Fuel cell studies in acid liquid ammonia solutions
by David Alan Strah

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University

Abstract:
A fuel cell has been developed which will operate at temperatures down to -20 °C using a liquid ammonia solution (NH3/NHNO3) as the electrolyte. The cell used a mixture of hydrogen and ammonia gases as the fuel and iodine (dissolved in the electrolyte) as the oxidizer, The anode (hydrogen electrode)was a commercial porous gas diffusion electrode (American Cyanamid Company) which consisted of platinum black electrocatalyst(9 mg/cm2) bonded to a tantalum screen. The cathode (iodine electrode), which consisted of platinized porous stainless steel, was developed in these studies and was of the porous flow-through type. The open circuit voltage of the cell was 1.15 volts.

A number of preliminary studies on potential fuels, oxidizers, and. electrocatalysts were made in liquid ammonia solutions using the electrochemical technique of cyclic voltammetry. Iodine reduction at various electrode surfaces was also studied using this technique. Polarization characteristics of each electrode used in the final cell design were obtained by fixing the cell current using a D.C. power supply and recording the resulting electrode voltage with respect to a Pb/Pb+2 reference electrode.

Hydrogen electrode polarization was high at extreme NH3/H2 ratios (1:5 and 5:1) and was a minimum at NH3/H2 ratios approaching 1:1. A decrease in cell operating temperature led to increased hydrogen electrode polarization. Typical polarization of the hydrogen electrode at an operating temperature of -18 °C and NH3/H2 ratio of 1:1 was 0.2 volts at a current density of 80 ma/cm2.

Polarization at the stainless steel cathode was studied at three different platinum loadings (0.5, 4.0, and 20 mg/cm2) using three different electrode pore sizes (5, 20, and 65 microns). Polarization at the cathode decreased with an increase in platinum loading and with a decrease in electrode pore size. Electrolyte flow rate (1.0-9.5 cc/min.) and iodine concentration (1.0 to 3.0 g/100 cc solution) were found to affect iodine electrode polarization only if their values were such that a shortage of iodine existed at the cathode for maintaining the current density being drawn from the cell.

The fuel cell developed in these studies was operated continuously at 30 ma/cm2 and 0.75 volts for 72 hours with no apparent electrode deterioration. Operating conditions were as follows: NH3/H2 ratio, 1:1; ambient temperature, -15 to -18 °C; iodine concentration, approximately 3.0 g/100 cc solution; electrolyte flow rate, 1.0 to 2.0 cc/min.

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Bozeman, Montana

December, 1969

ACKNOWLEDGMENT

The author wishes to thank the staff of the Chemical Engineering Department of Montana State University for their suggestions and criticisms which led to the completion of this project. A special thanks goes to Dr. Michael J. Schaer, who directed this research, for his encouragement and guidance throughout this investigation. In addition, thanks are also due Mr. Silas Huso and Mr. James Tillery for their assistance in equipment fabrication and maintenance.

The author is also indebted to the National Science Foundation and to the Chemical Engineering Department of Montana State University for their financial support and the opportunity to conduct this investigation.

Finally, the author gratefully acknowledges the help and encouragement of his family and wife, Ann Marie.

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ABSTRACT

A fuel cell has been developed which will operate at temperatures down to -20 °C using a liquid ammonia solution (NH_3/NH_4NO_3) as the electrolyte. The cell used a mixture of hydrogen and ammonia gases as the fuel and iodine (dissolved in the electrolyte) as the oxidizer. The anode (hydrogen electrode)was a commercial porous gas diffusion electrode (American Cyanamid Company) which consisted of platinum black electrocatalyst(9 mg/cm^2) bonded to a tantalum screen. The cathode (iodine electrode), which consisted of platinized porous stainless steel, was developed in these studies and was of the porous flow-through type. The open circuit voltage of the cell was 1.15 volts.

A number of preliminary studies on potential fuels, oxidizers, and electrocatalysts were made in liquid ammonia solutions using the electrochemical technique of cyclic voltammetry. Iodine reduction at various electrode surfaces was also studied using this technique. Polarization characteristics of each electrode used in the final cell design were obtained by fixing the cell current using a D.C. power supply and recording the resulting electrode voltage with respect to a Pb/Pb^{+2} reference electrode.

Hydrogen electrode polarization was high at extreme NH_3/H_2 ratios (1:5 and 5:1) and was a minimum at NH_3/H_2 ratios approaching 1:1. A decrease in cell operating temperature led to increased hydrogen electrode polarization. Typical polarization of the hydrogen electrode at an operating temperature of -18 °C and NH_3/H_2 ratio of 1:1 was 0.2 volts at a current density of 80 ma/cm^2.

Polarization at the stainless steel cathode was studied at three different platinum loadings (0.5, 4.0, and 20 mg/cm^2) using three different electrode pore sizes (5, 20, and 65 microns). Polarization at the cathode decreased with an increase in platinum loading and with a decrease in electrode pore size. Electrolyte flow rate (1.0-9.5 cc/min.) and iodine concentration (1.0 to 3.0 g/100 cc solution) were found to affect iodine electrode polarization only if their values were such that a shortage of iodine existed at the cathode for maintaining the current density being drawn from the cell.

The fuel cell developed in these studies was operated continuously at 30 ma/cm^2 and 0.75 volts for 72 hours with no apparent electrode deterioration. Operating conditions were as follows: NH_3/H_2 ratio, 1:1; ambient temperature, -15 to -18 °C; iodine concentration, approximately 3.0 g/100 cc solution; electrolyte flow rate, 1.0 to 2.0 cc/min.

I. INTRODUCTION

Although the fuel cell principle has been known for over a hundred years, it has only been in recent years that the fuel cell has become the object of wide and varied research. The advent of the space age and the need for a light, compact power source for space applications probably did more to rekindle interest in fuel cells than anything else. Since 1959, which was about the time of the beginning of the space age, hundreds of laboratories, government, industrial, and academic, have entered the area of fuel cell research (1,2,3,4).

The major attraction of the fuel cell is its potentially high efficiency of energy conversion. In a fuel cell the chemical energy of a fuel is converted directly into electrical energy without intermediate conversion into heat. Consequently, the thermodynamic Carnot limitation does not apply, and thermal efficiencies approaching 90% are theoretically possible (5).

Of course, fuel cells have other advantages in addition to their high efficiency of energy conversion, including reliability and silence of operation, ease of maintenance, cleanliness, and continuous, indefinite operation without recharging. On the other hand, fuel cells have their disadvantages, chief of which is their high cost due to expensive cell components. Thus, the foregoing advantages and disadvantages of fuel cells determine their application. If economics is the prime consideration, fuel cells are generally not competitive with conventional power sources and are not used.

A. Principle of Operation

The principle of operation of a fuel cell is, in theory, very simple. A fuel cell is nothing more than an electrochemical device which consists of two electrodes (anode and cathode), an electrolyte (which separates the electrodes), fuel and oxidizer, and suitable controls. Figure 1 shows a schematic diagram of a typical fuel cell and can be used to explain the principle of operation. A fuel (gas, liquid, or solid) is fed to the anode where it is electrochemically oxidized to yield electrons and an ionized species. The electrons flow from the anode through an external circuit as D. C. electric current, through some electrical load (electric motor, light bulb, etc.), and back to the cathode. At the cathode these electrons react electrochemically with the oxidizer to again produce an ionized species. The circuit is completed by transfer of one of the ionized species through the highly conductive electrolyte. The net effect is the production of electricity in the form of electrons flowing through the external circuit.

B. Measurement of Fuel Cell Performance

The ideal fuel cell delivers high current with a minimum of internal voltage loss. But, in any fuel cell, as current being drawn from the cell is increased, the cell voltage invariably decreases due to fuel cell polarization. In the development of any fuel cell one of the main objectives is to minimize this polarization effect.

There are three major contributions to fuel cell polarization:

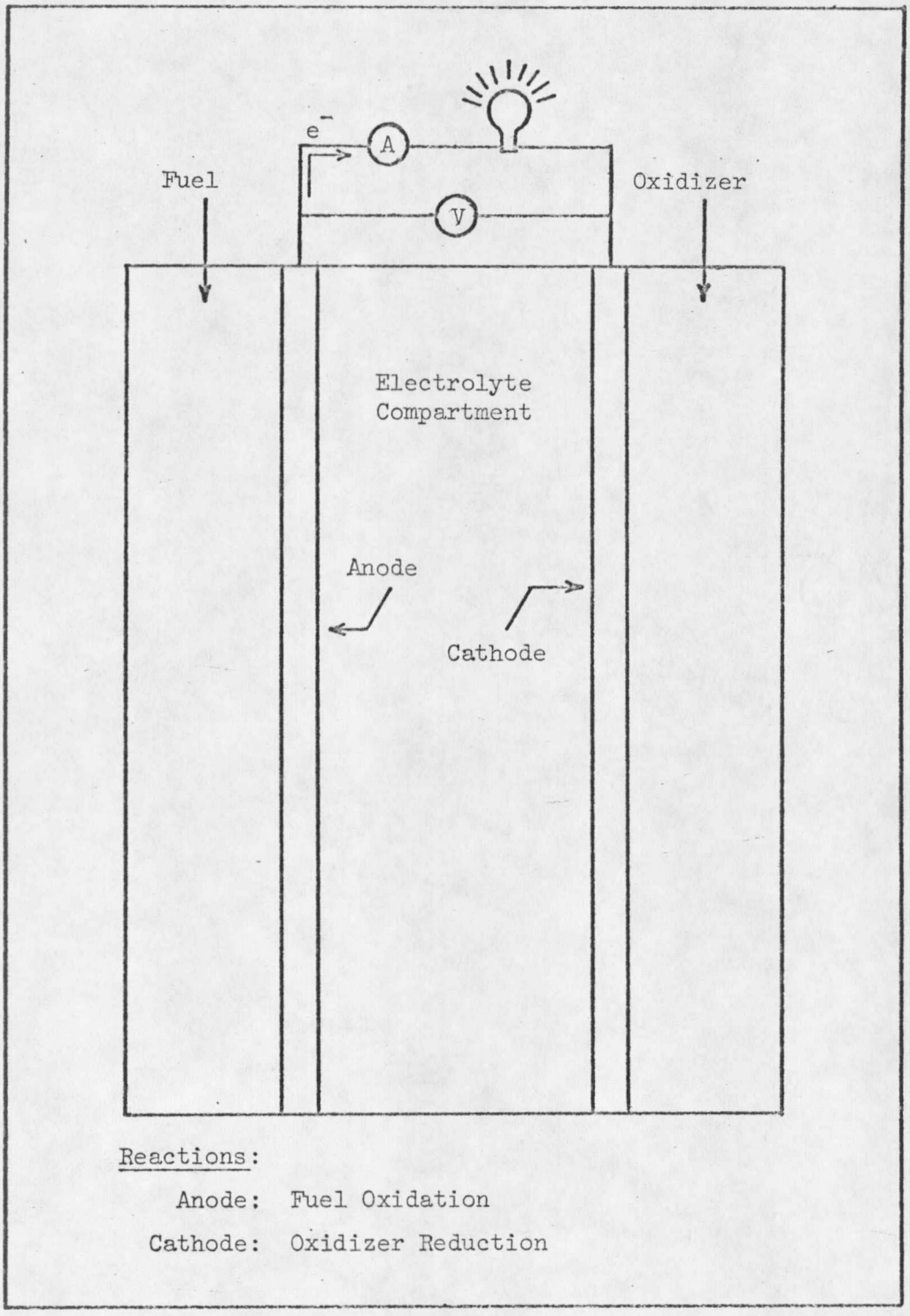


Figure 1. Schematic diagram of a typical fuel cell.

1. Ohmic polarization is nothing more than a cell voltage decrease due to the ohmic resistance of the electrodes and electrolyte. This effect is minimized by having high electrolyte conductivity and as thin a space between electrodes as possible.

2. Concentration polarization is caused by slow supply of reactants to the electrode surface and slow diffusion away of reaction products, i.e., a decrease in reactant concentration at the electrode surface.

3. Activation polarization is caused by slow kinetics of the electrochemical reaction at the electrodes. It is generally minimized by increasing operating temperature and by improving the catalytic powers of the electrodes.

A theoretical discussion of polarization has been presented by a number of authors (3,4,5,6,7).

Of course, polarization data is not the only performance parameter of interest to fuel cell researchers. Life studies, power densities, and efficiency of operation are also important performance characteristics which are frequently studied (5). In initial studies such as the present one, however, performance is most frequently measured by obtaining the polarization characteristics of the cell.

C. Liquid Ammonia Fuel Cells

At the present time there are hundreds of fuel cell investigations being conducted throughout the world, both by private industry and

governmental agencies. These investigations encompass a wide variety of fuel cell types which employ a number of different reactants, electrocatalysts, and electrolytes at widely divergent operating conditions.

Notably absent from this wide realm of fuel cell research are fuel cells which can be operated at cold temperatures (<20 °C). An extensive literature survey has shown that most fuel cell investigations are being carried out at or above room temperature. For example, Yeager (8) presents the stage of development and future outlook of a variety of fuel cell systems presently under study as well as the electrodes, electrolyte, and operating temperature of each of these systems. All of the fuel cells which Yeager discusses normally operate at 20 °C or above and employ aqueous, fused salt, or solid electrolytes. It appears that the temperature region below 20°C has been virtually neglected by researchers as far as fuel cell studies are concerned. With this fact in mind, a cold temperature fuel cell research program was undertaken.

Liquid ammonia was chosen as the ionizing solvent for cold temperature fuel cell studies for a number of reasons:

1. Although the freezing point of liquid ammonia solutions will vary according to the concentration of the conducting salt present, the freezing point will always be low enough so as to provide a wide temperature range for cold temperature studies. The freezing point of pure liquid ammonia is -77.7 °C, and most salt solutions will freeze at

or below this temperature.

2. Liquid ammonia is an excellent solvent which exhibits high electrolytic conductivity even at very cold temperatures (9,10).

3. Liquid ammonia approaches water very closely in its physical properties (10,11). It was felt that results from aqueous fuel cells might be drawn by analogy to a liquid ammonia system.

Thermodynamically, liquid ammonia has only a .04 volt potential difference between anodic and cathodic solvent decomposition (hydrogen and nitrogen evolution). The solvent decomposition reactions and their oxidation potentials in volts at 25 °C are given below (9).

Acid Solutions ($1M\ NH_4^+$)

$$\frac{1}{2} H_2 + NH_3 = NH_4^+ + e^- \qquad E^\circ = 0.0\ v$$

$$4NH_3 = \frac{1}{2} N_2 + 3NH_4^+ + 3e^- \qquad E^\circ = -0.04\ v$$

Basic Solutions ($1M\ NH_2^-$)

$$\frac{1}{2} H_2 + NH_2^- = NH_3 + e^- \qquad E^\circ = 1.59\ v$$

$$3NH_2^- = \frac{1}{2} N_2 + 2NH_3 + 3e^- \qquad E^\circ = 1.55\ v$$

The electrokinetics of these decomposition reactions are slow on most electrode surfaces and both reactions usually exhibit overvoltages of about 1 volt. Thus, in acid solutions the practical range of potentials for dissolved species is from 1.0 to -1.0 volts, while in basic solutions the practical range is from 2.6 to 0.6 volts. Of course, these limits are extremely rough, and exceptions are to be found, especially among

nitrogen compounds which react very slowly (12). In general, then, solutions of liquid ammonia exhibit fairly wide potential ranges for carrying out electrochemical studies between anodic and cathodic solvent decomposition.

The chemistry of liquid ammonia has been well studied and most of its physical properties have been determined. In addition, electrolyte solutions of liquid ammonia have been subjected to extensive research (9). Nevertheless, very little research has been done toward developing fuel cells which use liquid ammonia as the electrolyte.

Laitinen and his co-workers (13,14,15) used liquid ammonia solutions for the polarographic study of the reduction of a number of metal ions. However, very little of their work has been directly applied to fuel cell development.

A great deal of research has been done regarding the properties and applications of metal-ammonia solutions (16), but little of this research has been applied to fuel cells. Only Bennett (17) has done research in this area. He made a study of lithium-ammonia solutions as preliminary research toward development of a fuel cell which would use liquid ammonia as the electrolyte. His research showed that very high current densities (1000 ma/cm^2) could be obtained with low polarization using lithium as the fuel in liquid ammonia solutions. The development of a low temperature liquid ammonia electrolyte fuel cell in the present research program would, hopefully, contribute to the further development

of the results which Bennett obtained.

Electrochemical studies involving liquid ammonia have been made in abundance at the Naval Ordnance Laboratory at Corona, California. Most of the research conducted at Corona has been directed toward development of ammonia batteries (18), although some liquid ammonia fuel cell work has been done. For example, Wilcox and Harris (19) made a study of the reduction of m-dinitrobenzene in a liquid ammonia electrolyte fuel cell which they developed. Their results appeared to be quite promising, although they used no anode feed (fuel) in the evaluation of their cell and its associated controls.

Miles and Kellett (20) reported on the electrochemical oxidation of a variety of fuels on a number of electrode surfaces in a liquid ammonia electrolyte. Overvoltage measurements for the hydrogen and nitrogen evolution reactions were made on these electrode surfaces in order to evaluate them as potential electrocatalysts for hydrogen oxidation. Their research represents one of the biggest steps that have been taken toward development of a liquid ammonia fuel cell.

II. RESEARCH OBJECTIVES

As seen from the foregoing discussion, research data on liquid ammonia fuel cells are limited. In light of this fact a research program was undertaken with the following general research objectives.

1. Conduct preliminary electrochemical studies on a number of possible electrocatalysts and fuels in a liquid ammonia electrolyte.

2. Develop and make operable a cold temperature liquid ammonia fuel cell based on the results of these preliminary studies.

3. Optimize, at least briefly, the performance of this fuel cell with respect to its operating variables and study the effect of these variables on cell polarization characteristics.

III. EXPERIMENTAL

A. Voltammetric Studies

In the development of this cold temperature liquid ammonia fuel cell a number of preliminary half cell studies were made using liquid ammonia solutions. These half cell studies required the use of a number of chemicals and electrode materials. The ammonia used in these studies was Matheson anhydrous, of 99.95% stated minimum purity. Inorganic salts used for conductivity purposes were reagent grade chemicals, while the various materials studied as possible fuels were all of industrial or reagent grade. Metals used as electrodes in electrocatalyst studies were of 99.9% minimum purity and were used in wire form.

For these preliminary studies electrochemical measurements were made in a three compartment glass cell in which the three compartments were separated by glass frits (Figure 20). All half cell voltammetric studies were made using a platinum disc counter electrode and a Pb/Pb^{+2} reference electrode. In studying various potential fuels the working electrode was always a platinum or platinum black wire which was sealed into the end of a glass tube with epoxy resin. All metals used as working electrodes in electrocatalyst studies were also sealed into glass with epoxy.

Single sweep and cyclic voltammetric curves were obtained using an all-transistor chronopotentiostat (21) as the scanning instrument, while current-potential curves were recorded on an X-Y recorder (Hewlett-Packard, model 7030AM).

The technique of single sweep and cyclic voltammetry has found extensive use only in recent years. Briefly, this technique involves the linear change of potential across a working (test) electrode and a non-polarized reference electrode. As the potential is changed, a point will be reached at which an electrochemical reaction will occur. This electrochemical reaction is observed as current flowing through the working and counter electrodes and is recorded as a function of the potential applied using an X-Y recorder. Using this technique diffusion is the sole mode of mass transfer and the working electrode potential is scanned linearly at a rapid rate (several mv/sec. to several hundred mv/sec.). In these particular studies the scan rate was usually 125 mv/sec. A more extensive discussion of this electroanalytical technique, including mathematical analysis, is given by Kublic (22), Adams et al. (23), and Nicholson and Shain (24).

B. Polarization Studies

Chemicals used in polarization studies (ammonia, inorganic salts, etc.) were, as in half cell voltammetric studies, of reagent grade and high purity.

A flow diagram of the system used in obtaining fuel cell polarization data is shown in Figure 2. The principle of operation of this system is as follows. Constant nitrogen pressure was used to force the electrolyte from reservoir A through the fuel cell to reservoir B. Flow rate of electrolyte was regulated with a precision needle valve at

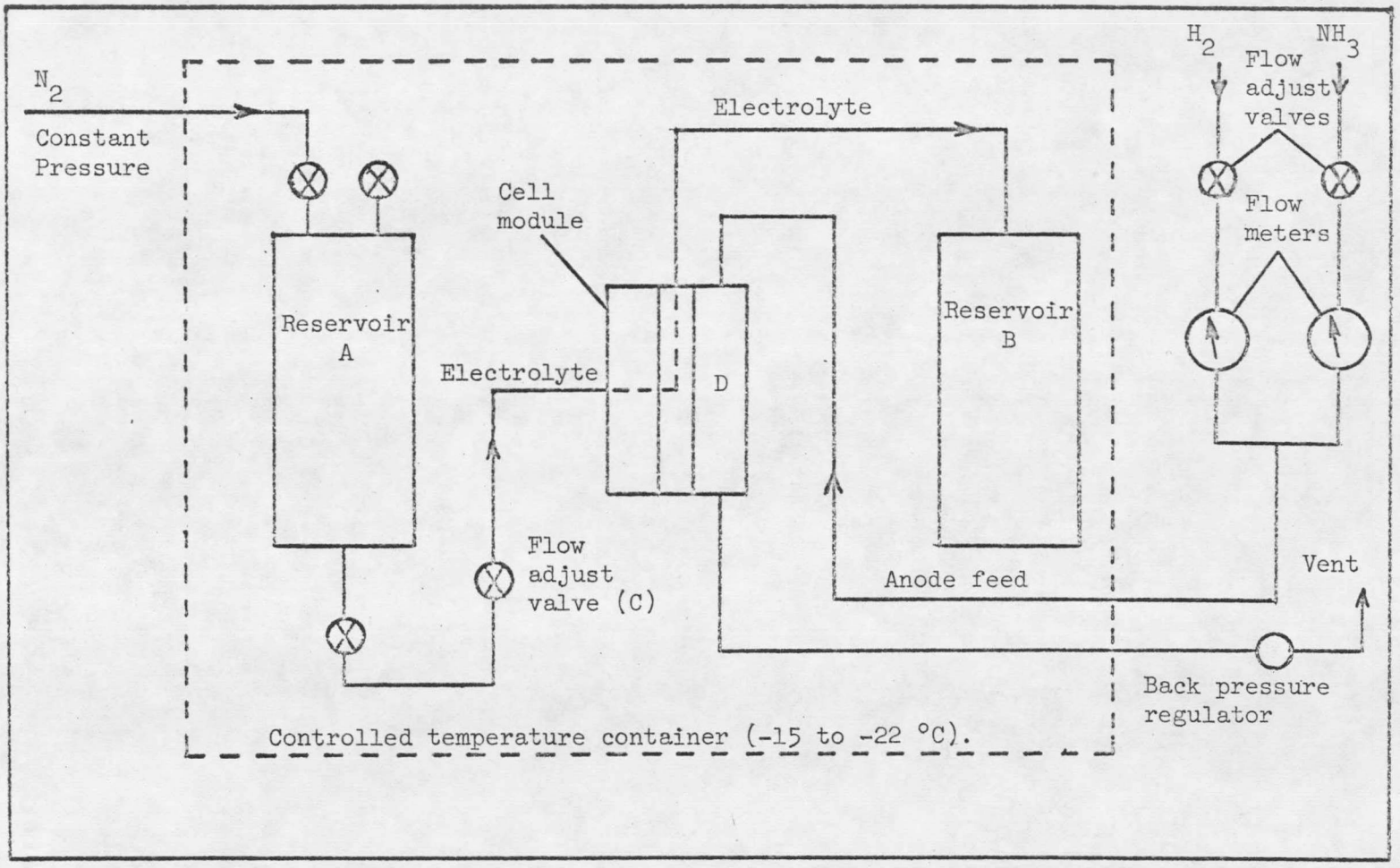


Figure 2. Flow diagram of fuel cell system.

C and was measured periodically at the cell outlet using a stopwatch and graduated cylinder. Fuel to the cell (a mixture of hydrogen and ammonia gases) flowed into the gas compartment at D and excess was vented to the atmosphere. A back pressure of approximately six inches of water was maintained on the gas side electrode (anode). The electrolyte (containing the dissolved oxidizer, iodine) flowed either adjacent to or through the cathode. In most cases a flow-through type of cathode was employed. Electrolyte was manually transferred from reservoir B to reservoir A when recirculation was necessary. The cell and reservoirs were maintained at cold temperatures (-15 to -22 °C) by keeping them in a five cubic foot chest freezer.

Figure 21 shows a cross-sectional sketch of the fuel cell itself. The cell module was constructed of polypropylene which proved to be resistant to ammonia solutions. Gasketing material used was 1/16-inch thick silicone rubber, rated to remain resilient and flexible down to -60 °C. In all cases the anode used was a commercial porous electrode material manufactured by American Cyanamid Company. Physical properties of this electrode material as stated by the manufacturer are as follows:

Catalytic material	Platinum black: 8.4 g ± 1 g/ft^2
Screen material	Tantalum: 50 mesh, 3 mil wire
Electrode thickness	6-7 mils
Porosity	Very open
Electrode weight	40 g/ft^2

The reference electrode used in polarization studies was constructed following a procedure recommended by Panzer and McWilliams(25).

It consisted of a piece of lead (Pb) metal enclosed in a thin glass tube which contained a saturated solution of ammonium nitrate in ammonia. The Pb/Pb^{+2} reference was separated from the liquid ammonia electrolyte by means of thin microcracks in the end of the glass tube. The microcracks were formed by sealing a short length of soft glass capillary tubing into the end of larger diameter pyrex tubing and allowing to cool. Best results were attained when the impedence across the microcrack fell between 5000 and 20000 ohms. Electrochemically these Pb/Pb^{+2} electrodes were relatively stable and reproducible.

A number of different electrode materials were used as the cathode in these polypropylene cell studies. The materials used and a brief description of each is given below.

Platinum foil -- 99.9% purity, 20 mils thick, electrode area of 11.4 sq. cm.

Porous platinum black -- Commercial gas diffusion electrode, same as that used at anode (American Cyanamid), electrode area of 1.27 sq. cm.

Platinum-rhodium screen -- 90% platinum, 10% rhodium, 80 mesh, electrode area of 1.27 sq. cm.

Porous stainless steel -- 20 mils thick, pore size unknown, electrode area of 1.27 sq. cm. (Mallory Metallurgical Company).

Porous stainless steel -- 1/16-inch thick, pore sizes of 5, 20, and 65 microns, electrode area of 1.27 sq. cm. (Pall Trinity Micro Corporation).

All of the above materials were used as porous flow-through electrodes except the platinum foil, in which case the electrolyte was passed adjacent to the cathode. The porous stainless steels and platinum-rhodium

screen were platinized to increase their catalytic activity. The platinizing procedure is explained in detail in the following section.

Electrolyte solutions used in these polarization studies were mixed at room temperature such that they were nearly saturated at -25 °C. This permitted usage of the electrolyte at -20 °C without the threat of precipitation of the conducting salt. Electrolytes prepared in this manner consistently exhibited identical electrolytic conductivities. Solubility data for the conducting salt used is presented in the Appendix (Figure 22).

Polarization data from the polypropylene cell were obtained as follows. Cell current was set at a fixed value using a regulated D.C. power supply. The resulting electrode (vs. Pb/Pb^{+2} reference) or complete cell voltage was recorded as a function of the cell current using an X-Y recorder. Voltages would be maintained constant for four to five minutes before going to the next current setting. Internal ohmic resistance was periodically recorded using an A.C. (60 or 1000 cps.) conductivity bridge (Industrial Instruments, Inc., model RC 16B2). Knowledge of internal resistance allowed calculation of IR free voltages.

In obtaining data for cell life studies, the cell module was modified so that the electrodes were only about 3/32 of an inch apart so as to minimize ohmic resistance (not shown in Figure 21). Cell current was set at a fixed value, and electrode or cell voltage was recorded as a function of time using a strip chart recorder.

C. Platinizing Procedure

In the development of a flow-through cathode for use in the final cell design a number of possible porous electrode materials were studied. The performance of two of these electrode materials (platinum-rhodium screen and porous stainless steel) was improved considerably by platinizing them to improve their catalytic properties. Following is a description of the platinizing procedure used. The plating solution used was a 3% solution of chloroplatinic acid containing .06% lead acetate as recommended by MacNevin and Levitsky (26).

Platinum-rhodium: The platinizing of platinum and its alloys has been reported on by many authors (26, 27, 28). Most researchers recommend cleaning the platinum with a solution of aqua regia to remove surface deposits; the platinum-rhodium screen used in this study was cleaned in this manner. After cleaning, the electrode was platinized using a plating current of 10 ma until the desired platinum loading was attained. The amount of platinum deposited was determined by weight difference and the area used to determine platinum loading (mg/cm^2) was the geometric area of the electrode. It was assumed that the platinum was evenly distributed over the entire electrode surface.

316 Stainless steel: No information could be found in the literature concerning the platinizing of stainless steel. Drazic and his co-workers (29) reported on the activiation of nickel fuel cell electrodes with platinum catalysts using the technique of immersion plating (chemical exchange), but this technique has not been used to

platinize stainless steel. Thus, a brief experimental study was undertaken to develop a technique for platinizing stainless steel.

