NASA CR- 72364

A PROGRAM TO DEVELOP A HIGH-ENERGY DENSITY PRIMARY BATTERY WITH A MINIMUM OF 200 WATT HOURS PER POUND OF TOTAL BATTERY WEIGHT

by

William E. Elliott and Robert F. Amlie

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-6015

FINAL REPORT
July 1964 – September 1967

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A Program to Develop a High-Energy Density Primary Battery With a Minimum of 200 Watt-Hours per Pound of Total Battery Weight

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William E. Elliott and Robert F. Amlie

ABSTRACT

This extensive study included a large number of non-aqueous electrolytes, electrodes and cell systems which were theoretically promising for high-energy density batteries. Conductivity and stability were emphasized in the electrolyte investigation, and the solvent N-nitrosodimethylamine (NDA) was found to be particularly promising in both respects. Lithium and calcium were found to be the most satisfactory anode metals. Discharge capacities and rates of experimental cells were limited by the cathodes. Impurities usually exhibit a critical effect on performance, and the necessity to detect and remove them in order to characterize an electrochemical system was demonstrated.

SUMMARY

The principal objective of this program was to develop a primary battery possessing an energy density of 200 WH/lb of total battery weight. The extensive amount of work on nonaqueous electrochemical systems carried out during this contract is most conveniently considered under the general areas of electrolytes, anodes and cathodes. This outline is followed in the body of the report and roughly approximates the chronological order of investigation. Concurrent studies of system components were usually necessary throughout this program.

An extensive study of nonaqueous electrolytes, which was started during the preceding contract (NAS 3-2790), was completed under this contract. This study was directed toward finding the most suitable electrolyte, and the primary experimental emphasis was placed on electrolyte conductivity and stability in contact with electrode active materials. An empirical equation was formulated which satisfactorily relates the conductance of a large number of nonaqueous electrolytes with their solute concentration, solvent dielectric constant and solution viscosity.

The upper limit of conductance of the organic electrolytes studies was found to be at least an order of magnitude lower than that of aqueous electrolyte systems. Limited solute solubility, high solution viscosity and high solvent molecular weight were shown to be the parameters which usually limit the conductivity of organic electrolytes.

N-nitrosodimethylamine (NDA) was found to be a particularly promising aprotic solvent since solutions of relatively excellent conductivity were obtained. This solvent has a very low viscosity (η = 0.865 cps, as compared with 2.5 cps for propylene carbonate), high dielectric constant (ϵ = 53 at $20^{\circ}C$), and wide liquid range (-21 to $150^{\circ}C$). The principal disadvantage is its high toxicity.

This work demonstrated that anodes of lithium and calcium metals can be discharged at current densities as high as 100mA/cm^2 in nonaqueous electrolytes without excessive polarization, i.e., at potentials negative to -2.0V vs a Ag/AgCl reference electrode. Eleven lithium and one calcium anode-electrolyte combinations were found which operated at the 100mA/cm^2 rate, at least for short periods of time. The stability of the calcium anode in various electrolytes was found to be superior to that of lithium.

Magnesium is not a suitable anodic material since its potential in organic solutions, as in aqueous solutions, is considerably below the theoretical thermodynamic value. The potential was only about half that of the theoretical value in the organic electrolytes.

Eighty-four anode-electrolyte combinations which exhibited current density capabilities of at least 10mA/cm^2 are also enumerated in this report. In addition, many anode systems showing lower discharge rates were defined by this work.

Cell discharge rates and capacities were limited by the positive electrode. Although a battery with a lithium-cupric fluoride electrode combination can theoretically yield well over 200WH/lb, this energy density was not attained experimentally at even a low (1mA/cm^2) discharge rate in this laboratory. Cell discharge performance was often poorly reproducible and was dependent upon many variables such as purification, water content, techniques of fabrication, additives, active material conductivity, etc. A satisfactory cathode exhibiting good shelf life, high discharge rate and efficiency, and reproducibility was not demonstrated. This result is in agreement with the existing state of the art. Cathode failure was apparently due to the formation of a passivating film, and additional work was carried out with thin film CuF_2 electrodes to investigate this phenomena. Performance of the silver oxide cathodes was similarly affected by fabrication, composition and impurities.

For all cathodes tested, the highest current densities obtained were 80mA/cm^2 with a soluble organic cathode. This organic compound was hexachloromelamine, which was discharged on a carbon electrode in a solution of lithium hexafluorophosphate in dimethylformamide. Like all the high-energy organic cathodic materials tested, it was soluble in the organic electrolytes used in this study.

The highest cell energy densities obtained in this laboratory were with the lithium-silver oxide electrode combination in 2" x 2" sandwich type cells with two outer cathodes and a central anode. These gave values of 108WH/lb of total battery weight at the 0.5mA/cm^2 rate and about 81WH/lb at the 5mA/cm^2 discharge rate. Following a five-day stand period, this system delivered only 78WH/lb at the 0.5mA/cm^2 rate.

The need for more exacting purification and characterization methods for individual components and systems became increasingly evident as this work continued. Vacuum distillation of solvents, vacuum and inert atmosphere drying of solutes and electrode components and the exclusion of moisture were studied. Characterization by vapor phase chromatography, x-ray diffraction, and linear sweep voltammetry were employed extensively in this work.

INTRODUCTION

The objective of this program was to develop a primary battery with an energy density of at least 200 watt-hours per pound of total battery weight. The needs of military and space exploration agencies for high energy density power sources have recently revitalized interest in aprotic nonaqueous electrolyte batteries. This interest arises from the widely recognized possibility of using alkali and alkaline earth metals as anodes to obtain theoretical energy densities far greater than is now possible in aqueous media.

This project is a continuation of work carried out under a prior contract(1) which had the same objective as stated above. The initial project was primarily devoted to a systematic investigation of nonaqueous electrolytes with emphasis on obtaining the optimum conductivity and stability. Over thirty (30) solute-solvent combinations (one molal solute concentration) were found during the previous study with specific conductivities in excess of 10^{-2} ohm^{-1} cm^{-1}.

Effort during the first and second quarters of the present contract was also primarily concerned with the development of highly conductive nonaqueous electrolytes and a clarification of the basic factors governing conductance. Emphasis was then shifted to a study of anode-electrolyte phenomena, and the latter part of the program was concerned with cathode behavior. This study is, therefore, reported under the main headings of electrolytes, anodes and cathodes in the body of this report which approximates the chronological order of investigation.

I. ELECTROLYTES

It was recognized initially in this high-energy density primary battery program that very little was known about high conductance organic electrolyte systems. In our previous work(1) emphasis was placed upon obtaining an understanding of those factors which affect electrolyte conductance in concentrated nonaqueous solutions. Further work along these lines was carried out in the early part of the present program(2-5).

I-A. Solvents

Solvent properties which are recognized as important in the ability of solvents to provide satisfactory electrolyte solutions are the following:

1. Dielectric constant
2. Viscosity
3. Solvent power
4. Structure, i.e., influence of functional groups on solvent performance
5. Molecular weight and molecular volume
6. Temperature range of utility
7. Decomposition potentials
8. Purity and stability

The role of the dielectric constant (ϵ) of the solvent in forming conducting solutions is two-fold; as ϵ increases, (1) the solubility of ionic salts is increased, and (2) the degree of ionic dissociation also increases. In the work done in this investigation it was established that the specific conductance is proportional to the dielectric constant of the solvent. To establish the proportional influence of the dielectric constant on organic solvent power and conductance, mixtures of ethylene carbonate (ϵ = 95 at 36°C) and propylene carbonate (ϵ = 64.6 at 25°C), which is functionally identical, were prepared. The dielectric constants of the mixtures are given in Table I and ranged from 69.1 to 87.2. Potassium hexafluorophosphate at various molar concentrations was used as the solute. Results are shown in Figure 1, p. V-2 and Figure 2, p. V-3. The mixtures are observed to have almost identical viscosities which minimize viscosity as a variable. The highest solubility and specific conductance were observed with the mixed solvent of highest dielectric constant. Other factors can exert an influence in increasing or decreasing the conductance and frequently exhibit greater influence than that of the solvent dielectric constant, providing that the latter exceeds a value of about 20.

The viscosity of the solvent is an extremely important factor since it is inversely proportional to the conductance. Thus, high viscosity nonaqueous solvents are generally not suitable for battery electrolytes even though they possess a high dielectric constant. Our evidence has consistently indicated that solvents of low viscosity and moderate dielectric constants will yield higher conductance solutions of the same salt at the same concentration than will solvents of relatively high viscosity and high dielectric constant. For example, the influence of viscosity on the conductance of mixtures of acetonitrile and dimethylcyanamide (closely related in structure and possessing almost equivalent dielectric constants) demonstrates this effect. Acetonitrile (low viscosity) is seen to to give better conductance values than any mixture with dimethylcyanamide or dimethylcyanamide alone since the viscosity increases from pure acetonitrile to pure dimethylcyanamide as shown in Table II, p. V-4 and Figure 2, p. V-5.

The following tabular comparison of a few common solvents and their 0.7m (molal) solutions of KPF_6 demonstrates the principle of inverse proportionality of conductance to solution viscosity.

Name of Solvent	ϵ	η_0 (cp)	η (cp) (.7mKPF_6)	L $ohm^{-1}cm^{-1}$
Propylene carbonate(PC)	64	2.52 (25°C)	4.38 (25°C)	6.8×10^{-3}
Dimethylformamide (DMF)	36.7	0.80 (25°C)	1.36 (25°C)	2.05×10^{-2}
Acetonitrile (AN)	37.5	0.345(25°C)	0.59 (25°C)	3.70×10^{-2}

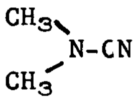
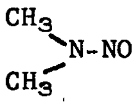
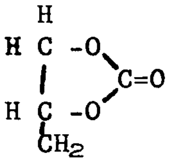
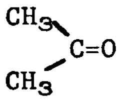
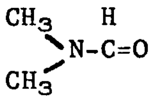
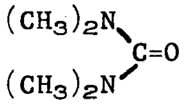
where ϵ = dielectric constant
η_0 = solvent viscosity
η = solution viscosity
L = specific conductance

In general, solution viscosity has been shown to be an exponential function of solute concentrations. The exact form of this function will vary for different solvents.

Solvent power is extremely hard to define, but it is recognized that substantial concentrations of dissociated solutes (forming low viscosity systems) are required for very high specific conductances. Solubility is usually a function of the dielectric constant and functional structure of the solvent molecule. It may also be assumed that the solvent's molar volume is related to solvent power and ability to solvate ions.

Solvent structure influences both solubility and specific conductance as exemplified by the fact that solvents with oxygen-containing functional groups are generally preferable for the dissociation and solution of alkali metal salts. Thus, acetone, dimethylformamide, tetramethyl urea and other compounds possessing carbonyl groups are usually superior solvents for alkali metal compounds. Compounds of similar structure which do not contain a carbonyl group do not perform as well. This comparative solubility behavior is illustrated by data presented in the following table which also demonstrates the influence of the dimethyl amino group on solubility.

SOLUBILITY AS A FUNCTION OF SOLVENT STRUCTURE

Solvent	Structure-functional group	ϵ	Solubility (max) KPF$_6$	Solubility (max) (Pr)$_4$NPF$_6$
acetonitrile (AN)	CH_3 -CN	37.5	0.75M	1.10M
dimethylcyanamide (DMC)	 $(CH_3)_2N\text{-}CN$	36	0.83	--
nitrosodimethylamine (NDA)	 $(CH_3)_2N\text{-}NO$	53	1.0	1.30
propylene carbonate (PC)		64	1.2	--
acetone	 $(CH_3)_2C{=}O$	20.7	1.28	1.31
dimethylformamide (DMF)	 $(CH_3)_2N\text{-}CH{=}O$	36.7	2.33 (not sat'd)	1.45
tetramethyl urea (TMU)	 $((CH_3)_2N)_2C{=}O$		--	1.27

With quaternary ammonium salts the effect of the solvent functional group on solubility is not readily apparent. This is illustrated by the solubility data for tetrapropylammonium hexafluorophosphate ($(Pr)_4NPF_6$) included in the above table.

The effect of a high solvent molecular weight can be two-fold, namely: (1) the liquid is too viscous to be usable, and (2) the molar volume is extremely large. It is apparent that the molar volume must be low if sufficient ion concentration and mobility are to be obtained. The effect of high molecular weight and molar volume can be seen from data obtained at the beginning of this contract[2,3].

It is obvious that a solvent of wide liquid range, i.e., low meling point and high boiling point is desirable for a battery which is required to operate over a wide temperature range.

The decomposition potentials are extremely important in determining the available working range for an electrolyte system. Decomposition potentials can be altered by the introduction of a solute, and the solution decomposition potential is of practical importance.

Purity and stability of the system components influence the interactions between electrodes and solutes which can occur on stand or during use of a battery. Purity is a more or less nebulous property since one must be able to define what constitutes purity or what degree of purity is required in a particular nonaqueous solvent. This is an extremely difficult problem. For example, on a smooth platinum surface containing roughtly 1-2 x 10^{15} platinum atoms per cm^2, certain impurities in very low ranges, e.g., 5-10 ppm, may be more significant than gross amounts of other impurities. On a 1:1 atomic or molecular ratio basis, coverage of 1 cm^2 of low roughness platinum can be accomplished with less than 5 ppm of electrolyte impurity. Modern purification and measuring techniques may be far from adequate to prevent substantial electrode-impurity interactions from occurring and thereby influence the electrochemical performance of the electrode.

I-B. Solutes

In the selection of solutes for conducting solutions several factors appear to be critical. Naturally the solute must be of such a structure as to dissolve easily. Since specific conductance also is directly related to concentration, sufficient material must dissolve and dissociate to establish an adequate conductance. Crystalline materials of low lattice energy will often dissolve more readily than solutes of high lattice energy. In addition, the ability of the solute to interact, coordinate, or solvate with the solvent is important as noted in the discussion of solvents. For most systems, salts which yield solvated or unsolvated ions that are sufficiently large, so as to have a relatively low charge density, will dissolve most readily. For example, it is not unusual to find salts with large anions are more soluble and easily dissociated than those with small anions. It is frequently found that the halide and group VI perfluoro compounds of a given cation have the solubility relationship.

a) $I^- > Br^- > Cl^- > F^-$ and b) $SbF_6^- > AsF_6^- > PF_6^-$

Examination of the conductivity data of Table IV, p. V-6 to V-11, demonstrate this and other effects. Quaternary ammonium salts of sufficient cation size are usually soluble in the nonaqueous solvents. The tetramethylammonium salt is usually less soluble than the higher tetraalkylammonium salts. As the alkyl groups approach the optimum size, solubility and specific conductance increase. As the size of the quaternary alkyl groups is further increased, the resultant increase in viscosity reduces the specific conductance. Examples are given below:

Solvent	Solute	C	L
DMF	$(CH_3)_4NPF_6$	1 molar	1.09×10^{-2}
DMF	$(C_3H_7)_4NPF_6$	1 molar	2.09×10^{-2}
DMF	$(C_{12}H_{25}C_6H_4CH_2)CH_3NPF_6$	1 molar	1.15×10^{-2}

The purities of commercial salts which yield the highest conductances leave much to be desired, and some analytical work and purification is almost always required. We have noticed differences in appearance and performance of quaternary ammonium salts from different lots. Lithium hexafluorophosphate has been the solute compound studied most thoroughly in this laboratory. The commercial anhydrous salt has been found to differ markedly from lot to lot and required pretreatment prior to using. We have attempted several procedures for both purification and identification of the impurities. Titration of the "as received" materials with a standard base usually resulted in detecting a small amount of free acid in the salt. Utilizing linear sweep voltammetry it was found that electrochemically active impurities were present. Additions of various impurities such as water, HF, and HPF_6 indicated that both water and HPF_6 may be the major contaminants since both resulted in larger current peaks in the voltammetric sweeps at peak voltages corresponding to those of the impurities. Analysis of the salt was made by x-ray diffraction, and most lots showed free lithium fluoride to be present in addition to other extraneous lines. An x-ray diffraction pattern of pure $LiPF_6$ was received from Professor D. W. Sharp, University of Strathclyde, Glasgow, Scotland, and compared with those obtained here. Substantial differences were observed as seen in Table V, pages V-12 and V-13. In attempting to purify $LiPF_6$, a number of techniques were attempted, none of which gave reproducible products. Some of the methods used were: (1) drying the $LiPF_6$ in a nitrogen atmosphere at 110°C for 24 hours, (2) drying the salt under vacuum from 4 to 60 hours at 50°C, and (3) drying in an argon stream at 50°C for 24 hours.

There is also some instability of the $LiPF_6$ itself which makes it difficult to prepare in pure anhydrous form, and maintain its purity. This instability was also reported by the supplier in discussions of the purity problem.

The above analysis and purification techniques (discussed more thoroughly in a later section of this report) indicate the complex nature of some of the problems with solute materials for nonaqueous electrolytes. Such materials, when purified, must demonstrate a capability for long range stability if they are to be satisfactory as battery electrolytes.

I-C. ELECTROLYTIC SOLUTIONS

When the solute is dissolved in the solvent the interactions previously discussed are most important in determining the effective performance of this solution as an electrolyte.

Conductance is one of the most important characteristics of an electrochemical solution. A large number of electrolyte specific screening tests were therefore obtained under a preceding contract(1) and during the first part of the present contract(2,3). Specific conductance and viscosity values for some of the better electrolytes investigated are shown in the graphs which comprise Table VI, pp. V-14 to V-27. Other data related to conductance measurements are presented in references(1,2,3).

It was usually found that the maximum specific conductance for different solvents occurred at approximately a one molar solute concentration. One purpose of the screening and analytical tests was to determine, if possible, from the relationships discussed under solvents and solutes, which of these factors most affect the specific conductance of the electrolyte. It was found that the most significant factors are (1) concentration, (2) dielectric constant, (3) viscosity of the solution and (4), stability in contact with the electrode active materials.

A few temperature coefficient determinations were run, and the results appear in Figure 4, p. V-28. It is apparent that the more concentrated solutions are more temperature dependent.

I-C-1 An Empirical Method for Calculating the Conductance of Electrolyte Solutions

Our work on electrolytes was directed toward understanding those factors which affect conductance such as solution viscosity, dielectric constant, concentration and solvent-solute interactions. The concepts were evolved to a point where the interrelationship of the above properties has been established to some extent. Thus we have been able to develop an empirical equation relating most of the properties. It is:

$$L = \frac{k\, C \epsilon^m}{1000 \eta}$$

in which L = specific conductance in $ohm^{-1}cm^{-1}$

C = concentration in terms of normality (equivalents per liter) or molarity (where 1:1 electrolytes are involved)

$C/1000$ = equivalents per ml

ϵ^m = dielectric constant of the solvent to the m power

η = viscosity in centipoises of the solution at the concentration C

k = arbitrary constant with units centipoise cm^2/ohm-equivalent

In Figure 5 which is shown on pages V-29 through V-34, respectively, experimental curves and calculates curves for six systems are presented. In the calculates curves, the following assumptions were made.

1. The exponent, m, on the dielectric constant, ϵ , is unity.

2. The constant, k, is unity in many cases.

3. In specific cases, a k value calculated at a single concentration, C, would hold over the entire range of concentration and improve the correlation.

It is noteworthy that the calculated conductance curves correlate closely (less than an order of magnitude difference) with the actual experimental curves. Other facts to observe are:

1. k is near unity for most systems including the aqueous systems.

2. The equation holds even for the aqueous system H_2SO_4-H_2O except that the true k is quite high, 2.5, as might be expected with the highly mobile hydrogen ion present.

Since the equation has been developed only recently, it cannot be assumed as yet that it will be applicable in all cases. Indeed, it is likely that limitations exist. In the next section our logic in developing the equation is given.

Derivation of the Equation

In previous studies we found that the viscosity of the electrolyte solutions is highly important in determining the conductance. Walden made similar observations many years ago$^{(4)}$, but Walden's rule, ($\Lambda_0 \eta_0 \cong$ Constant) related only the limiting equivalent conductance, Λ_0 , and the solvent viscosity, η_0 .

We chose to evaluate the Walden Product, $\Lambda \eta \cong$ Constant, where Λ is the equivalent conductance at high concentration and η is the viscosity of the solution at high concentration. We found that the Walden Product is nearly constant over a fairly wide range of concentration for several systems as shown in the following tables.

TABLE A. WALDEN PRODUCTS OF LITHIUM CHLORIDE SOLUTIONS

	Water			Dimethylformamide		
C	Λ^*	η	$\Lambda\eta$	Λ	η	$\Lambda\eta$
0	99	0.89	88	60	0.8	48
0.5	70	0.9	63	16.2	1.4	23
0.955	63	0.95	60	9	2.1	19

TABLE A. WALDEN PRODUCTS OF LITHIUM CHLORIDE SOLUTIONS (Cont'd)

	Water			Dimethylformamide		
c	Λ*	η	$\Lambda\eta$	Λ	η	$\Lambda\eta$
1.42	--	--	--	5.5	3.3	18
1.88	--	--	--	3.3	5.0	16.5
2.33	50	1.2	60	1.9	6.2	12
5.38	30	1.95	59	--	--	--
6.92	22.6	2.56	58	--	--	--
8.33	17	3.25	55	--	--	--
9.68	11	4.43	51	--	--	--

---

* Lange's Handbook of Chemistry, Tenth Edition, 1961.

TABLE B. WALDEN PRODUCTS OF POTASSIUM HEXAFLUOROPHOSPHATE SOLUTIONS

C	DMF①			DMC②			PC③			TMU④		
(moles/ℓ)	Λ	η	$\Lambda\eta$	Λ	η	$\Lambda\eta$	Λ	η	$\Lambda\eta$	Λ	η	$\Lambda\eta$
0.26	45.4	1.00	45	35.0	0.80	28.0	14.8	3.10	48.9	17.7	2.30	40.6
0.42	38.8	1.15	44.6	27.4	0.90	24.7	13.1	3.55	46.5	13.3	2.85	38.0
0.58	34.3	1.30	44.6	22.9	1.05	24.1	11.0	4.05	44.7	10.3	3.45	35.7
0.75	29.8	1.50	44.6	19.6	1.25	24.5	9.2	4.60	42.4	8.0	4.15	33.2
1.10										4.59	6.55	30.0
1.20	20.8	2.20	45.6				6.08	6.40	38.9			
1.60	15.0	3.20	48.2									
2.20	8.96	6.00	53.8									
2.80	4.97	12.15	60.3									

---

[1] Dimethylformamide

[2] Dimethyl Cyanamide

[3] Propylene Carbonate

[4] Tetramethylurea

From this, we see that:

(1) $\Lambda\eta \cong K$ where Λ = equivalent conductance ($cm^2 ohm^{-1} equiv.^{-1}$)
η = viscosity of the solution (centipoises)
K = a constant

By definition:

(2) $\Lambda = \frac{1000L}{C}$ where L = specific conductance ($ohm^{-1} cm^{-1}$)
C = concentration (moles $liter^{-1}$)

Then, substituting for Λ in equation (1) we get:

(3) $$\frac{1000L\eta}{C} \cong K$$

Rearranging, we get:

(4) $$L \cong \frac{KC}{1000\eta}$$

Now the assumption was made that K should involve the dielectric constant (ϵ);

(5) $K \propto \epsilon^m$ where m is a constant,

or:

(6) $$K = k\,\epsilon^m$$

Then, substitution into equation (4) gives the final form:

(7) $$L \cong \frac{k\,C\,\epsilon^m}{1000\eta}$$

Thus, it is immediately apparent that this simple equation assumes the Walden Product to be constant and will be most accurate in cases where it is constant. It also assumes that the dielectric constant plays a significant role in the equation.

It can be observed that in the derivation no assumption was made as to the value of the exponent, m.

There is some indication in the preliminary examination of our data that it is less than one, but even with an assumed value of $m = 1$, the correlation with experimental data was quite good. The next section describes more details of the use and limits of the equation.

Use of the Equation

To use the equation, certain data such as the viscosity of solutions over the concentration range of interest must be known. It is also necessary to know the dielectric constant of the solvent at 25°C. In addition, since the equation includes concentration, it implicitly assumes that the solute solubility is known to cover the region of interest since values beyond saturation are meaningless.

Perhaps it is well to state the built-in limitations at this point.

1. It does not include a term to correct for temperature.

2. It says nothing about solubility.

3. It undoubtedly deviates from experimental values at very low concentrations where the Onsager relationship holds.

4. It may be that the value of k is related to solvent-solute interactions and mobility, but no firm statement can be made on this point.

The above discussion merely points up the need for further research to establish other relationships for electrolyte solutions which can be useful.

I-D. Purification and Analytical Procedures

I-D-1 Organic Solvents

Stability tests for solvents normally involve measurements at or near an equilibrium condition. The sequence of measurements usually followed to establish the purity of a solvent was to obtain a vapor phase chromatogram, a conductance value and an index of refraction value(2).

The solvent was (and is) first vacuum distilled from a drying agent which was often a molecular sieve. The vacuum distillation apparatus used includes a 1000 ml distilling flask and a vacuum-jacketed column which is strip-silvered (supplied by the Scientific Glass Co.). This column has an internal diameter of 2.5 cm. and is packed with a 90 cm. bed of glass helices 1/8" in diameter. Distillations were carried out at a 1:1 reflux ratio. This ratio was maintained by means of a swinging funnel fitted with a soft iron core mounted in this distillation head. An electromagnet regulated by a General Electric type TSA-14 timing device moves this funnel into position for either total reflux or collection. The timer cycle of 20 seconds is divided into the desired ratio of total reflux to collection, in this case, 1:1. Variations up to a ratio of 1:100 with 1% accuracy are possible by appropriate setting of the timer. Distillate was collected in a flask designed to allow transfer to the argon atmosphere dry box without exposure to the atmosphere or interruption of the distillation process. Vacuum is maintained with a No. 1400B Welch Duoseal pump capable of achieving a pressure of 1 micron. Vapor pressure was measured by a closed-end manometer mounted on the distillation flask(5).

Vapor pressure in the system during distillation was dependent upon the solvent being distilled and was kept as low as proper reflux conditions would permit. In each case, 700 ml were distilled with the first and last 100 ml fractions discarded.

Following vacuum distillation, the analytical measurements were repeated to determine the nature and amounts of impurities which remain. The distilled (and undistilled) solvents were characterized by measuring the refractive index and specific conductivity of each of the collected fractions during the first part of this program(5). An F and M Gas Chromatograph was later acquired and became the principal analytical tool during the latter part of the contract.

Solvent samples were stored in a dry argon atmosphere and specific conductivities were measured in the argon atmosphere. Refractive indices and specific conductivities were measured at one, two, four, twelve and twenty-four-week intervals after distillation according to the original test procedure set up to evaluate aging effects. Changes in these test values were observed during the stand test as exemplified in Table VII, pages V-35 through V-37, which includes acetonitrile, N, N-dimethylformamide, N-nitrosodimethylamine and propylene carbonate during a twelve-week period.

A modified procedure for purification of N-nitrosodimethylamine (NDA) was adopted during the last part of this program. The NDA was first given two pretreatments with Union Carbide Type 4A molecular sieves. The molecular sieves were reactivated by drying at 200°C. Pretreatment with molecular sieves was superior to pretreatment with calcium hydride, lithium and P_2O_5. The water content of the distilled NDA fractions was less than 50 ppm and often less than 30 ppm.

The vapor phase chromatograph was invaluable in determining impurity contents and in evaluating the efficiencies of various methods for removing these impurities from the solvents. The columns and operating conditions for the chromatograms were as follows:

Detector Temperature - 125°C
Injection Port Temperature - 150°C
Bridge Current - 150 ma
Columns and Packing - 1-1/2 ft., 1/4 inch copper tubing packed with 10% Carbowax 20M on Fluoropak 80 0.02ml
Sample Size - 0.02ml
Oven Temperature Program - Initial temperature = 100°C, increase to 150°C at 30°/min., then held for 3 min.
Helium Flow Rate - 40ml/min.
Attenuations - as shown on curve

In Figure 6a, page V-38 the chromatograms for NDA as received from the supplier and after vacuum distillation are compared. The "as received" material contains 30,000 ppm H_2O which, after distillation from molecular sieves 4A, has been reduced to 600-1200 ppm. The effect of adding 1000 ppm H_2O to the distilled NDA is illustrated in Figure 6-b, page V-39. Figure 6-c, page V-40 demonstrates the effect of treating distilled NDA with lithium for 24 hours. The H_2O content is reduced from about 1000 ppm to 425 ppm or less. The effect of treating distilled NDA with P_2O_5 for 1 hour is shown in Figure 6-D, page V-41. Here, the H_2O content has been reduced from about 1000 to 70 ppm.

I-D-2 Solutes and Organic Electrolytes

The linear voltage potentiometric (LVP) technique was used to determine the presence and reactivity of impurities in the solution which might obscure or alter the actual electrode performance. Most of the solutes used were dried before use in a stream of dry nitrogen at $110^{\circ}C$ or at another temperature known to be satisfactory. Voltammetric and discharge test results indicated that impurities added to most solutions with these "dried" solutes were not appreciable.

The LVP technique was of particular importance in investigating the nature of the electroactive impurities found to be present in lithium hexafluorophosphate which were readily reduced at the CuF_2 cathode during discharge. It was found that two reduction waves existed in the voltammetric sweeps of the electrolyte composed of lithium hexafluorophosphate (as received) in vacuum distilled N-nitrosodimethylamine. One occurred at -0.7V versus Ag/AgCl and the other at -1.75 or more negative values. It appeared to be due to water as shown in Figure 7, pages V-42 through V-47. The more negative wave was enhanced by the addition of water and decreased by the addition of drying agents such as lithium metal or phosphorous pentoxide.

The exit gasses from the drying of lithium hexafluorophosphate under nitrogen which may contain either a volatile impurity or decomposition product exhibited acidic properties when absorbed in water. A titration of the aqueous solution of collected exit gas when 55.5g of lithium hexafluorophosphate was dried required 18.8 milliequivalents of base. Sodium bifluoride, $NaHF_2$, and hexafluorophosphoric acid (65% aqueous solution) were investigated in hopes of providing further information about the nature of the electroactive impurities in lithium hexafluorophosphate.

Sodium bifluoride had only a limited solubility in N-nitrosodimethylamine (NDA), less than 0.3m. A voltammetric sweep study of a saturated solution of sodium bifluoride in NDA is shown in Figure 8-a, page V-48. The low currents obtained are probably due to the low conductivity of the electrolyte. Figure 8-b on page V-49 shows the effect of saturating a solution of "as received" lithium hexafluorophosphate-NDA with sodium bifluoride. The initial wave, the reduction of interest, showed no enhancement by this addition, and it is therefore doubtful that the bifluoride ion or any of its possible dissociation products, e.g., HF, are the electroactive impurities in lithium hexafluorophosphate.

Voltammetric sweep studies of 0.1m and 1.0m hexafluorophosphoric acid in NDA are shown in Figure 8-c, page V-50. The peak positions in these solutions are not dissimilar from those found in "as received" lithium hexafluorophosphate-NDA. The addition of hexafluorophosphoric acid to a dried lithium hexafluorophosphate-NDA solution (see Figure 8-d, page V-51) enhances the initial peak considerably. Similarly, the addition of hexafluorophosphoric acid to "as received" lithium hexafluorophosphate-NDA (as shown in Figure 8-e, page V-52) enhances the initial peak. Of the materials tested to date, hexafluorophosphoric acid gives voltammograms most closely resembling that shown by the electroactive impurities found in lithium hexafluorophosphate as received from the supplier.

Attempts were made to duplicate the work on lithium hexafluorophosphate and hexafluorophosphoric acid in propylene carbonate (PC) as the solvent. The electrochemical tests were hampered by severe filming of the silver electrodes which led to irreproducible results. After each scan, the working electrode was covered with a heavy blue-gray film. Repeated scans gave different peak heights, peak positions and sometimes no peaks at all. These results are quite different from those obtained in NDA. Because of the problems encountered in propylene carbonate, the studies of lithium hexafluorophosphate and hexafluorophosphoric acid in this solvent were discontinued.

A more detailed study of the electroactive impurities in lithium hexafluorophosphate in NDA was made using a pyrolytic graphite disk with a geometric area of 7.8mm^2 as a working electrode, a silver-silver chloride reference electrode with a non-aqueous salt bridge (see Section IV-B) and a pyrolytic graphite rod counter electrode. The solutions to be investigated were purged with nitrogen prior to investigation to eliminate any oxygen and kept under a nitrogen blanket during the tests. This precaution was taken because preliminary studies showed that while oxygen did not have a pronounced influence on the reduction waves found in lithium hexafluorophosphate solutions, a small wave was present prior to the reduction peaks of lithium hexafluorophosphate when samples were exposed to oxygen.

The effect of lithium metal contact was investigated by LVP scans of a solution of lithium hexafluorophosphate as received from the supplier dissolved in N-nitrosodimethylamine (NDA) and a similar solution neutralized with lithium metal. The voltammetric sweep studies of the neutralized solution showed only one reduction peak which apparently corresponds to the second peak found in the unneutralized solution (see Figure 8-f, page V-53). Since adsorption is time, potential and concentration dependent, the linearly varying potential techniques allowed the study of the two solutions in more detail by varying the first two parameters over a wide range. In Figure 8-g, page V-54, curve 1 shows the cyclic voltammetric scan obtained at a scan rate of two volts per second on an electrode which had only been held at potentials more negative than -1.5V relative to the Ag/AgCl reference electrode. Under these conditions, only residual current is obtained. When the same electrode was held at -0.76V for 5 to 10 seconds, curve 2 is typical of the results obtained when the electrode was scanned cathodically. The peak height was found to be related to the holding time and to the applied potential (for potentials more positive than -1.5V). The peak height is limited to a maximum value which is determined by the equilibrium for adsorption. During the holds, the current was very close to zero and cathodic.

In the unneutralized solution, both reduction processes were adsorption dependent as seen by the voltammetric curves in Figure 8-h, page V-55. If the adsorption of the impurities on the working electrode was prevented through the use of very fast scan rates, only residual current was obtained between -1.5V and -2.5V vs Ag/AgCl (curve 1). Holds for 500 and 800 seconds at -1.5V gave appreciable adsorption of one species, and both resulted in scans represented by curve 2. Rapid scans from -0.5V to -2.5V and from -1.5V to -.3V show some reduction of the species adsorbed at voltages more positive than -1.5V. Again, a 500 second hold at -0.5V resulted in curve 4 where both species have been adsorbed and their reduction waves appear.

When the adsorbed species are reduced, it is possible to reoxidize them at more positive potentials. Figure 8-i on page V-56 shows these anodic and cathodic scans. The anodic peak at +0.8V (vs Ag/AgCl) is only obtained if the first impurity is reduced (cycle 1) and the peak at +0.3V appears when the second species is reduced (cycle 2). The actual identification of the impurities responsible for these peaks appears to be a problem not within the scope of this project. The first reduction peak seems to be related to the acidic impurity, the concentration of which varies markedly from one lot of lithium hexafluorophosphate to another. Neutralization of this acidic impurity with lithium removes the material giving rise to the wave at -1.1V vs Ag/AgCl (see Figure 8-f, page V-53) and extends the potential range where only residual current is apparent from 0 to -1.5V (vs Ag/AgCl). Thus, linear sweep voltammetry or cyclic voltammetry can be used to provide a rapid and simple check of the composition of lithium hexafluorophosphate solutions of each new lot of solute.

In addition to the electrochemical characterization of lithium hexafluorophosphate reported earlier, x-ray diffraction patterns were obtained for each lot of the material used in the program to date and for a sample of lithium hexafluorophosphate monohydrate(10).

Attempts were made to recover the $LiPF_6$ from a lithium pretreated solution of $LiPF_6$-NDA in order to determine if its x-ray pattern matches that of $LiPF_6$ dried under nitrogen at 110°C. This is of interest since the $LiPF_6$-NDA electrolyte, which has been pretreated with lithium, shows LVP behavior similar to that obtained for an electrolyte prepared from the dried $LiPF_6$, and there seems less likelihood of contamination by decomposition products if the lithium pretreatment is used. About 200ml of a 1m $LiPF_6$-NDA solution was pretreated with pieces of Li for one day. The solution was filtered and an LVP scan made on a small portion. The scan matched those previously obtained for both pretreated and dried $LiPF_6$-NDA systems. Approximately half of the NDA was removed by vacuum distillation at 50°C. At this point, the temperature began to rise so the distillation was halted to avoid any possible decomposition. Small portions of the solution were then treated with benzene and heptane to see if precipitation could be initiated, but both solvents were immiscible with the solution. No further work was carried out to recover the $LiPF_6$ during this contract.

II. ANODES

II-A. Introduction

In early 1965, a significant achievement was obtained in anode performance in nonaqueous electrolytes with constant current screening tests in this laboratory. This achievement was the discovery of electrolyte systems permitting active metal anodes such as lithium and calcium to deliver current densities of 100 ma/cm^2. This high value was almost an order of magnitude above the best results previously reported by investigators in this field. The first such system investigated in this program contained a lithium anode in a 1 molal morpholinium hexafluorophosphate - N-nitrosodimethylamine electrolyte. Anode potentials were measured against a Ag/AgCl reference electrode, and a large Ag/AgCl electrode was used as the counter electrode. Unfortunately, the morpholinium salt is protic, and attacks lithium with the release of hydrogen as a by-product. After the original system had been studied, other lithium anode-electrolyte systems with improved stability were discovered. In addition, a few calcium anode-electrolyte systems were also studied.

These significant developments resulted from work carried out during the second phase of this contract which was primarily concerned with finding and characterizing such anode-electrolyte systems. Several reactive metals were evaluated as anode materials in the more promising organic electrolytes according to a systematic study which included the following measurements:

1. Constant current screening at 0.1, 1.0, 10.0, and 100 ma/cm^2 for 5 minutes to evaluate the initial voltage-time performance of the metallic anode in a number of electrolytes in order to determine:

   a. At what maximum current density an apparent steady state anode performance can be realized,

b. what magnitude of iR loss can be expected,

c. a qualitative idea of the effects of such properties as activation polarization, concentration polarization and passivation.

2. Chemical stability of anode materials in solvents and electrolyte systems.

3. Voltammetric sweep studies of anode-electrolyte interactions.

4. Impurity effects on anode performance.

5. Fabrication of lithium electrodes.

II-B. Procedures and Results

II-B-1 Constant Current Screening Tests

Evaluation of the individual electrodes was based on the determination of the degree of polarization which an electrode undergoes when discharged at different magnitudes of current density in a particular electrolyte. Visual observations of reaction phenomenon, precipitation, electrolyte color changes, anode surface charges, etc. were included in this screening test. The screening method is described in detail below:

The anode (1 cm^2 area) under study was made to undergo successive discharges of five minutes' duration in comcombination with a suitable counter electrode at successively increasing values of constant current, corresponding to 0.1, 1, 10 and 100 milliamperes per square centimeter. The system is allowed to stand on open circuit after discharge at each current density until a stable open circuit voltage is observed, i.e., very, very slow change in potential.

The voltage of the test electrode versus a reference electrode was recorded during discharge at each current density and on open circuit. The open circuit voltage was chosen as a reference value for assessing the degree of polarization. Current was maintained constant during the discharges by means of a versatile electrochemical apparatus utilizing DeFord type operational amplifier circuitry(22). All experiments of this kind were performed in an argon atmosphere. Individual silver-silver chloride reference and counter electrodes were used in virtually all of the screening tests. In addition, it was thought desirable to employ the same reference and counter electrodes in all systems for the purpose of comparison. Reference electrodes were immersed directly in the test solution without employing a Luggin capillary modification. This may introduce iR errors at high current densities, but did not cause trouble in most of the screening work.

In the analysis of the polarization data, classification of each electrode-electrolyte system was according to the magnitude of current density (i.e., 0.1, 1, 10 or 100 ma/cm^2) which the electrode could sustain during discharge. The arbitrary basis used for separation into these categories was as follows. If the electrode was observed to be polarized by less than fifty per cent at a given current density, it was judged to be capable of sustaining discharge at that current density. On the other hand, if the degree of polarization was greater than fifty per cent, the system was classified in a lower current density category. Obviously, since each current density is an order of magnitude greater than the preceding one, classification of a system in a particular category does not necessarily represent the upper limit of current density which the system can sustain. Hence, in some cases, where the behavior of a system was particularly interesting, discharges were carried out at current densities other than those cited. In such cases the system was still classified under one of the magnitude categories in the specified manner.

Classification of some systems was uncertain because the degree of polarization varied appreciably during the discharge period at a given current density. Hence, in some cases, polarization was greater than fifty per cent during the first part of the discharge but less than fifty per cent later in the period, or vice versa. In these cases, further arbitrary rules of classification were applied. If the polarization at the end of the discharge period at a given current density was greater than fifty per cent for only a short time at the beginning but less than fifty per cent for the duration of the discharge, the system was considered capable of sustaining discharge at the given current density.

In the constant current screening tests, it was found that fifteen (15) of the systems studied could operate at the 100ma/cm^2 rate, but only a few of these were truly stable. These were lithium in $LiPF_6$-NDA, lithium in 1m $LiClO_4$-NDA and lithium in lithium pretreated in morpholinium hexafluorophosphate-NDA. At least forty-one (41) of the lithium-electrolyte and twenty-eight (28) of the calcium electrolyte systems were able to perform at the 10 ma/cm^2 rate. A list of both stable and unstable lithium and calcium anode systems which were satisfactory at the 100 ma/cm^2 and 10 ma/cm^2 discharge rates are given in Table VIII, pages V-57 through V-82. Data for other anode systems which operated at lower current densities can be found in the quarterly reports of this contract (2,3,4).

Magnesium anode-electrolyte systems were also screened using the above methods, but the magnesium voltage was always much lower (i.e., about 1/2) than the theoretical thermodynamic electrode potential. Thus its only utility would probably be in low voltage batteries of considerably less energy density than desired of high-energy systems. To review the results of these tests the reader is referred to the quarterly reports(2-6).

II-B-2 Chemical Stability of Anode-Electrolyte Systems

In general, two types of anode-electrolyte stability tests were carried out which depended primarily on the length of the test. These were: (a) short-term (24 hr.) tests for severe corrosion and reaction, and (b) long-term (2-18 week) stability tests depending upon promise of the system. The initial screening for stability of anodes was of 24 hours' duration, and the rate of reaction was estimated by visual observation which included effects such as anode gassing and changes in electrolyte color or precipitation.

In prolonged tests of two weeks or more, weight losses or gains and specific conductance changes were measured in addition to color changes or other visually observable effects. Chemical stability tests of the anode-electrolyte systems listed in Table VIII (100 ma/cm^2 and 10 ma/cm^2) and other systems of interest are given in Table IX pages V-83 through V-106. It will be noted that most of the tests listed in Table IX are for two weeks' duration only, and these were usually adequate to determine the extent of reaction. Stability tests of lithium in N-nitrosodimethylamine electrolytes are given on pages V-103 and V-104.

II-B-3 Effect of Pretreatment on Anode Performance

It was readily observed in the work with lithium and calcium electrodes that gassing occurred in several situations where either protic materials were contained in the solvent as structural components (enol-keto type shifts, hydrogen bonds, etc.) or as solvent impurities (water, protic acids, etc.). Proticity could also be introduced with the solutes in the electrolyte (water or protons on ammonium or quaternary ammonium ions are acidic and replaceable). Removal of these protic materials from the electrolytes generally reduces corrosive attack on the active metals, and should promote higher coulombic efficiencies. However, it was found that in the more purified aprotic media the polarization of the electrode was often greater under load. In some circumstances the protic materials therefore appear to either clean and/or activate the electrode surface or result in an increase in the area of the active metal electrode.

Electrochemical half-cell screening tests of lithium anodes in pretreated electrolytes are summarized in Table X, pages V-105 through V-113.

II-B-4 Fabrication of Lithium Electrodes

Very little developmental work was done on the fabrication of lithium electrodes. Small half-cell tests were made with half inch lithium ribbon of 15 mils thickness. No substrate was used in tests of this type. In fabricating 2" x 2" lithium electrodes, a silver Exmet grid was most frequently used. Some reaction with and separation of the lithium from the silver metal was observed. Copper Exmet screen was also tested as a grid material, and the limited data obtained indicated that this metal is superior to silver as a supporting member. A comparison of the performance of lithium metal on both copper and silver Exmet screen is given in Table XI, page V-114.

II-B-5 Voltammetric Anode Studies

Voltammetric studies of anodes were carried out in those electrolytes which appeared to be the most promising. These tests indicated that the active metals do not behave as reversible systems in the organic electrolytes since iR losses, activation polarization and concentration polarization all play significant roles. When the anodes were discharged by linear sweep voltammetry, activation polarization shifted the initial anodic rise of the current-potential curves, along the zero current axis toward more positive values. The slope of the rise of the linear sweep curve is related to the activation polarization as well as to the normal electrochemical iR polarization of the system. For most metals the increase in current as a function of increasing anode potential should yield a curve with a slope which is close to infinity (i.e. vertical) and which exhibits minimal iR polarization. This is not usually observed in nonaqueous media where iR effects are more dominant than in aqueous systems. Concentration polarization should normally be most evident in its effect on the limiting current and the slope of the voltammetric sweep wave after the peak current has been passed. These evaluations are primarily qualitative in nature because scan rate, initial potential and other factors can influence the wave's peak potential and curve form.

The data plotted in Figures 9 and 10, pages V-115 through V-123, indicate that in different electrolytes, the magnitudes of activation, iR, and concentration polarization are dependent on the electrolyte. This merely points to the need for better electrolytes. Voltammetric and half cell studies of calcium electrodes were not carried out.

II-C. Summary

Of the systems examined, the best lithium anode performance at the highest drain rates and lowest polarization was obtained with a lithium hexafluorophosphate - N-nitrosodimethylamine electrolyte.

Screening studies and two half cell tests indicate that there may be advantages in the utilization of a calcium anode since, (1) it possesses relatively high (negative vs SHE) anodic voltages, (2) it is more stable in electrolytes than lithium, thus opening a wider range of utility to calcium systems, and, (3) it has demonstrated capability to perform at high current densities in screening tests, specifically up to 120 ma/cm^2 at -1.6V vs Ag/AgCl.

There is, as yet, no basic understanding of lithium electrode discharge mechanisms in various electrolytes. The wide variation in the open circuit voltage of anodes should be studied to determine the cause of these deviations. It is likely that organic electrolyte components or impurities are adsorbed on the anode and thereby reduce the effective active surface in certain cases. This could be verified by further voltammetric studies of specific systems.

III. CATHODES

III-A Introduction

An important objective of the program was to study and, if possible, select promising cathode materials for a nonaqueous high-energy density primary battery. The selection is dependent on other factors in addition to the theoretical energy density of the electrode active material. The two cathodes which were studied in most detail were (1) cupric fluoride (CuF_2) and (2) silver oxide (AgO). The best capacity results were obtained with silver oxide, 108 WH/lb. at the low 0.5 ma/cm^2 rate and 81 WH/lb. at the medium 5 ma/cm^2 rate. Cupric fluoride cathodes have been reported to deliver better energy densities than found in this work at the low (0.5 ma/cm^2) rate(12), and at higher rates with limited shelf life and low temperature range systems(13). The silver oxide-lithium couple possesses a theoretical energy density of about 500 WH/lb., and a battery with this combination should yield between 100-200 WH/lb. at medium discharge rates. It appears that the silver oxide system is of sufficient promise to warrant further work.

Experimental work done in this laboratory and by other investigators working on high energy systems indicate that the cathode problem is the most complex and difficult to solve(14). This is not too surprising if one considers that solid cathodes are much more complex than metal anodes. For example, it is usual that a cathode is comprised of most or all of the following components:

1. An active material consisting of a compound of varying complexity ranging from dissolved metal ions to simple binary metal salts and to complex metal salts or even more complex organic compounds.

2. A conductive additive which must be a good electronic conductor and be stable in the system.

3. A binder which must at least provide mechanical reinforcement of the active material. It must adhere to the solid particles without appreciably masking the surfaces or inactivating the surface interface. It may also perform other functions such as wicking the electrolyte into the cathode, etc.

4. An electron conducting substrate or support which is usually a metal of low resistivity and both retains the active materials and performs the function of a current collector and path to the external circuit. It is often preferable that this collector does not enter either chemically or electrochemically into the cathode reaction(s).

5. Other additives to improve electrode properties may also be used.

It was recognized that certain of the above constituents might not be essential or that one constituent might serve several functions. Therefore, an attempt at isolating the key characteristics of cathodes was made in this program. A further consideration of this approach suggests that these factors might have to be evaluated in a comparative way by the fabrication and study of different types of electrodes, namely:

1. Pasted cathodes (insoluble)

2. Thin film cathodes

3. Soluble cathodes

4. Organic cathodes

5. Nonstoichiometric or semiconducting cathodes requiring no conductive additives

The thin film electrode, or cathode in this case, is defined as one which is formed or grown directly on the metal substrate (base). Thin film electrodes are employed extensively in single electrode studies since intimate contact of the active material with the substrate is obtained, and the formation conditions are usually more reproducible. Thin film CuF_2 electrodes were formed on copper in an anhydrous HF - 1m KF solution as the final effort of the cathode study (section III-F).

Variations in the methods of fabricating a particular type of cathode further complicates the problem of evaluation. Examples of such fabrication variables include:

1. Nature of support (substrate), i.e., material or element
2. Substrate form (sheet, expanded, sintered, screen metal)
3. Active material nature (chemical composition)
4. Active material form (crystals, sheets, powders)
5. Conductive additive nature (chemical composition)
6. Conductive additive form (particle size, powder, wire, surface area)
7. Composition (amounts of substrate, active material, and additives)
8. Physical factors affecting fabrication
    a. Temperature
    b. Pressure of compression
    c. Electrolytic formation

  - d. Sizing of mix particles
  - e. Impregnation and drying
  - f. Other

Thus, it can be seen that the possible variables in cathode preparation alone can be considered overburdening from a scientific standpoint, and one is therefore inclined to resort initially to an empirical approach.

III-B Experimental

A brief outline of the research program which was followed during this project to study cathodes is given below:

1. Cathode fabrication
2. Chemical stability of cathode materials in electrolytes
3. Constant current screening tests
4. Film formation studies of cathodes
5. Cathode polarization and discharge studies
   - a. Coulombic efficiency
   - b. Effect of drying materials and assembled cathodes
   - c. Voltammetric analysis
   - d. Silver oxide
6. Organic cathode materials
7. Thin film CuF_2 electrode potential and discharge tests

III-B-1 Fabrication

The principal method of fabrication was to form pasted electrodes. Most of these electrodes contained either cupric fluoride powder or silver oxide powder as the active material. Expanded metal grids or wire screens of silver, copper and nickel served as the electrode support members. The most frequently used conductive additives were Columbian Carbon Co. carbon black (14R-22), Fisher Scientific metallic copper powder, copper powder formed by hydrogen reduction of cupric fluoride, Shawinigan acetylene black, Dixon graphite, and silver powder. Either Solka Floc (Brown Co.) or filter paper pulp (Fisher) were utilized as a binder. To increase electrode porosity several attempts were made to add materials to the cathode mix which would or could be removed later to increase porosity. The first material used for this purpose was phenol which was removed by sublimation after the electrode had been fabricated. With filter cake type cupric fluoride electrodes, lithium perchlorate solid or phenyltrimethylammonium hexafluorophosphate solid was added in small amounts in the expectation that as these salts dissolved from the cathode, voids would be formed and porosity increased. The only other additives used in pressed electrodes for specific purposes were LiF, SbF_3 and "Maracel E", a lignosulfonate derivative from the Marathon Division of the American Can Company.

Other fabrication techniques which were tried included:

1. Sintering CuF_2 onto grids of copper and aluminum foil, copper-nickel screen and aluminum, silver and nickel expanded metal.

2. Soluble cathode active materials were usually not tested as a solid matrix. Rather the cathode active material was dissolved either in the electrolyte or in some other suitable solvent. Carbon in various forms was usually employed as the cathode current collector. Nickel screen, platinized nickel screen, and platinized carbon were also used. Porous carbon cups were used to contain the cathode solution in those cases in which it appeared desirable to separate the cathode solution from the electrolyte and anode. Organic cathode materials were soluble to varying extents in the electrolytes. In a very few cases attempts were made to utilize organic cathode active materials in pasted electrodes (see section III-e).

3. Some experimental work was done with nonstoichiometric compounds such as PbO_2 and MnO_2. A limited effort was made to improve the cathodic reactivity of nickel oxide, nickel fluoride and cupric fluoride by impurity "doping" but this work was not successful.

In the fabrication of compressed types of electrodes, two important variables are temperature and pressure. All pasted electrodes were dry pressed, cold pressed or hot pressed. Pressures ranged from about 1,400 to 15,00 lbs/cm^2. Temperatures for hot pressing or sintering were usually relatively low, i.e., from 50-300°C. For pressed, sintered thin layers of CuF_2, the active material was sized to pass a 120 mesh sieve. The electrode fabrication technique utilized most often involved pasting in which the same sequence of steps was usually followed. As an example, cupric fluoride was blended with 5% acetylene black and 5% Solka-floc plus small amounts of other additives. The components of the cathode mix were placed in an electric blender with 600 ml of hexane and blended for 5 minutes. After blending, the mixture was filtered on a Buchner funnel and dried in a vacuum desiccator at ambient temperature. The screen grid electrodes were made with an area of either 2 cm^2 (both sides) or 52 cm^2 (2" x 2"). Electrodes prepared most recently were usually compressed at pressures of 2500 lb/cm^2.

In summary it can be stated that of the various fabrication techniques used in this program, not one was completely satisfactory. However, the pasted-pressed electrode was usually prepared because it appeared to be the most satisfactory technique for making high capacity cathodes.

III-B-2 Cathode Stability Studies

Stability tests for cathode materials were made in both the organic solvents alone and in the various electrolyte systems. The majority of cathode materials were eliminated from further evaluation because they showed some deterioration or solubility. The criteria for evaluation were visual observations of decomposition or dissolution and specific conductance measurements of the solutions to indicate ionic contamination as shown in Table XII, pp. V-124 through V-144. It will be noted that the first group of tests listed in Table XII were of 24 hours' duration and were therefore used to screen a large number of cathode-electrolyte combinations. The more extensive stability tests selected for this table are for CuF_2, AgO and lithium metal in contact with NDA solvent and NDA electrolytes. Toward the end of the program both CuF_2 and AgO were studied under well controlled conditions in regard to drying, purification and characterization. These later experiments were therefore much more definitive than the initial experiments.

III-B-3 Constant Current Screening Tests

The constant current discharge method used to screen anodes (see Section II) was used with cathodes as well. It was found that considerably lower current densities were permissible for most cathode materials used in this test, and modification of the anode polarization procedure was necessary. The inorganic compounds which were tested as cathode active materials in this program are listed in the following table in which active material mixtures tested are also included.

INORGANIC CATHODE MATERIALS

Insoluble

cupric fluoride (CuF_2)
cobalt trifluoride (CoF_3)
manganese dioxide (MnO_2)
lead dioxide (PbO_2)
nickel oxide (NiO)
nickel hydroxide $Ni(OH)_2$

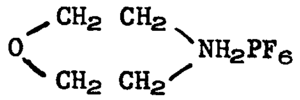
nickel fluoride (NiF_2)
cuprous sulfide (Cu_2S)
silver (II) oxide (AgO)
titanium trifluoride (TiF_3)
silver III oxynitrate ($Ag_7O_8NO_3$)
silver difluoride (AgF_2)

Mixtures

CuF_2 - CoF_3
CuF_2 - FeF_3
CuF_2 - LiF
CuF_2 - SbF_3
$CuCl_2 \cdot 3CuO \cdot 4H_2O$
Ag_2O - AgF_2
AgO - CuF_2

Soluble

aresenous tribluoride (AsF_3)
cupric chloride ($CuCl_2$)
morpholinium hexafluorophosphate



sulfuric acid
cuprous chloride ($CuCl$)
cupric-cuprous chloride
water (H_2O)

Some of the cathode materials listed above were evaluated in only small cell tests at constant current since it was already known that they were electrochemically active. This particularly was true of a few of the soluble salts such as cupric chloride.

Many half-cell constant current screening tests of cathodes were made during this program and are fully described in the quarterly reports(5-11). Both CuF_2 and AgO were studied extensively in NDA electrolytes by this screening procedure, and the results given in Table XIII, pp. V-145 through V-148, for these cathodes illustrate variables introduced and the data obtained from this technique. The importance of pretreatment of the NDA solvent and solutions was stressed in these tests.

III-B-4 Film Formation Studies

Cupric fluoride cathodes have demonstrated poor reproducibility and low efficiency in most of our tests. This lack of reporducibility and low efficiency might be attributed to several factors, and one of the more important of the possible factors is passivation due to film formation. Our work has definitely indicated that film formation does occur with cupric fluoride cathodes in certain organic electrolytes.

Test results for KPF_6 and $LiPF_6$ in NDA indicate the passivation is occurring at the cathode in both electrolytes. The inability of the cathodes to perform at the same voltage levels at 10 ma/cm^2 after being loaded to higher current densities supports this conclusion. A further demonstration of passivation was found with lithium salts, for which repeated runs at 10 ma/cm^2 showed an increase in polarization. However, scraping the cathode surface to remove the film led to a recovery of the open circuit potential to approximately its original value or more positive values and regenerated the cathode's ability to perform at 10 ma/cm^2. Thus, the passivation is most likely caused by film formation. In a single test with the $LiClO_4$-PC electrolyte, similar behavior was observed, although after a three-day stand, it was no longer possible to improve performance by scraping the cathode surface. The behavior with phenyltrimethylammonium hexafluorophosphate was somewhat different in that even though the initial open circuit value was not recovered by repeated scraping, the performance at 10 ma/cm^2 was approximately the same after each scraping.

The current-time behavior of CuF_2 cathodes held at constant potentials in $LiPF_6$-NDA and KPF_6-NDA electrolytes are depicted in Figure 11, pages V-150 and V-151. In light of the evidence for film formation taking place at higher current densities during constant current screening in these electrolytes, it is interesting to note in the single run shown in Figure 11b, page V-151, that the CuF_2 in KPF_6-NDA was still operating after 45 hours with its potential held constant at -0.25V vs. Ag/AgCl. This result indicates that film formation is dependent on other factors in addition to the rate of discharge.

X-ray diffraction studies of discharged cupric fluoride electrodes show that lithium fluoride is generally present on the discharged cupric fluoride electrode surface. The CuF_2 cathodes used in the electrochemical tests were removed from the electrolyte at the end of the test and allowed to dry in an argon atmosphere. Their surfaces were then examined by x-ray diffraction to determine what reaction products might be present.

The results of the x-ray analysis of sixteen (16) discharged CuF_2 cathodes are given in Table XIV, page V-152. The patterns were identified by comparison with standard patterns run for all the materials which might possibly be present, namely, LiF, KF, NH_4F, $LiPF_6$, KPF_6, NH_4PF_6, CuF_2, $CuF_2 \cdot 2H_2O$, CuOHF, CuO, and Cu_2O. The fact that CuF_2 was not found in every case indicates that preferred orientation may result in incomplete determinations. It is interesting to note that LiF was the only fluoride product found, even in the presence of excess K and NH_4 ions. The appearance of Cu_2O may be attributed to reaction of the active cathode material with water inasmuch as the gas chromatographic results demonstrate that approximately 1000ppm H_2O may be present in the solvent.

Prevention of the formation of lithium fluoride requires that either fluoride or lithium ions must not be permitted in the region of the cathode surface. Since fluoride ions are released at the cathode, the major sources of lithium ions at the cathode have to be eliminated if lithium fluoride formation is to be prevented, and two major sources are evident. The first is the lithium anode, and the second could be the electrolyte solute. If we simply do not use a lithium salt as the electrolyte solute, this eliminates one of the possible sources, but a lithium anode presents a difficult problem with a practical cell. The introduction of a soluble fluoride could possibly result in the precipitation of insoluble LiF at or near the anode and prevent lithium ions from reaching the cathode. Since the cesium, potassium and lithium fluoride salts exhibit the solubility relationship $CsF > KF > LiF$ in water, several experiments were tried using these dried solutes in NDA solutions. These experiments were not valid in NDA, however, since an inverse solubility relationship ($LiF > KF > Cs$) was actually found(10).

III-B-5 Cathode Polarization and Discharge Studies

The initial work indicated that a more comprehensive investigation of electrode passivation was necessary to determine the cause(s) and eliminate or minimize them. Single electrode tests showed that the open circuit values of passivated electrodes did not recover overnight. To provide a more comprehensive investigation, half-cell constant current discharges, voltammetry, vapor phase chromatography, and x-ray diffraction were used as tools in this work. The areas studied included the effect of electrolyte constituents and their pretreatment on the performance as well as the effects of mass transport, cathode composition, cathode drying techniques and of high and low rate discharges on coulombic efficiency. Voltammetric sweep studies were conducted with electrolytes and cathode-electrolyte systems. Thin film CuF_2 electrodes were prepared by anodization of a copper substrate in anhydrous hydrogen fluoride and investigated as the final phase of the cathode study.

The electrolyte solvent emphasized in these studies was N-nitrosodimethylamine (NDA). In addition, a few voltammetric studies were carried out in propylene carbonate. The solutes studied were as follows: lithium hexafluorophosphate ($LiPF_6$), potassium hexafluorophosphate (KPF_6), ammonium hexafluorophosphate (NH_4PF_6), and lithium perchlorate ($LiClO_4$) in NDA. Lithium perchlorate was the only solute studied in propylene carbonate. After studying the effect of electrolyte composition on performance, we selected and emphasized the 1 molal potassium hexafluorophosphate (KPF_6) in nitrosodimethylamine (NDA). This system was selected because it gave better and more reproducible results than other solutes with pressed cupric fluoride cathodes.

Cathodes were prepared in most cases by blending 90% cupric fluoride (CuF_2), 5% filter paper pulp (FPP), and 5% acetylene black (AB). In a few cases, additional additives to those mentioned above were used, and the amount of cupric fluoride was then reduced slightly to 89 or 89.5%. All cathode mixes contained 5% filter paper pulp as a binder, and 5% acetylene black as a conductive addive. When other additives were used, they were either Maracel "E"*, lithium fluoride or both. Cathode blends were all prepared by placing the components in an electric blender with 600 ml of hexane and mixing for 5 minutes. The material was then collected on a filter and dried in a vacuum desiccator at ambient temperature. Test pellet was prepared by pressing approximately 0.3g of the cathode blend onto a 1 cm^2 Cu expanded metal screen at 2500 lbs load for 2 minutes at ambient temperature.

III-B-5a Efficiency Studies of Cathodes

Half-Cell Constant Current Discharges of Cupric Fluoride Cathodes

A specific constant current discharge test program was set up initially to accomplish two purposes: (1) to backup and verify voltammetric studies indicating passivation and film formation, and (2) to study the effect of electrolyte components and pretreatments on film formation(11). This test program was later altered after it became evident that film formation occurred. The test program utilized in the verification of film formation and electrolyte effects is described in the 10th Quarterly Report(11).

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* Product of Marathon Division, American Can Company

The solutes and electrolytes used in the screening tests were usbjected to a variety of treatments. The effect of these treatments on cathode performance at 2.5 ma/cm^2 is illustrated by the test results in the voltage-time curves, given in Figures 12a, 12b and 12c, pages V-153 to V-155. Comparison of the coulombic efficiencies obtained in these constant current tests, as demonstrated by the plotted curves, was used as the basis for deciding which treatment had resulted in the best cathode performance.

Cathode Performance Using Electrolyte Solutes as Received From the Supplier

The first set of tests was run using the hexafluorophosphate solutes as received from the supplier in NDA which had been vacuum distilled from the molecular sieves 4A and contained approximately 600-1000 ppm of moisture. These tests provide a starting point for comparison to determine what beneficial effects, if any, are derived from various treatments of the solutes and electrolytes. The average coulombic efficiencies in these tests were 5.4% and 3.8% for the $LiPF_6$ and KPF_6 electrolytes, respectively. The efficiency for the NH_4PF_6 electrolyte was 8.6%; however, most of this discharge took place at voltages more negative than -0.9V vs Ag/AgCl where, the electrolyte participated in the reduction.

III-B-6 Effects of Drying and Pretreatment

III-B-6a Solutes and Electrolytes

The effect on cathode performance of drying the electrolyte solutes for 4 hours under vacuum at 50°C was investigated(11). Tests with the $LiPF_6$-NDA electrolyte gave erratic results, but the results with KPF_6-NDA demonstrated a definite improvement in cathode performance with the dried solute as compared to the tests with the "as received" material. The poor results and lack of performance changes with changes of variables in the $LiPF_6$-NDA tests make it impossible to draw any conclusions about cathode performance in this electrolyte.

Inasmuch as improved performance was obtained by drying the solutes for 4 hours, $LiPF_6$ and KPF_6 were dried for 24 hours under vacuum at 50°C to determine whether a longer drying time has a definite effect on cathode performance. The $LiPF_6$-NDA system yielded an efficiency of 3% which again is not significantly different from the results with other treatments. With KPF_6-NDA, efficiencies of only 9.6% and 8.8% were obtained with two tests.

The effect of contacting the electrolytes, prepared with the dried solutes, with lithium metal was also examined. Lithium metal pieces were placed in the electrolytes, and the solutions were stirred for 2 hours. With the $LiPF_6$-NDA, an efficiency of 4.4% was obtained.

After the electrolyte had stood in contact with the Li overnight, a second test was run which yielded a 3.3% coulombic efficiency. These results are not significantly different from those obtained in tests without the Li treatment. Similar behavior was found with the KPF_6-NDA system where the 7.8% coulombic efficiency obtained was approximately the same as those resulting without Li treatment. Since all the discharges in NH_4PF_6-NDA appeared to involve reduction of some component of the electrolyte, no further tests were made with this solute.

In general, the results with $LiPF_6$-NDA electrolytes were not satisfactory, and since the reason for the unsatisfactory performance is not resolved, it does not yet lend itself without further characterization to a systematic study of cathode performance. With NDA and PC electrolyte systems tested, there was evidence of film formation in that cleaning of the electrode surface by scraping allows further discharge to be carried out. Some of the filming problem may be ascribed to the electrolyte solute since purification of this material, particularly in the case of KPF_6, caused significant changes in the discharge characteristics of the cathodes. A one (1) molal potassium hexafluorophosphate (KPF_6) in nitrosodimethylamine (NDA)(11) was therefore selected for further study. This system was selected because better performance and reproducibility were obtained with cupric fluoride electrodes with this electrolyte than with other electrolytes tested. The 1m KPF_6-NDA electrolyte was prepared with potassium hexafluorophosphate which had been vacuum dried at 50°C for 24 hour and N-nitrosodimethylamine which had been vacuum distilled. The quantity of electrolyte required for each test was 10 ml unless otherwise noted. In the remaining tests, the cathodes of cupric fluoride utilized in the above electrolyte were prepared in the same manner as reported earlier. In general, the cathodes all contained 5% filter paper pulp (FPP) as a binder and 5% acetylene black (AB) as a conductive filler. The amount of cupric fluoride varied from 89 to 90% depending upon the amount of additional additives (Maracel "D" or lithium fluoride) used.

III-B-7 Other CuF_2 Cathode Studies

The Effect of a Lignosulfonate Dispersive (Maracel "E") on Performance and Filming of Cupric Fluoride Cathodes

It is well known in the battery art that additives are sometimes necessary to obtain good performance, e.g., expanders in lead-acid batteries, lithium in nickel-cadmium cells, etc. One component of such expanders is a dispersive material known as Maracel "E", a mixture of sodium lignosulfonates which are derivatives of lignin from the paper making process. It must also be recognized that the Maracel "D" might contribute impurities such as moisture to the system.

With the addition of 0.5% Maracel "E", the coulombic efficiencies (13.4 and 13.6%) were significantly improved over runs without the additive, but unfortunately cathode performance was still far from satisfactory. Other quantities of Maracel "E" and additions of lithium fluoride did not improve results significantly although efficiencies between 14 and 24% were obtained. Thus, the use of the Maracel "E" or combinations of it with lithium fluoride while improving performance did not eliminate the problem of poor cathode performance at medium rates of discharge.

The Effect of Drying Techniques on CuF_2 Performance

A group of cathodes was tested which contained no additives except filter paper pulp and acetylene black. This group was dried 24 hours with flowing argon at 50°C. The results are not very good as shown in runs 1-6, (Table XV-B, pages V-157 and V-158).

In order to further compare the effectiveness of different drying techniques, a group of cathodes was dried 24 hours at 50°C under vacuum, and another group was dried 24 hours in an argon stream at 50°C. Both groups contained 0.5% Maracel "E" and 0.5% LiF, and solvent vacuum distilled off of P_2O_5. There was no significant performance difference between the two groups.

The Effect of Mass Transport on CuF_2 Performance

The effect of mass transport on performance and filming of cupric fluoride electrodes was investigated in cells in which the electrolyte was quiescent and in cells in which the electrolyte was stirred. The coulombic efficiencies (see Table XV, page V-156, Nos. 1-5) indicated that with cupric fluoride electrodes the quiescent solutions yielded higher efficiencies, 8.2 and 9.0%, than electrodes in the stirred solutions, which yielded only 5.5 and 6.0%. In one case where 50 ml of electrolyte were utilized instead of 10 ml and the solution was stirred, the efficiency was only 7.0% (not significantly improved over the stirred 10 ml runs). It is possible that one or more species (e.g., H_2O in the electrolyte reacts at the cathode surface, and stirring brings these materials to the cathode surface more rapidly than diffusion or convection which would be the modes of transport in quiescent solutions. Another possibility is that the products of the anode (lithium) reaction are swept over to the cathode more rapidly by stirring and interact with the fluoride ion as a deposit on the cathode.

III-C Voltammetric Sweep Studies of Cathode-Electrolyte Systems

Linearly varying potential studies were made of a number of cathode-electrolyte systems to determine whether they would show passivation or filming phenomena. LVP characteristics of various types of CuF_2 cathodes in KPF_6-NDA, $LiClO_4$-NDA, $LiClO_4$-PC, $(C_6H_5)(CH_3)_3NPF_6$-NDA; AgSCN in KPF_6-NDA and $CuCl_2 \cdot 2H_2O$ in KPF_6-NDA were investigated. In addition, the characteristics of a Cu wire in KPF_6-NDA were examined over the voltage region of interest to determine residual effects. The results of these studies are illustrated in Figures 13 and 14, pages V-159 through V-176. With the exception of the Cu wire and $CuCl_2 \cdot 2H_2O$, all of the initial scans were started at the open circuit voltage of the cathode. The voltage was scanned towards more negative voltages, reversed, and scanned back to approximately 0V, (vs Ag/AgCl). Then, without interruption, the second scan was run. All of the CuF_2 systems and the AgSCN system showed a loss in peak current in the second scan which is ascribed to passivation of the electrode surface during the first scan. The $CuCl_2 \cdot 2H_2O$ cathode did not show any signs of passivation. In Figures 19-b and 19-c, scan 3 was run after the cathode had been held at a positive potential for a short time (30 seconds), and some oxidation had taken place. The scans obtained after this oxidation indicated that the surface had been activated.

In general, the passivation of the CuF_2 cathodes appears to be a function of the cathode and may not be simply related to any specific electrolyte. The reactivation of the cathode by oxidation indicates that either the material causing passivation is removed by oxidation or that a new active material has been formed. The similarity of initial scans and scans after oxidation support the former explanation. The lack of passivation of the $CuCl_2 \cdot 2H_2O$ cathode is no doubt in part due to the solubility of this material in the electrolyte used.

III-D Silver Oxide Cathode Studies

The immediate objective of the experimental work performed with silver oxide (AgO) cathodes was to make a preliminary comparison of the passivation during discharge with that of the cupric fluoride (CuF_2) cathodes under similar conditions. The electrodes and the electrolytes as well as the electrolyte constituents were pretreated (primarily dried) in a manner which had given the best coulombic efficiencies (15-16%) with cupric fluoride cathodes. No additives such as Maracel "E" were used. The studies were all made with N-nitrosodimethylamine (NDA) as the electrolyte solvent. This solvent was pretreated to remove impurities, mainly water, by vacuum distillation from phosphorous pentoxide (P_2O_5). It was characterized by vapor phase chromatography to contain approximately 100 ppm of H_2O.

The potassium hexafluorophosphate (KPF_6) and lithium hexafluorophosphate ($LiPF_6$) solutes were vacuum-dried for 24 hours at 50°C before use.

Each of the pretreated solutes was then used to prepare 1 molal electrolyte solutions with NDA. For each experiment, a volume of 10ml of the required electrolyte solution was used. All of the experiments were carried out in a dry argon atmosphere in a drybox. The counter electrode in all cases was lithium. The reference electrode was silver-silver chloride (Ag/AgCl).

