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CONTRACT REPORT

ORGANIC ELECTROLYTE BATTERY
(FINAL REPORT)

MASTER

Prepared by
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Globe-Union Inc.

SANDIA LABORATORIES

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Prepared by

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Globe-Union Inc., Milwaukee, Wisconsin

for

Sandia Corporation

under

Contract Numbers 53-0690, 58-4116, 58-5214

April 1969

i

Abstract

A technique was developed to rapidly screen potential cathode materials for a wide temperature range, $-54^{\circ}C$ to $+121^{\circ}C$, non-aqueous electrolyte battery. This screening technique, involving the testing of thin anodic films of materials, was applied to the chlorides, oxides and fluorides of silver, copper, nickel, cobalt, iron, manganese and chromium. The requirement that an anodic film of the material could be formed which was stable in at least one of the five organic test solvents, limited the applicability of the screening technique. Of the materials to which this technique could be applied, cobalt oxide, iron oxide and copper oxide failed to establish a reproducible open circuit potential in non-aqueous solvents. The remaining materials, silver chloride, silver oxide and cupric fluoride, gave potentials in a non-aqueous medium which were repro- ducible to within one millivolt and behaved reversibly to the application of anodic and cathodic potential (10 mv). Silver chloride and silver oxide were shown to be able to produce considerably more current at the same polarization from open circuit potential than copper fluoride and should therefore be more extensively investigated as electrode materials for a wide temperature range, non-aqueous battery. Evaluation of the materials which could not be studied as thin anodic films will have to await the development of suitable macro electrode techniques.

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Foreword

This report, "Organic Electrolyte Battery", is the final research report covering studies performed under SANDIA Corporation contracts Number 58-0690, 58-4116 and 58-5214, by the Electrochemical Research Department, Corporate Applied Research Group, Globe-Union Inc., in Milwaukee, Wisconsin. Work under these contracts was initiated on November 1, 1967 and completed on December 31, 1968.

Project Leader and principal investigator was Dr. Guy Mc-Donald. He was assisted by B. Cornilsen, T. Roemer, and K. Murphy. The Research Manager was Dr. E. Y. Weissman.

Chemical analyses required in this work were performed by Globe-Union's Materials Testing Laboratory under the direction of Dr. A. C. Eckert.

Technical monitoring of this project was performed by Dr. Samuel Levy of the SANDIA Corporation. His valuable assistance and encouragement are gratefully acknowledged.

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ORGANIC ELECTROLYTE BATTERY
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1. Introduction

The objective of this work is the development of a primary battery, either active or reserve type, which is capable of producing fifty watt-hours per pound of total battery weight over the temperature range $-54^{\circ}C$ to $+121^{\circ}C$. Our approach to the development of such a system is first to determine if there are suitable electrolytes for such a battery, then to evaluate the performance of potential electrode materials in these electrolytes and finally to determine fabrication variables affecting the performance of electrodes prepared from these electrode materials.

This is the second report issued relating to the development of this wide temperature range battery. The first report [1] dealt primarily with the study of electrolytes. It was shown that there are electrolytes, solvents plus conductive solutes, which are liquid and highly conductive over this temperature range. In addition, the important variables affecting electrolyte conductivity were shown to be viscosity, dielectric constant, and solvating ability of the solvent. It was demonstrated that electrolytes could be prepared whose conductivity changed very little with temperature (less than one order of magnitude over the temperature range) by using mixed solvents.

The work described in this report is concerned with the development of a rapid method for the screening of potential electrode materials and the application of this screening technique to twenty-nine materials.

Various approaches have been used for electrode screening in the past [2-9]. In general, the results of these studies have been ambiguous. One source of ambiguity has arisen from the methods used in fabricating test electrodes. In many cases subtle changes in fabrication techniques rather than in the active materials used, have been found to influence

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performance appreciably [2,9]. Reproducibility of electrode performance has been poor. In general, the optimized electrode structure for one electrode material cannot be assumed to be so for another material. For the rapid screening of a sizeable number of electrode materials, it is obviously too time consuming to attempt to prepare an optimized electrode structure in each case. Another source of ambiguity in the results reported, is that in some cases, the nature of the active material is not identified. For example, the anodization of a metal electrode in an organic electrolyte containing a hexafluorophosphate salt is assumed to give a metal fluoride electrode [8]. This supposition has not been substantiated as yet.

To circumvent the aforementioned pitfalls, the present study uses thin anodic films of the desired electrode materials formed on the parent metal under appropriate conditions for the formation of this material.

2. Experimental

2.1 Purification and Characterization of Chemicals

All chemicals used were of the highest purity commercially available and were handled in an inert atmosphere box. Solvents used for this work were obtained from the Eastman Organic Chemical Company (Rochester, N.Y.) and were treated as described in a previous report, namely: the solvents were dried over molecular sieves, distilled, and the moisture content was determined by gas chromatography or Karl-Fisher titration. If the solvent contained less than 50 ppm of water it was stored in sealed glass ampules until used.

Thermogravimetric analyses were run on all solid materials obtained to determine the maximum temperature to which they could be heated to remove

moisture without decomposition. The suppliers and the treatment given

each solute and electrode material are given in tables 1 and 2. After

that treatment, an x-ray powder pattern was taken to confirm the purity

of the material. Each material was stored in evacuated glass ampules

until used.

Tetrabutylammonium hydroxide was not commercially available. It

was prepared by the reaction

$$Ag_2O + 2Bu_4NI + H_2O \quad ---------- \quad 2AgI + 2Bu_4NOH$$
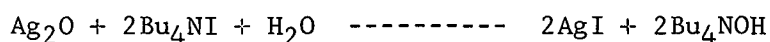
in aqueous medium, according to previously reported techniques [10,11].

The product was shown to be free of the iodide ion. Titration of the

product of this reaction with acid showed that the yield was 86% based on

the original tetrabutylammonium iodide.

Anhydrous hydrogen fluoride was obtained from the Matheson

Company.

The suppliers and dimensions of the metals used as substrates

in the preparation of anodic films are given in table 3.

2.2 Equipment

The following equipment was used: General Radio Type 1650A

impedance bridge; Hewlett-Packard Vacuum Tube Voltmeter, Model 412A;

Hewlett-Packard X-Y recorder, Model 2D-2AM; Malmstadt-Enke polarographic

unit with a chopper stabilized operational amplifier system; Keithley Solid

State Electrometer, Model 602; North Hills Electronics, Model CS-120,

constant current supply; and F and M Model 810 gas chromatograph. The

argon-filled inert atmosphere box equipped with a vacuum exchange entry

post and the distillation equipment have been previously described [1].

TABLE 1

CATHODE MATERIAL SUPPLIERS AND TREATMENT

Material	Supplier	Decomp.Temp.*	Treatment Before Use
AgF	Alfa Inorganics, Inc.	$80^{\circ}C$	$25^{\circ}C$ at 10 μ pressure
CuF_2	Alfa Inorganics, Inc.	$100^{\circ}C$	$25^{\circ}C$ at 15 μ pressure
$CuCl_2$	Fisher Scientific	$200^{\circ}C$	$125^{\circ}C$ at 15 μ pressure
CuCl	Fisher Scientific	$> 25^{\circ}C$	$25^{\circ}C$ at 3 μ pressure
CuO	Fisher Scientific	$> 500^{\circ}C$	100° at 15 μ pressure
Cu_2O	Fisher Scientific	$250^{\circ}C$	100° at 15 μ pressure
CoF_2	Ozark Mahoning	$25^{\circ}C$	$25^{\circ}C$ at 15 μ pressure
$CoCl_2$	Fisher Scientific	$360^{\circ}C$	$200^{\circ}C$ at 15 μ pressure
CoO	Alfa Inorganics, Inc.	$>500^{\circ}C$	$25^{\circ}C$ at 15 μ pressure
Co_2O_3	Alfa Inorganics, Inc.	$>500^{\circ}C$	$105^{\circ}C$ at 3.5 μ pressure
CrF_2	Ozark Mahoning	$250^{\circ}C$	$25^{\circ}C$ at 15 μ pressure
CrF_3	Ozark Mahoning	$>500^{\circ}C$	$25^{\circ}C$ at 15 μ pressure
$CrCl_2$	Fisher Scientific	$250^{\circ}C$	$100^{\circ}C$ at 15 μ pressure
$CrCl_3$	Fisher Scientific	$350^{\circ}C$	$25^{\circ}C$ at 15 μ pressure
Cr_2O_3	Fisher Scientific	$>500^{\circ}C$	$150^{\circ}C$ at 15 μ pressure
FeF_3	Ozark Mahoning	$25^{\circ}C$	$25^{\circ}C$ at 15 μ pressure
$FeCl_3$	Fisher Scientific	$250^{\circ}C$	$25^{\circ}C$ at 15 μ pressure
$FeCl_2$	Fisher Scientific	$300^{\circ}C$	$200^{\circ}C$ at 15 μ pressure
Fe_3O_4	Fisher Scientific	$180^{\circ}C$	$150^{\circ}C$ at 15 μ pressure
Fe_2O_3	Fisher Scientific	$> 500^{\circ}C$	$150^{\circ}C$ at 15 μ pressure
MnF_2	Optovac, Inc.	$450^{\circ}C$	$25^{\circ}C$ at 5.5 μ pressure
$MnCl_2$	Fisher Scientific	$400^{\circ}C$	$250^{\circ}C$ at 5 μ pressure
MnO_2	Fisher Scientific	$> 500^{\circ}C$	$250^{\circ}C$ at 15 μ pressure
MnO	Sergent and Co.	$250^{\circ}C$	$250^{\circ}C$ at 20 μ pressure
NiF_2	Ozark Mahoning	$100^{\circ}C$	$250^{\circ}C$ at 15 μ pressure
$NiCl_2$	Fisher Scientific	$>500^{\circ}C$	$300^{\circ}C$ at 15 μ pressure
NiO	Fisher Scientific	$>500^{\circ}C$	$110^{\circ}C$ at 15 μ pressure

* As determined from Thermogravimetric Analysis.

TABLE 2

SOLUTE SUPPLIERS AND TREATMENT

Material	Supplier	Decomp. Temp.*	Treatment Before Use (pressure)
$(CH_3CH_2)_4NF$	Southwestern Chem. Co.	$80°C$	$25°C$ at $10\,\mu$
Phenyl$(CH_3)_3NCl$	K and K Laboratories	--	$25°C$ at $10\,\mu$
KF	Baker and Adamson	$>500°C$	$200°C$ at $10\,\mu$
CaF_2	Fisher Scientific Co.	$>500°C$	$200°C$ at $10\,\mu$
$LiClO_4$	G. Frederick Smith Chem. Co.	$>500°C$	$160°C$ at $10\,\mu$

* As determined from thermogravimetric analysis.

TABLE 3

METAL SUBSTRATES

Metal	Supplier	Dimensions
Cobalt	Var Lac Oid Chemical Co. Elizabeth, New Jersey	0.040" drawn wire 99.9% pure
Nickel	Var Lac Oid Chemical Co. Elizabeth, New Jersey	0.080" drawn wire 99.5% pure
Copper	Central Steel and Wire Co. Milwaukee, Wisconsin	0.050" drawn wire 99.9% pure
Manganese	Foote Mineral Knoxville, Tennessee	Various Size Electrolytic flakes 99.99% pure
Iron	Semi Elements, Inc. Saxonburg, Pennsylvania	0.050" drawn wire 99.99% pure
Chromium	Atlantic Equipment Engineers Bergenfield, New Jersey	0.080" hot pressed wire 99.9% pure
Silver	Leach and Garner Co. Attleboro, Massachusetts	0.020" drawn wire 99.99% pure

2.3 Techniques used for Screening of Potential Cathode Materials

2.3.1 Selection of Materials

There are a large number of potential electrode materials which could be screened for battery applications. Since the desired battery requires 50 watt-hours per pound of total battery weight, evaluation of materials which theoretically cannot supply this specific energy can be excluded. For that matter, electrode couples which are not capable of providing a minimum of 200 watt-hours per pound can likewise be excluded because of the extent of anticipated parasitic weight increases in the system caused by electrolyte, separator, current collectors, additives, battery cases, and unused portions of the active materials. There remains, however, a large number of materials which are still theoretically capable of providing the desired specific energy. Since the amount of time and effort that can be spent on such a screening program (cathode materials in this case) is limited, it was decided to concentrate on the oxides, fluorides and chlorides of transition metals. The selected materials along with the specific energy of various electrode couples are given in the table 4 . This group contains what appears at this time to be the most promising materials for this study.

2.3.2 Test Electrolytes

The electrochemical evaluation of electrode materials requires special electrolytes which are capable of providing the appropriate ions required by the electrode mechanism. Two types of mechanisms for the study of positive electrodes can be proposed in which the electrolyte does not have to provide specific ions for the reaction to occur (the nature of the ions present in the electrolyte does, however, control the nature of the product formed and therefore influences the reaction).

In one case, the reaction product is soluble, and in the other it is insoluble at the electrode surface. For example, one could propose to use an electrolyte containing lithium perchlorate for the evalua-

TABLE 4

SPECIFIC ENERGY OF ELECTRODE COUPLES IN WHr/lb.