Before electroplating a given metal surface with another metal it is first necessary to clean and activate the surface of the base metal so that strong bonding can occur between the two metals involved. At the beginning of this study on platinization of stainless steel the author had no access to recommended cleaning procedures for stainless steel, and while awaiting such information, it was decided to experiment with different cleaning solutions. It has already been noted that aqua regia was used to clean platinum before plating; based on this fact aqua regia was tried as a cleaning solution for stainless steel and was found to work quite well.

Thus the following procedure was developed for platinizing stainless steel. The porous electrode to be platinized was immersed in an aqua regia solution for 60-90 seconds in order to remove surface deposits and activate the surface. Following this, the electrode was washed and soaked in water to remove all aqua regia, then dried using compressed air and weighed to the nearest 0.1 mg. before platinizing. Using the plating solution mentioned previously, the electrode was platinized at currents between 10-20 ma. The electrode was periodically weighed to determine the amount of platinum that had been added and a typical electrode took 45-60 minutes to complete. In determining platinum loading it was again assumed that the platinum deposit was evenly

distributed over the geometric electrode surface, although a cross sectional cut of the finished electrode showed that some of the platinum was deposited within the electrode pores. Electrodes produced using this technique showed highly reproducible initial performance regardless of the platinum loading or electrode pore size.

Subsequent to the platinizing technique developed in this research for stainless steel, a chemical cleaning procedure for stainless steel was acquired (30). This cleaning procedure was not used in this research.

IV. RESULTS AND DISCUSSION

The major objective of this research program was to develop a fuel cell which would operate at cold ambient temperatures. In the initial stages of this program, the only thing that was definite was that the ionizing solvent for this fuel cell would be liquid ammonia, for reasons previously stated. There was no initial decision made concerning the other major components of a fuel cell, i.e., electrode type, electrocatalysts, fuel, oxidizer, conducting salt, etc. All of these other cell components had to be either developed in the research program, or obtained commercially and proven usable.

The end result of this research program has been the development of a working liquid ammonia electrolyte fuel cell which operates at temperatures down to -20 °C. The evolution and development of this fuel cell came about through a number of preliminary studies on each of the above basic cell components (excluding ionizing solvent).

A. Voltammetric Studies

As mentioned previously, voltammetric techniques were used to make preliminary studies on possible fuels, oxidizers, and electrocatalysts. Results of these preliminary voltammetric studies were used in the development of a complete fuel cell. Figure 23 shows the convention used in obtaining voltammetric curves.

1. Reaction of potential fuels and oxidizers in NH_3/NH_4SCN:

   A number of potential fuels and oxidizers were studied in

liquid ammonia using voltammetric techniques. The reactants were arbitrarily chosen from a number of chemicals which were readily available or easily obtained, but attempts were made to study a group representative of the different types of organic compounds as fuels (along with hydrogen and hydrazine) and several inorganic compounds as possible oxidizers. Most of the reactants chosen were soluble in liquid ammonia.

For these preliminary studies ammonium thiocyanate was chosen as the conducting salt. Solutions of ammonium thiocyanate exhibit high electrolytic conductivity and the boiling point of a saturated ammonium thiocyanate-ammonia (NH_3/NH_4SCN) solution is about 64 °C (31), thus permitting the use of this solution at room temperature without the threat of boiling of ammonia.

Table I presents a summary of the reactants studied, the extent of electrochemical reaction occurring, and the potential (voltage) at which the reaction occurred with respect to a Pb/Pb^{+2} reference electrode. The working electrode in all cases was a shiny platinum wire or a platinum wire coated with platinum black.

It can be seen from Table I that most of the reactants studied showed no electrochemical reaction in liquid ammonia. This was verified by making voltammetric scans with and without the reactant present in solution. Absence of current peaks in the voltammetric curves indicates a lack of electrochemical reaction. Note also that

TABLE I. Electrochemical reaction of various chemicals in a saturated solution of NH_3/NH_4SCN.

Reactant	Electrochemical Reaction[a]
Benzene[b]	None
Acetone[b]	None
Ethylene glycol	None
Methanol	None
Ethanol	None
n-Propyl alcohol	None
n-Propyl amine	None
2-Amino ethanol	None
Cyclohexanol	None
Hydrazobenzene	None
Diphenylamine	None
Nitrobenzene[b]	Oxidation at 0.5 v, reductions at 0.5 and 0.1 v
Hydrazine	Oxidation at 0.25 v
Chlorine[b]	Reacts chemically
Bromine[b]	Reacts chemically
Nitrogen dioxide	Reacts chemically
Iodine	Reduction at 0.75 v
Hydrogen[b]	Oxidation at -0.10 v

[a]Reaction determined using cyclic voltammetry and cell configuration shown in Figure 20.
Reference electrode: Pb/Pb^{+2}
Counter electrode: Shiny Pt
Working electrode: Pt black, unless otherwise noted.

[b]Working electrode: Shiny Pt wire.

some of the materials studied reacted chemically with the ammonia solution employed (chlorine, bromine, nitrogen dioxide).

All of the materials which showed no chemical or electrochemical reaction in liquid ammonia were carbon containing compounds which were being studied as possible fuels. There have been numerous studies made on the electrochemical oxidation of carbon containing compounds in aqueous electrolytes (4, 32). Several mechanisms have been proposed for the oxidation of these compounds (4, 33); all of these mechanisms require oxygen in some adsorbed state. Generally the oxygen comes from the aqueous solvent and is used to convert the carbonaceous species to carbon dioxide. In liquid ammonia the only oxygen present is that which may be contained in the reactant (fuel) itself, and this is generally insufficient for oxidizing all carbon atoms to carbon dioxide. If the reaction mechanism in liquid ammonia were analogous to aqueous systems, electrochemical oxidation of carbonaceous materials in ammonia would be even less than in water since adsorbed NH_2 species are poorer oxidizing agents than adsorbed oxygen containing species. According to Miles and Kellett (20), carbonaceous fuel oxidation will probably be more favorable in solvents containing chlorine, fluorine, and oxygen, while ammonia should be useful for fuels such as hydrazine, hydrogen, and metals since the solvent is not directly involved in the oxidation reaction.

Of the materials studied, only four exhibited electrochemical

oxidation or reduction in NH_3/NH_4SCN. These materials and their reactions are discussed individually below.

Hydrogen: The oxidation of hydrogen in a saturated NH_3/NH_4SCN solution occurs at -.10 volts with respect to the Pb/Pb^{+2} reference electrode, as seen in Figure 3. Two voltammetric scans are shown in this figure, one with hydrogen absent (curve A) and one with hydrogen present (curve B). These two curves were produced in the following manner. In acid solutions of liquid ammonia (excess NH_4^+) the solvent decomposition reaction at cathodic potentials is $NH_4^+ + e^- \rightarrow NH_3 + \frac{1}{2} H_2$ (8). Curve A of Figure 3 was made by scanning from negative to positive potentials without first allowing this decomposition reaction to occur. Curve B was made after allowing this decomposition reaction to occur for thirty seconds, i.e., long enough for hydrogen to be produced and adsorbed on the working electrode. In other words, with hydrogen absent no oxidation peak appears, but with hydrogen present electrochemical oxidation occurs (as indicated by the current peak). The oxidation reaction that occurs is the reverse of the cathodic decomposition reaction, i.e., $\frac{1}{2} H_2 + NH_3 \rightarrow NH_4^+ + e^-$.

To further verify that the oxidation reaction occurring at -.10 volts with respect to Pb/Pb^{+2} was due to hydrogen oxidation, the potential was held near this value while hydrogen was externally added to the electrolyte-electrode interface in the three compartment cell. A slight increase in current was observed, indicating that electrochemical

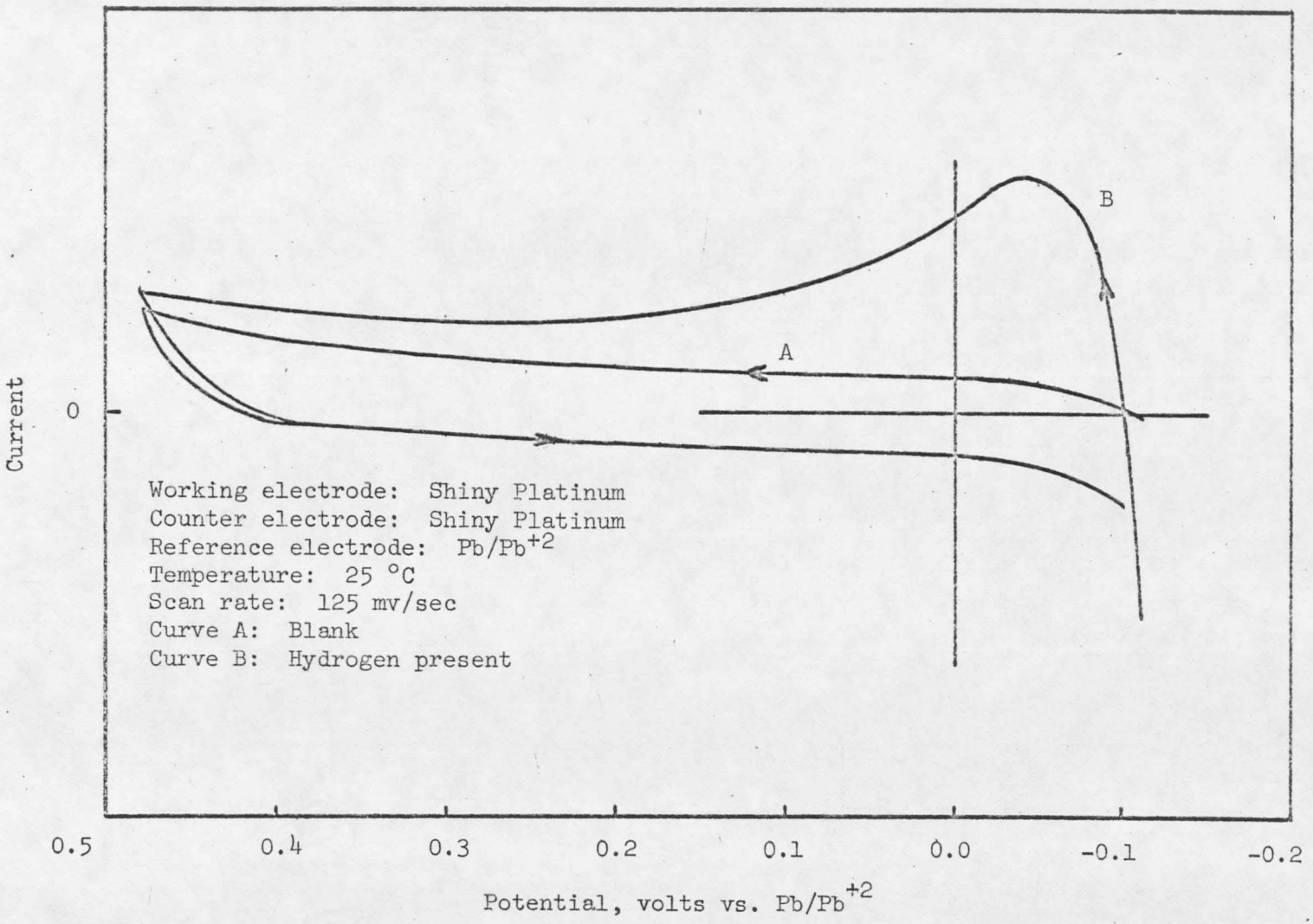


Figure 3. Voltammetric trace for hydrogen oxidation in NH_3/NH_4SCN.

reaction was occurring.

Hydrazine: Figure 4 shows the voltammetric scans obtained with and without hydrazine in liquid NH_3/NH_4SCN. Electrochemical oxidation of hydrazine occurs at about 0.25 volts with respect to the Pb/Pb^{+2} reference. The net oxidation reaction is $4NH_3 + N_2H_4 \rightarrow N_2 + 4NH_4^+ + 4e^-$ (20). The oxidation of hydrazine appears to be fast kinetically (as indicated by the steep slope of the current-potential curve at 0.25 v), but would be more favorable if it occurred at a lower potential with respect to the reference. However, hydrazine shows some promise as a fuel in liquid ammonia, especially if a suitable oxidant can be found to couple with it.

Nitrobenzene: Figure 5 shows the voltammetric scan made with nitrobenzene in liquid ammonia. The true electroreduction of nitrobenzene occurs at 0.1 volts with respect to the reference and is represented by the peak labeled A. Reactions for the peaks labeled B and C are not known, but Figure 6 helps explain what is happening. Curve 1 of Figure 6 shows the cyclic scan made without nitrobenzene reduction occurring at 0.1 v. Curve 2 shows the cyclic scan made after reduction of nitrobenzene at -0.2 v for thirty seconds. Finally, curve 3 was produced by reducing nitrobenzene at -0.2 v for thirty seconds, scanning the voltage from negative potential to 0.5 v, and then reversing the scan direction. The interpretation of these curves is as follows. Peak B appears only after nitrobenzene reduction (peak A) is allowed to occur and must be due to

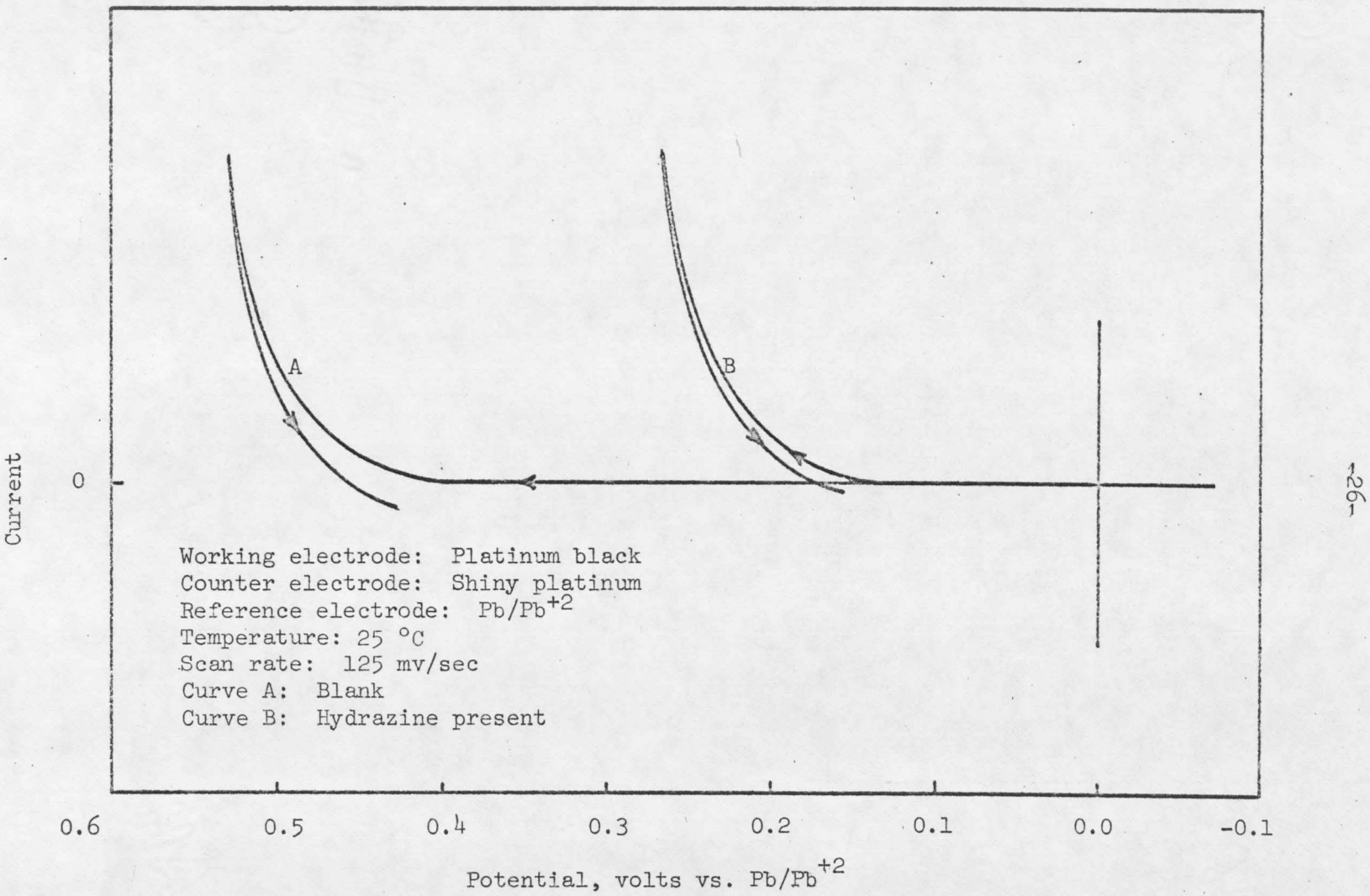


Figure 4. Voltammetric trace for hydrazine oxidation in NH_3/NH_4SCN.

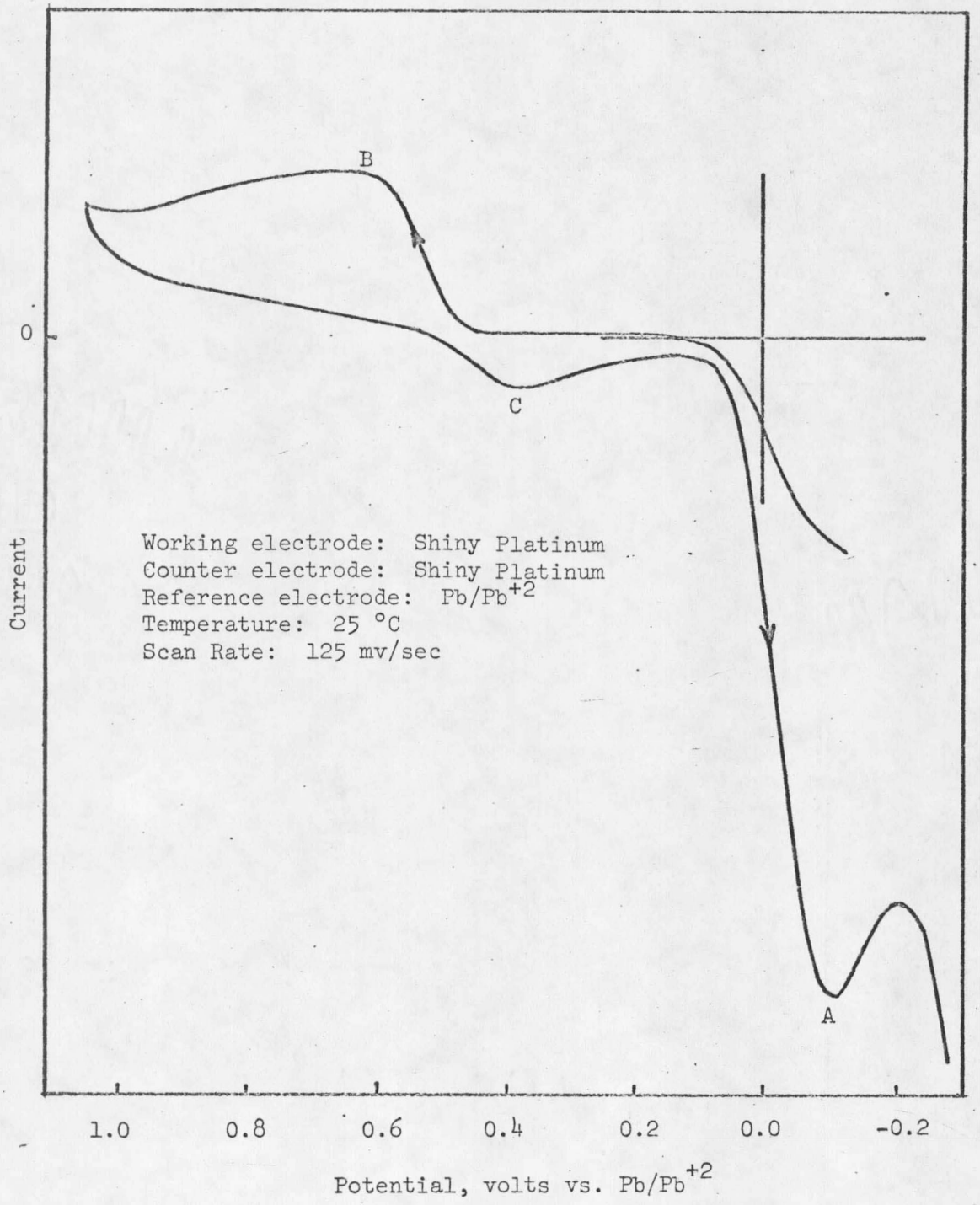


Figure 5. Voltammetric trace for nitrobenzene in NH_3/NH_4SCN.

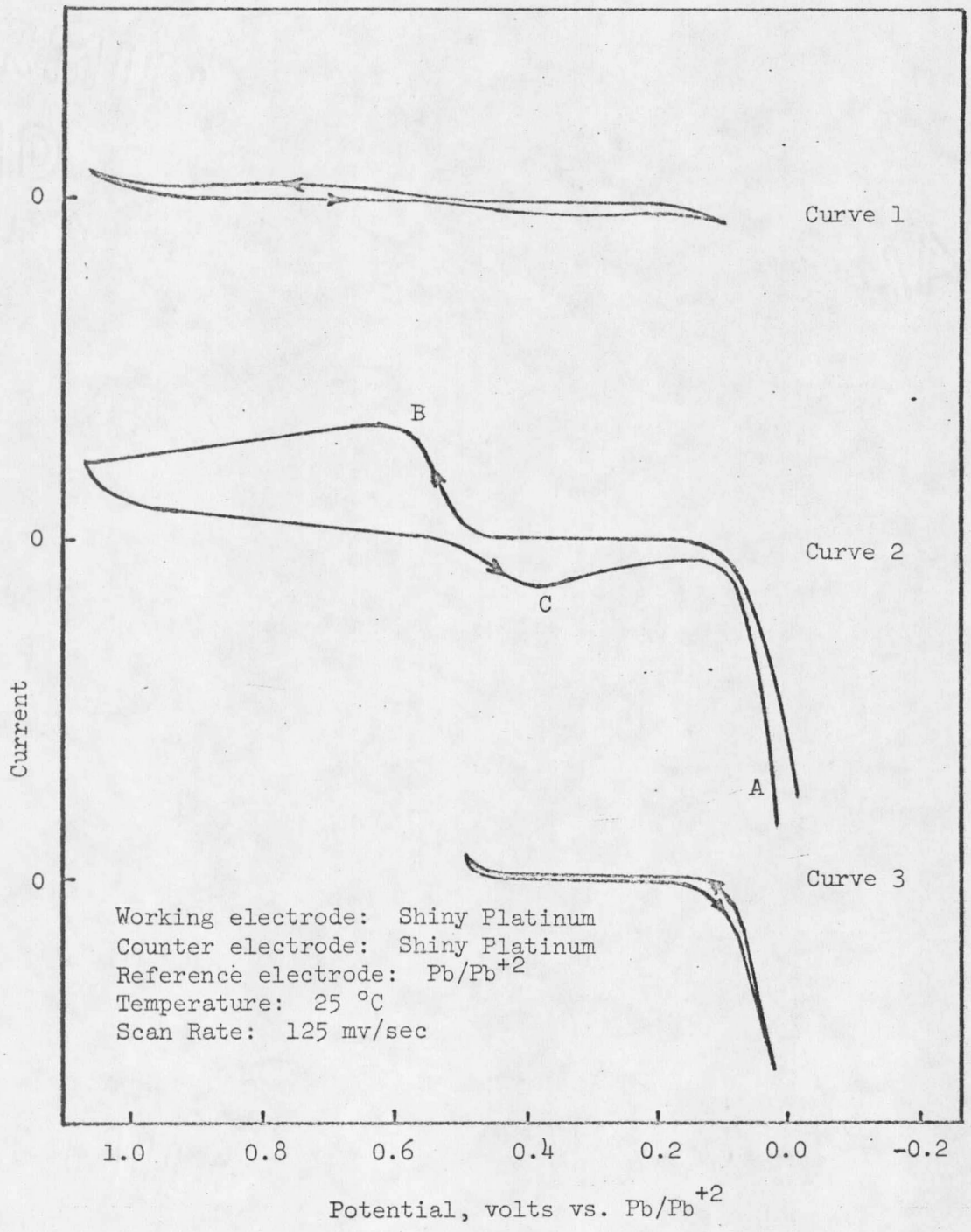


Figure 6. Voltammetric scans for explaining nitrobenzene behavior in NH_3/NH_4SCN.

the product of nitrobenzene reduction. Peak C appears only if the oxidation causing peak B is allowed to occur and must be due to the reduction of the product formed at oxidation peak B. The oxidation-reduction pair at 0.5 v appears to be fairly reversible, but the true reaction is not known.

The purpose of these voltammetric studies was to find an oxidizer for fuel cell development. Unfortunately, reduction of nitrobenzene occurred very close to cathodic solvent decomposition and nitrobenzene did not appear feasible for use in these studies. Consequently, voltammetric studies on nitrobenzene in liquid ammonia were terminated and the reversible oxidation-reduction couple at 0.5 volts was not studied further.

Electroreduction of nitrobenzene in liquid ammonia has previously been studied by Harris and his co-workers (19,31) at Corona, California. They claim that the end products of the reduction of nitrobenzene in liquid ammonia are phenylhydroxylamine (C_6H_5NHOH) and hydrazobenzene ($C_6H_5NH{=}NHC_6H_5$). It has already been shown that hydrazobenzene does not react electrochemically in NH_3/NH_4SCN (Table I). Whether or not phenylhydroxylamine causes the oxidation-reduction couple at 0.5 volts is not known, but future work along this line should prove interesting.

Iodine: Three halogens (chlorine, bromine, iodine) were studied as possible oxidizers because their reduction potentials in acid liquid ammonia are quite high compared to the Pb/Pb^{+2} reference. However,

Bergstrom (34) claims that chlorine and bromine react energetically with liquid ammonia to form the respective ammonium salts. This fact was borne out by the present studies. Bergstrom also claims that iodine is very soluble in a small volume of liquid ammonia, but reacts reversibly with it on dilution in the sense of the equation $I_2 + 2NH_3 \leftrightarrows INH_2 + NH_4I$ to form iodine-amine and ammonium iodide. This reaction is analogous to the following reaction between chlorine and water: $Cl_2 + H_2O \leftrightarrows HOCL + HCl$.

The voltammetric scan for iodine in NH_3/NH_4SCN is shown in Figure 7. A strong reduction peak appears at 0.75 volts with respect to the reference and is assumed to be due to iodine reduction, i.e., $I_2 + 2e^- \rightarrow 2I^-$.

2. Electrocatalyst studies in NH_3/NH_4SCN:

The noble metals have been used extensively as electrocatalysts for fuel cell studies in aqueous systems. However, since few fuel cell studies have been made in liquid ammonia, electrocatalyst studies in liquid ammonia solutions are at a premium. Only Miles and Kellett (20) have done research in this area.

Using voltammetric techniques, studies were made on a number of metals in liquid NH_3/NH_4SCN to determine, first of all, the potential range which each metal exhibits between anodic and cathodic solvent decomposition, and secondly, their ability to oxidize hydrogen in liquid ammonia. The metals studied included many of the noble metals as

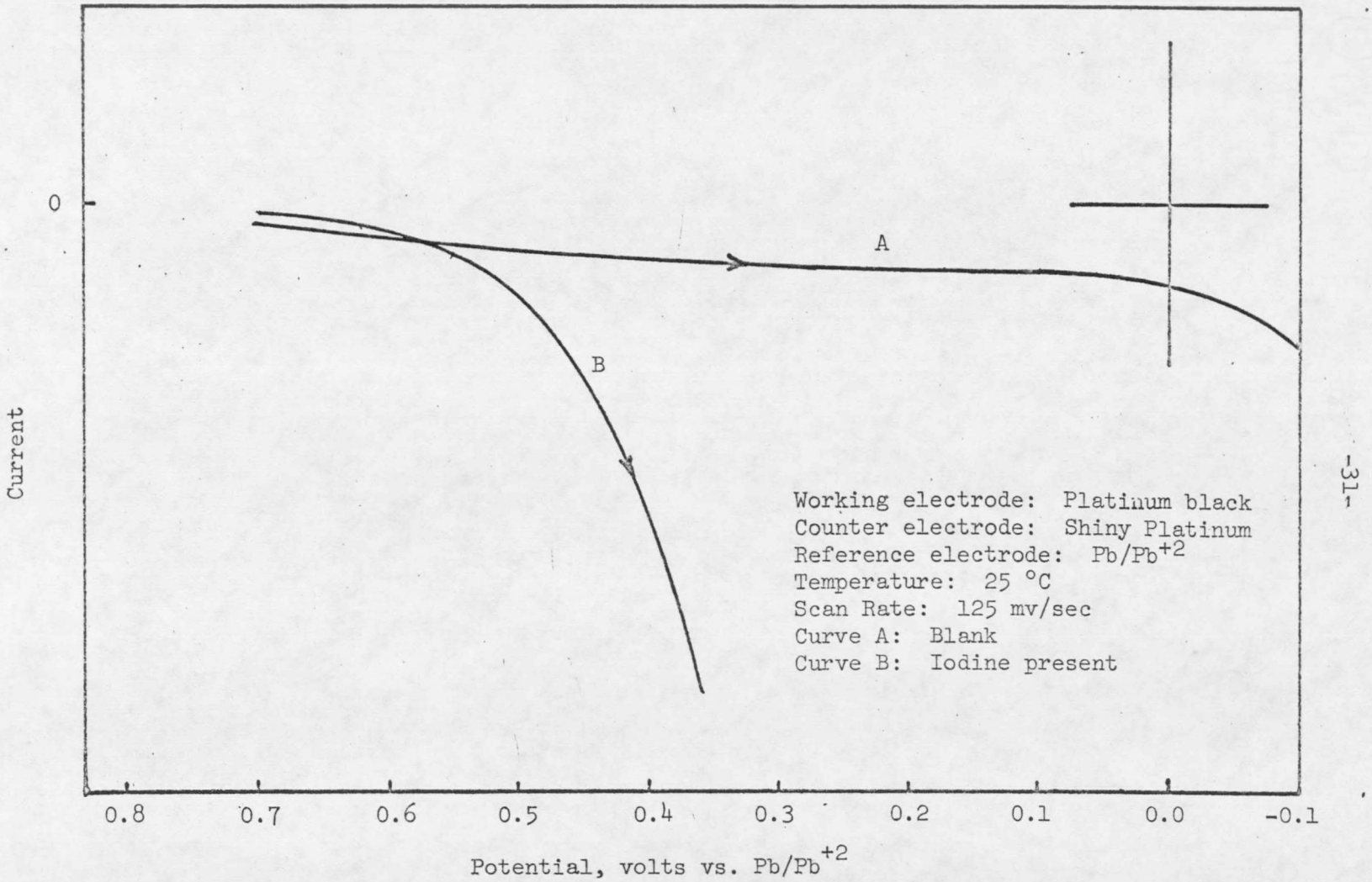


Figure 7. Voltammetric trace for iodine reduction in NH_3/NH_4SCN.

well as others which were readily obtainable in pure form. Table II summarizes the results of these studies, while Figures 24 - 31 show cyclic voltammetric traces for the metals studied.

