



The electrochemical oxidation of lithium-ammonia solutions
by John Edwin Bennett

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in CHEMICAL ENGINEERING
Montana State University
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Abstract:

The electrochemical oxidation of lithium-ammonia solutions has been successfully studied by the methods of single and cyclic sweep solid electrode voltammetry. The oxidation reaction which occurs is actually that of the solvated electron, and cyclic voltage scans confirm its reversibility.

Complete oxidation waves have been obtained up to a concentration of 0.2 moles/liter by single sweep voltammetry. These curves show a linear relationship between peak current and concentration, and some reach current densities of 1000 ma/cm². Unfortunately, because of instrumental limitations, complete curves could not be obtained in the concentrated region.

Polarization studies were carried out up to a concentration of 2.0 moles/liter. Solutions in the "bronze" or concentrated region showed a potential deviation of only about 3 mV at a current density of ma/cm².

Other tests showed current efficiencies to be at least 92%, with the majority of losses probably being caused by non-electrochemical reactions.

The electrochemical oxidation of lithium in liquid ammonia is a powerful reaction which appears to be well suited for application in an electrical power generating device such as a fuel cell and further development toward this goal is recommended.

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ABSTRACT

The electrochemical oxidation of lithium-ammonia solutions has been successfully studied by the methods of single and cyclic sweep solid electrode voltammetry. The oxidation reaction which occurs is actually that of the solvated electron, and cyclic voltage scans confirm its reversibility.

Complete oxidation waves have been obtained up to a concentration of 0.2 moles/liter by single sweep voltammetry. These curves show a linear relationship between peak current and concentration, and some reach current densities of 1000 ma/cm². Unfortunately, because of instrumental limitations, complete curves could not be obtained in the concentrated region.

Polarization studies were carried out up to a concentration of 2.0 moles/liter. Solutions in the "bronze" or concentrated region showed a potential deviation of only about 3 mV at a current density of ma/cm².

Other tests showed current efficiencies to be at least 92%, with the majority of losses probably being caused by non-electrochemical reactions.

The electrochemical oxidation of lithium in liquid ammonia is a powerful reaction which appears to be well suited for application in an electrical power generating device such as a fuel cell and further development toward this goal is recommended.

INTRODUCTION

Fuel cells have been a subject of investigation since the early part of the twentieth century, but it has only been in the past decade that this work has become intense (1,2). Fuel cells are an attractive source of power for several reasons. They can presently be made to operate at nearly 80% efficiency compared to about half that figure for steam turbines and generators, which are limited by the Carnot cycle. Fuel cells produce no noxious fumes or objectionable combustion products. Noise and maintenance are minimized because there are no moving parts. Beyond ten hours operating time, fuel cells become the best systems by far in terms of power-per-unit-volume and power-per-unit-weight. Because of these factors, fuel cells are finding important uses in military and space applications today, and significant commercial applications are believed to be less than ten years away.

Even more recent has been the study of lithium as a possible source of electric power. This interest has been primarily because of its favorable position on the potential scale, and because of its light weight. Thus, lithium could prove advantageous for space application or any other use where weight is critical.

Most of the work with lithium to date has been done using a high temperature fused salt electrolyte. One such program (3) culminated in the operation of a lithium-hydrogen cell with a current density of 1300 ma/cm^2 at a potential of 0.325 volts. Fused salt

is a logical choice as an electrolyte since, in addition to having favorable electrical properties, it is inert to the highly reactive lithium. There are, however, serious disadvantages to such high temperature operation. These include corrosion problems, operating problems, and construction problems.

As a possible solution, we have chosen to study the lithium/lithium ion reaction in a liquid ammonia electrolyte. Alkali metals dissolve in ammonia to form unique stable solutions which have been laboratory curiosities since the latter part of the nineteenth century.

Ammonia, itself, is second only to water as a general solvent.

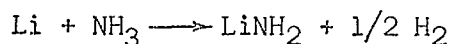
(4,5). To quote from an article by Franklin and Kraus (6):

"Of all known liquids, ammonia most closely approaches water in all those properties which give water its conspicuous position among solvents. In its capacity as a general solvent for salts it is secondary to water, but superior to all other solvents."

There are few anhydrous solvents, either inorganic or organic, which can compete with liquid ammonia as a solvent on the basis of cost. The use of ammonia offers no great experimental difficulties and is used widely in organic and inorganic synthetic chemistry today.

Our primary concern here is the ability of ammonia to form unique solutions with the alkali metals. The solutions of alkali and alkaline earth metals all possess a characteristic deep blue color in the dilute concentration ranges; the more soluble alkali metals give a coppery-bronze lustre in the more concentrated region.

The metal ammonia solutions possess varying stability. If solutions of lithium or sodium are prepared with enough care, they may be stored for weeks or even months without appreciable decomposition. The decomposition reaction



is unfortunately catalyzed by most electrode materials. Burgess and Kahler (7) investigated qualitatively the catalytic action of a few materials, but this seems to be one field in which a great deal more investigation is necessary.

A. Metal-Ammonia Solutions Background

Weyl (8) made the first investigation of metal-ammonia solutions in 1864. Weyl reported both blue and bronze solutions of sodium and potassium, and attributed the phenomena to the ammonia substituted radicals NaNH_3 and KNH_3 . A few scattered investigations in the years following confirmed the observations reported by Weyl.

It was not until the turn of the century that Charles A. Kraus began his significant series of investigations. Even though Kraus completed his conductance and vapor pressure experiments over sixty years ago, his data is still used today. Everyone familiar with non-aqueous solvents is aware of Kraus' exceptional work with metal-ammonia solutions.

Kraus (9) first demonstrated by vapor pressure determinations that no compounds existed in the cases of sodium, potassium, and lithium, and they were true solutions. Calcium, he reported, associated with ammonia in the compound $\text{Ca}(\text{NH}_3)_6$. Today it is well known that calcium, lithium, and the alkaline earths, unlike the other alkali metals, form definite compounds. Lithium forms $\text{Li}(\text{NH}_3)_4$, but only at extremely low temperatures, and is of no concern in this work.

Previously, Cady (10) had first measured some electrical properties of alkali metals in liquid ammonia and reported an excellent conductivity. He also noticed that passage of current in bronze solutions involved little or no mass transport, but in dilute solutions a passage of current resulted in an increase of metal concentration at the cathode. Cady also reported that the electrodes acted reversibly with respect to electrode processes.

Kraus (11) found the conductance-temperature coefficient to be positive, and later showed (12) that the cation of the metal was identical to the same cation of ordinary salts. The anion, however, appeared to be a new species for which he coined the term "solvated electron".

From EMF measurements carried out in concentration cells (12), he determined the relative speeds of these ions. Mobility of the positive cation remains relatively constant, but the negative species is seven times more effective in dilute solutions, and 280 times more

effective in bronze solutions. Thus, the solvated electron carries 87% of the current in dilute solutions and nearly 100% in concentrated solutions.

Further studies by Kraus (13,14,15) reveal the following:

1. The electrical conductivity is higher for these solutions than that found for any known salt in any known solvent.
2. The conductance for the alkali metals in ammonia goes through a minimum and then increases sharply with increasing concentration.
3. Conductance in the concentrated region is very high. Near saturation, a sodium solution has a specific conductance one-half that of mercury even though there are over five molecules of ammonia for each atom of metal at this point. This seems to indicate metallic conductance of some kind.

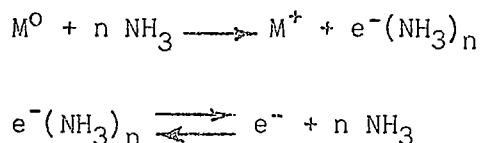
Let us consider Dr. Kraus' analysis for a moment. He summarized the nature of metal-ammonia solutions as follows (13):

"These solutions therefore constitute a connecting link between metallic and electrolytic conductors. In dilute solutions the process is, at least in part, electrolytic. A portion of the current is carried by

the positive carriers as they appear in solution of the common salts. The negative carrier is chemically uncombined, but is associated with one or more molecules of the solvent. These carriers are identical for solutions of all metals, and when discharge takes place, the only material process which takes place is that a portion of the solvent is left behind in the immediate vicinity of this electrode. As the concentration of the solution increases, the nature of phenomena changes only insofar as the combination of the negative carrier with ammonia is affected. At higher concentrations the negative carriers are free from association with the ammonia molecules to a greater and greater extent. Since under these conditions the negative carrier is associated with no matter of atomic dimensions, it follows that all the material effects cease so far as these carriers are concerned. It is not to be understood that these carriers are free from association with the solvent molecules for any considerable period of time. Certainly an equilibrium must exist between the free carriers, combined carriers, and ammonia which results in a constant interchange between free and bound carriers. During the interval over which these carriers are free from the solvent molecules, they conduct just as they do in metals. As the concentration is increased, the number must be relatively small, since at higher concentrations their equivalent conductance reaches values one hundred times as great as that at one normal concentration. It is not possible to determine the actual number of carriers in the more concentrated solutions. In the more dilute solutions, however, it appears that the number of carriers decreases with increasing concentration, just as it does in the case of normal electrolytes in ammonia.

"There is nothing to distinguish the more concentrated solutions from actual metallic substances. It may be concluded, therefore, that the process of conduction in the case of ordinary metals is effected by means of the same negative carrier. Since this carrier is negatively charged and has sub-atomic dimensions, we may conclude that it is identical with the negative electron as it appears in radioactive and other phenomena."

Kraus, therefore, assumed the following equilibria to exist in solution:

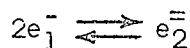


Because of its simplicity and workability, this model is often referred to in this paper. One should certainly be aware, however, of a great many other models. Many become very complicated in their effort to explain the behavior of metal solutions. It is not the primary purpose of this paper to propose or substantiate any physical model. For this reason, only brief descriptions of the more significant models are given. The proposals are many and varied, yet none sufficiently explains all aspects of the unusual metal-ammonia solutions.

A concentrated solutions model was first proposed by Farkas (16) and later extended by Jolly (17). Farkas assumed that the metal ions form a well-ordered structure in the concentrated region. This structure provides a periodic potential field in which the electrons reside in square potential wells. The higher the concentration, the closer these wells are to one another. Jolly postulated that at concentrations less than one molar the potential wells are too widely separated to permit quantum tunneling, but an appreciable amount of conduction

may occur by thermal excitation of bound electrons to the conductance band. In very concentrated solutions, the electrical conductivity is of both types, excitation of the bound electron to the conductance level, and quantum tunneling from potential well to potential well in the bound state.

One of the most popular proposals is the cavity model first proposed by Ogg (18) and later extended by several authors. Ogg postulated that the solvated electron in liquid ammonia is trapped in a spherical cavity created by the solvent molecules. The electrons may be confined in these cavities either singly or paired, according to the equilibrium:



At infinite dilution the electrons should all be in singly occupied cavities, while at higher concentrations the energetically favored paired sites should predominate.

Hill (19), Lipscomb (20), and Stairs (21) improved the primitive cavity model proposed by Ogg. The basic concept was retained, but mathematical treatment was improved to make the model more compatible with experimental observations.

Kaplan and Kittel (22) made a major contribution giving credence to the idea of a cavity model. They proposed the complete ionization

of the alkali metal at all concentrations with the electrons located in solvent cavities as before. These cavities would have approximately the volume of two to four ammonia molecules. Furthermore, the electrons in the cavities are regarded as being in molecular orbital states on the protons of the adjacent ammonia molecules. A mathematical treatment of this model compares well with most experimental results, but does not appear to be compatible with electrical conductivity data.

The Becker, Lindquist, and Alder (23), or BLA model, is another proposal which has received considerable attention. The BLA model proposes an equilibrium between four solute species: the solvated metal ion, the electron, a monomer, and a dimer. The metal ion is solvated by a sheath of about six molecules of ammonia, with the electron moving around the hydrogen atoms which form the outer surface. The dimer is a unit composed of two monomers bound together principally by exchange forces.

Symons (24) proposed a hybrid model, postulating that in dilute solutions the electron resides in a cavity while at higher concentrations, dimer formation of the BLA type occurs.

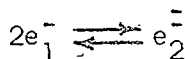
Gold, Jolly, and Pitzer (25) introduced a model which incorporates a solvated cation and an electron in a cavity. As the concentration is increased, the solvated metal ion and the electron in a cavity form an ion pair.

Extensions of these models and other models have been advanced by several authors since 1940 (26-31).

The optical properties of metal-ammonia solutions have been a subject of interest ever since investigators first noticed the intense blue color which appears. This blue color for dilute solutions arises from the existence of an adsorption maximum in the infrared with a tail extending into the red region of the visible spectrum.

Jolly (32) reported the absorption peak maximum at 6666 cm^{-1} . Jolly proposed that this energy, equivalent to 0.83 volts, is the energy needed for the excitation of the unpaired "solvated" electron in the solution into a conductance band. The electron, once in the conductance band, is free to move without becoming trapped by solvent molecules.

Blades and Hodgins (33) investigated the absorption spectra in greater detail and learned that the peak's maximum and width depended strongly on temperature and metal concentration. These environmental changes point to a dynamic equilibrium existing between species of some kind. The postulated equilibrium in this case is



as proposed by the cavity model.

Some knowledge of more concentrated solutions was gained by Beckman and Pitzer (34), who made reflection spectral studies on the sodium-ammonia system.

Photoelectric measurements complement the spectral data by providing some information about the nature of the binding between the various species present in metal-ammonia solutions. Studies in this area appear to be somewhat conflicting, however (35-37).

Based on X-ray studies, Schmidt (38) supported the BLA rather than the cavity model. But similar X-ray studies by Brady and Varimbi (39) appear to be conflicting.

Until magnetic susceptibility measurements were made, the Kraus (13) model for metal-ammonia solutions provided an adequate explanation for the physical properties of these solutions. Freed and Sugarman (26) determined that molar magnetic susceptibility was dependent on metal concentration. This is contrary to the behavior predicted by the simple Kraus model.

Nuclear magnetic resonance (40) and electron spin resonance (41) studies have also supplied useful information concerning the physical nature of the metal-ammonia solutions.

None of the models proposed to date accurately describes the metal-ammonia solutions in all respects, and there is considerable

debate concerning which of the proposed models is best. The true metal-ammonia system must be a complicated equilibrium, indeed.

Another interesting phenomenon is the remarkable volume expansion which occurs when an alkali metal is dissolved in liquid ammonia. This expansion is most marked for lithium and decreases with increasing atomic weight of the metal. A saturated lithium-ammonia solution, in fact, is the lightest known liquid at room temperature, having a density of only 0.477 g/cc.

Johnson (43) first pointed out in 1931 that saturated solutions of sodium and potassium in liquid ammonia are among the lightest known liquids. Johnson noted that the increase in volume cannot be attributed to the metal ions, but must be due to the negative electron associated with the solvent molecules.

Evers and Filbert (44) reported the volume change of sodium in liquid ammonia at -45°C . Their results show an expansion of about 41 cc/g-atom sodium near 1 n, decreasing to a minimum of 30 cc/g-atom at 0.04 n, and then increasing to a limiting value of 41 cc/g-atom at infinite dilution.

Gunn and Green (45,46) reported volume change data for sodium and lithium at 0°C and sodium at -45°C . This phenomenon is further evidence of the unique physical structure of the metal-ammonia solutions.

