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
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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 ($NH_3/NHNO_3$) 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/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 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/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: 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.

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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.

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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.

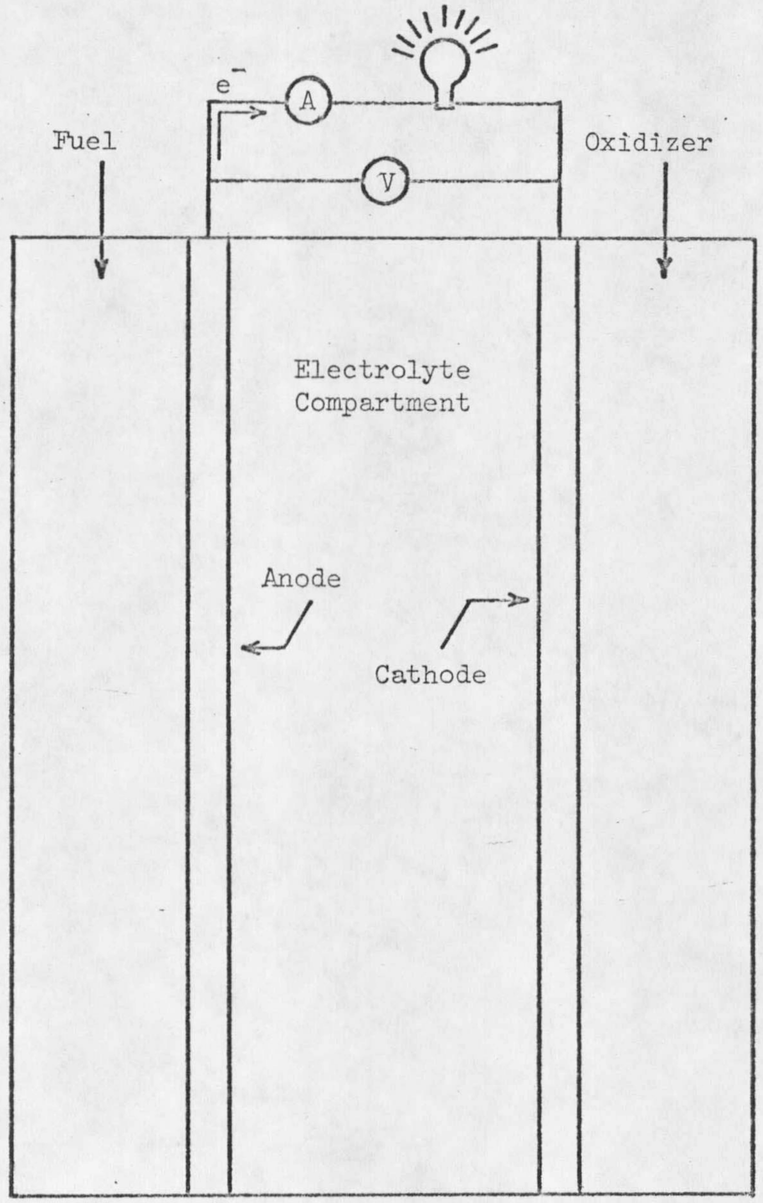
A. Principle of Operation

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:


e^-
A
V
Fuel
Oxidizer
Electrolyte Compartment
Anode
Cathode

Reactions:

Anode: Fuel Oxidation

Cathode: Oxidizer Reduction

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 ($1M\ NH_4^+$)

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

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

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

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

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