Reprinted from ADVANCES IN CHEMISTRY SERIES, Number 47, Page 9, 1965
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Fuel Cell Electrodes for Acid Media

WALTER G. TASCHEK

U. S. Army Electronics Research and Development Laboratories, Fort Monmouth, N.J.

Investigations have been conducted toward developing high drain fuel cell electrodes for acid media. Activated carbon electrodes have been prepared, wetproofed with paraffin or Teflon, and catalyzed with platinum. The wetproofing agent was applied by immersion or electrodeposition and the catalyst applied by chemical decomposition of H_2PtCl_6 solutions. Half cell studies with hydrogen anodes and oxygen (air) cathodes have shown that electrochemical performance is essentially the same for paraffin and Teflon-treated electrodes; however, the life of the Teflon-treated electrodes under equal conditions of load is greater than that for paraffin-treated electrodes. An equation that describes the cathode's polarization behavior for heterogeneous porous electrodes expresses a simple relationship between current density and polarization and is valid in the range of practical current densities.

The long range goal of fuel cell research is the development of fuel cell batteries operating directly or indirectly on inexpensive fuels—for example, hydrocarbons, and air as the oxidant. The batteries must operate at high efficiency at practical current densities and have long operational life if they are to compete with present forms of power generation. The batteries must employ electrolytes which are not affected by carbon dioxide. For this approach, acid electrolytes are mandatory. Consequently, a part of our program is concerned with liquid acid electrolytes. Also, the development of an efficient air cathode operating under these conditions is necessary.

Original work on hydrogen and oxygen electrodes for acid media was reported in 1962 (3). It was found that by means of a new preparation technique for catalyzed, activated carbon electrodes, wetproofed with paraffin, high performance of hydrogen anodes and oxygen cathodes could be obtained. The life of the paraffin wetproofed electrodes was short. Initial tests made with Teflon wetproofed electrodes showed performances close to that of paraffin wetproofed electrodes.

In continuation of this work, investigations have been conducted on hydrogen, oxygen, and air electrodes operating in liquid, acid media. Various electrode preparation techniques have been used, employing paraffin and Teflon as wetproofing agents. The electrochemical performance of the electrodes has been measured over extended periods of operation.

The carbon electrodes used in these investigations were supplied by Speer Carbon Co., grade 7716, dimensions 1 × 1 × $^1/_8$ inch.

The preparation techniques used most extensively were:

Paraffin-Treated Electrodes (A)

Activation. The raw carbon electrodes were weighed and then fired in a carbon dioxide atmosphere at 800° C. for eight minutes. After that, the electrodes were cooled in a stream of carbon dioxide to prevent air oxidation of the hot carbon. Finally, the electrodes were weighed and their weight loss calculated. A 7 to 10% weight loss was desired.

Wetproofing. The activated carbon electrodes were immersed in a wetproofing solution for $^1/_2$ hour. The wetproofing solution contained 2 grams of paraffin per 100 ml. of petroleum ether. The electrodes were then dried by drawing air through the pores for several hours. This was accomplished by means of a water aspirator. The activated and wetproofed electrodes were then ready for catalyzation with platinum.

Catalyzation. A solution of H_2PtCl_6 were prepared containing from 50 to 100 mg. of platinum per ml. of solution. The volume of solution which was necessary to cover the electrodes with 2 mg. of platinum per sq. cm. of geometric electrodes surface was measured. The electrodes were heated in an oven at 200° C. The solution was then applied to the surface of the hot electrodes with a brush. Finally, the electrodes were placed in a vacuum oven at 150° to 175° C. for several hours.

Teflon-Treated Electrodes (Teflon Applied by Immersion) (B)

Activation. Same as with paraffin-treated electrodes.

Wetproofing. The activated electrodes were immersed for 15 minutes in a dispersion containing 10 ml. of Teflon 41-BX per 100 ml. of water. Prior to drying, the excess of Teflon resin was rinsed from the carbon surface with distilled water. The electrodes were then dried as in the case of paraffin wetproofing. Teflon 41-BX is a fluorocarbon resin of hydrophobic negatively charged particles in an aqueous medium of pH = 10. The average size of the resin particles is about 0.2 micron. The dispersion was obtained from E. I. DuPont de Nemours & Co. (*1*).

