

PERFORMANCE OF A REFORMED NATURAL GAS-ACID
FUEL CELL SYSTEM

Part II. Fuel Cell Battery

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INTRODUCTION

This is a report on a joint effort of Ionics, Inc. and The Institute of Gas Technology to develop an air-breathing fuel cell system powered by natural gas. The long range objective of the project is the development of an economical power source using this readily available fuel, and which has a high degree of reliability and safety for relatively long periods of unattended operation. The system selected for this program was a low temperature, hydrogen-oxygen fuel cell with an acid electrolyte.

The hydrogen-oxygen system is well advanced. It provides relatively high efficiency with fuels and oxidants that are easy to obtain. The fuel can be generated from natural gas or other hydrocarbons and the oxidant is available from the air. The process to generate hydrogen for this fuel cell has been presented in an earlier publication in this series.¹ The description of a 100-CFH reformer unit has been discussed in another paper during this session.²

A low temperature system was selected for the investigation because of its long life, reduced corrosion problems, and low pressure operation. These advantages are counterbalanced in part by the present high cost of the catalyst.

An acid electrolyte system was dictated by the need for compatibility with the carbon dioxide which is formed during the reforming of natural gas and which is also present in room air. With the acid system, expensive steps to purify the hydrogen are not required. Also, the air does not have to be scrubbed to remove carbon dioxide.

A dual ion-exchange membrane battery was chosen for its inherent safety and reliability. With the acid electrolyte contained between two membranes, and the gases on the outside of these membranes, the chances of gas intermixing are minimized. A pinhole in one membrane does not bring two reactant species together in the presence of an active catalyst which would cause failure. The safety of operation is consistent with the goals of the project.

BATTERY CONSTRUCTION AND OPERATION

General Description

The battery is an internally manifolded stack of cells wired in series and with parallel flows of gas and electrolyte. An individual cell is diagramed in Figure 1. The acid compartment, in the center of this diagram, is filled with a polyethylene-

polypropylene woven cloth (70% void) to maintain the electrolyte spacing. On either side of the acid compartment are cationic ion-exchange membranes with woven glass backing. Each of these membranes is intimately contacted by an electrode, either anode or cathode. These, in turn, are held in place by ribbed plates. The plates are embossed niobium sheets, 5 mils thick. They electrically connect one cathode to the adjacent anode and simultaneously distribute the flow of gas to the electrodes. The gas and electrolyte compartment frames are made of 65 durometer butyl rubber. This is sufficiently firm to retain dimensional stability but still has enough flexibility for sealing. The electrodes are platinum-black bonded to a tantalum screen as manufactured by the American Cyanamid Company.³ The catalyst loading in the present battery is 9 grams per square foot. The total thickness for a single cell is 140 mils or about 1/7 inch.

The internal manifolding technique is shown in Figure 1. The manifolds for the movement of fresh and spent material are holes punched in the margins of the components. Channels connect the appropriate compartments and manifolds. In the present geometry, 70 percent of the total area is active. The active area of a cell is 1/4 square foot.

In operation, the reactant gases are fed to the top of their respective compartments. Spent gas is removed from the bottom of the battery to sweep out the liquid formed by the reaction or which has passed through the membrane by osmosis. The 25 percent sulfuric acid electrolyte flows from the bottom of the compartment to the top. This removes gas which may be in the compartments during start-up. The current is taken from the battery from the terminal collector plates. These are heavier than the interior sheets to reduce the battery's electrical resistance.

Heat and Mass Balance

A detailed analysis of the heat and mass balance problems within the cathode compartment of the cell was performed on a digital computer using finite difference techniques. This study indicated that the air required for a thermal balance is greater than that for a water balance by a factor of approximately 30. Therefore, the heat of reaction must be removed by other means.

Figure 2 shows the heat and mass balances during steady-state operation on reformed natural gas. The operating conditions are typical of those realized in the laboratory. All of the heat generated in the battery, plus that which is equivalent to the water condensed, is removed by the rise in the acid's temperature. If the humidity of the inlet air were lower during operation, water would be removed from the battery and the acid concentration would rise. The exit air is a few degrees higher than the acid temperature because most of the irreversibility of the reaction is at the cathode. The inlet air temperature and humidity are maintained at the conditions of the exit air. The fuel, on the other hand, need not be excessively heated or humidified for stable operation.

