

SYMPOSIUM ON FUEL CELLS
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THE PRELIMINARY APPRAISAL OF THE AMMONIA
FUEL CELL SYSTEM

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INTRODUCTION

During the past five to ten years there has been a decided increase in fuel cell research. The result has been the development of several prototype fuel cell systems which fall into two types. In one type, hydrogen-oxygen for example, both the fuel and oxidant are gases. The second type uses a liquid fuel and gaseous oxidant and can be exemplified by the methanol-oxygen system.

The oxidant most generally employed has been pure oxygen or air. The fuel, however, has been picked from a wide range of compounds and prototypes have been operated on such gaseous fuels as hydrogen, carbon monoxide, and hydrocarbons. The liquid fuels most commonly used have been partially oxygenated hydrocarbons, such as alcohols or aldehydes, and special fuels, such as sodium amalgam.

In this preliminary report attention has been centered upon ammonia as a fuel with minor emphasis on the complete ammonia-oxygen system. The material presented covers two areas. First, a discussion of ammonia and some of its characteristics, and second, a report of some of the typical data obtained on several preliminary, but very impractical, ammonia-oxygen fuel cells.

APPLICATION METHODS

Several methods are available for employing ammonia as a fuel for fuel cell consumption. They are:

1. Decomposition of ammonia into its elements and (a) separate the pure hydrogen, or (b) use the nitrogen-hydrogen mixture directly.
2. Direct consumption of ammonia: (a) as a gas, or (b) dissolved in the electrolyte.

Simple equipment has been designed for cracking ammonia. This reverts it to the 75-25 mixture of hydrogen and nitrogen, respectively. This represents a convenient way of securing supplies of hydrogen, one cylinder of ammonia being the equivalent of nine or ten cylinders of hydrogen. Pure hydrogen generating units have been reported (1) which yield hydrogen of 99.995 per cent purity, the nitrogen being removed by liquification. The cost is quoted at less than pure cylinder gas and no more than the "impure" electrolytic grade.

The scope of this report will be limited to the study of the direct use of ammonia as a fuel since cracked ammonia is essentially a hydrogen-oxygen fuel cell and both the cracking and the hydrogen-oxygen fuel cell have already been developed.

When one uses ammonia as an anodic reactant in electrochemical system, two properties should be kept in mind. The first is that the nitrogen-hydrogen bond energy of 118 kcal/mole in the ammonia molecule indicates stability and that the bonds are not readily broken in electrochemical oxidation. Thus, one can anticipate that at room temperature, difficulty will be experienced in the cleavage of the nitrogen-hydrogen bond. As will be shown later, in this report this was found to be the case even under open circuit conditions.

The second important property is the high solubility of ammonia in all conventional electrolyte solutions, both aqueous and non-aqueous. This means that ammonia can readily be supplied to the electrode-solution interface, at the anode, through either the gas or the solution phases. This high solubility, however, has the disadvantage that

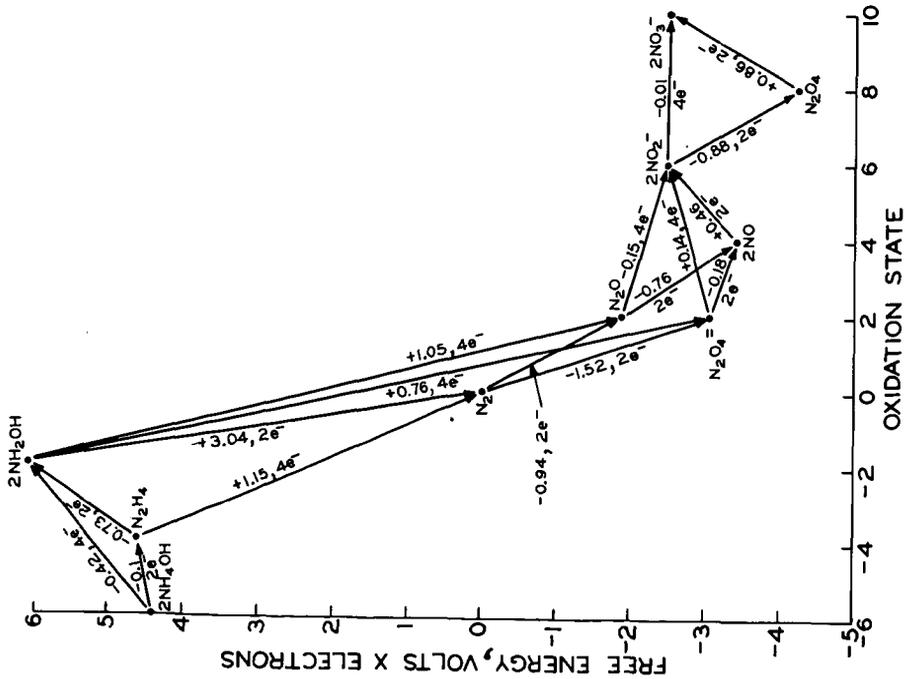


Figure 1. Free Energy of the Nitrogen System in Alkaline Solution at 25° C.