A very recent paper by Gordon and Sundheim (46) is of considerable interest in this discussion. They made a chronopotentiometric study of the anionic diffusion in potassium-ammonia solutions. These investigations were made at various temperatures both with and without potassium iodide as a supporting electrolyte. They report diffusion coefficients for the electron of approximately $5 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, supporting the view that the electron in dilute solutions shows no evidence of any unique transport properties as compared with ordinary electrolytes. They obtained pseudo-diffusion coefficients of approximately 1×10^{-5} in pure potassium-ammonia solutions. Diffusion coefficients obtained in this way refer to the electrolyte as a whole. They reported their investigations to a maximum concentration of 0.164 M. Further progress into the high concentration region was blocked by problems of "phase separations" and "Joule heating". At the higher concentrations and higher current densities, the latter part of the chronopotentiograms appeared to show the onset of boiling. It should also be noted that their reproducibility was not very good, and the general morphology of the chronopotentiograms was poor.

This recent article by Gordon and Sundheim confirms the strong oxidation of the solvated electron at a potential within the range of liquid ammonia. This suggests the possibility of practical application of this oxidation in the form of electrical power generation.

This concludes the historical review presented here. The reader is reminded, however, that many excellent reviews (17,47,48, 49,50) are available on this fascinating subject.

B. Analytical Procedure Background

Solid electrode voltammetry, the principal analytical method used, has only recently found extensive use. Basically, this technique involves the linear change of potential between a stationary working electrode and a non-polarized reference electrode. Electrochemical reactions are observed in the form of current between the working electrode and a third electrode, the counter. This current-potential curve is recorded on an X-Y recorder. This method gives a better qualitative picture of the system than chronopotentiometry, or constant current operation, but is usually more difficult to treat quantitatively.

This method is analogous to polarography but the latter is generally applied to the branch of voltammetry in which a dropping mercury electrode is used as the working or polarized electrode. The dropping mercury electrode, or D.M.E., has been investigated more thoroughly and is generally considered more accurate and reproducible than solid electrodes. It is indeed unfortunate that the rapid amalgamation tendencies of alkali metals preclude its use here.

The first application of this method was made by Matheson and Nichols (51). Randles (52) was the first to consider the single scan method for a reversible reaction taking place at a plane electrode. The theory was later extended to totally irreversible charge transfer reactions by Delahay (53). Reinmuth (54,55) also contributed to the theory of both reversible and irreversible reactions taking place at flat electrodes. Unfortunately, even in cases involving complete diffusion control and plane electrodes, the theoretical treatment is relatively difficult, ultimately requiring some sort of numerical analysis.

Other electrode geometries become quite formidable mathematically. Despite its complexity, however, the theory of the single scan method has been extended to reversible reactions taking place at cylindrical electrodes (56) and at spherical electrodes (54,44).

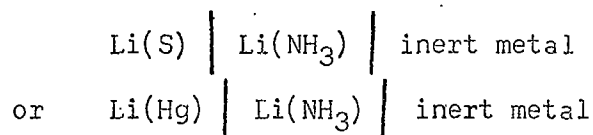
Mathematical complexity has also prevented extensive study of the cyclic triangular wave methods, in spite of their value. Zublik (57) and Adams et al (58) discussed the cyclic method qualitatively. An excellent treatment of the theory of stationary electrode polarography was presented in a recent paper by Nicholson and Shain (59). They discuss both single scan and cyclic methods as applied to reversible, irreversible, and kinetic systems.

The reader is referred to Treatise on Analytical Chemistry by Kolthoff and Elving (60) for a more complete discussion of various electro-analytical techniques.

STATEMENT OF THE PROBLEM

The unique "blue solutions" formed by the solution of alkali metals in liquid ammonia have been laboratory curiosities since their discovery in 1864. Their unusual properties have prompted considerable investigation but as yet practical applications are undeveloped. It has been established (46) that these solutions undergo a strong electrochemical oxidation which could be favorable if applied to the production of electrical energy.

This oxidation has long been known (10) to be nearly perfectly reversible due to extremely fast kinetic processes. This suggests that application of this reaction in a device such as a fuel cell could provide a system capable of very high current densities and low polarization. A complete electrochemical study of the characteristics of this oxidation would be the first step in the fabrication of such a fuel cell. It would be ideal to use a cell without transference for these studies, such as



Indeed, electrochemical studies have been conducted utilizing lithium as the anode in solvents of propylene carbonate (61) and cyclic esters (62), but not in liquid ammonia.

One cannot use the free metals as electrodes in ammonia because of their high solubility, nor can the amalgam electrodes be used because of the nearly complete extraction of the metals from ammonia into mercury. Inert electrodes, such as platinum, are then the logical approach to lithium-ammonia electrochemical studies. Unfortunately, most inert electrode materials catalyze an undesirable side reaction to lithium amide. This also seems to be a subject which has received little attention to date (7).

With these criteria in mind, an attempt was made to study the electrochemical oxidation of lithium in liquid ammonia. The objectives of this investigation were the following:

1. Observe the lithium oxidation reaction with single sweep voltammetry.
2. Make a systematic study of several electrodes and their effects on both the electrochemical reactions and catalyzing the undesirable amide reaction.
3. Compile quantitative electrochemical data.
4. Make recommendations concerning application of these results to further development of a lithium fuel cell at Montana State University.

EXPERIMENTAL PROCEDURES

In performing precise experiments on the quasi-stable metal-ammonia system, extreme care and purity are necessary. Because of this requirement, experimental procedures become involved and tedious.

Lithium samples were prepared and handled in an inert argon atmosphere contained by dry box model HE-43-2 manufactured by Vacuum/Atmospheres Corporation. The argon atmosphere was maintained pure by circulation through NaK-56 eutectic which was also contained inside the glove box. This simple purification system seemed adequate but proved bothersome and difficult to maintain.

In order to determine lithium concentrations, a small piece of lithium was cut and cleaned, placed in a small weighing bottle, removed from the dry box, weighed accurately to $1/10$ of a milligram, and returned to the dry box. The empty weighing bottle was then removed and weighed again, containing only the argon atmosphere of the box. This known quantity of lithium was then placed in the electrolytic cell while in the dry box. The sealed cell could then be removed and the experiment performed. Care was taken in all cases to keep the cell completely sealed until the experiment had been completed.

The anhydrous ammonia was purchased from The Matheson Company in a commercial cylinder with a minimum purity analysis of 99.99%. The ammonia as supplied was found to be totally unsatisfactory.

Lithium blue solutions prepared with ammonia directly from the cylinder were unstable and usually decomposed to a white precipitate in less than an hour. The product is presumed to be lithium amide. Therefore, all ammonia referred to in this report was distilled from the cylinder into a glass condensing flask immersed in a dry ice-isopropanol bath (Figure 1). During the distillation into this flask, the flask was connected to a mercury manometer blowoff by means of Tygon tubing to prevent excessive pressure buildup. Pressure could be easily controlled by positioning a leveling bulb containing mercury. Application of a few millimeters of mercury pressure in this way facilitated the condensation of ammonia. Following the condensation, the liquid ammonia could be forced from the condensing flask through a dip tube and into the electrolytic cell by again applying pressure in this manner.

It should be noted that most investigators studying metal-ammonia solutions use more scrupulous purification procedures. Some, involved in precise quantitative determinations, distilled the ammonia several times over sodium to insure a minimum of impurities. In view of other factors limiting accuracy, however, this single distillation is considered adequate.

Low temperatures were maintained with a tandem refrigeration system (Figure 2). A conventional Freon refrigeration unit was used to cool a methanol bath contained in a large Dewar flask to approxi-

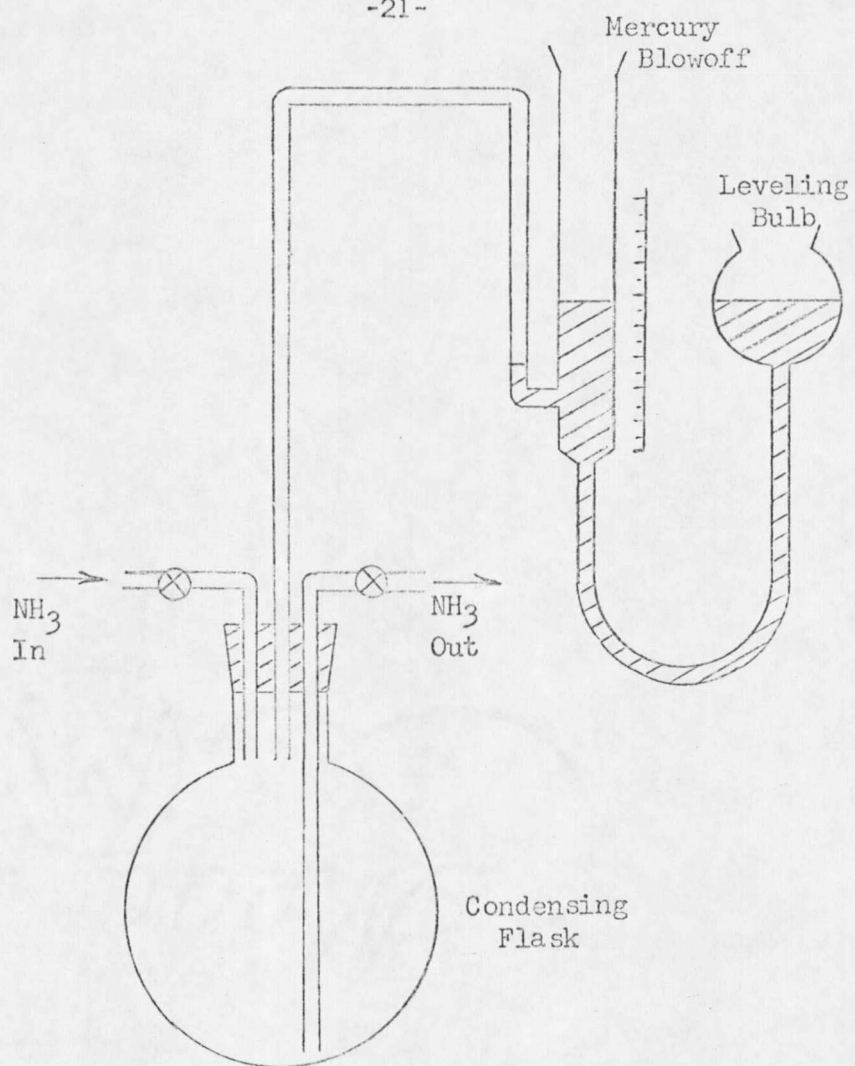


Figure 1. Ammonia Condensation Apparatus.

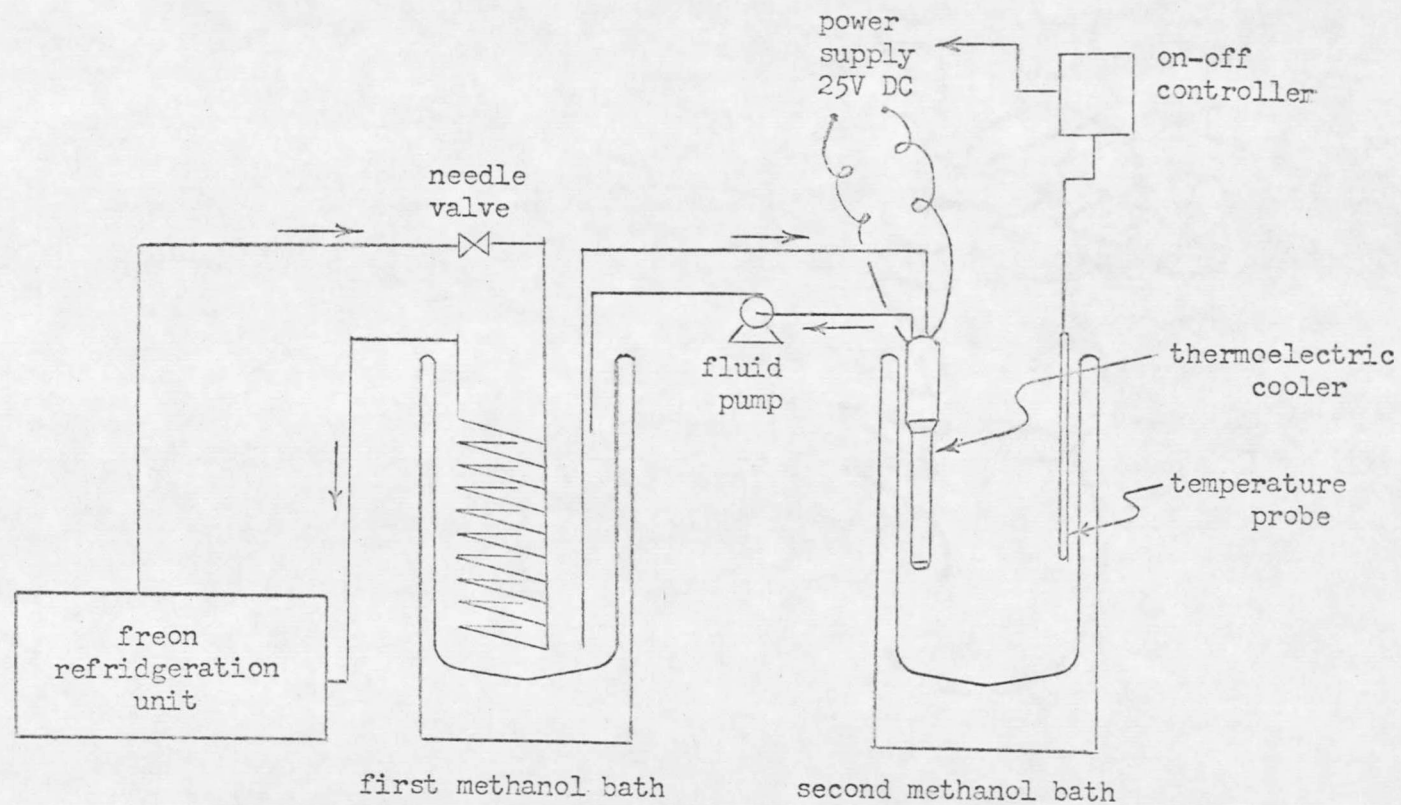


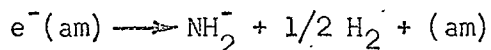
Figure 2. Refrigeration System.

mately -20°C . This chilled fluid was then circulated through an Eberbach thermo-electric immersion cooler which was immersed in a second methanol bath also contained in a large Dewar flask. An on-off Thermistemp temperature controller model 63 was used to control the second bath temperature $\pm 0.1^{\circ}\text{C}$ between -20°C and -40°C .

A. Electrode Catalysis Study

A brief qualitative study was made on the catalysis of the deterioration reaction of lithium-ammonia solutions to the corresponding amide. The reader should recognize that this is actually a reaction of the solvated electron since lithium is presumed to ionize completely in liquid ammonia.

The reaction is, then,



This amide ion is then free to couple with the cation in solution.

Burgess and Kahler (7) investigated qualitatively the catalytic action of a few materials, but it was desirable to determine the effects of other possible electrode materials. This was done by condensing the ammonia as previously described directly on a small piece of lithium, forming a dilute blue solution in the condensing flask. This solution was then transferred as described to a small tube containing a sample of electrode material. The catalytic effect of each material could then be determined by observing the characteristic

blue color and timing its disappearance.

The qualitative nature of this experiment is acknowledged. Nevertheless, the results are informative.

B. Three-Compartment Cell

A three-compartment cell was used for potential measurements and a few voltage scans. This cell is shown in Figure 3.

The three compartments are joined below the liquid level by glass frits and above the liquid level by a pressure equalization arm. Each compartment is sealed by a ground glass joint and a glass stopcock, as shown.

A lead/lead nitrate electrode was used as a reference. This electrode was found to be a suitable reference in previous studies on liquid ammonia (63). Unfortunately, a high and variable resistance between the reference and working electrodes contributed some doubt as to its accuracy.

A typical run in the three-compartment cell was made in the following manner:

1. A known quantity of lithium, weighed in the manner previously described, was placed in the working compartment of the cell while in the dry box.

