

FUEL CELLS

History, Operation, and Applications

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A FUEL cell may be defined as an electrochemical cell in which the chemical energy of a conventional fuel is converted directly and usefully into electrical energy. By way of emphasis some parts of this definition merit further mention. The fuel cell does not differ fundamentally in its operation from primary cells with which we are all familiar; e.g., the Leclanché and mercuric-oxide-zinc dry cells. Use of a conventional fuel which is continuously fed to the anode, rather than an expensive metallic "fuel" such as zinc, is a distinguishing feature of the fuel cell. The category of conventional fuels includes the fossil fuels or substances readily derived from them. Hydrogen qualifies if it is sufficiently cheap; i.e., impure. Similarly, under our definition, oxygen or air is the only oxidant used in fuel cells and it too is fed continuously, but to the cathode.

In the course of the discussion we shall develop the basis for the considerable interest today in fuel cells as energy converters. They differ from primary cells in that they do not store the energy they convert. It may be of value to summarize at the outset the historical interest in these devices. At the turn of the century, fuel cells appeared to hold out a realizable hope for producing electrical power more cheaply and easily than thermal plants. This hope is not dead. After World War II, there was a resurgence of effort on fuel cells in Europe, and this effort was spurred by the dwindling of coal reserves. An efficiency of energy conversion approaching the theoretical would, if achieved, extend the fuel reserves. The advent of nuclear power has made this need less pressing and the level of the effort has diminished in recent years. Fuel cells, in particular

those operating on hydrogen, are currently of great interest as low-cost, light-weight, and otherwise very convenient sources of electricity for special applications.

History

SPACE will permit no more than touching the high spots of fuel cell history. Credit for being the pioneer in the field, and an unusually keen pioneer at that, goes unquestionably to W. R. Grove. In 1839, he reported that two strips of platinum immersed in sulfuric acid, one in contact with hydrogen and the other with oxygen, caused the steady deflection of a galvanometer connected to them.¹ Further experiments resulted in the construction of a battery of such hydrogen-oxygen cells with sufficient electromotive force to electrolyze water.² It was this feature of his "battery" which most intrigued Grove. We shall refer again to Grove when discussing fuel cell operation. A more elaborate hydrogen-oxygen cell employing platinum foil electrodes (perforated and platinized) pressed against absorbent layers saturated with sulfuric acid was described by Mond and Langer in 1889.³ This cell had a rating of about 2 watts per square foot, but suffered rather severe concentration polarization.

An important landmark in fuel cell history is the address of Ostwald at the first meeting of the Bunsen Society in 1894.⁴ He called for the replacement of heat engines by fuel cells as the most practical way of bringing the conversion efficiencies substantially above the 10% then current. It will be appreciated that the relatively primitive engineering of that era made for a relatively easy bogey. From about 1910 until World War II, the foremost contributor to fuel cell knowledge