A number of observations can be made from Table II. First of all, note that a number of electrode materials are limited anodically by oxidation of the electrode itself. Materials which oxidize at low positive potentials (e.g., nickel, cobalt, silver) would thus be poor materials of construction for a liquid ammonia cell since they would corrode rapidly. On the other hand, materials which oxidize at high positive potentials would probably be acceptable materials of construction for a liquid ammonia cell.

Secondly, it can be seen that, of the materials studied, only platinum, palladium, and a platinum-iridium alloy effectively oxidize hydrogen in liquid ammonia. Titanium, tantalum, and tungsten all show questionable catalytic activity, but other materials studied did not oxidize hydrogen.

Decomposition potential in these studies was defined as the potential at which the current density attained a value of 10 ma/cm^2 using a scan rate of 125 mv/sec. The potential range is the region that exists between anodic and cathodic solvent decomposition. Electrochemical studies outside this region cannot be made.

For a more extensive study of electrocatalysts in liquid ammonia the reader is referred to an article by Miles and Kellett (20).

TABLE II. Electrocatalyst studies in a saturated solution of NH_3/NH_4SCN.

Electrode	Decomposition Potential (v)[a] Anodic	Cathodic	Potential Range (v)	Hydrogen Oxidation
Titanium	3.15	-1.00	4.15	Q[d]
Tantalum	3.00	-1.15	4.15	Q
Zirconium	2.00[b]	-1.05	3.05	No
Tungsten	1.75	-0.75	2.50	Q
Aluminum	0.75[b]	-1.40	2.15	No
Molybdenum	1.40	-0.70	2.10	No
Rhodium	1.25[b]	-0.40	1.65	No
Gold	0.80[b]	-0.60	1.40	No
Platinum	1.15	-0.25	1.40	Yes
Platinum-Iridium[c]	1.15	-0.25	1.40	Yes
Palladium	1.10	-0.15	1.25	Yes
Bismuth	0.35[b]	-0.75	1.10	No
Silver	0.25[b]	-0.70	0.95	No
Tin	-0.10[b]	-0.90	0.80	No
Cobalt	0.10[b]	-0.50	0.60	No
Nickel	0.05[b]	-0.45	0.50	No

[a]Measured against a Pb/Pb^{+2} reference electrode using cell configuration shown in Figure 20. Counter electrode was shiny platinum. Decomposition potential is that required to attain a current density of 10 ma/cm^2 at a scan rate of 125 mv/sec.

[b]Limited by electrode oxidation rather than solvent decomposition.

[c]90% Pt, 10% Ir

[d]Questionable

They made studies similar to those reported here, but looked at over thirty possible electrode surfaces. Their conclusions and observations were much the same as those reported here, at least where the same electrode materials were studied.

3. Iodine reduction using various electrocatalysts:

Before an attempt was made to design and construct a liquid ammonia fuel cell, a third preliminary voltammetric study was made in the three compartment cell. Based on the voltammetric study of potential oxidizers (Table I) it was decided to try to develop a cell which would use iodine as the oxidizer. Thus a brief study of iodine reduction at various electrode surfaces in liquid ammonia was made. Table III summarizes the results of this study.

The scan rate for these studies was 130 mv/sec. and the conducting salt used was ammonium nitrate (NH_4NO_3), for reasons to be explained later. Voltammetric scans were made at temperatures between -10 and -12 °C.

From Table III it can be seen that several electrocatalysts will reduce iodine in a solution of NH_3/NH_4NO_3 (saturated). Of course the best electrocatalyst for iodine reduction is one which will reduce iodine at the highest positive potential with respect to the reference electrode. Based on this criteria, palladium, gold, and platinum appear to be equivalent electrocatalysts for iodine reduction.

TABLE III. Iodine reduction at various electrode surfaces in a saturated solution of NH_3/NH_4NO_3.

Electrocatalyst	Potential at which reduction occurs (v)[a]
Titanium	0.05
Tungsten	0.60
Tantalum	No reduction
Zirconium	0.70
Molybdenum	0.75
Aluminum	No reduction
Palladium	1.05
Gold	1.05
Rhodium	0.90
Platinum	1.05
Stainless steel (316)	0.80

[a]Reaction determined using single sweep voltammetry and cell configuration shown in Figure 20.
Reference electrode: Pb/Pb^{+2}
Counter electrode: Shiny Pt.
Temperature: -10 °C
Scan rate: 130 mv/sec.

B. Evolution of Final Cell Design

Based on the brief but informative voltammetric studies just discussed, the development of a liquid ammonia electrolyte fuel cell was undertaken. Since it is important that the fuel oxidation occur at as low a potential as possible and the oxidizer reduction occur at as high a potential as possible, hydrogen was chosen as the fuel and iodine (dissolved in the electrolyte) as the oxidizer. Platinum was chosen as the electrocatalyst for both hydrogen oxidation and iodine reduction since it appeared to be as good or better than any other material studied (see Tables II and III). Ammonium thiocyanate was chosen as the conducting salt initially, although ammonium nitrate was subsequently used, for reasons to be stated later.

The theoretical open circuit voltage (OCV) for a liquid ammonia fuel cell (at 25 °C) with hydrogen as fuel and iodine as oxidizer is 1.28 volts and was determined using standard oxidation potentials for hydrogen and iodine in ammonia (12) as follows.

Anode: $\frac{1}{2} H_2 + NH_3 \rightarrow NH_4^+ + e^-$	$E^\circ = 0.0$ v
Cathode: $\frac{1}{2} I_2 + e^- \rightarrow I^-$	$E^\circ = 1.28$ v
Overall: $\frac{1}{2} H_2 + NH_3 + \frac{1}{2} I_2 \rightarrow NH_4^+ + I^-$	$E^\circ = 1.28$ v

The theoretical OCV of 1.28 volts holds provided that the hydrogen and ammonia are at one atmosphere pressure and the iodine, iodide ion, and ammonium ion are at unit activity. Electrolyte concentration, hydrogen pressure, iodine concentration, and operating temperature are all

variables which can cause deviations from the theoretical OCV, and their effect can be calculated by using the Nernst equation (6), which is as follows:

$$E = E^{\circ} - \frac{RT}{nF} \ln \left(\frac{a_p}{a_r}\right)$$

where E° = standard electrode potential at unit activity of products and reactants (v)

E = reversible electrode potential (v)

R = gas constant (joules/°C/mole)

T = absolute temperature (°K)

n = number of electrons involved (equivalents/mole)

F = Faraday's constant (96500 coulombs/equivalent)

a_p = activity of products

a_r = activity of reactants

The particular cell developed in these studies exhibited an OCV of 1.15 volts; deviation from the theoretical OCV for such a cell is undoubtedly due to the above mentioned Nernst equation variables.

Having decided to use the cell components already mentioned (i.e., hydrogen, iodine, platinum electrocatalysts) in developing a liquid ammonia electrolyte fuel cell, it was next necessary to develop a physical design for utilizing these components. A summary of the other components used in the final cell design and some of the operating problems encountered is given below.

1. Anode: Numerous fuel cells have been developed which employ aqueous electrolytes and gaseous fuels, and invariably the anode is a

porous gas diffusion electrode of one type or another (4). In using gaseous fuels it is mandatory that a three phase interface (fuel-electrode-electrolyte) be established in order to enhance the electrochemical reaction, since the solubility of most gaseous fuels in water is low and diffusion limitations occur. In recent years a good deal of developmental work on porous gas diffusion electrodes has occurred (4). Recent trends in electrode development are toward thin electrode structures as opposed to thicker porous electrodes used in years past (e.g., porous carbon). One type of thin electrode structure which has proved quite successful is the type which consists of a catalytic material bonded to a thin metallic screen. Since these thin porous electrodes work quite well in aqueous systems, it was decided to obtain some of this material commercially and try it as anode material for hydrogen oxidation in liquid ammonia. It will be shown later that this type of electrode does indeed work as far as physical performance goes, although electrochemical performance was not as good as desired.

2. Cathode: Most aqueous fuel cell research has been carried out using gaseous oxidizers. However, a few fuel cells exist which operate with the oxidizer dissolved in the electrolyte (35), and some cells have been developed which employ dissolved fuels (32). Generally, when a dissolved fuel or oxidizer is employed, the electrode used is of the porous flow-through type. The electrolyte containing the dissolved species flows through the electrode to establish intimate contact between the fuel and electrode, thus eliminating diffusion as the major

mass transfer factor. In principle, this type of electrode should be simple to operate, since it is not necessary to establish a three phase interface for reaction as in the case of a gaseous reactant.

Since the oxidizer chosen for these studies was to be dissolved in the electrolyte, it was decided to design the cell so that a flow-through type of electrode could be used as the cathode. The development of a reproducible flow-through cathode which would give reasonable electrochemical performance became one of the problems to be solved in this research.

3. Reference electrode: The reference electrode used in the liquid ammonia fuel cell polarization studies has already been described in the Experimental section. However, it should be noted at this point that the reference used in polarization studies differed in its zero point by 0.08 volts from the lead (Pb) metal used as a reference in three compartment cell studies (Table IV).

TABLE IV. Voltage deviation of reference electrodes used in three compartment cell and polypropylene cell.

	Reference electrode	Open circuit voltage H_2 Oxid.	I_2 Red.	Overall OCV
Three compartment cell	Lead metal directly in contact with electrolyte	-.10 v	1.05 v	1.15 v
Polypropylene cell	Lead metal separated from electrolyte by glass microcracks	-.18 v	0.97 v	1.15 v

This difference in the two reference electrodes employed could be due

to a number of factors, including ionic concentrations of conducting salts and the impedence across the glass microcracks. In any event, each electrode was fairly stable and reproducible and the overall OCV was the same in both cases.

4. Cell module and gasketing: In the past, fuel cell modules have been constructed of both metallic and plastic materials. Metals have the advantage of strength and durability, but must be electrically insulated from the electrodes to prevent short circuits, while plastics are nonconductive and easier to work with. For this particular cell it was necessary to find a material which was resistant to ammonia solutions, and polypropylene seemed to work quite well. The part that polypropylene plays in the cell design has already been shown in Figure 21.

To prevent leakage of fuel and electrolyte from the cell it was necessary to employ gasketing material between cell parts. A number of gasketing materials were used (neoprene, Viton*, Buna-n), but only silicone rubber worked well at cold temperatures. Most gasketing materials became rigid at very cold temperatures, but silicone rubber remained elastic and flexible even down to -55 °C.

5. Conducting Salt: Preliminary voltammetric studies on fuels, oxidizers, and electrocatalysts were made using ammonium thiocyanate (NH_4SCN) as the conducting salt, for reasons already stated. However,

* E. I. DuPont & Company

use of a saturated solution of NH_3/NH_4SCN with the commercial porous anode material that was chosen for study caused poisoning of the anode and complete loss of catalytic activity. No attempt was made to determine the mechanism of this poisoning, although use of the same electrode material in an aqueous solution to which NaSCN had been added again resulted in electrode poisoning and loss of catalytic activity. In other words, thiocyanate ion (SCN^-) appears to have a deleterious effect on the electrode.

Rather than work on the development of a new porous electrode for hydrogen oxidation, it was decided to try other ammonium compounds as the conducting salt. Ammonium nitrate was chosen for study because it, like NH_4SCN, tends to raise the boiling point of ammonia by forming a so called Divers' solution (31). A saturated solution of NH_3/NH_4NO_3 was used in the polypropylene cell and was found to work satisfactorily as the electrolyte, showing high electrolytic conductivity. Thus, all subsequent studies, including those reported in Table III on iodine reduction at various electrode surfaces, were made using NH_3/NH_4NO_3 as the electrolyte.

6. Operating procedure and problems: The principle of operation of the final fuel cell design used in these studies has already been presented in the Experimental section of this thesis. On paper the mode of operation of this system appears simple, but there are a couple of subtleties of the system about which the reader should be advised.

First of all, if iodine is dissolved in ammonia and then the ammonia is allowed to evaporate, the highly unstable and explosive compound ammonium tri-iodide (NH_4I_3) is formed. However, if iodine is dissolved in an ammonium nitrate-ammonia solution, the ammonium nitrate appears to prevent this compound from forming upon evaporation of the ammonia. In any event, the reader is cautioned about the explosive nature of ammonium tri-iodide.

Secondly, it is important that the nitrogen pressure that is impressed upon the system to cause electrolyte flow be much larger than the hydraulic head of the liquid ammonia electrolyte in reservoir A (Figure 2). Otherwise, if this nitrogen pressure is small, the flow rate of electrolyte will vary with the level of ammonia in the reservoir. Generally, the nitrogen pressure was kept between 10-20 psig.

Finally, a few words are in order with respect to the anode material used. As noted previously this electrode material is on the order of 6-7 mils thick. For optimum efficiency of operation of this electrode material, it is necessary to establish a three phase interface somewhere within the interior of the electrode. If the pressure on the electrolyte side of the electrode (due to hydraulic head) becomes too great, the electrolyte floods the electrode and performance is very poor. Similarly, if the gas side pressure becomes too great the gaseous fuel will bubble into the electrolyte compartment and performance is again destroyed.

There are a couple of methods of overcoming this problem. A commonly used method of preventing electrolyte leakage with this type of membrane electrode is to use a matrix material which absorbs the electrolyte but still keeps the electrodes wet (36), although this approach was not used here. An alternative method of preventing electrolyte leakage is to balance the pressure on each side of the electrode so that there is no pressure differential across the electrode. The author found that best results were obtained if there was a slight positive pressure (0.5 to 1.0 inches of water) on the gas side of the electrode. This seemed to establish a three phase interface for electrochemical reaction. Installation of a glass plate into the end plate of the cell so that the electrode could be observed visually helped considerably with the control of the leakage problem.

Some difficulty was also encountered in initial operation of the cell with electrolyte leakage around the edges of the electrode. This problem was overcome by sealing the electrode material to the gasketing material using silicone rubber adhesive.

C. Polarization Studies

Having decided upon a final design for a liquid ammonia electrolyte fuel cell, it was next decided to measure the performance of the cell with respect to a number of operating variables. Performance was measured by obtaining the polarization characteristics of the cell as described in the Experimental section. Polarization studies were

broken into three distinct parts, hydrogen electrode polarization, iodine electrode polarization, and life studies.

1. Hydrogen electrode polarization:

The commercial porous platinum black electrode material used in these studies has worked quite well in aqueous systems. Current densities up to 400 ma/cm^2 at 0.1 volts hydrogen electrode polarization have been reported for a single cell (4). Since the performance of this electrode material was so good in aqueous systems, it was chosen for use in the present studies.

Figure 8 presents the polarization characteristics of this electrode material using a nearly saturated solution of NH_3/NH_4NO_3 as electrolyte. The hydrogen to ammonia ratio in the fuel was 1:1 by volume and operating temperature was -18 °C. The maximum current density attainable with this electrode material at these conditions is about 80-90 ma/cm^2 at about 0.2 volts polarization. Above 90 ma/cm^2 polarization becomes very high, mainly due to a concentration polarization effect. Note that the current-potential curve exhibits a slight inflection at a current density of about 40 ma/cm^2. Almost invariably in these studies this inflection appeared for hydrogen electrode polarization, although a few cases were observed where the inflection was absent. There is no immediate explanation for this behavior.

The electrochemical reaction occurring at the anode is

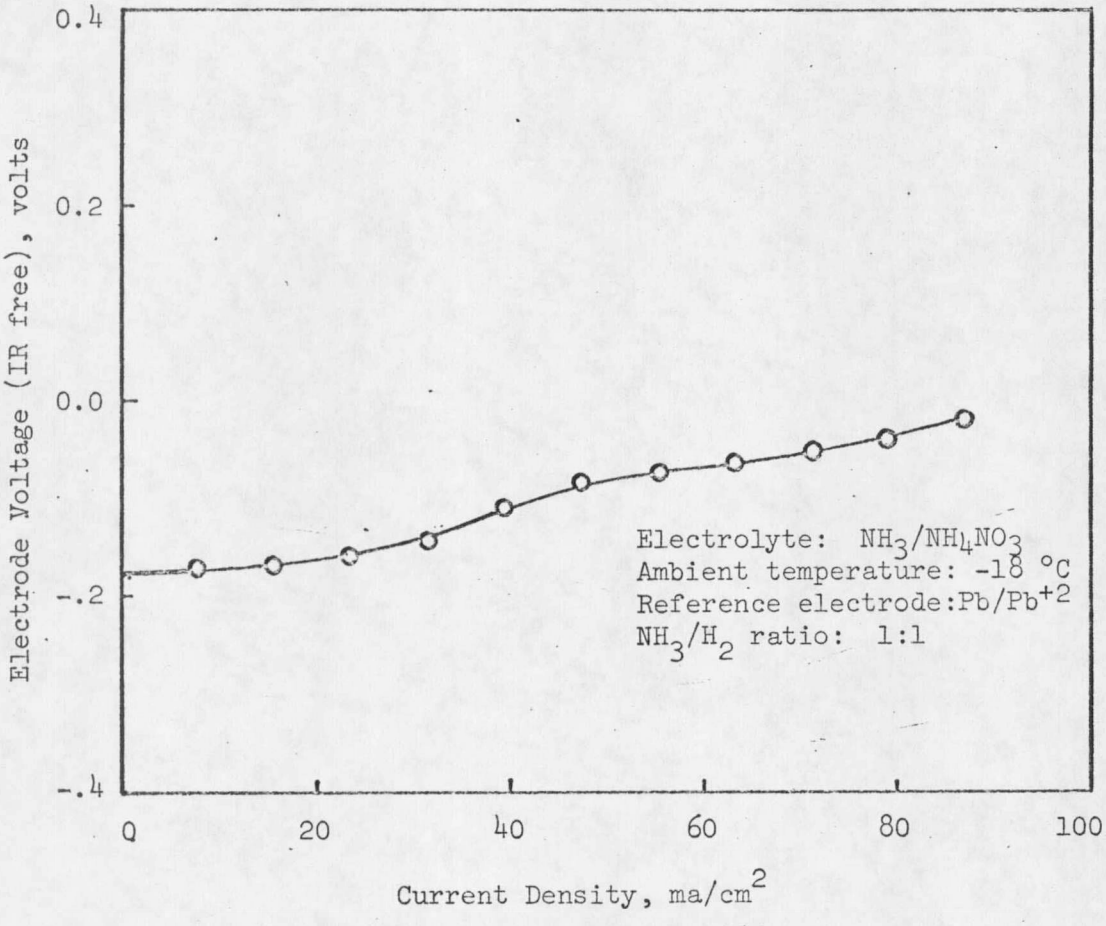


Figure 8. Hydrogen electrode polarization as a function of current density.

$H_2 + 2NH_3 \rightarrow 2NH_4^+ + 2e^-$. For each mole of hydrogen that is consumed two moles of ammonia are used up in the reaction. Ammonia for this reaction could come from the liquid ammonia electrolyte, or it could be fed to the cell with the hydrogen fuel. It was found through experimental study that feeding hydrogen alone to the anode led to excessive polarization even at very low current densities (<10 ma/cm^2). In other words, it was found necessary to add ammonia gas with the hydrogen fuel in order to sustain electrochemical reaction. Figure 9 shows the effect of NH_3/H_2 ratio on the hydrogen electrode performance. Note that polarization is highest at the extreme NH_3/H_2 ratios and that performance is essentially the same for a 2:1 ratio (theoretical optimum) and a 1:1 ratio.

It is reasonable that performance is poorer at a high NH_3/H_2 ratio (5:1) since the concentration of hydrogen at the electrode is diluted because of the excess ammonia. Poor performance at low NH_3/H_2 ratios (e.g., 1:5 or less) might be explained as follows. Since two moles of ammonia are required for each mole of hydrogen reacted there is a good chance that some of the required ammonia is coming from the electrolyte itself. This results in a certain amount of "drying out" of the electrode surface and thus an increase in electrode polarization.

Figure 10 presents the polarization characteristics for different pieces of the porous platinum black material and can be used to illustrate the degree of reproducibility of results using this

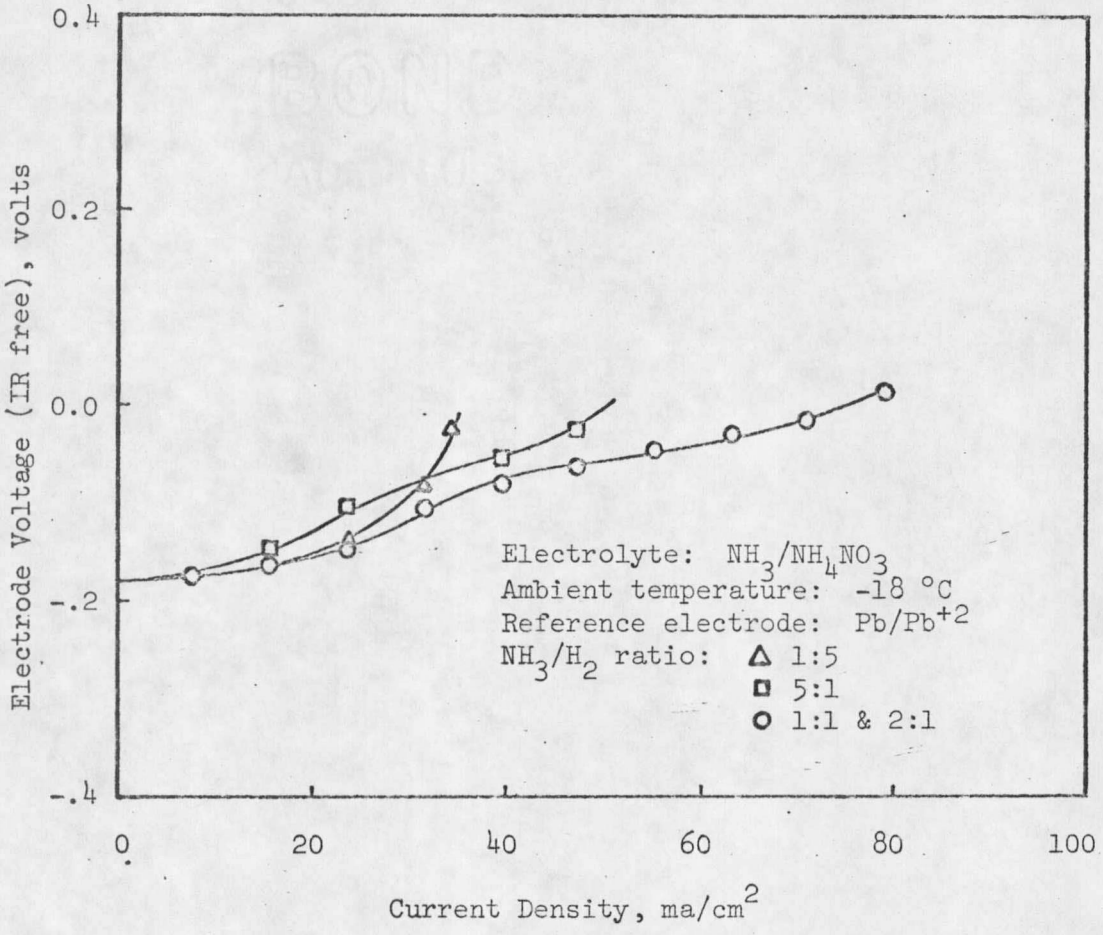


Figure 9. Hydrogen electrode polarization at different NH_3/H_2 ratios.

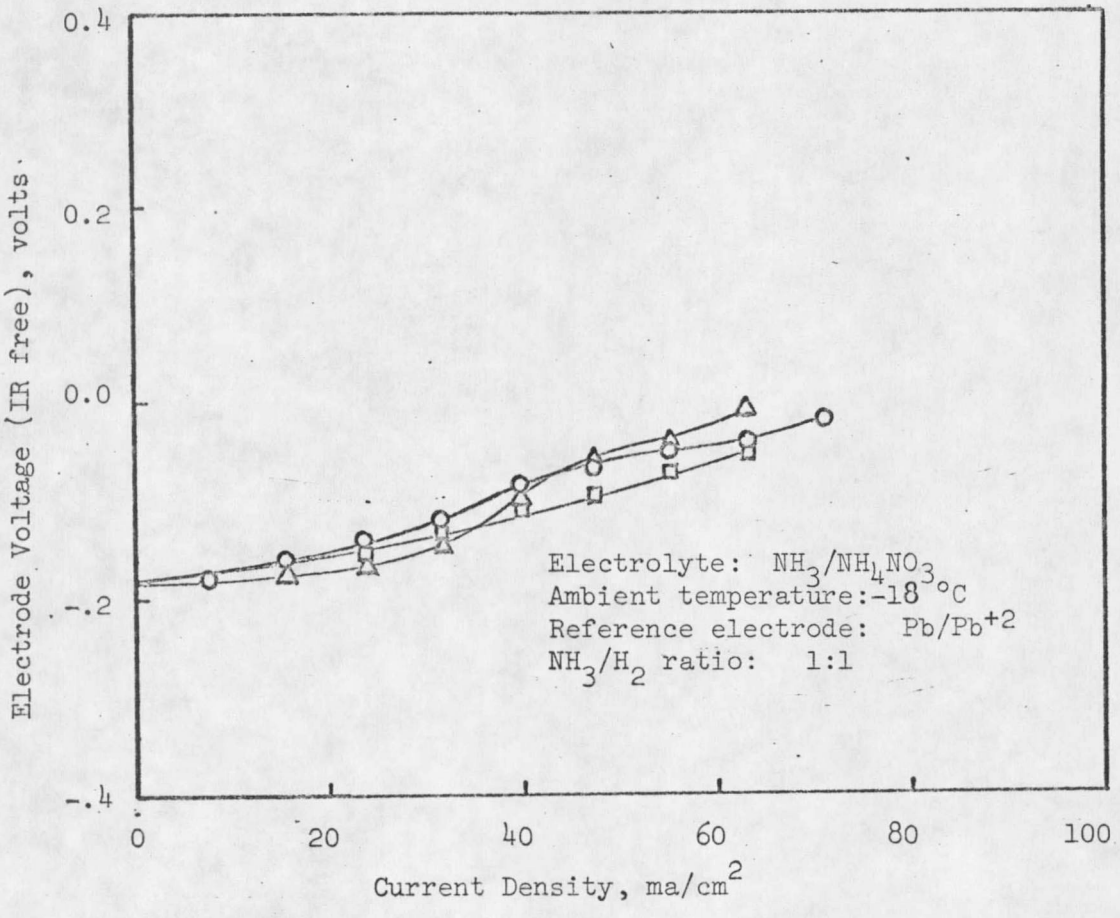


Figure 10. Hydrogen electrode polarization for different pieces of the same electrode material.

electrode. Note that there is a slight deviation in performance shown for different pieces of the same electrode material. The pore size and platinum loading for each piece of electrode material varied at different points on the electrode surface. Undoubtedly the variability of the electrode surface had much to do with the deviation in performance for different pieces of electrode. In other words, reproducibility of the polarization characteristics of this electrode material is well within the range of experimental error.

The performance of this commercial electrode material as an anode in a liquid ammonia electrolyte fuel cell is not too bad, although current densities attainable with this electrode material in aqueous systems are four to five times as great as those obtained here. There are a number of possible reasons for this poorer performance.

First of all, this commercial electrode material was designed and developed for use with aqueous electrolytes. There is a good chance that ammonia does not exhibit the same wetting characteristics with respect to this electrode material as does water.