Pressure Drop

The pressure drop of the gas streams within the battery is important in the design of the entire system. Air must be supplied at enough pressure to overcome the losses in the humidification process and within the battery. Of greater importance, the reformer must be designed to supply gas at enough pressure to overcome the losses on the anode side of the battery from a line pressure of six inches.

The pressure drop in the present battery design is shown in Figure 3. From this graph, it can be observed that the flow in the cathode chamber is laminar; the pressure drop varies directly with the flow rate. With the same design, the pressure drop for an 80 percent hydrogen-20 percent carbon dioxide fuel mixture, similar to the generator product, should be significantly less than that of the air. The pressure drop with this fuel mixture is so low that uneven distribution within the battery results. To correct the distributional problem, the resistance in the inlet to the fuel compartment from the fuel manifold is increased. In the present design, the restriction is 1/2 inch of 19 mil. I.D. tantalum tubing. With this restriction, the pressure drop to fuel flow is about the same as the pressure drop to air flow. The flow within the anode compartment, according to the slope of the line in Figure 3, is not laminar but is in the transition region.

The pressure drop at expected operating conditions is three to five inches wc. From the earlier paper on the reformer construction, it will be noted that this fuel pressure is readily obtainable from the hydrogen generating system. Enough energy is available in the reformer flue gas to generate steam for ejecting the air required. As the air must be heated and humidified, according to Figure 2, an ejector is a convenient technique for air movement.

If extrapolated, the pressure drops, at increased power levels, would be quite high. This problem can be avoided by embossing the bipolar plates more deeply and shortening the length of the restrictive tubing in the anode compartment.

The plates are now pressed manually and are not identical. This non-uniformity presents a problem with uneven flow distribution within the battery. Relatively high pressure drops must be used in the experimental units for uniform gas distribution.

BATTERY PERFORMANCE

The initial investigations of this program were performed on cells having an area of four square inches. Performance of the batteries is better than that of the small cells. This is due to improved control facilities. Four of these batteries have been constructed and tested. Each has 13 cells with 1/4 square foot of active area. The power is nominally rated at 100 watts each when operated on reformed natural gas and air.

Hydrogen-Oxygen Performance

Polarization curves for a 13 cell battery operating on various fuel and oxidant gases are shown in Figure 4. The data for Figure 4 were taken with 500 hours total operation on the electrodes, and just after a 100 hour run, to minimize the effects of fresh catalyst. The hydrogen-oxygen performance of the battery at 60°C is the standard of comparison for the operating conditions. When these data are plotted IR-free, with each electrode against a reference, it is found that the anode reaction is essentially reversible over the range of current density. By contrast, the oxygen electrode shows substantial polarization, even when the circuit is open. The irreversibility of oxygen electrodes is well-known. It is an area for further catalyst investigation.

Internal Resistance

Preliminary measurements of the internal resistance of the battery show 0.002 ohms-square foot for each cell. This value was determined by interrupting the load on the battery and instantaneously measuring the voltage rise on an oscilloscope. This resistance figure is probably high. More accurate determinations will be possible when faster battery switching techniques have been perfected. Figure 4 shows a curve for the hydrogen-oxygen performance on an IR-free basis.

Conductivity measurements of the membranes and electrolyte indicate that a negligibly small fraction of the internal resistance is in the metallic components of the battery. The liquid electrolyte area resistance is 0.00046 ohm-square foot and the membranes, which act very much like porous media containing 25 percent electrolyte, are responsible for the balance.

Hydrogen-Air Performance

The goals of the project require a system that operates with air at the cathode. The prime disadvantage in the use of air is the loss of cathode potential because of dilution. This potential loss ranges from 40 to 80 millivolts per cell if sufficient air is used. The voltage loss increases as current is increased. The loss at 60 amps per square foot (ASF) is approximately 70 millivolts per cell or .91 volts for the battery. A polarization curve for hydrogen-air operation is included in Figure 4.