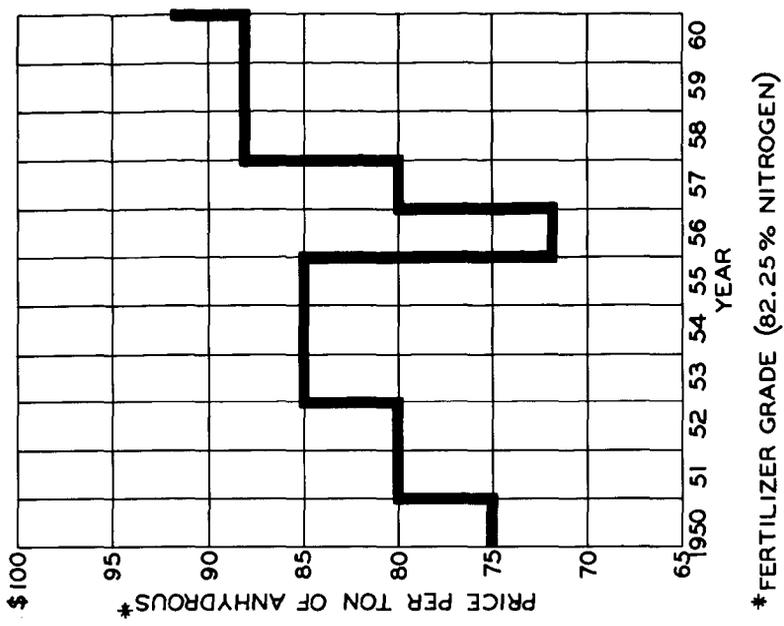


Figure 2. Cost of Anhydrous Ammonia for the Period 1950-1960.

ammonia transport from the anode, through the solution phase, to the cathode is not negligible unless proper operating precautions are taken. High pressure operation will further increase the solubility of ammonia in the electrolyte solution. Thus, ammonia can be introduced through the rear of a porous electrode resulting in a gas-gas fuel cell or through the solution phase giving a "liquid"-gas fuel cell, similar to the methanol-oxygen cell mentioned earlier.

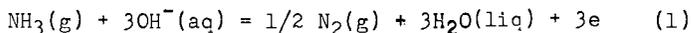
The discussion and experimental results to follow are limited to the use of gaseous ammonia as the fuel.

THERMODYNAMICS AND ELECTRODE REACTIONS

In order to understand the ammonia fuel cell, it is important to establish what chemical reactions are occurring during discharge of the cell. The reactions occurring at the cathode, when using an alkaline electrolyte and oxygen as the oxidant, have been characterized and reported by others. (2-4)

In figure 1 are plotted the free energies and potential relationships for the various oxidation states associated with nitrogen in an alkaline solution at 25°C. These results were tabulated from data reported by Latimer. (5) One can obtain the standard free energy change, ΔF°_{298} , for a half-reaction by multiplying the corresponding values by the Faraday constant, 23.06 kcal/volt/gm. equivalent. Also included are the values of the standard oxidation potentials, E°_{298} , and the number of electrons released for the reactions indicated in the direction of the arrows.

The anode reaction was characterized by first analyzing for the reaction products. As will be pointed out later, the principle products were found to be nitrogen and water. Assuming the half-cell reaction



a value of 0.77 volts can be calculated for E°_{298} , using the expression relating potential values to free energies,

$$\Delta F^{\circ}_{298} = -nFE^{\circ}_{298} \quad (2)$$

where the symbols mean,

ΔF°_{298} - change in the standard free energy at 25°C.
with all reacting substances at unit activity.

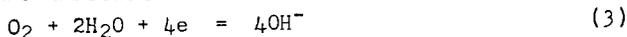
n - number of electrons in the reaction.

F - Faraday's constant, 23.06 kcal/volt/gm. equivalent.

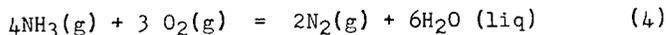
E°_{298} - standard oxidation potential at 25°C.

The American sign convention has been used, i. e., the electrons are on the right-hand side of the equation and therefore a positive value for E°_{298} means that the reduced form of the couple is a better reducing agent than hydrogen. All the potentials are referred to the standard hydrogen electrode.

