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The Hydrogen-Oxygen (Air) Fuel Cell with Carbon Electrodes  
by Karl Kordesch

Research Laboratories  
National Carbon Company  
Division of Union Carbide Corporation  
Cleveland, Ohio

### Introduction

The reversal of water electrolysis on platinum electrodes in the first hydrogen-oxygen cell was demonstrated by W. Grove in 1839.<sup>1</sup> Early theoretical publications appeared shortly after 1900. Very extensive competitive efforts to build practical fuel cells started after World War I, ending in the mid-thirties without practical results. The improved heat engine, in spite of the efficiency limit set by Carnot's cycle, discouraged all efforts to construct fuel battery power plants. It is beyond the scope of this paper to mention all the various fuel cell constructions tried during this period. For a comprehensive summary, see the review written in 1933 by E. Baur and J. Tobler.<sup>2</sup>

Practical oxygen carbon electrodes became well known from experiments with air depolarized zinc batteries. Around 1930 G. W. Heise and E. A. Schumacher at the National Carbon Company<sup>3</sup> constructed long lasting "Air-Cells" with caustic electrolyte, more powerful than the earlier cells operating with ammonium chloride. But not before 1943, when W. G. Berl published his studies,<sup>4</sup> was the peroxide mechanism of the carbon oxygen electrode accepted.

After World War II scientists became strongly aware of the need to preserve fossil fuels by obtaining higher energy conversion efficiencies and fuel cell research was revived.

Again it is impossible to mention all the progress made in recent years on many different fuel cell systems, but fortunately most communications are already collected in survey publications and papers.<sup>5, 6, 7</sup>

As far as the carbon electrode fuel cell is concerned, O. Davtyan in Russia<sup>8</sup> experimented with catalyzed carbon electrodes with unconvincing results. E. Justi in Germany<sup>9</sup> worked initially with carbon, switching later to porous metal electrodes. The lack of durable catalysts and good carbon materials was obvious. The high pressure cell of F. T. Bacon seemed to be the only prospective fuel cell.<sup>10</sup>

In the meantime, realizing that the simplest gas element was a carbon electrode cell operating at room temperature on air, A. Marko and the author, at the University of Vienna, investigated catalyzing procedures which led to high current oxygen electrodes for alkaline cells.<sup>11</sup> A short time later F. Kornfeil,<sup>7</sup> F. Martinola<sup>12</sup> and H. Hunger<sup>13</sup> joined the research group. The performance of hydrogen-oxygen carbon fuel cells looked very promising, but it was still difficult to obtain reliable carbon material.

In 1955 the author joined the National Carbon Company and could make use of the carbon production experience accumulated at this organization. Together

with R. R. Witherspoon and J. F. Yeager, the present fuel cells have been developed.

In the following part of this paper the fundamental principles and the performance parameters of our cells will be stressed. Technical descriptions of the performance of practical batteries have already been presented by G. E. Evans at the Twelfth and Thirteenth Annual Power Sources Conferences of the U.S. Army Signal Research & Development Laboratories.<sup>5</sup>

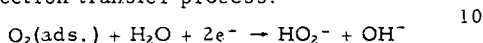
### The Characteristics of the National Carbon Fuel Cell

The construction of a laboratory type hydrogen-air fuel cell with two concentric electrodes is shown in Figure 1. The electrolyte is 30 per cent KOH. The cell produces electricity as soon as hydrogen is fed into the inner carbon tube. The outer tube is exposed to air. With more cells in series a common electrolyte circulation system is provided to remove water or carbonate if necessary. It should be noted that the CO<sub>2</sub>-pickup from the air is astonishingly slow. The larger surface of the outer tube offsets the lower current density of the air electrode. With pure oxygen-hydrogen cells we prefer equal-surface electrodes to obtain proper cell balance. Tube bundle cells or plate cells are chosen in this case.

