

## FUEL CELL ELECTRODES FOR ACID MEDIA

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The long range goal of fuel cell research is the development of fuel cell batteries operating directly or indirectly on inexpensive fuels, e.g., 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 was conducted on "Hydrogen and Oxygen Electrodes for Acid Media," and was reported at the 16th Annual Power Sources Conference in 1962.<sup>(1)</sup> 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 effect of electrolyte concentration on performance was investigated with 3N, 6N, and 10N sulphuric acid. Little change in performance was observed. In measuring the electrochemical characteristics of the oxygen electrodes, a peculiar effect was observed. This effect is shown in Figure 1. By increasing the current density over 8 mA/cm<sup>2</sup>, a decrease in polarization was observed. However, tests with careful temperature control eliminated this behavior termed "Heat Effect". 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 Company, grade 7716, dimensions 1 x 1 x 1/8 inch.

The preparation techniques used most extensively were:

## A. Paraffin Treated Electrodes

(1) Activation: The raw carbon electrodes were weighed and then fired in a carbon dioxide atmosphere at 800°C for 8 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 - 10% weight loss was desired.

(2) Wetproofing: The activated carbon electrodes were immersed in a wetproofing solution for 1/2 hour. The wetproofing solution contained 2 g 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.

(3) Catalyzation: A solution of  $H_2PtCl_6 \cdot nH_2O$  was prepared containing from 50 - 100 mg of platinum per ml of solution. The volume of solution which was necessary to cover the electrodes with 2 mg platinum per sq cm of geometric electrode surface was measured. The electrodes were heated in an oven at  $200^\circ C$ . 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  $150 - 175^\circ C$  for several hours.

#### B. Teflon Treated Electrodes (Teflon Applied by Immersion)

(1) Activation: Same as with paraffin treated electrodes.

(2) Wetproofing: The activated electrodes were immersed for 15 minutes in a dispersion of Teflon in water, 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 like 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 microns. The dispersion was obtained from E. I. DuPont de Nemours, Inc. (2)

(3) Catalyzation: Same as with paraffin treated electrodes.

#### C. Teflon Treated Electrodes (Teflon Applied by Electrodeposition)

(1) Activation: Same as with paraffin treated electrodes.

(2) Wetproofing: An activated electrode was placed in the electrodeposition bath containing 4 ml Teflon 41-BX per 100 ml water. Figure 2 shows a diagram of the electrodeposition apparatus. A DC 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 V 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.

(3) Catalyzation: Same as with paraffin electrodes. The carbon surface lean of Teflon deposits was catalyzed.

A diagram of the cell used to test electrodes is shown in Figure 3. The electrolyte used in all tests was 5N sulphuric 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 Kordeš and Marko was used to eliminate the IR drop in potential measurements. (3) A saturated calomel electrode was used as the reference electrode.

An equation was found that described the polarization behavior of the oxygen or air electrodes. The equation is given by:

$$(1) \log \eta = \log a + \log i$$

$\eta$  is the polarization in volts,  $i$  is the current density in amps 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  $5 \times 10^{-4}$  to  $10^{-1}$  A/cm<sup>2</sup>. Its validity could be established for 19 out of 21 current voltage curves using various electrodes. The log-log plot of the polarization versus the current density was obtained by superimposing the measured potential values on the polarization ordinate (Figure 4) and assigning an arbitrary open circuit potential of 1.1 volts for oxygen and air electrodes vs the standard hydrogen electrode. We used an 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 volts to 1.1 volts. This range is probably caused by mixed potentials whose value depend on various factors. The reversible open circuit potential of 1.229 V was not chosen because related investigations indicate the presence of another reaction mechanism.<sup>(4)</sup>

The equation (1) can also be expressed in the exponential form:

$$(2) \eta = a i^b$$

Dividing both sides of the equation by  $i$  results in:

$$(3) \frac{\eta}{i} = a i^{(b-1)}$$

Grouping  $a i^{b-1}$  and setting it equal to the variable term  $R_1$ , the equation is then arranged in the following form:

$$(4) \eta = R_1 i$$

$R_1$  is a variable term that is a function of the current density  $i$ .  $R_1$  can be considered as an over all "Reaction Resistance".<sup>(5)</sup>