The loss of cathode potential, as stated above, depends upon the use of sufficient air. This is designated as a maximum effective feed rate - that is, the point at which any further increase in air flow does not measurably increase the electrode potential. A determination for this air flow rate is presented in Figure 5. For a single cell, the air flow rate at which a potential drop occurs is only slightly more than the stoichiometric equivalent. This is less than 20 percent excess air for 300 millivolt drop from a linear extrapolation of the polarization curve, and less than 25 percent excess air for

100 millivolt drop. At twice stoichiometric flow (100 percent excess air), no deviation from the straight line curve can be observed.

If the oxidant gas supply is interrupted briefly while current can flow through the battery, a noticeable improvement occurs in the battery's performance. This may amount to .65 volts at 60 ASF with a decay time of up to 6 hours depending upon the past history of the battery. Since this lack of reactant shifts the cathode potential almost to the anode potential, a strongly reducing condition is produced at the cathode which apparently cleans the electrode.

Dilute Fuel Performance

The product of the hydrogen generator is primarily 80 percent hydrogen and 20 percent carbon dioxide, with trace amounts of methane and carbon monoxide. The methane and carbon dioxide dilute the anode feed whereas carbon monoxide has a polarization effect which will be discussed later.

The investigation of reactant dilution is straightforward since only hydrogen and carbon dioxide need be considered. The concentration effects due to the dilution of the hydrogen are shown in Figures 6 and 7. Polarization data is included on Figure 4. In treating the data, it is convenient to define a unit gas flow rate as a stoichiometric equivalent (or stoich). This is a gas flow equal to the rate at which the reactant gas is consumed under specified conditions. For example, with a 13-cell battery operating at 15 amperes current, 1 stoich equals 1460 milliliters per minute of hydrogen. Figure 6 shows the stoichiometric relationships. Lines of constant fresh feed (j), and recycle ratio (R), are shown for an 80-20 percent mixture of hydrogen and carbon dioxide.

Experimentally, the indicated feed and recycle rates were simulated by feeding a mixture of the corresponding values of the pure gases. The average potential loss at 60 ASF was then calculated for each condition. This voltage, expressed as millivolts per cell, appears on Figure 6 near the intersection of the corresponding lines. The average potential loss is strongly influenced by excess feed and only slightly affected by the recycle ratio.

The arithmetic mean of battery inlet and outlet conditions was used for average reactant concentration. A graph of potential loss against the average concentration is presented in Figure 7. The correlation is good. The three poorest points occurred at low total flow rates. With this condition, poor distribution between cells was the most likely cause, that is, one or two cells behaved differently from the rest. According to Figure 7, there is a wide range of conditions under which the potential loss can be held to approximately 20 millivolts at 60 ASF.

Figure 7 is plotted on semilog paper for convenient presentation of the data. Also included on this graph is the line for the Nernst Equation which expresses the theoretical open

circuit potential loss. At low average feed concentrations, there appears to be a significant diffusion problem at 60 ASF current. In the range of probable operation, without recycle, the concentration effect is not large.

Figure 4 includes a curve for the polarization of the 13-cell battery on 80 percent hydrogen-20 percent carbon dioxide fuel mixture vs. air. Approximately 200 percent excess fuel was used in the collection of these data.

To check for carbon monoxide production in the anode chamber, the carbon monoxide concentrations of the battery inlet and outlet gases were measured with a sensitive infra-red analyzer. With an inlet concentration from a bottled mixture of 80 percent hydrogen-20 percent carbon dioxide containing 3 ppm of carbon monoxide, the battery outlet concentration was 4 to 5 ppm of carbon monoxide without load. The thermodynamic equilibrium of the reverse water gas shift reaction at 60°C is 20 ppm. Under the flow conditions in the battery, the reaction does not proceed rapidly over the platinum catalyst.

