"Investigation of Electrochemistry

of

High Energy Compounds in Organic Electrolytes"

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by

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Abstract

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The investigation of high energy compounds in organic electrolytes is proceeding along two lines. The first involves the study of the electrochemical properties of six solvents selected because of their reported physical and chemical properties. These are acetonitrile, dimethylformamide, α - picoline, propylene carbonate, γ - butyrolactone, and γ - valerolactone. Solutions of butyrolactone have decomposition potentials exceeding 4 volts and are greatly dependent on the supporting electrolyte. Dimethylformamide solutions have decomposition potentials greater than 5.5 volts if easily reducible species are not introduced. e.g. by drying procedures.

The second effort involves the study of high energy cathodic compounds, popularly known as "depolarizers". Attention is being devoted to the nitrogen-halogen compounds on the basis of their reported high potential and high capacity, and their expected suitability for non-aqueous systems.

Author

I. SCOPE

This research deals with the electrochemistry of high energy compounds in organic electrolytes. The term, "high energy", is defined by, and restricted to, those elements and compounds useful in the conversion by electrochemical processes of chemical to electrical energy. In defining the scope of the work, it is convenient to consider a galvanic cell in which a compound participates in a cell reaction as an electrode-active material. The electrical energy (joules) available from a galvanic cell is the product of the capacity (coulombs) and the voltage. The energy relationship points out the need to consider compounds from the standpoint of their potentials as well as their capacities.

In this investigation, attention will be given to oxidizing agents rather than reducing agents. As a preliminary indication of the usefulness of a compound a <u>theoretical capacity</u> can be calculated on the basis of the number of electrons accepted per mole or per gram during complete reduction. Thus, nitro compounds have high capacities, with six electrons involved in the reduction of each nitro group. The available capacity for a dinitrobenzene is then 2 x 6 x 96,487 ampere-second per mole or in conventional terms,

$$\frac{2 \times 6 \times 96,487}{60 \times 168.11} = 114.78 \text{ ampere-minute per gram}$$

Most inorganic compounds have lower theoretical capacities, e. g. manganese dioxide with 18.5 ampere-minute per gram, mercuric oxide with 14.9 ampere-minute per gram. For this reason the investigation is directed toward the investigation of organic cathode materials. One of the first steps is to correlate the <u>structure</u> of organic molecules with capacity, potential, and energy.

To achieve a high energy system this compound would be expected to participate in a galvanic cell reaction whose cell voltage is three volts or higher. There are two implications.

The first is that, because of the low "decomposition potential" of
water (about 1.7 volts for many electrolyte-electrode combinations), the
system must be non-aqueous. Not only must the decomposition potential
of the non-aqueous solvent be high but the overpotential in both anodic
and cathodic directions must be high.

The second implication is derived from the expected potential of
the anode. A reasonable value would be approximately 2.0 volts. Then
the cathode reaction must furnish about 1 volt to the total galvanic cell
voltage. These considerations restrict the scope of the investigation.

A further restriction describes the nature of the work. The main
effort will be to establish principles. These principles, optimistically,
would describe the character of the non-aqueous solvent, the type and
structure of high-energy organic compounds, and the kinetics and mechanism
of the electrode processes leading to the utilization of the thermodynamical-
ly available energy.

II. ORGANIC ELECTROLYTES -- DECOMPOSITION VOLTAGE

A. BACKGROUND.

The term, "decomposition voltage", is not generally considered to be a term of substantial theoretical significance. For example, MacInnes (1) does not discuss the term at all and many authors use it as an introduction to a discussion of overpotential. This results to a large extent from the traditional concentration on aqueous electrochemistry.

The early electrochemical investigations (2) yielded observations of the type illustrated below. When a voltage was applied to an electrolysis cell a current density-voltage curve was obtained.

Applied voltage
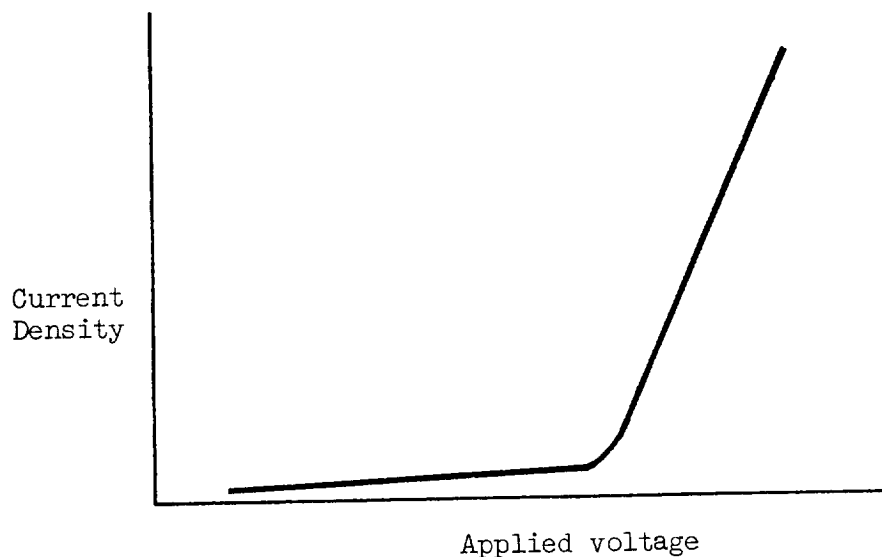
A certain voltage was required before a current of reasonable magnitude was observed to pass between the electrodes in the solution. Le Blanc (3), in the period of 1891-3, measured the decomposition voltage of a number of aqueous solutions of acids and bases. These were all approximately 1.7 volts. The decomposition voltages of solutions of NaNO$_3$, K$_2$SO$_4$, Ca(NO$_3$)$_2$, and other solutions of salts formed from strong acids and the alkali

and alkaline earths were about 2.2 volts. It was concluded that this was due to processes which must be common to all these solutions -- the evolution of hydrogen at the cathode and oxygen at the anode. The higher value observed for solutions of salts of strong acids and the alkali or alkaline earth elements was explained by the evolution of hydrogen or oxygen from unbuffered solutions. Thus, the minimum decomposition voltage of an aqueous solution would be the potential difference between the cathode (hydrogen potential) and the anode (oxygen potential). For water at 25° C, hydrogen at one atmosphere, a hydrogen ion activity of unity, an activity of OH^- of 10^{-14}, and an oxygen partial pressure of 1/5 atmosphere this value is 1.23 volts. The fact that it is actually greater is due to polarization as initially studied by Caspari in 1899, Tafel in 1905 and discussed in hundreds of publications since then. Thus, after the individual electrode reactions were identified, attention was focussed exclusively on these reactions.

Potter (4) identifies a reversible decomposition potential, D_o by

$$D_i = D_o + \eta_c + \eta_a + iR$$

where D_i is the applied potential to maintain a current $\underline{i}$ in the cell, η_c and η_a are the activation overpotentials for the cathode and anode reaction respectively, and R is the internal resistance of the cell. Further, this may be written as

$$D_i = (Ec - Ea) + \eta_c + \eta_a + iR$$

wherein the E's are the reversible potentials for the electrode reaction. The current achieved in the cell before the onset of the decomposition potential is dependent on the presence of extraneous materials in the solution (4). Three types of curves are possible depending on the concentration of electroactive impurities in the solution.

Applied potential
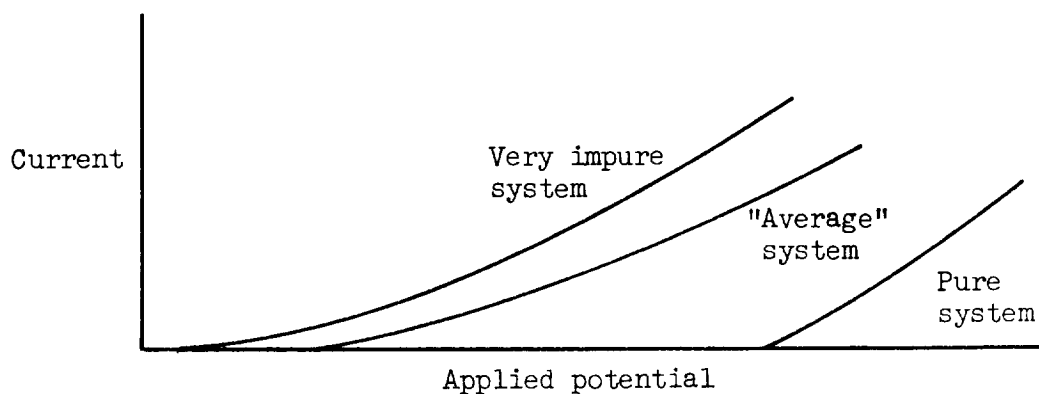
This general review leads to the conclusion that, if a finite current density is selected, and a "minimum decomposition potential" is measured, then the concept of decomposition potential of a solvent has some meaning. A specific finite current is required because if modern thinking in terms of exchange current is correct, then an anodic (and cathodic) current will flow at any potential varying from the equilibrium potential of the electrode.

The problem then becomes one of measuring the minimum decomposition voltage for the electrolytic solution and identifying the electrode reactions.

Charlot, et. al (5) discuss the decomposition of the solvent as the important consideration in the use of non-aqueous solvents in electrochemistry. They picture the electrochemical properties of solvents in the preferred way, that is, indicating both cathodic and anodic limitations.

A desirable preliminary step is to attempt to correlate the structure of the organic molecule with electrochemical stability. The literature of electro-organic chemistry is of limited help here. By and large this literature is composed of reports of electrolyses carried out under ill-defined conditions. In fact, until recently much of the experimental work has been reported without reference to potential, this in spite of the fact that Haber pointed out in his work in 1898 that in cathode reductions it was the cathode potential that determined the products obtained.

In spite of the limited quantitative information, certain observations may be made from these experimental reports. If the oxidation or reduction is carried out in aqueous solution and at a given current density the potential can be estimated in an approximate way.

The oxidation and reduction characteristics of the common typical structures are briefly reviewed (6)*.

R-OH

Aliphatic alcohols are oxidized to the corresponding acid, for example, propyl alcohol in dilute sulfuric acid solution gives a 90% yield of propionic acid when oxidized at a PbO_2 electrode. Glycol is oxidized to a mixture of products.

R-CHO and R_2=C=O

Aliphatic and aromatic aldehydes are oxidized to the corresponding acids in acid and basic media. Ketones are also readily oxidized. Both aliphatic and aromatic aldehydes and ketones are susceptible to reduction to the alcohols. Methyl ethyl ketone is reduced to secondary butyl alcohol at a lead cathode in a sodium bicarbonate medium. When p-hydroxyacetophenone is reduced at a potential of -2.2 v. (versus S.C.E.) in aqueous NaOH a 77% yield of the pinacol is obtained.

