



The electrochemical reduction of basic liquid ammonia solutions
by Shoou-I Wang

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirement for the degree of
MASTER OF SCIENCE in Chemical Engineering
Montana State University
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Abstract:

The electrochemical reduction of a basic liquid ammonia solution (NH_3/KNH_2) has been studied by the method of cyclic voltammetry.

A qualitative study of heterogeneous catalysis in liquid ammonia, solutions for the preparation of potassium amide were made* Platinum black, rusted iron, and powdered nickel were the most efficient catalysts.

A microcracked glass electrode has been prepared and adopted as a reference electrode for a one-compartment cell.

A number of studies on oxidizers and electrocatalysts were made in a liquid ammonia solution (NH_3/KNH_2) by using the electrochemical technique of cyclic voltammetry.

Electrochemical reduction of iodine and tin dioxide in this solution occurred at -1.5 and -1.65 volts versus Pb reference electrode respectively. Platinized platinum was the best electrocatalyst.

An example of the calculation of an oxidation potential from thermodynamic data was made and compared with the result obtained by experiment.

A reversibility study of the electrochemical reductions of iodine and tin dioxide was made by changing scan rates. It was found that the reduction of iodine in NH_3/KNH_2 solution to be irreversible and tin dioxide to be reversible. .

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Date Jan 26, 1970

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of *MS*

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in

Chemical Engineering

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Bozeman, Montana

March, 1970

ACKNOWLEDGMENT

The author wishes to thank the staff of the Chemical Engineering Department of Montana State University, and in particular, Dr. Michael J. Schaer who directed this research, for their suggestions which led to the completion of this project. In addition, thanks are also due to professor Robert L. Nickelson, William E. Genetti, and Myron S. Henry, who have served on his graduate committee.

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

The author acknowledges the help and encouragement of his wife, Jeanny Kao.

TABLE OF CONTENTS

	Page
Vita	ii
Acknowledgment	iii
Table of Contents	iv
List of Tables	v
List of Figures	vi
Abstract	vii
Introduction	1
A. Liquid-Ammonia Fuel Cells	1
B. Metal-Ammonia Solutions	3
C. Analytical Background	4
Research Objectives	6
Experimental Procedures	7
A. Preparation of Potassium Amide	7
B. One-Compartment Cell	9
C. The Scanning Instrumentation	12
Result And Discussion	13
A. Catalytic Study of Potassium-Ammonia Solution	13
B. Voltammetric Studies	14
C. Reference Electrode And Working Electrode	19
D. Method of Calculation the Oxidation Potential from Thermodynamic Function	24
E. Reversibility Study	26
Conclusions	33
Literature Cited	34

LIST OF TABLES

	Page
Table I. Electrochemical Reactions of Various Chemicals in a Saturated Solution of NH_3/KNH_2	16
Table II Peak Currents of Scans in the One Compartment Cell on Various Electrode Materials	23

LIST OF FIGURES

	Page
Figure 1.	Comparison of Pb & Pt Reference Electrode at Various Concentration of SnO_2 11
Figure 2	Voltammetric Curve for Iodine in NH_3/KNH_2 17
Figure 3	Voltammetric Curve for Tin Dioxide in NH_3/KNH_2 18
Figure 4	Voltammetric Curves for Tin Dioxide in NH_3/KNH_2 at Various Concentration 20
Figure: 5	Photograph of Microcrack in Tip of Glass Electrode 21
Figure: 6	Full-Length View of Microcracked Glass Electrode 22
Figure 7	Voltammetric Curves of SnO_2 Reduction in Saturated NH_3/KNH_2 Solution at Various Scan Rates 28
Figure 8	Voltammetric Curves of Iodine Reduction in Saturated NH_3/KNH_2 Solution at Various Scan Rates 29
Figure 9	Peak Current Relationship for the Reduction of SnO_2 in Saturated NH_3/KNH_2 Solution at Different Concentrations 30
Figure 10	Peak Current Relationship for the Reduction of SnO_2 in Saturated at Different Scan Rates 31
Figure 11	Peak Current Relationship for the Reduction of Iodine in Saturated NH_3/KNH_2 Solution at Different Scan Rates 32

ABSTRACT

The electrochemical reduction of a basic liquid ammonia solution (NH_3/KNH_2) has been studied by the method of cyclic voltammetry.

A qualitative study of heterogeneous catalysis in liquid ammonia solutions for the preparation of potassium amide were made. Platinum black, rusted iron, and powdered nickel were the most efficient catalysts.

A microcracked glass electrode has been prepared and adopted as a reference electrode for a one-compartment cell.

A number of studies on oxidizers and electrocatalysts were made in a liquid ammonia solution (NH_3/KNH_2) by using the electrochemical technique of cyclic voltammetry.