2. A small, undetermined quantity of lithium was placed in the counter electrode compartment. This was necessary to make the compartment conductive.
3. Enough lead nitrate was placed in the reference electrode compartment to make a saturated solution.
4. The sealed cell was then removed from the dry box and placed in the controlled temperature cold bath.
5. Each compartment of the cell was filled to the desired level with liquid ammonia from the condensing flask as previously described. The condensing flask dip tube was connected to the cell stopcocks by Swagelok fittings. Positive pressure was kept on the system at all times during transference of the ammonia with the mercury blowoff manometer. Ammonia was transferred by bleeding gas from one of the cell stopcocks.
6. The proper electrode connections were made and the cell was ready for the experiment.

The glass frits proved to be a source of difficulty for several reasons. To clean the cell completely, acid, water, and acetone had to be successively forced through the frits and the entire cell was

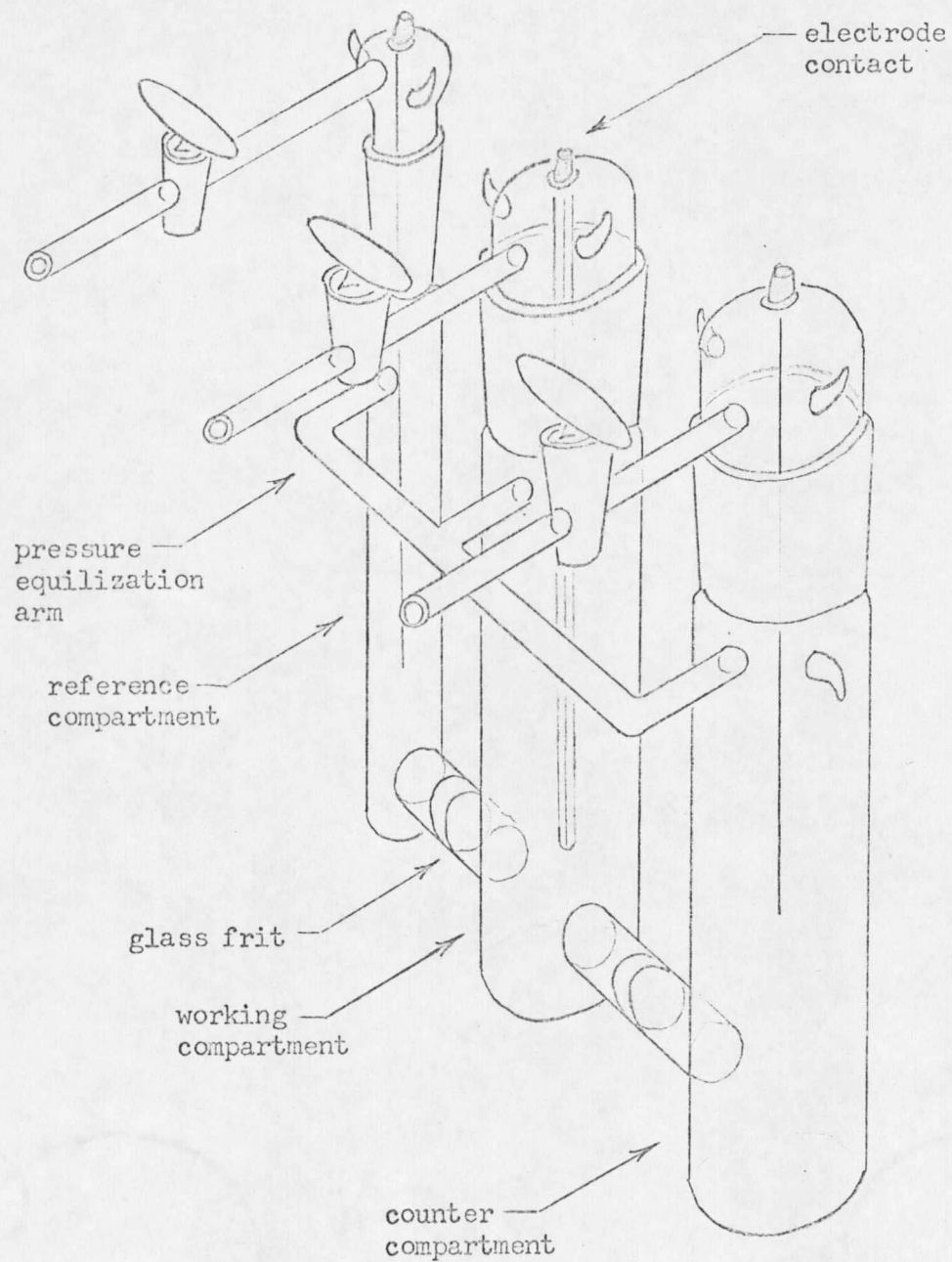


Figure 3. Three-Compartment Cell.

then baked at 200°C under vacuum overnight. The frits frequently broke following a run due to the immediate exothermic reaction of lithium solution which remained in them after the cell had been emptied.

The most serious difficulty was a result of high resistance through the frits. The action of the lithium often raised this resistance to over 5000 ohms. A high resistance between the working and counter compartments, for example, caused a correspondingly higher potential difference for a given current flow. Since the scanning instrument will only function for a set range of potential between these two electrodes, this had the effect of seriously limiting the currents, and thus the concentration range which could be examined. A complete current-voltage curve could therefore be obtained only for a very dilute solution in the three-compartment cell. This was undesirable since any practical application, such as a fuel cell operating at high current densities, would utilize a more concentrated solution.

A high and variable resistance between the working and reference electrodes made accurate potential measurements difficult by introducing an IR drop.

For these reasons the three-compartment cell was used only for potential measurements and a few specialized scans. A one-compartment cell, described below, was utilized for most potential runs.

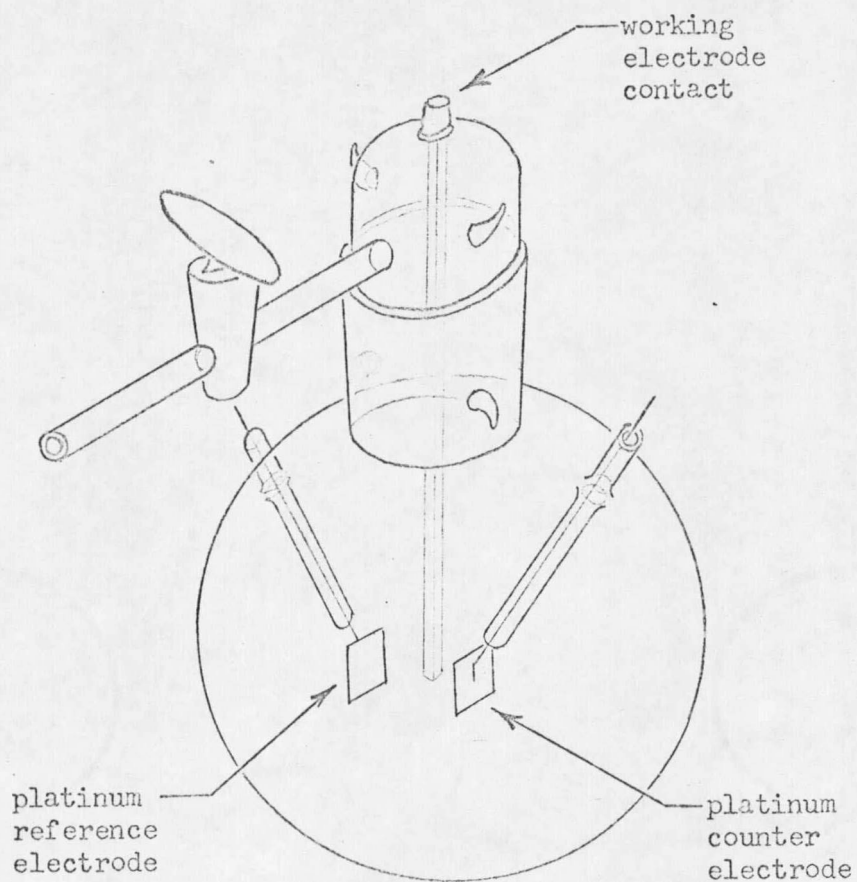


Figure 4. One-Compartment Cell.

C. One-Compartment Cell

Because of the difficulties described in the preceding section, most voltage scans were made in a one-compartment cell. This cell, (Figure 4), contained two fixed platinum plates, one which served as a reference electrode and one which served as a counter. The working electrode and top assembly was identical to that used with the three-compartment cell.

A typical run in the one-compartment cell was performed in the following manner:

1. A known quantity of lithium, weighed as previously described, was placed in the cell while in the dry box.
2. The sealed cell was then removed from the dry box and placed in the controlled temperature cold bath.
3. The cell was filled to the desired level with liquid ammonia from the condensing flask as described for the three-compartment cell.
4. The proper electrode connections were made and the cell was ready for the voltage scan.

This one-compartment cell simplified the experimental procedure and eliminated a few problems. The cell did have two serious disadvantages, however.

First, the platinum plate used as a reference electrode was not ideal. Although for any given run it served as a constant reference point, its potential varied with the lithium concentration of each experiment. Thus, the potential of the oxidation reaction had to be determined first using the three-compartment cell and the saturated lead/lead nitrate reference.

Second, for long periods of operation the one-compartment cell would become contaminated with products from the reaction occurring at the counter electrode. This meant that current efficiency experiments could not be carried out with this arrangement.

D. The Scanning Instrumentation

The scanning instrument was an all-transistor chronopotentiostat recently described by Martin and Vogt (64) (Figure 5). The performance specifications are: The controller current range is -50 to +50 ma. without discontinuity at zero. Sensitivity is about one amp per one volt error signal. Input impedance is about one megohm. The fixed reference voltage is variable from -5 to +5 volts without discontinuity at zero. The ramp reference voltage is linear with time between -10 and +10 volts. The ramp slope is vari-

able from zero to 100 mV/sec, and is subject to hold or reversal at any time. Meters provided indicate the ramp voltage, test electrode current, and test cell voltage.

Current-voltage curves are recorded on a Hewlett-Packard, Moseley Division, 7030AM X-Y recorder.

Lithium-ammonia solutions were stirred by glass-coated magnetic stirring bars spun by a submersible magnetic stirrer in the controlled temperature bath.

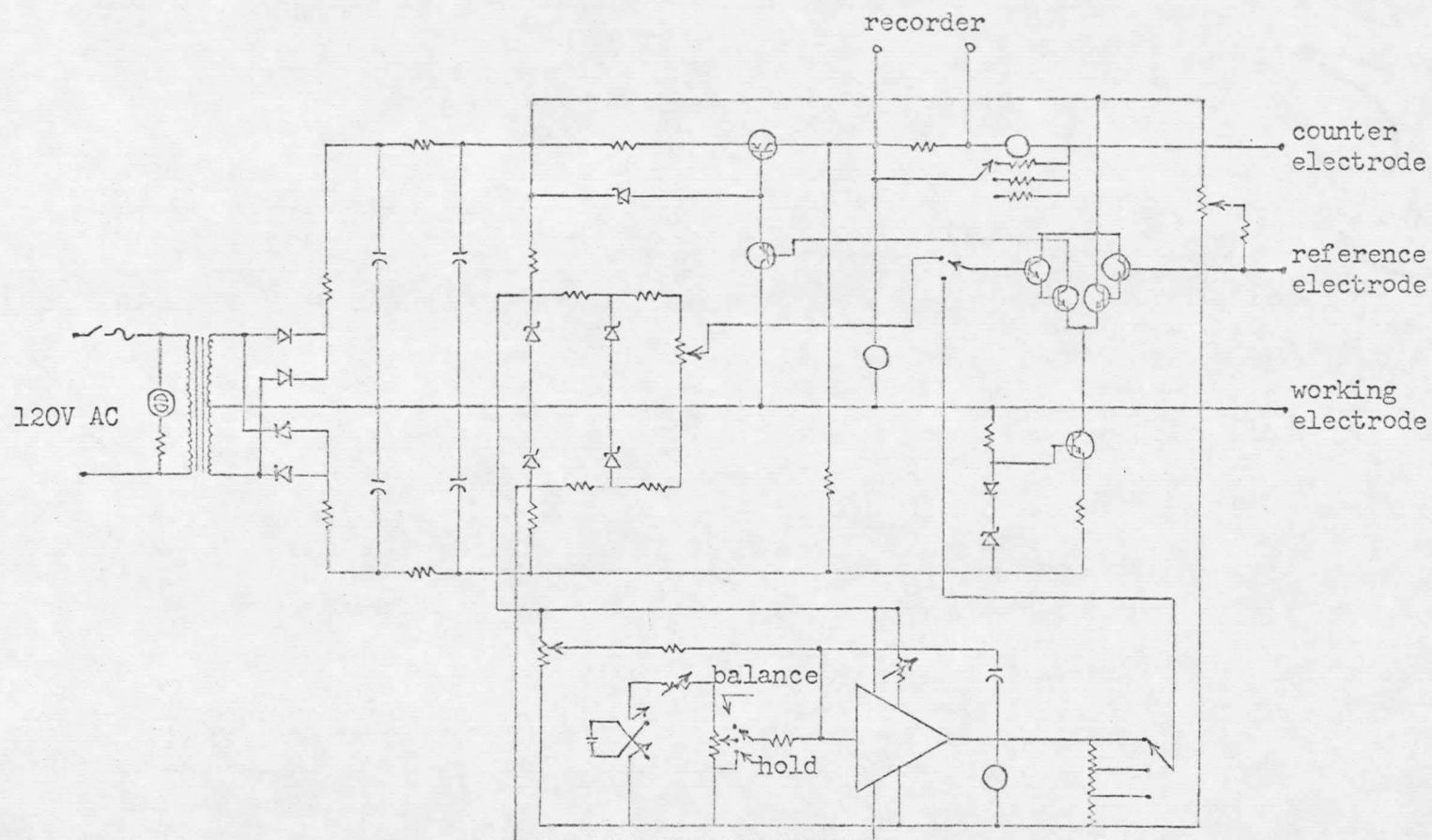


Figure 5. Chronopotentiostat Circuit.

EXPERIMENTAL RESULTS

A. Electrode Catalytic Study

A study of the catalytic action of several prospective electrode materials on the deterioration of the lithium-ammonia solution was conducted first. The results of this study are qualitative only, and therefore materials are classified as excellent, good, fair, or poor. For example, platinum black, which is a strong catalyst for the undesirable reaction, would be classified as "poor". An "excellent" rating would indicate little or no catalytic action.

The results are the following:

<u>Material Tested</u>	<u>Result</u>
mercury*	poor
platinum black	poor
rusted iron	poor
nickel	poor
gold	fair
pure iron	fair
smooth platinum	fair
zinc	fair
silver	good
gray platinum	good
paladium	good

<u>Material Tested (cont.)</u>	<u>Result (cont.)</u>
aluminum	excellent
tungsten	excellent
carbon	excellent

*Mercury appears very poor, primarily because of the rapid amalgamation of the dissolved lithium into the mercury rather than because of its catalytic action.

Since these results are not quantitative, a few words concerning the significance of this catalysis seem appropriate.

Even in the presence of a strong catalyst such as platinum, the amide reaction occurs very slowly and can be observed only in a very dilute solution. This author feels, after having directly observed this effect, that losses in the practical operation of a fuel cell would be small. Nevertheless, effective catalysts should be avoided in construction if possible. Additional difficulty of operation due to the insoluble amide in the system would probably be of greater significance than actual fuel loss.