R - COOH and R - CO - OR

Anodic oxidations involving fatty acids and their salts go readily and have been investigated extensively (e. g. the considerable amount of the work on Kolbe reaction). Straight chain acids from acetic to stearic give the Kolbe reaction. The yield of various products varies with the chain length. Benzoates are also readily oxidized. Carboxylic acids are reduced in aqueous solution to aldehydes and ketones. The response of the ester depends on the acid portion of the molecule. For example, ethyl esters of acetic, phenylacetic, and cyanoacetic acids are not reduced while fumaric, tartaric, and succinic acids react slowly, and oxalic, malonic, acetoacetic, oxalacetic, benzoic, halobenzoic, and phthalic acids react readily.

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  The observations reported here were taken from the mongraph reference 6. For primary reference see (6).

Alicyclic compounds

Cyclohexane is easily oxidized.

Heterocyclic compounds

Pyridine is oxidized at a platinum anode in an aqueous sulfuric acid solution to yield 2-pyridyl-pyridinium sulfate. The compound is reduced to piperidine in aqueous sulfuric acid with a Pb electrode. Quinoline reacts in a similar way.

Aromatic compounds

Benzene is oxidized in ethanolic-sulfuric acid. Anthracene in suspension is oxidized to anthraquinone in a acetone-sulfuric acid medium.

R-NO$_2$

Nitrocompounds are reduced at potentials of less than 1.0 volt.

R-NH$_2$

Primary aromatic amines are anodically oxidized to imines or azo compounds in aqueous sodium sulfate solutions. Imines or imidic esters can be reduced to the respective amines in either an acidic or basic medium.

General

One electrolytic reaction of interest occurs with a so-called catalytic electrode, as follows.
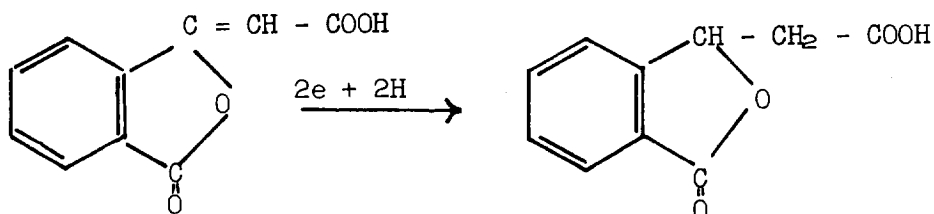
This is indicative of the stability of the structure of the condensed ring. Similar structures observed in the cyclic esters have a high degree of electrochemical stability.

The assumption has been made in the foregoing that, if the oxidation or reduction could be conducted in aqueous solution, then the particular structure was susceptible to oxidation or reduction at a potential lower than the applicable overpotential of oxygen or hydrogen. There would be one important point to be kept in mind as the attempt is made to extrapolate this knowledge in an estimation of the stability of an organic structure for use as an electrochemical solvent. If the mechanism of oxidation or reduction were such as to require a concentration of protons or hydroxyl ions that reaction would not go in the anhydrous solvent. Thus, in the absence of water the decomposition voltage of the solvent would be extended.

There are very few data of a quantitative sort reported on the decomposition voltages of solvents.* One limitation often encountered is that of the reduction of the cation of the electrolyte before the solvent limitation is reached.

Of the organic non-aqueous solvents most work has been done with acetonitrile. Charlot, et. al. (5) estimate the decomposition potential as greater than 4 volts. It has been reported that electrochemical reactions can be conducted over a 6 volt range in this solvent (7). This agrees approximately with measurements made and reported below in "experimental".

The cyclic esters as solvents for electrochemical reactions have been investigated by Harris (8). These include ethylene carbonate, propylene carbonate, γ-butyrolactone, and γ-valerolactone. In discussing the stability of propylene carbonate it is stated that chlorine can be liberated at a platinum electrode in the anhydrous liquid without decomposing the solvent. Solutions of bromine and iodine are not decolorized after standing for long periods of time. The standard potential for the Cl_2 electrode is -1.36 v. (8) Harris further reports that Li, Na, and K were deposited from their halide solutions. With the Li potential 3.04 v. it would appear that the decomposition potential of propylene carbonate exceeds 4.4 volts.

* The literature on the six solvents shown in Table I and several other closely related structures has been reviewed. This bibliography, which includes over 100 pertinent references, will be published in the near future.
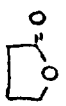
Therefore, one of the first objectives of the investigation has been to collect quantitative data on the decomposition potential of six solvents of particular interest.

B. EXPERIMENTAL

Solvents Investigated

The open literature and recent reports were studied to select solvents for the organic electrolyte system. This subject has been given considerable attention recently (10, 11, 12). The first consideration here was one of suitable physical and chemical properties. Six solvents were selected for experimental investigation. Generally speaking the compounds had broad liquid ranges of about 200° C. With the exception of acetonitrile the vapor pressure at room temperature was quite low. These solvents had fairly high dielectric constants, and this, coupled with the possibility of entering into solvent-solute interactions, indicated that they would be good solvents for various salts. The physical characteristics of these liquids are given in Table I.

Table I Solvents for Electrochemical Investigation

Liquid	Formula	Formula Weight	Melting Point (°C)	Boiling Point (°C)	Dielectric Constant	Viscosity (cp)	Density	Refractive Index, n_D
1. Acetonitrile	CH_3-CN	41.05	-45.72 (13)	80.06 (13)	36 (20° C) (14)	0.345 (25°C) (14)	$0.7856^{20}_{}$ (13)	1.3441 (20°C) (13)
2. Dimethyl-formamide	$(CH_3)_2-N-\overset{O}{\underset{H}{C}}$	73.09	-61 (15)	153^{760} (15)	36.71(25°) (15)	0.802 (25°C) (15)	0.9445^{25}_{4} (15)	1.4269 (25°C) (15)
3. α-picoline	C_6H_7N	93.13	-70 (16)	128.8 (13)	9.8 (20°) (13)		0.9497^{15}_{4} (13)	1.5029 (17°C) (13)
4. Propylene carbonate	$CH_3 \cdot \overset{H}{C}-O$ $\underset{CH_2-O}{\big|} C \cdot O$	102.09	-49.2 (17)	241.7 (17)	69.0 (23°) (17)	1.916 (40°) 2.530 (25°) (8)	1.2057^{20}_{4} (17)	1.4209 (20°C) (13)
5. γ-butyrolactone	(ring $O=$, O)	86.09	-43.53 (19)	204 (19)	39 (20°) (18)	1.751 (25°) (8)	1.1254 (25°) (19)	1.4348 (25°) (17)
6. γ-valerolactone	(ring CH_3, O, $=O$)	100.11	-31 (20)	205.9-206.6 (20)		2.15 (25°) (20)	1.0518 (25°) (20)	1.4301 (20)

Solvent Purification and Characterization

Dimethylformamide

Dimethylformamide (Eastman Kodak Co. No. 5870 and Matheson, Coleman and Bell Co.. No. 5974,) was distilled at a reduced pressure. Three cuts were made. The first cut was taken between 25-30°C. over a pressure range of 3.8 - 5.1 mm Hg.. The second cut was taken between 26-29.75°C. over a range of 4.25 - 5.10 mm Hg.. The third cut was the residue. The physical characteristics of these cuts were as follows:

Cut	Refractive index* $(n_D 25°)$	Boiling Pt. °C. (760 mm)	Density
No. 1	1.42582		
No. 2	1.42646	151.64	0.93314(26°)
No. 3	1.42619		
Reported**	1.4269	153	

Attempts were made to characterize DMF using gas chromatography. A Nester/Faust Anakro gas chromatograph with a zeolite column was used with the trace being recorded on an L and N Speedomax G recorder. Nitrogen was employed as the carrier gas. Column flow was approximately 60 cc/min. Amperage was set at 150 milliamps. At all temperatures below 200°C for both column and preheat, only slight deviations from the base line were recorded. It is planned to characterize these cuts more completely.

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   Checked with standard sucrose solutions
**
   Reference (15)

<u>γ-Butyrolactone</u>

γ-Butyrolactone (Eastman Kodak Co., No. 6922) was fractionally distilled at reduced pressure. Three cuts were made, the first at 70°C. and 6 mm Hg, the second, which represented 4/5 of the volume, came off between 78-83° and 9 - 13 mm Hg, and the third being the residue. The refractive indices of these cuts were as follows:

<u>Sample</u>	<u>Refractive index $n_D 25°$</u>
Original Eastman Sample	1.4349
Reported (Reference 18)	1.435
Cut No. 1	1.4335
Cut No. 2	1.4319-1.4344
Residue	1.4311

Since there was a large discrepency between the reported and observed refractive indices, the second cut was distilled under reduced pressure again. Four cuts were made. The first fraction of redistilled second cut was taken at 82-83° C. and 9.25 - 11.25 mm Hg, the second fraction was taken at 82° and 10 mm and the third fraction was taken off at 86° and 11.25 mm Hg. The refractive indices of these cuts are as follows:

<u>Cut</u>	<u>Refractive index, $n_D 25°$</u>
No. 1	1.4308
No. 2	1.4337
No. 3	1.4325
No. 4	1.4334
Reported*	1.435

The γ-butyrolactone is being characterized further by infrared and vapor chromatography.

<u>2 - Picoline</u>

2-Picoline (Eastman Kodak Co. No. P209) was distilled at reduced pressure with six fractions being obtained. The first cut was taken at

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Reference (18)

36°C and 11 mm Hg, the second at $34 - 35^\circ$C and $12 - 14$ mm Hg, the third at $31 - 32^\circ$C and $12.75 - 13.25$ mm Hg, the fourth at $31.5 - 33^\circ$C and $9.75 - 13.25$ mm Hg, the fifth at 33°C and 12.5 mm Hg, and the sixth cut was the residue. The corresponding refractive indices are as follows:

Cut	Refractive index, $n_D 25^\circ$
No. 1	1.4966
No. 2	1.4953
No. 3	1.4970
No. 4	1.4964
No. 5	1.4969
No. 6	1.4972
Original	1.49705
Reported*	1.5061

Acetonitrile

Acetonitrile (Eastman Kodak Co., No. P488) was distilled at atmospheric pressure and five fractions were taken. The first cut was taken at $80-81^\circ$C. and 750.0 mm Hg, the second at $80.5-81^\circ$C. and 750.0 mm Hg. the third at 81°C and 753.0 mm Hg, the fourth at 81° and 753 mm Hg and the residue was the fifth cut. The refractive indices of these fractions are as follows:

Cut	Refractive index, $n_D 25^\circ$
No. 1	1.3415
No. 2	1.3427
No. 3	1.3426
No. 4	1.3426
No. 5	1.3406
Original	1.3407
Reported**	1.3461

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* Reference (13)

** Reference (13)

- 13 -

Propylene carbonate

Propylene carbonate (Eastman No. P7050) is now being fractionated under reduced pressure.