In Figure 5 a conventional Tafel plot is compared with a  $\log \eta$  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  $\log \eta$  vs  $\log i$  plot shows that equation (1) is valid for practical ranges of current density. Deviations occur below current densities of  $5 \times 10^{-4}$  and above current densities of  $10^{-1}$  A/cm<sup>2</sup>. For low polarizations, small errors in experimental measurements are magnified due to the structure of the log-log plot. Above  $10^{-1}$  A/cm<sup>2</sup>, apparent effects of high concentration polarization are observed.

Determination of the constants  $a$  and  $b$  in equation (3) 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  $I_1$  are tabulated in Figure 6 showing the differences arising from different 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, 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/cm<sup>2</sup>. 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 8 hours per day. Figure 7 shows the results. Life tests of hydrogen electrodes showed nearly constant performance over all periods of operation.

With Teflon treated oxygen electrodes, over 850 hours of operation were obtained at  $10 \text{ mA/cm}^2$  without loss in performance. Previously with paraffin treated electrodes, only 80 hours of operation at  $10 \text{ mA/cm}^2$  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 V to 0.76 V vs S.H.E. 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  $10 \text{ mA/cm}^2$ , 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 0, 296, and 800 hours. Figure 8 shows the curves for the oxygen electrodes in a  $\log \eta$  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 can be seen from the table in Figure 8. A decrease in the  $a$  value and a considerable increase in the  $b$  and  $I_1$  values is observed from 0 to 296 hours. After that, little change in these values was observed.

Further, current voltage curves were taken for air cathodes and compared with curves obtained with pure oxygen cathodes. 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 9. 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.

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. This has been established so far for current densities up to  $10 \text{ mA/cm}^2$ .
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. It was found that the polarization of oxygen electrodes can be described by the equation  $\log \eta = \log a + b \log i$ . The equation was found to be valid for the range of current densities investigated.

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2. "Teflon", Inf. Bull. No. X-916, Polychemicals Dept., E. I. DuPont de Nemours & Co., (Inc), Wilmington, Delaware.
3. Kordesch, K., Marko, A., J. El. Chem. Soc., 107, 6, 480 (1960).
4. Wynn, J.E., "A Study of the Cathodic Reduction of Oxygen at Carbon Electrodes in Acid Electrolytes," presented at the Electrochemical Society Meeting, Detroit, Michigan, Oct 61, Extended Abstract No. 25 of Battery Division.
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Preparation Technique	a	a	b	b	$I_1$ (A/cm <sup>2</sup> )	$I_1$ (A/cm <sup>2</sup> )
		Average		Average		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