Silver oxide cathodes were prepared with blends consisting of 95% AgO and 5% filter paper pulp. Mixing was carried out in an electric blender by adding the cathode constituents to 600ml of hexane previously placed in the blender. This mixture was then blended for 5 minutes at ambient temperature after which the slurry was removed and filtered. The filter cake mixture of AgO and filter paper pulp was dried in a vacuum desiccator at ambient temperature. Cathode test pellets were prepared by pressing approximately 0.33g of the cathode blend onto a 1 cm^2 silver expanded metal substrate at 2500 lb. for 2 minutes at ambient temperature. Fabricated electrodes were then dried 24 hours in a flowing stream of dry argon at $50^\circ C$.

III-D-1 Half-Cell Constant Current Discharges of Silver Oxide Cathodes

The performance of silver oxide cathodes in molal KPF_6-NDA electrolyte was very poor. The coulombic efficiency in four runs (1-4) Table XVI, page V-177, was always less than 1%. Polarization under the normal 5ma ($\sim$ 2.5ma/cm^2) load was severe. Therefore, a reduced current, 2ma, (1ma/cm^2) was used for the coulombic efficiency studies. Even with this reduced load, the silver oxide performed as poorly as noted above. Silver oxide was essentially passivated in 1m KPF_6-NDA, whereas cupric fluoride performed best and most reproducibly in this solution with similar pretreatment.

In contrast to the performance of silver oxide in 1m KPF_6-NDA, the performance of silver oxide cathodes in 1m $LiPF_6$-NDA was much improved. The coulombic efficiencies ranged from 17.1 to 67.2% for three runs (5-7), Table XVI, pp. V-177 and V-178. Although the performance was not reproducible, the extent of passivation and premature failure is greatly reduced. Cupric fluoride electrodes showed much less polarization (0.21 volts) under similar conditions, but the coulombic efficiency was poor ($< 15\%$). The two NDA electrolyte systems discussed above were the only ones investigated with the AgO cathode. It is also evident that much more experimental work is required to characterize this system.

III-E Organic Cathode Material Studies

Organic compounds are of particular interest for high-energy batteries due to the theoretically high energy densities which they exhibit. An extensive survey of organic depolarization has recently been reported by Gruber et al(16). These authors state that the best organic cathodes are generally of four types, namely: nitro compounds (RNO_2), positive halogen compounds (ROX and RNX), halogen addition compounds (R_3NX_3) and peroxides (ROOR). Almost all of the organic materials evaluated in this laboratory were from the group of nitro compounds studied by Morehouse and Glicksman in tests with aqueous electrolytes(17-21). The compounds shown to be most active in aqueous solutions were selected for study in the nonaqueous solutions. In addition to the materials suggested by Morehouse and Glicksman, we also examined several chlorinating or bleaching materials produced by Monsanto Chemical Company. These were trichloroisocyanuric acid (ACL-85), dichloroisocyanuric acid (ACL-70), and the potassium salt of dichloroisocyanuric acid (ACL-59). None of the organic cathode materials tested was found to be insoluble, and films were observed on the inert HP10 Speer carbon working electrodes during the screening tests. It was, therefore, felt that these materials are not suitable for use in their present forms. Either insoluble compounds or good electrode separators must be obtained before these organic cathodes can be of use in stable high-energy density batteries. Organic cathodes might find application in reserve batteries which are activated just prior to use.

III-F Thin Film CuF_2 Cathode Study

III-F-1 Introduction

Since the investigation of compressed cupric fluoride powder cathodes showed low, variable discharge efficiencies and poor potential reproducibility, the final effort in the program was devoted to the study of thin film CuF_2 cathodes in the expectation that a more definitive explanation of these problems could be obtained. The CuF_2 powder cathode studies indicated that electrode failure in PC and NDA electrolytes was due to the formation of a passivating surface film (possibly LiF). The possibility of a poor electronic contact between the copper substrate and the CuF_2 film is minimized or eliminated by the thin film technique since the film is formed by directed anodization of this substrate. Compacted powder and pasted electrodes, by comparison, are often poorly defined, primarily due to poor electronic contact or the formation of other solid phases the active materials/conductor interface. In addition, the formation of intermediate species, such as CuF, should be more evident with thin film electrodes using controlled discharge technique.

Extensive variations in the open circuit potential and discharge capacities of cupric fluoride and other cathodes in organic electrolytes were found, and this situation was not improved by careful preparation, (See section III-B-3). Deviations of about 0.4 volt in the open circuit potentials of CuF_2 electrodes in NDA electrolytes containing either $LiPF_6$ or KPF_6 were not uncommon as illustrated by the data presented in Tables XIII and XV and Figure 17.

The CuF_2 thin film electrode study is the only phase of this program which was not fully reported in previous quarterly progress reports and is therefore reported in more detail in this report.

III-F-2 Experimental

AHF Apparatus and Procedure

Thin film CuF_2 electrodes were prepared by anodizing copper in a solution of anhydrous hydrogen fluoride (AHF) with KF as a solute by a technique which was similar to that used at Tyco Laboratories(21). Due to the extremely corrosive nature of anhydrous hydrogen fluoride the apparatus train which is illustrated in Figure 15, page V-179, was constructed from Teflon, Kel-F and polypropylene (when necessary) components. The initial collection cell and the test cell were machined from a 3" diameter Teflon rod, and the platinum wire probes shown in place in these cells (Figure 15) made possible the determination of liquid levels (volumes) as well as comparative conductivities in the collection cell. Pure anhydrous hydrogen fluoride (Matheson Company, 99.9% min.) was removed from the cylinder as a vapor (b.p. = 19.5°C) and condensed at -30°C in the collection cell. The collected liquid HF was transferred to the adjoining test cell held at 0°C by either vaporizing and recollecting, or pumping the liquid over directly. A constant stream of dried nitrogen or argon was passed through the apparatus during each experiment to remove the air which would otherwise be present. This stream could also be used to transfer liquid AHF as is seen in the apparatus schematic of Figure 15. The AHF was transferred as a liquid in all of the later experiments since this procedure was rapidly done and the probability of H_2O pick-up was reduced.

The test cell cover was provided with openings for three copper wire test electrodes, a copper wire coil reference electrode, a platinum wire counter electrode and a platinum wire liquid-level sensing electrode. Copper electrodes were usually prepared from either 50 mil or 65 mil electrolytic copper wire. Platinum and copper wires were covered with heat-shrinkable Teflon tubing which made possible a defined electrode area in the AHF-KF solution as well as a tight seal at the cover opening. In most of the experiments, the Teflon sheathing was removed to expose from 1mm (.053cm^2 of 50 mil and .074cm^2 of 65 mil wire) to 1cm (0.412cm^2 of 50 mil and 0.54/cm^2 of 65 mil wire) sections of the copper. The exposed copper was first cleaned in nitric acid and rinsed with distilled water before dipping in acetone and drying in an argon atmosphere. The copper reference electrode and the platinum wire electrode were treated by the same procedure. Kel-F wax was used as a sealant around each wire at the cover opening, and the cover was held tightly against the cell base with a special clamp.

Either 50 or 75 mls of liquid AHF was added to the test cell which contained a weighed amount of dried KF necessary to produce a 1 molal solution. Other concentrations were tested in initial experiments and provided no evident advantage.

At the end of each experiment the AHF solution was transferred to trap A from which an option of two methods existed for its disposal as shown in Figure 15. The HF could be removed either as a vapor by warming trap A and applying a gentle vacuum with the water pump, or the liquid HF could be run into an open stainless steel flask containing MgO powder in a large excess of CaF_2 crystals as a diluent. The latter procedure was usually followed since it was found to be the most rapid and safest disposal method. All operations were carried out in a laboratory hood.

The electrodes and apparatus were prepared and cleaned prior to each experimental run which required from 6 to 12 hours to complete.

Electrochemical Instrumentation

Cupric fluoride thin films were formed and reduced by a voltammetric procedure in which the current-potential curves are recorded on an X-Y plotter. The versatile electrochemical instrument employed was almost identical to that described by Underkofler and Shain(23), and the linear varying potential technique has been discussed in this program(5). Well-regulated constant currents (for micropolarization and reduction measurements) were provided by a North-Hills model CS-120 Precision Current Source. The Moseley Model 2D-2AM X-Y Recorder is provided with a built-in time base which was used in certain film reduction measurements. Potentials were measured with either a Hewlett-Packard 412A VTVM or a Kiethley Model 601 electrometer.

III-F-3 Chemicals and Purification

Particular effort was devoted to obtaining the purest materials possible for studies in the AHF and organic electrolyte media. The purest chemicals available were obtained and further purified with specific attention to the removal of water. Water contents of particulate crystals were determined by the Karl Fisher method which has an accuracy of about ± 10% in the 100 ppm range. Water concentrations of the NDA and PC solvents were determined by gas chromatography which has been found to be a reliable technique for measuring down to the 30 ppm range. Both solutes and solvents were stored in stoppered containers in an argon-atmosphere dry box, and all handling and electrochemical testing was carried out in this dry box.

Sources, pretreatments and analyses of the materials employed in this study are summarized below:

Solutes

Lithium hexafluorophosphate, anhydrous ($LiPF_6$) -- Purchased from Ozark Mahoning Company. No purification was attempted. Karl Fisher water analysis showed the water concentration to be 43.7 ppm.

Potassium hexafluorophosphate, anhydrous (KPF_6) -- Purchased from Matheson Scientific Company. Dried under vacuum at 200°C for four days. Karl Fisher water analysis showed the water concentration to be 135 ppm.

Potassium floride, anhydrous (KF) -- Purchased from Allied Chemical Company. Dried under vacuum at 130°C for four days. Karl Fisher water analysis showed the water concentration to be 41 ppm.

Lithium perchlorate, anhydrous ($LiClO_4$) -- Purchased from Fisher Scientific Co. Recrystallized from distilled water and dried at 180°C for seven days. Karl Fisher water analysis showed the water concentration to be 600 ppm.

Solvents

Hydrogen fluoride, anhydrous (HF) -- Purchased from Matheson Scientific Company. Specified as 99.9% min mole per cent HF. Used as received.

N-nitrosodimethylamine (NDA) -- Purchased from Eastman Kodak Company. Pretreated with molecular sieve to reduce the water concentration under 100 ppm, then vacuum distilled using a reflux to collection ratio of 1:1 and discarding the first fraction. Impurities were determined by gas chromatography. A water peak showing the water concentration to be 34 ppm was the only impurity observed. A test for peroxides was negative.

Propylene Carbonate (PC) -- From Aldrich Chemical. Gas chromatographic analysis showed a low concentration of impurities. Pretreated with lithium metal to eliminate any peroxides present. Passed through dried molecular sieve to bring the water concentration under 100 ppm. The low and high boiling impurities were removed by vacuum distillation using a reflux to collection ratio of 1:1 and discarding the first fractions as well as the PC remaining in the distilling flask. The middle fractions were then vacuum distilled to remove the impurities which boil just below the boiling point of PC (241.7°C at 760mm Hg). This last distillation was accomplished by refluxing for over 24 hours and then collecting until pure PC was obtained. The PC analysis was done by gas chromatography and showed the absence of all impurity peaks except for water (approximately 50 ppm concentration) and what is suspected to be propylene glycol (approximately 70 ppm concentration).

Electrodes

Electrolytic copper wire was used as the electrode substrate in electrolysis experiments in 1 molal KF-HF (anhydrous). Spectrographic analysis from Spectro-Chemical Research Laboratories, Inc. showed the copper to be more than 99.99% pure copper.

III-F-4 Results and Discussion

Cu/CuF_2 Electrode in AHF-KF

The standard electrode potential of the $Cu/CuF_2(s)$ couple has been reported to be 0.52V positive to that of the HF (liq.)/H_2 couple in the AHF medium(24). One would, therefore, expect that copper metal would not be attacked in the absence of oxygen or other oxidizing agents and that a defined potential would not be attained in such a pure media. It was found that a thin CuF_2 film was formed on the copper wire when immersed in the AHF-KF electrolyte, and this film increased slowly with time. This finding is in agreement with that reported by Tyco Laboratories(22) in which the probable influence of oxygen impurity is discussed. The potential of the copper electrodes often varied as much as 0.2V following immersion and slowly approached a common value on standing. A comparison of the three test electrodes usually showed a potential difference of less than 10mV after standing one hour as summarized for 10 different days in the following table. The averaged result includes the three test electrodes and the Cu reference electrodes.

Daily Absolute Mean Potential Variation (mV)

Day	Unanodized (1 hr)	Anodized (1 hr)
1	7.01	2.30
2	7.90	4.70
3	7.10	3.23
4	4.10	1.23
5	6.95	16.45
6	3.33	3.60
7	7.53	6.63
8	21.0	8.87
9	12.8	3.07
10	13.86	9.17
Mean daily [absolute variation =]	9.16	5.93

Cupric fluoride film formation and electrode potential uniformity and stability were more rapidly attained following anodization as also shown in the above table. A typical voltammetric (i-v) curve is shown in Figure 16, page V-180, in which the anodic sweep is initiated at the hydrogen reduction potential region. Our results agreed in most respects with those previously reported by Tyco Laboratories, particularly in regard to the excellent reversibility of what must be the Cu/CuF_2 electrode couple and the suitability of this couple as a reference electrode in an AHF media(22). The sharp, well-defined anodic peak shown in Figure 16 was taken at a linear varying potential (LVP) scan rate of 3mV/sec and exhibits a peak current of about 100ma/cm^2 of geometric surface area. After the peak value, the current rapidly drops to a very low level which is characteristic of a highly passivating film.

No additional anodic waves were found even when the potential was allowed to increase to about 2.0V vs Cu/CuF_2. Using other voltammetric scan rates and initial potentials, it showed neither additional anodic nor cathodic peaks at potentials positive to that of the Cu/CuF_2 couple. This result is contrary to that of Tyco Laboratories which reported well-defined anodic and cathodic peaks at 0.5V(22).

In the majority of experiments the area of the anodic CuF_2 peak was equivalent to a charge input of 0.5 to 1.5 coulombs per square centimeter of geometrical surface area. Anodic charge inputs as high as 3.3 coulombs/cm^2 and as low as 25 millicoulombs/cm^2 were obtained. These low values were usually accompanied by potential instability and irreproducibility.

The appearance of the anodized electrodes was also indicative of the system purity since one might expect a white film, if only CuF_2 is obtained, and a dark gray or black film with H_2O present due to the formation of $CuF_2 \cdot 2H_2O$. The anodically prepared films ranged between these visible conditions, and the blackest deposits were accompanied by poor potential stability. Several attempts were made to determine film composition by x-ray diffraction techniques, but the results were inconclusive. This work indicated that an x-ray powder diffraction technique would be most suitable since the sample could be protected from the atmosphere.

The relatively slow cathodic reduction kinetics of the CuF_2 films in the AHF-KF solutions are also illustrated in Figure 16, page V-180. The slow discharge capability made determination of the coulombic efficiency difficult due to the increase in the background current as the hydrogen evolution potential is approached. Film reduction was investigated by constant voltage and constant current techniques, but a very slow cathodic LVP sweep (1-2mV/sec.) was found to provide the most practical method for determining coulombic efficiency. This is actually the basis for stripping analysis procedures which are becoming more widely used in electroanalytical chemistry. Calculated coulombic discharge efficiencies averaged 82% and varied from extremes of 51 to 98% with the slow LVP scan reduction procedure. This result is at variance with that reported by Tyco Laboratories which showed better reversibility and higher discharge efficiencies(22).

As an additional check on the reversibility of the electrode when it was at a potential assumed to be that of the Cu/CuF_2 couple, micropolarization measurements were also carried out on seven different days. In this test the electrode should be displaced no more than ± 10mV from its open circuit potential value by passing microampere currents in both anodic and cathodic directions, and coincident straight lines passing through the original potential indicate that the electrode couple is reversible.

A copper plate ($8cm^2$) and a copper wire coil were used as test electrodes in these measurements, and a small test wire served as the reference electrode. A small amount of hysteresis was experimentally observed and this effect is illustrated by the curve plotted in Figure 17, page V-181. This result indicates that the anodized copper electrodes are at a potential defined by a fairly reversible electrode couple.

Much of the effort in this part of the program was devoted to purification of the solute (KF) and solvents (NDA and PC) and to improvements in the apparatus and procedures to obtain higher purity in the electrochemical system.

Behavior of Thin Film CuF_2 Electrodes in PC and NDA Solutions

The reversibility and reproducibility of the thin film CuF_2 were determined in propylene carbonate and N-nitrosodimethylamine electrolytes to make a comparison with the pressed CuF_2 powder cathodes in these electrolytes. Potential reproducibility and discharge characteristics were investigated in five organic electrolytes, namely 1m KPF_6, 1m $LiPF_6$ and 1m $LiClO_4$ in propylene carbonate (PC), and 1m KPF_6 and 1m $LiPF_6$ in NDA. Further understanding of the CuF_2 electrode is gained by comparison of the behavior in the organic electrolytes with that in the AHF-1m KF solution in which the films were formed.

Preparation of the thin film CuF_2 electrodes for organic electrolyte tests was carried out in the manner described in the previous section. Potential variations between the test and reference electrodes were measured in the HF-KF media both before and after anodization. The test electrodes were first reduced and then anodized at the 2mV/sec. LVP sweep rate and the coulombic input determined with a planimeter from the area of the i-v (converted to an i-t) peak on the X-Y plot. Previous work had shown that the capacity of an anodized CuF_2 decreased relatively slowly on open-circuit stand in the AHF-KF media. This loss was found to be several per cent per hour and was determined by repeated anodic LVP scans starting at the 0.0V (vs Cu/CuF_2) potential. It has been shown that the solubility of CuF_2 in anhydrous HF is less than $2.10^{-5}M$(27) and increases with increasing water content. These results indicated that capacity decay prior to removal was not a problem during the times involved.

Transfer of the anodized electrodes to the organic solutions was accomplished by disconnecting the cover-electrode assembly and placing it on a beaker containing the purified solvent of the organic solution to be used. This assembly with submerged electrodes was immediately evacuated in the dry box entrance chamber and then transferred into the argon atmosphere. The cover assembly was finally placed on a Pyrex cell containing the purified organic test solution. Electrical connections were made, and the cell was mounted on a magnetic stirrer.

Test Results

Thin film CuF_2 cathodes were first investigated in a solution of 1m KPF_6 in PC. The averages discharge efficiency of three test electrodes was 88% in the AHF-1m KF solution. Potential reproducibility in the 1m KPF_6-PC was poor with deviations of up to 0.2V after 45 minutes of immersion. The electrode potentials were decreased at the -2mV/sec LVP cathodic scan, and no reduction was obtained before -1.8V (vs Cu/CuF_2 reference). The electrodes remained in this solution overnight, and the organic electrolyte was then analyzed for copper content. The analysis was sufficiently sensitive to show the total copper in solution to be less than 500 millicoulombs whereas the total anodized CuF_2 film content was 6.1 coulombs. This result indicates effective passivation of the electrodes in this media.

The discharge procedure 1m KPF_6-PC was repeated the following day with essentially the same result.

Thin film CuF_2 electrodes were next investigated in a 1m $LiPF_6$-PC solution, and relatively excellent discharge results were obtained as shown in Figure 18, page V-182. Well defined reduction peaks were obtained with a maximum at -0.7V (vs Ag/AgCl, see section IV-B), and more favorable reduction kinetics than found in the AHF-KF media are indicated. An average discharge efficiency of 68% was obtained for a total of four electrodes discharged on two different days. The average open circuit potential variation was about 30mV which also compares more favorably with AHF-KF electrolyte values.

Very poor potential reproducibility and discharge capacities were obtained in the 1m $LiClO_4$-PC electrolyte. One test was made with the 1m $LiClO_4$-PC electrolyte, and the result was inconclusive due in our inability to obtain a sufficiently pure system. A cathodic peak was found at -0.7V vs Ag/AgCl, but the reduction was obscured by interfering processes.

Only negligible capacities were obtained on reduction of the CuF_2 film electrodes in a 1m KPF_6-NDA electrolyte at a -2mV/sec scan rate. This result was confirmed when the experiment was repeated the following day. Residual currents measured with both silver and copper working electrodes were minimal until about -1.8V vs Ag/AgCl. Open circuit electrode potential differences were found to increase with stand time prior to cathodization. No copper was detected in the used electrolyte after standing overnight.

Essentially the same result found for the 1m KPF_6-NDA electrolyte was obtained for the 1m $LiPF_6$-NDA electrolyte. Reduction in this electrolyte was particularly difficult to evaluate due to excessive background cathodic currents. These background currents were markedly reduced by pretreatment of the solution with metallic lithium, but no improvement in capacity was thereby obtained. No copper was found by analysis of the solutions after experimentation. Four different experiments with the 1m $LiPF_6$-NDA electrolyte were conducted over a four-day period.

Cupric fluoride (Alpha Inorganics) was found to be soluble in NDA to the extent of less than 50 ppm. This solubility is undoubtedly highly dependent on water content.

III-F-5 Conclusions

The average film thickness of the CuF_2 film formed by anodization in copper in AHF-KF media can be readily calculated. If the copper surface is assumed to be covered with 3.0 coulombs of CuF_2 per cm^2 in a pure system, and the density of CuF_2 is taken as $4.85 g/cm^3$, the film thickness if found to be 3.26μ . This thickness is equivalent to approximately 7000 unit-cell layers which should be readily analyzed by x-ray diffraction.

Comparable discharge characteristics of compressed CuF_2 powder electrodes in KPF_6-PC and $LiPF_6$-PC electrolytes were not obatined in this program, and a direct comparison with the thin film results is therefore not possible. Other investigators have reported a coulombic efficiency of only 2% when a pasted CuF_2 electrode was discharged in a 1.0F KPF_6-PC electrolyte(26) which is in substantial agreement with the thin film cathode result.

Cyclic voltammetric sweep data for CuF_2 electrodes in both $LiPF_6$-PC and KPF_6-PC solutions are reported by the Whittaker Corporation(26), and their findings are in substantial agreement with those herein reported. Their CuF_2 electrodes were prepared by direct fluorination, and weight gains indicated that thin coatings were obtained. Results for copper were reported to be similar in the KPF_6-PC solution(27).

The present work has indicated that thin film electrode techniques have definite applications for the study of cathodes in nonaqueous media.

III-G Summary and Conclusions (Cathodes)

Discharge capacity results with cupric fluoride were generally poorer than the corresponding discharge capacities with silver oxide cathodes. The best performance attained with the silver oxide-lithium electrode combination gave 108WH/lb at the 0.5ma/cm^2 discharge rate. At the 5ma/cm^2 rate the energy density decreased to 80WH/lb. The electrolyte in both of these experimental systems was 1 molal lithium hexafluorophosphate ($LiPF_6$ - as received) in N-nitrosodimethylamine. After an open-circuit stand of five days, the AgO-Li cell yielded only 78WH/lb at the 0.5ma/cm^2 discharge rate.

Dried and/or pretreatment of the electrode and electrolyte components consistently reduced performance values below those obtained with the less pure materials. It was our finding and that of other investigators(14) that water impurity plays a significant role in improving the performance of cupric fluoride cathodes. Silver oxide cathodes gave only negligible coulombic efficiencies when predried electrodes were used in a dried 1m KPF_6-NDA electrolyte. On the basis of this work it appears that neither cathode can function in a truly aprotic medium.

The most significant conclusions which were derived from cathode investigation in this program are the following:

Conclusions

1. Presumably both cupric fluoride and silver oxide perform better in the presence of some moisture (or other protic impurities) rather than in a completely anhydrous environment.

2. Many of the most promising cathode materials are too soluble in the electrolyte to serve as good cathodes. This is particularly true of organic cathode materials.

3. Many cathode materials of high theoretical energy density possess virtually no semi-conducting or electronic conductance.

4. Fabrication methods are not well defined.

5. Film formation (not defined as to nature of film) causes failure of CuF_2 cathodes in both hexafluorophosphate-NDA and lithium perchlorate-propylene carbonate electrolytes.

6. Because even relatively low drain rates reduce the coulombic efficiency of CuF_2 (5ma/cm^2), it may be that film formation is also dependent on the electrode potential.

7. Highest efficiencies are generally obtained at low drain rates, but even the best coulombic efficiencies are below 75%.

8. Electrode (cathode) mechanisms in nonaqueous solutions are complex and very poorly understood.

9. Many more substances, particularly organic compounds, could be utilized as high-energy cathodes if suitable separators could be developed.

10. Ion exchange membranes examined for use with soluble cathodes have such high resistivities as to be of little value in batteries.

11. Thin film CuF_2 electrodes, formed by the anodization of pure copper wires in an HF-1mKF solution, gave reproducible open circuit potentials and discharge capacities in this media.

12. These CuF_2 thin film electrodes did not exhibit the excellent potential reproducibility in PC and NDA solutions that was found in the HF-KF solutions. Favorable discharge behavior was found with a $LiPF_6$-PC electrolyte but not in KPF_6-PC, $LiPF_6$-NDA or KPF_6-NDA solutions.

13. Thin film electrode techniques should have definite applications for the study of cathodes in organic electrolytes.

IV. OTHER COMPONENTS AND REFERENCE ELECTRODES

IV-A Separator and Case Materials

A few materials were investigated for use as separators. Among these were some "Ionics" ion exchange resins, certain filter papers, porous glass and microporous rubber. The only stable and low resistance material was the Gelman porous glass. It was, therefore, used in most of the cell tests. The ion exchange resins caused excessive iR losses in reducing the cell terminal voltage by more than one volt.

Polypropylene was tested as a case material and was found to be resistant to all the organic electrolytes to which it was exposed.

IV-B Reference Electrode Study

Silver electrodes were widely used as reference electrodes in non-aqueous solutions. The stability of the potential of these electrodes is in doubt. An alternative electrode was constructed which had the simplicity and versatility of the silver electrode, but which demonstrated considerably greater potential stability than the silver electrode. This electrode will be used in place of silver whenever precise potential measurements are required.

Figure 19, page V-183 is a schematic drawing of this alternative reference electrode. It consists of a conventional silver-silver chloride electrode in an aqueous 0.1M KCl solution separated from the working electrolyte by a suitable nonaqueous salt bridge (e.g., 1M $LiClO_4$-NDA). Small pieces of a porous glass rod (Vycor No. 7930) are used to isolate the KCl solution from the salt bridge and the salt bridge from the solution of interest. The lower end of the salt bridge is curved to permit positioning of the reference electrode very close to the working electrode. The salt bridge is designed for easy cleaning after it has been contaminated by ions from the working electrolyte and the reference electrode.

The reversibility of this electrode was investigated using the classical method of applying small overpotentials to both sides of the equilibrium and determining if there is any hysteresis, i.e., a micropolarization test. For this experiment the cell consisted of the electrode shown in Figure 24 as the working electrode, a saturated Calomel Electrode (Beckman 39170) as reference, a pyrolytic graphite rod as counter electrode and 1M $LiPF_6$-N-nitrosodimethylamine (distilled) as electrolyte. The electrolyte was neutralized with excess Li metal before use. The overpotentials were applied using potentiostatic equipment and were measured with a digital voltameter through the use of a load resistor. The overpotentials were applied manually, and the measurements were made within 10-20 seconds (after a steady value was achieved). The results are shown in Figure 20, page V-184.

On the first run, a maximum hysteresis of only 0.6mv was observed. All subsequent runs duplicated this hysteresis curve. The potential, as determined from Figure 20, of the Ag/AgCl (0.1m KCl), 1m $LiClO_4$-NDA reference electrode is -0.0249 ± 0.0003V relative to the saturated Calomel Electrode (SCE). For our experiments, a value of -0.025V versus SCE will be used. The same reversibility test was attempted with a silver electrode, but steady potentials could not be obtained.

V. FIGURES AND TABLES

TABLE I. PROPERTIES OF ETHYLENE CARBONATE-PROPYLENE CARBONATE MIXED SOLVENT

Solvent Composition			
Weight % EC	Weight % PC	Viscosity*(25°C) (Centipoises)	Dielectric Constant(25°C)
0	100	2.52	64.6
20	80	2.52	69.1
40	60	2.52	74.6
60	40	2.52	80.5
80	20	2.55	87.2
100	0	Solid	Solid

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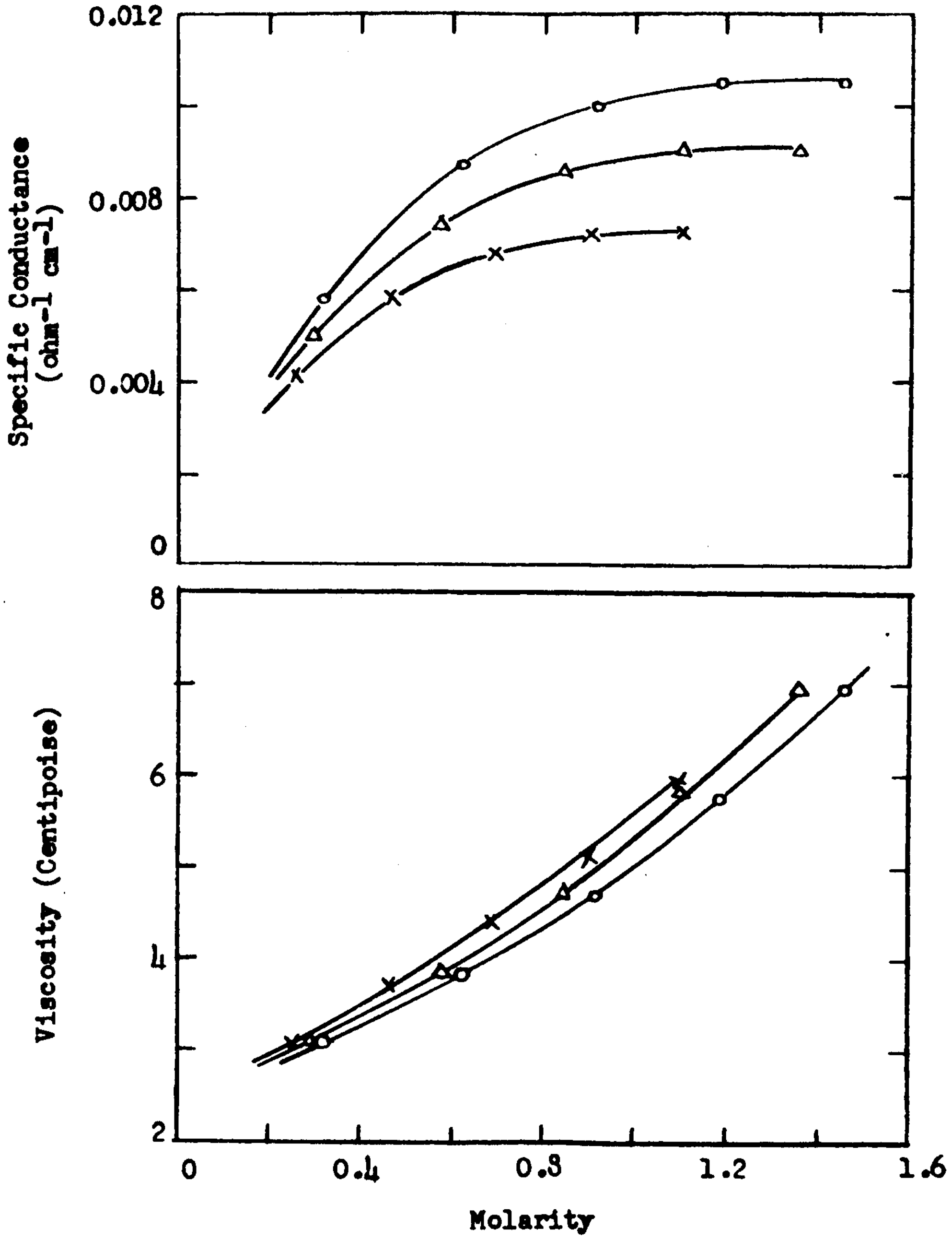
* Determined Experimentally.

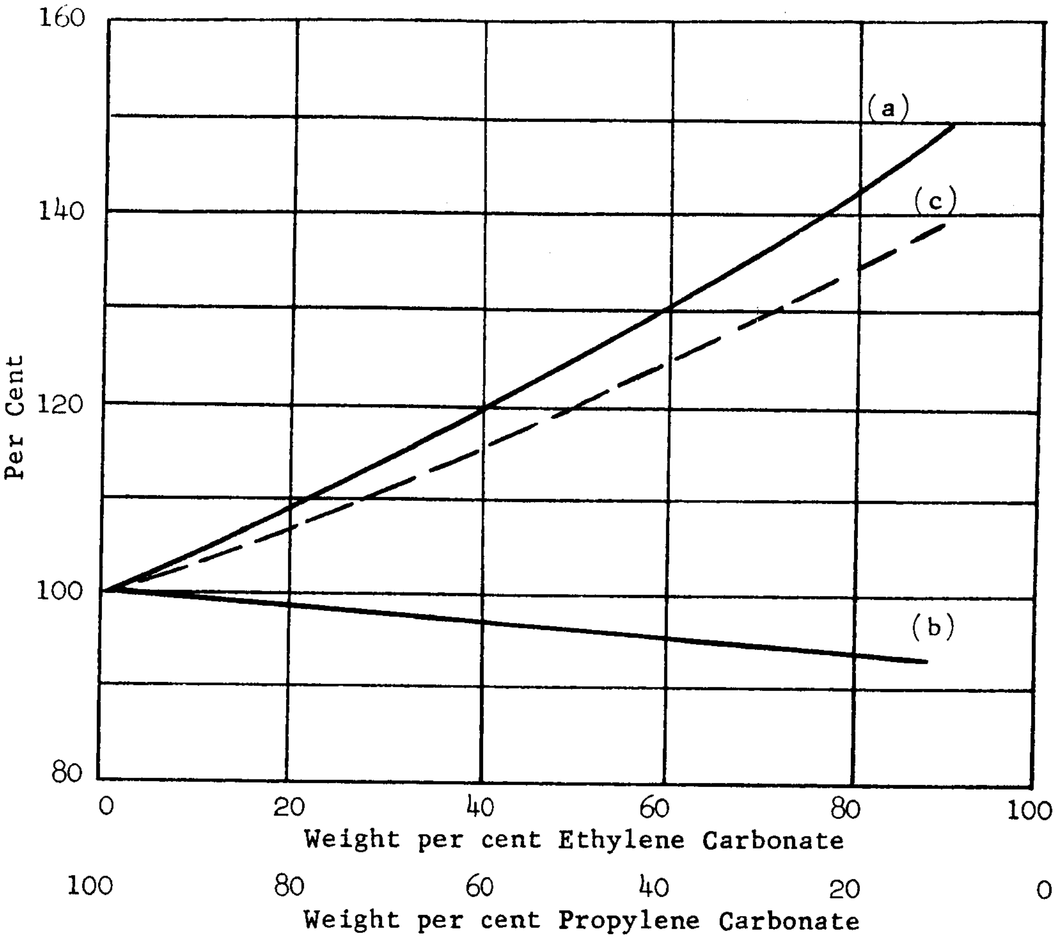
FIGURE 1. PROPERTIES OF KPF_6-ETHYLENE CARBONATE-PROPYLENE CARBONATE SYSTEM (Continued)



o KPF_6 in 80% EC + 20% PC ($\epsilon_{25°C}$ = 87.2)

△ KPF_6 in 40% EC + 60% PC ($\epsilon_{25°C}$ = 74.6)

x KPF_6 in PC ($\epsilon_{25°C}$ = 64.6)



Curves:

(a) Specific conductances (29-30°C) of one-molal KPF_6.

(b) Viscosities (25°C) of one-molal KPF_6.

(c) Dielectric constants (25°C) of solvent.

100% Values (one-molal KPF_6-PC):

Specific conductance = 8.10×10^{-3} ohm^{-1} cm^{-1} at 29°C.

Viscosity = 6.25 centipoises at 25°C.

FIGURE 2. PROPERTIES OF KPF_6 SOLUTIONS VS. EC-PC SOLVENT COMPOSITION

TABLE II. PROPERTIES OF ACETONITRILE-DIMETHYL CYANAMIDE MIXED SOLVENTS

Symbol	Volume Percent Acetonitrile	Density(25°C) (g/c.c.)	Viscosity(25°C) (Centipoise)	* Dielectric Constant(25°C)
AN	100	0.778	0.346	36.2
80 AN/20 DMC	80	0.799	0.389	36.2
60 AN/40 DMC	60	0.821	0.436	37.6
40 AN/60 DMC	40	0.842	0.499	37.8
20 AN/80 DMC	20	0.863	0.569	36.6
DMC	0	0.883	0.673	37.2

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* Relative dielectric constants based on dielectric constant of DMF = 36.7 at 25°C

FIGURE 3. PROPERTIES OF KPF_6-ACETONITRILE-DIMETHYL CYANAMIDE SYSTEM (Continued)

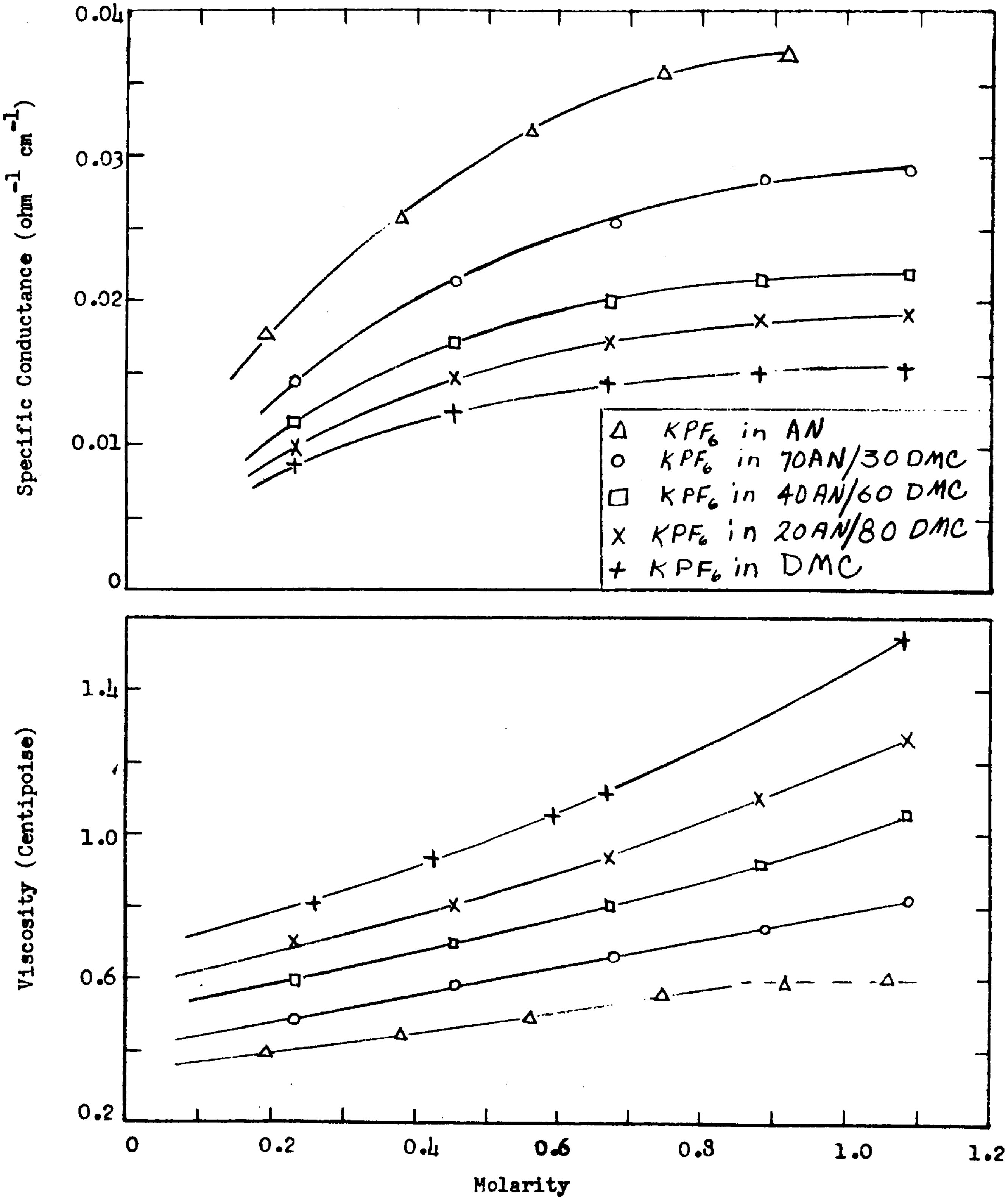

TABLE IV. SPECIFIC CONDUCTANCE OF SOLUTIONS

Solute	Specific Conductance ($\text{ohm}^{-1}\ \text{cm}^{-1}$)	Visual Observations		
		Solution	Solid	Others
	b. Acetonitrile			
* KPF_6	3.30×10^{-2} (27°C)	Clear	White	--
LiCl	4.67×10^{-4} (28°C)	Clear	White	--
* $(n\text{-}C_3H_7)_4NPF_6$ (tetra-n-propylammonium hexafluorophosphate)	3.36×10^{-2} (27°C)	Brown	--	--
$AlCl_3$	3.18×10^{-2} (26°C)	Clear	None	Exothermic heat of dissolution
NH_4PF_6 (Ammonium hexafluorophosphate)	4.20×10^{-2} (24°C)	Clear	White	None
$(n\text{-}C_4H_9)_4NCl$ (Tetra-n-butylammonium chloride)	2.23×10^{-2} (26°C)	Clear, Orange	None	None
* $(n\text{-}C_3H_7)_4NBF_4$ (Tetra-n-pro-ylammonium tetrafluoroborate)	3.60×10^{-2} (25°C)	Orange	--	--
* $(C_6H_5)(CH_3)_3NPF_6$ (N-Phenyl N,N,N-trimethylammonium hexafluorophosphate)	3.86×10^{-2} (26°C)	Clear	Slight Amount Black	--
* $(n\text{-}C_4H_9)_2H_2NAsF_6$ (Di-n-butylammonium Hexafluoroarsenate)	4.23×10^{-2} (26°C)	Clear	--	--
* $(n\text{-}C_3H_7)_3HNAsF_6$ (Tri-n-propylammonium hexafluoroarsenate)	4.40×10^{-2} (26°C)	Tan	Slight Amount Tan	--
* $(n\text{-}C_3H_7)_4NAsF_6$ (Tetra-n-propylammonium hexafluoroarsenate)	3.44×10^{-2} (25°C)	Brown	Slight Amount Gray	--
$(n\text{-}C_3H_7)_4NSbF_6$ (Tetra-n-propylammonium hexafluoroantimonate)	3.60×10^{-2} (25°C)	Light Yellow	White	--

* 1 molal solution

TABLE IV. SPECIFIC CONDUCTANCE OF SOLUTIONS (Continued)

Solute	Specific Conductance (ohm^{-1} cm^{-1})	Visual Observations		
		Solution	Solid	Others
	i. N-nitrosodimethylamine			
Black	2.37×10^{-5} (28°C)	Yellow	--	--
CaCl	9.36×10^{-5} (31°C)	Yellow	White	--
$CsPF_6$	1.42×10^{-2} (30°C)	Yellow	White	--
$KAsF_6$	2.29×10^{-2} (29°C)	Yellow	Slight Amount White	--
$NaSbF_6$	2.34×10^{-2} (29.5°C)	Yellow	White	--
* $O\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}NH_2PF_6$ (morpholinium hexafluorophosphate)	2.73×10^{-2} (29.5°C)	Yellow	--	--
* $(n\text{-}C_3H_7)_4NPF_6$ (tetra-n-propylammonium hexafluorophosphate)	2.39×10^{-2} (27.5°C)	Brown	--	--
* $(n\text{-}C_4H_8)_2NH_2AsF_6$ (di-n-butylammonium hexafluoroarsenate)	2.74×10^{-2} (30.5°C)	Yellow	--	--
$(C_6H_5CH_2)N(CH_3)_3SbF_6$ (N-benzyl N,N,N-trimethylammonium hexafluoroantimonate)	2.08×10^{-2} (28°C)	Yellow	Slight Amount Brown	--

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* One molal solutions.

TABLE IV. SPECIFIC CONDUCTANCE OF SOLUTIONS (Continued)

Solute	Specific Conductance (ohm^{-1} cm^{-1})	Visual Observations		
		Solution	Solid	Others
	i. N-nitrosodimethylamine (Continued)			
KCl	4.51×10^{-5} (30°C)	Yellow	White	---
* KPF_6	2.03×10^{-2} (29°C)	Yellow	Slight Amount White	---
* $KPF_6 \cdot 4TMU$	1.46×10^{-2} (31°C)	Turbid	---	---
LiCl	1.08×10^{-3} (30°C)	Yellow	White	---
NH_4SO_3F	1.20×10^{-2} (24.5°C)	Clear	White	---
$NaBF_4$	1.91×10^{-3} (25°C)	Clear	White	---
$NaPF_6$	2.15×10^{-2} (27°C)	Tan	Small Amount Tan	---
* $(n\text{-}C_3H_7)_4NBF_4$ (Tetra-n-propylammonium tetrafluoroborate)	2.15×10^{-2} (25°C)	Orange	---	---
* $(n\text{-}C_3H_7)_3HNAsF_6$ (Tri-n-propylammonium hexafluoroarsenate)	2.35×10^{-2} (25°C)	Yellow	---	---
$(n\text{-}C_4H_9)_4NCl$ (Tetra-n-butylammonium chloride)	1.16×10^{-2} (27°C)	Yellow	---	0.99 Molal Solution
$(C_6H_5)_4PCl$ (Tetraphenylphosphonium chloride)	1.37×10^{-2} (24.5°C)	Orange	White	---

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* One molal solution

TABLE IV. SPECIFIC CONDUCTANCE OF SOLUTIONS (Continued)

Solute	Specific Conductance (ohm^{-1} cm^{-1})	Visual Observations		
		Solution	Solid	Others
	i. N-nitrosodimethylamine (Cont'd)			
* $(CH_3)_4NPF_6$ (Tetramethylammonium	8.21×10^{-3} (26°C)	Clear, yellow	Large amount, white	None
$(C_6H_5)(CH_3)_3NPF_6$)N-Phenyl N,N,N-trimethylammonium hexafluorophosphate)	2.32×10^{-2} (28°C)	Dark green	Small amount, dark	None
$(p\text{-}C_{12}H_{25}C_6H_4CH_2)(CH_3)_3NPF_6$ (N-(p-Dodecylbenzyl) N,N,N-trimethylammonium hexafluorophosphate)	1.13×10^{-2} (26°C)	Clear, yellow	Tan	None
$(n\text{-}C_3H_7)_4NAsF_6$ (Tetra-n-propylammonium hexafluoroarsenate)	2.08×10^{-2} (26°C)	Clear, brown	Tan	None
$(C_6H_5)_4AsCl$ (tetraphenylarsonium chloride)	1.32×10^{-2} (26°C)	Clear, yellow	White	None
$AlCl_3$	2.06×10^{-2} (27°C)	Clear, tan	Slight amount, white	Exothermic heat of dissolution
$FeCl_3$	1.72×10^{-2} (26°C)	Clear, brown	Tan	None
** $K_3Cr(SCN)_6$	1.94×10^{-2} (30°C)	Clear, purple	None	None
* KI	8.82×10^{-3} (30°C)	Clear, orange	Large amount, white	None
* $MgCl_2$	1.08×10^{-2} (27°C)	Clear, yellow	Large amount, white	None

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All solutions were one molal unless noted to be saturated or of another concentration

* saturated

** 0.5 molal

TABLE IV. SPECIFIC CONDUCTANCE OF SOLUTIONS (Continued)

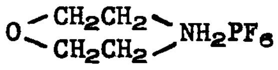
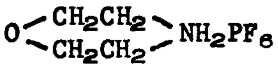
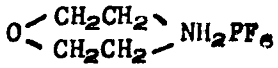
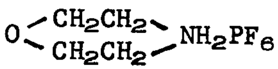
Solute	Specific Conductance (ohm^{-1} cm^{-1})	Visual Observations		
		Solution	Solid	Others
	j. Propylene Carbonate			
$KAsF_6$	8.80×10^{-3} (25°C)	Clear	White	--
$NaSbF_6$	7.26×10^{-3} (26.5°C)	Turbid	White	--
* $(C_6H_5)N(CH_3)_3PF_6$ (N-phenyl N,N,N-trimethylammonium hexafluorophosphate)	9.70×10^{-3} (28+°C)	Cloudy	--	--
* $(n\text{-}C_3H_7)_4NPF_6$ (tetra-n-propylammonium hexafluorophosphate	1.00×10^{-2} (29°C)	Clear Brown	--	--
 $O{<}\genfrac{}{}{0pt}{}{CH_2CH_2}{CH_2CH_2}{>}NH_2PF_6$ (morpholinium hexafluorophosphate)	1.03×10^{-2} (26°C)	Clear	Slight Amount White	--
* $(C_6H_5CH_2)N(CH_3)_3SbF_6$ (N-benzyl N,N,N-trimethylammonium hexafluoroantimonate)	8.15×10^{-3} (25°C)	Yellow	--	--
	k. 60% Propylene Carbonate + 40% Ethylene Carbonate			
KPF_6	9.78×10^{-3} (29°C)	Clear	Slight Amount White	--
 $O{<}\genfrac{}{}{0pt}{}{CH_2CH_2}{CH_2CH_2}{>}NH_2PF_6$ (morpholinium hexafluorophosphate)	1.14×10^{-2} (26°C)	Clear	Slight Amount White	--
$(C_6H_5)N(CH_3)_3PF_6$ (N-phenyl N,N,N-trimethylammonium hexafluorophosphate)	1.05×10^{-2} (26°C)	Gray	Black	--
	l. 40% Propylene Carbonate + 60% Ethylene Carbonate			
KPF_6	1.06×10^{-2} (30°C)	Clear	Slight Amount White	--
 $O{<}\genfrac{}{}{0pt}{}{CH_2CH_2}{CH_2CH_2}{>}NH_2PF_6$ (morpholinium Hexafluorophosphate)	1.22×10^{-2} (26.5°C)	Clear	White	--

TABLE IV. SPECIFIC CONDUCTANCE OF SOLUTIONS (Continued)

Solute	Specific Conductance (ohm^{-1} cm^{-1})	Visual Observations		
		Solution	Solid	Others
m. 20% Propylene Carbonate + 80% Ethylene Carbonate				
FeF_3	1.14×10^{-4} (27°C)	Turbid	White	--
LiCl	9.31×10^{-4} (26°C)	Turbid	White	--
$KAsF_6$	1.21×10^{-2} (25°C)	Clear	White	--
KPF_6	1.16×10^{-2} (29°C)	Clear	Slight Amount White	--
$NaSbF_6$	8.81×10^{-3} (26°C)	Clear	White	--
$Na(CF_3COO)$ (sodium trifluoroacetate)	1.38×10^{-3} (27°C)	Turbid	White	--
* $SbCl_3$	2.76×10^{-4} (27°C)	Clear	--	--
SbF_3	1.21×10^{-4} (30°C)	Clear	White	--
 $O(CH_2CH_2)_2NH_2PF_6$ (morpholinium hexafluorophosphate)	1.31×10^{-2} (25°C)	Clear	Slight Amount White	--
$(C_6H_5)N(CH_3)_3PF_6$ (N-phenyl N,N,N-trimethylammonium hexafluorophosphate)	1.12×10^{-2} (25°C)	Gray	Black	--
$(C_6H_5CH_2)N(CH_3)_3SbF_6$ (N-benzyl N,N,N-trimethylammonium hexafluoroantimonate)	9.85×10^{-3} (25°C)	Yellow	Slight Amount Black	--
* $MgCl_2$	4.52×10^{-3} (27°C)	Turbid	Large amount, white	None
$(n\text{-}C_3H_7)_4NPF_6$ (Tetra-n-propylammonium ammonium hexafluorophosphate)	1.20×10^{-2} (27°C)	Clear, orange	None	None
$(n\text{-}C_4H_9)_4NCl$ (Tetra-n-butylammonium chloride	8.15×10^{-3} (27°C)	Clear, orange	None	None
n. 10% Propylene Carbonate + 90% Ethylene Carbonate				
KPF_6	1.22×10^{-2} (30°C)	Clear	Slight Amount White	--

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* 1 molal solution

TABLE V. X-RAY POWDER PATTERN DATA FOR VARIOUS LITHIUM HEXAFLUOROPHOSPHATE SAMPLES

	$LiPF_6$[a]		Lot 1				Lot 2		$LiPF_6$ (dried)		$LiPF_6 \cdot H_2O$		LiF
			1a		1b								
	"d" (A)	I	"d" (A)	I	"d" (A)	I	"d" (A)	I	"d" (A)	I	"d" (A)	I	
1.	4.23	4	4.33	13	4.20	10	6.36	7	4.23	23	4.57	36	2.31
2.	4.03	10	4.23	19	4.00	os[b]	5.30	5	4.04	36	4.41	8	2.01
3.	3.54	10	4.07	69	3.85	5	4.18	83	4.00	50	4.13	39	1.42
4.	2.551	3	3.92	7	3.51	os[b]	4.04	55	3.52	59	3.86	30	1.22
5.	2.418	2	3.54	os[b]	2.80	2	3.81	5	2.32	58	3.06	6	
6.	2.186	1	2.83	3	2.54	3	3.53	os[b]	2.13	68	3.03	3	
7.	2.124	10	2.57	20	2.17	12	2.54	22.5	2.01	63	2.98	3	
8.	2.019	2	2.43	52	2.12	40	2.12	33	1.77	9	2.81	7	
9.	1.853	2	2.20	38	2.01	5	2.10	7	1.60	12	2.77	2	
10.	1.768	8	2.13	45	1.77	9	1.78	17	1.56	5	2.56	33	
11.	1.629	1	2.11	5	1.63	2	1.76	15	1.42	29	2.43	21	
12.	1.600	8	2.05	2	1.60	74	1.60	13	1.38	2	2.33	os[b]	
13.	1.562	5	2.02	3	1.56	5	1.597	16	1.36	3	2.28	28	
14.	1.528	1	1.85	49	1.43	5	1.55	44	1.27	3	2.20	49	
15.	1.502	1	1.77	71	1.42	3	1.44	8	1.21	10	2.11	33	
16.	1.435	3	1.60	32	1.38	3	1.43	4			2.03	9	
17.	1.421	3	1.57	10	1.36	6	1.42	3			2.02	os[b]	
18.	1.378	3	1.53	9	1.35	7	1.36	3			1.93	2	
19.	1.360	4	1.51	9	1.25	3	1.35	2			1.85	32	
20.	1.346	2	1.47	1	1.23	2	1.27	5			1.65	10	
21.	1.269	3	1.44	6	1.22	18	1.268	7			1.53	13	
22.	1.220	3	1.42	3	1.21	2	1.24	3			1.50	12	
23.	1.202	2	1.38	3			1.22	4			1.49	2	
24.	1.178	4	1.36	8							1.47	3	
25.	1.163	4	1.30	3							1.43	37	
26.	1.128	2	1.27	17							1.37	3	
27.	1.109	1	1.23	3							1.32	2	
28.	1.0721	2	1.22	11							1.30	3	
29.	1.0619	3	1.20	2							1.28	4	
30.	1.0517	3									1.24	5	

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[a] Prof. D. W. Sharp, The University of Strathclyde, Glasgow, Scotland, private communication.

[b] Off scale.

TABLE V. X-RAY POWDER PATTERN DATA FOR VARIOUS LITHIUM HEXAFLUOROPHOSPHATE SAMPLES (Continued)

	$LiPF_6$[a]		Lot 1				Lot 2		$LiPF_6$ (dried)		$LiPF_6 \cdot H_2O$		LiF
			1a		1b								
	"d" (A)	I	"d" (A)	I	"d" (A)	I	"d" (A)	I	"d" (A)	I	"d" (A)	I	
31.	1.0112	2									1.23	2	
32.	0.9945	3									1.22	8	
33.	0.9754	1											
34.	0.9670	2											
35.	0.9480	2											
36.	0.9344	3											
37.	0.9090	2											
38.	0.8827	2											
39.	0.8635	2											
40.	0.8609	1											
41.	0.8514	2											
42.	0.8317	2											
43.	0.7996	2											
44.	0.7816	1											
45.	0.7757	1											

TABLE VI. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS

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* No viscosity data are available for these solutions.

TABLE VI. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

a. KPF_6-Acetonitrile

Molarity	Specific Conductance (ohm^{-1} cm^{-1})	Density (g/c.c.)	Viscosity (Centipoise)
0.193	1.75×10^{-2} (28.5°C)	0.809 (25°C)	0.396 (25°C)
0.380	2.56×10^{-2} (28.5°C)	0.831 (25°C)	0.438 (25°C)
0.563	3.16×10^{-2} (28.5°C)	0.853 (25°C)	0.490 (25°C)
0.747	3.57×10^{-2} (28.5°C)	0.885 (25°C)	0.550 (25°C)
>0.747 *	3.70×10^{-2} (28.5°C)	0.903 (25°C)	0.592 (25°C)
>0.747 *	3.66×10^{-2} (28.5°C)	0.900 (25°C)	0.601 (25°C)

* Saturated

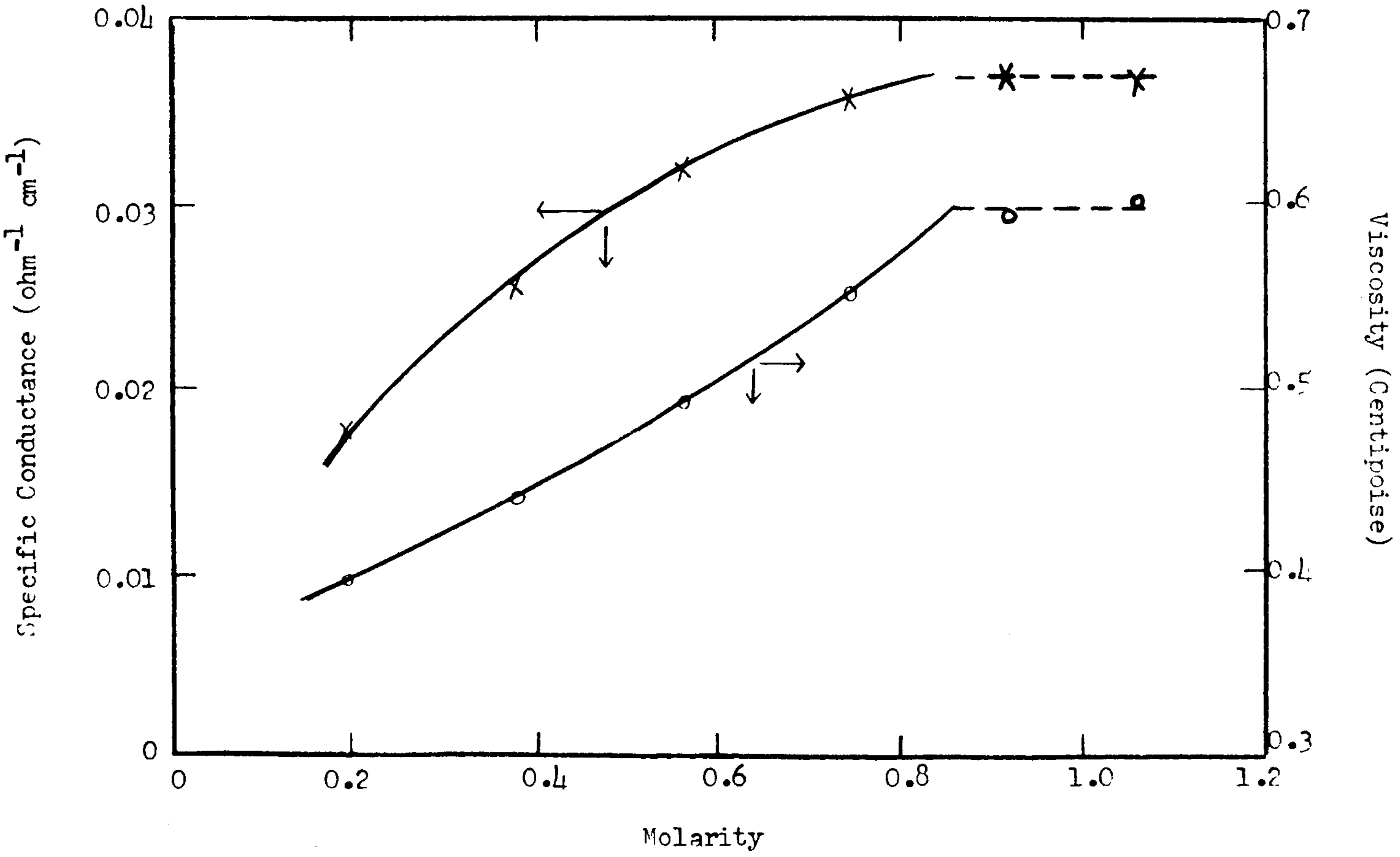


TABLE VI. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Cont'd)

b. $NaPF_6$-Acetonitrile

Molarity (25°C)	Specific Conductance (ohm^{-1} cm^{-1})	Density(25°C) (g/c.c.)	Viscosity(25°C) (Centipoise)
0.382	3.08×10^{-2} (25°C)	0.829	0.453
0.568	3.83×10^{-2} (25°C)	0.853	0.515
0.750	4.30×10^{-2} (27°C)	* 0.876	--
0.929	4.80×10^{-2} (25°C)	0.899	0.649
** .929	5.08×10^{-2} (25°C)	0.918^{+}	0.710
** .929	5.08×10^{-2} (25°C)	0.916^{+}	--

* Interpolated value
** Saturated

Note: Small amount of solid impurity present in every sample.

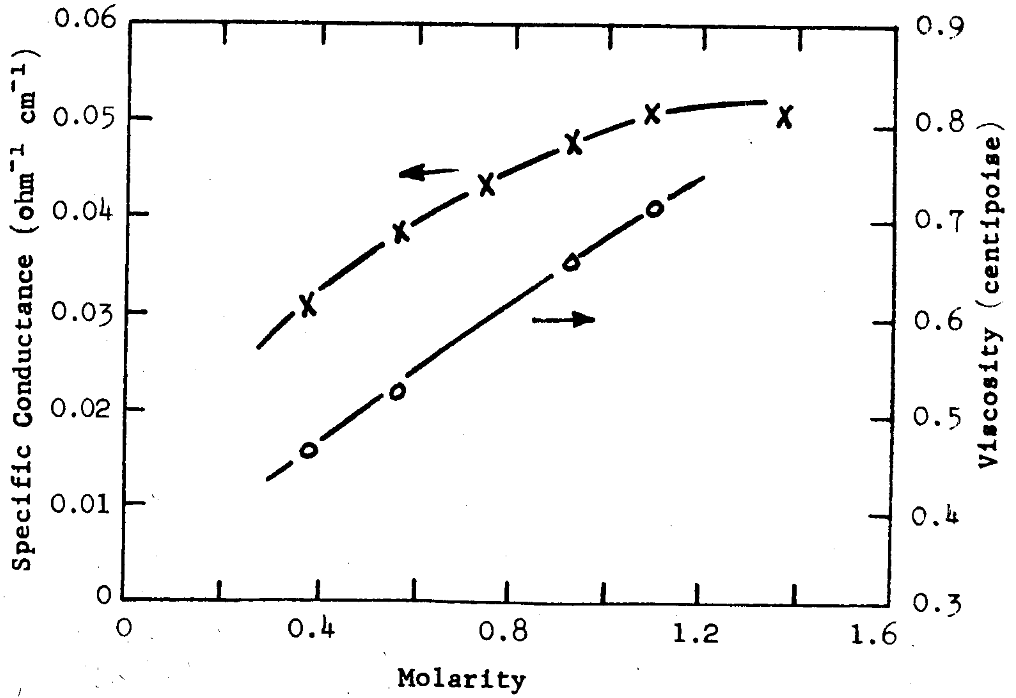


TABLE VI. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Cont'd)

c. $NaSbF_6$-Acetonitrile

Molarity (25°C)	Specific Conductance (ohm^{-1} cm^{-1})	Density(25°C) (g/c.c.)	Viscosity(25°C) (Centipoise)
0.379	3.10×10^{-2} (25°C)	0.856	0.454
0.560	3.92×10^{-2} (25°C)	0.891	0.505
0.735	4.63×10^{-2} (27°C)	* 0.925	--
0.902	5.00×10^{-2} (25°C)	0.956	0.624
** 0.902	5.02×10^{-2} (25°C)	0.962	0.647
** 0.902	5.02×10^{-2} (25°C)	0.966	--

* Interpolated value
** Saturated

Note: White solid impurity present in every sample.

