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AFAPL-TR-65-128

LITHIUM-NICKEL HALIDE
SECONDARY BATTERY INVESTIGATION

A. Lyall
H.N. Seiger
R.C. Shair

GULTON INDUSTRIES, INC.

TECHNICAL REPORT AFAPL-TR-65-128

MARCH 1966

AIR FORCE AERO PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

NOTICES

AFALPL-TR-65-128

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Air Force Aero Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

FOREWORD

This Final Technical Report was prepared by Gulton Industries, Inc., Metuchen, N. J. for the Research and Technology Division, Wright-Patterson Air Force Base, Ohio, under Contract No. AF33(615)-1266, Project No. 8173, Task No. 817304. Mr. J. E. Cooper and Mr. W. S. Bishop were task engineers for the Air Force Aero Propulsion Laboratory. We wish to acknowledge the helpful discussions held with them.

The studies reported cover the contract period from December 1964 to November 1965.

This report was submitted by the authors on December 10, 1965.

ABSTRACT

Two methods of protecting the tabs of the $NiCl_2$ electrode from corrosion by chlorine have been developed. The first is a protective coating and the second is the use of Monel 400 alloy instead of nickel. These methods have also shown to be satisfactory for the nickel fluoride system. The Monel 400 alloy method is the most favorable.

Half cell tests indicate that thinner sintered nickel plaques reduce polarization of the positive electrode, but the degree of success is not significant.

Polarization tests with thin film electroformed nickel chloride showed that concentration polarization was only part of the problem. A major improvement was noted when the sintered nickel plaque was absent.

Pasted electrodes of $NiCl_2$ and graphite are superior to impregnated plaques. Using carbonyl nickel as a conductive diluent gave results similar to the impregnated plaques.

Tests were conducted using sulphur magnesium chloride and stannous chloride as doping agents. Experiments were conducted in which the amount of sulphur doping of the $NiCl_2$ was varied from 0.01% to 0.08%. Results show that there are two effects, one from sulphur and the other from the MCl_2 dopants. Each has advantages and disadvantages. Electrodes were also prepared having 0.04% sulphur and 0.05% $MgCl_2$ co-dopants. The effects of co-doping has been found to be additive.

A pasted nickel fluoride electrode was developed. Doping with MgF_2 had no discernable effect on polarization.

Half cell studies were conducted to investigate the effects of the ratio of nickel halide to graphite, and the effect of compressing the electrodes.

Laboratory cell studies showed the PC-$AlCl_3$ $LiCl/Cl_2$ electrolyte to be a major problem in self-discharge and subsequent reduction of available capacity. Polarographic tests were conducted on propylene carbonate and dimethyl sulfoxide electrolytes. The selection of propylene carbonate with KPF_6 as an electrolyte resulted. The state of dryness of the KPF_6 salt before dissolving it in the solvent influences the conductivity.

Various binders were tried to find a substitute for carboxy methyl cellulose. A binder of USP grade gelatine has been found to be the best.

The use of two types of graphite were investigated. UCET acetylene black is superior for the chloride system, but a blend must be used for the fluoride electrodes.

The design of the prototype cell is given.

PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

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I. INTRODUCTION

The work covered by this report is a continuation of the project started under AF33(615)-1266 and described in Technical Report AFAPL-TR-65-11, Lithium-Nickel Halide Secondary Battery Investigation. A satisfactory electrolyte for purposes of electrode study, a good lithium anode, two good separators, and materials for cell cases and hardware were the four major achievements under this contract.

The electrolyte was propylene carbonate containing 100 g/L of $AlCl_3$ and saturated with LiCl. The propylene carbonate is saturated with chlorine gas at room temperature before adding the $AlCl_3$. This prevents the darkening of the electrolyte due to heating when the $AlCl_3$ is added. After saturating with LiCl, the excess chlorine gas is scavenged with lithium metal.

The lithium anode is a pasted electrode of lithium and carbonyl nickel powder. A carboxymethyl cellulose binder improves adhesion of the discharged material to the expanded nickel screen used as a base. Low polarization potentials and relatively high utilization of theoretical capacity (80%) on both charge and discharge have been found.

The separators used have been a non-woven polypropylene and an asbestos-fiberglass paper. Both have been equally successful and have been used interchangeably. The polypropylene has the advantage of being heat sealable, so that electrode "bags" can be made for easier cell assembly.

Cell cases can be made of polyethylene or polypropylene. Teflon is completely inert and can be used, but sealing a Teflon cell is difficult. Type 304 stainless steel is satisfactory as a cell case. Some metals such as aluminum can be used if they are in contact with lithium. Because of the high activity of lithium, it will react before the case material and, thus, give anodic protection.

The problem that still had to be resolved was the excessive polarization of the nickel halide electrode. Both the nickel chloride and the nickel fluoride electrodes show a high degree of polarization on both discharge and charge, the latter being so great as to allow almost no current. This prevented discharge rates from approaching any satisfactory level while maintaining cell voltages above 2.0 volts. The major emphasis was placed on finding a way to reduce the polarization of the nickel chloride electrode, and in finding a way to produce a nickel fluoride electrode which could be discharged.

II. ELECTRODE TAB CORROSION

A. PROBLEM

The nickel chloride electrode is a sintered nickel plaque formed on a perforated nickel sheet approximately 3 mils thick. To this plaque, a nickel tab has been welded for electrical contact.

In order to improve the utilization of the present $NiCl_2$ electrode, it is necessary to subject these electrodes to a formation cycle. During this formation cycle, there is an anodization taking place at the nickel tabs. This anodization necessitates the replacing of the tabs after two such cycles, making accurate weight gain determination impossible.

This same anodization takes place in a cell and the tabs are soon corroded away causing open circuits. The resulting rough edges of the tabs may also cause a short circuit.

B. APPROACH TAKEN

There were two approaches planned to solve this problem. The first was a protective coating and the second was to find a material with an anodization potential greater than nickel.

1. Protective Coatings

One of the earlier protective coatings applied was an epoxy paint (No. 7263 F.P./K by Markem Machine Co.). This material was satisfactory for tab protection when applied to a finished electrode. The epoxy was cured by heating to just under 150°F for one hour. However, if it was heated at this temperature in excess of an hour, it would become brittle. The tabs were coated with this epoxy, the plates impregnated and subjected to a formation cycle. After the formation discharge, the plates were washed, dried, and impregnated again. They were dried and subjected to another formation cycle. Inspection of the tabs at this time revealed that the epoxy was brittle, even though the temperature had been kept below 150°F. The total time, however, was over 2 hours. This indicates the epoxy being used becomes brittle on prolonged exposure to heat as well as temperatures above 150°F. There is apparently a time-temperature dependence whereby, given a long enough time, the epoxy will become brittle even at room temperature.

A successful technique was developed in which the tabs were coated with a fluorinated ethylene-propylene copolymer. Electrode tabs are spot welded to the unimpregnated nickel plaques. Masking off the area where active material will be deposited and also where the tabs will be welded to the terminal studs, a coat of FEP #856-301 Primer (DuPont) is sprayed on. This, as well as the #856-204 Teflon coat, is a water suspension. The primer is air dried and the plaques are fired at 625° to 650°F for 30 minutes. After cooling, the same mask is used as before and the tabs sprayed with the FEP #856-204 dispersion. After drying, the plaque is again fired, this time at 650° to 675°F for a period of from 45 to 60 minutes. A second coat of FEP #856-204 is applied and fired as before. The FEP Teflon flows at the temperatures used. The tetrafluoroethylene (TFE) Teflon is sintered and is somewhat porous and cannot be used for this application. Two coats of the FEP Teflon are applied to insure no pin holes in the surface.

The plaque is now ready for impregnation and formation. Figure 1 contains two photographs of a pair of electrodes. Note that the Teflon coating is carried into the sintered plaque area. This is done to prevent oxidation of the sinter surface near the tabs which may result in loss of contact.

2. New Alloys for Tabs

The second approach, that of finding an alloy that is more noble than nickel to the oxidation by chlorine, has produced a satisfactory alloy. Monel 400 has been found to resist anodization in the nickel chloride-lithium cell. This material has been tested using the double ammeter technique. Figure 2 is a schematic of the apparatus used. Two ammeters of equal internal resistance are connected in the parallel legs of the circuit. The positive leg of the circuit is connected through a third ammeter used to control the total current. From one of the parallel ammeters, a lead is connected to the test electrode. The other meter is connected to a nickel anode. The cathode is a $NiCl_2$ electrode. The spacing between the electrodes is the same. The stack is placed in a polyethylene cell or a beaker shimmed with polyethylene. The cell is placed in a glove bag with a dry argon atmosphere and propylene carbonate - $AlCl_3/Cl_2$ electrolyte added. Voltage is applied and the current values recorded. The test continues until the current stabilizes with respect to time.

C. EXPERIMENTAL RESULTS

1. Protective Coating

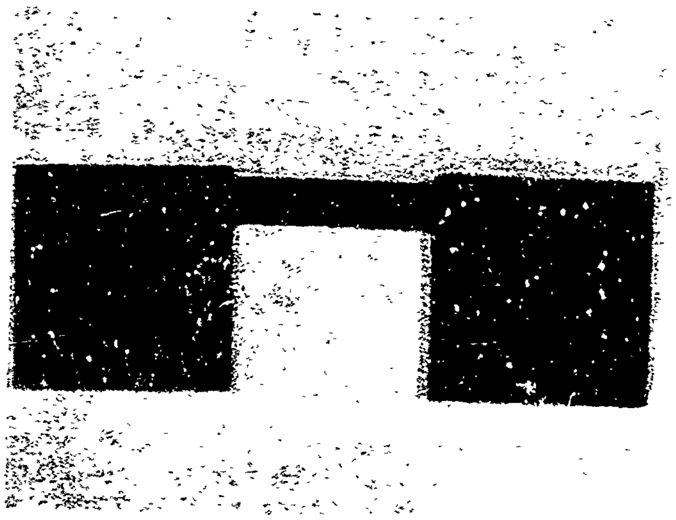
Extensive testing of the FEP coated tabs was not done. Initial tests indicated that additional coating was necessary in the region of the weld between the tabs and the terminal stud. In a cell flooded with electrolyte, there was corrosion of the tabs at the weld to the terminal stud. After welding, another coat of primer was applied and firing was accomplished with an electric heat gun. The same technique was used for the Teflon coats. It is difficult to control the heat, and temperatures can only be estimated with this technique. In the experiments conducted, this secondary coating method had been satisfactory, but better control was needed to insure uniform quality. These tests were abandoned with the advent of the pasted nickel halide electrodes using Monel 400 screen.

2. New Alloys for Tabs

The materials tested were initially selected by consulting various engineering handbooks and through direct consultation with technical representatives of companies which produce corrosion resistant alloys. Without going to the expense of using the more exotic or precious metal alloys, the selections were limited to largely nickely base alloys. Silver was also used, since it was thought to form a protective coating and would not corrode seriously. Silver was found to form a coating on exposure to the electrolyte, but under the influence of electrochemical cycling, the penetration continued with use.

All stainless steels were eliminated as well as iron-nickel alloys. This left the Monel types and Hastelloy types.

Front Side



Back Side

FIGURE 1 DOUBLE POSITIVE ELECTRODE PLAQUES SHOWING TEFLON COATING ON TABS.

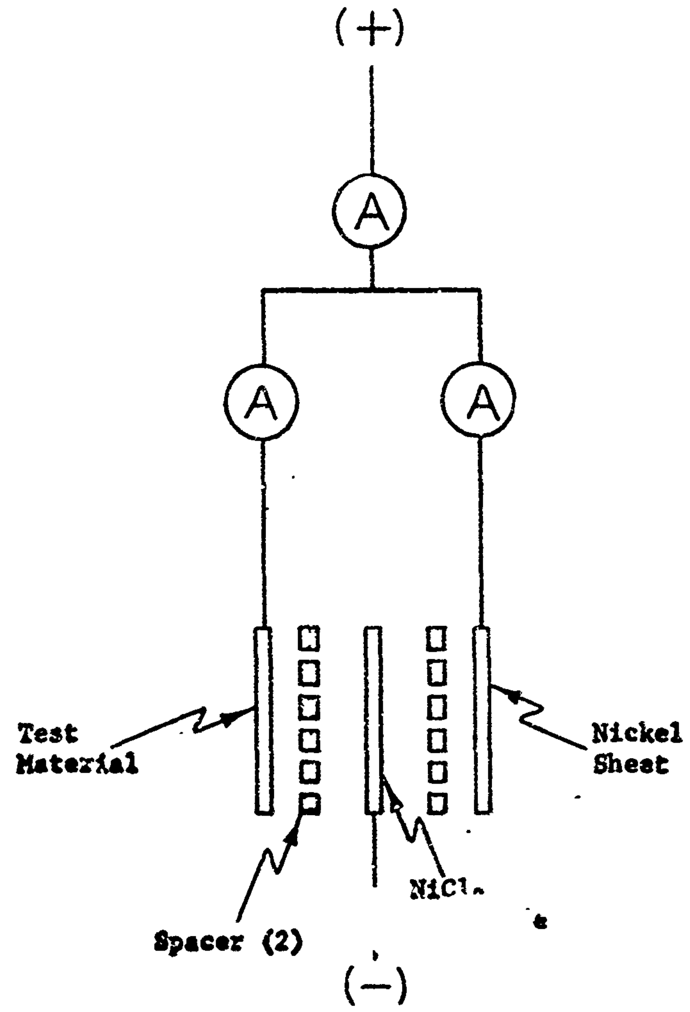


FIGURE 2 SCHEMATIC OF DOUBLE AMMETER TEST

When the metal under test was more noble than nickel, the majority of the current passed between the nickel sheet and the $NiCl_2$ electrode. As the nickel sheet became covered with $NiCl_2$, the current shifted to the test metal where either chlorine gas was liberated, or anodization of the alloy took place. It was during this period, representing the overcharge period of the electrode, that corrosion of the tabs took place. After the current stabilized, it was continued for 10 minutes. The cell was disassembled, the test electrode washed and examined for corrosion. Figure 3 is a plot of the two ammeter readings for the Monel 400 test. Figure 4 is the ammeter readings for the Hastelloy C.

From these tests, Monel 400 has been found to be the best material with Hastelloy C useable. Since the tests were conducted at a constant current, the plots of the ammeter readings in Figures 3 and 4 form mirror immages. In Figure 3, the period from 30 to 40 minutes is where gassing was visible at both electrodes. The jump at 17 minutes was probably due to decomposition of the electrolyte. In Figure 4, there was some gassing at the Hastelloy C electrode at the beginning. After 15 minutes, the gassing was the same on both electrodes.

Figure 5 contains photographs of the test and nickel electrodes used for these experiments. These photographs were made with oblique lighting. The Monel 400 (Figure 5a) shows a small amount of corrosion in the lower portion of the exposed circle. The nickel electrode on the right shows the effect of oxidation when $NiCl_2$ was formed. The Hastelloy C (left side of Figure 5b) shows a larger area of corrosion than the nickel, but the depth of penetration was less than the nickel. The etched surface of the Monel 400 was discernible only with oblique lighting, whereas, the other samples could be seen with diffused lighting.

Hastelloy C is a hard alloy and exhibits little plasticity. Even an annealed or "soft heat" sample was not very pliable.

Monel 400 is more flexible than Hastelloy C, but at times, it has been found to become brittle when it is spot welded to the stud or to the electrode. This is due to the excessive local heating. A minimum amount of power (about 2700 amperes for 50 ms or 3 cycles of 60 cps AC) is used that will produce a good weld, thereby eliminating excessive heating.

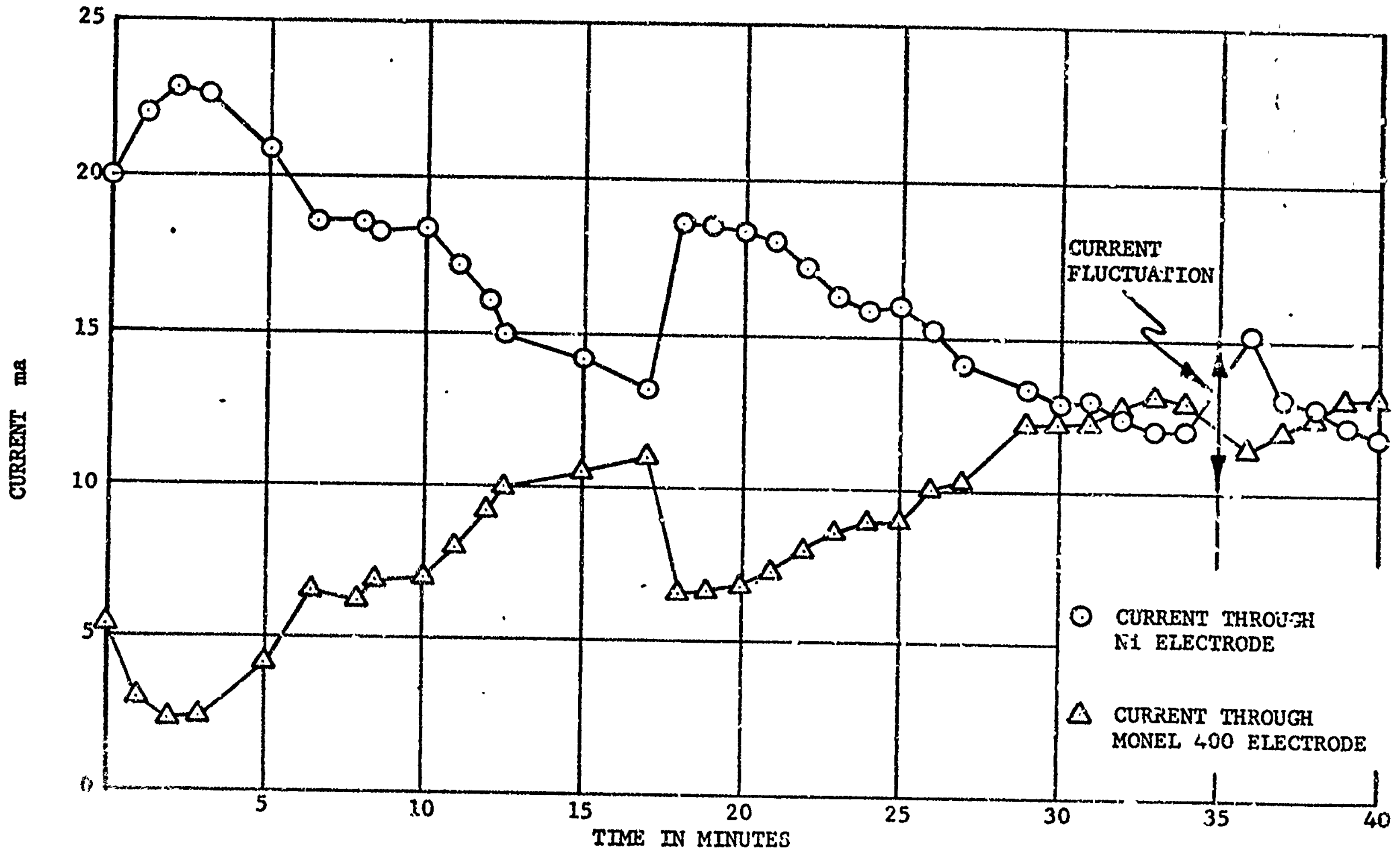


FIGURE 3 - DOUBLE-AMMETER TEST - MONEL VS NICKEL

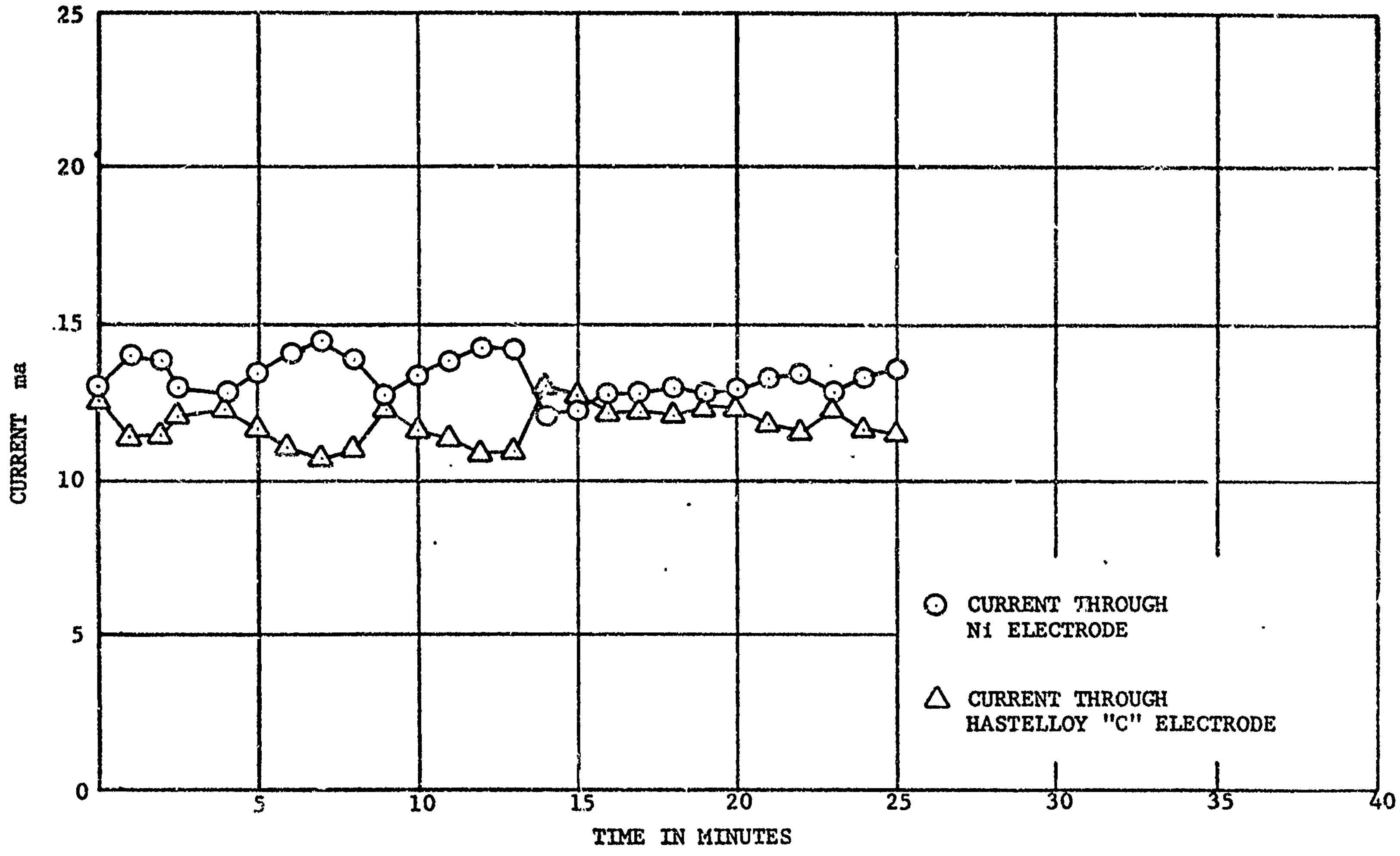
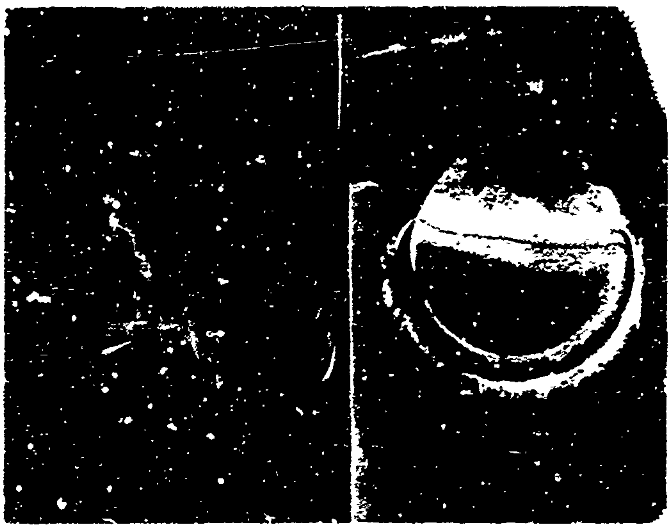
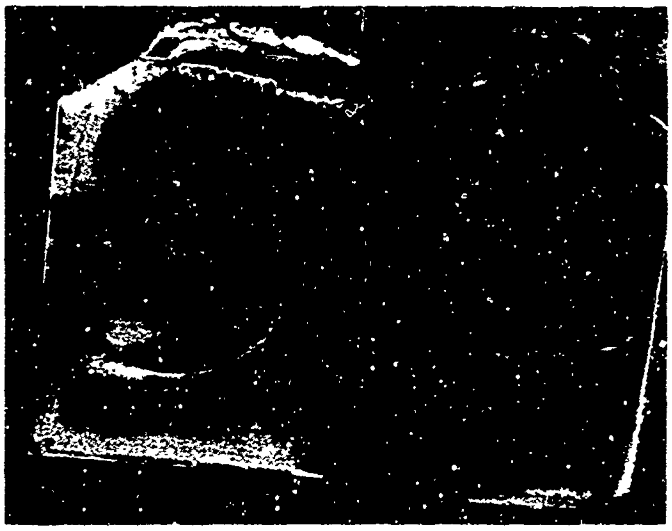


FIGURE 4 - DOUBLE-AMMETER TEST - HASTELLOY "C" VS NICKEL



a. Left-Monel 400, Right-Nickel A (or Nickel 200)



b. Left-Hastelloy "C", Right-Nickel A (or Nickel 200)

FIGURE 5 DOUBLE-AMMETER TEST SAMPLES - COMPARATIVE AMOUNTS OF CORROSION

III. NICKEL CHLORIDE SYSTEM

A. PROBLEM

Initially, the nickel chloride electrodes were sintered nickel plaques impregnated with nickel chloride. These electrodes exhibited a high degree of polarization on discharge. There was a constant decrease in potential with discharge.

The cause of the polarization was believed to be partially due to a concentration polarization within the pores of the sintered nickel plaque. Formation cycling improved the usable capacity, but did not affect the polarization potential to a degree that would make it acceptable. There seemed to be a combination of ohmic, concentration and chemical polarization influencing the positive electrode.

Experiments were conducted using thin films of nickel chloride deposited on a non-porous surface. These experiments revealed that the sintered nickel plaque was contributing greatly to the polarization, and not exclusively through concentration polarization in the pores.

Because of this, and with the success of the pasted lithium electrode, a new approach was taken, that of a pasted nickel chloride electrode. This improved the electrode somewhat, but the current densities were limited to 1 ma/cm^2 at best and utilization of the active material was about 10%.

The problem then became one of trying to improve the utilization of the active material and reduction of the polarization.

B. METHOD OF APPROACH

1. Cathode Preparation

a. Sintered Plates

The original approach taken with the sintered nickel plaque was concerned with the reduction of concentration polarization taking place within the pores of the sinter. Experiments reported in Technical Report AFAPL-TR-65-11 indicated that a flow of electrolyte through the pores reduced polarization. It was proposed that if the path through the pores could be shortened, it would be reasonable to assume that the concentration polarization taking place in the plaque could be reduced. The standard sintered nickel plaque used for the $NiCl_2$ electrodes had been 30 mils thick with about 70% to 80% porosity on 4 mil thick perforated nickel sheet. Samples of sintered nickel plaques with a 17 mil thickness on the same base and a 67% porosity were prepared by the nickel-cadmium Plate Facility Dept. at Gulton Industries. These plaques were cut to squares 1¼ inches on a side. A similar set of 30 mil thick plaques were prepared as controls. This plaque is the same as is used for the cadmium electrode of the nickel-cadmium cell.

The nickel chloride is introduced as a saturated solution of $NiCl_2 \cdot 6H_2O$ in methanol. The concentration is 330g $NiCl_2$ per liter of solution. This solvent was used because of its low surface tension which facilitates the penetration of the solution into the pores of the nickel matrix. The plaques are placed in the solution in a beaker. The beaker is put in a bell jar and a vacuum of 27 inches pulled. After 5 minutes, the pressure is returned to atmospheric and the plates removed. The excess solution is wiped off with a glass doctor knife.

The plates are air dried at room temperature to remove all surface wetting. They are further dried at 75° to 80° under 20 inches of vacuum for 2 hours. The vacuum jar in which the plates are dried is placed in the oven at room temperature, allowing the temperature to come up over a period of several minutes. The temperature is kept low to prevent creeping of the nickel chloride to the surface during drying. If the pressure is reduced below 20 inches of vacuum, the plates weep, even at room temperature, and a large percentage of the nickel chloride migrates to the surface of the plate.

The process is continued until the desired weight is obtained or a specified number of cycles is completed. Experimentally, 7 cycles has been found to give a fully "loaded" electrode. The plates are then dried for 16 hours while the temperature is increased to 130°C and the pressure kept at 20 inches of vacuum. At this point a greater vacuum could be used, but it is kept constant for simplicity.

While still in the vacuum jar, the plates are cooled to room temperature. The jar and plates are transferred to a glove box having a dry atmosphere and the plates removed. They are stored in a desiccator over calcium sulfate until needed.

The average pickup of $NiCl_2$ was 0.125 g/in^2 for the 17 mils thick plaques and 0.150 g/in^2 for the 30 mils thick plaques. Three electrodes of each thickness were given only one impregnation and three were given seven such impregnations to yield a set of fully loaded electrodes. The fully loaded electrodes averaged 0.4 g/in^2 and 0.7 g/in^2 for the 17 and 30 mils thick sinter respectively. The electrodes were not subjected to any formation cycles.

The electrodes were tested in the apparatus shown in Figure 6, which is the same apparatus reported in the aforementioned Technical Report. Electrolyte was placed in the funnel and the electrodes discharged. A vacuum was applied to the funnel forcing electrolyte through the plaque while the electrodes were being discharged.

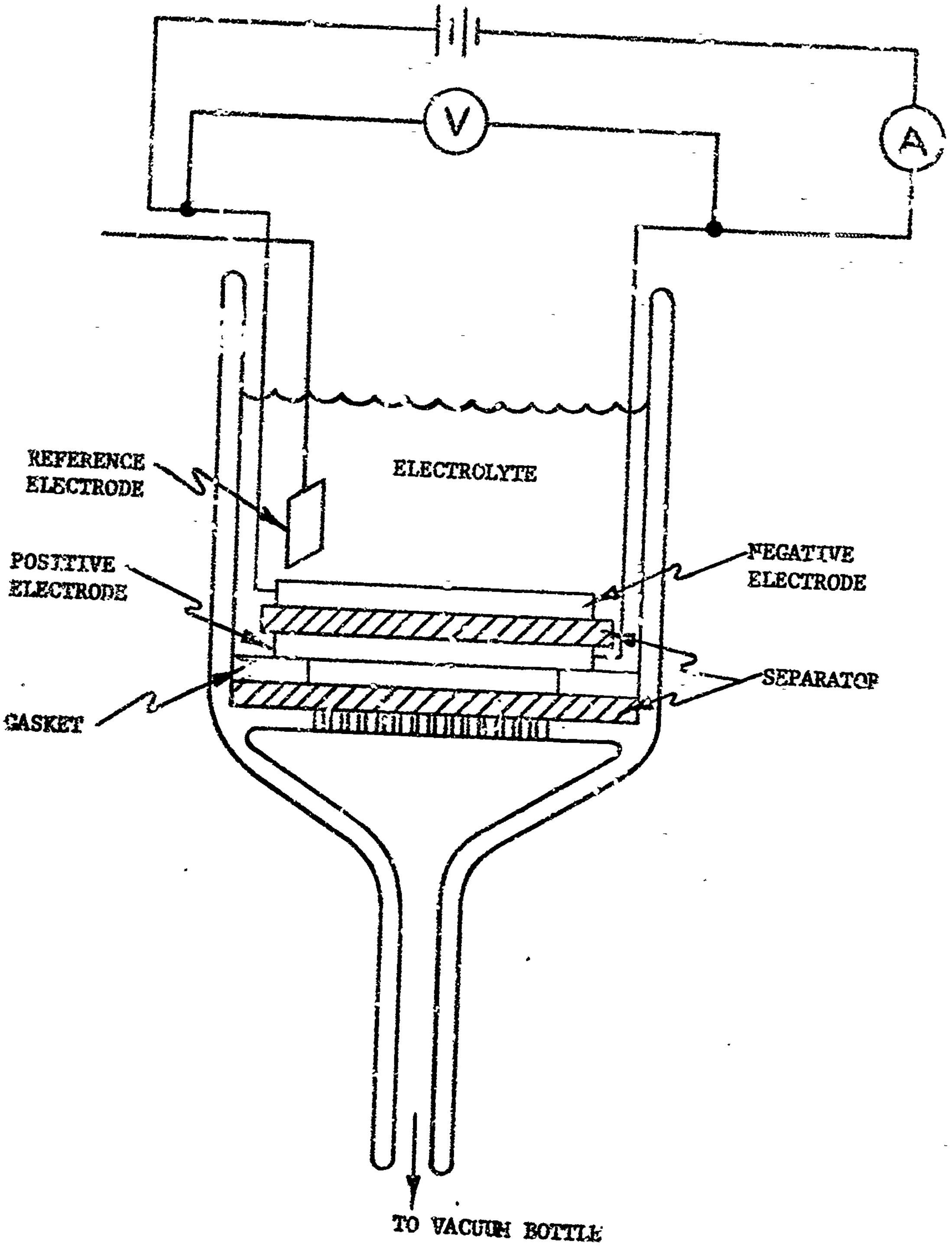


FIGURE 6 - APPARATUS FOR CONCENTRATION POLARIZATION STUDIES

The results of these tests indicated that the polarization found with the sintered nickel plaque was not wholly due to the porosity of the sintered nickel. To further investigate this problem, the approach of using a thin film of nickel chloride on a non-porous substrate was followed.

b. Thin Plates

Plates of Monel 400 were electroplated with nickel using a commercial nickel sulfamate bath, at 2 ma/cm^2 and 140°F for 10 minutes. The plates were dipped in an aqueous solution of CMC to form a binder film on the surface. Such a film is porous and insoluble in the electrolyte. These plates were placed in cells with nickel chloride electrodes prepared by the impregnation of a sintered nickel plaque with $NiCl_2$ as previously described. Polypropylene separator and PC-$AlCl_3 \cdot LiCl/Cl_2$ electrolyte were used. Films of $NiCl_2$ were formed on the surface at various current densities. Several attempts were made to produce a uniform layer. Each trial resulted in a mottled coating, showing the chloride built up, presumably, wherever a nucleus first originated. There seemed to be a migration of nickel chloride to these areas and the buildup was in thickness rather than area. By varying the current density, 3 to 60 ma/cm^2 were tried; the best results were at 13 ma/cm^2. The conversion was only about 50% of the available nickel and the area was about 25% of the surface.

The plates were washed with isopropyl alcohol since $NiCl_2$ is insoluble in it and the electrolyte is. They were dried and stored in the dessicator until used, usually within a day or two.

The results of these tests showed that the sintered plaque technique was not satisfactory.

c. Pasted $NiCl_2$ - Carbonyl Nickel Electrodes

A sample of about 50 grams of $NiCl_2 \cdot 6H_2O$ was heated in an evaporating dish in the drying oven at 110°C. A crust formed on the surface which had to be periodically broken to insure continuing evaporation of the water. When all the $NiCl_2$ appeared to be yellow instead of green, the temperature was increased to 180°C for 16 hours. The dried $NiCl_2$ was ground in a mortar and pestle in a dry atmosphere until it all passed through an 80 mesh screen ($<$0.175 mm). The material was reheated at 180°C for 2 hours and placed in a jar while hot and sealed.

A sample of $NiCl_2$ powder was weighed out and an equal amount of carbonyl nickel powder added. The mixture was tumbled to thoroughly mix the powders. A carboxy methyl cellulose binder was added, but this was later replaced with the use of USP gelatine powder from Baker & Adamson. This binder has been found to actually be superior since it is easier to use and the adhesive properties are good. Half cell polarographs indicated there are no electrochemical effects observed from the binders used. The CMC binder became gelatinous during the discharge of the $NiCl_2$ electrode, which could affect cycle life. An aqueous dispersion of the binder is [illegible] to give 2% (dry weight) of the final mixture.