Figure 6  
Tabulation of a, b, and  $I_1$  Values

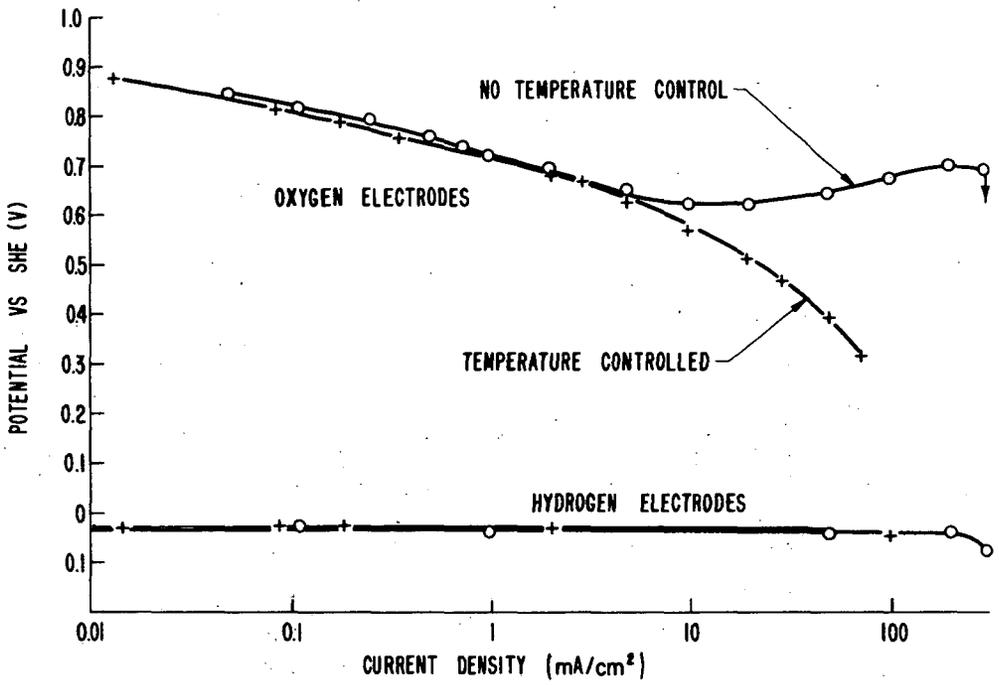


FIG. 1 HEAT EFFECT IN 6NH<sub>2</sub>SO<sub>4</sub>

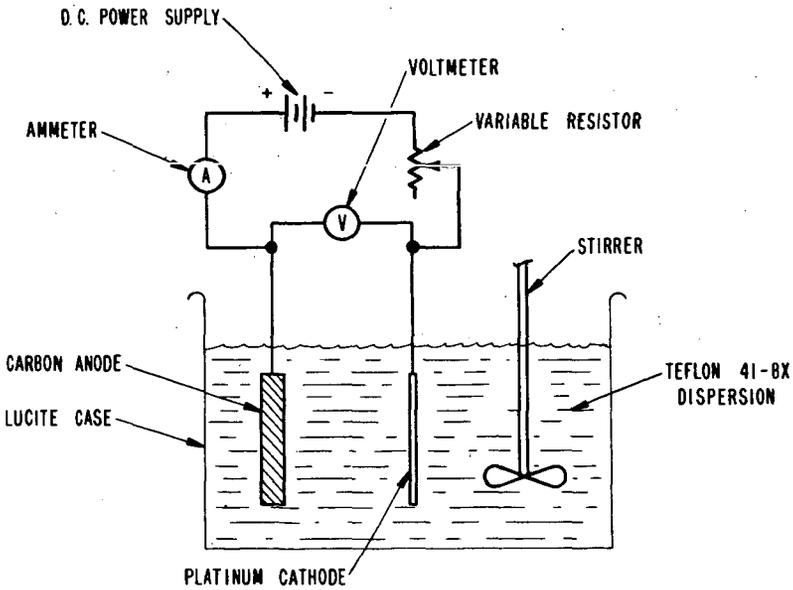


FIG. 2 SCHEMATIC OF ELECTRODEPOSITION APPARATUS