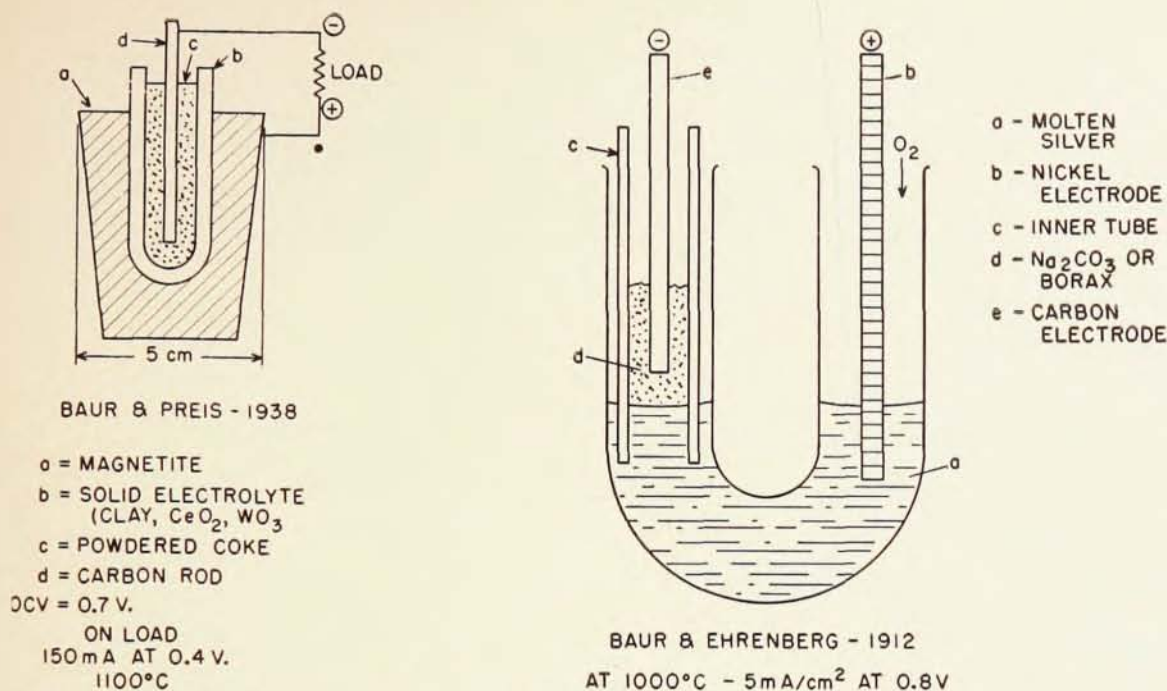


Fig. 1. Examples of early attempts by Baur, et al., to make carbon-oxygen cells.

was the Swiss, Emil Baur.⁵ The work of Baur and his colleagues covered nearly all types of cells, two high-temperature versions being shown in Fig. 1. These cells were designed to use carbon or coal directly and met with indifferent success. The main shortcoming was a very short operating life.

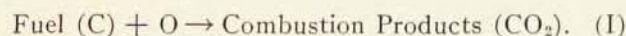
A comprehensive review of fuel cell research up to 1945 will be found in the paper by Howard.⁶

Operation

FUEL cell thermodynamics can be discussed from a number of points of view. The General Electric Company must obviously be interested in the possible generation of central station power from the least expensive fossil fuels. The simplest such fuel cell would be one in which carbon (coal) is fed directly to the anode and oxygen (air) to the cathode (Fig. 2). At the anode the reaction of carbon with oxide ions from the electrolyte forms carbon dioxide and releases electrons to the circuit. These electrons do work on the way to the cathode, where they form oxide ions by combination with oxygen from the air. Through the electrolyte, the current to complete the circuit is all carried by oxide ions. Here it is worthwhile to digress momentarily to stress a critical feature of fuel cell electrolytes, namely, invariance. Invariance is the requirement that the composition of a fuel cell electrolyte not change appreciably as the cell operates. In other words, ions removed by reaction at one electrode must be replaced one for one at the other electrode. The carbon-oxygen cell shown in Fig. 2 illustrates this principle. Note that this requirement distinguishes fuel cells from the usual primary and some secondary batteries and that it

markedly restricts the selection of electrolytes for any given fuel.

Returning to purely thermodynamic considerations, we see that the over-all reaction accomplished by the cell is the oxidation of a fuel (carbon to carbon dioxide in our example):



If the reaction is carried out under the boiler in a conventional steam plant (boiler-turbine-alternator), the chemical energy is randomized as heat. The amount of heat produced is equal to the change in heat content

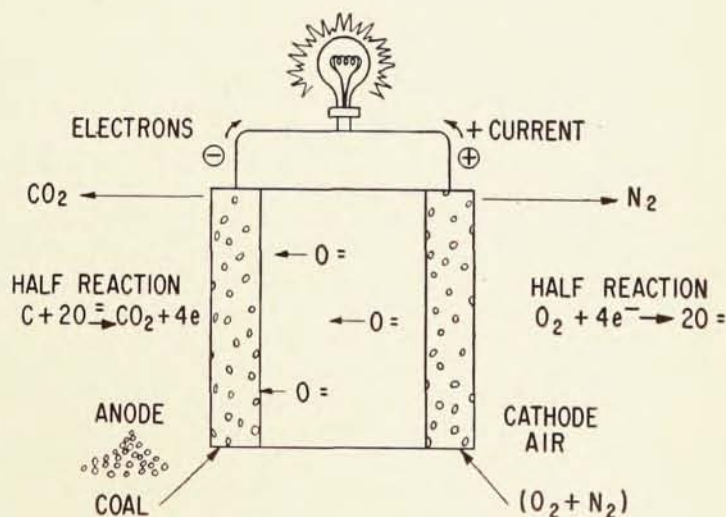


Fig. 2. Schematic diagram of carbon-oxygen fuel cell.