Electrochemical reduction of iodine and tin dioxide in this solution occurred at -1.5 and -1.65 volts versus Pb reference electrode respectively. Platinized platinum was the best electrocatalyst.

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INTRODUCTION

A fuel cell is an electrochemical device composed of a nonconsumable anode and cathode, an electrolyte, and suitable controls. The free energy of the reactants, which are stored outside the cell itself, is converted into electrical energy.

Fuel cells have been a subject of investigation since the nineteenth century, but it has only been in the past twenty years that this work has become intense (1,2). Fuel cells are an attractive source of power for the following reasons.

1. They can be made to operate at about 80% efficiency in comparison with about 40% for turbines and generators, which are limited by Carnot Cycle.
2. In passing from chemical energy into electricity, no mechanical conversion is required.
3. No noxious fumes or noise is emitted and they do not require much maintenance since there are no moving parts.

Of course, fuel cells also have their disadvantages, chief of which is their high cost due to expensive cell components. If economics is the most important factor, fuel cells are generally not competitive with conventional power sources and are not used.

A. Liquid Ammonia Fuel Cells

At the present time there are hundreds of fuel cell investiga-

tions being conducted throughout the world. These investigations include a wide variety of fuel cell types which employ a number of different reactants, electrocatalysts, and electrolytes at widely divergent operating conditions. Most of the work has been done by using aqueous, fused salt, or solid electrolytes. But, notably absent in the area of fuel cell research are fuel cells which operate at low temperatures, that is, less than 0°C. We have therefore decided to study low temperature fuel cells with liquid ammonia as the ionizing solvent.

Liquid ammonia has been used as a polarographic solvent for investigations into the reduction of many metal ions; the most comprehensive and extensive work has been done by Pleskov (3); Pleskove and Monorson (4); and Laitinen and Coworkers (5,6,7). The interest in liquid ammonia for many years has been due to the solvated electron.

Liquid ammonia with its self-dissociation constant of 1.9×10^{-33} may be considered an aprotic solvent with proton availability between that of common aprotic solvents such as acetonitrile, dimethylformamide, or dimethylsulfoxide and of solvents such as alcohols. Its dielectric constant is 22 at -34°C (9) which compares to the values of 38 at 25°C for acetonitrile (10), of 36.7 at 25°C for dimethylformamide (11) and 46.7 at 25°C for dimethylsulfoxide (12). It is rather surprising, in view of its fairly low dielectric constant, that liquid ammonia serves as a solvent for a wide variety of inorganic salts and organic

molecules.

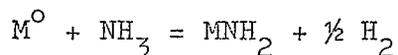
In addition, liquid ammonia is an excellent solvent (13) and approaches water very closely in its physical properties (14,15). Therefore, the results from aqueous fuel cells might be drawn by analogy to a liquid ammonia system. Furthermore, in acid liquid ammonia solutions the practical range of potentials 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. Many exceptions are to be found, particularly among the nitrogen compounds which often react very slowly with liquid ammonia (16). Therefore, solutions of liquid ammonia exhibit fairly wide potential ranges for carrying out electrochemical studies between the anodic and cathodic solvent decomposition.

B. Metal-Ammonia Solutions

A lot of research has been done regarding the properties and applications of metal-ammonia solutions (17). The proposals are many and varied, yet none sufficiently explains all aspects of the unusual metal-ammonia solutions, and there is considerable debate concerning which of the proposed mode is best (18). The true metal-ammonia system must be a complicated equilibrium, indeed.

The metal-ammonia solutions exhibit varying stability. If they are prepared with enough care, they may be stored for weeks or even months without appreciable reaction between the metal and the

solvent ammonia. Yet a slow reaction does occur. The reaction is as follows:



The rate of the reaction between metal and ammonia could be speeded up by the presence of impurities. This fact was first observed by Franklin (33) who noticed that in tubes containing bits of asbestos fiber, the time for preparation of potassium amide was shortened appreciably. Other catalytic agents were tried by a lot of authors (32,33,23).

C. Analytical Background

Solid electrode voltammetry has been used in this experiment. 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 electrode. 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 similar to polarography but the latter is generally applied to the branch of voltammetry in which a dropping mercury electrode is used as the working electrode. The dropping mercury electrode is considered more accurate and reproducible than solid electrodes. But, unfortunately, because of the rapid amalgamation.

tendencies of alkali metals from ammonia into mercury, it can not be used in this study.

RESEARCH OBJECTIVES

As described in the foregoing discussion, research data on liquid ammonia fuel cell are notably absent. Bennett (18) 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. Recently, Strah (34) has done research in acid, liquid ammonia solutions. He has developed and made operable a cold temperature liquid ammonia fuel cell using a liquid ammonia solution ($\text{NH}_3/\text{NH}_4\text{NO}_3$) as the electrolyte. However, no work on basic liquid ammonia solutions. In light of this fact, a research program was undertaken with the following objectives.