γ-Valerolactone

γ-Valerolactone (Eastman No. P6123) has been obtained for these studies. At present it is not intended to purify further the compound. It is assumed that its properties will approximate those of γ-butyrolactone. The only characterization consisted of the measurement of the refractive index.

	$n_D 25°$
Sample	1.4310
Reported (reference 17)	1.4301

Salts

Potassium hexafluorophosphate was obtained from Ozark-Mahoning Co. -- their lot No. PR 14-1-8 -- and used without further purification. Analysis of this salt (21) by the tetraphenylarsonium chloride method gave 77.63% PF_6^- which corresponds to 98.56% purity of KPF_6.

Sodium tetrafluroborate, Ozark-Mahoning, lot No. KW1-1-151, analyzed (21) as 74.60% BF_4^- corresponding to 94.35% $NaBF_4$. The fluoride analysis gave 67.14% F^- which corresponds to a purity of 97.02%.

Potassium tetrafluoroborate-Ozark-Mahoning lot No. KW-1-148- gave an analysis (21) of 58.36% total F^- which corresponds to 96.70% KBF_4.

The usual procedure in making up a solution was to dissolve the amount of salt to supply the particular molarity (known not to saturate the solution (10)) taking into account the purity. This solution was made up in a volumetric flask and a small amount of insoluble material was present. The solution was then filtered through fiber-glass paper into a glass-stoppered flask and allowed to stand over molecular sieves type 4A to remove traces of H_2O. Analysis of the above salts showed that there was a small amount of water present. No attempt was made to remove this from the salt but the final solution was dried.

Tetramethylammonium chloride was Eastman No. 3592. The solution, after being made up volumetrically was dried over molecular sieve type 4A.

In several cases saturated solutions of tetramethylammonium chloride, sodium tetrafluoroborate, and potassium tetrafluoroborate were prepared by adding an excess to butyrolactone, placing the stoppered flask in a water bath at 40°, allowing the flask to stay in the bath for six hours with occasional shaking and then allowing the bath to cool to 25° overnight.

Apparatus and Procedure

The electrical arrangement for the decomposition potential measurements is shown in figure 1. The potential control was achieved with a precision potentiostat, components of which are within the dotted line. The potentiostat was an Anotrol Model 4101 Research Potential Controller, Serial Number 64-0155; it was modified to supply 10 amperes cathodic current at 10 volts. This potentiostat is capable of control over the range of 0 to $\pm$ 5.0 volts within 1 millivolt. The rated capacity is 15 amperes anodic current or 10 amperes cathodic current at 10 volts. It has a sensitivity of $\pm$ 0.5 millivolt, and a response time of 2-5 microseconds.

The electrolysis cell was held in a constant temperature bath (Blue M MW-1120 A) usually at $25^{\circ} \pm 0.2^{\circ}C$. The cell is illustrated in figure 2. Because of the solubility of most of the common plastics in these organic solvents, the cell components were constructed from glass and teflon. Teflon tape was used to prevent slipping of glass-to-Teflon joints. The electrodes were smooth platinum, 0.076 mm thick, 2.54 cm x 1.95 cm or an area in each face of approximately 5 cm^2. This meant that the current measurement can be changed to a current density measurement by division by 10 if it is assumed that both faces of the electrode participate in the electrochemical reaction. The electrodes are separated from each other and from the silver reference electrode by glass-fiber paper. The reference electrode was a silver wire 1 mm in diameter with a surface area of about 0.16 cm^2. The platinum electrodes were separated by approximately 3 mm. The potential was controlled by the silver wire which was positioned very closely to the control electrode. The gas which bubbled through the solution was prepurified nitrogen passed through Drierite and Linde Molecular Sieves type 4A.

The typical procedure was as follows. The platinum electrodes were mounted in the Teflon stopper, cleaned with concentrated nitric acid, distilled water, and acetone. The assembly was dried by passing dry nitrogen into the cell. The silver reference electrode
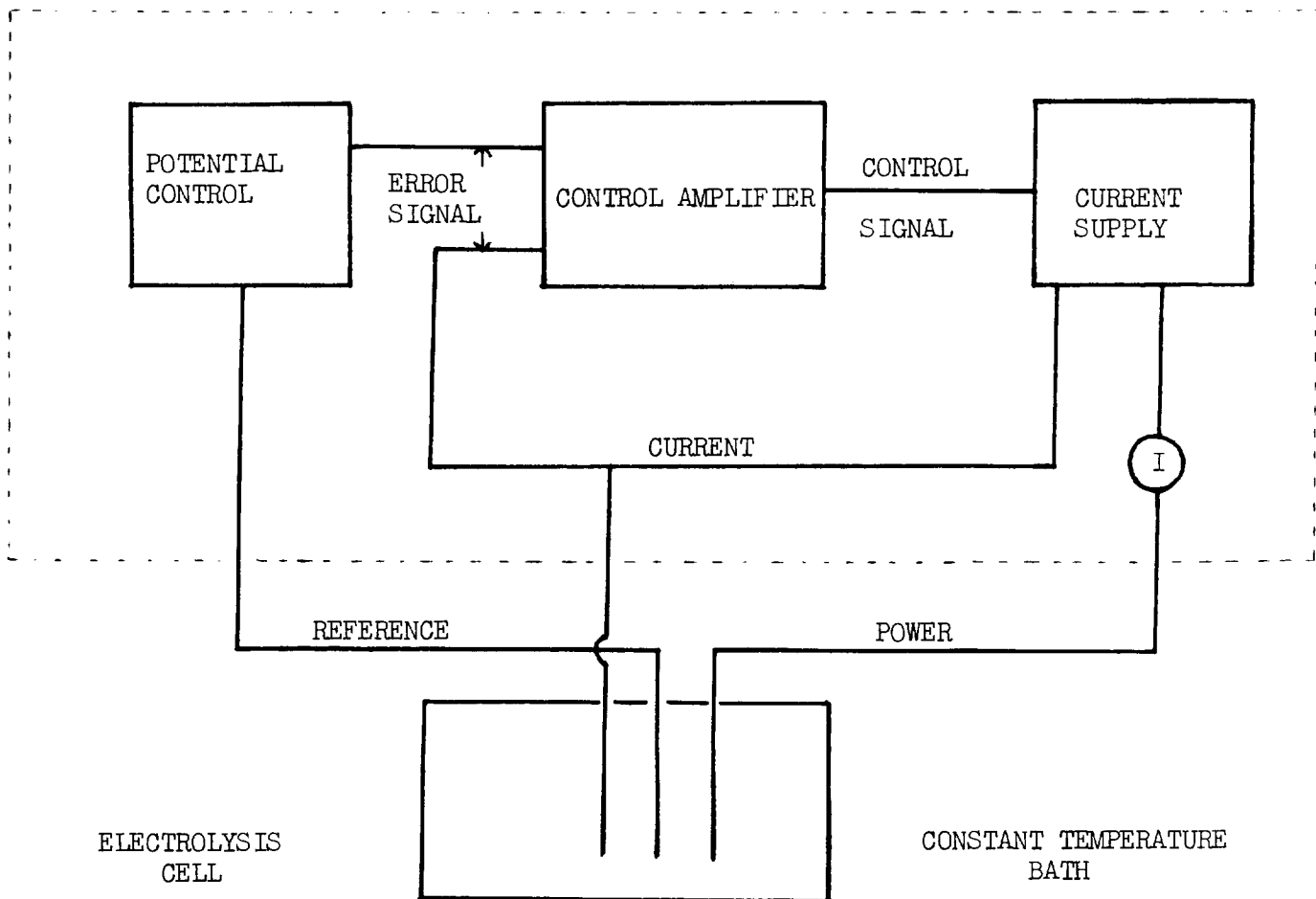
Figure 1. POTENTIOSTAT AND ELECTROLYSIS CELL ARRANGEMENT