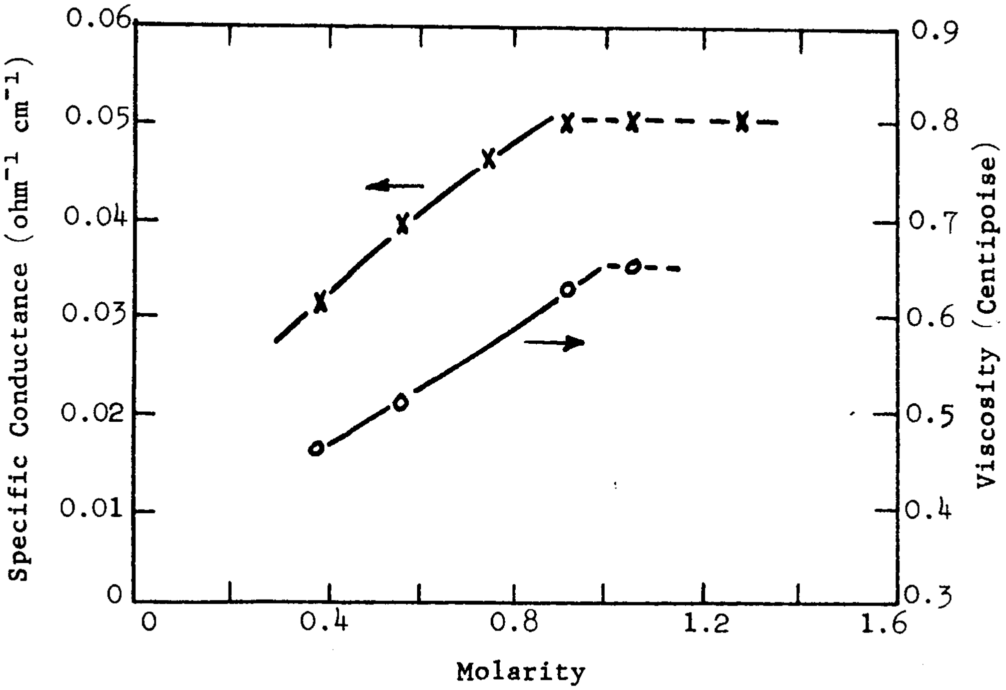


TABLE VI. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

d. N-Phenyl N,N,N-Trimethylammonium Hexafluorophosphate-Acetonitrile

Molarity	Specific Conductance (ohm^{-1} cm-1)	Density (g/c.c.)	Viscosity (Centipoise)
0.189	1.67×10^{-2} (25°C)	0.809 (25°C)	0.396 (25°C)
0.364	2.70×10^{-2} (26°C)	Δ 0.831 (25°C)	---
0.685	3.86×10^{-2} (26°C)	Δ 0.877 (25°C)	---
0.991	4.31×10^{-2} (26°C)	0.926 (25°C)	0.693 (25°C)
1.24 *	4.45×10^{-2} (26°C)	Δ 0.968 (25°C)	---
1.315 *	4.55×10^{-2} (26°C)	Δ 0.982 (25°C)	---
1.43 *	4.50×10^{-2} (27°C)	0.985	0.976 (25°C)

* Solid present (concentration uncertain).
Δ Interpolated values

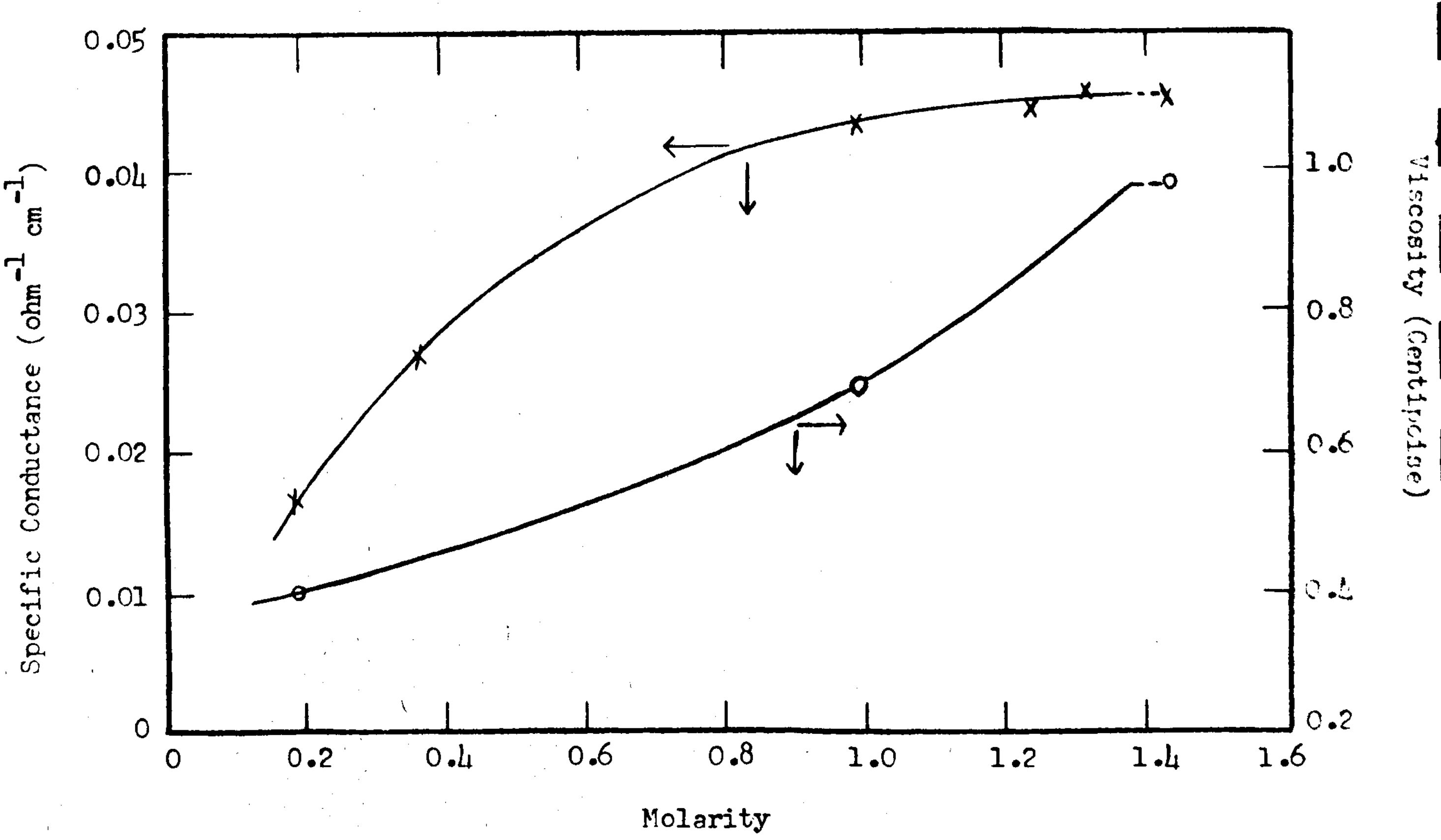


TABLE VI. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Cont'd)

e. $NaPF_6$-Dimethylformamide

Molarity (25°C)	Specific Conductance (ohm^{-1} cm^{-1})	Density(25°C) (g/c.c.)	Viscosity(25°C) (Centipoise)
0.370	1.53×10^{-2} $(26^{-\circ}C)$	* 0.986	--
0.482	$1.83^{-} \times 10^{-2}$ $(27^{+\circ}C)$	0.999	1.18^{+}
0.637	2.12×10^{-2} $(27^{-\circ}C)$	* 1.017	--
0.898	$2.37^{+} \times 10^{-2}$ $(25^{+\circ}C)$	* 1.048	--
0.991	2.44×10^{-2} $(26.5^{\circ}C)$	1.059	1.94
1.15	2.43×10^{-2} $(26^{+\circ}C)$	* 1.077	--
1.41	2.39×10^{-2} $(26.5^{\circ}C)$	1.102	2.98
1.63	2.22×10^{-2} $(26.5^{\circ}C)$	* 1.130	--

* Interpolated or extrapolated value

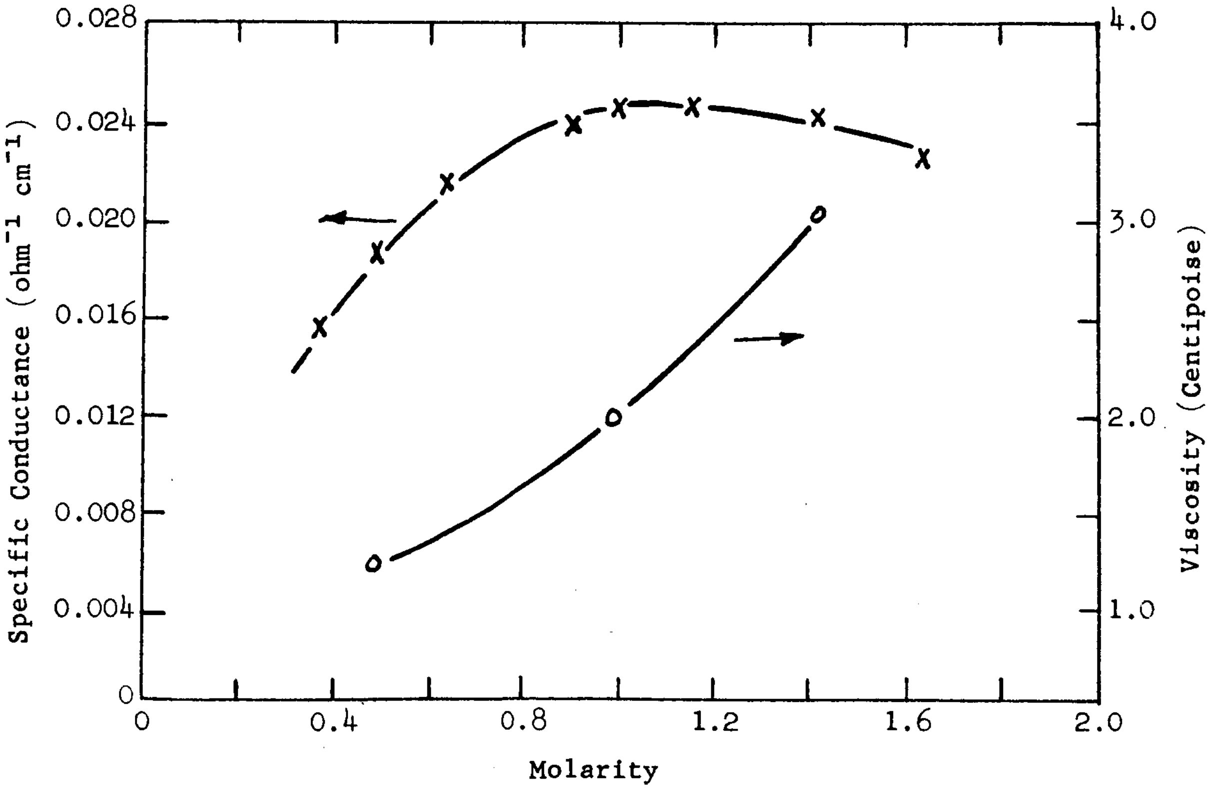


TABLE VI. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

f. Morpholinium Hexafluorophosphate-Dimethylformamide

Molarity	Specific Conductance (ohm^{-1} cm^{-1})	Density (g/c.c.)	Viscosity (Centipoise)
0.229	1.21×10^{-2} (29°C)	Δ 0.967 (25°C)	---
0.442	1.99×10^{-2} (30°C)	Δ 0.988 (25°C)	---
0.835	2.70×10^{-2} (29°C)	1.029 (25°C)	1.44 (25°C)
1.515	3.00×10^{-2} (29°C)	1.111 (25°C)	2.59 (25°C)
2.05	2.67×10^{-2} (29°C)	1.163 (25°C)	4.25 (25°C)
2.50	2.23×10^{-2} (30°C)	1.204 (25°C)	7.01 (25°C)
2.86	1.66×10^{-2} (28.5°C)	1.239 (25°C)	11.6 (25°C)
3.18	1.29×10^{-2} (30°C)	1.270 (25°C)	17.9 (25°C)

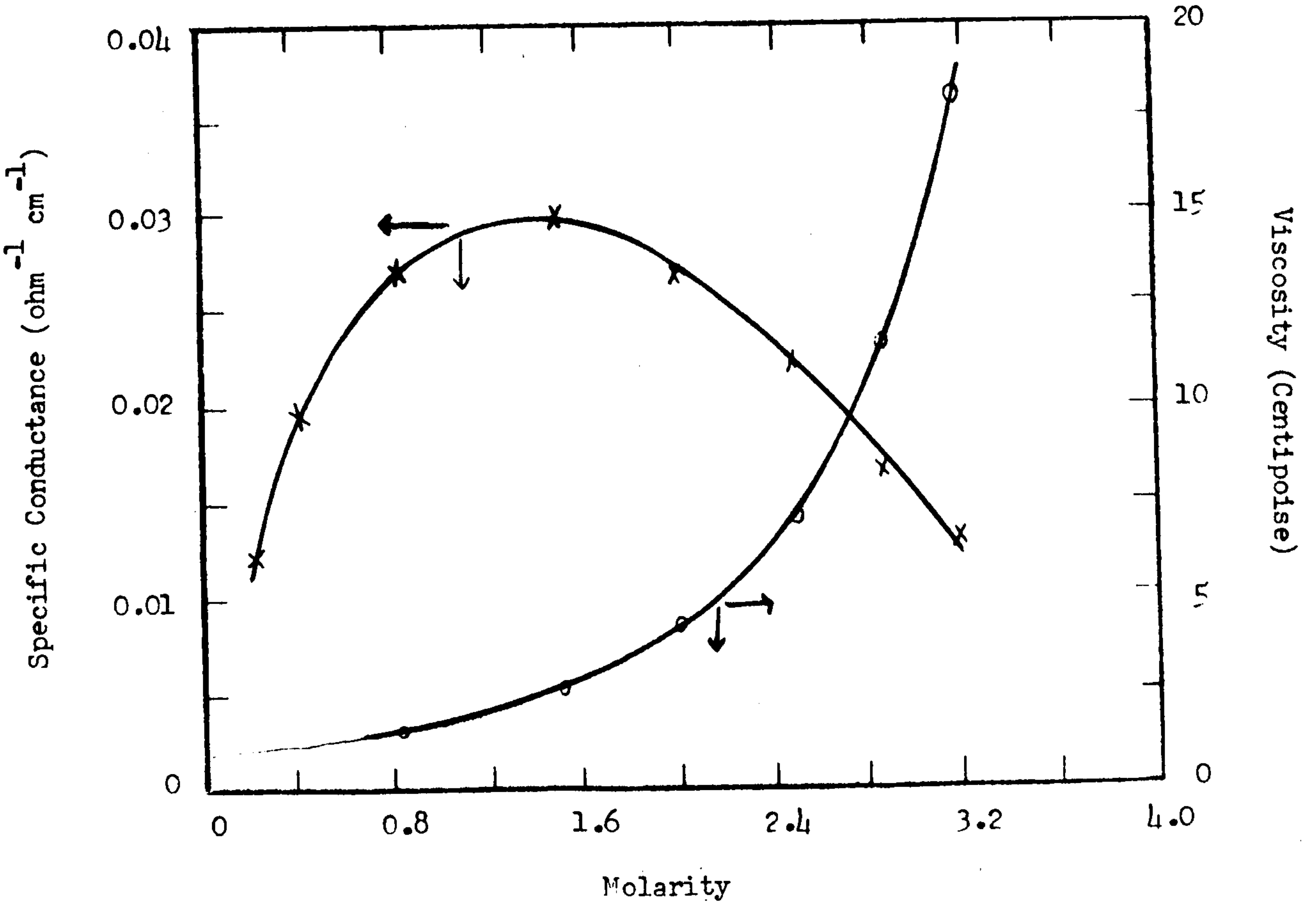


TABLE VI. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

g. N-Phenyl N,N,N-Trimethylammonium Hexafluorophosphate-Dimethylformamide

Molarity (25°C)	Specific Conductance (ohm^{-1} cm^{-1})	Density (25°C) (g/c.c.)	Viscosity (25°C) (Centipoise)
0.433	1.605×10^{-2} (26^{-}°C)	0.990	1.135
0.802	$2.12^{+} \times 10^{-2}$ (26°C)	1.027	1.475
1.115	$2.26^{+} \times 10^{-2}$ (26^{-}°C)	1.058	1.90^{+}
1.39	$2.18^{+} \times 10^{-2}$ (26^{-}°C)	1.085	2.39
1.63^{-}	2.04×10^{-2} (26^{-}°C)	1.109	3.04

NOTE: Slight amount solid impurity present in every sample.

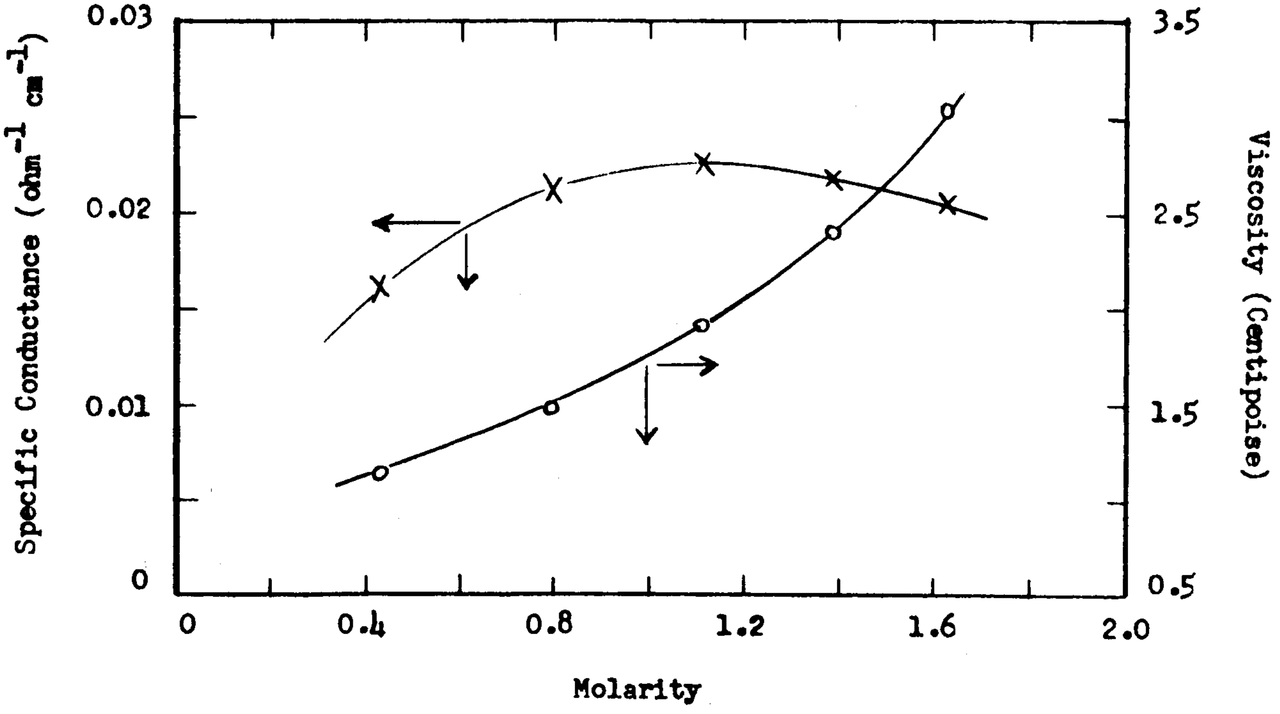


TABLE VI. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Cont'd)

h. $NaPF_6$-N-nitrosodimethylamine

Molarity (25°C)	Specific Conductance (ohm^{-1} cm^{-1})	Density(25°C) (g/c.c.)	Viscosity(25°C) (Centipoise)
0.391	1.495×10^{-2} $(25^{+o}C)$	* 1.043	--
0.675	1.94×10^{-2} $(25^{+o}C)$	1.074	1.385
0.946	2.10×10^{-2} $(25^{+o}C)$	* 1.104	--
1.21	2.13×10^{-2} $(25^{+o}C)$	1.133	2.27
1.46^{+}	2.05×10^{-2} $(25^{+o}C)$	* 1.160	--
1.70^{+}	1.96×10^{-2} $(25^{+o}C)$	1.182	3.40^{-}

* Interpolated or extrapolated value

Note: Small amount of tan solid present in every sample.

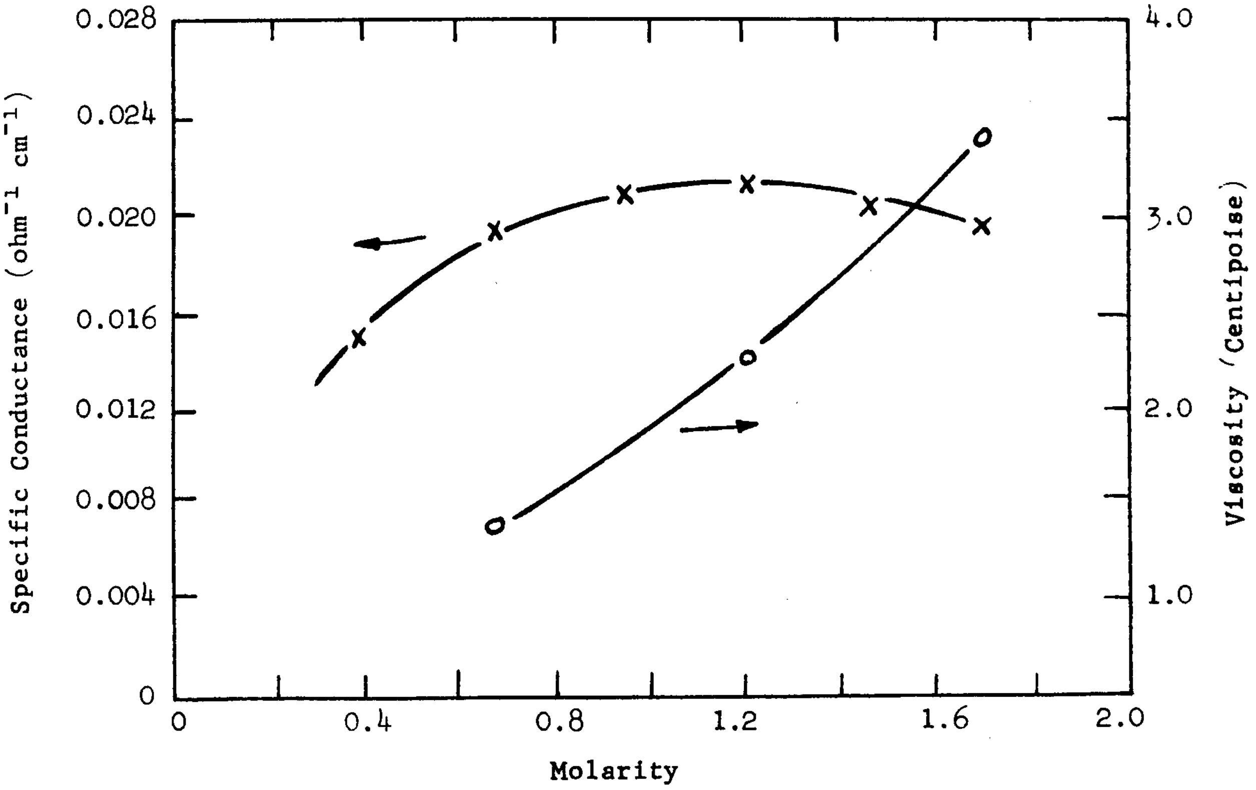


TABLE VI. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

i. Tetra-n-propylammonium hexafluorophosphate-N-nitrosodimethylamine

Molarity (25°C)	Specific Conductance (ohm^{-1} cm^{-1})	Density(25°C) (g/c.c.)	Viscosity(25°C) (Centipoise)
0.235	1.20 x 10^{-2} (27°C)	1.016	0.966
0.441	1.79 x 10^{-2} (31°C)	1.028	1.125
0.789	2.26 x 10^{-2} (30°C)	1.050	1.485
1.07	2.25 x 10^{-2} (29°C)	1.066	1.92
1.30	2.12 x 10^{-2} (29°C)	1.080	2.39

Note: Small amount of brown solid present in every sample

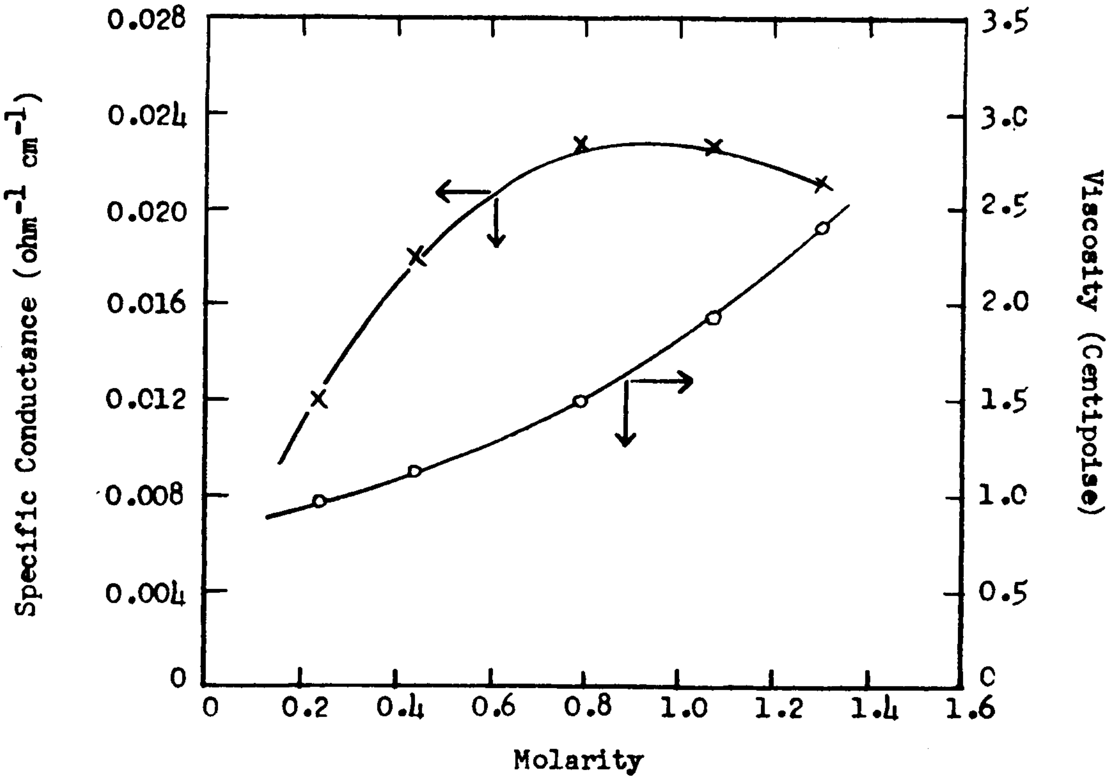


TABLE VI. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

j. KPF_6-Nitrosodimethylamine

Molality		Specific Conductance (ohm^{-1} cm^{-1})
0.199		1.05×10^{-2} (31°C)
0.398		1.51×10^{-2} (30°C)
0.580		1.83×10^{-2} (30°C)
0.796		2.00×10^{-2} (30°C)
0.995		2.10×10^{-2} (30°C)
1.195	(Solid Present)	2.14×10^{-2} (30°C)
1.39	(Solid Present)	2.14×10^{-2} (30°C)
1.99	(Solid Present)	2.15×10^{-2} (31°C)

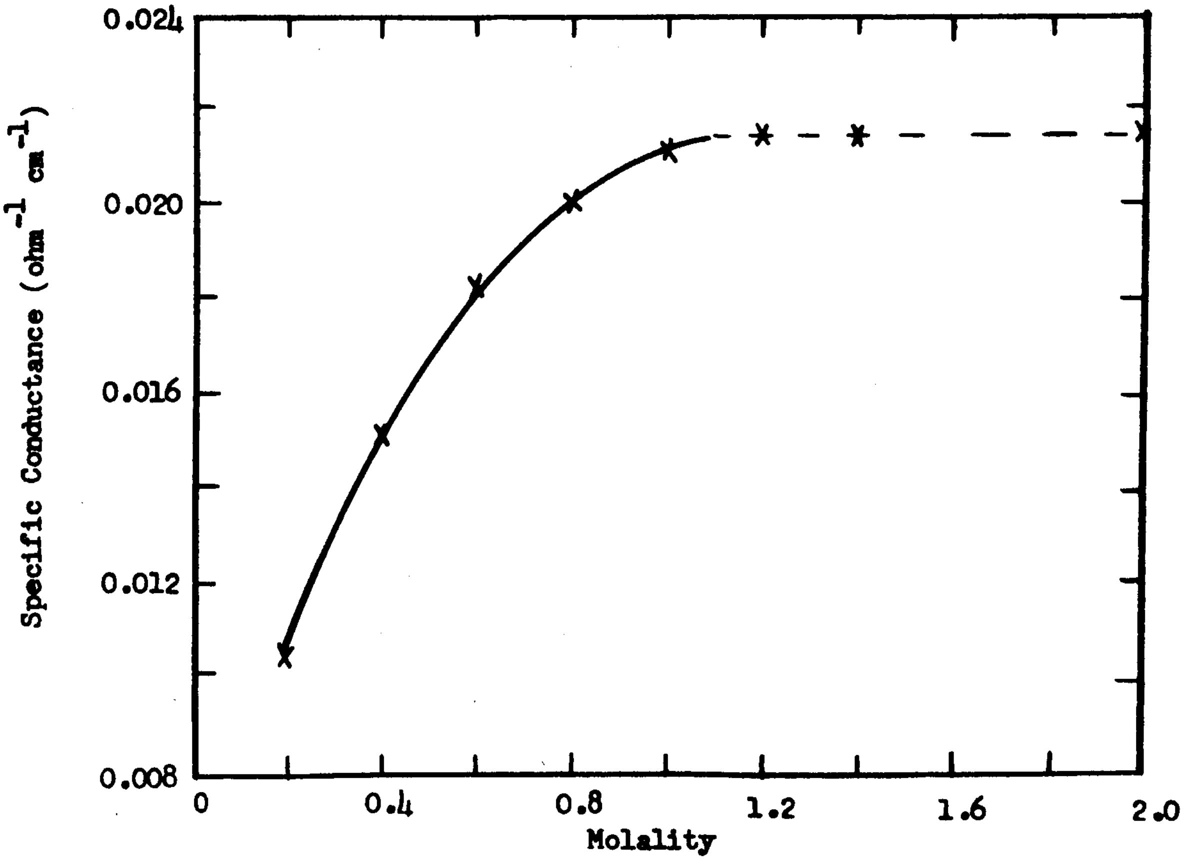


TABLE VI. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

k. Morpholinium Hexafluorophosphate-Nitrosodimethylamine

Molarity (25°C)	Specific Conductance (ohm^{-1} cm^{-1})	Viscosity(25°C) (Centipoises)	Density (25°C)
0.210	1.16×10^{-2} (31°C)	0.946	1.025
0.408	1.82×10^{-2} (31°C)	1.08	1.043
0.597	2.26×10^{-2} (31°C)	1.245	1.064
0.774	2.60×10^{-2} (30°C)	1.390	1.080
0.943	2.72×10^{-2} (30°C)	1.560	1.096
1.100	2.65×10^{-2} (30°C)	1.750	1.111
1.255	2.73×10^{-2} (29°C)	----	* 1.130
1.59-	2.69×10^{-2} (29°C)	2.720	1.162

* Interpolated value.

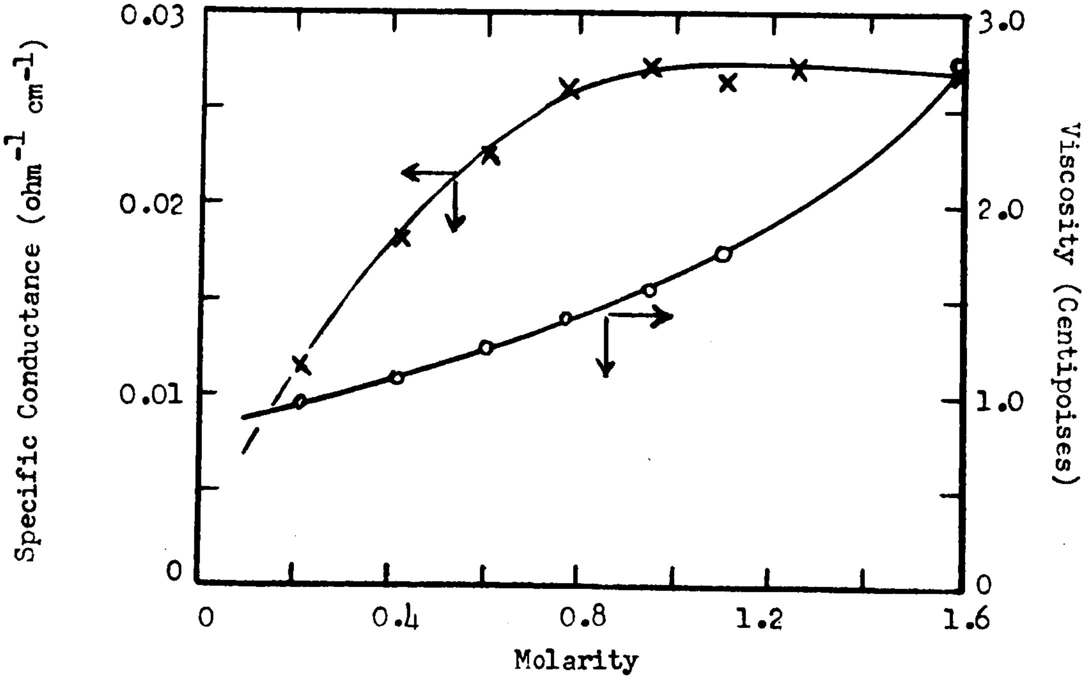


TABLE VI. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

1. $AlCl_3$-(80% Ethylene Carbonate + 20% Propylene Carbonate)

Molality	Specific Conductance ($ohm^{-1}\ cm^{-1}$)
0.297	4.46×10^{-3} (28°C)
0.70	7.85×10^{-3} (27.5°C)
0.987	8.63×10^{-3} (27°C)
1.295	9.03×10^{-3} (28°C)
1.72	8.34×10^{-3} (28°C)
2.01	7.08×10^{-3} (27°C)

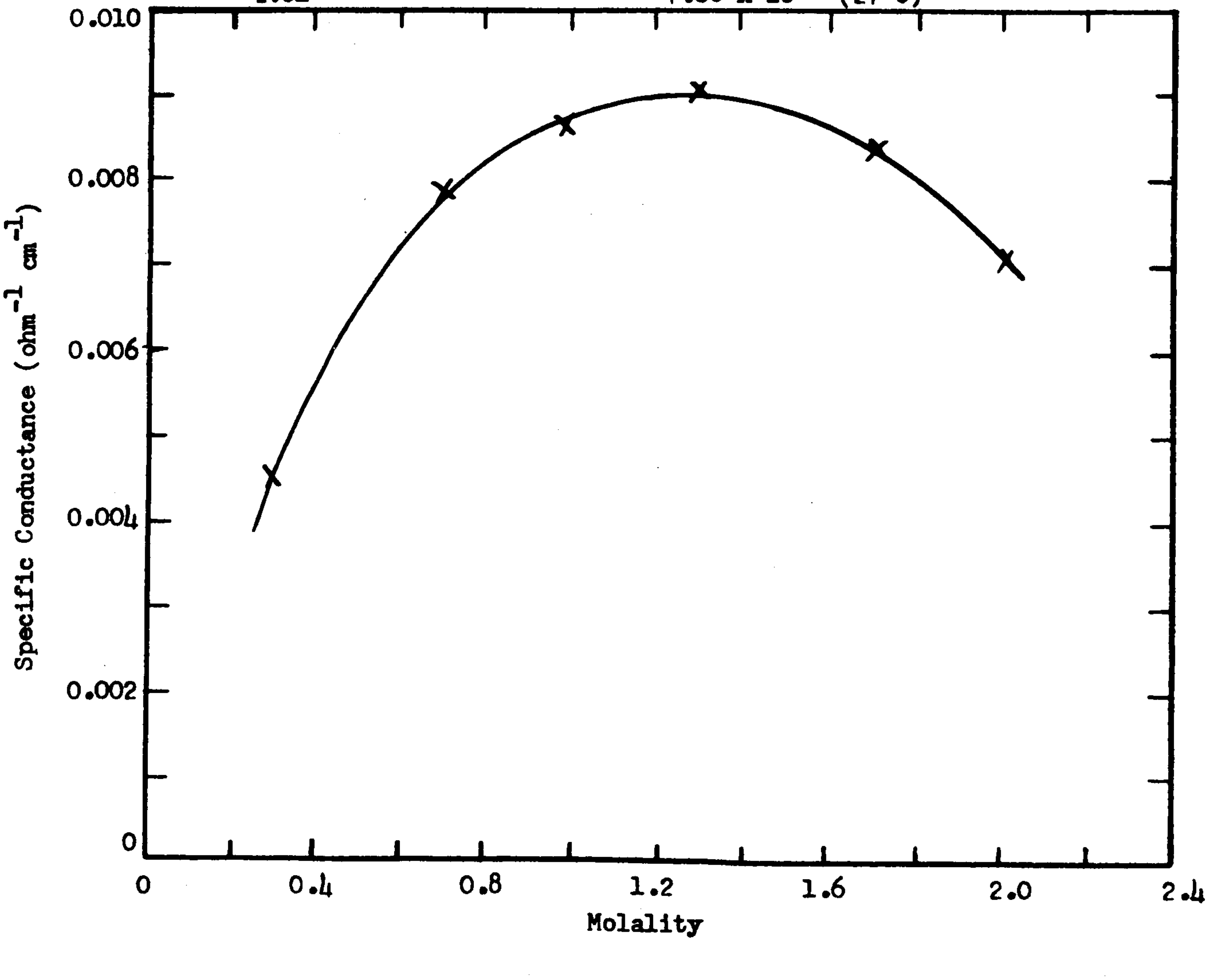
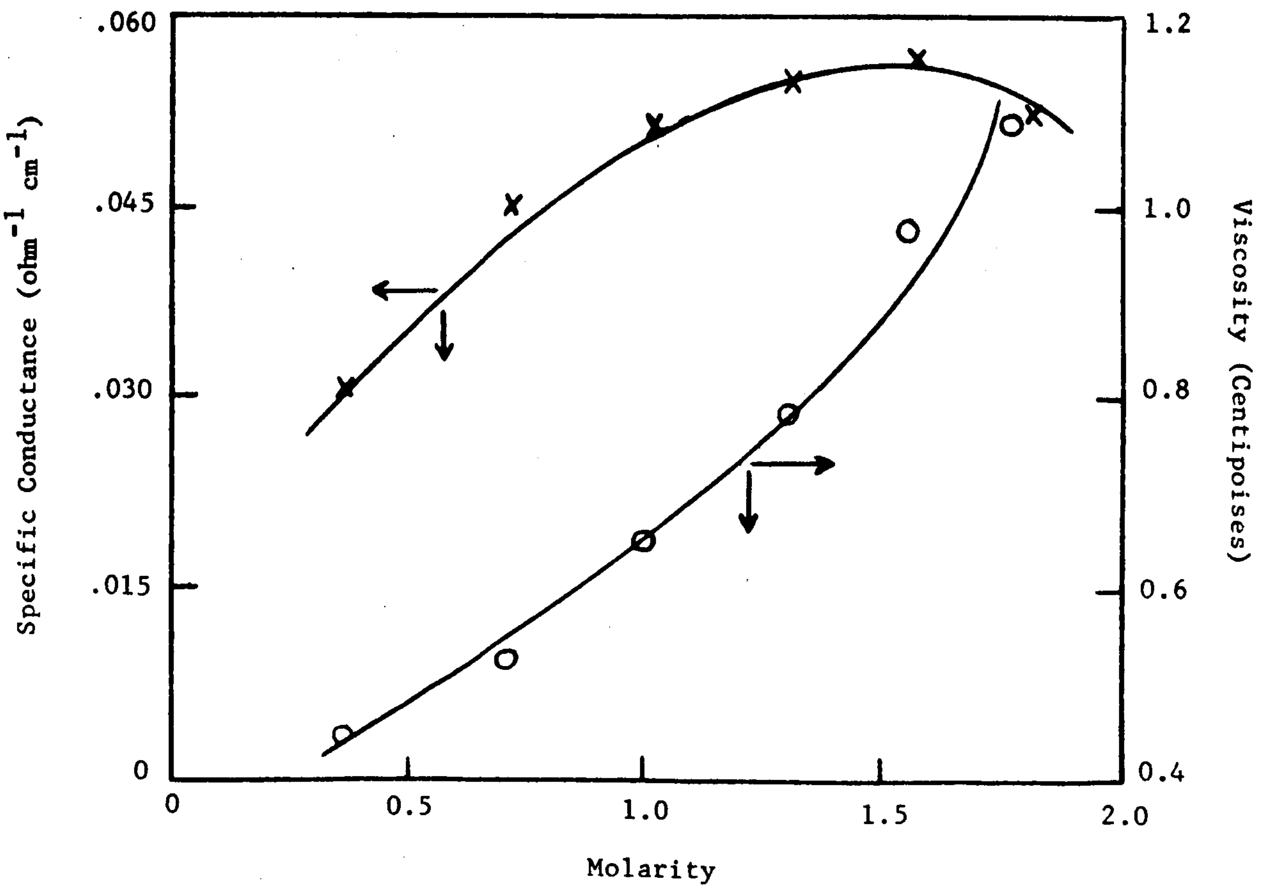


TABLE VI. (m) SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF MORPHOLINIUM HEXAFLUOROPHOSPHATE-ACETONITRILE SOLUTIONS

Molarity (25°C)	Specific Conductance (ohm^{-1} cm^{-1}) (25°C)	Density (25°C) (g/cc)	Viscosity (25°C) (Centipoise)
0.373	3.05×10^{-2}	0.831	0.447
0.722	4.50×10^{-2}	0.877	0.525
1.021	5.12×10^{-2}	0.920	0.649
1.310	5.47×10^{-2}	0.960	0.782
1.565	5.69×10^{-2}	0.992	0.926
1.811	5.24×10^{-2}	1.024	1.09



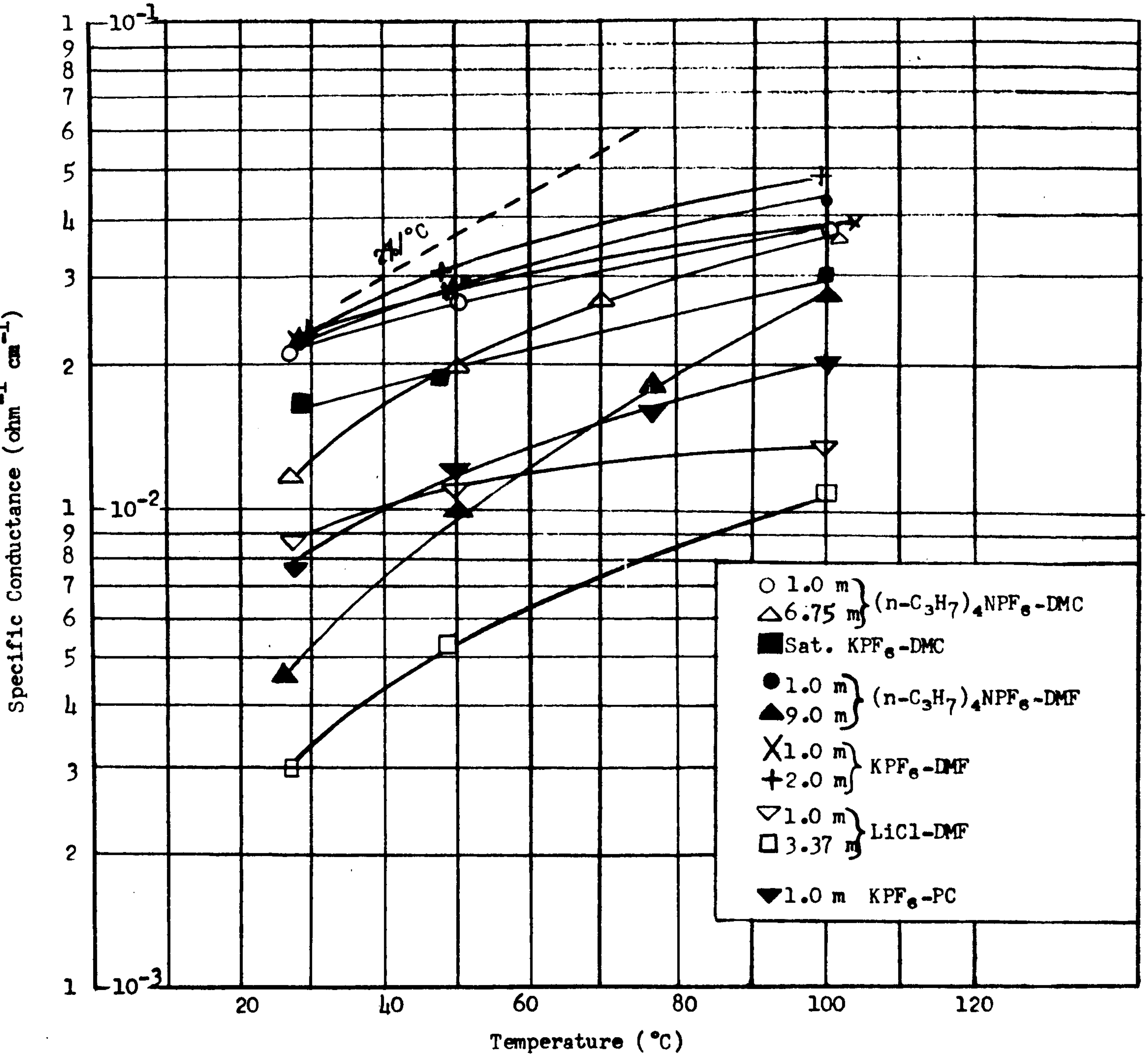


FIGURE 4. SPECIFIC CONDUCTANCE OF SOLUTIONS VS. TEMPERATURE

FIGURE 5

COMPARISON OF PREDICTED AND EXPERIMENTAL ELECTROLYTE CONDUCTANCES

FIGURE 5. COMPARISON OF PREDICTED AND EXPERIMENTAL CONDUCTANCES

a. Water - H_2SO_4

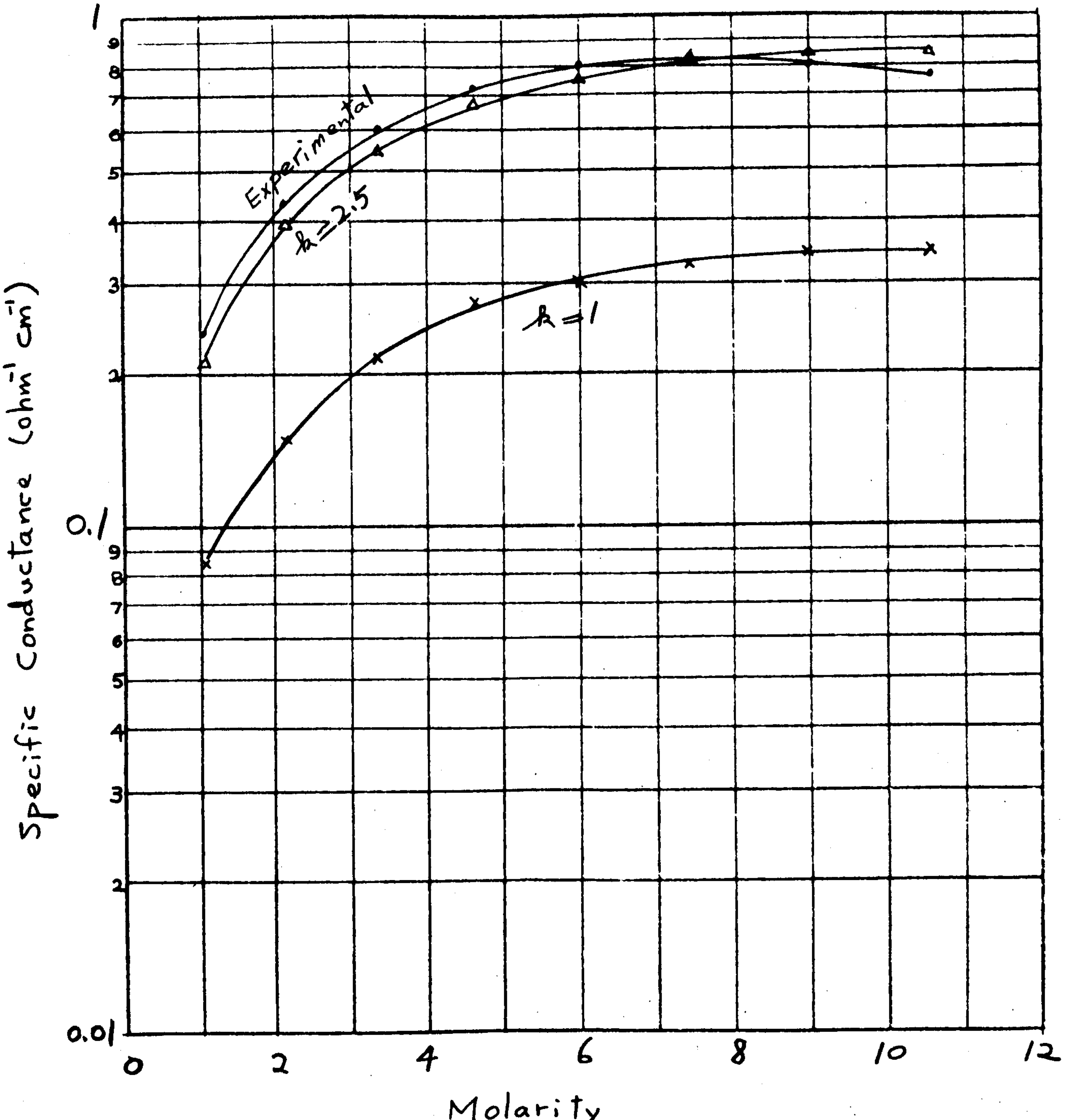


FIGURE 6. COMPARISON OF PREDICTED AND EXPERIMENTAL CONDUCTANCES (Continued)

b. Acetonitrile - KPF_6

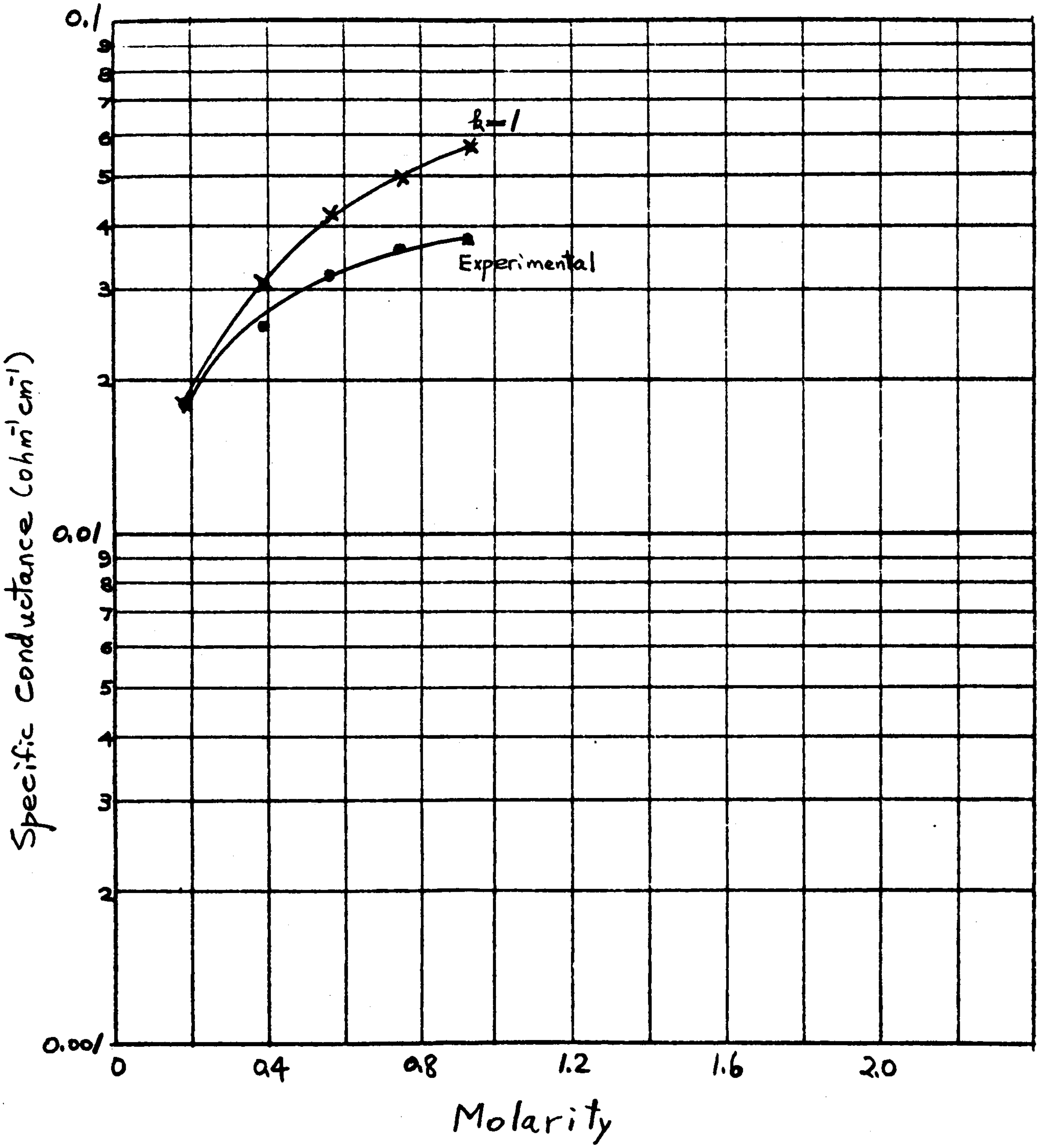


FIGURE 7. COMPARISON OF PREDICTED AND EXPERIMENTAL CONDUCTANCES (Continued)

c. Dimethylformamide - KPF_6

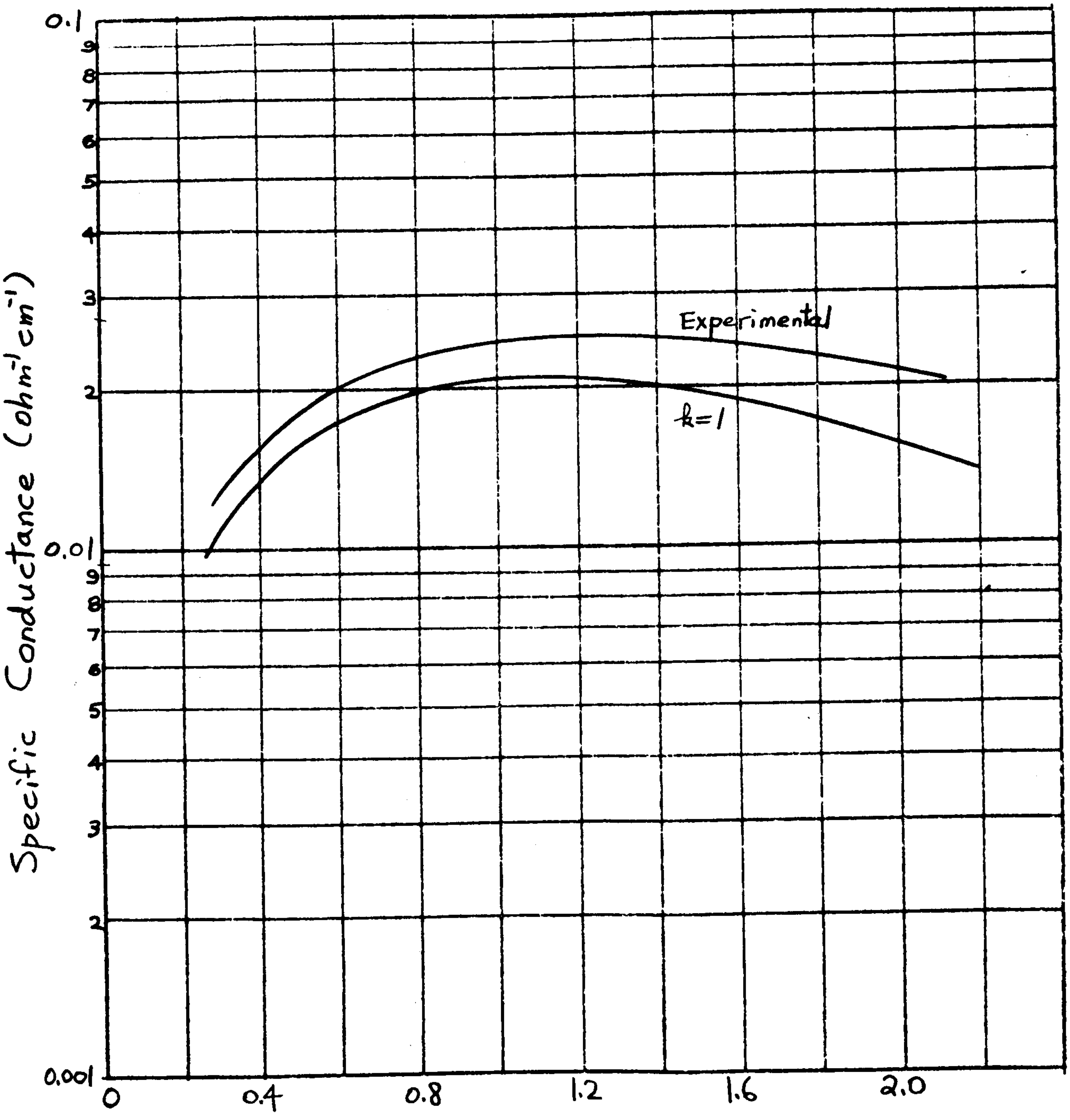


FIGURE 8. COMPARISON OF PREDICTED AND EXPERIMENTAL CONDUCTANCES (Continued)

d. Dimethylformamide — Morpholinium hexafluorophosphate

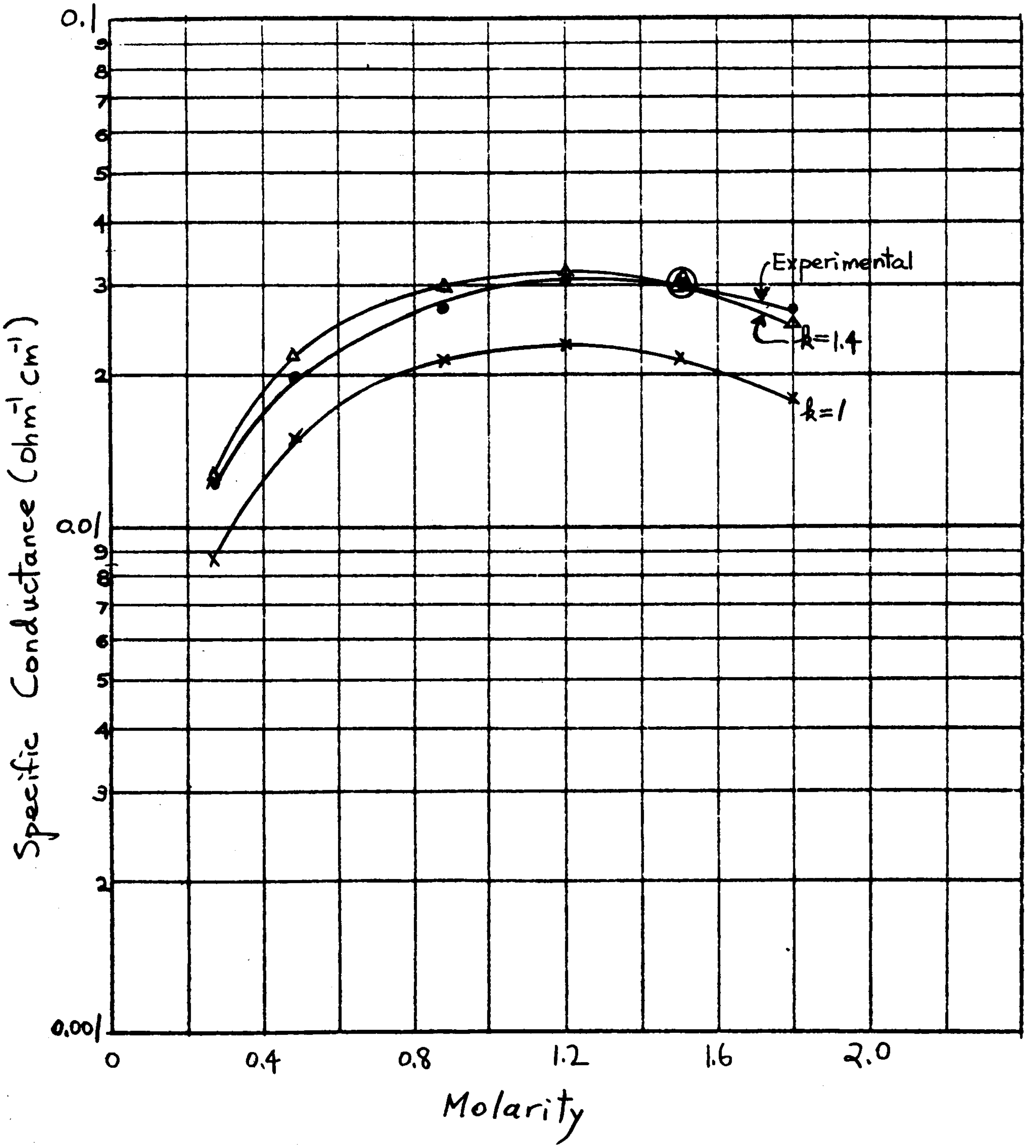


FIGURE 9. COMPARISON OF PREDICTED AND EXPERIMENTAL CONDUCTANCES (Continued)

e. Nitrosodimethylamine — Morpholinium hexafluorophosphate

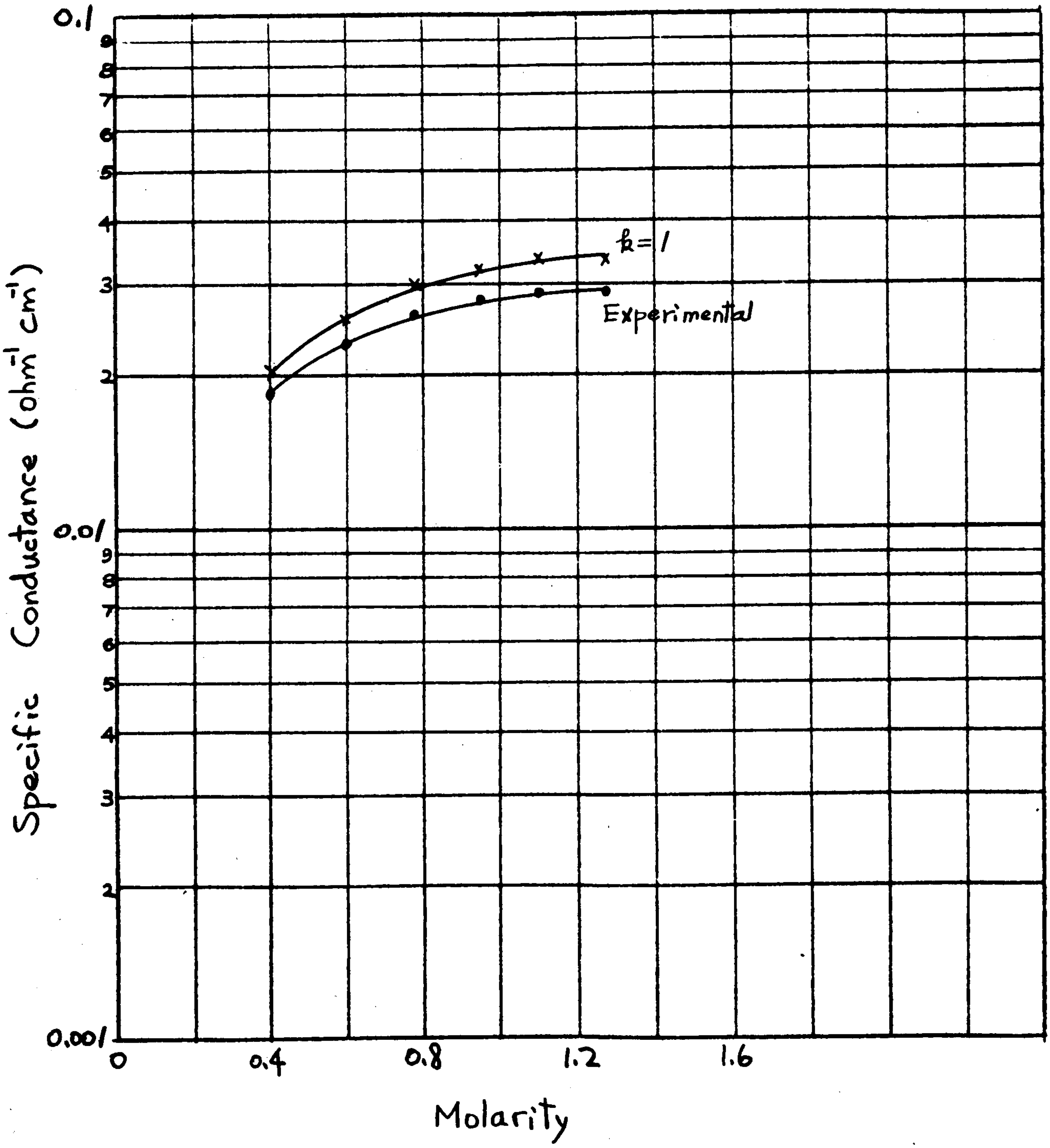


FIGURE 10. COMPARISON OF PREDICTED AND EXPERIMENTAL CONDUCTANCES (Continued)

f. Tetramethyl urea — KPF_6

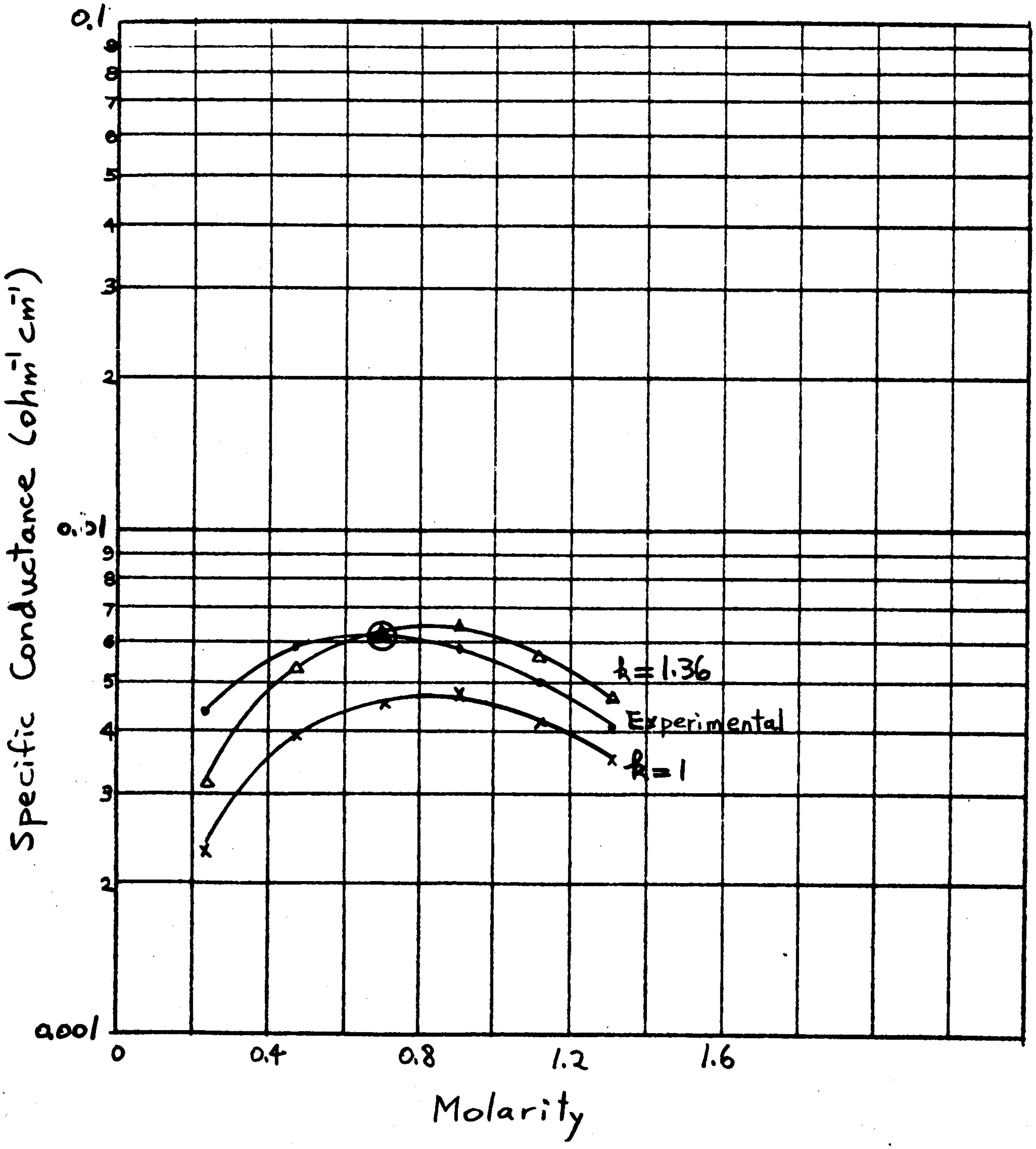


TABLE VII. DISTILLATION AND TESTING OF SOLVENTS EMPLOYED IN ELECTROLYTIC SOLUTIONS (Continued)

A. Refractive Indices of Distilled Solvent Fractions at 25°C.

Fraction	Original	One Week	Two Weeks	Four Weeks	Twelve Weeks
1. Acetonitrile. ($n_D^{16.5}$ = 1.34596, Handbook of Chem. & Physics, Chem. Rubber Co., 44th Ed.)					
Undistilled Sample	1.3415	1.3415	1.3420	1.3414	1.3415
1 (Discard)	---	---	---	---	---
2 (100 ml)	1.3414	1.3418	*	*	1.3415
3 (100 ml)	1.3412	1.3416	1.3416	1.3416	1.3415
4 (100 ml)	1.3415	1.3415	1.3415	1.3417	1.3418
5 (12 ml)	1.3416	1.3415	1.3418	1.3416	1.3418
2. N,N-Dimethylformamide. (n_D^{25} = 1.4269, DMF, Dupont Product Information Bulletin; n_D^{25} = 1.4294, J. Electrochem. Soc., 99, 28, (1952).					
Undistilled Sample	1.4281	1.4281	1.4280	1.4275	1.4281
1 (Discard)	---	---	---	---	---
2 (100 ml)	1.4279	1.4281	1.4281	1.4283	1.4279
3 (100 ml)	1.4280	1.4282	1.4281	1.4283	1.4281
4 (100 ml)	1.4279	1.4282	1.4281	1.4281	1.4281
5 (100 ml)	1.4281	1.4281	1.4281	1.4280	1.4282
6 (100 ml)	1.4279	1.4280	1.4281	1.4282	1.4280
3. N-Nitrosodimethylamine. ($n_D^{18.4}$ = 1.43743, Handbook of Chem. & Physics, Chem. Rubber Co., 44th Ed.)					
Undistilled Sample	1.4339	1.4339	1.4340	1.4340	1.4341
1 (Discard)	---	---	---	---	---
2 (100 ml)	**	1.4344	1.4344	1.4345	1.4344
3 (100 ml)	**	1.4344	1.4344	1.4346	1.4346
4 (100 ml)	**	1.4343	1.4345	1.4345	1.4345
5 (100 ml)	**	1.4344	1.4344	1.4345	1.4345
6 (100 ml)	**	1.4345	1.4344	1.4346	1.4345

---

* Field of refractometer was indistinct. Values were ca. 1.3465.

** Not measured.

TABLE VII. DISTILLATION AND TESTING OF SOLVENTS EMPLOYED IN ELECTROLYTIC SOLUTIONS (Continued)

B. Refractive Indices of Distilled Solvent Fractions at 25°C. (Continued)

Fraction	Original	One Week	Two Weeks	Four Weeks	Twelve Weeks
4. Propylene Carbonate.					
Undistilled Sample	1.4194	1.4177	1.4196	1.4193	1.4195
1 (Discard)	---	---	---	---	---
2 (100 ml)	1.4197	1.4190	1.4194	1.4199	1.4199
3 (100 ml)	1.4195	1.4198	1.4193	1.4196	1.4200
4 (100 ml)	1.4198	1.4168	1.4176	1.4195	1.4199
5 (100 ml)	1.4198	1.4162	1.4190	1.4196	1.4198
6 (100 ml)	1.4198	1.4163	1.4179	1.4192	1.4199

TABLE VII. DISTILLATION AND TESTING OF SOLVENTS EMPLOYED IN ELECTROLYTIC SOLUTIONS (Continued)

C. Specific Conductivities of Distilled Solvent Fractions.

Fraction	Original	One Week	Two Weeks	Four Weeks	Twelve Weeks
1. Acetonitrile. (L = 5.9×10^{-8} ohm^{-1} cm^{-1}, J. Electrochem. Soc., 112, 104, (1965).					
Undistilled Sample	2.13×10^{-6}	2.62×10^{-6}	3.04×10^{-6}	4.78×10^{-6}	4.62×10^{-6}
1 (Discard)	---	---	---	---	---
2 (100 ml)	7.25×10^{-7}	3.22×10^{-6}	4.44×10^{-6}	6.84×10^{-6}	8.00×10^{-6}
3 (100 ml)	8.58×10^{-7}	1.69×10^{-6}	2.94×10^{-6}	4.98×10^{-6}	7.83×10^{-6}
4 (100 ml)	3.10×10^{-7}	1.28×10^{-6}	2.94×10^{-6}	5.37×10^{-6}	8.56×10^{-6}
5 (12 ml)*	---	---	---	---	---
2. N,N-Dimethylformamide. (L = $0.6\text{-}2.0 \times 10^{-7}$ ohm^{-1} cm^{-1}, J. Phys. Chem., 59, 16-17, (1955).					
Undistilled Sample	1.30×10^{-6}	1.33×10^{-6}	3.24×10^{-6}	5.61×10^{-6}	2.89×10^{-5}
1 (Discard)	---	---	---	---	---
2 (100 ml)	1.65×10^{-6}	5.91×10^{-6}	1.96×10^{-5}	2.50×10^{-5}	3.08×10^{-5}
3 (100 ml)	6.66×10^{-7}	1.78×10^{-6}	3.66×10^{-6}	4.23×10^{-6}	7.27×10^{-6}
4 (100 ml)	5.34×10^{-6}	8.25×10^{-6}	9.15×10^{-6}	1.07×10^{-5}	1.52×10^{-5}
5 (100 ml)	4.46×10^{-6}	7.95×10^{-6}	8.45×10^{-6}	1.00×10^{-5}	1.16×10^{-5}
6 (100 ml)	7.43×10^{-7}	2.82×10^{-6}	3.69×10^{-6}	4.20×10^{-6}	6.22×10^{-6}
3. N-Nitrosodimethylamine.					
Undistilled Sample	2.64×10^{-5}	9.95×10^{-6}	1.34×10^{-5}	1.78×10^{-5}	6.78×10^{-5}
1 (Discard)	---	---	---	---	---
2 (100 ml)	**	1.25×10^{-5}	7.59×10^{-5}	7.90×10^{-5}	1.26×10^{-4}
3 (100 ml)	**	2.18×10^{-6}	9.3×10^{-6}	6.88×10^{-5}	8.90×10^{-5}
4 (100 ml)	**	3.41×10^{-6}	1.05×10^{-5}	5.28×10^{-5}	7.57×10^{-5}
5 (100 ml)	**	3.34×10^{-6}	2.96×10^{-5}	6.53×10^{-5}	7.47×10^{-5}
6 (100 ml)	**	1.05×10^{-5}	5.15×10^{-5}	8.16×10^{-5}	1.46×10^{-4}
4. Propylene Carbonate.					
Undistilled Sample	1.37×10^{-5}	1.37×10^{-5}	1.38×10^{-5}	1.45×10^{-5}	1.39×10^{-5}
1 (Discard)	---	---	---	---	---
2 (100 ml)	6.97×10^{-8}	5.85×10^{-7}	1.07×10^{-6}	1.22×10^{-6}	1.42×10^{-6}
3 (100 ml)	4.01×10^{-8}	4.20×10^{-7}	4.64×10^{-7}	7.43×10^{-7}	1.01×10^{-6}
4 (100 ml)	6.06×10^{-8}	8.30×10^{-8}	2.32×10^{-7}	3.50×10^{-7}	7.93×10^{-7}
5 (100 ml)	9.71×10^{-8}	1.22×10^{-7}	2.30×10^{-7}	3.78×10^{-6}	1.15×10^{-6}
6 (100 ml)	6.37×10^{-8}	1.02×10^{-7}	2.22×10^{-7}	3.02×10^{-6}	1.05×10^{-6}

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* Specific conductivity could not be measured because of small volume.

