CURRENT PROBLEMS IN RESEARCH

Fuel Cells

They produce more electricity per pound of fuel than any other nonnuclear method of power production.

Ernest Yeager

In a postscript to a letter to the editor of *The Philisophical Magazine* in 1839, Sir William Grove (*1*) first reported the production of electrical energy by means of an electrochemical cell consuming hydrogen and oxygen gases. In his postscript Grove was not concerned with the generation of electrical power but rather with the demonstration that the electrolysis of water on platinum electrodes could be reversed. Grove's cell was capable of doing nothing more than deflecting a galvanometer. Nevertheless, this work was the forerunner of present-day fuel cells. Of the various fuel cells now available, the hydrogen-oxygen fuel cells appear to be the most advanced.

Much of the incentive for work on fuel cells in the latter half of the 19th century and the early 20th century was derived from the desire to burn coal electrochemically at efficiencies far higher than is possible with conventional heat engines. The direct electrochemical combustion of coal has not yet been accomplished on a practical basis, but other fuels, including some derived from coal, have been used successfully in electrochemical cells.

In the broad sense, any anodic reactant in a battery can be considered a fuel. Originally the designation "fuel cell" was reserved, however, for electrochemical cells which were to generate power from low-cost fuels. In recent years the term has been extended to include electrochemical cells consuming fuels which hardly can be considered low in cost. Projected space applications and exotic military applications, in good part, have prompted this extension of the term.

A particular feature of almost all fuel cells is that the electrode reactants are not stored in appreciable amounts within the cells but are fed into the system as they are consumed, usually in a continuous fashion. Thus, only a relatively small amount of either the fuel or the oxidizing agent is within the cell at any instant. The oxidizing agent for fuel cells, with few exceptions, is either pure oxygen or oxygen derived from air, since other oxidizing agents, such as the halogen gases, are far more expensive, heavier, and more difficult to handle than oxygen.

In the ordinary combustion of a fuel, the electrons are rearranged within the molecules and transferred between molecules without the opportunity to do any useful work directly, and hence their excess energy is degraded to heat. Only a portion of this heat can be converted to useful work or electrical energy by means of a heat engine because of limitations imposed by thermodynamics. Thus the efficiency (f) associated with the conversion of chemical to electrical energy with a heat engine is set by the Carnot-cycle expression:

$$f = \frac{W}{Q} = \frac{T_2 - T_1}{T_2} \qquad (1)$$

where W represents the work derived from the heat engine, Q represents the heat introduced into the heat engine at the higher temperature T_2, and T_1 represents the lower temperature at which heat is rejected to the surroundings. In the most advanced types of turboelectric generating equipment available today, not much more than 40 percent of the chemical energy released as heat during the combustion of the fuel can be converted to electrical energy.

During electrochemical oxidation, the electrons are transferred from the fuel to the oxidizing reactant (usually oxygen) through an external electrical circuit and hence can lose much of their excess energy by doing useful electrical work. As a result, the efficiency associated with the conversion of chemical to electrical energy in an electrochemical cell is not limited by the Carnot cycle equation mentioned previously (Eq. 1). The theoretical limit for the thermal efficiency of an electrochemical cell is given thermodynamically as

$$f = \frac{W}{Q} = \frac{\Delta F}{\Delta H} \qquad (2)$$

where W is the electrical work derived from the system; Q is the heat that would have been released if the fuel were oxidized directly, nonelectrochemically; ΔF is the free energy of oxidation of the fuel; and ΔH is the enthalpy (or heat content) of oxidation of the fuel. Since ΔF is numerically somewhat less than ΔH for the fuel cells now under development, the efficiency for these cells must be less than unity. Actual values for f in excess of 60 percent have already been achieved for some of these cells.

In addition to more electrical energy per pound of fuel, fuel cells offer the potential advantages of relative simplicity and long life in unattended operation. High-speed moving parts operating in high-temperature environments, such as are encountered with conventional heat engines, are not involved. Fuel cells, however, provide low-voltage direct-current power rather than alternating-current power—a decided disadvantage in certain types of applications.

Despite the present enthusiasm in the United States for fuel cells, no system as of this date appears to have advanced beyond the developmental stage, and many are still at the basic research level. This situation does not reflect a lack of effort but reflects, rather, the substantial technical difficulties which must be overcome before practical fuel-cell systems are available.

Polarization

When power is drawn from an electrochemical cell, the terminal voltage of the cell decreases from that which would be anticipated thermodynamically. This decrease in cell voltage reflects not only IR drop within the cell but also potential losses associated with irreversibility of various processes at the electrode-solution interfaces. These

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deviations in the potentials of the electrodes from the values predicted thermodynamically are referred to as electrode polarization. Many electrochemical fuels which appear to be advantageous for fuel-cell applications on a thermodynamic basis cannot be used successfully because of excessive electrode polarization which prohibits the operation of the cells at practical power levels; that is, whenever any appreciable current is drawn from the cells, the cell voltage rapidly drops to a very low value.

The reversibility of a given electrode reaction, and therefore the electrode polarization, is often very dependent upon the catalytic properties of the electrode surface. For example, the electrochemical oxidation of hydrogen at a given electrode potential may be able to proceed 10^3 to 10^6 times faster with a platinum-impregnated porous carbon electrode than with a similar carbon electrode containing no such catalyst. Part of this improved performance with the platinum catalyst is due to the intrinsic catalytic properties of platinum for the hydrogen oxidation reaction, while part is due to the very high surface area associated with the platinum metal as it is incorporated in the carbon electrodes. Fundamental electrochemical research on the kinetics of electrode processes on various surfaces should prove of considerable importance in the future in pointing the way to development of more active surfaces for use as electrodes in fuel-cell systems operating at high current densities with a minimum of polarization.