The paste of $NiCl_2$-carbonyl nickel powder and binder is applied to a 4/0 expanded metal screen at a 1 gram/$10cm^2$. The best material for the screen is, again, Monel 400, although pure nickel has been used. A Monel 400 tab is spot welded on before pasting the electrode. The electrode is air dried at room temperature until dry to the touch. It is then compressed at 2 tons/in^2. The electrode is thoroughly air dried at 110°-120°C for 16 hours.

d. Pasted $NiCl_2$-Graphite Electrode

A paste was made of the anhydrous $NiCl_2$ powder and an equal part of graphite (National Carbon No. 38). An electrode was prepared using 2% USP gelatine binder. The $NiCl_2$-graphite electrode was prepared the same as the $NiCl_2$-carbonyl nickel electrode.

Pasted electrodes of $NiCl_2$ and graphite showed some improvement over impregnated sintered nickel plaques. Doping of the $NiCl_2$ electrode had produced both desirable and undesirable effects. The sulphur doped electrodes yielded a higher initial voltage for a given current density However, the rate of increase in polarization with time was such that after the same number of ampere minutes had passed, the voltage was the same as an undoped electrode.

The magnesium or stannous chloride doped electrodes showed a lower voltage for a given current density, but the increase in polarization with time was much less than undoped electrodes. Although, there was considerable variability in the $MgCl_2$ results, they seem more favorable than the $SnCl_2$ doped electrodes.

The amount of sulfur and $MgCl_2$ doping was arbitrarily chosen as 0.1%. The effect of varying the amount of dopant and the effect of co-doping with both sulfur and magnesium chloride were yet to be resolved.

The $NiCl_2$ electrodes had been pressed at 2 tons/in^2 in order to obtain a smooth, even electrode and ensure good contact between the particles for conductivity. The fact that the electrodes had to be compressed for smoothness was obvious, yet the effect of such compression or polarization and utilization were not known This also, had to be investigated.

The amount of sulfur dopant was varied in the $NiCl_2$ by successive dilutions of the 0.1% doped material with pure $NiCl_2$. Since both the doped and undoped portions are soluble, when a paste is made using water as the solvent, the sulfur is presumably dispersed uniformly. The amounts of sulfur were 0.1%, 0.08%, 0.04%, 0.02%, and 0.01%.

Electrodes were also prepared by mixing equal parts of 0.08% sulfur doped $NiCL_2$ with 0.1% $MgCl_2$ doped $NiCl_2$. All of the electrodes were made by taking 50% of the $NiCl_2$ and 50% graphite (National Carbon No. 38) plus the binder. Electrolyte was $PC\text{-}AlCl_3 \cdot LiCl/Cl_2$.

To test the effect of compressing the electrode, four $NiCl_2$-graphite electrodes were prepared from a mix of 1 part $NiCl_2$ (0.08% S doped) and 3 parts graphite. After air drying at room temperature, two electrodes were pressed at 3 tons/in^2 and two were not. They were all dried at 120°C overnight before testing.

To determine if the ratio of $NiCl_2$ to graphite has any significant effect, two ratios were chosen. One was 10% $NiCl_2$ (containing 0.08% S) and 90% graphite; the other was the inverse.

2. Polarographic Tests

A small plastic test cell was made to hold 3 electrodes and a reference electrode. Each electrode had a 10 cm^2 area. The electrode under test and two pasted lithium electrodes were placed in the cell using polypropylene separator and the standard $PC\text{-}AlCl_3 \cdot LiCl/Cl_2$ electrolyte. The system was wired according to the schematic in Figure 7. When the switch was in the open position, the cell voltage was recorded on the X axis of the X-Y recorder. A precision, one ohm resistor was in series with the cell and the voltage drop across this resistor was recorded on the Y axis and recorded as the current.

A motor driven potentiometer with a total resistance of 100 ohms was put in series. The total resistance could be varied linearly in 2.5 minutes and the motor was capable of being reversed in direction.

When the switch was closed in the discharge position, the cell discharged through the potentiometer, which acted as the load. When the switch was closed in the charge position, the charge current was varied by the potentiometer and the bucking voltage of the cell.

In discharging the cell, the potentiometer was started at 100 ohms and driven to zero ohms, hence, varying the load from 101 to 1 ohm. At this point, it was reversed and brought back to 101 ohms. The charges were performed in the same manner. Modifications in the procedure are noted under experimental results.

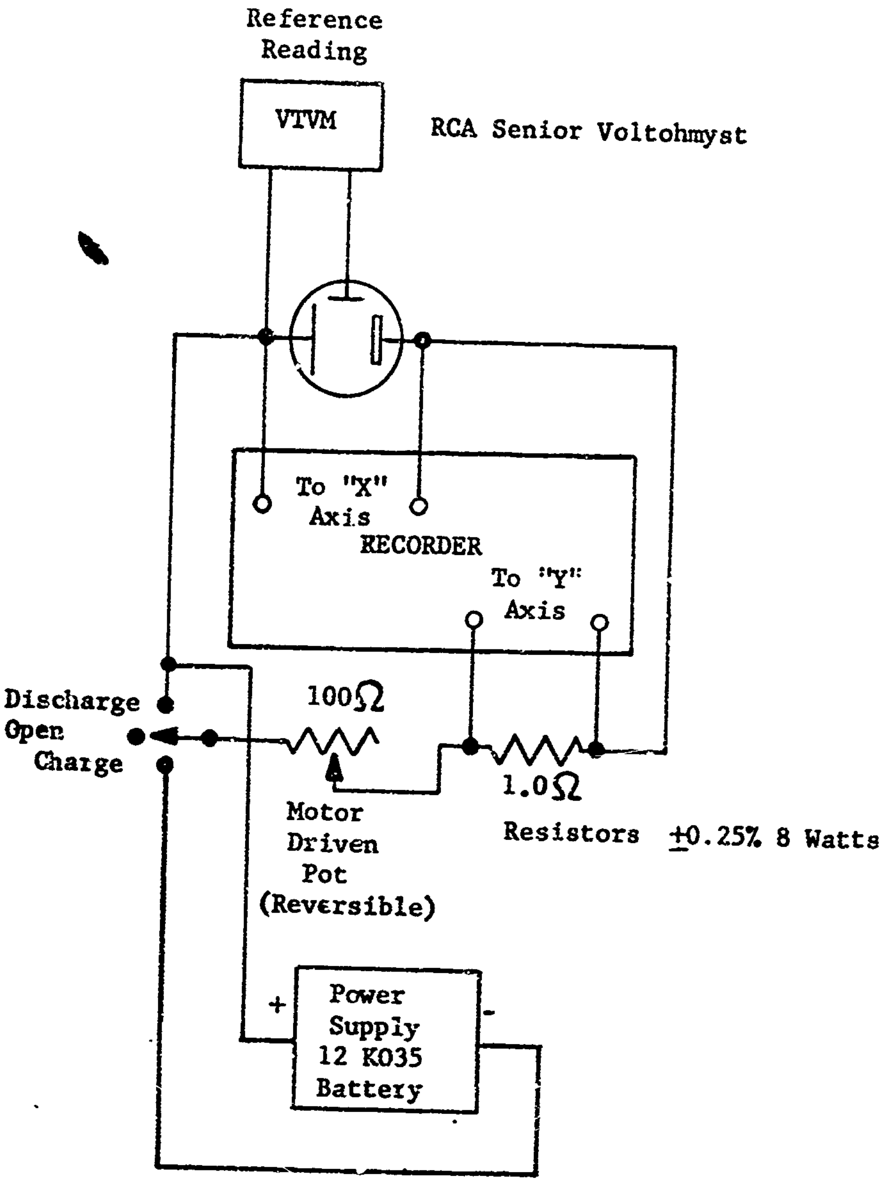


FIGURE 7 POLAROGRAPHIC STUDY - SCHEMATIC FOR X-Y RECORDER SETUP

Subsequent testing was done using a Wenking Potentiostat and the X-Y recorder. The Wenking Potentiostat is also a Galvanostat and was used in this way as shown in Figure 8.

C. EXPERIMENTAL RESULTS

1. Sintered Plaques - Polarization Tests

Figure 9 is a typical plot of the cell voltage and the positive to reference voltage during the polarization tests. The cell was allowed to remain on open circuit about 12 minutes and then discharged at 3.0 ma/cm^2. There is an immediate decrease in voltage. At the end of one minute, the amount of this decrease in voltage was noted. Table I summarizes the data. During the next nine minutes, the change in voltage with time was determined and tabulated as increase in polarization with time. The vacuum was then applied and the increase in voltage (decrease in polarization) was noted. The initial polarization potentials (columns 4 and 5) favor the 30 mil thick electrode. However, the polarization with time (columns 6 and 7) favor the 17 mil thick electrodes. Using the Fisher "t" test, (Facts From Figures, M. J. Moroney, Penquin Books, London, 1956) the probability of the difference between the data on the 17 mil thick and the 30 mil thick electrodes due to cause (not error) is 93% in column 7. This is a strong indication that the 17 mil thick electrode does not polarize as much with discharge as the 30 mil thick does. The fact that, initially, some thin plate electrodes showed a high polarization is due to differences in surface coating of $NiCl_2$. This facet is eliminated with formation cycling.

The high degree of variability in the results of the decrease in polarization with electrolyte flow (column 8) was due to the lack of control of the flow rate of the electrolyte through the electrodes. Further testing was planned using a modification of the apparatus to control the flow rate. This work was abandoned after the results of the thin film electrode studies were obtained.

2. Thin Film Plates - Polarographic Tests

A 3 plate cell was assembled in the polyethylene test cell. Using the apparatus shown in Figure 7, the thin film electrode was discharged and charged. When the cell discharged through the 100 ohms, the voltage dropped to 1.75 volts and the cell delivered 1.4 ma/cm^2. The motor drive was started as soon as the switch was closed and the resistive load decreased. The current increased and the voltage approached zero. Since there was always at least one ohm in the circuit, the voltage did not reach zero. The drive was reversed and, as the resistance increased, the current-voltage trace returned on the same line as when in the decreasing resistance mode. This indicated that there was little if any change in polarization with time during discharge. The original open circuit voltage was 2.95 V and the positive to reference voltage was -0.10V. After discharge it was 2.075 V, and the positive to reference voltage was

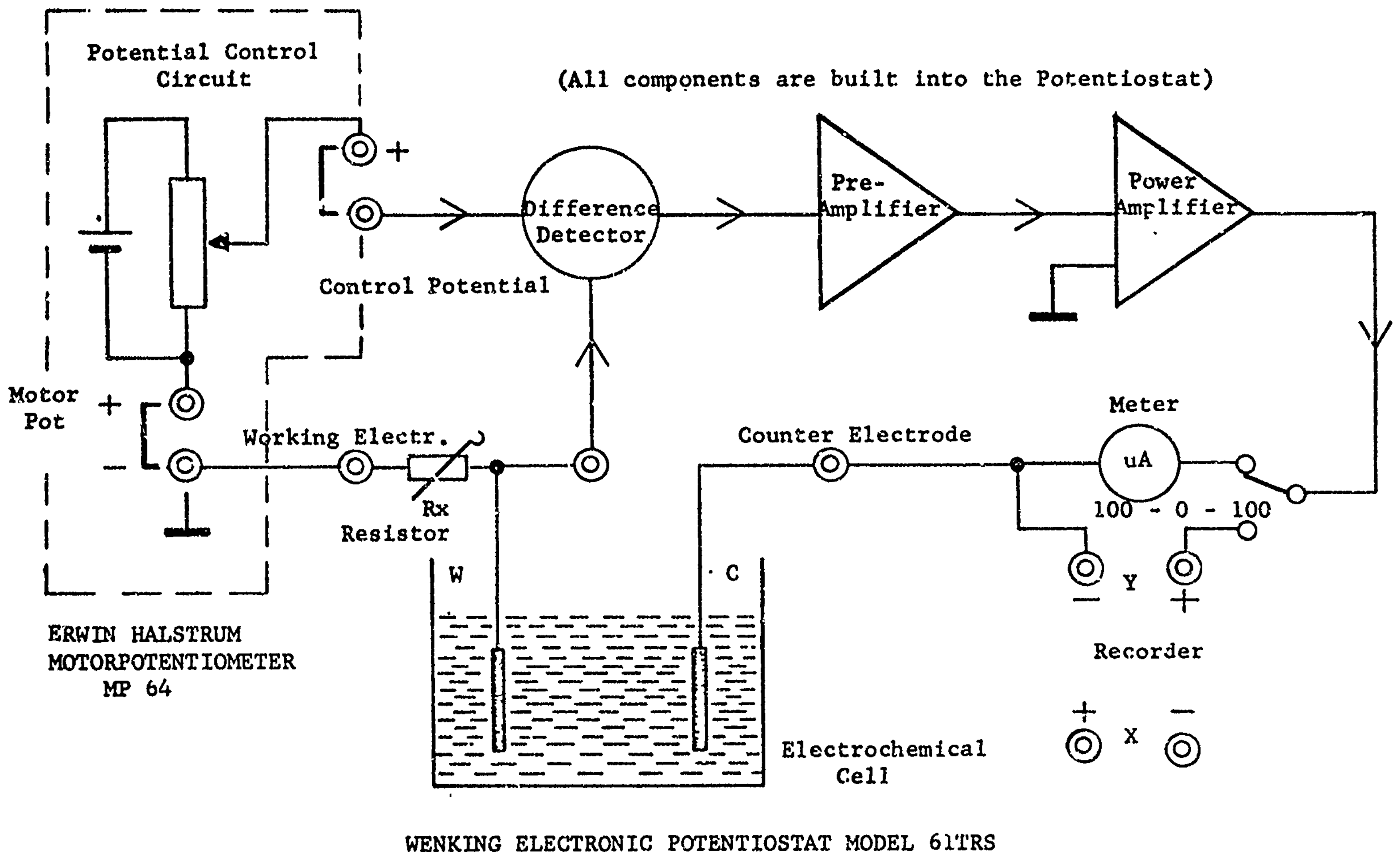


FIGURE 8 OPERATING PRINCIPLE GALVANOSTAT

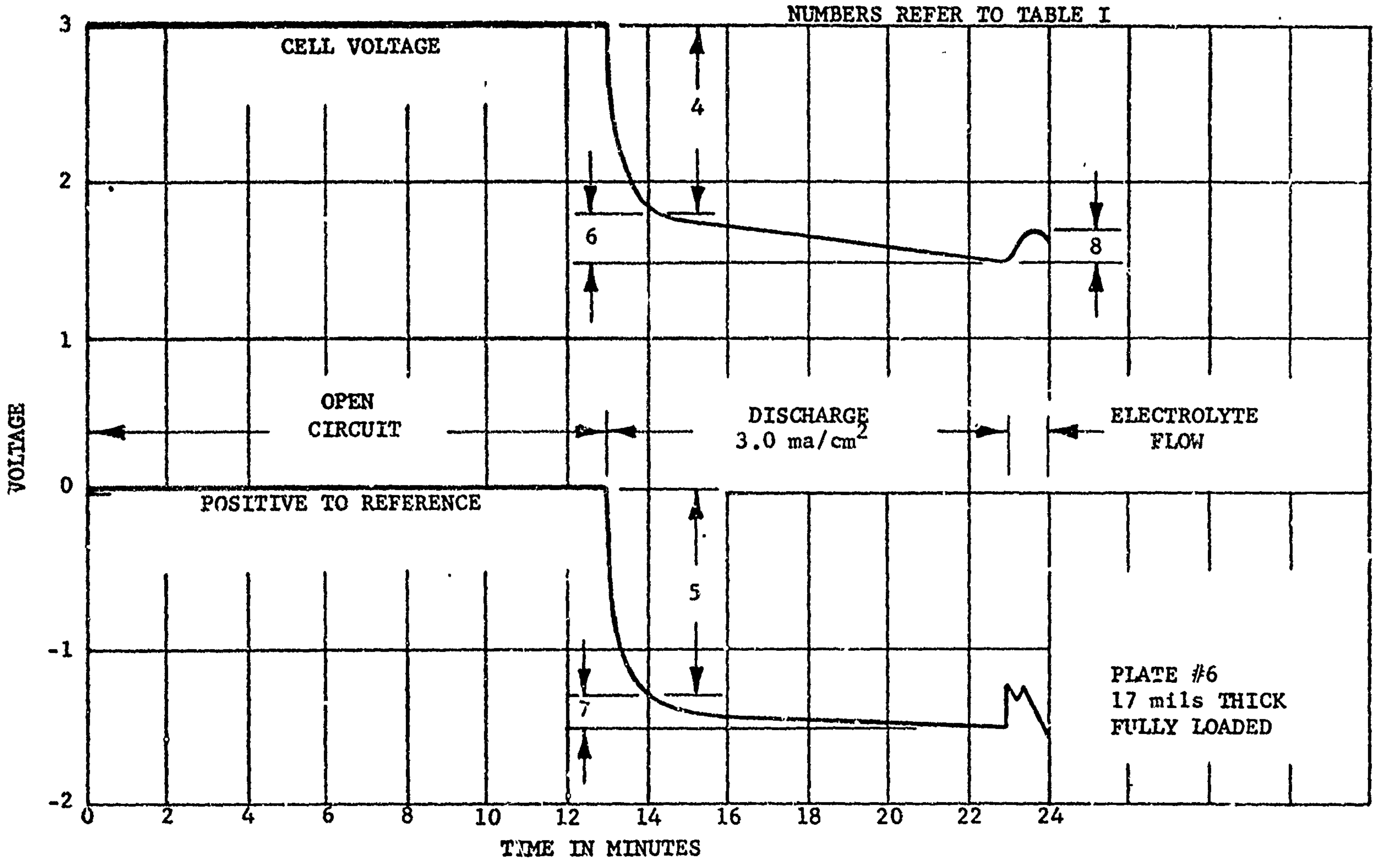


FIGURE 9 - TYPICAL POLARIZATION TEST OF $NiCl_2$ IMPREGNATED SINTERED Ni PLAQUE

TABLE I

THE EFFECT OF PLATE THICKNESS ON POLARIZATION

			INITIAL POLARIZATION VOLTAGE		INCREASE IN POLARIZATION WITH TIME mv/min		DECREASE IN POLARIZATION WITH ELECTROLYTE FLOW V in Volts
PLATE NO. (1)	THICKNESS (mils) (2)	LOADING (3)	POS. TO NEG (4)	REF. TO POS. (5)	POS. TO NEG (6)	REF. TO POS (7)	(8)
2	17	P	1.60	1.35	45.9	15.3	.55
3	17	F	1.25	1.25	28.6	16.2	.10
4	17	F	1.30	1.30	20.0	20.0	.65
5	17	P	1.00	1.12	31.9	31.9	.20
6	17	F	1.20	1.30	30.0	20.0	.30
AVG		All	1.27	1.26	31.7	20.7	.36
AVG		F	1.25	1.28	26.2	18.7	.35
AVG		P	1.30	1.24	35.9	23.6	.38
13	30	F	1.20	1.20	54.5	45.4	.50
14	30	F	1.10	1 12	26.1	26.1	.15
17	30	F	1.10	1.10	44.2	28.8	.25
18	30	P	1.80	--	40.0	30.0	1.15
19	30	P	1.10	1.18	40.0	25.0	.05
20	30	P	1.10	1.10	33.3	38.1	.20
AVG		All	1.23	1.14	39.7	32.2	.38
AVG		F	1.13	1.14	41.6	33.4	.30
AVG		P	1.33	1.14	37.8	31.0	.48
Probability of difference being due to cause			80%	82%	74%	93%	

F = Fully Loaded (0.4 g/in^2 for 17 mil and 0.7 g/in^2 for 30 mil)
P = Partially Loaded(0.125 g/in^2 for 17 mil and 0.150 g/in^2 for 30 mil)

slowly increasing from -1.45 V towards -0.10 V. During the discharge, the positive to reference voltage ranged from -1.40 to -2.70 volts and back to -1.45 volts. The difference from start to finish was 0.05 volts, which does not account for the 0.875 volts difference in open circuit voltage.

The cell was placed on charge (through 100 ohms) using a 6.5 volt power supply. As the resistance in the charge circuit decreased, the current density increased with the voltage to 3.5 ma/cm^2 at 4.15 to 4.20 V. It suddenly decreased and at 4.85 volts there was a sharp break and the current rose again with the voltage.

When the variable resistor reached zero ohms, the drive was reversed. As the current and voltage decreased, they followed the same path as the increase to the 4.85 volt point. The trace continued on an almost straight line. The charge was stopped when the resistor reached 100 ohms. The open circuit voltage returned to 2.95 volts and the positive to reference potential was -0.10 volts.

The following discharge, and all subsequent discharges, followed the original current density-voltage relationship shown in Figure 10. From this, and the fact that the curves return as the resistance increases, it can be concluded that the polarization does not change even when the state of charge changes by a factor of 2. There is an indication that the open circuit voltage does decrease some, immediately after discharging, but it slowly returns to 2.95 volts on stand.

The experiment was repeated with another electrode using the galvanostat, and the X-Y recorder trace is shown in Figure 11. The discharge trace is not as close as shown in Figure 10. In the charge portion of the curve, the "hump" seen in Figure 10 is best seen in the lower loop of the trace in Figure 11. This is believed to be due to a breakdown of the electrolyte near the 4.8 volt region. The value does not hold consistently and can be traced to the amount of excess chlorine in the electrolyte.

An alcoholic solution of $NiCl_2 \cdot 6H_2O$ and carboxy methylcellulose (CMC) was painted on a nickel support material and dried. The polarization tests were done as before, using the variable resistor. Figure 12 is of the plots obtained for the first three discharges. The charges all followed the same trace as the first. These results were very different from the results obtained with electroformed $NiCl_2$ on Monel, (Fig. 10). The charges did not show the "hump" in the c.d. vs voltage plot. The discharges showed a variation from cycle to cycle and also a considerable increase in polarization with time. This increase with time became more acute each cycle.

3. Pasted $NiCl_2$-Carbonyl Nickel Electrode - Polarographic Test

Figure 13 is a plot of the first three discharges and charges of the pasted electrode. The variable resistor equipment (Fig. 7) was used. The first discharge showed an almost linear c.d. vs voltage

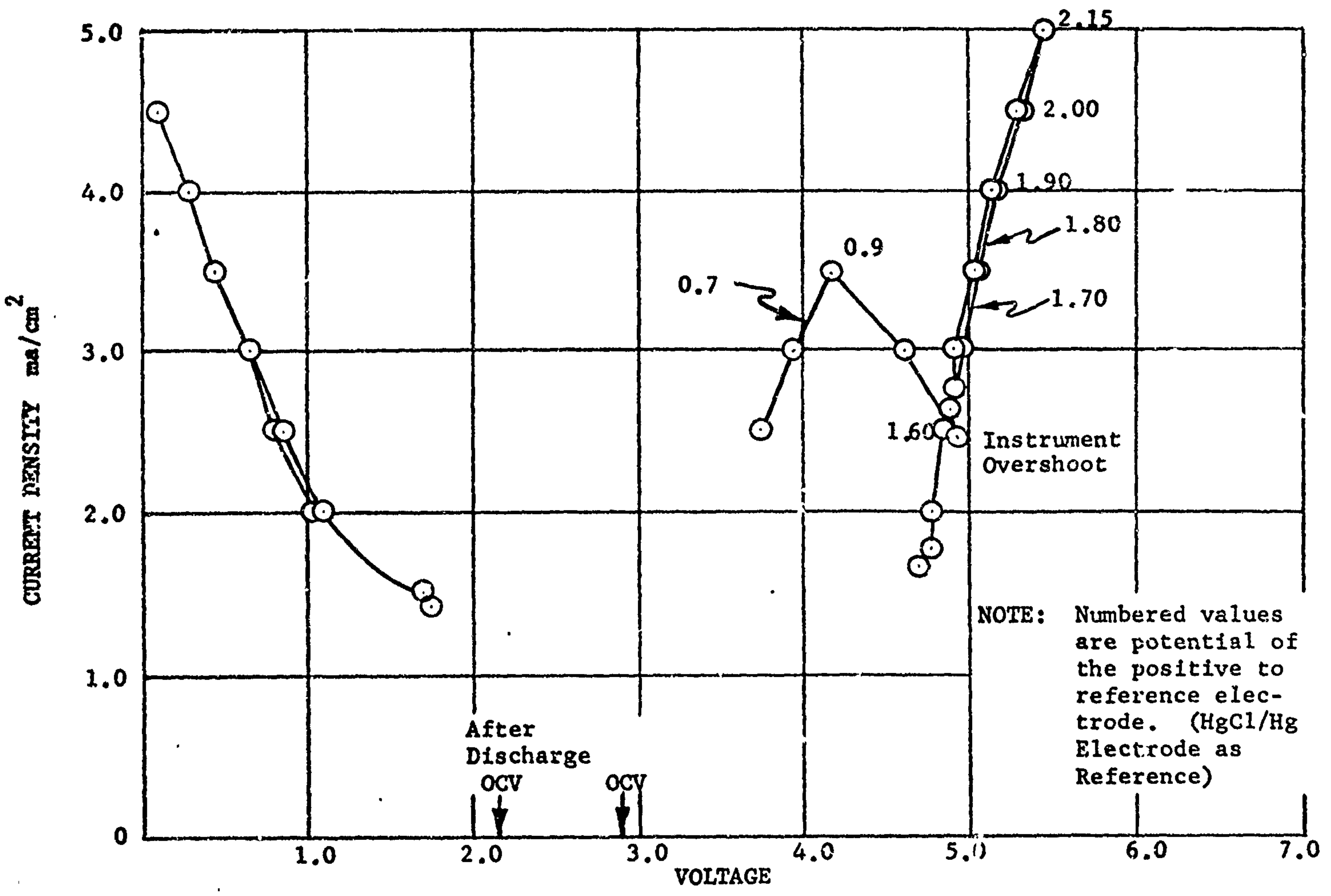


FIGURE 10 - POLARIZATION TEST - $NiCl_2$ THIN FILM (PLATED) ELECTRODE

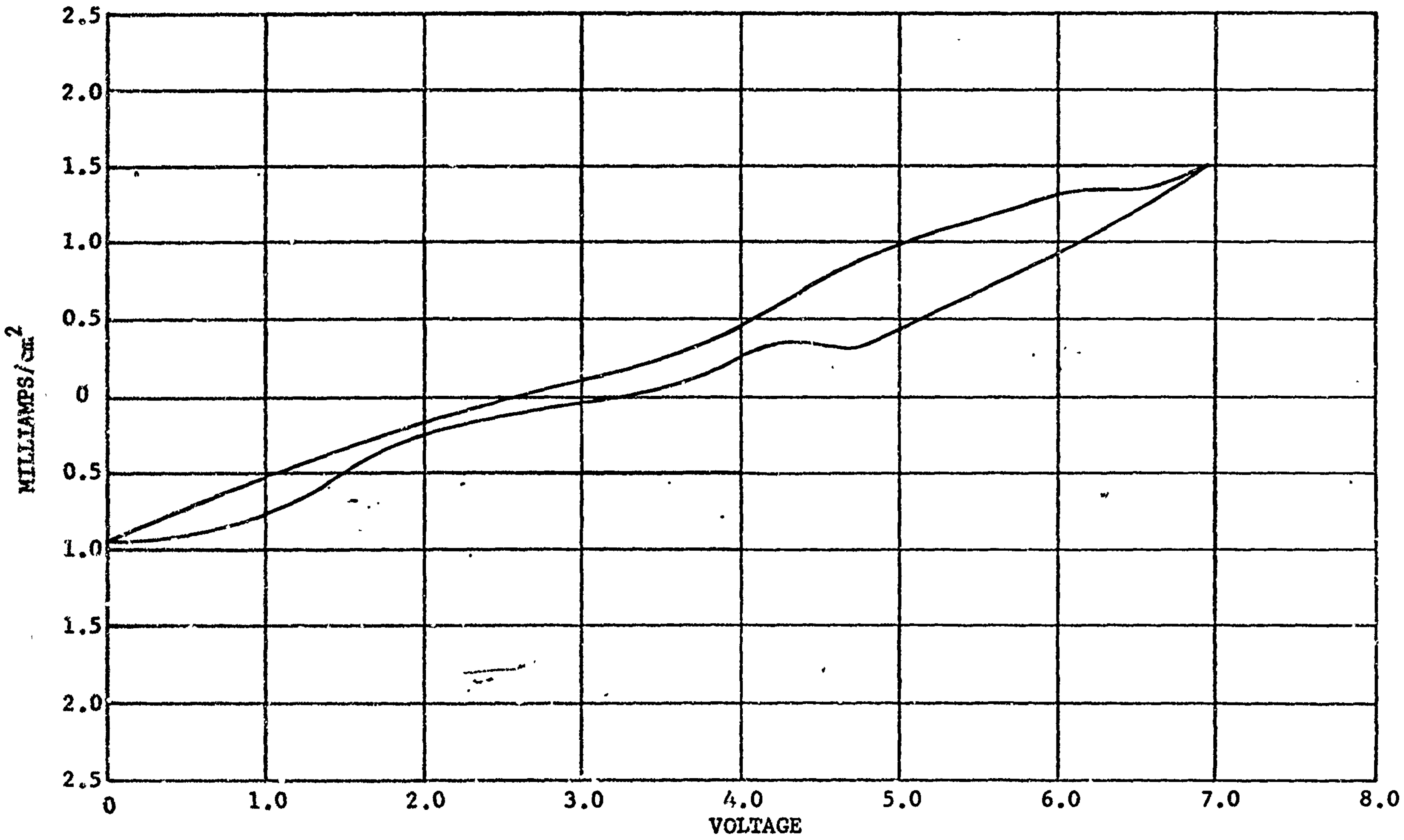


FIGURE 11 - THIN FILM NiCl ELECTROFORMED FROM Ni PLATE ONTO MONEL 400 + Li ANODE + PROPYLENE CARBONATE WITH $AlCl_3$, LiCl, AND Cl_2

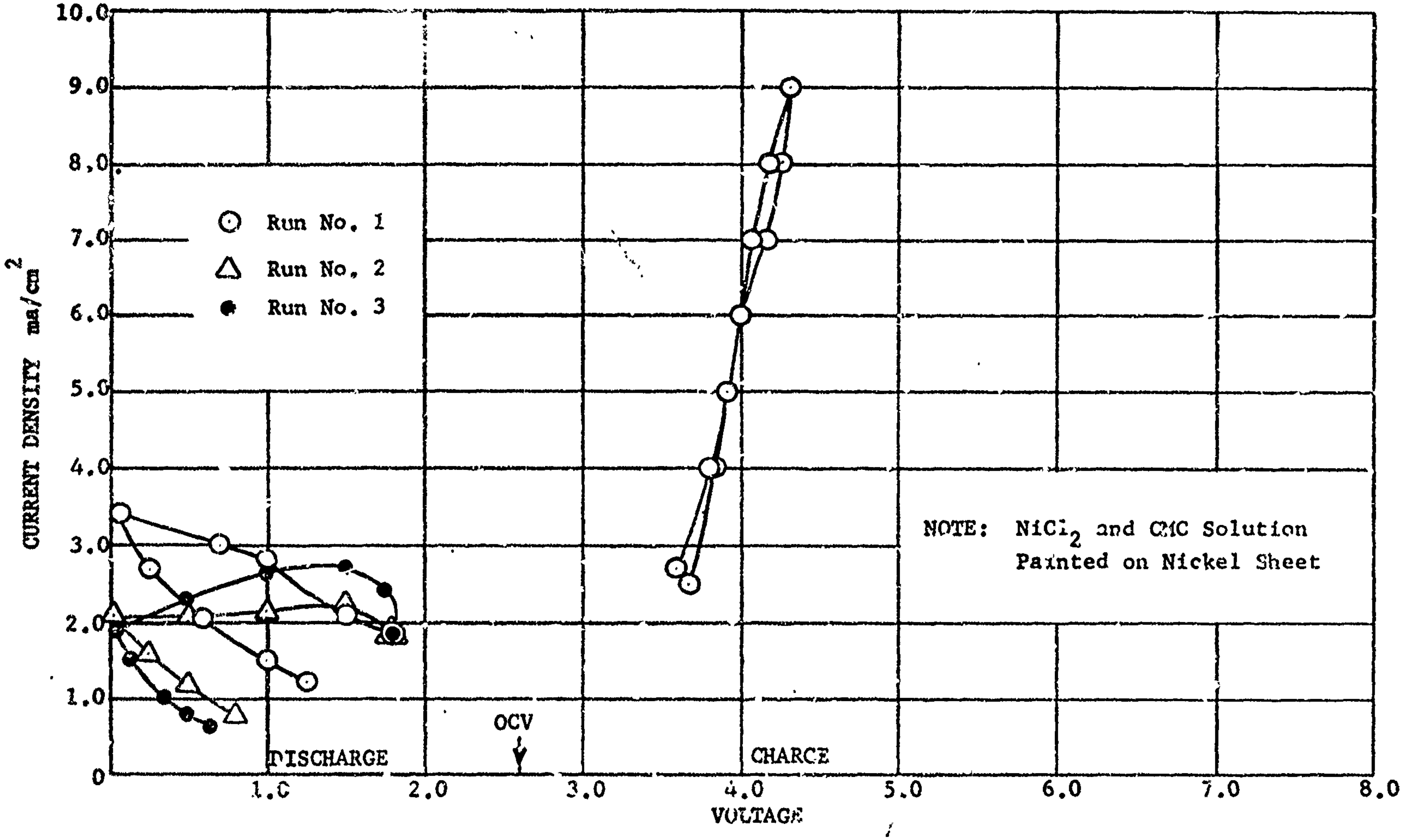
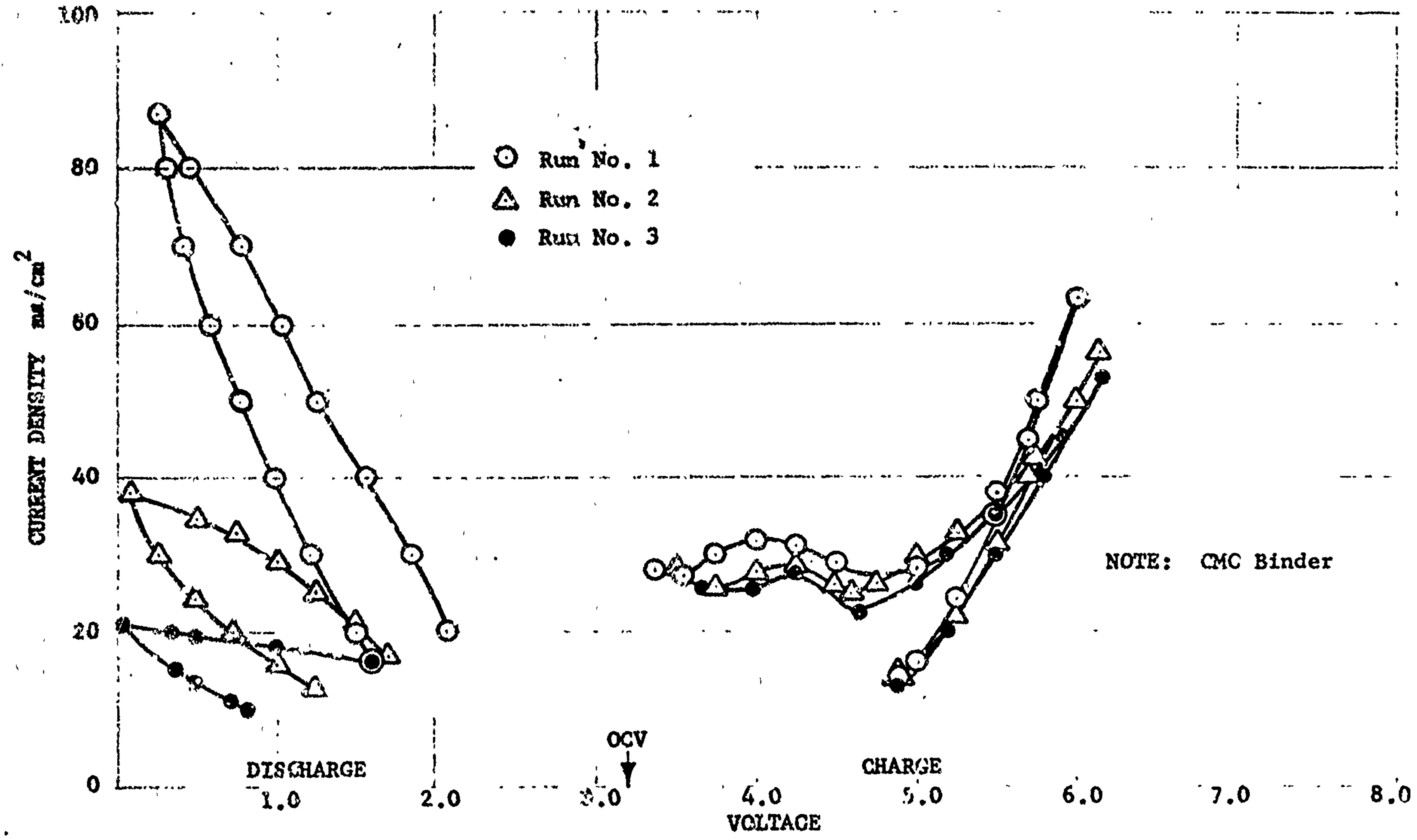


FIGURE 12 - POLAROGRAPHIC TEST - PAINTED THIN FILM NiCl$_2$ ELECTRODE



NOTE: CMC Binder

FIGURE 13 - POLAROGRAPHIC TEST - PASTED $NiCl_2$ CARBONYL NICKEL ELECTRODE

relationship. There was no downward trend in the curve. The cell voltage immediately dropped to 2.05 volts at 2.0 ma/cm^2. The c.d. ran to 8.7 ma/cm^2 at 0.25 volts. The return trace showed the change in polarization with time. The charge curve showed a partial hump, the results being somewhat between those of a thin film electroformed $NiCl_2$ electrode and the $NiCl_2$-graphite pasted electrode (covered in the next section).