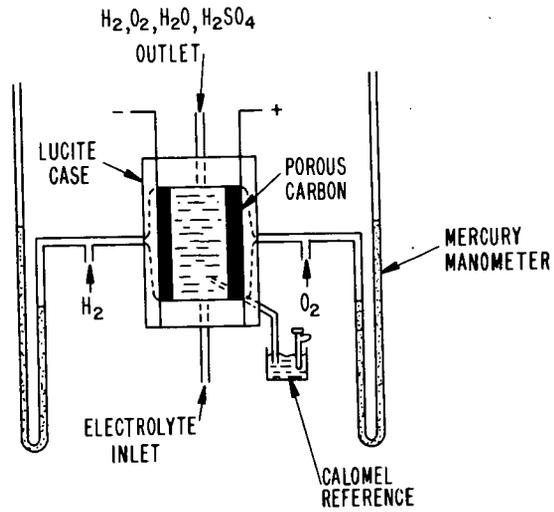


FIG. 3 SCHEMATIC OF EXPERIMENTAL CELL

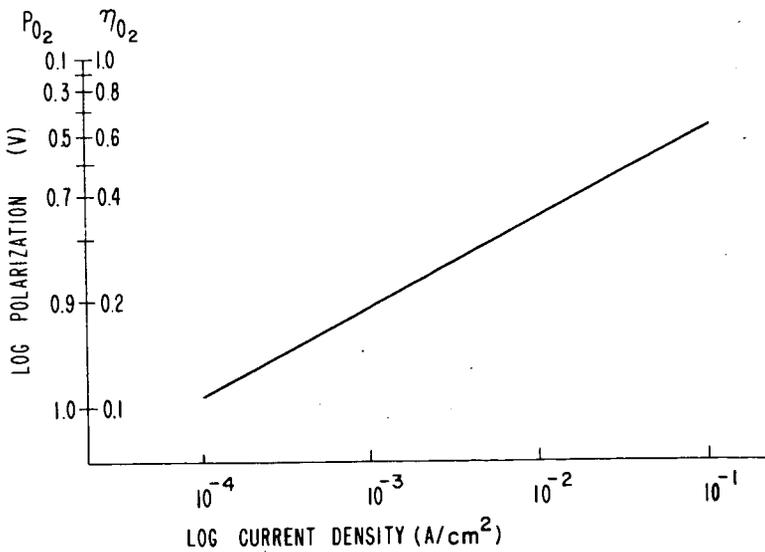


FIG. 4 CATHODE POTENTIAL SUPERIMPOSED ON POLARIZATION ORDINATE

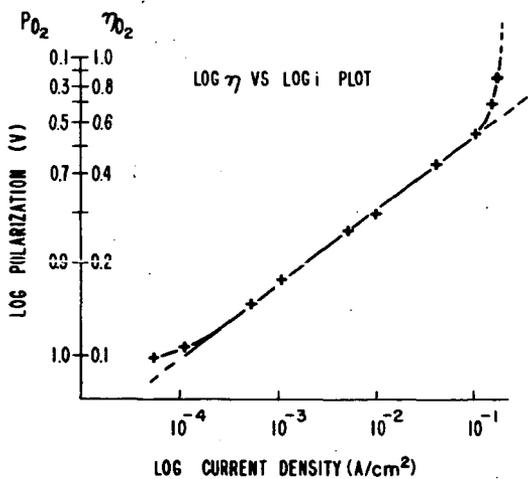
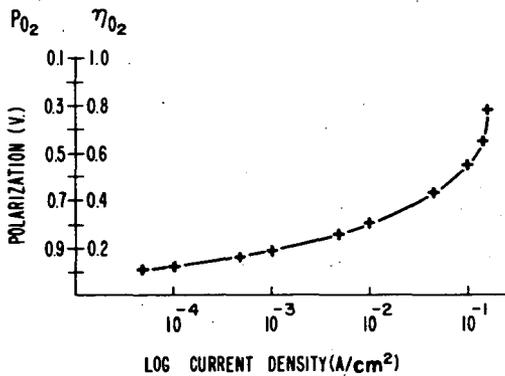