In addition, the cold temperature (-18 °C) of operation may have had a deleterious effect on the catalytic powers of the platinum. It was difficult to obtain data for the cell at temperatures above -10 °C since boiling of the electrolyte occurred and performance was very unsteady. Thus the effect of temperature on cell performance could not accurately be measured by increasing the operating temperature. On the

other hand, it was possible to obtain polarization data for the cell at -55 °C by packing the cell in a dry ice atmosphere. Figure 11 compares the performance of the hydrogen electrode at operating temperature of -18 °C and -55 °C, with all other operating conditions fixed. Note that performance is much worse at -55 °C than at -18°C; this is undoubtedly due to the effect of extremely cold temperature on the catalytic powers of platinum. By analogy, we would say that performance is worse at -18 °C than it is at 25 °C because of a similar decrease in catalytic powers of platinum, although this is only speculation and no concrete data exists to back this statement.

2. Iodine electrode polarization:

It has already been noted that one of the problems to be solved in producing a liquid ammonia fuel cell was the development of a reproducible cathode that showed fairly good performance. Since the oxidizer(iodine) was dissolved in the electrolyte, it was felt that a porous flow-through type of electrode should be used. This was verified by obtaining polarization data for iodine reduction using shiny platinum foil as the cathode; the electrolyte with dissolved oxidizer was passed adjacent to the shiny platinum foil. From Figure 32 it can be seen that polarization was quite high at current densities above 1 ma/cm^2 with this cathode. Undoubtedly diffusion problems existed and there was a minimum of contact between electrode and oxidizer.

Cathode development: There has not been a great deal of developmental

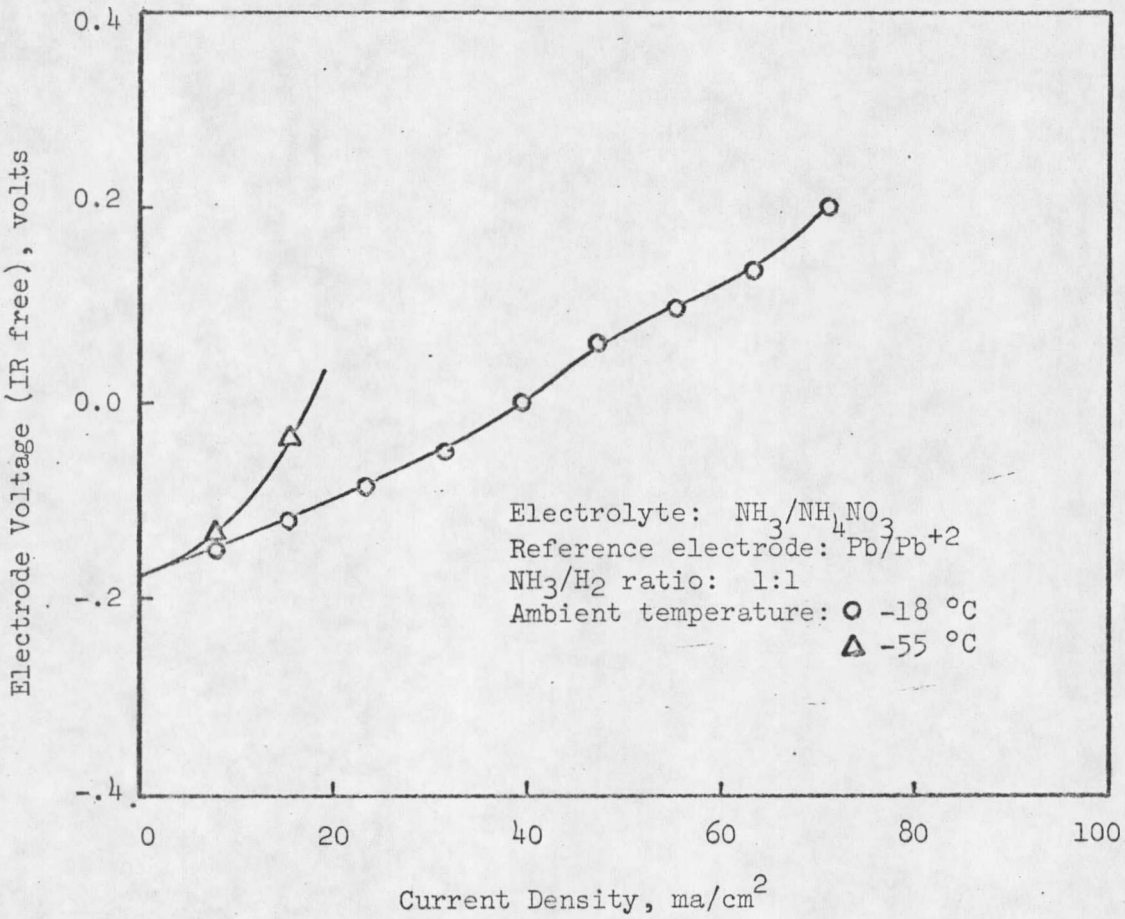


Figure 11. Hydrogen electrode polarization as a function of operating temperature.

work done on porous flow-through electrodes. Some investigations have been made using dissolved fuels in aqueous electrolytes (32), but little detailed information is available on the types of flow-through electrodes employed. Generally flow-through electrodes are of two types: (1) thin metallic screens (catalyzed or uncatalyzed), and (2) porous metals that contain pores that are small in diameter compared to electrode thickness (4).

If the flow-through electrode is composed of a metallic screen then the electrode area is not very much different from an equivalent solid, plane electrode. However, the flow of electrolyte through the screen cuts down the diffusion layer through which mass transfer limitations occur. Flow velocities with this type of electrode must be relatively high to minimize mass transfer effects and it is usually difficult to consume all of the reactant in one pass through the screen. On the other hand, in using porous metals the internal area of the electrode is very high and mass transfer to the walls of the pores is rapid due to the small distances involved (on the order of microns). Therefore it is theoretically possible to consume all of the reactant in one pass through the electrode.

The first step toward development of a flow-through electrode in this research program was to use some of the commercial porous platinum black anode material as the cathode. This material was certainly not designed for use as a flow-through electrode, and in fact, was designed

to prevent electrolyte from passing through it. Nevertheless, to gain experience with a flow-through design it was decided to go ahead and use this material as a cathode.

The polarization characteristics of this porous platinum black material as a flow-through electrode are presented in Figure 33. Polarization data from three individual test runs are presented in this figure (several tests were made); the data for each individual test run were obtained at identical operating conditions.

The immediate thing to note from this figure is the very poor reproducibility obtained using this electrode material as a cathode. No doubt this was due, at least in part, to the variability of the electrode surface. By holding this electrode material up to the light, one could detect a wide variation in electrode pore size. Thus with one electrode the pore size might be quite constant and flow through the electrode would be fairly uniform, giving good contact between electrode and oxidizer, and thus fairly good performance. On the other hand, if the electrode showed a variation in pore size, flow would not be uniform, and polarization would be higher because less electrode surface was used for reaction. Of course, even if this reproducibility problem did not exist with this electrode material, polarization was high enough that the electrode would have been rejected for use in the final cell design.

One other screen material was tried as the cathode in these studies. Figure 34 shows the polarization characteristics for iodine reduction at

a platinum-rhodium screen. Note that polarization was very high, although platinization of the screen improved the results to some extent. Even so, current densities attainable with this electrode were low enough so as to cause its rejection for use in the final cell design.

Since results obtained using screen materials as flow-through electrodes were poor, it was next decided to look at porous metals as a possible basis for cathode development. In referring to Table III it can be seen that 316 stainless steel was found to electrochemically reduce iodine at 0.8 volts with respect to the Pb/Pb^{+2} reference. This fact, coupled with the availability of porous stainless steel both as a thin rolled sheet material (much like tin foil) and as a thicker sintered material (> 1/32 of an inch thick), made this the logical first choice for study as a flow-through electrode.

Figure 35 shows iodine reduction using very thin (10-20 microns) porous stainless steel as the flow-through cathode. It can be seen that polarization was very high with the pure stainless steel, but that platinization of the stainless steel improved performance considerably. However, even with platinization of this electrode material, performance was poor and only low current densities were attained. The fact that this particular porous stainless steel material was so thin caused it to behave much like the metal screens discussed previously since there was no large internal electrode area for reaction to occur. However, the increased performance due to platinization of this electrode was

encouraging.

The final porous flow-through electrode used in these studies was developed by platinizing sintered porous stainless steel that was 1/16 of an inch thick. Performance was better for this type of electrode than for any other cathode material used; consequently it was chosen for use in the final cell design. Using this type of electrode a number of operating variables were studied and the effect of the variables on performance is reported in the following sections.

Effect of platinum loading: Figure 12 shows polarization data for iodine reduction at a porous stainless steel electrode using different platinum loadings but with all other operating variables fixed. Note first of all that polarization for a stainless steel electrode with no platinum loading is high. As expected, the platinization of the electrode increases performance considerably because of the increased surface area for electrochemical reaction.

There is no appreciable difference in the polarization data obtained with the two electrodes of lowest platinum loading (0.5 and 4.0 mg/cm^2). The reader should be reminded at this point that the polarization data presented here were obtained over short periods of time, i.e., the potential reading at each current setting was maintained for only 4-5 minutes before going on to the next current setting. Thus, even though the two electrodes with the lowest platinum loadings showed nearly identical performance (Figure 12), this does not mean that their

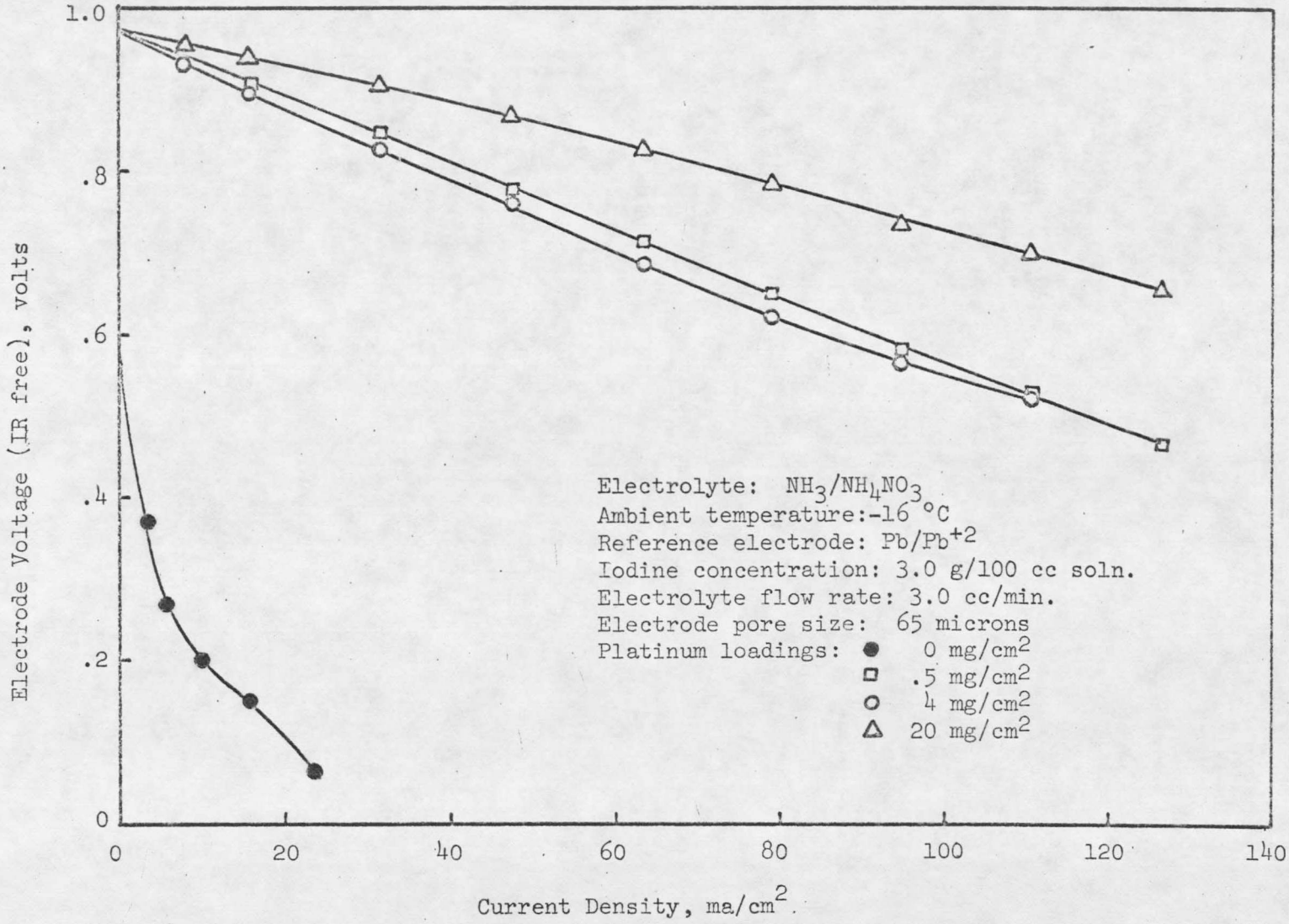


Figure 12. Iodine electrode polarization at different platinum loadings.

performance will be the same over extended periods of time.

It can also be seen from Figure 12 that a platinum loading of 20 mg/cm^2 results in improved performance over the other two platinum loadings. At the high platinum loading the electrode polarization was 0.25 volts at 100 ma/cm^2, although this again was only short time data.

Effect of electrode pore size: Figure 13 shows polarization data for iodine reduction with a platinized stainless steel electrode as a function of electrode pore size; platinum loading was 4.0 mg/cm^2 and all other operating variables were fixed. It can be seen that, as pore size of the electrode is decreased, the polarization of the electrode likewise decreases, although the two largest pore sizes used showed little difference in performance. It seems logical that electrode performance should increase with a decrease in pore size since mass transfer to the electrode walls is speeded up due to the small distances involved. Of course, as the electrode pore size is decreased, the pressure drop across the electrode increases, although this had no noticeable effect in these studies.

Effect of iodine concentration: To measure the effect of iodine concentration on iodine electrode performance, three different iodine concentrations were arbitrarily chosen for study (1.0, 2.0, and 3.0 grams of iodine/100 cc of solution). Solubility data for iodine in ammonia could not be found in the literature, but saturation was rapidly approached when an attempt was made to dissolve 4.0 grams of iodine in

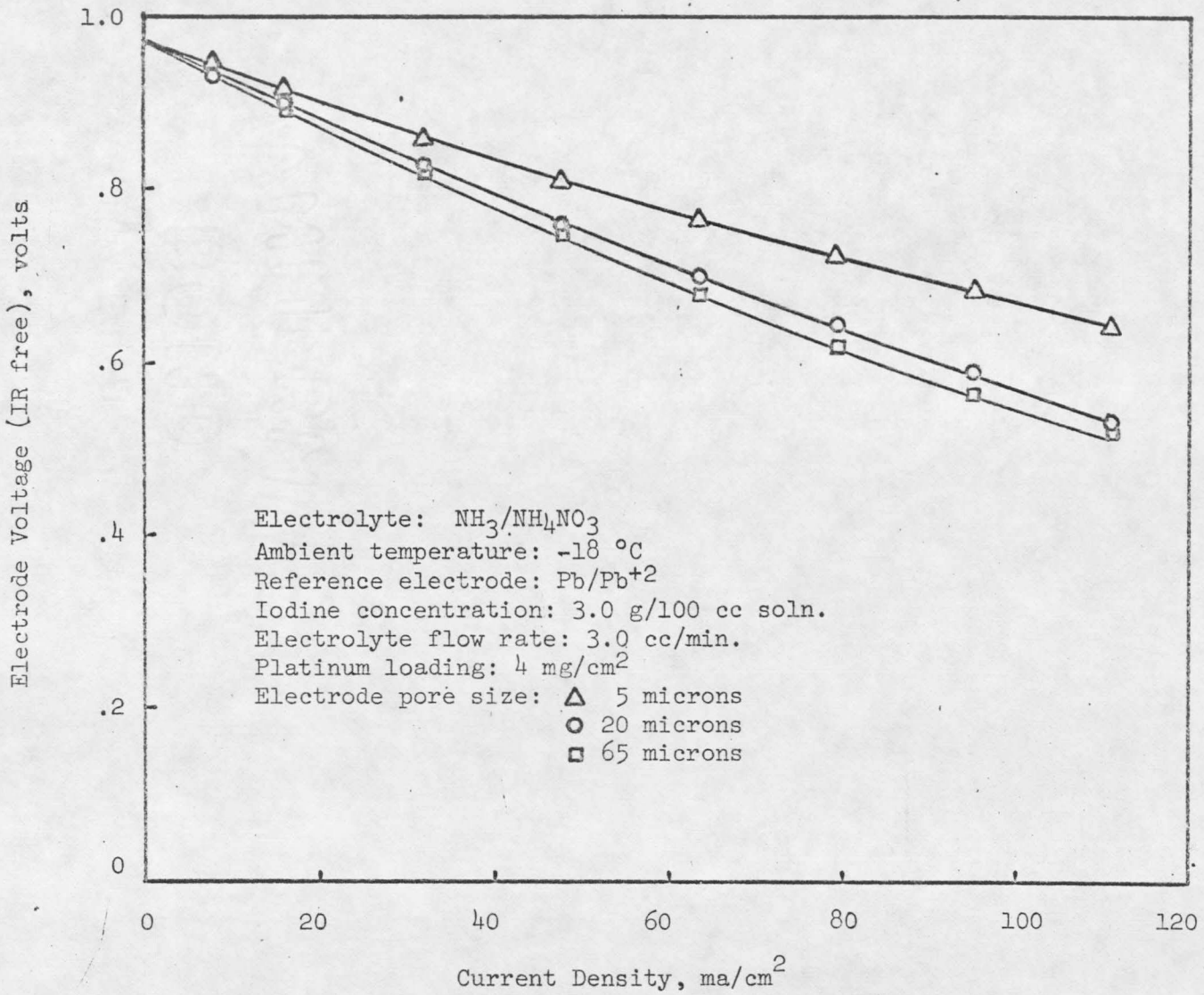


Figure 13. Iodine electrode polarization as a function of electrode pore size.

100 cc of solution at about -10 °C. Figure 14 shows the effect of iodine concentration on the iodine electrode with all other variables fixed, including platinum loading and electrode pore size. At low current densities there is no appreciable difference in performance with change in iodine concentration, but as current density is increased above 30 ma/cm^2 polarization increases with decreased iodine concentration. This is to be expected since the amount of iodine available at the electrode surface decreases with a decrease in iodine concentration (all other variables being constant), and is no doubt less than the theoretical amount necessary to sustain higher current densities (concentration polarization).

Effect of electrolyte flow rate: Figure 15 shows the effect of electrolyte flow rate on iodine electrode polarization with all operating variables fixed. At low current densities there is little change in electrode polarization with flow rate, but as current density is raised it can be seen that polarization increases with a decrease in flow rate. This again is due to concentration polarization, i.e., not enough iodine is reaching the electrode surface to sustain electrochemical reaction.

The ideal situation using this type of electrode material is to have complete reaction of the oxidant in one pass through the electrode. No attempt was made in these studies to attain this optimum situation. To achieve complete reaction of the iodine in one pass through the electrode it is first necessary to know the current to be drawn from

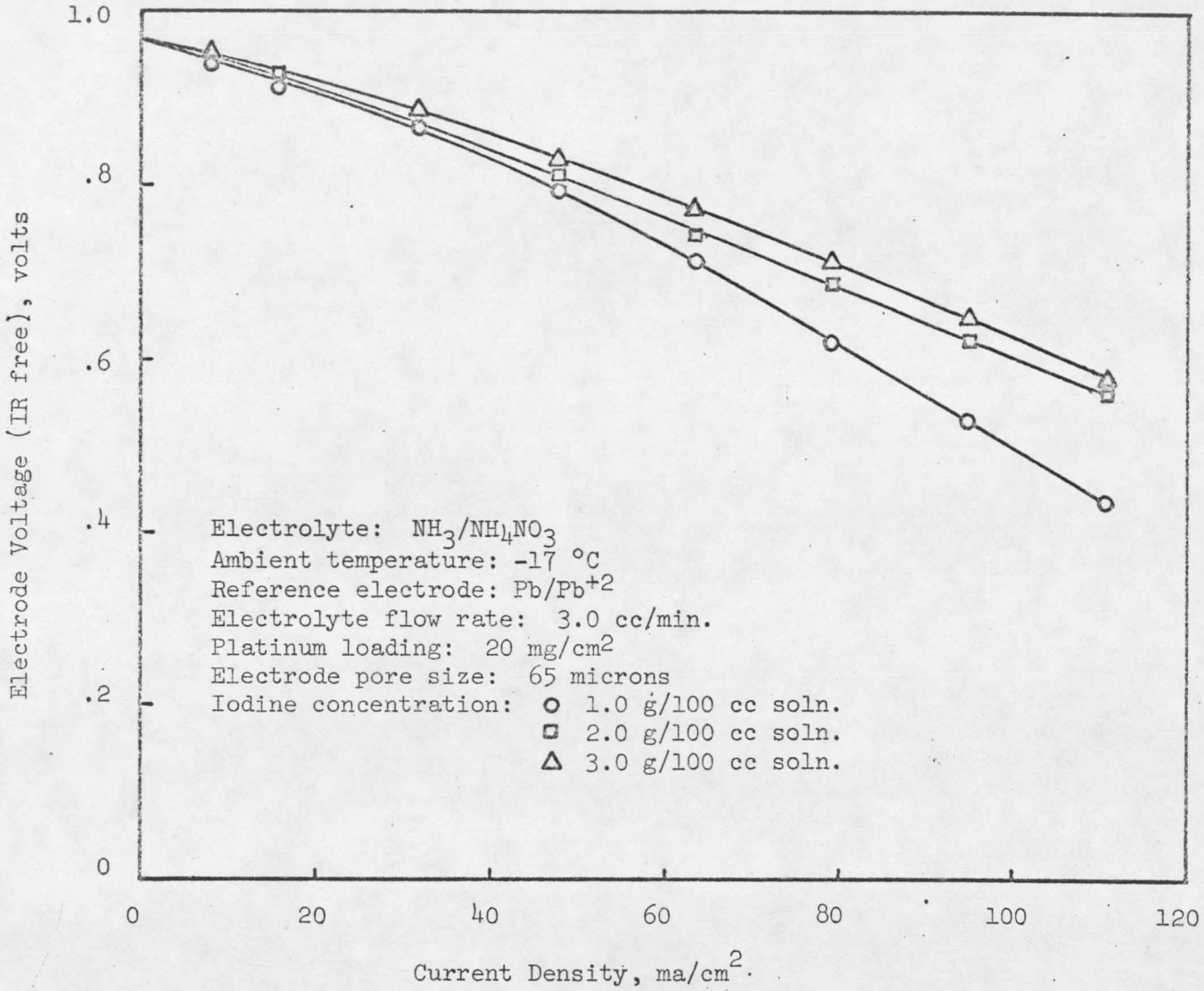


Figure 14. Iodine electrode polarization as a function of iodine concentration.

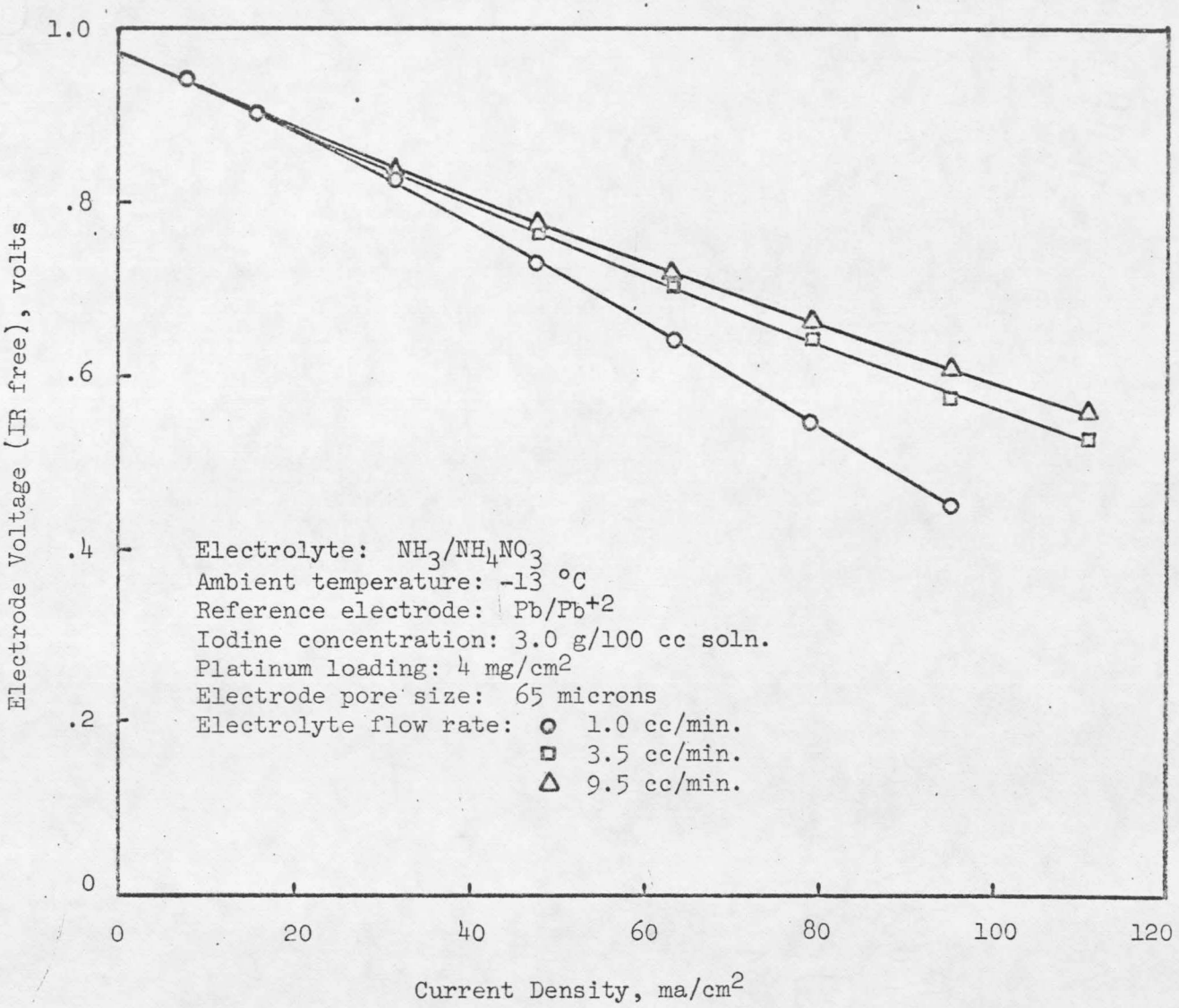


Figure 15. Iodine electrode polarization as a function of electrolyte flow rate.

the cell. It is then possible to calculate the rate at which iodine must reach the electrode surface to sustain such a current. The rate at which iodine reaches the electrode surface is a function of the two variables just discussed, i.e., iodine concentration and electrolyte flow rate. Thus once the flow rate and current were fixed, it would be simple to calculate the theoretical iodine concentration required to sustain electrochemical reaction. In any event, the effect of iodine concentration and electrolyte flow rate are interrelated and behavior of the electrode with respect to these two variables is as expected.

Effect of operating temperature: The objective of this research program was to develop a fuel cell that would operate at cold temperatures. Most studies were made between -15 to -22 °C since this was as cold as the chest freezer which contained the apparatus could be operated. To measure the effect of very cold temperature on iodine electrode performance, the cell was packed in a dry ice atmosphere such that the temperature was -55 °C. Electrolyte was fed to the cell and a black gummy mixture was emitted at the cell outlet. According to Ruff (37), at -60 °C iodine and ammonia form a black powder which slowly dissolves to a yellow solution; if enough iodine is added, $NI_3 \cdot 12NH_3$ separates. Thus results of this cold temperature study were inconclusive and no further attempt was made to operate at extremely cold temperatures because of the added problems involved.

Reproducibility of results: The reader will recall that one of the

problems with the porous platinum black electrode material which was used as a flow-through cathode was that electrode performance was not reproducible. To measure the reproducibility of the porous stainless steel electrodes being used in the final cell design, a number of electrodes of identical pore size and platinum loading were made and tested. Figures 36-38 show the degree of reproducibility of these electrodes with respect to electrode polarization; each figure compares initial results for different electrodes. From these three figures it can be seen that initial performance of these stainless steel electrodes is highly reproducible and well within the range of experimental error. This high degree of reproducibility is due, at least in part, to uniform pore size over the entire electrode surface; thus electrolyte flow through the electrode is very uniform, even for different electrode pieces.

Degradation of electrode performance after initial usage: Many of the platinized stainless steel electrodes developed in this study were used more than once in obtaining polarization data. After each usage the electrode was washed with water, soaked in water for several hours to remove salts which might have precipitated in the electrode interior, and then washed again and stored in water until needed for further study. Without exception, electrodes which were used more than once exhibited a degradation of performance with each successive usage. This fact is verified by Figures 39-43 which show performance degradation for a number of electrodes of different pore size and different platinum

loading. Note that each subsequent electrode usage shows poorer performance (higher polarization).