The second and third discharges showed something of the non-reversible phenomenon seen with the impregnated sintered nickel plaques. This is further discussed in the conclusion. The charges seemed to repeat each other satisfactorily.

4. Pasted $NiCl_2$-Graphite Electrode - Polarographic Tests

Figure 14 is a plot of the polarization test using the apparatus in Figure 7. Although there is an initial polarization and an increase in polarization with time, the three runs are almost identical. This shows a reversible polarization which was not the case with the $NiCl_2$-Carbonyl nickel electrode.

This new approach became the major portion of the endeavor.

5. Pasted $NiCl_2$-Graphite Electrodes - Doping Test

a. Procedure

Tests had been made during the first contract in 1964 using 5% $MgCl_2$ and 5% $SnCl_2$ dopants to improve the electrochemical reactivity of the $NiCl_2$ electrode. The results were the opposite, producing electrodes which were almost passive. DiBari and Petrocelli (1) list several elements in the order of their effectiveness as additives to increase the electrochemical reactivity of nickel. For equal atomic concentrations, they are:

$$S > Se > Te > P > C > Si$$

Based on this, a new series of doping tests were started. These were done using sulphur as a dopant.

The addition of sulphur is not the same type of dopant as $MgCl_2$ or $SnCl_2$. The latter are crystal lattice defect producing dopants, whereas the sulphur reportedly catalyzes the electron transfer on rearrangement of the nickel. Because of the two different mechanisms involved, both types were studied.

In order to prepare $NiCl_2$ containing small amounts of S in a uniform distribution, wet chemical means were employed. An aqueous saturated solution of $NiCl_2 \cdot 6H_2O$ was stirred rapidly and water saturated with H_2S gas slowly added. At 25°C, 100 grams of water will dissolve 0.3375 grams of H_2S.(2) Sufficient H_2S was added to result in a $NiCl_2$ salt containing

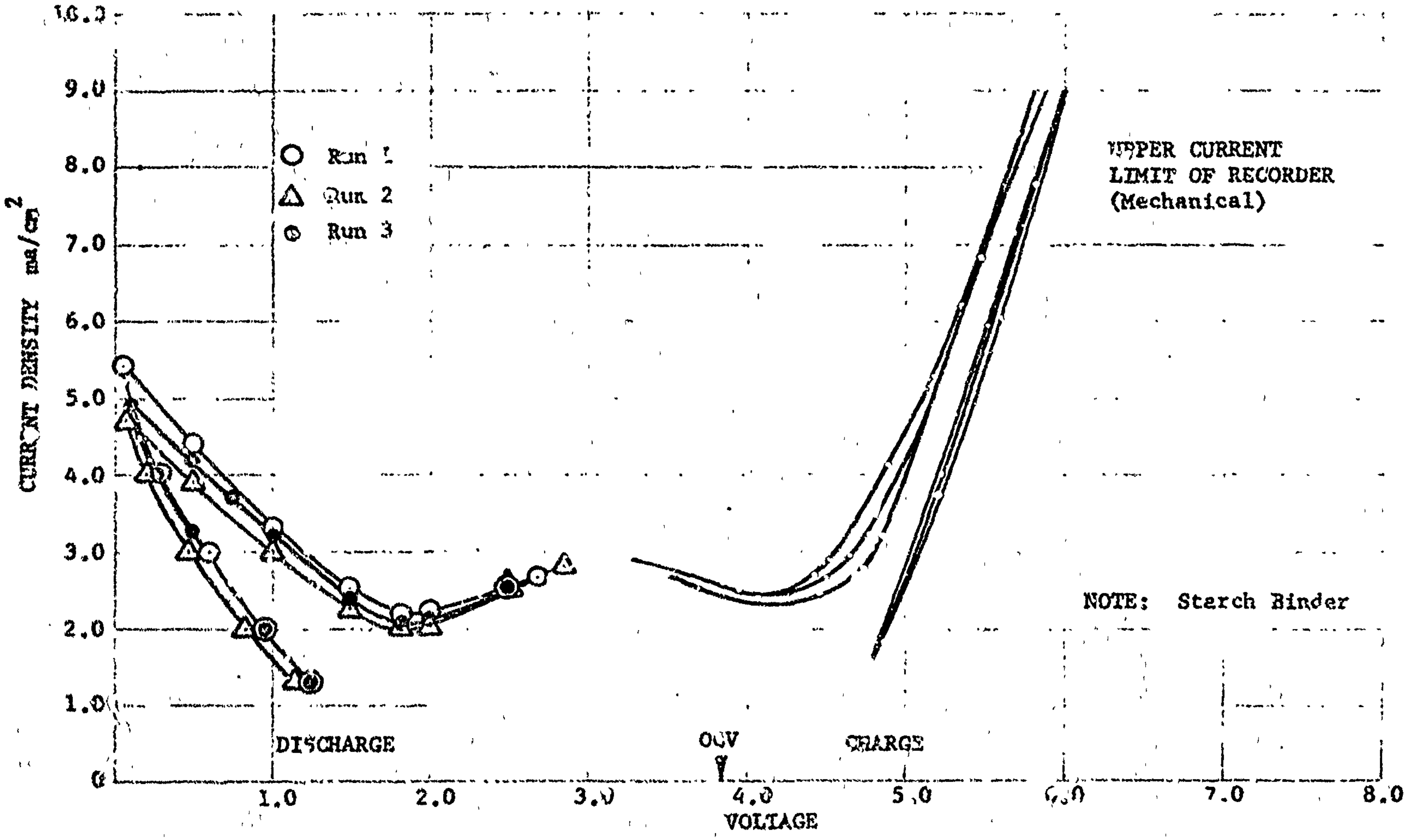


FIGURE 14 - POLAROGRAPHIC TEST - PASTED $NiCl_2$-GRAPHITE ELECTRODE

0.1% sulfur based on the nickel content. That is, if the $NiCl_2$ were reduced to nickel, it would contain 0.1% sulfur. The solution was placed in an evaporating dish. It was then evaporated at 110°C using the same technique described in Section IV, B., 1., c. for the $NiCl_2$ powder.

The same technique was used to prepare $NiCl_2$ powders containing 0.1% $MgCl_2$ and $SnCl_2$. These were 0.1% $\underline{M}Cl_2$ based on the $NiCl_2$.

Electrodes were prepared by mixing 1.0 gram of the doped $NiCl_2$ with 1.0 gram of National Carbon Co. grade 38 graphite. One cc of USP gelatine binder (B&A) was added and the electrode pasted with this on a 4/0 expanded nickel screen. A Monel 400 tab was previously spot welded to the screen. The electrode was air dried and then pressed at 2 ton/in^2. The $NiCl_2$ was further dried at 110°-120°C for 16 hours.

Testing was done using a plastic cell and two lithium anodes. 0.75M PC-$AlCl_3$/Li/Cl_2 electrolyte was used. The cell was connected to a galvanostat (Fig. 2) and the current and voltage recorded on an X-Y recorder.

b. Experimental Results

Figure 15 shows the result of a pasted $NiCl_2$ electrode doped with 0.1% sulfur. The solid line in Figure 15 is a plot of a $NiCl_2$-graphite electrode without doping and is used for comparison.

Higher voltages were obtained at given current densities, but the polarization with time of discharge is still great.

The upper traces of the discharge and the lower traces of the charge portions show agreement. This indicates that although the initial c.d. of the S doped electrode is higher, the polarization with time is initially greater and after a given period of time, the effect of doping is lost.

Figure 16 is a plot of the $MgCl_2$ and $SnCl_2$ doped electrodes. The scale for current density is half that of Figure 8. The encouraging feature of the $MgCl_2$ doped electrode is the spread between the lower line and the upper trace. This spread is an indication of the increase in polarization with time. In the case of the $SnCl_2$ and $MgCl_2$ doped electrodes, this is much less than the undoped or sulphur doped electrodes.

Figure 17 through 20 show the effect of diluting the sulphur. The potentiometer sweep rate of the galvanostat was 10 amperes/hour. Since the desired cut-off voltage is 2.0 volts, (the battery voltage requirements are such that the cells should not vary more than 0.30 volts during use) the final c.d. (return sweep) at this voltage is important. As a figure of merit for comparison, the initial voltage after charge at this c.d. is also important, as is the time to reach 2.0 volts.

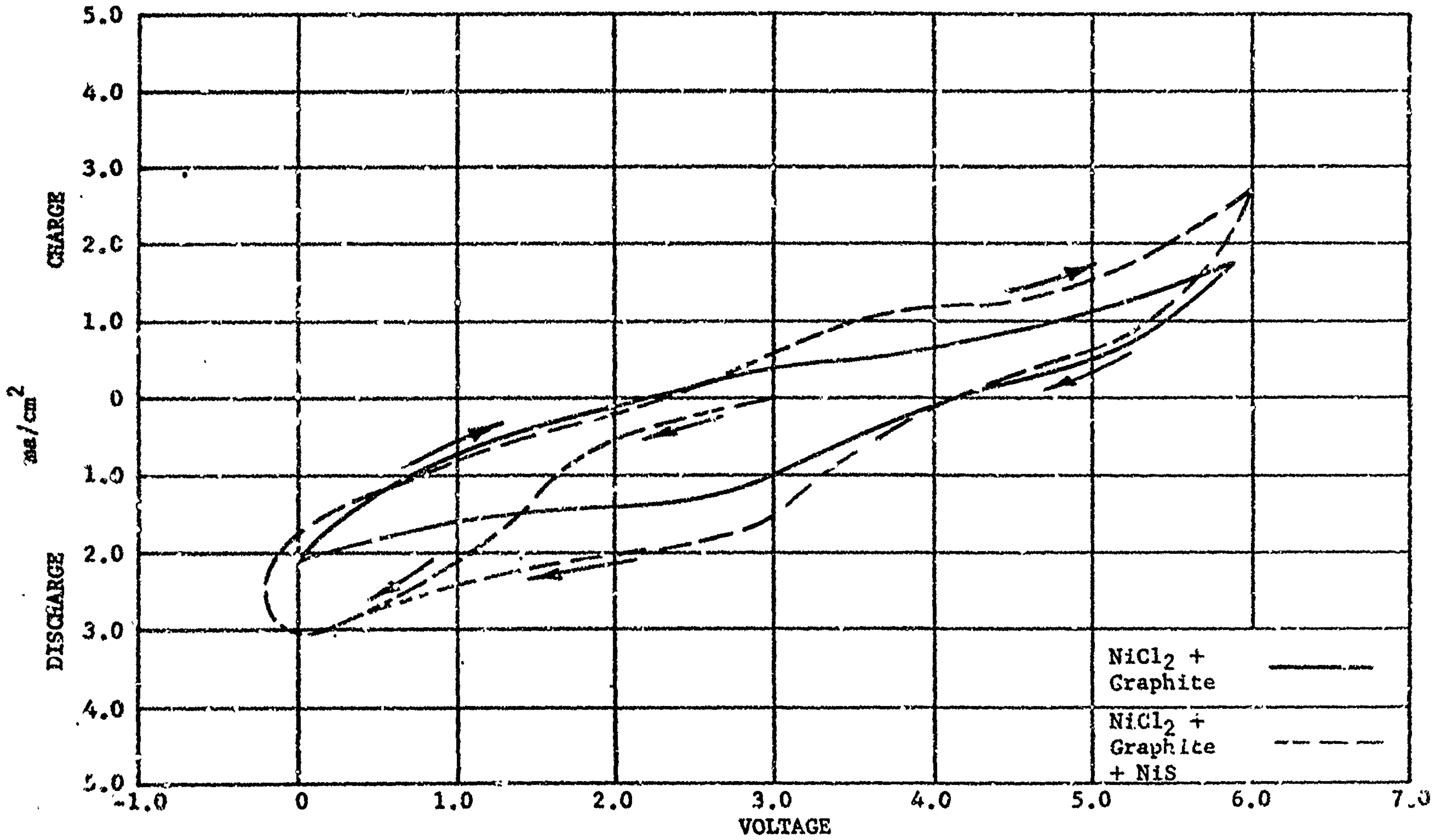


FIGURE 15 - POLAROGRAPHIC TEST - NiCl$_2$ + GRAPHITE Vs NiCl$_2$ + GRAPHITE + 0.1% NiS

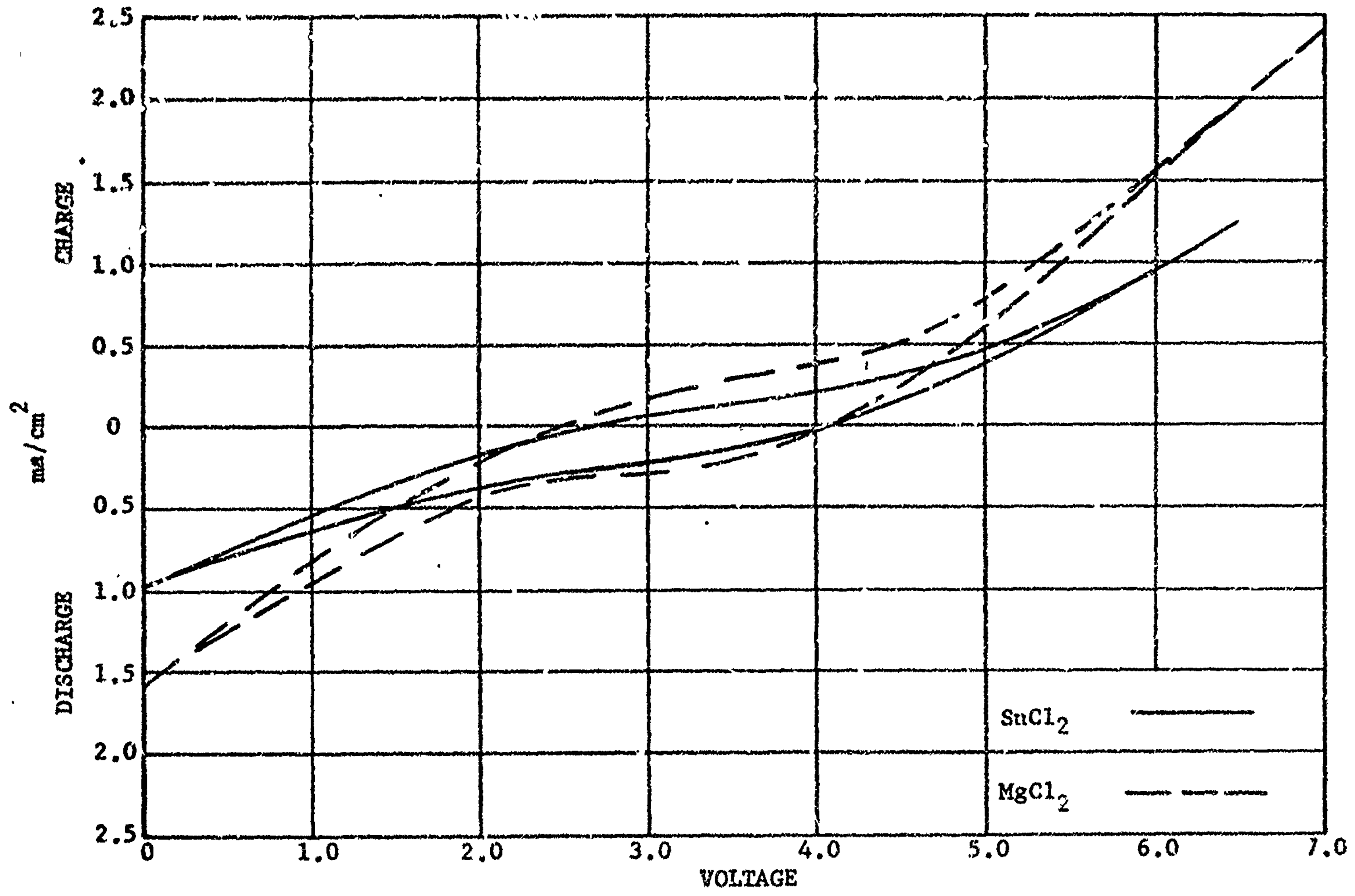


FIGURE 16 - POLAROGRAPHIC TEST - NiCl$_2$ AND GRAPHITE WITH 0.1% DOPANTS

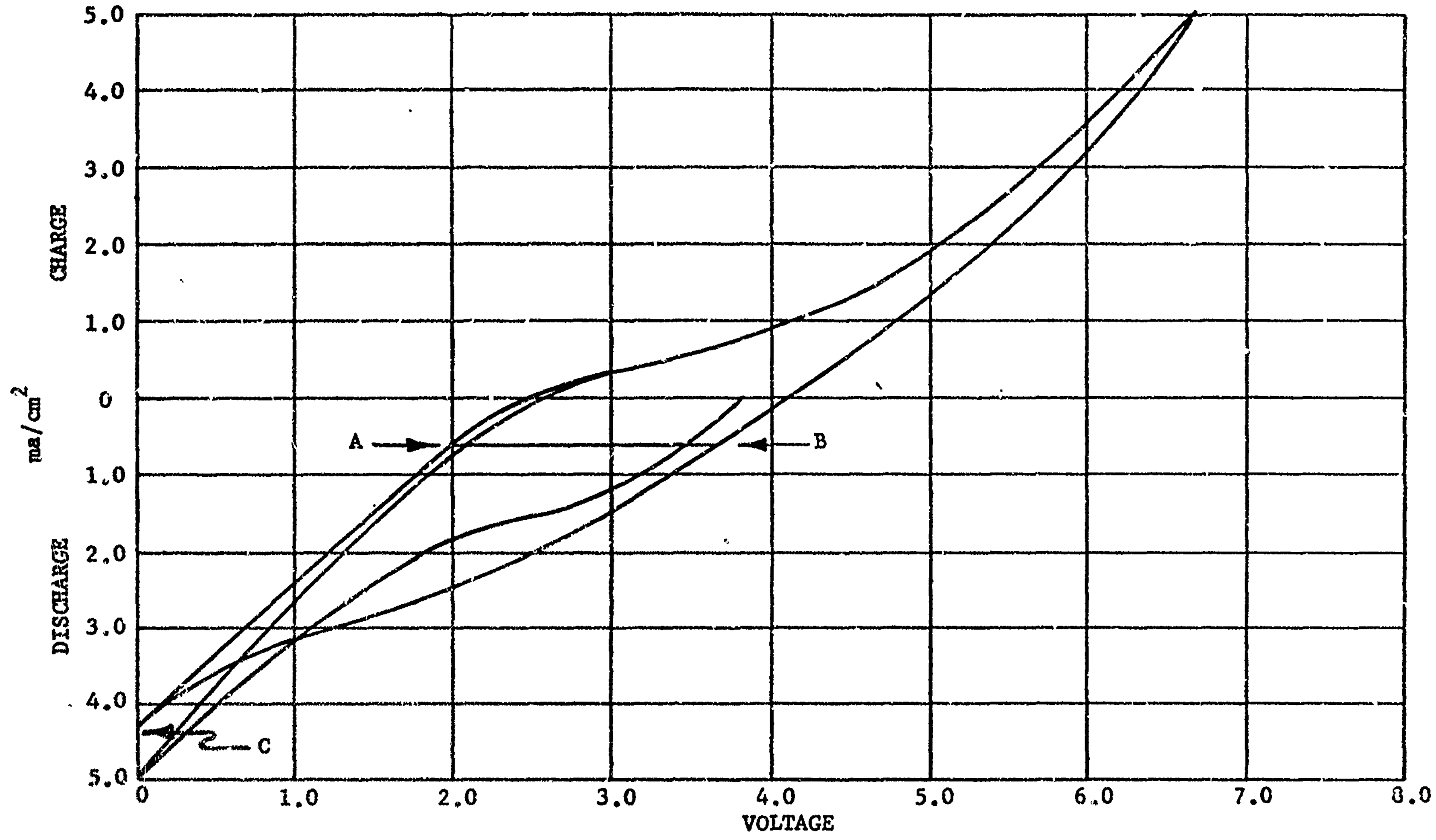


FIGURE 17 - POLAROGRAPHIC TEST - 50% $NiCl_2$ (+0.08% NiS DOPANT) AND 50% C

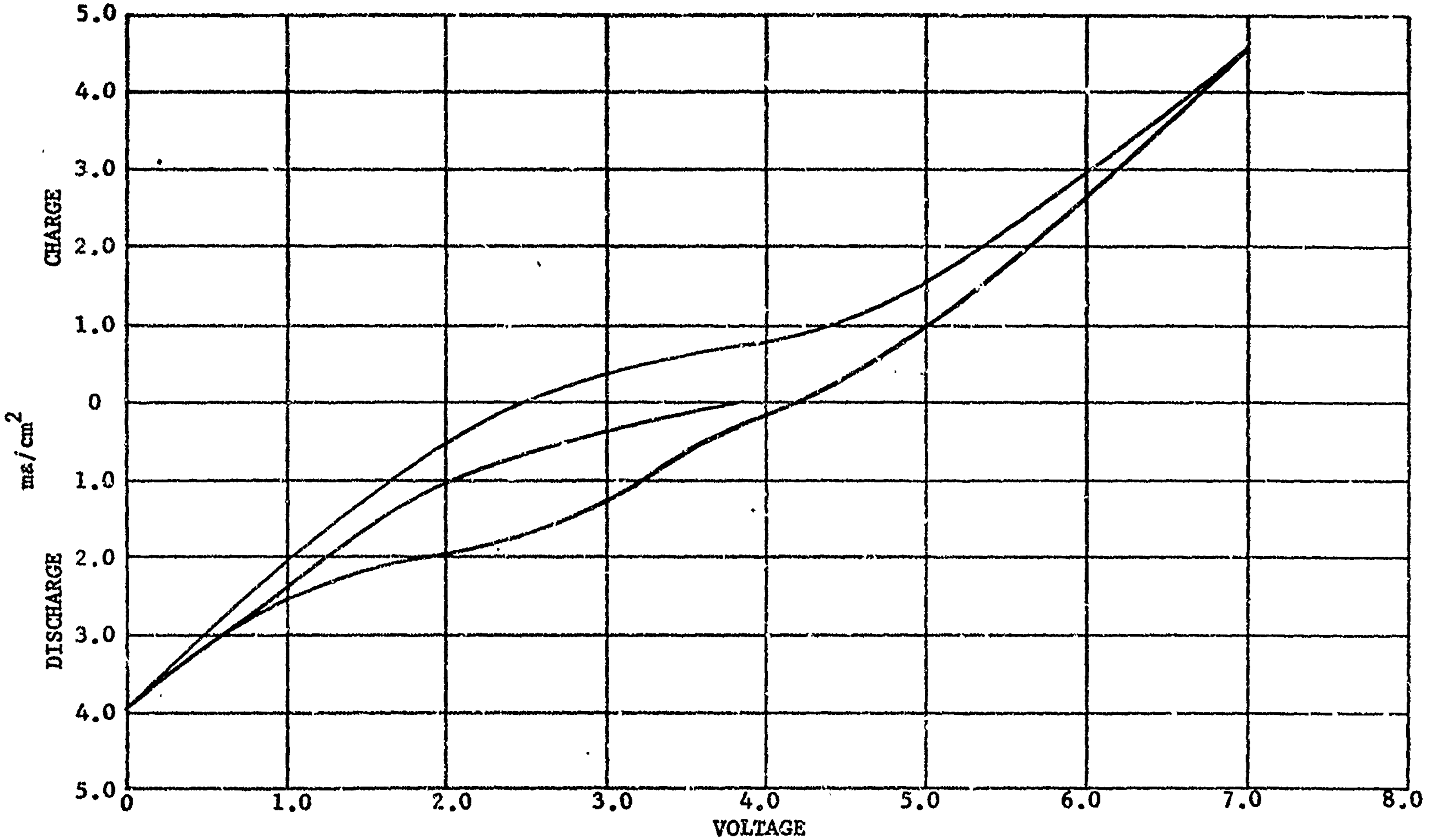


FIGURE 18 - POLAROGRAPHIC TEST - 50% $NiCl_2$ (+0.04% DOPANT) AND 50% C

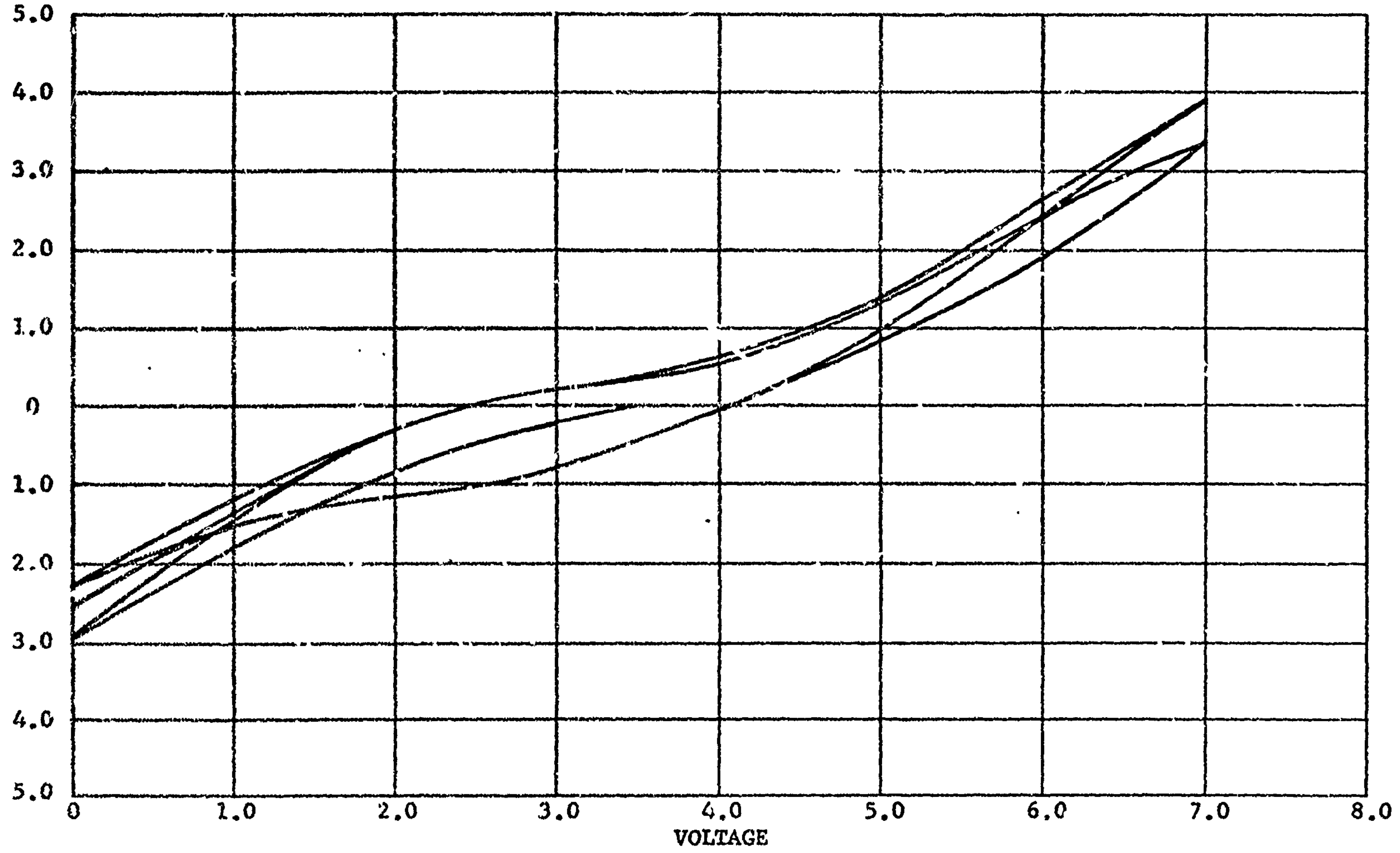


FIGURE 19 - POLAROGRAPHIC TEST - 50% $NiCl_2$ (+0.02% DOPANT) AND 50% C

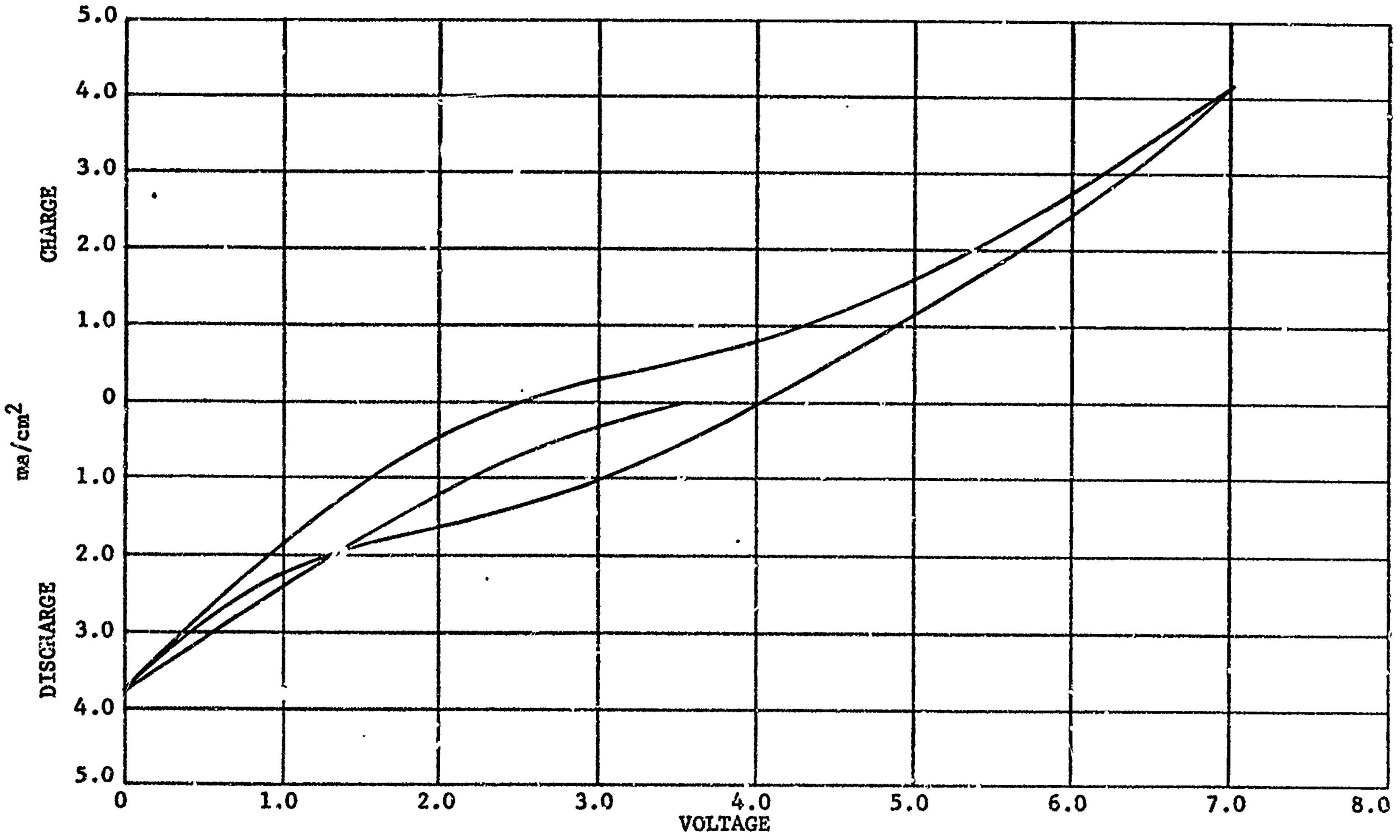


FIGURE 20 - POLAROGRAPHIC TEST - 50% $NiCl_2$ (+0.01% NiS DOPANT) AND 50% C

Table II. summarizes these data from Figure 15 through 22.

Referring to Figure 17, the final c.d. at 2.0 volts is shown at point A. The initial voltage at this c.d. is shown at point B, and the maximum c.d. is point C.

The time in seconds is a function of the sweep rate and the maximum current density. The sweep rate was 10 amperes/hour (except where noted differently). In the first case (Figure 15), the maximum c.d. was 2.1 ma/cm^2, and the final c.d. was 0.1 ma/cm^2. The electrode area is 10 cm^2 so the currents are 21 ma and 1 ma. The time to sweep from 1 ma to 21 ma and back to 1 ma is:

$$2 \times (21-1)/10 \text{ amperes}/3600 \text{ sec.} = 14.4 \text{ sec.}$$

The $\Delta V / \Delta t$ represents the increase in polarization voltage with time. It is desired to have as little increase in polarization voltage with time as possible. ΔV is the initial voltage (B) minus the cutoff voltage (A) which is 2.0 volts. Again, in the case of Figure 15, this is 4.00 - 2.00 - 2.00 volts. The time interval was 14.4 sec. and the ratio is 2.00/14.4 = 0.139.

The last column incorporates the change in polarization with time $\Delta V/ \Delta t$ with the final c.d. at 2.0 volts. However, a low value of polarization increase with time alone is not enough. It is desired to have the lowest Δ V/sec. and the highest c.d. Therefore, a quotient rate of voltage change and c.d. having the lowest value is a reasonable significance test. Based on these preliminary tests, the sulphur dopant should be in the region of 0.08%. The variability found between 0.08% and 0.10% is too high compared with 0.08% and 0.04%. Also, the values at 0.02% are out of line with those obtained at 0.01% and 0.04%. These tests will be duplicated.

Figures 21 and 22 are duplicate runs using a mixture of equal parts of 0.08% sulphur doped and 0.1% $MgCl_2$ doped $NiCl_2$. This gave a mix containing 0.04% S and 0.05% $MgCl_2$. Note that the ordinates are marked differently than the earlier figures. Figure 22 was initially run at a sweep rate of 3.0 amperes/hour for one cycle and then changed to the ratio of 10 amperes/hour used for the other tests. From Table I, it can be seen that at the current density to produce 2.0 volts after the sweep, the time does not affect the potential drop. Points A and B are the same at either sweep. Somewhat higher current densities are obtained at the faster sweep, especially below 3.0 volts.