** Not measured.

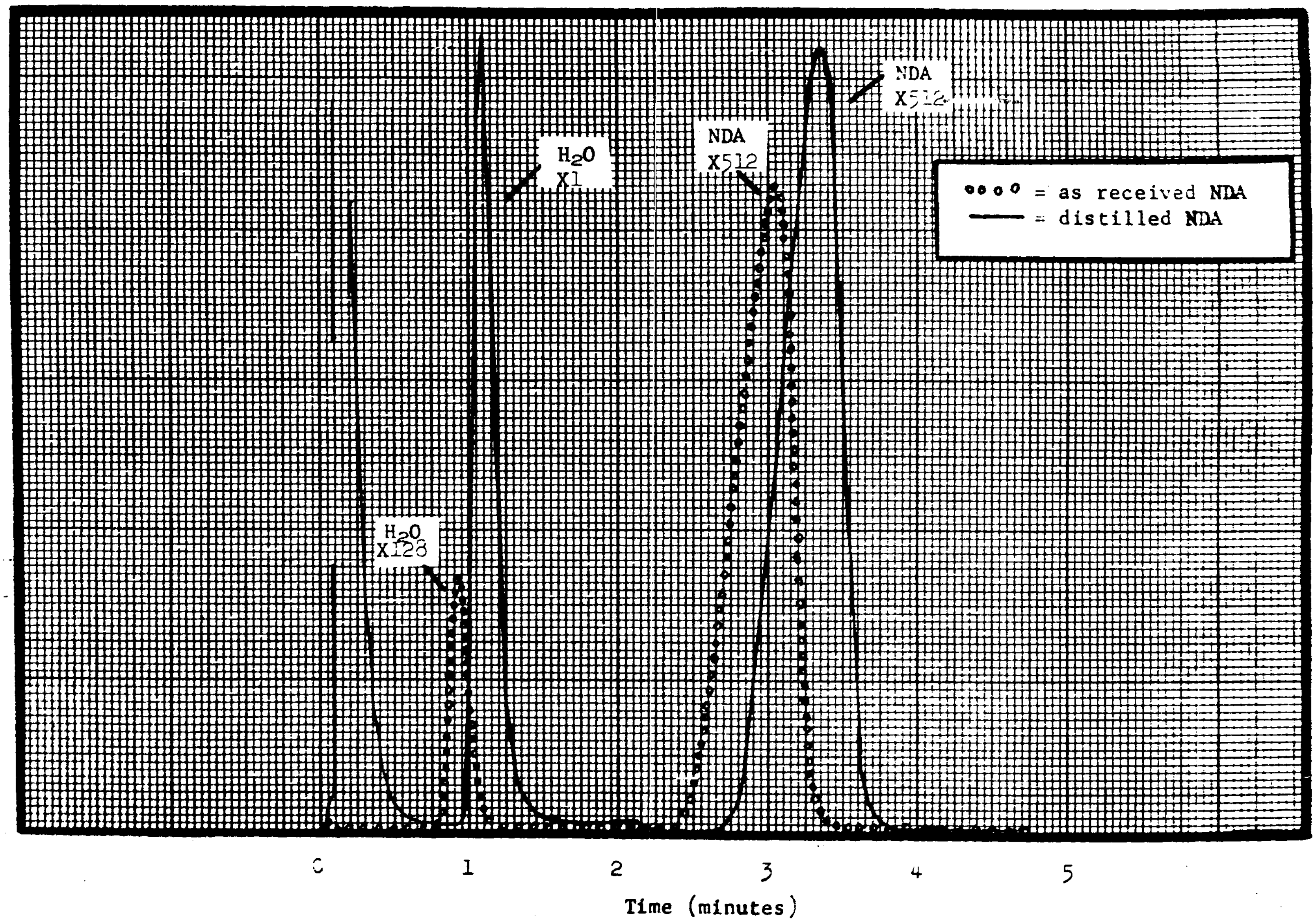

FIGURE 6. GAS CHROMATOGRAMS OF N-NITROSODIMETHYLAMINE (NDA)

Figure 6-a. Comparison of NDA as received from the supplier and after vacuum distillation

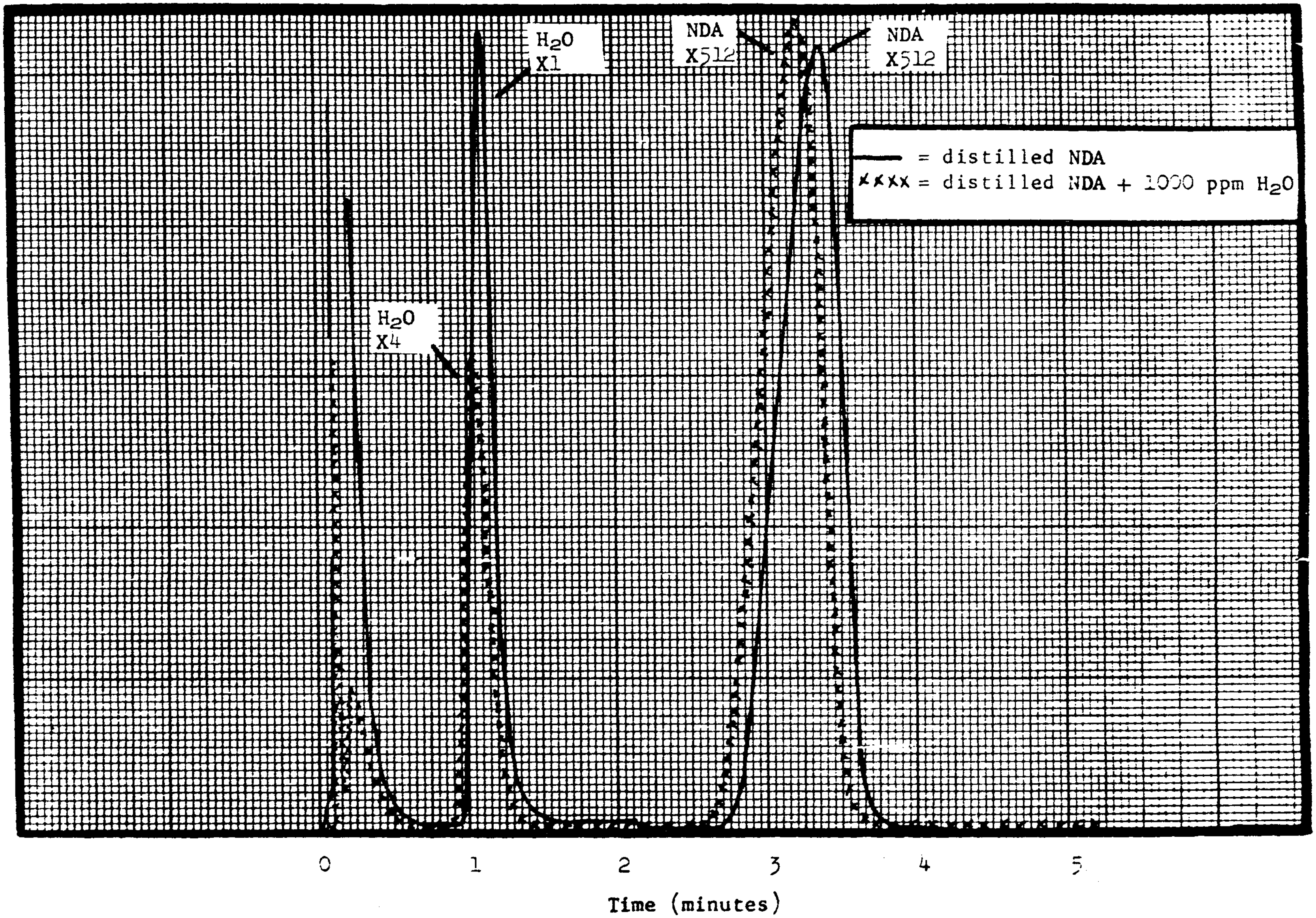

FIGURE 6. <u>GAS CHROMATOGRAMS OF N-NITROSODIMETHYLAMINE (NDA)</u> (Continued)

Figure 6-b. Comparison of distilled NDA and distilled NDA + 1000 ppm H_2O

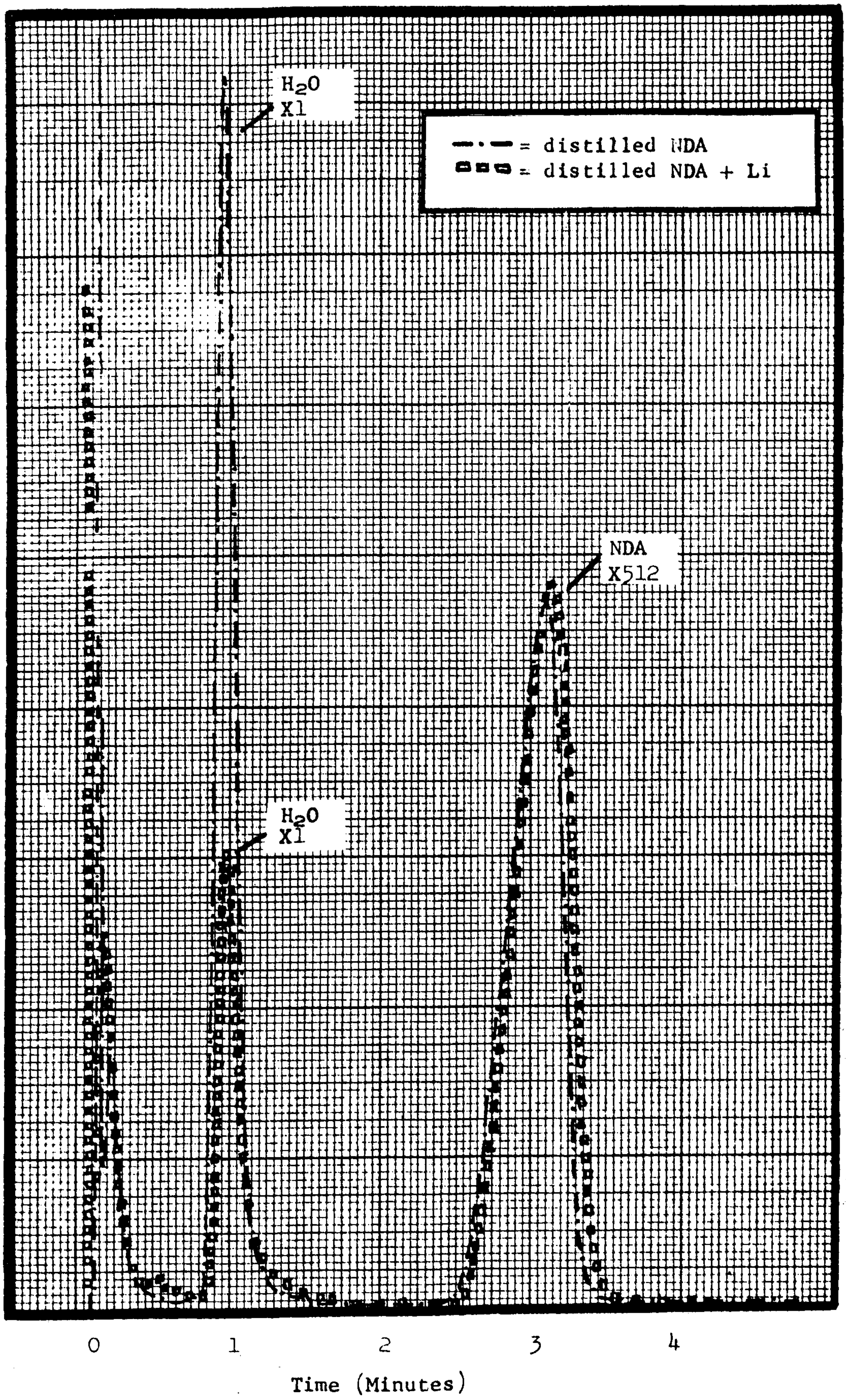

FIGURE 6. GAS CHROMATOGRAMS OF N-NITROSODIMETHYLAMINE (NDA) (Continued)

Figure 6-c. Comparison of the H_2O content of vacuum distilled NDA and vacuum distilled NDA treated with Li

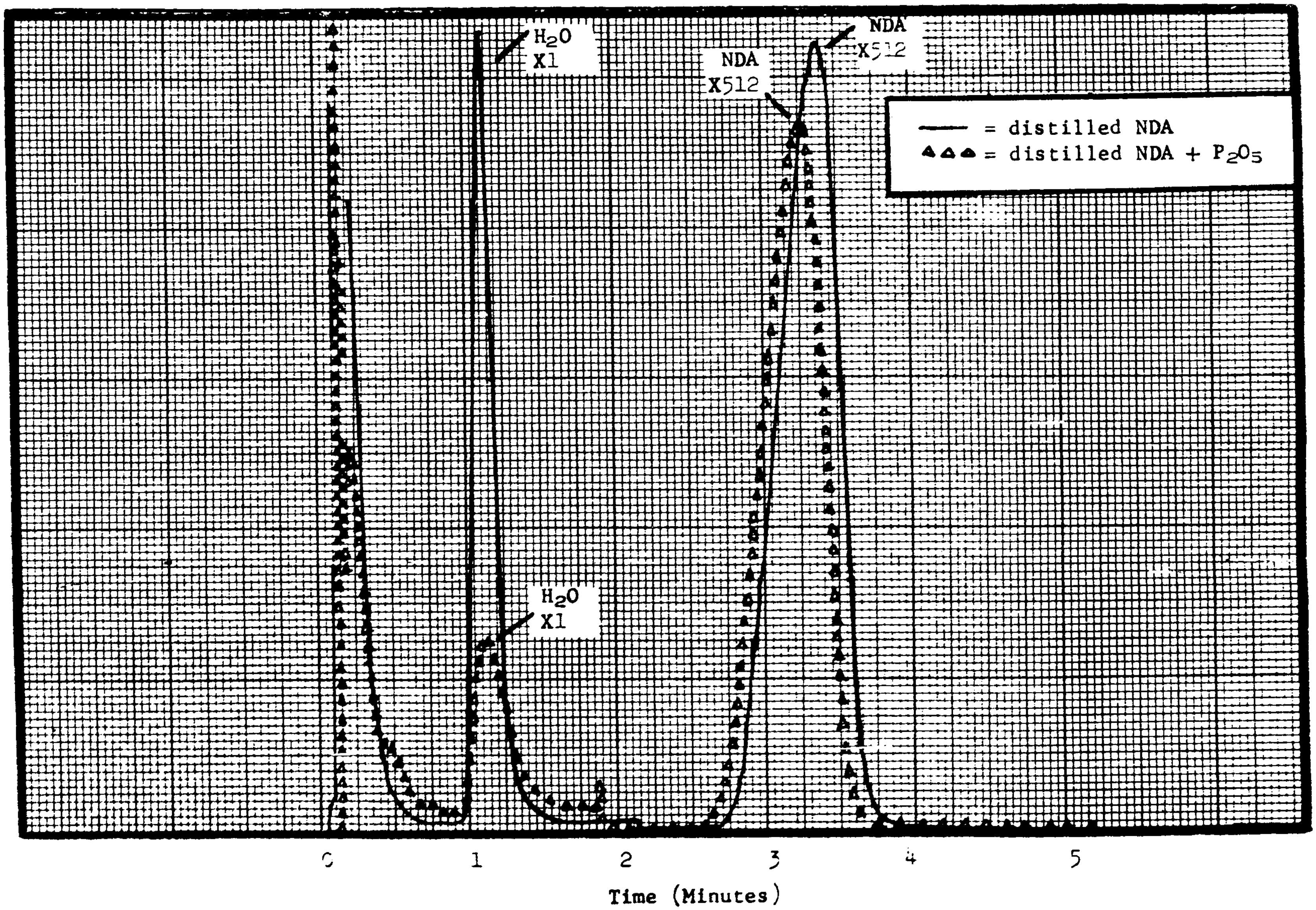

FIGURE 6. GAS CHROMATOGRAMS OF N-NITROSODIMETHYLAMINE (NDA) (Continued)

Figure 6-d. Comparison of the H_2O content of vacuum distilled NDA and vacuum distilled NDA treated with P_2O_5

FIGURE 7. LINEARLY VARYING POTENTIAL STUDIES TO DETERMINE THE IMPURITY PRESENT IN $LiPF_6^*$-N-NITROSODIMETHYLAMINE

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* "As received" $LiPF_6$

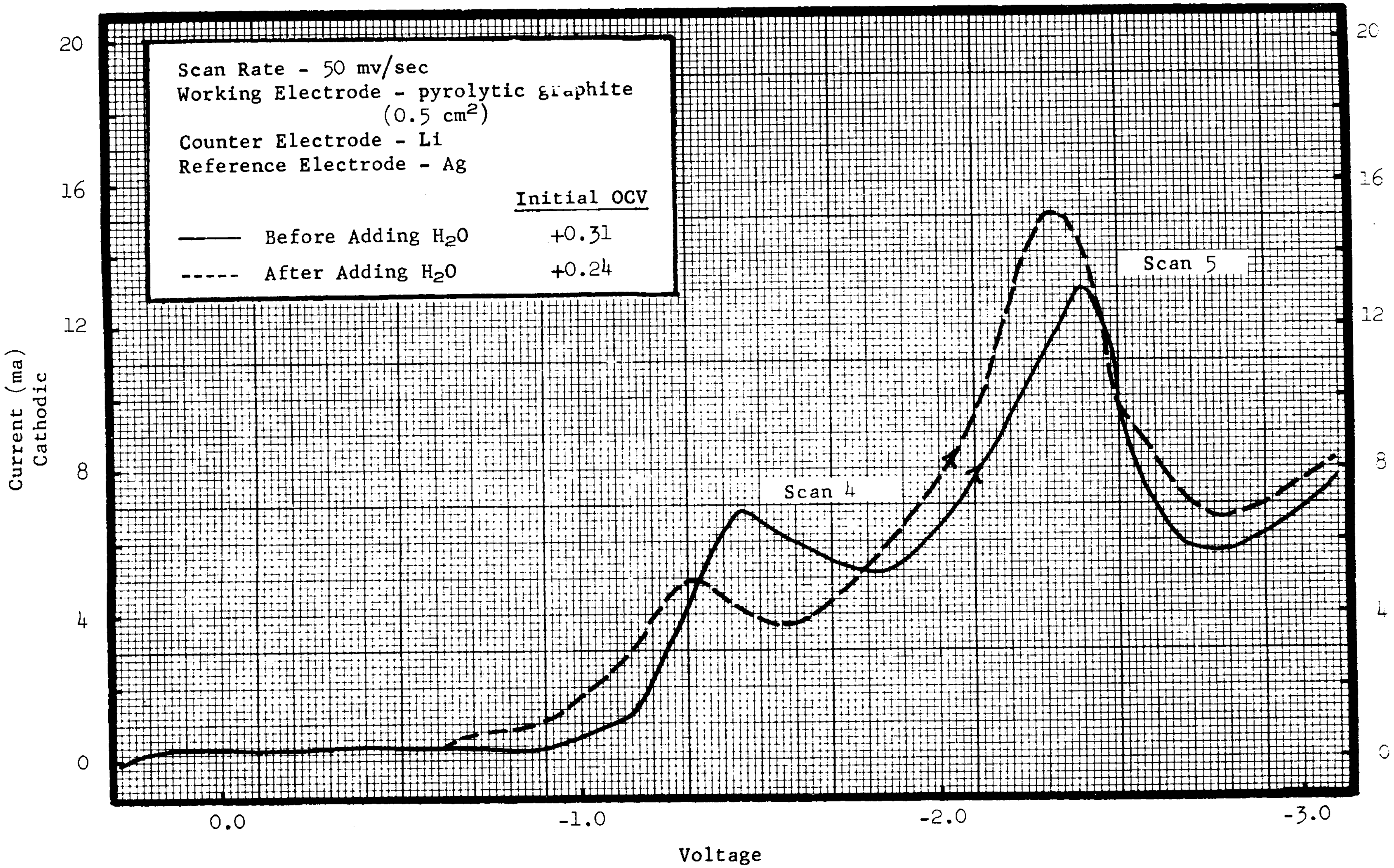

FIGURE 7. LINEARLY VARYING POTENTIAL STUDIES TO DETERMINE THE IMPURITY PRESENT IN $LiPF_6^*$-N-NITROSODIMETHYLAMINE

Figure 7-a. The Effect of Adding Water to One Molal $LiPF_6^*$-N-Nitrosodimethylamine.

* "As received" $LiPF_6$.

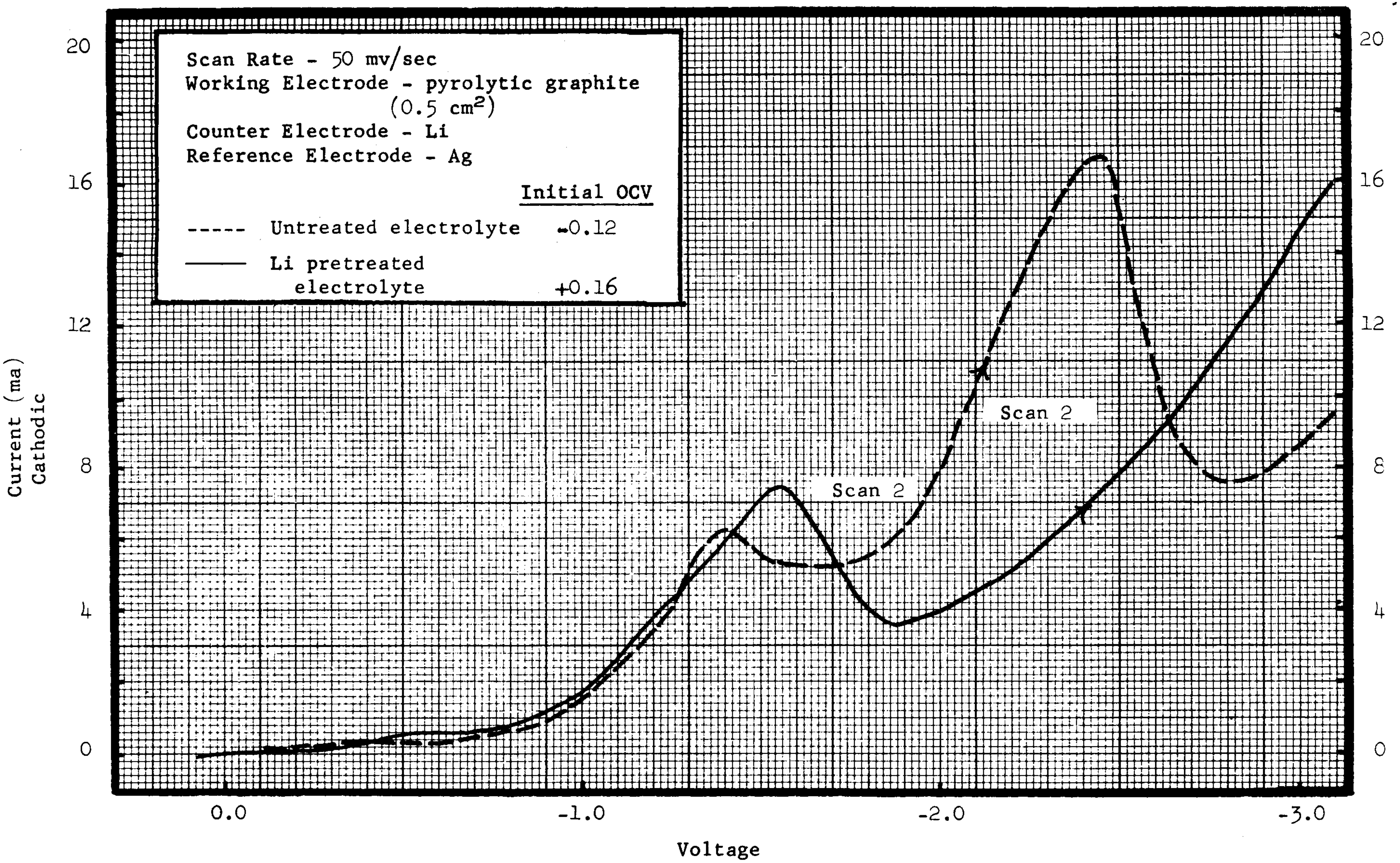

FIGURE 7. LINEARLY VARYING POTENTIAL STUDIES TO DETERMINE THE IMPURITY PRESENT IN $LiPF_6^*$-N-NITROSODIMETHYLAMINE (Continued)

Figure 7-b. The Effect of Pretreating One Molal $LiPF_6^*$-NDA With Lithium.

* "As received" $LiPF_6$.

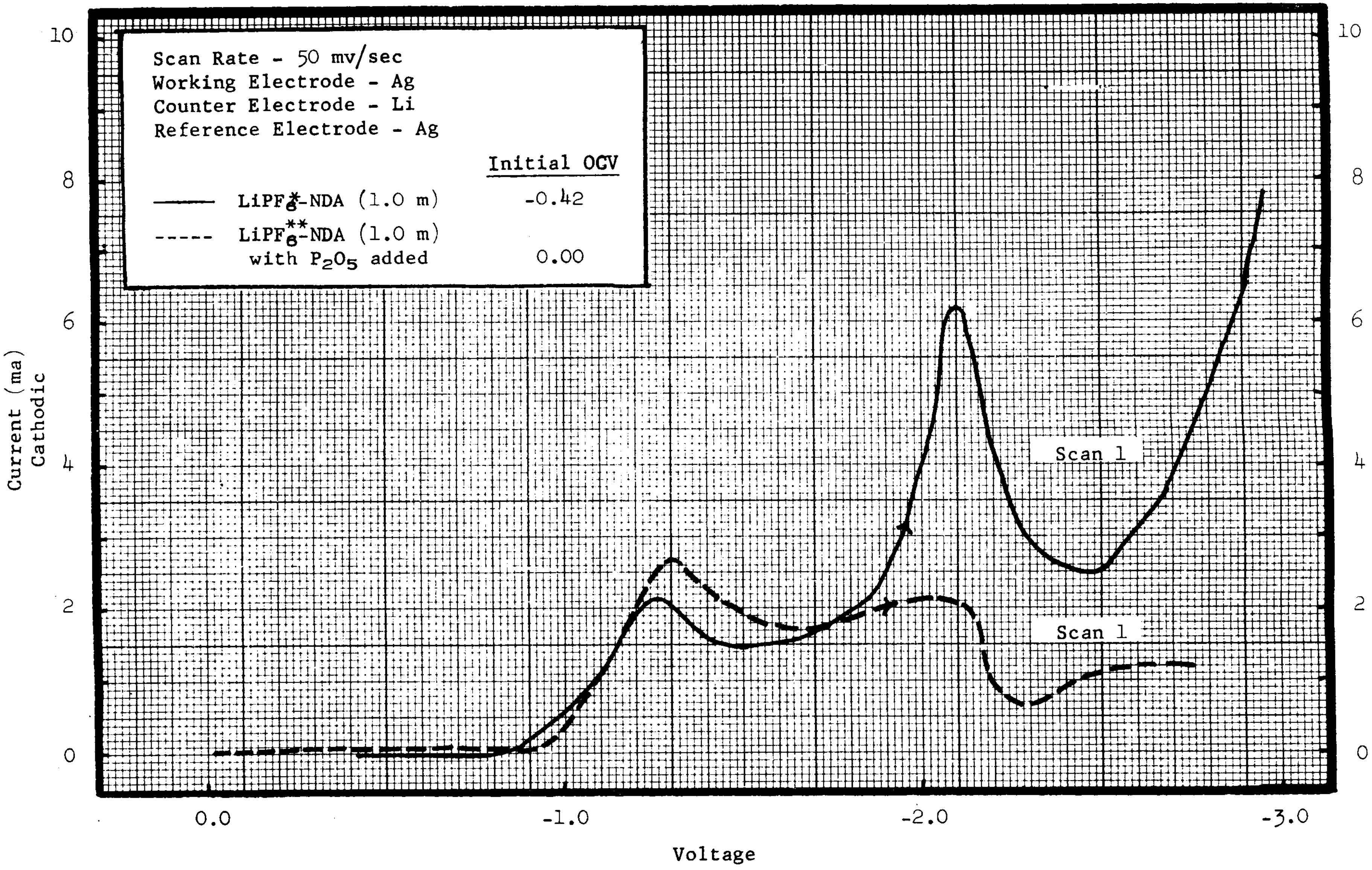

FIGURE 7. <u>LINEARLY VARYING POTENTIAL STUDIES TO DETERMINE THE IMPURITY PRESENT IN LiPF$_6^{**}$-N-NITROSODIMETHYLAMINE</u> (Continued)

Figure 7-c. The Effect of Adding Phosphorous Pentoxide to One Molal LiPF$_6^{**}$-N-Nitrosodimethylamine.

* The LiPF$_6$ was dried at 110°C in a nitrogen atmosphere before use.

** "As received" LiPF$_6$.

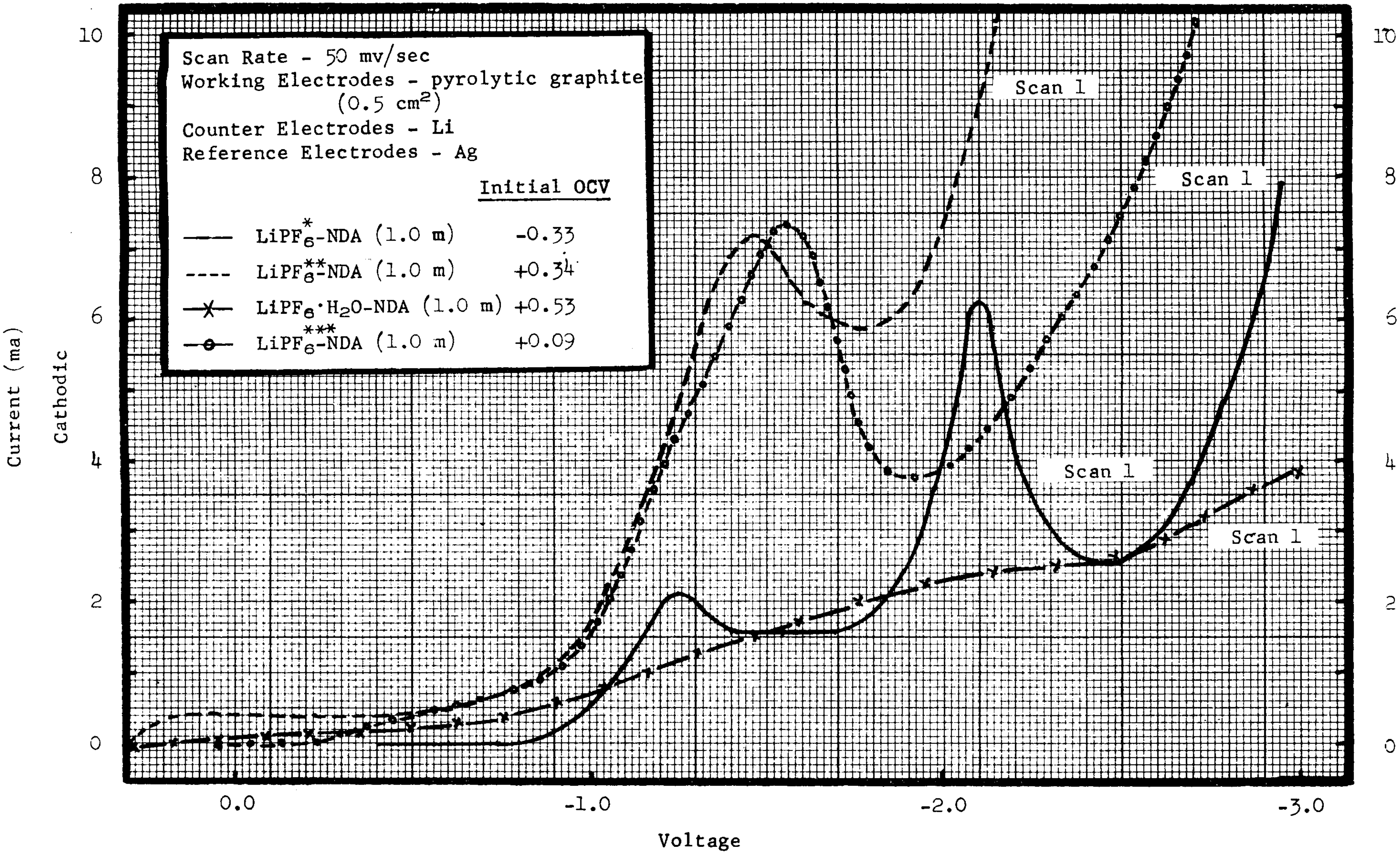

FIGURE 7. LINEARLY VARYING POTENTIAL STUDIES TO DETERMINE THE IMPURITY PRESENT IN $LiPF_6^{**}$-N-NITROSODIMETHYLAMINE (Continued)

Figure 7-d. $LiPF_6$- and $LiPF_6 \cdot H_2O$-N-Nitrosodimethylamine Electrolytes.

* The $LiPF_6$ was dried at 110°C in a nitrogen atmosphere before use.
** "As received" $LiPF_6$.
*** The $LiPF_6$(as received)-NDA solution was pretreated with Li for 48 hours before use.

FIGURE 8

VOLTAMMETRIC SWEEP STUDIES OF ELECTROACTIVE IMPURITIES IN LITHIUM HEXAFLUOROPHOSPHATE

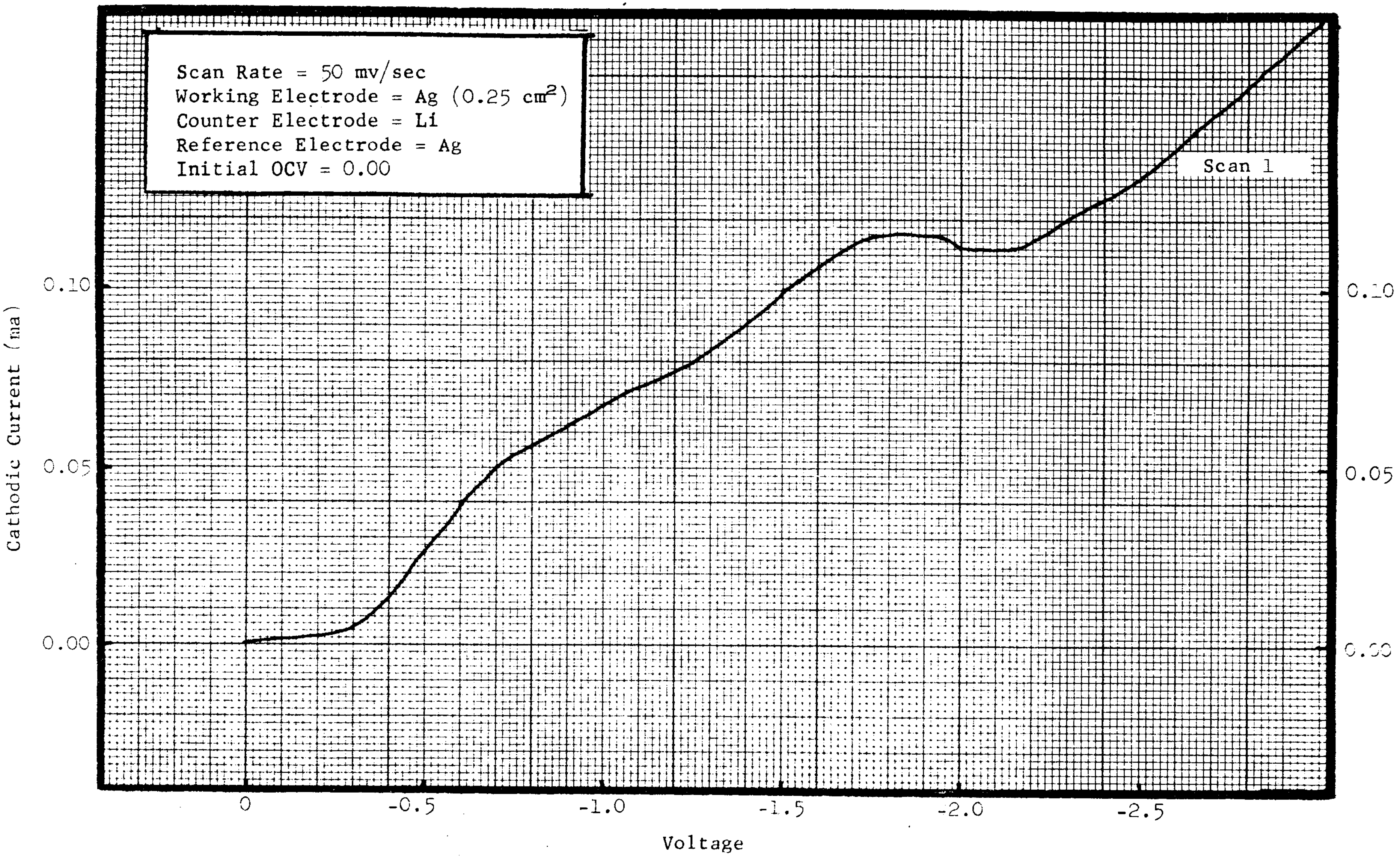

FIGURE 8. VOLTAMMETRIC SWEEP STUDIES OF ELECTROACTIVE IMPURITIES IN LITHIUM HEXAFLUOROPHOSPHATE

Figure 8-a. Voltammetric Sweep Study of Saturated Sodium Bifluoride in N-Nitrosodimethylamine. The initial potential was set equal to the open circuit voltage and the scan run towards more negative voltages.

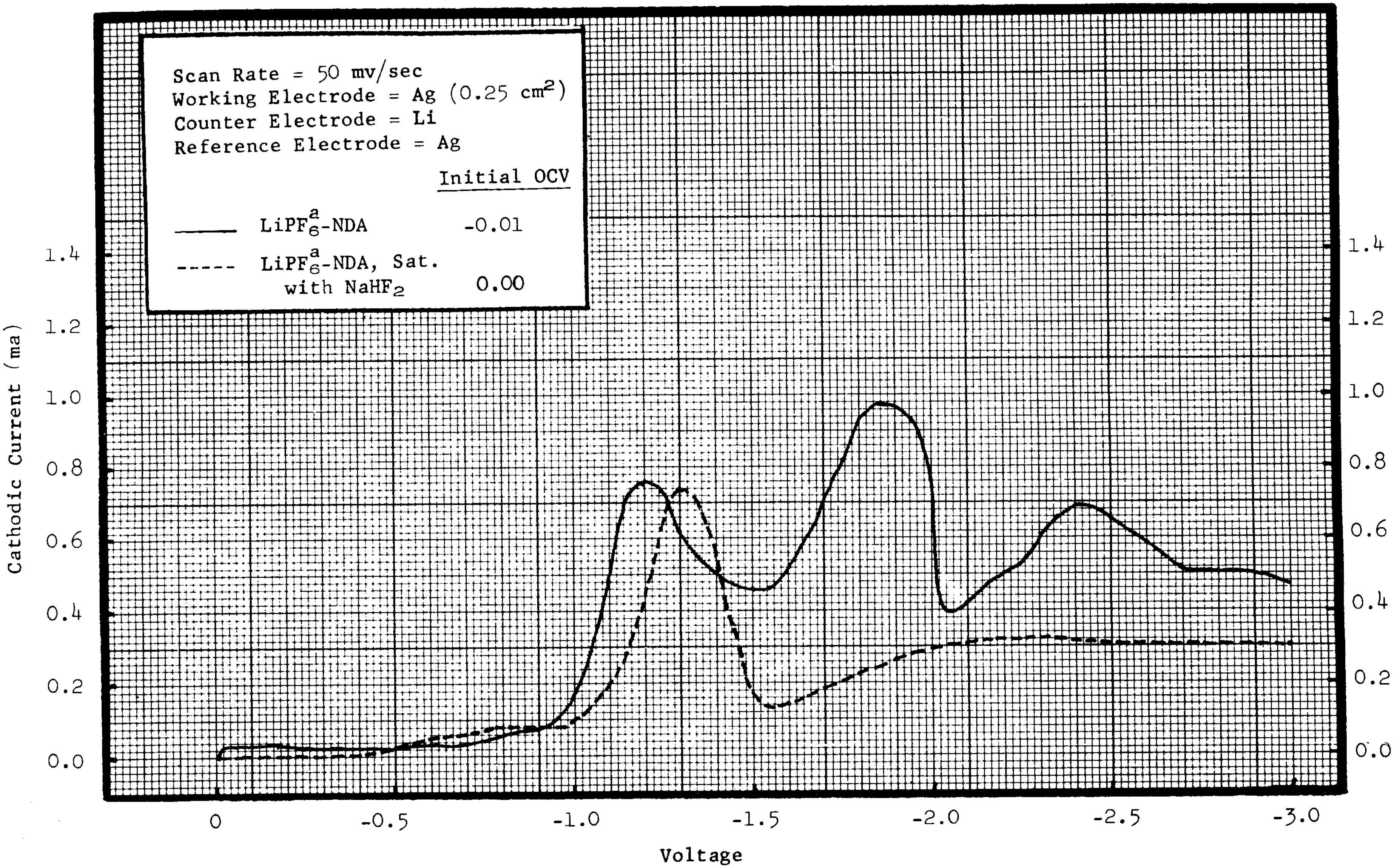

FIGURE 8. VOLTAMMETRIC SWEEP STUDIES OF ELECTROACTIVE IMPURITIES IN LITHIUM HEXAFLUOROPHOSPHATE (Continued)

Figure 8-b. Voltammetric Sweep Study of 1m $LiPF_6$-NDA and 1m $LiPF_6$-NDA Saturated with Sodium Bifluoride.

The initial potentials were set equal to the open circuit voltages and the scans run towards more negative voltages.

[a] $LiPF_6$ used "as received."

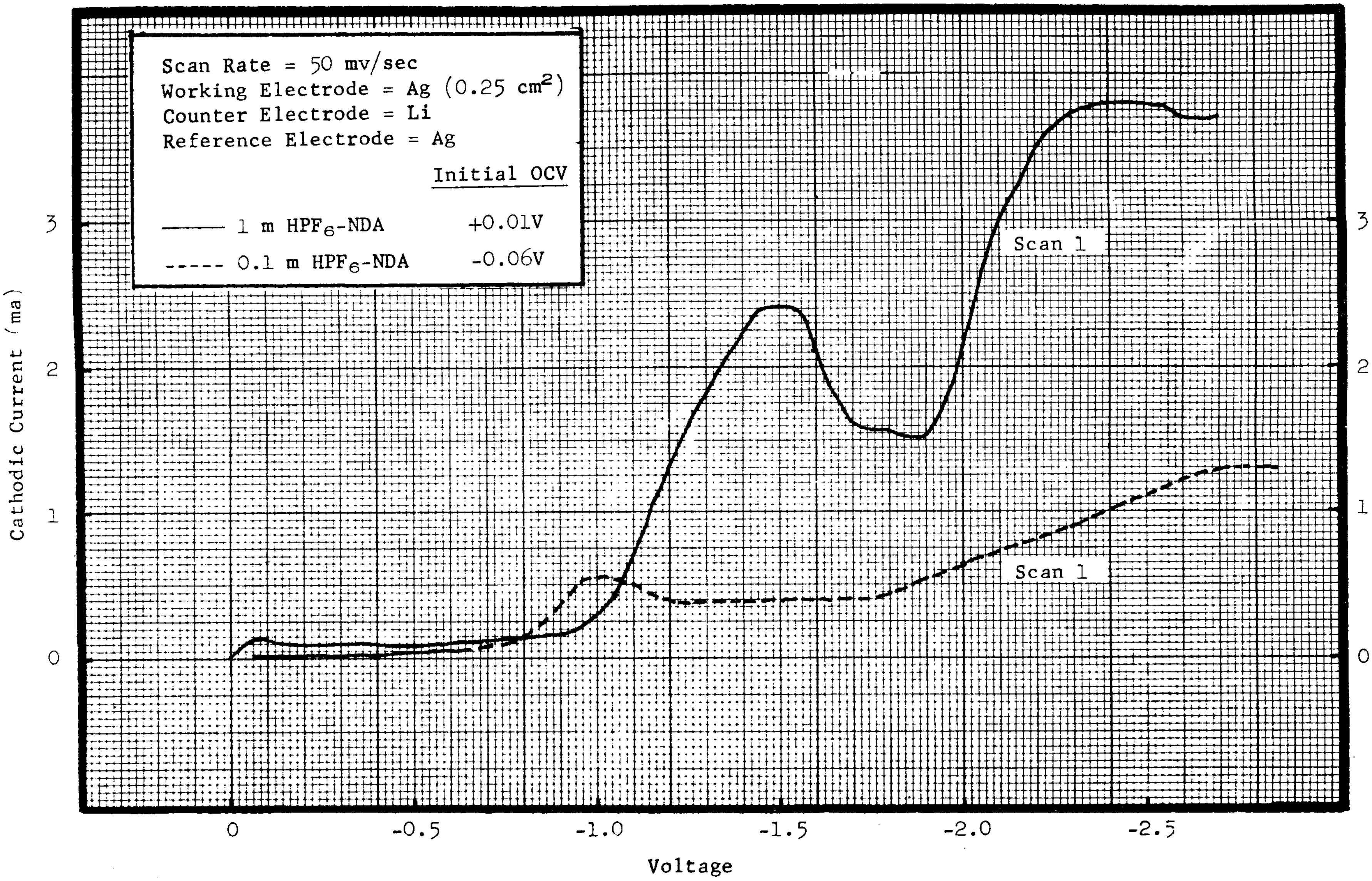

FIGURE 8. <u>VOLTAMMETRIC SWEEP STUDIES OF ELECTROACTIVE IMPURITIES IN LITHIUM HEXAFLUOROPHOSPHATE</u> (Continued)

Figure 8-c. Voltammetric Sweep Study of Hexafluorophosphoric Acid[a] in N-Nitrosodimethylamine. **The initial potentials were set equal to the open circuit voltages and the scans run towards more negative voltages.**

[a] Hexafluorophosphoric acid used was a 65% aqueous solution.

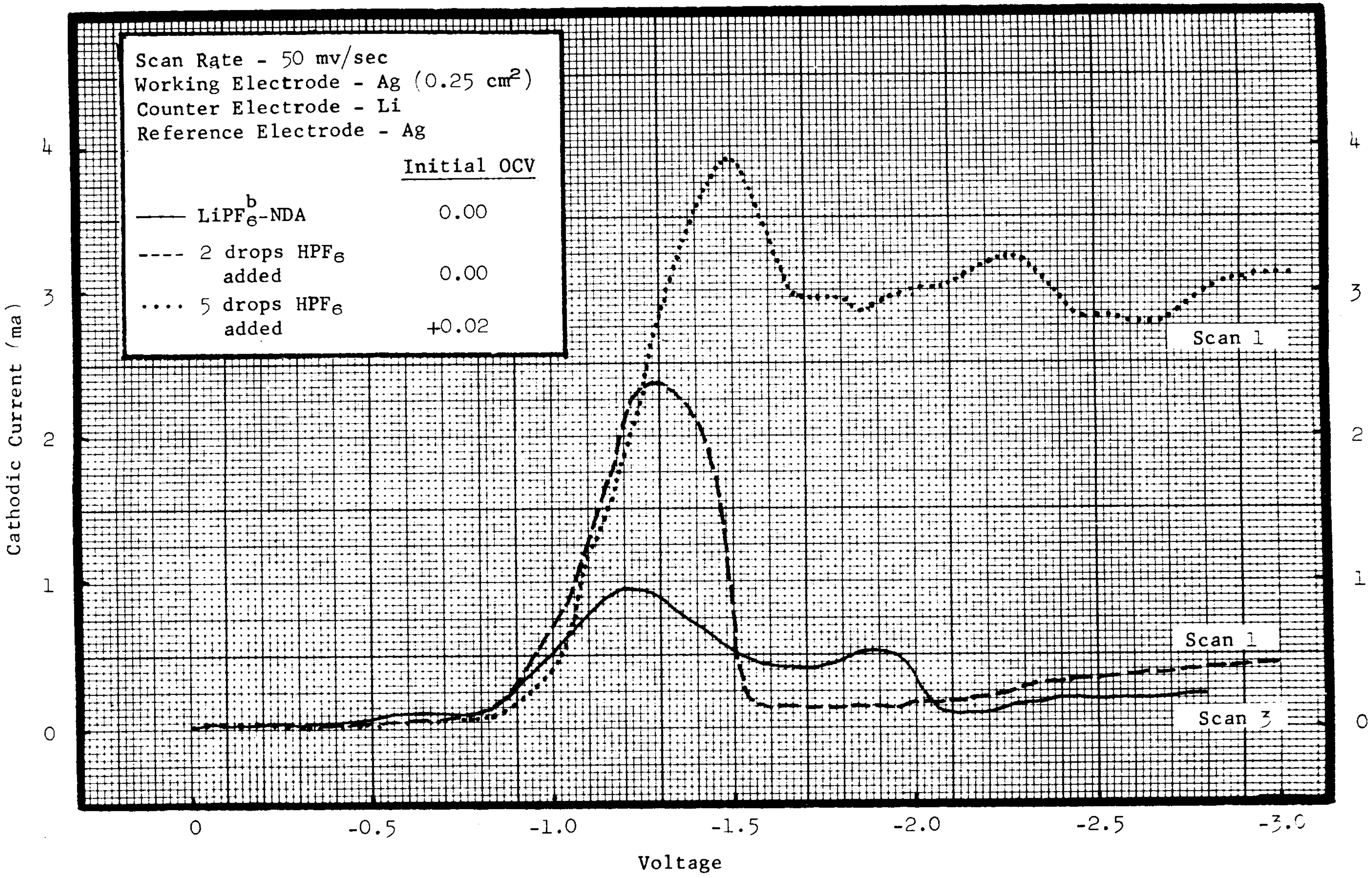

FIGURE 8. VOLTAMMETRIC SWEEP STUDIES OF ELECTROACTIVE IMPURITIES IN LITHIUM HEXAFLUOROPHOSPHATE (Continued)

Figure 8-d. **Voltammetric Sweep Study of Adding Hexafluorophosphoric Acid[a] to $LiPF_6$[b]-N-Nitrosodimethylamine**

The initial potentials were set equal to the open circuit voltages and the scans run towards more negative voltages.

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[a] Hexafluorophosphoric acid used was a 65% aqueous solution.

[b] $LiPF_6$ used was dried at 110°C under nitrogen.

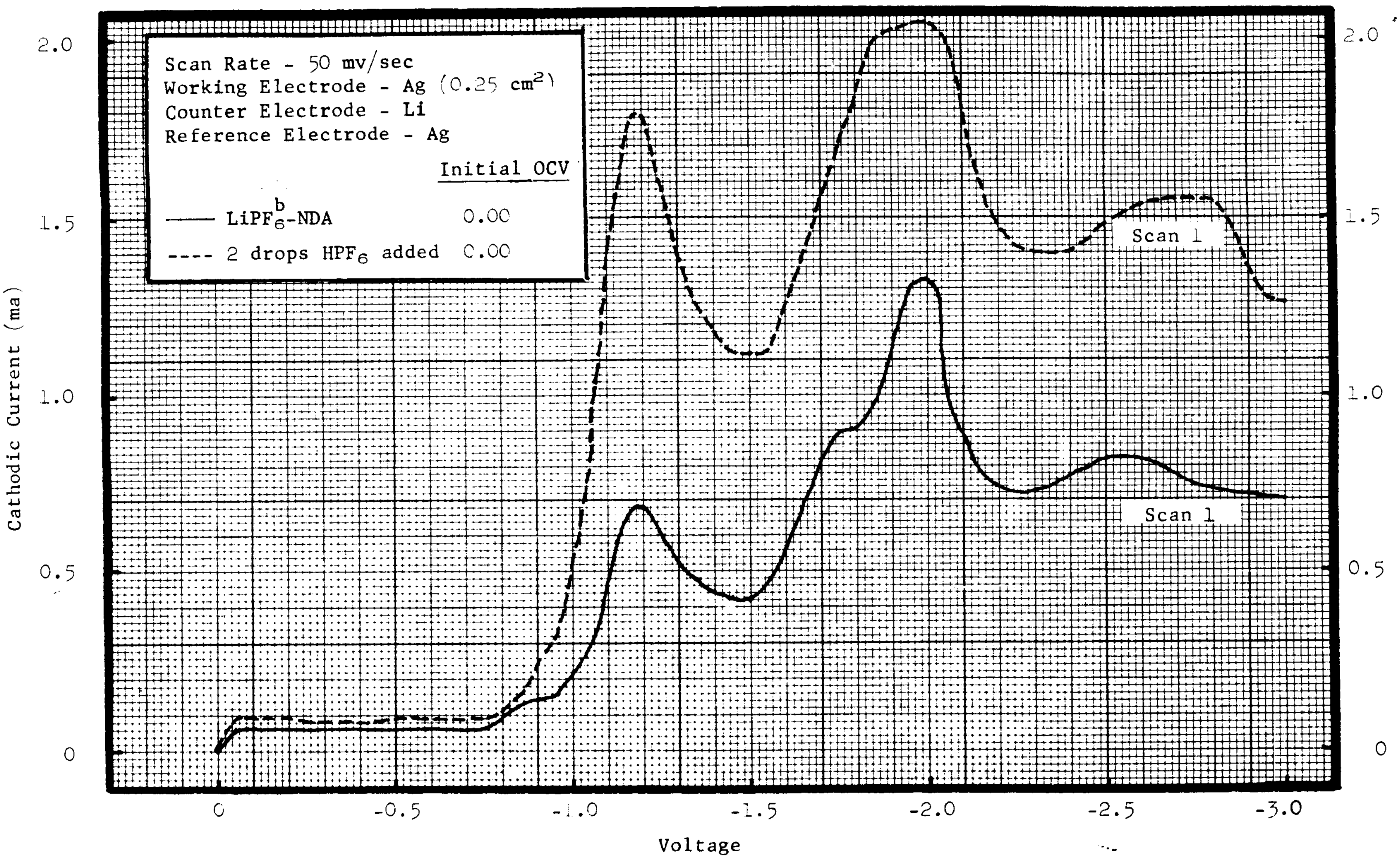

FIGURE 8. VOLTAMMETRIC SWEEP STUDIES OF ELECTROACTIVE IMPURITIES IN LITHIUM HEXAFLUOROPHOSPHATE (Continued)

Figure 8-e. Voltammetric Sweep Study of Adding Hexafluorophosphoric Acid[a] to $LiPF_6$[b]-N-Nitrosodimethylamine. The initial potentials were set equal to the open circuit voltages and the scans run towards more negative voltages.

[a] Hexafluorophosphoric acid used was a 65% aqueous solution.

[b] $LiPF_6$ used "as received."

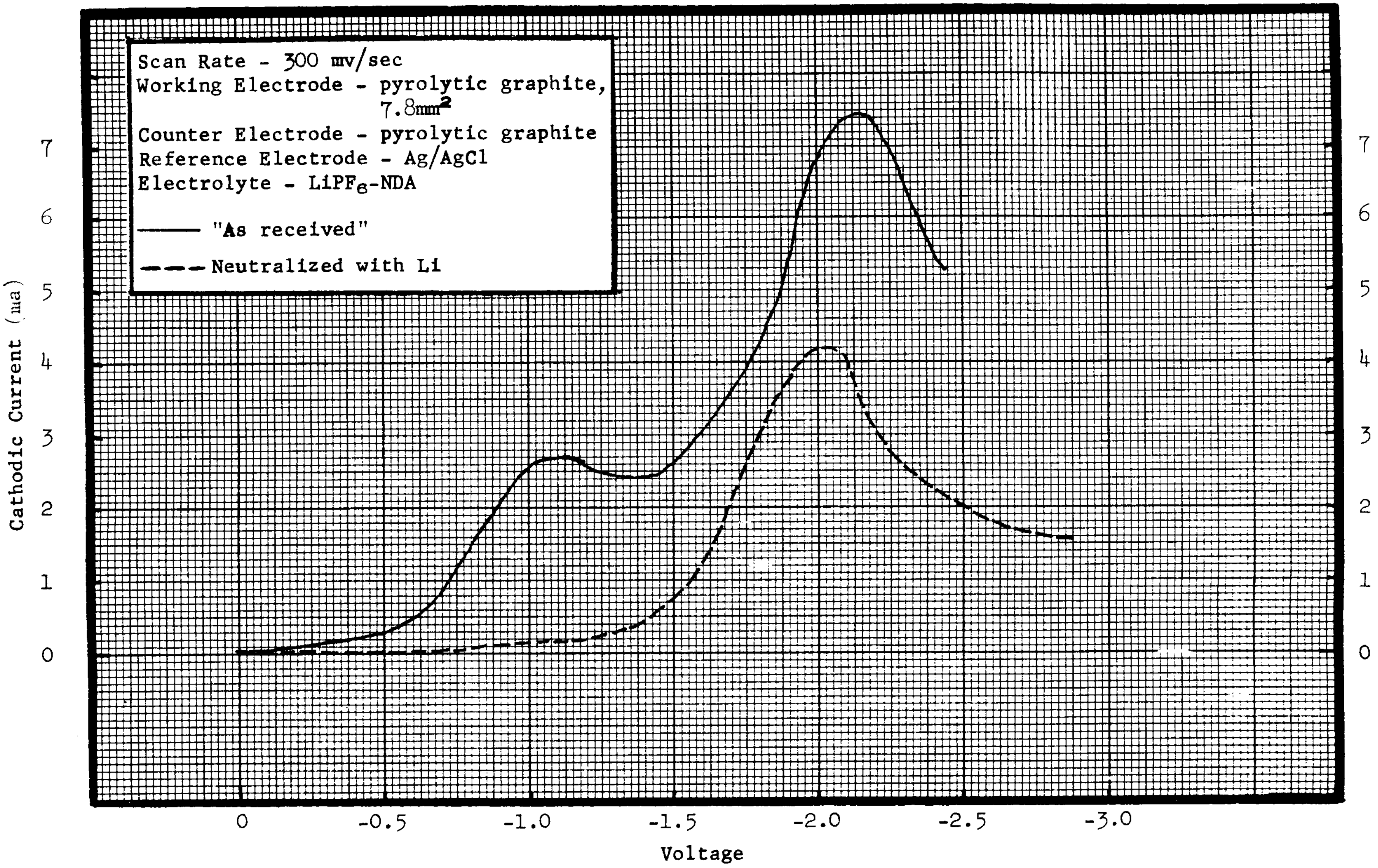

FIGURE 8. VOLTAMMETRIC SWEEP STUDIES OF ELECTROACTIVE IMPURITIES IN LITHIUM HEXAFLUOROPHOSPHATE (Continued)

Figure 8-f. The Effect of Neutralizing the Lithium Hexafluorophosphate-N-Nitrosodimethylamine Solution with Lithium Metal.

The initial potentials were set equal to the open circuit voltages and the scans run towards more negative voltages.

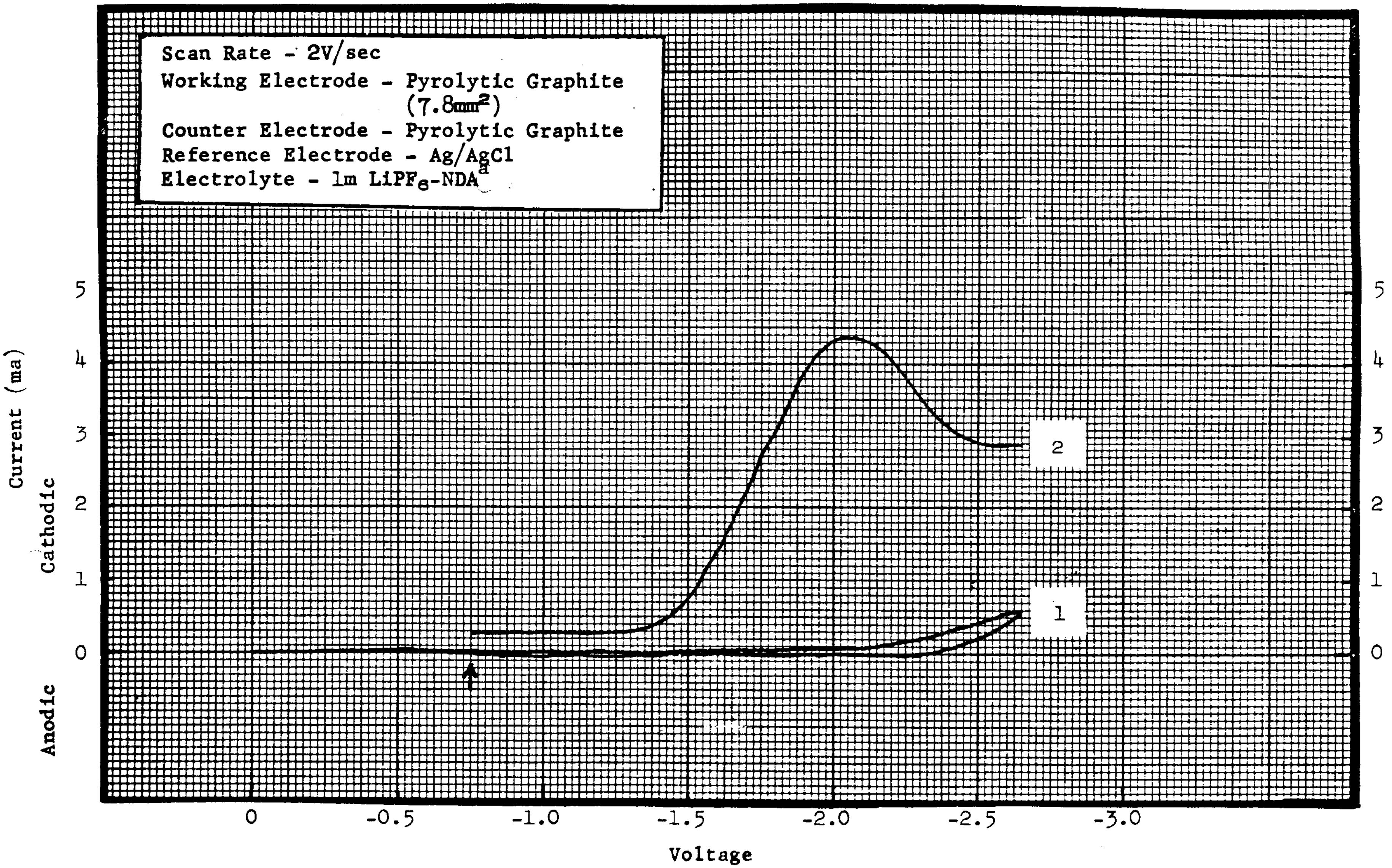

FIGURE 8. VOLTAMMETRIC SWEEP STUDIES OF ELECTROACTIVE IMPURITIES IN LITHIUM HEXAFLUOROPHOSPHATE (Continued)

Figure 8-g. Reduction of the Absorbed Species Found in Lithium Hexafluorophosphate-N-Nitrosodimethylamine. Curve 1 was obtained when the electrode had never been held at potentials more positive than -1.5V (vs. Ag/AgCl). Curve 2 is typical of the scans obtained when the electrode was held at -0.76V (vs. Ag/AgCl) for 5 to 10 seconds. (Voltage indicated by the arrow.)

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[a] The $LiPF_6$-NDA was neutralized with an excess of lithium prior to the electrochemical testing.

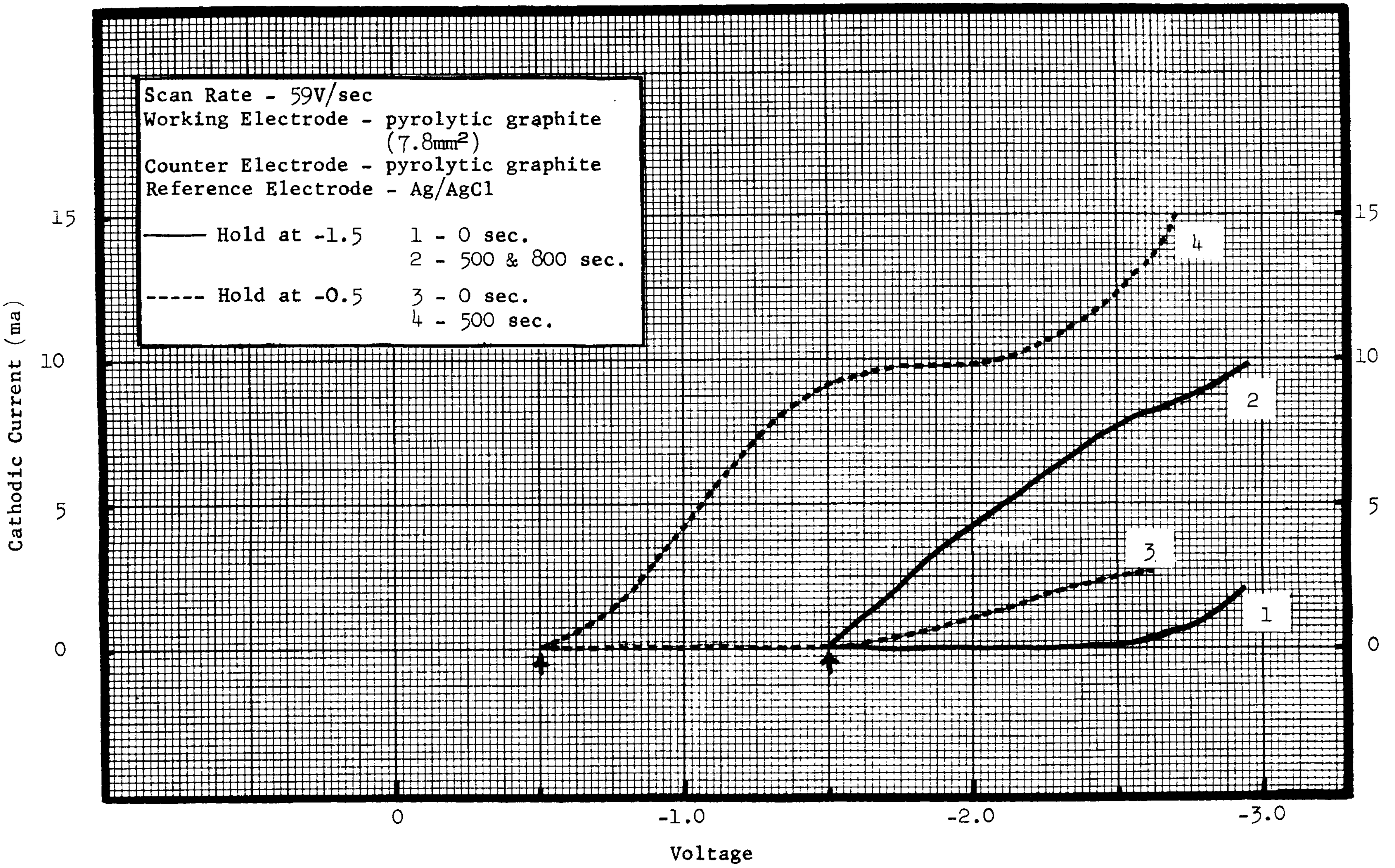


FIGURE 8. VOLTAMMETRIC SWEEP STUDIES OF ELECTROACTIVE IMPURITIES IN LITHIUM HEXAFLUOROPHOSPHATE (Continued)

Figure 8-h. Voltammetric Sweep Studies of the Electroactive Impurity Present in Lithium Hexafluorophosphate[a] N-Nitrosodimethylamine.

Curves 1 and 3 were obtained by making rapid scans over the voltage ranges indicated. Curves 2 and 4 represent the results obtained when the electrode was held at the potentials indicated by the arrows for the given lengths of time.

[a] LiPF[illegible]sed [illegible] re[illegible]ed.

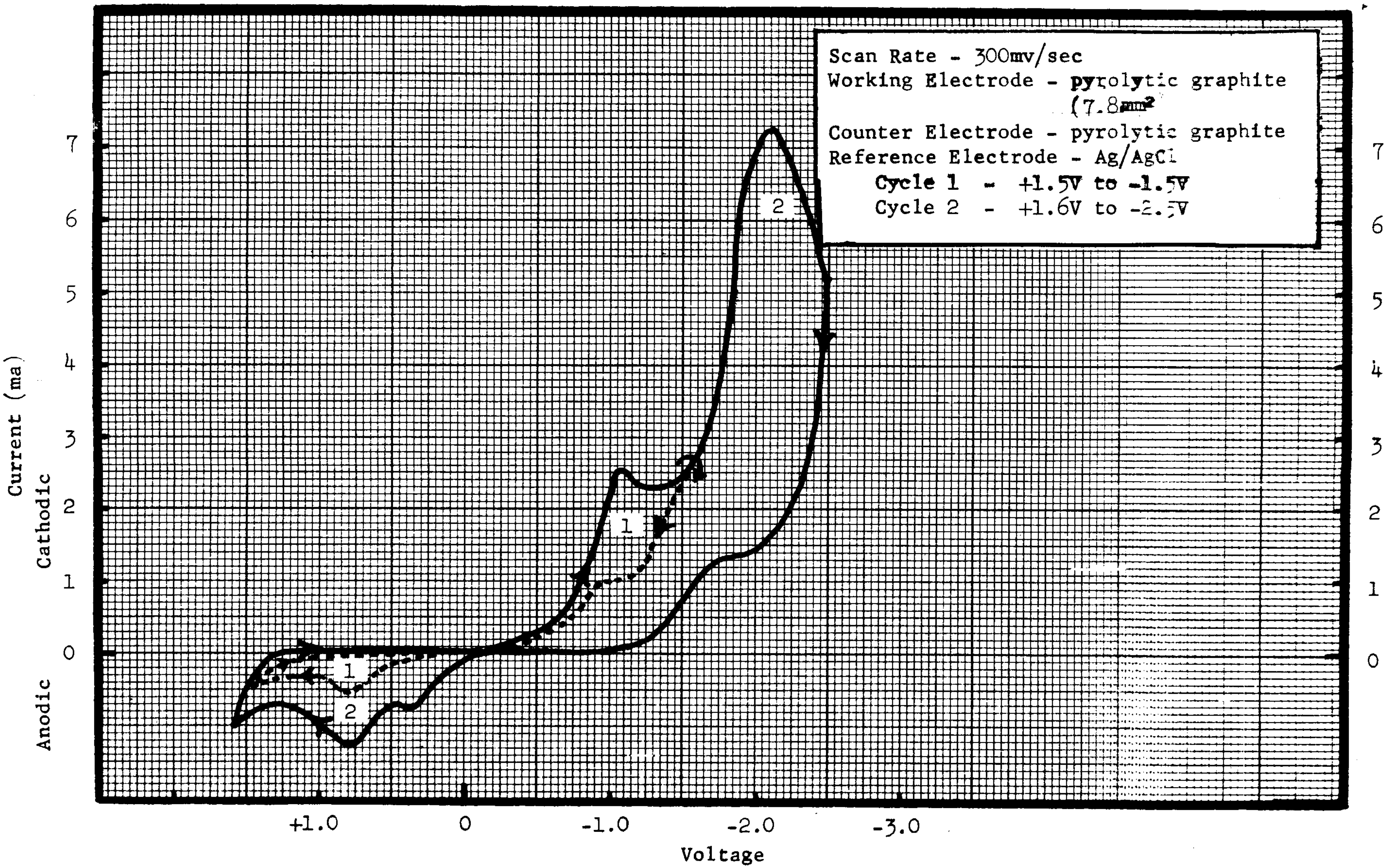


FIGURE 8. <u>VOLTAMMETRIC SWEEP STUDIES OF ELECTROACTIVE IMPURITIES IN LITHIUM HEXAFLUOROPHOSPHATE</u> (Continued)

Figure 8-1. Cyclic Voltammetric Study of the Electroactive Impurities Present in Lithium Hexafluorophosphate[a]-N-Nitrosodimethylamine.

The changes in the anodic portion of the scan as a function of increasing reduction are demonstrated by the differences between cycles 1 and 2.

[a] $LiPF_6$ used "as received."

TABLE VIII

ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES

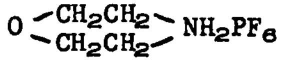
TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES

I. Anode-Electrolyte Systems Capable of Sustaining 100 ma/cm^2.

A. Lithium Anode Systems

	Electrolyte									
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities: Initial	Final	Further Observations and Remarks
1.	NDA	LiPF$_6$*	Ag/AgCl	Ag/AgCl	-3.33	-3.37	0.1	-3.32	-3.37	Continuous gassing of the lithium anode. Slight gassing occurred at the counter electrode during the 100 ma/cm^2 discharge. At the end of the discharges the lithium was covered with a gray film.
						-3.36	1	-3.36	-3.37	
						-2.85	10	-3.20	-2.76	
						-2.83	100	-1.98	-1.84	
2.	NDA	(m-C$_3$H$_7$)$_4$ NPF$_6$**	Ag/AgCl	Ag/AgCl	-2.95	-2.98	0.1	-2.92	-2.92	Moderate gassing at lithium electrode on open circuit and during discharge. A slight amount of a precipitate was observed near the lithium electrode. No change was apparent in the reference and counter electrode.
						-2.95	1	-2.90	-2.88	
						-2.95	10	-2.74	-2.68	
						-2.90	100	-1.80	-1.54	
3.	NDA	M PF$_6$*	Ag/AgCl	Ag/AgCl	-3.01	-3.01	0.1	-2.94	-2.94	Vigorous gassing at lithium electrode on open circuit and during discharge. A gelatinous material was formed in solution, and the surface of the counter electrode had deteriorated somewhat.
						-3.00	1	-2.92	-2.92	
						-2.92	10	-2.75	-2.75	
						-2.92	100	-2.34	-2.18	

* Morpholinium hexafluorophosphate -



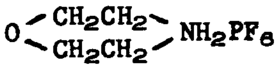
$O\begin{smallmatrix}\diagup CH_2CH_2 \diagdown \\ \diagdown CH_2CH_2 \diagup\end{smallmatrix}NH_2PF_6$

** Tetra-n-propylammonium hexafluorophosphate - $(n\text{-}C_3H_7)_4NPF_6$

TABLE VIII. ELECTROCHEMICAL HALF CELL SCREENING OF ANODES (Cont'd)

I. Anode-Electroltye Systems Capable of Sustaining 100 ma/cm^2. (Cont'd)
A. Lithium Anode Systems. (Cont'd)

	Electrolyte				Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
	Solvent	Solute	Reference Electrode	Counter Electrode				Initial	Final	
4.	DMF	NH_4PF_6	Ag/AgCl	Ag/AgCl	-3.10	-3.03 -3.02 -3.00 -2.99	0.1 1 10 100	-3.08 -3.03 -2.96 -2.00	-3.04 -3.02 -2.90 -1.80	Vigorous gas evolution occurred when the lithium was immersed. The solution became slightly turbid and turned yellow-brown by the 10 ma discharge. A new lithium anode was inserted for the 100 ma discharge because the first anode dissolved completely. The counter electrode gassed heavily at 100 ma and the anode potential flucturated considerably. A strong ammonia odor was detected.
5.	DMF	$KAsF_6$	Ag/AgCl	Ag/AgCl	-3.48	-3.46 -3.43 -3.37 -3.33	0.1 1 10 100	-3.42 -3.03 -2.98 -2.22	-3.37 -3.10 -2.98 -2.32	Gas evolution occurred at the lithium anode and at the counter electrode at 100 ma. The solution turned black and turbid.
6.	DMF	$M\ PF_6$*	Ag/AgCl	Ag/AgCl	-3.20	-3.25 -3.22 -3.18 -3.22	0.1 1 10 100	-3.24 -3.25 -3.04 -1.94	-3.28 -3.23 -3.00 -1.72	Vigorous gassing at lithium electrode on open circuit and during discharge. Lithium was gradually consumed, and a precipitate formed in the solution. The appearance of the reference and counter electrodes was unchanged.