REFERENCE

POWER

CONTROL

DRY N$_2$

CAPILLARY

TEFLON STOPPER

GAS DIFFUSER

ELECTROLYTIC SOLUTION

PLATINUM ELECTRODE

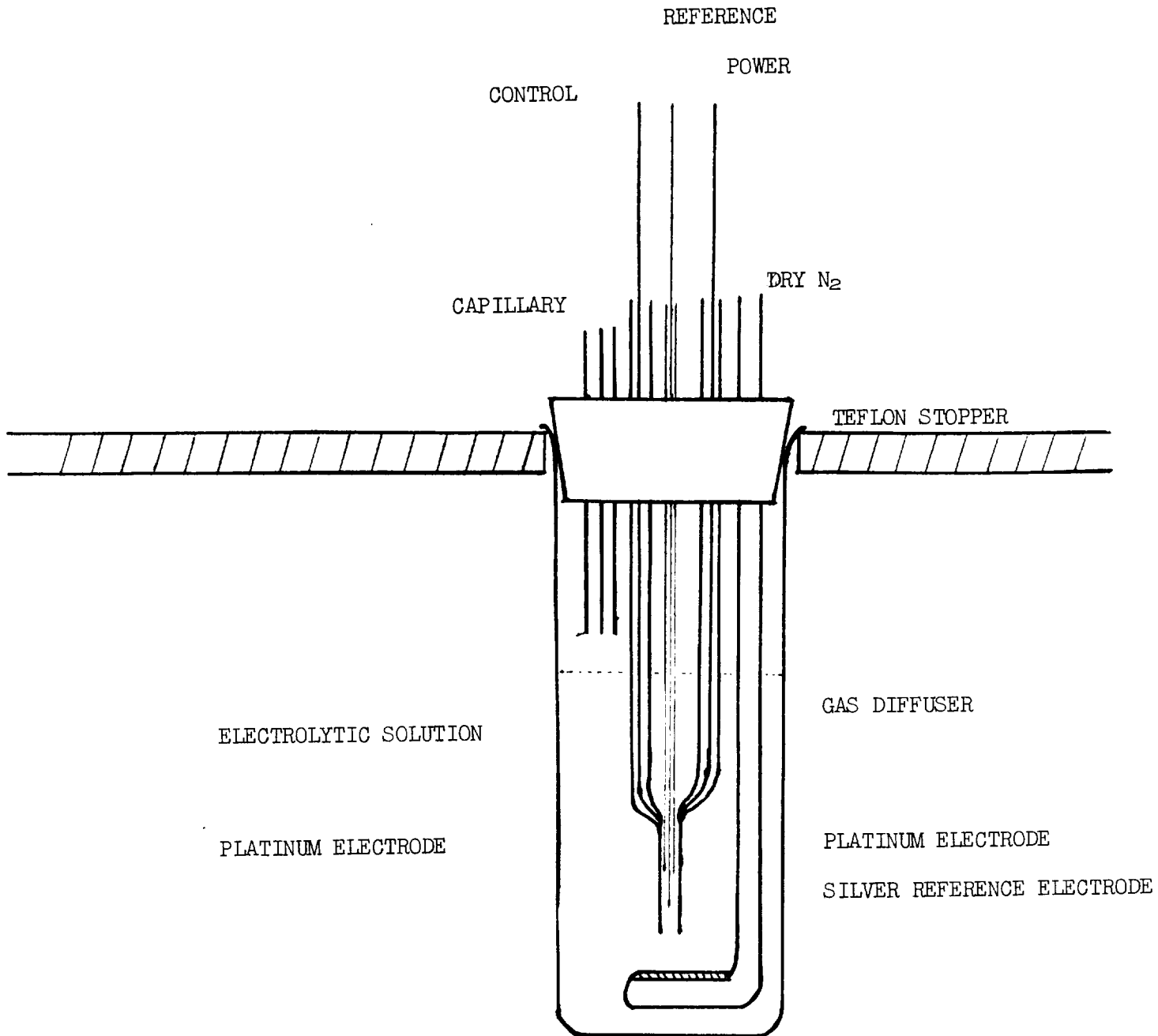PLATINUM ELECTRODE

SILVER REFERENCE ELECTRODE

Figure 2. ELECTROLYSIS CELL

was then inserted and the space between the silver wire and the tubing above the stopper was closed with epoxy cement. The fiberglass filter paper was positioned and the gas diffuser tube run through the stopper. The electrolytic solution, usually 75 - 90 ml in volume, was added and the bottom of the electrolysis beaker was covered with molecular sieve. The top of the cell with the stopper was then wrapped with Parafilm "M" Paper.* Dry nitrogen was then passed through the cell for 15 minutes to remove the air and the assembly was then stoppered and allowed to stand overnight. Prior to a electrolysis experiment the cell was purged again with dry nitrogen for 20 minutes. The electrolysis was conducted anodically and cathodically at 0.2 v intervals. In the preliminary experiments the potential was set and then a wait of one minute occurred before the current was read.
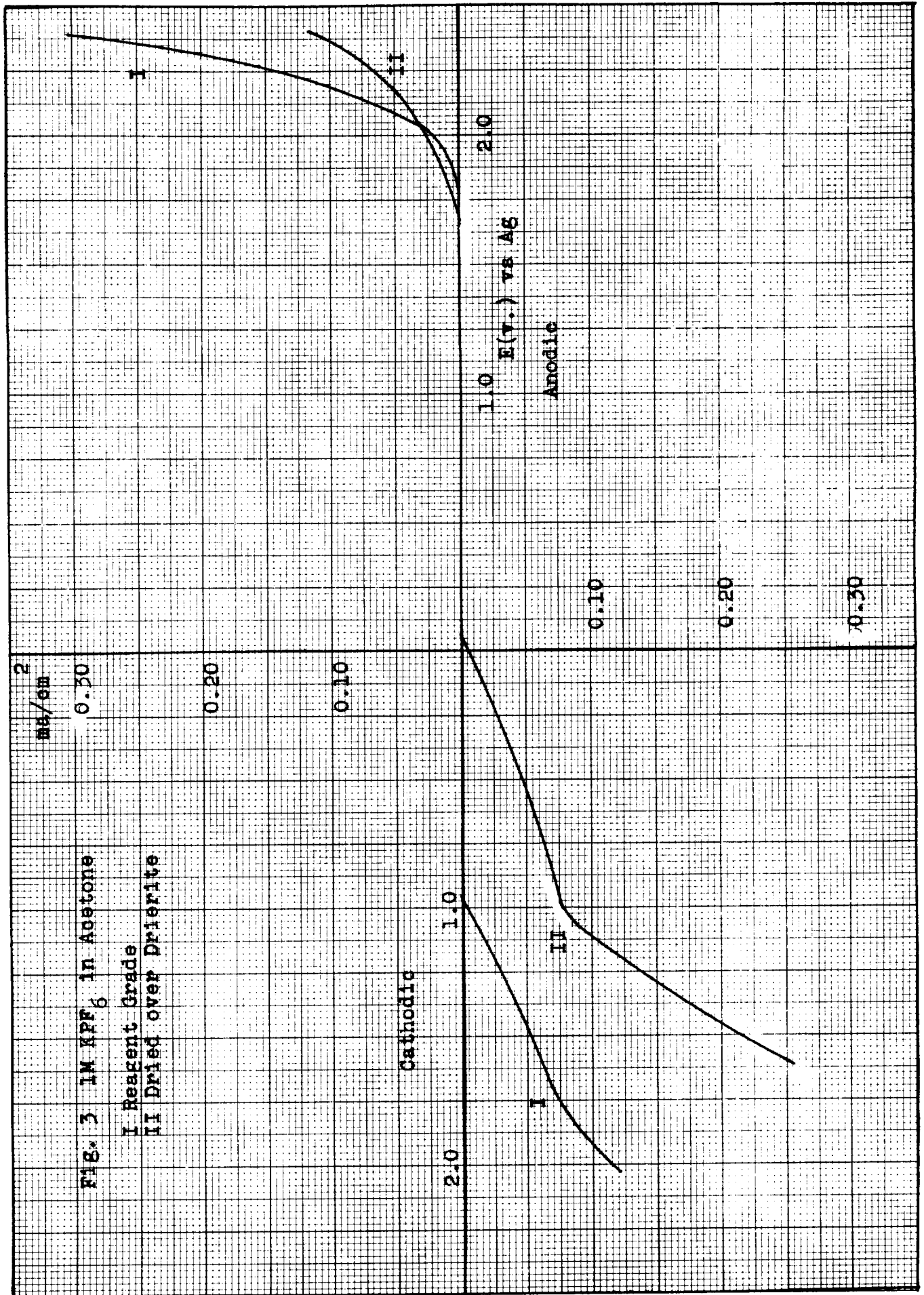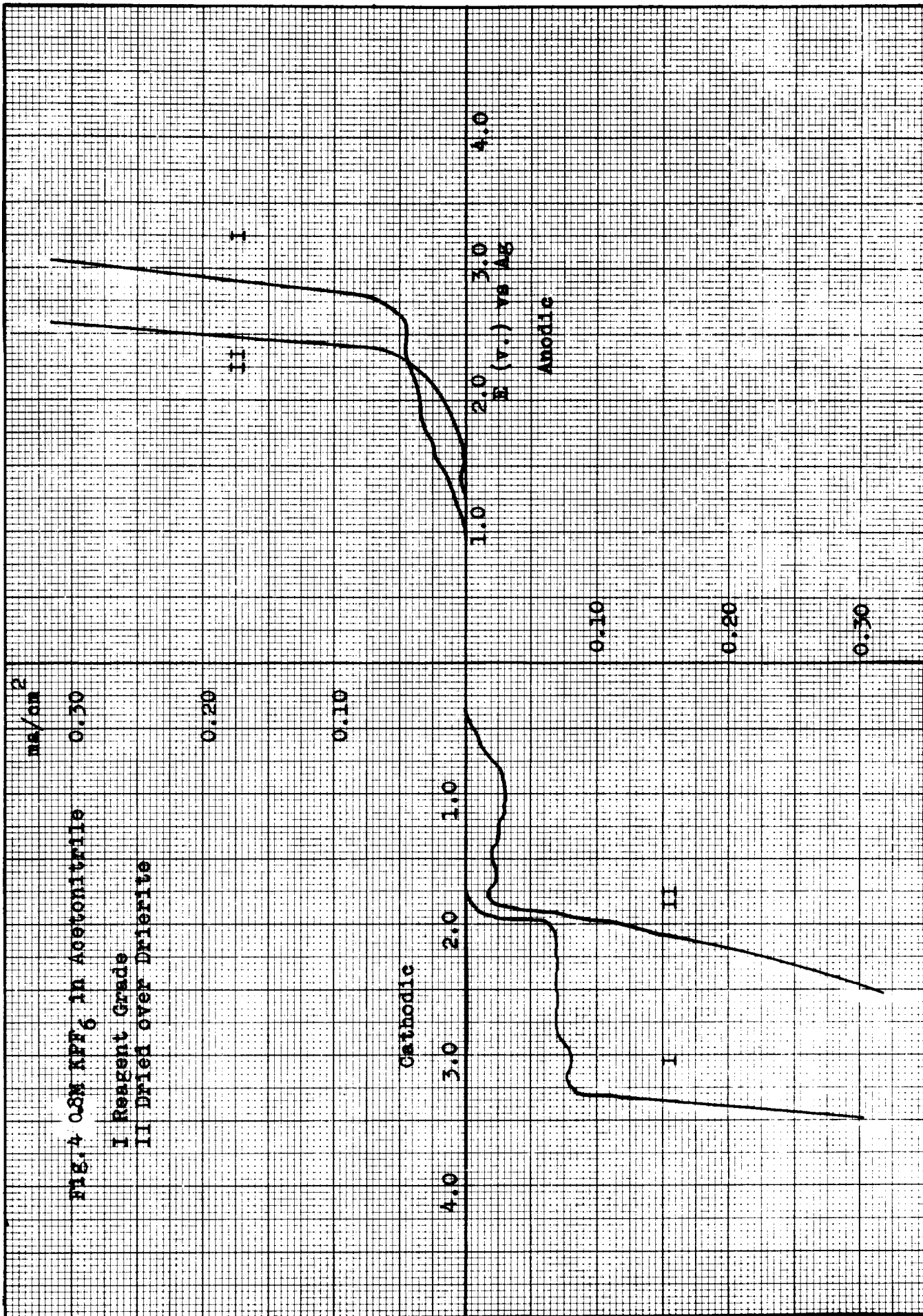
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* Marathon - American Can Co.

Results and Discussion

Some of the preliminary experimentation involved learning the effect on decomposition potential of drying the organic solvent with some of the conventional drying agents. The reagent grade solvents themselves are anhydrous but water is introduced by the salts and the transferring of the solutions. Figure 3 shows anodic and cathodic decomposition curves for a solution 1 M in KPF_6 in reagent grade acetone. This curve is compared with that obtained from the same solution dried over Drierite (anhydrous calcium sulfate) for one week. The anodic side of the curve is affected very little but the cathodic side indicates that a more easily reduced new species has been introduced into the solution. This is very likely the sulfate ion. An acetonitrile solution, 0.8 M in KPF_6, dried over Drierite is affected in somewhat similar fashion as shown in figure 4. A species, reducible below 1.0 volt, very likely the sulfate ion, appears in the solution. The anodic side is also affected, probably by the removal of the easily oxidizable water.