6. Pasted $NiCl_2$-Graphite Electrode - Compression Test

Figures 23 and 24 show the results of the tests of com-

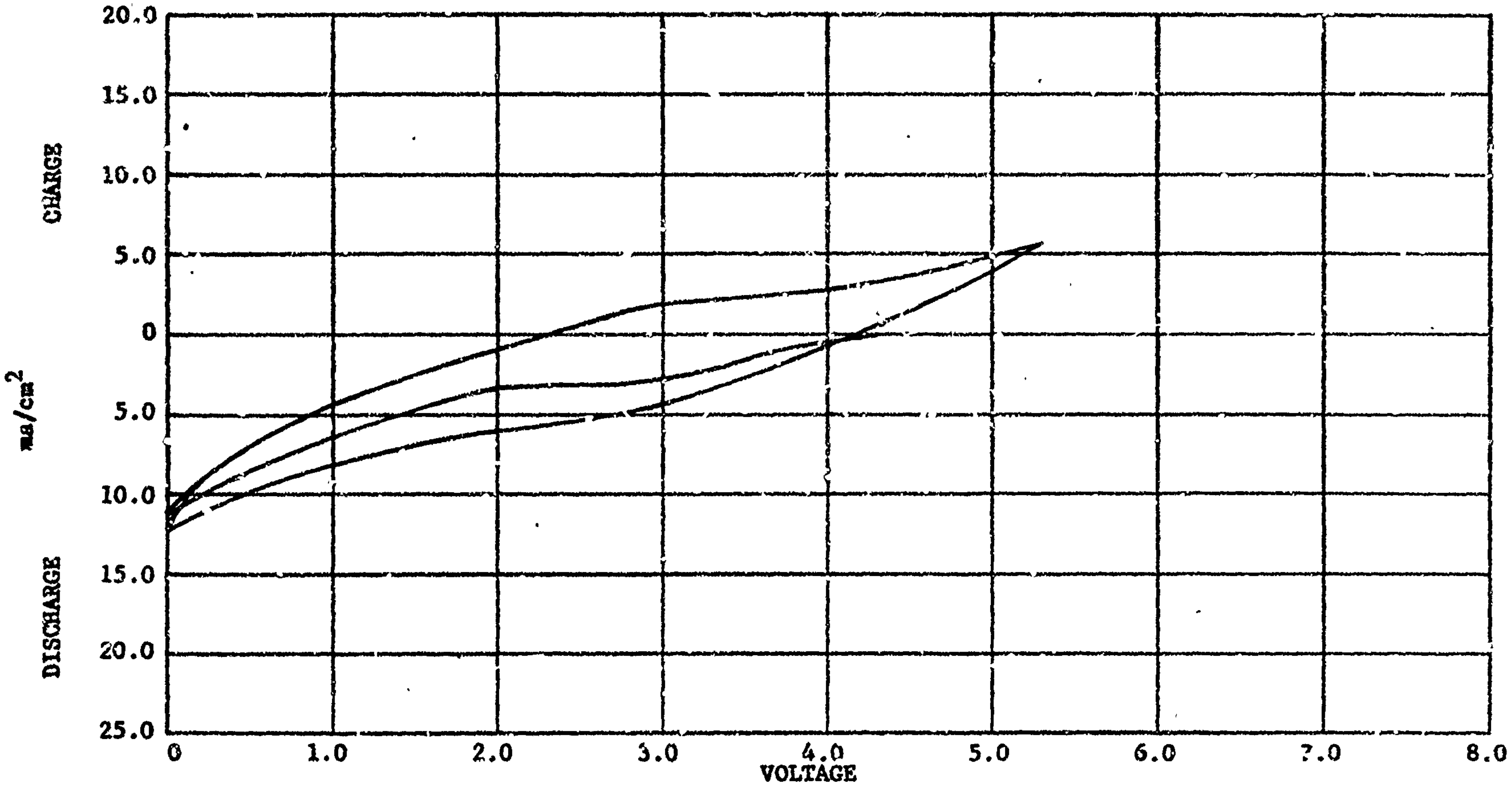


FIGURE 21 - POLAROGRAPHIC TEST - 50% $NiCl_2$ (+0.05% $MgCl_2$ AND 0.04% NiS DOPANTS) AND 50% C

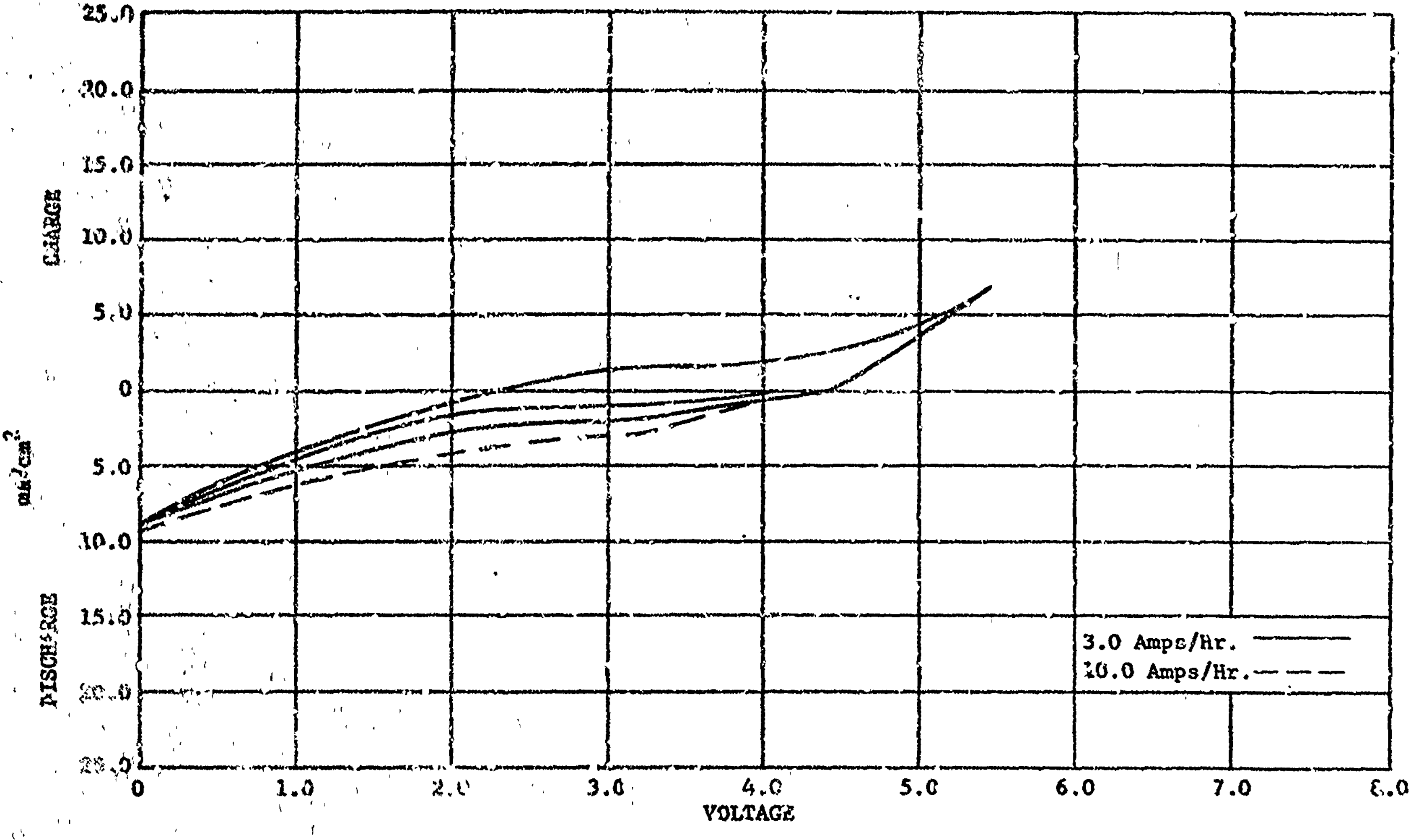


FIGURE 22 - POLAROGRAPHIC TEST - 50% $NiCl_2$ (+0.05% $MgCl_2$ AND 0.04% NiS DOPANTS) AND [illegible] C

TABLE II

SUMMARY OF POLARIZATION DATA

FIGURE NO.	% DOPANT	MAX. C.D. (ma/cm^2) (zero volt) (C)	FINAL C.D.* AT 2.0 VOLTS (ma/cm) (A)	INITIAL VOLTAGE AT C.D.* (B)	TIME (seconds)	$\frac{\Delta V}{\Delta t}$	$\frac{\Delta V/SEC.}{C.D.*}$
15	0	2.1	0.10	4.00	14.4	0.139	1.39
20	0.01	3.7	0.50	3.50	23.0	0.065	0.13
19	0.02	2.3	0.30	3.70	14.4	0.118	0.39
18	0.04	3.0	0.50	3.60	24.5	0.065	0.13
17	0.08	4.3	0.60	3.65	26.6	0.062	0.10
15	0.10	3.1	0.20	4.00	20.9	0.096	0.48
21	0.04 S 0.05 $MgCl_2$	12.5	1.00	3.95	82.8	0.024	0.024
22	0.04 S 0.05 $MgCl_2$	9.0	1.00	3.65	192 (3 amps/hr.)	0.010	0.010
22	0.04 S 0.05 $MgCl_2$	9.5	1.00	3.85	61.2	0.030	0.030

* Same Current Density

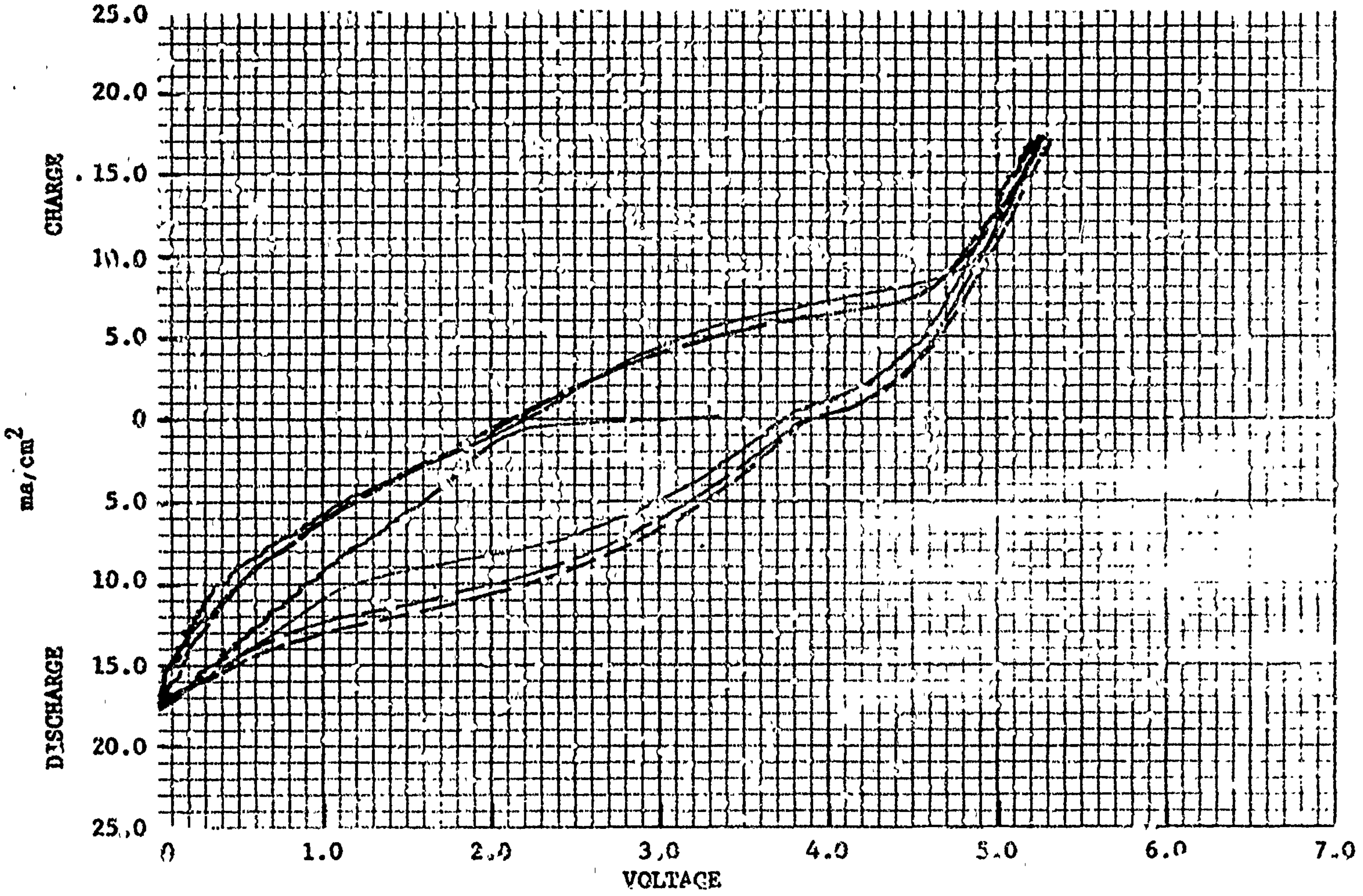


FIGURE 23 - POLAROGRAPHIC TEST - 25% $NiCl_2$ (WITH 0.08% NiS) AND 75% C - PLATE COMPRESSED AT 3 TONS PER IN^2

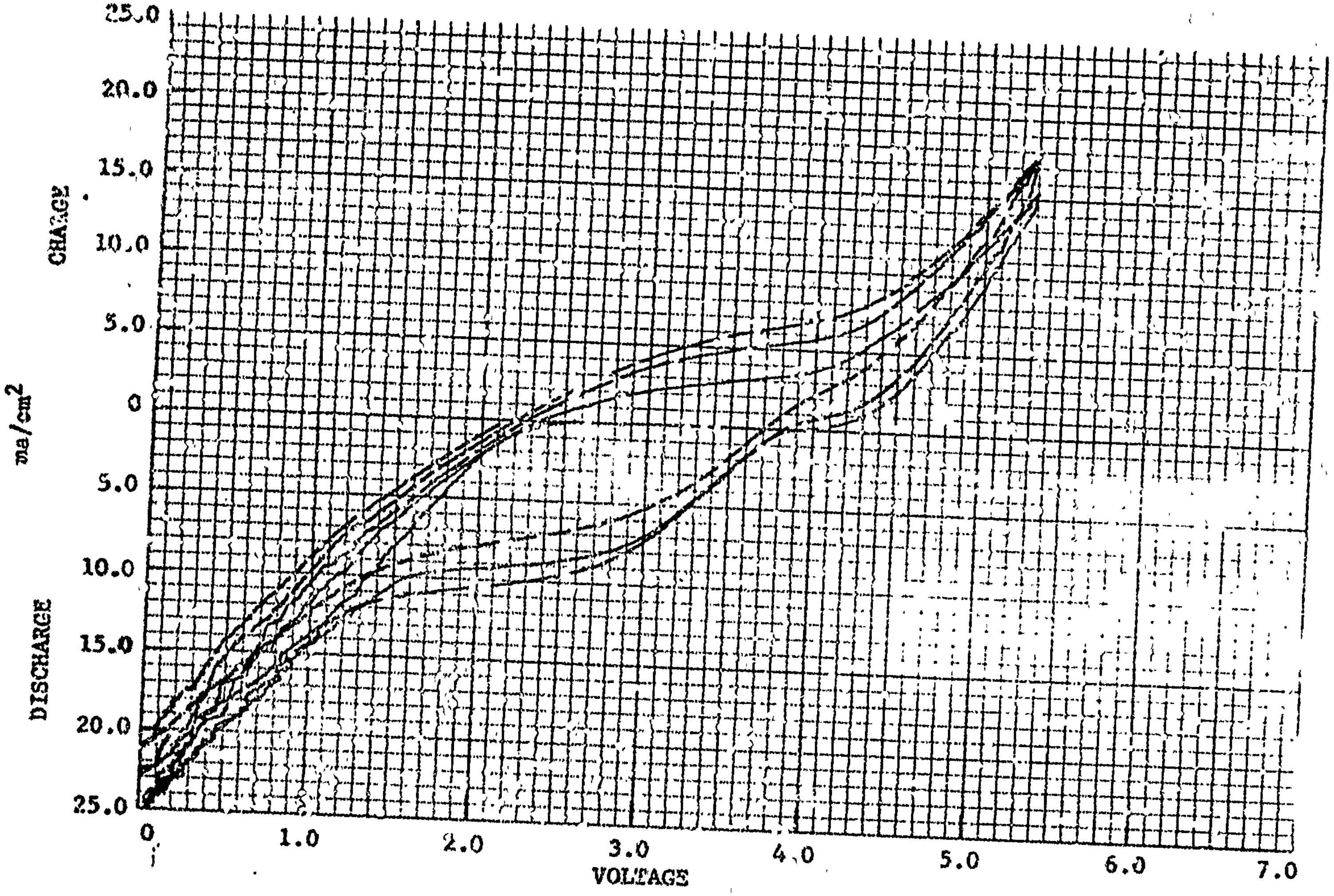


FIGURE 24 - POLAROGRAPHIC TEST - 25% $NiCl_2$ (WITH 0.08% NiS) AND 75% C - UNCOMPRESSED PLATE

pressed (3 tons/in^2) and uncompressed plates. The uncompressed plates showed less polarization than the compressed electrodes. However, each cycle (there were 3) of the compressed electrode improved it, while the uncompressed electrode appeared to increase in polarization each cycle.

The repeatability was good between duplicate runs and showed the same results.

It is felt that some compression (500 to 1000 psi) of the electrode may be beneficial, but that the high compression used here was detrimental to the polarization characteristics of the $NiCl_2$ electrode.

7. Pasted $NiCl_2$-Graphite Electrodes - Ratio Test

a. Type 38 Graphite

Figure 25 is a plot of the results from the 90% graphite and 10% $NiCl_2$ with 2% USP gelatine binder. The numbers are the order of sweeps starting at the discharge. It is noted that each discharge increased the initial c.d., but all the return sweeps were essentially the same.

Figure 26 shows the results obtained with 90% $NiCl_2$ and 10% graphite with 2% USP gelatine. The c.d. scale is 1/5 of Figure 25. In this case, each successive discharge yielded a lower c.d. These results are reminiscent of those obtained with impregnated sintered nickel plaques.

These results combined with Figure 23 show that there is little difference between a 1:9 and a 1:3 ratio of $NiCl_2$ and graphite. The results do show more favorable characteristics than even the co-doped electrodes of the 1:1 ratio shown in Figure 21.

b. UCET Graphite

In the last month of experimental work, a new special grade of graphite (sold by Union Carbide Division of National Carbon Co., under the name of UCET Acetylene Black - 50% compressed) was obtained.

Because of its extremely low bulk density, a 1:1 mix of UCET graphite and $NiCl_2$ had a volume almost 20 times that of a similar mixture using Type 38 graphite. Blends of Type 38 and UCET graphite were tried. The majority of the work consisted of making pastes and applying them to screens in attempts to get a workable technique that would give a paste containing enough $NiCl_2$ to give the capacity needed. From these tests, the following procedure was obtained.

A blend of 90% UCET and 10% Type 38 graphite was made.

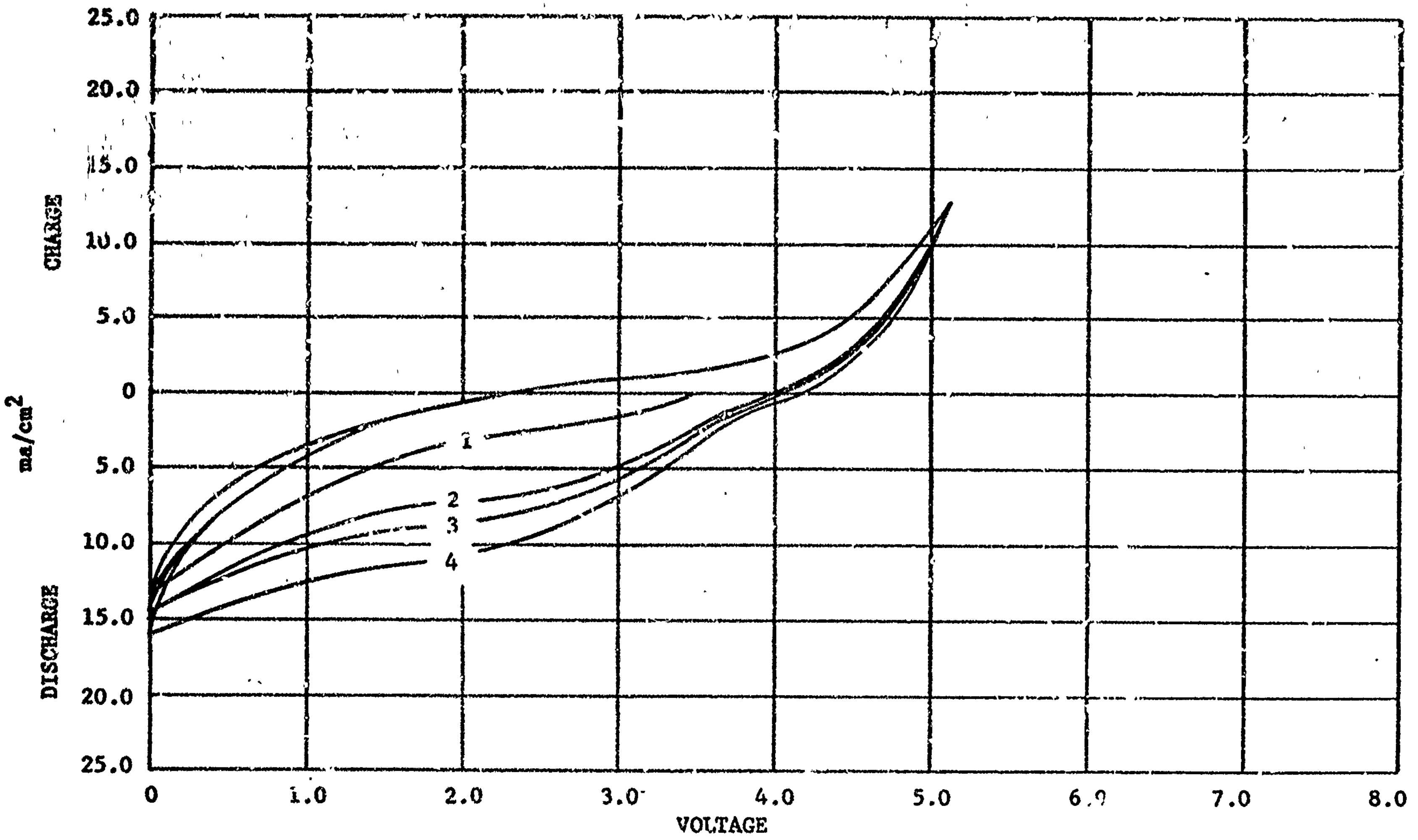


FIGURE 25 - POLAROGRAPHIC TEST - 90% C + 10% $NiCl_2$ (+0.08% NiS DOPANT)

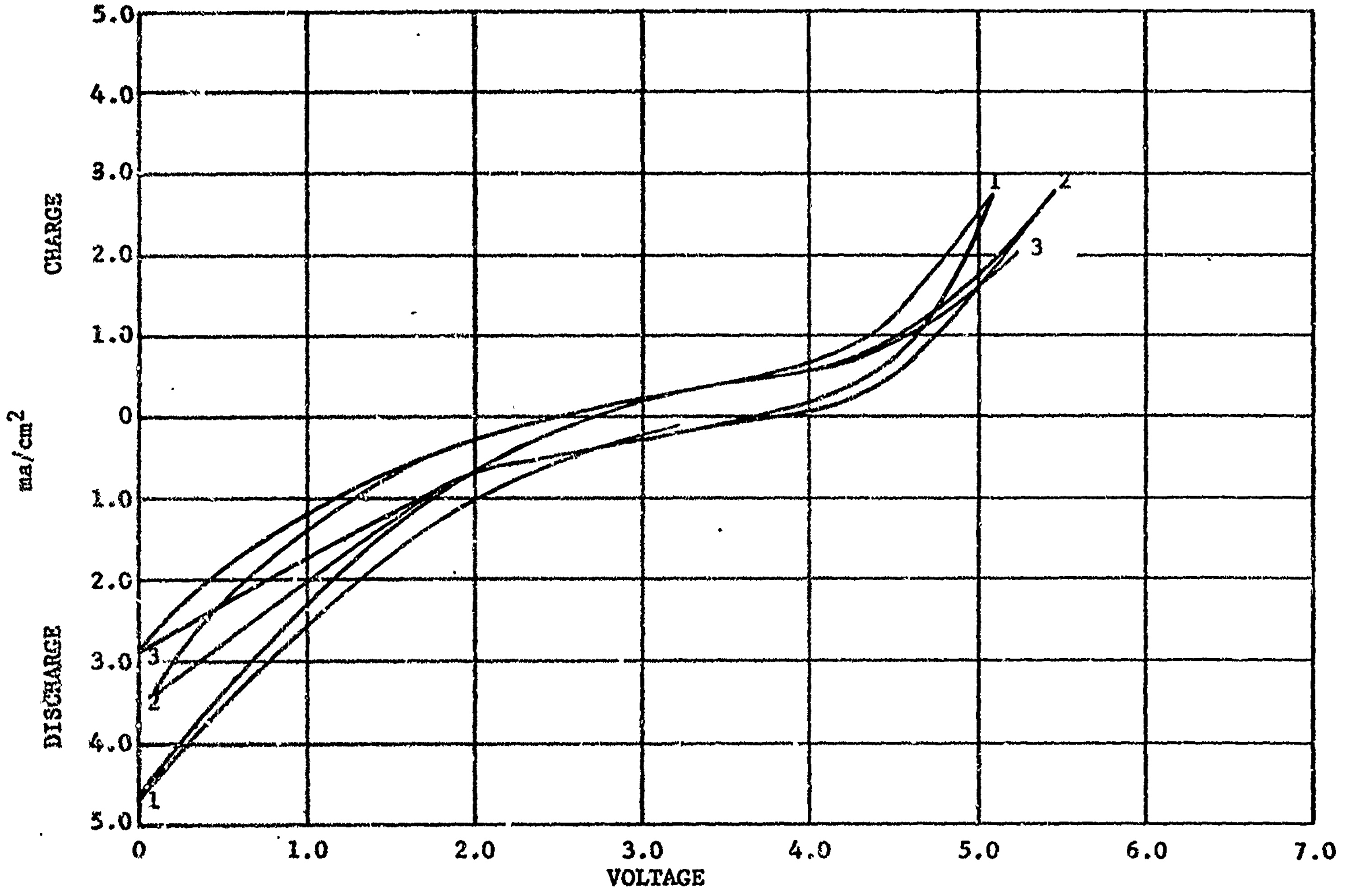


FIGURE 26 - POLAROGRAPHIC TEST - 90% $NiCl_2$ (+0.08% NiS DOPANT) AND 10% C

A Methanol solution of $NiCl_2 \cdot 6H_2O$ containing 330 g/L of $NiCl_2$ was made. Sufficient nickel-chloride solution was added to the graphite blend to give a 3:1 ratio of $NiCl_2$ to graphite when dried. An aqueous solution of 100 g/L of USP gelatine (B&A) was added to give a mix containing 2% dry weight of gelatine. Enough water was added to result in a paste with a consistency of whipped cream. A thin film of the paste was applied to the screen and dried. At 100°C in a humid ($\sim$70% RH) air stream. The plate was then compressed at 2 tons/in.^{2} between sheets of polyethylene. Another coat of the paste was applied and the procedure repeated. This routine was repeated until at least 0.1 gram/cm^2 had been applied to the electrode. After the last compression, the electrode was immersed in thionyl chloride to remove all water.

Figure 27 is a polarographic test of one of these electrodes. The electrolyte used was propylene carbonate saturated with KPF_6 and then saturated with LiCl. This electrode is the type used for laboratory cell studies and the prototype cells.

D. DISCUSSION

Pasted electrodes of $NiCl_2$ powder and a conductive diluent give results far superior to the best $NiCl_2$ impregnated sintered nickel plaques. The use of carbonyl nickel powder as a diluent, however, is not satisfactory. It is believed that both the sintered nickel plaque and the carbonyl nickel powder become coated with $NiCl_2$ from electroforming and the intimate contact necessary between the conductive material and the support screen is lost. For this reason, the $NiCl_2$-graphite electrode is the best so far.

Doping the $NiCl_2$ electrode has produced both desirable and undesirable effects. The sulphur doped electrodes show a higher initial voltage for a given current density. However, the rate of increase in polarization with time is such, that after the same ampere minutes have been passed, the voltage is the same as an undoped electrode.

The magnesium or stannous chloride doped electrodes show a lower voltage for a given current density, but the increase in polarization with time is much less than undoped electrodes. Although there is considerable variability in the $MgCl_2$ results, they seem more favorable than the $SnCl_2$ doped electrodes, even taking the lower values.

Because each type of dopant seems to show some advantages, a mixture of sulphur and $MgCl_2$ doping was tried. The results indicated that the advantages of both types can be utilized in a co-doped electrode.

The incorporation of the co-doped electrodes with the UCET graphite diluent was tested in a laboratory cell and is discussed under that heading in Section VIII. C.3.

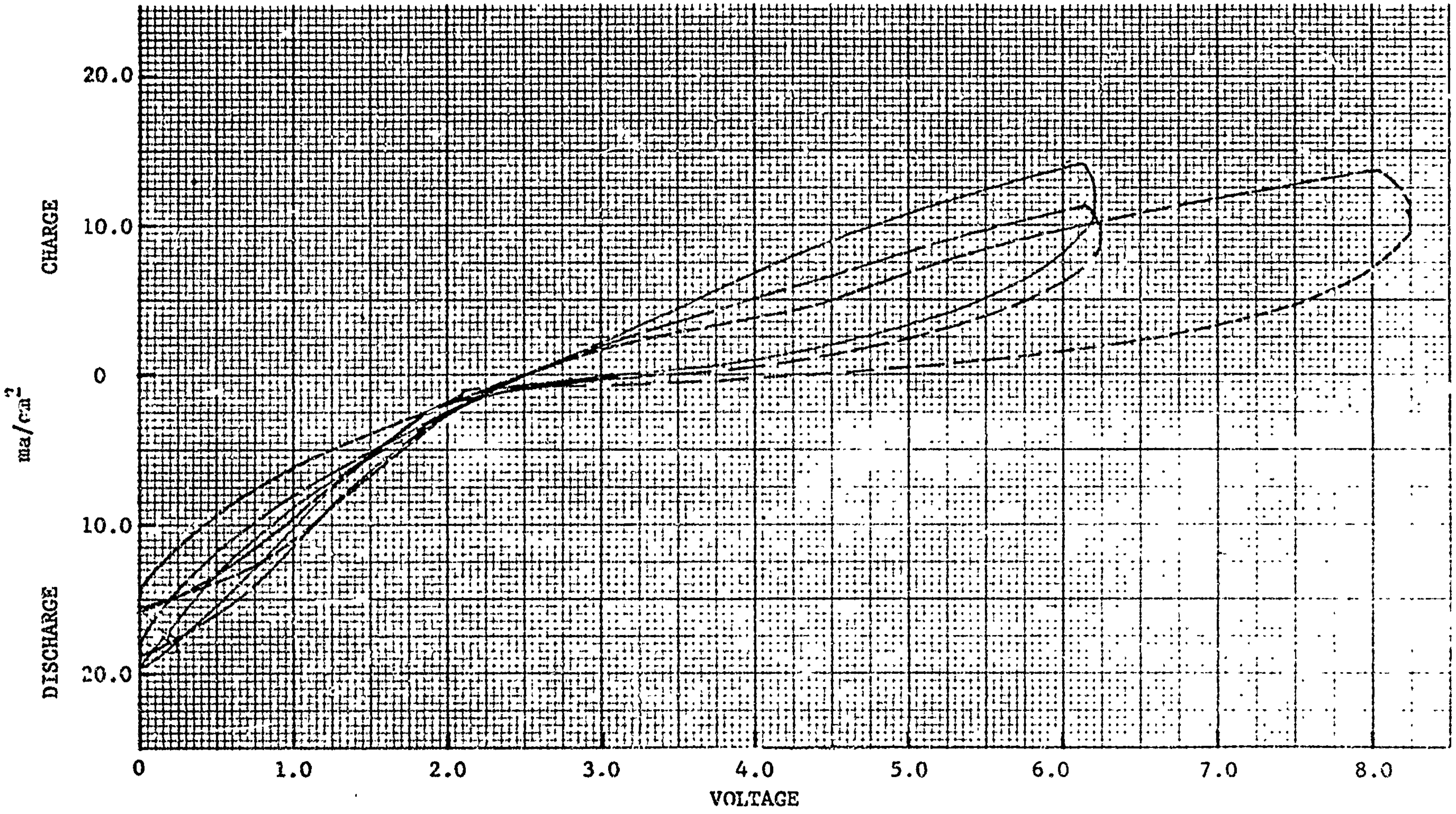


FIGURE 27 - POLAROGRAPHIC TEST - $NiCl_2$ AND UCET ACETYLENE BLACK (3:1 RATIO)

IV. NICKEL FLUORIDE ELECTRODES

A. PROBLEM

Previous attempts to make a nickel fluoride electrode by converting $Ni(OH)_2$ impregnated in a sintered nickel plaque to NiF_2 resulted in electrodes with extremely high polarization on discharge. After the initial success of the pasted $NiCl_2$ electrodes, pasted NiF_2-graphite electrodes were proposed. The same problems of improving current density of the NiF_2 graphite electrode existed as in the chloride system.

Attempts were made to dope the NiF_2 electrode with MgF_2 using wet chemistry, but these showed no significant change in polarization characteristics. The validity of the results were questioned, since the mode of doping was not considered the most efficient.

Doping by melting the NiF_2 proved to be a satisfactory method of incorporating the dopant, but results showed that the MgF_2 had no effect on the polarization of the electrode.

The same problems of the ratio of NiF_2 to graphite and the effect of compression of the electrode were present in the NiF_2 electrode studies as in the $NiCl_2$ system.

B. METHOD OF APPROACH

Because NiF_2 is not soluble in water to any extent, the use of the UCET acetylene black was limited. Electrodes made with a 3:1 ratio of NiF_2 to UCET graphite were too bulky and tended to check on drying. Although all of the data presented here was obtained with NiF_2 electrodes using Type 38 graphite, a new paste has been made using a blend of 90% Type 38 graphite and 10% UCET acetylene black. These electrodes have excellent physical properties and are easily pasted, the same as the $NiCl_2$ electrodes described in Section III. C.7.b.

Two methods of doping the NiF_2 with MgF_2 were tried. The first was a wet chemical method, and the second method was a melt technique.

Since NiF_2 has a limited solubility (.02 grams/100 cc of water at 20°C), the same technique used for doping $NiCl_2$ could not be used. The NiF_2 was ground and sieved through a 200 mesh screen ($< 74\mu$). A portion of the powder was weighed out and added to 20 times as much water. Magnesium fluoride was weighed out to equal 0.1% of the NiF_2 and was added. The slurry was slowly evaporated, first on a hot plate-stirrer, then in the drying oven at 110°C. The resulting powder was again ground and sieved through a 200 mesh screen.

It was believed that the MgF_2 doping could best be done by incorporating it into molten NiF_2. The NiF_2 and MgF_2 were ground and sieved through a 200 mesh screen. MgF_2 was weighed out to equal 0.1% of the NiF_2 and added. Two graphite crucibles were filled, one with the doped material and one with the undoped. The crucibles were heated in an inert atmosphere to 1100°C to melt the NiF_2, then cooled to recrystallize the material. The resulting pellets were reground and sieved through a 200 mesh screen.

The nickel fluoride powder obtained from Fisher Scientific Co. is reported by them to be the purest commercially available. When the NiF_2 was melted to introduce dopants, a control sample of undoped NiF_2 was melted also. There was a considerable (from 30 - 50%) weight loss, some to to sublimation and water loss, and the resulting color was a definite green, whereas the starting material had a grayish cast when ground to <~ 200 mesh.

A pair of X-ray diffraction patterns were made to see if there was any major change occurring in the NiF_2. It was not until the experimental work was completed that the X-ray pattern was interpreted to show a high percentage of NiO present.

An electrode was made of NiF_2 and graphite, 1:1 ratio, to use as a control. Other electrodes were made using the MgF_2 doped NiF_2 from the wet chemical method in ratios of 1:1, 1:3, and 9:1 NiF_2 to graphite. The electrolyte was PC-KPF_6 (saturated).

From the NiF_2 powders which had been fired at 1100°C, a series of electrodes were prepared with a NiF_2 to graphite ratio of 3:1. Two electrodes were prepared with only 1/2 gram of mix on a 10 cm^2 Monel 400 screen. Three electrodes were given 1.0 gram of the mix on a 10 cm^2 screen and two more were given successive coats until 2.0 grams of mix had been applied to 10 cm^2.

One of each of the above electrodes was prepared by not compressing it between coatings or at the end. One of each type was compressed at 1000 psi between each coat and at the end. The third electrode of the 1.0 gram/10 cm^2 type was compressed at 2 tons/square inch.

The electrodes were evaluated in a polyethylene plastic cell with polypropylene separator. Each NiF_2 electrode was tested against 2 lithium anodes. The Wenking potentiostat was used as shown in Fig. 8

C. EXPERIMENTAL RESULTS

Figures 28 and 29 are the X-ray patterns of the unfired and fired NiF_2 samples respectively. It was believed that there would be a substantial quantity of NiO (green) in the fired material, but this was not true.

