Thin Fuel Cell Electrodes

R. G. Haldeman, W. P. Colman, S. H. Langer, and W. A. Barber

Central Research Division, American Cyanamid Company
Stamford, Connecticut

I. Introduction

There is considerable current interest in low temperature, light-weight, high-performance H_2-O_2 fuel cell components. This company has had for several years a research program directed toward development of thin electrode structures for the "equilibrated matrix" hydrogen-oxygen or hydrogen-air cells. Electrodes developed for this system should be useful also in the ion exchange membrane fuel cell, and with some modification in the free electrolyte fuel cell.

As a short range objective, we have required that such electrodes, when assembled into an H_2-O_2 cell, should sustain currents of at least 200 ma/cm^2, developing a potential corrected for internal resistance of 0.8-0.9 volts. They should be useful with suitable modification of support material in either strong acid or base and should be capable of sustained operation at temperatures from ambient to 100°C. They should be capable of manufacture in large sizes, e.g., one foot square, and have good uniformity and reproducibility. Further, material costs/kw of power should be minimum.

II. Experimental

A. Procedures

Much of the initial evaluation work has been carried out in one inch diameter (5 cm^2) matrix cells. We have found that scale up to 2" x 2" cells (25 cm^2 active area) can be readily achieved, and the larger cell is preferred for life testing.

For the alkaline system, asbestos is a suitable matrix material, while glass-fiber paper performs well in the acid system. Several types of organic matrix may also be used.

In life testing, in order to obtain stable operation, it is necessary to remove water from the system as fast as it is formed by the electrochemical reaction. In our work this has been accomplished by using just sufficient gas flow to permit evaporation of the proper amount of water.

B. Electrodes

For the equilibrated matrix system electrodes have been developed consisting of a porous layer of platinum black and a waterproofing agent with or without extenders, spread uniformly on and supported by a wire mesh screen. The thickness of the electrode and platinum loading can be varied by using screens of differing mesh and wire diameter, and also by varying the amount of extender used. Two major variations are under study.

In Type A no extender is used. Thus, with screens in the range 50-100 mesh and .002-.004 inch wire diameter, platinum loadings are typically in the range 7-10 mg/cm^2 and electrode thickness 0.004-0.008 inch. Resistivity is nearly that of the support screens. In Type B electrodes, platinum is supported on a carbon or graphite extender. Electrodes of this type may contain 0.5 to 4 mg Pt/cm^2 electrode area and have the same thickness and resistivity characteristics as Type A electrodes.

C. Studies of Type A Electrodes

Comprehensive studies have been made with platinum black-metal screen electrodes, since these are capable of sustaining very high currents at low polarization.

1. Acid System

In Figure 1, we show typical polarization curves for 50 mesh tantalum screen electrodes containing 7-9 mg Pt/cm^2 as used on both sides of H_2-O_2 and H_2-air cells. Temperature was ambient and the electrolyte 2N H_2SO_4 in a glass fiber paper matrix. The polarization curve for H_2-O_2 uncorrected for internal resistance indicates a potential of about 0.72 volts at 200 ma/cm^2. Indeed, similar curves have been found to be approximately linear to 600 ma/cm^2 and 0.55 volts. The H_2-O_2 curve corrected for internal resistance (based on open current measurements with a Universal AC bridge) indicates an essentially constant IR free potential of about 0.82-0.87 volts.

The performance of this type of electrode in a hydrogen-air cell is shown in the lower curve of Figure 1. It will be seen that the increase of polarization is only 50 mv at 50 ma/cm^2 and 60 mv at 200 ma/cm^2 and apparently indicates that at these current densities performance is not limited by inadequate diffusion of oxygen into or nitrogen out of the electrode structure.

Performance of these electrodes seems to be substantially independent of temperature as indicated in Figure 2. Somewhat higher performance might be expected at elevated temperature; however, these cells have not yet been optimized for performance at higher temperature.

Some indication of life performance has been obtained with the tantalum screen electrodes in the H_2-O_2 system at ambient temperature. These electrodes have been operated for over 1000 hours at currents up to 150 ma/cm^2 without evidence of deterioration.

2. Base System

Extensive studies have been made of platinum black spread on 100 mesh nickel screens. In Figure 3 we show initial polarization for H_2-O_2 and H_2-air of the system consisting of these electrodes with 5N KOH in a matrix cell. The uncorrected H_2-O_2 curve indicates a cell potential of 0.76 volts at 200 ma/cm^2. This curve has also been extended to 600 ma/cm^2, a potential of 0.6 volts being obtained. Thus, the electrodes are capable of sustaining very high electrochemical rates in the alkaline system.