Anode Cathode	Lithium	Magnesium	Calcium	Zinc
AgF_2	786.0	650.0	--	--
AgF	375.4	307.5	339.3	124.8
AgCl	229.8	150.9	204.5	53.6
AgO	520.9	491.0	472.0	219.0
CuF_2	749.0	566.0	--	151.4
$CuCl_2$	477.2	332.0	415.0	122.0
CuCl	316.3	201.8	271.8	63.8
CuO	583.5	538.0	503.0	166.1
Cu_2O	331.7	318.4	314.5	103.8
CoF_2	633.0	454.0	504.7	57.1
$CoCl_2$	425.5	259.9	352.7	61.5
CoO	493.4	465.0	436.8	101.3
Co_3O_4	635.9	572.0	522.8	130.8
CrF_2	551.4	369.0	433.1	--
CrF_3	628.0	463.1	523.9	--
$CrCl_2$	378.8	201.8	304.3	8.67
$CrCl_3$	462.5	255.0	363.8	29.6
Cr_2O_3	420.0	370.4	354.0	--
FeF_3	--	--	--	--
$FeCl_3$	513.9	349.7	446.6	105.2
$FeCl_2$	320.6	241.9	338.1	44.1
Fe_3O_4	540.7	483.8	450.4	66.0
Fe_2O_3	590.7	523.7	481.8	75.6
MnF_2	495.5	322.6	390.8	--
$MnCl_2$	294.2	126.6	234.3	--
MnO_2	724.1	626.0	560.0	99.2
MnO	295.0	272.7	273.3	--
NiF_2	571.0	445.0	496.2	49.4
$NiCl_2$	434.9	262.0	354.4	62.6
NiO	490.4	449.0	425.2	91.7

tion of a fluoride electrode material, i.e., AgF. The reaction occurring
at the cathode would be:

$$e^- + AgF + Li^+ \text{ ----------- } Ag + LiF$$
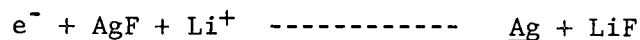
On the other hand, one could study AgF under conditions which gave a
soluble reaction product. One could use phenyltrimethylammonium perchlorate
as a solute since phenyltrimethylammonium fluoride is soluble in organic
solvents. The electrode reaction would then be:

$$e^- + AgF \text{ ------------------ } Ag + F^-$$
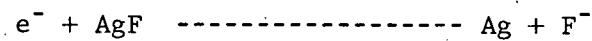
One sees, however, that the electrode would immediately polarize on dis-
charge since the potential of the electrode would be controlled by the
Nernst equation:

$$E = E_o - 0.059 \log F^-$$

A plot of this relationship is shown in figure $\underline{1}$. To avoid the initial
polarization exhibited by the left hand portion of the curve, it would be
desirable to discharge the electrode in a medium already containing fluoride
ions. To do this requires the use of an electrolyte containing a soluble
fluoride.

Similar reasoning can be applied to the chloride studies.

The oxide studies pose an additional complication. To form an
insoluble product, one could use lithium perchlorate as before:

$$Ag_2O + 2Li^+ + 2e^- \text{ ----- } 2Ag + 2Li_2O$$
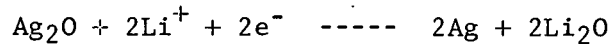
To form a soluble reaction product, however, the following reaction would
have to occur:

$$Ag_2O + H_2O + 2e^- \text{ ------ } 2Ag + 2OH^-$$

and one would have to develop an electrolyte which contained a soluble
hydroxide while tolerating an appreciable concentration of water.

With the objective of developing these special electrolytes in

Figure 1

Effect of Fluoride Ion Concentration
on Silver Fluoride Electrode Potential

Fluoride Ion Concentration
(moles/liter)

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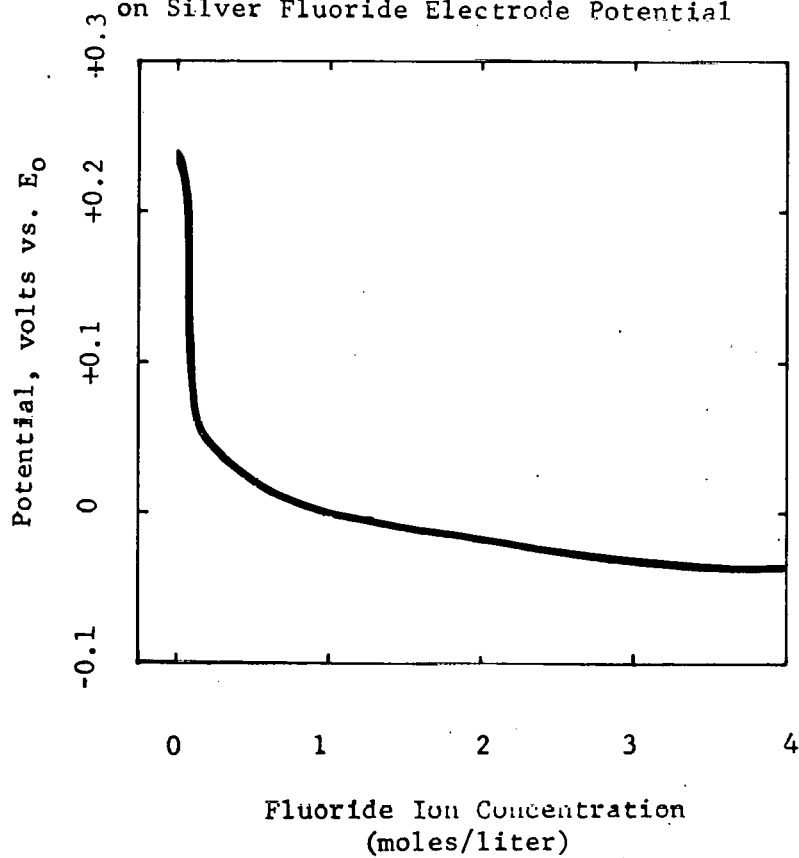
mind, five of the solvent systems found in previous electrolyte studies[1] were chosen on the basis of their general high conductivity with the solutes studied, and compatibility with the temperature range required. They are acrylonitrile (AcN), 60% acetonitrile - 40% dimethylformamide (AN-DMF), 60% acetronitrile - 40% N-nitrosodimethylamine (AN-NDA), 55% acetonitrile - 45% 2-butanone (AN-2B) and 2-butanone (2B). The solubility and conductivity of lithium perchlorate has already been shown to be quite good in **these solvent** systems [1]. One could then evaluate the performance of metal oxides, chlorides **and fluorides** under the condition of insoluble reaction products (formation of insoluble lithium salts). Suitable solutes, however, had to be found to evaluate these materials under conditions which would not precipitate the reaction products on the electrodes.

Two fluoride-containing solutes were investigated as possible sources of soluble fluoride: calcium fluoride and tetraethylammonium fluoride. Calcium fluoride was found to be insoluble in the solvents chosen. Tetraethylammonium fluoride was found to react vigorously with acrylonitrile. While tetraethylammonium fluoride was not completely soluble in the other (four) electrolytes at one molal concentration, the conductivity of saturated solutions of it in these solvents was reasonably good (see table 5).

Two chloride-containing solutes were tested, magnesium chloride and phenyltrimethylammonium chloride ($\emptyset Me_3 NCl$). Five of the possible eight combinations of these solutes with the solvents were found to give reasonably conductive solutions. The conductivities of these five electrolytes are given in table 5 .

The development of a suitable hydroxide containing electrolyte requires not only a soluble hydroxide which gives a conductive electrolyte

TABLE 5

ELECTROLYTE CONDUCTIVITY

Solute (1m)	Solvent(s)	Conductivity (25°C) ohm^{-1} cm^{-1}
Et$_4$NF	AN-2B	1.8 x 10^{-2}
Et$_4$NF	AN-DMF	1.4 x 10^{-2}
Et$_4$NF	AN-NDA	6.9 x 10^{-3}
Et$_4$NF	2B	1.0 x 10^{-3}
MgCl$_2$	AN-DMF	1.6 x 10^{-2}
MgCl$_2$	AN-NDA	1.6 x 10^{-2}
ØMe$_3$NCl	AcN	1.6 x 10^{-3}
ØMe$_3$NCl	AN-DMF	2.5 x 10^{-3}
ØMe$_3$NCl	AN-NDA	2.2 x 10^{-3}
Bu$_4$NOH	AN-DMF	9.1 x 10^{-3}
Bu$_4$NOH	AN-NDA	9.8 x 10^{-3}
Bu$_4$NOH	AN-2B	9.1 x 10^{-3}
Bu$_4$NOH	2B	2.5 x 10^{-3}
LiClO$_4$	AN-DMF	3.0 x 10^{-2}
LiClO$_4$	AN-NDA	2.3 x 10^{-2}
LiClO$_4$	AN-2B	2.5 x 10^{-2}
LiClO$_4$	2B	1.5 x 10^{-2}

Key:

AN-2B	55 mole % Acetonitrile - 45 mole % 2-Butanone	
AN-DMF	60 mole % Acetonitrile - 40 mole % Dimethylformamide	
AN-NDA	60 mole % Acetonitrile - 40 mole % N-nitrosodimethylamine	
2B	2-butanone	
AcN	Acrylonitrile	
Et$_4$NF	Tetraethylammonium fluoride	
ØMe$_3$NCl	Phenyltrimethylammonium chloride	
Bu$_4$NOH	Tetrabutylammonium hydroxide	

but also an electrolyte which is capable of tolerating appreciable amounts of water, since water is required in the proposed mechanism for oxide reduction. Water was found to be immiscible with acrylonitrile, eliminating this solvent from the screening of oxides. The experimentally determined phase diagrams for three solvent mixtures (acetonitrile - 2-butanone, acetonitrile - N-nitrosodimethylamine, and acetonitrile - dimethylformamide) are given in figure 2 . Table 6 gives the composition of organic solvents and water which freeze below -54°C. The conductivity of solutions of tetrabutylammonium hydroxide (Bu$_4$NOH) in organic solvents were found to be reasonably good at room temperature, (table 5).

2.3.3 Stability of Cathode Materials in the Electrolytes

For the initial rapid screening of electrode materials, the stability criteria were: 1) no visible interaction between the electrode material and the organic solvent; 2) sufficiently low solubility of the electrode materials in the solvents to permit thin film evaluations.

The stability of each material of interest in five organic solvents was determined by adding some of the organic solvent (approximately 5 ml) to a small quantity of the material (approximately 5 grams) in a glass tube in an inert atmosphere box. After filling, the tubes were immediately sealed. The tubes were checked initially, after two hours, after 24 hours, two days, one week and thirty days to determine if any visible interaction had occurred. A material was called stable only if there was no apparent interaction with the solvent after thirty days.

2.3.4 Preparation of Test Electrodes

The approach used to fabricate test electrodes was to anodically form films of the materials to be studied, using the parent metal or substrate and appropriate experimental conditions. In general, this meant

Figure 2

Phase Diagram of Mixtures of Organic
Solvents with Water
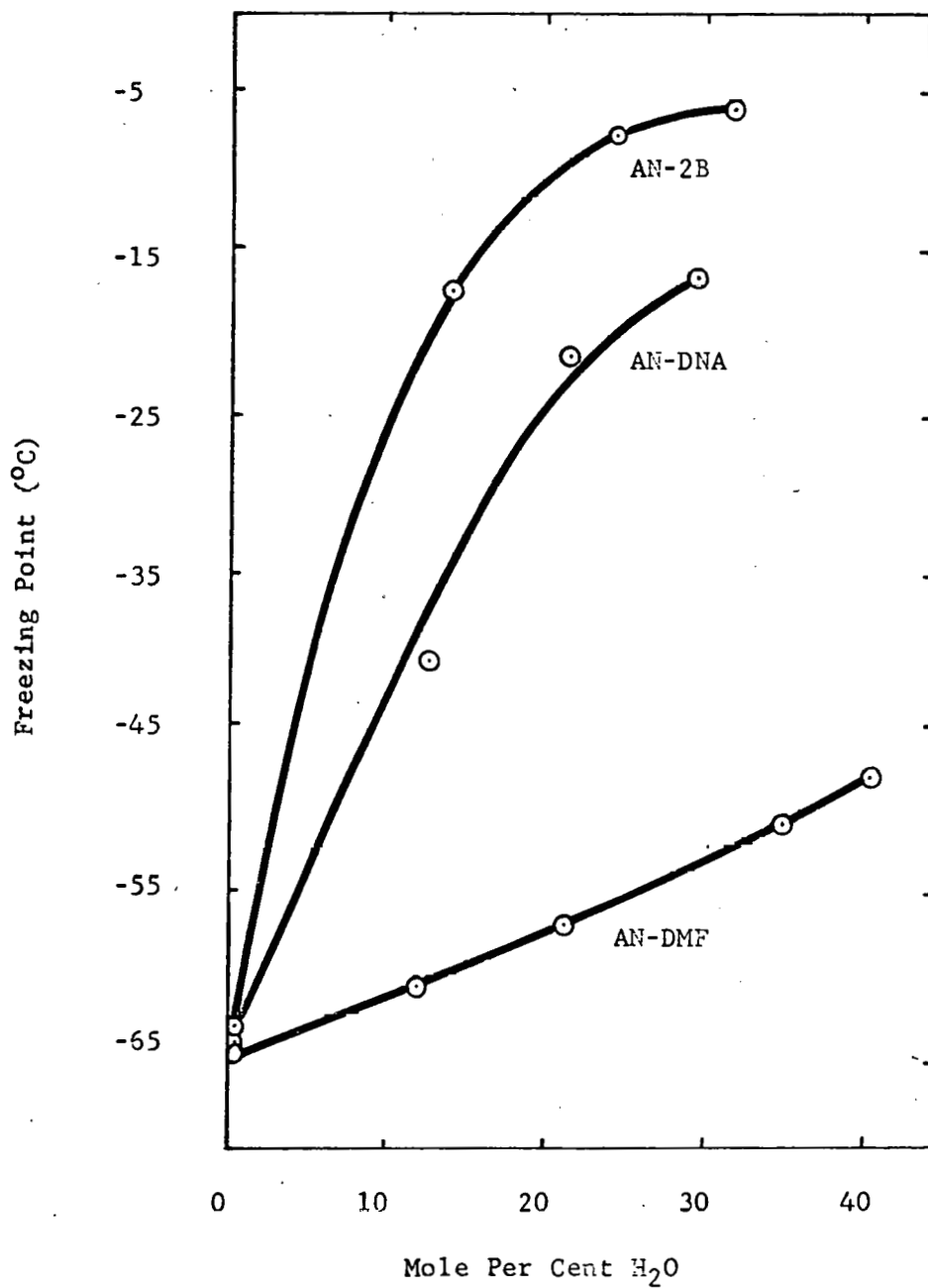
TABLE 6

COMPOSITION OF SOLVENTS FREEZING BELOW $-54^\circ C$

Solvent	Maximum Water Content
60 mole % Acetonitrile - 40 mole % Dimethylformamide	25 mole % H_2O
60 mole % Acetonitrile - 40 mole % N-nitrosodimethylamine	4.5 mole % H_2O
55 mole % Acetonitrile - 45 mole % 2-Butanone	2.5 mole % H_2O
2-Butanone	4 mole % H_2O

anodizing a piece of metal in an appropriate electrolyte and then testing the film formed in the desired non-aqueous medium. Since no conductive additives, expanders, binders, current collectors, etc. are required for thin films of material in intimate contact with a conductive metal surface, the results obtained from such an electrode should be optimum for that electrode material, so long as deep discharges are not required.