Coupled with the anodic reaction is an oxygen electrode process. Assuming a very active peroxide decomposing catalyst on the cathode surface greatly simplifies the cathodic process and the two electron process changes to an apparent four electron mechanism. Thus for the half reaction



the value of E°_{298} is 0.40 volts. Coupling the two half reactions, equation (1) and (3), one obtains for the overall fuel cell reaction



and an E°_{298} value of 1.17 volts. As will be apparent later, the actual conditions employed during operation of the ammonia-oxygen cell varied considerably from the standard conditions assumed. Therefore, this value, although accurate for the conditions assumed in its calculation, represents only a first approximation of the theoretical value for the experimental conditions employed. Since the open circuit potential of the fuel cell is related to the change in the thermodynamic functions of free energy, enthalpy and entropy, the calculated effect of temperature and pressure changes could, in principle, be obtained through standard thermodynamic calculations. However, care must be exercised in making these calculations due to such typical factors as:

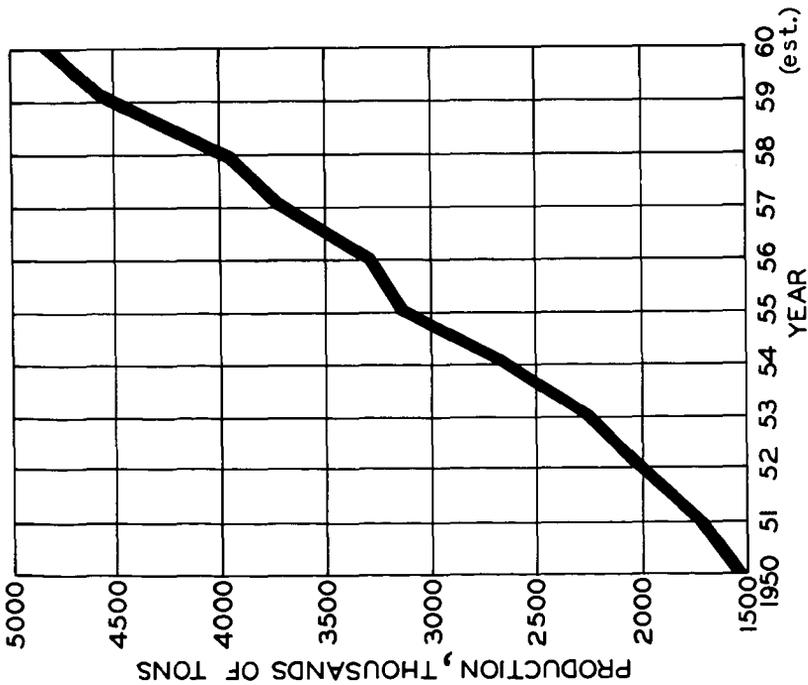


Figure 3. Volume Output of Anhydrous Ammonia for the period 1950-1960.

SOURCE: BUREAU OF THE CENSUS, U.S. DEPT. OF COMMERCE.

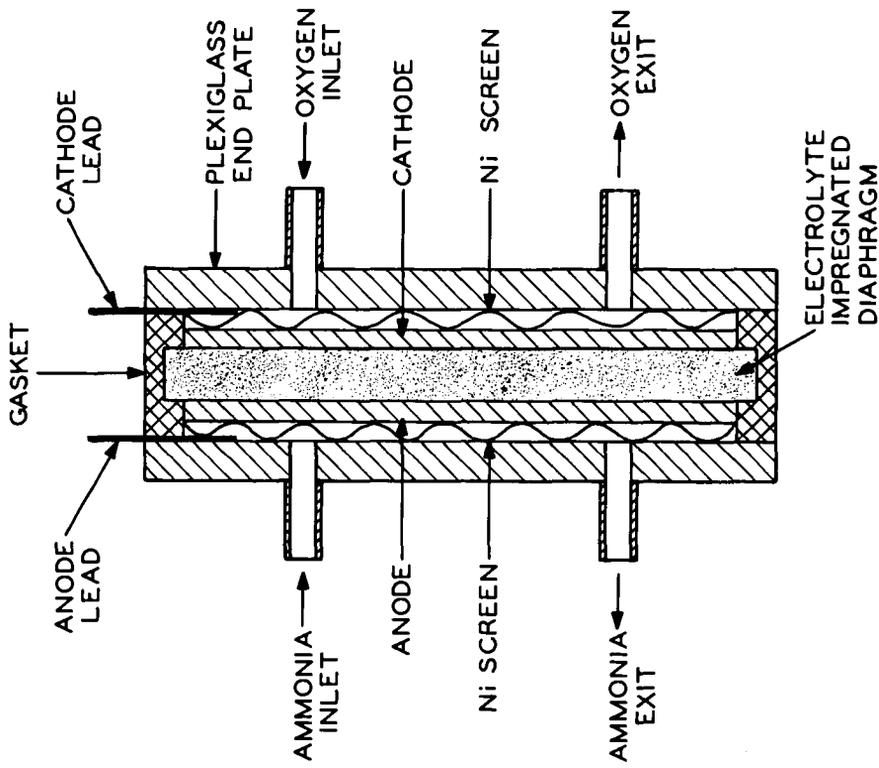


Figure 4. Cross Sectional Diagram of the Experimental Ammonia-Oxygen Fuel Cell.