* morpholinium hexafluorophosphate = 

$$O\begin{matrix} \diagup CH_2CH_2 \diagdown \\ \diagdown CH_2CH_2 \diagup \end{matrix} NH_2PF_6$$

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Cont'd)

I. Anode-Electrolyte Systems Capable of Sustaining 100 ma/cm^2. (Cont'd)
   A. Lithium Anode Systems (Cont'd).

	Electrolyte									
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities: Initial	Final	Further Observations and Remarks
7.	DMF	*	Ag/AgCl	Ag/AgCl	-3.32	-3.32	0.1	-3.32	-3.32	Vigorous gassing at lithium electrode at all times. Discharges at each current density were limited to two minutes instead of the usual five minutes because the rate of self-discharge appeared to be quite high. Brown product formed at lithium surface.
						-3.31	1	-3.30	-3.29	
						-3.26	10	-3.13	-3.15	
						-3.17	100	-2.32	-2.38	
8.	DMF	**	Ag/AgCl	Ag/AgCl	-3.52	-3.52	0.1	-3.52	-3.52	Vigorous gassing at lithium electrode at all times. Rate of gassing decreased slightly as the test progressed. Discharges at each current density were limited to two minutes because of high apparent rate of self-discharge.
						-3.51	1	-3.50	-3.48	
						-3.28	10	-3.08	-2.95	
						-3.26	100	-2.28	-2.35	
9.	DMF	***	Ag/AgCl	Ag/AgCl	-3.12	-3.18	0.1	-3.12	-3.17	Moderate rate of gassing at lithium after 4 minutes at 100 ma, accompanied by blackening of the lithium. Slow gassing continued on open circuit. The counter electrode deteriorated slightly. No change in appearance of the solution or reference electrode.
						-3.19	1	-3.03	-3.06	
						-3.20	10	-2.77	-2.85	
						-3.18	100	-1.65	-1.77	

* Di-n-butylammonium hexafluoroarsenate - $(n\text{-}C_4H_9)_2NH_2AsF_6$

** Tri-n-propylammonium hexafluoroarsenate - $(n\text{-}C_3H_7)_3NHAsF_6$

*** N-phenyl N,N,N-trimethylammonium hexafluorophosphate - $(C_6H_5)(CH_3)_3NPF_6$

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Cont'd)

I. Anode-Electrolyte Systems Capable of Sustaining 100 ma/cm^2.

B. Calcium Anode Systems

	Electrolyte				Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
	Solvent	Solute	Reference Electrode	Counter Electrode				Initial	Final	
10.	AN	*	Ag/AgCl	Ag/AgCl	-2.10	-2.13	0.1	-2.03	-2.04	At 1, 10 and 100 ma, a loosely adhering gray solid formed on the calcium. At 100 ma, gas evolved at the calcium electrode. No change in the appearance of the solution or counter and reference electrodes.
						-2.30	1	-1.75	-1.98	
						-2.32	10	-1.58	-1.72	
						-2.27	100	-1.10	-1.27	
11.	AN	**	Ag/AgCl	Ag/AgCl	-2.13	-2.14	0.1	-2.12	-2.12	Slight gas evolution occurred when the calcium was immersed in the solution. A slight amount of gray solid formed at the anode upon discharge. The counter electrode gassed at 100 ma and the solution became turbid.
						-2.14	1	-2.08	-2.09	
						-2.20	10	-1.74	-1.95	
						-2.21	100	-1.12	-1.45	

* Tetra-n-propylammonium hexafluorophosphate - $(n\text{-}C_3H_7)_4NPF_6$

** Ammonium hexafluorophosphate - NH_4PF_6

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES

I. Anode-Electrolyte Systems Capable of Sustaining 100 ma/cm^2.
B. Calcium Anode Systems (Cont'd).

	Electrolyte									
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities Initial	Final	Further Observations and Remarks
12.	AN	M PF$_6$*	Ag/AgCl	Ag/AgCl	-2.08	-2.05	0.1	-2.05	-2.00	Continuous moderate gassing at calcium electrode. Precipitate formed near surface of the calcium. When this was removed, substantial voltages (-2.16 to -1.50) were observed at 20, 30, 40 and 70 ma/cm^2. This system had been tentatively classified in the 10 ma/cm^2 because a temporary failure in instrumentation did not permit measurements at 100 ma/cm^2. Subsequent tests have indicated that the system can sustain 100 ma/cm^2. (Refer to data for discharge of this system through fixed resistors.)
						-2.00	1	-1.94	-1.90	
						-2.00	10	-1.58	-1.72	
						--	100	--	--	

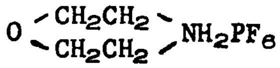
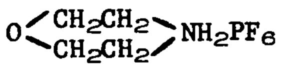
* Morpholinium Hexafluorophosphate - 
$O\begin{matrix}\diagup CH_2CH_2 \diagdown \\ \diagdown CH_2CH_2 \diagup\end{matrix}NH_2PF_6$

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2. (Continued)
B. Lithium Anode Systems.

	Electrolyte							Voltage of Anode vs. Reference Electrode at Various Current Densities		
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Initial	Final	Further Observations and Remarks
1.	DMC	* M PF$_6$	Ag/Agcl	Ag/AgCl	-3.15	-3.12 -3.10 -3.02 -3.00	0.1 1 10 100	-3.12 -3.06 -2.64 -1.20	-3.08 -3.04 -2.40 -0.40	Moderate gassing at lithium electrode initially. This slowly decreased, and finally ceased after discharges were made. At this point lithium had a white film on it. The counter electrode had deteriorated somewhat.
2.	DMF	KPF$_6$	PbO$_2$	PbO$_2$	-3.15	-3.05 -3.00 -2.90 -2.70	0.1 1 10 100	-3.08 -2.80 -2.45 -1.0	-3.03 -2.78 -2.45 -0.4	Solution slowly became cloudy. No gassing at any current density. Lithium remained shiny in appearance. At 20 and 30 ma/cm^2 the voltages were -1.6 and -1.2, respectively.
3.	DMF	LiCl	PbO$_2$	PbO$_2$	-3.08	-2.95 -2.92 -2.80 -2.85	0.1 1 10 100	-2.84 -2.60 -2.20 Reversed Polarity	-2.80 -2.62 -2.18 ----	At 40 ma/cm^2, voltage varied between -1.60 and -1.54. No gassing at any current density. The appearance of the electrodes and electrolyte did not change during the screening period.
4.	DMF	MgCl$_2$	Ag/AgCl	Ag/AgCl	-3.10	-3.00 -2.92 -2.84 -2.85	0.1 1 10 100	-3.02 -2.55 -1.94 Reversed Polarity	-2.97 -2.35 -2.05 ----	A black product formed at lithium surface and diffused into the solution. Reference and counter electrodes deteriorated somewhat.

* Morpholinium hexafluorophosphate -



$O\langle{}^{CH_2CH_2}_{CH_2CH_2}\rangle NH_2PF_6$

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Cont'd)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2. (Cont'd)
B. Lithium Anode Systems (Cont'd).

	Electrolyte		Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
	Solvent	Solute						Initial	Final	
5.	DMF	$(m\text{-}C_4H_9)_4NCl$*	Ag/AgCl	Ag/AgCl	-3.08	-3.10 -3.05 -2.96 -2.89	0.1 1 10 100	-3.08 -3.00 -2.35 Reversed Polarity	-3.08 -2.93 -1.65 --	Lithium became appreciably blackened. Reference and counter electrodes deteriorated somewhat, and the electrolyte becamse cloudy.
6.	DMF	$(C_8H_5)_4PCl$**	Ag/AgCl	Ag/AgCl	-2.93	-2.90 -2.86 -2.83 -2.10	0.1 1 10 100	-2.90 -2.84 -2.42 -0.55	-2.88 -2.84 -2.47 Reversed Polarity	Lithium gassed at moderate rate upon immersion in the electrolyte and became appreciably blackened upon discharge. Brown solid was suspended in the solution. AgCl electrodes deteriorated somewhat.
7.	80 WT % EC 20 WT % PC	$AlCl_3LiCl$	Ag/AgCl	Ag/AgCl	-2.92	-2.92 -2.85 -2.85 --	0.1 1 10 100	-2.88 -2.70 -1.70 Reversed Polarity	-2.88 -2.70 -2.33 --	A solid material was produced during reaction which floated at the surface of the solution. Slow gassing was observed only at 100 ma/cm^2. Lithium also became
8.	80 WT % EC 20 WT % PC	$(m\text{-}C_4H_9)_4NCl$*	Ag/AgCl	Ag/AgCl	-2.93	-2.89 -2.85 -2.84 -2.83	0.1 1 10 100	-2.88 -2.62 -1.18 Reversed Polarity	-2.84 -2.67 -1.68 --	No changes in the appearance of the entire system.

* Tetra-n-butylammonium chloride - $(n\text{-}C_4H_9)_4NCl$

** Tetraphenylphosphonium chloride - $(C_8H_5)_4PCl$

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Cont'd)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2. (Continued)
B. Lithium Anode Systems (Cont'd).

	Electrolyte				Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
	Solvent	Solute	Reference Electrode	Counter Electrode				Initial	Final	
9.	80 WT % EC 20 WT % PC	$(m-C_3H_9)_4NOF_8$*	Ag/AgCl	Ag/AgCl	-3.33	-3.15	0.1	-3.30	-3.11	Slow gassing at lithium upon immersion in the electrolyte. Gassing ceased at 10 ma/cm^2. No change in the appearance of the system.
						-3.04	1	-2.98	-2.86	
						-3.00	10	-2.30	-2.20	
						-3.00	100	Reversed Polarity	--	
10.	80 WT % EC 20 WT % PC	M PF_6 **	Ag/AgCl	Ag/AgCl	-2.97	-3.02	0.1	-2.97	-2.97	Discharges were repeated at 10 ma/cm^2 after the 100 ma/cm^2 discharge, and yielded steady voltages of -2.30. At 20 ma/cm^2 voltage was steady at -1.74. The appearance of lithium was changed very little after the discharges. Is the steadiness at -1.74V indicative of a limiting capability of the surface.
						-2.98	1	-2.88	-2.76	
						-2.88	10	-1.68	-2.40	
						-2.83	100	Reversed Polarity	--	
11.	NDA	$AlCl_3$	Ag/AgCl	Ag/AgCl	-2.88	-2.88	0.1	-2.84	-2.82	White film formed on lithium. No gassing except at 100 ma/cm^2 (slow). At 20 ma/cm^2 voltage was -2.40; at 40 ma/cm^2 voltage was -1.90; at 10 ma/cm^2 (repeated) voltage was -2.60.
						-2.88	1	-2.80	-2.79	
						-2.85	10	-2.34	-1.94	
						-2.88	100	-0.8	-0.4	
12.	NDA	***	Ag/AgCl	Ag/AgCl	-3.15	-3.10	0.1	-3.05	-3.02	Lithium became somewhat draker in appearance. No gassing at any time. No change in appearnce of the solution.
						-3.02	1	-2.84	-2.82	
						-2.90	10	-2.16	-2.18	
						-2.90	100	Reversed Polarity	--	

* Tetra-n-propylemmonium hexafluorophosphate $(n-C_3H_7)_4NPF_6$

** Morpholinium hexafluorophosphate - $O\genfrac{}{}{0pt}{}{\diagup CH_2CH_2 \diagdown}{\diagdown CH_2CH_2 \diagup}NH_2PF_6$

[redacted]*** [redacted]p-D[redacted]ylb[redacted]l)N[redacted]-tr[redacted]thy[redacted]oni[redacted]exa[redacted]rop[redacted]pha[redacted] (p[redacted]$_{25}$[redacted]CH$_2$[redacted]$_3$)[redacted] [redacted] [redacted] [redacted] [redacted]

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Cont'd)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2. (Cont'd)
B. Lithium Anode Systems. (Cont'd)

	Electrolyte Solvent	Electrolyte Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities Initial	Voltage of Anode vs. Reference Electrode at Various Current Densities Final	Further Observations and Remarks
13.	NDA	$MgCl_2$	Ag/AgCl	Ag/AgCl	-3.00	-3.00	0.1	-2.80	-2.80	At 40 ma/cm^2 voltage was steady at -1.08. At 30 ma/cm^2 voltage was steady at -1.48. At 20 ma/cm^2 voltage was steady at -2.02. No gassing at any time. Lithium became darker in appearance at high current densities.
						--	1	-2.44	-2.60	
						-2.90	10	-1.60	-2.26	
						--	100	Reversed Polarity	--	
14.	NDA	M PF_6-$NaSbF_6$*	Ag/AgCl	Ag/AgCl	-3.42	-3.20	0.1	-3.35	-3.10	Moderate gassing at lithium at all times. Rate of gassing decreased somewhat as experiment proceeded. Lithium became dark at high current densities. No change in appearance of the solution.
						-2.90	1	-3.00	-2.40	
						-2.70	10	-2.20	-2.00	
						--	100	-0.60	-0.40	
15.	NDA	$(m\text{-}C_4H_9)_2NH_2AsF_6$**	Ag/AgCl	Ag/AgCl	-3.15	--	0.1	--	--	Lithium remains shiny in appearance at 100 ma/cm^2. Moderate gassing at lithium at all times. No change in appearance of the solution or counter and reference electrodes.
						-3.05	1	-3.08	-2.94	
						-3.00	10	-2.78	-2.74	
						-2.95	100	-1.47	-1.10	
16.	NDA	$(m\text{-}C_4H_9)_4NCl$***	Ag/AgCl	Ag/AgCl	-2.88	-2.82	0.1	-2.80	-2.83	Lithium became darkened in appearance. Slow gassing began at 100 ma/cm^2. No change in appearance of the solution.
						-2.88	1	-2.70	-2.72	
						-2.85	10	-2.28	-2.30	
						-2.85	100	Reversed Polarity	--	

* Morpholinium hexafluorophosphate - $O\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}NH_2PF_6$ - $NaSbF_6$

** Di-n-butylammonium hexafluoroarsenate - $(n\text{-}C_4H_9)_2H_2NAsF_6$

*** Tetra-n-butylammonium chloride - $(n\text{-}C_4H_9)_4NCl$

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2. (Continued)
B. Lithium Anode Systems. (Continued)

	Electrolyte				Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
	Solvent	Solute	Reference Electrode	Counter Electrode				Initial	Final	
17.	NDA	$(CH_3)_4NPF_6$*	Ag/AgCl	Ag/AgCl	-3.50	-3.10 -3.10 -2.95 -2.90	0.1 1 10 100	-3.40 -2.36 -2.00 Reversed Polarity	-2.86 -2.54 -2.10 ----	No change in appearance of the solution, counter, and reference electrodes. No gassing at any time.
18.	NDA	$(C_6H_5)_4AsCl$**	Ag/AgCl	Ag/AgCl	-3.05	-3.05 -3.02 -2.95 -2.95	0.1 1 10 100	-3.02 -2.85 -2.48 Reversed Polarity	-3.02 -2.84 -2.52 ----	White film formed at surface of lithium. Slow gassing observed at 100 ma/cm^2. No change in appearance of the solution. Counter electrode had deteriorated slightly.
19.	NDA	$(C_6H_5)_4PCl$***	Ag/AgCl	Ag/AgCl	-3.05	-3.05 -3.02 -2.98 -2.90	0.1 1 10 100	-2.98 -2.78 -2.44 -0.68	-2.98 -2.78 -2.52 Reversed Polarity	No change in appearance of the solution. Lithium became black in appearance and gassed continuously after 10 ma/cm^2 discharge. Counter and reference electrodes had deteriorated somewhat.
20.	NDA	$(m\text{-}C_3H_7)_3NHAsF_6$****	Ag/AgCl	Ag/AgCl	-3.28	-3.05 -2.98 -2.95 -2.90	0.1 1 10 100	-3.25 -2.90 -2.75 -1.28	-2.92 -2.88 -2.70 -1.20	At 150 ma/cm^2 voltage varied from -0.40 to -0.24. Lithium remained shiny but was gassing moderately at all times, and was eventually consumed. A brown precipitate formed in the solution.

* Tetramethylammonium hexafluorophosphate - $(CH_3)_4NPF_6$

** Tetraphenylarsonium chloride - $(C_6H_5)_4AsCl$

*** Tetraphenylphosphonium chloride - $(C_6H_5)_4PCl$

**** Tetra-n-propylammonium hexafluoroarsenate - $(n\text{-}C_3H_7)_4NAsF_6$

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2. (Continued)
B. Lithium Anode Systems. (Continued)

	Electrolyte				Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
	Solvent	Solute	Reference Electrode	Counter Electrode				Initial	Final	
21.	NDA	$(m\text{-}C_3H_7)_4NBF_4$*	Ag/AgCl	Ag/AgCl	-2.95	-2.90 -2.95 -2.95 -2.95	0.1 1 10 100	-2.90 -2.83 -2.50 Reversed Polarity	-2.90 -2.83 -2.54 ----	White film formed at surface of lithium. Very slow rate of gassing at all times. No change in appearance of the solution or in the counter and reference electrodes.
22.	NDA	**	Ag/AgCl	Ag/AgCl	-3.20	-3.15 -3.05 -3.05 -2.90	0.1 1 10 100	-3.06 -2.78 -2.36 Reversed Polarity	-3.04 -2.82 -2.12 ----	Lithium became blackened at 100 ma/cm^2. No gassing at any time. No change in appearance of the solution or the counter and reference electrodes.
23.	NDA	$(C_6H_5)(CH_3)_3NPF_6$***	Ag/AgCl	Ag/AgCl	-3.42	-3.20 -3.05 -3.05 -2.95	0.1 1 10 100	-3.35 -2.84 -2.20 -1.20	-3.10 -2.78 -2.18 -0.8	Solution became dark in color. No gassing was apparent. Lithium became somewhat darker in appearance.
24.	PC	$AlCl_3$-LiCl	Ag/Agcl	Ag/AgCl	-2.90	-2.95 -2.90 -2.90 -2.90	0.1 1 10 100	-2.78 -2.70 -1.98 Reversed Polarity	-2.80 -2.78 -2.48 ----	Lithium became dark gray in appearance. Slow gassing at lithium began at 100 ma/cm^2. Counter electrode also gassed at 100 ma/cm^2. No change in appearance of the solution or the counter and reference electrodes.

* Tetra-n-propylammonium tetrafluoroborate - $(n\text{-}C_3H_7)_4NBF_4$

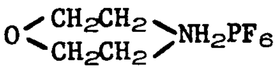
** N-Benzyl N,N,N-trimethylammonium hexafluoroantimonate - $(C_6H_5CH_2)(CH_3)_3NSbF_6$

*** N-Phenyl N,N,N-trimethylammonium hexafluorophosphate - $(C_6H_5)(CH_3)_3NPF_6$

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2. (Continued)
B. Lithium Anode Systems. (Continued)

	Electrolyte							Voltage of Anode vs. Reference Electrode at Various Current Densities		
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Initial	Final	Further Observations and Remarks
25.	PC	M PF$_6$*	Ag/AgCl	Ag/AgCl	-3.02	-3.05 -2.95 -2.92 -2.90	0.1 1 10 100	-3.10 -2.69 -1.52 Reversed Polarity	-3.00 -2.74 -1.84 ----	Lithium became light gray in appearance. No gassing at any time. No change in appearance of the solution or counter and reference electrodes.
26.	TMU	M PF$_6$*	Ag/AgCl	Ag/AgCl	-3.21	-3.20 -3.20 -3.15 -3.12	0.1 1 10 100	-3.14 -3.12 -2.86 Reversed Polarity	-3.14 -3.09 -2.89 ----	At 20 ma/cm^2 voltage varied from -2.80 to -2.71. At 30 ma/cm^2 voltage varied from -2.32 to -1.68. At 40 ma/cm^2 voltage varied from -2.08 to -0.04. Moderate gassing at lithium at all times. A gray film formed at the lithium surface.
27.	TMU	M. PF$_6$-LiCl**	Ag/AgCl	Ag/AgCl	-3.10	-3.12 -3.12 -3.12 -3.12	0.1 1 10 100	-3.08 -3.04 -2.74 Reversed Polarity	-3.08 -3.06 -2.73 ----	Moderate gassing at lithium electrode at all times. No change in appearance of the solution or reference or counter electrodes.

* Morpholinium hexafluorophosphate -

$O<\begin{smallmatrix}CH_2CH_2\\CH_2CH_2\end{smallmatrix}>NH_2PF_6$

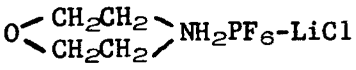
** Morpholinium hexafluorophosphate -

$O<\begin{smallmatrix}CH_2CH_2\\CH_2CH_2\end{smallmatrix}>NH_2PF_6\text{-}LiCl$

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2. (Continued)
B. Lithium Anode Systems. (Continued)

	Electrolyte							Voltage of Anode vs. Reference Electrode at Various Current Densities		
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Initial	Final	Further Observations and Remarks
28.	80 WT % EC 20 WT % PC	*	Ag/AgCl	Ag/AgCl	-3.20	-3.17	0.1	-3.20	-3.18	Lithium gassed moderately at all times. No changes in the appearance of the solution or counter and reference electrodes.
						-3.11	1	-3.13	-3.10	
						-3.04	10	-2.82	-2.83	
						-2.98	100	Reversed Polarity	----	

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* Tri-n-propylammonium hexafluoroarsenate - $(n\text{-}C_3H_7)_3NHAsF_6$

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES IN PRETREATED ELECTROLYTES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2.

A. Lithium Anode Systems.

	Electrolyte Solvent	Electrolyte Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities: Initial	Voltage of Anode vs. Reference Electrode at Various Current Densities: Final	Further Observations and Remarks
29.	NDA	*	Ag/AgCl	Ag/AgCl	-2.90	-2.90	0.1	-2.88	-2.88	During the 100 ma discharge, both the lithium and the counter electrodes gassed lightly. A gray-white film formed at the lithium surface and the counter electrode became blackened. No change in the appearance of the reference electrode or the electrolyte.
						-2.90	1	-2.81	-2.83	
						-2.90	10	-2.48	-2.64	
						-2.83	100	-1.20	-1.00	

* $(n\text{-}C_3H_7)_3NHAsF_6$ - Tri-n-propylammonium hexafluoroarsenate (1 molal). The solution was pretreated with lithium until gas evolution ceased. In addition to evolving an appreciable amount of gas, this reaction resulted in the formation of a second liquid which was immiscible with the rest of the solution and amounted to ca. 10% of the total volume. Solid was also formed. After filtering the solution, it had a specific conductance of 1.85×10^{-2} ohm^{-1} cm^{-1} (larger liquid phase) as compared to 2.36×10^{-2} ohm^{-1} cm^{-1} for the untreated solution. The combination of the two immiscible liquids was used for the screening test, but the electrodes were not in contact with the smaller (upper) phase.

The results for the same system (not pretreated with lithium) are listed below for comparison. Conductance of the electrolyte was 2.35×10^{-2} ohm^{-1} cm^{-1}.

	Electrolyte Solvent	Electrolyte Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities: Initial	Voltage of Anode vs. Reference Electrode at Various Current Densities: Final	Further Observations and Remarks
30.	NDA	**	Ag/AgCl	Ag/AgCl	-3.40	-3.00	0.1	-3.30	-2.92	Vigorous gassing at lithium electrode at all times. No discharge was carried out at 1 ma, and at 10 ma the discharge was interrupted after two minutes. At this point, much of the lithium had been consumed. Discharge was then carried out at 100 ma for 20 seconds.
						----	1	----	----	
						-3.00	10	-2.74	----	
						----	100	-1.44	----	

** $(n\text{-}C_3H_7)_3NHAsF_6$ - Tri-n-propylammonium hexafluoroarsenate (1 molal)

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2. (Continued)

B. Lithium Anode Systems. (Continued)

	Electrolyte									
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities: Initial	Voltage of Anode vs. Reference Electrode at Various Current Densities: Final	Further Observations and Remarks
31.	NDA	*	Ag/AgCl	Ag/AgCl	-2.93	-2.87	0.1	-2.92	-2.87	The lithium electrode gassed continuously. During the 100 ma/cm^2 discharge gassing began at the counter electrode and deterioration was evident. There was no change in the appearance of the reference electrode or the electrolyte.
						-2.87	1	-2.85	-2.85	
						-2.87	10	-2.67	-2.68	
						-2.83	100	-1.40	-1.36	

The system whose reaction products might be LiPF$_6$ and morpholine is listed below for comparison.

	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Initial	Final	Further Observations and Remarks
32.	NDA	**	Ag/AgCl	Ag/AgCl	-2.90	-2.91	0.1	-2.90	-2.91	Counter electrode gassed at 100 ma. No change in the appearance of the lithium, the reference electrode, or the electrolyte.
						-2.91	1	-2.87	-2.88	
						-2.90	10	-2.72	-2.68	
						-2.88	100	-1.60	-1.64	

* LiPF$_6$ (1 molal) and $O{<}\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}{>}NH$ - morpholine (1 molal). Specific conductance = 1.85 x 10^{-2} ohm^{-1} cm^{-1}.

** $O{<}\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}{>}NH_2PF_6$-morpholinium hexafluorophosphate (1 molal). The solution was pretreated with lithium metal until gas evolution ceased. This reaction resulted in the formation of a gelatinous yellow solid in addition to the evolution of an appreciable quantity of gas. After filtering the solution had a specific conductance of 1.81 x 10^{-2} ohm^{-1} cm^{-1} as compared to 2.74 x 10^{-2} ohm^{-1} cm^{-1} for the untreated solution.

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2.
A. Calcium Anode Systems.

	Electrolyte							Voltage of Anode vs. Reference Electrode at Various Current Densities		
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Initial	Final	Further Observations and Remarks
33.	AN	$LiPF_6$	Ag/AgCl	Ag/AgCl	-2.66	-2.60	0.1	-2.43	-2.07	The calcium anode became covered with a black film during the 10 ma/cm^2 discharge. During the 100 ma/cm^2 discharge vigorous gassing occurred at the calcium electrode and a black solid fell from its surface. The counter electrode also began gassing vigorously during the 100 ma/cm^2 discharge. There was no change in the appearance of the reference electrode or the electrolyte.
						-2.61	1	-1.83	-2.01	
						-2.17	10	-1.72	-1.63	
						-2.27	100	-1.28	-1.10	
34.	DMF	NH_4PF_6	Ag/AgCl	Ag/AgCl	-2.48	-2.50	0.1	-2.48	-2.50	Continuous moderate gassing at the calcium anode. The solution became slightly turbid during discharge. The counter electrode began gassing during the 100 ma/cm^2 discharge. The calcium anode was partially black at the end of the discharges. No change in the appearance of the reference electrode.
						-2.48	1	-2.47	-2.48	
						-2.34	10	-2.35	-2.25	
						-2.16	100	-1.35	Reversed Polarity	

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2. (Continued)
A. Calcium Anode Systems. (Continued)

	Electrolyte									
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities: Initial	Voltage of Anode vs. Reference Electrode at Various Current Densities: Final	Further Observations and Remarks
35.	NDA (Distilled)	$LiPF_6$	Ag/AgCl	Ag/AgCl	-2.13	-2.27	0.1	-2.13	-2.22	The calcium gassed continuously and turned black. There were no other changes in the system.
						-2.26	1	-2.06	-2.06	
						-2.00	10	-1.83	-1.25	
						-1.87	100	Reversed Polarity	----	

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2.

A. Calcium Anode Systems.

	Electrolyte							Voltage of Anode vs. Reference Electrode at Various Current Densities		
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Initial	Final	Further Observations and Remarks
36.	AN	*	Ag/AgCl	Ag/AgCl	-2.00	-1.97	0.1	-1.94	-1.92	After the 100 ma discharge, a small amount of white solid was suspended in the electrolyte. No change in appearance of calcium or counter and reference electrodes.
						-2.07	1	-1.65	-1.77	
						-2.08	10	-1.45	-1.34	
						-2.10	100	Reversed Polarity	----	
37.	DMF	*	Ag/AgCl	Ag/AgCl	-2.32	-2.25	0.1	-2.32	-2.27	At 50 ma, voltage was initially -1.00 but reversed to +0.25 within 30 seconds. Calcium became blackened upon discharge at 0.1 ma.
						-2.17	1	-2.15	-2.12	
						-2.49	10	-1.50	-1.96	
						-2.22	100	-0.50	Reversed Polarity	
38.	DMF	**	Ag/AgCl	Ag/AgCl	-2.44	-2.39	0.1	-1.98	-1.98	At 50 ma, voltage varied between -0.60 and -0.79. Black material formed at calcium surface and diffused into the solution.
						-2.53	1	-1.65	-1.92	
						-2.57	10	-1.00	-1.63	
						-2.48	100	Reversed Polarity	----	

* Tetramethylammonium hexafluorophosphate - $(CH_3)_4NPF_6$

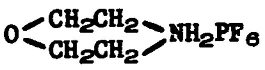
** Morpholinium hexafluorophosphate - 
$O\begin{matrix}\diagup CH_2CH_2 \diagdown \\ \diagdown CH_2CH_2 \diagup\end{matrix}NH_2PF_6$

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2.(Continued)
A. Calcium Anode Systems. (continued)

	Electrolyte							Voltage of Anode vs. Reference Electrode at Various Current Densities		
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Initial	Final	Further Observations and Remarks
39.	DMF	NaPF$_6$	Ag/AgCl	Ag/AgCl	-2.25	-2.48	0.1	-2.05	-2.04	Calcium blackened during the 10 ma and 100 ma discharges and gas evolution began at the counter electrode at 100 ma. No change in the appearance of the reference electrode or the solution.
						-2.57	1	-2.04	-2.03	
						-2.63	10	-1.97	-1.88	
						-2.65	100	Reversed Polarity	---	
40.	DMF	KAsF$_6$	Ag/AgCl	Ag/AgCl	-2.18	-2.23	0.1	-1.75	-1.75	Calcium blackened during the 10 ma and 100 ma discharges and gassed at 100 ma. The counter electrode began gassing at 100 ma with the formation of a black solid.
						-2.43	1	-1.60	-1.72	
						-2.48	10	-1.48	-1.56	
						-2.36	100	-0.25	-0.24	
41.	DMF	KPF$_6$	Ag/AgCl	Ag/AgCl	-2.36	-2.38	0.1	-2.07	-2.04	At 100 ma calcium blackened, the counter electrode gassed vigorously, and the solution changed from colorless to brown.
						-2.45	1	-2.00	-1.98	
						-2.58	10	-1.87	-1.84	
						-2.63	100	-1.14	-1.03	
42.	DMF	LiCl	Ag/AgCl	Ag/AgCl	-2.22	-2.17	0.1	-2.10	-2.15	Both counter and reference electrodes deteriorated to some extent. Beginning at the 1 ma discharge, the calcium gassed continuously. At 10 ma, the calcium blackened and a brown turbidity appeared in the solution around it.
						-1.95	1	-2.05	-2.10	
						-1.80	10	-1.78	-1.11	
						-1.85	100	Reversed Polarity	----	

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2. (Continued)

A. Calcium Anode Systems (Continued)

	Electrolyte							Voltage of Anode vs. Reference Electrode at Various Current Densities		
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Initial	Final	Further Observations and Remarks
43.	DMF	*	Ag/AgCl	Ag/AgCl	-2.16	-2.34	0.1	-2.02	-2.02	At 100 ma, calcium blackened, the solution changed from colorless to a turbid brown, and the counter electrode deteriorated slightly.
						-2.41	1	-2.02	-2.02	
						-2.42	10	-1.80	-1.82	
						-2.42	100	-0.65	Reversed Polarity	
44.	DMF	**	Ag/AgCl	Ag/AgCl	-1.88	-1.87	0.1	-1.70	-1.82	After the 10 ma discharge, the calcium gassed at all times. It also blackened with the formation of a black turbidity under it. At 50 ma, voltage varied between -1.0 and -1.38. No changes in counter or reference electrodes.
						-2.03	1	-1.40	-1.82	
						-2.23	10	-1.00	-1.77	
						-2.43	100	Reversed Polarity	----	
45.	80 WT % EC 20 WT % PC	$AlCl_3$	Ag/AgCl	Ag/AgCl	-2.57	-2.57	0.1	-2.55	-2.57	Calcium gassed slowly at all times. No changes in appearance of the solution or counter and reference electrodes.
						-2.57	1	-2.52	-2.53	
						-2.57	10	-2.18	-2.20	
						-2.57	100	Reversed Polarity	----	
46.	80 WT % EC 20 WT % PC	KPF_6	Ag/AgCl	Ag/AgCl	-2.57	-2.32	0.1	-1.74	-1.81	Moderate gassing at calcium at 100 ma. No changes in the appearance of the solution or counter and reference electrodes.
						-2.28	1	-1.72	-1.72	
						-2.23	10	-1.50	-1.49	
						-2.39	100	Reversed Polarity	----	

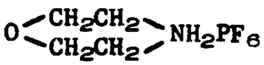
* N-(p-Dodecylbenzyl)N,N,N-trimethylammonium hexafluorophosphate - $(p\text{-}C_{12}H_{25}C_6H_4CH_2)(CH_3)_3NPF_6$

** N-phenyl N,N,N-trimethylammonium hexafluorophosphate - $(C_6H_5)(CH_3)_3NPF_6$

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2. (Continued)
A. Calcium Anode Systems. (Continued)

	Electrolyte							Voltage of Anode vs. Reference Electrode at Various Current Densities		
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Initial	Final	Further Observations and Remarks
47.	80 WT % EC 20 WT % PC	*	Ag/AgCl	Ag/AgCl	-2.32	-2.24	0.1	-2.18	-1.94	Calcium gassed slowly at all times and became darkened at 10 ma.
						-2.47	1	-1.85	-2.04	
						-2.48	10	-1.65	-1.35	
						-2.48	100	Reversed Polarity	----	
48.	80 WT % EC 20 WT % PC	**	Ag/AgCl	Ag/AgCl	-2.04	-2.09	0.1	-1.99	-2.06	Calcium began gassing at 0.1 ma and continued to do so at all times until coated gray-black during the 100 ma discharge. No changes in the appearance of the solution or counter and reference electrodes.
						-2.13	1	-1.85	-1.90	
						-2.23	10	-1.35	-1.32	
						-2.20	100	Reversed Polarity	----	
49.	80 WT % EC 20 WT % PC	***	Ag/AgCl	Ag/AgCl	-2.07	-2.11	0.1	-1.53	-1.64	At 100 ma, calcium gassed vigorously and a gray film formed at the surface. No changes in the appearance of the solution or counter and reference electrodes.
						-2.17	1	-1.53	-1.56	
						-2.18	10	-1.35	-1.34	
						-2.15	100	Reversed Polarity	----	
50.	NDA	**	Ag/AgCl	Ag/AgCl	-1.83	-1.77	0.1	-1.58	-1.54	At 10 ma, calcium began to gas and continued to do so at all times; solid formed at the calcium surface. No changes in the appearance of the solution or counter and reference electrodes.
						-1.88	1	-1.26	-1.43	
						-2.08	10	-1.25	-1.32	
						-2.10	100	Reversed Polarity	----	

* Morpholinium hexafluorophosphate - 

$O\begin{smallmatrix}CH_2CH_2\\CH_2CH_2\end{smallmatrix}NH_2PF_6$

** N-phenyl N,N,N-trimethylammonium hexafluorophosphate - $(C_6H_5)(CH_3)_3NPF_6$

*** Tetramethylammonium hexafluorophosphate - $(CH_3)_4NPF_6$

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2. (Continued)
A. Calcium Anode Systems. (Continued)

	Electrolyte Solvent	Electrolyte Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities: Initial	Voltage of Anode vs. Reference Electrode at Various Current Densities: Final	Further Observations and Remarks
51.	NDA	KPF$_6$	Ag/AgCl	Ag/AgCl	-2.30	-2.18	0.1	-1.50	-1.62	Calcium became blackened during the discharges.
						-2.13	1	-1.40	-1.43	
						-2.10	10	-1.27	-1.28	
						-2.15	100	Reversed Polarity	----	
52.	NDA	*	Ag/AgCl	Ag/AgCl	-2.18	-2.24	0.1	-1.54	-1.69	Moderate rate of gas evolution at calcium at 10 ma/cm^2. Calcium somewhat darkened. Gas evolution at counter electrode.
						-2.28	1	-1.50	-1.63	
						-2.32	10	-1.23	-1.10	
						-2.30	100	Reversed Polarity	----	

* Tetramethylammonium hexafluorophosphate - $(CH_3)_4NPF_6$

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2. (Continued)
A. Calcium Anode Systems. (Continued)

	Electrolyte				Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities		Further Observations and Remarks
	Solvent	Solute	Reference Electrode	Counter Electrode				Initial	Final	
53.	NDA	$AlCl_3$	Ag/AgCl	Ag/AgCl	-2.30	----	0.1	-2.31	-2.31	No change in the appearance of the entire system. Very slow gassing at calcium began at 1 ma/cm^2.
						-2.25	1	-2.25	-2.18	
						-2.12	10	-1.30	-1.45	
						-2.15	100	Reversed Polarity	----	

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2. (Continued)
A. Calcium Anode Systems. (Continued)

	Electrolyte							Voltage of Anode vs. Reference Electrode at Various Current Densities		
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Initial	Final	Further Observations and Remarks
54.	DMF	$MgCl_2$	Ag/AgCl	Ag/AgCl	-2.34	-2.35	0.1	-2.25	-2.30	Calcium became blackened somewhat upon discharge. Slight gassing at calcium at 10 ma/cm^2. At 10 ma/cm^2, potential was constant at about -1.40 after 1 minute. Reference and counter electrodes were deteriorated appreciably.
						-2.40	1	-1.95	-2.12	
						-2.33	10	Reversed Polarity	-1.40	
						-2.32	100	Reversed Polarity	----	
55.	DMF	$(m\text{-}C_3H_7)_4NPF_6$*	Ag/AgCl	Ag/AgCl	-2.21	-2.22	0.1	-2.00	-2.19	At 10 ma/cm^2, potential rose rapidly from initial low value to -1.92. Very slow gassing at calcium at 10 ma/cm^2. Calcium was blackened and solution became cloudy.
						-2.31	1	-1.80	-2.10	
						-2.43	10	-0.40	-1.92	
						-2.42	100	-0.60	-0.82	
56.	DMF	$(m\text{-}C_4H_9)_4NCl$**	Ag/AgCl	Ag/AgCl	-2.24	-2.30	0.1	-2.21	-2.28	Calcium became appreciably corroded and gassed vigorously upon discharge. Reference and counter electrodes deteriorated somewhat.
						-2.29	1	-2.13	-2.21	
						-1.91	10	-1.80	-1.85	
						-1.15	100	Reversed Polarity	----	
57.	DMF	$(C_6H_5)_4PCl$***	Ag/AgCl	Ag/AgCl	-2.05	-2.13	0.1	-1.98	-2.05	Calcium became blackened and the reference and counter electrodes deteriorated somewhat.
						-2.14	1	-1.60	-2.05	
						-2.15	10	-1.50	-1.66	
						-2.05	100	Reversed Polarity	----	

* Tetra-n-propylammonium hexafluorophosphate - $(n\text{-}C_3H_7)_4NPF_6$

** Tetra-n-butylammonium chloride - $(n\text{-}C_4H_9)_4NCl$

*** Tetraphenylphosphonium chloride - $(C_6H_5)_4PCl$

TABLE VIII. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Continued)

II. Anode-Electrolyte Systems Capable of Sustaining 10 ma/cm^2.
A. Calcium Anode Systems.

	Electrolyte Solvent	Electrolyte Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities Initial	Voltage of Anode vs. Reference Electrode at Various Current Densities Final	Further Observations and Remarks
58.	AN	$AlCl_3$	Ag/AgCl	Ag/AgCl	-2.53	-2.52	0.1	-2.52	-2.52	No change in the appearance of the entire system. Very slow gassing at calcium at 100 ma/cm^2.
						-2.52	1	-2.49	-2.49	
						-2.53	10	-2.20	-2.20	
						-2.55	100	-1.20	-0.98	
59.	AN	$(m\text{-}C_3H_7)_3NHAsF_6$*	Ag/AgCl	Ag/AgCl	-2.09	-2.09	0.1	-2.01	-2.01	Continuous moderate gassing at calcium electrode. Calcium gradually became darker in appearance. No change was apparent in the solution, or in the counter and reference electrodes.
						-2.50	1	-1.98	-1.94	
						-2.50	10	-2.04	-2.00	
						-2.35	100	-1.20	-0.94	
60.	AN	$(m\text{-}C_3H_7)_4NPF_4$**	Ag/AgCl	Ag/AgCl	-2.45	-2.45	0.1	-2.24	-2.17	Calcium electrode began gassing slowly at 10 ma/cm^2. After this point it continued to gas at all times, even on open circuit. Counter electrode had deteriorated somewhat. Electrolyte and reference electrode were not changed in appearance.
						-2.35	1	-1.68	-2.13	
						-2.35	10	-1.80	-1.96	
						-2.35	100	-0.80	-0.65	
61.	AN	$(C_6H_5)(CH_3)_3NPF_6$***	Ag/AgCl	Ag/AgCl	-1.84	-1.82	0.1	-1.70	-1.79	Calcium became blackened somewhat upon discharge. Solution became cloudy after 100 ma discharge, apparently because of some deterioration of the counter electrode. Slight gassing of calcium at 100 ma/cm^2.
						-2.03	1	-1.60	-1.57	
						-1.99	10	-1.35	-1.36	
						-1.88	100	-0.85	-0.55	

* Tri-n-propylammonium hexafluoroarsenate - $(n\text{-}C_3H_7)_3HNAsF_6$

** Tetra-n-propylammonium tetrafluoroborate - $(n\text{-}C_3H_7)_4NBF_4$

*** N-Phenyl N,N,N-trimethylammonium hexafluorophosphate - $(C_6H_5)(CH_3)_3NPF_6$

TABLE IX

CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS

Tests of Two Weeks Duration.

A. Stability in Acetonitrile Solutions.

	Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Two Week Exposure
1.	$(CH_3)_4NPF_6$ (Tetramethyl-ammonium hexa-fluorophosphate)	Ca	Before Exposure	1.1082	1.14×10^{-2} (24°C)	1.14×10^{-2} (24°C)	No change in the appearance of the calcium. A slight amount of fluffy white solid appeared at the bottom of the solution.
			After Two Weeks	1.1100	1.12×10^{-2} (25°C)	1.12×10^{-2} (25°C)	
		Mg	Before Exposure	0.4685	1.14×10^{-2} (24°C)	1.14×10^{-2} (24°C)	Several white spots appeared on the magnesium surface. A slight amount of fluffy white solid appeared at the bottom of the solution.
			After Two Weeks	0.4741	1.13×10^{-2} (25°C)	1.12×10^{-2} (25°C)	
2.	$(n\text{-}C_3H_7)_4NPF_6$ (Tetra-n-propyl-ammonium hexa-fluorophosphate)	Mg	Before Exposure	0.3900	3.66×10^{-2} (24°C)	3.66×10^{-2} (24°C)	The original brown solution became lighter and a white percipitate appeared. A thin white film formed on the magnesium surface.
			After Two Weeks	0.4082	3.62×10^{-2} (25°C)	3.68×10^{-2} (25°C)	
3.	$(C_6H_5)(CH_3)_3NPF_6$ (N-phenyl-N,N,N-trimethylammonium hexafluorophosphate)	Mg	Before Exposure	0.4249	3.77×10^{-2} (24°C)	3.72×10^{-2} (24°C)	Light gassing occurred on immersion. A white gelatinous solid appeared in both the blank and the exposed electrolyte. A heavy, white, gelatinous film formed on the magnesium surface.
			After Two Weeks	0.8406	3.82×10^{-2} (25°C)	3.71×10^{-2} (25°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS

Tests of Two Weeks Duration.
A. Stability in Acetonitrile Solutions.

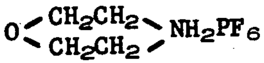
	Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Two Week Exposure
4.	$(n\text{-}C_4H_9)_2NH_2AsF_6$ (Di-n-butyl-ammonium hexa-fluoroarsenate)	Ca	Before Exposure	0.5840	4.17×10^{-2} (25°C)	4.06×10^{-2} (25°C)	Darkening of the entire calcium surface; thick black film formed on part of the calcium.
			After Two Weeks	0.6217	4.34×10^{-2} (25°C)	4.25×10^{-2} (25°C)	
		Mg	Before Exposure	0.2140	4.12×10^{-2} (25°C)	4.06×10^{-2} (25°C)	Formation of thin, white film on part of the magnesium surface.
			After Two Weeks	0.2202	4.38×10^{-2} (25°C)	4.25×10^{-2} (25°C)	
5.	$AlCl_3$	Mg	Before Exposure	0.6123	2.87×10^{-2} (28°C)	2.94×10^{-2} (28°C)	A loosely adhering black solid formed at the magnesium surface.
			After Two Weeks	0.5880	2.65×10^{-2} (26°C)	2.84×10^{-2} (26°C)	
6.	 $O<\begin{smallmatrix}CH_2CH_2\\CH_2CH_2\end{smallmatrix}>NH_2PF_6$ (Morpholinium hexafluorophos-phate)	Ca	Before Exposure	0.2826	4.61×10^{-2} (27°C)	4.44×10^{-2} (27°C)	Some consumption of the calcium. Formation of a thick, black film on the calcium surface. White solid formed in the solution.
			After Two Weeks	0.1848	4.64×10^{-2} (26°C)	4.20×10^{-2} (26°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration. (Continued)

A. Stability in Acetonitrile Solutions. (Continued)

	Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Two Week Exposure
7.	$(n\text{-}C_3H_7)_4NPF_6$ (Tetra-n-propylammonium hexafluorophosphate)	Ca	Before Exposure	0.3387	4.15×10^{-2} (27°C)	4.05×10^{-2} (27°C)	Formation of a thin, gray film on the calcium. The calcium had a duller appearance. Slight amount of orange-brown solid formed in solution.
			After Two Weeks	0.3319	4.10×10^{-2} (26°C)	4.01×10^{-2} (26°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.

A. Stability in Acetonitrile Solutions.

Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Two Week Exposure
8. KPF_6	Ca	Before Exposure	1.1338	3.10×10^{-2} (28°C)	3.10×10^{-2} (28°C)	Calcium surface appeared to be slightly duller than initially.
		After Two Weeks	1.1380	3.53×10^{-2} (24°C)	3.48×10^{-2} (24°C)	
9. $(C_6H_5)(CH_3)_3NPF_6$ (N-Phenyl N,N,N-trimethylammonium hexafluorophosphate)	Ca	Before Exposure	1.0417	3.96×10^{-2} (26°C)	3.94×10^{-2} (27°C)	A few small brown spots formed at calcium surface.
		After Two Weeks	1.0484	3.97×10^{-2} (24°C)	3.94×10^{-2} (25°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.

B. Stability in N,N-Dimethylformamide Solutions.

	Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Two Week Exposure
1.	KPF_6	Li	Before Exposure	0.6446	2.28×10^{-2} (24°C)	2.32×10^{-2} (24°C)	The solution color changed from colorless to orange and a large amount of yellow solid appeared in the solution. The small amount of lithium remaining was covered with a thick yellow film.
			After Two Weeks	5.3802	2.24×10^{-2} (25°C)	2.36×10^{-2} (25°C)	
2.	$(CH_3)_4NPF_6$ (Tetramethyl-ammonium hexa-fluorophosphate)	Li	Before Exposure	0.6065	1.10×10^{-2} (24°C)	1.11×10^{-2} (24°C)	Light gassing occurred initially. The solution color changed from colorless to light yellow with a great reduction in the volume of the solution. The small amount of lithium remaining was covered with a large amount of white solid. The deterioration of the system made any measurements at the end of the test period impossible.
			After Two Weeks	----	----	1.13×10^{-2} (25°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration. (Continued)
B. Stability in Dimethylformamide Solutions.

	Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Two Week Exposure
3.	$(CH_3)_4NPF_6$ (Tetramethyl-ammonium hexa-fluorophosphate)	Mg	Before Exposure	0.2091	1.15 x 10^{-2} (26°C)	1.15 x 10^{-2} (26°C)	No change.
			After Two Weeks	0.2210	1.10 x 10^{-2} (25°C)	1.10 x 10^{-2} (25°C)	
4.	$(n\text{-}C_4H_9)_2NH_2AsF_6$ (Di-n-butyl-ammonium hexa-fluoroarsenate)	Ca	Before Exposure	0.5633	2.33 x 10^{-2} (25°C)	2.38 x 10^{-2} (25°C)	Calcium surface somewhat darkened.
			After Two Weeks	0.6018	2.28 x 10^{-2} (25°C)	2.33 x 10^{-2} (25°C)	
		Li	Before Exposure	0.7214	2.33 x 10^{-2} (27°C)	2.35 x 10^{-2} (27°C)	Extensive consumption of the lithium. Remaining lithium covered with a thick, yellow-brown solid. The original colorless solution became an opaque red-brown. Some black solid was present.
			After Two Weeks	3.9874	1.29 x 10^{-2} (25°C)	2.31 x 10^{-2} (25°C)	
		Mg	Before Exposure	0.2055	2.34 x 10^{-2} (25°C)	2.38 x 10^{-2} (25°C)	No change.
			After Two Weeks	0.2106	2.29 x 10^{-2} (25°C)	2.33 x 10^{-2} (25°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration. (Continued)

B. Stability in Dimethylformamide Solutions. (Continued)

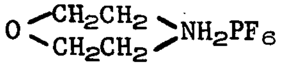
	Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Two Week Exposure
5.	 $O(CH_2CH_2)_2NH_2PF_6$ (Morpholinium hexafluorophosphate)	Ca	Before Exposure	0.5656	2.71 x 10^{-2} (26°C)	2.68 x 10^{-2} (26°C)	Formation of thick white film at calcium surface. Solution cloudy.
			After Two Weeks	0.8281	2.65 x 10^{-2} (25°C)	2.65 x 10^{-2} (25°C)	
		Mg	Before Exposure	0.2232	2.73 x 10^{-2} (26°C)	2.68 x 10^{-2} (26°C)	Entire surface of magnesium was blackened. Some white solid was also formed.
			After Two Weeks	0.3167	2.68 x 10^{-2} (25°C)	2.65 x 10^{-2} (25°C)	
6.	$(C_6H_5)(CH_3)_3NPF_6$ (N-phenyl N,N,N-trimethylammonium hexafluorophosphate)	Ca	Before Exposure	0.4221	2.21 x 10^{-2} (27.5°C)	2.25 x 10^{-2} (27.5°C)	Calcium became slightly dull.
			After Two Weeks	0.4198	2.15 x 10^{-2} (25°C)	2.15 x 10^{-2} (25°C)	
		Li	Before Exposure	0.4824	2.12 x 10^{-2} (26°C)	2.14 x 10^{-2} (26°C)	Complete consumption of the lithium. Change in the solution from clear and colorless to opaque orange-brown. Considerable amount of orange-white solid formed in solution.
			After Two Weeks	---	1.61 x 10^{-2} (26°C)	2.08 x 10^{-2} (26°C)	
		Mg	Before Exposure	0.6225	2.23 x 10^{-2} (27.5°C)	2.25 x 10^{-2} (27.5°C)	Magnesium became slightly dull.
			After Two Weeks	0.6217	2.19 x 10^{-2} (25°C)	2.15 x 10^{-2} (25°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration. (Continued)
B. Stability in Dimethylformamide Solutions. (Continued)

	Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1})		Visible Change After Two Week Exposure
					Exposed Electrolyte	Blank Electrolyte	
7.	$(n\text{-}C_3H_7)_3NHAsF_6$ (Tri-n-propyl-ammonium hexa-fluoroarsenate)	Ca	Before Exposure	0.3011	2.20×10^{-2} (27°C)	2.20×10^{-2} (27°C)	Formation of a thick, black film on the calcium. A white solid formed in solution.
			After Two Weeks	0.3717	2.06×10^{-2} (26°C)	2.15×10^{-2} (26°C)	
8.	"	Li	Before Exposure	0.6745	2.20×10^{-2} (27°C)	2.22×10^{-2} (27.5°C)	Extensive consumption of the lithium. Remaining lithium covered with a thick, yellow-brown solid. The original light orange solution separated into a small, clear, colorless upper layer and an opaque, dark brown lower layer.
			After Two Weeks	4.9617	1.65×10^{-2} (26°C)	2.15×10^{-2} (26°C)	
9.	"	Mg	Before Exposure	0.6375	2.20×10^{-2} (27°C)	2.20×10^{-2} (27°C)	No change.
			After Two Weeks	0.6399	2.15×10^{-2} (26°C)	2.15×10^{-2} (26°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.

B. Stability in Dimethylformamide Solutions.

Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1}) 25°C ± 1 Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) 25°C ± 1 Blank Electrolyte	Visible Change After Two Week Exposure
10. $MgCl_2$	Ca	Before Exposure	2.1523	1.01×10^{-2}	1.01×10^{-2}	No change.
		After Two Weeks	2.2400	1.01×10^{-2}	1.01×10^{-2}	
	Mg	Before Exposure	0.1700	1.01×10^{-2}	1.01×10^{-2}	No change.
		After Two Weeks	0.1892	1.01×10^{-2}	1.01×10^{-2}	
11. NH_4SO_3F	Ca	Before Exposure	2.1124	2.09×10^{-2}	2.09×10^{-2}	Entire surface of calcium blackened.
		After Two Weeks	2.1602	2.04×10^{-2}	2.04×10^{-2}	
	Mg	Before Exposure	0.2060	2.09×10^{-2}	2.09×10^{-2}	Large number of black spots formed on magnesium surface.
		After Two Weeks	0.4117	2.01×10^{-2}	2.04×10^{-2}	
12. $NaBF_4$	Ca	Before Exposure	1.7440	2.02×10^{-2}	2.02×10^{-2}	No change.
		After Two Weeks	1.7715	2.05×10^{-2}	2.04×10^{-2}	
	Mg	Before Exposure	0.1528	2.02×10^{-2}	2.02×10^{-2}	A few small black spots formed on magnesium surface.
		After Two Weeks	0.1829	2.06×10^{-2}	2.04×10^{-2}	
13. $NaPF_6$	Ca	Before Exposure	2.1598	2.30×10^{-2}	2.30×10^{-2}	No change.
		After Two Weeks	2.1673	2.25×10^{-2}	2.22×10^{-2}	
	Mg	Before Exposure	0.1542	2.30×10^{-2}	2.30×10^{-2}	No change.
		After Two Weeks	0.2088	2.27×10^{-2}	2.22×10^{-2}	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.
B. Stability in Dimethylformamide Solutions. (Continued)

	Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1}) 25°C ± 1		Visible Change After Two Week Exposure
					Exposed Electrolyte	Blank Electrolyte	
14.	$NaSbF_6$	Ca	Before Exposure	2.0969	2.20×10^{-2}	2.20×10^{-2}	Entire surface of calcium blackened.
			After Two Weeks	2.1417	2.20×10^{-2}	2.23×10^{-2}	
		Mg	Before Exposure	0.1324	2.20×10^{-2}	2.20×10^{-2}	No change.
			After Two Weeks	0.1767	2.20×10^{-2}	2.23×10^{-2}	
15.	$(n\text{-}C_3H_7)_4NPF_6$ (Tetra-n-propylammonium hexafluorophosphate)	Ca	Before Exposure	2.4111	1.97×10^{-2}	1.97×10^{-2}	A few black spots formed on calcium surface.
			After Two Weeks	2.5189	1.99×10^{-2}	1.98×10^{-2}	
		Mg	Before Exposure	0.1383	1.97×10^{-2}	1.97×10^{-2}	Appreciable blackening of magnesium; holes in magnesium.
			After Two Weeks	0.1220	1.89×10^{-2}	1.98×10^{-2}	
16.	KPF_6	Ca	Before Exposure	1.7519	2.74×10^{-2} (27°C)	2.75×10^{-2} (27°C)	No change.
			After Two Weeks	1.7588	2.25×10^{-2} (25°C)	2.27×10^{-2} (25°C)	
17.	$(CH_3)_4NPF_6$ (Tetramethylammonium hexafluorophosphate)	Ca	Before Exposure	1.6560	1.19×10^{-2} (17°C)	1.09×10^{-2} (27°C)	No change.
			After Two Weeks	1.6617	1.12×10^{-2} (25°C)	1.11×10^{-2} (25°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.

C. Stability in Ethylene Carbonate (80 Wt. %)-Propylene Carbonate (20 Wt. %) Solutions.

	Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1})		Visible Change After Two Week Exposure
					Exposed Electrolyte	Blank Electrolyte	
1.	$AlCl_3$	Ca	Before Exposure	0.3909	6.03×10^{-3} (23°C)	6.03×10^{-3} (23°C)	The calcium gassed on immersion. Considerable consumption of the calcium occurred. The original light brown solution was colorless after two weeks.
			After Two Weeks	0.0377	4.78×10^{-3} (26°C)	5.07×10^{-3} (26°C)	
2.	"	Li	Before Exposure	0.3767	6.03×10^{-3} (23°C)	6.03×10^{-3} (23°C)	The lithium gassed on immersion. After two weeks, some consumption of the lithium had occurred and the remaining lithium was covered with a thin gray film. Both the exposed and unexposed electrolyte changed from light to dark brown.
			After Two Weeks	0.3513	4.79×10^{-3} (26°C)	5.07×10^{-3} (26°C)	
3.	"	Mg	Before Exposure	0.2360	6.03×10^{-3} (23°C)	6.03×10^{-3} (23°C)	The magnesium gassed on immersion. There were no other changes in the system.
			After Two Weeks	0.1829	5.13×10^{-3} (26°C)	5.07×10^{-3} (26°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.
C. Stability in 80 Wt. % Ethylene Carbonate, 20 Wt. % Propylene Carbonate Solutions. (Continued)

	Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Two Week Exposure
4.	$(CH_3)_4NPF_6$ (Tetramethyl-ammonium hexa-fluorophosphate)	Ca	Before Exposure	0.7964	4.82×10^{-3} (24°C)	4.82×10^{-3} (24°C)	The calcium surface was partly covered by a thin black film.
			After Two Weeks	0.8104	4.87×10^{-3} (25°C)	4.91×10^{-3} (25°C)	
5.		Li	Before Exposure	0.6661	4.82×10^{-3} (24°C)	4.82×10^{-3} (24°C)	Light gassing occurred on immersion. A black film formed on the lithium surface. A white percipitate formed in solution.
			After Two Weeks	0.8149	4.85×10^{-3} (25°C)	4.91×10^{-3} (25°C)	
6.		Mg	Before Exposure	0.4821	4.82×10^{-3} (24°C)	4.82×10^{-3} (24°C)	Approximately 30% of the magnesium surface was covered with a thin layer of black solid.
			After Two Weeks	0.4914	4.90×10^{-3} (25°C)	4.91×10^{-3} (25°C)	
7.	$(n\text{-}C_3H_7)_3NHAsF_6$ (Tri-n-propyl-ammonium hexa-fluoroarsenate)	Li	Before Exposure	0.4307	5.63×10^{-3} (27°C)	5.12×10^{-3} (27°C)	The lithium gassed on immersion. There was no change in the system.
			After Two Weeks	0.4567	1.22×10^{-2} (26°C)	1.22×10^{-2} (26°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.

C. Stability in Ethylene Carbonate (80 Wt. %)-Propylene Carbonate (20 Wt.%). (Continued)

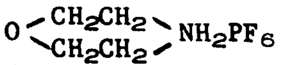
	Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Two Week Exposure
8.	 $O\langle\begin{smallmatrix}CH_2CH_2\\CH_2CH_2\end{smallmatrix}\rangle NH_2PF_6$ (Morpholinium hexafluorophosphate)	Li	Before Exposure	0.4298	1.18×10^{-2} (23°C)	1.16×10^{-2} (23°C)	Vigorous gassing occurred at the lithium surface upon immersion. At the end of two weeks, most of the lithium had been consumed and a white gelatinous precipitate had formed in solution.
			After Two Weeks	0.0896	5.43×10^{-3} (27°C)	1.30×10^{-2} (27°C)	
9.	$(C_6H_5)(CH_3)_3NPF_6$ (N-phenyl N,N,N-trimethylammonium hexafluorophosphate)	Ca	Before Exposure	0.4858	1.23×10^{-2} (28°C)	1.23×10^{-2} (28°C)	Formation of a black film which partially covered the calcium surface.
			After Two Weeks	0.4993	1.19×10^{-2} (25°C)	1.19×10^{-2} (25°C)	
10.	"	Li	Before Exposure	0.5461	1.22×10^{-2} (26°C)	1.20×10^{-2} (26°C)	Formation of a thick, gray film on the lithium surface. Some white solid was present in solution.
			After Two Weeks	1.1810	1.13×10^{-2} (26°C)	1.13×10^{-2} (26°C)	
11.	"	Mg	Before Exposure	0.6127	1.23×10^{-2} (28°C)	1.23×10^{-2} (28°C)	Gray spots appeared at random over approximately 30% of the magnesium surface.
			After Two Weeks	0.6151	1.19×10^{-2} (25°C)	1.19×10^{-2} (25°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration. (Continued)
C. Stability in 80 WT % Ethylene Carbonate-20 WT % Propylene Carbonate Solutions. (Continued)

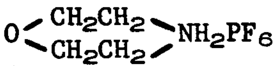
	Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1})		Visible Change After Two Week Exposure
					Exposed Electrolyte	Blank Electrolyte	
12.	 $O{<}\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}{>}NH_2PF_6$ (Morpholinium hexafluorophosphate)	Ca	Before Exposure	0.5134	1.33 x 10^{-2} (28°C)	1.28 x 10^{-2} (28°C)	Formation of a thick, black film on the calcium surface.
			After Two Weeks	0.5331	1.27 x 10^{-2} (25°C)	1.26 x 10^{-2} (25°C)	
	"	Mg	Before Exposure	0.6284	1.34 x 10^{-2} (28°C)	1.28 x 10^{-2} (28°C)	The magnesium surface became slightly covered with black spots.
			After Two Weeks	0.6560	1.28 x 10^{-2} (25°C)	1.26 x 10^{-2} (25°C)	
13.	$(n\text{-}C_3H_7)_3NHAsF_6$ (Tri-n-propylammonium hexafluoroarsenate	Ca	Before Exposure	0.2633	1.23 x 10^{-2} (28°C)	1.23 x 10^{-2} (28°C)	The calcium dulled and was partially covered with a gray-black film.
			After Two Weeks	0.2704	1.15 x 10^{-2} (26°C)	1.15 x 10^{-2} (26°C)	
14.	"	Mg	Before Exposure	0.5785	1.26 x 10^{-2} (28°C)	1.23 x 10^{-2} (28°C)	No change.
			After Two Weeks	0.5824	1.16 x 10^{-2} (26°C)	1.15 x 10^{-2} (26°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.

D. Stability in N-Nitrosodimethylamine Solutions.

Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1})		Visible Change After Two Week Exposure
				Exposed Electrolyte	Blank Electrolyte	
1. $AlCl_3$	Ca	Before Exposure	0.3445	9.64×10^{-3} (23°C)	4.64×10^{-3} (23°C)	The calcium became covered with a thick gray film.
		After Two Weeks	0.3622	1.89×10^{-2} (27°C)	1.91×10^{-2} (27°C)	
2. "	Mg	Before Exposure	0.2676	9.64×10^{-3} (23°C)	9.64×10^{-3} (23°C)	The color of the solution changed from yellow-green to orange-brown. The magnesium appeared unchanged.
		After Two Weeks	0.2113	1.81×10^{-2} (27°C)	1.91×10^{-2} (27°C)	
3. KPF_6	Li	Before Exposure	0.4181	1.72×10^{-2} (24°C)	1.68×10^{-2} (24°C)	The lithium gassed on immersion and became covered with a gray film. There was no other change in the system.
		After Two Weeks	0.5627	1.65×10^{-2} (22°C)	1.67×10^{-2} (22°C)	
4. "	Mg	Before Exposure	0.3116	1.70×10^{-2} (24°C)	1.68×10^{-2} (24°C)	There was no change in the system.
		After Two Weeks	0.3119	1.67×10^{-2} (22°C)	1.67×10^{-2} (22°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.

D. Stability in N-Nitrosodimethylamine Solutions. (Continued)

	Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Two Week Exposure
5.	$MgCl_2$	Mg	Before Exposure	0.2831	9.27×10^{-3} (25°C)	9.37×10^{-3} (25°C)	The magnesium surface became slightly dull. There was no other change in the system.
			After Two Weeks	0.2899	8.70×10^{-3} (22°C)	8.58×10^{-3} (22°C)	
6.	$(CH_3)_4NPF_6$ (Tetramethylammonium hexafluorophosphate)	Ca	Before Exposure	0.3759	5.82×10^{-4} (23°C)	5.82×10^{-4} (23°C)	There was no change in the appearance of the system.
			After Two Weeks	0.3761	9.25×10^{-4} (26°C)	9.03×10^{-4} (26°C)	
7.	"	Li	Before Exposure	0.3847	5.82×10^{-4} (23°C)	5.82×10^{-4} (23°C)	A slight amount of light brown solid formed on the lithium surface.
			After Two Weeks	0.4012	8.65×10^{-4} (26°C)	9.03×10^{-4} (26°C)	
8.	"	Mg	Before Exposure	0.2565	5.82×10^{-4} (23°C)	5.82×10^{-4} (23°C)	There was no change in the appearance of the system.
			After Two Weeks	0.2625	9.47×10^{-4} (26°C)	9.03×10^{-4} (26°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.
D. Stability in N-Nitrosodimethylamine Solutions. (Continued)

	Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1})		Visible Change After Two Week Exposure
					Exposed Electrolyte	Blank Electrolyte	
9.	$(n\text{-}C_3H_7)_4NPF_6$ (Tetra-n-propylammonium hexafluorophosphate)	Mg	Before Exposure	0.2253	1.78×10^{-2} (23°C)	1.85×10^{-2} (23°C)	The magnesium surface was covered with several black spots at the end of two weeks. The solution changed from yellow to light orange-brown.
			After Two Weeks	0.2444	1.96×10^{-2} (27°C)	1.99×10^{-2} (27°C)	
10.	$(C_6H_5)(CH_3)_3NPF_6$ (N-phenyl N,N,N-trimethylammonium hexafluorophosphate)	Ca	Before Exposure	0.3933	2.13×10^{-2} (23°C)	2.13×10^{-2} (23°C)	The calcium gassed slightly on immersion. The calcium surface became covered with a gray film. A yellow precipitate formed and the solution changed from yellow to orange-brown.
			After Two Weeks	0.5295	2.20×10^{-2} (26°C)	2.20×10^{-2} (26°C)	
11.	"	Li	Before Exposure	0.3656	2.13×10^{-2} (23°C)	2.13×10^{-2} (23°C)	The lithium gassed slightly on immersion. The lithium surface became covered with a gray film and a slight amount of orange-brown solid. The solution color changed from yellow to orange-brown.
			After Two Weeks	0.8170	2.19×10^{-2} (26°C)	2.20×10^{-2} (26°C)	
12.	"	Mg	Before Exposure	0.2941	2.13×10^{-2} (23°C)	2.13×10^{-2} (23°C)	The magnesium gassed slightly on immersion. The magnesium surface became covered with a gray film. A yellow precipitate formed in solution.
			After Two Weeks	0.4937	2.14×10^{-2} (26°C)	2.20×10^{-2} (26°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration. (Continued)
D. Stability in N-Nitrosodimethylamine Solutions.

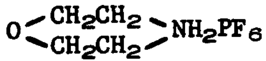
	Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Two Week Exposure
13.	$(n\text{-}C_4H_9)_2NH_2AsF_6$ (Di-n-butylammonium hexafluoroarsenate)	Mg	Before Exposure	0.2033	2.37 x 10^{-2} (26°C)	2.40 x 10^{-2} (26°C)	No change.
			After Two Weeks	0.2062	2.31 x 10^{-2} (25°C)	2.36 x 10^{-2} (24°C)	
14.	 $O\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}NH_2PF_6$ (Morpholinium hexafluorophosphate)	Li	Before Exposure	0.5365	2.74 x 10^{-2} (26°C)	2.59 x 10^{-2} (26°C)	Some consumption of the lithium. Formation of thin, gray film at lithium surface. White gelatinous suspension in the solution.
			After Two Weeks	0.3488	1.81 x 10^{-2} (26°C)	2.68 x 10^{-2} (26°C)	
15.	"	Mg	Before Exposure	0.2048	2.65 x 10^{-2} (26°C)	2.70 x 10^{-2} (26°C)	No change.
			After Two Weeks	0.2089	2.67 x 10^{-2} (25°C)	2.67 x 10^{-2} (25°C)	
16.	$(n\text{-}C_3H_7)_3NHAsF_6$ (Tri-n-propylammonium hexafluoroarsenate)	Li	Before Exposure	0.6344	2.36 x 10^{-2} (27°C)	2.38 x 10^{-2} (27°C)	Formation of a thin, gray film on the lithium surface. Original yellow-orange solution separated into a small, clear, colorless upper layer and a larger slightly yellow-brown lower layer. A dark brown solid formed.
			After Two Weeks	0.6347	1.85 x 10^{-2} (25°C)	2.30 x 10^{-2} (25°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.
D. Stability in N-Nitrosodimethylamine Solutions.

Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1})		Visible Change After Two Week Exposure
				Exposed Electrolyte	Blank Electrolyte	
17. $AlCl_3$	Li	Before Exposure	0.6442	2.06×10^{-2} (27°C)	2.12×10^{-2} (27°C)	Color of solution changed from yellow to amber.
		After Two Weeks	0.7602	1.92×10^{-2} (24°C)	2.02×10^{-2} (24°C)	
18. $MgCl_2$	Ca	Before Exposure	1.0533	1.09×10^{-2} (28°C)	1.09×10^{-2} (28°C)	No change.
		After Two Weeks	1.0788	9.47×10^{-3} (24°C)	9.42×10^{-3} (24°C)	
19.	Li	Before Exposure	0.6608	1.09×10^{-2} (28°C)	1.09×10^{-2} (28°C)	No change.
		After Two Weeks	0.6845	8.13×10^{-3} (24°C)	9.42×10^{-3} (24°C)	
20. KPF_6	Ca	Before Exposure	1.0293	2.00×10^{-2} (28°C)	1.99×10^{-2} (28°C)	Calcium surface appeared to be slightly duller than initially.
		After Two Weeks	1.0449	1.95×10^{-2} (25°C)	1.92×10^{-2} (25°C)	

TABLE IX. CHEMICAL STABILITY OF ANODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Two Weeks Duration.