There were two possible explanations for this performance degradation which occurred. First of all, it was possible that there was some trace impurity in the ammonia solutions being used that was poisoning the platinum catalyst, although electrodes exhibited no weight change after being used in the cell. Secondly, it was possible that storage of the electrodes in tap water between test runs was causing a poisoning of the electrode.

To determine whether or not these electrodes were deteriorating during use in the cell, a series of extended studies on the cell were undertaken in order to monitor electrode performance as a function of time. The results of these extended test runs are reported in the next section on life studies.

3. Life studies:

It has been noted previously that the bulk of the polarization data obtained in this research program was obtained over short periods of time, i.e., potentials were held constant only 4-5 minutes at each current setting. Consequently there was little indication as to how the electrodes used in this cell would hold up over extended time periods. It has just been noted in the previous section that the platinized stainless steel electrodes developed in this study showed a decrease in performance with each subsequent usage. On the other hand, the

porous platinum black hydrogen electrode could be used several times for short studies with little or no change in performance. To determine the life of the electrodes used in this liquid ammonia cell, a number of life studies were made.

The first study (Run LS-1) was made using the cell configuration which has been used all along. Cell current density was fixed at 30 ma/cm^2 using a D.C. power supply and the resulting voltage of each electrode (with respect to Pb/Pb^{+2}) was recorded as a function of time. For all life studies made the anode was porous platinum black on tantalum screen and the cathode was platinized stainless steel (20 micron pore size, 4 mg/cm^2 platinum loading). The current density, iodine concentration, and electrolyte flow rates used were such that an excess of iodine was present at the cathode at all times for electrochemical reaction. Each batch of electrolyte was passed through the cell twice in this initial study by manually transferring it from the outlet reservoir to the inlet reservoir. The results of this first life study on the cell are shown in Figure 16.

It can be seen from Figure 16 that performance of both electrodes was fairly good for the first six hours of the run; there was little decrease in the voltage of either electrode at constant current operation. Beyond six hours of operation the two electrode voltages began to steadily converge. Concurrent with this increase in polarization at each electrode there was a decrease in electrolyte flow

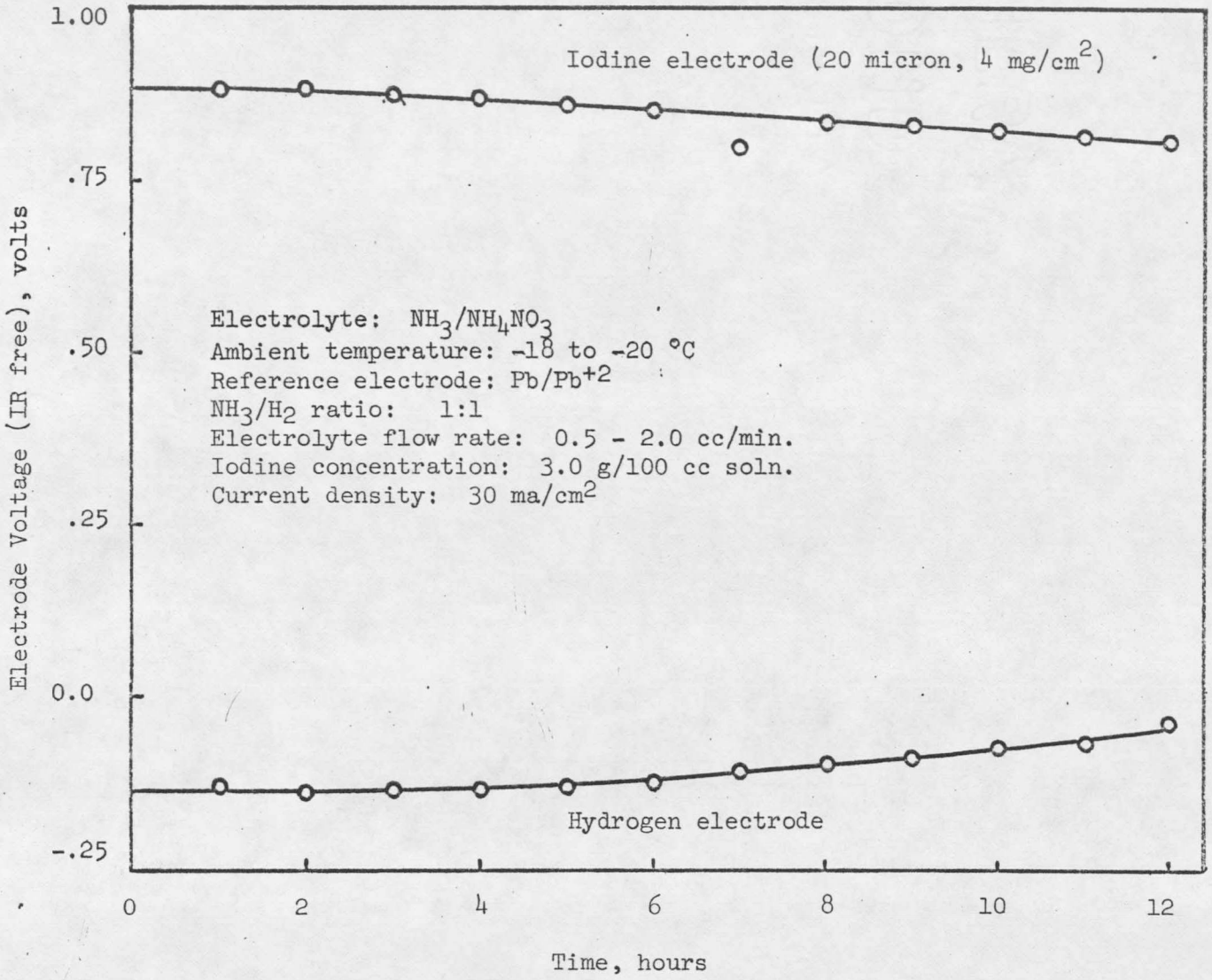


Figure 16. Electrode voltage as a function of time at constant current operation (Run LS-1).

through the cell. Continued decrease in electrolyte flow and cell voltage led to termination of this run after twelve hours of operation.

Upon taking the cell apart it was found that a fairly large amount of impurity had built up on the inlet side of the porous stainless steel cathode. Since the impurity had built up on the inlet side of the electrode, it was felt that it had probably come from the electrolyte, i.e., the electrode was acting as a filter by removing impurities from the electrolyte. If the impurity was a reaction product, it would probably have built up on both sides of the flow-through electrode. In any event, enough impurity had collected to completely prohibit flow through the electrode.

The cell was modified slightly before the next life studies were made. To minimize IR drop (ohmic polarization) across the electrolyte the space between the electrodes was decreased to 3/32 of an inch and the reference electrode was eliminated. Then two more life studies were made, though no steps were yet taken to eliminate the problem of electrode plugging.

Figures 17 and 18 show the results of these two life studies, which were designated as runs LS-2 and LS-3. Operating conditions for these runs were the same as those used in run LS-1. Run LS-2 (Figure 17) was made using newly constructed electrodes and was terminated after 22 hours of operation due to very low electrolyte flow rate and plugging of the cathode. For this run the electrolyte was manually circulated as

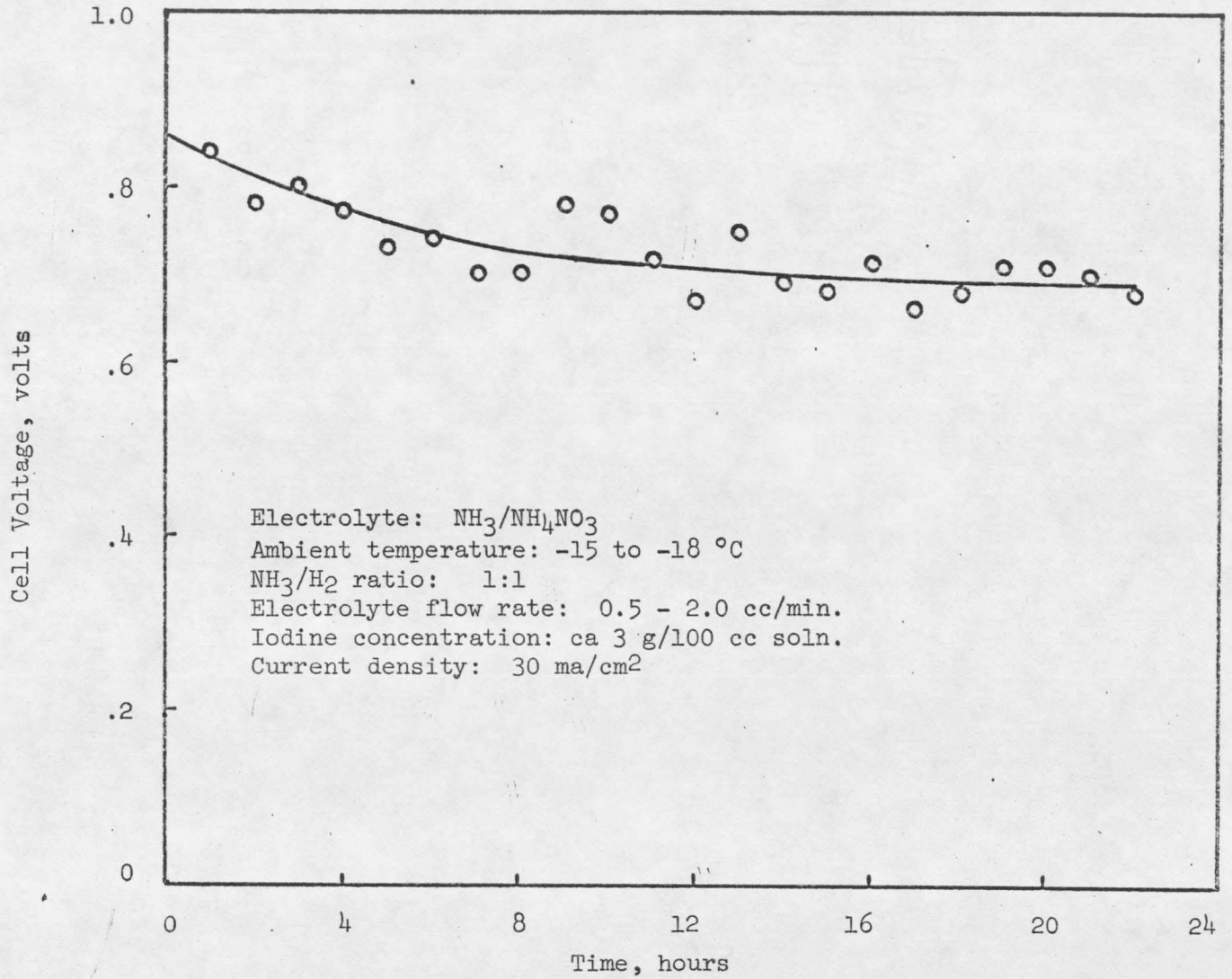


Figure 17. Fuel cell voltage as a function of time at constant current operation (Run LS-2).

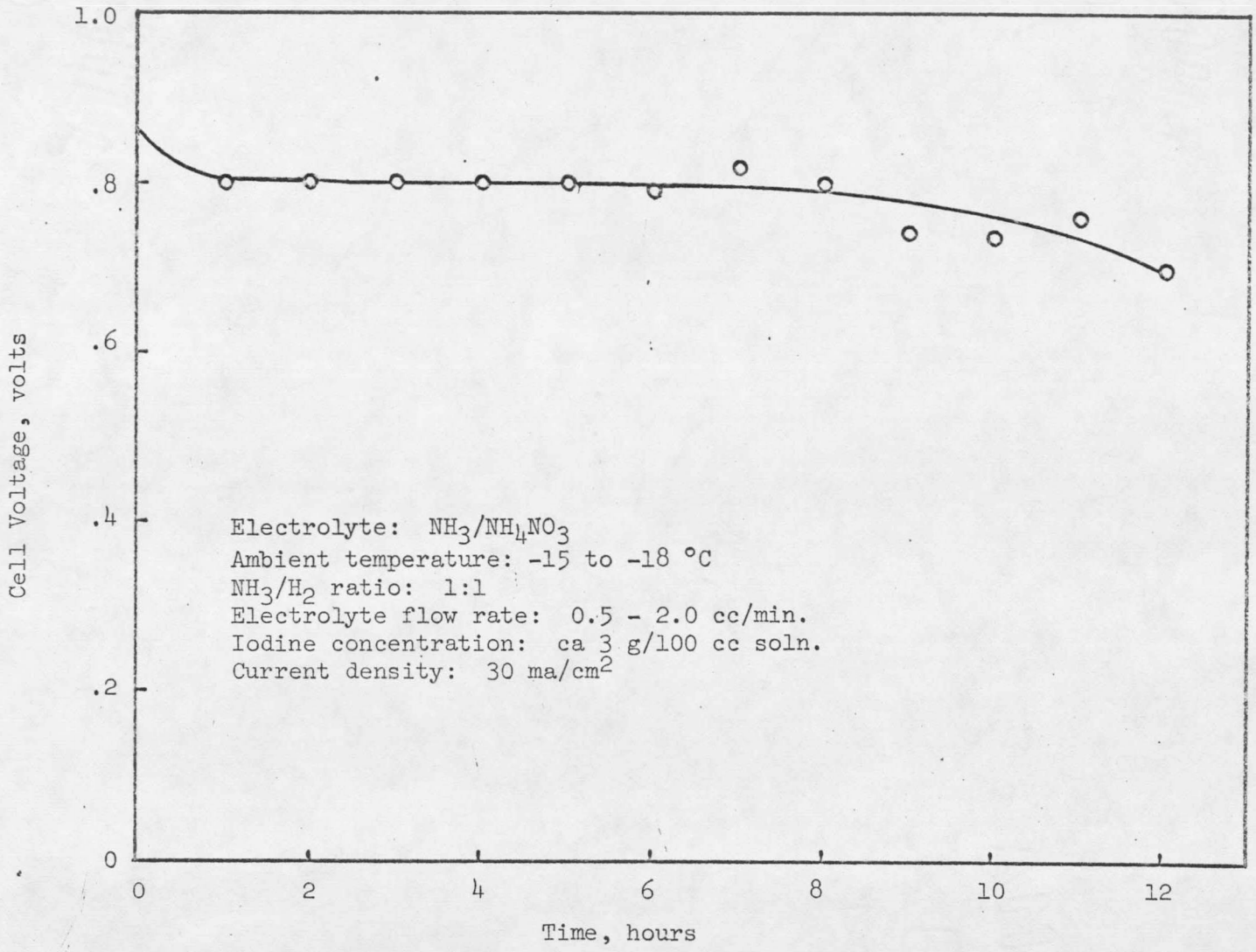


Figure 18. Fuel cell voltage as a function of time at constant current operation (Run LS-3).

in run LS-1. For run LS-3 (Figure 18) fresh electrolyte was continually fed to the cell in an attempt to eliminate the plugging problem, since it was felt that the circulated electrolyte might be adding reaction product impurities to the feed reservoir. However, the cathode became plugged again and the run was terminated after twelve hours.

The unsteady behavior observed in these two runs made it difficult to determine just how much the electrodes were deteriorating (if at all), but there was no radical change in cell performance. It appeared that decrease in performance of the cell was due to the plugging of the cathode rather than a deterioration of the electrodes.

In an attempt to eliminate the problem of plugging of the flow-through cathode, a glass fiber filter was installed in the electrolyte feed line in order to remove impurities from the electrolyte before it entered the cell. Then run LS-4 (Figure 19) was made using two electrodes which had been briefly used in a previous study. During this particular run the electrolyte was passed through the cell only once and then discarded; the filter was periodically changed whenever the electrolyte flow rate began to decrease. It was found that the filter did indeed remove impurities from the electrolyte and that plugging of the filter (rather than the flow-through electrode as in previous runs) caused the flow to be variable. Identifiable impurities removed by the filter included small undissolved iodine particles and what appeared to be rust,

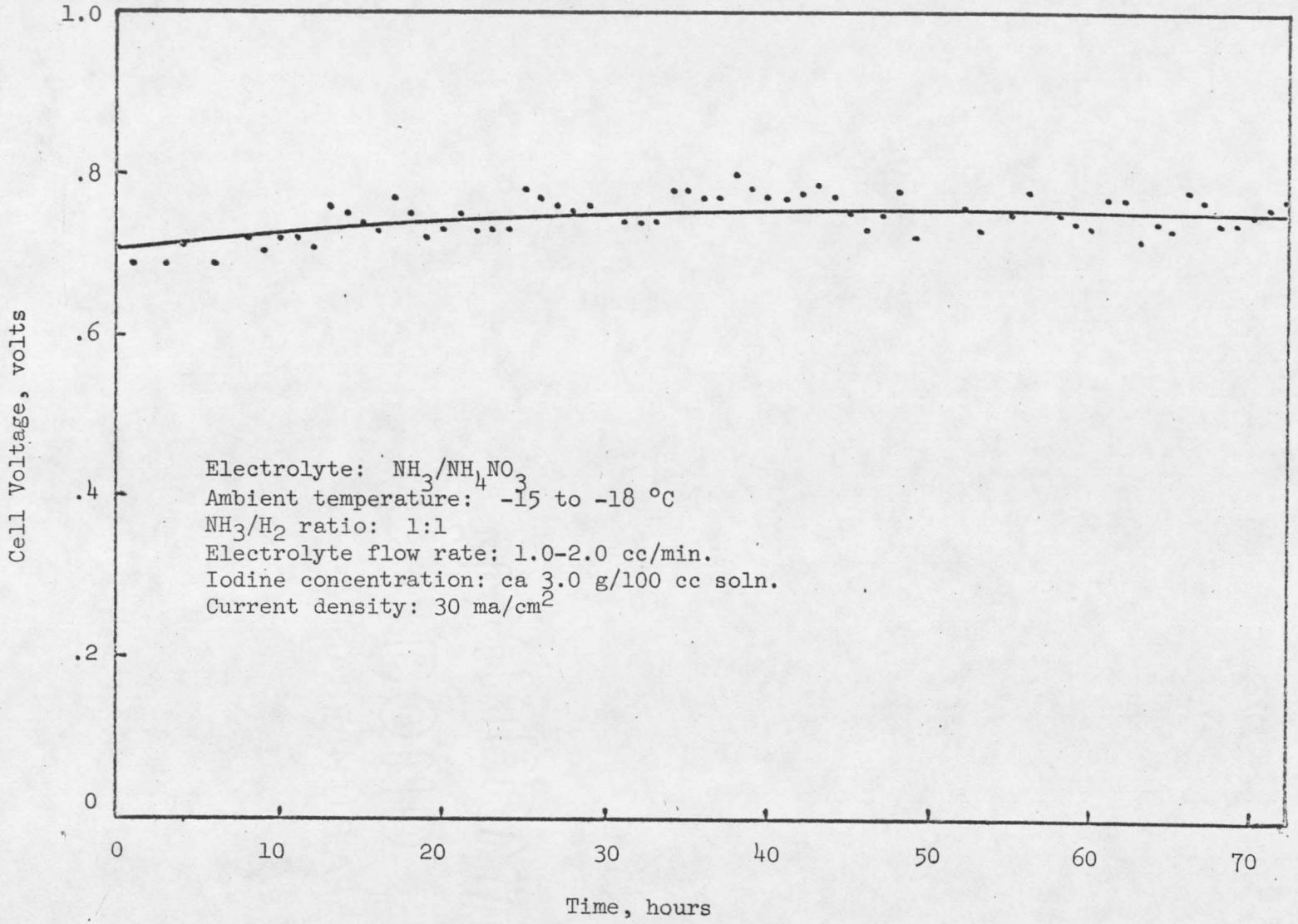


Figure 19. Fuel cell voltage as a function of time at constant current operation (Run LS-4).

apparently from the ammonia cylinder.

The cell was operated continuously at constant current before the run was terminated at 72 hours. Cell voltage was low initially, perhaps due to previous usage of the cathode, but showed some increase with time before reaching a plateau at about 0.75 volts. The considerable scatter of data shown in Figure 19 is undoubtedly due to the variability of electrolyte flow. As the filter became plugged, flow rate of electrolyte would decrease and cell voltage would drop. When a new filter was installed, flow rate would return to normal, and cell voltage would show an increase. In any event, there was no radical decrease in cell voltage over the 72 hour period, indicating that the electrodes were holding up quite well. Apparently the degradation of performance shown by the stainless steel electrodes in short time studies (Figures 39-43) was due to storing of the electrodes in water between runs rather than use of the electrodes in the cell.

When the cell was taken apart there was no visible impurity built up on the cathode, confirming that previous electrode plugging was due to electrolyte impurities rather than reaction products.

V. CONCLUSIONS

1. The operation of a fuel cell at temperatures down to -20 °C using a liquid ammonia solution (NH_3/NH_4NO_3) as the electrolyte is indeed possible. For such a fuel cell hydrogen works well as the fuel, while iodine dissolved in the electrolyte works adequately as the oxidizer.

2. A commercial porous platinum black electrode material (American Cyanamid Company) works adequately as the anode material for hydrogen oxidation with a liquid ammonia electrolyte; electrochemical performance with this electrode material is reproducible.

3. Gaseous ammonia must be added with the hydrogen fuel in the fuel stream to prevent very high electrode polarization even at low current densities. Hydrogen electrode polarization is high at extreme NH_3/H_2 ratios and is at a minimum at NH_3/H_2 ratios near 1:1.

4. Hydrogen electrode polarization increases as the temperature of operation of the cell is decreased.

5. Platinized porous stainless steel shows fair performance as a cathode for iodine reduction using a liquid ammonia electrolyte. This electrode material exhibits reproducible initial performance but shows a degradation of performance for each subsequent usage regardless of platinum loading or electrode pore size. Degradation of performance does not occur while the electrode is being used in the cell, however.

6. Polarization of the platinized stainless steel electrode material decreases as the platinum loading of the electrode is increased and as the electrode pore size is decreased.

7. Iodine concentration and electrolyte flow rate determine the amount of iodine which is available at the cathode per unit time for electrochemical reaction. These variables affect electrode performance (polarization) only if a shortage of iodine exists at the electrode for maintaining the current density being drawn from the cell.

8. The fuel cell developed in this research can be operated for at least 72 hours at 30 ma/cm^2 and 0.75 volts with no apparent electrode deterioration.

VI. APPENDIX

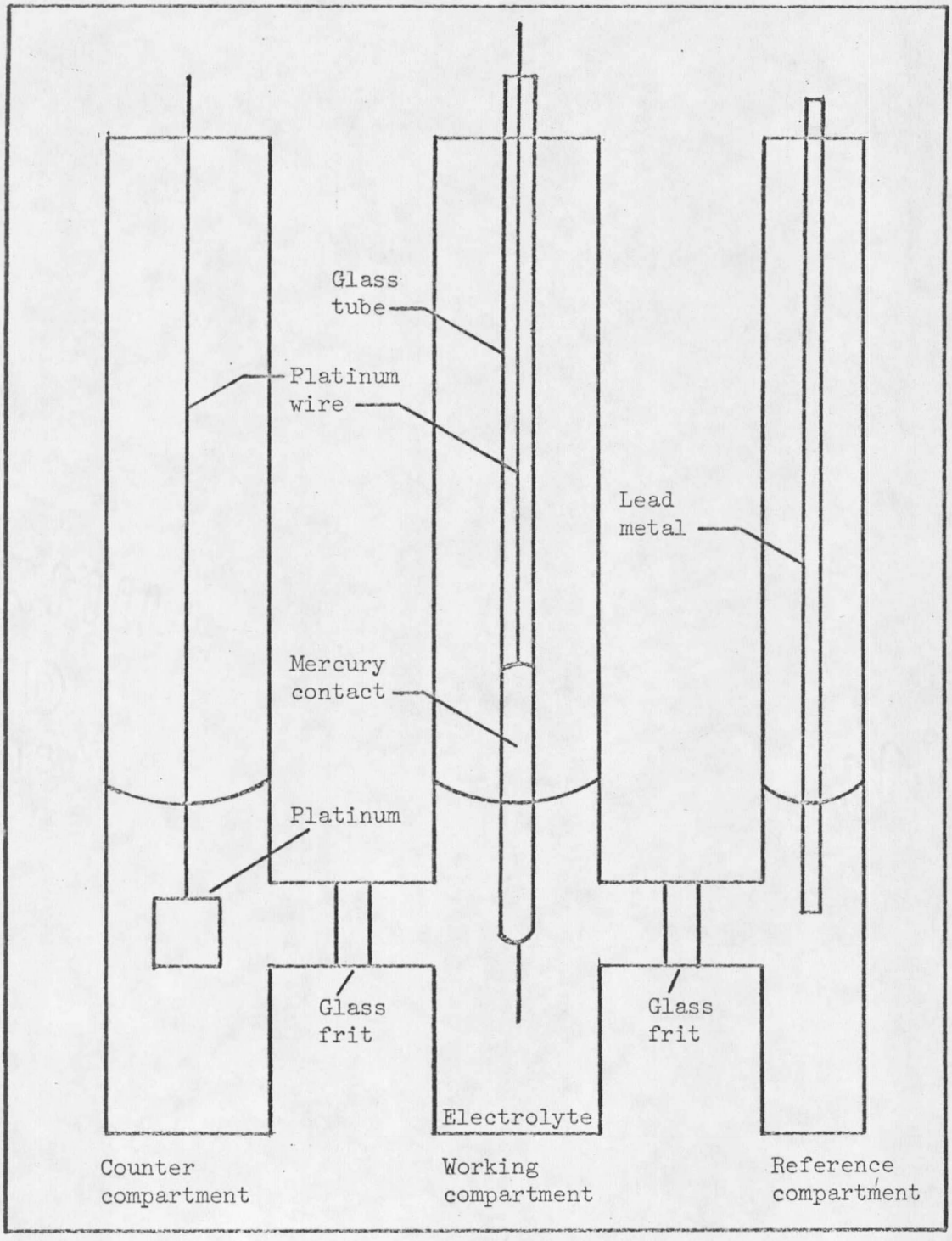
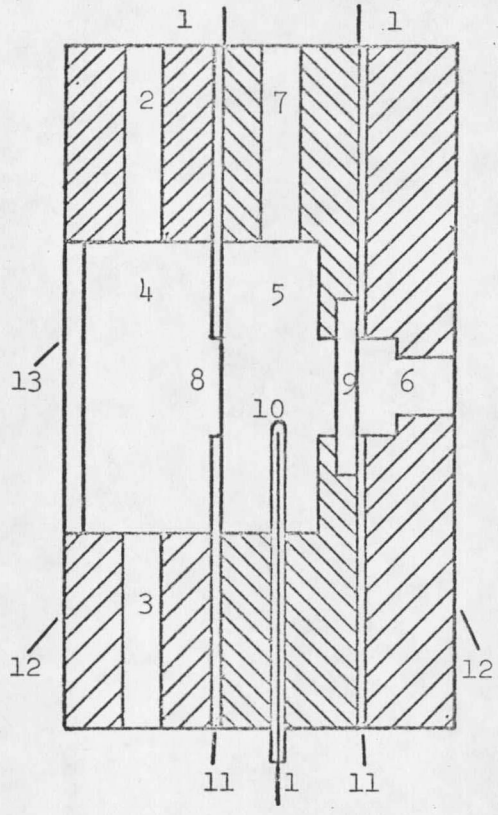


Figure 20. Three compartment glass cell for voltammetric studies (approximate size).



1. Electrode leads
2. Fuel inlet
3. Fuel outlet
4. Fuel compartment
5. Electrolyte compartment
6. Electrolyte inlet
7. Electrolyte outlet
8. Porous anode
9. Porous cathode
10. Reference electrode
11. Silicone rubber gasketing
12. Polypropylene cell module
13. Anode viewing window

Figure 21. Cross-sectional view of liquid ammonia fuel cell.

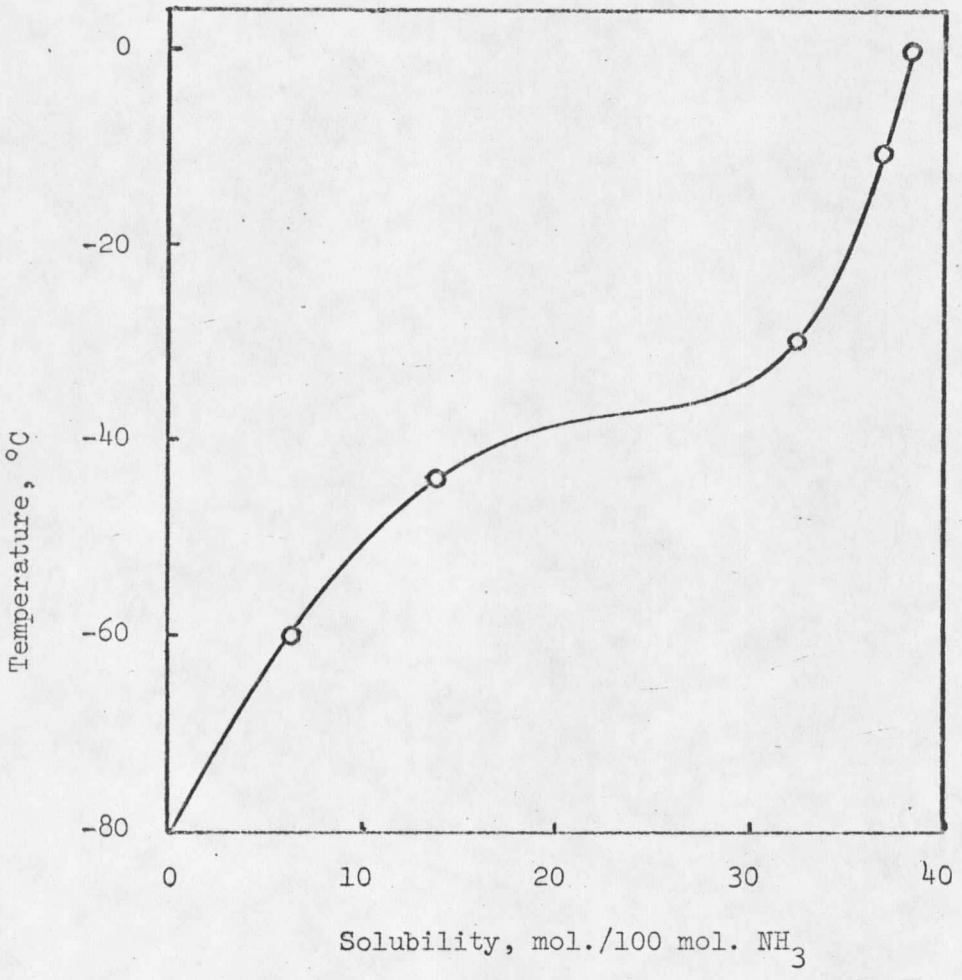


Figure 22. Solubility of ammonium nitrate in ammonia (38).