1. Practical cells are operated in a highly alkaline solution and therefore the activities of the hydroxyl ion and water are not unity.

2. Although activity coefficients can be employed, they should be for individual ionic species, but experimentally only mean activity coefficients can be determined.

3. Several electrons are involved in the electrochemical steps and therefore, mixed electrode potentials might be obtained experimentally which would be difficult to compensate for in the calculations.

CRITERIA

Many criteria have been proposed for evaluating fuel cells and the fuels used in them. To date little can be said concerning how the ammonia-oxygen fuel cells meets these general criteria such as ultimate current density, cell efficiency, power per unit weight or volume, etc. These factors can only be appraised after sufficient scaling-up has been done and an engineering investigation and feasibility study has been made. Nevertheless, from a preliminary appraisal, the ammonia-oxygen fuel cell has many advantages which center around the use of ammonia as the fuel.

Ammonia is economical. The present cost is 4.6 cents per pound, based upon ton quantities. (5) It is produced from readily available raw materials and has a wide increasing range of applications. This serves to guarantee the stability of its market. As figure 2 points out, the cost of anhydrous ammonia only varied over a very narrow range during the period from 1950 to 1960. It should be remembered, however, that as the quantity required decreases, the cost increases rapidly. This is exemplified in Table I where, in addition to various size and weight factors, the cost of ammonia is listed as a function of volume or quantity purchased. It is also obvious that as the required purity of the ammonia increases so does the cost.

TABLE I
GROSS SIZE, WEIGHT AND COST OF ANHYDROUS AMMONIA
AS A FUNCTION OF AMOUNT DESIRED

Cylinder Dimensions, (1) Inches	Gross Weight, lbs.	Ammonia Content, lbs.	Cost	
			Cents per lb. (2)	Cents per Mole (2)
Ton Quantities (Carload Lots)			4.6 (3)	
14 x 59	340	150	20	0.8
8 x 53	112	40	25	0.9
8 x 25	52	15	52	2.0
5 x 24	28	5	87	3.3
4 x 14	17	2	165	6.2
2 x 15	4	0.4	400	15.0

(1) Diameter x height.

(2) 99.99 percent purity.

(3) Fertilizer grade.

Ammonia production is already a large tonnage item. From the data presented in figure 3, it can be seen that the output has tripled since 1950. Presently, this rise in production stems from the increased use of ammonia as a fertilizer. (6) This leads one to conclude that in view of the large quantity of ammonia produced one can assume that in the future the price of ammonia should remain relatively constant regardless of any demand caused by fuel cells.

Ammonia is a gas which can readily be liquified. Thus high pressure tanks are not required for its storage. In spite of this, however, the storage facilities needed to stock ammonia is a large cost factor. It has been reported (5) that amortization costs

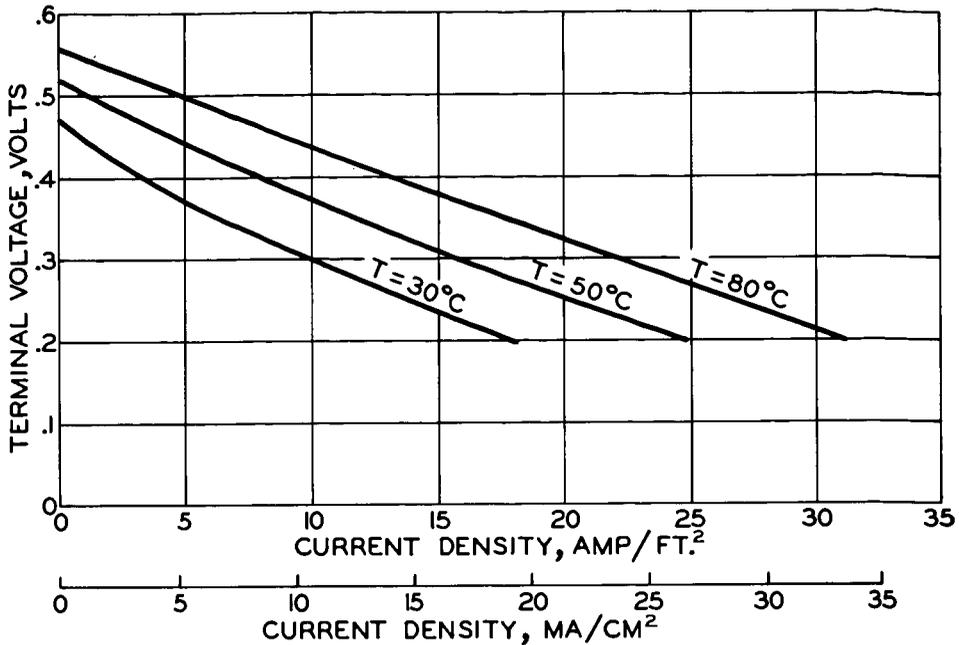


Figure 5. Typical Performance Curves Obtained for the Ammonia-Oxygen Fuel Cell at 30, 50 and 80° C., Atmospheric Pressure and Flowrates of Three Times That Needed to Maintain Reaction.