1. Search for a good catalyst to prepare potassium amide solution.
2. Find an electrochemical oxidizer by the method of voltammetry in a liquid ammonia solution.
3. Prepare an improved reference electrode and platinized platinum working electrode.
4. Calculate an oxidation potential from free energy data and compare with experimental data.
5. Measure the reversibility of reactions by changing scan rates in the voltammetric study.

EXPERIMENTAL PROCEDURES

In performing these experiments, extreme care is necessary and because of this requirement, some tedious experimental procedures should be mentioned.

This half cell study required the use of a number of chemicals and equipments. The potassium metal used in this study was purchased from J. T. Baker Chemical Co. with a minimum purity analysis of 99.9%. Potassium samples were prepared and handled in an inert argon atmosphere contained in a dry box model HE-43-2 manufactured by Vacuum/Atmosphere Corporation. A piece of potassium was cut, cleaned, and placed in the electrolytic cell while in the dry box. A small amount of catalyst was then added to the cell and then sealed. 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 ammonia used in these studies was Matheson anhydrous, of 99.95% stated minimum purity. Liquid ammonia was introduced directly from the cylinder into the electrolytic cell.

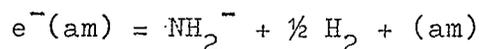
Low temperature was maintained to approximately -40°C by adding dry ice into a methanol bath contained in a large Dewar flask.

A. Preparation of Potassium Amide

Solutions of the alkali-metals in liquid ammonia are known to

be relatively stable, existing for many hours without appreciable reaction between the metal and the ammonia. However, a slow reaction does occur, and earlier workers (19-21) with liquid ammonia as a solvent, prepared the amides of sodium and potassium in this way. In some cases, days and even months were required for complete reactions. The rate of the reaction between metals and liquid ammonia can be increased by the presence of other substances.

As reported by Kraus (23), when the metal amide is formed the real reaction that occurs is one between ammonia and the solvated electrons. The reaction is



Because the preparation of potassium amide is not the main purpose of this research, the study was only qualitative. Liquid ammonia was introduced directly into the electrolytic cell (described previously), and a dark blue solution was formed. Since the reaction between potassium metal and liquid ammonia in the absence of a catalyst is very slow, the reaction that occurs in this solution can be assumed to take place completely on the surface of the catalyst. Therefore, the rate of supplying the reactants to the surface is an important factor in the time of reaction and this rate of supply is largely dependent on the mechanical stirring. A glass-coated magnetic stirring bar, spun by a submersible magnetic stirrer in the controlled temperature bath, was used in this study. In order to determine how

the rate of stirring affected the time of reaction, several runs were carried out in which the rate of stirring was changed. Several kinds of powdered catalysts were tested and the catalytic effect of each material was determined by observing the characteristic blue color and timing its disappearance.

B. One-Compartment Cell

Because of a high and variable resistance between the working and reference electrodes in three compartment cells, accurate potential measurement was difficult (17-19). Hence, all voltage scans were made in a one-compartment cell. This cell contained a counter electrode, a reference electrode, and a Pt-wire working electrode. In many of the earlier runs, two platinum plates, one electrode a reference electrode and the other a counter, were employed.

A typical run in the one-compartment cell was conducted as follows:

1. A piece of potassium metal (3 grams/100 ml solution) was cleaned and placed in the cell and a catalyst was added while in the dry box.
2. The sealed cell was removed from the dry box, and placed in the cold bath.
3. Liquid ammonia was introduced into the cell to the desired level.

4. The solution was stirred until a saturated potassium amide solution was formed. A small amount of the chosen reactant was then added to serve as the oxidizer in the saturated NH_3/KNH_2 solution.
5. The cell was then ready for the voltage scan.

The one-compartment cell simplified the experimental procedure and eliminated the problems that occurred in the three compartment cell, but it still has two serious disadvantages.

First, the platinum plate used as a reference electrode was not defined. Although for any given run it served as a constant reference point, its potential changed with the various concentrations of oxidizer in the solution (Figure 1).

Second, for a long period of operation, the counter electrode would be contaminated with products of the electrochemical reaction.

In light of this, a lead/lead nitrate electrode was used as a reference. This electrode has been shown to be a suitable one in liquid ammonia (24). It was found that the performance of the electrode material (platinum) was improved considerably by platinizing to improve its catalytic properties (25-27). The counter electrode was cleaned in nitric acid or sulfuric acid-chromate cleaning solutions, washed in distilled water and then heated in a flame.