Catalyzation. Same as with paraffin-treated electrodes.

Teflon-Treated Electrodes (Teflon applied by electrodeposition) (C)

Activation. Same as with paraffin-treated electrodes.

Wetproofing. The activated electrode was placed in the electrodeposition bath containing 4 ml. of Teflon 41-BX per 100 ml. water. A d.c. power supply connected to a variable resistor served as the source of current. The electrode to be wetproofed was the anode (+) and a platinum strip was the cathode (−). A potential of 6 volts was applied across the electrodes and the resulting current was about 65 ma. The distance between the anode and cathode was 1 to 2 inches. Direct current passing through the dispersion of Teflon 41-BX caused the negatively charged dispersed particles to migrate toward the positive carbon anode by electrophoresis. The particles were discharged and deposited there. The only occurrence at the platinum cathode was the evolution of hydrogen gas. It was observed that a heavier deposit of Teflon was formed at the carbon surface facing away from the cathode.

Catalyzation. Same as with paraffin-treated electrodes. The carbon surface clean of Teflon deposits was catalyzed.

A diagram of the cell used to test electrodes is shown in Figure 1. The electrolyte used in all tests was 5*N* sulfuric acid. All cells were operated at room temperature. Gas pressures of hydrogen, oxygen, and air were maintained at the bubble pressure of the electrode. The bubble pressure was defined as the minimum pressure required to maintain visible bubbling at the electrode-electrolyte interface. The interrupter technique described by Kordesch and Marko was used to eliminate the IR drop in potential measurements (2). A saturated calomel electrode was used as the reference electrode.

An equation was found that described the polarization behavior of the porous gas diffusion type oxygen (or air) electrodes. The equation is given by:

$$\eta = ai^b$$

η is the polarization in volts; i is the current density in amp. per square centimeter, and a and b are constants of the equation. The equation was found to be valid in the range of current densities from 5×10^{-4} to 10^{-1} amp./sq. cm. Its validity could be established for 19 out of 21 current voltage curves using various electrodes. By plotting the polarization and the current density on a log-log plot, the constants a and b can be readily

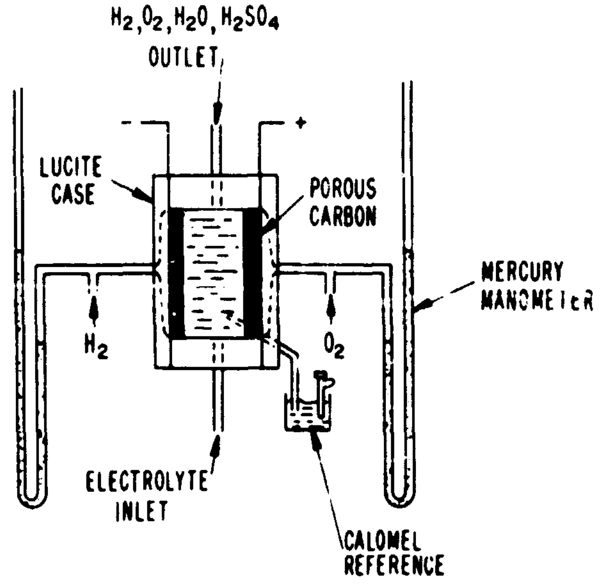


Figure 1. Schematic drawing of experimental cell

evaluated. The log-log plot of the polarization versus the current density was obtained by superimposing the measured potential values on the polarization ordinate and assigning an arbitrary open-circuit potential of 1.1 volts for oxygen and air electrodes versus the standard hydrogen electrode (SHE). We used arbitrary open-circuit potential since the experimental open-circuit potentials are difficult to reproduce from one electrode to the next. The range of the experimental open-circuit potentials observed was about 0.8 volt to 1.1 volts. This range is probably caused by mixed potentials whose values depend on various factors. The reversible open-circuit potential of 1.229 volts was not chosen because related investigations indicate the presence of another reaction mechanism(*4*).

In Figure 2 a conventional Tafel plot is compared with a log η *vs.* log i plot representing a typical set of data. It can be observed that there is no straight line portion in the Tafel plot. The log η *vs.* log i plot shows that equation $\eta = ai^b$ is valid for practical ranges of current density. Deviations occur below current densities of 5×10^{-4} amp./sq. cm. and above current densities of 10^{-1} amp./sq. cm. For low polarizations, small errors in experimental measurements are magnified because of the structure of the log-log plot. Above 10^{-1} amp./sq. cm. apparent effects of high concentration polarization are observed.