The main effect appears to be the removal of some water of crystallization and some volatile impurities.

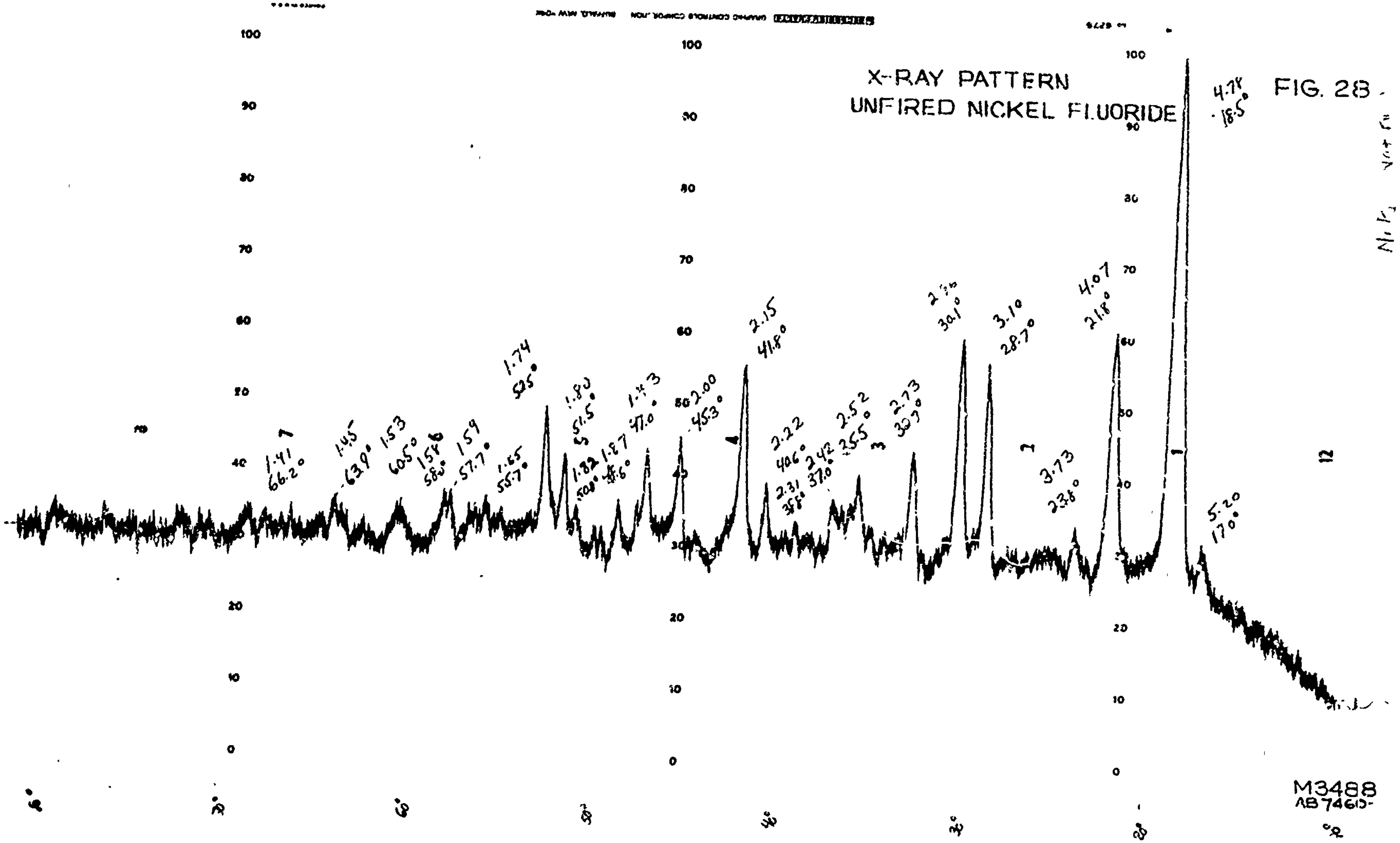
Figure 30 is a plot of the results from the undoped and unfired NiF_2 electrode. Figure 31 is the X-Y trace of the same NiF_2-graphite ratio with 0.1% MgF_2 doping from the wet chemical method. There is a scale change in the c.d. (anticipation of higher c.d. results) but the results are essentially the same as the undoped plates.

Figures 32 and 33 are the results of the 1:3 and 9:1 NiF_2 to graphite ratios. The 1:3 is the same as 1:1, and the 9:1 ratio is similar in proportion to the results obtained with $NiCl_2$ electrodes.

All of the above experiments were run in duplicate with excellent repeatability of results. The sequence of sweeps on the recorder were:

FIG. 28

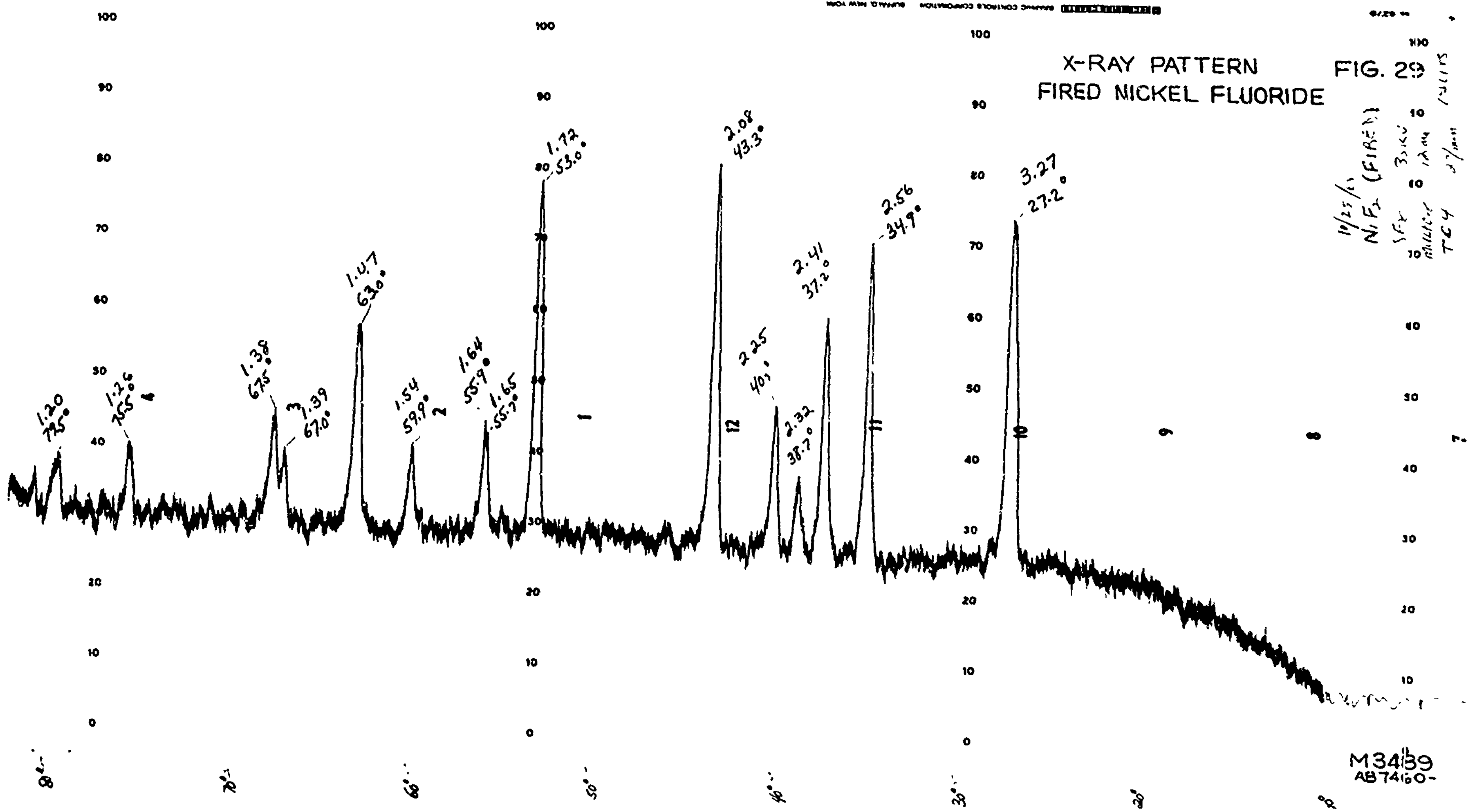
X-RAY PATTERN
UNFIRED NICKEL FLUORIDE



M3488
AB7461-

FIG. 29

X-RAY PATTERN
FIRED NICKEL FLUORIDE



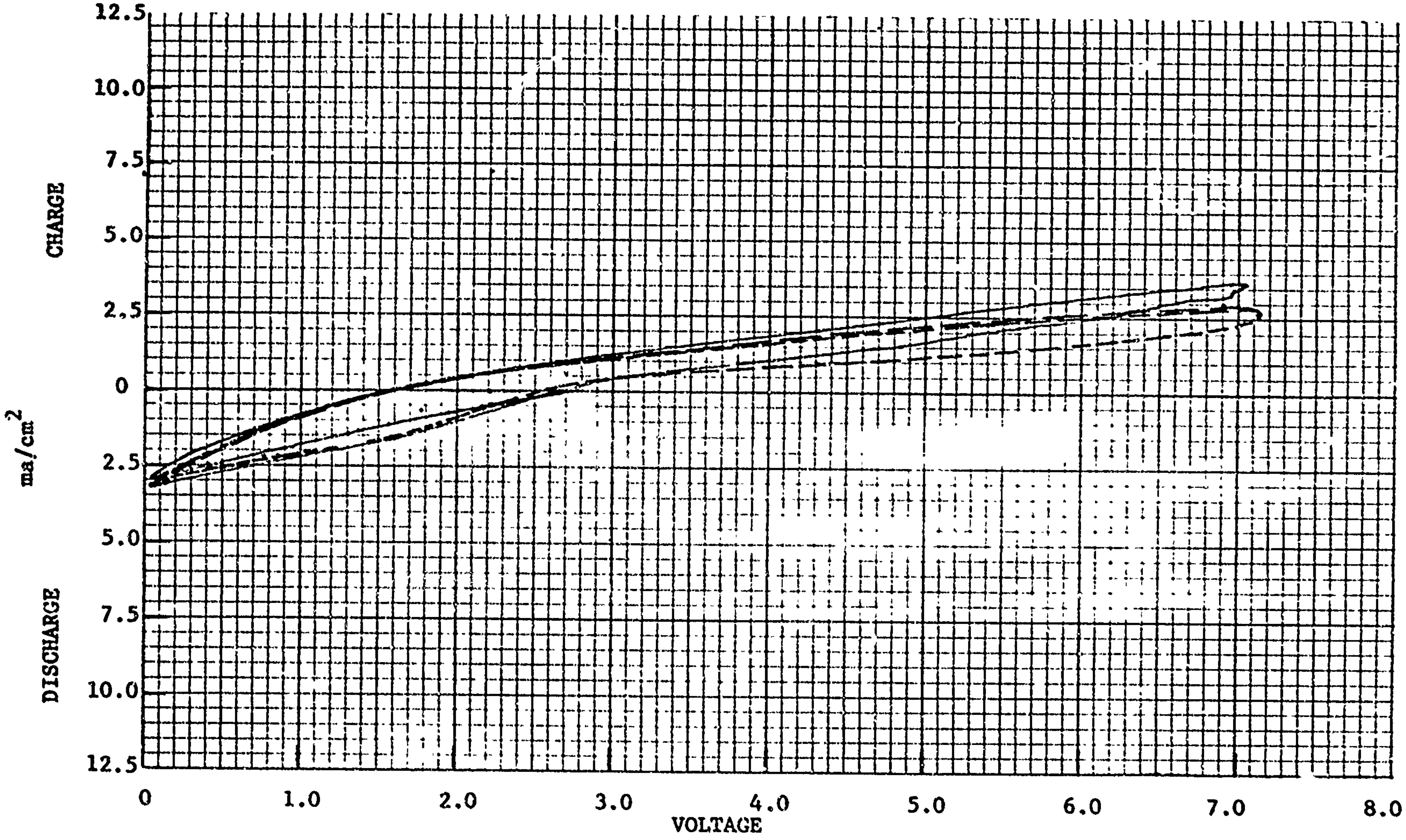


FIGURE 30 - POLAROGRAPHIC TEST - 50% NiF_2 + 50% C

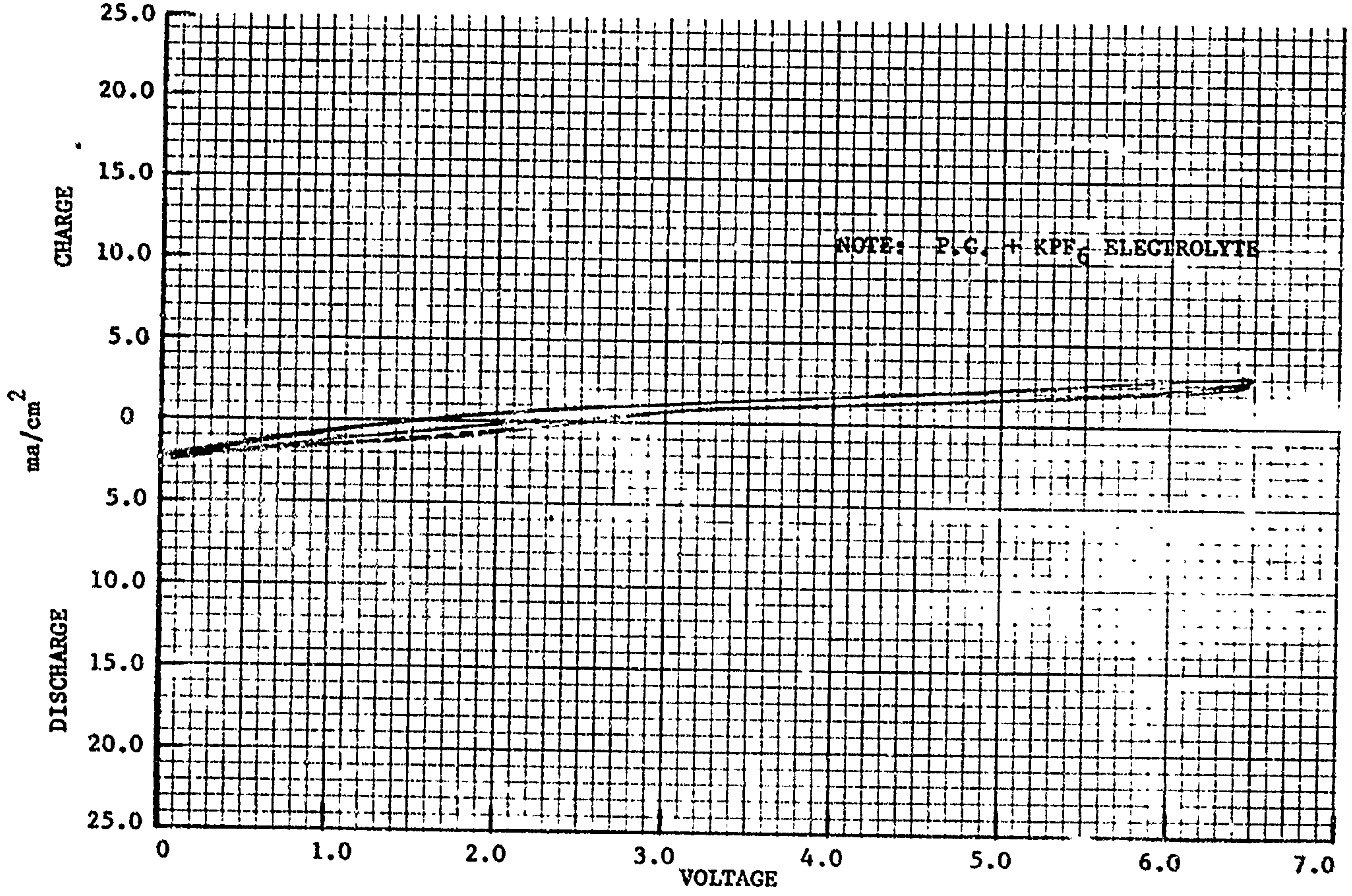


FIGURE 31 - POLAROGRAPHIC TEST - 50% NiF_2 (+0.1% MgF_2 DOPANT) + 50% C

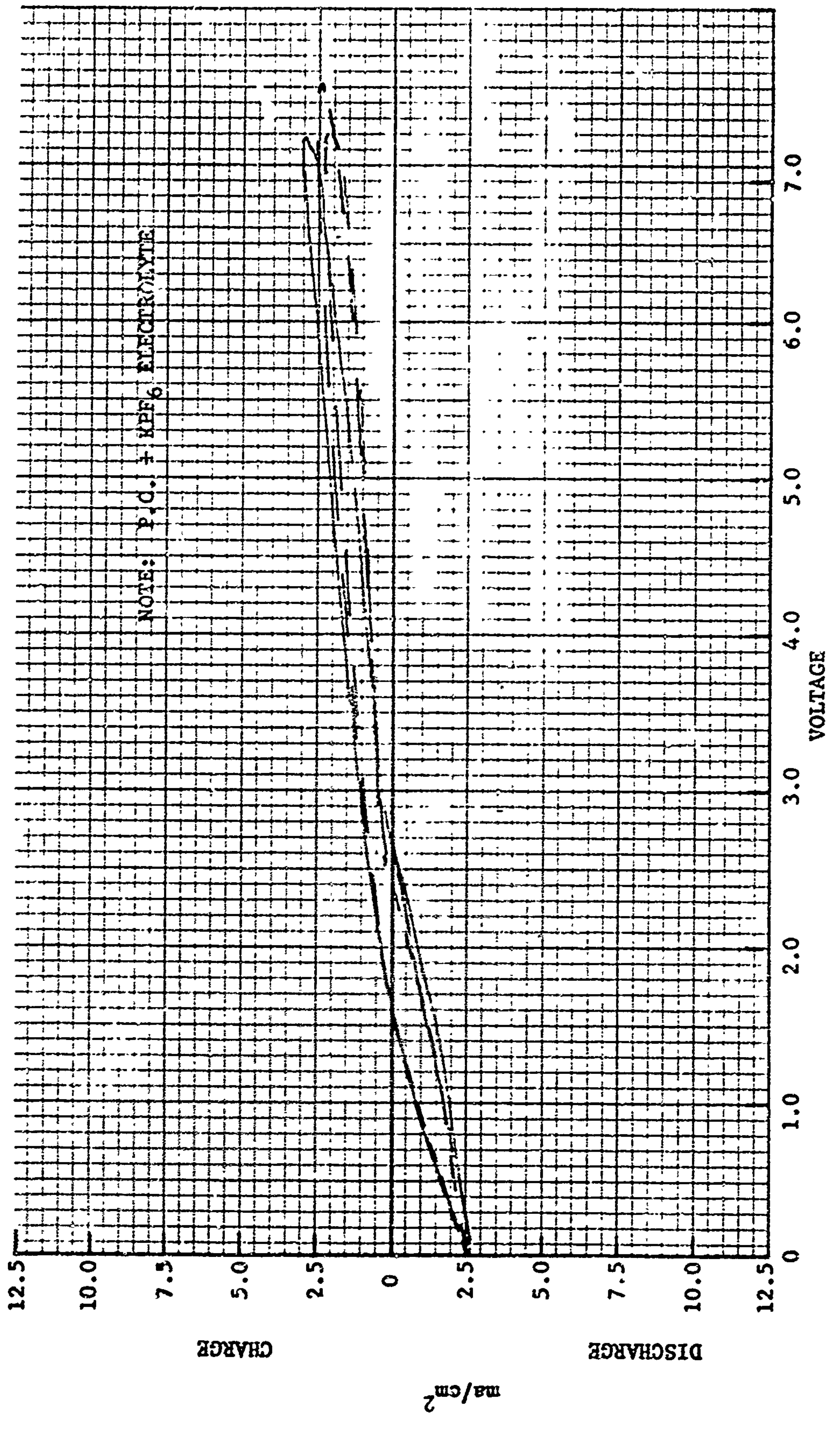


FIGURE 32 - POLAROGRAPHIC TEST - 25% NiF_2 (+0.1% MgF_2 DOPANT) + 75% C

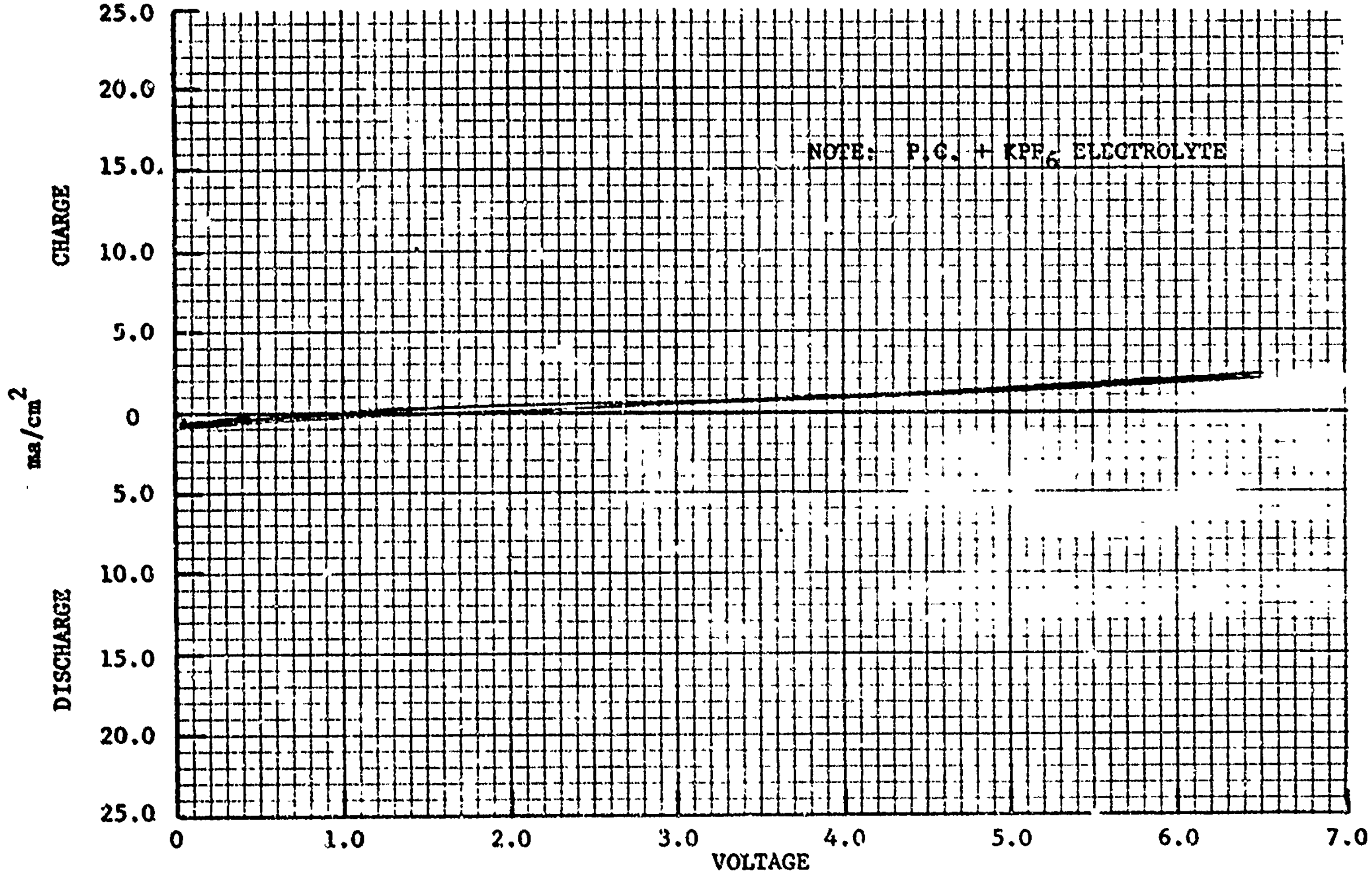


FIGURE 33 - POLAROGRAPHIC TEST - 90% NiF_2 (+0.1% MgF_2 DOPANT) + 10% C

(1) the solid line, (2) the long dashed line, and (3) the short dashed line.

It should be noted that the electrolyte used was PC saturated with KPF_6. Improvements in this electrolyte were later found to reduce resistivity (see Section V.). This could affect the slope of the curve slightly because of an increase in IR drop, but R varies in this cell by a factor of 0.00125ρ, so the total IR drop is negligible.

Figures 34, 35 and 36, show electrodes coated with 0.5. 1.0 and 2.0 grams of mix per 10 cm^2 of screen. These show an increase in polarization with increased loading. There is also an improvement in repeatability of cycles with increased loading.

Figures 37 through 40 are the same as 34 through 36, except that these cathodes were doped with 0.1% MgF_2. Figure 40 is the only one which does not follow the same pattern. This electrode should be a duplicate of Figure 38 except that it was compressed at twice the pressure. The effect of compressing the electrode is shown by the increase in current density with each sweep.

D. DISCUSSION

The initial results of wet chemistry MgF_2 electrodes were thought to be invalid because of the manner in which they were doped. In the case of the chloride, the salts are soluble and can be co-crystallized. In this manner, the $MgCl_2$ is incorporated into the crystal lattice. In the case of the fluoride, the dopant was primarily a surface coating of heavily doped NiF_2 on the undoped nucleus. However, the melt technique should have overcome this problem. The results of these tests still show the effect of doping with MgF_2 was insignificant but they may have been masked by the NiO impurity. Since doping of the $NiCl_2$ electrode showed some changes. it is felt that other dopants should be tried in a future program, such as SrF_2 (ionic radius double Ni).

There were three factors under test: (1) thickness or loading, (2) compression, and (3) doping. The thickness of the active material does not affect the polarization at 0.1 and 0.2 grams per cm^2. At 0.05 grams per cm^2, there is a slight improvement, which is reminiscent of the thin film electrode experiments. These tests were made on 10 sq. cm electrodes.

The experiments with ratios of NiF_2 to graphite show no advantage in using less than 50% NiF_2. The use of UCET acetylene black indicates that the ratio of 3:1 NiF_2 to graphite is practical using a 9:1 blend of Type 38 and UCET graphites.

In the case of the NiF_2 electrode at a 1:3 ratio, compression of the material is beneficial. This may be due to the fact that, since NiF_2 is insoluble in water, the pasting operation does not insure intimate contact of NiF_2 particles with the graphite. In the case of the $NiCl_2$ the pasting operation wets the $NiCl_2$ and this coats the surface of the graphite. Formation cycling of compressed NiF_2 electrodes should improve the utilization, as should the use of the UCET graphite in the mix. Cycling of the electrode should cause a better intermixing of the NiF_2 with the conductive diluent by reducing the particle size of the NiF_2.

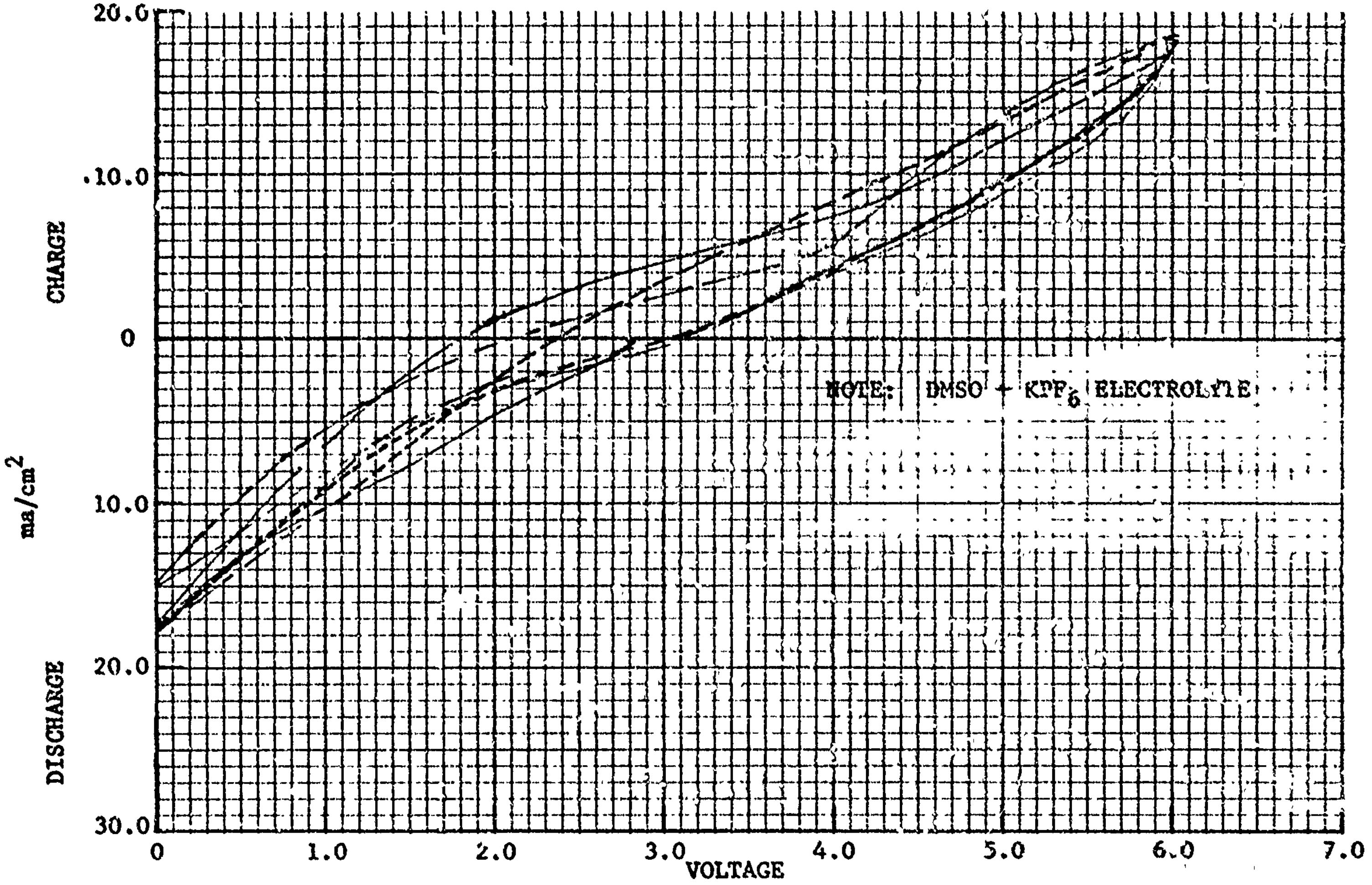


FIGURE 34 - POLAROGRAPHIC TEST - 25% NiF$_2$ + 75% C - 1/2 G/10.0 cm^2

UNCOMPRESSED PLATE

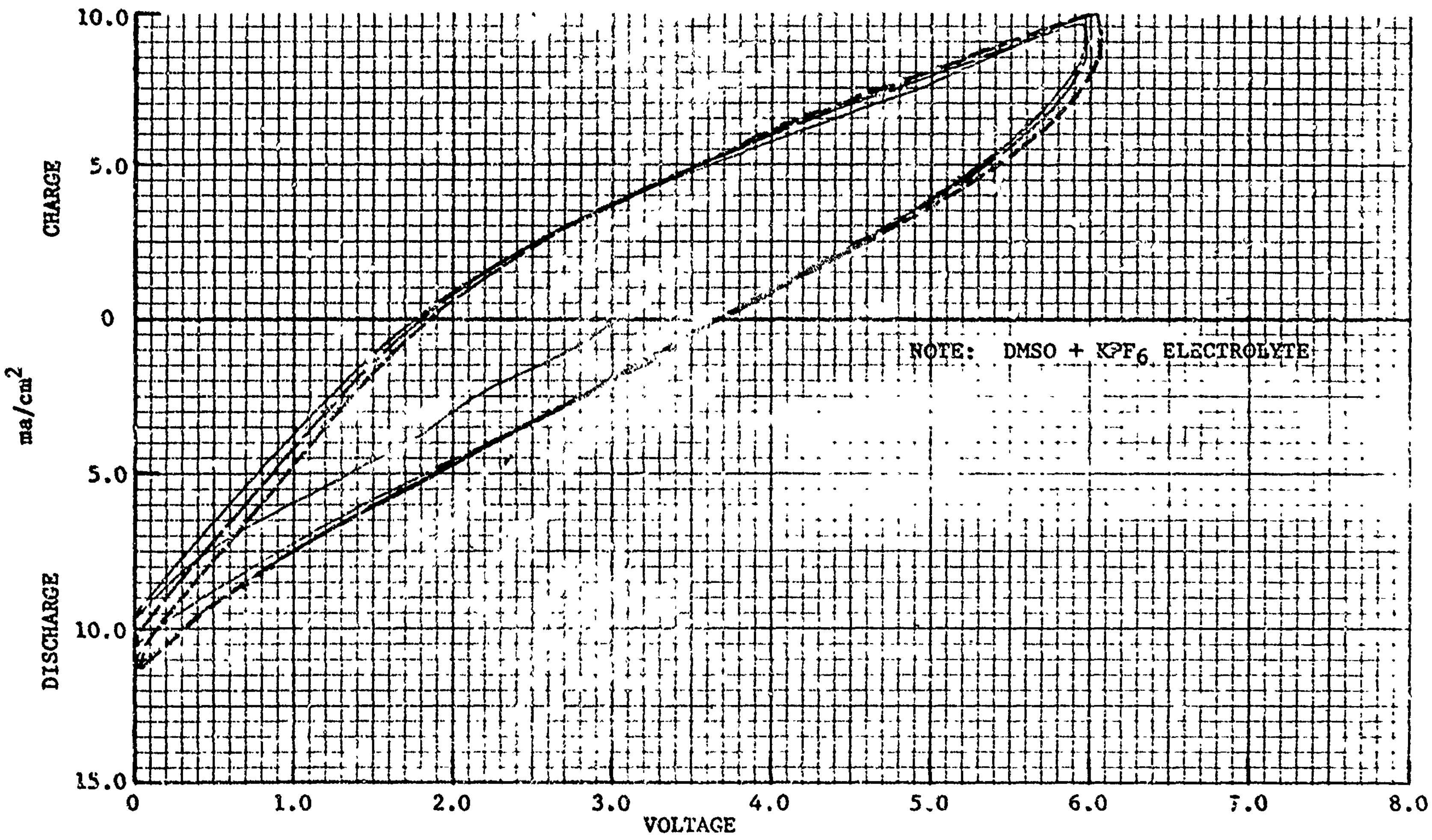


FIGURE 35 - POLAROGRAPHIC TEST - 25% NiF_2 + 75% C - 1.0 G/10.0 cm^2

UNCOMPRESSED PLATE

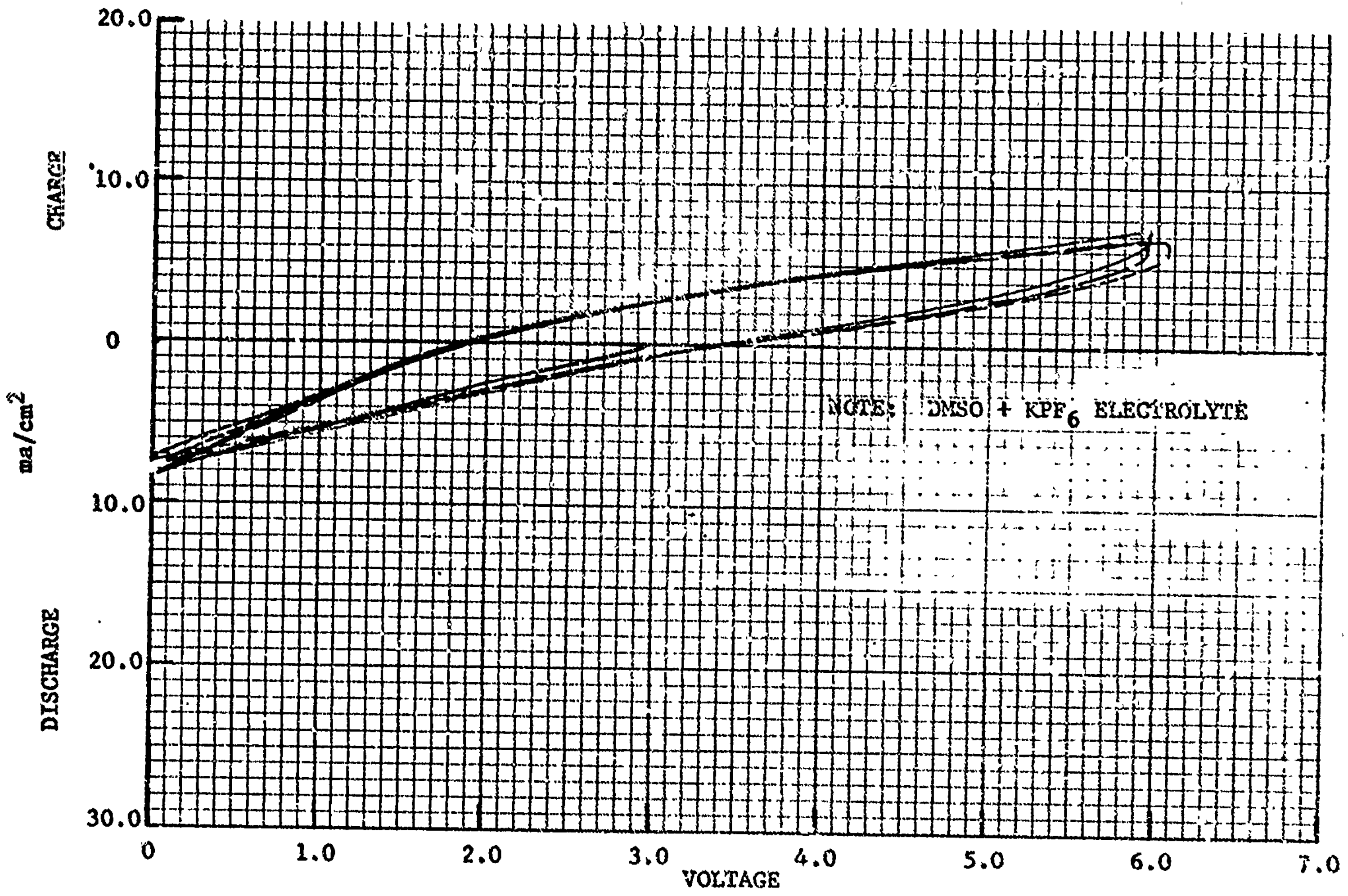


FIGURE 36 - POLAROGRAPHIC TEST - 25% NiF$_2$ + 75% C - 2.0 G/10.0 cm^2
PLATE COMPRESSED AT 10^3 P.S.I.