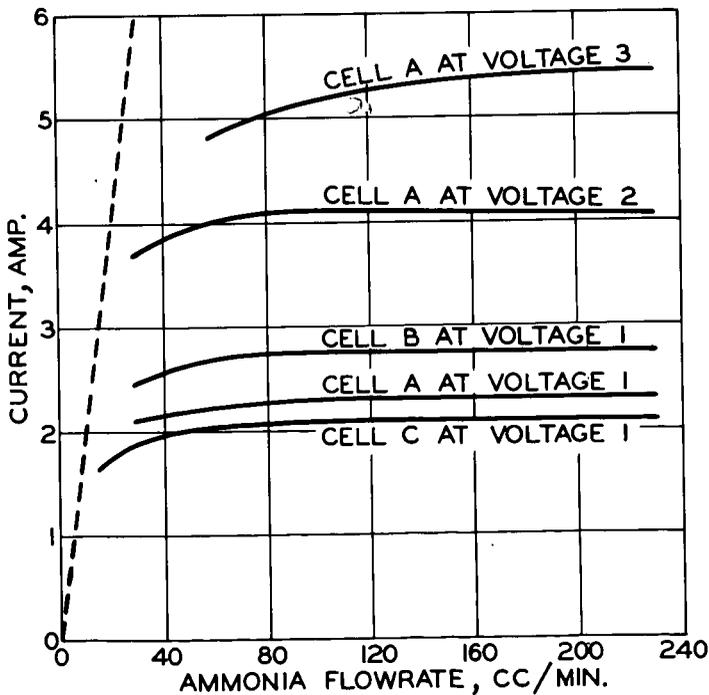


Figure 6. Cell Current As a Function of Ammonia Flow Rate (Atmospheric Pressure, Constant Oxygen Flow Rate, 25° C.).

for anhydrous ammonia storage facilities run between 15 to 20 dollars per ton a year. A Horton sphere, of 2500 ton capacity, costs about \$275,000. A new technique for storing refrigerated ammonia at atmospheric pressure, rather than in pressurized tanks, has been reported (7) to cut the storage cost in half. The low storage temperature is obtained by surface evaporation of the ammonia. The vapor is recompressed and circulated back into the storage unit.

Ammonia can be handled easily on a wide-scale. The practicality of wide-scale usage of ammonia might be questioned from a safety standpoint. The limits of inflammability, as reported by Lewis and von Elbe (8), are found in Table II. Such mixtures can be ignited by a spark and would explode if confined to a closed space. Higher temperatures increase the danger of combustion or explosion. The dangers that exist, however, are less than those found with hydrogen.

TABLE II
LIMITS OF INFLAMMABILITY OF AMMONIA IN AIR AND OXYGEN
AT ROOM TEMPERATURE AND ATMOSPHERIC PRESSURE

	<u>Percentage-by-Volume Basis</u>	
	<u>Lower</u>	<u>Upper</u>
Air	15.50	27.00
Oxygen	13.50	79.0

Ammonia is toxic, but its pungent odor provides amply warning of its presence. It can be detected in air at concentrations as low as 20 parts per million by volume. In air concentrations of 200 p. p. m. are dangerous and may prove lethal. (9) The American Conference of Governmental Industrial Hygienists has recommended that the maximum allowable concentration for an eight hour daily exposure should be 100 p. p. m. (10) Ammonia solutions produce caustic burns on the skin, a 3 per cent concentration being the maximum that can be tolerated for more than a few seconds.

In conclusion, ammonia is an economical gas which can readily be condensed. It is produced from nonstrategic elements in large volume. Although it is inflammable and toxic, its characteristic odor serves as a warning of its presence.

EXPERIMENTAL

The construction of a laboratory type ammonia-oxygen fuel cell is illustrated diagrammatically in figure 4. The design was chosen as one of convenience in testing various fuel cell components.

Fuel and oxidant were supplied to the cell in such a manner as to permit the gas flow to be controlled. The gas-diffusion electrodes were made of a commercially available porous carbon. Only a preliminary effort was made to use electrodes of controlled pore size distribution. The electrode porosity was 48 per cent. A wire screen was used to manifold the gas and to improve the contact between the electrode and the external circuit. The two electrodes had the same geometric area and were spaced about 0.2 cm. apart. The untreated carbon electrodes were not able to activate the ammonia and for this reason a catalyst was deposited onto the electrode. It was found experimentally that platinum black was suitable, to a limited extent, and was the catalyst employed in this preliminary study. Platinum black also served as the catalyst at the oxygen electrode.