Determination of the constants a and b in the equation shows that low polarization is associated with low a values and high b values for b values less than one. No b values greater than one were observed. The high, low, and average values of a, b, and the limiting current density I_l are given in Table I and show the differences arising from different

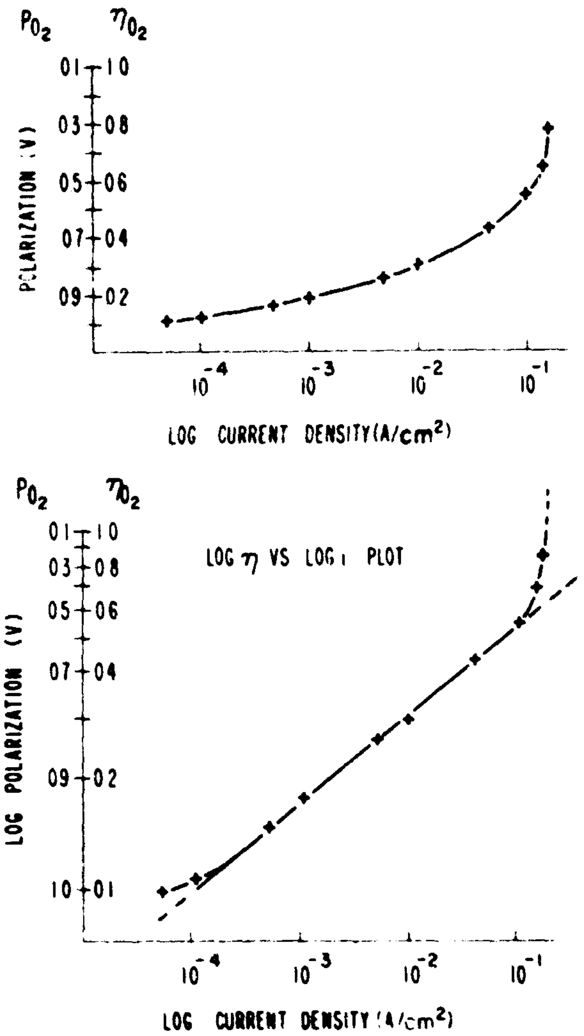


Figure 2. Tafel vs. log η-log i plot

preparation techniques. The table was compiled from nine trials of *A*, four trials of *B*, and four trials of *C*. No significant deviations were observed in average *a* values for the three preparation techniques, although there was considerable variation in these values from one electrode to the next. Close agreement was found in all *b* values for techniques *A* and *B*.

Table I. Tabulation of *a*, *b*, and I_L Values

Preparation Technique	*a*	*a*, Average	*b*	*b*, Average	I_L, Amp./Sq. Cm.	I_L, Amp./Sq. Cm., Average
A	0.72-1.10	0.90	0.12-0.145	0.13	0.07-0.3	0.19
B	0.87-1.05	0.96	0.13-0.14	0.13	0.08-0.2	0.12
C	0.59-1.15	0.89	0.13-0.22	0.18	0.05-0.1	0.08

but C showed higher b values and more variation from one electrode to another. However, technique C was connected with strong effects of concentration polarization above current drains of 50 ma. per sq. cm.

The hydrogen electrodes tested showed low polarization in the order of 50 mv. up to 100 ma./sq. cm. No limiting current densities could be observed over the range of current density investigated.

Life tests were conducted on hydrogen and oxygen electrodes with paraffin and Teflon treated electrodes. The electrodes were operated for eight hours per day. Figure 3 shows the results. Life tests of hydrogen electrodes showed nearly constant performance over all operation periods.