#### 1. The Oxygen Electrode

The transpiration of oxygen through the wall of the carbon tube determines the current of the electrode. Fick's law for linear diffusion allows a calculation of the pressure drop between gas side and electrolyte side of the carbon wall.<sup>7</sup> Under a number of operating conditions, it amounts to several percent of the applied gas pressure, depending on the load. No gas escapes into the electrolyte in a properly operating cell. The pore structure is chosen such that a large pressure differential is required to produce gas bubbles on the electrolyte-carbon interface. Penetration of the electrolyte into the carbon is effectively stopped by a special carbon repellency treatment.

The oxygen molecule adsorbed on the carbon surface is ionized in accordance with the 2-electron transfer process:



Using special peroxide decomposing catalysts, the hydrogen peroxide concentration is reduced beyond the sensitivity of analytical tests to an estimated value of 10<sup>-10</sup> molar. Suitable catalysts for this purpose are described in the patents by Marko and Kordesch.<sup>14</sup> The low concentration of peroxide corresponds to the open circuit potential of 1.10 to 1.13 volts against the hydrogen electrode. The oxygen formed by decomposition of the H<sub>2</sub>O<sub>2</sub> is entirely reused. This fact changes the 2-electron process to an apparent 4-electron mechanism. Only the 0.1 volt differences in the open circuit potential of the oxygen-water electrode reveals that the electrode is not following the equation



The hydrogen peroxide mechanism on carbon electrodes was also confirmed by E. Yeager and co-workers.<sup>15</sup> The temperature coefficient of the oxygen electrode open circuit potential is -1 mv/°C (negative). Under a load condition of 10 ma/cm<sup>2</sup> we found a positive coefficient of +0.75 mv/°C, increasing with the load.<sup>12</sup>

In accordance with the theory, the oxygen electrode potential must be dependent on the alkali concentration of the electrolyte. The pH function is shown

in Figure 2. The slope of the oxygen-H<sub>2</sub>O<sub>2</sub>-electrode curve is about 30 to 32 mv per pH unit, in good agreement with the postulated value of 29 mv for a 2-electron process. In solutions containing less than 0.01N-caustic, the potential values are not reproducible. The non-linearity at higher caustic concentration is a direct measure of the activity coefficient. The abscissa indicates normality of the KOH, determined by titration with 1-N-sulfuric acid.

The potential of the oxygen-carbon electrode follows the Nernst equation. As a result, such electrodes can be used for the determination of oxygen partial pressures. The practical usefulness of such electrodes for oxygen sensing elements is very much increased by the fact that a 1 ma/cm<sup>2</sup> load does not cause marked deviations from this behavior in the range between 0.1 to 10 atmospheres pressure.<sup>16</sup> Total pressure changes give the same indication as partial pressure changes on open circuit measurements but not under heavy load conditions. In the latter case the diffusion through the blocking inert gas causes an additional pressure drop across the carbon electrode wall.

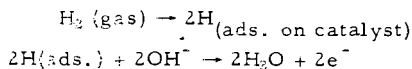
Figure 3 shows typical pressure curves of oxygen carbon electrodes, measured against an HgO reference electrode.

The effect of hydrogen peroxide concentrations in the electrolyte has been studied by E. Yeager and co-workers<sup>15</sup> and recently again by W. Vielstich.<sup>17</sup> The influence of the pH value of the caustic electrolyte on the hydrogen peroxide decomposition with and without catalysts was studied by Hunger<sup>13</sup> and led to the remarkable result that a minimum half life of peroxide is observed around pH-14. Different catalysts change the half lifetime several magnitudes but the minimum stays in the same pH region. In strong caustic solutions only the best catalysts are useful. Under pH-13 no catalyst was found which prevented a rapid increase in H<sub>2</sub>O<sub>2</sub> half life to values one hundred and one thousand fold that at pH-14.

## 2. The Hydrogen Electrode

Hydrogen is not active on untreated carbon electrodes as shown by careful experiments with carbons free of heavy or precious metals. On our hydrogen electrodes we deposit a catalyst on the electrode surface.