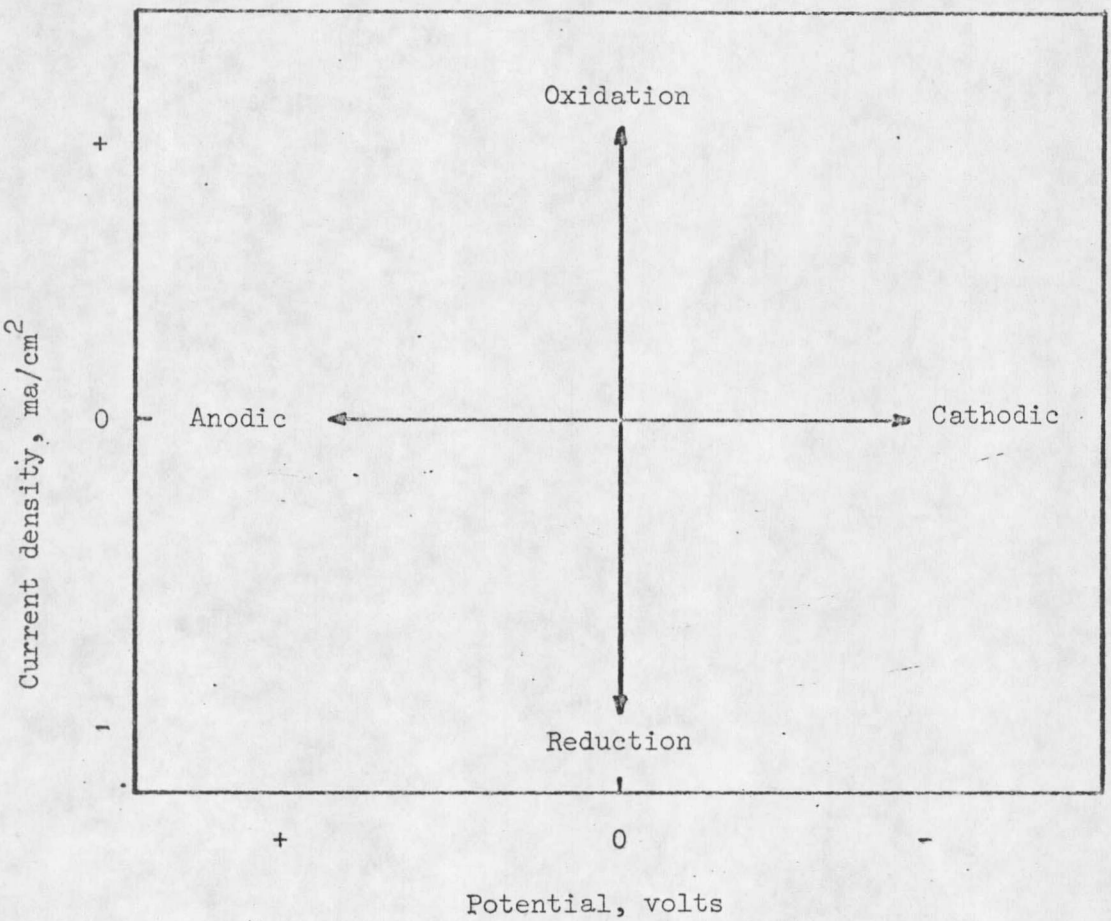


Figure 23. Convention used in obtaining voltammetric data.

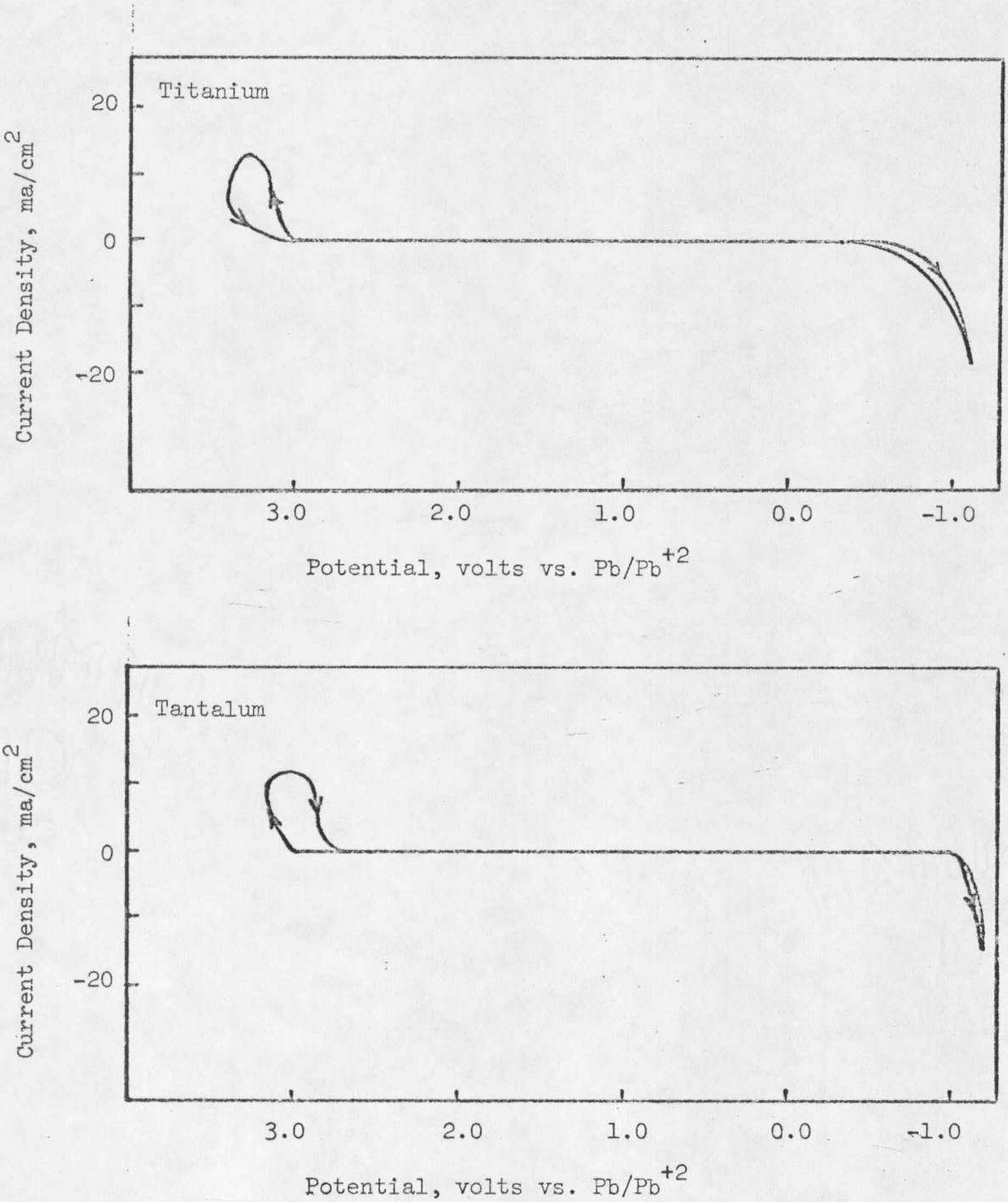


Figure 24. Cyclic voltammetric scans for titanium and tantalum.

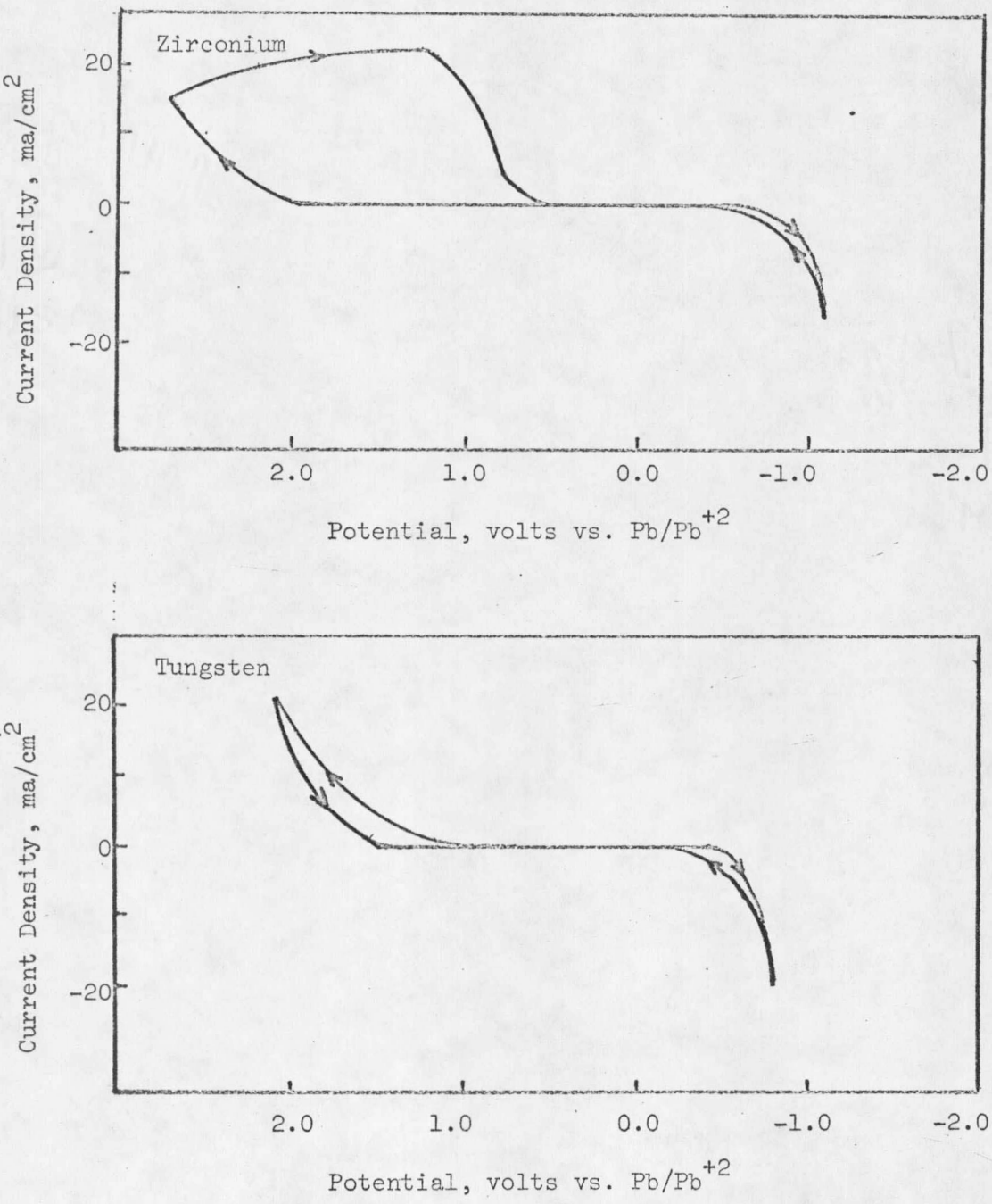


Figure 25. Cyclic voltammetric scans for zirconium and tungsten.

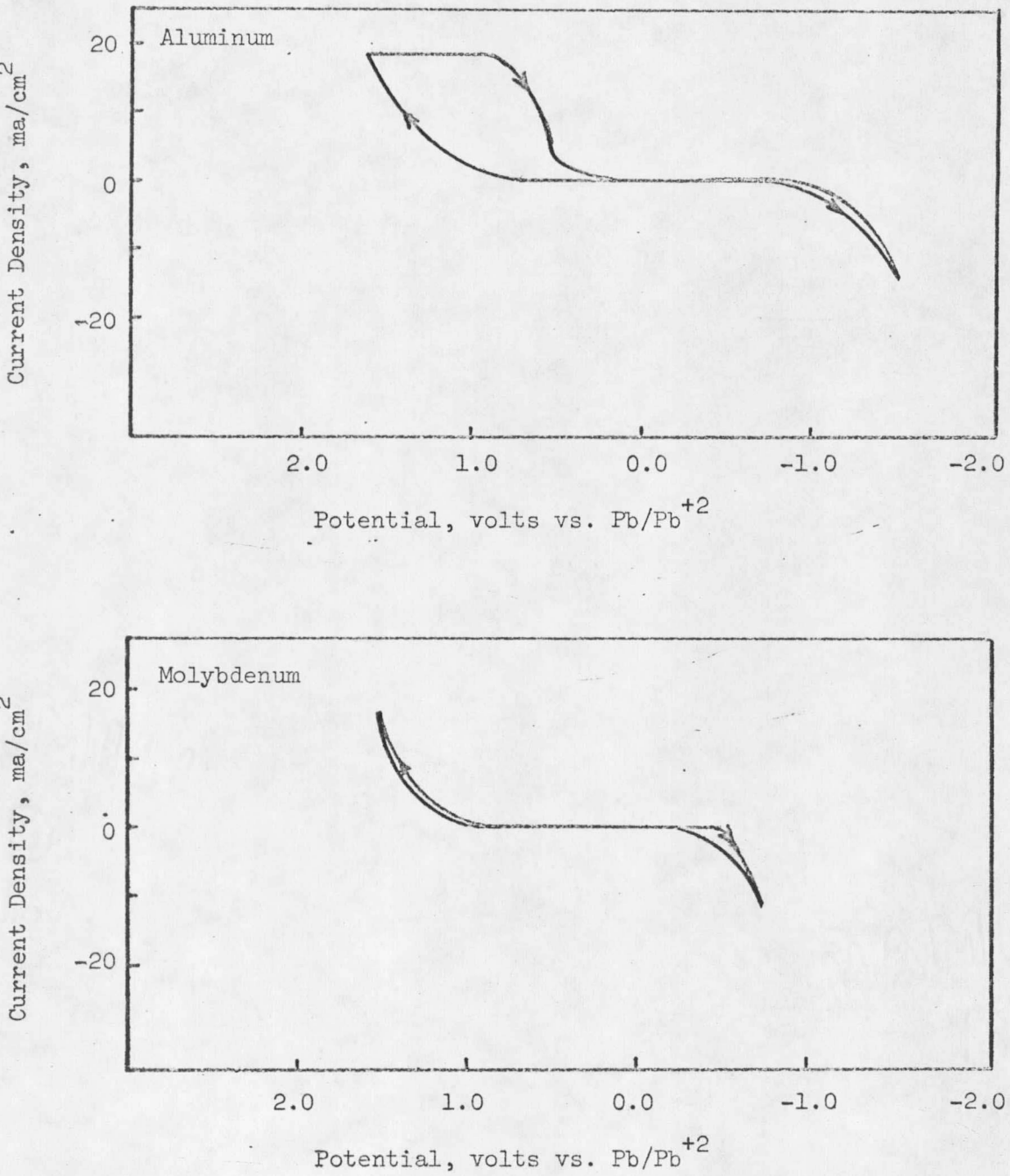


Figure 26. Cyclic voltammetric scans for aluminum and molybdenum.

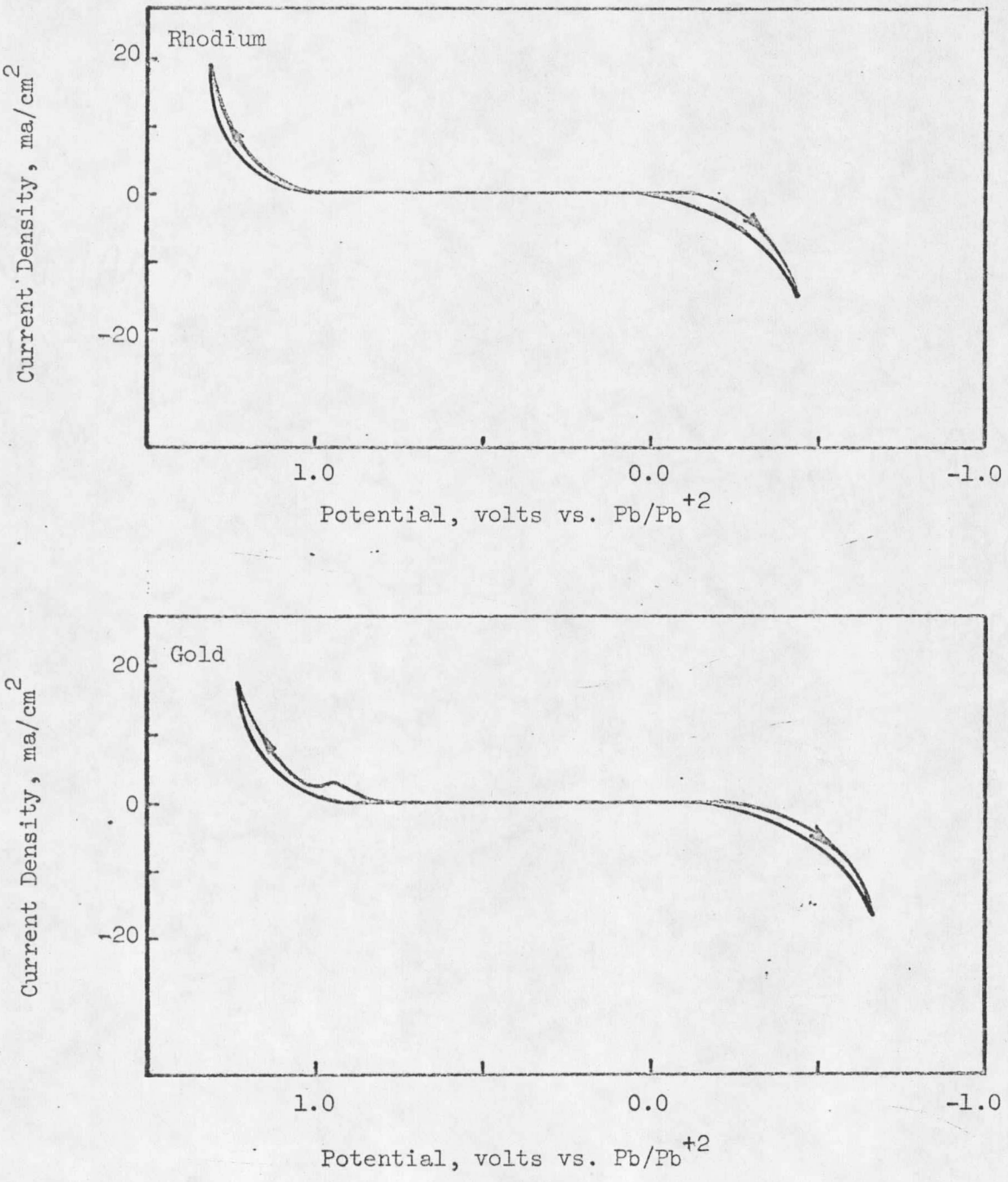


Figure 27. Cyclic voltammetric scans for rhodium and gold.

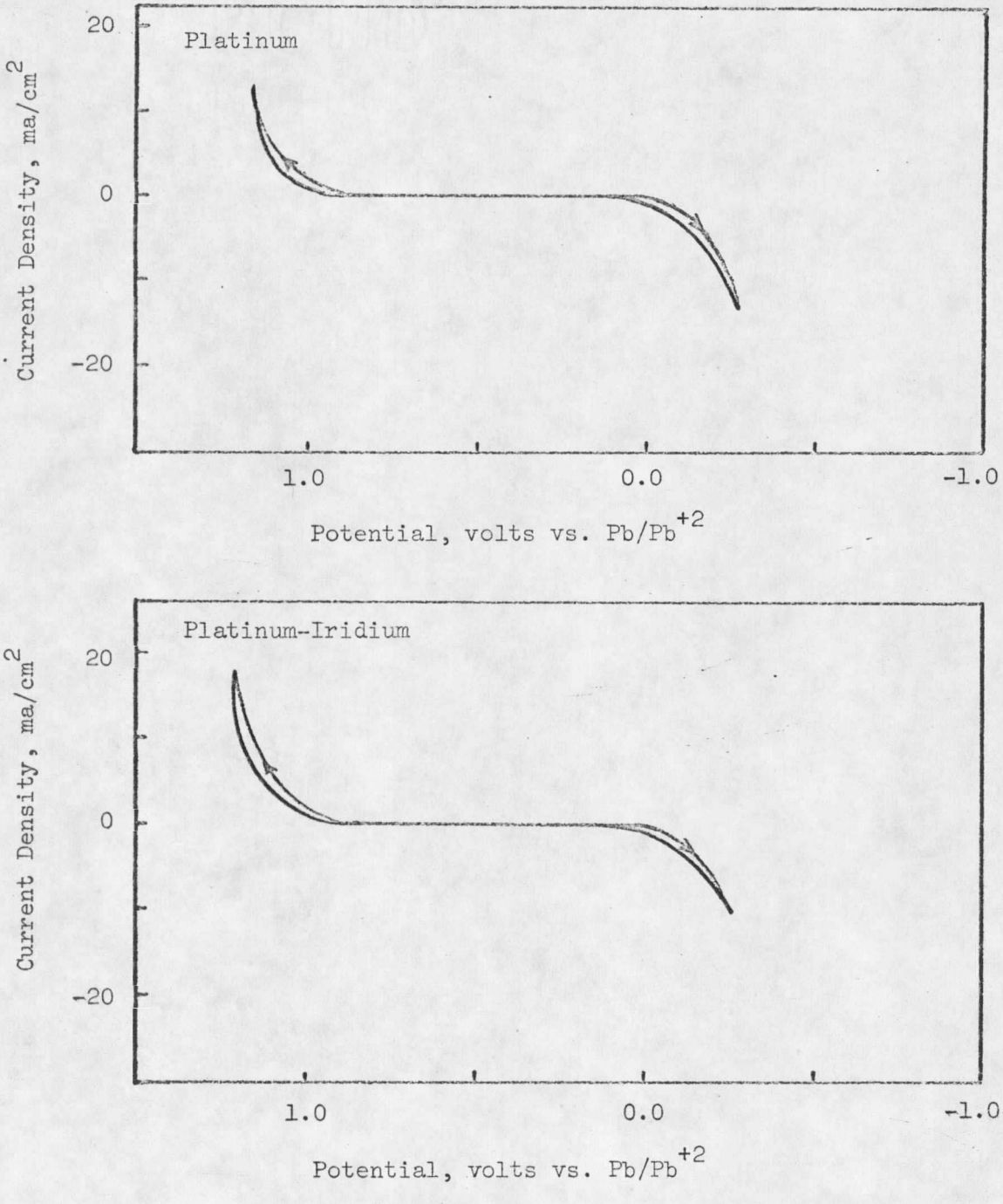


Figure 28. Cyclic voltammetric scans for platinum and platinum-iridium.

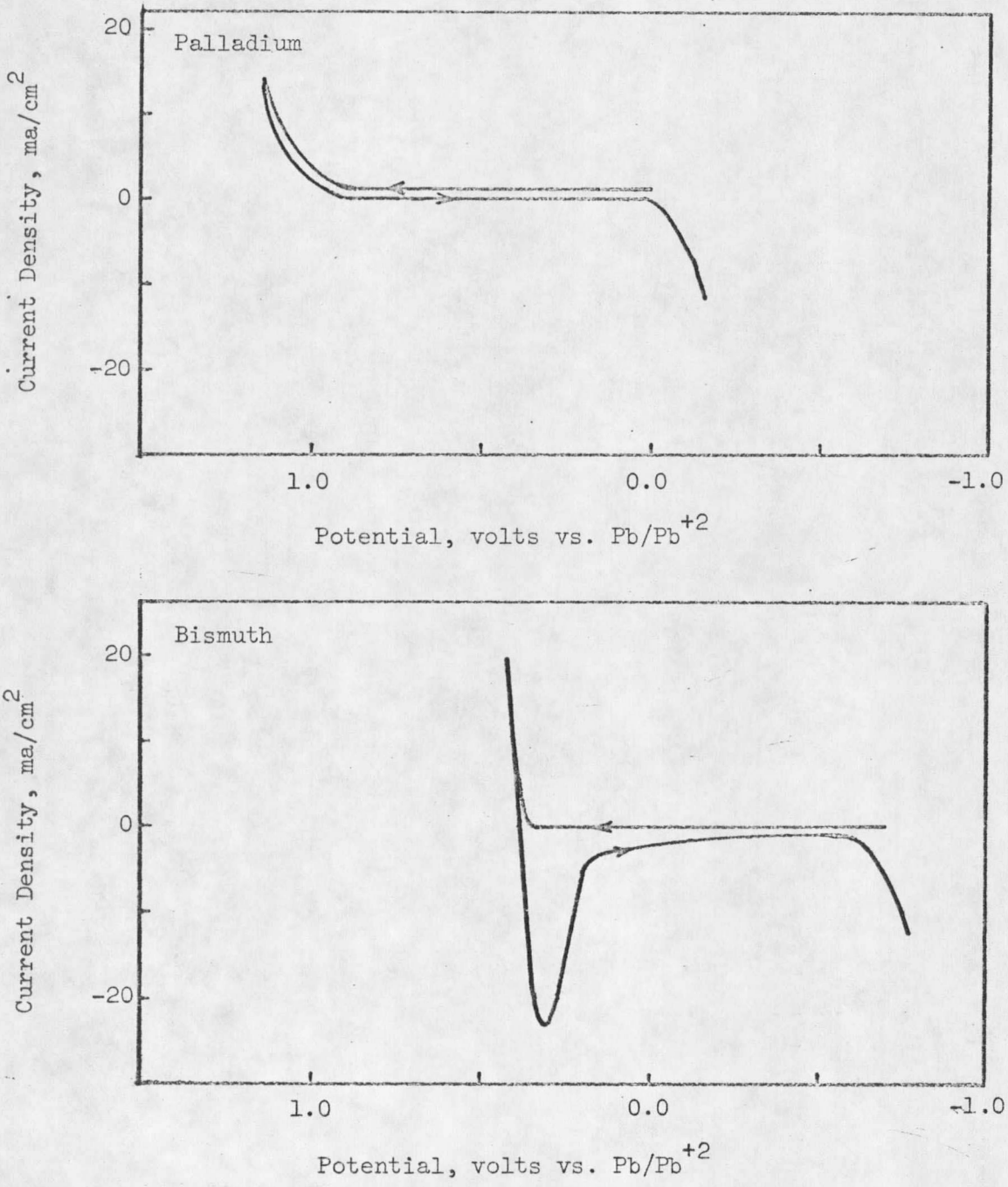


Figure 29. Cyclic voltammetric scans for palladium and bismuth.