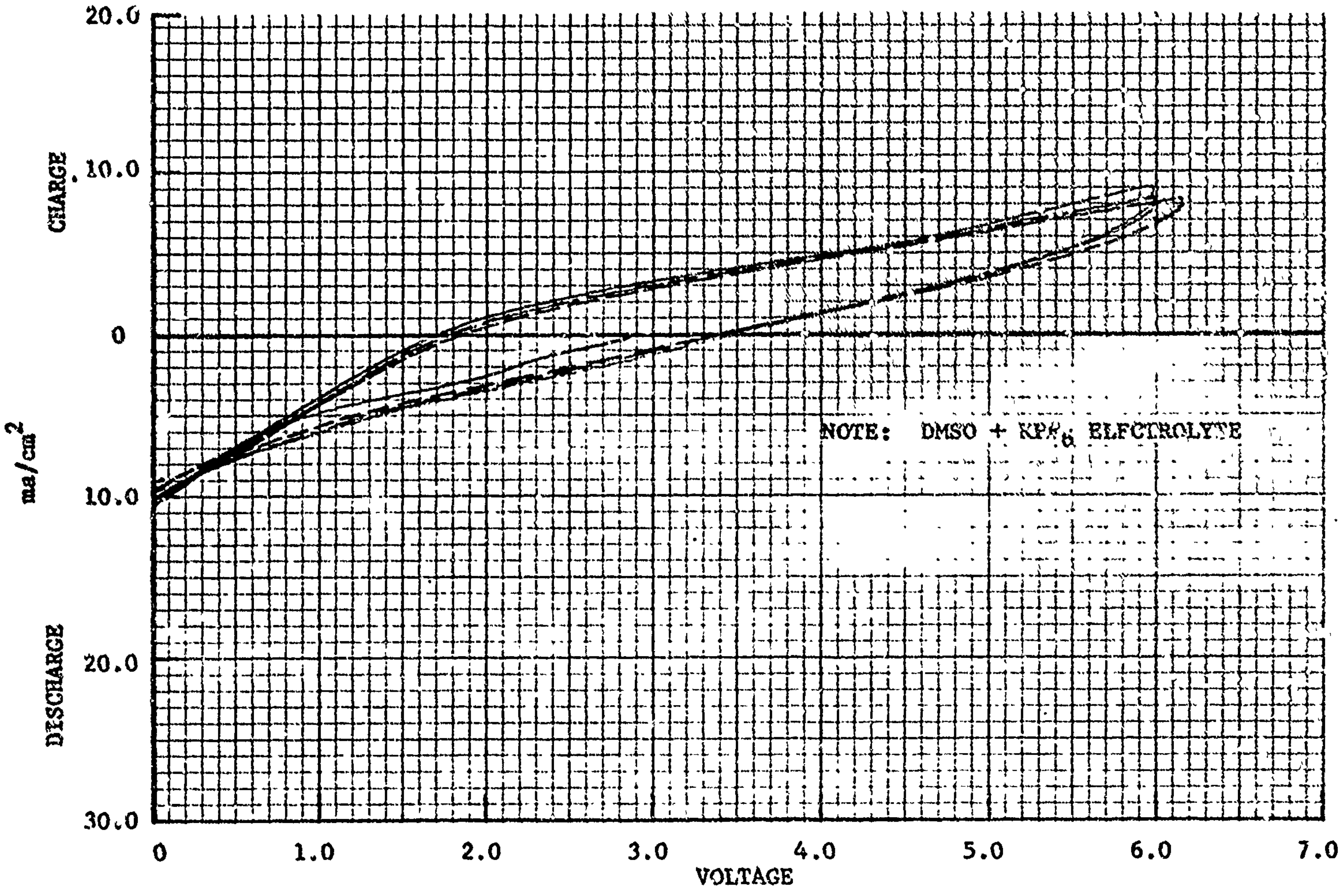


FIGURE 37 - POLAROGRAPHIC TEST - 25% NiF_2 (+0.01% MgF_2) + 75% C - 1/2 G/10.0 cm^2 - UNCOMPRESSED PLATE

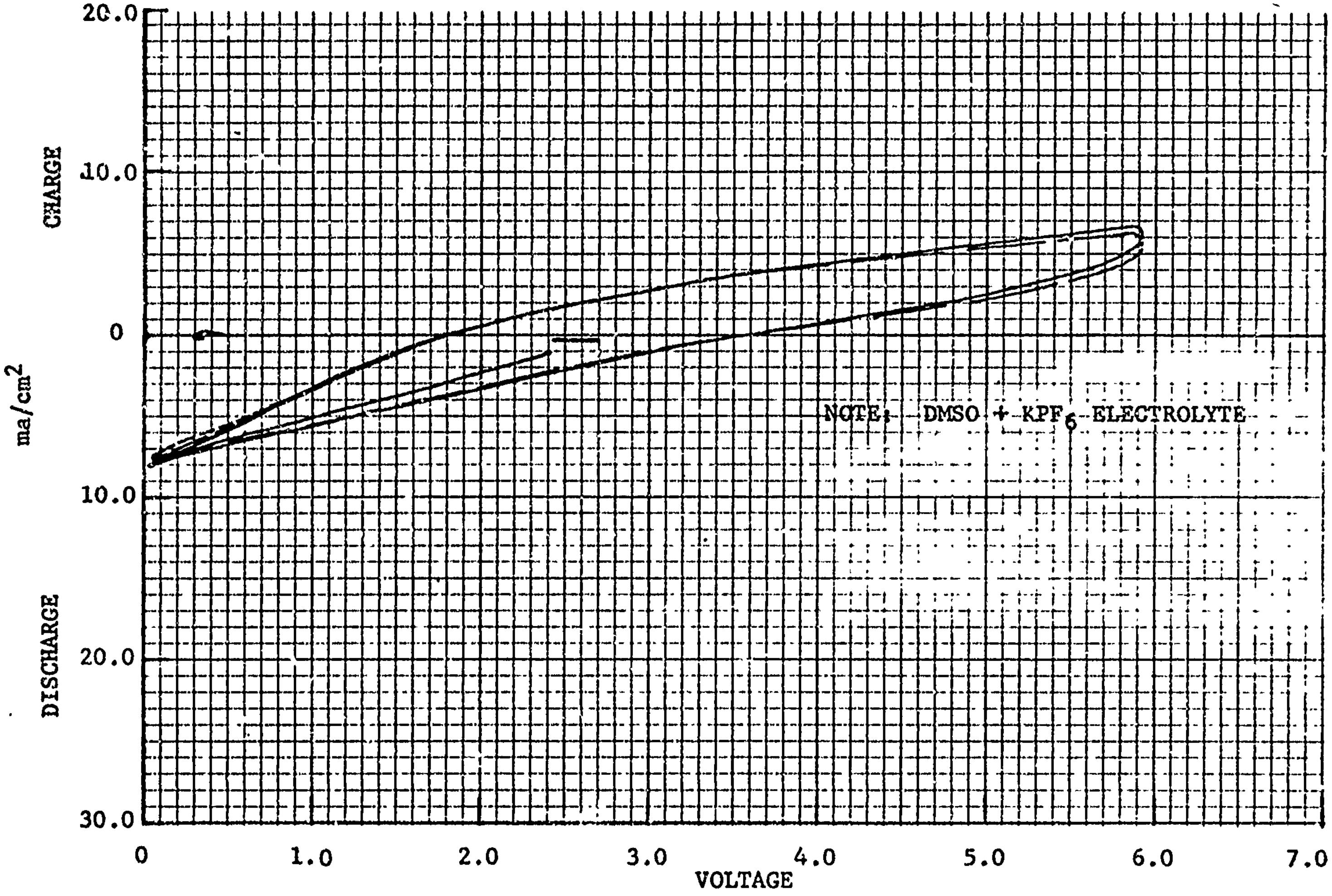


FIGURE 38 - POLAROGRAPHIC TEST - 25% NiF_2 (+0.01% MgF_2) + 75% C -
1.0 G/10.0 cm^2 -
PLATE COMPRESSED AT 10^3 P.S.I.

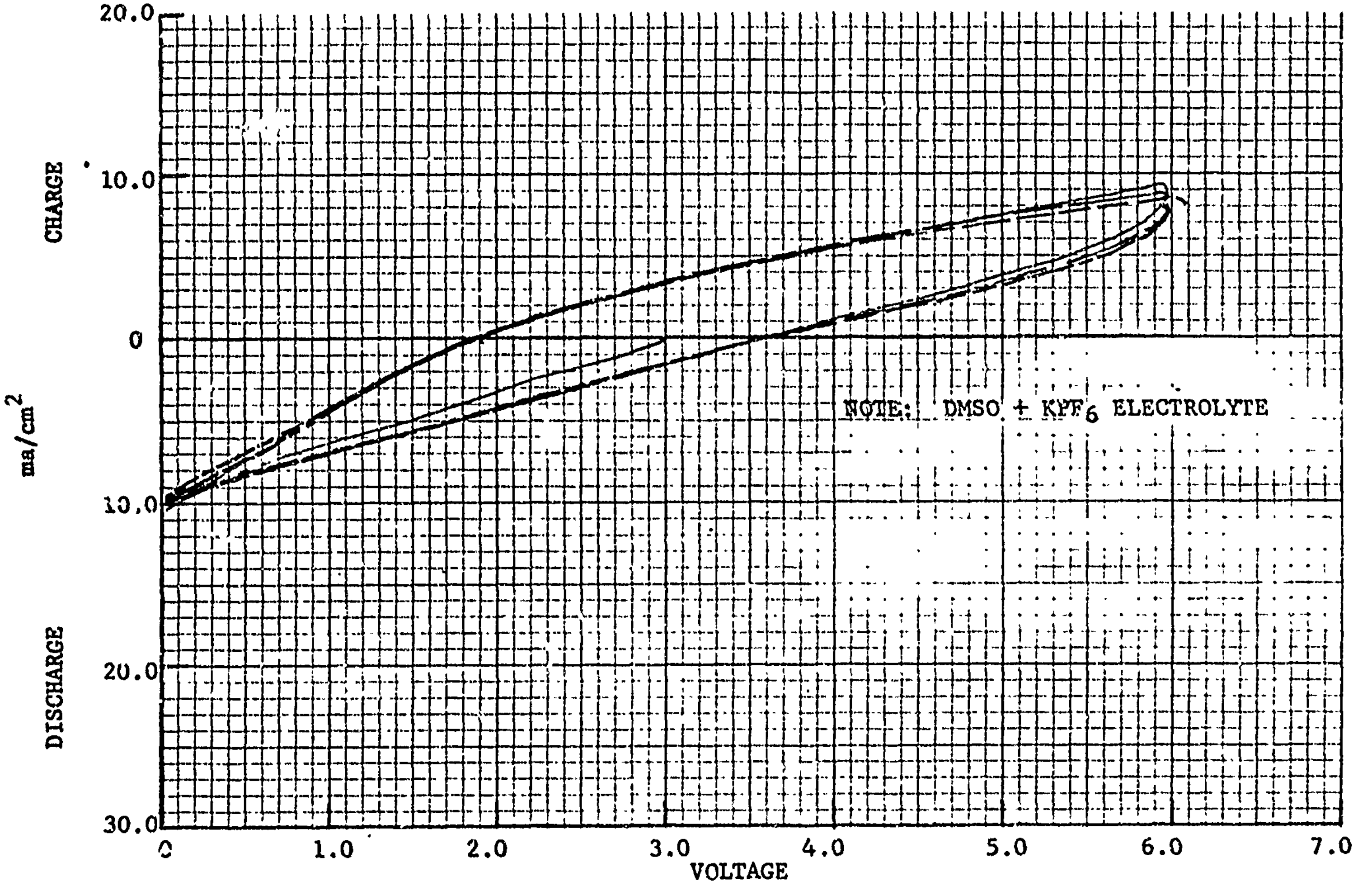


FIGURE 39 - POLAROGRAPHIC TEST - 25% NiF_2 (+0.01% MgF_2) + 75% C
2.0 G/10.0 cm^2 -
PLATE COMPRESSED AT 10^3 P.S.I.

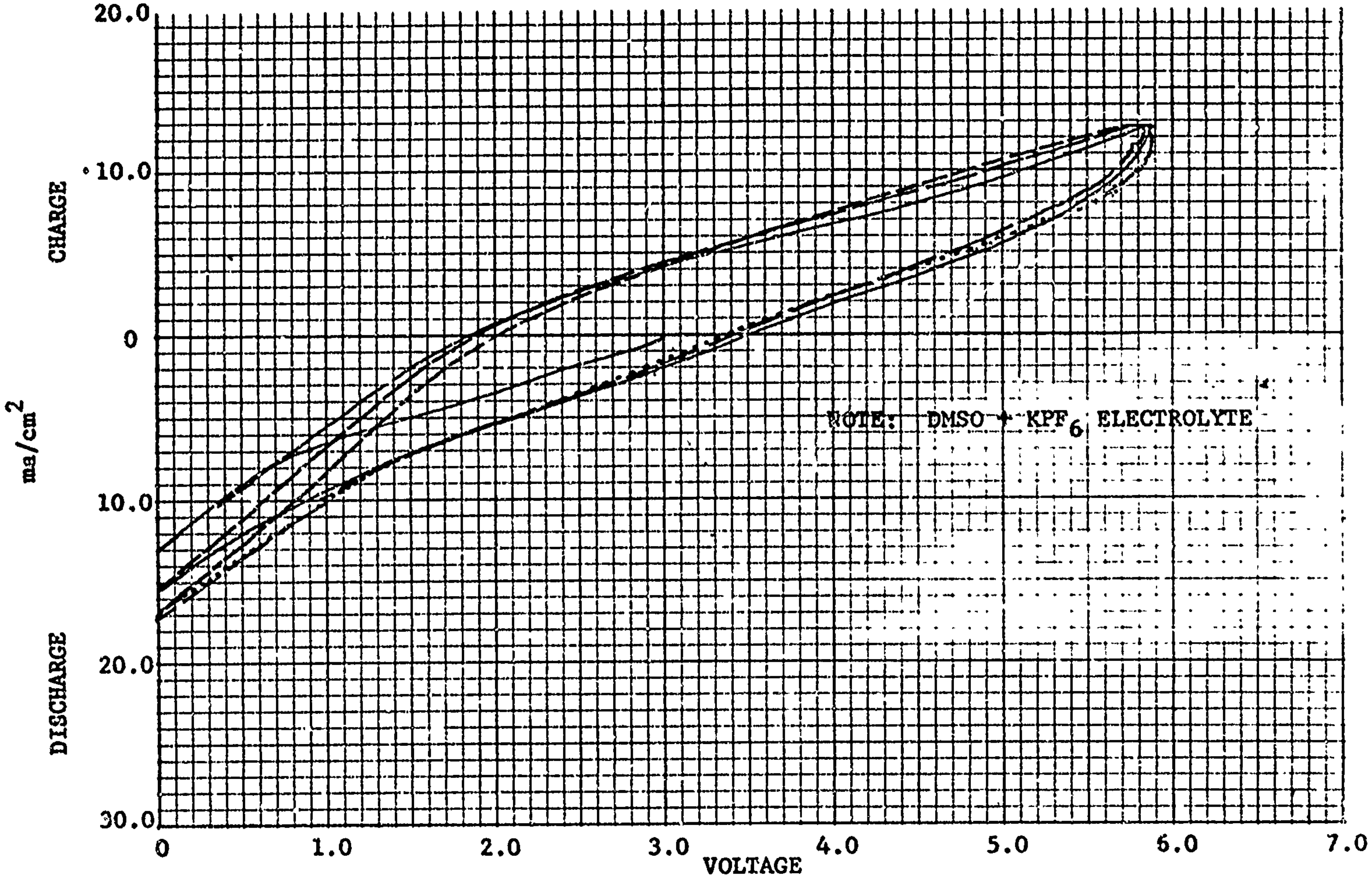


FIGURE 40 - POLAROGRAPHIC TEST - 25% NiF_2 (+0.01% MgF_2) + 75% C -
1.0 G/10.0 cm^2 -
PLATE COMPRESSED AT ONE TON/IN^2

V. ELECTROLYTE STUDIES

A. PROBLEM

Laboratory cell studies have revealed a potential decay on open circuit of $NiCl_2$-Li cells using PC-$AlCl_3\cdot LiCl/Cl_2$ electrolyte. It was postulated that there was some reaction occurring which did not show in the compatibility tests. It was also observed that there was gassing at both electrodes of a cell during charge at voltages over 4.95 volts. Because of these problems, further study of the electrolyte system was undertaken.

The problems of polarization, self discharge, and utilization may well be related to the electrochemical properties of the electrolyte used. Conductivity, decomposition potential, and static compatibility have been evaluated. However, the effect of impurities has not been investigated.

B. METHOD OF APPROACH

The decomposition potential of an electrolyte may be determined by the dropping mercury electrode method. Stationary microelectrodes have been little used in polarography, both because they are very sensitive to vibration and because the current depends on the length of time over which the electrolysis has been conducted, and so a dropping mercury electrode is usually employed as the polarized electrode. This consists of a very fine glass capillary immersed in the solution and connected to a column of mercury. As mercury flows through the capillary a droplet forms on the capillary tip. This grows for several seconds, until it has attained an accurately reproducible size which depends on the geometry of the capillary and the interfacial tension between the mercury and the solution; then it falls and another droplet begins to grow in its place. The dropping mercury electrode has several advantages over a stationary microelectrode. First, each drop behaves in exactly the same way as the preceding one, and the average current measured with a galvanometer or other long-period current-measuring instrument is accurately reproducible from drop to drop. Second, since a jar or shock which causes one drop to behave erratically does not affect the following one, the dropping electrode is much less sensitive to mechanical disturbances than is a stationary microelectrode. Third, the very high overvoltage for the deposition of hydrogen on a mercury surface makes it possible to secure well-defined waves for ions whose standard potentials lie far above that of hydrogen ion. In neutral solutions, even sodium and potassium ions can be determined polarographically.

Figures 41a and 41b are photographs of the apparatus used. The electrode shown in Fig. 41b is 24 inches to the top of the mercury. This controls the drop speed to 2 seconds per drop. In Fig. 41a, the X-Y recorder is an 11 x 17 inch chart size. Top center is the Erwin Halstrup Motorpotentiometer MP 64. To the right of this is a VTVM used to make course adjustments. Under the Motorpotentiometer and VTVM is the Wenking Electronic Potentiostat.

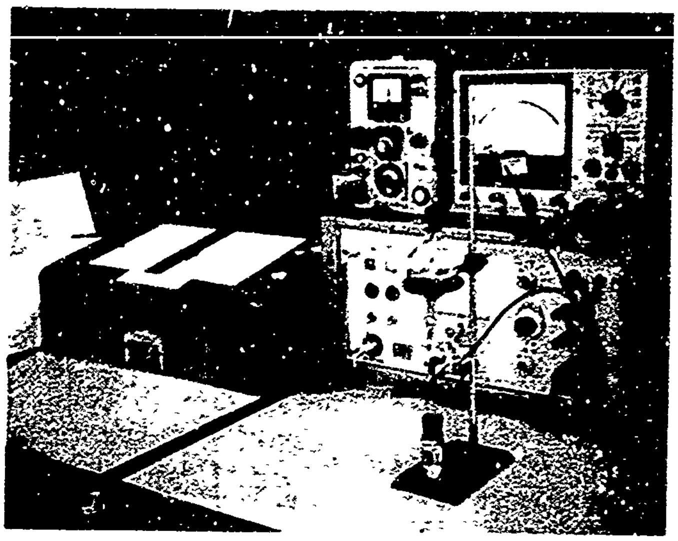


Fig. 41A POLAROGRAPHIC APPARATUS SHOWING CELL, POTENTIOSTAT, MOTOR DRIVE, AND RECORDER

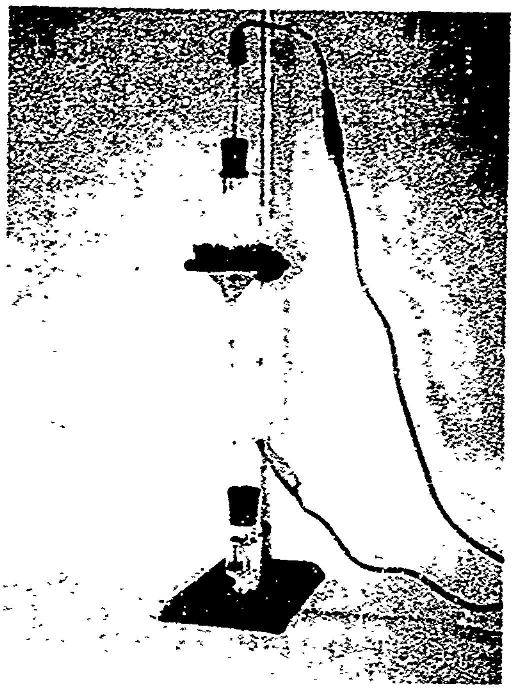


Fig. 41B DROPPING MERCURY ELECTRODE

A wide range of specific conductivities was encountered with both the propylene carbonate and the dimethyl sulfoxide solvent when electrolytes were prepared with KPF_6. Attempts were made to produce a very dry sample of KPF_6 and to test this as an electrolyte salt.

C. EXPERIMENTAL RESULTS

Figure 42 is a trace of the polarograph of the decomposition of PC-$AlCl_3 \cdot LiCl/Cl_2$ electrolyte. The drop time was approximately one per two seconds using a scan rate of 30 volts/hour. The voltage and current were recorded on an X-Y recorder which has little dampening. The frequency response of the recorder is 1 cps. With the high sensitivity of the recorder, average current values were taken directly from the chart. This electrolyte had been pre-electrolyzed with a pasted lithium anode and a Monel 400 screen cathode. At the beginning of the polarograph, there is a gradual increase in current. The products of electrolysis formed on the electrodes do not remain there, but slowly diffuse back into solution. A small current must pass in order to compensate for this loss by diffusion.(3) The decrease in current at 0.7 volts is referred to as a maximum of the second kind.(4) It is postulated that, prior to this maximum, there is no concentration polarization at the dropping mercury electrode. Immediately after the maximum, the electrode becomes completely concentration polarized.(5) The curve reaches a minimum and starts to increase rapidly at 0.9 volts. The extension of this line to the $I = 0$ axis, gives the decomposition potential of 0.75 volts. The voltage was increased, and at 2.6 volts, there was another maximum. This subsequent curve indicated a second decomposition potential at 1.6 volts but a very highly polarized electrode.

It was postulated that the difference in conductivity found in two lots of DMSO - KPF_6 might be caused by trace amounts of water in the electrolyte. A fresh sample of high purity DMSO (freezing point checked at 18.40°C) was used. The KPF_6 was dried with thionyl chloride and immediately dissolved in the DMSO. The KPF_6 was added until the solution became turbid. The total content was 460 g/liter. The resistivity was determined at 24.8°C. A portion of the electrolyte was successively diluted and conductives determined. Figure 43 is a plot of the resistivity versus concentration of dried DMSO - KPF_6 electrolyte. The remaining amount of the original lot was diluted to give 40 ohms. A drop of water was added to 6 cc of electrolyte with no effect on the conductivity. Up to 1 cc of water was added before there was a change in conductivity, and then only to the degree obtained by dilution with DMSO.

A sample of KPF_6 which had been dried with thionyl chloride a week earlier and had been exposed to the air on several occasions during that time was used to prepare electrolyte from the same DMSO as used for Fig. 43. Only a few grams would dissolve and the best conductivity obtained was with no dilution. The resistivity was 132 ohms.

The addition of 2% water to the DMSO prior to dissolving a freshly dried sample of KPF_6 had no effect on the solubility or resistivity of the electrolyte.

Figure 44 shows the results of a DME test of dried DMSO, but KPF_6 which had been exposed to air. Figure 45 shows the difference using dried KPF_6.

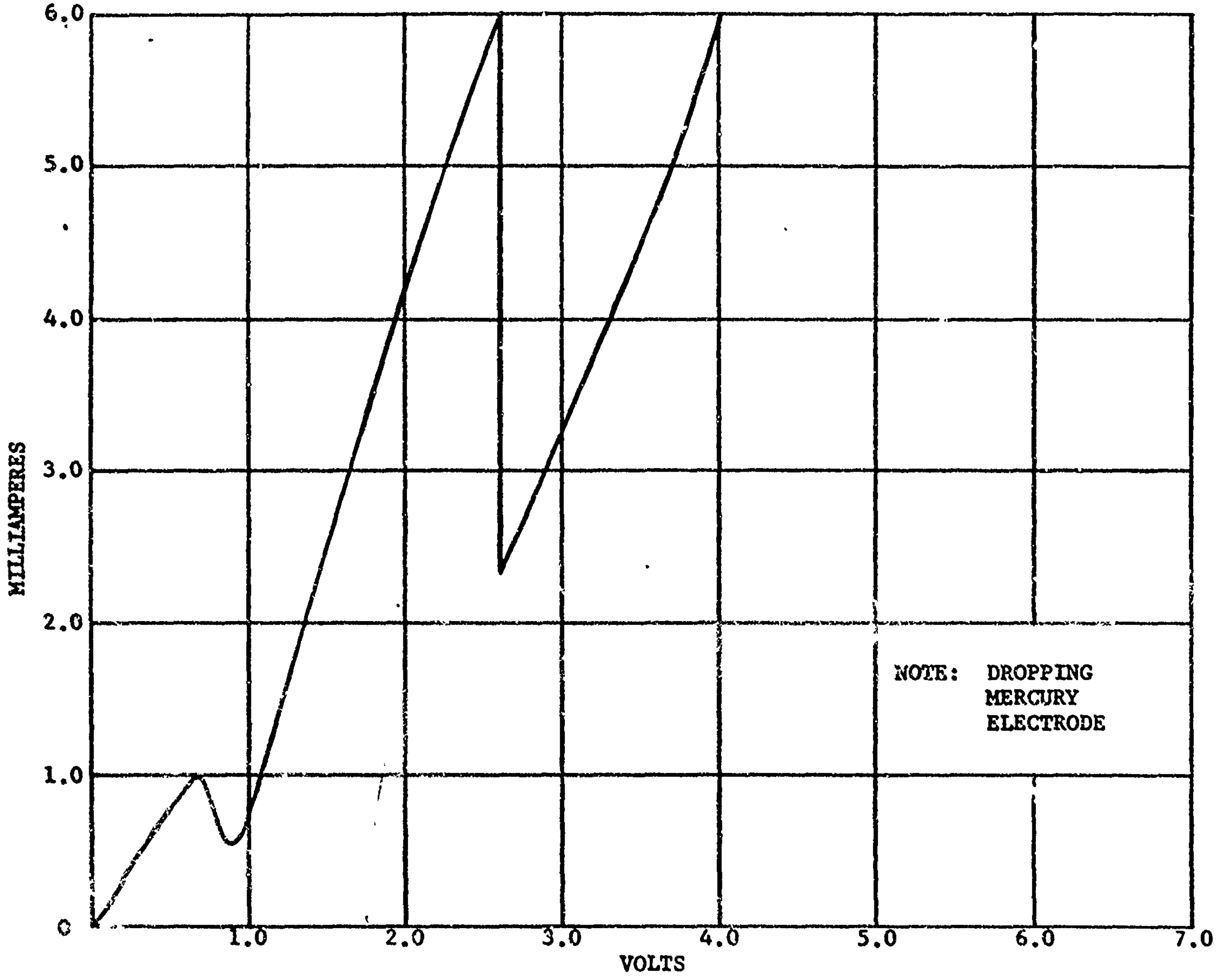


FIGURE 42 - DECOMPOSITION POTENTIAL OF PC-$AlCl_3$/LiCl-Cl_2

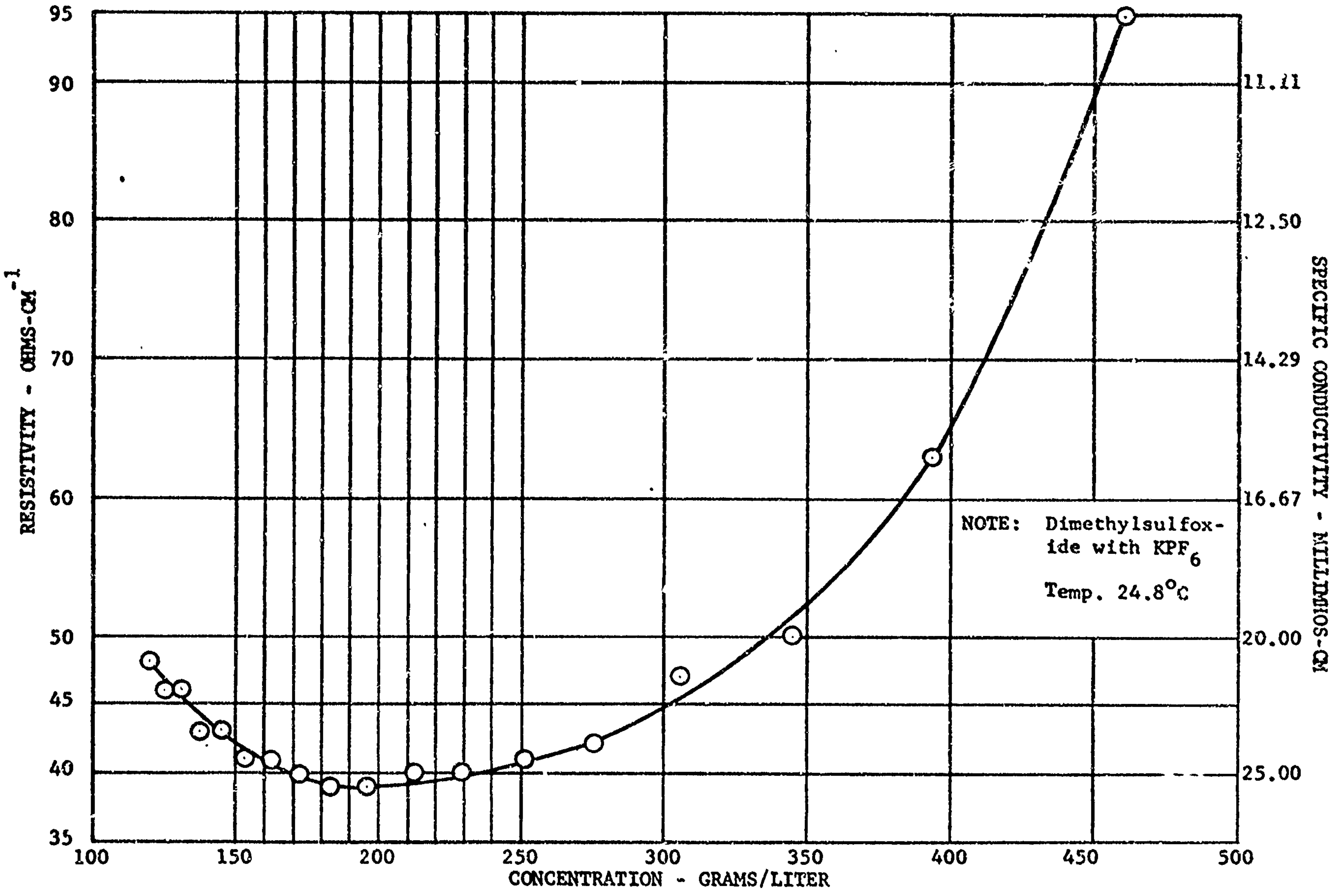


FIGURE 43 - CONDUCTIVITY Vs CONCENTRATION - DMSO-KPF_6

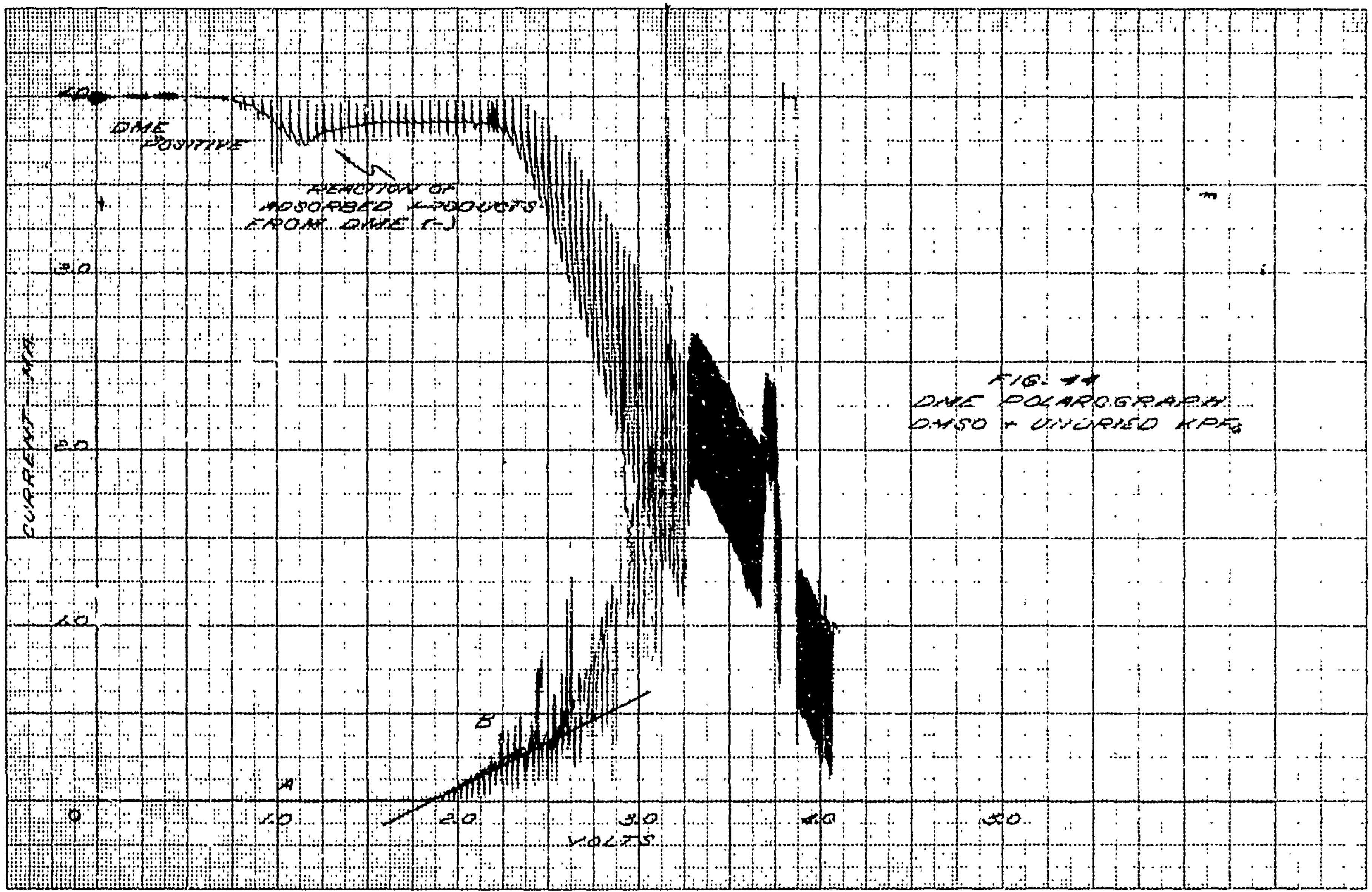


FIG. 44
DME POLAROGRAPH
DMSO + UNDRIED KPF_6

M3503
AB7460

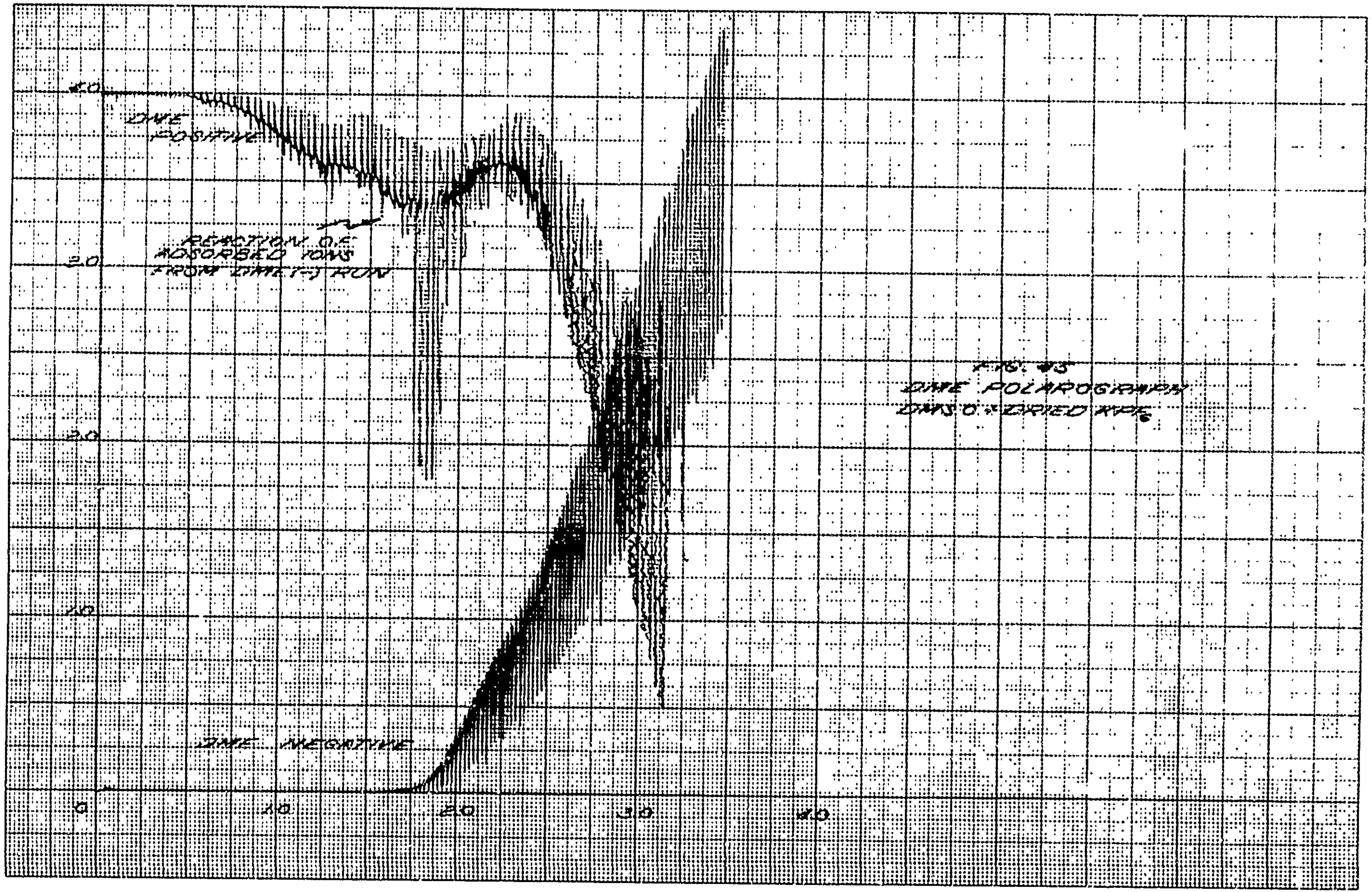


FIG. #3
DME POLAROGRAPHY
DMSO. + DRIED KPF6

M3504
AB7460

A sample of the same electrolyte lot used for Fig. 45 was electrolyzed at 1 ma/cm^2 using a lithium anode and a Monel 400 screen cathode for 30 minutes. The electrolyte was then placed in the polarographic cell and the trace shown in Figure 46 recorded. The first trace, made with a 5 μa/in chart scale would be indiscernible at the 0.5 ma/in chart scale since 25 μa is equal to 1/20 inch or the smallest division. There was no change in conductivity or DME trace noted.