B. Voltage Scans

In order to discuss the characteristics of the current-voltage curves, let us first consider how such a curve is generated. Basically, a linear or ramp potential is impressed on the working

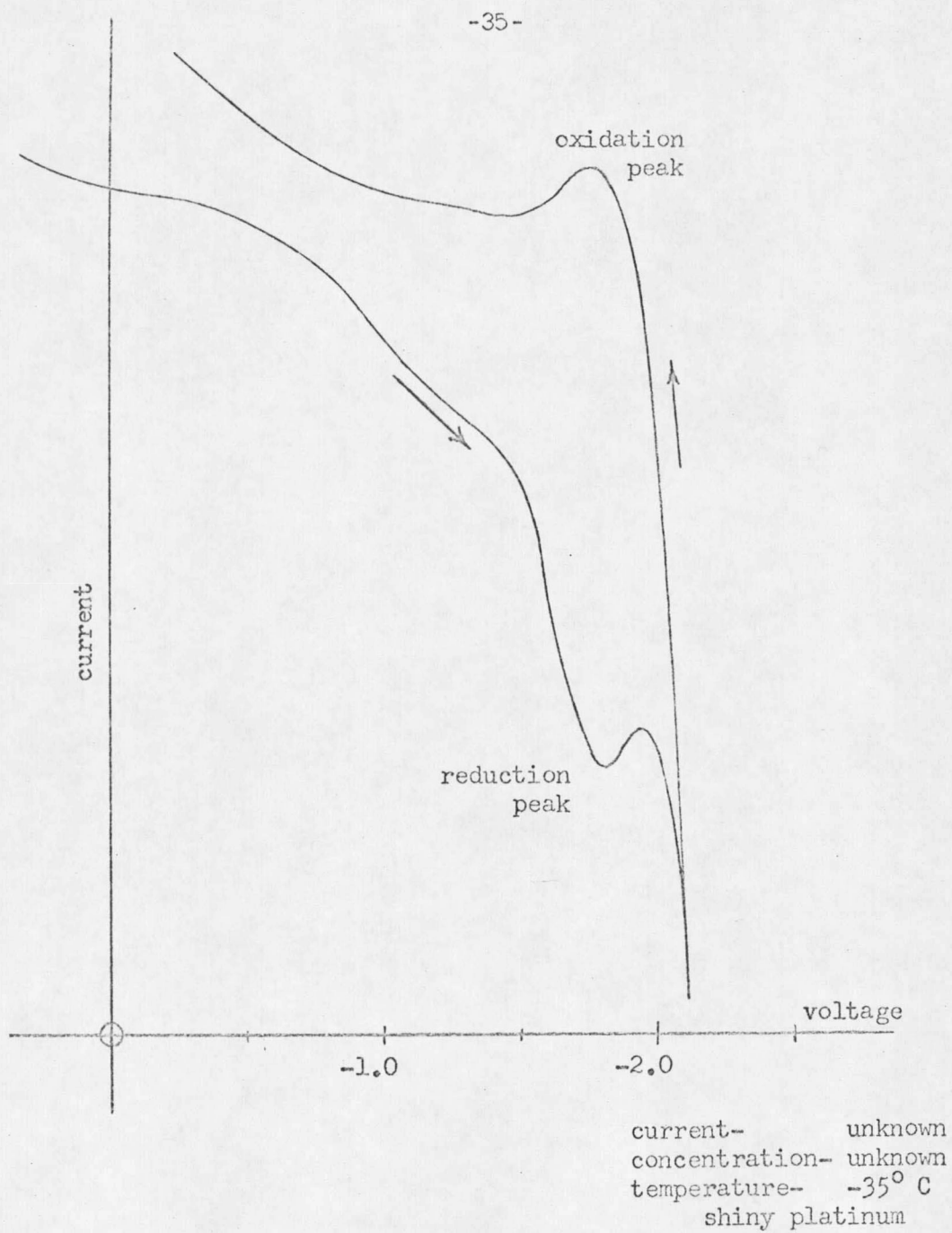


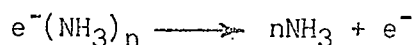
Figure 6. Cyclic Scan of Lithium-Ammonia Solution in the Three-Compartment Cell.

electrode. Since we are primarily interested in oxidations in this case, the ramp potential is scanned from negative to positive, or toward the anodic. When this potential becomes sufficiently anodic, an electrochemical oxidation occurs, and can be observed by a positive increase in current. A reduction wave is generated in an analogous manner, except that the potential is scanned from positive to negative and the current increase is negative when a reaction occurs. Thus, a positive current indicates a net oxidation and a negative current a net reduction. Both oxidation and reduction waves are shown in Figure 6.

The rate of electrochemical reaction, and hence the current, is controlled in part by the rate of the electron-transfer reaction and in part by the transport of a solution species to the electrode surface. The rate of current flow is governed by the slowest of these two processes. An investigation of the relative effects of kinetics and diffusion is therefore an important part of this study.

The fact that diffusion plays a significant role is apparent by noticing that the oxidation wave exhibits a peak or maximum. This is caused by a depletion of the reacting species at the electrode surface and the formation of a diffusion layer between the electrode and the bulk of the solution.

Assuming that lithium ionizes completely in liquid ammonia, as first proposed by Kraus, the electrochemical oxidation which occurs is



This reaction has been called reversible by many investigators. Let us consider for a moment what makes a reaction reversible, and how it can be recognized. A reversible reaction is basically one with very fast kinetic processes. This causes the reacting species to undergo electron transfer immediately on contact with the electrode and the diffusion~~al~~ process is controlling. Irreversible reactions are, therefore, those with slow kinetics. Considering this, one might expect the oxidation of the solvated electron to be very reversible since it is bound rather loosely to the solvent molecules.

The separation of the oxidation and reduction peaks can be a measure of the reversibility. Actually, for a truly reversible system the anodic and cathodic peaks are not at exactly the same potential but are separated by about 56 mV. Figure 6 shows the solvated electron reaction to conform to this requirement of reversibility. Furthermore, Figure 7 shows that the position of the reduction peak does not change with a variation of scan rate. If the reaction were irreversible, an increase in scan rate would cause the reduction peak to move to a more cathodic potential, thus separating the oxidation and reduction peaks further. This characteristic is often used to

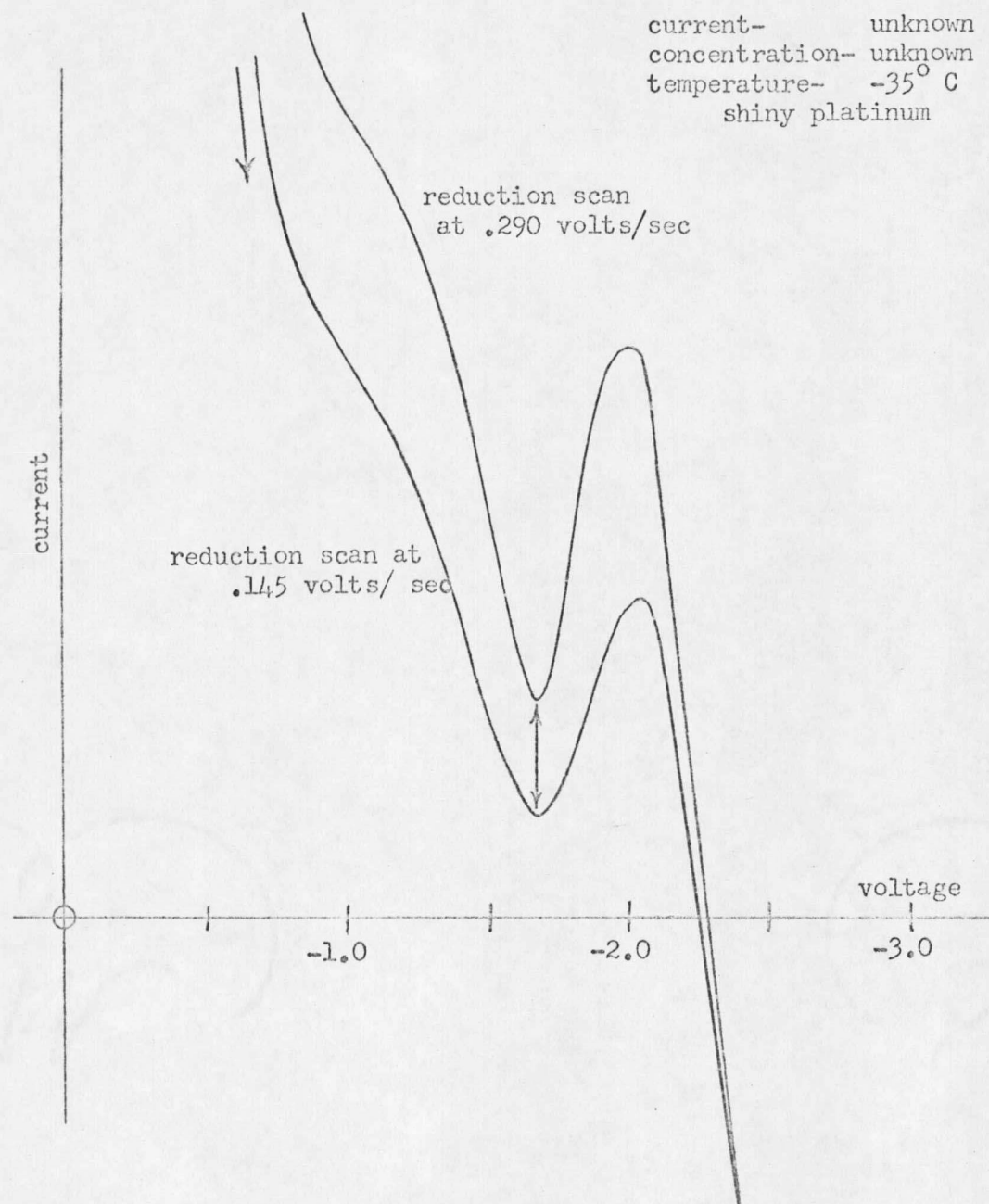


Figure 7. Effect of Scan Rate on Reduction Waves in the Three-Compartment Cell.

study electron transfer rates. For example, if a reaction behaves reversibly, as the solvated electron reaction does, it should be possible to increase the scan rate until the point is reached where the reaction rate becomes significant and the peaks begin to separate. Unfortunately, for very fast electron transfer steps, sophisticated equipment is necessary to generate and record the extremely fast scan rates required. Therefore, such analysis was not possible in this laboratory.

Further evidence of a reversible reaction is a linear relationship between peak height and reactant concentration. A series of voltage scans to establish this relationship was made at varying concentrations and are shown in Figures 8 through 14. Figure 15 shows a plot of concentration vs. current, and although the points show some scatter, they do approximate a straight line.

Complete voltage scans were made on solutions up to 0.208 M. Beyond this concentration complete waves could not be obtained because of two limitations. First, the peak current became greater than the chronopotentiostat could accommodate. In practice this resulted in an automatic stop in the voltage scan. Second, the oxidation waves became very rough at high current densities. This appears to be the same difficulty experienced by Gordon and Sundheim (46) in their constant current diffusion studies. They reported that at higher concentrations the latter part of the chronopotentiograms appeared to

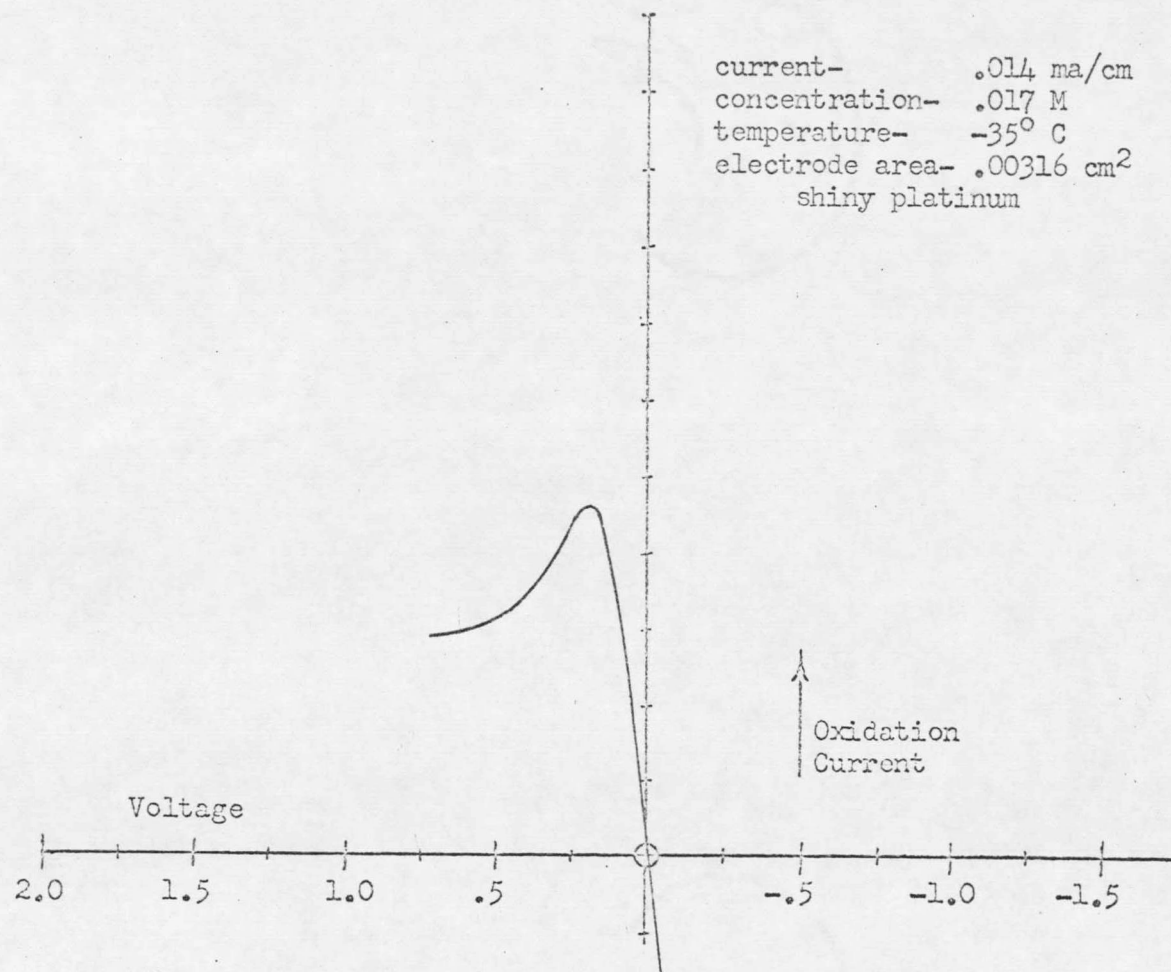


Figure 8. Oxidation Wave in the One-Compartment Cell.