D. Stability in N-Nitrosodimethylamine Solutions. (Continued)

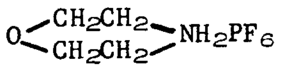
	Solute	Anode Material	Time of Measurement	Weight of Anode Material (Grams)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Two Week Exposure
21.	$(n\text{-}C_4H_9)_4NCl$ (Tetra-n-butylammonium chloride)	Ca	Before Exposure	1.0058	1.15×10^{-2} (28°C)	1.16×10^{-2} (27°C)	Calcium surface appeared to be very slightly darker than initially.
			After Two Weeks	1.0073	1.10×10^{-2} (25°C)	1.11×10^{-2} (25°C)	
22.	$(n\text{-}C_3H_7)_4NPF_6$ (Tetra-n-propylammonium hexafluorophosphate)	Ca	Before Exposure	1.5178	2.27×10^{-2} (27°C)	2.25×10^{-2} (27°C)	Calcium surface dull and partially blackened. A small amount of a solid product also appeared at the surface.
			After Two Weeks	1.7518	2.29×10^{-2} (25°C)	2.25×10^{-2} (27°C)	
23.	 $O{<}^{CH_2CH_2}_{CH_2CH_2}{>}NH_2PF_6$ (Morpholinium hexafluorophosphate)	Ca	Before Exposure	1.1857	2.86×10^{-2} (27°C)	2.87×10^{-2} (27°C)	Formation of large amount of black product at calcium surface. White solid formed in solution.
			After Two Weeks	1.0479	2.70×10^{-2} (25°C)	2.70×10^{-2} (25°C)	

TABLE IX. CHEMICAL STABILITY OF ELECTRODE MATERIALS IN ELECTROLYTE SOLUTIONS

D. Stability in N-Nitrosodimethylamine Solutions.

Solute	Electrode Material	Time of Measurement	Weight of Electrode Material (g)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Exposure
1. None	Li	Initial	0.1632	1.07×10^{-4} (24°C)	1.08×10^{-4} (24°C)	A gray film formed on the lithium after one week. No further visible changes occurred.
		After Two Days		1.02×10^{-4} (26°C)	1.31×10^{-4} (26°C)	
		After One Week		1.17×10^{-4} (26°C)	1.56×10^{-4} (26°C)	
		After Three Weeks		1.29×10^{-4} (24°C)	1.44×10^{-4} (24°C)	
		After Four Weeks		1.38×10^{-4} (29°C)	1.65×10^{-4} (29°C)	
		After Nine Weeks		1.66×10^{-4} (26°C)	1.77×10^{-4} (26°C)	
		After Fourteen Weeks		1.62×10^{-4} (27°C)	1.97×10^{-4} (27°C)	
		After Fifteen Weeks		1.65×10^{-4} (25°C)	2.01×10^{-4} (25°C)	
		After Sixteen Weeks		1.69×10^{-4} (25°C)	2.11×10^{-4} (25°C)	
		After Seventeen Weeks		1.70×10^{-4} (23°C)	2.05×10^{-4} (23°C)	
		After Eighteen Weeks	0.1840	1.71×10^{-4} (24°C)	2.07×10^{-4} (24°C)	
2. $LiPF_6$ (as received)	Li	Initial	0.2069	2.08×10^{-2} (24°C)	2.03×10^{-2} (24°C)	Gassing occurred initially. A white film formed on the lithium during the first day. After fourteen weeks a white precipitate had formed. No further visible changes occurred.
		After Two Days		1.98×10^{-2} (26°C)	2.03×10^{-2} (26°C)	
		After One Week		1.98×10^{-2} (26°C)	2.06×10^{-2} (26°C)	
		After Three Weeks		1.96×10^{-2} (24°C)	2.03×10^{-2} (24°C)	
		After Four Weeks		1.94×10^{-2} (29°C)	2.06×10^{-2} (29°C)	

TABLE IX. CHEMICAL STABILITY OF ELECTRODE MATERIALS IN ELECTROLYTE SOLUTIONS (Cont'd)

D. Stability in N-Nitrosodimethylamine Solutions. (Continued)

Solute	Anode Material	Time of Measurement	Weight of Electrode Material (g)	Specific Conductance (ohm^{-1} cm^{-1})		Visible Change After Exposure
				Exposed Electrolyte	Blank Electrolyte	
2. (Cont'd)	Li	After Nine Weeks		1.97×10^{-2} (26°C)	2.04×10^{-2} (26°C)	
		After Fourteen Weeks		2.03×10^{-2} (27°C)	1.59×10^{-2} (27°C)	
		After Fifteen Weeks		1.87×10^{-2} (25°C)	2.02×10^{-2} (25°C)	
		After Sixteen Weeks		1.92×10^{-2} (25°C)	2.03×10^{-2} (25°C)	
		After Seventeen Weeks		1.94×10^{-2} (23°C)	2.04×10^{-2} (23°C)	
		After Eighteen Weeks	0.2230	1.96×10^{-2} (24°C)	1.86×10^{-2} (24°C)	
3. $LiPF_6$[a]	Li	Initial	0.2205	1.90×10^{-2} (24°C)	1.87×10^{-2} (24°C)	Gassing occurred initially. A white film formed on the lithium during the first day. After fourteen weeks a white precipitate had formed. No further visible changes occurred.
		After Two Days		1.82×10^{-2} (26°C)	1.88×10^{-2} (26°C)	
		After One Week		1.85×10^{-2} (26°C)	1.17×10^{-2} (26°C)	
		After Three Weeks		1.81×10^{-2} (24°C)	1.77×10^{-2} (24°C)	
		After Four Weeks		1.85×10^{-2} (29°C)	1.93×10^{-2} (29°C)	
		After Nine Weeks		1.82×10^{-2} (26°C)	1.92×10^{-2} (29°C)	
		After Fourteen Weeks		1.87×10^{-2} (29°C)	1.96×10^{-2} (28°C)	
		After Fifteen Weeks		1.81×10^{-2} (25°C)	1.80×10^{-2} (25°C)	
		After Sixteen Weeks		1.80×10^{-2} (25°C)	1.78×10^{-2} (25°C)	
		After Seventeen Weeks		1.84×10^{-2} (23°C)	1.78×10^{-2} (23°C)	
		After Eighteen Weeks	0.2384	1.76×10^{-2} (24°C)	1.71×10^{-2} (24°C)	

[a] $LiPF_6$ dried at 110°C in N_2 atmosphere before use.

TABLE X

ELECTROCHEMICAL HALF-CELL SCREENING OF LITHIUM ANODES IN PRETREATED ELECTROLYTES

TABLE X. ELECTROCHEMICAL HALF-CELL TESTING OF ANODES

A. Lithium-Electrolyte Systems Capable of Sustaining 100 ma/cm^2.

	Electrolyte Solvent	Electrolyte Solute	Electrolyte Reference Electrode	Electrolyte Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities Initial	Voltage of Anode vs. Reference Electrode at Various Current Densities Final	Further Observations and Remarks
1.	NDA	*	Ag/AgCl	Ag/AgCl	-2.90	-2.91	0.1	-2.90	-2.91	Counter electrode gassed at 100 ma. No change in the appearance of the lithium, the reference electrode, and the electrolyte.
						-2.91	1	-2.87	-2.88	
						-2.90	10	-2.72	-2.68	
						-2.88	100	-1.60	-1.64	

2. * $O \begin{matrix} CH_2CH_2 \\ CH_2CH_2 \end{matrix} NH_2PF_6$ - Morpholinium hexafluorophosphate (1 molal). The solution was pretreated with lithium metal until gas evolution ceased. This reaction resulted in the formation of a gelatinous yellow solid in addition to the evolution of an appreciable quantity of gas. After filtering the solution, it had a specific conductance of 1.81×10^{-2} ohm^{-1} cm^{-1} as compared to 2.74×10^{-2} ohm^{-1} cm^{-1} for the untreated solution.

The results for the same system (not pretreated with lithium) are listed below for comparison. The conductance of the solution in this case was 2.80×10^{-2}.

	Electrolyte Solvent	Electrolyte Solute	Electrolyte Reference Electrode	Electrolyte Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode at Various Current Densities Initial	Voltage of Anode vs. Reference Electrode at Various Current Densities Final	Further Observations and Remarks
3.	NDA	**	Ag/AgCl	Ag/AgCl	-3.01	-3.01	0.1	-2.94	-2.94	Vigorous gassing at lithium electrode on open circuit and during discharge. A gelatinous material was formed in solution and the surface of the counter electrode had deteriorated somewhat.
						-3.00	1	-2.92	-2.92	
						-2.92	10	-2.75	-2.75	
						-2.92	100	-2.34	-2.18	

** $O \begin{matrix} CH_2CH_2 \\ CH_2CH_2 \end{matrix} NH_2PF_6$ - Morpholinium hexafluorophosphate (1 molal)

TABLE X. ELECTROCHEMICAL HALF-CELL TESTING OF ANODES

A. Lithium

	Electrolyte							Voltage of Anode vs. Reference Electrode at Various Current Densities		
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Initial	Final	Further Observations and Remarks
4.	NDA	$LiPF_6$(undried)	Ag/AgCl	Ag/AgCl	-3.33	-3.37	0.1	-3.32	-3.37	Continuous gassing of the Li anode. Slight gassing occurred at the counter electrode during the 100 ma/cm^2 discharges the lithium was covered with a gray film.
						-3.36	1	-3.36	-3.37	
						-2.85	10	-3.20	-2.76	
						-2.83	100	-1.98	-1.84	
5.	NDA	$LiPF_6$**	Ag/AgCl	Ag/AgCl	-3.45	-3.45	0.1	-3.45	-3.45	The counter electrode turned black during the discharges.
						-3.45	1	-3.43	-3.43	
						-2.93	10	-3.25	-3.15	
						-2.98	100	-1.82	-1.89	

* N-Nitrosodimethylamine.

** The $LiPF_6$ was dried for ca. 24 hours at 110°C in the apparatus described on page 2.

TABLE X. ELECTROCHEMICAL HALF-CELL TESTING OF ANODES (Cont'd)

A. Lithium (Cont'd)

	Electrolyte							Voltage of Anode vs. Reference Electrode at Various Current Densities		
	Solvent	Solute	Reference Electrode	Counter Electrode	Initial Open Circuit Voltage of Anode vs. Reference Electrode	Open Circuit Voltage After Discharge at Various Current Densities	Current Density (ma/cm^2)	Initial	Final	Further Observations and Remarks
6.	NDA (Distilled)	*	Ag/AgCl	Ag/AgCl	-2.67	-2.76	0.1	-2.68	-2.75	The lithium anode gassed continuously. During the 0.1 ma/cm^2 discharge a gray solid began to form on the lithium. At the end of the discharges the counter electrode had turned black but whitened on standing. System capable of sustaining 100 ma/cm^2.
						-2.76	1	-2.72	-2.73	
						-2.78	10	-2.53	-2.57	
						-2.83	100	-1.35	-1.67	
7.	NDA (Not Distilled)	*	Ag/AgCl	Ag/AgCl	-3.42	-3.20	0.1	-3.35	-3.10	Solution became dark in color. No gassing was apparent. Lithium became somewhat darker in appearance. System capable of sustaining 10 ma/cm^2.
						-3.05	1	-2.84	-2.78	
						-3.05	10	-2.20	-2.18	
						-2.95	100	-1.20	-0.8	

* N-Phenyl-N,N,N-trimethylammonium hexafluorophosphate - $(C_6H_5)(CH_3)_3NPF_6$

TABLE X. ELECTROCHEMICAL HALF-CELL TESTING OF ANODES

A. Lithium

	Electrolyte	Reference Electrode	Counter Electrode	Current Density (m2/cm^2)	Voltage of Anode vs. Reference Electrode[a] Initial	Final	Open Circuit Voltage After Discharge	Observations and Remarks
8.	1m LiPF$_6$-NDA[b]	Ag/AgCl	Ag/AgCl	0.0	-2.93	---	---	Lithium gassed slightly during 50 through 100ma discharges.
				10.0	-2.73	-2.60	-2.85	
				20.0	-2.38	-2.52	-2.85	
				30.0	-2.20	-2.42	-2.85	
				40.0	-2.09	-2.33	-2.85	
				50.0	-2.14	-2.18	-2.85	
				60.0	-2.00	-2.06	-2.85	
				70.0	-1.93	-1.79	-2.85	
				80.0	-1.74	-1.63	-2.83	
				90.0	-1.57	-1.49	-2.83	
				100.0	-1.53	-1.09	-2.81	
9.	1m LiPF$_6$-NDA[b]	Ag/AgCl	Ag/AgCl	0.0	-2.72	---	---	
				10.0	-2.49	-2.50	-2.75	
				20.0	-2.32	-2.28	-2.74	
				30.0	-2.12	-2.10	-2.75	Li gassing slightly.
				40.0	-1.94	-1.92	-2.75	
				50.0	-1.74	-1.66	-2.75	
				60.0	-1.50	-1.39	-2.75	
				70.0	-1.30	-1.03	-2.75	Counter gassing.
				80.0	-1.13	-0.69	-2.75	
				90.0	-1.00	-0.72	-2.75	
				100.0	-0.83	-0.43	-2.75	Li appeared unchanged at the end of the test.

---

[a] Duration of discharge at each current density - 5 minutes unless otherwise indicated.

[b] Electrolyte pretreated with lithium and filtered before use.

TABLE X. ELECTROCHEMICAL HALF-CELL TESTING OF ANODES
(Continued)

A. **Lithium** (Continued)

	Electrolyte	Reference Electrode	Counter Electrode	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode[a]		Open Circuit Voltage After Discharge	Observations and Remarks
					Initial	Final		
10.	1m $LiPF_6$-NDA[b]	Ag/AgCl	Ag/AgCl	0.0	-3.27	------	------	
				10.0	-3.0	-2.55	-2.82	
				20.0	-2.30	-2.35	-2.82	
				30.0	-2.16	-2.22	-2.82	
				40.0	-2.02	-2.08	-2.82	
				50.0	-1.90	-1.95	-2.85	
				60.0	-1.78	-1.81	-3.00	Counter electrode gassing.
				70.0	-1.73	-1.52	-2.92	
				80.0	-1.44	-1.59	-3.18	
				90.0	-1.28	-1.19	-3.05	
				100.0	-1.18	-0.83	-2.93	Li appeared unchanged at the end of the test.
11.	1m KPF_6^c-NDA	Ag/AgCl	Ag/AgCl	0.0	-3.39	------	------	
				10.0	-2.60	-2.80	-3.31	
				20.0	-2.40	-2.61	-3.26	
				30.0	-1.90	-2.32	-3.07	
				40.0	-1.20	-1.81	-2.85	Counter gassing.
				50.0	-1.10	-1.45	-2.78	
				60.0	-0.90	-1.21	-2.71	
				70.0	-0.65	-0.79	-2.64	Electrolyte brown near counter.
				80.0	-0.30	-0.39	-2.62	
				90.0	Reversed polarity	-0.24	-2.54	Li unchanged.
12[d].	1m KPF_6^c-NDA	Ag/AgCl	Ag/AgCl	0.0	-3.26	------	------	
				0.1	-3.23	-3.19	-3.22	
				1.0	-2.95	-2.88	-3.11	
				10.0	-2.55	-2.71	-3.05	
				100.0	-1.24	-1.24	-3.00	

---

[a] Duration of discharge at each current density - 5 minutes unless otherwise indicated.

[b] Electrolyte pretreated with lithium and filtered before use.

[c] The KPF_6 was used "as received" from the supplier.

[d] Previously reported in the Eighth Quarterly.

TABLE X. ELECTROCHEMICAL HALF-CELL TESTING OF ANODES
(Continued)

A. Lithium (Continued)

	Electrolyte	Reference Electrode	Counter Electrode	Current Density (ma/cm^2)	Voltage of Anode vs. Reference Electrode[a] Initial	Final	Open Circuit Voltage After Discharge	Observations and Remarks
13.	1m KPF_6^c + 0.001M KF^e-NDA	Ag/AgCl	Ag/AgCl	0.0	-3.15	------	------	
				10.0	-2.40	-2.66	-3.05	
				20.0	-2.20	-2.56	-3.03	
				30.0	-1.80	-2.36	-2.98	
				40.0	-1.60	-2.25	-3.00	Counter gassing, electrolyte near counter turning brown.
				50.0	-1.60	-2.16	-3.00	
				60.0	-1.60	-1.95	-3.00	
				70.0	-1.50	-1.66	-2.94	
				80.0	-1.20	-1.54	-2.89	
				90.0	-1.10	-1.40	-2.95	
				100.0	-1.10	-1.22	-2.94	Li unchanged.
14.	1m KPF_6^c + 0.01M KF^e-NDA	Ag/AgCl	Ag/AgCl	0.0	-3.47	------	------	
				10.0	-2.80	-2.88	-3.22	
				20.0	-2.30	-2.85	-3.29	
				30.0	-2.20	-2.75	-3.31	
				40.0	-2.00	-2.62	-3.25	Counter gassing, electrolyte darkening near counter.
				50.0	-2.00	-2.44	-3.14	
				60.0	-1.80	-2.05	-2.84	
				70.0	-1.50	-1.60	-2.73	
				80.0	-1.00	-1.43	-2.70	
				90.0	-0.90	-1.17	-2.72	
				100.0	-0.60	-1.03	-2.70	Li unchanged.

---

[a] Duration of discharge at each current density - 5 minutes unless otherwise indicated.

[c] The KPF_6 was used "as received" from the supplier.

[e] The KF was dried for 16 hours at 100°C.

TABLE X. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Cont'd)

A. Lithium (Cont'd)

	Electrolyte Solute-Solvent	Reference Electrode	Counter Electrode	Current Densities (ma/cm^2)	Voltage of Anode vs. Reference Electrode[a] Initial	Voltage of Anode vs. Reference Electrode[a] Final	Open Circuit Voltage After Discharge	Observations and Remarks
15.	1m$(n\text{-}C_3H_7)_4NPF_6$-NDA	Ag/AgCl	Ag/AgCl	0.0	-2.83	--	--	
				40.0	-2.27	-2.04	-2.82	
				50.0	-2.06	-1.76	--	
				60.0	-1.94	-1.66	-2.80	
				75.0	-1.70	-1.60	--	
				100.0	-1.38	-1.35	-2.80	
				0.0[b]	-3.00	--	--	
				0.1	-2.92	-2.92	-2.95	
				1.0	-2.90	-2.88	-2.95	
				10.0	-2.74	-2.64	-2.90	
				100.0	-1.80	-1.54	--	
16.	1m$C_6H_3(CH_3)_3NPF_6$-NDA	Ag/AgCl	Ag/AgCl	0.0	-2.83	--	--	
				20.0	-2.35	-2.52	-2.82	
				50.0	-2.13	-2.22	-2.84	
				75.0	-1.95	-1.23	-2.84	
				100.0	-1.78	-0.50	-2.84	Test stopped after 30 seconds.
				0.0[b]	-3.25	--	--	
				0.1	-3.25	-3.10	-3.20	
				1.0	-2.84	-2.78	-3.05	
				10.0	-2.20	-2.18	-3.05	
				100.0	-1.20	-0.80	-2.95	
17.	1m$NaPF_6$-NDA	Ag/AgCl	Ag/AgCl	0.0	-3.24	--	--	
				0.1	-3.24	-3.24	-3.24	
				1.0	-3.16	-3.20	-3.24	
				10.0	-2.73	-2.81	-3.08	
				100.0	-1.68	-1.85	-2.75	
				0.0[b]	-3.30	--	--	
				0.1	-3.24	-3.25	-3.40	
				1.0	-2.94	-2.42	-2.80	
				10.0	-2.10	-1.52	-2.85	
				100.0	--	--	--	

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[a] Duration of discharge at each current density - 5 minutes (unless otherwise noted).

[b] Test previously reported in Third Quarterly Report at which time undistilled solvents were being used.

TABLE X. ELECTROCHEMICAL HALF-CELL SCREENING OF ANODES (Cont'd)

A. Lithium (Cont'd)

	Electrolyte Solute-Solvent	Reference Electrode	Counter Electrode	Current Densities (ma/cm^2)	Voltage of Anode vs. Reference Electrode[a] Initial	Voltage of Anode vs. Reference Electrode[a] Final	Open Circuit Voltage After Discharge	Observations & Remarks
18.	1m KPF_6-NDA	Ag/AgCl	Ag/AgCl	0.0	-3.23	--	--	
				0.1	-3.23	-3.19	-3.22	
				1.0	-2.95	-2.88	-3.11	
				10.0	-2.55	-2.71	-3.05	
				100.0	-1.24	-1.24	-3.00	
				0.0[b]	-3.20	--	--	
				0.1	-3.10	-3.10	-3.20	
				1.0	-2.70	-2.83	-2.85	
				10.0	-2.04	-1.28	-2.35	
				100.0	-0.20	-0.30	--	
19.	1m KPF_6-NDA[c] (undistilled)	Ag/AgCl	Ag/AgCl	0.0	-3.12	--	--	
				0.1	-3.08	-3.07	-3.12	
				1.0	-2.90	-2.86	-3.09	
				10.0	-2.30	-2.58	-2.92	
				100.0	-1.10	-1.42	--	

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[a] Duration of discharge at each current density - 5 minutes (unless otherwise noted).

[b] Test previously reported in Third Quarterly Report at which time undistilled solvents were being used.

[c] This test is a repeat of the preceeding test.

TABLE XI. A COMPARISON OF THE PERFORMANCE OF Li ON Cu AND Li ON Ag ANODES[a]

Li on Cu Exmet			Li on Ag Exmet		
Time (Hours)	Anode Voltage Vs. Ag Ref. Electrode	Current (ma)	Time (Hours)	Anode Voltage Vs. Ag Ref. Electrode	Current (ma)
0	-2.8V	260	0	-3.1V	260
1	-2.7V	250	1	-2.8V	260
2	-2.5V	260	2	-2.6V	255
3	-2.3V	260	3	-2.3V	255
4	-2.3V	260	4	-2.2V	250
5	-2.3V	255	5	-2.2V	250
6	-2.3V	250	6	-2.2V	250
7	-2.3V	240	7	-2.2V	250
8	-2.3V	235	8	-2.2V	200
9	-2.3V	215	9	-2.2V	130
10	-2.2V	195	10	-2.2V	100
11	-2.2V	175	11	-2.1V	80
12	-2.2V	160	12	-2.1V	70
13	-2.1V	125	13	-2.0V	55

---

[a] The tests were run in 45ml of $LiPF_6$-NDA electrolyte which had been pretreated with Li and filtered prior to use. AgO cathodes and a Ag wire reference electrode were used in each test.

FIGURE 9. LINEARLY VARYING POTENTIAL STUDIES OF LITHIUM ANODES

Electrolyte
(1 Molal) Page

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* "As received" and dried LiPF_6.
** "As received" LiPF_6.
*** Dried LiPF_6.

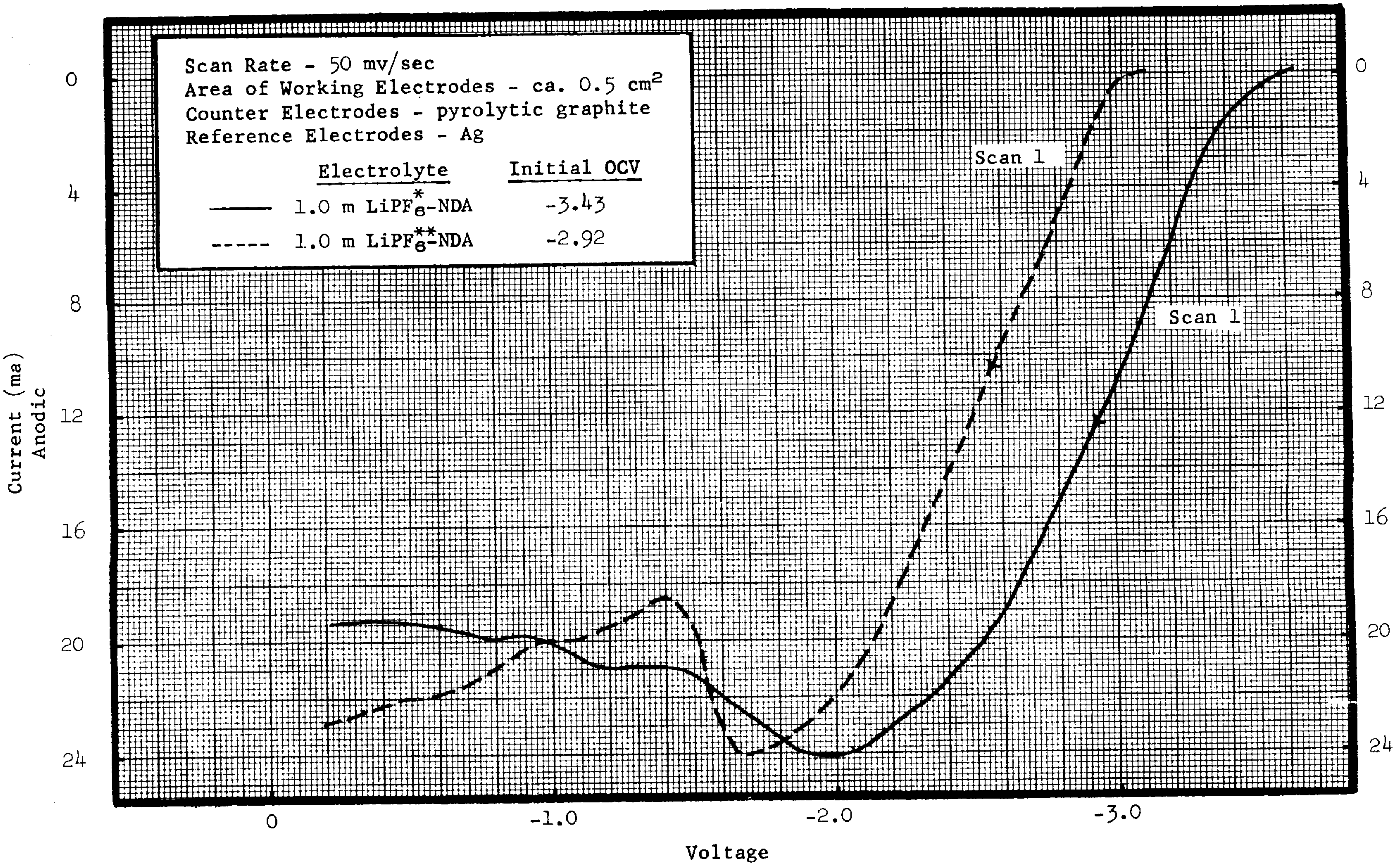


FIGURE 9. LINEARLY VARYING POTENTIAL STUDIES OF LITHIUM ANODES

Figure 9-a. The Effect of Drying the $LiPF_6$ Solute.

* "As received" $LiPF_6$.

** The $LiPF_6$ was dried at 110°C in a nitrogen atmosphere before use.

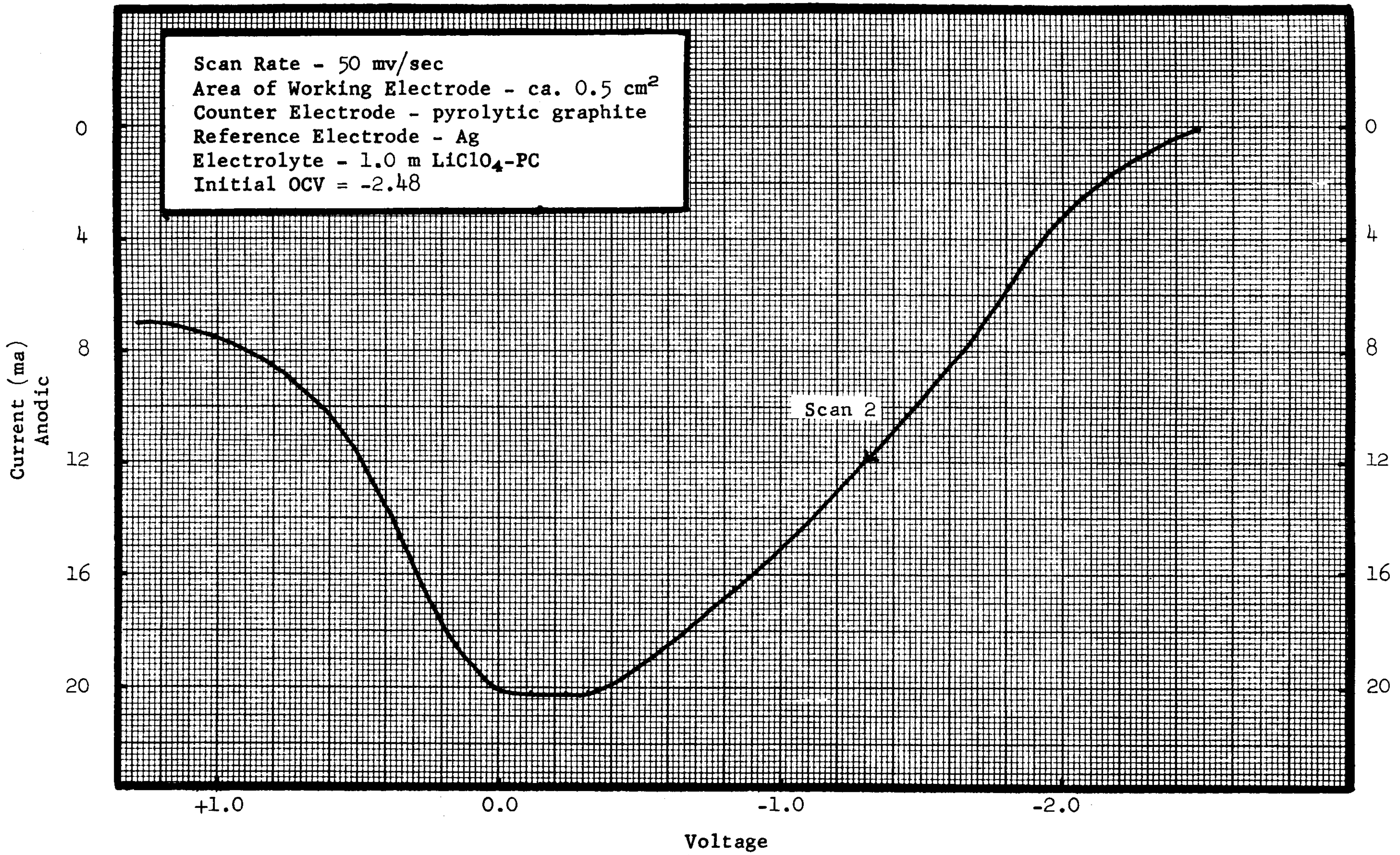


FIGURE 9. <u>LINEARLY VARYING POTENTIAL STUDIES OF LITHIUM ANODES</u> (Continued)

Figure 9-b. The Effect of Using a $LiClO_4$-Propylene Carbonate Electrolyte.

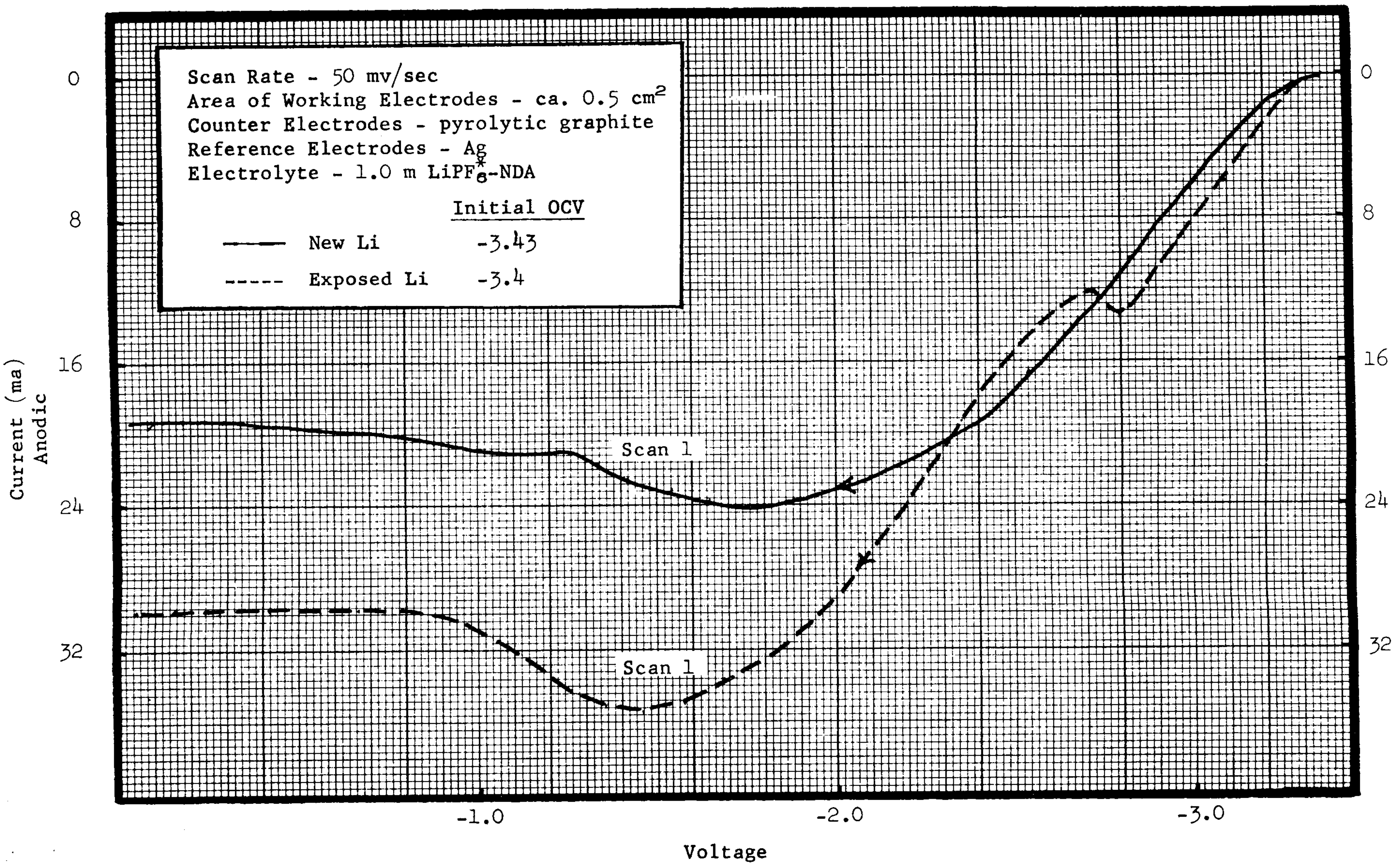


FIGURE 9. LINEARLY VARYING POTENTIAL STUDIES OF LITHIUM ANODES (Continued)

Figure 9-c. LVP Scans Before and After Twenty-Four Hour Exposure to the Electrolyte.

* "As received" LiPF$_6$.

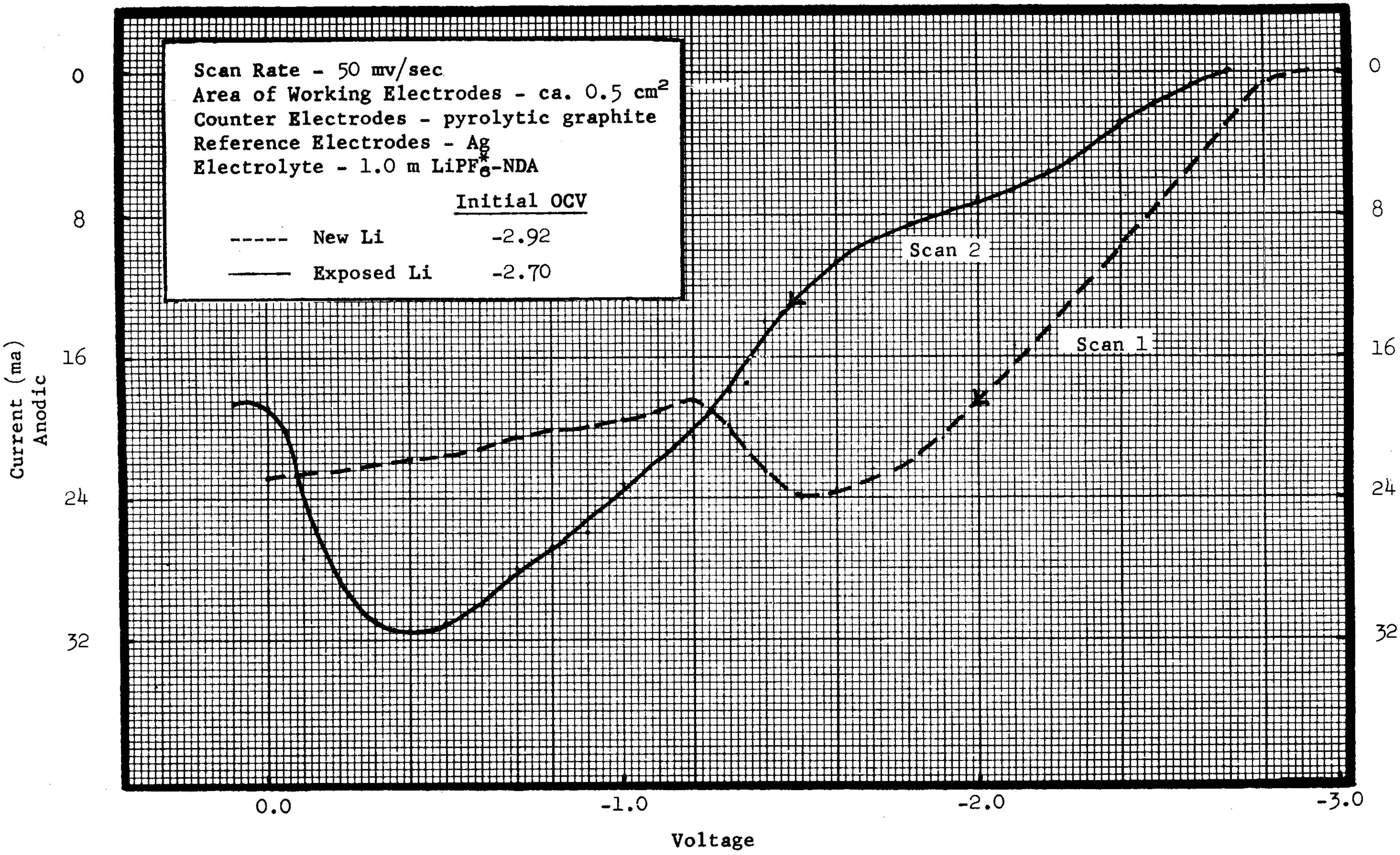


FIGURE 9. LINEARLY VARYING POTENTIAL STUDIES OF LITHIUM ANODES (Continued)

Figure 9-d. LVP Scans Before and After Twenty-Four Hour Exposure to the Electrolyte.

* The $LiPF_6$ was dried at 110°C in a nitrogen atmosphere before use.

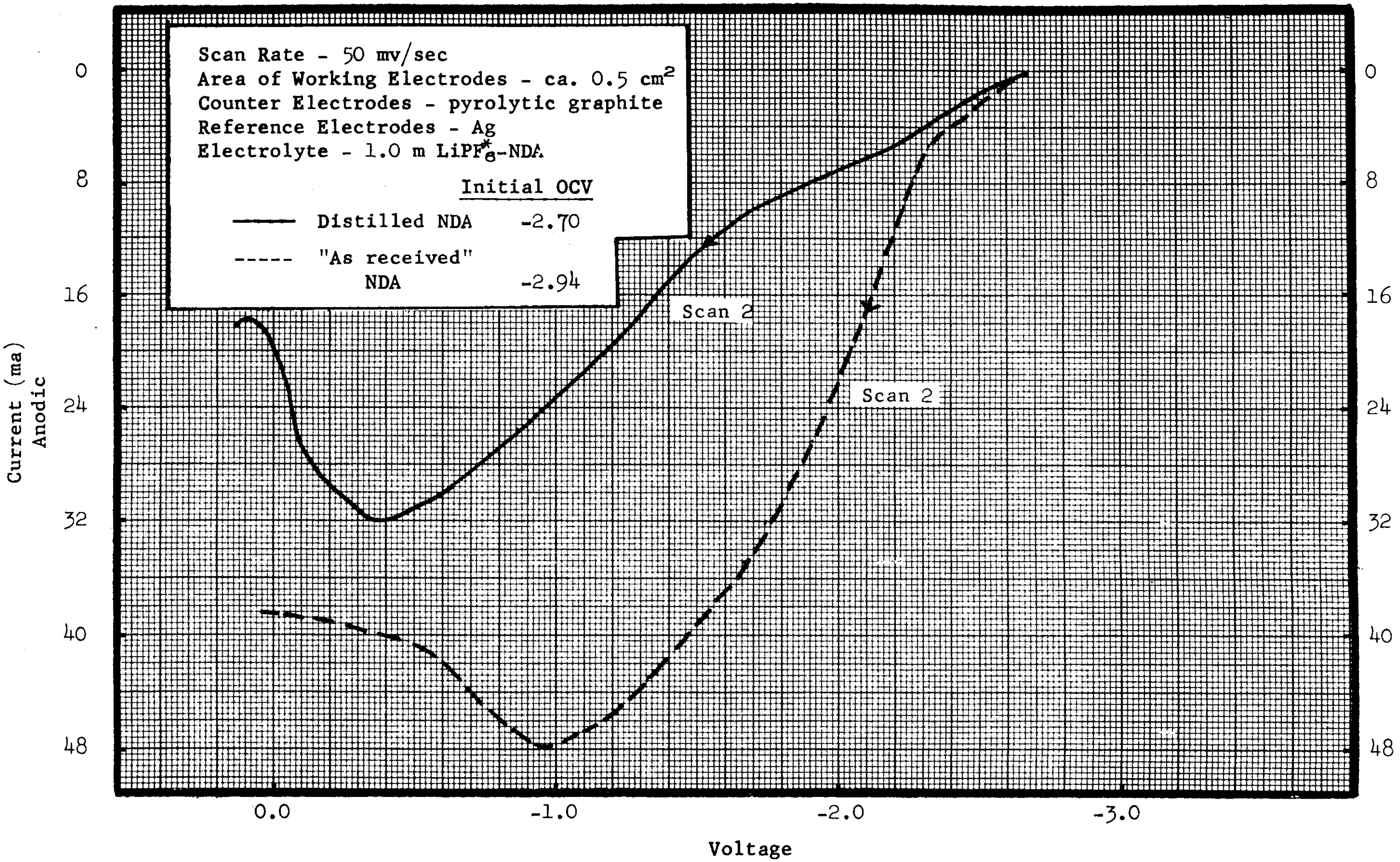


FIGURE 9. LINEARLY VARYING POTENTIAL STUDIES OF LITHIUM ANODES (Continued)

Figure 9-e. LVP Scans After Twenty-Four Hour Exposure to One Molal $LiPF_6^*$-N-Nitrosodimethylamine Prepared from Distilled and "As Received" Solvent.

* The $LiPF_6$ was dried at 110°C in a nitrogen atmosphere before use.

FIGURE 10. VOLTAMMETRIC STUDIES OF LITHIUM ANODES

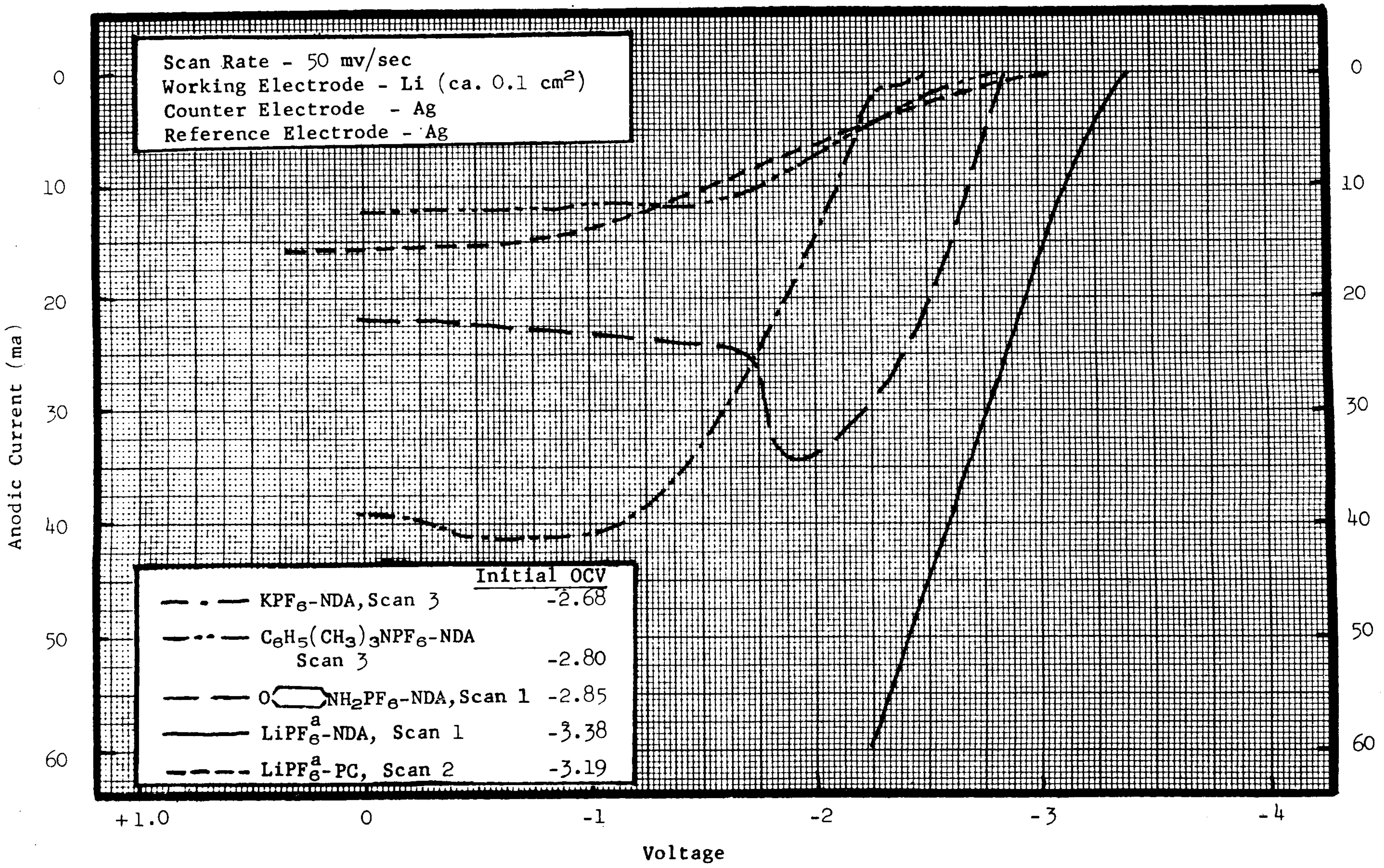


FIGURE 10. VOLTAMMETRIC SWEEP STUDIES OF ANODES

Figure 10-a. Voltammetric Sweep Studies of Lithium in Various Electrolytes.

The initial potential for each electrode was set equal to the open circuit voltage and the scan taken towards more positive voltages.

[a] LiPF$_6$ used was dried at 110°C under nitrogen.

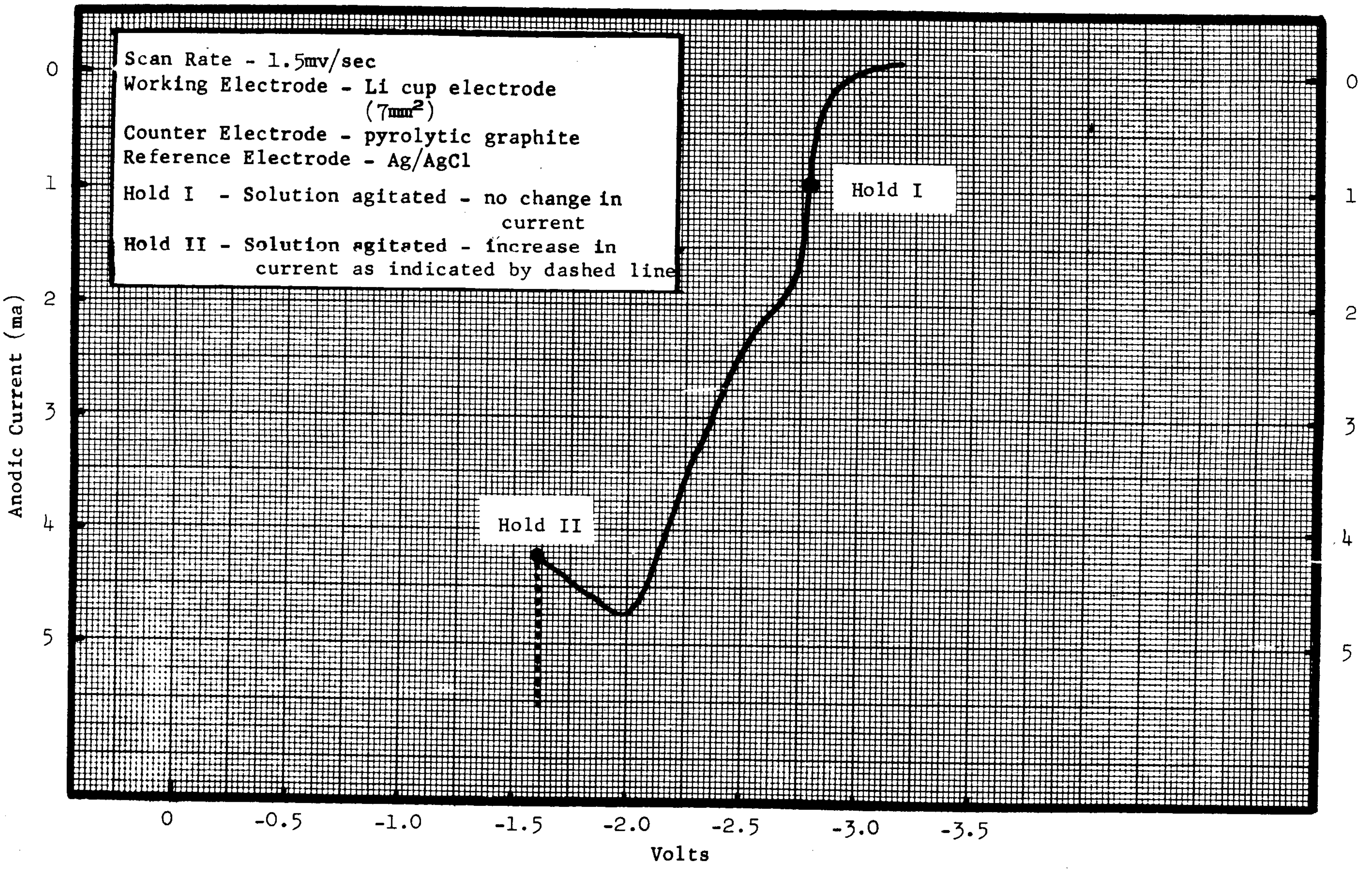


FIGURE 10. VOLTAMMETRIC SWEEP STUDIES OF ANODES (Continued)

Figure 10-b. Electrochemical Study of Lithium in Lithium Hexafluorophosphate-N-Nitrosodimethylamine[a].

The initial potential for the electrode was set at -3.2V vs. Ag/AgCl and the scan run towards more positive voltages. At the Hold I point, the potential was held constant for approximately 30 seconds, then the scan was continued to Hold II when the potential was again held constant for 30 seconds.

[a] The $LiPF_6$-N-nitrosodimethylamine solution was pretreated with lithium prior to this study.

TABLE XII. CHEMICAL STABILITY OF ELECTRODE MATERIALS IN NONAQUEOUS SOLVENTS AND ELECTROLYTES

I. Tests of 24 Hours Duration

TABLE XII. CHEMICAL STABILITY OF CATHODE MATERIALS IN ELECTROLYTE SOLUTIONS

I. Tests of Twenty-Four Hours Duration.

A. Stability in N-Nitrosodimethylamine Solutions.

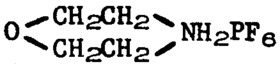
Solute	Cathode Material	Visible Change After 24 Hour Exposure
1. $MgCl_2$	CuF_2	Solution color became amber; green and orange solids formed.
	MnO_2	No change.
	CoF_3	Formation of green solid and green solution.
	Cu	No change.
2. KPF_6	CuF_2	Color of solution changed from yellow to dark green; gray-green solid formed.
	MnO_2	No change.
	CoF_3	Solution color became dark blue-green; black solid formed.
	Cu	No change.
3. $(n\text{-}C_3H_7)_4NPF_6$ (Tetra-n-propylammonium hexafluorophosphate)	CuF_2	No change.
	MnO_2	No change.
	CoF_3	Color of the CoF_3 solid appeared to be somewhat darkened.
	Cu	No change.
4.  $O\begin{smallmatrix}CH_2CH_2\\CH_2CH_2\end{smallmatrix}NH_2PF_6$ (Morpholinium hexafluorophosphate)	CuF_2	Solution color became green; green solid formed.
	MnO_2	No change.
	CoF_3	Color of the CoF_3 solid appeared to darken.
	Cu	No change.

TABLE XII. CHEMICAL STABILITY OF CATHODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Twenty-Four Hours Duration. (Continued)

A. Stability in N-Nitrosodimethylamine Solutions.

Solute	Cathode Material	Visible Change After 24 Hour Exposure
5. $AlCl_3$	CuF_2	CuF_2 color changed from light gray to light brown.
	MnO_2	Solution color changed from amber to deep yellow-green.
	CoF_3	Solution color changed from amber to dark green; CoF_3 color changed from brown to blue.
	Cu	Solution color changed from amber to orange.
6. LiCl	CuF_2	Solution color changed from yellow to amber. CuF_2 color changed from gray to yellow.
	MnO_2	No change.
	CoF_3	Solution color changed from yellow to blue-green.
	Cu	No change.
7. $(p\text{-}C_{12}H_{25}C_6H_4CH_2)(CH_3)_3NPF_6$ (N-(p-Dodecylbenzyl)N,N,N-trimethylammonium hexafluorophosphate)	CuF_2	Solution color changed from yellow to yellow-green.
	MnO_2	Solution color changed from yellow to yellow-green.
	CoF_3	Solution color changed from yellow to yellow-green.
	Cu	Solution color changed from yellow to yellow-green.

TABLE XII. CHEMICAL STABILITY OF CATHODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of 24 Hours Duration. (Continued)

A. Stability in N-Nitrosodimethylamine Solutions. (Continued)

Solute	Cathode Material	Visible Change After 24 Hour Exposure
8. $(CH_3)_4NPF_6$ (Tetramethylammonium hexafluorophosphate)	CuF_2	No change.
	MnO_2	No change.
	CoF_3	CoF_3 color darkened.
	Cu	No change.
9. $(C_6H_5)(CH_3)_3NPF_6$ (N-Phenyl N,N,N-trimethylammonium hexafluorophosphate)	CuF_2	No change.
	MnO_2	No change.
	CoF_3	CoF_3 color darkened appreciably.
	Cu	No change.
10. $(n\text{-}C_3H_7)_3NHAsF_6$ (Tri-n-propylammonium hexafluoroarsenate)	CuF_2	No change.
	MnO_2	No change.
	CoF_3	CoF_3 color darkened.
	Cu	No change.
11. $(n\text{-}C_4H_9)_2H_2NAsF_6$ (Di-n-butylammonium hexafluoroarsenate)	CuF_2	No change.
	MnO_2	No change.
	CoF_3	No change.
	Cu	No change.

TABLE XII. CHEMICAL STABILITY OF CATHODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

Tests of Twenty-Four Hours Duration. (Continued)
B. Stability in Dimethylformamide Solutions.

Solute	Cathode Material	Visible Change After 24 Hour Exposure
1. LiCl	CuF_2	Solution color changed from colorless to orange. CuF_2 changed from gray to yellow.
	MnO_2	No change.
	CoF_3	Solution color changed from colorless to dark blue. CoF_3 color changed from brown to black.
	Cu	No change.
2. $(p\text{-}C_{12}H_{25}C_6H_4CH_2)(CH_3)_3NPF_6$ (N-(p-Dodecylbenzyl)N,N,N-trimethylammonium hexafluorophosphate)	CuF_2	No change.
	MnO_2	No change.
	CoF_3	No change.
	Cu	No change.
3. $(CH_3)_4NPF_6$ (Tetramethylammonium hexafluorophosphate)	CuF_2	Color of CuF_2 changed from light gray to darker gray.
	MnO_2	No change.
	CoF_3	Solution changed from colorless to faint red; CoF_3 color darkened.
	Cu	No change.
4. $(C_6H_5)(CH_3)_3NPF_6$ (N-Phenyl N,N,N-trimethylammonium hexafluorophosphate)	CuF_2	No change.
	MnO_2	No change.
	CoF_3	Solution color changed from clear gray to clear brown. CoF_3 color darkened.
	Cu	No change.
5. $(n\text{-}C_3H_7)_3NHAsF_6$ (Tri-n-propylammonium hexafluoroarsenate)	CuF_2	No change.
	MnO_2	Solution color somewhat deeper.
	CoF_3	Solution color somewhat deeper; CoF_3 color darker.
	Cu	No change.

TABLE XII. CHEMICAL STABILITY OF CATHODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

I. Tests of Twenty-Four Hours Duration.

B. Stability in Dimethylformamide Solutions.

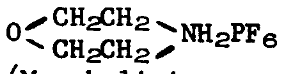
Solute	Cathode Material	Visible Change After 24 Hour Exposure
6. $MgCl_2$	CuF_2	Solution color became deep amber. Yellow-green solid produced.
	MnO_2	No change.
	CoF_3	Solution color became deep blue; blue-green solid produced.
	Cu	No change.
	Co	No change.
7. KPF_6	CuF_2	Solution color changed from colorless to light blue. Blue solid formed.
	MnO_2	No change.
	CoF_3	Solution color changed from colorless to faint red; CoF_3 solid somewhat darker.
	Cu	No change.
8. $(n\text{-}C_3H_7)_4NPF_6$ (Tetra-n-propylammonium hexafluorophosphate)	CuF_2	Solution became yellow-green; small amount of green solid produced.
	MnO_2	Solution color changed from yellow to amber.
	CoF_3	Solution color became deep amber.
	Cu	No change.
	Co	No change.
9.  $O\begin{smallmatrix}CH_2CH_2\\CH_2CH_2\end{smallmatrix}NH_2PF_6$ (Morpholinium hexafluorophosphate)	CuF_2	Solution color became light blue. Blue solid produced.
	MnO_2	No change.
	CoF_3	Color of the CoF_3 solid appeared to darken.
	Cu	No change.

TABLE XII. CHEMICAL STABILITY OF CATHODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

I. Tests of Twenty-Four Hours Duration. (Continued)
C. Stability in Ethylene Carbonate (80 Weight %)-Propylene Carbonate (20 Weight %) Solutions.

Solute	Cathode Material	Visible Change After 24 Hour Exposure
1. $AlCl_3$	CuF_2	Solution color changed from light brown to deep amber. CuF_2 color changed from gray to black.
	MnO_2	Solution color changed from light brown to dark green.
	CoF_3	Solution color changed from light brown to dark blue. CoF_3 color changed from brown to blue.
	Cu	No change.
2. LiCl	CuF_2	Solution color changed from colorless to orange-yellow. CuF_2 color changed from gray to yellow-green.
	MnO_2	No change.
	CoF_3	Solution color changed from colorless to blue.
	Cu	No change.
3. $(p\text{-}C_{12}H_{25}C_6H_4CH_2)(CH_3)_3NPF_6$ (N-(p-Dodecylbenzyl)N,N,N-trimethylammonium hexafluorophosphate)	CuF_2	No change.
	MnO_2	No change.
	CoF_3	CoF_3 color darkened.
	Cu	No change.
4. $(CH_3)_4NPF_6$ (Tetramethylammonium hexafluorophosphate)	CuF_2	No change.
	MnO_2	No change.
	CoF_3	CoF_3 color darkened.
	Cu	No change.

TABLE XII. CHEMICAL STABILITY OF CATHODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

I. Tests of 24 Hours Duration. (Continued)

C. Stability in Ethylene Carbonate (80%)-Propylene Carbonate (20%) Solutions. (Continued)

Solute	Cathode Material	Visible Change After 24 Hour Exposure
5. $(C_6H_5)(CH_3)_3NPF_6$ (N-Phenyl N,N,N-trimethylammonium hexafluorophosphate)	CuF_2	Solution color changed slightly from light gray to light green.
	MnO_2	Solution color became green.
	CoF_3	CoF_3 color darkened appreciably; solution color became yellow.
	Cu	No change.
6. $(n\text{-}C_3H_7)_3NHAsF_6$ (Tri-n-propylammonium hexafluoroarsenate)	CuF_2	No change.
	MnO_2	No change.
	CoF_3	Solution color changed from yellow to brown; CoF_3 darkened.
	Cu	No change.
7. $(n\text{-}C_4H_9)_2H_2NAsF_6$ (Di-n-butylammonium hexafluoroarsenate)	CuF_2	No change.
	MnO_2	No change.
	CoF_3	No change.
	Cu	No change.

TABLE XII. CHEMICAL STABILITY OF CATHODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

I. Tests of Twenty-Four Hours Duration.

C. Stability in Ethylene Carbonate (80 Weight %)-Propylene Carbonate (20 Weight %) Solutions.

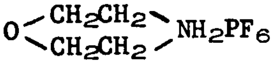
Solute	Cathode Material	Visible Change After 24 Hour Exposure
8. $MgCl_2$	CuF_2	Solution became orange-yellow colore
	MnO_2	No change.
	CoF_3	Solution became blue colored. Blue solid formed.
	Cu	No change.
9. KPF_6	CuF_2	No change.
	MnO_2	No change.
	CoF_3	Color of CoF_3 solid somewhat darkene
	Cu	No change.
10. $(n\text{-}C_3H_7)_4NPF_6$ (Tetra-n-propylammonium hexafluorophosphate)	CuF_2	Solution color changed from amber to light yellow. Yellow solid formed.
	MnO_2	No change.
	CoF_3	No change.
	Cu	No change.
11.  $O\left<\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}\right>NH_2PF_6$ (Morpholinium hexafluorophosphate)	CuF_2	No change.
	MnO_2	No change.
	CoF_3	No change.
	Cu	No change.

TABLE XII. CHEMICAL STABILITY OF CATHODE MATERIALS IN NONAQUEOUS SOLVENTS

II. Tests of 2 Weeks Duration

Cathode Material	Specific Conductance ($ohm^{-1}cm^{-1}$) At 25°C - After 2 Week Exposure: Exposed Solvent	Blank Solvent	Visible Change After Two Week Exposure
	a. Stability in Acetonitrile		
CoF_3	1.13×10^{-4}	4.71×10^{-6}	No change.
MnO_2	4.74×10^{-6}		No change.
CuF_2	1.02×10^{-5}		No change.
	b. Stability in Dimethylformamide		
CoF_3	1.64×10^{-4}	1.54×10^{-6}	CoF_3 somewhat darkened.
MnO_2	4.86×10^{-6}		No change.
CuF_2	6.80×10^{-6}		No change.
	c. Stability in Ethylene Carbonate (80 Weight %)-Propylene Carbonate (20 Weight %)		
CoF_3	2.06×10^{-4}	4.92×10^{-6}	Solution colored faintly red.
MnO_2	3.48×10^{-6}		No change.
CuF_2	6.60×10^{-6}		No change.
	d. Stability in N-Nitrosodimethylamine		
CoF_3	5.90×10^{-5}	2.48×10^{-5}	CoF_3 somewhat darkened.
MnO_2	3.31×10^{-5}		No change.
CuF_2	2.49×10^{-5}		No change.

TABLE VII. CHEMICAL STABILITY OF ELECTRODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

A. Stability in N-Nitrosodimethylamine Solutions.

	Solute		Time of Measurement	Weight of Electrode Material (g)	Specific Conductance (ohm^{-1} cm^{-1})		Visible Change After Exposure
					Exposed Electrolyte	Blank Electrolyte	
1.	None	CuF_2	Initial	0.4576	1.05×10^{-4} (24°C)	1.08×10^{-4} (24°C)	The cathode pellet turned green immediately. No further visible change occurred.
			After Two Days		1.26×10^{-4} (26°C)	1.31×10^{-4} (26°C)	
			After One Week		1.42×10^{-4} (26°C)	1.56×10^{-4} (26°C)	
			After Three Weeks		1.71×10^{-4} (24°C)	1.44×10^{-4} (24°C)	
			After Four Weeks		2.21×10^{-4} (29°C)	1.65×10^{-4} (29°C)	
			After Nine Weeks		2.59×10^{-4} (26°C)	1.72×10^{-4} (26°C)	
			After Fourteen Weeks	0.4685	2.79×10^{-4} (27°C)	1.97×10^{-4} (27°C)	
2.	$LiPF_6$ (as received)	CuF_2	Initial	0.3179	1.98×10^{-2} (24°C)	2.01×10^{-2} (24°C)	The electrolyte changed from yellow to green after two days. After fourteen weeks a dark green precipitate had formed. No further visible changes occurred.
			After Two Days		1.81×10^{-2} (26°C)	2.03×10^{-2} (26°C)	
					2.07×10^{-2} (26°C)	2.06×10^{-2} (26°C)	
					1.91×10^{-2} (24°C)	2.03×10^{-2} (24°C)	
					2.13×10^{-2} (29°C)	2.06×10^{-2} (29°C)	

TABLE XII. CHEMICAL STABILITY OF ELECTRODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

A. Stability in N-Nitrosodimethylamine Solutions. (Continued)

Solute	Electrode Material	Time of Measurement	Weight of Electrode Material (g)	Specific Conductance (ohm^{-1} cm^{-1})		Visible Change After Exposure
				Exposed Electrolyte	Blank Electrolyte	
3. (Continued)	CuF_2	After Nine Weeks		1.97×10^{-2} ($26^\circ C$)	2.04×10^{-2} ($26^\circ C$)	
		After Fourteen Weeks	0.1461	1.88×10^{-2} ($27^\circ C$)	1.59×10^{-2} ($27^\circ C$)	
4. $LiPF_6$[a]	CuF_2	Initial	0.1932	1.89×10^{-2} ($24^\circ C$)	1.87×10^{-2} ($24^\circ C$)	The cathode pellet remained intact. The electrolyte changed from yellow to green after two days. After fourteen weeks a blue-green precipitate had formed. No further visible changes occurred.
		After Two Days		1.86×10^{-2} ($26^\circ C$)	1.88×10^{-2} ($26^\circ C$)	
		After One Week		1.89×10^{-2} ($26^\circ C$)	1.17×10^{-2} ($26^\circ C$)	
		After Three Weeks		1.83×10^{-2} ($24^\circ C$)	1.77×10^{-2} ($24^\circ C$)	
		After Four Weeks		1.93×10^{-2} ($29^\circ C$)	1.93×10^{-2} ($29^\circ C$)	
		After Nine Weeks		1.88×10^{-2} ($26^\circ C$)	1.92×10^{-2} ($26^\circ C$)	
		After Fourteen Weeks	0.1942	1.72×10^{-2} ($27^\circ C$)	1.96×10^{-2} ($28^\circ C$)	

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[a] The $LiPF_6$ was dried at 110°C in a nitrogen atmosphere before use.

TABLE XII. CHEMICAL STABILITY OF ELECTRODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

A. Stability in N-Nitrosodimethylamine Solutions. (Continued)

	Solute	Electrode Material	Time of Measurement	Weight of Electrode Material (g)	Specific Conductance (ohm^{-1} cm^{-1})		Visible Change After Exposure
					Exposed Electrolyte	Blank Electrolyte	
5.	$LiPF_6$ (as received)	CuF_2 & Li (2 electrodes)	Initial	0.2372[c] (CuF_2) 0.0691 (Li)	2.06×10^{-2} (28°C)	2.01×10^{-2} (28°C)	Gassing occurred initially and the solution turned green. The cathode pellet disintegrated completely after four weeks.
			After One Day		1.95×10^{-2} (27°C)	1.96×10^{-2} (27°C)	
			After One Week		1.98×10^{-2} (26°C)	1.91×10^{-2} (26°C)	
			After Two Weeks		2.01×10^{-2} (27°C)	2.01×10^{-2} (27°C)	
			After Three Weeks		1.97×10^{-2} (27°C)	2.06×10^{-2} (27°C)	
			After Four Weeks	0.0433 (Li)	1.89×10^{-2} (27°C)	2.01×10^{-2} (27°C)	
6.	$LiPF_6$[b]	CuF_2 & Li (2 electrodes)	Initial	0.2523[c] (CuF_2) 0.0643 (Li)	1.89×10^{-2} (28°C)	1.94×10^{-2} (28°C)	The solution turned green when the cathode was inserted. After four weeks the cathode pellet had disintegrated completely.
			After One Day		1.92×10^{-2} (27°C)	1.92×10^{-2} (27°C)	
			After One Week		1.91×10^{-2} (26°C)	1.86×10^{-2} (26°C)	
			After Two Weeks		1.87×10^{-2} (27°C)	1.93×10^{-2} (27°C)	
			After Three Weeks		1.93×10^{-2} (27°C)	1.90×10^{-2} (27°C)	
			After Four Weeks	0.1463 (Li)	1.90×10^{-2} (27°C)	1.92×10^{-2} (27°C)	

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[b] The $LiPF_6$ was dried at 110°C in a nitrogen atmosphere before use.

[c] Includes substrate weight.

TABLE XII. CHEMICAL STABILITY OF ELECTRODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

A. Stability in N-Nitrosodimethylamine Solutions. (Continued)

Solute	Electrode Material	Time of Measurement	Weight of Electrode Material (g)	Specific Conductance $(\text{ohm}^{-1}\ \text{cm}^{-1})$		Visible Change After Exposure
				Exposed Electrolyte	Blank Electrolyte	
7. None	AgO	Initial	0.3591	7.96×10^{-5} (29°C)	8.03×10^{-5} (29°C)	The electrolyte changed from yellow to green after four weeks. After ten weeks a dark precipitate had formed and the cathode pellet was disintegrating. No further visible changes occurred.
		After One Day		9.59×10^{-5} (26°C)	8.22×10^{-5} (26°C)	
		After One Week		1.07×10^{-4} (27°C)	8.58×10^{-5} (27°C)	
		After Two Weeks		1.14×10^{-4} (28°C)	1.12×10^{-4} (28°C)	
		After Three Weeks		1.22×10^{-4} (26°C)	1.07×10^{-4} (26°C)	
		After Four Weeks		1.45×10^{-4} (27°C)	1.11×10^{-4} (27°C)	
		After Five Weeks		1.58×10^{-4} (29°C)	1.24×10^{-4} (29°C)	
		After Six Weeks		1.68×10^{-4} (28°C)	1.24×10^{-4} (28°C)	
		After Seven Weeks		1.72×10^{-4} (27°C)	1.36×10^{-4} (28°C)	
		After Eight Weeks		1.85×10^{-4} (26°C)	1.25×10^{-4} (25°C)	
		After Nine Weeks		1.96×10^{-4} (25°C)	1.25×10^{-4} (25°C)	
		After Ten Weeks		2.03×10^{-4} (26°C)	1.26×10^{-4} (26°C)	
		After Eleven Weeks		2.06×10^{-4} (25°C)	1.30×10^{-4} (25°C)	
		After Twelve Weeks		2.20×10^{-4} (27°C)	1.47×10^{-4} (27°C)	
		After Thirteen Weeks		2.26×10^{-4} (26°C)	1.39×10^{-4} (26°C)	
		After Fourteen Weeks		2.24×10^{-4} (22°C)	1.50×10^{-4} (22°C)	
		After Fifteen Weeks[b]		2.44×10^{-4} (23°C)	1.48×10^{-4} (23°C)	

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[b] Weight change of AgO cannot be calculated because pellet disintegrated.

TABLE XII. CHEMICAL STABILITY OF ELECTRODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

A. Stability in N-Nitrosodimethylamine Solutions. (Continued)

Solute	Electrode Material	Time of Measurement	Weight of Electrode Material (g)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Exposure
8. $LiPF_6$ (as received)	AgO	Initial	0.4480	2.04×10^{-2} (29°C)	2.04×10^{-2} (29°C)	Moderate gassing occurred initially. A white precipitate formed during the first day. The cathode pellet disintegrated considerably after two weeks.
		After One Day		2.00×10^{-2} (26°C)	1.98×10^{-2} (26°C)	
		After One Week		2.03×10^{-2} (27°C)	2.06×10^{-2} (27°C)	
		After Two Weeks		2.07×10^{-2} (28°C)	2.06×10^{-2} (28°C)	
		After Three Weeks		2.06×10^{-2} (26°C)	1.95×10^{-2} (26°C)	
		After Four Weeks		2.05×10^{-2} (27°C)	1.94×10^{-2} (27°C)	
		After Five Weeks		2.08×10^{-2} (29°C)	2.06×10^{-2} (29°C)	
		After Six Weeks		2.07×10^{-2} (28°C)	2.03×10^{-2} (28°C)	
		After Seven Weeks		2.00×10^{-2} (26°C)	1.87×10^{-2} (26°C)	
		After Eight Weeks		2.05×10^{-2} (26°C)	2.00×10^{-2} (26°C)	
		After Nine Weeks		2.05×10^{-2} (26°C)	1.90×10^{-2} (26°C)	
		After Ten Weeks		2.05×10^{-2} (26°C)	1.90×10^{-2} (26°C)	
		After Eleven Weeks		1.96×10^{-2} (25°C)	1.94×10^{-2} (25°C)	
		After Twelve Weeks		1.98×10^{-2} (27°C)	2.02×10^{-2} (27°C)	
		After Thirteen Weeks		2.01×10^{-2} (26°C)	1.89×10^{-2} (26°C)	
		After Fourteen Weeks		1.88×10^{-2} (22°C)	1.59×10^{-2} (22°C)	
		After Fifteen Weeks[b]		1.82×10^{-2} (23°C)	1.88×10^{-2} (23°C)	

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[b] Weight change of AgO cannot be calculated because pellet disintegrated.