Another sample from the lot used for Fig. 45 was contaminated with 1 drop of water and the polarograph shown in Figure 47 made. Two things of note are the plateau during the μa portion with the sharp peak at 1.5 volts. Second, the first break in the polarogram at B is reminiscent of the one in Fig. 44. Both cases can be attributed to water but may not necessarily be due to the electrolysis of water. KPF_6 is a double salt of KF and PF_5, the latter reacting vigorously with water as does PCl_5. There is the possibility of some secondary action involving PF_5 with water at this potential.

To determine if the decompositions were caused by the DMSO or the KPF_6, two tests were made, one with $NaPF_6$ and the other with LiF in DMSO. The results are shown in Figures 48 and 49. The $NaPF_6$ gave results almost identical to the KPF_6. The resistivity was 42 ohms. The LiF showed the same break point but due to the higher resistivity (510 ohms) gave an almost flat curve.

Figure 50 shows the polarogram of PC with KPF_6. There is a low plateau starting at 1.95 volts which may be due to water or some other impurity such as alcohol. The decomposition is, however, at a greater potential than DMSO with KPF_6 and even though the conductivity is slightly less (.022 mhos) it may be more desirable.

Figure 51 is a composite of results using the DME and either a lithium electrode or a nickel fluoride-graphite electrode. The lithium trace is a double sweep - from 0 to 4 volts and back. Using the DME as a reference value, the only point where current does not pass is at a potential difference of 2.1 volts. The currents for the lithium versus DME are in microamps.

The passage of current first entails a capacitative portion and then a faradaic portion. To sustain a faradaic current suitable oxidation-reduction reactions must occur. In the case of Li and the dropping mercury electrode, a possible faradaic cell is:

$$\text{Li, Li}^{+}/\text{KPF}_6\text{, DMSO}/\text{P}^{+5}\text{, p}^{+3}\text{; Hg.}$$

Oxidation occurs in the left electrode and reduction in the right electrode. It appears like on thermodynamic considerations that phosphorous is the species being reduced.

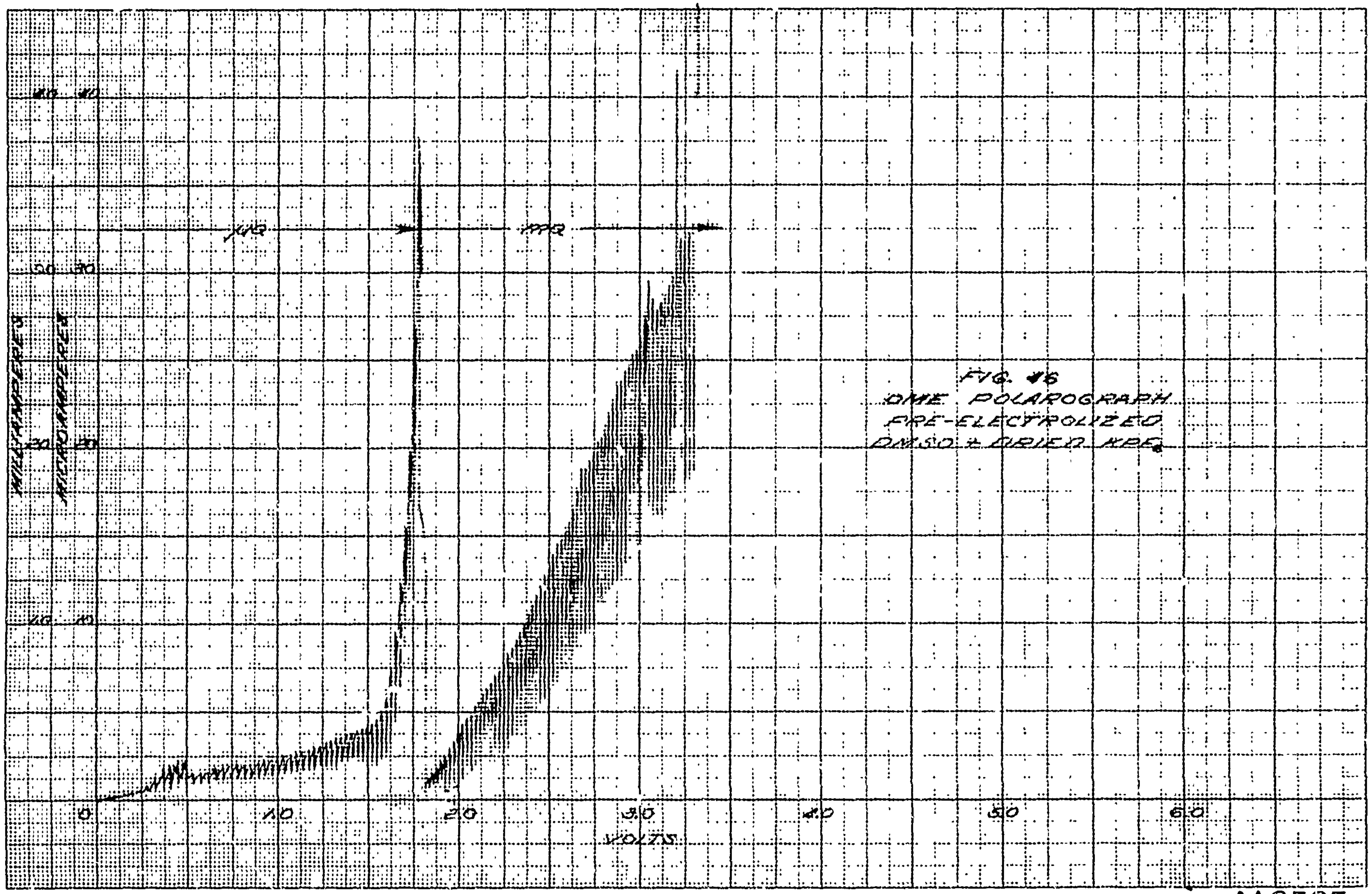


FIG. #6
DME POLAROGRAPH
PRE-ELECTROLIZED
DMSO + DRIED KPF$_6$

M 3505
AB7460

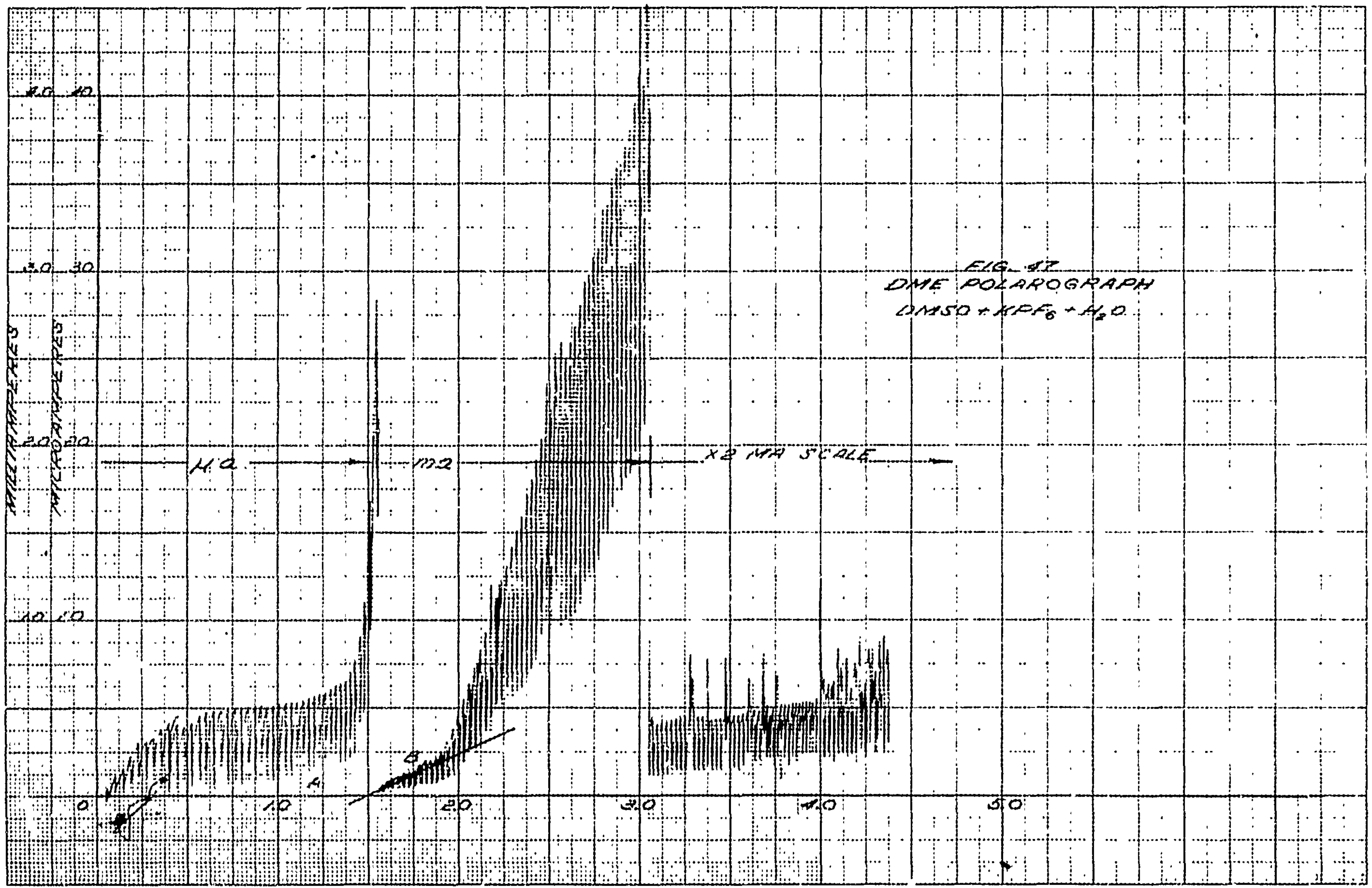


FIG. 47
DME POLAROGRAPH
DMSO + KPF_6 + H_2O

M3506
AB7460

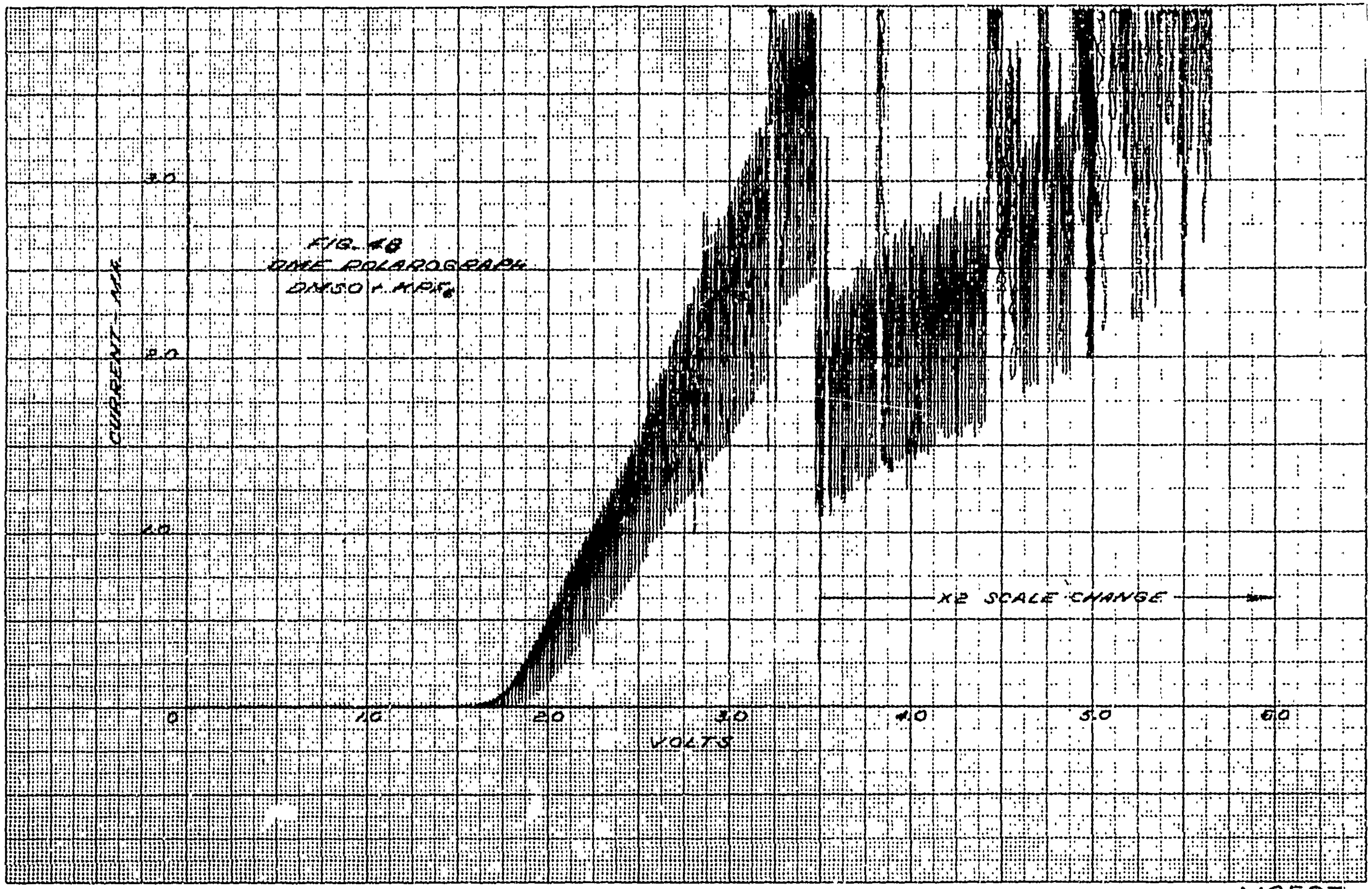


FIG. 48
DME POLAROGRAPH
DMSO + KPF$_6$

M3507
AB7460

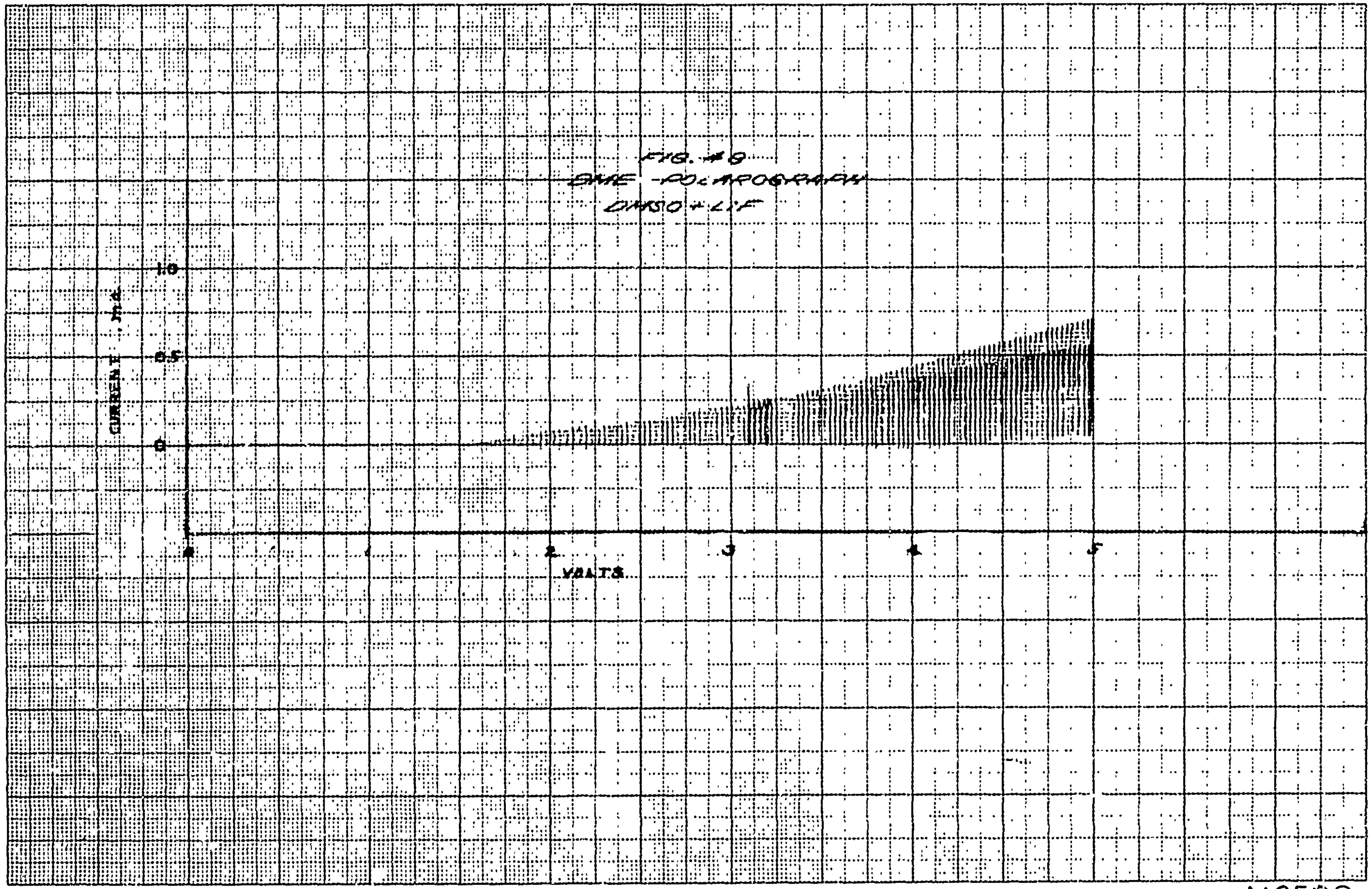


FIG. #8
DME - POLAROGRAPH
DMSO + LiF

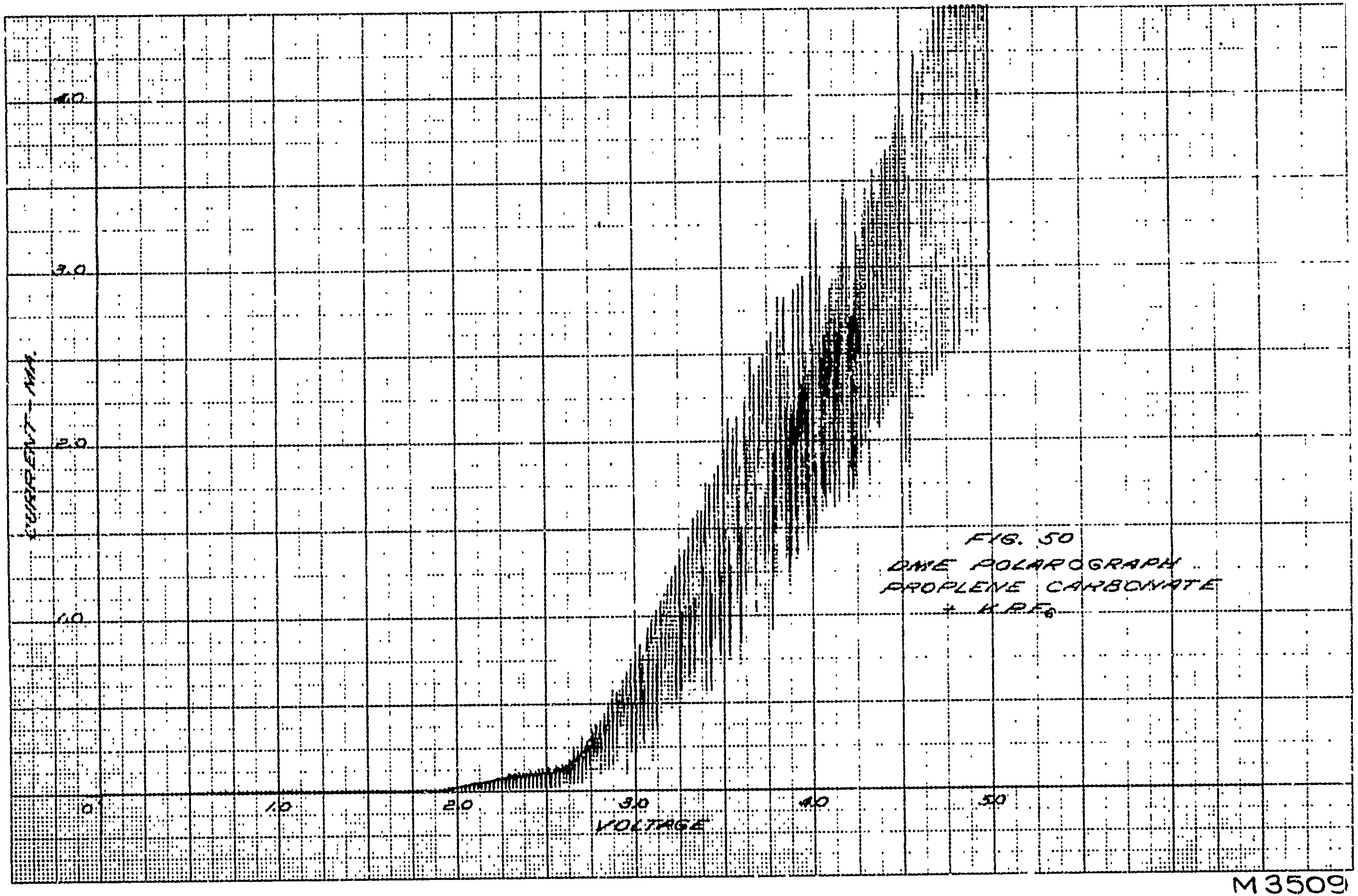
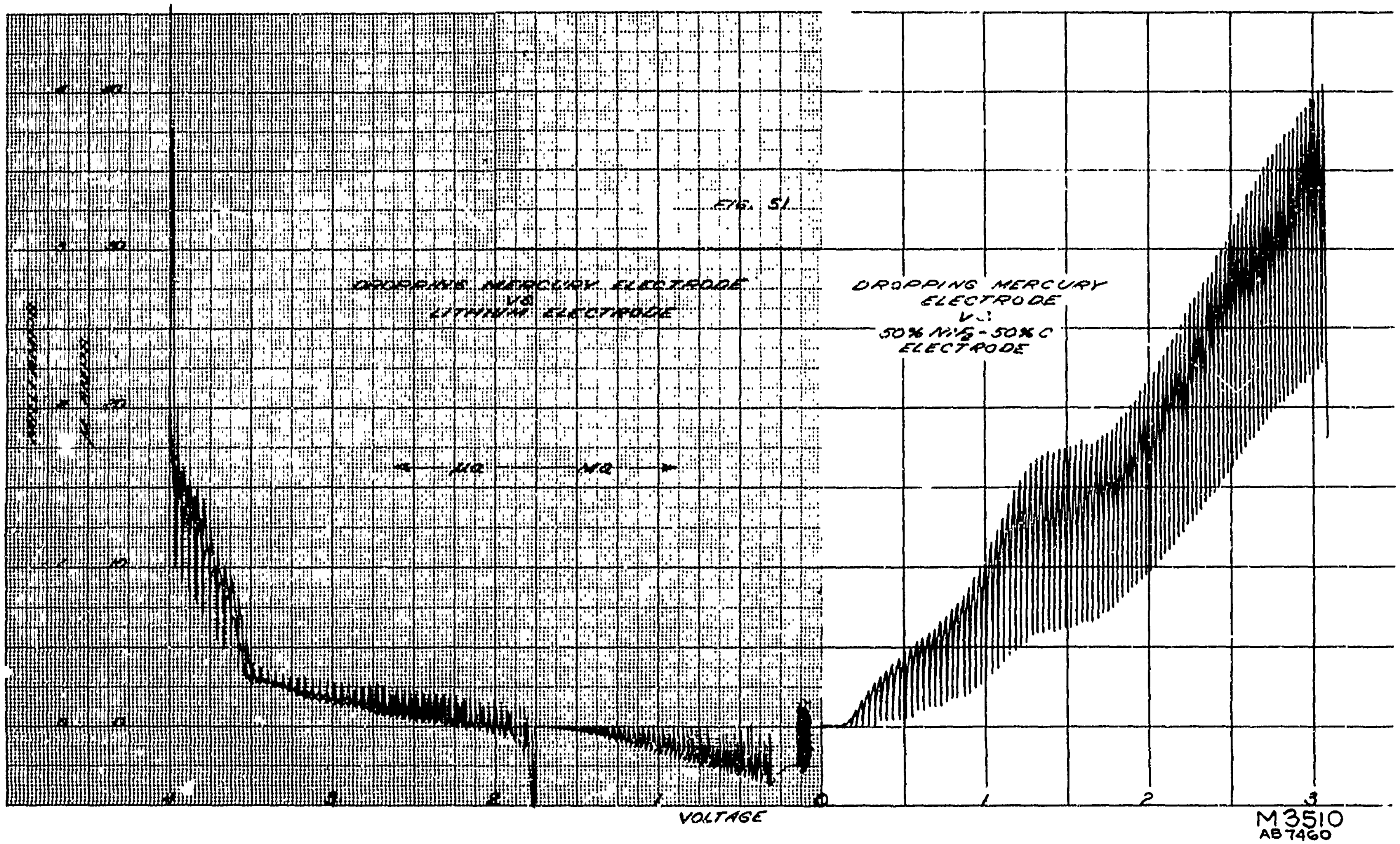


FIG. 50
DME POLAROGRAPH
PROPLENE CARBONATE
+ KPF$_6$

M3509
AB7460

FIG. 51



M3510
AB7460

VI. BINDER STUDIES

A. PROBLEM

The binder used for the lithium electrode is carboxy methyl cellulose (CMC). When this binder, made in an aqueous solution, was used for the nickel chloride electrode, it became gelatinous after a few cycles. Although it did not dissolve, the electrodes swelled and there was the probability of a poor contact between the support screen and the active material.

B. METHOD OF APPROACH

Several commercially available materials were obtained from vendors. Also, a hydrolyzed form of starch (corn starch treated with Nd OH) and gelatine (Baker & Adamson USP) were selected. These were made into viscous solutions and coated on Monel 400 screens. When dried, these screens were placed in the electrolyte solvents (DMSO and PC) in sealed bottles for 7 days. If, upon removing and drying, the film was unaffected, the binder was tried in a test electrode.

Test electrodes were prepared, both $NiCl_2$ and NiF_2 types using both DMSO and PC electrolytes with KPF_6. These were cycled in polyethylene test cells by discharging at 1 ma/cm^2 ($\sim$C/20) for two hours and charged at 6 volts constant potential for 3 hours. After 5 cycles they were removed and examined.

C. EXPERIMENTAL RESULTS

A summary of the test data on binders is given in Table III below. The material which gave the best physical properties of ease in pasting and uniform drying was gelatine. Its adhesion after cycling was also excellent. All of the co-polymers failed in cell operation. The hydrolyzed starch, formed by adding a small amount of NaOH to a starch (Argo corn starch) solution, was moderately successful, but not as good as the gelatine.

TABLE III

	BINDER TEST		
BINDER	PASTING QUALITY	ADHESIVE QUALITY	ADHESIVE QUALITY UNDER TEST
	WET	DRY	
Gelatine (B&A USP Grade)	excellent	excellent	excellent
"Polectron 450" (Vinyl Pyrrolidone-styrene co-polymer)	excellent	good	poor
Hydrolyzed Starch	excellent	good	good
Polyvinyl Alcohol	good	poor	poor
"Polectron 130" (Vinyl Pyrrolidone-ethylacrylate co-polymer)	excellent	good	poor

VII. LABORATORY CELL TESTING

A. PROBLEM

Half cell studies were conducted in a plastic cell open to the atmosphere in the test chamber. In order to test the results obtained in half cell studies under conditions closer to a prototype cell, a special laboratory cell was designed.

B. METHOD OF APPROACH

Four laboratory cell cases were made according to the drawing given in Figure 52. These cells can be sealed and resealed for evaluation of the inside of the cell.

C. EXPERIMENTAL RESULTS

There were many attempts to assemble a laboratory cell, each failing for some mechanical reason. Some of the first cells failed because the tabs were corroded after the first cycle. Most failures were due to shorting, usually as a result of a sharp edge of the expanded screen cutting through the separator.

Three of the more significant test cells are reported here. Each used the standard lithium electrode. The negative electrodes were pasted lithium-carbonyl nickel anodes. The carbonyl nickel powder is 10 microns. Using a 10 mole percent nickel admixture gives an electrode coating containing 50.6% lithium, 47.4% nickel, and 2% binder. A 10% solution of CMC in dimethylsulfoxide was added to the lithium-nickel oil dispersion so as to leave about 2% CMC in the pasted material after drying.

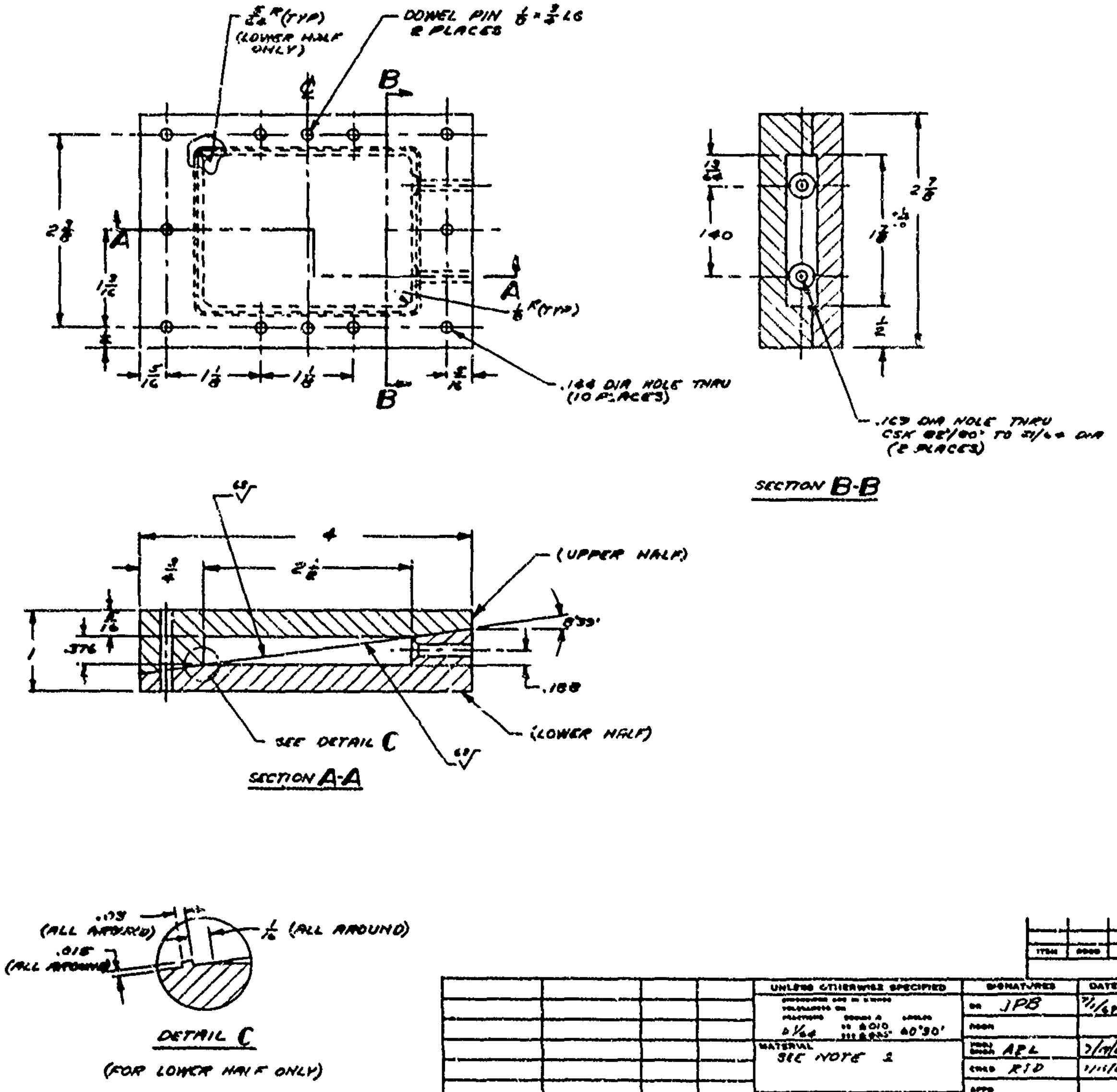
The materials are weighed out. The lithium-oil dispersion is placed in a weighing bottle in the glove box. Based on this weight, the weight of the nickel and binder are calculated. The binder is dissolved in DMSO. All ingredients are returned to the glove box when they are mixed. The lithium-nickel mixture is applied with a spatula to a base. Although this is done in a glove box under argon, it can be handled in the atmosphere as long as there is oil on the lithium surface. The electrode tabs were welded to the terminal studs before the screens were pasted with lithium. After a uniform layer of mix has been applied, the electrode stack is removed from the glove box, each electrode placed between two plates of polyethylene, and compressed at 2 tons per square inch. The electrodes are placed in a small glass vacuum chamber heated with resistance heating tapes.