Solutions of dimethylformamide which had been dried over Drierite and P_2O_5 are compared to the reagent grade solution in figure 5. The anodic part of the electrolysis reaction is not affected. P_2O_5 is not soluble in dimethylformamide (15) but does introduce into the solution a species which is reducible below 1.0 volt. Further, at voltages below 4.0 volts on the cathodic side, appreciable currents are observed. Calcium sulfate also has a very low solubility in dimethylformamide. Whereas the easily reduced species observed in acetonitrile solutions does not appear to be added to the solution the reduction wave at the higher voltage similar to that seen in solutions allowed to stand over P_2O_5 is observed.

These results suggest that the (chemical) formation of hydrates in solution does not represent a desirable method of removing traces of water.
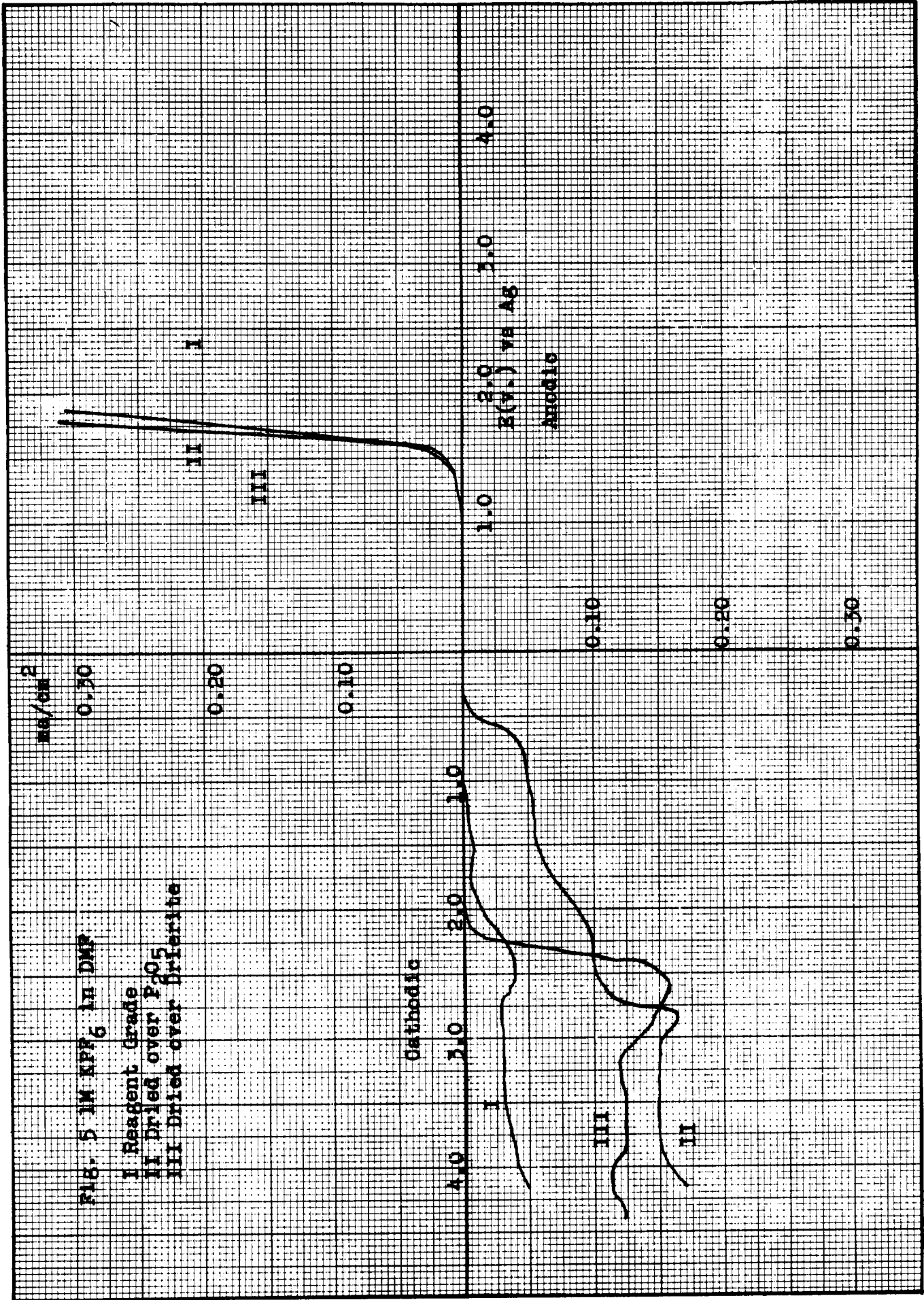
Fig. 3 1M KPF$_6$ in Acetone

I Reagent Grade
II Dried over Drierite

Cathodic

Anodic

E(v.) vs Ag

ma/cm^2

FIG. 4 0.8M KPF6 in Acetonitrile

I Reagent Grade
II Dried over Drierite

Fig. 5. 5 1M KPF6 in DMF

I Reagent Grade
II Dried over P2O5
III Dried over Drierite

ma/cm2

Cathodic

Anodic

E(v.) vs Ag

The unusual results achieved with these chemical techniques suggested the employment of physical adsorption techniques, specifically the use of "molecular sieve" materials. The "molecule sieves" are synthetically produced metal aluminosilicates that adsorb H_2O by virtue of a controlled pore size. In this work Linde Molecule Sieve type 4 A which will adsorb molecules with diameters less than 4 angstroms was used. This zeolite is a sodium aluminosilicate with unit cell formula of $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27 H_2O$. The water of hydration is removed by heating before it is used as a drying agent. In figure 6 the anodic and cathodic behavior of a 1 M solution of KPF_6 in butyrolactone run under two conditions are compared. Curve I was observed following the procedure described above. Curve II was a similar solution held over molecule sieve type 4A for 12 days. The anodic decomposition potential is extended to a higher potential. Also, on the cathode side a species reducible under one volt is decreased in concentration.

It would appear at this point that the employment of molecular sieves (in addition to careful manipulation of solutions, equipment, etc.) offers the desirable way to remove H_2O from essentially anhydrous solutions. The present work was done by using the adsorbents statically simply allowing the solution to stand over the prepared solution. It is intended in the future to run the solution through a column before filling the electrolysis cell. This is a more efficient method of water removal.

The use of molecular sieves does pose two questions and apparently the data are not available to give good answers to either at this point. The particular zeolite used in these experiments is a sodium aluminosilicate. When held in contact with a solution of a potassium salt the possibility exists of exchange of potassium ions for sodium ions. This should be minimized in anhydrous solvents but the extent of this cannot be estimated at this point. The second question has to do with residue water. It has not been possible to learn the residue water in an "anhydrous" organic liquid in contact with these zeolites. It is known that these adsorbents are more efficient than activated alumina or silica gel but literature search
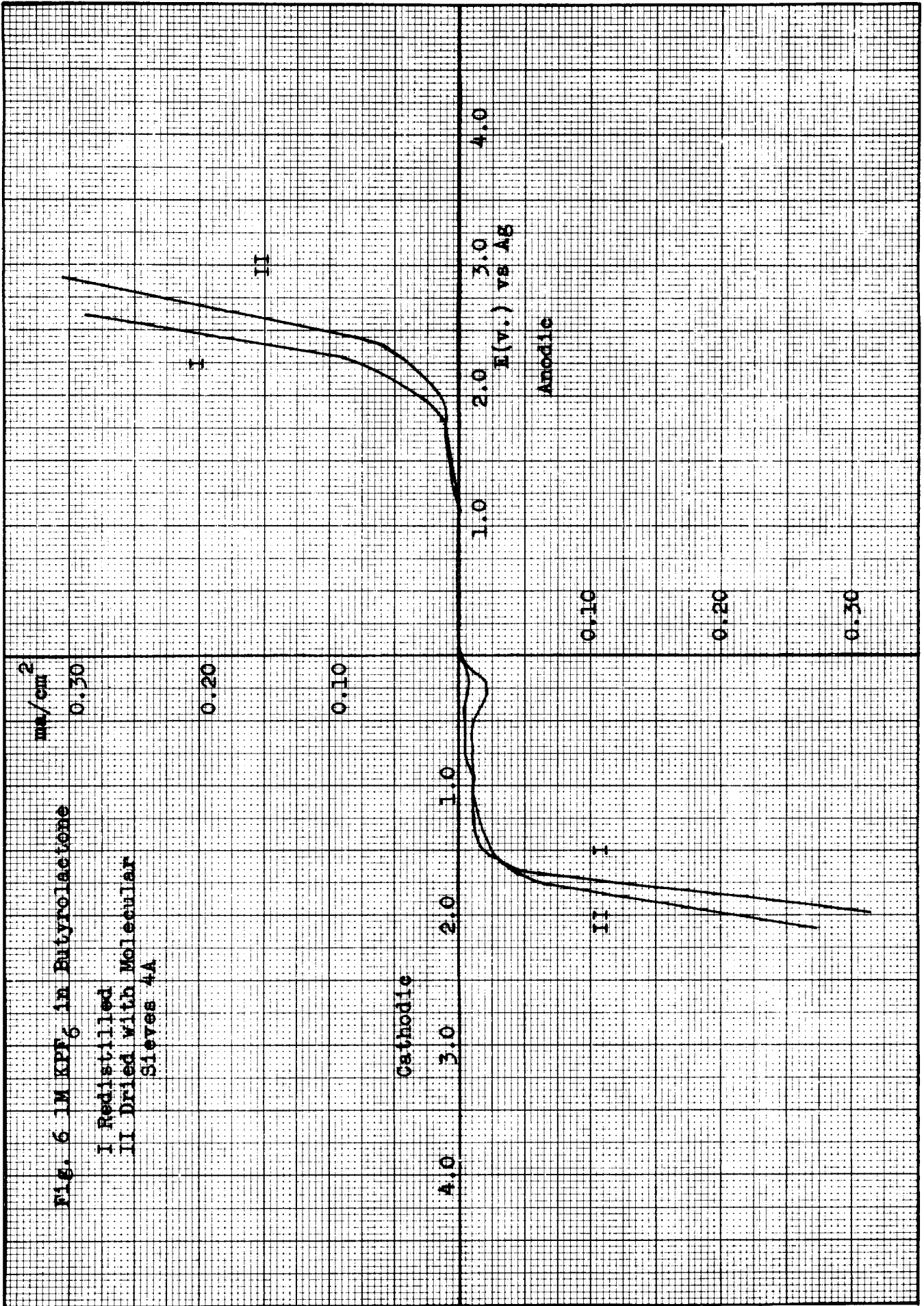
Fig. 6 .1M KPF$_6$ in Butyrolactone

I Redistilled
II Dried with Molecular
    Sieves 4A

and discussion with Linde specialists fail to allow a precise estimate of the value. Both of these points are being investigated further.