The uses of wire substrates embedded in an epoxy resin has a distinct advantage over other electrode configurations because of the ease of reproducing the surface area of the electrode. All that would be required is to polish the ends of the wires to renew the electrode surface. It was found, however, that a satisfactory bond along the edges of the metal wire could not be obtained and therefore, the surface area of the electrode could not be controlled. To circumvent this problem, a metal disc electrode was used. The size of the metal disc (66.1 mm^2) was large enough so that effects caused by the contact wire (spot welded to the disc) was minimal. This electrode was found to be satisfactory for the initial studies. Later, it was found that a suitable electrode could be obtained using heat-shrinkable teflon tubing (Penntube Plastics Company, Clifton Heights, Pa.) provided not too much force was applied to the wire during polishing. All subsequent electrodes (other than the silver electrodes) were therefore prepared using the heat-shrinkable tubing.

The study of manganese was hampered by the lack of manganese rod. No suppliers could be found who were able to supply 50 thousandths manganese rods. Attempts to fabricate manganese substrates from electrolytic flake met with only limited success. The roughness of these flakes and the problems encountered in attempting to polish such a refractory and brittle material made it impossible to produce a series of electrodes of uniform area.

Films of the desired materials were formed on these metal substrates by anodization in appropriate electrolytes. In the case of metal fluorides, anhydrous hydrogen fluoride was used. To make the hydrogen fluoride conductive, the solutions were made one molal in potassium fluoride. The handling of anhydrous hydrogen fluoride required the development of special equipment and techniques. A line was fabricated for handling the anhydrous hydrogen fluoride from commercially available teflon tubing, valves, tees and adaptors (Fisher Scientific Company, Chicago, Illinois). A diagram of this line is shown in figure 3 . An all teflon cell was constructed (figure 4) which was sealed with an "ethylene-propylene" type 559N rubber o-ring (Minnesota Rubber Company , Minneapolis, Minnesota). No problems were encountered in the the use of this equipment and hydrogen fluoride was found to be relatively easily handled. With reference to figure 3 , the first (upstream) cell was filled with hydrogen fluoride by cooling it with a dry ice-acetone bath and passing hydrogen fluoride through. After filling the cell, the flow was shut off. The hydrogen fluroide was transferred into the second (downstream) cell by passing high purity nitrogen through the first cell and through the cooled second cell. Total time to fill the first cell and transfer the hydrogen fluoride to the second cell was usually less than one hour. At first, hydrogen fluoride was removed from the cell by passing nitrogen over it until it evaporated. This was found to be unsatisfactory because the potassium fluoride in the hydrogen fluoride would deposit on the electrodes. A syphon was placed in the bottom of the cell so that the hydrogen fluoride could be transferred in liquid form to a trap from which it could be vaporized and disposed of by passing through a magnesium oxide and calcium fluoride trap. All electrodes were mounted through the teflon cell, size on size (i.e., 20 thousandths wire in a 20

Figure 3

Anhydrous Hydrogen Fluoride System
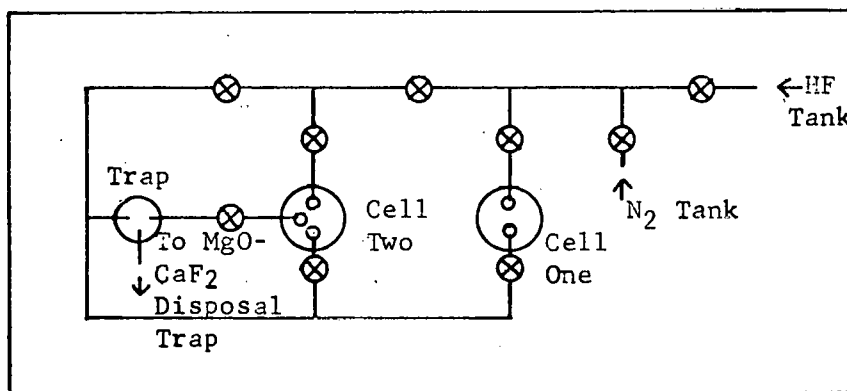
$\otimes$ - Stopcock

Figure 4

Teflon Hydrogen Fluoride Cell

Teflon Pipe Adapter

Electrolyte Syphon
"Ethylene-propylene"
O-ring.
Platinum Electrolyte
Level Electrode.
Working and Reference
wires embedded in heat-
shrinkable tubing.

Counter Electrode

Teflon Container with
50 ml capacity.

Potassium Fluoride
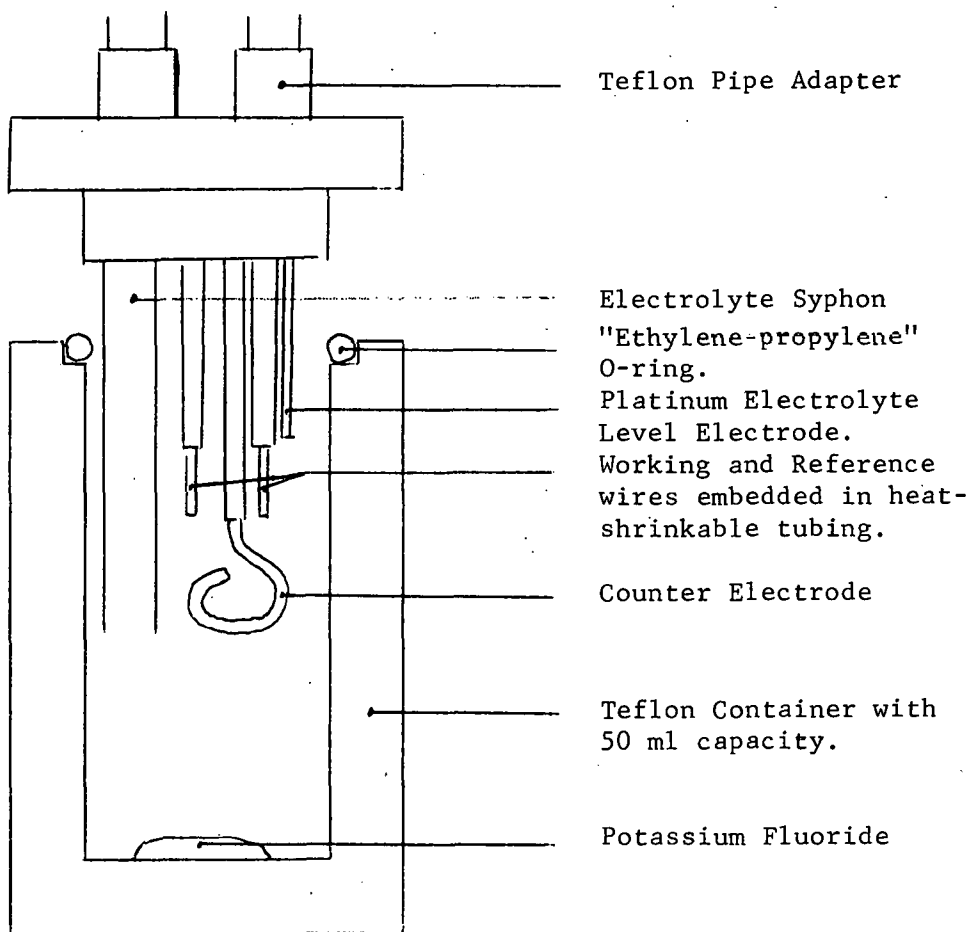
thousandths hole). No leakage was detected. No evidence was found for
the presence of an impurity peak on the cyclic voltammograms of the 1M
KF - hydrogen fluoride electrolyte, which has been reported by Burrows
and Jasinski [12]. The fluoride electrodes were left in the teflon cells
and brought directly into the inert atmosphere box via the vacuum exchange
port so as to avoid any contact with the atmosphere.

The formation of oxide and chloride electrodes required no
special equipment other than that needed to maintain an inert atmosphere
over the formation cell. All electrodes, once formed, were rinsed in
distilled water and immediately transferred to the vacuum exchange part of
the inert atmosphere box. They were held under vacuum for a minimum of
thirty minutes before being allowed to enter the box proper for testing.

A summary of the techniques and conditions used for forming
each of the electrode materials is given in table 7 .

2.3.5 Electrochemical Testing Criteria

The performance criteria required to qualify an electrode
material for future evaluation were: establishment of a reproducible open
circuit potential ($\pm$ 1 mv) in the organic electrolyte, ability to return
to this potential after small overpotentials (10 mv) had been applied and
the ability to produce reasonable current densities (greater than 40 $\mu a/cm^2$)
at limited polarizations (5 mv).

TABLE 7

PREPARATIVE TECHNIQUES FOR THIN FILM ELECTRODES FORMATION

Material To Be Deposited	Tech. No.	Electrolyte	Technique	Ref.
AgF	1	1mKF-HF	Potentiostatic anodization of silver.	--
AgCl	1	1M KCl aq.	Galvanostatic 0.5ma.	13
	2	0.1M HCl aq.	Galvanostatic 0.5ma.	--
	3	Molten AgCl	Silver wires dipped into molten AgCl.	--
	4		Pressed silver chloride onto silver substrates.	--
	5		Pressed silver chloride + 10% acetylene black onto silver substrate.	--
AgO	1	1M KOH aq.	Galvanostatic 0.5ma.	13
CuF_2	1	1m KF-HF	Potentiostatic anodization +0.5V vs Cu/CuF_2	12
CuO	1	1M KOH aq.	Galvanostatic 4ma/cm^2.	--
Cu_2O	1	1M KOH aq.	Galvanostatic 4ma/cm^2.	--
CoF_2	1	1m KF-HF	Potentiostatic +0.5V	--
CoO	1	6N KOH aq.	Potentiostatic cathodes cleaning at -1.40V vs calomel followed by potentiostatic anodization at +0.35 volts.	--
CrF_3	1	1m KF-HF	Potentiostatic +0.5V.	--
Cr_2O_3	1	1m KOH	Galvanostatic 0.01-4ma/cm^2.	14-18
FeF_3	1	1m KF-HF	Potentiostatic +0.5V.	--
Fe_2O_3	1	Borate buffer	Potentiostatic anodization of iron at -750mv vs calomel reference.	19-22
	2	Borate buffer	Potentiostatic anodization of iron at -730mv vs calomel.	19-22
MnO_2	1	1m KOH aq.	Galvanostatic 0.01 -4ma/cm^2.	--
NiF_2	1	1m KF-HF	Potentiostatic +0.5V.	--
$NiCl_2$	1	1m KCl aq.	Galvanostatic 0.01 -4ma/cm^2.	--
NiO	1	0.2M KOH aq.	Potentiostatic cathodic cleaning at -0.4V vs calomel followed by anodic scan (2mv/sec.).	23
	2	1M KOH aq.	Galvanostatic 0.01 -4ma/cm^2.	--

3. Results and Discussion

3.1 Stability Tests

The results of the stability test of the electrode materials are summarized in table 8 . It should be noted that the only materials which were excluded from the screening program because of the lack of stability in any of the five solvents were the chlorides of copper, cobalt, chromium and iron.

In the case of one material, silver chloride, the stability criteria were found to be inadequate. Silver chloride seemed to be somewhat soluble in the organic solvent but the extent of solubilization could not be estimated from visual observations. The solubility of silver chloride was therefore determined in each of the solvents at room temperature, see table 9 . On the basis of this additional information, silver chloride was deemed sufficiently insoluble in one molal phenyltrimethylammonium chloride -- 60 mole % acetonitrile - 40 mole % dimethylformamide and one molal phenyltrimethylammonium chloride -- acrylonitrile to permit its evaluation.