The reaction occurring at the catalytically active sites of the hydrogen electrode can be represented by the equation



As with the oxygen electrode, the structure of the hydrogen electrode is important for the best gas diffusion rate. A permanent three phase zone: solid/gas/liquid, has to be established by wetproofing of the carbon material. In addition we had to take precautions against "internal drowning" of the H<sub>2</sub>-electrode by the reaction product water. As indicated by the equation above, water forms at the anode and this creates a second current-limiting situation, at least at low temperatures. (Water-removing measures will be discussed in a later paragraph.)

The hydrogen electrode also follows the theoretical pH function very closely as is shown in Figure 2. The good reproducibility of measurements makes the carbon-hydrogen electrode a tool for determination of activity coefficients. Electrode equilibria are reached in minutes instead of many hours as is required with the Pt/Pt black electrode.

It is not easy to poison our carbon hydrogen electrodes. In four years of experimental testing of hydrogen electrodes, no electrode has failed as the result of catalyst poisoning, except for experiments in which large amounts of cyanide were deliberately introduced. Oxygen is detrimental only if mixed into the hydrogen in such quantities that large amounts of water form catalytically. This catalytic recombination feature prevents accumulation of a dangerous gas mixture above the electrolyte. In case of accidental gas leakage, this is important.

The open circuit potential has a small negative temperature coefficient. Under load the voltage increases rapidly with temperature, especially in the range between 20°C and 70°C.

The pressure sensitivity on open circuit follows the Nernst equation. Under heavy load conditions, the pressure effect is magnified because of the faster gas diffusion and higher adsorption values reached under pressure.

### 3. Removal of Reaction Water

In principle there are four ways of disposing of the reaction water:

- a. Operation at a temperature near or above 100°C, in the latter case under higher pressure.
- b. Operation at low temperatures under reduced pressure; current densities even at 100 mm Hg are above 20 ma/cm<sup>2</sup> at 0.8 volt.
- c. Use of gas circulating principle. Water from the electrolyte evaporates through the porous carbon wall especially if a temperature difference is set up. The water removal speed depends also on gas flow rates and is limited by the saturation value of water vapor. With a cell temperature of 70°C and a condenser temperature of 20°C, 180 g of water is transferred by each cubic meter of gas streaming through the electrodes. Evaporation of water occurs on both electrodes, however, we find more water at the anode if the cell is operating.
- d. Operation at low cell temperatures, allowing all the water to enter the electrolyte, with concentration of the electrolyte in a separate thermal or low pressure unit. For low power applications considerable dilution of electrolyte can be tolerated. The cell operates as well in 20 per cent KOH as in 50 per cent KOH. For example, a one ampere cell can be operated for one thousand hours with the production of less than one pound of water.

### 4. Cell Geometry

Because of the many possible fuel cell constructions, a comparison of different electrode arrangements and cell constructions had to be made. Figure 4 shows five basic arrangements of electrodes used in fuel cell constructions. The two-electrode tube cell (A) is the laboratory test cell model, several hundreds of which have been built to investigate electrode performance. The other constructions show remarkable improvements as can be seen from the table in Figure 4. The current factor given in this comparison represents the lower average polarization achieved by a more uniform potential distribution in the cell. The influence of ohmic resistance variations is eliminated by using the pulse current technique.<sup>19</sup> This method made our comparison insensitive to the distance between the electrodes.

The improvement factor in respect to current output per unit volume or weight is more spectacular than the mentioned polarization drop. Cell D, for

instance, is 10 times more efficient in volume utilization than type A. The internal resistance is a major factor to be considered in high current cells. Construction E is many times better than type C at 100 ma/cm<sup>2</sup> current densities, but the difference is negligible at 10 ma/cm<sup>2</sup>. These few examples show how important the engineering of fuel cells for special applications can be, independent of electrode performance.