The initial attention has been devoted to electrolytic solutions in which the solvent was gamma-butyrolactone. As has been mentioned previously a major problem exists in the decomposition or deposition, not of the solvent but of the dissolved salts. For this reason it is necessary to conduct experiments with a number of salts whose ions are stable to reasonably high potentials. The experimental plan for the investigation of butyrolactone was as follows:

Dissolved salt	Probable Species Decomposed	
	at the anode	at the cathode
KPF_6	PF_6^-; BL	K^+,BL
$NaBF_4$	BF_4^-, BL	Na^+, BL
$(CH_3)_4NCl$	Cl^-,BL	$(CH_3)_4N^+$, BL
KBF_4	BF_4^-,BL	K^+, BL

BL indicates direct reaction with the solvent. The data obtained with a 0.4 M solution of sodium tetrafluoroborate in butyrolactone are plotted in figure 7. The polarizations were conducted in two ways. In one case (Curve I) the working electrode was first made the anode, the current-potential curve run, then made the cathode, and the current potential curve run. In the second case (Curve II) the cathodic curve was run first, then the anodic curve. The difference in behavior then might be attributed to the accumulation of reaction products on or adjacent to the working electrode. Solutions of sodium tetrafluoroborate in butyrolactone exhibit different cathodic behavior depending on whether the anodic or cathodic polarization was run first. One explanation is that there is initially present in the solution some impurity that is reduced by the product obtained by anodic oxidation.

The anodic and cathodic behavior of a 0.02 M solution of tetra-methylammonium chloride is shown in figure 8. The oxidation of chloride ion occurs at a potential of approximately 1.4 v. This
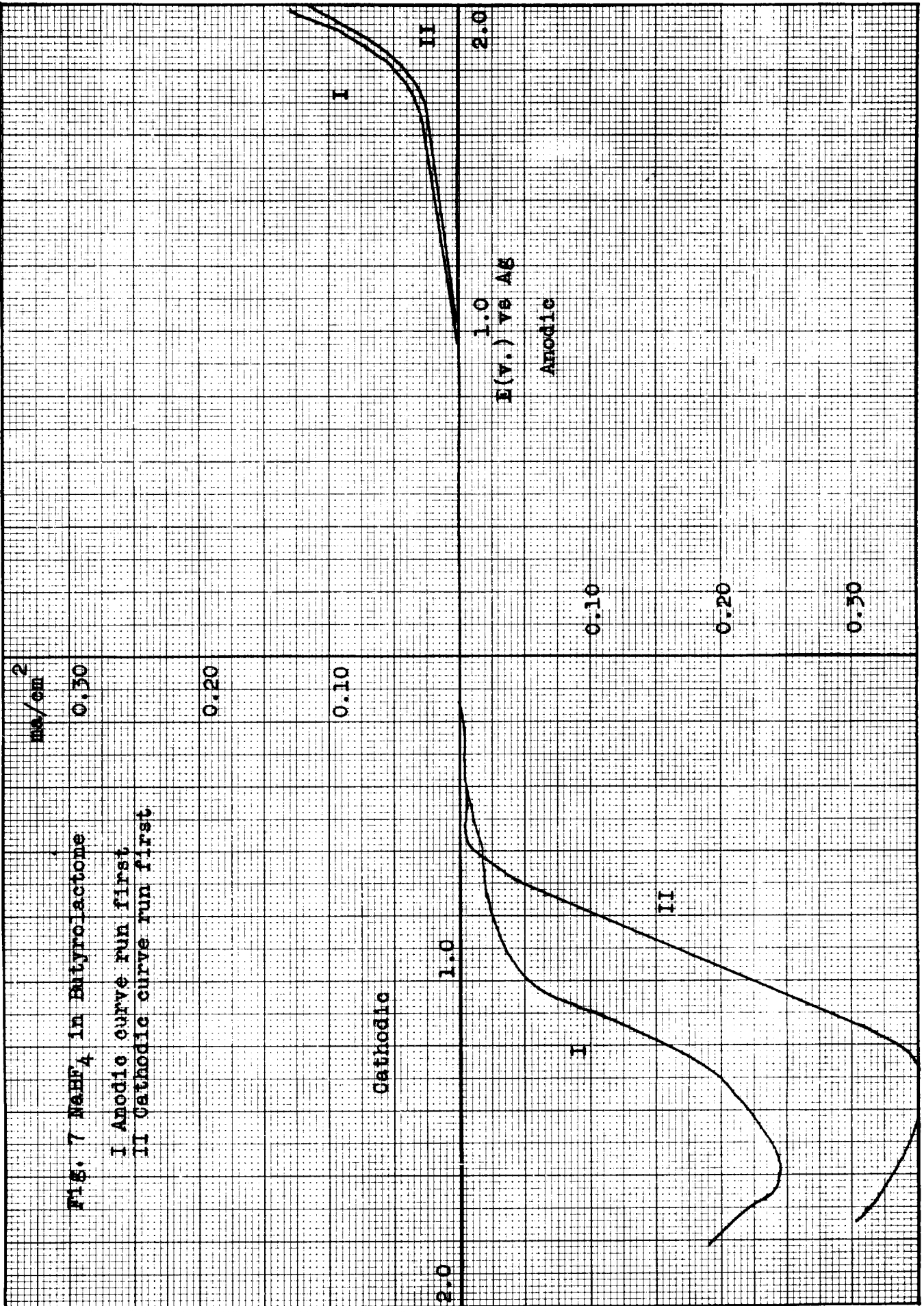
Fig. 7 NaBF$_4$ in Butyrolactone

I Anodic curve run first
II Cathodic curve run first

ma/cm^2

0.30

0.20

0.10

Cathodic

1.0

2.0

E(v.) vs Ag

Anodic

1.0

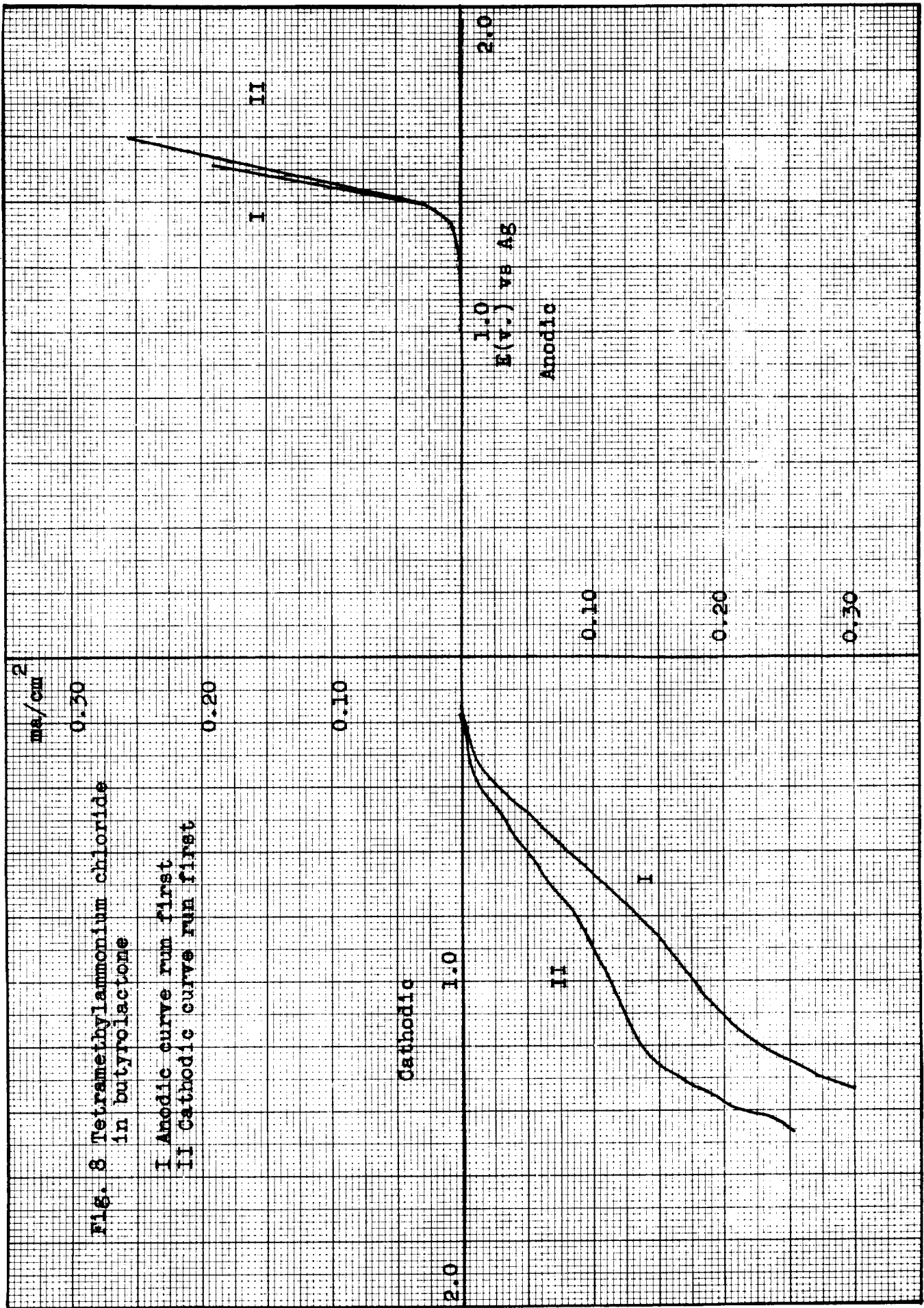2.0

0.10

0.20

0.30

I

II

Fig. 8 Tetramethylammonium chloride in butyrolactone

I Anodic curve run first
II Cathodic curve run first

may influence the cathodic behavior as well because to achieve cathodic potentials of about one volt it is required to go to cell voltages of such a magnitude that anodic potentials equivalent to the discharge of chlorine are reached. Once this occurs it is likely that there is sufficient material in solution to maintain a small residue current until chlorine can diffuse to the cathode.

The anodic and cathodic behavior of a 1 $\underline{M}$ KPF$_6$ solution has been given in figure 6.

As established above, in order for the decomposition potential to have meaning, it is necessary to specify some finite current. The value of 0.1 ma/cm^2 is arbitrarily selected as the point at which to measure the decomposition potential.

The decomposition values measured in butyrolactone to this point are as follows:

Dissolved salt	Decomposition potential		Decomposition Voltage
	Anodic	Cathodic	
KPF$_6$	2.52	1.82	4.34
NaBF$_4$	1.94	1.09	3.03
(CH$_3$)$_4$NCl	1.46	0.92	2.38

It is apparent that, with the exception of KPF$_6$ solutions, the measurement is determined by the electrode activity of the solute rather than the solvent.