When the H_2-O_2 polarization curve is corrected for internal resistance a steady potential of 0.85-0.90 is obtained over most of the range of current density. This is roughly 20-30 mv higher than was observed for the acid system. Individual electrode polarization studies have been made which indicate that at these platinum levels the major part of the initial 0.3-0.4 volt polarization occurs at the oxygen electrode in both acid and base systems.

The H_2-air performance is plotted in the lower curve of Figure 3. Additional polarization on air is 40 mv at 50 ma/cm^2 and 100 mv at 150 ma/cm^2. These electrodes have not been optimized for operation on air.

Performance at higher temperatures has been examined at 70° and 95°C and, again essentially no change from ambient is found. The data indicate maintenance of a high level of performance of the electrodes at higher temperatures, at which operation is probably desirable to facilitate removal of product water.

Life tests for over 1000 hours at ambient temperature and several hundred hours at 80°C at currents up to 125 ma/cm^2 indicate excellent performance stability.

D. Studies of Type B Electrodes

Type B electrodes represent an approach to more effective utilization of catalytic materials. Carbons added to the formulation act as extenders and substrates for the spreading of platinum or other activating ingredient. Excellent control of distribution of catalyst and waterproofing agent is achieved.

1. Choice of Carbons

As the result of a survey of over seventy-five carbons, half a dozen promising carbons have been discovered with good chemical stability and high catalytic activity when platinized, ranging in structure from graphitic to amorphous, and in surface area from 8 to 800 m^2/g. One of these is Cyanamid 99% graphite, which is a byproduct of the manufacture of calcium cyanamide from calcium carbide. Some properties of this material are listed in Table I.

This material can be compacted into a rather uniform porous structure having a conductivity characteristic of graphite. Its surface area and pore structure are such that no appreciable amount of catalytic material need be buried in tiny inaccessible pores.

2. Base System

Electrodes were prepared from platinized Cyanamid 99% graphite by methods similar to those described for electrodes of Type A. Waterproofing level was held constant. Platinum loadings of 1 and 2.5 mg/cm^2 on appropriate screens were obtained. Electrode thickness was approximately 0.007 inches. In Figure 4 is shown the performance of these electrodes in the base type matrix cell. Platinum loadings on each side are indicated in the table in the lower part of the graph. It is evident that reduction of platinum loading at either electrode produces some loss in performance. However, even at a total loading of 3.5 mg/cm^2 for both sides, the additional polarization is only about 100 mv at 200 ma/cm^2. It is believed that substantial improvement in performance by improved methods of platinization can be achieved. Additional polarization when these electrodes are operated on air is similar to that obtained at high platinum loadings. Life studies conducted for over 1000 hours, including substantial periods at 150 ma/cm^2, indicate no significant change in electrode properties when operated as either anode or cathode.

Similar studies have been made of Type B electrodes in acid systems.

III. Discussion

Based on the above performance and physical characteristics, we can project that cells constructed with these electrodes will have very desirable weight and volume characteristics. A typical electrolyte matrix with two thin electrodes would have a total thickness of about 0.030 inches and a weight of about 0.3 lbs/ft^2. For a fuel cell operating at 75 $watts/ft^2$ total electrode-electrolyte weight would be about 4 lbs/kw.

If it is assumed that individual cells could be stacked at 4 to the inch and operate at 100 $amps/ft^2$ with the potential indicated in the above polarization curves, power levels of 65-85 $watts/ft^2$ could be achieved on either oxygen or air, and power densities in excess of 3 kw/ft^3 of battery exclusive of auxiliaries should be feasible.

It is believed a power density of 75 $watt/ft^2$ can be achieved in the near future with a platinum usage of about 2 g/ft^2 of cell area (including both electrodes). This represents an investment in platinum of about $80/kw. Moreover, it is believed that major part of this platinum value can be recovered when the useful life of the battery has ended.

TABLE I

PROPERTIES OF CYANAMID 99% GRAPHITE

Purity	99.0 Wt. %
Impurities	SiO_2, CaO, Fe_2O_3, Al_2O_3
Particle Size	Approximately 0.25 to 2.0 Microns
Surface Area	11.4 $m^2/gram$
Conductivity*	50 mho/cm
Bulk Density*	1.28 g/cc
% Porosity*	40
X-ray	Graphitic

* Measured at 2000 psi.