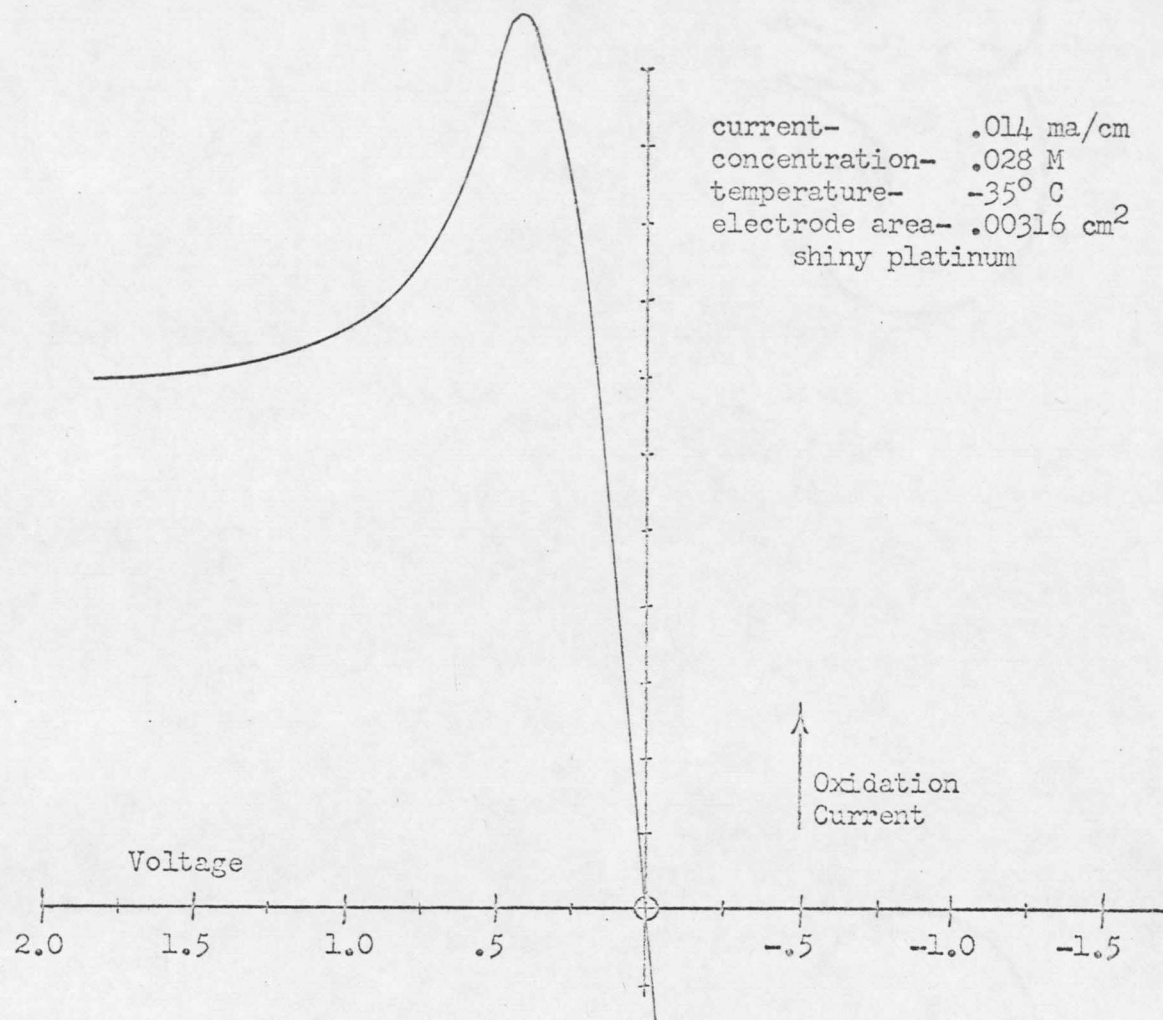


Figure 9. Oxidation Wave in the One-Compartment Cell.

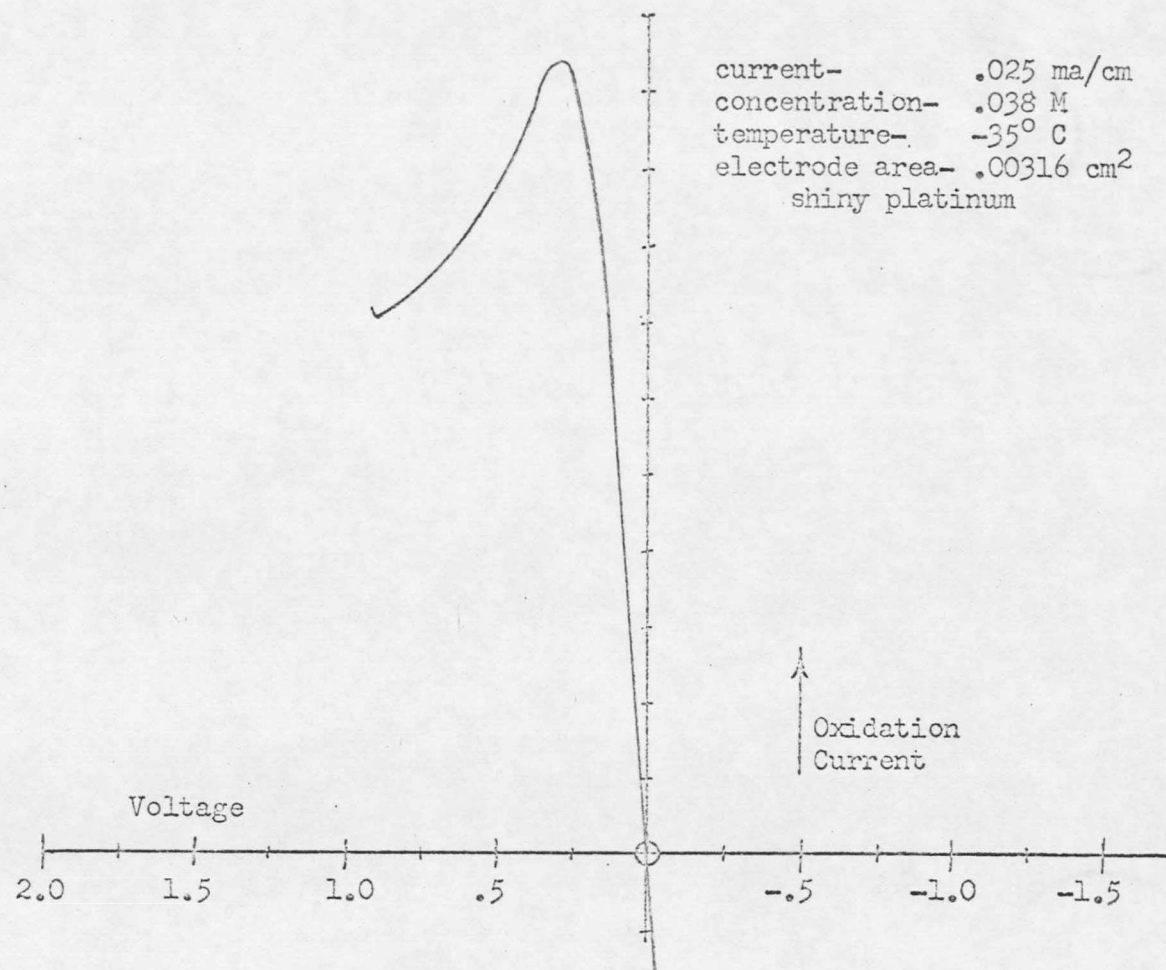


Figure 10. Oxidation Wave in the One-Compartment Cell.

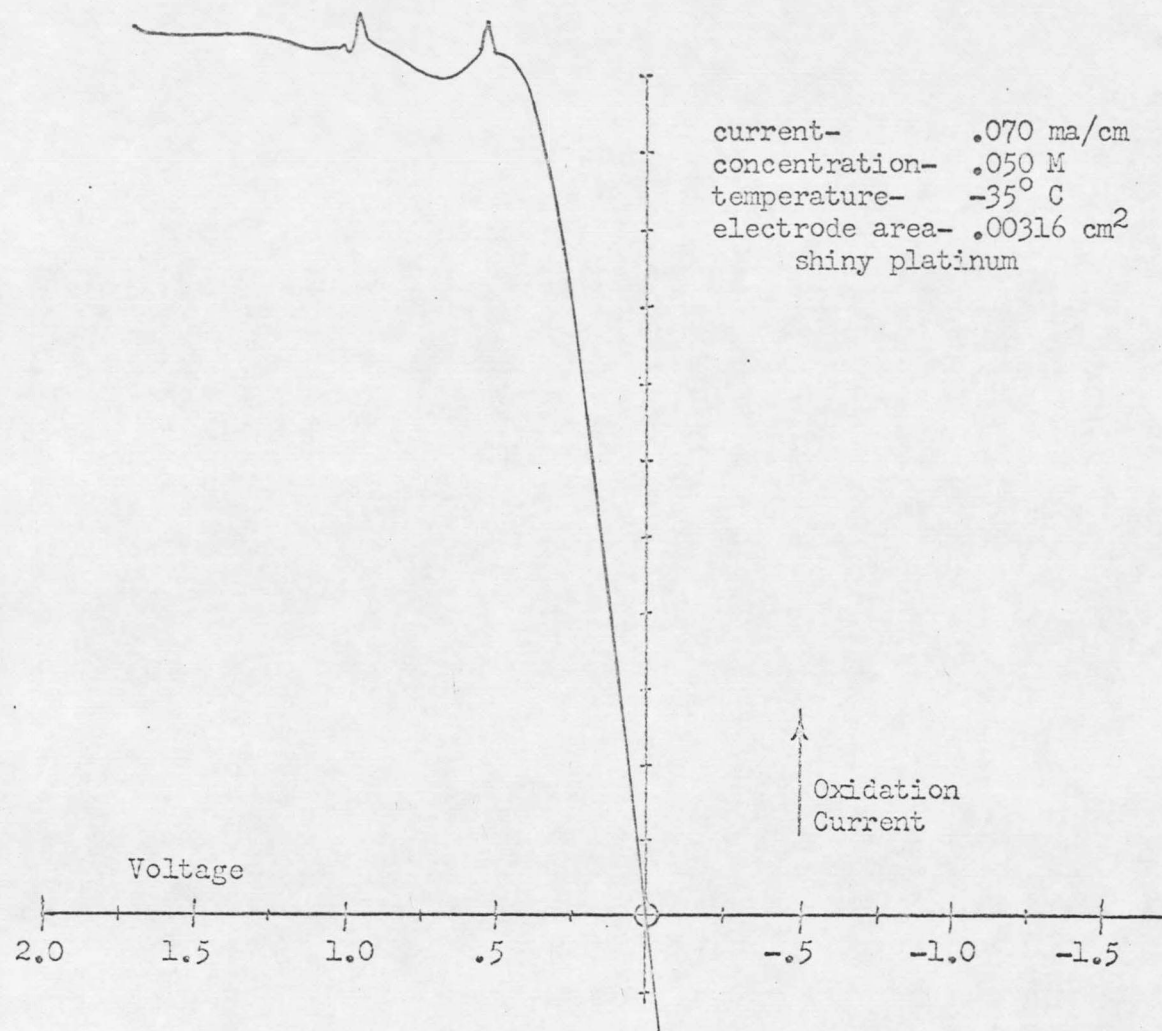


Figure 11. Oxidation Wave in the One-Compartment Cell.

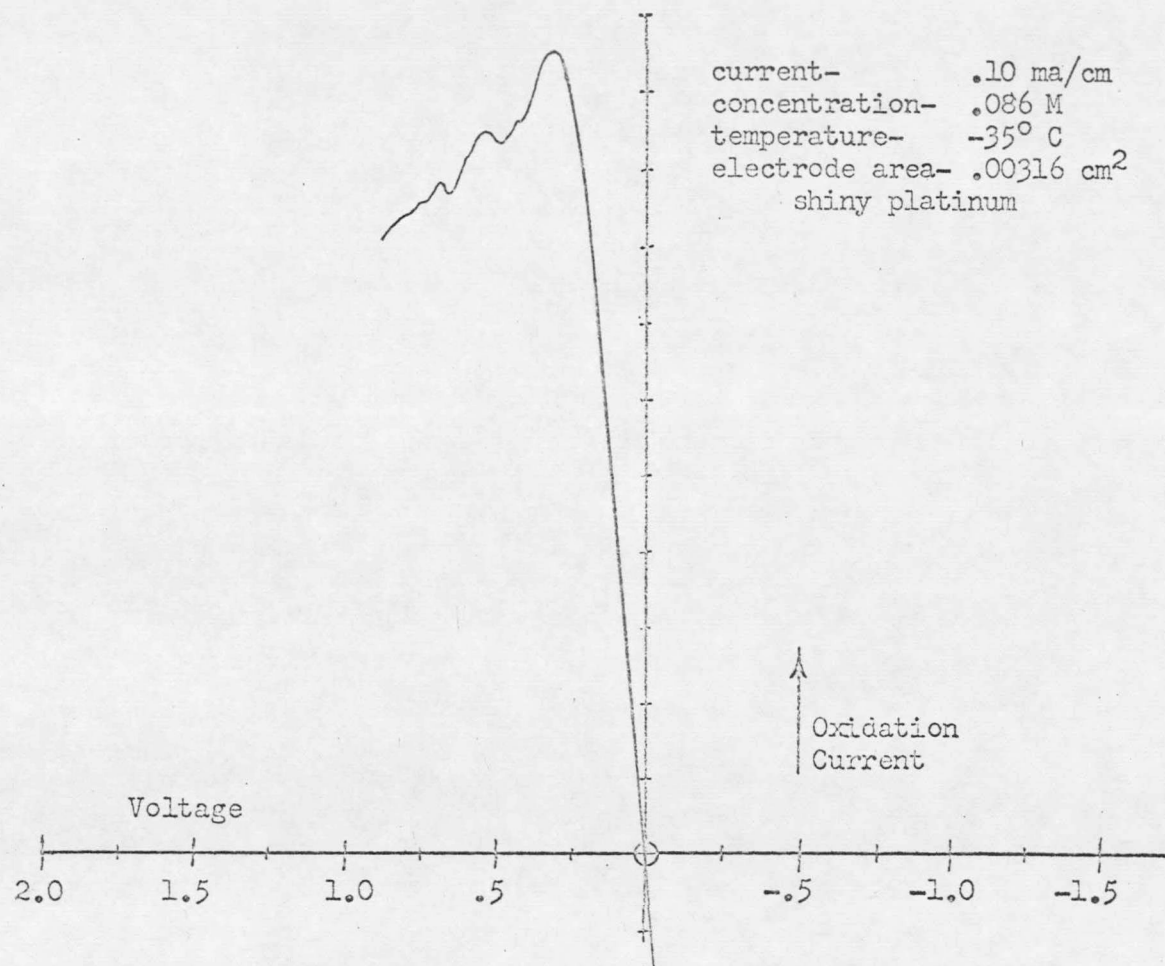


Figure 12. Oxidation Wave in the One-Compartment Cell.

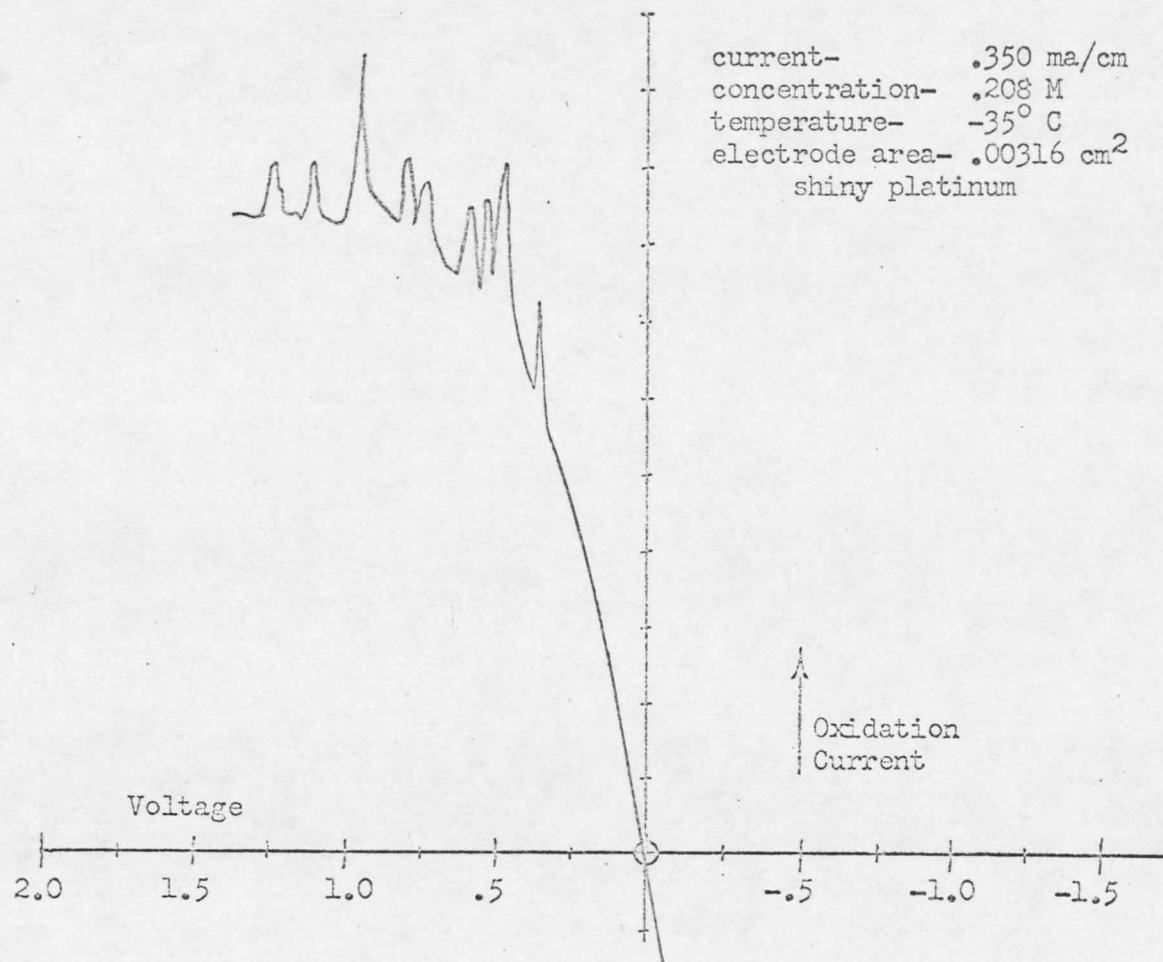


Figure 13. Oxidation Wave in the One-Compartment Cell.