FIG. 5 TAFEL VS LOG η-LOG i PLOT

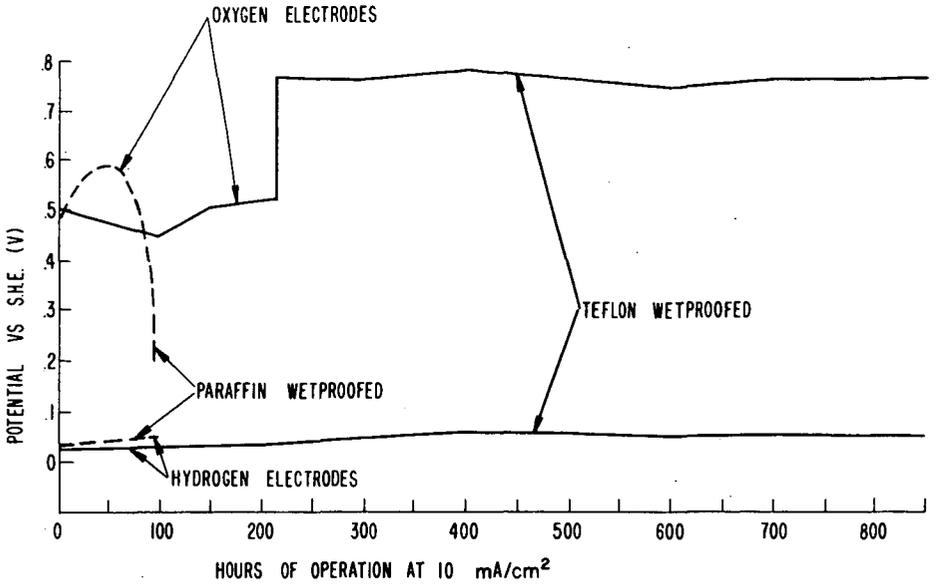


FIG. 7 LIFE TESTS

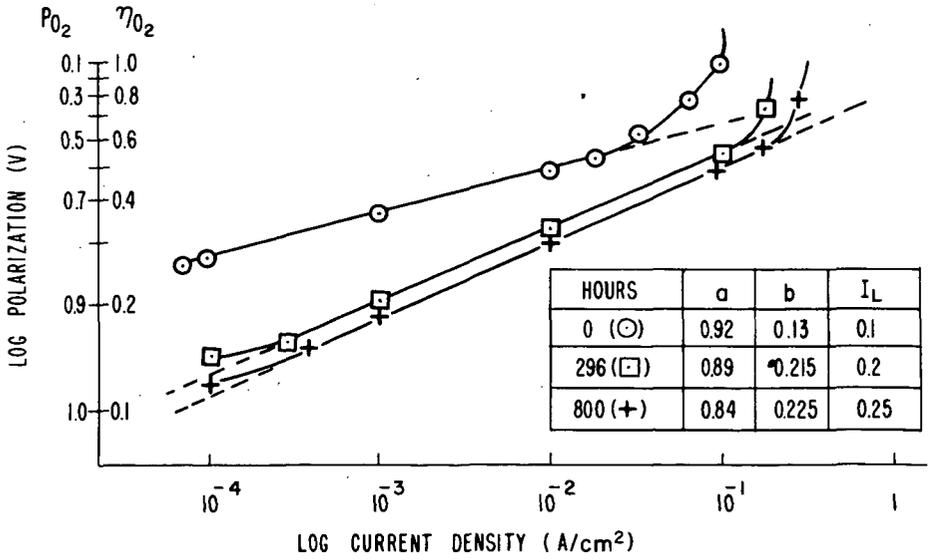


FIG. 8 LOG  $\eta$  - LOG  $i$  PLOT AS A FUNCTION OF TIME

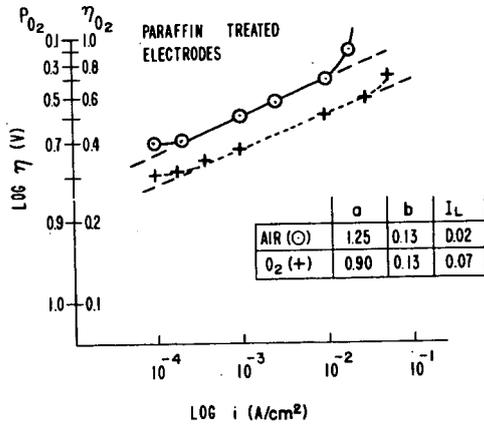
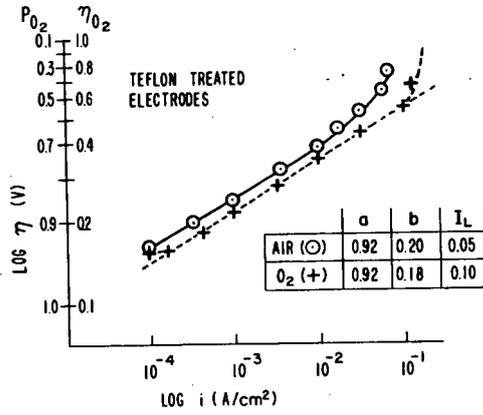


FIG. 9 AIR VS OXYGEN