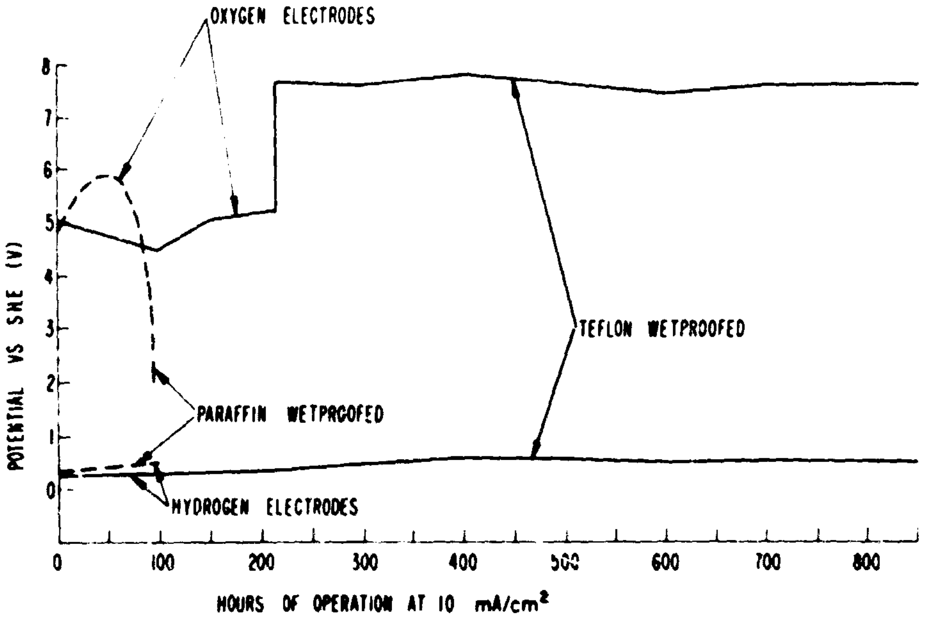
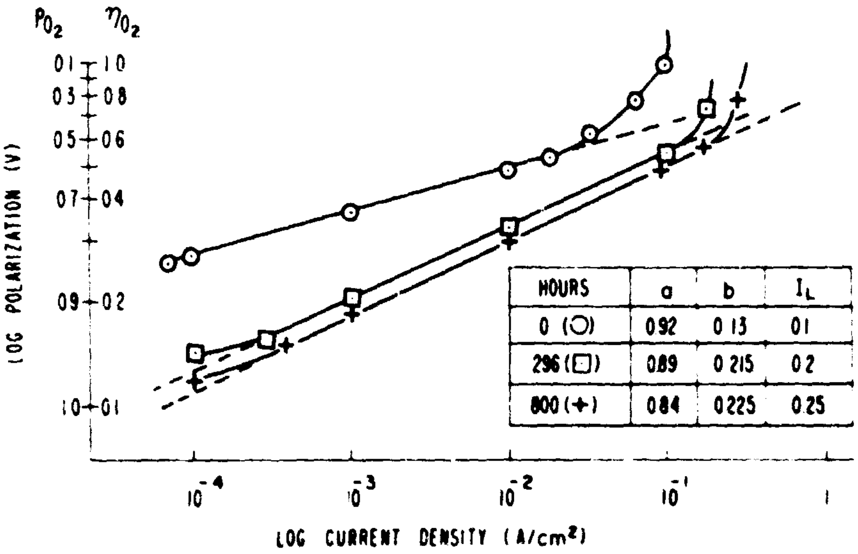


Figure 3. Life tests

With Teflon-treated oxygen electrodes, over 850 hours of operation were obtained at 10 ma. sq. cm. without loss in performance. Previously with paraffin treated electrodes, only 80 hours of operation at 10 ma./sq. cm. were obtained before the oxygen cathode failed. It was observed that after 230 hours of operation, the Teflon-treated electrodes showed a sharp rise in performance. This potential jump from 0.52 to 0.76 volt vs. SHE resulted from an increase of the oxygen gas pressure from 0.13 atm. to 0.35 atm. At the start of the test the bubble pressure for the oxygen electrode was 0.13 atm. This pressure was maintained for 230 hours of operation. It was then observed that the bubble pressure rose to 0.35 atm. The bubble pressure then remained stable from 296 to 850 hours of operation.

From these results it is evident that at relatively low drains of 10 ma./sq. cm., Teflon wetproofing does not impede the electrodes performance but increases the life of the electrodes considerably over that of paraffin wetproofed electrodes.