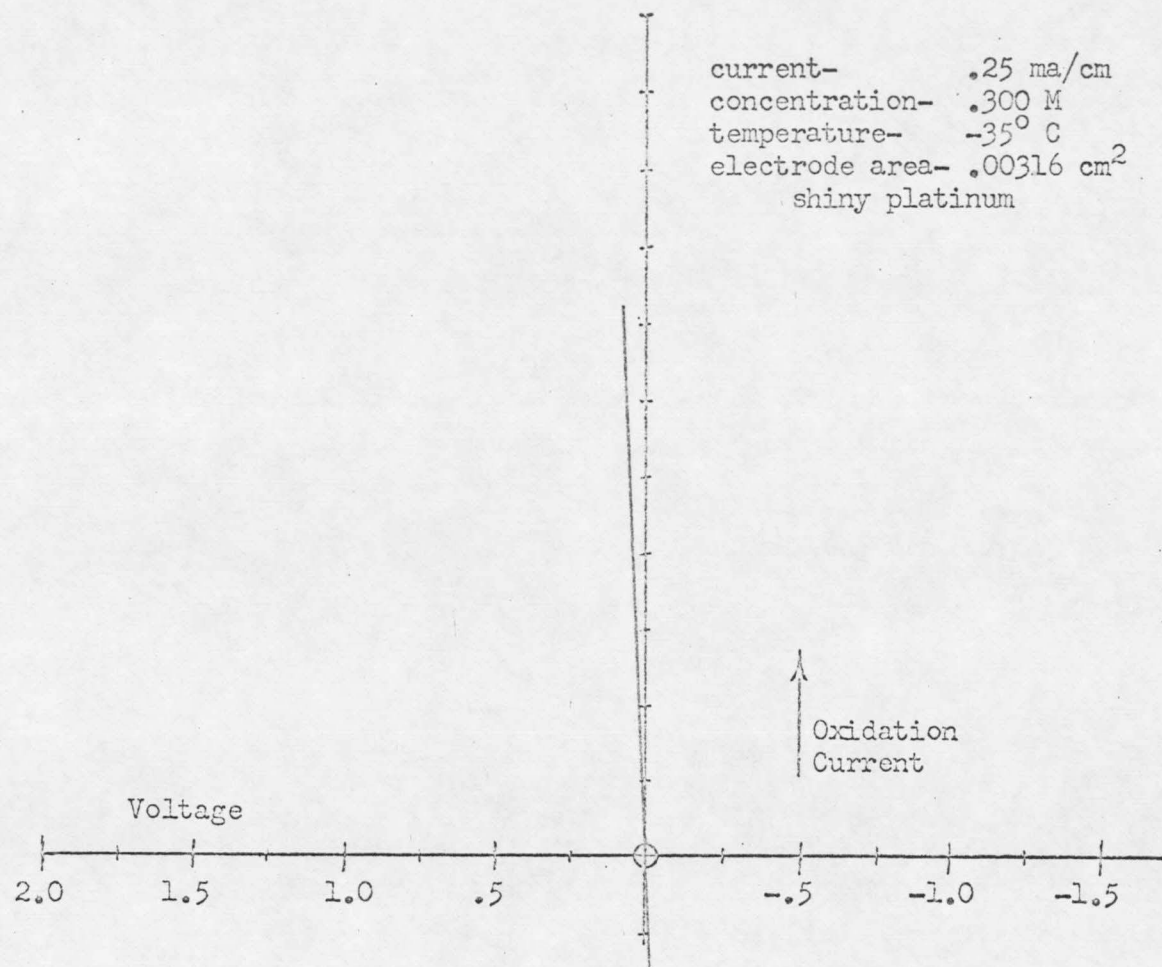


Figure 14. Oxidation Wave in the One-Compartment Cell.

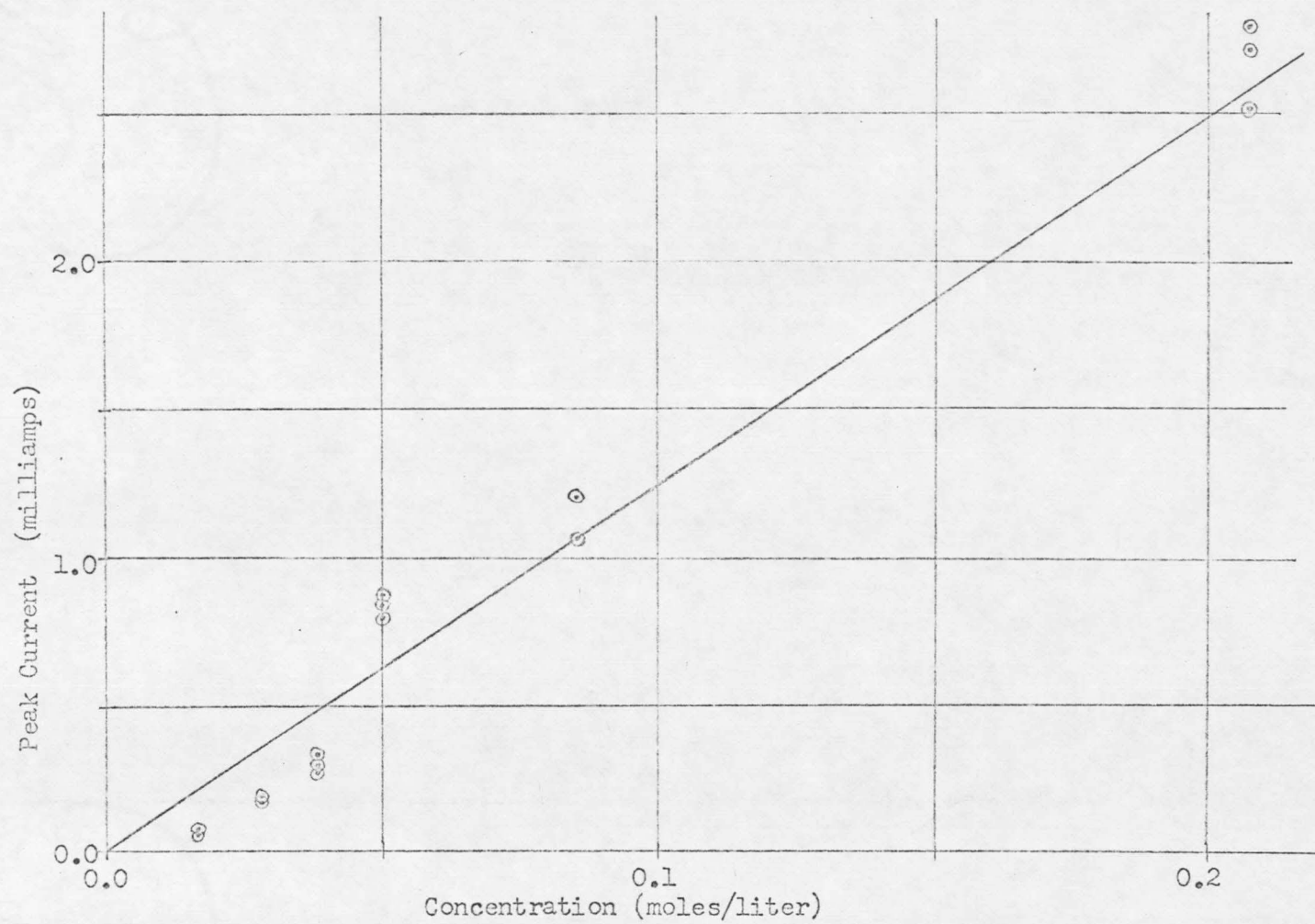


Figure 15. A Plot of Concentration vs. Peak Current.

show the onset of boiling, and blamed this disturbing effect on Joulean heating. This ragged behavior is often typical of high current density operation, and in this case the maximum current density was nearly 1000 ma/cm². This high value would be a definite advantage if it could be attained in practical application.

Polarization or overpotential is another parameter important to the operation of a fuel cell and the concept of reversibility. Polarization is a deviation of the reaction potential from its equilibrium value due to the passage of a net current. Here again, this parameter may be divided into two classes: that caused by a slow kinetic process in the electron-transfer reaction, called activation polarization, and that arising from a depletion of surface concentrations of the reacting species, called concentration polarization. In fact, electrode processes are classified to be reversible if the activation polarization is immeasurably small and irreversible if the activation polarization is measurable.

In the case of the electrochemical oxidation of the solvated electron, this overpotential is relatively easy to measure but difficult to interpret. One of the most significant characteristics of the oxidation is that it occurs in the same proximity as the solvent reduction. Therefore, at zero current where polarization is usually determined, two reactions are actually occurring, resulting in a net zero current. Despite this complication, the value of this over-

voltage is an important factor in a practical device such as a fuel cell where a small deviation is naturally desirable to maintain a high working potential.

Polarization measurements were made at varying concentrations from oxidation waves by determining the slope of the current-potential curve at zero current. This value of polarization per milliamp has the dimensions of resistance, and is usually termed the polarization resistance. Figure 16 shows a plot of this value vs. concentration on semi-log paper. The deviation from the equilibrium potential is seen to be only about 3 mV at a current density of nearly 1000 ma/cm² for the most concentrated solutions. Fortunately, since these measurements were taken at nearly zero current, the problems which prevented the generation of oxidation waves above 0.20 M did not inhibit polarization experiments into the concentrated region.

The fact that the oxidation wave of the solvated electron does in fact overlap the reduction decomposition of ammonia is a definite disadvantage from an analytical point of view. Therefore, several attempts were made to separate the two reactions in order to isolate the oxidation being observed.

Since the solvated electron oxidation had been established to be completely diffusion controlled, and the reduction of ammonia was known to be largely kinetically controlled, it was thought that a

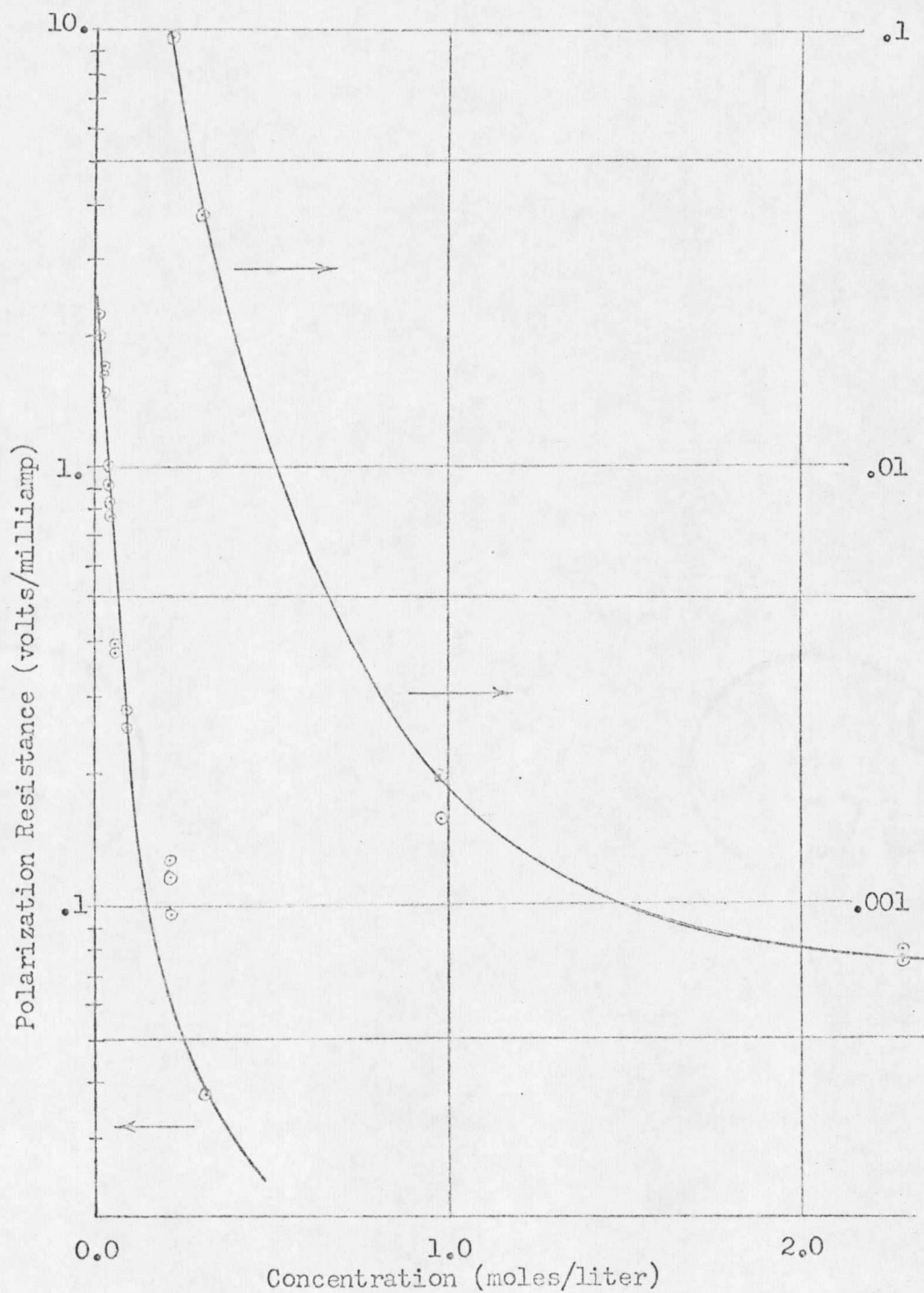


Figure 16. A Plot of Polarization/Milliamp vs. Concentration.

significant change of temperature might affect the two reactions differently enough to effect some separation. For this reason a cold scan was made at -60°C . As can be seen from this scan, shown in Figure 17, lowering the cell temperature had little effect. The most significant change resulting from the drop to -60°C was a decrease in peak current, due to the corresponding decrease in the reactant diffusion coefficient.