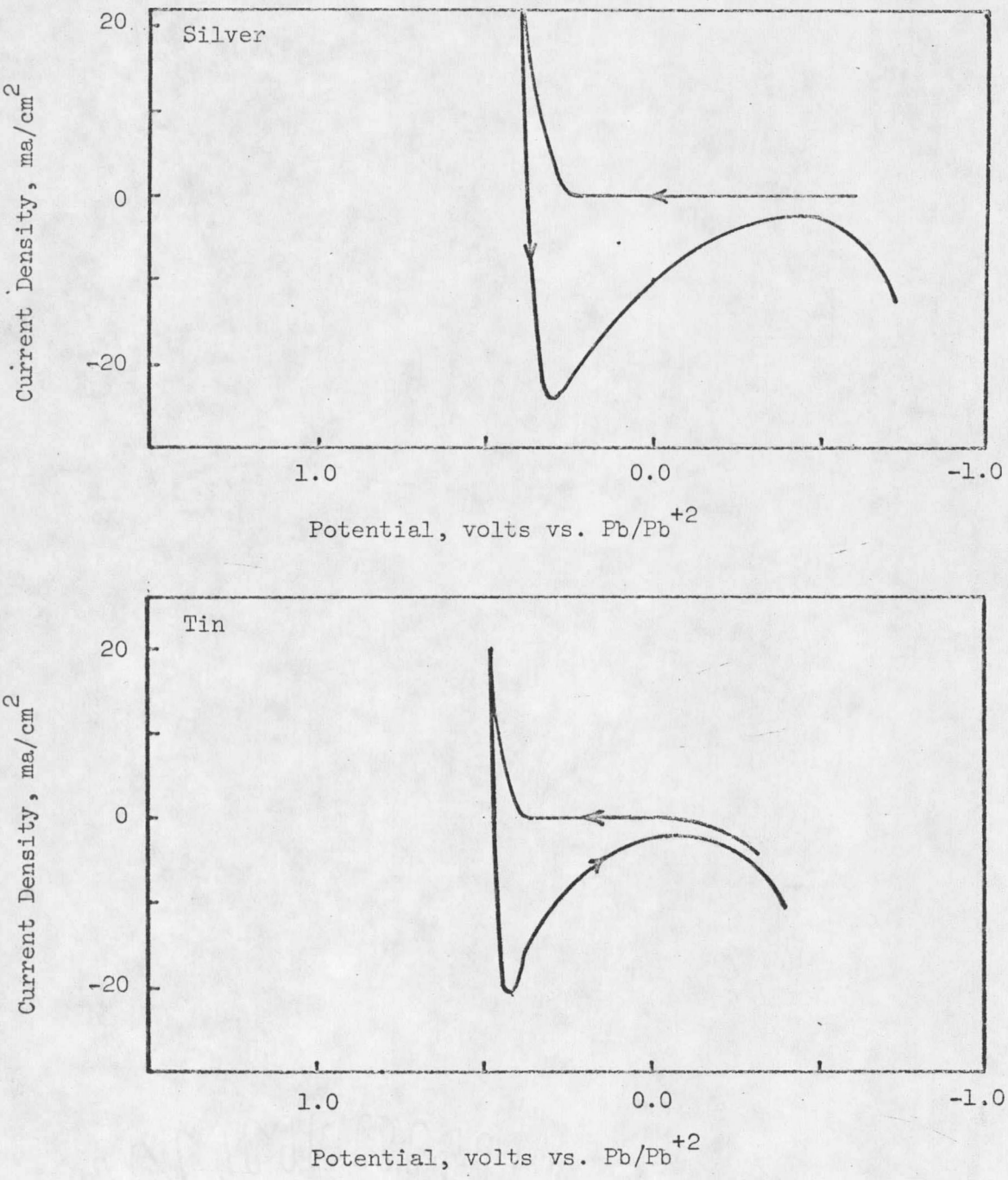


Figure 30. Cyclic voltammetric scans for silver and tin.

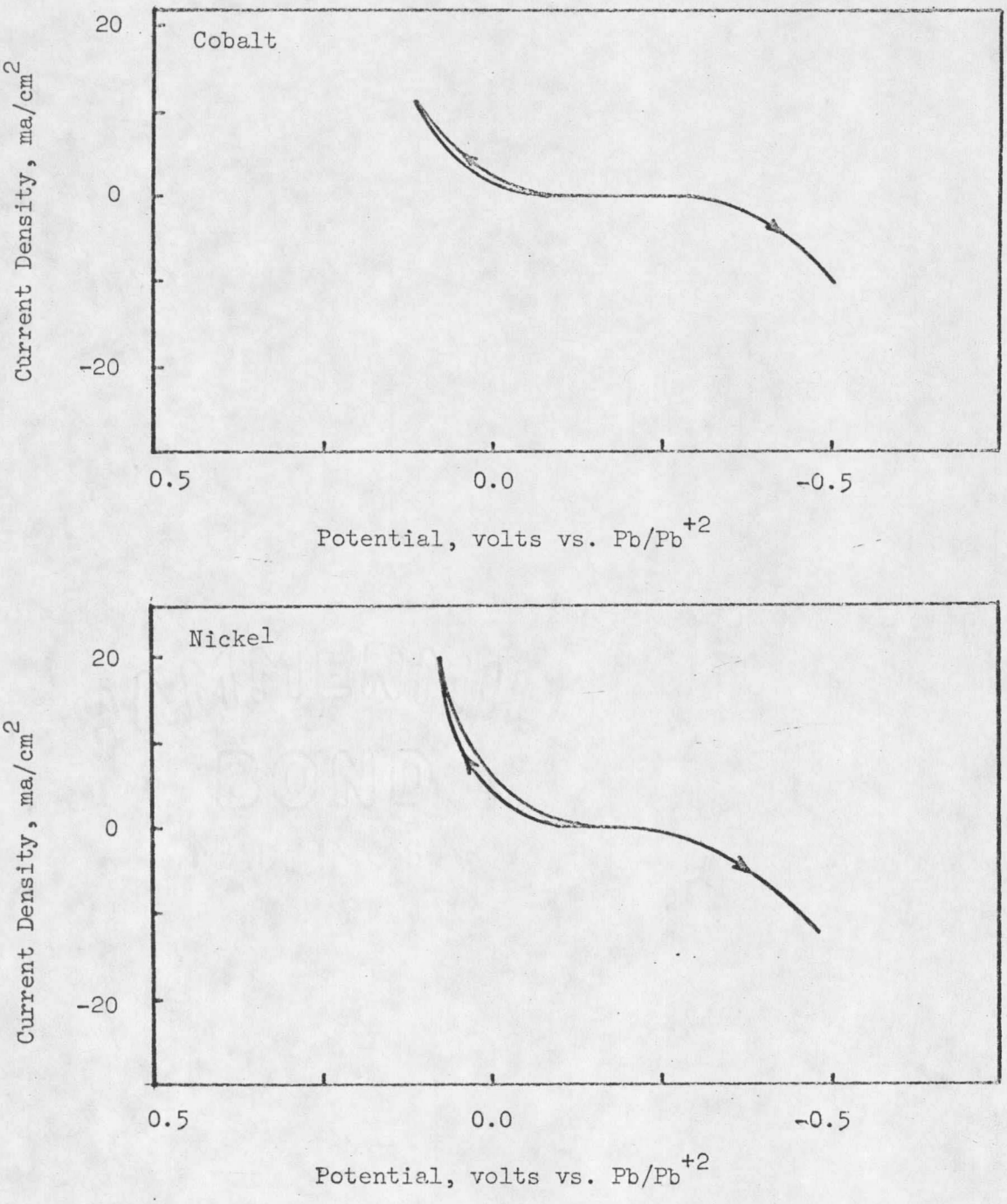


Figure 31. Cyclic voltammetric scans for cobalt and nickel.

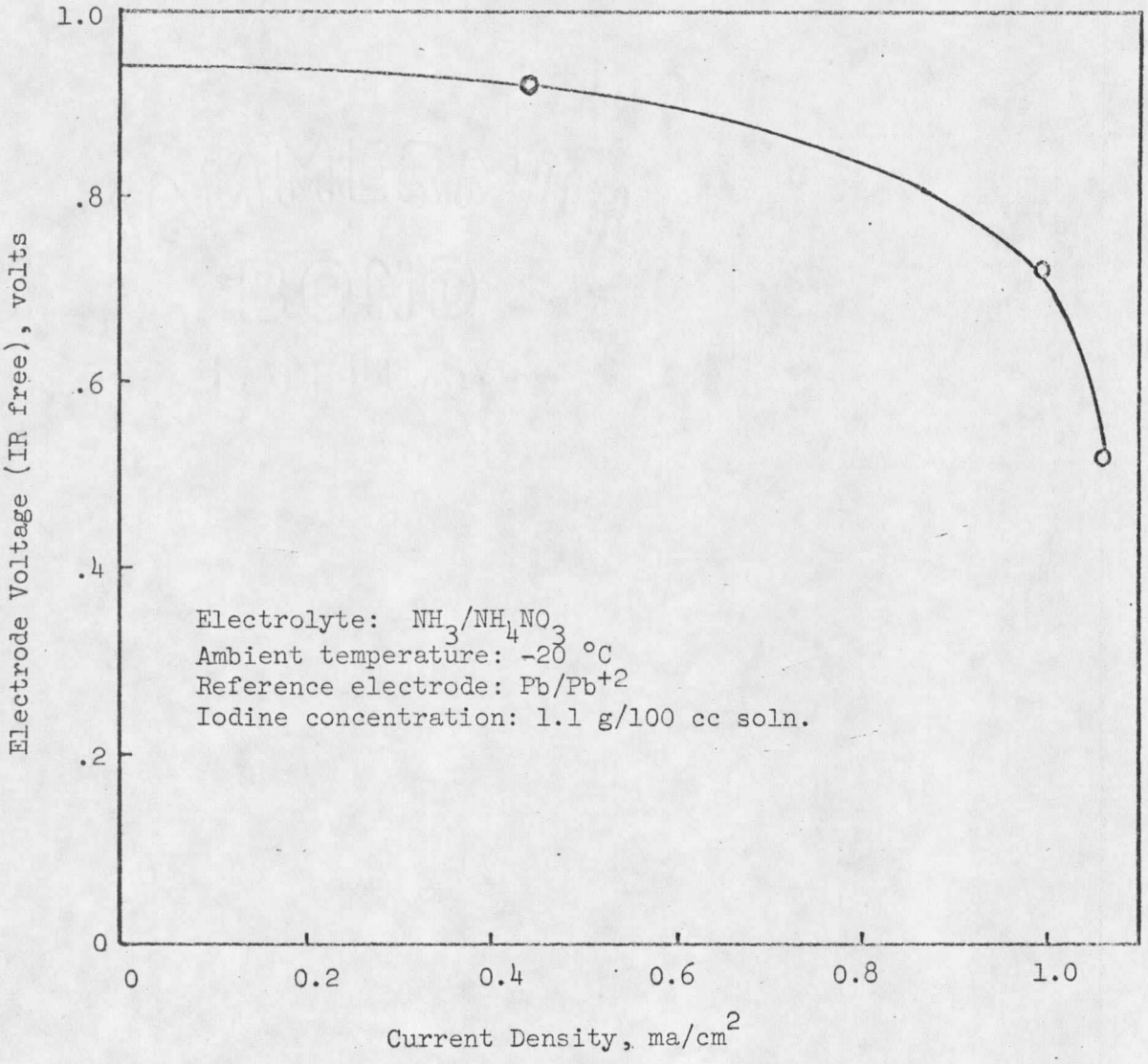


Figure 32. Iodine reduction at a shiny platinum foil cathode.

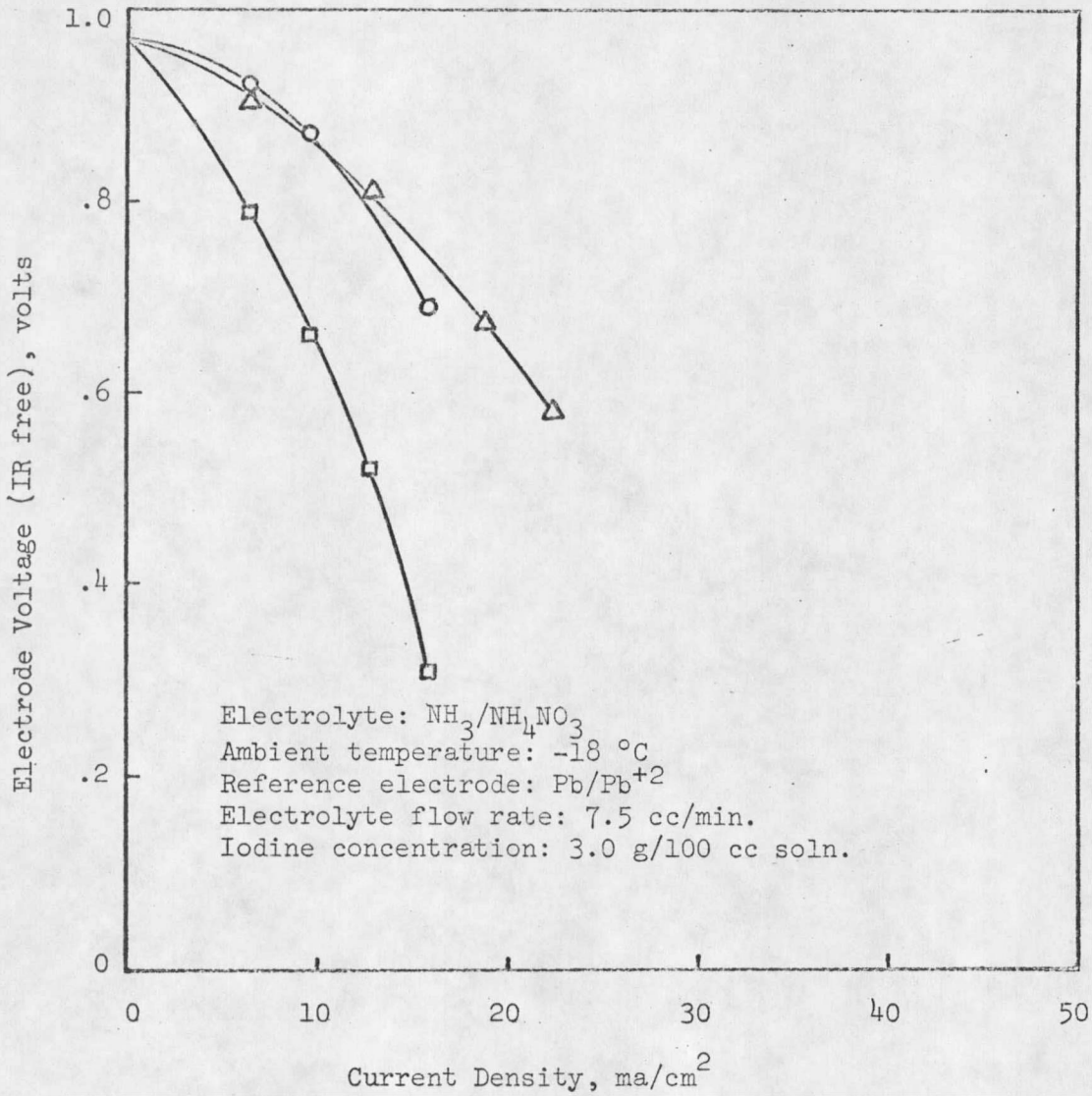


Figure 33. Iodine electrode polarization with different pieces of a porous platinum black flow-through cathode.

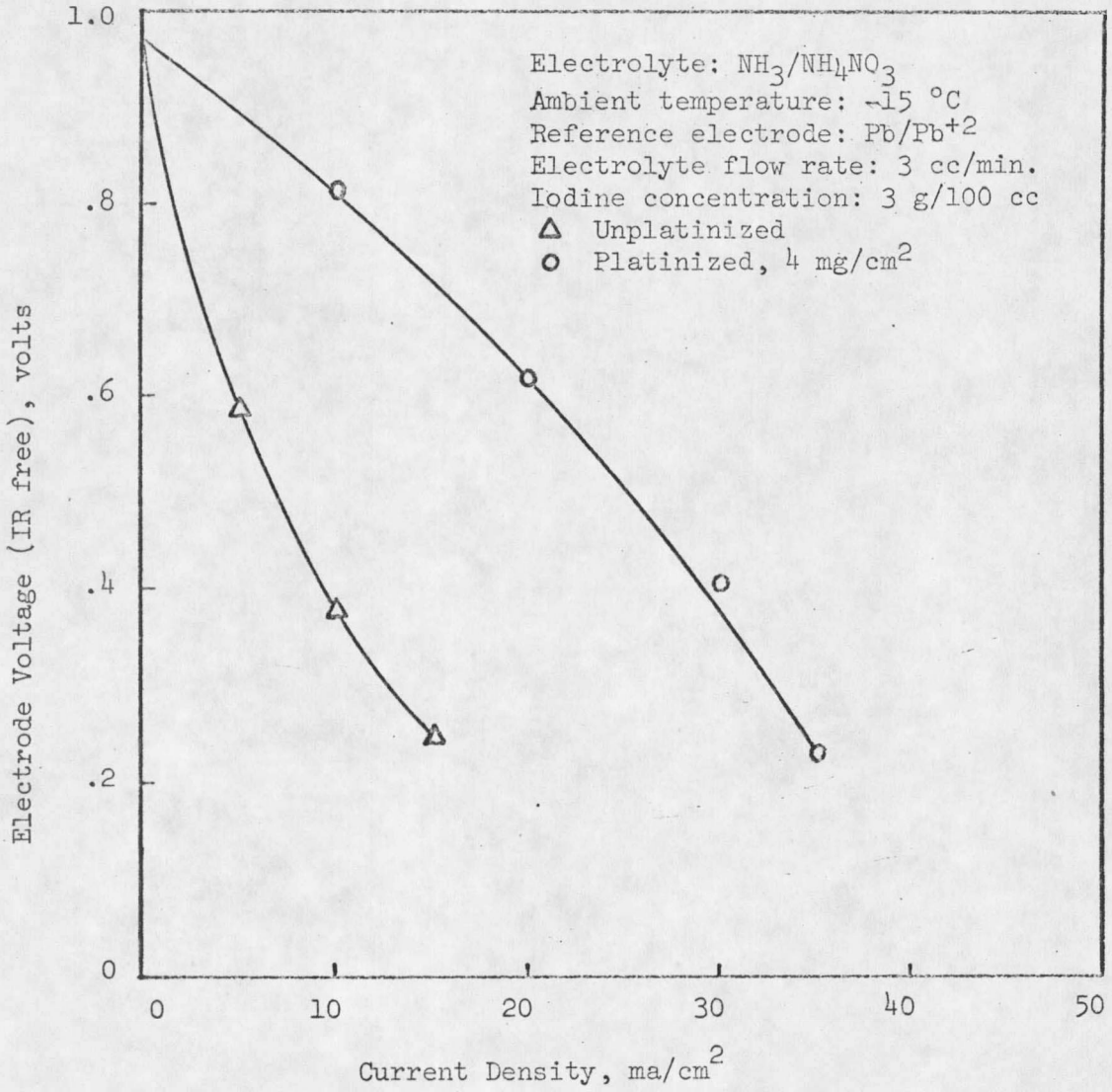


Figure 34. Iodine reduction at a platinum-rhodium screen flow-through electrode.

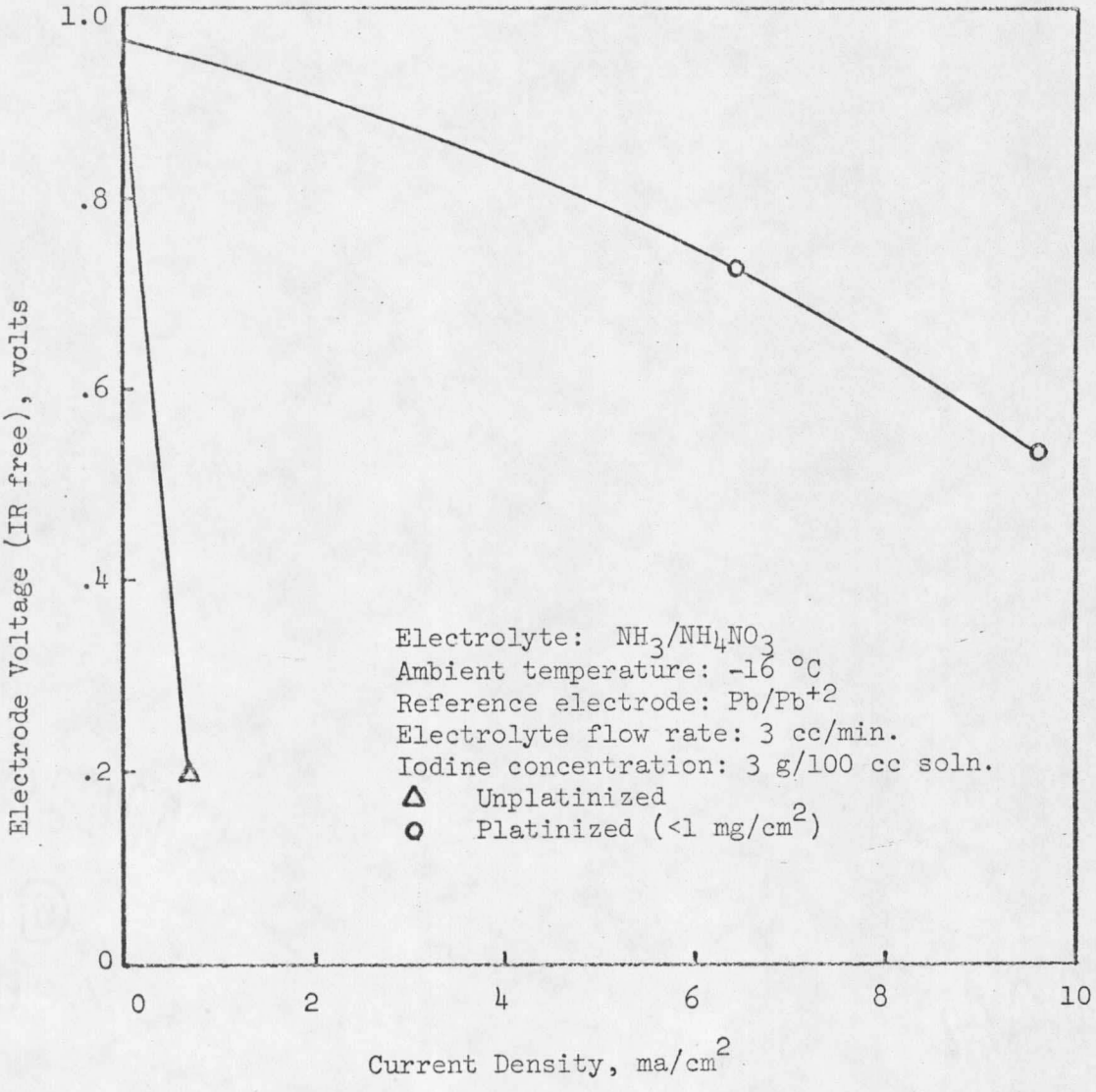


Figure 35. Iodine reduction at a thin porous stainless steel flow-through electrode.

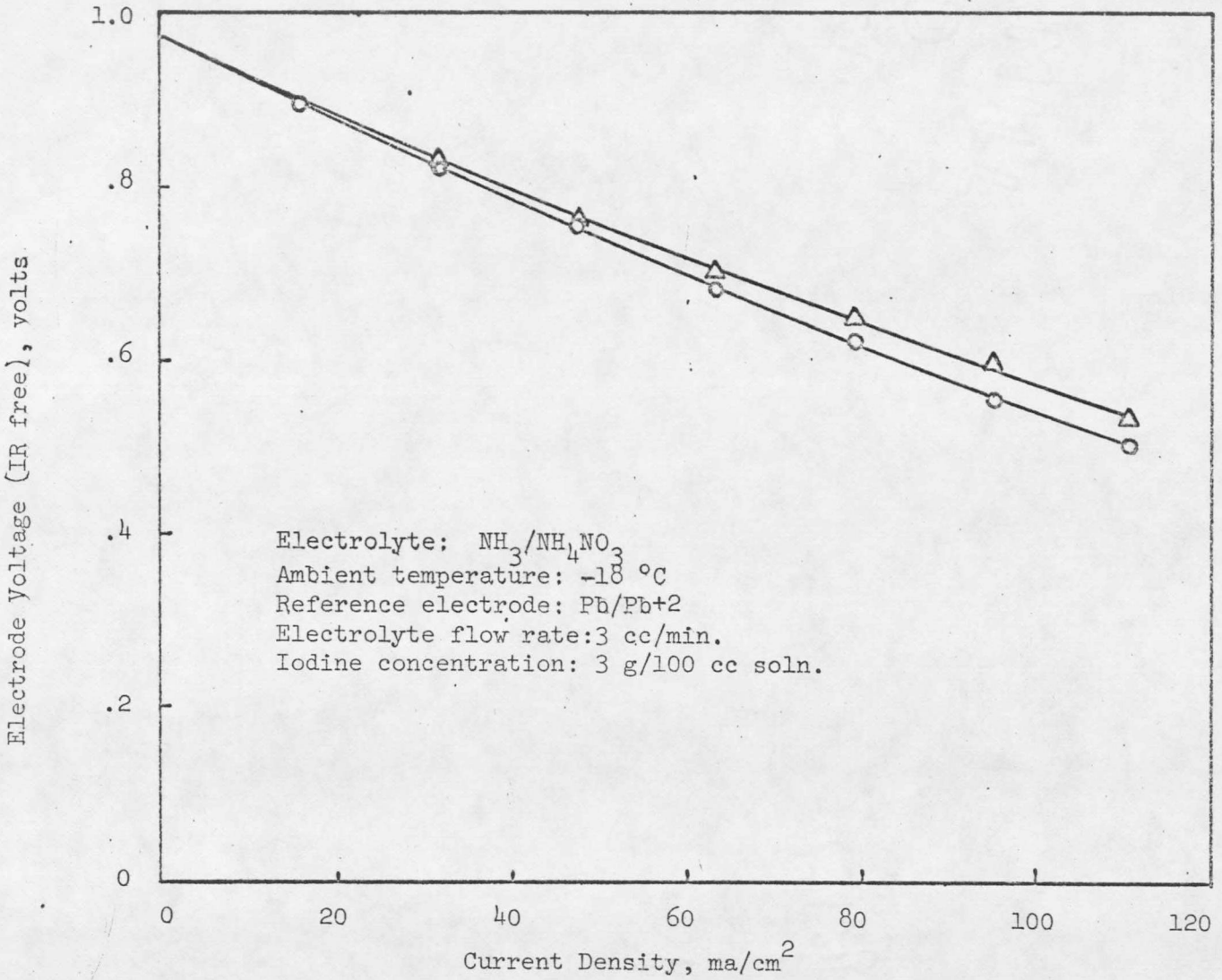


Figure 36. Initial performance of different electrodes of same pore size and platinum loading (20 micron, 4 mg/cm^2).

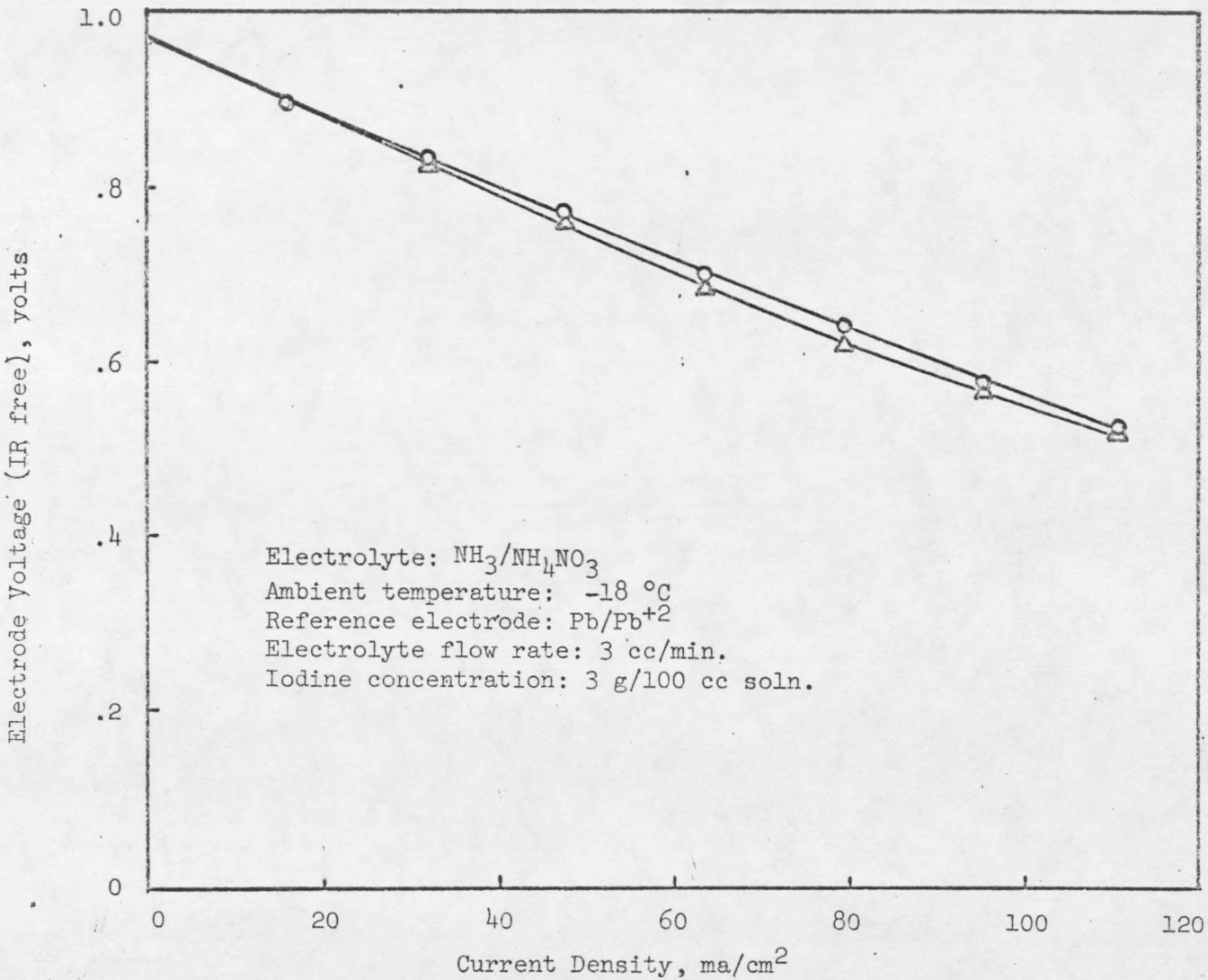


Figure 37. Initial performance of different electrodes of same pore size and platinum loading (65 micron, 4 mg/cm^2).