In addition to the constant performance test, complete current-voltage curves were taken at zero, 296, and 800 hours. Figure 4 shows the curves for the oxygen electrodes in a log η *vs.* log i plot. The curves show that a values decreased, b values increased, and I_1 values increased during the course of the life test. This means an increase in performance with aging of the electrode. This can be expected since the Teflon wetproofing initially prevents the electrolyte from making extended contact with the electrode surface. As the life test continues, the electrode surface becomes more wetted and the performance improves. This is shown in the table in Figure 4. A decrease in the a value and a considerable increase in the b and I_1 values are observed from zero to 296 hours. After that, little change in these values was observed.



HOURS	a	b	I_L
0 (○)	0.92	0.13	0.1
296 (□)	0.89	0.215	0.2
800 (+)	0.84	0.225	0.25

Figure 4. Log η-log i plot as function of time

Further, current voltage curves were taken for air cathodes and compared with curves obtained with pure oxygen. Paraffin and Teflon-treated electrodes were used. First, a current-voltage curve was taken of the hydrogen-oxygen cell. Then, after thoroughly flushing the cathode with air for several hours, the second current voltage curve was taken of the hydrogen-air cell. The results are shown in Figure 5. In both cases the oxygen electrode performed better than the air electrode. The performance of the Teflon-treated electrode decreased only slightly when air was used instead of oxygen. In the case of the paraffin wetproofing, the air performance was poor.

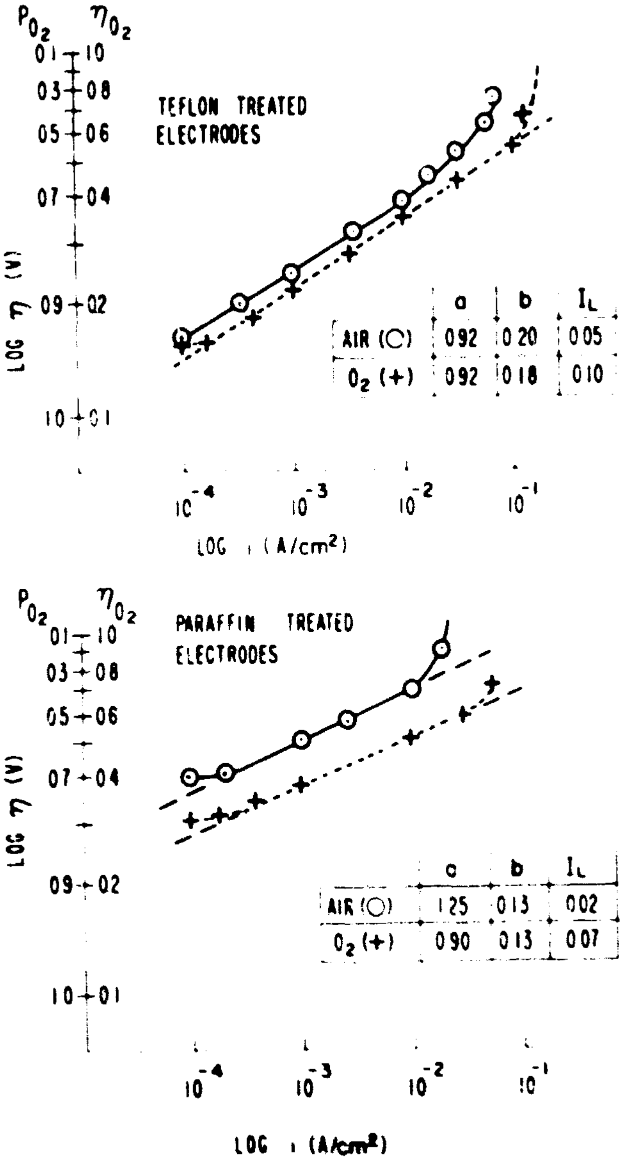


Figure 5. Air vs. oxygen

In conclusion:

1. Paraffin wetproofed electrodes show high initial performance but do not have long life.

2. Teflon wetproofed electrodes (by immersion) show excellent life characteristics without loss of electrochemical performance.

3. Teflon wetproofed electrodes (by electrodeposition) show high performance at low current densities but have low limiting current densities. Life of the electrodes has not been established.

4. Polarization of oxygen (or air) electrodes can be described by the equation $\eta = ai^b$. The equation is valid for the range of current densities investigated.

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RECEIVED February 17, 1964.

PRINTED IN U. S. A.