TABLE XII. CHEMICAL STABILITY OF ELECTRODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

A. Stability in N-Nitrosodimethylamine Solutions. (Continued)

Solute	Electrode Material	Time of Measurement	Weight of Electrode Material (g)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Exposure
9. $LiPF_6$[a]	AgO	Initial	0.4071	1.86×10^{-2} (29°C)	1.93×10^{-2} (29°C)	Slight gassing occurred initially. A small amount of white precipitate formed after two weeks. The cathode pellet remained intact. No further visible change occurred.
		After One Day		1.89×10^{-2} (26°C)	1.83×10^{-2} (26°C)	
		After One Week		1.90×10^{-2} (27°C)	1.91×10^{-2} (27°C)	
		After Two Weeks		1.96×10^{-2} (28°C)	1.84×10^{-2} (28°C)	
		After Three Weeks		1.91×10^{-2} (26°C)	1.87×10^{-2} (26°C)	
		After Four Weeks		1.94×10^{-2} (27°C)	1.92×10^{-2} (27°C)	
		After Five Weeks		1.91×10^{-2} (29°C)	1.93×10^{-2} (29°C)	
		After Six Weeks		1.97×10^{-2} (28°C)	1.42×10^{-2} (28°C)	
		After Seven Weeks		1.97×10^{-2} (27°C)	1.82×10^{-2} (27°C)	
		After Eight Weeks		1.94×10^{-2} (26°C)	1.88×10^{-2} (26°C)	
		After Nine Weeks		1.80×10^{-2} (26°C)	1.91×10^{-2} (25°C)	
		After Ten Weeks		1.93×10^{-2} (26°C)	1.95×10^{-2} (26°C)	
		After Eleven Weeks		1.88×10^{-2} (25°C)	1.90×10^{-2} (25°C)	
		After Twelve Weeks		1.95×10^{-2} (27°C)	1.85×10^{-2} (27°C)	
		After Thirteen Weeks		2.01×10^{-2} (26°C)	1.88×10^{-2} (26°C)	

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[a] The $LiPF_6$ was dried at 110°C in a nitrogen atmosphere before use.

TABLE XII. CHEMICAL STABILITY OF ELECTRODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

A. Stability in N-Nitrosodimethylamine Solutions. (Continued)

	Solute	Electrode Material	Time of Measurement	Weight of Electrode Material (g)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Exposure
9.	(Continued)	AgO	After Fourteen Weeks		1.86×10^{-2} (22°C)	1.79×10^{-2} (22°C)	
			After Fifteen Weeks[b]		1.81×10^{-2} (23°C)	1.82×10^{-2} (23°C)	
10.	None	AgO & Li (2 electrodes)	Initial	0.3237 (AgO) 0.0756 (Li)	1.09×10^{-4} (29°C)	8.03×10^{-5} (29°C)	The cathode pellet remained intact. After four weeks the solution had changed from yellow to yellow-green and was slightly turbid. After ten weeks a dark precipitate had formed. No further visible change occurred.
			After One Day		1.06×10^{-4} (26°C)	8.22×10^{-5} (26°C)	
			After One Week		1.21×10^{-4} (27°C)	8.58×10^{-5} (27°C)	
			After Two Weeks		1.27×10^{-4} (28°C)	1.12×10^{-4} (28°C)	
			After Three Weeks		1.27×10^{-4} (26°C)	1.07×10^{-4} (26°C)	
			After Four Weeks		1.37×10^{-4} (27°C)	1.11×10^{-4} (27°C)	
			After Five Weeks		1.45×10^{-4} (29°C)	1.24×10^{-4} (29°C)	
			After Six Weeks	0.0554[c] (Li)	1.46×10^{-4} (28°C)	1.24×10^{-4} (28°C)	
			After Seven Weeks		1.52×10^{-4} (27°C)	1.36×10^{-4} (28°C)	
			After Eight Weeks		1.56×10^{-4} (26°C)	1.25×10^{-4} (25°C)	

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[b] Weight change of AgO cannot be calculated because pellet disintegrated.

[c] Lithium was not visibly attacked up to this time. However, between tests it apparently worked loose from the connecting clip and dropped into solution. To avoid disturbing the test excessively, a new piece of lithium was used.

TABLE XII. CHEMICAL STABILITY OF ELECTRODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

A. Stability in N-Nitrosodimethylamine Solutions. (Continued)

Solute	Electrode Material	Time of Measurement	Weight of Electrode Material (g)	Specific Conductance (ohm^{-1} cm^{-1})		Visible Change After Exposure
				Exposed Electrolyte	Blank Electrolyte	
10. (Continued)	AgO & Li (2 electrodes)	After Nine Weeks		1.60×10^{-4} ($26^{\circ}C$)	1.25×10^{-4} ($25^{\circ}C$)	
		After Ten Weeks		1.66×10^{-4} ($26^{\circ}C$)	1.26×10^{-4} ($26^{\circ}C$)	
		After Eleven Weeks		1.76×10^{-4} ($25^{\circ}C$)	1.30×10^{-4} ($25^{\circ}C$)	
		After Twelve Weeks		1.80×10^{-4} ($27^{\circ}C$)	1.47×10^{-4} ($27^{\circ}C$)	
		After Thirteen Weeks		1.87×10^{-4} ($26^{\circ}C$)	1.39×10^{-4} ($26^{\circ}C$)	
		After Fourteen Weeks		1.82×10^{-4} ($22^{\circ}C$)	1.50×10^{-4} ($22^{\circ}C$)	
		After Fifteen Weeks	0.0813 (Li)[b]	1.85×10^{-4} ($23^{\circ}C$)	1.48×10^{-4} ($23^{\circ}C$)	
11. $LiPF_6$ (as received)	AgO & Li (2 electrodes)	Initial	0.2960 (AgO) 0.0921 (Li)	2.05×10^{-2} ($29^{\circ}C$)	2.04×10^{-2} ($29^{\circ}C$)	After one week the lithium turned black. After four weeks the solution's color changed from yellow to yellow-green and it was slightly turbid. The AgO pellet remained intact for six weeks after which time it began to disintegrate slowly.
		After One Day		1.96×10^{-2} ($26^{\circ}C$)	1.98×10^{-2} ($26^{\circ}C$)	
		After One Week		1.99×10^{-2} ($27^{\circ}C$)	2.06×10^{-2} ($27^{\circ}C$)	
		After Two Weeks		1.97×10^{-2} ($28^{\circ}C$)	2.06×10^{-2} ($28^{\circ}C$)	
		After Three Weeks		1.93×10^{-2} ($26^{\circ}C$)	1.95×10^{-2} ($26^{\circ}C$)	
		After Four Weeks		1.93×10^{-2} ($27^{\circ}C$)	1.94×10^{-2} ($27^{\circ}C$)	

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[b] Weight change cannot be calculated because pellet disintegrated.

TABLE XII. CHEMICAL STABILITY OF ELECTRODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

A. Stability in N-Nitrosodimethylamine Solutions. (Continued)

Solute	Electrode Material	Time of Measurement	Weight of Electrode Material (g)	Specific Conductance (ohm^{-1} cm^{-1}) Exposed Electrolyte	Specific Conductance (ohm^{-1} cm^{-1}) Blank Electrolyte	Visible Change After Exposure
11. (Continued)	AgO & Li (2 electrodes)	After Five Weeks		1.87×10^{-2} (29°C)	2.06×10^{-2} (29°C)	
		After Six Weeks		1.82×10^{-2} (28°C)	2.03×10^{-2} (28°C)	
		After Seven Weeks		1.86×10^{-2} (26°C)	1.87×10^{-2} (26°C)	
		After Eight Weeks		1.77×10^{-2} (26°C)	2.00×10^{-2} (26°C)	
		After Nine Weeks		1.85×10^{-2} (26°C)	1.90×10^{-2} (26°C)	
		After Ten Weeks		1.83×10^{-2} (26°C)	1.90×10^{-2} (26°C)	
		After Eleven Weeks		1.74×10^{-2} (25°C)	1.94×10^{-2} (25°C)	
		After Twelve Weeks		1.69×10^{-2} (27°C)	2.02×10^{-2} (27°C)	
		After Thirteen Weeks		1.88×10^{-2} (26°C)	1.89×10^{-2} (26°C)	
		After Fourteen Weeks		1.66×10^{-2} (22°C)	1.59×10^{-2} (22°C)	
		After Fifteen Weeks	0.1327 (Li)[b]	1.85×10^{-2} (23°C)	1.88×10^{-2} (23°C)	

---

[b] Weight change of AgO cannot be calculated because pellet disintegrated.

TABLE XII. CHEMICAL STABILITY OF ELECTRODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

A. **Stability in N-Nitrosodimethylamine Solutions.** (Continued)

Solute	Electrode Material	Time of Measurement	Weight of Electrode Material (g)	Specific Conductance (ohm^{-1} cm^{-1})		Visible Change After Exposure
				Exposed Electrolyte	Blank Electrolyte	
12. $LiPF_6$[a]	AgO & Li (2 electrodes)	Initial	0.4209 (AgO) 0.2350 (Li)[b]	1.94×10^{-2} (29°C)	1.93×10^{-2} (29°C)	Slight gassing occurred initially. The lithium was black after one week. After four weeks the solution was dark green and a black precipitate was present. After seven weeks the lithium showed signs of extensive disintegration.
		After One Day		1.94×10^{-2} (26°C)	1.83×10^{-2} (26°C)	
		After One Week		1.91×10^{-2} (27°C)	1.91×10^{-2} (27°C)	
		After Two Weeks		1.96×10^{-2} (28°C)	1.84×10^{-2} (28°C)	
		After Three Weeks		1.79×10^{-2} (26°C)	1.87×10^{-2} (26°C)	
		After Four Weeks		1.95×10^{-2} (27°C)	1.92×10^{-2} (27°C)	
		After Five Weeks		1.88×10^{-2} (29°C)	1.93×10^{-2} (29°C)	
		After Six Weeks		1.93×10^{-2} (28°C)	1.42×10^{-2} (28°C)	
		After Seven Weeks		1.86×10^{-2} (27°C)	1.82×10^{-2} (27°C)	
		After Eight Weeks		1.85×10^{-2} (26°C)	1.88×10^{-2} (26°C)	
		After Nine Weeks		1.93×10^{-2} (26°C)	1.91×10^{-2} (25°C)	
		After Ten Weeks		1.87×10^{-2} (26°C)	1.95×10^{-2} (26°C)	

---

[a] The $LiPF_6$ was dried at 110°C in a nitrogen atmosphere before use.

[b] Weight change of AgO cannot be calculated because pellet disintegrated.

TABLE XII. CHEMICAL STABILITY OF ELECTRODE MATERIALS IN ELECTROLYTE SOLUTIONS (Continued)

A. Stability in N-Nitrosodimethylamine Solutions. (Continued)

	Solute	Electrode Material	Time of Measurement	Weight of Electrode Material (g)	Specific Conductance (ohm^{-1} cm^{-1})		Visible Change After Exposure
					Exposed Electrolyte	Blank Electrolyte	
12.	(Continued)	AgO & Li (2 electrodes)	After Eleven Weeks		1.76×10^{-2} (25°C)	1.90×10^{-2} (25°C)	
			After Twelve Weeks		1.87×10^{-2} (27°C)	1.85×10^{-2} (27°C)	
			After Thirteen Weeks		1.94×10^{-2} (26°C)	1.88×10^{-2} (26°C)	
			After Fourteen Weeks		1.79×10^{-2} (23°C)	1.79×10^{-2} (23°C)	
			After Fifteen Weeks	0.2350	1.74×10^{-2} (23°C)	1.82×10^{-2} (23°C)	

TABLE XIII. HALF-CELL CONSTANT CURRENT DISCHARGES OF CuF_2 AND AgO CATHODES

TABLE XIII. HALF-CELL CONSTANT CURRENT DISCHARGES OF CUPRIC FLUORIDE CATHODES

A. EFFECT OF ELECTROLYTE AND ELECTROLYTE PRETREATMENT ON SCREENING PERFORMANCE OF CATHODES[a]

	Electrolyte	Current Density ma/cm^2	Voltage of Cathode Vs. Reference Electrode Initial	Voltage of Cathode Vs. Reference Electrode Final	Voltage of Anode Vs. Reference Electrode Initial	Voltage of Anode Vs. Reference Electrode Final	Time at Each Current Density Seconds	Coulombs at Each Current Density	Total Theoretical Coulombs Based on Cathode	Observations and Remarks
1.[f]	LiPF$_6$-NDA	0.00	-0.22		-3.43				5.19	
		1.25	-0.27	-0.39	-3.37	-3.36	1000	2.5		
		2.50	-0.50	-0.61	-3.31	-3.27	500	2.5		
		5.00	-1.00	-----	-----	-----	0	0.0		
		0.00	-0.29^{c}							
		0.00	-0.21		-3.35					
		2.50	-0.29	-1.00^{c}	-3.30	-3.30	3540	17.7		
		0.00	-0.05		-3.15					
		1.25	-0.11	-0.29	-2.99	-3.14	1000	2.5		
		2.50	-0.41	-1.00	-3.06	-3.06	67	0.7		
		0.00	-0.13^{c}							
		0.00	-0.07		-3.21					
		2.50	-0.15	-1.00	-2.94	-3.06	1530	7.65		

---

a The cathode mix for all tests was 90% CuF$_2$, 5% acetylene black and 5% filter paper pulp. It was pressed onto a 1cm^2 Cu expanded metal substrate at 2,500 lbs for 2 min. at ambient temperature. Li anodes and Ag/AgCl reference electrodes were used in all cells. Ten milliliters of electrolyte were used unless noted. Both sides of the cathode were exposed.

c Cathode removed from electrolyte, surface scraped, then reinserted in electrolyte and next test run.

d The solute was dried for 4 hours under vacuum at 50°C.

f A new sample of the solute was dried and used in this test.

TABLE XIII. HALF-CELL CONSTANT CURRENT DISCHARGES OF CUPRIC FLUORIDE CATHODES

A. EFFECT OF ELECTROLYTE AND ELECTROLYTE PRETREATMENT ON SCREENING PERFORMANCE OF CATHODES[a]

Electrolyte	Current Density ma/cm^2	Voltage of Cathode Vs. Reference Electrode Initial	Voltage of Cathode Vs. Reference Electrode Final	Voltage of Anode Vs. Reference Electrode Initial	Voltage of Anode Vs. Reference Electrode Final	Time at Each Current Density Seconds	Coulombs at Each Current Density	Total Theoretical Coulombs Based on Cathode	Observations and Remarks
2. $LiPF_6^g$-NDA	0.00	-0.20		-3.40				514	Electrolyte light yellow-green
	1.25	-0.23	-0.26	-3.33	-3.32	1000	2.5		
	2.50	-0.30	-0.38	-3.25	-3.26	500	2.5		
	5.00	-0.49	-0.47	-3.15	-3.06	250	2.5		
	10.00	-0.70	-1.00	-2.82	-2.80	180	3.6		
	0.00	-0.18[c]		-3.31					
	0.00	-0.18		-3.32					
	2.50	-0.24	-1.00[c]	-3.22	-3.20	4560	22.8		
	0.00	+0.22		-3.04					
	1.25	+0.17	+0.05	-2.95	-2.95	1000	2.5		
	2.50	-0.02	-0.11	-2.85	-2.92	500	2.5		
	5.00	-0.25	-0.45	-2.77	-2.81	250	2.5		
	10.00	-1.00[c]	-----	-----	-----	0	0.0		
	0.00	+0.09							
	0.00	+0.24		-3.00					
	2.50	+0.16	-1.00	-2.69	-2.92	1554	7.77		
3. $LiPF_6^h$-NDA	0.00	+0.12		-3.13				514	
	1.25	+0.08	+0.02	-3.03	-3.04	1000	2.5		
	2.50	-0.02	-0.10	-2.94	-2.98	500	2.5		
	5.00	-0.19	-0.21	-2.84	-2.86	250	2.5		
	10.00	-0.37	-1.00	-2.62	-2.68	551	11.0		
	0.00	-0.02[c]		-3.19					

---

[a] The cathode mix for all tests was 90% CuF_2, 5% acetylene black and 5% filter paper pulp. It was pressed onto a 1cm^2 Cu expanded metal substrate at 2,500 lbs. for 2 min. at ambient temperature. Li anodes and Ag/AgCl reference electrodes were used in all cells. Ten milliliters of electrolyte were used unless noted. Both sides of the cathode were exposed.

[c] Cathode removed from electrolyte, surface scraped, then reinserted in electrolyte and next test run.

[g] A portion of the electrolyte prepared for Test 2 was pretreated with lithium for 2 hours and then used.

[h] A portion of the same electrolyte prepared for Test 5 stood in contact with lithium overnight and was then used for this test.

HALF-CELL CONSTANT CURRENT DISCHARGES OF CUPRIC FLUORIDE CATHODES

A. EFFECT OF ELECTROLYTE AND ELECTROLYTE PRETREATMENT ON SCREENING PERFORMANCE OF CATHODES[a]

	Electrolyte	Current Density ma/cm^2	Voltage of Cathode Vs. Reference Electrode		Voltage of Anode Vs. Reference Electrode		Time at Each Current Density Seconds	Coulombs at Each Current Density	Total Theoretical Coulombs Based on Cathode	Observations and Remarks
			Initial	Final	Initial	Final				
3.	(Continued)	0.00	+0.08		-3.09					
		2.50	0.00	-1.00	-2.69	-3.03	3460	17.3		
4.	LiPF$_6^i$-NDA	0.00	-0.11		-3.25				524	The electrolyte turned green within a few minutes.
		1.25	-0.14	-0.22	-3.19	-3.24	1000	2.5		
		2.50	-0.28	-0.33	-3.19	-3.20	500	2.5		
		5.00	-0.50	-0.79	-3.12	-3.14	250	2.5		
		10.00	-1.11	-----	-----	-----	0	0		
		0.00	-0.18^c							
		0.00	-0.08		-3.28					
		2.50	-0.15	-1.00	-3.12	-3.16	3124	15.62		
5.	KPF$_6^b$-NDA	0.00	+0.18		-3.20				520	
		1.25	+0.14	-0.05	-2.94	-2.97	1000	2.5		
		2.50	-0.10	-0.15	-2.88	-2.94	500	2.5		
		5.00	-0.24	-0.26	-2.84	-2.85	250	2.5		
		10.00	-0.46	-1.00	-2.65	-2.70	445	8.9		
		0.00	-0.05^c							
		0.00	-0.05							
		2.50	-0.15	-1.00^c	-2.77	-2.96	3942	19.7		

---

[a] The cathode mix for all tests was 90% CuF$_2$, 5% acetylene black and 5% filter paper pulp. It was pressed onto a 1cm^2 Cu expanded metal substrate at 2,500 lbs. for 2 min. at ambient temperature. Li anodes and Ag/AgCl reference electrodes were used in all cells. Ten milliliters of electrolyte were used unless noted. Both sides of the cathode were exposed.

[b] The solute was used "as received" from the supplier.

[c] Cathode removed from electrolyte, surface scraped, then reinserted in electrolyte and next test run.

[i] The solute was dried for 24 hours under vacuum at 50°C.

TABLE XIII. HALF-CELL CONSTANT CURRENT DISCHARGES OF CUPRIC FLUORIDE CATHODES

A. EFFECT OF ELECTROLYTE AND ELECTROLYTE PRETREATMENT ON SCREENING PERFORMANCE OF CATHODES[a]

	Electrolyte	Current Density ma/cm^2	Voltage of Cathode Vs. Reference Electrode		Voltage of Anode Vs. Reference Electrode		Time at Each Current Density Seconds	Coulombs at Each Current Density	Total Theoretical Coulombs Based on Cathode	Observations and Remarks
			Initial	Final	Initial	Final				
5.	(Continued)	0.00	-0.06		-3.17					
		1.25	-0.18	-1.00[c]	-2.93	-3.05	726	1.8		
		0.00	-0.14	-1.00	-3.17					
		2.50	-0.40		-2.79	-2.89	31	0.2		
6.	KPF$_6^f$-NDA	0.00	+0.03		-3.32				522	
		1.25	0.00	-0.07	-3.19	-3.15	1000	2.5		
		2.50	-0.12	-0.16	-3.04	-3.06	500	2.5		
		5.00	-0.24	-0.28	-2.95	-2.96	250	2.5		
		10.00	-0.44	-1.00[c]	-2.82	-2.82	570	11.4		
		0.00	-0.01		-3.15					
		2.50	-0.10	-1.00[c]	-2.80	-3.04	8344	41.7		
		0.00	+0.15		-3.06					
		1.25	+0.08	-1.00[c]	-2.83	-2.96	951	2.4		
		0.00	+0.07		-3.10					
		2.50	-0.15	-1.00	-2.61	-2.82	85	0.4		

---

[a] The cathode mix for all tests was 90% CuF_2, 5% acetylene black and 5% filter paper pulp. It was pressed onto a 1cm^2 Cu expanded metal substrate at 2,500 lbs for 2 min. at ambient temperature. Li anodes and Ag/AgCl reference electrodes were used in all cells. Ten milliliters of electrolyte were used unless noted. Both sides of the cathode were exposed.

[c] Cathode removed from electrolyte, surface scraped, then reinserted in electrolyte and next test run.

[d] The solute was dried for 4 hours under vacuum at 50°C.

TABLE XIII. SCREENING PERFORMANCE OF AgO CATHODES

	Electrode	Electrolyte	Reference Electrode	Counter Electrode	Current (ma)	Voltage of Cathode vs. Reference Electrode[a]		Open Circuit Voltage After Discharge	Observations & Remarks
						Initial	Final		
1.	AgO	1m $LiClO_4$-DMSO	Ag/AgCl	Li	0.0	+0.26	--	--	No changes noted.
					0.1	+0.24	+0.21	+0.24	
					1.0	0.00	-0.23	+0.18	
					5.0	-0.50	-0.57	0.00	
					10.0	-0.84	-1.12	-0.06	
					15.0	-1.22	-1.45	-0.22	
					20.0	-1.30	-1.56	-0.32	
					25.0	-1.30	-1.72	-0.43	
					30.0	-1.20	-1.88	-0.37	
2.	AgO	1m $(C_6H_5)(CH_3)_3NPF_6$-DMSO	Ag/AgCl	Li	0.0	+0.30	--	--	No Changes noted.
					0.1	+0.29	+0.23	+0.25	
					1.0	+0.12	-0.21	+0.12	
					5.0	-0.47	-0.83	-0.24	
					10.0	-1.00	-1.16	-0.34	
					15.0	-1.40	-1.37	-0.45	
					20.0	-1.46	-1.51	-0.57	
					25.0	-1.46	-1.73	-0.60	
					30.0	-1.50	-1.96	-0.63	

---

[a] Duration of discharge at each current density was 5 minutes. Both sides of cathode were exposed to electrolyte.

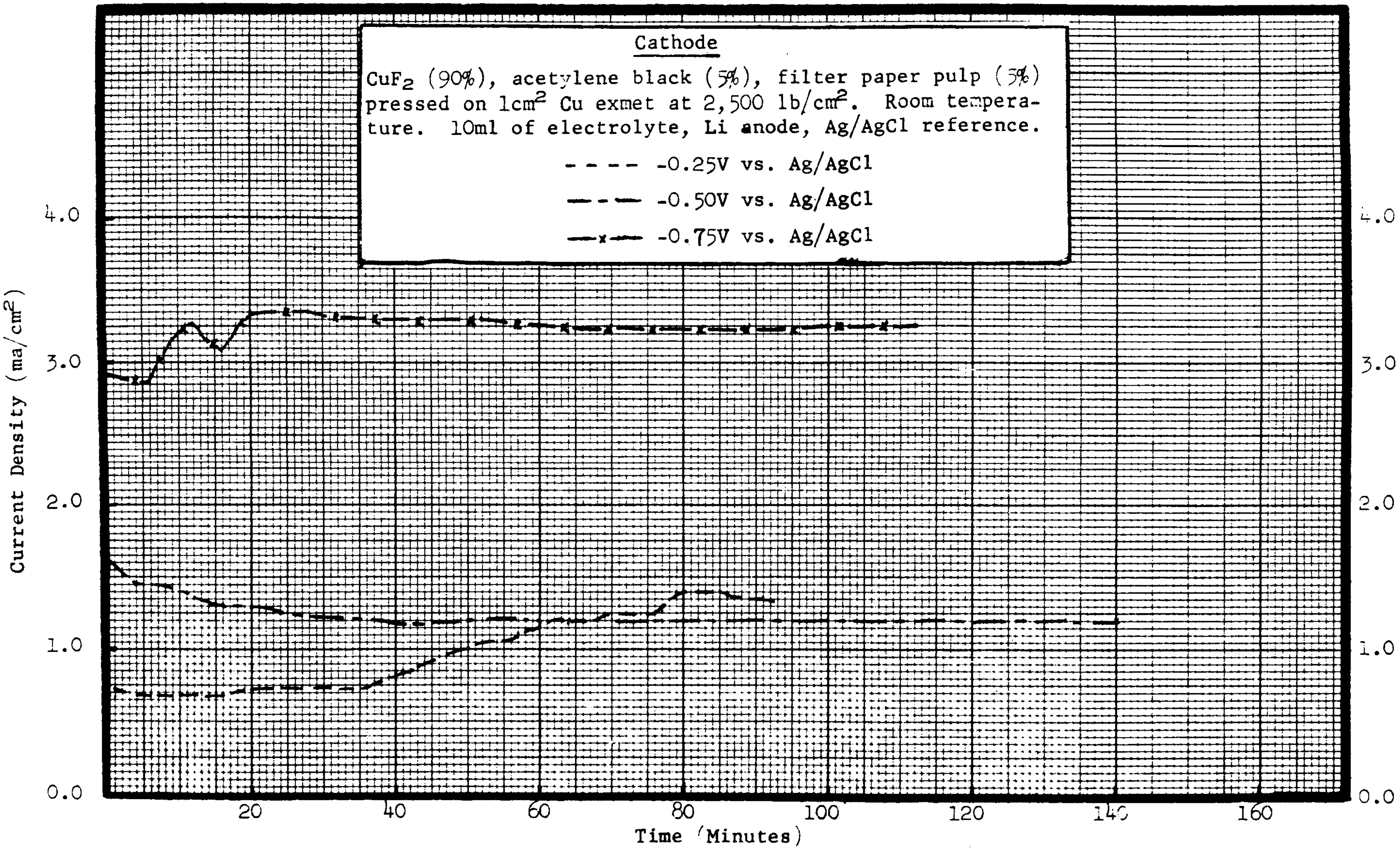


FIGURE 11. CONSTANT VOLTAGE DISCHARGES OF CuF_2 CATHODES IN N-NITROSODIMETHYLAMINE ELECTROLYTES WITH HEXAFLUOROPHOSPHATE SOLUTES

Figure 11-a. Discharges[a] at -0.25V, -0.50V and -0.75V vs. Ag/AgCl in $LiPF_6$[b]-NDA.

[a] Tests were terminated before cathodes were fully discharged.

[b] The electrolyte was pretreated with Li and filtered before use.

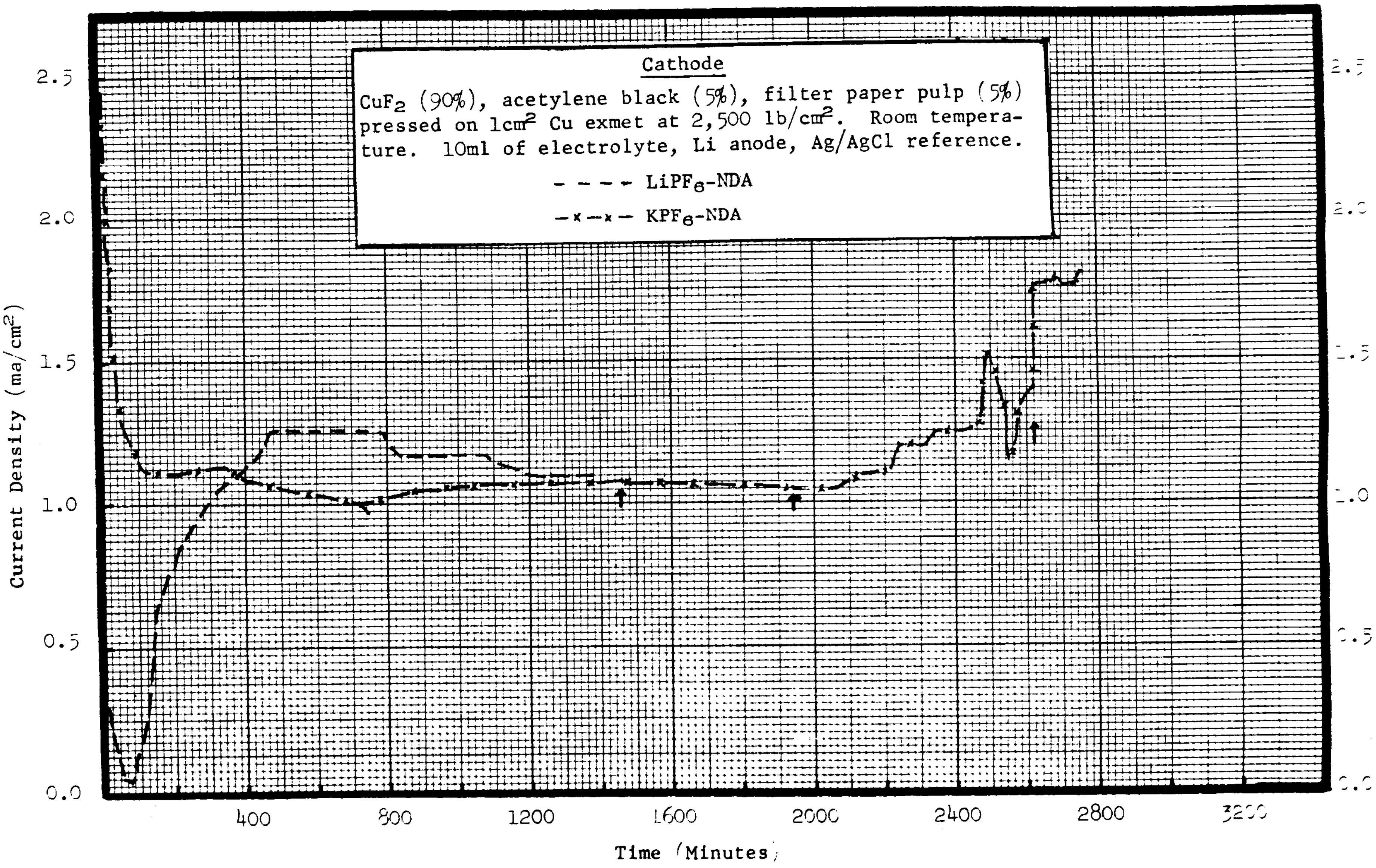


FIGURE 11. CONSTANT VOLTAGE DISCHARGES OF CuF_2 CATHODES IN N-NITROSODIMETHYLAMINE ELECTROLYTES WITH HEXAFLUOROPHOSPHATE SOLUTES

Figure 11-b. Comparison of the Discharge Characteristics[a] of $LiPF_6$-NDA[b] and KPF_6-NDA[c] at -0.25V vs. Ag/AgCl.

[a] Tests were terminated before cathodes had failed. Cathode in $LiPF_6$ had delivered 33% of its theoretical coulombs, the one in KPF_6-67%.

[b] The electrolyte was pretreated with Li and filtered before use.

[c] [illegible]ll [illegible] pla[illegible] on [illegible] c[illegible]it [illegible]ime[illegible]dic[illegible] by[illegible]rows

FIGURE 12. CONSTANT CURRENT DISCHARGES OF CuF_2 CATHODES IN NDA SOLUTIONS

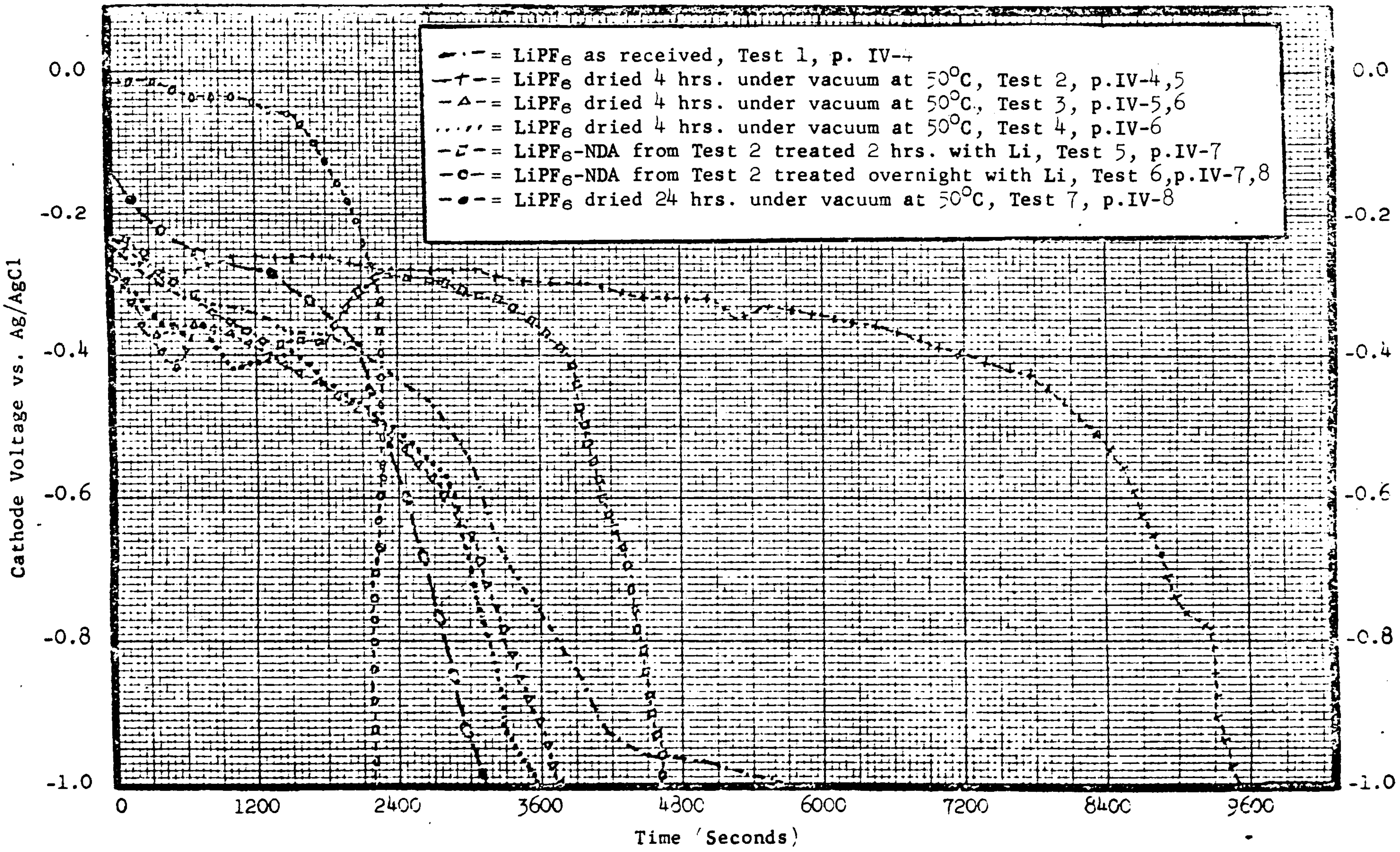


FIGURE 12. CONSTANT CURRENT[a] DISCHARGES OF CuF_2 CATHODES

Figure 12-a.Discharges in $LiPF_6$-N-Nitrosodimethylamine Electrolytes.

[a] All discharges were carried out at 2.5ma/cm² (5ma).

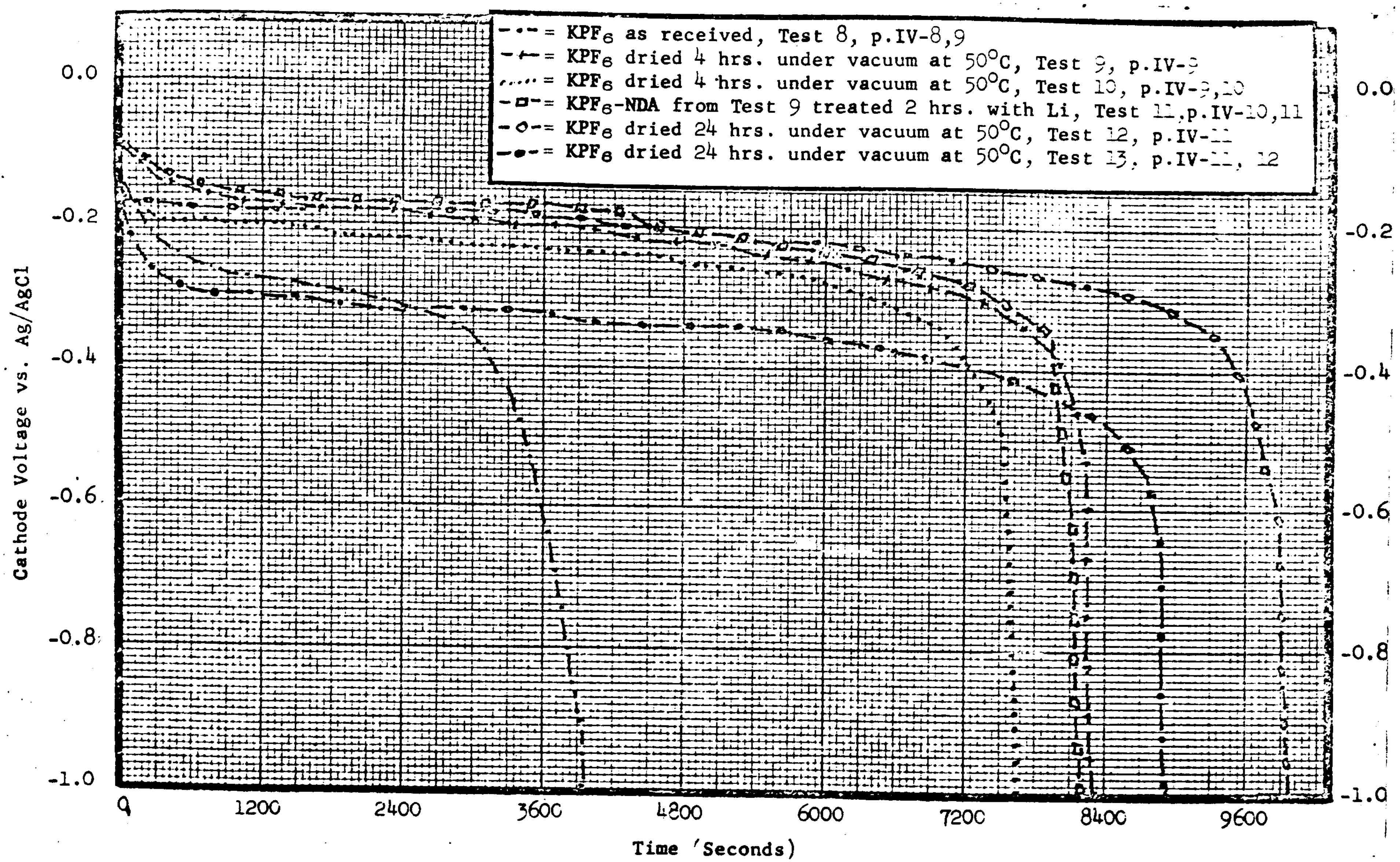


FIGURE 12. CONSTANT CURRENT[a] DISCHARGES OF CuF_2 CATHODES

Figure 12-b. Discharges in KPF_6-N-Nitrosodimethylamine Electrolytes.

[a] All discharges were carried out at 2.5ma/cm^2 (5ma).

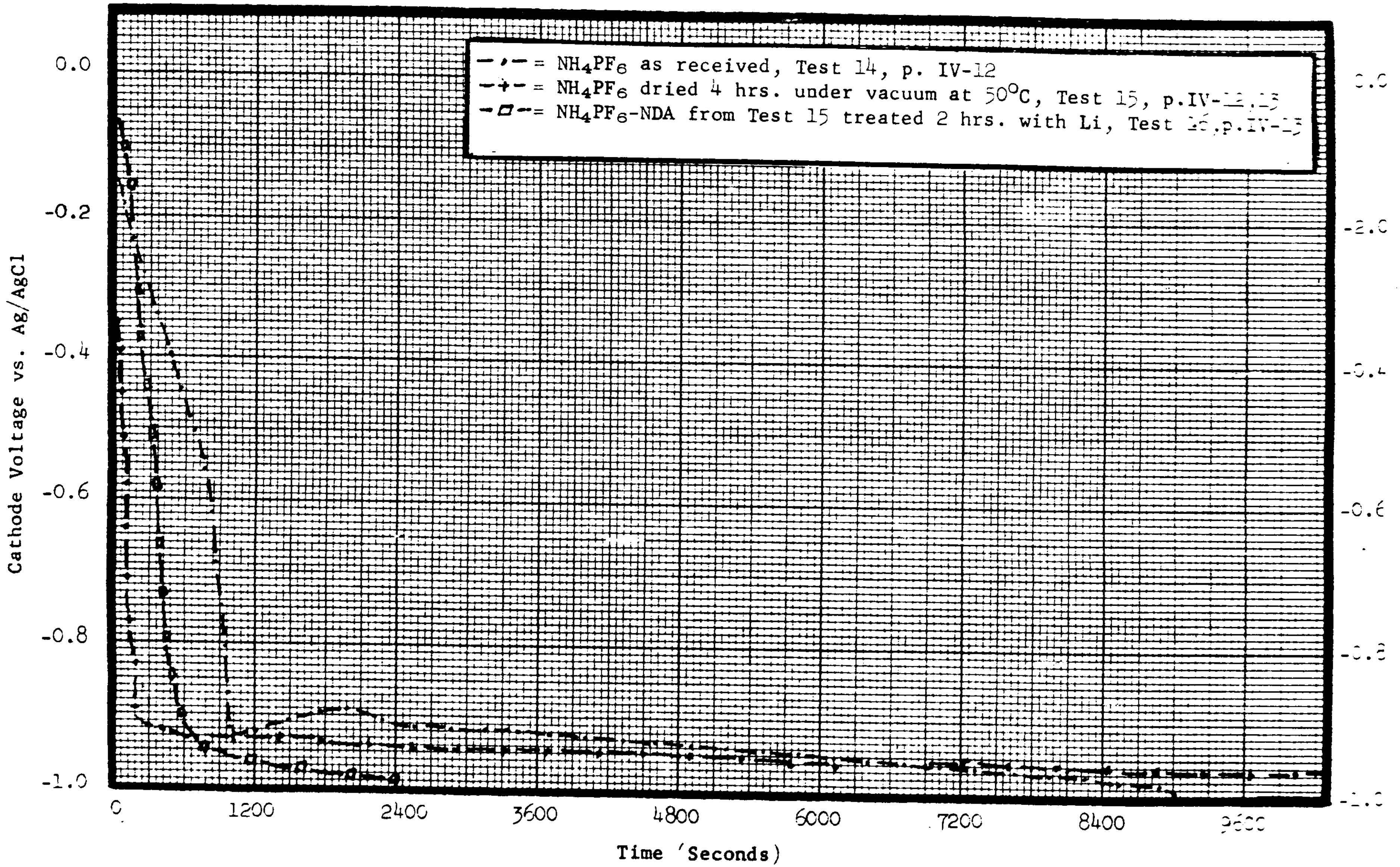


FIGURE 12. <u>CONSTANT CURRENT</u>[a] <u>DISCHARGES OF CuF_2 CATHODES</u> (Continued)

Figure 12-c. Discharges in NH_4PF_6-N-Nitrosodimethylamine Electrolytes.

a All discharges were carried out at 2.5ma/cm^2 (5ma).

TABLE XIV. X-RAY DIFFRACTION ANALYSIS OF THE SURFACE OF DISCHARGED CuF_2 CATHODES

Test No. (See Table IA)	Electrolyte Solute	Materials Found in Cathode Surface From X-ray Diffraction Pattern
1	$LiPF_6$	LiF, unknown[a]
2	$LiPF_6$	LiF, Cu_2O, CuF_2
4	$LiPF_6$	No definite pattern
5	$LiPF_6$	LiF
6	$LiPF_6$	LiF, unknown[a]
8	KPF_5	Cu_2O, unknown[a]
9	KPF_6	LiF, Cu_2O, unknown[a]
10	KPF_6	LiF, Cu_2O
11	KPF_6	LiF, Cu_2O, unknown[a]
12	KPF_6	Cu_2O, unknown[a]
13	KPF_6	Cu_2O, unknown[a]
14	NH_4PF_6	CuF_2
15	NH_4PF_6	LiF, CuF_2
16	NH_4PF_6	LiF, Cu_2O, CuF_2

---

[a] The same unknown was found with these cathodes. It had a definite pattern which has not been identified as yet.

TABLE XV. HALF-CELL CONSTANT CURRENT DISCHARGES OF CUPRIC FLUORIDE CATHODES

TABLE XV. HALF-CELL CONSTANT CURRENT DISCHARGES OF CUPRIC FLUORIDE CATHODES[a]

A. EFFECT OF MASS TRANSPORT ON COULOMBIC EFFICIENCY

Run Number	Cathode Composition[b]	Experimental Details[c]	Cathode vs. Reference Electrode: Open Circuit Voltage	Cathode vs. Reference Electrode: Median Load Voltage[d]	Wt. of CuF_2 (grams)	Theoretical Coulombs	Actual Coulombs	Coulombic Efficiency %
1.	90% CuF_2		+0.21	-0.25	0.2703	514	42.3	8.2
2.	90% CuF_2		-0.03	-0.21	0.2688	511	46.2	9.0
3.	90% CuF_2	The electrolyte was stirred throughout the discharge.	-0.08	-0.21	0.2750	523	28.6	5.5
4.	90% CuF_2	The electrolyte was stirred throughout the discharge.	-0.01	-0.26	0.2652	504	30.2	6.0
5.	90% CuF_2	The electrolyte was stirred throughout the discharge. 50ml of electrolyte were used.	+0.15	-0.16	0.2768	526	37.5	7.1

---

[a] Counter electrode: lithium. Reference electrode: Ag/AgCl. Current: 5ma, current density: ~ 2.5ma/cm^2.

[b] Cathodes all contain 5% acetylene black, and 5% filter paper pulp in addition to components listed above.
Substrate: 1cm^2 expanded copper.
Cathode Assembly: cathode mix pressed on substrate at 2,500 lbs. for 2 min. at ambient temperature.

[c] Electrolyte: 10ml of 1 molal KPF_6 in nitrosodimethylamine unless otherwise noted.
KPF_6 vacuum dried at 50°C for 24 hours.
Nitrosodimethylamine vacuum distilled. Water content approximately 600 - 1000 ppm.
Electrolyte quiescent unless otherwise noted.

[d] Cut Off Voltage: -1.0V vs Ag/AgCl. A sharp knee occurred just prior to end points unless otherwise noted.

TABLE XV. HALF-CELL CONSTANT CURRENT DISCHARGES OF CUPRIC FLUORIDE CATHODES[a]
(Continued)

B. EFFECT OF CATHODE DRYING TECHNIQUE ON COULOMBIC EFFICIENCY

Run Number	Cathode[b] Composition	Experimental[c] Details	Cathode vs. Reference Electrode Open Circuit Voltage	Cathode vs. Reference Electrode Median Load Voltage[d]	Wt. of CuF_2 (grams)	Theoretical Coulombs	Actual Coulombs	Coulombic Efficiency %
1.	90% CuF_2	The cathode was dried in a stream of argon for 24 hours. The solvent was distilled from P_2O_5..	+0.14	-0.24	0.2695	512	16.2	3.2
2.	90% CuF_2	The cathode was dried in a stream of argon for 24 hours. The solvent was distilled from P_2O_5.	+0.20	-0.29	0.2754	523	9.0	1.7
3.	90% CuF_2	The cathode was dried in a stream of argon for 24 hours. The solvent was distilled from P_2O_5.	+0.16	-0.25	0.2696	512	18.5	3.6

---

[a] Counter electrode: lithium. Reference electrode: Ag/AgCl. Current: 5ma, current density: ~2.5ma/cm^2.

[b] Cathodes all contain 5% acetylene black, and 5% filter paper pulp in addition to components listed above.
Substrate: 1cm^2 expanded copper.
Cathode Assembly: cathode mix pressed on substrate at 2,500 lbs. for 2 min at ambient temperature.

[c] Electrolyte: 10ml of 1 molal KPF_6 in nitrosodimethylamine unless other wise noted.
KPF_6 vacuum dried at 50°C for 24 hours.
Nitrosodimethylamine vacuum distilled.
Electrolyte quiescent unless otherwise noted.

[d] Cut Off Voltage: -1.0V vs Ag/AgCl. A sharp knee occurred just prior to end points unless otherwise noted.

TABLE XV. HALF-CELL CONSTANT CURRENT DISCHARGES OF CUPRIC FLUORIDE CATHODES[a]
(Continued)

B. EFFECT OF CATHODE DRYING TECHNIQUE ON COULOMBIC EFFICIENCY (Continued)

Run Number	Cathode Composition[b]	Experimental Details[c]	Cathode vs. Reference Electrode		Wt. of CuF_2 (grams)	Theoretical Coulombs	Actual Coulombs	Coulombic Efficiency %
			Open Circuit Voltage	Median Load Voltage[d]				
4.	90% CuF_2	The cathode was dried in a stream of argon for 24 hours at 50°C. The solvent was distilled from P_2O_5. $H_2O < 100$ ppm.	+0.21	-0.15	0.2696	512	20.9	4.1
5.	90% CuF_2	Cathode was dried in argon stream at 50°C for 24 hours.	+0.11	-0.24	0.2644	502	53.6	10.7
6.	90% CuF_2	Cathode was dried in argon stream at 50°C for 24 hours.	+0.22	-0.10	0.2685	510	60.3	11.8
7.	89% CuF_2, 0.5% Maracel "E", 0.5% LiF	The cathode was dried for 24 hours under vacuum at 50°C.	+0.18	-0.04	0.2631	500	120.6	24.1
8.	89% CuF_2, 0.5% Maracel "E", 0.5% LiF	The cathode was dried for 24 hours under vacuum at 50°C.	+0.28	+0.01	0.2683	510	84.6	16.6

---

[a] Counter electrode: lithium. Reference electrode: Ag/AgCl. Current: 5ma, current density: ~2.5ma/cm².

[b] Cathodes all contain 5% acetylene black, and 5% filter paper pulp in addition to components listed above.
Substrate: 1cm² expanded copper.
Cathode Assembly: cathode mix pressed on substrate at 2,500 lbs. for 2 min. at ambient temperature.

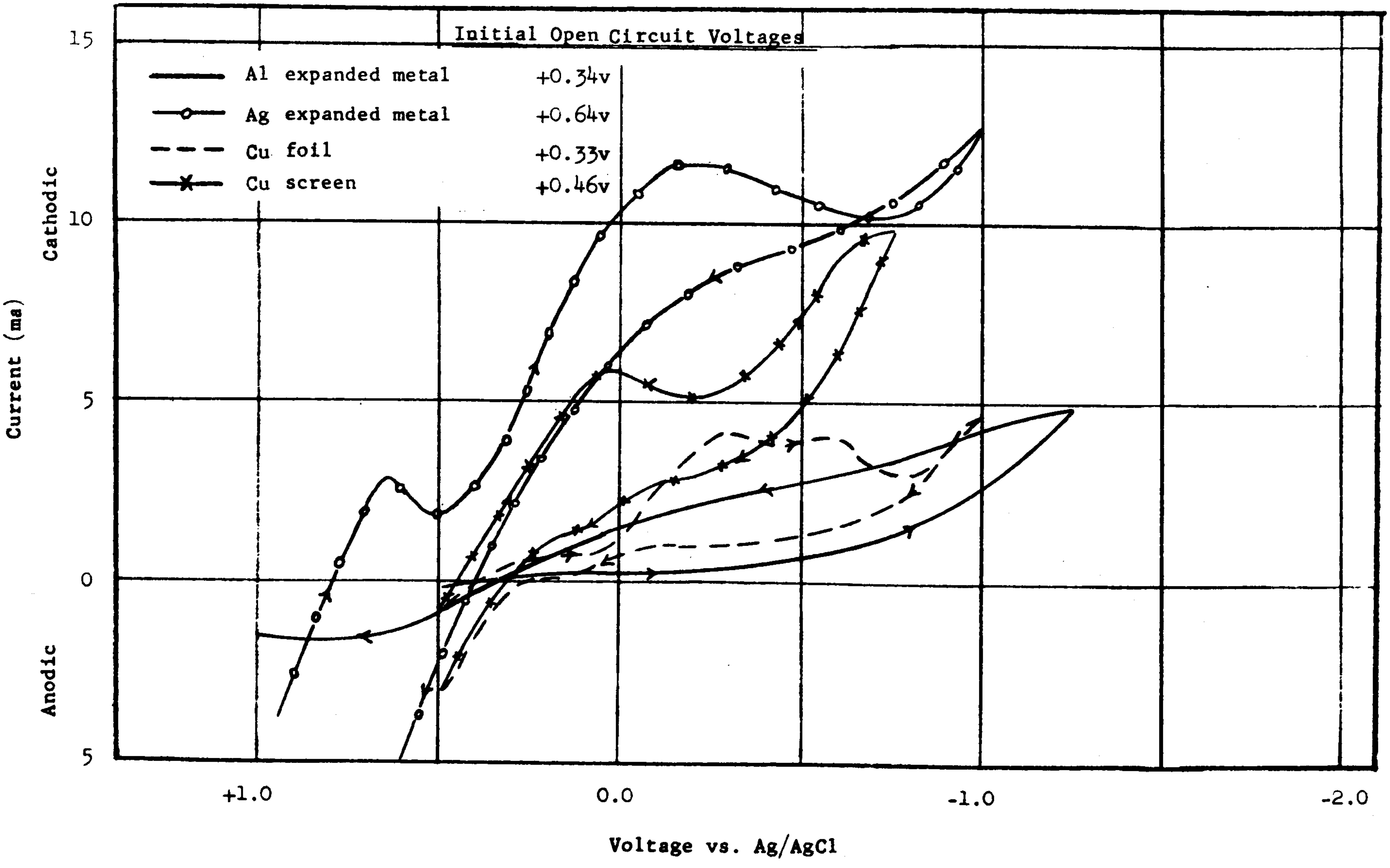
[c] Electrolyte: 10ml of 1 molal KPF_6 in nitrosodimethylamine unless otherwise noted.
KPF_6 vacuum dried at 50°C for 24 hours.
Nitrosodimethylamine vacuum distilled.
Electrolyte quiescent unless otherwise noted.

[d] Cut Off Voltage: -1.0V vs Ag/AgCl. A sharp knee occurred just prior to end points unless otherwise noted.

FIGURE 13. LINEARLY VARYING POTENTIAL STUDIES OF INORGANIC CATHODES

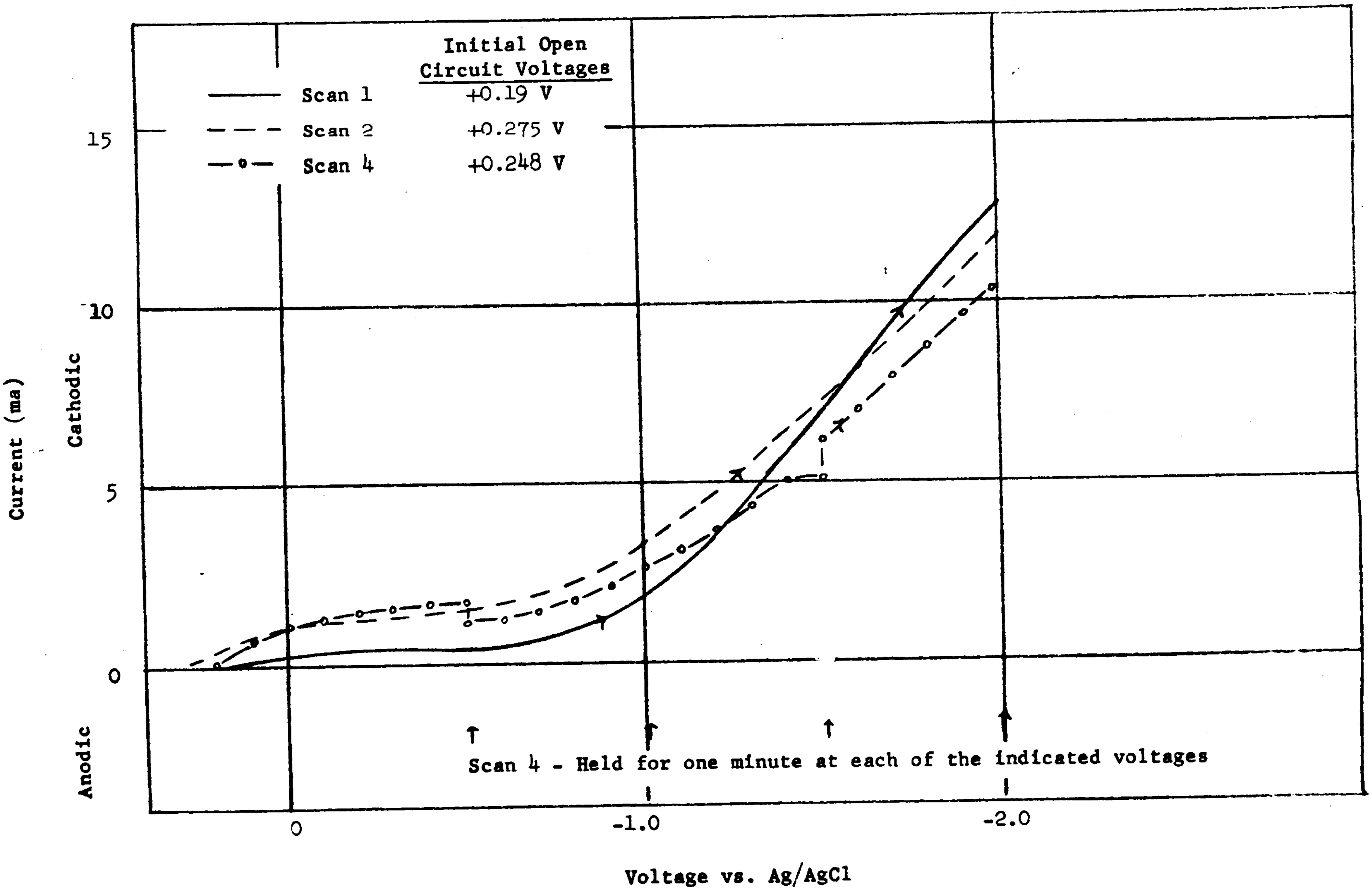
	Cathode	Electrolyte (1 molal)	Page
a.	Cupric Fluoride Sintered in a Nitrogen Atmosphere on a Variety of Substrates.	$LiClO_4$-Propylene Carbonate	V-160
b.	Cupric Fluoride Sintered in a Nitrogen Atmosphere on Aluminum.	$LiClO_4$-Propylene Carbonate	V-161
c.	Cupric Fluoride Sintered in a Metallurgical Press on Silver.	$LiPF_6$-N-Nitrosodimethylamine	V-162
d.	Cupric Fluoride Thin Films Formed on Copper Foil by Solvent Evaporation and by Electrolysis of 48% Hydrogen Fluoride.	$LiClO_4$-Propylene Carbonate	V-163
e.	Copper Oxides (I and II) Produced During an Electrolysis of 48% Hydrogen Fluoride.	$LiClO_4$-Propylene Carbonate	V-164
f.	Copper Sulfide Thin Film.	N-Phenyl-N,N,N-trimethylammonium Hexafluorophosphate-Dimethylformamide	V-165
g.	Cupric Fluoride Pressed Cathodes Containing Antimony Trifluoride and Carbon Additives.	$LiClO_4$-Propylene Carbonate	V-166
h.	Silver Oxide - Antimony Trifluoride Pressed Cathode.	$LiClO_4$-Propylene Carbonate	V-167
i.	Cupric Fluoride Filter Pad.	$LiClO_4$-Propylene Carbonate	V-168

FIGURE 13a. LINEARLY VARYING POTENTIAL SCANS OF CUPRIC FLUORIDE SINTERED IN A NITROGEN ATMOSPHERE ON A VARIETY OF SUBSTRATES. $LiClO_4$-PROPYLENE CARBONATE ELECTROLYTES (1 MOLAL). Li COUNTER ELECTRODES. Ag/AgCl REFERENCE ELECTRODES. AREA OF SUBSTRATES = 2.8cm^2*. 50mv/sec SCAN RATE.



* The substrates were not completely covered with CuF_2.

FIGURE 13b. LINEARLY VARYING POTENTIAL SCANS OF CUPRIC FLUORIDE SINTERED ON ALUMINUM IN A NITROGEN ATMOSPHERE. $LiClO_4$-PROPYLENE CARBONATE ELECTROLYTE (1 MOLAL). Li COUNTER ELECTRODE. Ag/AgCl REFERENCE ELECTRODE. AREA OF SUBSTRATE = 2.8cm^2*. 50mv/sec SCAN RATE.



* The substrate was almost completely covered with CuF_2.

FIGURE 13c. LINEARLY VARYING POTENTIAL SCANS OF CUPRIC FLUORIDE SINTERED IN A METALLURGICAL PRESS ON SILVER EXPANDED METAL. $LiPF_6$-N-NITROSODIMETHYLAMINE ELECTROLYTE (1 MOLAL). Li COUNTER ELECTRODE. Ag/AgCl REFERENCE ELECTRODE. AREA OF SUBSTRATE = 2.8cm^2. 50mv/sec SCAN RATE.

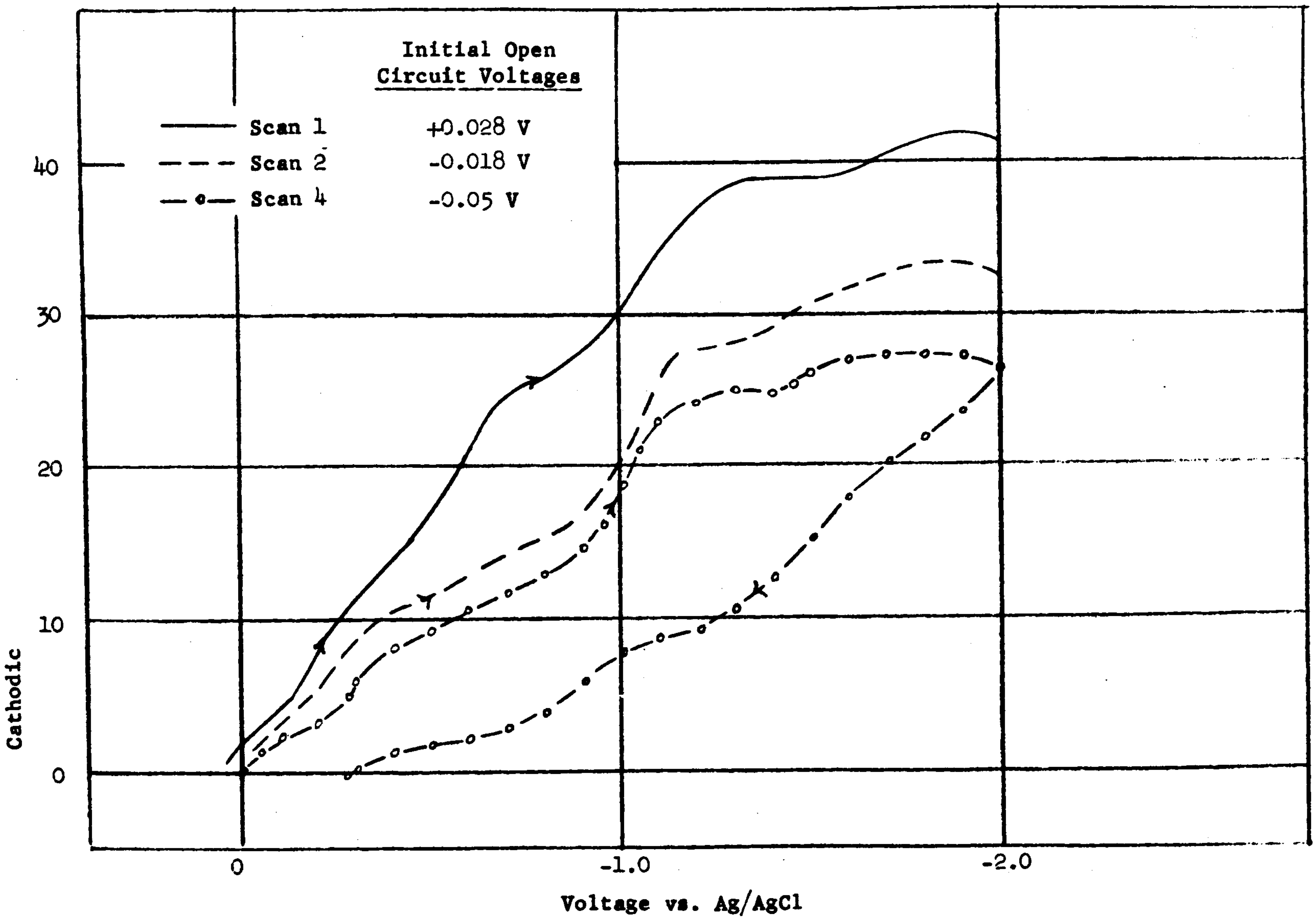
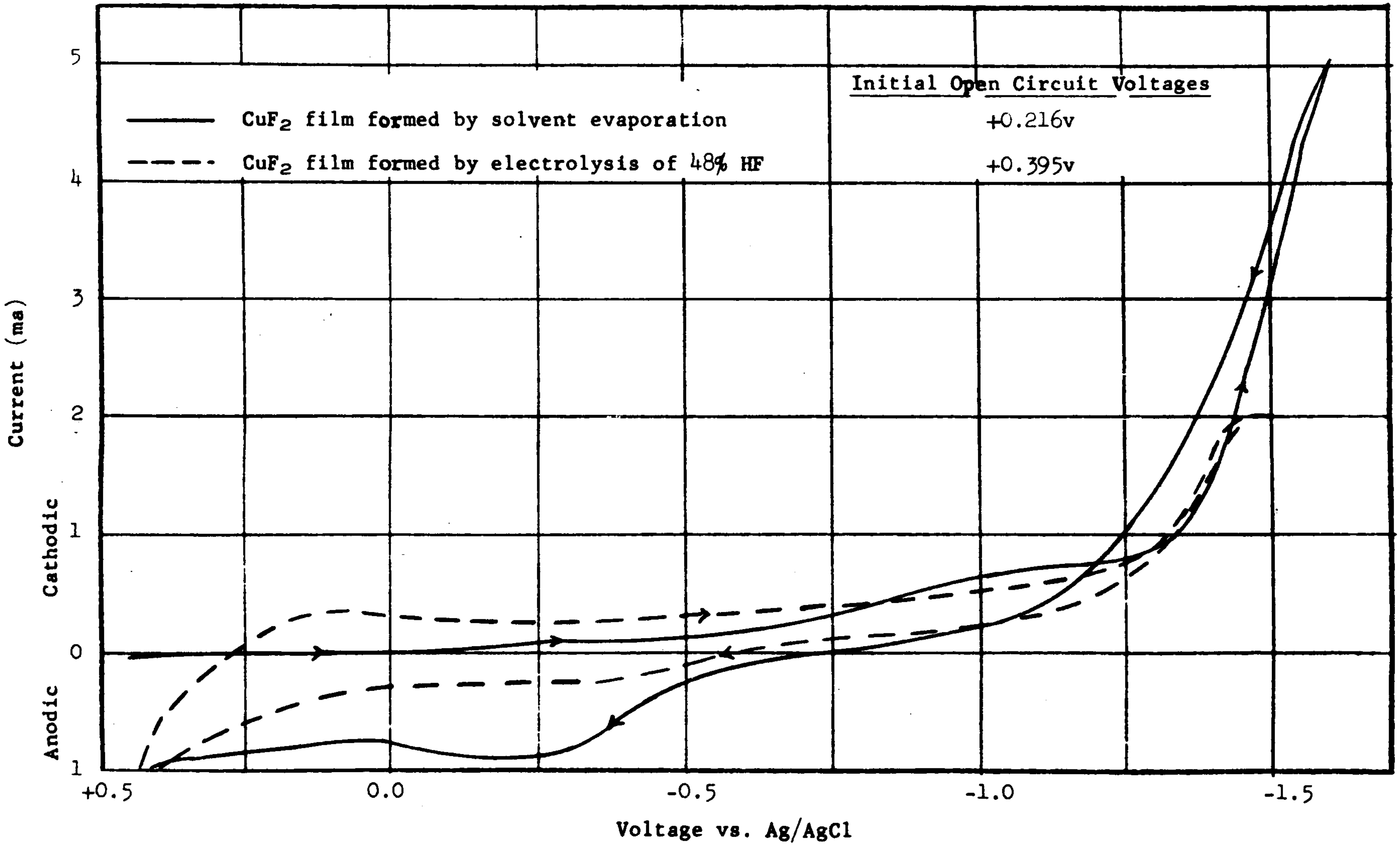
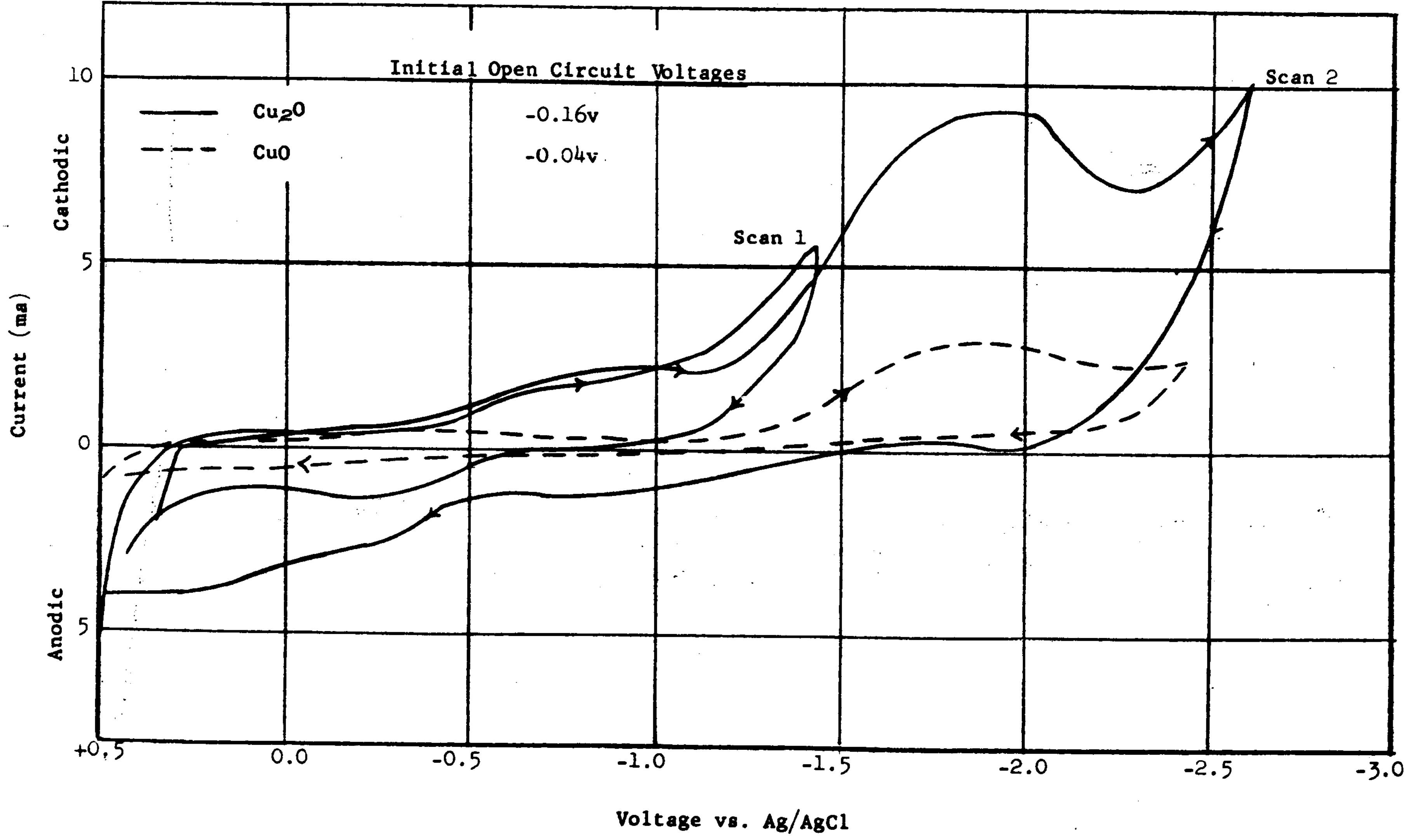


FIGURE 13d LINEARLY VARYING POTENTIAL SCANS OF CUPRIC FLUORIDE THIN FILMS FORMED ON COPPER FOIL BY SOLVENT EVAPORATION AND BY ELECTROLYSIS OF 48% HF.* $LiClO_4$-PROPYLENE CARBONATE ELECTROLYTES (1 MOLAL). Li COUNTER ELECTRODES. Ag/AgCl REFERENCE ELECTRODES. 50mv/sec SCAN RATE.



* The area of the CuF_2 electrodes was ca. 0.5 cm^2.