(ΔH) associated with the reaction. In 1824 Carnot pointed out the theoretical limit to the fraction of heat energy that can be converted into useful work. To be converted into electrical work, heat must flow from temperature T_h to temperature T_c , and maximum useful work recoverable is $\Delta H(T_h - T_c)/T_h$.

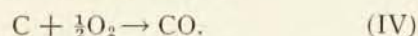
In contrast to the situation above, Reaction I is carried out isothermally and reversibly in an ideal fuel cell. The first and second laws of thermodynamics define the maximum useful work ΔG that can be recovered under these circumstances. From the relationship

$$\Delta G = \Delta H - T\Delta S \quad (\text{II})$$

we can at once write for the ideal efficiency of a fuel cell (operating isothermally and reversibly)

$$\eta_i = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \quad (\text{III})$$

With a single exception, all fuel cells currently considered reject heat to the surroundings even when operating isothermally and reversibly. The principal significance of this is that the ideal efficiencies of these cells will be less than unity and will decrease with increasing temperature. It is worth mentioning here that heat thus rejected need not be wasted. If the operating temperature is high enough the heat can be a valuable by-product. The exception mentioned above is the combustion of carbon to carbon monoxide:



For this reaction ΔS is positive, and at 1200°K the ideal efficiency is 200%. This is of no practical significance, for the cell must draw heat from the surroundings in order to maintain isothermal operation.

Two particularly important cases deserve further mention. For hydrogen as a fuel, ideal efficiencies at various absolute temperatures are as follows: 0.83 (298°K); 0.90 (500°K); 0.78 (1000°K); 0.54 (2000°K). (These efficiencies are based on the formation of liquid water at 298°K and gaseous water at the higher temperatures.) Clearly, hydrogen-oxygen cells lose their attraction at very high temperatures. In contrast to the behavior of hydrogen, cells accomplishing the oxidation of carbon to carbon dioxide have ideal efficiencies very close to 100% over the entire range of temperature cited above. The comparison of this number with the 40–42% over-all efficiency attained in the most modern steam plants explains the continued interest in carbon-based fuel cells. Practically this increased efficiency, if attained, would result in a greatly reduced fuel cost.

While the interest in fuel cells can be accounted for in large part by the thermodynamics above, we must turn to considerations of reaction kinetics in order to find the limitations to the application of fuel cells. Indeed, these limitations are so severe that the first commercial application has yet to be made.

The expression

$$-\Delta G = nE_rF = E_rIt \quad (\text{V})$$

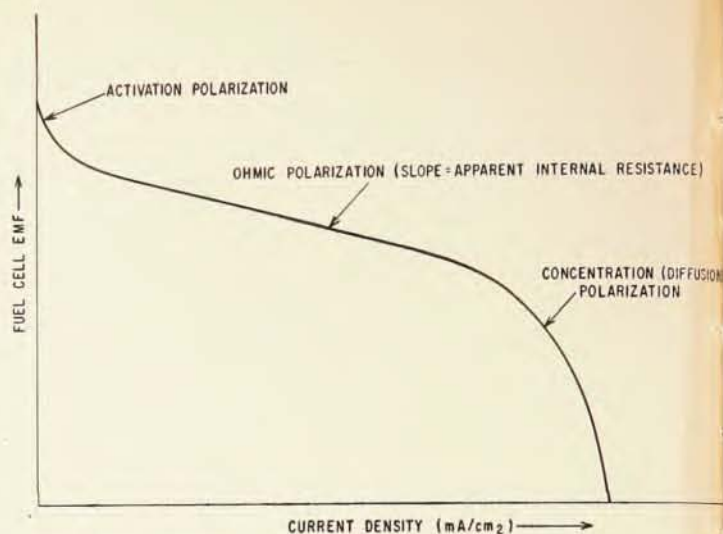


Fig. 3. Hypothetical polarization curve for galvanic cells.