Several attempts were made to isolate the solvated electron oxidation by changing the over-voltage of the ammonia reduction. Since this latter reaction involves a gas evolution, its position on the potential scale should largely depend on the state of the electrode surface, traces of impurities, and especially the electrode material. Selection of a metal electrode with a higher overvoltage than platinum should therefore shift the ammonia reduction to a more cathodic potential. Here, again, the rapid amalgamation of the alkali metals from solution is indeed unfortunate since mercury effects a very strong overvoltage.

Figures 18-21 show oxidation waves on working electrodes of aluminum, tungsten, palladium, and platinum-iridium, respectively. In all cases no significant change in the general morphology of the current-potential curve was effected. This result is both surprising and unfortunate. Other electrode materials generally showed less consistency than platinum (Table III), and none were pursued further.

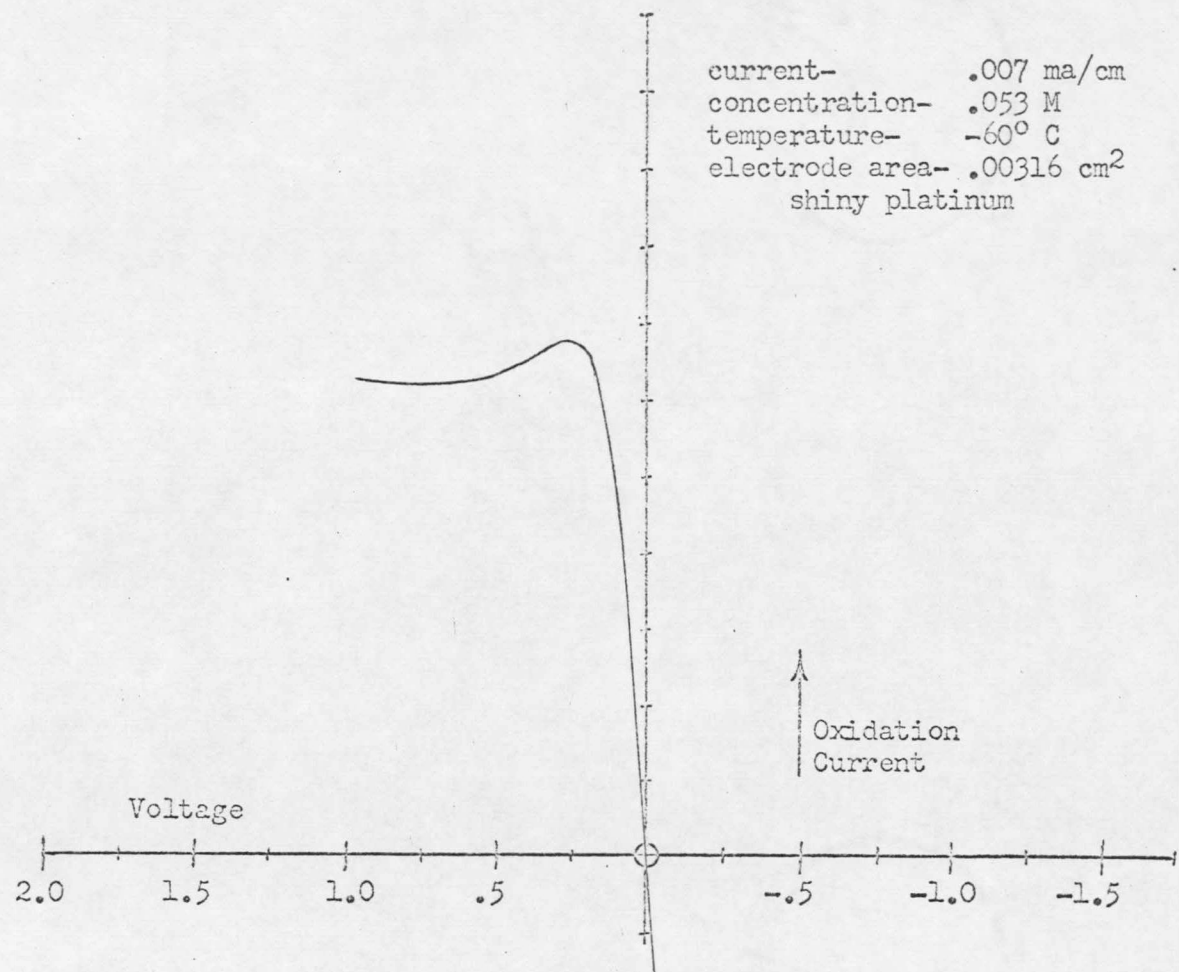


Figure 17. Oxidation Wave at -60° C.

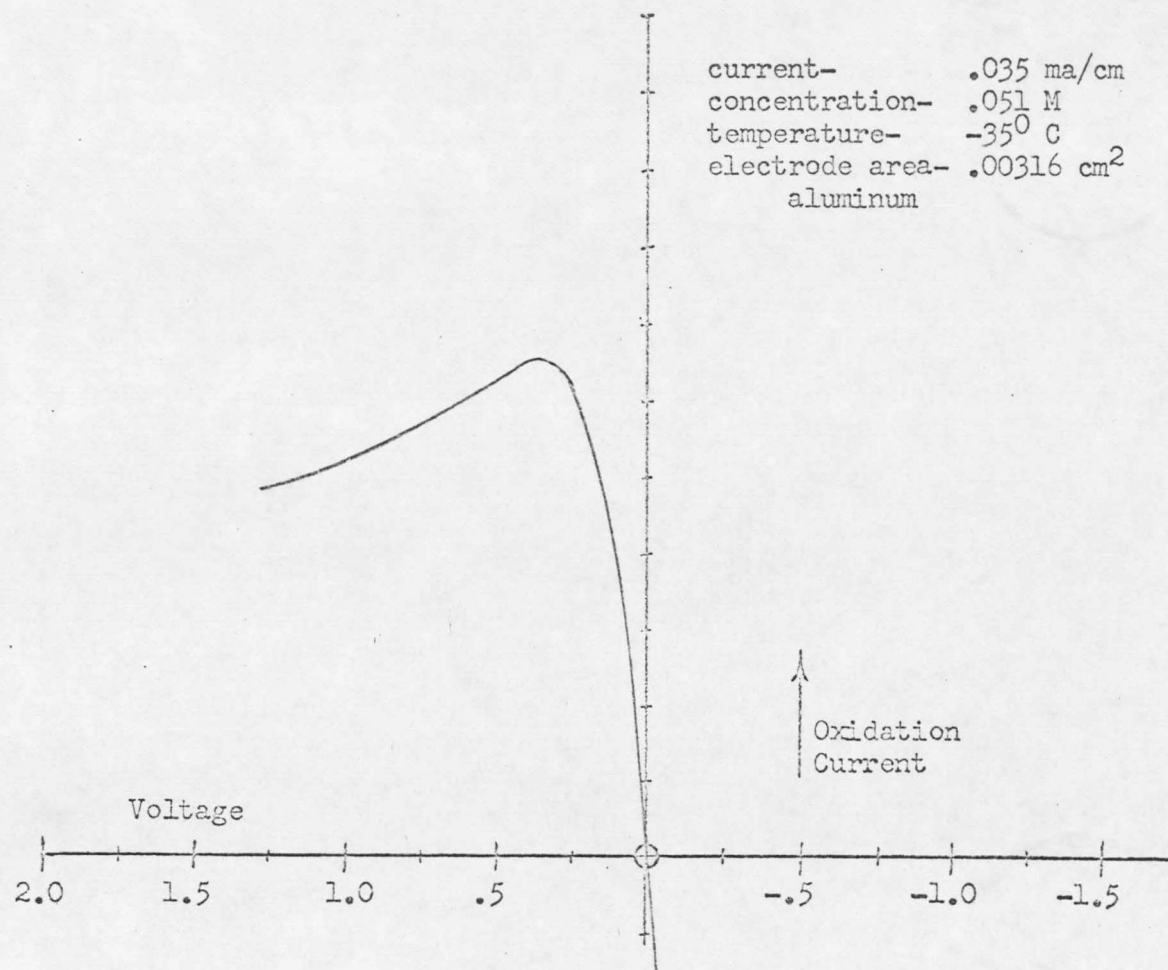


Figure 18. Oxidation Wave Using an Aluminum Electrode.

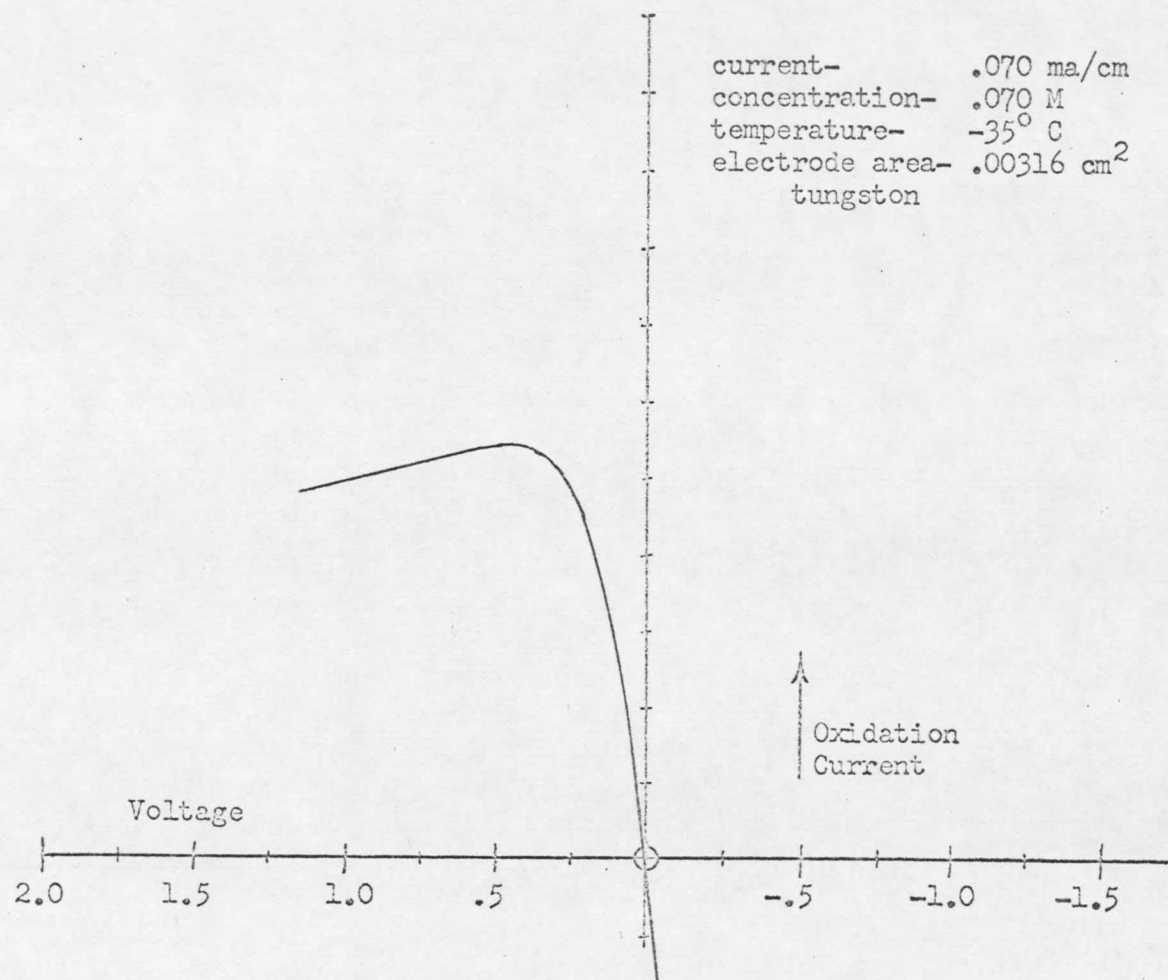


Figure 19. Oxidation Wave Using a Tungsten Electrode.

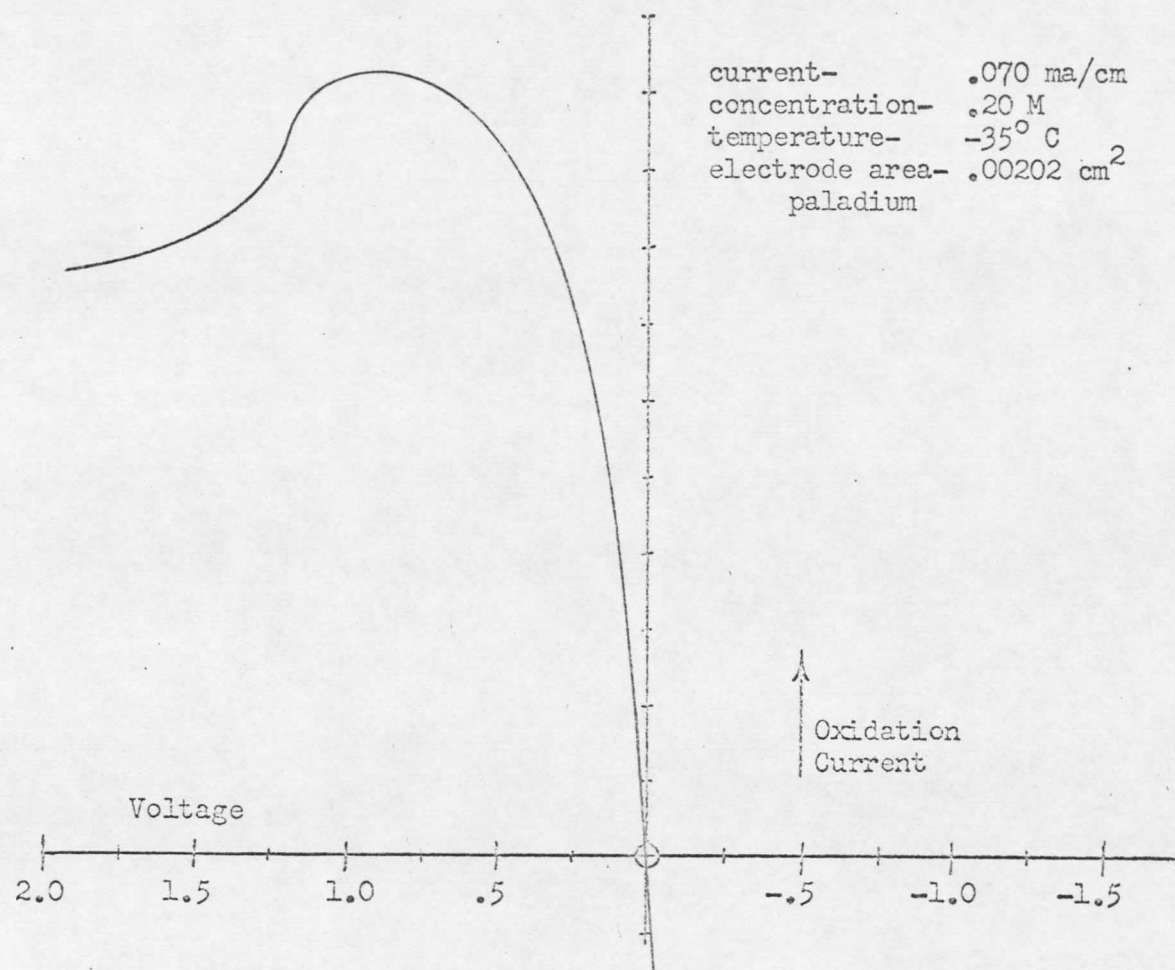


Figure 20. Oxidation Wave Using a Paladium Electrode.