Preliminary to the examination of the electrolyzed solution to determine reaction products metallic sodium, potassium, and lithium were allowed to stand in contact with the fractionated butyrolactone used in the above experiments. Infrared curves absorption curves were taken on the original solvent and after standing overnight. No changes were observed.

C. CONCLUSIONS AND DIRECTION OF FUTURE EFFORT

The concept of measuring and placing significance on a "minimum decomposition potential" appears to have merit. This is defined as the potential, anodic or cathodic, required to maintain a current density of the arbitrary value of $0.1 \ ma/cm^2$. The experimental data accumulated to this point indicate that the electrode activity of the solvent can be readily obscured by the activity of the supporting electrolyte. The nature and purity of the conducting ionic species must be given careful consideration. In a similar fashion careful attention must be given to the manner in which the solvent is dried. It appears that the desirable way to do this is to use physical adsorption techniques. To prevent cation exchange the molecule sieve should be selected on the basis of the cation in the supporting electrolyte. K^+, Na^+, or Ca^+ zeolites are available. This observation does not hold when the solvent itself is being dried.

From the standpoint of the direction of future effort it is intended to complete measurements on the decomposition potentials of the solvents indicated in Table I with specific attention being devoted to the nature and purity of supporting electrolyte. This electrochemical data will be supported by infra-red analysis of the solution for electrolytic products and gas chromatographic analysis of trace products in the solution and in the gas phase.

III. HIGH ENERGY CATHODE MATERIALS

A. BACKGROUND

The initial objective of this part of the program is to establish guiding principles relating the structure of organic molecules to their electrochemical activity, the latter being defined in terms of reduction potential, capacity, and electrode efficiency. The need to consider both potential and capacity has been discussed above. In the following section some rules developed by an analysis of previously reported work are given. The analysis of the experimental work, largely work done in the RCA Laboratory, is not complete. However, certain observations which point to the desirable electrochemical properties of N-halogen organic molecules and the nitro-substituted compounds are stated.

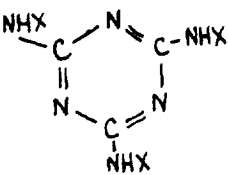B. STRUCTURE AND ELECTROCHEMICAL ACTIVITY
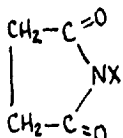
Nitrogen-Halogen Compounds
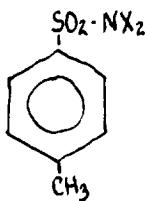
The nitrogen-halogen organic compounds have been studied in detail (22). The common feature of this class of compounds is the "positive" halogen attached to the nitrogen, and this halogen is electroactive by virtue of either hydrolysis and then reaction, or by direct reaction. There is evidence for both mechanisms and obviously this would be a significant point to establish if these co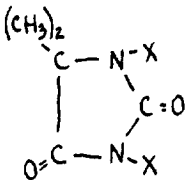mpounds were to be used in nonaqueous solvents. In the survey of Morehouse and Glicksman (22) the following type of halogen-substituted compounds were investigated: amides of carboxylic acids, amides of sulfonic acids, imides derived from dibasic acids, both straight chain and cyclic amides of carbonic acid (urea), amidines of carbonic acid (guanidine). The technique used to study these compounds involved discharging a cell, in which the compound was the cathode material, at a constant current drain equivalent to 0.03 0 amp/gram.

One of the significant points disclosed was the high potential developed by these compounds, many of them discharging initially at 0.8 to 1.0 v. (vs. hydrogen). It is possible that the potential represents that of the halogen electrode with a kinetic step accounting for differences in capacity.

Chloro compounds in several categories discharge at higher potentials and give a greater capacity than bromo compounds. In addition to the high potential, certain compounds discharge with relatively high efficiency with flat discharge curves.

A comparison of N-bromo compounds and N-chloro compounds is given in Table II.

Table II N-Cl and N-Br Compounds

Structure	Initial Potential		Electrode Efficiency		Shape of Discharge Curve	
	Cl	Br	Cl	Br	Cl	Br
(melamine derivative, NHX–C=N–C–NHX ring, NHX)	1.156	0.88	43.9	--		
(succinimide derivative, CH₂–C=O / NX / CH₂–C=O)	1.00	0.98	48.5	38.6		
(toluenesulfonamide, SO₂·NX₂ ... CH₃)	0.895	0.998	52.6	31.9		
(dimethylhydantoin, (CH₃)₂C–N–X / C=O / O=C–N–X)	0.98	0.80	46.0	49.9		

The influence of the electrolyte is quite pronounced as shown by discharge curves for hexachloromelamine, trichloromelamine, and the dichlorodimethylhydantoin in acid ($AlCl_3 \cdot 6H_2O$), neutral ($MgBr_2 \cdot 6H_2O$), alkaline (30% NaOH - 70% H_2O (satd. with ZnO) solutions. In the $AlCl_3 \cdot 6H_2O$ electrolyte, hexachloramelamine discharges at a potential of

approximately 1.20 v with a capacity of about 36 amp. min. per gram or 62% of theoretical. Cathode efficiencies calculated for the discharge of hexachloromelamine and trichloromelamine indicate that 5 and 2 chlorine atoms are used respectively.

Many of the N-halogen organic compounds have been observed to behave electrochemically like the hypohalous acids and their salts. It was observed that high solubility of the compound in the electrolyte was undesirable and for that reason within a certain class of compounds the cathode efficiency increased with increase in chain length of the compound.

The electrochemical properties of several N-chlorocompounds are such as to suggest more detailed attention on our program. These include dichlorobiuret, N, N'-dichlorodimethylhydantoin, hexachloromelamine,and trichloromelamine.

Cathode Material	Theoretical Capacity	Obtained	Efficiency
N,N' – dichlorobiuret	37.4	15.0	40.1
N,N' – dichlorodimethylhydantoin	32.6	15.0	46.0
Trichloromelamine	42.2	18.	43.9
Hexachloromelamine	58.0	19.5	33.6

This N-chloro class of compounds can be considered in the high energy category from a practical viewpoint. Reserve cells with magnesium anodes and dichlorodimethylhydantoin discharged on an energy basis of 2.7 to 6.2 watt-min/g. (22)

Aromatic nitro compounds

The systemic study of aromatic nitro compounds has disclosed certain groups of high energy compounds and principles which bear on the development of high potentials and capacities in compounds of this type. (23) In the nitrobenzene reduction scheme only nitrobenzene and nitrosobenzene can be considered to be high energy compounds. Certain reduction intermediates or side products such as azobenzene are removed from consideration. Substitution of various groups on the ring of aromatic nitro compounds
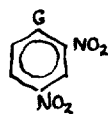
have a significant effect on potential. Empirical rules were developed and interpreted in terms of theory. One of the rule is that the substitution of an electron attracting group, such as NO_2, CN, and CHO, in the para-position causes the initial potential for reduction to be increased by 0.05 - 0.20v.

Electron - repelling groups, such as NH_2, - N $(C_2H_5)_2$, - CH_3, and ONa in the para-position result in compounds reducing at potentials 0.10 - 0.20 v. lower than nitrobenzene.

Such rules are not surprising in view of modern theory. Structure or functional groups that withdraw electrons from the oxidizing group would be expected to aid the reduction (gain of electrons) of the oxidizing group. That is, electron withdrawing groups should make the oxidizing group a more powerful electron acceptor. Electron-donating groups should have effects opposite to those of electron-withdrawing groups. Futhermore those molecules in which the electron-withdrawing groups are so located that a maximum of their electronic effects can act on the oxidizing group should be the best cathodic materials, at least on a molar basis.

The general rule with regard to the effect of substitution on nitrobenzene in the para-position is that the initial reduction potential will be varied as NO_2 > CHO, $CONH_2$, CN, CO_2H, SO_3H > H > CH_3 > NH_2 > $-O^-$. This is the order of electron withdrawing strength of the various groups.

This same effect is also found in polynitro compounds. For example in the 2,4-dinitrophenyl derivatives , as G varies, voltages are in the relative order SO_3K > Cl > H > CH_3 > NH_2. The effect of several electron withdrawing groups is cumulative in the sense that a second electron group will raise the potential still further. That is as might be predicted. The relative initial voltages of the following series are:
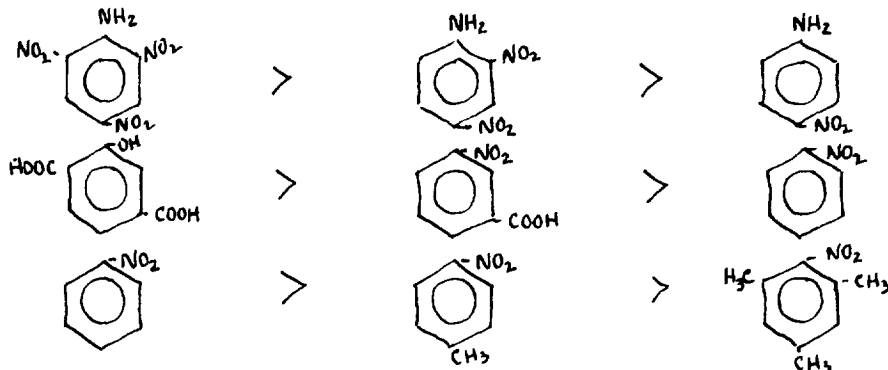
The effect of the position of the various groups also varies as would be expected. m-Nitrotoluene has a higher initial voltage than p-nitrotoluene because in the meta derivative only the inductive effect can donate electrons while in the para position both the resonance and the inductive effects can. para-Dinitrobenzene has a higher initial voltage than m-dinitrobenzene because in the para position both resonance and inductive effects can withdraw electrons whereas in the meta position only the inductive effects can act.

The electronic effects discussed here apply when the rate determining step is the electron transfer step. However, in many situations the rate limiting step is the supply of hydrogen ions. Changes of pH show up in the availability of hydrogen ions, the alteration of the chemical nature of the molecule, e.g. the neutralization of an acidic group or hydrolysis of other groups, and the encouragement of side reactions, e.g. coupling in alkaline solutions. In certain organic electrolytes, such as the esters, it is expected that such effects will be of great significance.

In many cases the reduction of the nitro compounds take place with the theoretical 6-electron change with an efficiency of 70-90%.

In the comparison of the ortho-, para-, and meta-dinitrobenzene it was observed that for the first step the ortho and para substituted compounds operate at an initially higher potential. Then when one of the nitro groups is reduced, the meta compound has the higher potential. This is explained on the basis that the potential reducing effect of the $-NH_2$ group is less when substituted in the meta position as compared to the ortho and para substitutions.

The electrode efficiency of aromatic nitro compounds also can be correlated with structure (Table III) The correlation however, is not as good as the structure-initial potential correlations discussed above.