3.2 Electrode Preparation Tests

The results of the electrode preparation studies are summarized in table 10. As can readily be seen from this table, the requirement that an anodic film of the test material be formable on the parent metal greatly limits the number of materials which can be screened. Only seven out of the sixteen materials which passed the stability tests could be deposited as anodic films. In the case of silver fluoride, it is known that silver (I) fluoride was soluble in anhydrous hydrogen fluoride (see table 4). It was hoped that silver (II) fluoride which is much less soluble could be formed. Visual observations of the electrode and cyclic voltammograms both confirm that only soluble products are formed on the anodizing of silver in hydrogen

TABLE 8

COMPATIBILITY OF ELECTRODE MATERIAL WITH ORGANIC SOLVENTS

Material	Solvent*	Observation**	Conclusion
CuF_2	2-B	No Reaction	Stable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	AcN polymerized	Unstable
	DMF	No Reaction	Stable
$CuCl$	2-B	No Reaction	Stable
	AN	Soluble, Reaction	Unstable
	NDA	No Reaction	Stable
	AcN	Soluble, Reaction, Black ppt.	Unstable
	DMF	Soluble, Reaction, green ppt.	Unstable
$CuCl_2$	2-B	Reaction, black ppt.	Unstable
	AN	Reaction, yellow solution	Unstable
	NDA	Soluble, Reaction, orange ppt.	Unstable
	AcN	Reaction, Soluble	Unstable
	DMF	Reaction, Sample changed color	Unstable
Cu_2O	2-B	No Reaction	Stable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	No Reaction	Stable
CuO	2-B	No Reaction	Stable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	No Reaction	Stable
CoF_2	2-B	No Reaction	Stable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	No Reaction	Stable
$CoCl_2$	2-B	Soluble - immediately	Unstable
	AN	Soluble - immediately	Unstable
	NDA	Soluble - immediately	Unstable
	AcN	Soluble - immediately	Unstable
	DMF	Soluble - immediately	Unstable

TABLE 8

COMPATIBILITY OF ELECTRODE MATERIAL WITH ORGANIC SOLVENTS (Cont'd)

Material	Solvent*	Observation**	Conclusion
CoO	2-B	No Reaction	Stable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	No Reaction	Stable
Co_2O_3	2-B	No Reaction	Stable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	No Reaction	Stable
CrF_2	2-B	No Reaction	Stable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	No Reaction	Stable
CrF_3	2-B	Possible Reaction	Unstable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	No Reaction	Stable
$CrCl_2$	2-B	Reaction, pink and green ppt.	Unstable
	AN	Reaction, green ppt.	Unstable
	NDA	Reaction, green ppt.	Unstable
	AcN	Reaction, green ppt.	Unstable
	DMF	Reaction, olive green ppt.	Unstable
$CrCl_3$	2-B	No Reaction	Stable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	No Reaction	Stable
Cr_2O_3	2-B	No Reaction	Stable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	No Reaction	Stable

TABLE 8

COMPATIBILITY OF ELECTRODE MATERIAL WITH ORGANIC SOLVENTS (Cont'd)

Material	Solvent*	Observation**	Conclusion
$FeCl_3$	2-B	Soluble	Unstable
	AN	Soluble	Unstable
	NDA	Soluble	Unstable
	AcN	Soluble	Unstable
	DMF	Soluble	Unstable
$FeCl_2$	2-B	Solution brown	Unstable
	AN	Brown ppt.	Unstable
	NDA	Red ppt.	Unstable
	AcN	No Reaction	Stable
	DMF	No Reaction	Stable
FeF_3	2-B	Red ppt. after two weeks	Unstable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	No Reaction	Stable
Fe_2O_3	2-B	No Reaction	Stable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	No Reaction	Stable
Fe_3O_4	2-B	No Reaction	Stable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	No Reaction	Stable
MnF_2	2-B	Slight white ppt.	Stable
	AN	Slight white ppt.	Stable
	NDA	Slight white ppt.	Stable
	AcN	Slight white ppt.	Stable
	DMF	Slight white ppt.	**Stable**
$MnCl_2$	2-B	White suspension, reaction	Unstable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	Soluble	Unstable

TABLE 8

COMPATIBILITY OF ELECTRODE MATERIAL WITH ORGANIC SOLVENTS (Cont'd)

Material	Solvent*	Observation**	Conclusion
MnO_2	2-B	No Reaction	Stable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	No Reaction	Stable
MnO	2-B	No Reaction	Stable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	No Reaction	Stable
NiF_2	2-B	No Reaction	Stable
	AN	No Reaction	Stable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	No Reaction	Stable
$NiCl_2$	2-B	No Reaction	Stable
	AN	30 days, orange-green ppt.	Unstable
	NDA	No Reaction	Stable
	AcN	No Reaction	Stable
	DMF	Reaction, blue solution	Unstable
NiO	2-B	No Reaction	Stable
	AN	No Reaction	Stable
	NDA	Fine white ppt.	Stable
	AcN	No Reaction	Stable
	DMF	Fine white ppt.	Stable
AgF	2-B	No Reaction	Stable
	AN	Reaction	Unstable
	NDA	Reaction	Unstable
	AcN	Reaction	Unstable
	DMF	Reaction	Unstable
AgCl	2-B	Reaction	Unstable
	AN	Partially Soluble	Questionable
	NDA	Partially Soluble	Questionable
	AcN	Partially Soluble	Questionable
	DMF	Partially Soluble	Questionable

TABLE 8

COMPATIBILITY OF ELECTRODE MATERIAL WITH ORGANIC SOLVENTS (Cont'd)

Material	Solvent*	Observation**	Conclusion
AgO	2-B	No Reaction	Stable
	AN	Reaction	Unstable
	NDA	Reaction	Unstable
	AcN	Reaction	Unstable
	DMF	Reaction	Unstable

* Key to Solvents: 2-B   2-Butanone
                    AN   Acetonitrile
                    NDA   N-nitrosodimethylamine
                    AcN   Acrylonitrile
                    DMF   Dimethylformamide

** No reaction means no apparent reaction.

TABLE 9

SOLUBILITY OF SILVER CHLORIDE IN CHLORIDE CONTAINING ELECTROLYTES

| Electrolyte	Solubility of AgCl
1m $MgCl_2$ - AN-DMF	1.006 moles/liter
1m ϕMe_3NCl - AN-NDA	0.339 moles/liter
1m $MgCl_2$ - AN-NDA	0.175 moles/liter
1m ϕMe_3NCl - AN-DMF	0.028 moles/liter
1m ϕMe_3NCl - AcN	0.009 moles/liter

Key:
    AN-DMF   60 mole % Acetonitrile - 40 mole % Dimethylformamide
    AcN   Acrylonitrile
    ϕMe_3NCl Phenyltrimethylammonium Chloride

TABLE 10

RESULTS OF ELECTRODE PREPARATION STUDY

Material	Technique	Nature of Deposit Formed	Conclusion
AgF	1	No film formed, material soluble in HF.	Unsatisfactory
AgCl	1	Film formed, potentials in aqueous medium very erratic.	Unsatisfactory
	2	Film formed.	Satisfactory
	3	Electrode coated.	Satisfactory
	4	Electrode area hard to control.	Satisfactory
	5	Electrode area hard to control.	Satisfactory
AgO	1	Film formed.	Satisfactory
CuF_2	1	Film formed, see figure 5.	Satisfactory
CuO	1	Thin film formed.	Satisfactory
Cu_2O	1	Thin film formed.	Satisfactory
CoF_2	1	Anodic current flow but no film formed, see figures 6 and 7.	Unsatisfactory
CoO	1	Non-uniform film, electrode covered.	Unsatisfactory
CrF_3	1	Anodic current flow but no film formed, see figure 10.	Unsatisfactory
Cr_2O_3	1	No film formed.	Unsatisfactory
FeF_3	1	No evidence of film formation, see figure 8.	Unsatisfactory
Fe_2O_3	1	Poor electrode coverage.	Unsatisfactory
	2	Thin film.	Satisfactory
MnO_2	1	Incomplete coverage of electrode, electrode area not well defined.	Unsatisfactory
NiF_2	1	No evidence of film formation, see figure 9.	Unsatisfactory
$NiCl_2$	1	No film formed.	Unsatisfactory
NiO	1	Nature of film variable and non-reproducible.	Unsatisfactory
	2	No film formed.	Unsatisfactory

Figure 5

Cyclic Voltammogram of Copper in Anhydrous
Hydrogen Fluoride (1M KF)

Potential, mv, vs. Cu/CuF_2
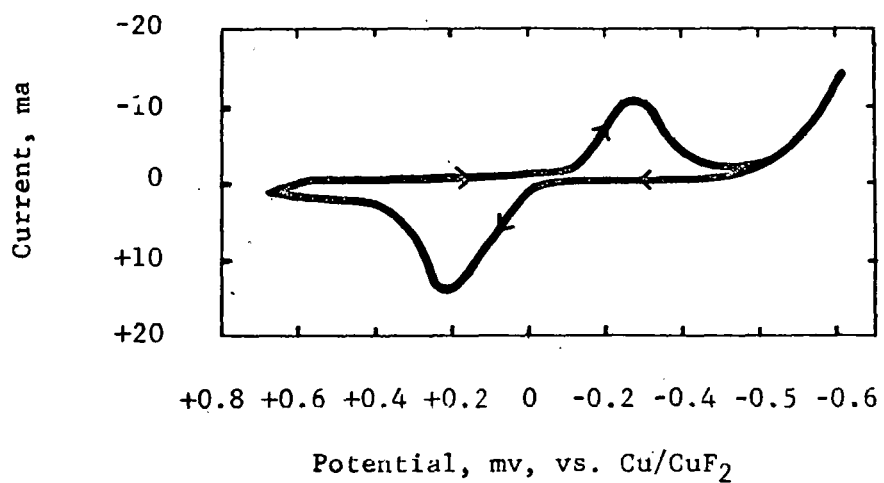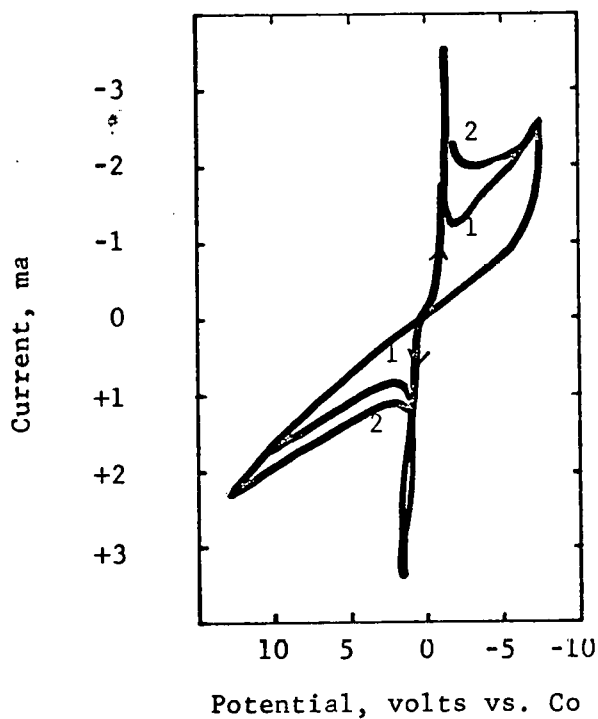
Scan Rate: 2v/sec

Electrodes: Working   Cu ($1cm^2$)
              .Counter   Platinum

Temperature: 23^oC

Figure 6

Cyclic Voltammogram of Cobalt in
Anhydrous Hydrogen Fluoride (1M KF)

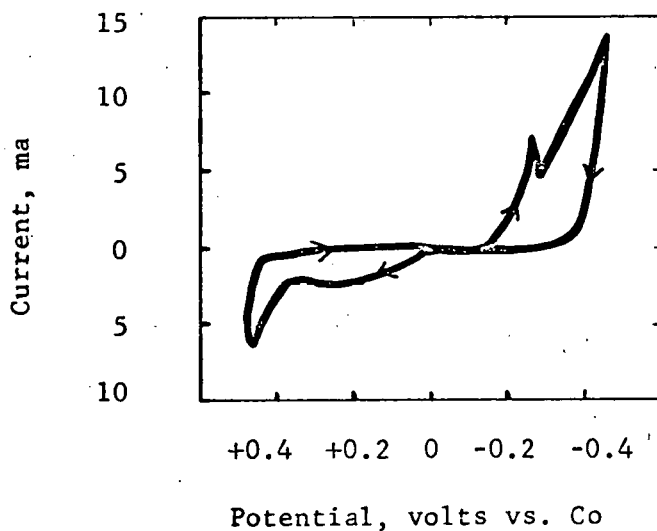
Scan Rate: 20 mv/sec

Electrodes:

  Working   Co (1 cm^2)

  Counter   Co

Temperature: 0°C

Figure 7

Cyclic Voltammogram of Cobalt in
Anhydrous Hydrogen Fluoride (1M KF)
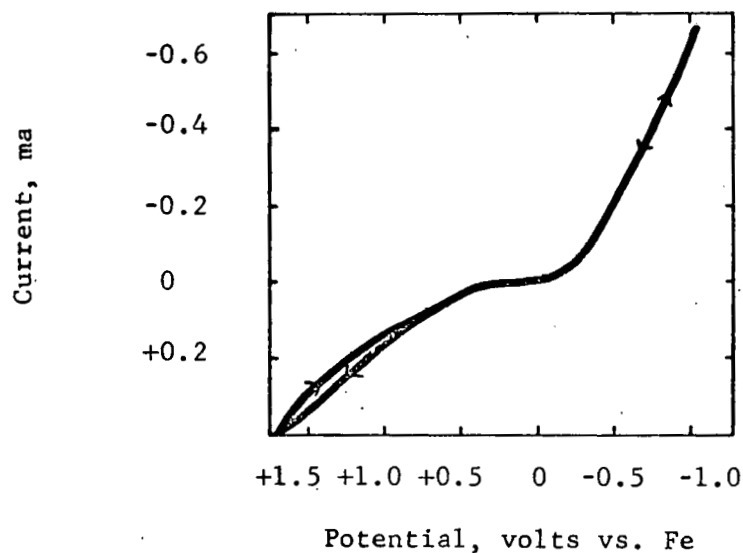

Scan Rate: 200 mv/sec

Electrodes:

  Working   Co   (1 cm^2)