relates the reversible electromotive force, E_r , to the current, I , and the time it is drawn, t . It is characteristic of most galvanic cells that the working voltage decreases as current drawn from the cell increases. A hypothetical curve relating working voltage to current is shown in Fig. 3. The decrease in voltage is attributed to "polarization" in the jargon of the electrochemist, and clearly represents a significant and unwelcome decrease in the operating efficiency below the ideal. Three contributing factors are internal resistance of the cell, formation of concentration gradients in the electrolyte, and any activation barriers in the electrode reactions. The first two are amenable to good structural design, while the third requires more sophisticated electrochemical stratagems, of which further discussion is in order.

The majority of promising fuel cells have both the fuel and oxidant in gaseous form. Coal, the only solid fuel of importance, requires temperatures of 1000°C and above before the sluggish electrode processes yield appreciable currents. Disposal of ash and provision of an invariant oxide-ion electrolyte (see Fig. 2) are two formidable barriers to success for such cells, but their potential attractiveness is great enough to justify their continued investigation. There is a limited amount of interest in cells which will burn liquid fuels, e.g., methanol. Such devices fall more properly into the category of continuous-feed batteries unless an invariant electrolyte is involved.

Two reasons for the emphasis on gaseous fuels may be cited: (1) ease of handling and, more important, (2) only the common fuel gases hydrogen and carbon monoxide have been shown to react rapidly enough at electrodes to provide acceptable current densities of the order of 100 mA/cm² (100 amps/ft²). (The propane-oxygen cell recently announced by Allis-Chalmers may be an exception to this, but judgment must be reserved until more information has been released.) A little thought will make one appreciate the difficulties in-

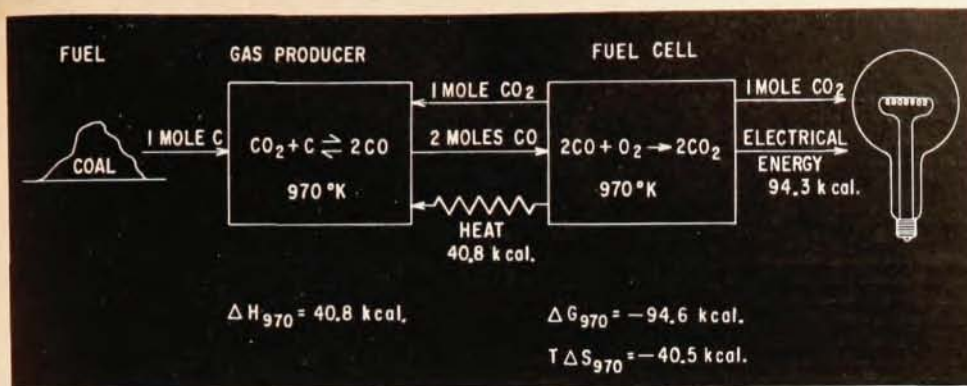


Fig. 4. Schematic integrated fuel cell-gas producer at 970°K.

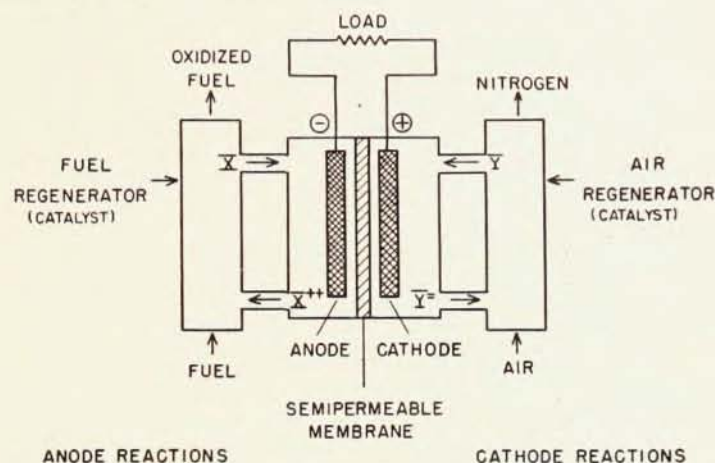
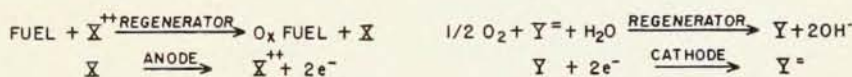