The electrodes are vacuum dried since the dimethylsulfoxide boils at approximately 190°C which would soften the lithium particles and cause sintering. The electrodes are heated to 90-100°C under 2 psia pressure for 15 minutes and then cooled. After the cooling, the vacuum chamber is placed in a dry box where it is opened, under argon, and the electrodes washed with hexane to remove any residual mineral oil.

Each electrode had an area of 20 cm^2. The capacity of each lithium electrode was over 1.0 ampere hour.

Fig. 52

REVISIONS



NOTES
1. CELL TO BE MADE FROM EITHER POLYSTYRENE OR POLYPROPYLENE. MATERIAL TO BE SUPPLIED BY GULTON

LIST OF MATERIAL

UNLESS OTHERWISE SPECIFIED
± 1/64 ± .010 ± .005 ± 0°30'
MATERIAL
SEE NOTE 1

SIGNATURES DATE
JPB 7/1/64
APL 7/17/64
RID 7/15/64

CELL

SCALE 1:1
DWG SIZE C

APPLICATION
QTY REQD

Separators were polypropylene bags of 3 mil thick non-woven material. One was placed over each electrode.

The make-up of the three cells is given in Table IV.

TABLE IV

MAKE-UP OF LABORATORY CELLS

CELL NO.	NO.OF POS.	NO.OF NEG.	RATIO $NiCl_2$ TO GRAPHITE	GRAPHITE TYPE	BINDER	DOPANTS	CAPACITY (THEORETICAL) AMP.HRS.
A-18	5	4	1:1	38	CMC	.08% S	0.775
A-22	3	2	1:1	38	CMC	.08% S .10% $MgCl_2$	2.40
A-23	2	3	3:1	UCET	Gelatine	.08% S .10% $MgCl_2$	1.2

1. Cell No. A-18

The $NiCl_2$ electrodes were compressed at 2 tons/in^2 during their preparation. The electrolyte used was PC-$AlCl_3 \cdot LiCl/Cl_2$.

Figure 53 is a plot of the first discharge. The rate was 10 ma, much lower than expected. This cell, based on half cell data should have delivered between 125 and 250 ma. A current density of 0.06 ma/cm^2 was actually drawn.

Even with the low capacity and current density, the cell was put on automatic cycling. The discharge was 10 ma to 1.0 volts cut-off. A rest period followed to allow a total of 60 minutes from start of discharge to charge. The charge was at constant potential of 4.8 volts for 2 hours. A constant potential charge was used because, at a constant current, a hump was found at 4.9 volts which seemed to represent a break-down of the electrolyte. If the cell was charged at 4.9 or 5 volts, the charge efficiency seemed to reduce to almost nothing.

The cell was cycled for 12 cycles when the discharge time started decreasing from 60 minutes. The 13th cycle was 58 minutes with a 2 minute rest. On the charge of the 13th cycle, an equipment malfunction caused the cell to fail on the 14th cycle and go into a 58 minute rest period. The 15th cycle was almost normal again, and after that, the cut-off voltage was reached in decreasing time intervals. By the 23rd cycle, the discharge was only 30 minutes, so the test was stopped.

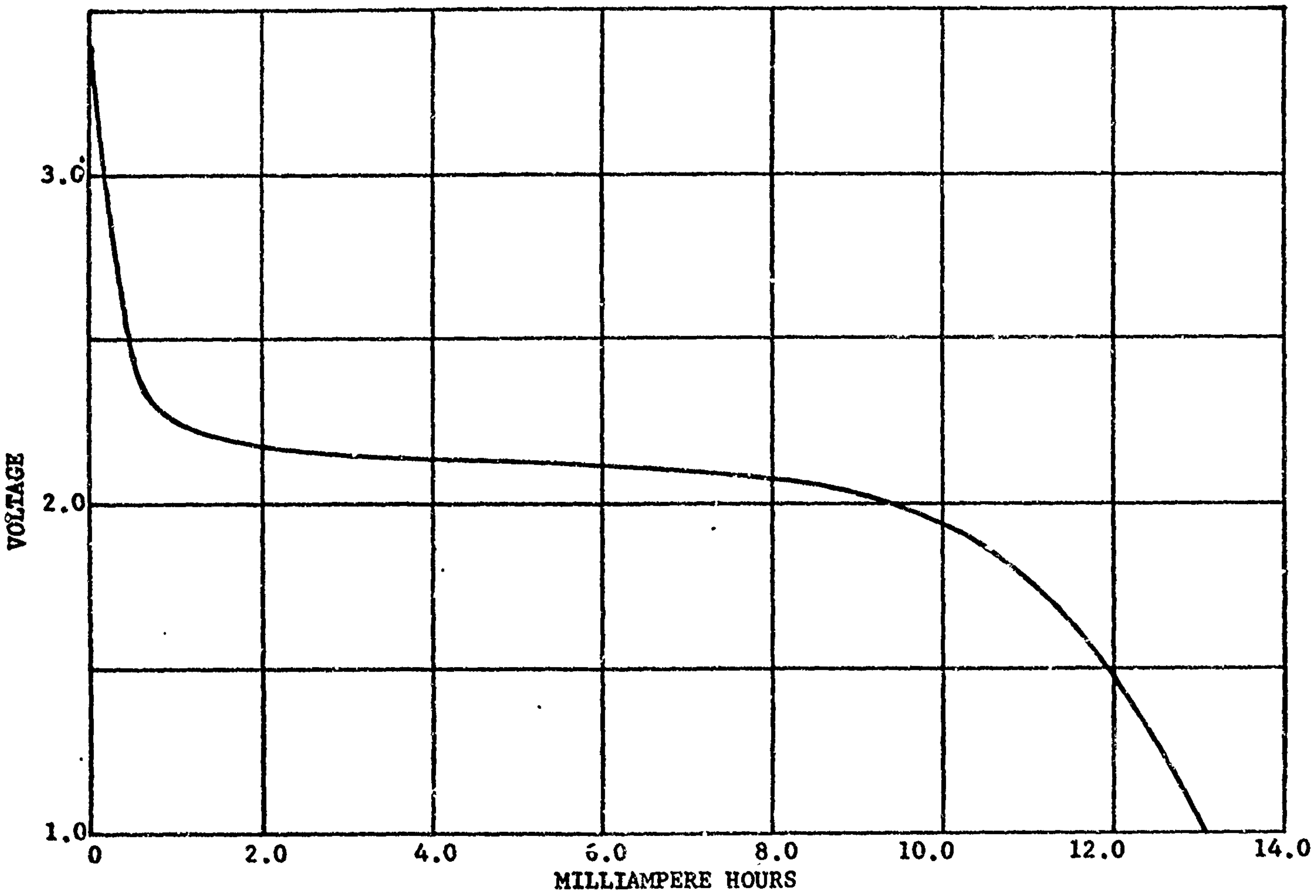


FIGURE 53 - DISCHARGE OF $NiCl_2$-Li LABORATORY CELL A-18

An examination of the cell showed no shedding or visible cause for the shortened discharge period. This phenomenon manifested itself in cell No. A-22.

2. Cell No. A-22

The positive electrodes were nickel chloride and graphite (Union Carbide Type 38). The $NiCl_2$ was doped with 0.08% sulfur and 0.1% $MgCl_2$. The binder was CMC and the mix was applied in two successive 1 gram/10 cm^2 applications to give 2.0 gm/10 cm^2 loading. The dried electrodes were compressed using 60 mil stops on the press to give a smooth electrode of that thickness. This is not much compression since the volume of $NiCl_2$-graphite used per plate has been found to give a plate approximately 60 mils thick when compressed at 500 psi. This procedure yields electrodes of more uniform thickness and loading than by just pasting on 2 grams and compressing the electrode.

The electrolyte was PC-$AlCl_3 \cdot LiCl/Cl_2$ which had been pre-electrolyzed with a pasted lithium anode and a Monel 400 screen cathode.

The electrode areas were 20 cm^2 each, giving 80 cm^2 surface to surface area for the positive to negative electrodes. The theoretical capacity was 2.4 AH based on the $NiCl_2$ present.

The cell was capable of delivering 250 ma for 15 minutes, a current density of 3 ma/cm^2, before reaching 1.90 volts. The cell was recharged at 4.85 volts constant potential. When left on open circuit over the week-end, the recorder indicated a self discharge to less than one volt.

As was later determined, the PC-$AlCl_3 \cdot LiCl/Cl_2$ electrolyte decomposes at a potential below the open circuit potential of the charged cell, discharging the lithium electrode with the evolved chlorine gas. This reduced the capacity of the negatives to a capacity below that of the positives so the cell became negative limiting on discharge but could still be overcharged without pressure build-up.

3. Cell No. A-23

This cell, the last made, has several changes. The positive electrodes were prepared using the UCET acetylene black following the procedure given in Section IV.C.7.b. The electrolyte was PC saturated with KPF_6, then with LiCl. The electrolyte was pre-electrolyzed with a lithium electrode and a Monel 400 screen.

The cell was discharged at 12 ma for 74 hours (equal to 0.888 AH or 74% of capacity). During that time the voltage made an almost linear plot from 2.85 volts to 1.10 volts. The cell was recharged at 6.0 volts constant potential for 21 hours.

A test was conducted after a 5 hour open circuit stand. The cell was discharged for 10 minutes at 10 ma. The current was raised to 20 ma for 5 minutes, keeping the milliampere minute discharge constant. The current was increased to 30 ma for 3.33 minutes, and so forth to 100 ma for one minute. The results are shown in Figure 54. The rate of change of voltage with a change in capacity $\Delta V/\Delta C$ (see insert in figure) is essentially a constant regardless of the rate from .125 ma/cm^2 to 1.25 ma/cm^2 current density. The large variations at the beginning can be extrapolated back to a high open circuit voltage of 2.95 volts.

The cell was left on open circuit for 24 hours. The OCV was 2.75 volts. The cell was then pulsed at 100 ma for 10 minutes as shown in Figure 55. A semi-log plot has been used to compress the time scale. The maximum OCV did not occur until almost 60 hours.

These tests strongly suggest an adsorbed layer) would take the amount of time to disperse that is found in these tests. The effect is cancelled when the cell is charged.

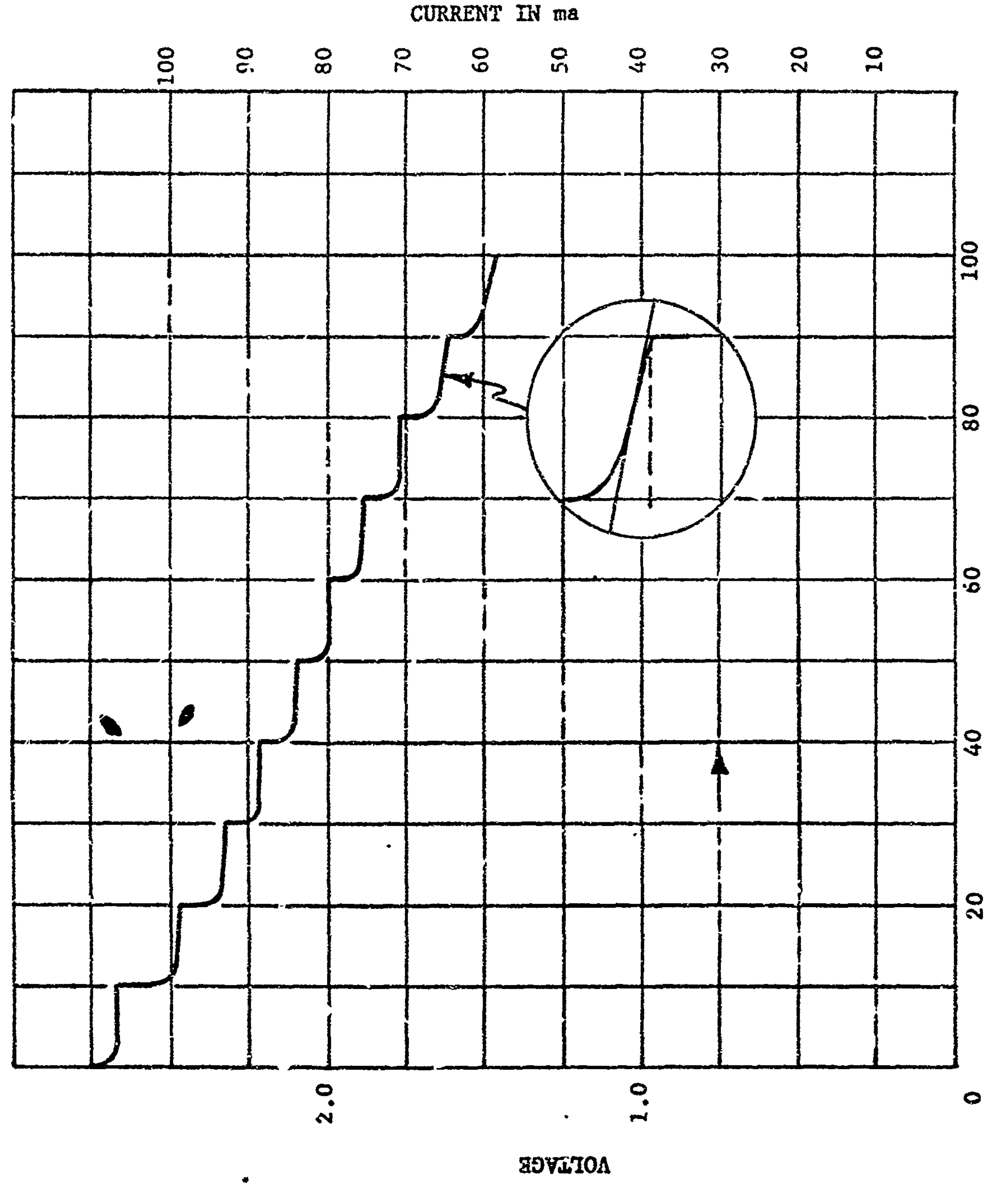


FIGURE 54 - POLARIZATION TEST - LABORATORY CELL A-23

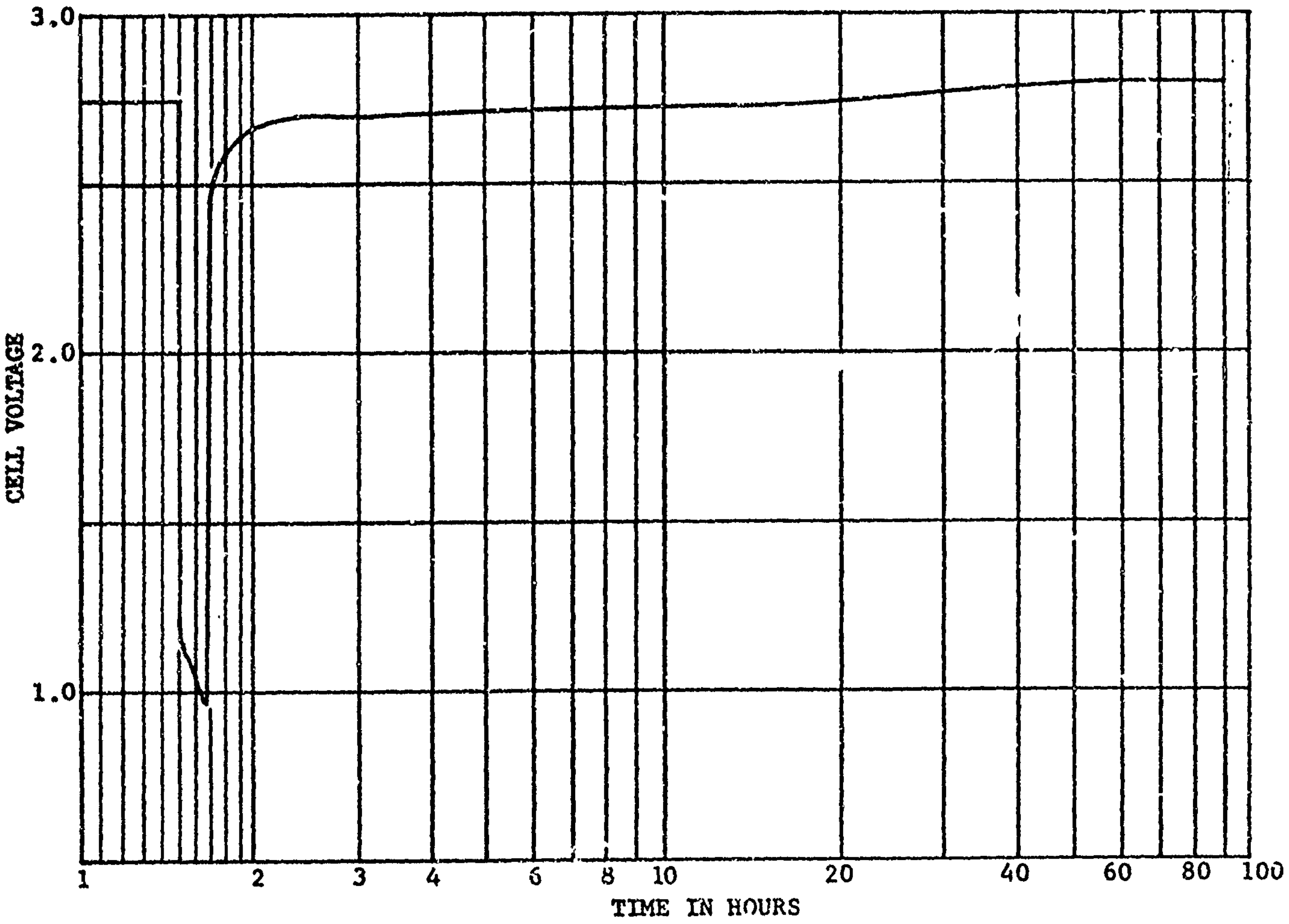


FIGURE 55 - PULSE-BOUNCE BACK TEST - LABORATORY CELL A-23

VIII. PROTOTYPE CELL ASSEMBLIES

A. PROBLEM

In accordance with Exhibit "A-1", dated 29 April 1964, paragraphs 2.3 and 2.5, two, 5 cell, 10 ampere hour batteries are to be prepared, one of the chloride system and the other a fluoride system.

B. METHOD OF APPROACH

Based on the data available from half cell studies and laboratory cell tests, a cell was designed to have a 10 ampere hour capacity. Because of the high polarization obtained with both nickel chloride and nickel fluoride electrodes, the discharge rates must be limited to very low values, in the region of C/100.

A cell, shown in Figure 56, was designed and built.

C. DESIGN DATA

Each electrode has an area of 57 cm^2. Based on the half cell data and laboratory cell tests, each positive electrode can be made 50 mils thick. Allowing for expansion of electrodes during cycling, a cell using 11 positive and 12 negative electrodes was designed. Polypropylene separator bags were used for the positive and negative electrodes.

The theoretical capacity of the cell, calculated from the weight of $NiCl_2$ present, is

$$\frac{0.414 \text{ AH}}{\text{gram of } NiCl_2} \times \frac{0.75 g \ NiCl_2}{10 \text{ cm}^2} \times \frac{57 \text{ cm}^2}{\text{plate}} \times \frac{11 \text{ plates}}{\text{cell}} = 19.5 \ \frac{\text{A.H.}}{\text{cell}}$$

This requires a utilization coefficient of 51% for the $NiCl_2$.

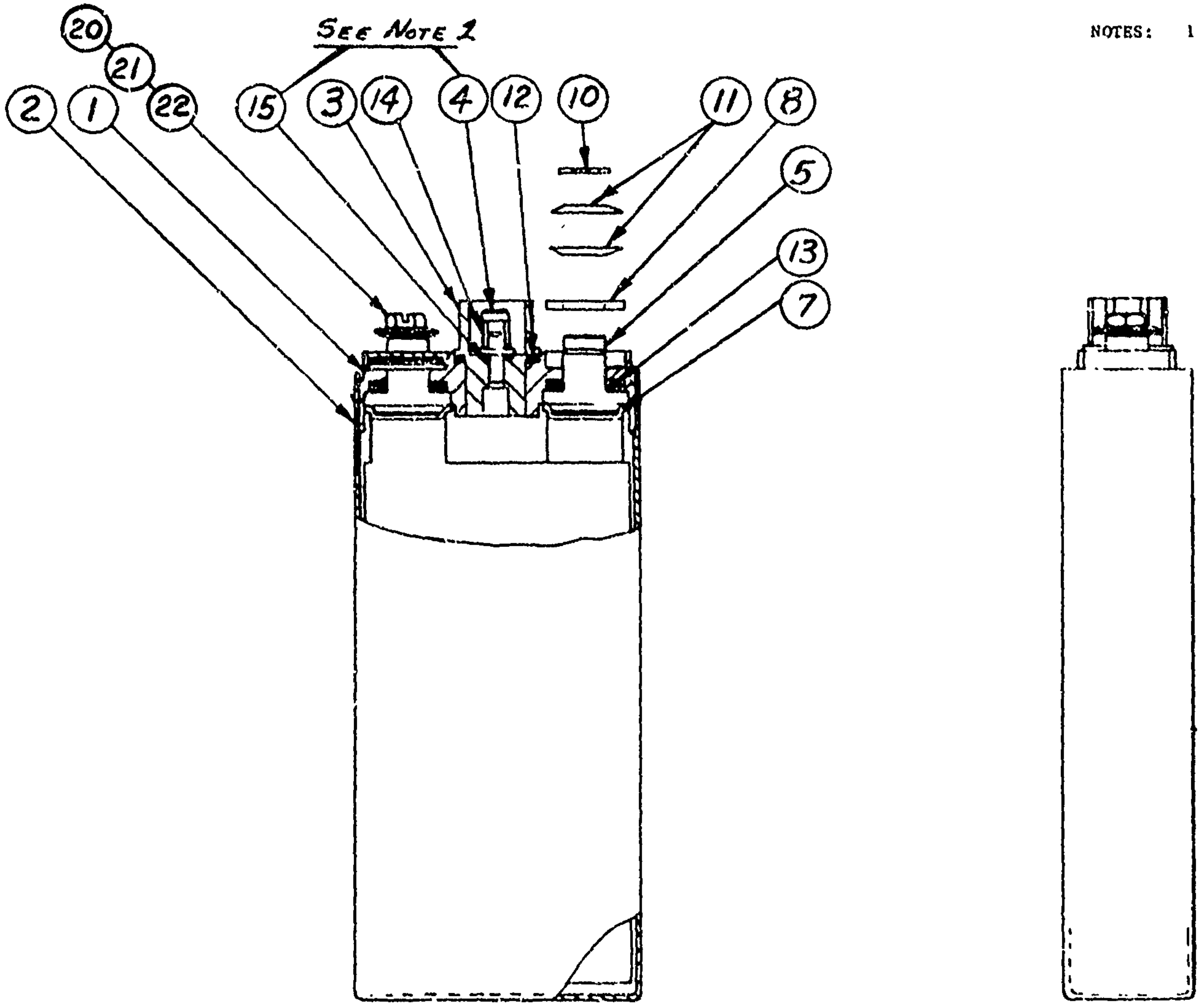
The fluoride system permits a slightly higher capacity for the same loading of the positive electrodes as the nickel chloride. Since half cell studies of the fluoride electrodes show that compression of the plates reduces polarization, 50 mil thick NiF_2 electrodes are desirable. In this case, 11 positive electrodes of 3:1 NiF_2 and graphite at 0.1 gm/cm^2 will have a theoretical capacity of

$$\frac{0.555 \text{ A.H.}}{\text{g. of } NiF_2} \times \frac{0.75 g \ NiF_2}{10 \text{ cm}^2} \times \frac{57 \text{ cm}^2}{\text{plate}} \times \frac{11 \text{ plates}}{\text{cell}} = 26.1 \ \frac{\text{AH}}{\text{cell}}$$

This requires a utilization coefficient of only 39% for a 10 ampere hour cell.

The electrolyte is propylene carbonate saturated with KPF_6. For the chloride system it is saturated with LiCl, and for the fluoride system with LiF. In both cases it is pre-electrolyzed with lithium.

To seal the polypropylene covers to the cases, a hot melt adhesive (#L7-1) manufactured by Commercial Paste, Inc. is used. The edges of the cover are precoated with the adhesive. When the electrodes are inserted in the case, the cover is sealed with an argon-electric welding torch (Bel-Arto Plastic Co., Inc.). The cells are checked for leaks



NOTES: 1 - AFTER TESTING:

A - REMOVE VENT VALVE, ITEM NO. 4, AND GASKET, ITEM NO. 15, FROM CELL AND PACKAGE IN A SEPARATE CONTAINER WITH EACH CELL TO FORM A COMPLETE CELL TEST ASSEMBLY.

B - REPLACE VENT VALVE AND GASKET IN CELL WITH VENT SCREW, ITEM NO. 23, AND VENT GASKET, ITEM NO. 9.

ITEM	DESCRIPTION
1	COVER
2	CONTAINER
3	VENT HOUSING
4	VENT VALVE
5	TERMINAL
6	SEALING SPEC
7	PLATE COMB
8	WASHER, FLAT
9	VENT GASKET
10	RETAINING RING
11	WASHER BELLEVILLE
12	"O" RING VENT
13	"O" RING TERMINAL
14	VENT BAND
15	GASKET VALVE
16	PLATE NEGATIVE
17	PLATE POSITIVE
18	SEPARATOR BAG
19	SEPARATOR
20	SCREW SLOTTED HEX HD.
21	WASHER, FLAT
22	WASHER BELLEVILLE
23	VENT SCREW

FIGURE 56 - NILI-10 CELL ASSEMBLY - NICKEL HALIDE-LITHIUM

with a GE Type H-2 halogen leak detector and freon gas. When they are free from leaks, the electrolyte is added through the vent hole on top and sealed.

After testing, the vent valve is removed and a seal put in. The top is then potted with a hot melt adhesive to insure a seal.

Figure 57 is a photograph of a finished cell.

FIGURE 57 - NiLi-10 PROTOTYPE CELL

IX. SUMMARY

The problem of corrosion of the tabs in half cells could well have manifested itself in attack on the terminals in laboratory or prototype cells. The use of protective coatings alone would have been insufficient. It became imperative that a resistant alloy be found. It is fortunate that Monel 400 is one such alloy, since it is readily available easily machined, and easily worked.

In retrospect, the problem of corrosion of the tabs of the sintered nickel plaques is indicative of the type of reaction taking place with the sinter itself. The purpose of the sintered plaque is to provide a conductive matrix, but if this matrix becomes oxidized, it no longer functions as such. A sintered plaque has advantages for space use. It is much more resistant to shock and vibration then a pasted electrode. The use of Monel 400 alloy for the grids and tabs leads one to believe that if a sintered plaque of Monel 400 alloy were used, it would show an improvement over the nickel.

Of the three types of positive electrodes (impregnated sinter, thin film, and pasted), the pasted nickel halide electrode has shown the greatest promise as a means of achieving a high energy to density ratio. By using UCET acetylene black with the chloride electrodes, a 3:1 ratio of active material to conductive diluent is available. This is the highest ratio yet obtained.

There is still the great problem of polarization preventing the acceptance of the lithium-nickel halide system on the basis of higher current density. The watt-hour per pound ratio can, no doubt, be met, particularly with higher capacity batteries, but the discharge rates are limited to values from C/40 to C/100.

Both the chloride and the fluoride batteries are capable of being cycled from 10 to 20 times. Both exhibit good charge retention under the limited test period studies (72 hours). The change in capacity after a 72 hour stand was within the variability between cycles. If there is an application for a low rate (C/100) rechargeable battery having a 100 watt-hour per pound ratio, either system could be used. There still remains the necessity of a development program for such a battery to find the optimum design. The work that must be done to change this system to a high rate battery now involves a basic study of the nickel halide electrode. The type of polarization, such as concentration or chemical, and the interaction of the cathode and electrolyte are two parameters which must be studied. The kinetics of the reactions a the influence of the conductive matrix (as was revealed when carbonyl nickel was used in place of graphite) will give an investigator an insight to the problem of polarization so that a remedy can be found.

The developments from this contract are summarized below.

A satisfactory lithium electrode has resulted from the previous contracts, and until such time as the positive electrodes obtain the degree of acceptability of the lithium electrode, no further changes are contemplated. The substrate is an expanded metal screen of Monel 400, although for the lithium electrode, pure nickel can be used. This screen is .005 inch thick with the long dimension of the expanded pattern as .046 inch. A paste of 90 mole percent lithium metal powder (<100 mesh) and 10 mole percent of carbonyl nickel powder are blended using mineral oil as a vehicle. The carbonyl nickel is added as a conductive material, not for the lithium, but for the lithium halide which is not a conductor, and causes a high charge polarization. A binder of carboxy methyl cellulose dissolved in dimethyl sulfoxide (DMSO) is added to result in 2% as dry weight of the lithium-nickel mixture.

The paste is applied to the screen in a glove box under a dry argon atmosphere using a spatula. The electrodes are then placed in polyethylene bags and sealed. They are removed from the glove box and pressed at 2 tons per square inch. They are returned to the glove box and removed from the bags. They are then transferred to a vacuum oven and the DMSO removed by heating to 120°C at 29" of mercury vacuum. The electrodes are returned to the glove box and the mineral oil removed by washing with hexane.

Three separator materials have been found to be acceptable. These are untreated cotton percale (Loenstein & Co.), non-woven polypropylene, and a Teflon-Fiberglas filter paper. Of the three, the non-woven polypropylene (Pellon T-12-892-2) is the most desirable. The drawbacks of this material lie with the manufacturers, who have not been able to supply uniform lots. This is a problem which could easily be remedied if the demand were sufficient for the manufacturers to exert some extra effort. Polypropylene can be heat sealed into envelopes and slipped over the negative electrodes. The cotton separator (a fine grade of broadcloth) has excellent electrolyte retention.

Cell cases and covers are made from molded polypropylene. Polypropylene can be welded, but recent developments in adhesives and epoxies have given us commercial materials to seal polypropylene or polyethylene cells. Polyethylene is difficult to mold to close tolerances, so polypropylene is the better material.

Aluminum can also be used providing there is always some unreacted lithium present to give a galvanic protection against corrosion from the NiX_2 and electrolyte.

Hardware, such as terminals, combs and seals, can be made from Monel 400. In the case of the negative electrode terminals and combs, pure nickel can be used, but there is no advantage in using two different metals since Monel 400 is a good working metal, easily welded and machined.

The nickel chloride and nickel fluoride electrodes are made similarly. For both, the substrate is the same expanded metal screen used for the lithium, except that only Monel 400 has been found to be satisfactory. The binder is U.S.P. gelatin (B & A) dissolved in water, (100 g/L) and added in an amount that results in about 2% of the final dry weight.

Graphite is used as the conductive diluent in the nickel halide electrode. Nickel halide salts are not soluble in the electrolyte and hence, are not ionic conductors. Since they are semiconductors at best in the dry state, an inert conductor must be admixed with the nickel halide. Carbonyl nickel was found to passivate (the term passivate is used here for the lack of a better one, or an understanding of the true mechanism) the electrode after a few minutes of discharge or after a single charge. Two grades of graphite are used: Type 38 and UCET acetylene black, both from Union Carbide Corporation. The UCET acetylene black has better contact properties, but is difficult to dry without checking. It can be used with the $NiCl_2$ electrodes, but for the NiF_2 electrodes, a blend of 90% Type 38 and 10% UCET is used.

At this point, the two systems diverge. The $NiCl_2$ electrodes are prepared by adding a saturated (330 g/L) $NiCl_2$ methanol solution to UCET graphite in a 3:1 ratio. The gelatine binder is added and the mix diluted with water to give a smooth consistency about like whipped cream. NiF_2 powder is dried with thionyl chloride to rid it of water which is usually found in NiF_2 in varying amounts. A mix of the 9:1 Type 38-UCET graphite is used. The NiF_2 and graphite are blended 1:1 and enough methanol added to wet the mix. The gelatine binder is added to give 2% of the total dry weight. Sufficient water is added to again give a consistency of whipped cream.

At this point the two processes are again alike. The paste is applied to the screen with a spatula and then the plates are passed between two blades .050 inch apart. The plates are dried in warm moist (60% RH) air until dry to the touch. They are compresed at 2 tons per in.^{2}. They are then put through the same coating cycle. This is continued until 0.1 g/cm^2 of the dry mix is on the plates. The thickness should be between .045 and .050 inches. The plates are then vacuum dried at -29 inches of Hg, slowly bringing the temperature up from room temperature to 100°C over a two hour period. The plates are now stored in a desiccator until used.

The electrolyte which has largely been used to date is propylene carbonate (P.C.) with $LiAlCl_4/Cl_2$ as the solute. This electrolyte has a good conductivity of 14.3 millimhos-cm^{-1} but due to some reaction with the lithium in the presence of the $NiCl_2$-Li couple, it cannot be used. There appears to be a decomposition potential below the OCV of the $NiCl_2$-Li couple.

Two alternate electrolytes have been found. PC saturated with KPF_6 which has been dried with thionyl chloride has a conductivity of 23.0 millimhos-cm^{-1} and DMSO with 190 g/L of KPF_6 with a conductivity of 25.5 millimhos-cm^{-1}. DMSO dissolves $NiCl_2$ but not NiF_2 so it is used for the fluoride system. When PC with KPF_6 is used for the chloride system, the electrolyte is first saturated with anhydrous LiCl and then pre-electrolyzed using a pair of partially discharged Li/LiCl electrodes to establish an equilibrium between the chloride and fluoride ions.

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Air Force Aero Propulsion Laboratory Wright-Patterson AFB, Ohio 45433

13. ABSTRACT

Two methods of protecting the tabs of the $NiCl_2$ electrode from corrosion by chlorine have been developed. The first is a protective coating and the second is the use of Monel 400 alloy instead of nickel. These methods have also shown to be satisfactory for the nickel fluoride system. The Monel 400 alloy method is the most favorable.

Polarization tests with thin film electroformed nickel chloride showed that concentration polarization was only part of the problem. A major improvement was noted when the sintered nickel plaque was absent.

Tests were conducted on pasted nickel chloride and nickel fluoride electrodes using graphite as a conductive diluent. Doping with sulphur on magnesium halide salts was tried.

The use of PC-$AlCl_3$ $LiCl/Cl_2$ has not been satisfactory due to some reaction taking place with the lithium electrode. Two electrolytes using KPF_6 were selected. Propylene carbonate is used for the nickel chloride system and dimethyl sulfoxide for the nickel fluoride system.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Energy Storage Primary and Secondary Batteries Lithium Anodes Nickel-Chloride Cathodes Nickel-Fluoride Cathodes Non-Aqueous Electrolytes						

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