  Counter   Co

Temperature: 0°C

Figure 8

Cyclic Voltammogram of Iron in
Anhydrous Hydrogen Fluoride (1M KF)

Scan Rate: 67 mv/sec

Electrodes:
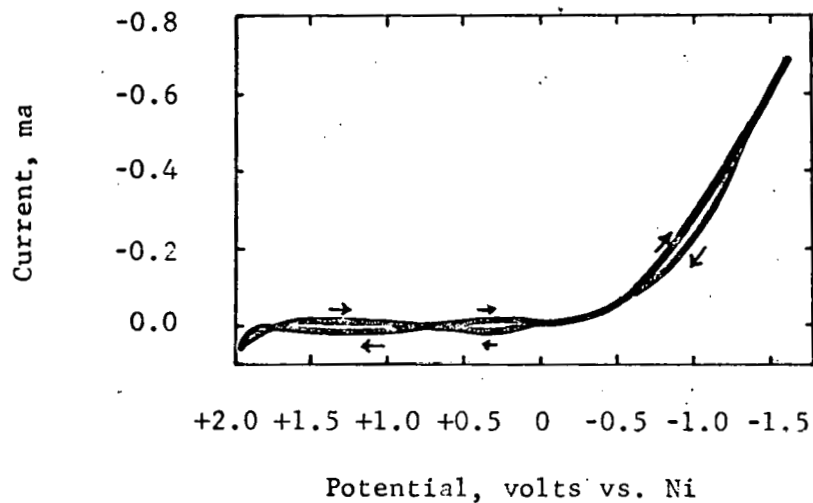
   Working   Fe   (1 cm^2)

   Counter   Fe

Temperature: $0^{o}C$

Figure 9

Cyclic Voltammogram of Nickel in
Anhydrous Hydrogen Fluoride (1M KF)

Scan Rate: 200 mv/sec

Electrodes:
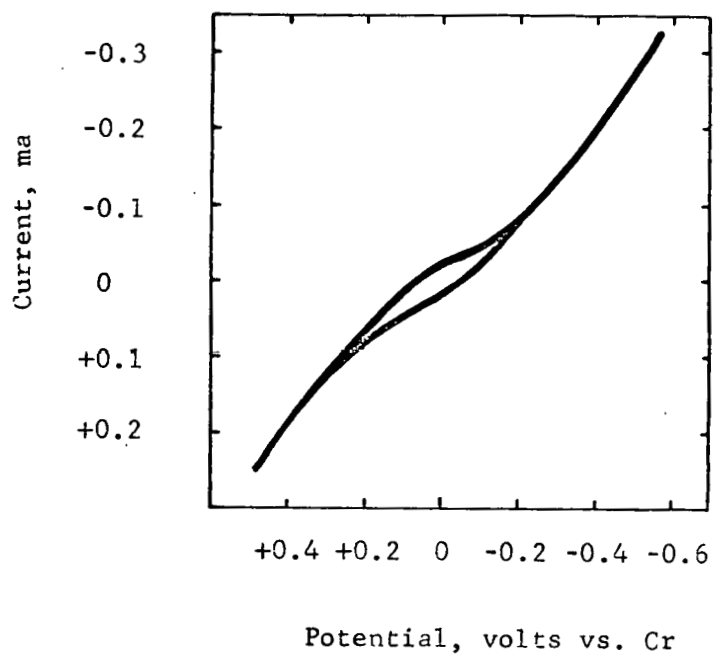
   Working   Ni (1 cm^2)

   Counter   Ni

Temperature: $0^{o}C$

Figure 10

Cyclic Voltammogram of Chromium in
Anhydrous Hydrogen Fluoride (1M KF)

Scan Rate: 200 mv/sec

Electrodes:

  Working   Cr (1 cm^2)

  Counter   Cr

Temperature: $0^{\circ}C$

Potential, volts vs. Cr

TABLE 11

SOLUBILITY OF METAL FLUORIDES IN ANHYDROUS HYDROGEN FLUORIDE

Metal Fluoride	Solubility g/100g HF
AgF	83.2
AgF_2	0.048
CuF_2	0.01
FeF_2	0.006
FeF_3	0.008
CrF_2	0.036
NiF_2	0.037
MnF_3	0.164
CoF_3	0.257

fluoride. No attempts were made to fabricate silver fluoride from commerically availabe material because it was felt that a meaningful comparison between results obtained from such an electrode with the previous tests made on anodic films could not be made until a detailed study of fabrication techniques was completed.

As previously noted, the manganese substrates could not be obtained in the desired form. The variation in surface areas was sufficiently great to give poor control of charge densities and therefore poor control of the anodically formed deposits.

3.3 Electrochemical Tests

A summary of the results of the electrochemical screening are given in table 12. The details of these tests are given below under the appropriate heading for each compound.

3.3.1 Silver Oxide Electrode

The potentials of five of these silver oxide disc electrodes when placed in 1m $LiClO_4$ - 2-butanone electrolyte or in 1m Bu_4NOH - 2-butanone (4 molal in H_2O) were within one millivolt of each other. After the application of small over potentials (10 mv) both negative and positive to the open circuit potential, the electrodes rapidly returned to the original open circuit potential in both electrolytes (figures 11 and 12). Cyclic voltammograms (at 1 mv per sec. scan rate) of silver oxide electrode in these electrodes showed that silver oxide was capable of producing approximately twice the current at a given polarization in 1m Bu_4NOH - 2-butanone than in 1m $LiClO_4$ - 2-butanone (see figures 13 and 14).

Cyclic voltammograms (60 mv/sec) of the silver oxide electrode in 1m $LiClO_4$ - 2-butanone gave evidence for the existence of a redox couple involving the electrolyte. The current was found to increase when the

TABLE 12

SUMMARY OF ELECTROCHEMICAL TESTS

Compound	Electrolyte*	Performance		
		Open Circuit (mv)	Polarization	i-v
AgCl	$LiClO_4$-AN-DMF	± 0.1	Rapid Recovery	Good
	phenyl$(CH_3)_3$Cl-AN-DMF	± 0.1	Rapid Recovery	Very Good
AgO	$LiClO_4$-AN-DMF	± 0.5	Rapid Recovery	Good
	$[CH_3(CH_2)_3]_4$NOH-AN-DMF	± 0.5	Rapid Recovery	Good
CuF_2	$LiClO_4$-AN-DMF	± 0.2	Fair Recovery	Poor
CuO	$LiClO_4$-AN-DMF	± 100	Fair Recovery	Poor
Cu_2O	$LiClO_4$-AN-DMF	± 5.0	Fair Recovery	Poor
CoO	$LiClO_4$-AN-DMF	± 50	Fair Recovery	Poor
MnO	$LiClO_4$-AN-DMF	± 125	Fair Recovery	Poor
Fe_2O_3	$LiClO_4$-AN-DMF	± 75	Fair Recovery	Poor

* AN-DMF = 60 mole % acetonitrile - 40 mole % dimethylformamide.

Figure 11

Effect of Over Potential on Silver Oxide in 1m LiClO$_4$ - 2-Butanone
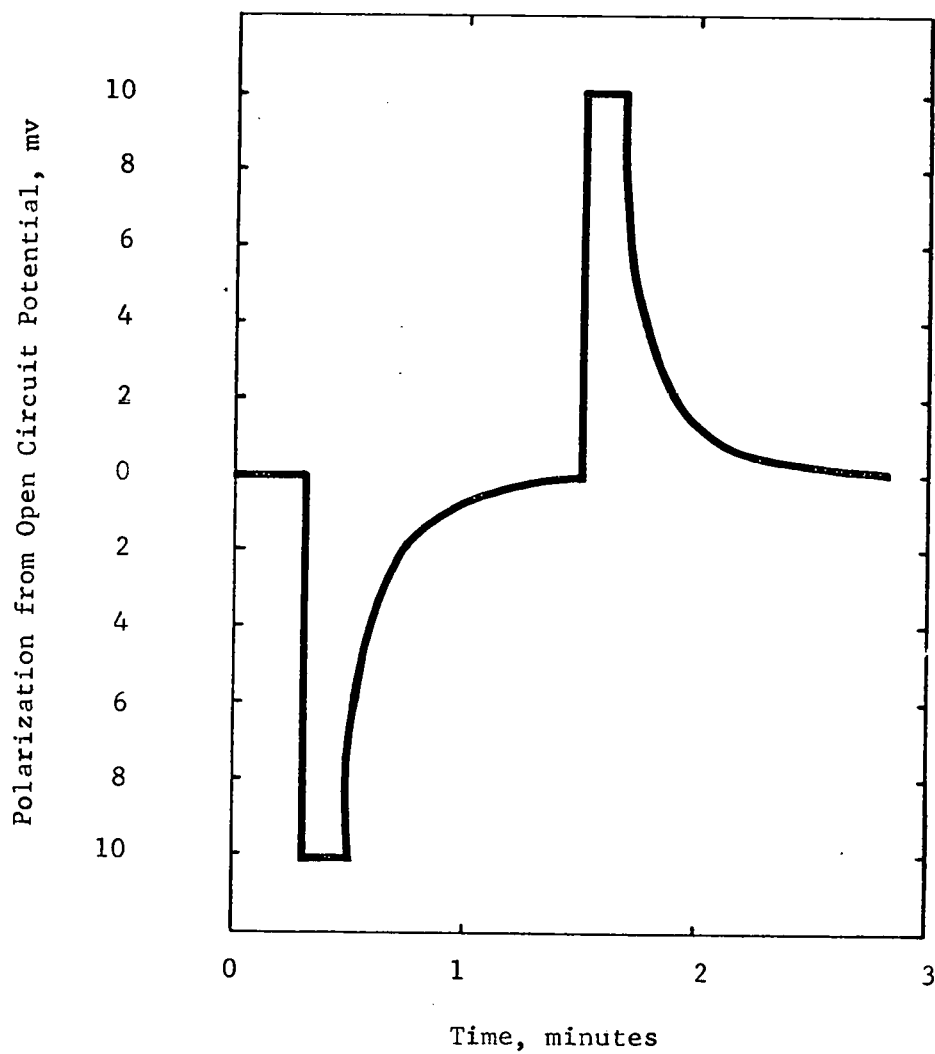

Polarization from Open Circuit Potential, mv

Time, minutes

Figure 12

Effect of Over Potential on Silver Oxide in
$1m\left[CH_3(CH_2)_3\right]_4$ NOH - 2-Butanone