#### 5. Performance Characteristics

Figures 5 and 6 show the voltage/current curves of hydrogen-oxygen carbon fuel cells under different conditions. The ohmic resistance is again eliminated by means of the pulse current (interrupter) technique.<sup>19</sup> All curves on the graph can be compared on an equal polarization basis. To calculate actual terminal voltages in special cells the following values should be used:

Electrolyte resistance: 1.0 to 2 ohm cm. (depending on temperature and concentration)

Electrode spacing: 0.1 to 0.3 cm.

As an example, the voltage drop due to the ohmic resistance in cell components is about 0.02 volt at 100 ma/cm<sup>2</sup> for a parallel plate battery, the terminal voltage of the cell can then be determined by combining this internal resistance loss with the appropriate polarization value from Figures 5 or 6.

#### 6. Life Expectancy

Low temperature, low pressure cells are not subject to electrode attack by electrolyte or oxidation. The only life limiting factor is wettability of the carbon electrodes.<sup>18</sup> The tendency of the electrode to wet appears to depend on the potential at which the electrode operates rather than the current density at which it operates. We have achieved two years' intermittent service on 10 ma/cm<sup>2</sup> and over one year continuous service on 20 ma/cm<sup>2</sup> at 0.8 volt, with tests still in progress. This at atmospheric pressure, between room temperature and 70°C. In the meantime better repellency treatments and more active catalysts have brought our expectations up to 30 to 50 ma/cm<sup>2</sup> over 0.8 volt for at least the same time period. The use of increased pressure gives us the benefit of very high currents at low temperature, at the price of more need of auxiliary equipment. The operation of completely "wet" carbon electrodes under high pressures might give us the additional advantage of reducing maintenance and control devices very considerably.

#### 7. Special Fuels

Hydrogen is an ideal fuel. One-eighth of one pound produces 1 kw hr in a fuel cell. In liquid state hydrogen can be stored for months, with a container weight approximately that of the hydrogen weight.

For every day purposes, hydrides, decomposed by water, are more convenient choices. One pound LiH is equivalent to 1 kw hr.

A practical, widely used fuel cell must operate on air, must be inexpensive and should use a readily available fuel. Our cells operate with high current densities on air with only a small potential difference to the pure oxygen-hydrogen cell. The use of carbonaceous fuels (liquids or gases) at low temperatures is one goal which we are attempting to accomplish. The need of removing carbonate from

the alkaline electrolyte complicates this system.

Unfortunately, the present oxygen-carbon electrode does not function in acid. The use of a redox-chemical intermediate (e.g., bromine) is necessary, which complicates the system.

All halogens operate on carbon electrodes with high current densities in acid systems. As a result hydrogen chlorine fuel cells can be operated at high power outputs for extended periods. Despite the higher voltages and high current densities which can be achieved in hydrogen chlorine fuel cells, the energy output per pound of combined fuel is less than that of the hydrogen-oxygen cell (because of the low equivalent weight of oxygen).

#### 8. Outlook

It may safely be assumed that the fuel cell will eventually become a major power source, replacing other systems in some applications. The fuel cell-operated flashlight is still a long way in the future. For the immediate present, fuel cell applications will probably be restricted to those in which the excellency of fuel efficiency, silence, freedom from fumes, simplicity of design and operation are important requirements.