Performance with Reformed Natural Gas Fuel

The purpose of this project is to achieve satisfactory battery operation on a fuel derived from natural gas. The product gas of the hydrogen generator contains 3000 ppm of methane and 20 ppm of carbon monoxide in addition to the hydrogen and carbon dioxide. The methane exerts a negligible dilution effect only, but the carbon monoxide, even in small amounts, significantly affects the battery's operation. It is believed that the carbon monoxide is adsorbed at the reaction site and results in a poisoning effect.

Figure 4 includes a line for the polarization of the 13-cell battery at 60°C when operating on reformed natural gas (RNG) fuel and air. These data were taken after 300 total hours on RNG fuel and immediately after a 100 hour run at 40 ASF. The polarization at 60 ASF is 1.2 volts for the 13 cells, or less than 100 millivolts per cell, when compared with pure hydrogen feed. As expected from the previous section, the concentration polarization due to the presence of carbon dioxide is less than 20 millivolts per cell. The remainder is due to the effect of the carbon monoxide. The maximum power of the battery is 112 watts at 80 ASF.

The poisoning effect just mentioned has occurred for 60°C operation. From tests on small cells, the effect at room temperature is approximately 300 millivolts per cell. The operating temperature of 60°C was selected to minimize the poisoning effect without reaching the temperature at which the fuel reduces the sulfuric acid to hydrogen sulfide.

The long term effects of carbon monoxide in the feed stream are now being investigated. At present, the total operating time on reformed natural gas is 800 hours.

Apparently, the anode can be rejuvenated by two techniques. If the battery load is removed for about an hour, the output

voltage of an 80-20 fuel mixture is produced when the load is restored. Another technique to remove the anode poisoning is to short circuit the battery without fuel. In this case, the carbon monoxide apparently is oxidized. It is not known if either of these rejuvenation techniques can be repeated indefinitely. There is evidence of increasing potential falloff rate with repeated anode treatment.

FUTURE IMPROVEMENTS

When this program was started two years ago, the approximate material cost was \$50,000 per kilowatt of power on hydrogen-oxygen feeds. The present cost is \$3,000 per kilowatt with an RNG-air feed. The cost must still be reduced significantly for this fuel cell battery to be an economical power source. There are several points of potential improvement in the battery.

The electrical resistance of the electrolyte accounts for a substantial loss of cell potential. A majority of the resistance is in the ion-exchange membranes. Research at Ionics has produced a membrane which could reduce the resistance by more than half, doubling the power output. It is likely that additional effort will result in further improvements in membrane technology.

Experimental electrodes with a greater tolerance for carbon monoxide are now being studied. These electrodes may reduce the load on the methanation system of the hydrogen generator and permit lower temperature operation. Improvement of the carbon monoxide polarization may be possible with increased unit power output.

Electrode costs are a significant fraction of the total battery material costs. Although the electrodes have a high scrap value, the platinum is a high cost investment. While it is unlikely that platinum will be replaced as a catalyst, at least on the oxygen side, the possibility of a more effective use of the catalyst is significant. Experiments with electrodes using different amounts of platinum indicate that the effectiveness of the platinum (at constant potential) increases significantly as the platinum loading decreases. Some success may be expected from attempts to place small amounts of catalyst on the electrode surface most favorable to the reaction. The anode polarization curve indicates that reduction in catalyst loading may be possible now without penalty to performance.