Polarization from Open Circuit Potential, mv

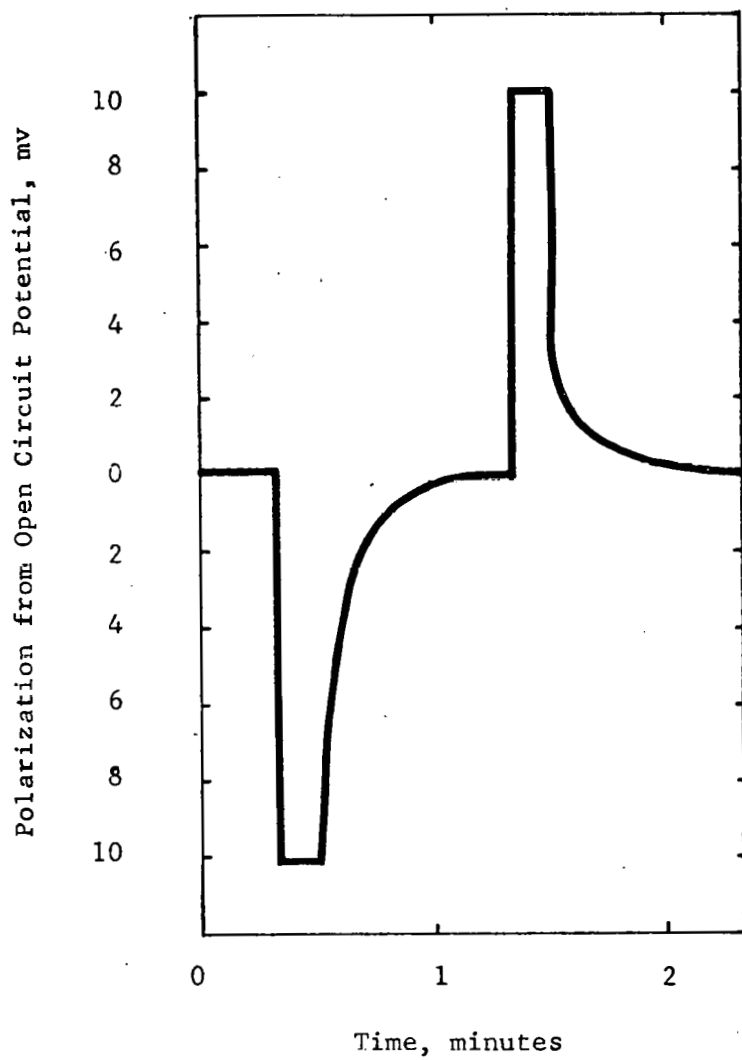Time, minutes

Figure 13
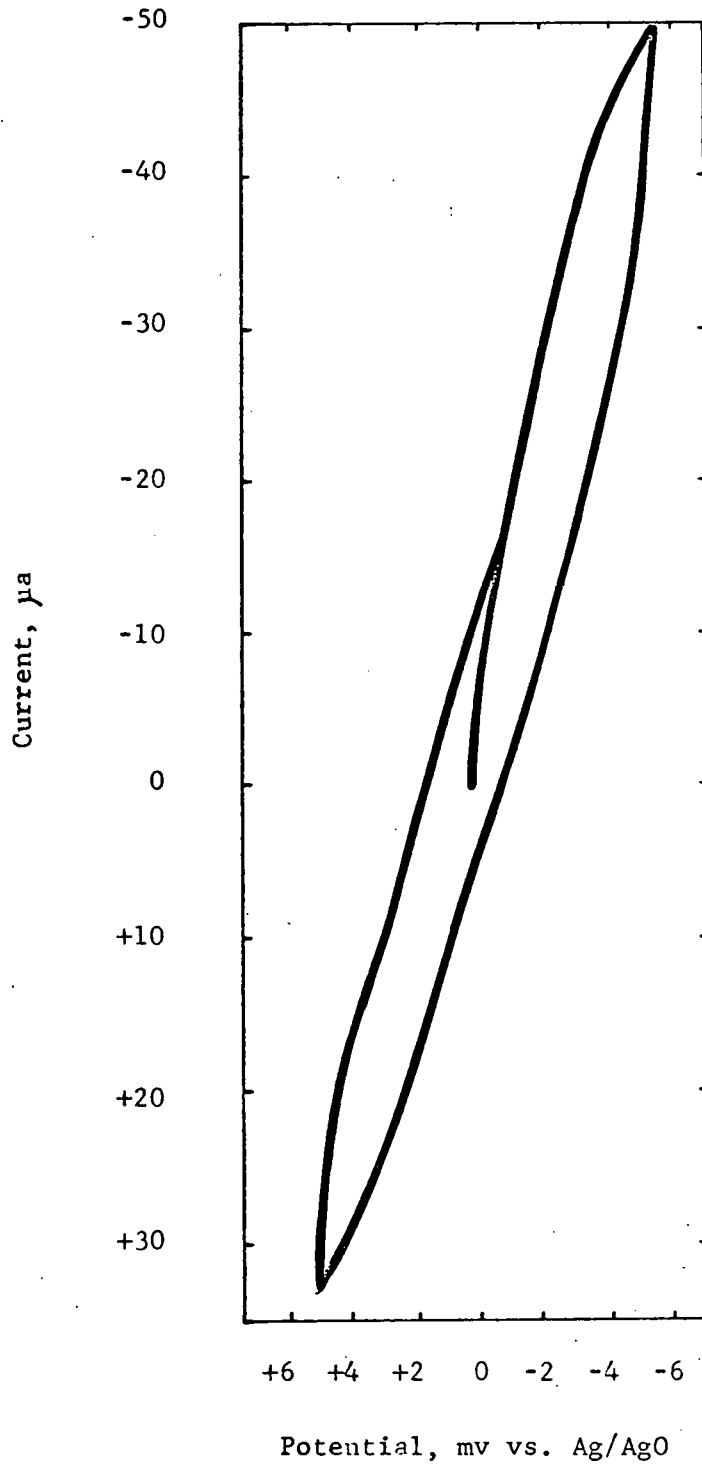
Cyclic Voltammogram of Silver Oxide
in 1m LiClO$_4$ - 2-Butanone

Scan Rate: 1 mv/sec

Electrodes:

  Working   AgO (66 mm^2)

  Counter   Ag

Temperature: 23°C

Potential, mv vs. Ag/AgO

Figure 14

Cyclic Voltammogram of Silver Oxide in
1m $\left[CH_3(CH_2)_3 \right]_4$ NOH - 2-Butanone
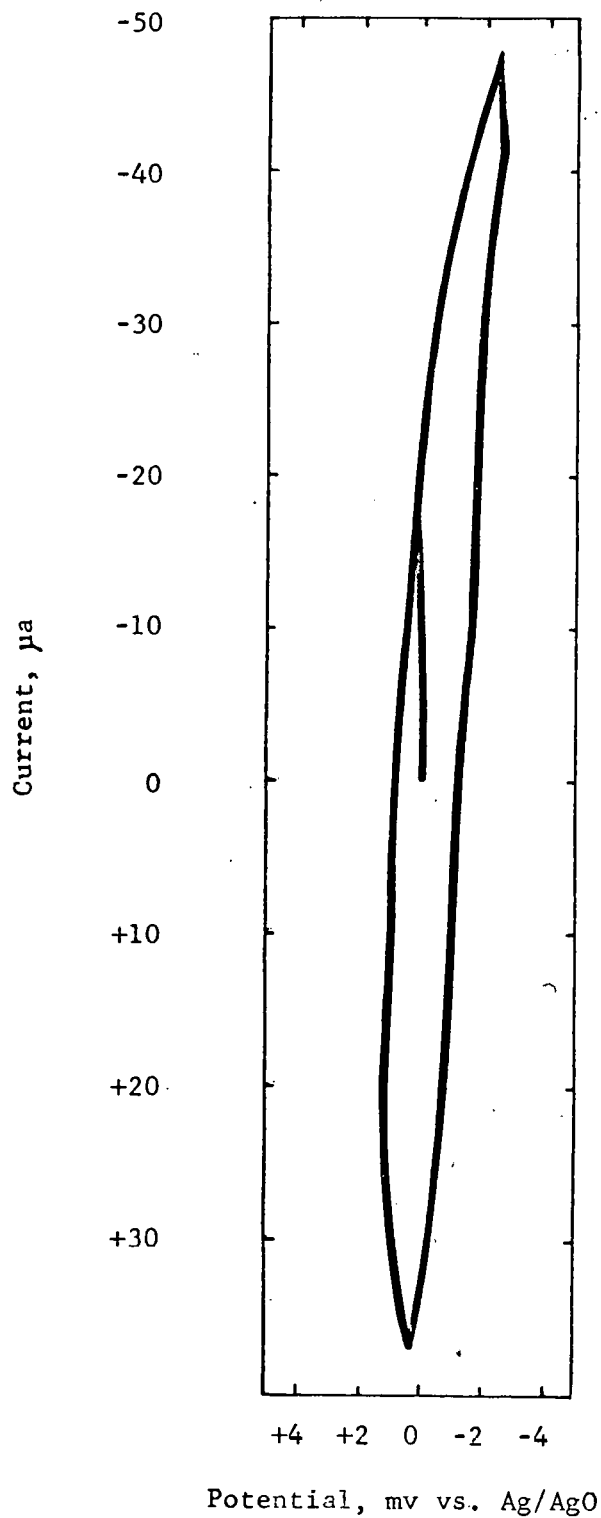
Scan Rate: 1 mv/sec

Electrodes:

    Working   AgO (66 mm^2)

    Counter   Ag

Temperature: 23°C

Potential, mv vs. Ag/AgO

40

electrolyte was agitated during a cathodic hold and less anodic current was obtained after a cathodic hold in a stirred solution then in a quiet one (figures 15 and 16). No such complication was found in the 1m Bu$_4$NOH - 2-butanone electrolyte.

3.3.2 Silver Choride Electrode

The silver chloride electrodes in 1m LiClO$_4$ -- 60 mole % acetonitrile - 40% dimethylformamide (AN-DMF) and in 1m phenyltrimethyl-ammonium chloride -- AN-DMF gave stable open circuit potentials which did not vary from electrode to electrode by more than 0.2 millivolts. Momentary ten millivolt polarizations (10 seconds) of the chloride electrodes in these solvents had no effect on the steady state open circuit potential. The rate of return to open circuit potential was comparable to that of the silver oxide electrode previously mentioned. (Compare figures 17 and 18). The current densities obtained on cyclic voltammograms (1 mv/sec) in these electrolytes were quite different. Considerably more current could be obtained from AgCl discharged in phenyltrimethylammonium chloride electro-lyte than LiClO$_4$ electrolyte (figures 19 and 20).

The open circuit potentials for the electrode formed from molten silver chloride (technique 3 on table 7) agreed to within two milli-volts of each other when screened in phenyltrimethylammonium -- AN-DMF elec-trolyte (compared with 0.2 mv agreement for the electrolytically formed electrodes). These electrodes rapidly returned to open circuit potential after polarization. Current densities of roughly 24 μa/cm^2 at 1 mv polari-zation were obtained. The area of these electrodes could only be roughly estimated so that not too much significance can be placed on these current densities.

Figure 15

Effect of Cathodic Hold on Cyclic Voltammogram of Silver Oxide in 1m $LiClO_4$ - 2-Butanone

10 second hold on
2nd Scan
at -210 mv

Scan Rate: 30 mv/sec

Electrodes:

Working AgO (66mm^2)

Counter Ag

Temperature: 23°C

1st Scan
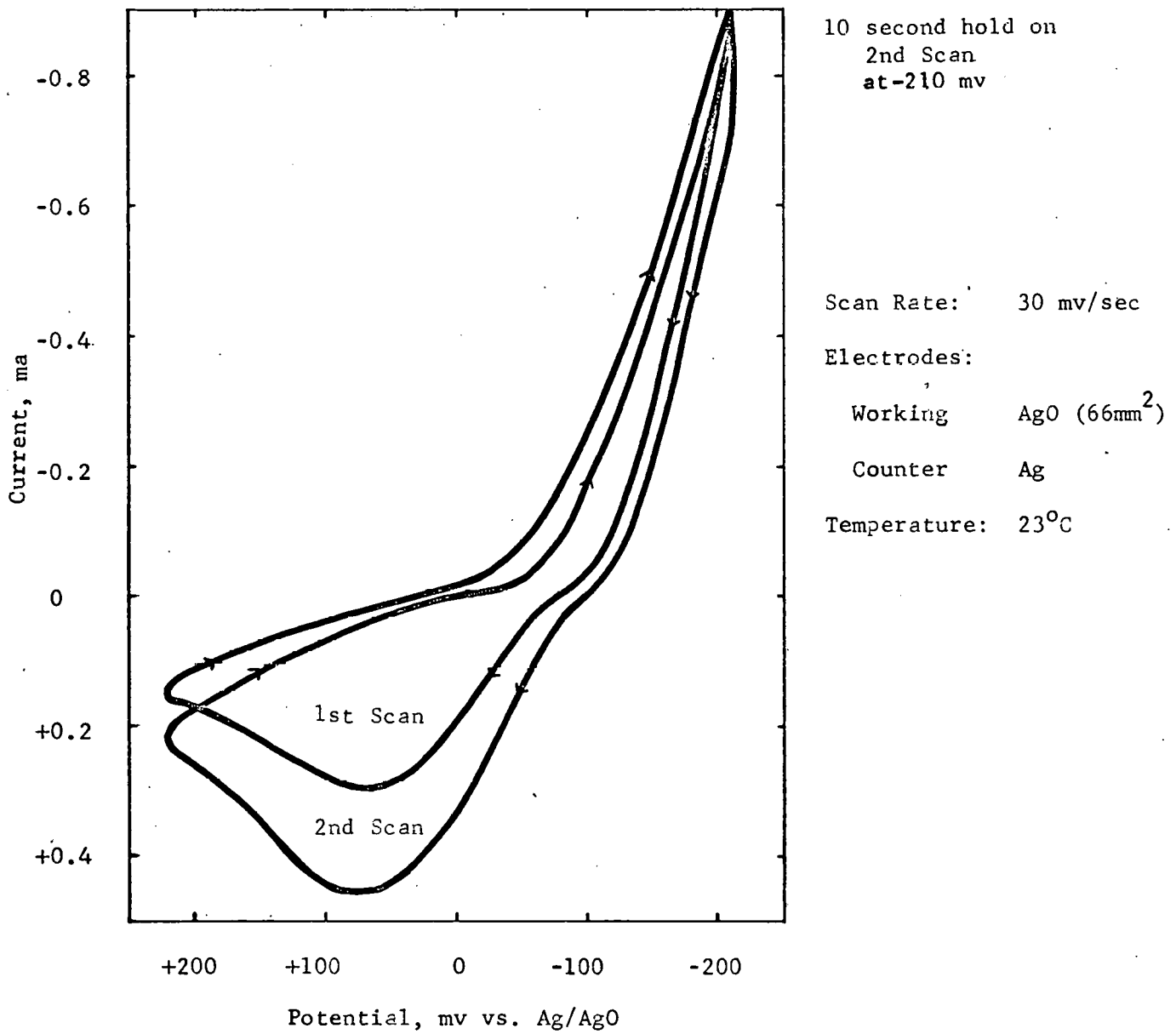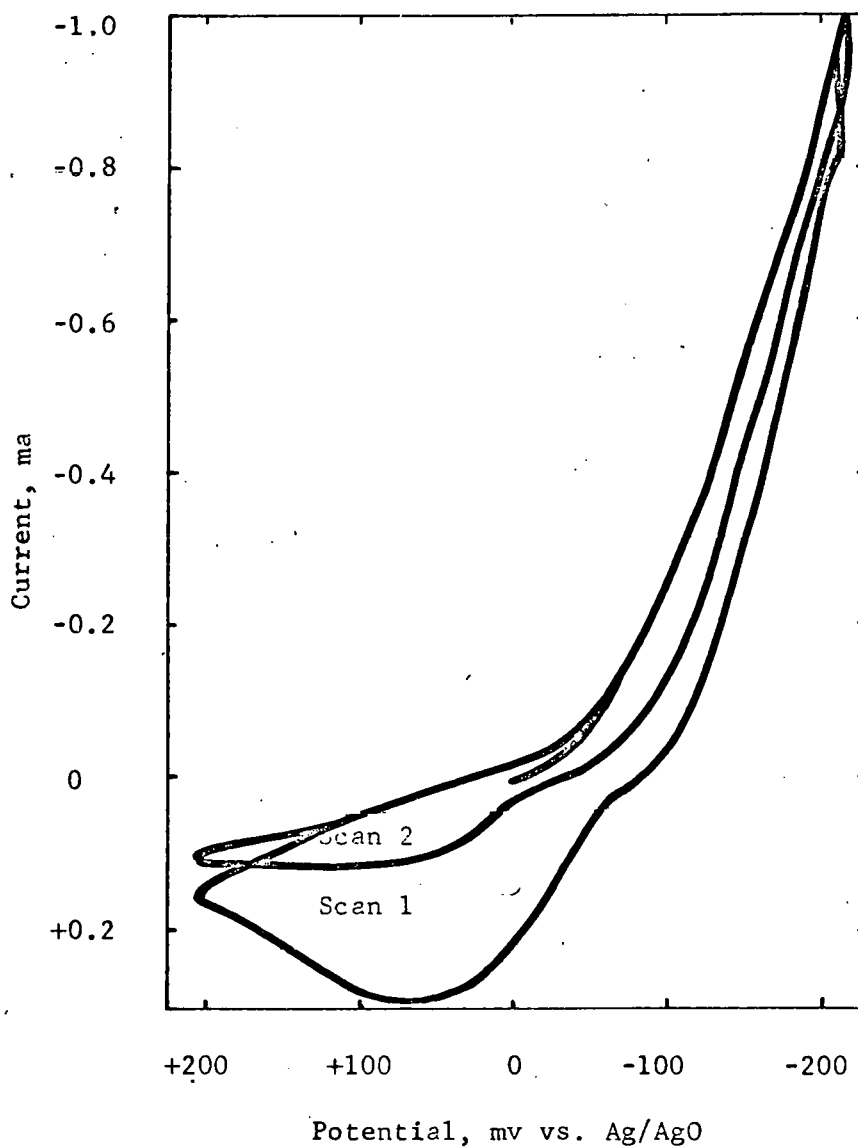
2nd Scan