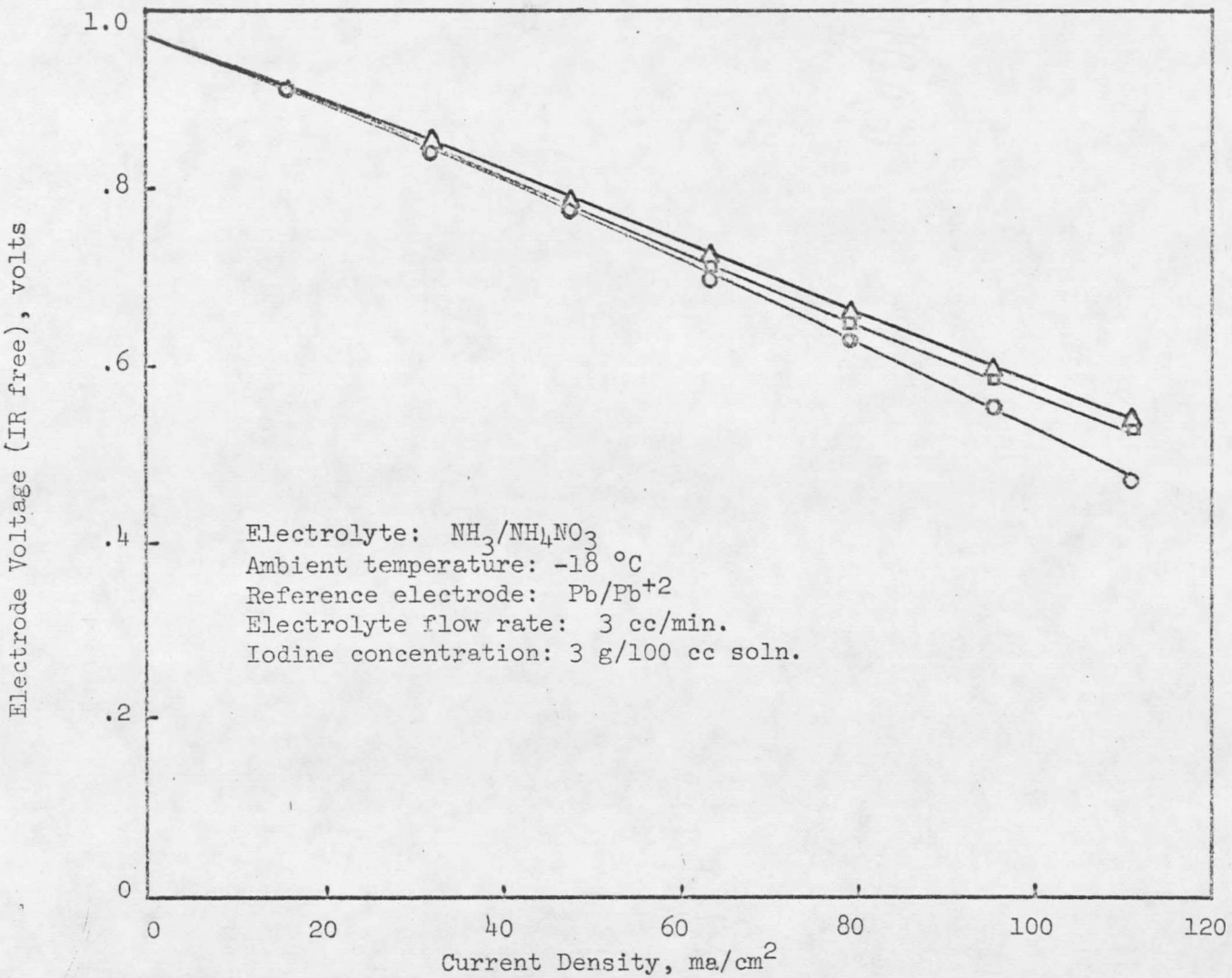


Figure 38. Initial performance of different electrodes of same pore size and platinum loading (65 micron, 0.5 mg/cm^2).

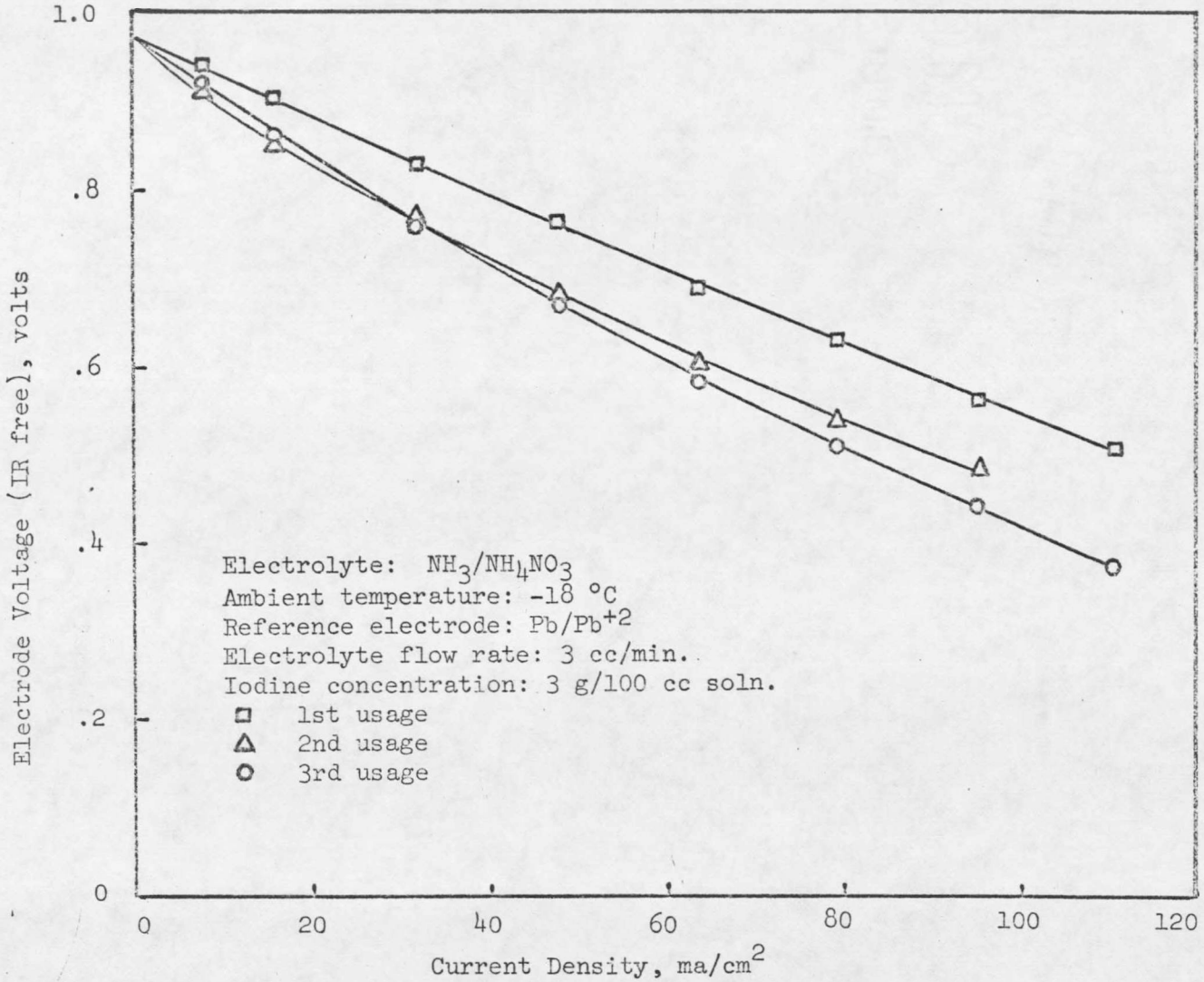


Figure 39. Degradation of performance for cathode number 15 (20 micron, 4 mg/cm^2).

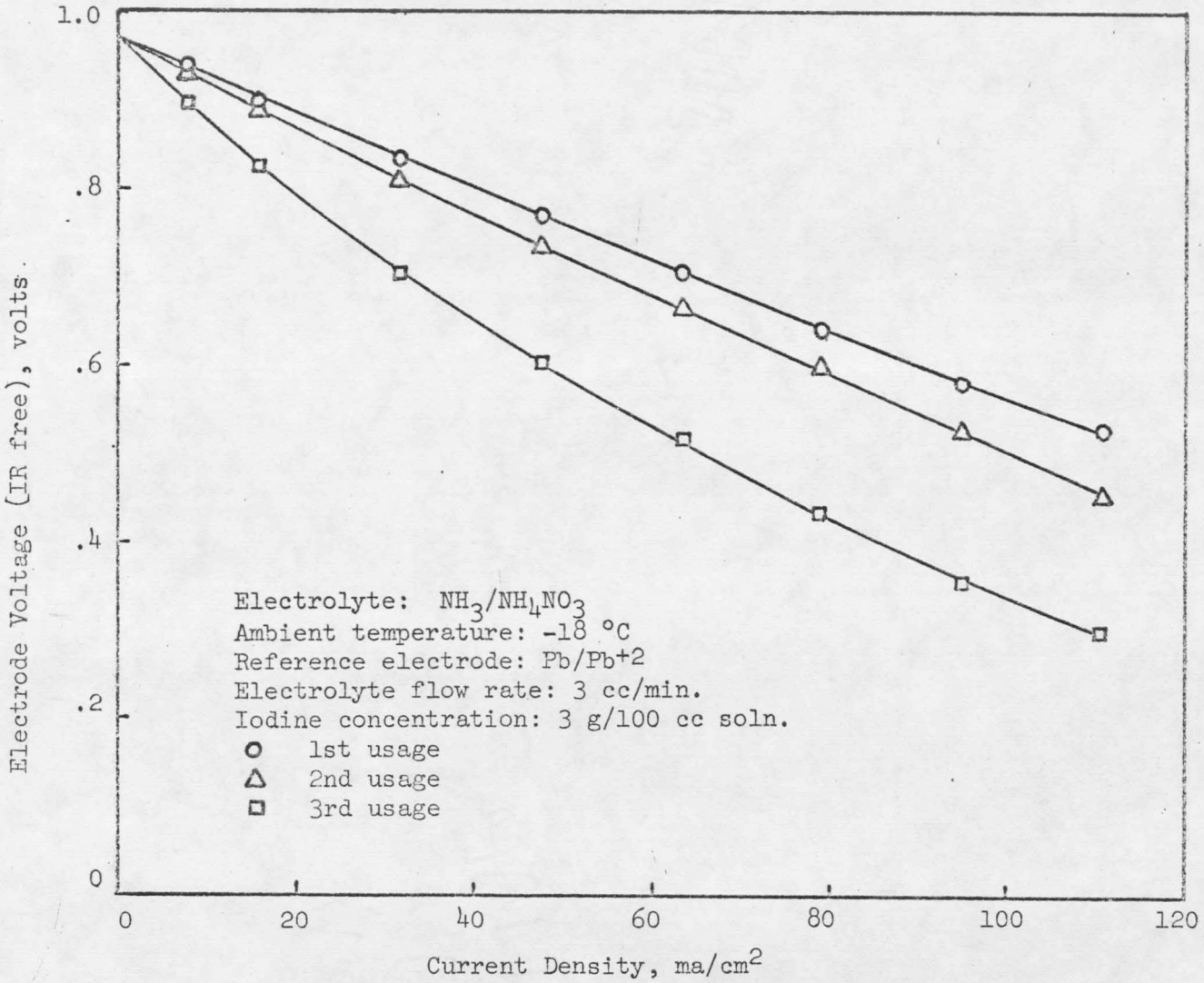


Figure 40. Degradation of performance for cathode number 17 (65 micron, 4 mg/cm^2).

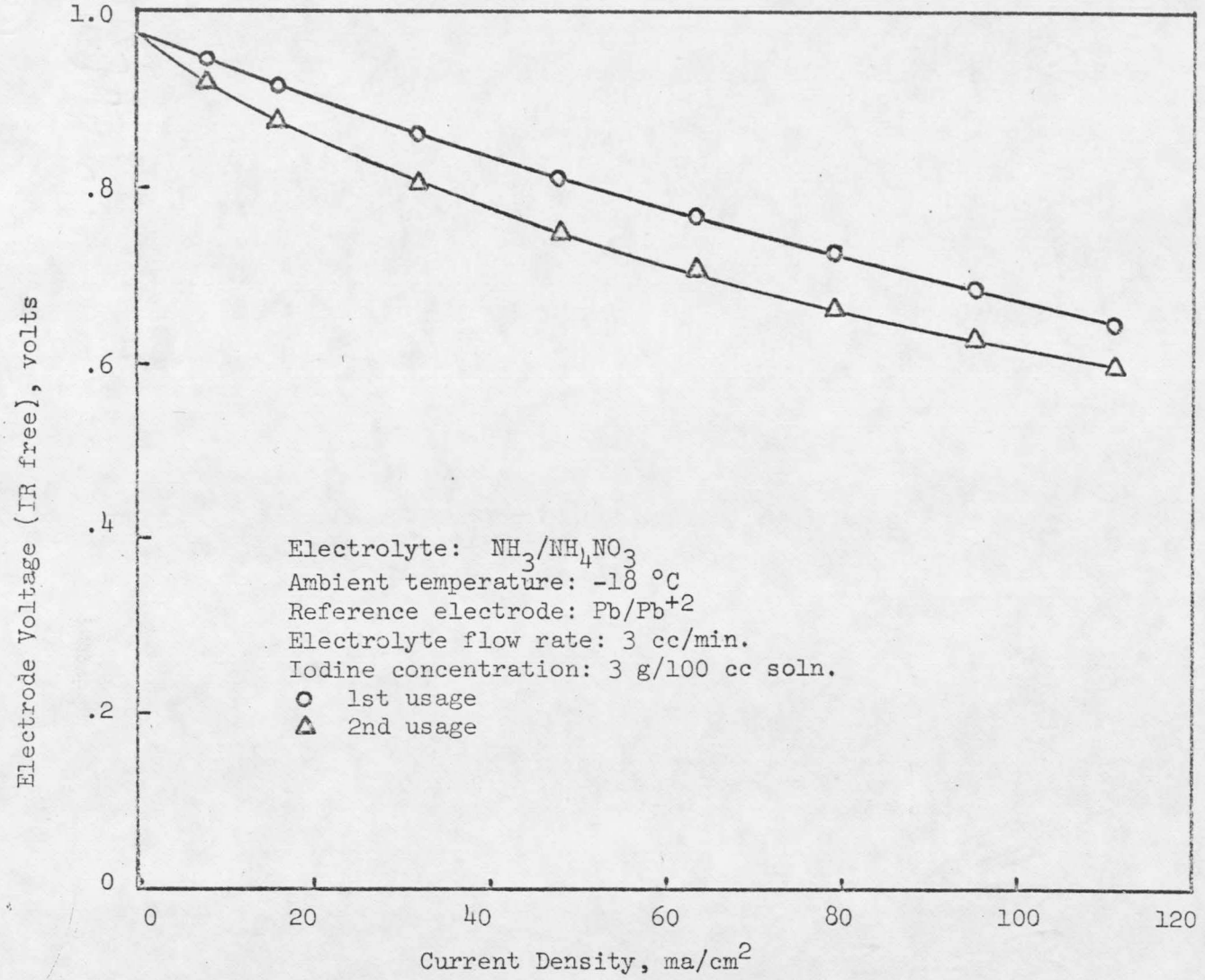


Figure 41. Degradation of performance for cathode number 19 (5 micron, 4 mg/cm^2).

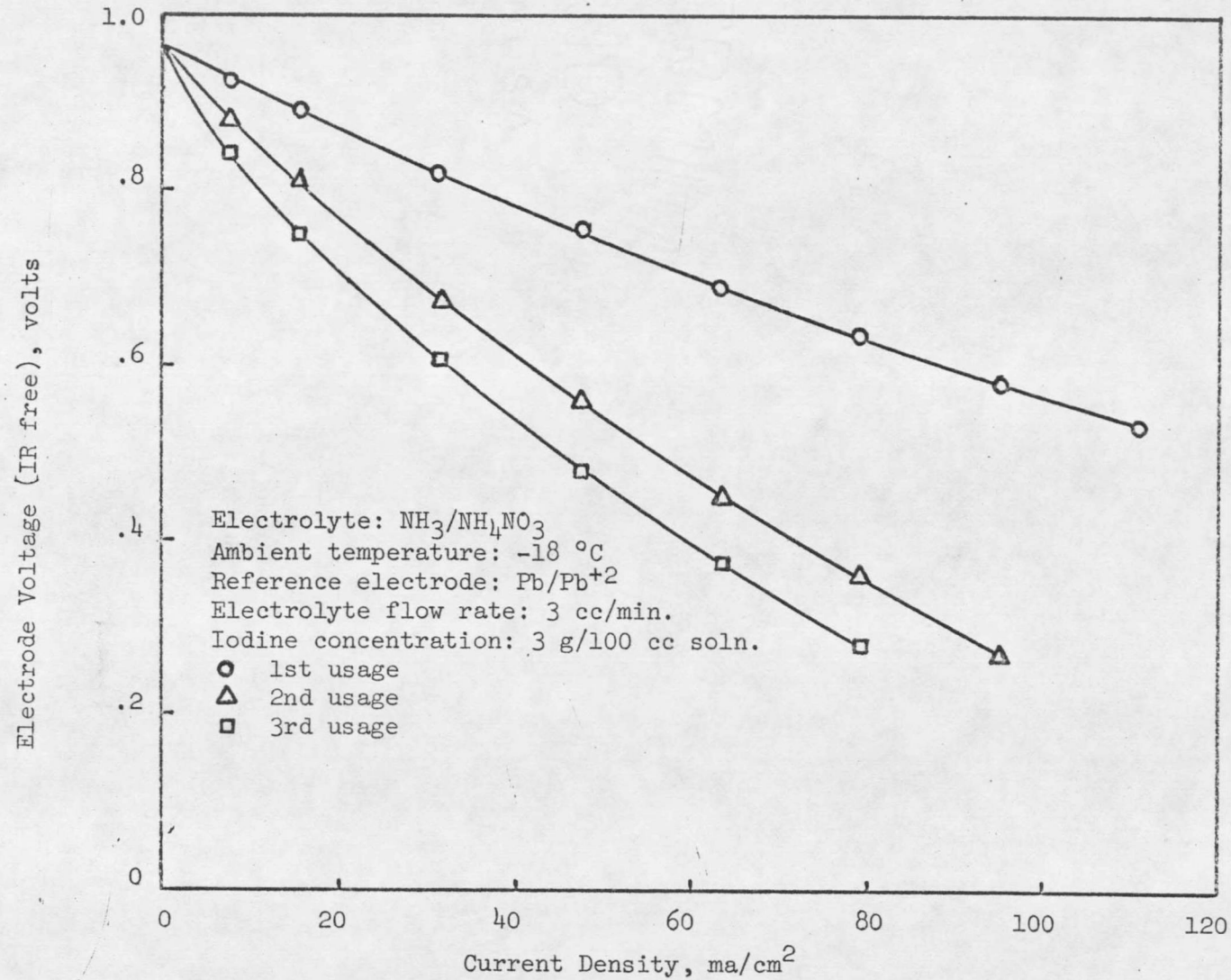


Figure 42. Degradation of performance for cathode number 20 (65 micron, .5 mg/cm^2).

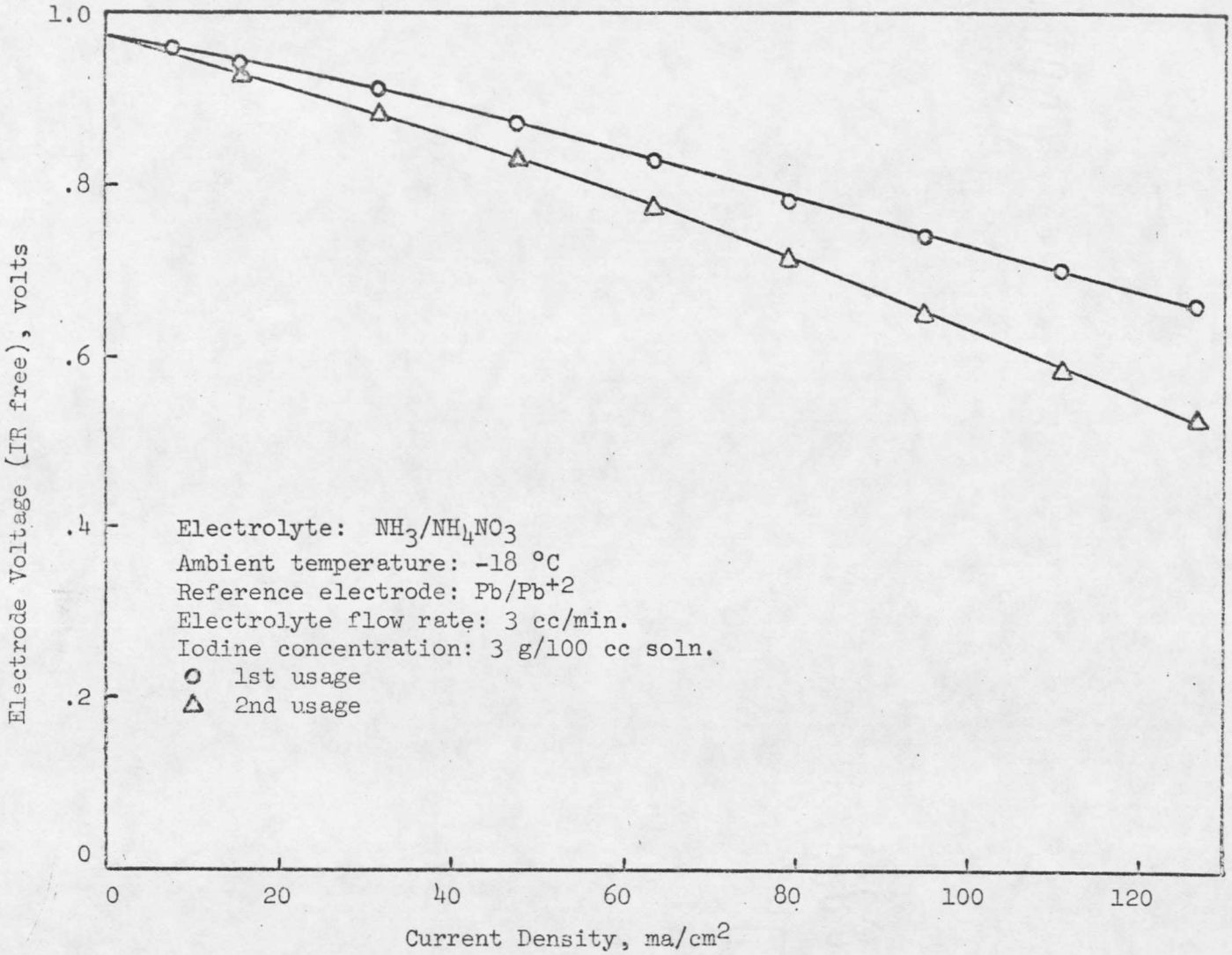


Figure 43. Degradation of performance for cathode number 23 (65 micron, 20 mg/cm^2).

VII. LITERATURE CITED

1. Young, G. J., ed., Fuel Cells, volumes I & II, Reinhold Publishing Corporation, New York (1960 & 1963).

2. Fuel Cell Systems, Advances in Chemistry Series, No. 47, American Chemical Society (1965).

3. Fuel Cells, American Institute of Chemical Engineers, New York (1963).

4. National Aeronautics and Space Administration. Fuel Cells - A Review of Government-Sponsored Research, 1950-1964, by L. G. Austin, Washington, D. C., NASA, 1967 (Report SP-120).

5. Mitchell, W., ed., Fuel Cells, Academic Press, New York (1963).

6. Williams, K. R., ed., An Introduction to Fuel Cells, Elsevier Publishing Company, New York (1966).

7. Austin, L. G., The Mode of Operation of Porous Diffusion Electrodes for Fuel Cells, Department of Fuel Technology, College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania (November, 1962).

8. Yeager, E., "Fuel Cells: Their Status and Future Outlook," C.E.P., 64, 92-96 (1968).

9. Jolly, W. L. and C. J. Hallada, "Liquid Ammonia," pp. 1-45 in Non-Aqueous Solvent Systems, by T. C. Waddington, Academic Press, New York (1965).

10. Audrieth, L. F., and J. Kleinberg, Non-Aqueous Solvents, John Wiley & Sons, Inc., New York (1956), chapter 3.

11. Holliday, A. K., and A. G. Massey, Inorganic Chemistry in Non-Aqueous Solvents, Permagon Press, New York (1965).

12. Jolly, W. L.,"Interpreting Liquid Ammonia Chemistry with Thermodynamics," J. Chem. Ed., 33, 512-517 (1956).

13. Laitinen, H. A., and C. J. Nyman, J. Am. Chem. Soc., 70, 2241 (1948); 70, 3002 (1948).

14. Laitinen, H. A., and C. E. Shoemaker, ibid., 72, 663, 4975 (1950).

15. McElroy, A. D., and H. A. Laitinen, J. Phys. Chem., 57, 564 (1953).

16. Lepoutre, G., and M. J. Sienko, Metal-Ammonia Solutions, W. A. Benjamin, Inc., New York (1964).

17. Bennett, J. E.,"The Electrochemical Oxidation of Lithium-Ammonia Solutions," M.S. Thesis, Montana State University, Bozeman, Montana (1968).

18. Naval Ordnance Laboratory Corona, Chemoelectric Energy Conversion for Nonaqueous Reserve Batteries, 13th Quarterly Report, July-September 1966, Corona, California, 15 January 1967, NOLC Report 701.

19. Naval Weapons Center Corona Laboratories, "Soluble Cathodes for Fuel Cells: Reduction of m-Dinitrobenzene in a Flow Fixture," by M. Wilcox and W. S. Harris, pp. 5-8 in Chemoelectric Energy Conversion for Nonaqueous Batteries and Fuel Cells, July-September 1968, 21st Quarterly Report, Corona, California, January, 1969 (NWCCL TP 822).

20. Miles, M. H. and P. M. Kellett, "Electrochemical Oxidation of Fuels in Liquid Ammonia," J. Electrochem. Soc., 115, 1225-1227 (1968).

21. Martin, T. F., and J. W. Vogt, "Simplified All-Transistor Chronopotentiostat," Anal. Chem., 38, 1102-1103 (1966).

22. Kublik, Z., "Cyclic Voltage Sweep Chronoamperometry with a Platinum Microelectrode," J. Electroanal. Chem., 5, 450-460 (1963).

23. Adams, R. N., Z. Galus, and H. Y. Lee, "Triangular Wave Cyclic Voltammetry," J. Electroanal. Chem., 5, 17-22 (1963).

24. Nicholson, R. S., and I. Shain, "Theory of Stationary Electrode Polarography," Anal. Chem., 36, 706-723 (1964).

25. Naval Ordnance Laboratory Corona, "Nonaqueous Solvent Electrochemistry" by R. E. Panzer and G. E. McWilliams, pp. 1-6 in Chemoelectric Energy Conversion for Nonaqueous Reserve Batteries, 12th Quarterly Report, April-June 1966, Research Department, Corona, California, 15 October 1966, NOLC Report 689.

26. MacNevin, W. M., and M. Levitsky, "Reproducible Platinized Platinum Electrode for Anodic Polarography," Anal. Chem., 24, 973-975 (1952).

27. Franklin, T. C., and S. L. Cooke Jr., "A Study of the Oxidation of Hydrogen at Platinized Platinum Electrodes," J. Electrochem. Soc., 107, 556-560 (1960).

28. Schumpelt, K., Trans. Electrochem. Soc., 80, 489-493 (1941).

29. Drazic, D. M., A. R. Despic, and N. D. Koselj, "Activation of Nickel Fuel Cell Electrodes with Platinum Catalysts," Electrochem. Tech., 6, 98-100 (1968).

30. Graham, A. K., ed., Electroplating Engineering Handbook, 2nd ed., Reinhold Book Corporation, New York (1968).

31. Naval Ordnance Laboratory Corona, The Electroreduction of Aromatic Nitro Compounds in Nonaqueous Solutions. Part I: The Reduction of Nitrobenzenes in Acid Liquid Ammonia Solutions, by W. S. Harris and G. B. Matson, Research Department, Corona, California, NOLC, 1 December 1962, NAVWEPS 7241.

32. Baker, B. S., ed., Hydrocarbon Fuel Cell Technology, Academic Press, New York (1965).

33. Bagotzky, V. S., and Y. B. Vassilyev, Electrochim. Acta., 12, 1323 (1967).

34. Bergstrom, F. W., J. Am. Chem. Soc., 48, 2319-2327 (1926).

35. Basic Research in Fuel Cells: Ammonia, Ethylene Glycol, and Urea Systems, Lockheed Missiles and Space Company, Sunnyvale, California, Government Report AD 273 049, November, 1961.

36. Colman, W. P., D. Gershberg, J. DiPalma, and R. G. Haldeman, Proc. Ann. Power Sources Conf., 19, 14-17 (1965).

37. Ruff, O., Ber., 33, 3025-3029 (1900).

38. Kuriloff, B., Z. physik. Chem., 25, 107-111 (1898).