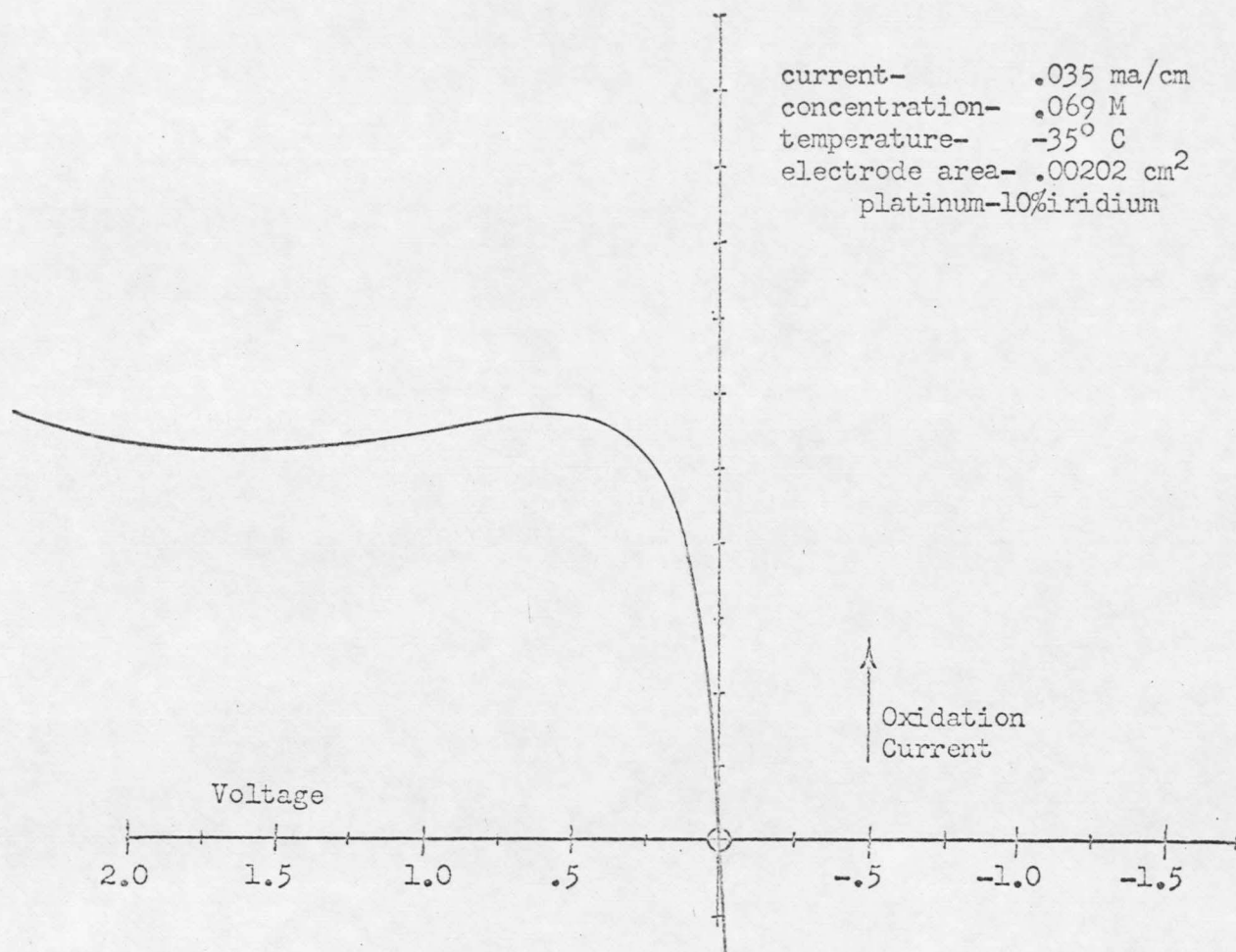
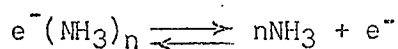


Figure 21. Oxidation Wave Using a Platinum-Iridium Electrode.

This is perhaps an appropriate point at which to discuss another interesting concept. It has been mentioned that metal-ammonia solutions above a concentration of about one molar behave as liquid metals in nearly every respect. Because of their remarkable conduction properties, these bronze solutions become, for all practical purposes, the electrodes themselves. Since the morphology of the current-voltage curves depend significantly on the electrode material, it would be extremely interesting to examine such a curve in this region. For this reason, the solution and instrumental limitations preventing such a study are particularly disappointing.

The oxidation was observed (Figure 22) to separate from the ammonia reduction on only one occasion in the presence of a considerable amount of iron impurity. This system, however, was very unstable and could not be quantitatively investigated.

In spite of its apparent perfect reversibility, the oxidation of the solvated electron does not appear reversible in at least two respects. These apparently result from the complex physical nature of metal-ammonia solutions. First, the peaks appear broader than one would expect for a perfectly reversible reaction. Second, one would expect from the equilibrium



that only ammonia is necessary for the reduction reaction forming the

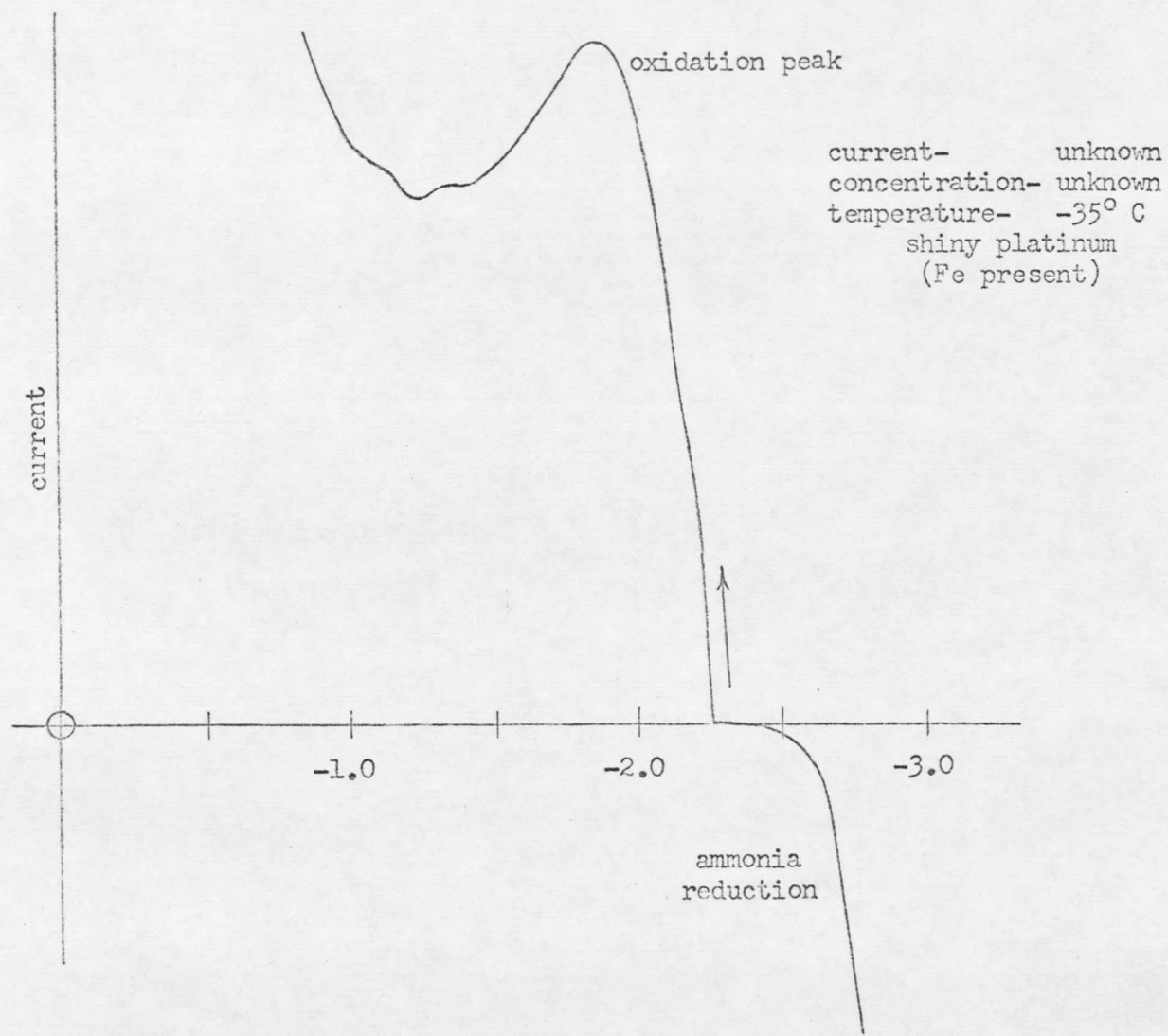


Figure 22. Oxidation Wave in the Presence of Iron Impurities.

solvated electron. Such is not the case. In the one-compartment cell, even at best only a slight inflection indicated the presence of the reduction reaction. In the three-compartment cell the reduction peak could be observed only if considerable oxidation occurred first, creating a large excess of Li^+ ion. The very fact that solvated electrons cannot be produced from any ammonia-salt solution confirms the importance of the cation in the unique blue and bronze solutions. The lithium ion itself, therefore, plays an important role in "solvating" the electron.

Some important procedural points should be mentioned before concluding the discussion of current-voltage curves. First, in order to obtain reasonable reproducibility it was found to be absolutely necessary to stir the solution between each scan and then wait a period of one minute to allow the solutions to become quiescent again. This procedure was used to destroy the diffusion layer at the electrode surface. A platinum electrode seems to exhibit a much better general reproducibility in these oxygen-free solutions than in aqueous systems. All platinum electrodes were stripped of their oxide layers previous to each test with aqua regia. No particular treatment of other electrodes was attempted, however.

It should also be pointed out that at no time was any supporting electrolyte used to eliminate migration currents. Thus, all currents refer more nearly to what might be expected in practical application rather than idealized diffusion currents.

C. Potential Measurements

An obvious disadvantage of operation of the one-compartment cell is the lack of a consistent voltage reference. For any given run the platinum plate used as a reference remained sufficiently constant, but varied from run to run with lithium concentration. For this reason, the potential of the zero current point was established in the three-compartment cell as a function of concentration. Actual potentials of points on the current-voltage curves obtained from the one-compartment cell can thus be referred to a saturated lead/lead nitrate reference electrode throughout this study. The results are shown in Table I.

The reader is reminded, however, that these potential measurements are subject to the possibility of error due to a high and variable resistance in the frit separating the reference and working electrodes.

D. Current Efficiency Study

A current efficiency study was conducted by holding the potential at a point sufficient for oxidation to occur until all the lithium had been electrochemically oxidized. The resulting current was recorded as a function of time until the endpoint was detected by both a drop of the oxidation current and a disappearance of the characteristic blue color. The area under such a current-time curve thus is a measure of coulombs, and can be related through Faraday's law to a specific weight of lithium. A ratio between this weight and the weight

actually used is, then, a measure of efficiency.

The potential was held at a point between the equilibrium potential and the current peak, thus approximating the potential where a practical device would operate. Although some drift was experienced, potential was maintained $\pm 0.05V$, approximately 0.1 V anodic of equilibrium. The three-compartment cell was used for these measurements in order to keep unwanted products from the counter electrode separate from the test solution.

Two separate runs yielded efficiencies of 92% and 95%. Since the amount of lithium used for this study was very small and the time involved was three and five hours, losses due to trace impurities and the amide reaction were probably significant. The author, therefore, feels that these figures represent minimum efficiencies.

It should be acknowledged that the quality of these curves was generally poor due to considerable noise.

SUMMARY

The electrochemical oxidation of a lithium-ammonia solution has been successfully studied, using the methods of single and cyclic sweep solid electrode voltammetry. This reaction has been shown to exhibit several characteristics which make it appear attractive as the anodic process for an electrical power producing device such as a fuel cell. Some of these characteristics are:

1. Cyclic scans at varying scan rates show the oxidation of the solvated electron to be reversible.
2. Current densities obtained appear to be very favorable for practical application. Current densities over 1000 ma/cm^2 have been experimentally observed.
3. Polarization studies show that the more concentrated lithium-ammonia solutions experience very small potential variations even at high current densities. Polarization in a 2.0 M solution was only about 3 mV at 1000 ma/cm^2 .
4. The oxidation occurs at a very negative potential which would permit operation of a

4. (continued)

fuel cell at a relatively large potential.

The reaction, in fact, occurs only slightly anodic of the solvent reduction at about -1.9 to -2.0 volts vs. a lead/lead nitrate reference.

5. High efficiencies can be expected from this reaction since two experiments yielded efficiencies of 92% and 95%.

In spite of these advantages there are some disadvantages presented by the application of a lithium-ammonia solution to a fuel cell. Such a cell would have to operate at either a temperature below -35°C or under pressure. Because of the inherent reactivity of lithium, great care is necessary during handling and operation. Also, the undesirable amide reaction may result in some fuel loss and cause some difficulty in construction and operation.

Nevertheless, this author feels that the advantages far overshadow the drawbacks, and that metal-ammonia solutions show great potential as the anodic process of a fuel cell or similar power-producing device. The greatest problem of any, in fact, may be finding a suitable reduction with which to couple it which could match its capabilities. This is the next logical step in development.

APPENDIX

TABLE I. Equilibrium Potential in Lithium-Ammonia Solutions
Measured vs. Lead/Lead Nitrate Reference.

	<u>Concentration (m)</u>	<u>Equilibrium Potential</u>
1.	0.10	2.04
2.	0.27	1.88
3.	0.47	1.76
4.	0.80	1.75
5.	1.32	1.68

TABLE II. Peak Current and Polarization of Scans in the One-Compartment Cell on Platinum.

<u>Concentration</u> <u>(moles/liter)</u>	<u>Peak Current</u> <u>(milliamps)</u>	<u>Polarization Resistance</u> <u>(volts/milliamper)</u>
0.017	0.0645	2.23
0.017	0.0545	1.99
0.028	0.171	1.43
0.028	0.164	1.65
0.028	0.161	1.62
0.038	0.312	0.77
0.038	0.268	1.00
0.038	0.278	0.91
0.038	0.260	0.83
0.050	0.875	0.385
0.050	0.835	0.385
0.050	0.791	0.375
0.086	1.20	0.250
0.086	1.06	0.275
0.208	2.52	0.115
0.208	2.80	0.123
0.208	2.73	0.0955
0.300	----	0.0375
0.975	----	0.00196
0.975	----	0.00156
2.29	----	0.000777
2.29	----	0.000762

TABLE III. Peak Currents and Polarizations of Scans in the One-Compartment Cell on Various Electrode Materials.

<u>*Electrode Material</u>	<u>Concentration (moles/liter)</u>	<u>Peak Current (milliamps)</u>	<u>Polarization Resistance (volts/milliamp)</u>
Aluminum	0.051	0.206	0.385
Aluminum	0.051	0.227	0.350
Aluminum	0.172	0.671	0.230
Aluminum	0.172	1.05	0.125
Tungsten	0.070	0.378	0.397
Paladium	0.080	0.304	1.02
Paladium	0.200	0.718	0.284
Paladium	0.200	0.710	0.179
Platinum-Iridium	0.069	0.200	0.446
Platinum-Iridium	0.186	0.287	0.298
Platinum-Iridium	0.186	0.325	0.255

* Electrode areas are:

Aluminum - 0.00316 cm^2

Tungsten - 0.00316 cm^2

Paladium - 0.00202 cm^2

Platinum-Iridium - 0.00202 cm^2

TABLE IV. Mean Molal Ionic Activity Coefficients of Lithium in Liquid Ammonia at -35° C (64).

<u>Molality</u>	<u>Activity Coefficient</u>
0.01	0.675
0.02	0.651
0.04	0.605
0.08	0.527
0.15	0.424
0.30	0.292
0.60	0.176
1.00	0.121
2.00	0.072
4.00	0.044
8.00	0.047
10.00	0.064
12.00	0.121
14.00	0.458
15.70 (Sat.)	1.11×10^3

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