ACKNOWLEDGEMENT

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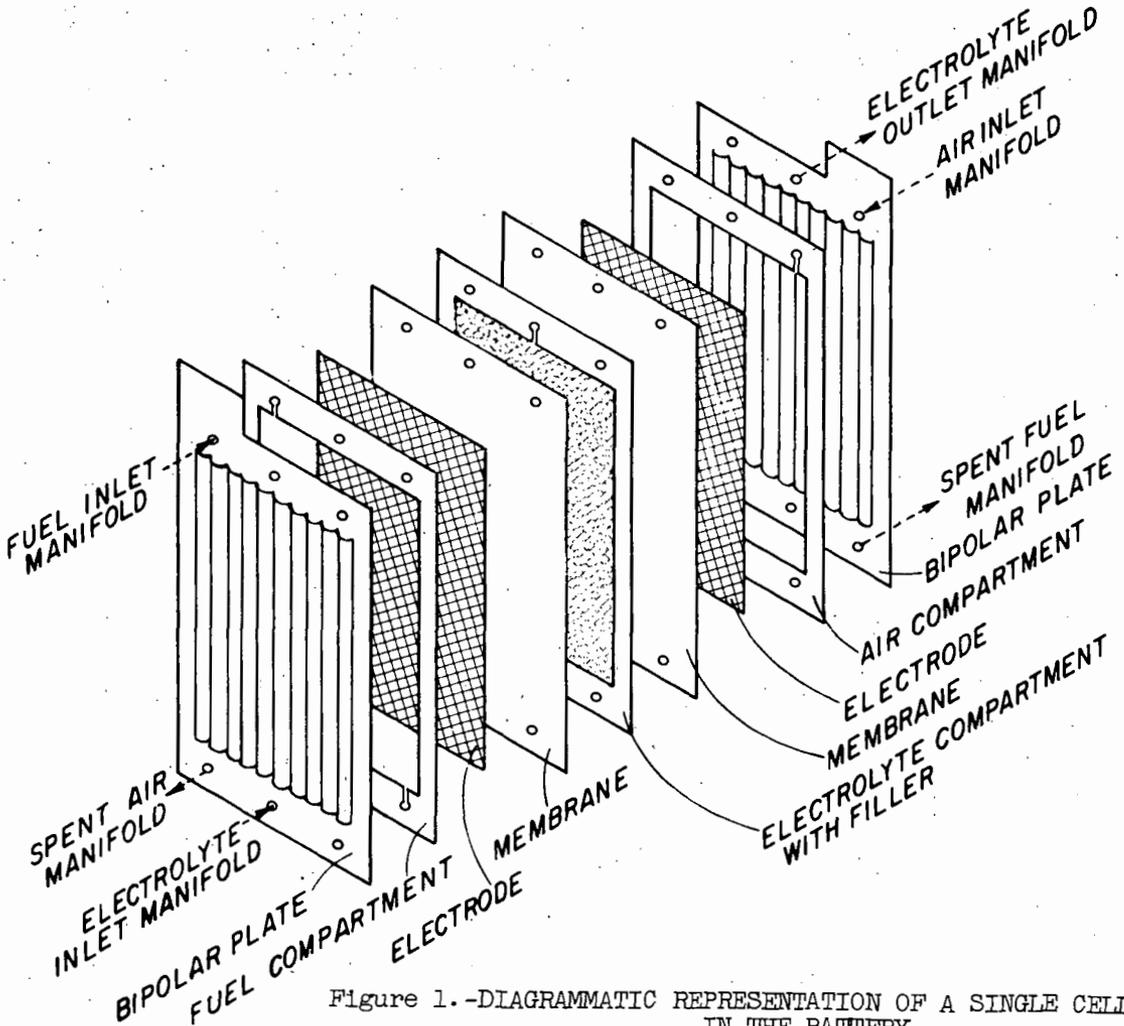


Figure 1. -DIAGRAMMATIC REPRESENTATION OF A SINGLE CELL IN THE BATTERY

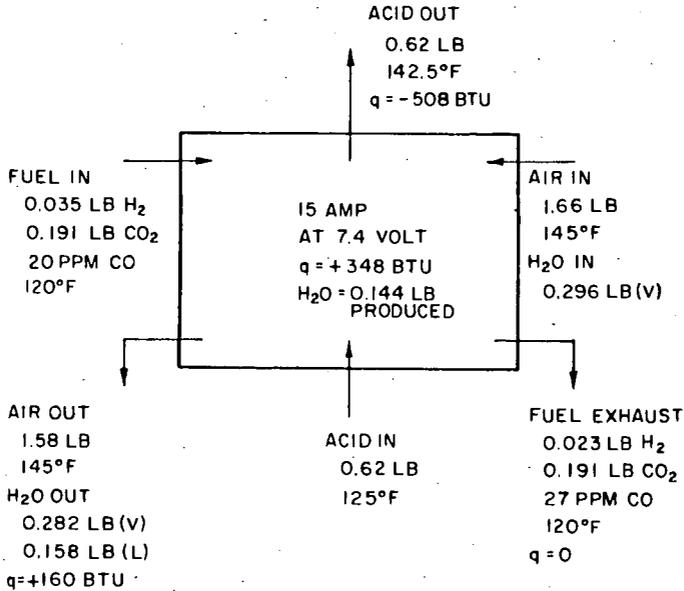


Figure 2.-HEAT AND MASS BALANCES AROUND THE OPERATING BATTERY
(13 CELLS, 1/4 SQ FT EACH, 1 HR OPERATION, STEADY STATE)