The ammonia and oxygen diffused through the carbon electrodes to the electrolyte interface where electrochemical reaction occurred. The electrolyte employed was a very concentrated potassium hydroxide solution which helped to prevent the transport of fuel to the cathode. In order to minimize flooding of the porous electrodes the electrolyte was held in a porous diaphragm and the electrodes pressed into the surface of the diaphragm.

Performance Characteristics

Figure 5 shows typical voltage-ampere curves for the ammonia-oxygen fuel cell operating at temperatures of 30, 50 and 80°C. The ammonia flow rate was three times that required to sustain the reaction. Because of the exploratory nature of these experiments the commutator technique (11) was not used in making the measurements.

It can be seen that the higher temperatures yield the expected higher outputs. However, the increase in open circuit voltage cannot be accounted for by the theoretical effect of temperature on the cell e. m. f. A more probable reason is a decrease in ammonia transport from the anode to the cathode with the increase in temperature. Open circuit voltages of 0.70 volts have been reported (12) when platinum and silver oxide catalysts were employed at the ammonia and oxygen electrodes, respectively.

Due to the observed variation of cell output with temperature, it was essential to control the cell temperature. This was accomplished with an air thermostat which held the working temperature constant to $\pm 0.5^{\circ}\text{C}$. The use of an air thermostat was chosen because of the ease with which the cells could be manipulated. However, a longer time was required to bring the cells to the proper operating temperature. The cell and thermostat temperatures were continuously recorded through separate, suitably positioned, thermocouples. Once the cell attained the operating temperature, there was very little temperature fluctuation.

In addition to careful control of the cell temperature, it is essential that close attention be given to the gas flow rate employed. Figures 6 and 7 serve to illustrate this point. The cells used for these experiments were all identically constructed according to the procedure described previously. The individual cells were designated as A, B, . . . G, to indicate that seven separate cells were used. An important point to note is that for each curve the cell voltage was held constant. The actual value of this voltage is not essential in illustrating the effect of flow rate on cell output, but does serve to indicate the type of reproducibility obtained (see cells A, B, and C at voltage 1).

Cells A, B, and C were all operated at voltage 1 (actually, 0.39 volt). In addition, cell A was operated at two other power levels, voltage 2 and 3 (0.31 and 0.25 volt, respectively). At the lower current levels it can be seen that the current remains essentially constant until the slower flow rates are approached when the current begins to drop relatively rapidly. The drop off occurs more readily when higher current levels are being maintained, e. g., cell A, voltage 3.

In figure 7 the current outputs of the four remaining cells are given at the lower flow rates, approaching those required to sustain the output. In this case the effect of flow rates on current delivered is very pronounced.

An exact analysis of this effect was not attempted because of its complex nature and the preliminary nature of this investigation. As long as the current remains independent of flow rate, the fuel cell is being limited by some other process than the ammonia flow rate. As the flow rate is decreased a point is reached when the current becomes dependent upon ammonia flow rate or some factor which is a function of the flow rate.

The dashed curves in figures 6 and 7 represent the ammonia flow rate required to just supply the electrode with sufficient fuel to maintain the current being delivered. For cells B, A and C a flow rate of 220 cc/min. represents a flow rate of about 16, 18 and 20 times that required, respectively. In the case of cell A at voltages of 2 and 3, a 220 cc/min. flow rate is 10 to 8 times that required, respectively. The increase in flow rate means an increase in ammonia concentration at the three phase reaction zone. A physical picture of the effect is very complicated since the result depends not only upon an electrochemical reaction, a three phase reaction zone which extends into the solution phase because of the solubility of the ammonia in the electrolyte and an electrode pore network, but also the geometrical shape of the fuel compartment adjacent to the electrode.

The important point stressed here is not the apparent explanation of the observed effect, rather that the consistency and correlation of fuel cell results is strongly tied in with environmental controls. This was further illustrated during a study of the importance of the nitrogen build-up, as reaction proceeds, on the operation of an ammonia fuel cell. A series of runs were carried out to determine the magnitude of this effect. The cell current was followed as a function of the percentage-by-volume of ammonia in a fuel mixture of ammonia and nitrogen. This problem is similar to that found in the use of air instead of pure oxygen. From the results obtained it was observed that the effect of nitrogen content was irregular unless the flow rate was also held constant. For example, figure 8 illustrates the results obtained as the ammonia percentage in the fuel stream was decreased when the total flow through the cell was held constant at 230 cc/min. From these results it can be concluded that the effect of nitrogen build-up is slight until over 50 percent of the fuel gas stream was nitrogen. As expected, the

effect of nitrogen percentage being more pronounced when heavier currents were being drawn. It was also observed that if a lower constant flow rate (less than 230 cc/min.) was used the current fall off appeared at greater ammonia percentages (i. e., with a lower percentage of nitrogen present). This serves to illustrate that the effect of the decreased partial pressure of ammonia is also a function of total flow rate.