Table III Structure and Electrode Efficiency

Compound	Electrode Efficiency (%)
1-nitronaphthalene	97.5
6-nitroquinoline	96.9
8-nitroquinoline	92.6
5-nitroisoquinoline	86.6
2-hydroxy-3-cyano-5-nitropyridine	86.5
2-hydroxy-5-nitropyridine	82.6
4-hydroxy-2-nitropyridine	82.3
5-nitroquinoline	81.2
2-hydroxy -3,5-dinitropyridine	76.8
m-dinitrobenzene	76.6
2-nitropyridine	66.3
3,5-dinitropyridine	62.4
4-nitropyridine	55.6
2-chloro-3,5-dinitropyridine	53.3
6,8-dinitroquinoline	49.1
2-nitro-1-(5-nitrofuryl) ethylene	27.1
2,5-dinitrofuran	25.2
2-nitrofuran	15.9

The obvious correlation from this table is that polynuclear nitro compounds have a higher efficiency than mononuclear nitro compounds. This might be expected because the π-electron systems of polynuclear aromatic systems act as better electron sinks than mononuclear systems because of the larger π cloud system. This is shown in many chemical reactions including electrophilic, free radical, and nucleophilic reactions. The last is the most closely related to the reductions of the cathodic material. Somewhat suprising is the fact that nitrogen heterocyclic compounds have lower electrode efficiencies than the corresponding benzenoid derivatives. This is not expected since a heterocyclic nitrogen atom in a six membered ring usually has a strong electron-withdrawing effect.

The cyano group shows the expected effect in raising the electrode efficiency. Hydroxy groups if not in the position where their electron-donating resonance effects can act, raise the electrode efficiency as the hydroxy group is electron-withdrawing by the inductive effect. Note the reported efficiencies for 2- and 4- hydroxynitropyridines in Table III.

Nitroso Compounds

Aromatic C-nitroso compounds were investigated by the RCA group because of their reported high potentials and their reversible character (24). Several general observations may be made on nitroso compounds. The C-nitroso compounds, compounds in which the nitroso group is attached to a carbon, are discharged at potentials 0.6 - 0.7 v higher than the corresponding N-nitroso compound. Nitrosobenzene is a stronger oxidizing agent than the corresponding N-nitroso compound. Nitrosobenzene is a stronger oxidizing agent than nitrobenzene and nitroso compounds are discharged at potentials 0.2 - 0.4 v higher than the corresponding nitro compound. Oximes (-C = N-OH) and N-oxide compounds operate at potentials low as compared with nitroso compounds. The potentials of aromatic nitroso compounds increases as the pH decreases as suggested by the mechanism that utilizes hydrogen ions in the reduction process and in view of the side reactions that take place in alkaline solutions. Of interest is, p-nitrosophenol which discharges in a flat discharge curve up to 92% of theoretical capacity at a potential of about 0.0 volts (hydrogen scale). The substitution of a second nitroso compound or of a nitro compound on the parent nitroso compound yields a compound of lower discharge potential. There is some uncertainty in the structure of nitroso compounds. They do not follow the theory developed and applicable to nitro compounds and this may be the reason.

Less data are available on the electrode efficiencies of aromatic nitroso compounds than on the electrode efficiencies of aromatic nitro compounds. There is some indication that here also electron-withdrawing groups raise the electrode efficiency. Surprisingly, amino and hydroxy

groups markedly raise the electrode efficiency if they are in the proper
position for their resonance effects to act. This is probably because
of strong contribution from resonance structures such as II and IV,
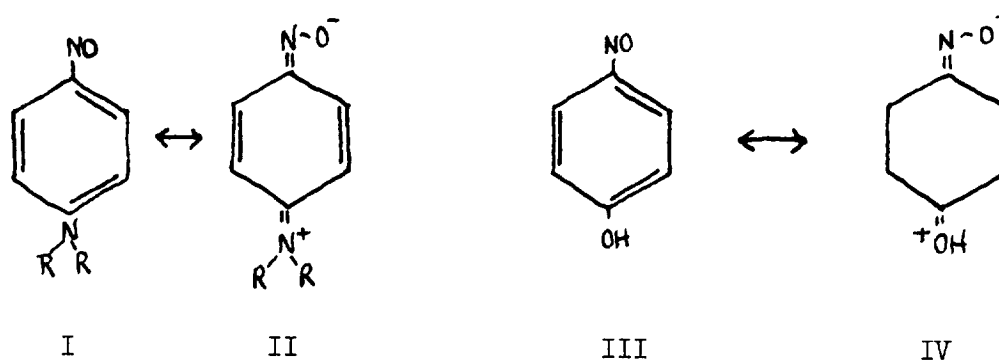
or from tautomerism so that what is actually being reduced is something
more nearly a quinoid-oxime structure than an aromatic nitroso compound.
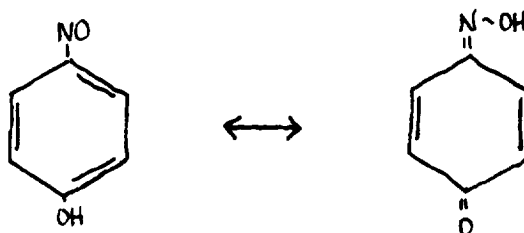
This is partly verified by the fact that allyl groups which cannot
contribute to any quinoid structure decrease electrode efficiency
and initial potential.

Nitroalkanes

The RCA group extended their investigation to the nitroalkanes
(25) and the cathodic behaviors of various compounds were explained
on the basis of a rate controlling electron transfer step dictated
by the electron-configuration of the molecule. Simple nitroalkane compounds
such as nitroethane and nitropropane operate at lower potentials than nitro-
benzene. The influence of substituted groups is based on their electron
attracting or repelling property as was the case in nitrobenzene.
Increasing the number of electron attracting group continues to raise
the initial potential.

Relative initial voltages for the chloronitroalkanes are in the following order: 1-chloro-1-nitropropane > 2-chloro-1-nitropropane > 3-chloro-1-nitropropane.

This would be expected as the farther away the chlorine atom is from the nitro group the weaker the inductive effect would be. The number and type of electron withdrawing groups also have the predicted effect on aliphatic compounds as is shown by the relative initial voltages in the following series:

$$C(NO_2)_4 > (NO_2)_3CCO_2 \ Et > (NO_2)_2C(CH_3)_2 > NO_2CH(CH_3)_2$$
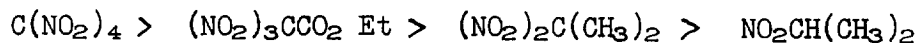
The first of the series had the highest potential, discharging at 0.8 volt.

The properties of some of these materials as compared with known cathode material are given in the following Table IV.

Table IV. Comparison of Cathode Materials

	Cathode	Physical State	Theoretical capacity amps-min/g.	Electrode efficiency (%)
1.	Manganese dioxide	solid	18.5	66
2.	Mercuric oxide	solid	14.9	70
3.	Nitrobenzene	liquid	78.4	
4.	m-dinitrobenzene	solid	115	77
5.	1,3,5-trinitrobenzene	solid	136	
6.	2-nitropropane	liquid	109	
7.	2,2-dinitropropane	solid	144	
8.	tetranitromethane	liquid	196	
9.	2,4,6-trichloro-2,4,6-trinitro heptane	solid	89.3	32
10.	4-bromo-4,4-dinitrobutyric acid	solid	75.1	36
11.	1,1,3,3-tetrabromo-2,2-dimethyl-1,3-dinitropropane	solid	40.4	50
12.	1,1,3,3-tetrachloro-2,2-dimethyl-1,3-dinitropropane	solid	64.3	48
13.	1,1,4,4-tetrabromo-1,4-dinitro-butane	solid	41.7	52

Of these sompounds, tetranitromethane has a capacity that is close to oxygen itself. When coupled with a magnesium electrode a galvanic cell with a potential of 2.0 - 2.1 v. is developed. The tetrabromo compound operates at a potential higher than the tetrachloro compound by about 0.2 v. The best performance is in acid solution but these compounds are not as pH dependent as the nitro aromatic compounds are.

Quinone-Type Compounds

A group of reactions involving the quinoid-benzenoid equilibria is of interest because it is a reversible system. The discharge characteristics of para and orthoquinone were measured. (26,27) The potentials of some of the quinone type compounds are high, although in the particular test (27) which involved discharge at 0.005 amp/g, the reversible potential was not approached. The initial discharge potentials of various of these structures were measured as follows:

p-quinone (neutral soln)	about	0.2 v.
1,4 napthoquinone	"	-0.1 v.
anthraquinone	"	-0.4 v.
2,5-dichloroquinone (neutral soln)	"	+0.28
p-quinone (acid soln)	"	+0.46
2,5-dichloro-p-quinone	"	+0.40

The actual capacities of these compounds were low because of the low efficiency, with the exception of p-quinonedioxime which operated at 93.3% of its 69.9 amp-min/g capacity (65.2 amp-min/g). The analogous 2,5-dichloro-p-quinone has a theoretical capacity of 18.2 and operated at 94.5% (17.2). The effects of substituent groups on the potential was similar to that predicted by Fieser based on the electron attracting ability of the groups.

- 40 -

C. EXPERIMENTAL

The preliminary correlation of <u>structure</u> and <u>electrochemical</u> activity suggested that experimental work be devoted to trichloromelamine, hexachloromelamine and related compounds. These compounds have high capacities and very high potentials. Moreover, halogenated compounds have been used as cathode "depolarizers" in non-aqueous solvents, e.g. inorganic halides in propylene carbonate.

The plan, then, is to work with trichloromelamine of high purity and reduce at controlled, constant potential, examine the reduction products, and outline the mechanism of reduction. This would be accomplished in a solvent such as propylene carbonate or butyrolactone.

Attempts were made to purify trichloromelamine (K and K Laboratories, Inc., No. 19117, lot 50575 L). In an ethanol-water mixture the compound was insoluble unless heated. However, upon heating the trichloromelamine was decomposed. Decomposition also occurred when recrystallization was attempted using concentrated HCl at room temperature (24°C). Attempts using cold H_2SO_4 (5 ml. 96% H_2SO_4 diluted with 25 ml. H_2O) and pouring over 100 g. of ice were also unsuccessful.

The reductions at constant potential are conducted with the Anotrol Potentiostat as schematically indicated in figure 1. Reductions at constant current are conducted with a Harrison Lab Constant Current Source No. 865C with a range of 1-40 volts, and 0-500 ma.

D. CONCLUSIONS AND DIRECTION OF FUTURE EFFORT

The analysis of the literature suggests that the most fruitful investigation would be on compounds including the nitrogen-halogen and nitro groups. However, attention will also be given to nitrogen heterocyclics and the pertinent literature on these compounds will be reviewed.

The experimental effort in the near future will be devoted to purification and reduction of the chlorinated melamines.

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