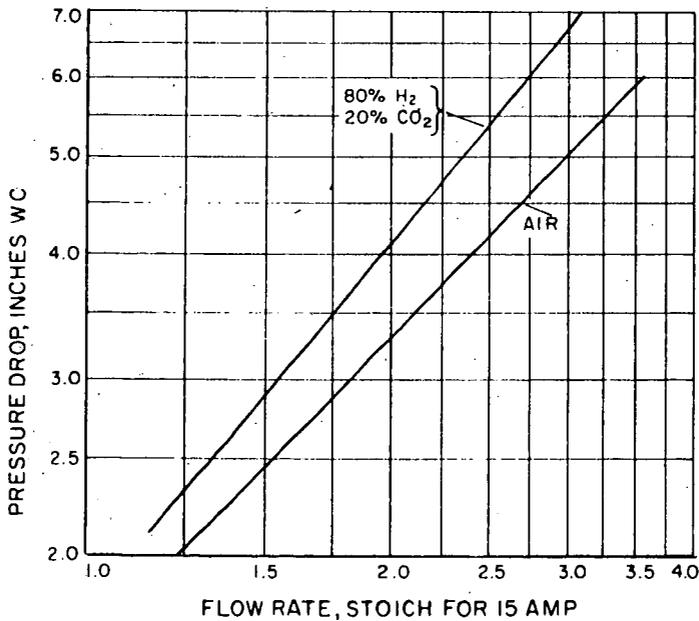


Figure 3.-PRESSURE DROPS IN THE BATTERY GAS STREAMS

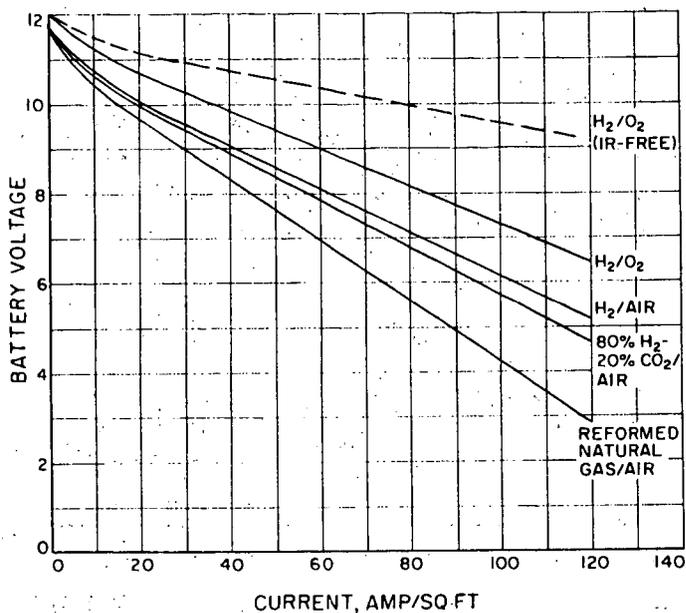


Figure 4.-OPERATING PERFORMANCE OF A 13-CELL BATTERY AT 60°C

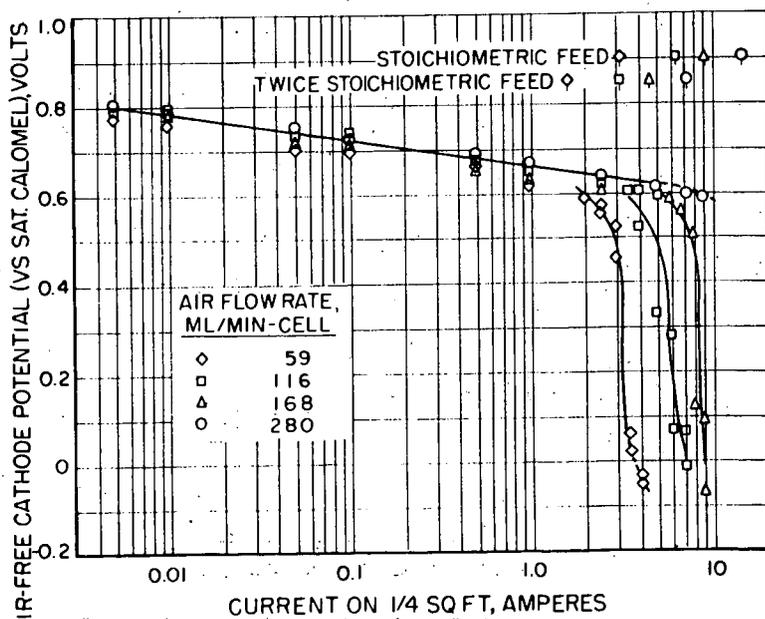


Figure 5.-POLARIZATION CURVE SHOWING POTENTIAL DROP AS