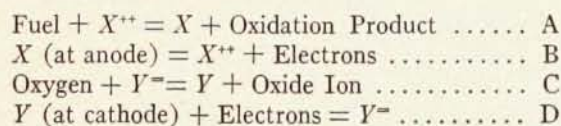
Fig. 5. Schematic Redox fuel cell.



involved in designing gas electrodes for high current densities. No better statement of the problem than that by W. R. Grove² can be found: "As the chemical or catalytic action . . . could only be supposed to take place . . . at the line or watermark where the liquid, gas, and platina met, the chief difficulty was to obtain anything like a notable surface of action." A common approach to obtaining "a notable surface of action" are the so-called gas-diffusion electrodes, the features of which are shown schematically in Fig. 4. The most effective of such electrodes have a distribution of pore sizes ranging from macropores of the order of ten microns in diameter to micropores with diameters from 10 to 100 Å. Gross transport of gas and electrolyte occurs in the large pores, while the network of micropores provides a very extended three-phase boundary between gas, electrolyte, and electrode. Gas-diffusion electrodes must neither permit appreciable gas to leak into the electrolyte nor suffer the electrolyte to fill their pores, which "drowns" them and makes them inactive. When hydrogen is the fuel, the water formed can be troublesome. If it is allowed to form as a liquid it can fill the micropores, and the electrode "drowns" in its own reaction product.

Other ways to increase reaction rates, and hence current density, are familiar in reaction kinetics: increase temperature and/or pressure and make the electrode surfaces more active by the incorporation of catalysts. A more roundabout method invokes the substitution of other, more rapid, reactions at the elec-

trodes by selecting suitable intermediates to react with fuel and oxygen in external regenerators. The intermediates form oxidation-reduction couples, represented in the following and in Fig. 5 as $\text{X}^{++} - \text{X}$ and $\text{Y} - \text{Y}^-$. They operate as follows:



These equations are not balanced, and the charges on the ions have been arbitrarily assigned. For the scheme to succeed, Reactions A-D must all be rapid, and they must remain in phase. The use of these "Redox" couples must necessarily invoke a decrease in the reversible electromotive force below the value of E_r for Reaction (I). This will be tolerable only if the electrode and regeneration reactions are sufficiently rapid.

One might conclude at first glance that, in retreating to the use of hydrogen and/or carbon monoxide in fuel cells, the hope of realizing the near 100% ideal efficiency associated with the carbon-oxygen reaction has been lost. E. Gorin has pointed out that this is not necessarily so.⁸ Inexpensive mixtures containing hydrogen and/or carbon monoxide are water gas and producer gas, both made by the gasification of coal. If the fuel gases are used in cells operating at high temperatures (600–700°C), the heat rejected by the cell may be used to carry out the endothermic gasification reactions.