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Figure 1

CONCENTRIC HYDROGEN-AIR-FUEL CELL

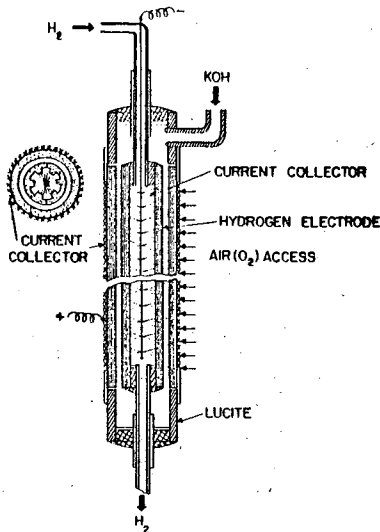


Figure 2

pH-FUNCTION OF THE OXYGEN AND HYDROGEN ELECTRODE

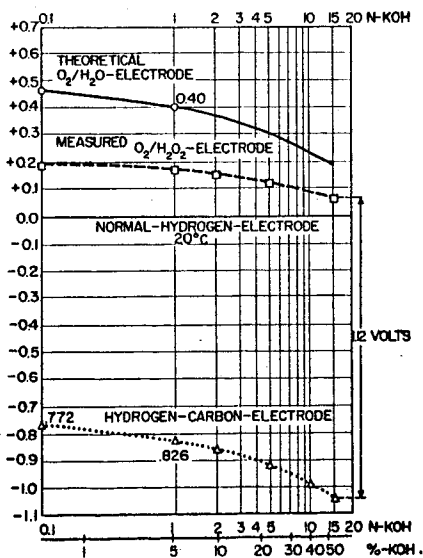


Figure 3.

THE POTENTIAL OF THE OXYGEN ELECTRODE AS A FUNCTION OF PRESSURE

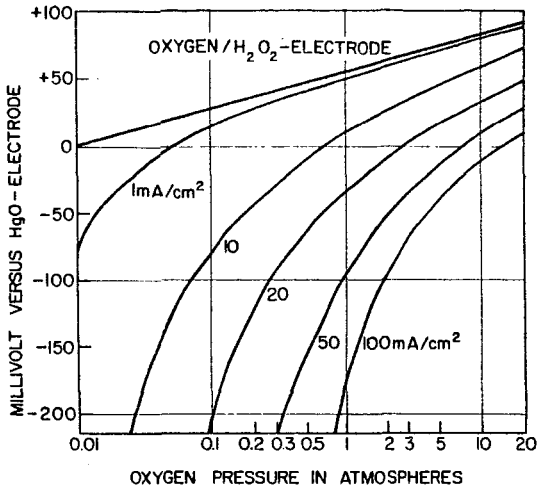
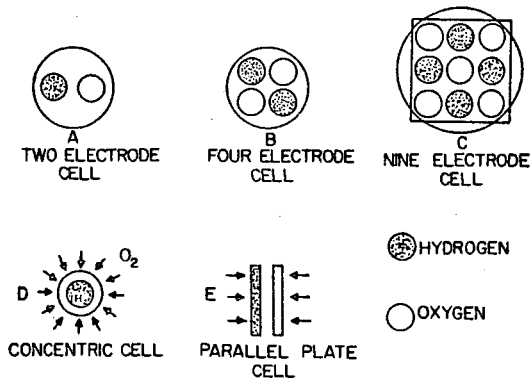


Figure 4

THE EFFECT OF CELL GEOMETRY ON THE CURRENT OUTPUT OF A CELL



CURRENT DENSITY mA/cm <sup>2</sup>	CURRENT FACTORS FOR TYPES				
	A	B	C	D	E
10	1	1.4	1.7	1.8	1.8
50	1	1.5	1.8	2.0	2.0
100	1	1.6	2.0	2.5	2.5



Figure 5

PERFORMANCE PARAMETERS  
OF NATIONAL CARBON FUEL CELLS

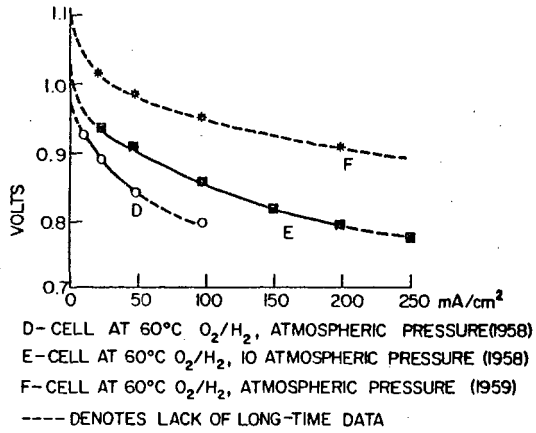


Figure 6

PERFORMANCE PARAMETERS  
OF NATIONAL CARBON FUEL CELLS