FIGURE 13e. LINEARLY VARYING POTENTIAL SCANS OF COPPER OXIDES (I AND II) PRODUCED DURING AN ELECTROLYSIS OF 48% HF.* LiClO$_4$-PROPYLENE CARBONATE ELECTROLYTES (1 MOLAL). Li COUNTER ELECTRODES. Ag/AgCl REFERENCE ELECTRODES. 50 mv/sec SCAN RATE.



* The area of the Cu$_2$O and CuO electrodes was approximately 0.5 cm^2.

FIGURE 13f. LINEARLY VARYING POTENTIAL SCANS OF A COPPER SULFIDE THIN FILM ELECTRODE IN A 1 MOLAL N-PHENYL-N,N,N-TRIMETHYLAMMONIUM HEXAFLUOROPHOSPHATE-DIMETHYLFORMAMIDE ELECTROLYTE. Li COUNTER ELECTRODE. AgS REFERENCE ELECTRODE. 50 mv/sec SCAN RATE.

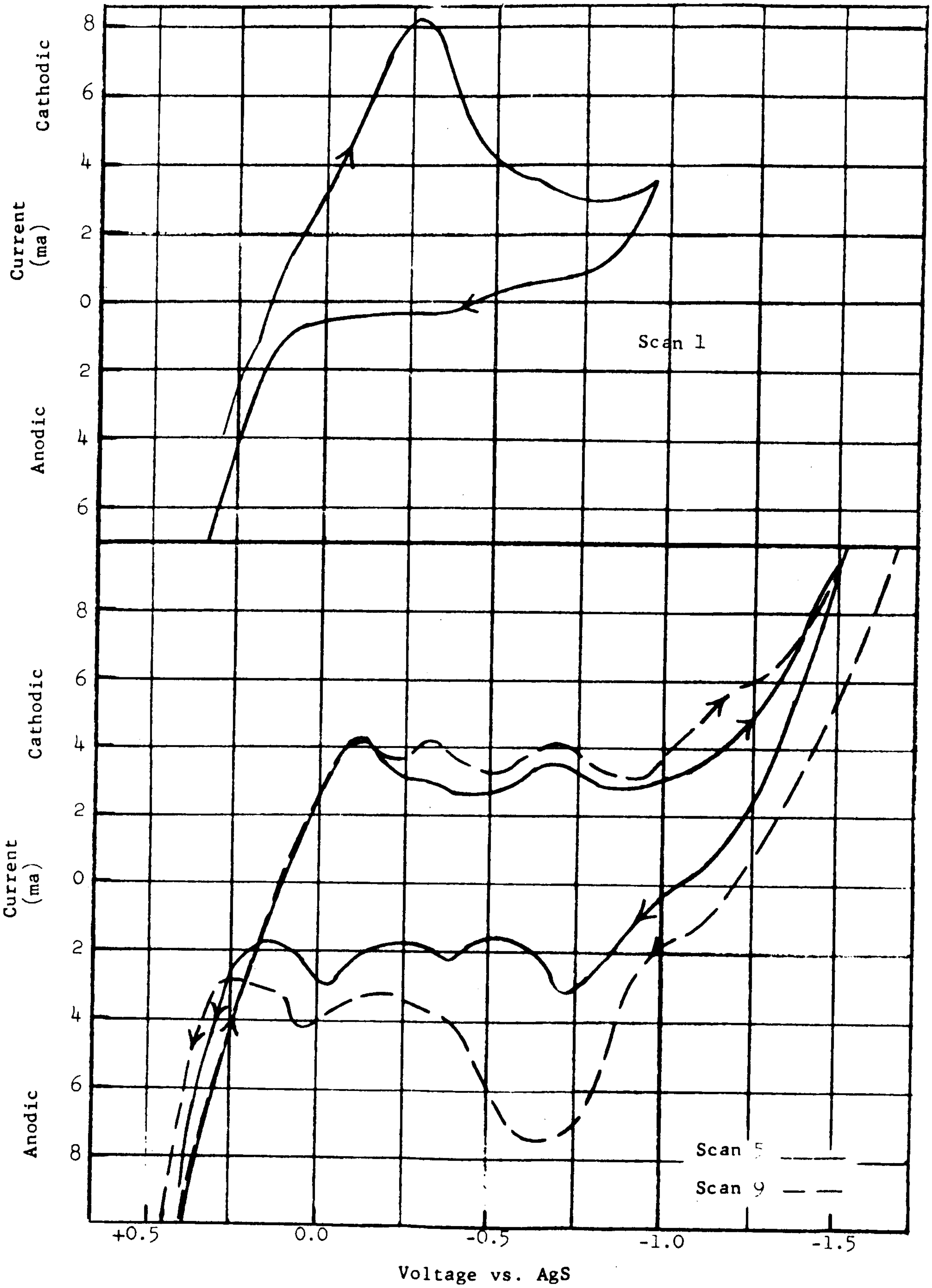


FIGURE 13g. LINEARLY VARYING POTENTIAL SCANS OF CUPRIC FLUORIDE PRESSED CATHODES CONTAINING ANTIMONY TRIFLUORIDE AND CARBON ADDITIVES. $LiClO_4$-PROPYLENE CARBONATE ELECTROLYTES (1 MOLAL). Li COUNTER ELECTRODES. Ag/AgCl REFERENCE ELECTRODES. SUBSTRATES - Cu EXPANDED METAL (AREA = 1 cm^2). 50 mv/sec SCAN RATE.

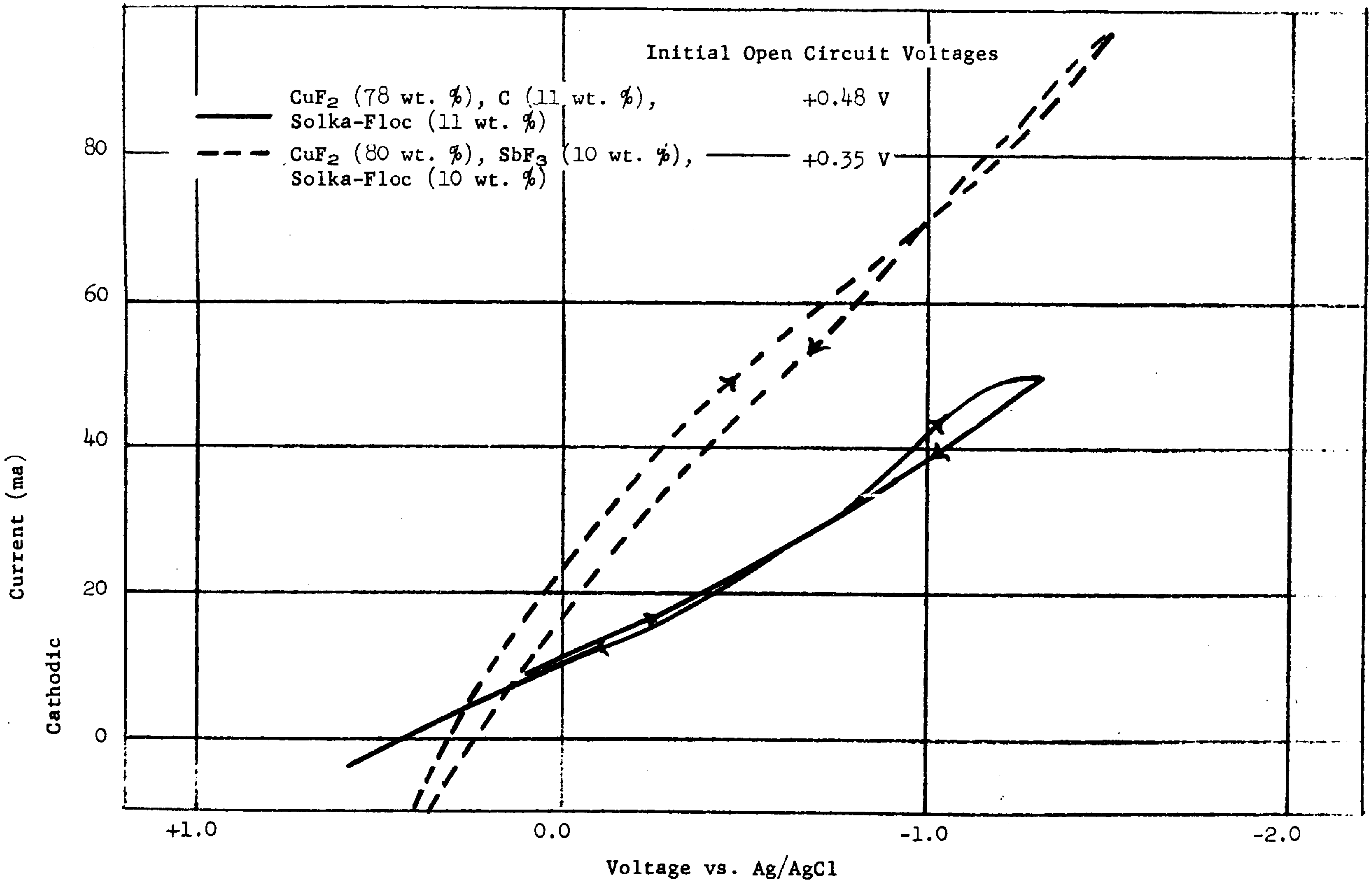


FIGURE 13h. LINEARLY VARYING POTENTIAL SCAN OF A SILVER OXIDE-ANTIMONY TRIFLUORIDE PRESSED CATHODE (85.5 WT. % AgO, 10 WT. % SbF_3, 4.5 WT. % SOLKA-FLOC). $LiClO_4$-PROPYLENE CARBONATE ELECTROLYTE (1 MOLAL). Li COUNTER ELECTRODE. Ag/AgCl REFERENCE ELECTRODE. SUBSTRATE - Ag EXPANDED METAL (AREA = 1 cm^2). 50 mv/sec SCAN RATE.

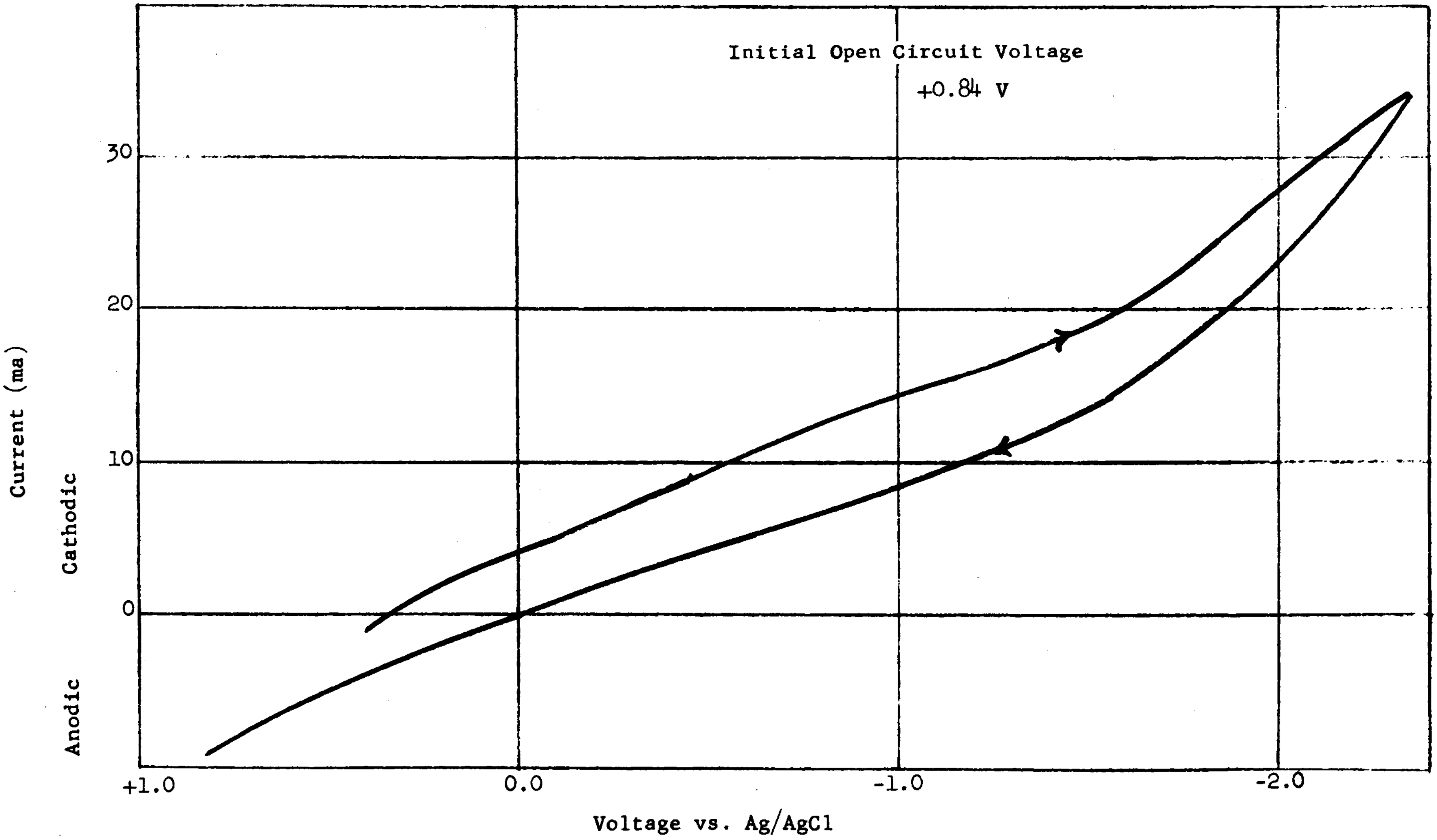


FIGURE 13i. LINEARLY VARYING POTENTIAL SCANS OF CUPRIC FLUORIDE FILTER PAD CATHODES IN 1 MOLAL $LiClO_4$-PROPYLENE CARBONATE ELECTROLYTE. Mg COUNTER ELECTRODE, Ag/AgCl REFERENCE ELECTRODE. 50 mv/sec SCAN RATE. CATHODE AREA - APPROXIMATELY 4 mm^2. (Continued)

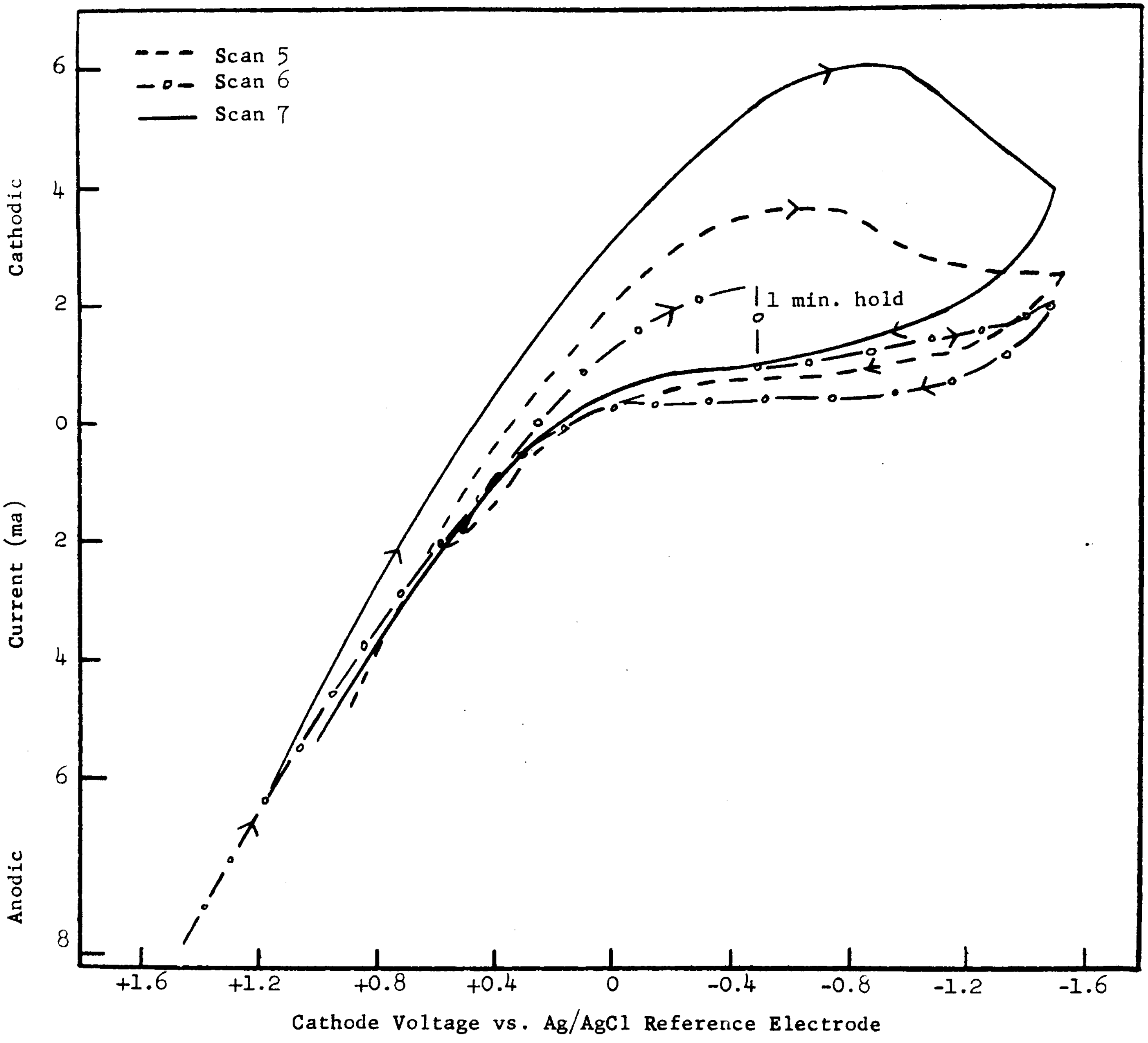


FIGURE 14. LINEARLY VARYING POTENTIAL STUDIES[a] OF CATHODE-ELECTROLYTE SYSTEMS

	Cathode	Electrolyte	Page
a.	Copper Wire	KPF_6-NDA	V-170
b.	CuF_2	$LiClO_4$-PC	V-171
c.	CuF_2	KPF_6-NDA	V-172
d.	CuF_2	$LiClO_4$-NDA	V-173
e.	CuF_2	$(C_6H_5)(CH_3)NPF_6$-NDA	V-174
F.	AgSCM	KPF_6-NDA	V-175
g.	$CuCl_2$-$2H_2O$	KPF_6-NDA	V-176

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[a] Pyrolytic graphite was used for the counter electtode in all tests. The solvents were all vacuum distilled and the solutes dried before use.

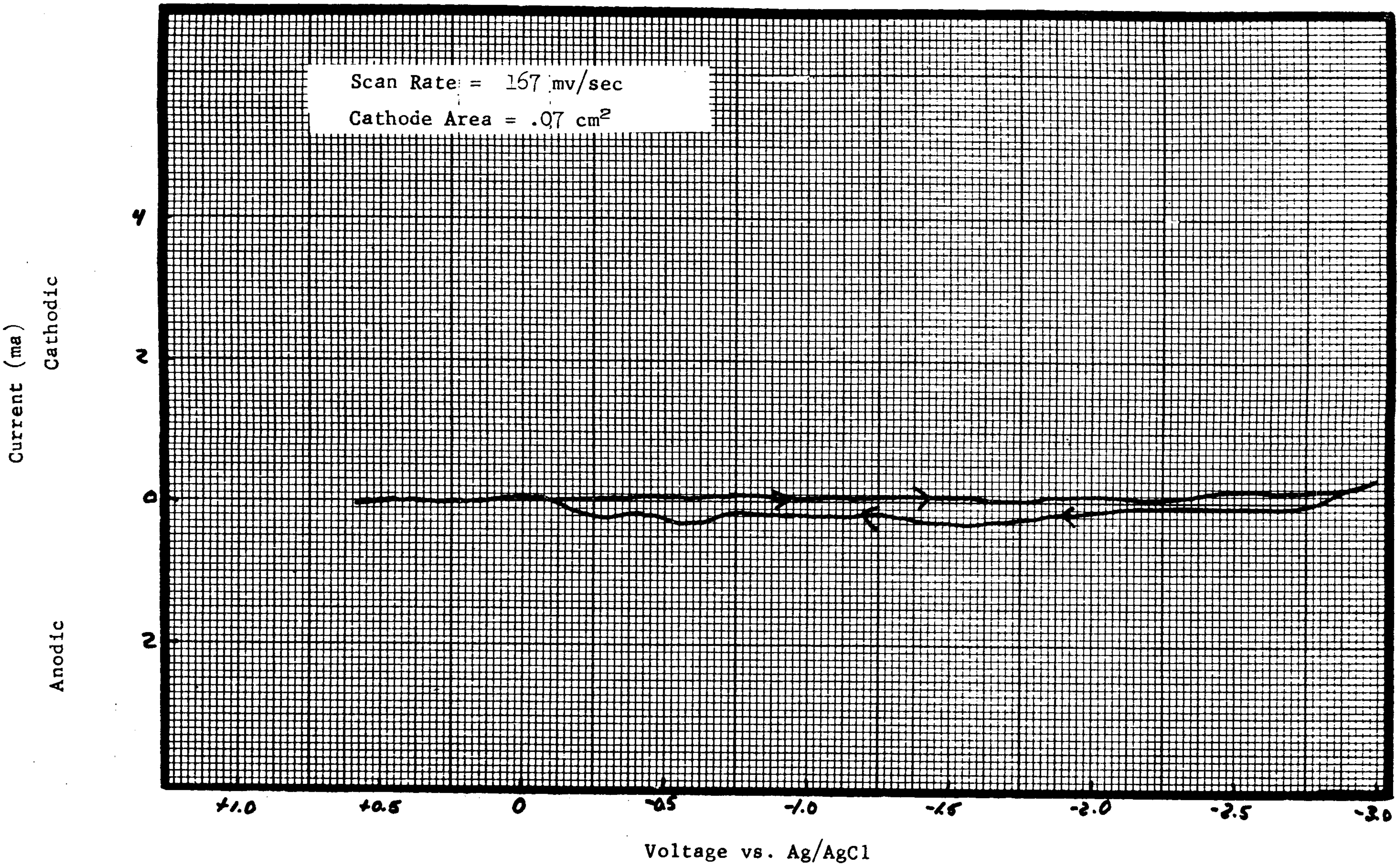


Figure 14-a. Cu wire in KPF_6-NDA electrolyte

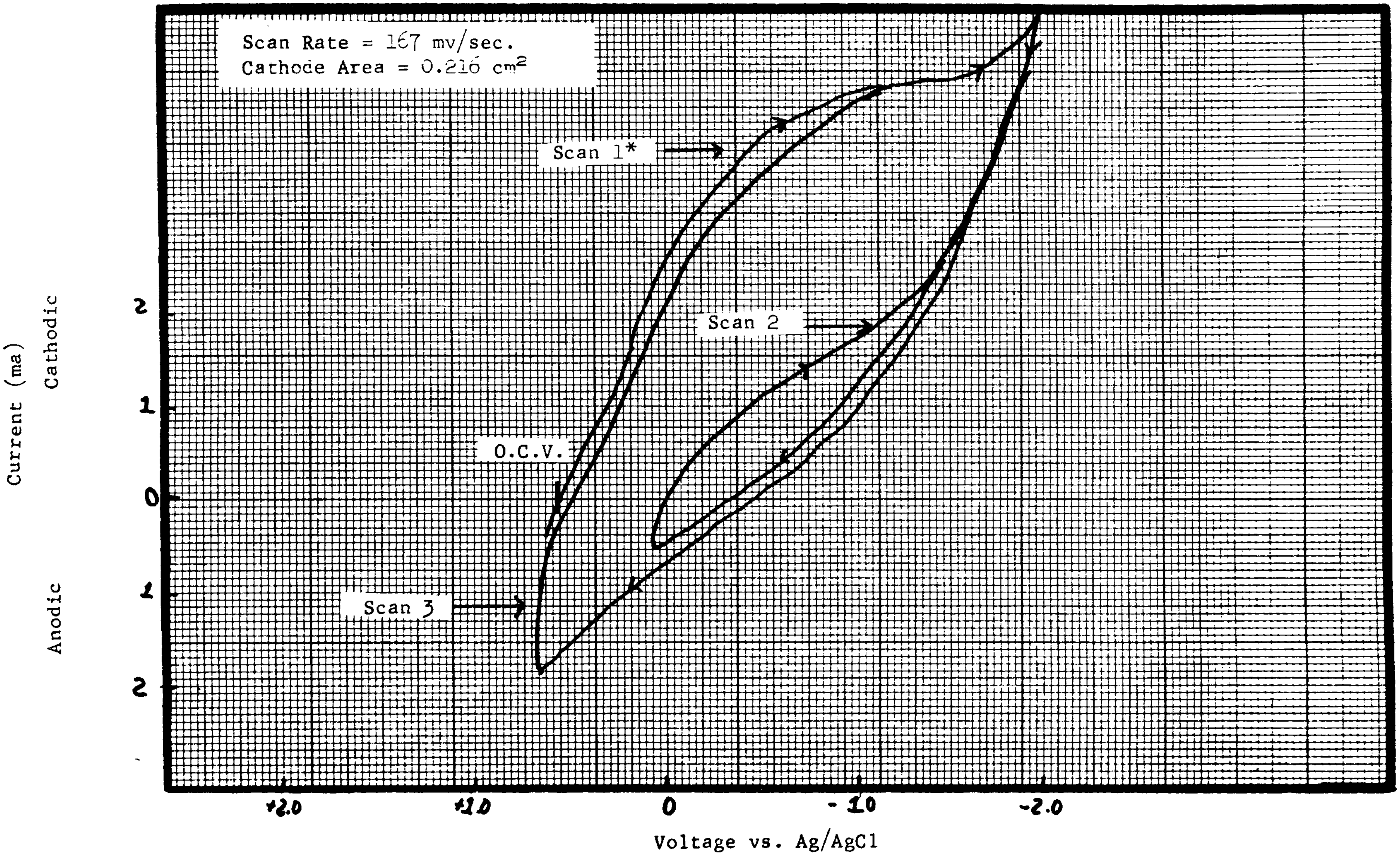


Figure 14b. CuF_2 cathode in $LiClO_4$-PC electrolyte

* Scan 1 starts at open circuit voltage and proceeds in cathodic direction.

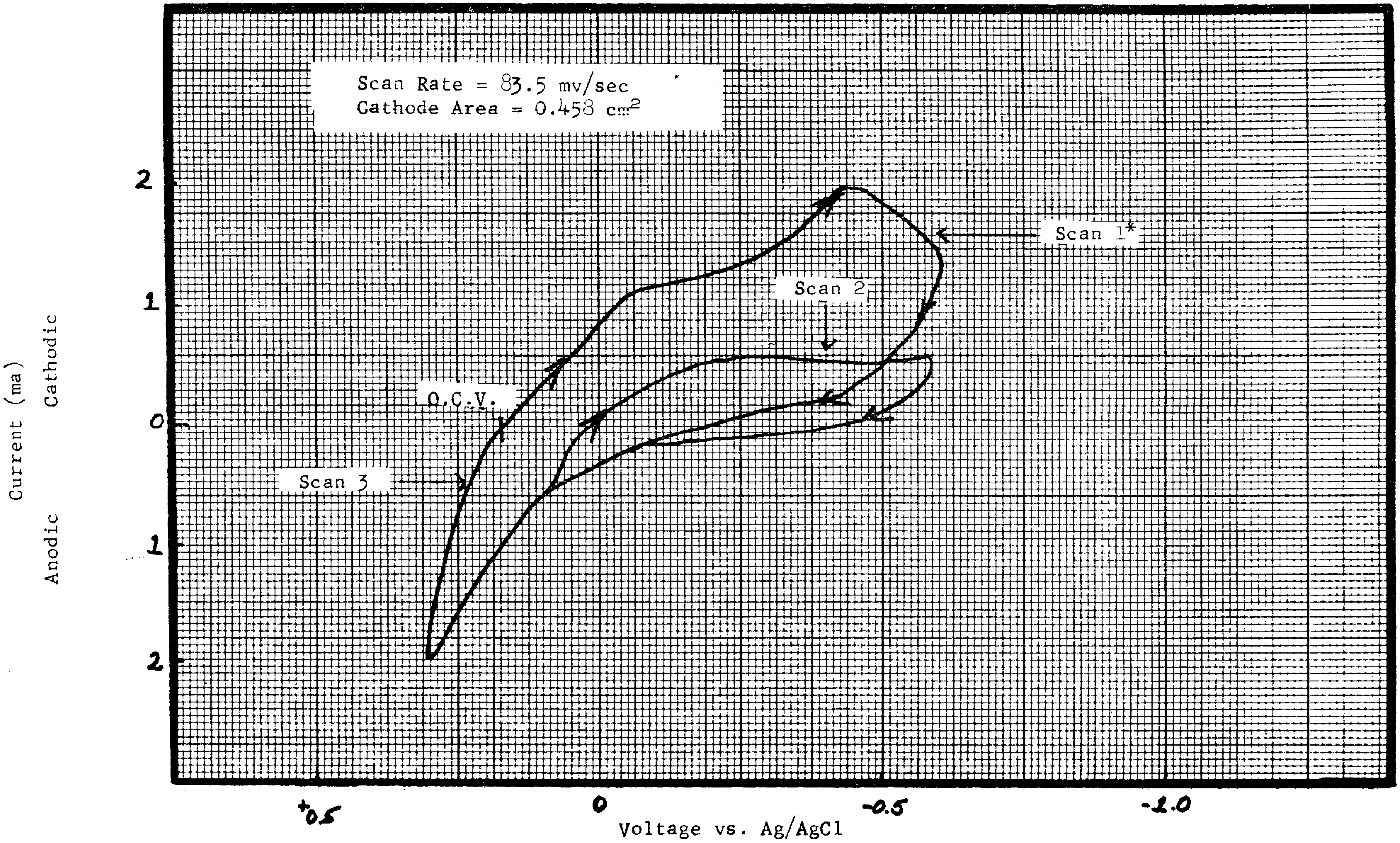


Figure 14c. CuF_2 cathode in KPF_6-NDA electrolyte

* Scan 1 starts at open circuit voltage and proceeds in cathodic direction

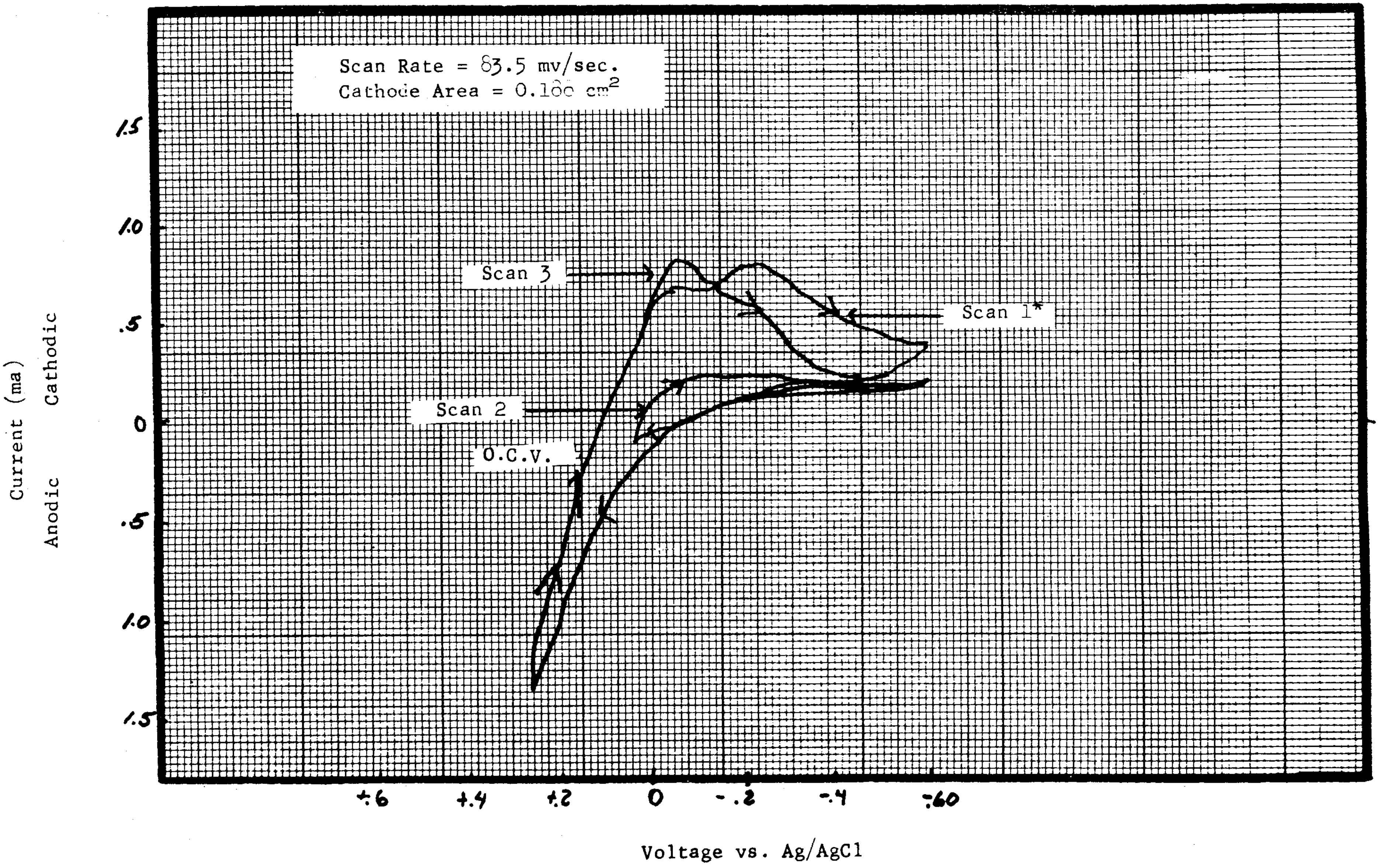


Figure 14d. CuF_2 cathode in $LiClO_4$-NDA electrolyte

* Scan 1 starts at open circuit voltage and proceeds in cathodic direction.

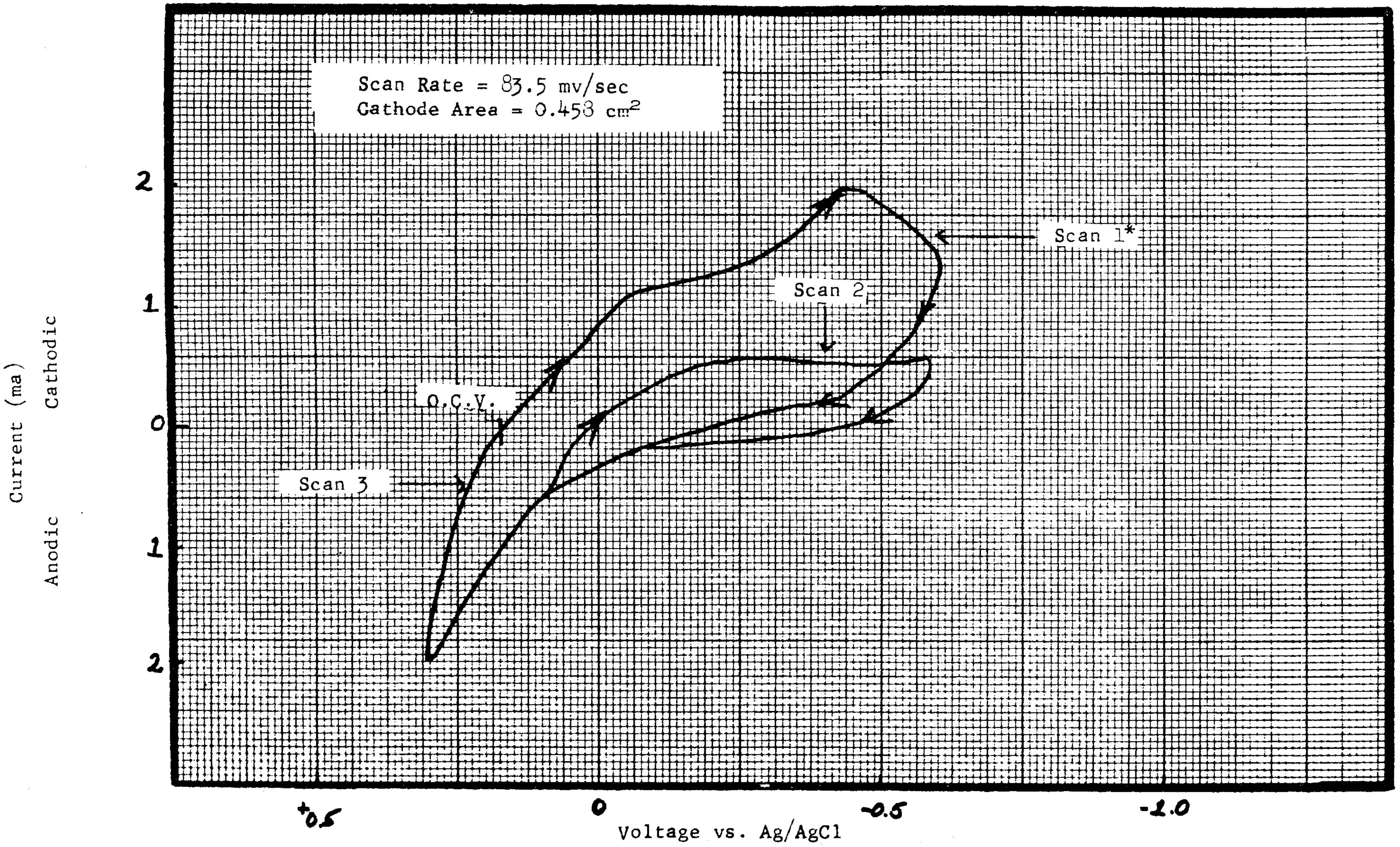


Figure 14c. CuF_2 cathode in KPF_6-NDA electrolyte

* Scan 1 starts at open circuit voltage and proceeds in cathodic direction

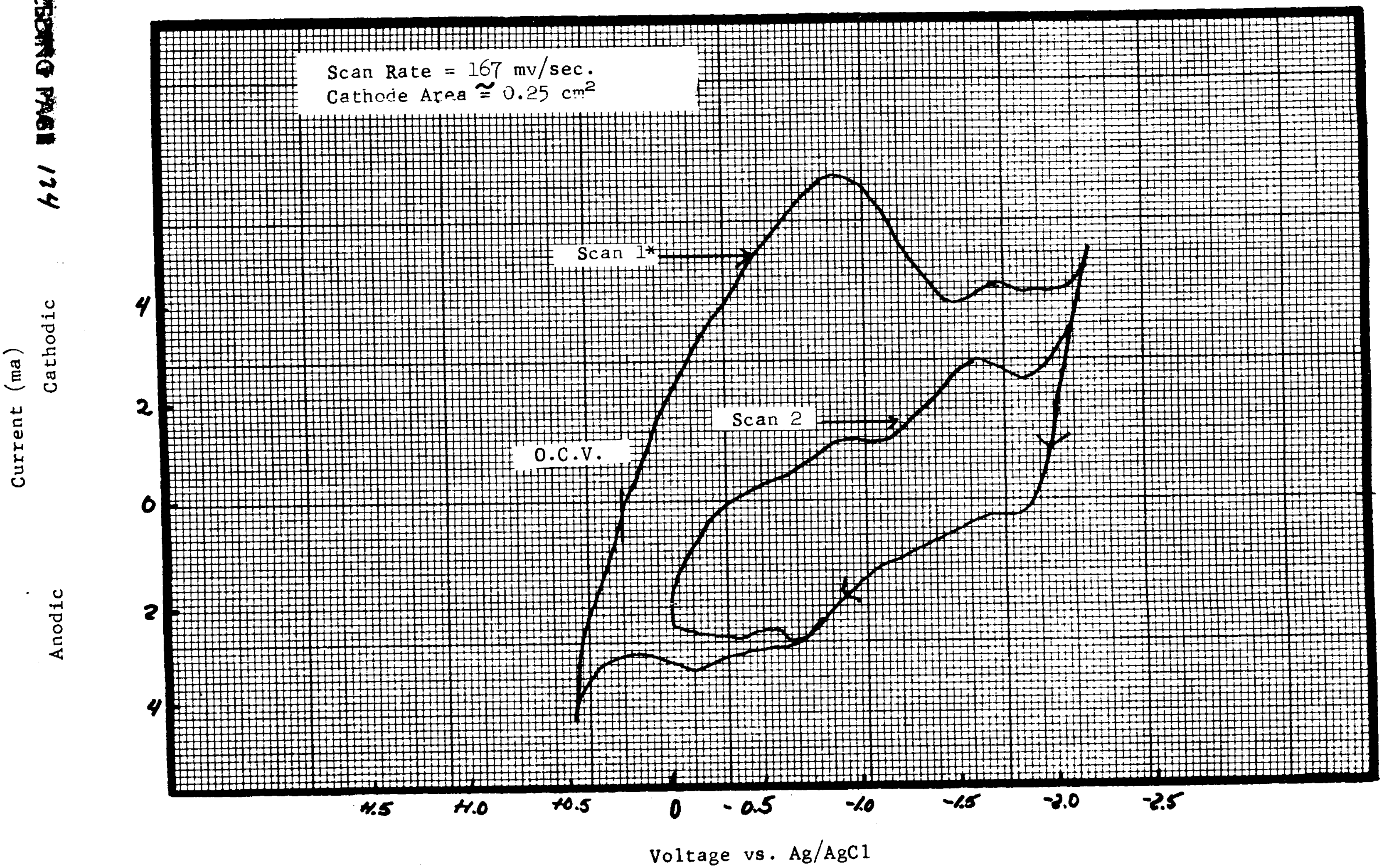


Figure 14f. AgSCN cathode in KPF_6-NDA electrolyte

* Scan 1 starts at open circuit voltage and proceeds in cathodic direction.

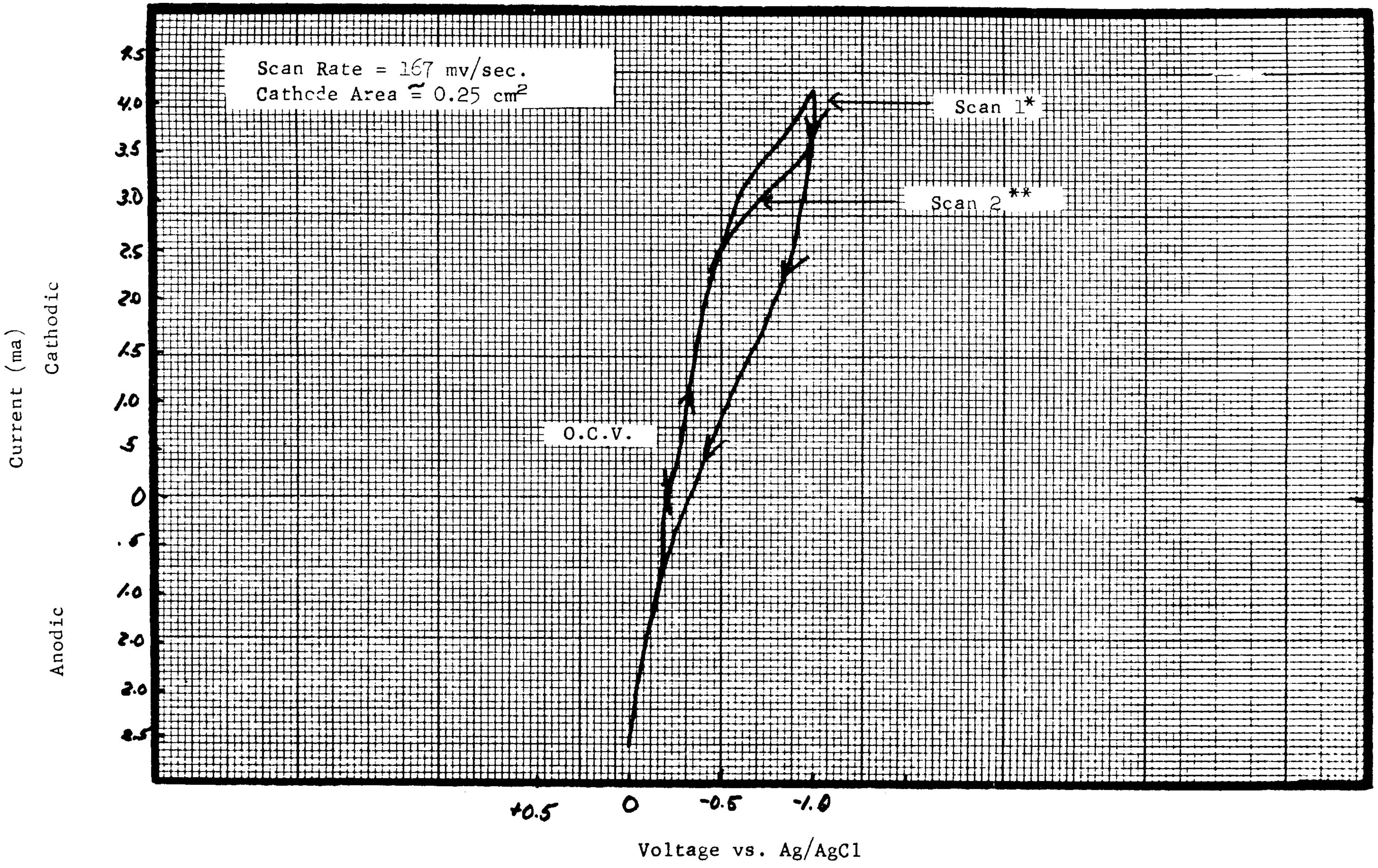


Figure 14g. $CuCl_2 \cdot 2H_2O$ cathode in $KPF_6 \cdot NDA$ electrolyte

* Scan 1 starts at open circuit voltage and proceeds in cathodic direction.
** Scan 2 and steady state scans following Scan 2.

TABLE XVI. HALF CELL CONSTANT CURRENT DISCHARGES OF SILVER OXIDE CATHODES

Run Number	Cathode[a] Composition	Experimental[b] Detail	Cathode vs Reference Electrode: Open Circuit Voltage	Cathode vs Reference Electrode: Median Load Voltage[e]	Wt. of AgO	Theor. Coulombs	Actual Coulombs	Coulombic Efficiency %
1	95% AgO 5% filter paper pulp (FPP)	Cathode dried[c] 24 hrs at 50°C in argon stream	+0.32	-0.84	0.3157	492	0.9	0.2
2	95% AgO 5% FPP	Cathode dried[c] 24 hrs at 50°C in argon stream	+0.31	-0.78	0.3254	507	3.06	0.6
3	95% AgO 5% FPP	Cathode dried[c] 24 hrs at 50°C in argon stream	+0.36	Polarized severely thru -1.0V	0.3145	490	0	0
4	95% AgO 5% FPP	Cathode dried[c] 24 hrs at 50° in argon stream	+0.32	Polarized severely thru -1.0V	0.3160	492	0.14	0.03
5	95% AgO 5% FPP	Cathode dried[d] 24 hrs at 50°C in argon stream	+0.45	-0.70	0.3180	495	180	36.4
6	95% AgO 5% FPP	Cathode dried[d] 24 hrs at 50°C in argon stream	+0.50	-0.69	0.3144	490	329.4	67.2

---

[a] Cathode was fabricated with 95% silver oxide (AgO) and 5% filter paper pulp (FPP). This mix was pressed onto 1cm^2 expanded silver substrate at 2500 lbs load for 2 minutes at ambient temperature.

[b] Anode: lithium. Reference: Ag/AgCl. Current: 2ma, current density ~1ma/cm^2 with the KPF_6-NDA electrolyte runs 1-4. Current 5ma, current density ~2.5ma/cm^2 for runs 1-4 $LiPF_6$-NDA electrolyte for runs 5-7.

[c] Electrolyte: 10ml of 1 molal KPF_6 in N-nitrosodimethylamine (NDA). The KPF_6 was vacuum dried for 24 hours at 50°C. The NDA was vacuum distilled from P_2O_5.

[d] Electrolyte: 10ml of 1 molal $LiPF_6$ in N-nitrosodimethylamine (NDA) for runs 5-7. The $LiPF_6$ was vacuum dried for 24 hrs at 50°C. i.e. as received. The NDA was vacuum distilled from P_2O_5. The electrolyte in runs 5 and 6 was also pretreated with lithium ribbon for 2 hours.

[e] Endpoint voltage for all runs was -1.0V vs Ag/AgCl.

TABLE XVI. HALF CELL CONSTANT CURRENT DISCHARGES OF SILVER OXIDE CATHODES (Continued)

Run Number	Cathode[a] Composition	Experimental[b] Detail	Cathode vs Reference Electrode Open Circuit Voltage	Cathode vs Reference Electrode Median Load Voltage[e]	Wt. of AgO	Theor. Coulombs	Actual Coulombs	Coulombic Efficiency %
7	95% AgO 5% FPP	Cathode dried[d] 24 hrs at 50°C in argon stream	+0.48	-0.62	0.3412	90.9	532	17.1

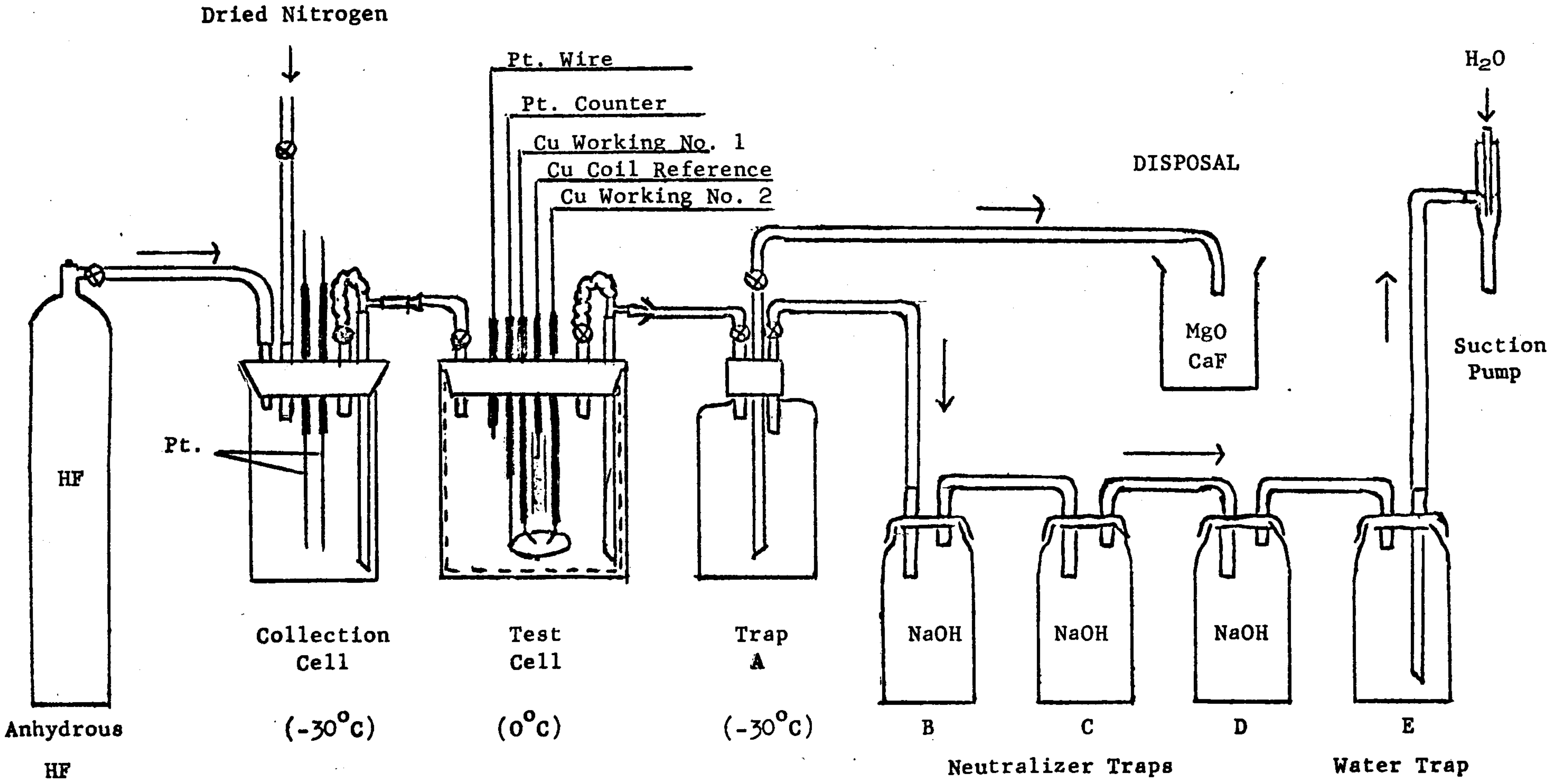
---

[a] Cathode was fabricated with 95% silver oxide (AgO) and 5% filter paper pulp (FPP). This mix was pressed onto expanded silver substrate at 2500 lbs load for 2 minutes at ambient temperature.

[b] Anode: lithium. Reference: Ag/AgCl. Current: 2ma, current density ~1ma/cm^2 with the KPF$_6$-NDA electrolyte runs 1-4. Current 5ma, current density ~2.5ma/cm^2 for runs 1-4 LiPF$_6$-NDA electrolyte for runs 5-7.

[d] Electrolyte: 10ml of 1 molal LiPF$_6$ in N-nitrosodimethylamine (NDA) for runs 5-7. The LiPF$_6$ was vacuum dried for 24 hrs at 50°C. i.e., as received. The NDA was vacuum distilled from P_2O_5. The electrolyte in runs 5 and 6 was also pretreated with lithium ribbon for 2 hours.

[e] Endpoint voltage for all runs was -1.0V vs Ag/Agcl.



APPARATUS FOR ELECTROLYSIS IN ANHYDROUS HF-KF

FIGURE 15

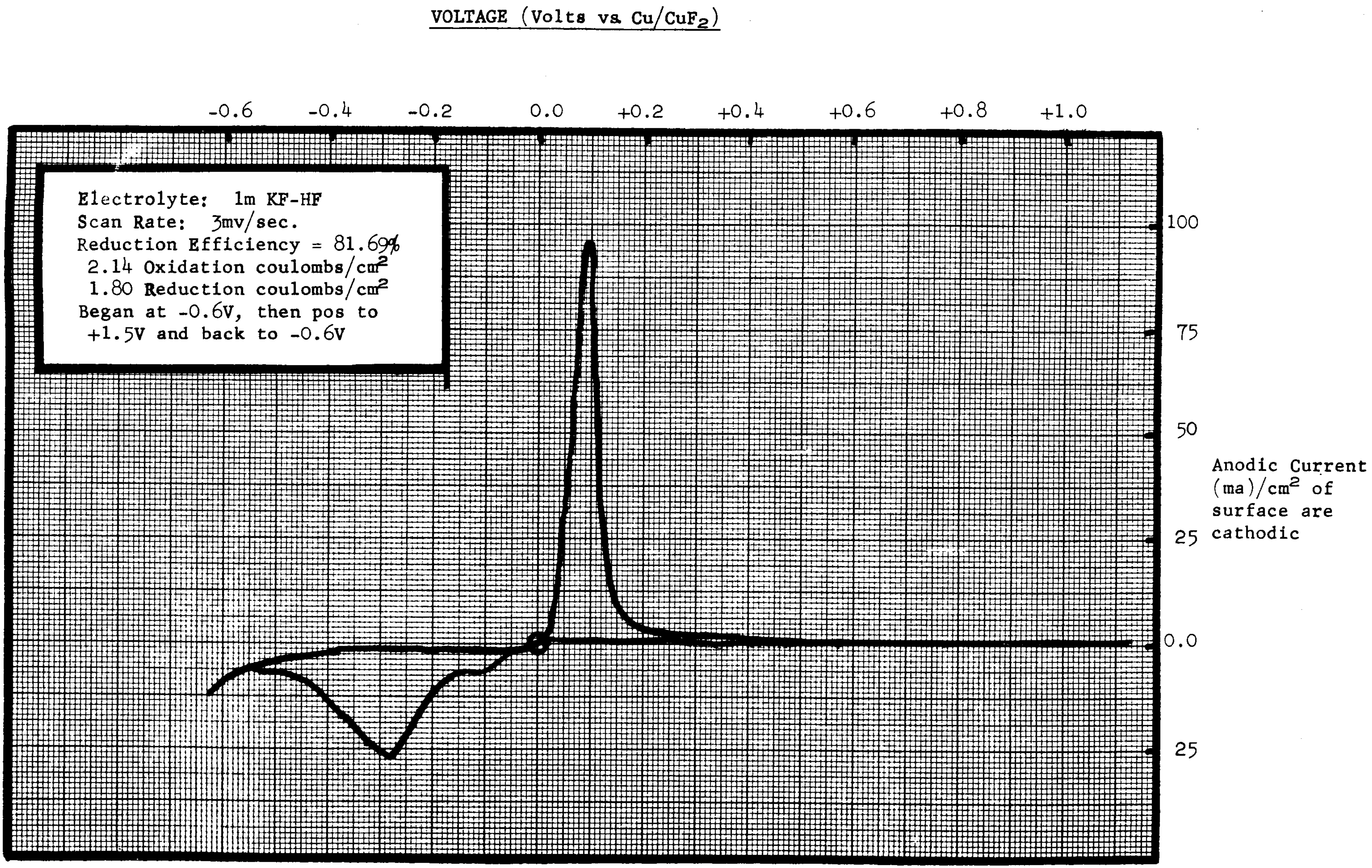


FIGURE 16. CYCLE VOLTAMMOGRAM OF Cu TEST ELECTRODE IN 1m KF-HF

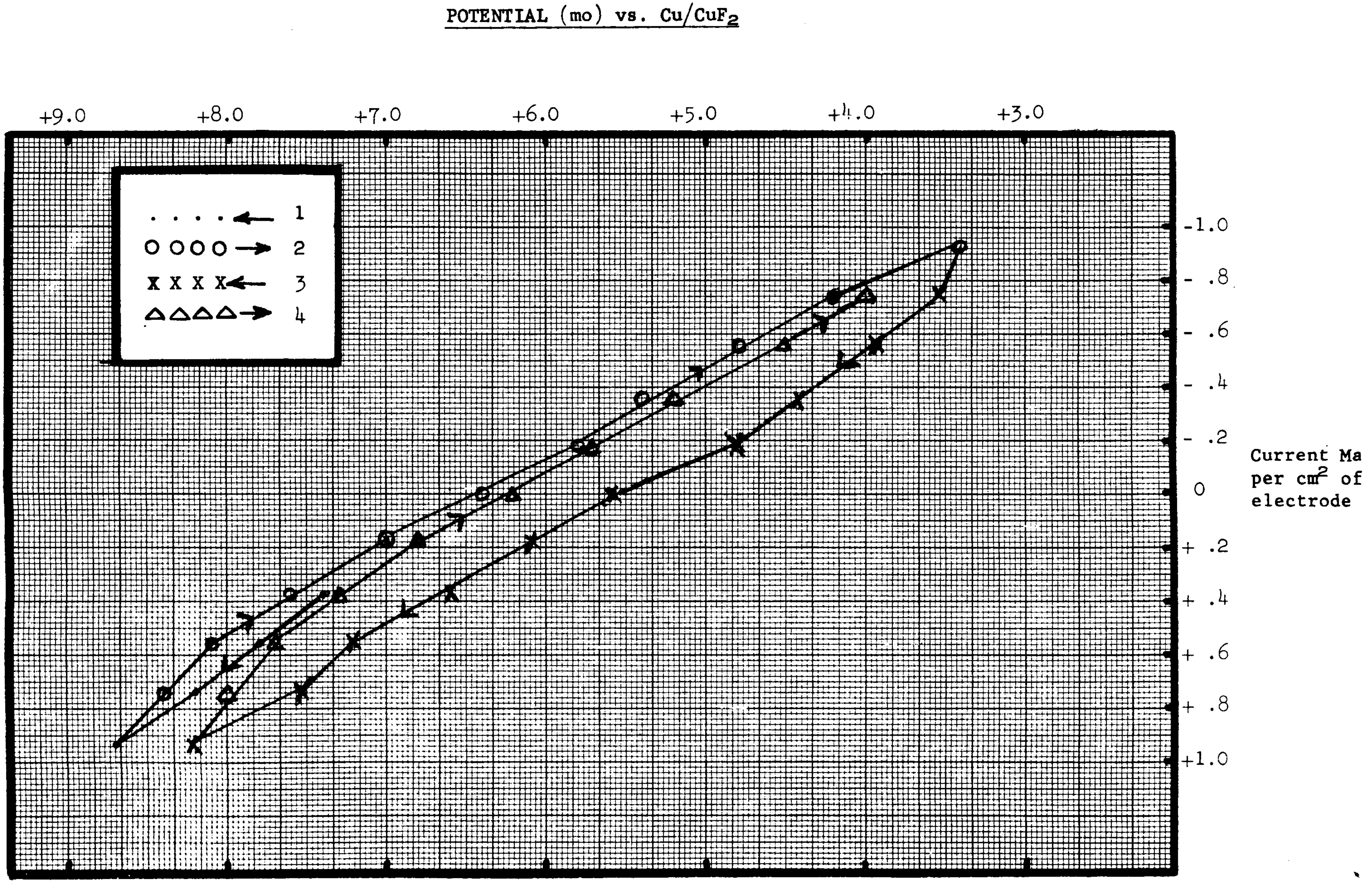


FIGURE 17. MICROPOLARIZATION OF Cu ELECTRODE IN 1m KF-HF

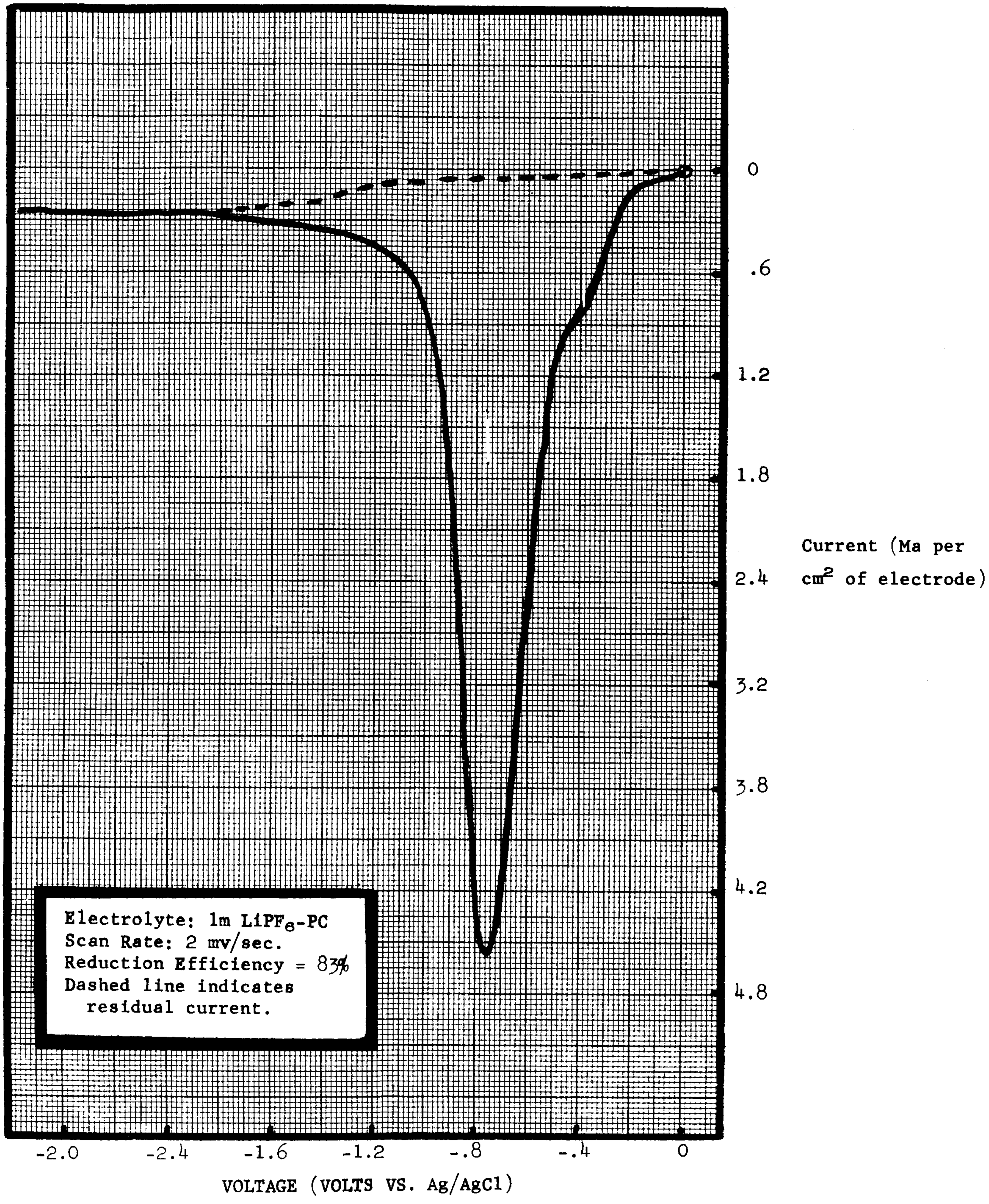
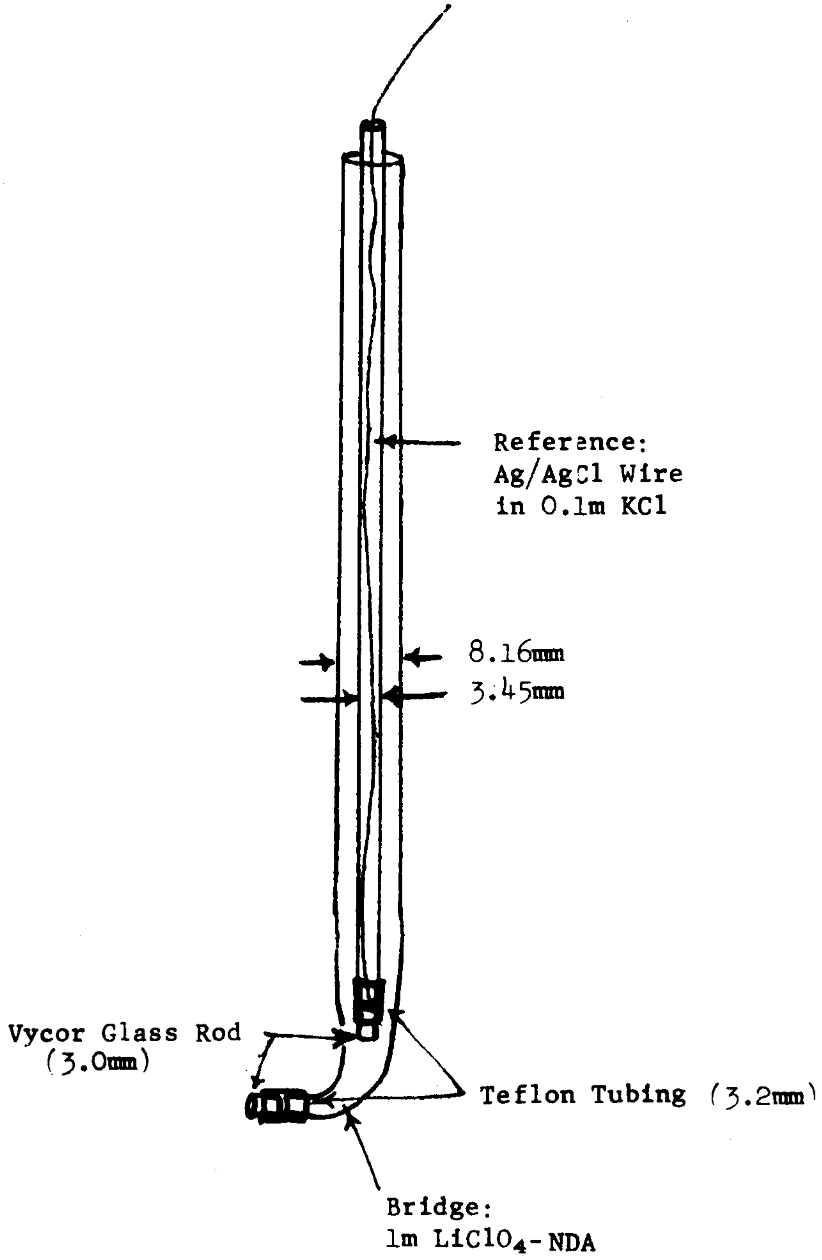


FIGURE 18. REDUCTION OF CuF_2 FILM IN 1m $LiPF_6$-PC

FIGURE 19. SILVER-SILVER CHLORIDE REFERENCE ELECTRODE



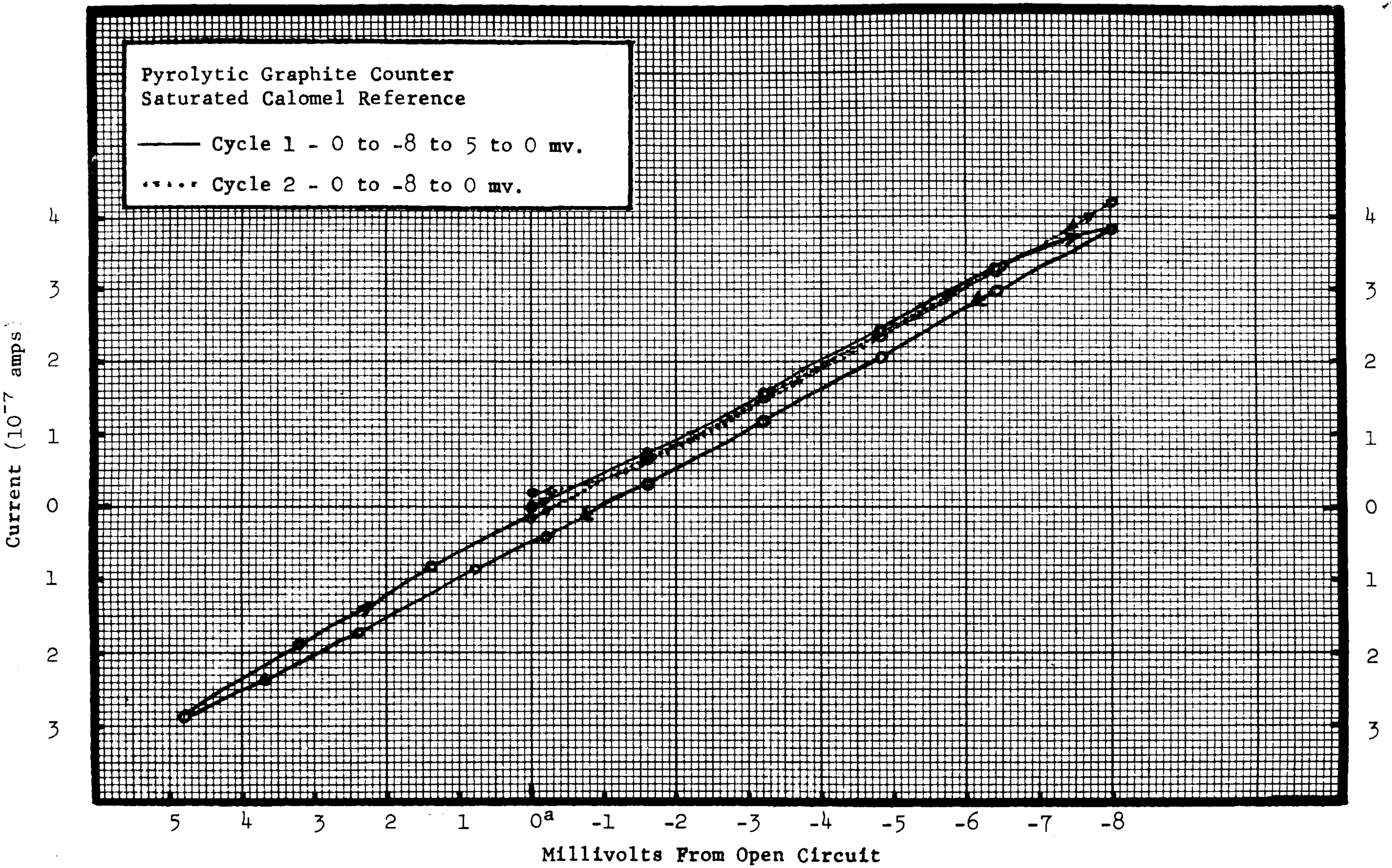


FIGURE 20. REFERENCE ELECTRODE STUDY - HYSTERESIS OF SILVER-SILVER CHLORIDE ELECTRODE

[a] Open circuit value of this reference electrode is -24.9mv versus a saturated calomel reference electrode.

VI. <u>REFERENCES</u>

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