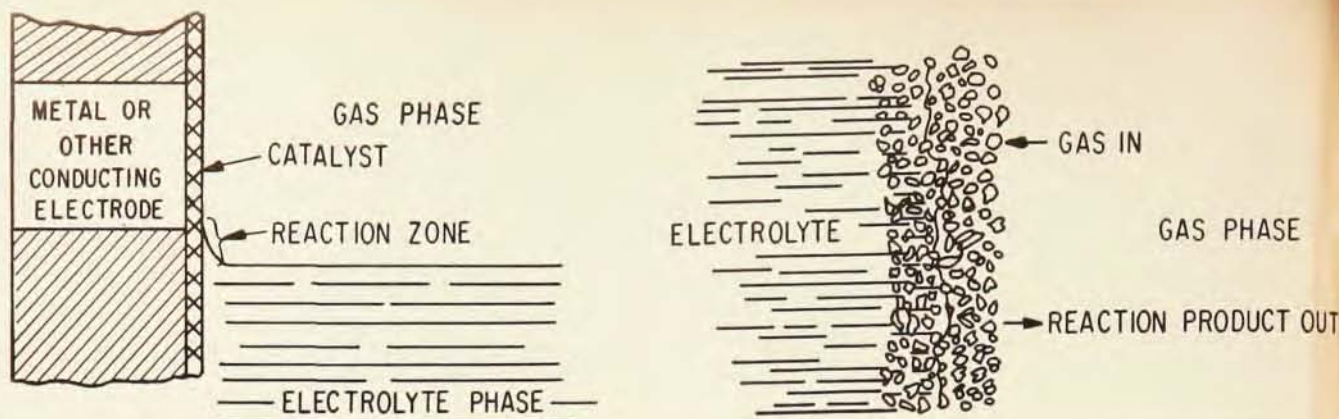


Fig. 6. Left, three-phase reaction zone in gas-diffusion electrode; right, electrode of porous conducting material.

Fig. 6 shows the thermodynamics of the carbon monoxide cycle at a particular temperature. With hydrogen the scheme is the same, but the numbers are slightly different. No integrated fuel cell-gasifier based on coal has been built, although several investigators have described high-temperature cells for hydrogen and carbon monoxide based on a molten alkali carbonate electrolyte.^{9, 10, 11}

One recent development along lines similar to the above deserves mention. If one works out the thermodynamics of the reforming of a hydrocarbon (say, methane) to hydrogen followed by use of the hydrogen in a high-temperature fuel cell, a heat balance precisely like that shown in Fig. 6 is obtained. Hydrocarbons have two important advantages over coal, viz., transportability in pipes and freedom from mineral residues or ash. The possibility of feeding a mixture of a hydrocarbon and water into the electrode of a high-temperature cell at once suggests itself. Broers¹⁰ and Chambers¹² have reported the operation of cells on methane and other hydrocarbons. At Soudes Place Research Institute in England, a considerable effort is being put into the development of molten alkali carbonate cells for use with hydrocarbons.¹²

Applications

FUEL cells may be conveniently classified under the following categories: (1) Fuel Cells for Central Station Power and (2) Fuel Cells for Special Applications.

In fuel cells for central stations (and here we do not necessarily mean stations to produce alternating current), cost will usually be the overriding consideration, although there may be an occasional special large installation for which cost is secondary. A successful central-station fuel cell is surely the most difficult to develop. But this application is well worth considering if only as the limiting case in which all the factors making for low cost will need optimization. The development of such a cell is much more difficult today than at the turn of the century, when the over-all efficiency of steam plants was only about 10%. According to present thinking, a central-station fuel cell would probably operate at temperatures above 500°C, contain an electrolyte of molten alkali carbonates, and have a silver-containing cathode. It goes without saying that only the least costly fuels can be considered for this appli-

cation. Only natural gas (methane), water gas, and producer gas seem to qualify. The ultimate in reduced fuel cost will require that the heat rejected by the cell be put to use—most likely to supply the heat for gasification and reforming reactions.

The most important consideration in fuel cells for special applications is convenience; cost is secondary. "Special applications" are numerous and diverse: space vehicles, automobiles, and portable power supplies are a few. Many of the fuel cells currently under development fall into this category. The majority of these are hydrogen-oxygen cells; e.g., the Bacon cell operating at 200°C and 600 psi, and that developed by the National Carbon Company, which operates at near room temperature and pressure. From the viewpoint of reactivity and availability of invariant electrolytes (common acids and bases qualify here), hydrogen is the superior fuel. It suffers from the disadvantage of relatively high cost for the pure variety needed in these cells and difficulty in packaging. LPG (liquid petroleum gas), as reportedly used by Allis-Chalmers,⁷ is readily transported in liquid form and enjoys a price advantage of a factor of eight over hydrogen in cylinders.

Mainly by virtue of the reactivity of hydrogen, cells using it have been brought to a high state of development. It seems likely that hydrogen-oxygen cells and hydrocarbon-oxygen cells will be seen in selected military and, perhaps, some commercial applications within a few years. The fuel cell for central station power is much further away. Present boiler-turbine-alternator plants will not be replaced in the foreseeable future.

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