CURRENT APPROACHES STOICHIOMETRIC EQUIVALENT OF AIR FEED

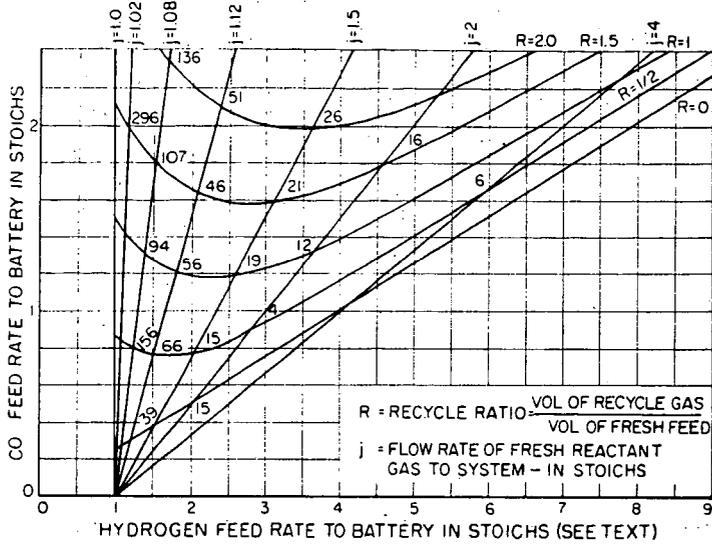


Figure 6.-VOLTAGE DIFFERENCE BETWEEN PURE HYDROGEN AND DILUTE ANODE FEEDS. NUMBERS ARE MILLIVOLTS LOSS PER CELL

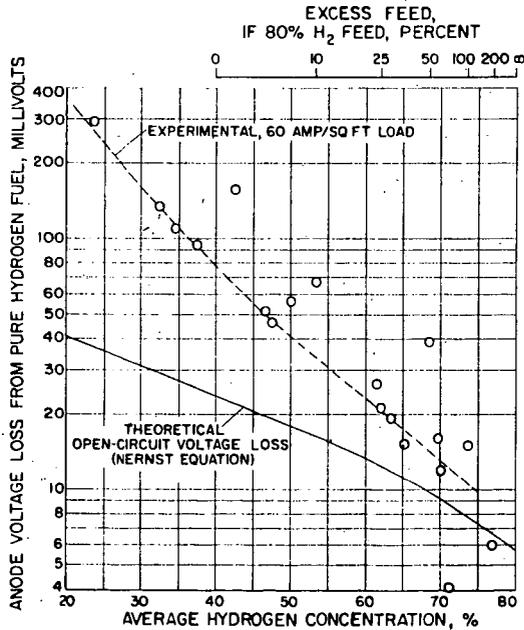


Figure 7.-VOLTAGE LOSS DUE TO DILUTE ANODE FEED.