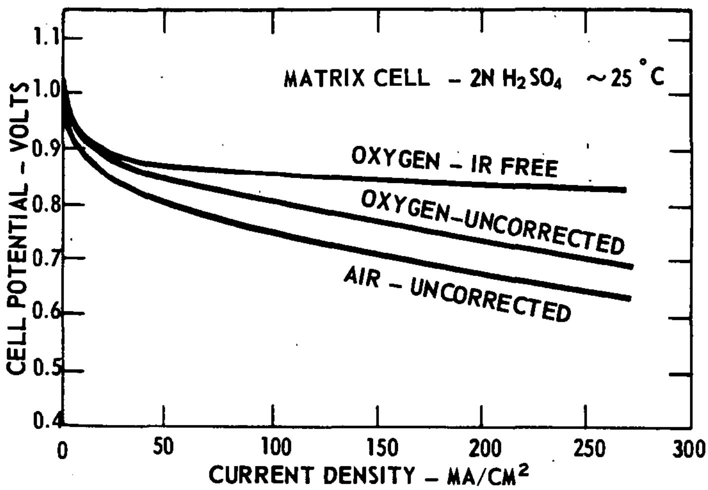

FIG.1 TYPE A ELECTRODES – ACID SYSTEM

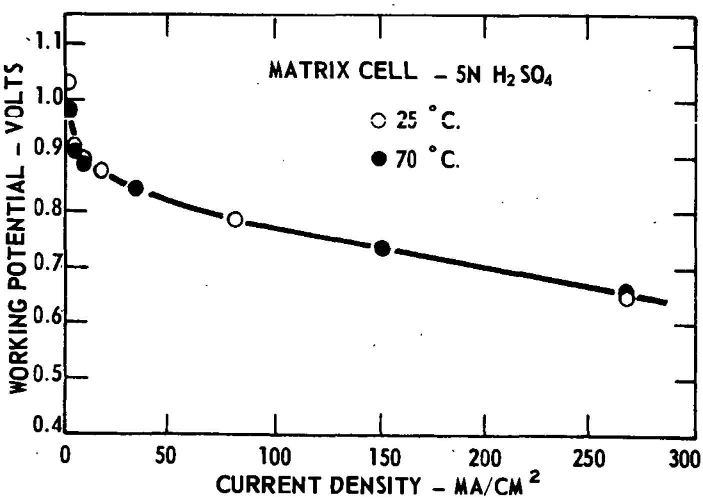

FIG.2 TYPE A ELECTRODES, EFFECT OF TEMPERATURE

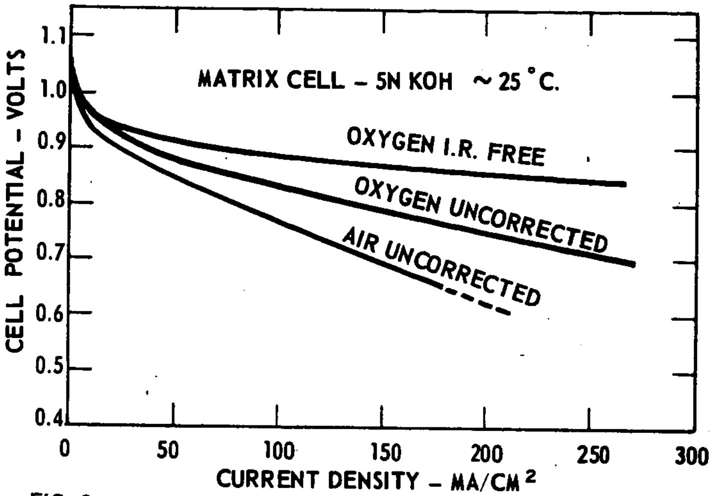

FIG. 3 TYPE A ELECTRODES – BASE SYSTEM

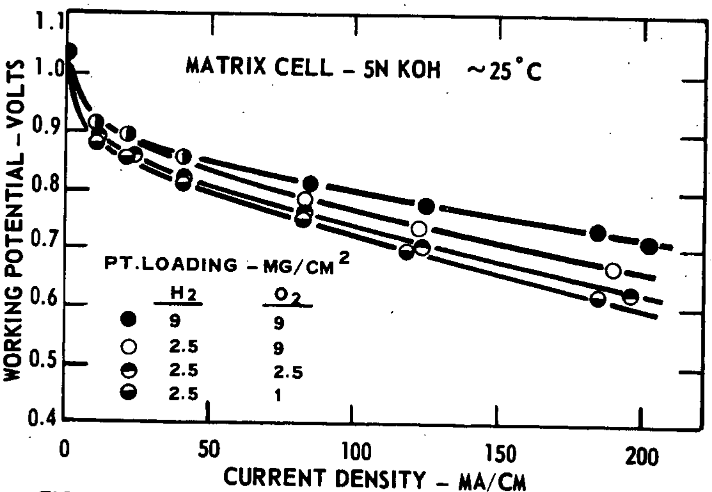

FIG. 4 TYPE B ELECTRODES – BASE SYSTEM