One of the initial measurements made on the fuel cell unit was a qualitative determination of the chemical reaction occurring at the anode. This work is still in progress and a more complete quantitative stoichiometric balance will be published later. A sample of ammonia was passed back and forth through the anode compartment of a cell operating at 80°C. With the circuit closed, the current flowing was recorded as a function of time. After observing a total of 14,000 to 20,000 coulombs; the fuel gas was collected and analyzed with a gas chromatograph. The components found were ammonia, nitrogen, and water vapor. No hydrogen was detected. A calculation of the number of coulombs was then obtained from the nitrogen volume observed and the assumption that a three electron process, reaction (1), was occurring. This value was then correlated with the coulombs obtained by integrating the area under the current-time curve. The results of this correlation varied over a range of 0.2 to 5 per cent. This corresponds to a current efficiency of 99.8 to 95 per cent, where the current efficiency, η_i , is defined as

$$\eta_i = \frac{\text{Observed Current} \times 100}{\text{Calculated Current}} \quad (6)$$

Although the experimental accuracy of these initial coulometric measurements was not as high as desired, they do serve to indicate that the major reaction is that represented by equation (1).

Of the many causes for the low voltages observed, two are of major importance. One being the inherent irreversibility of the oxidation resulting from the transfer of three electrons and the large bond energy associated with the molecule and two, the inadequacy of the catalyst to enhance the reaction rate and minimize the free energy losses.

At the present time an appraisal of the attainable power density, start-up time, attendant corrosion problems, necessary auxiliary equipment, construction materials, side reactions, and reliability have not been made. The low temperature and low pressure operation, however, is characteristic of rapid start-up, less rapid corrosion problems, minimum in auxiliary equipment and cheaper construction materials. The side reactions will be the subject of later studies. Experimental ammonia-oxygen units have not been in service for any long periods of time. It is, therefore, impossible to make any statement concerning the stability or reliability of the system.

SUMMARY

Attention has been centered on ammonia as a fuel with minor emphasis on the ammonia-oxygen system. Of the many ways in which ammonia can be used as a fuel, its application as a gas was studied. The open circuit voltage expected is about 1.1 to 1.2 volts depending upon conditions. The experimentally observed values were about one-half of this.

Criteria used to appraise final fuel cell systems are not applicable to preliminary experimental cells. Ammonia is manufactured from readily available raw materials in large tonnages. Ammonia is low in cost when purchased in large quantities. Although it is inflammable and toxic within certain defined limits, it has an easily detectable odor which warns of its presence. A major advantage in the use of ammonia results from its being an easily condensed gas and hence not difficult to store or transport.

The experimental results were very much dependent upon cell temperature and gas flow rate. The reaction products were found to be nitrogen and water. No attempt was made in the work reported to obtain significant power outputs. Ammonia represents, in many ways, an ideal fuel cell fuel.