Potential, mv vs. Ag/AgO

Figure 16

Effect of Agitation on Cyclic Voltammogram
of Silver Oxide in 1m LiClO$_4$ - 2-Butanone

Scan 1 - without agitation
Scan 2 - with agitation

Scan Rate: 30 mv/sec
Electrodes:
    Working   AgO (66mm^2)
    Counter   Ag
Temperature: 23°C

43

Figure 17

Effect of Over Potentials on Silver Chloride
in 1m LiClO₄ -- 60 Mole % Acetonitrile - 40
Mole % Dimethylformamide

Figure 18

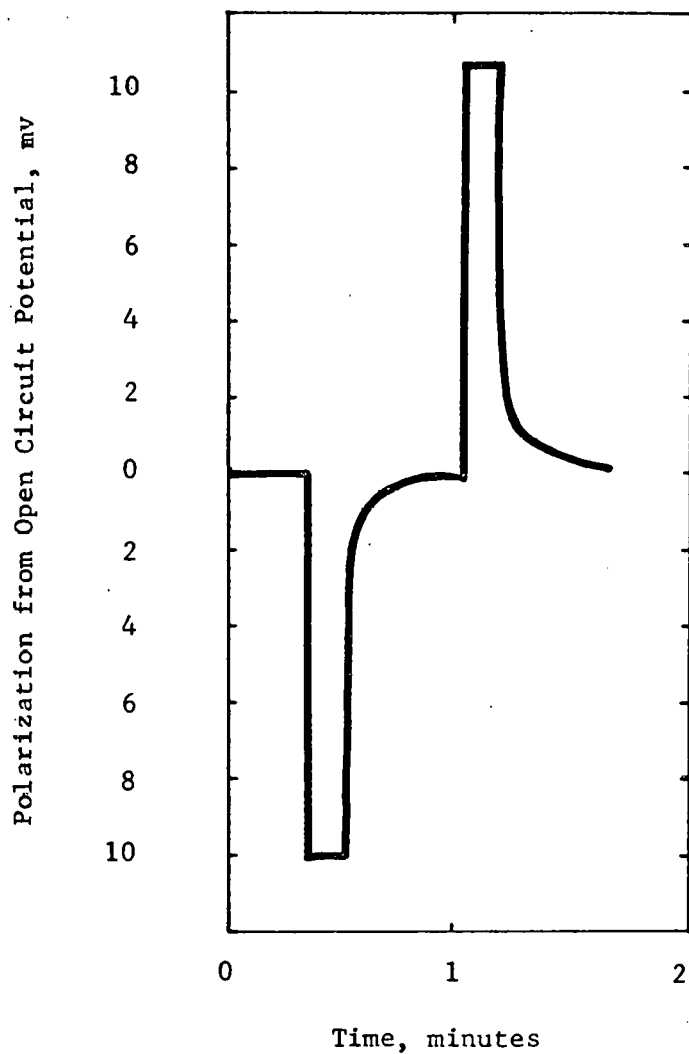Effect of Over Potentials on Silver Chloride
in 1m Phenyl $(CH_3)_3NCl$ -- 60 Mole % Acetoni-
trile - 40Mole % Dimethylformamide

45
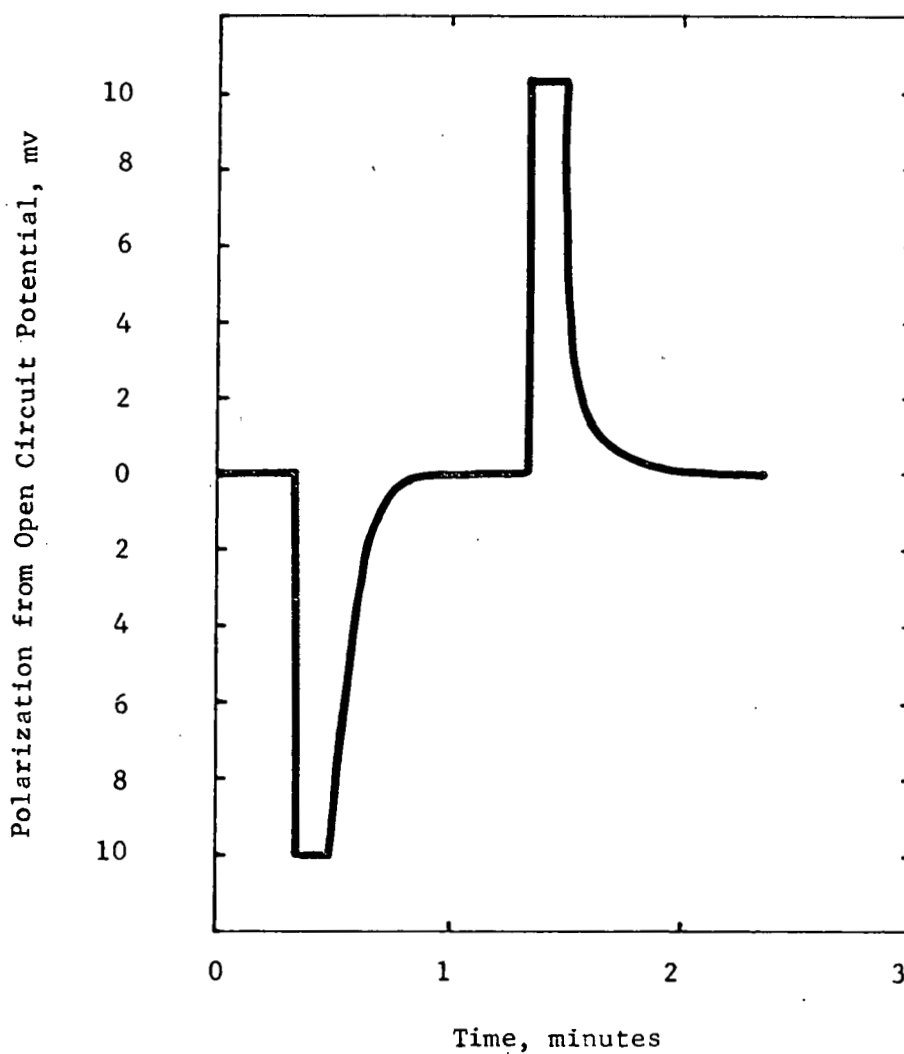
Figure 19

Cyclic Voltammogram of Silver Chloride in 1m
$LiClO_4$ -- 60 Mole % Acetonitrile - 40 Mole %
Dimethylformamide

Scan Rate: 1 mv/sec

Electrodes:

    Working   AgCl ($66mm^2$)

    Counter   Ag

Temperature: 23^oC

Potential, mv vs. Ag/AgCl

Figure 20

Cyclic Voltammogram of Silver Chloride in 1m
Phenyl $(CH_3)_3NCl$ -- 60 Mole % Acetonitrile -
40 Mole % Dimethylformamide

Scan Rate: 1 mv/sec
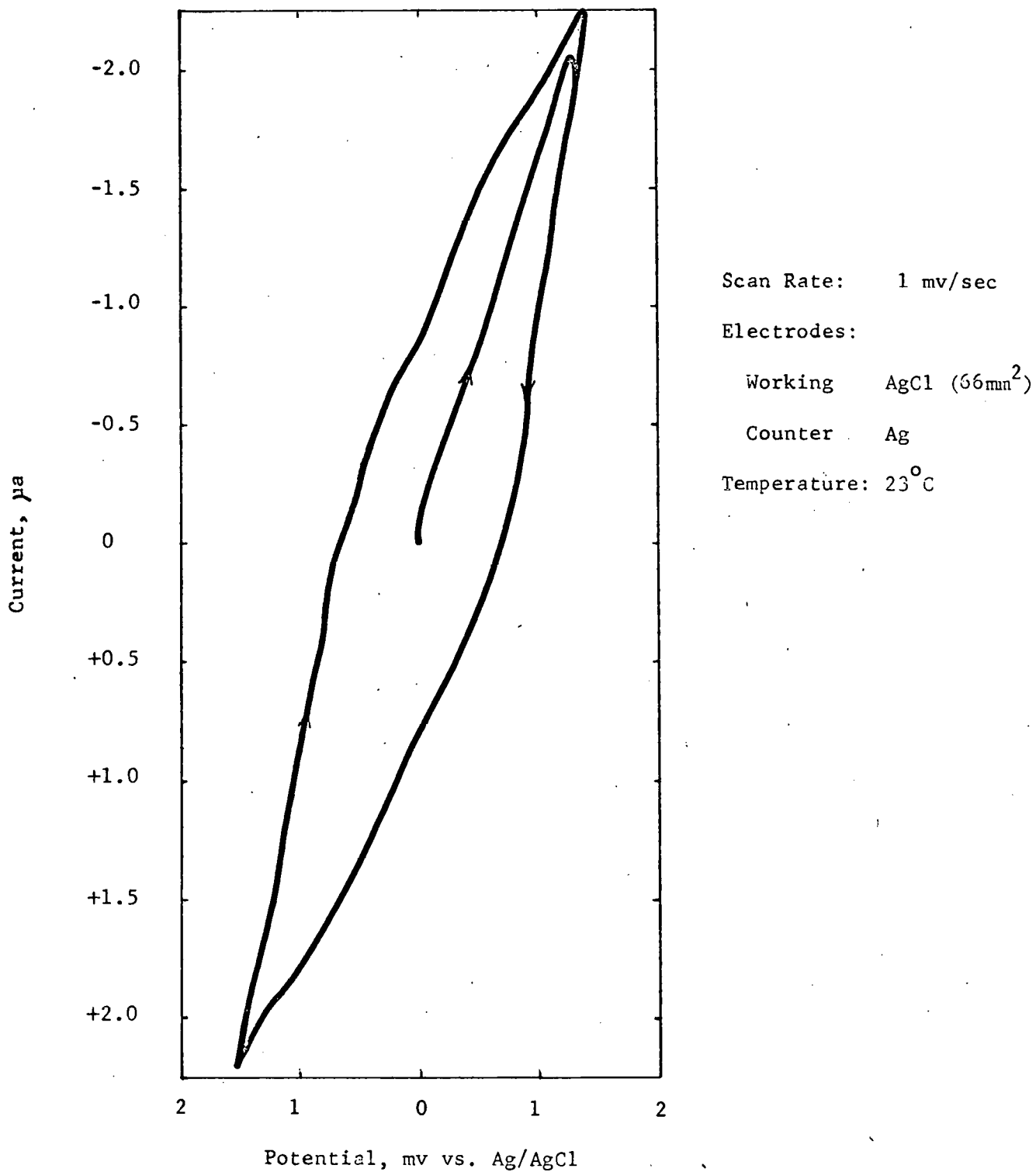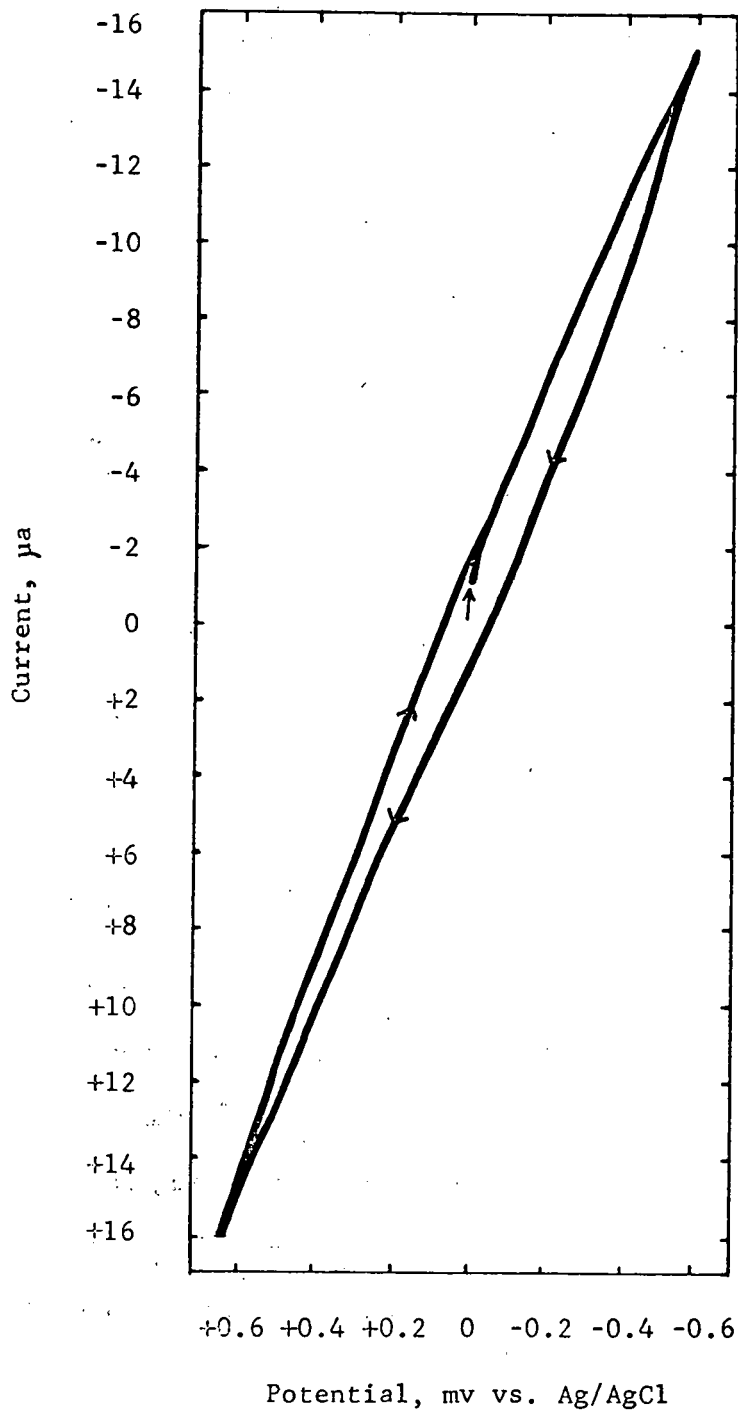
Electrodes:

   Working   AgCl (66 mm^2)

   Counter   Ag

Temperature: $23^{\circ}C$

Current, μa

Potential, mv vs. Ag/AgCl

The press-formed electrodes (techniques 4 and 5 on table 7)
agreed to within 3 mv on open circuit and returned rapidly to open circuit
potential after polarization. Again, current densities for these electrodes
could only be estimated because of uncertainty of the surface areas. Elec-
trodes containing only AgCl and those containing acetylene black could pro-
duce approximately 200 $\mu a/cm^2$ at 1 mv polarization). The presence of acetylene
black had no effect on the maximum current produced at a given potential, how-
ever, when the electrodes were held at various potentials, those containing
acetylene black could sustain higher currents than those without.

3.3.3 Copper Fluoride Electrode

The open circuit potential difference between three CuF_2 elec-
trodes in 1m $LiClO_4$ -- AN-DMF was found to be less than 1 mv. The copper
fluoride electrode was somewhat slow in recovering from the application of
over potentials (see figure 21) and gave only very low currents at moderate
polarization (i.e. 25 $\mu a/cm^2$ at 0.1v polarization from open circuit), see
figure 22.

3.3.4 Copper Oxide Electrode

Electrodes prepared with copper (II) oxide failed to produce
stable open circuit potentials in either 1m Bu_4NOH -- 60 mole % acetonitrile -
40 mole % dimethylformamide (AN-DMF) or in 1m $LiClO_4$ -- AN-DMF. There was
also evidence of meter-loading when the potential of the electrodes were
checked using an electrometer with an internal impedance of 10^{14} ohms.
Since copper (II) oxide showed little promise, electrodes containing only
copper (I) oxide were formed. Five of the copper (I) oxide electrodes were
tested in 1m $LiClO_4$ -- AN-DMF. The open circuit potential difference between

Figure 21

Effect of Over Potentials on Cupric Fluoride in
1m LiClO$_4$ -- 60 Mole % Acetonitrile - 40 Mole %
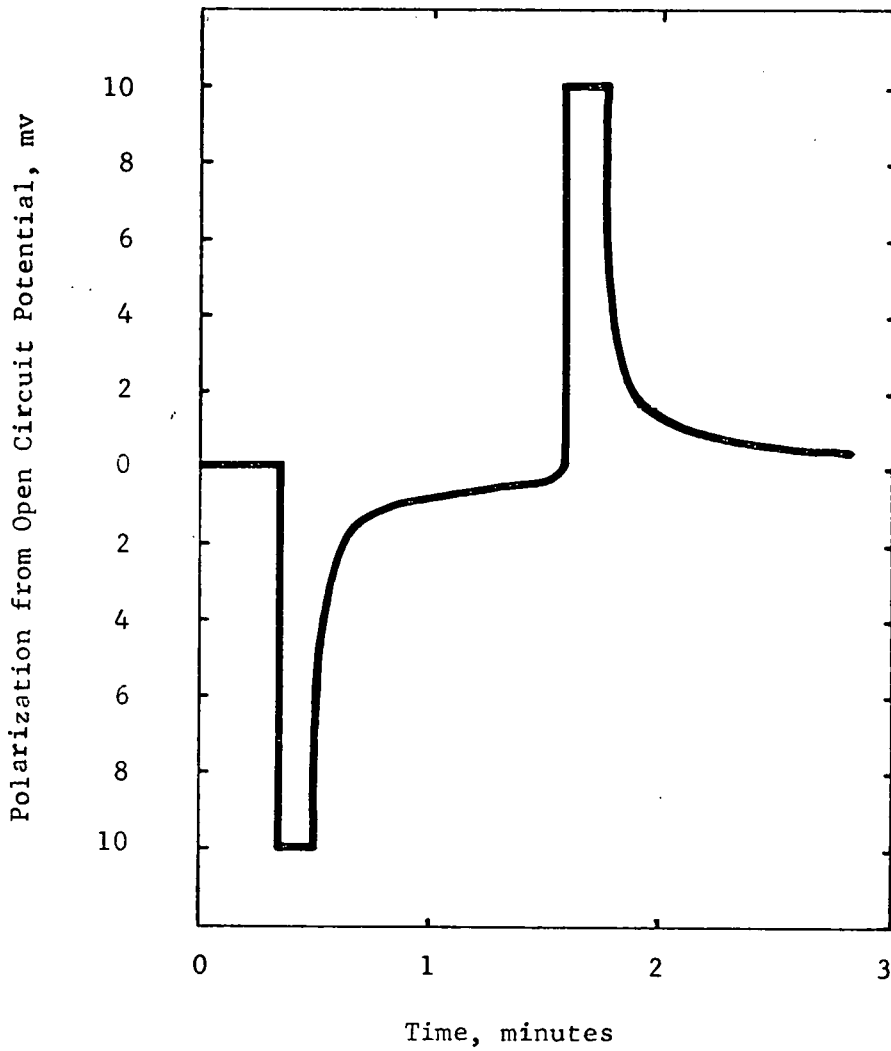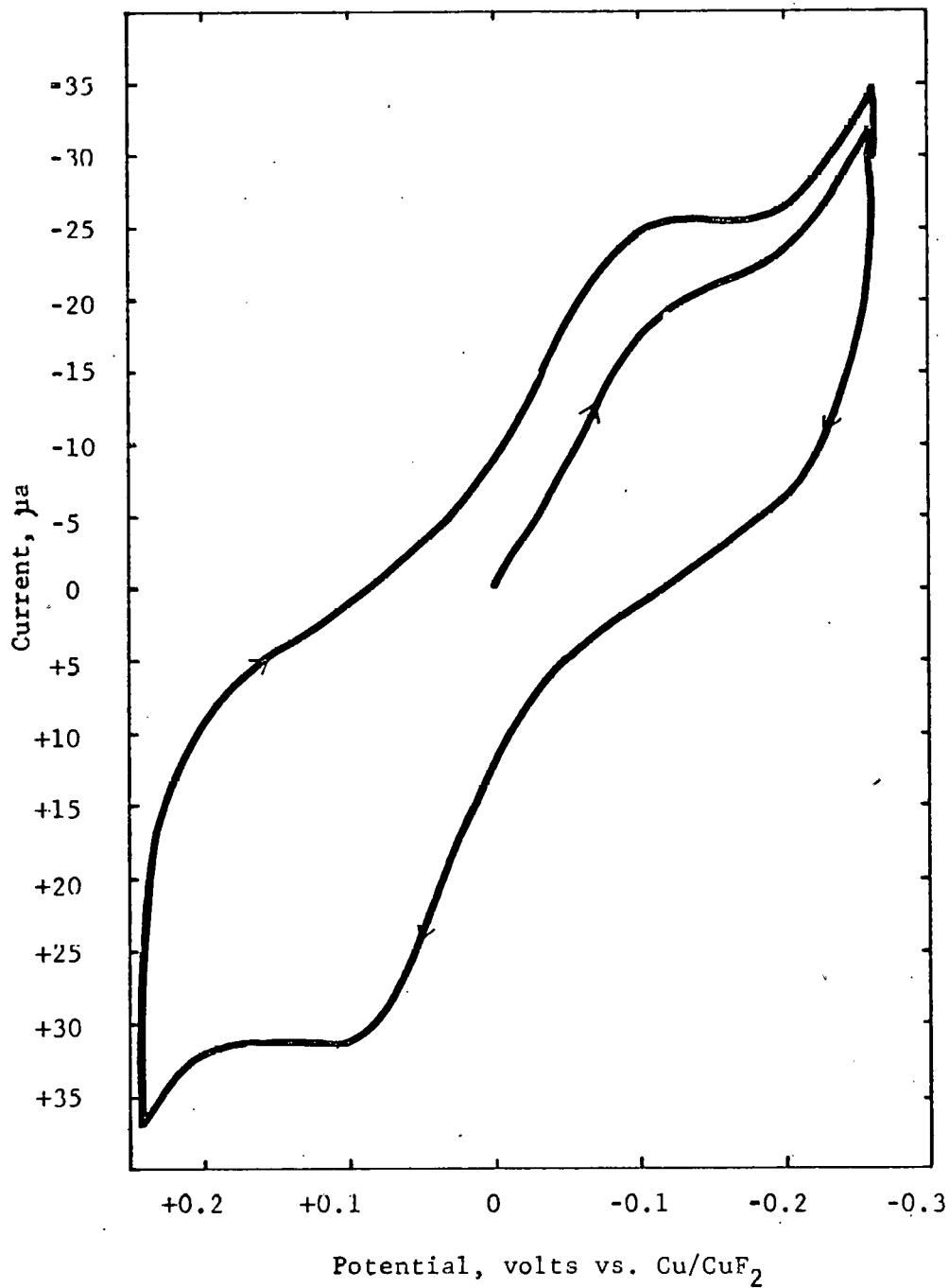Dimethylformamide

Figure 22

Cyclic Voltammogram of Cupric Fluoride in 1m
LiClO₄ -- 60 Mole % Acetonitrile - 40 Mole %
Dimethylformamide

Scan Rate: 30mv/sec

Electrodes:

    Working CuF$_2$(1cm^2)

    Counter   Pt

Temperature: 23°C

Potential, volts vs. Cu/CuF$_2$

the Cu_2O electrodes was excessive but remained steady upon standing in the electrolyte. No further tests were run with these electrodes.

4. Conclusions

A summary of the results of the screening program are given in table 13. A perusal of this table shows that silver chloride and silver oxide performed quite well on the screening test. Cupric fluoride, while not performing as well as the silver electrodes, did form a good test electrode. The current producing ability of this material was considerably less than that obtained from the silver salts. Copper oxide, cobalt oxide and iron oxide gave unsatisfactory performance and can therefore be rejected from further consideration. The chlorides of copper, cobalt, chromium and iron can be rejected because of their high solubilities in organic solvents. The metal fluorides, other than copper fluoride, nickel and manganese chloride, and nickel chromium and manganese oxide could not be screened because appropriate anodic films of these materials could not be formed. The screening of these materials will have to await developments suitable for macro-electrode fabrication techniques.

TABLE 13

SUMMARY OF RESULTS

Compound	Stable In (No. of soln.)	Test Electrode	Performance			Conclusion
			Open Circuit (mv)	Polarization	i-v	
Silver Fluoride	1	No Film	--	--	--	Method Inapplicable
Silver Chloride	4	Good Film	± 0.1	Rapid Recovery	Good	Satisfactory Material
Silver Oxide	1	Good Film	± 0.5	Rapid Recovery	Good	Satisfactory Material
Copper Fluoride	3	Good Film	± 0.2	Recovery Fair	Poor	Marginal
Copper Chloride	0	--	--	--	--	Method Inapplicable
Copper Oxide	5	Film Formed	± 5.0	--	--	Material Rejected
Cobalt Fluoride	4	No Film	--	--	--	Method Inapplicable
Cobalt Chloride	0	--	--	--	--	Method Inapplicable
Cobalt Oxide	5	Film Formed	± 50	--	--	Material Rejected
Chromium Fluoride	5	No Film	--	--	--	Method Inapplicable
Chromium Chloride	0	--	--	--	--	Method Inapplicable
Chromium Oxide	5	No Film	--	--	--	Method Inapplicable
Manganese Fluoride	5	Not Prepared	--	--	--	Material Not Tested
Manganese Chloride	3	Not Prepared	--	--	--	Material Not Tested
Manganese Oxide	4	Poor Film	± 125	--	--	Method Questionable
Nickel Fluoride	5	No Film	--	--	--	Method Inapplicable
Nickel Chloride	3	No Film	--	--	--	Method Inapplicable
Nickel Oxide	5	Inconsistent	± 75	--	--	Method Questionable
Iron Fluoride	3	No Film	--	--	--	Method Inapplicable
Iron Chloride	0	--	--	--	--	Method Inapplicable
Iron Oxide	5	Film Formed	± 75	--	--	Material Rejected

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