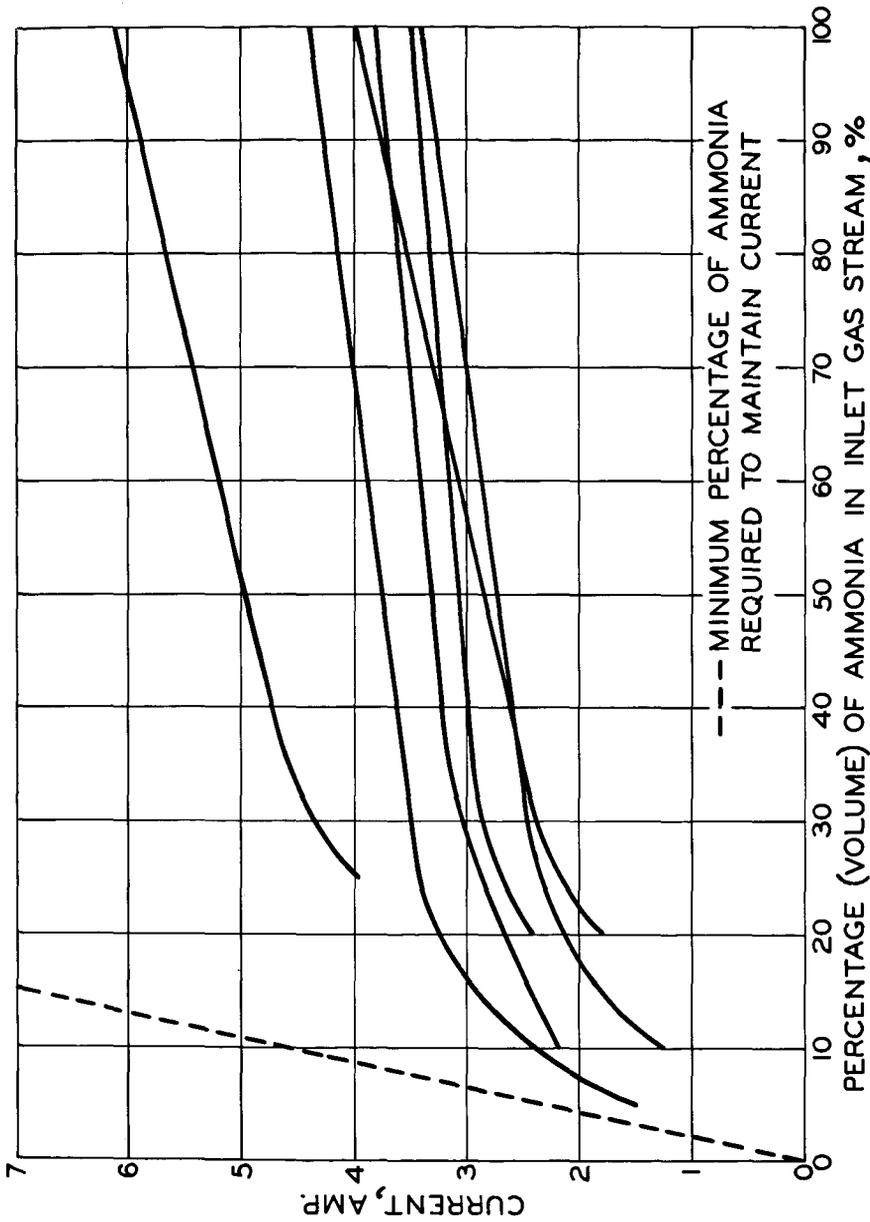


Figure 8. Cell Current as a Function of Ammonia Percentage in An Ammonia-Nitrogen Fuel Mixture (Atmospheric Pressure, Constant Oxygen Flow Rate, Constant Voltage). Flow Rate of Ammonia Plus Nitrogen Held Constant at 230 cc/min.

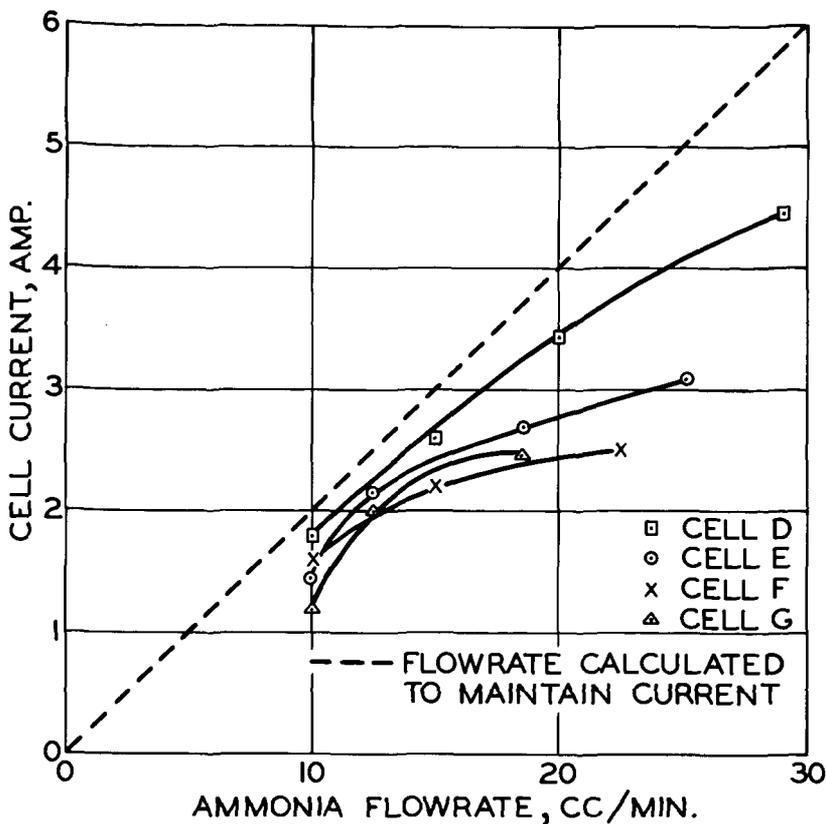


Figure 7. Cell Current As a Function of Ammonia Flow Rate, (Atmospheric Pressure, Constant Oxygen Flow Rate, Constant Voltage, 25° C.)

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