Specific Systems

In Table 1 are listed various fuel cells which appear to offer promise, and of which the performance has been documented in the literature or in published reports. All of the cells listed in Table 1 operate on oxygen. In some instances, however, it is not practical to derive the oxygen by feeding air directly to the cells, for reasons which will become evident in the evaluation of the specific systems.

Hydrogen-oxygen cells. The hydrogen-oxygen cells of Union Carbide (*2*), Bacon (*3*), and Justi (*4, 5*) listed in Table 1 all operate with strongly alkaline electrolytes. Alkaline electrolytes (usually KOH) have generally been favored because the reduction of oxygen at the cathode proceeds with a minimum of polarization in such solutions. The over-all reactions for these cells with alkaline electrolytes are as follows:

$$\text{Anode: } 2H_2 + 4OH^- \rightarrow 4H_2O + 4e^- \quad (1)$$

$$\text{Cathode: } O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (2)$$

$$\text{Cell: } 2H_2 + O_2 \rightarrow 2H_2O. \quad (3)$$

Thus the over-all cell reaction involves the generation of water from hydrogen and oxygen.

If no voltage losses occurred within hydrogen-oxygen fuel cells, the voltage expected thermodynamically should be slightly in excess of 1.2 volts, the value corresponding to the free-energy change associated with reaction 3 at temperatures below 100°C. In practice, cell voltages for the hydrogen-oxygen system rarely exceed 1.05 volts, and the operating voltages under load conditions do not exceed 0.9 volt, because of electrode polarization as well as IR drop within the cells.

Figure 1 is a functional diagram of a hydrogen-oxygen cell with an aqueous electrolyte. Porous electrodes are used to permit the sparingly soluble reacting gases (hydrogen and oxygen) to pass through the electrodes from the rear to the sites of the electrochemical reactions at the solution-electrode interfaces. Under proper operating conditions the electrolyte should penetrate only into the outermost pore structure of the electrode. Pores in the bulk of the electrodes should be free of solution, since the diffusion of sparingly soluble gases through liquid-filled capillaries is far too slow for operation at reasonable current densities.

One means of keeping the pores within the bulk of the electrode free of solution is to have the surfaces within the pores hydrophobic, as is the case with the porous carbon electrodes used in the Union Carbide hydrogen-oxygen cell. In such porous electrodes interfacial tension is the predominant factor which keeps the pores from filling with solution. With time and use, however, the hydrophobic properties of the electrode may be slowly modified and the solution may progressively penetrate into the pore structure, with the result that the electrodes eventually fail to function properly. The penetration of the solution into the pores of the hydrophobic-type electrodes is usually accelerated by operation at high current densities.

Table 1. Typical fuel cells.

Systems	Reactants	Electrode		Electrolyte	Typical temperature	State of development	Remarks
		Anode	Cathode				
Union Carbide (*2*)	$H_2 + O_2$	Carbon	Carbon	KOH	20°–60°C	Advanced	Requires H_2 free of CO and CO_2
Bacon (*3*)	$H_2 + O_2$	Ni	Ni	KOH	200°–240°C	Advanced	Requires 400 to 800 lb/in.^{2}; requires H_2 free of CO and CO_2
Justi (*4, 5*)	$H_2 + O_2$	Ni	Ag	KOH	20°–90°C	Moderately advanced	Requires H_2 free of CO and CO_2
G.E. ion-exchange membrane (*11*)	$H_2 + O_2$	Pt	Pt	Resin	20°–80°C	Advanced	No fluid electrolyte
Fused carbonate (*14, 17, 18*)	$H_2 + O_2$	Porous metals	Porous metals	Alkali metal carbonates	400°–600°C	Early	Capable of operation on H_2 containing CO and CO_2
Fused carbonates (*16–19*)	Hydrocarbon + O_2	Porous metals	Porous metals	Alkali metal carbonates	500°–700 C	Early	Deterioration of electrodes and gaskets at high temperatures a problem
Esso (*20*)	Hydrocarbon + O_2	Porous carbon plus catalysts	Porous carbon plus catalysts	KOH	65°–200°C	Early	Problem of CO_2 rejection from electrolyte, not solved
Alcohol cells (*5, 10*)	Alcohol + O_2	Porous metals	Porous metals	KOH	20°–90°C	Early	Problem of CO_2 rejection from electrolyte, not solved
Allis Chalmers alcohol-peroxide (*10*)	Alcohol + H_2O_2	Pt	Ag	NaOH	20°–45°C	Early	Available in the form of student demonstration kit; rather inefficient
Amalgam cell (*22*)	Na(Hg) + O_2	Steel	Carbon	NaOH	20°–70°C	Moderately advanced	Expensive to operate

With porous metal electrodes the internal surfaces are hydrophilic, and an excess pressure must be maintained in the gas phase at the rear of each electrode to prevent the electrolyte from flooding all the pores of the electrode. Gas bubbles, however, should not be forced into the solution, since such bubbles would interfere with cell operation. For this and other reasons, such porous metal electrodes are usually constructed with a relatively coarse pore structure for most of the electrode and a fine-pore-structure layer on the side of the electrode facing the solution. A stable zone for the gas-liquid interfaces can be established within the pores in the transition region from the coarse- to fine-pore layers by maintaining an excess gas pressure behind the electrode. With this arrangement some fluctuations in pressure can be tolerated without the electrode flooding or gas bubbles being blown into the solution.

The coarse and fine pores just described have radii in the range of 10^{-4} to 10^{-3} centimeter and often are referred to as macropores. In addition to the macropores, the electrodes used in hydrogen-oxygen cells have a micropore structure, involving pores principally of dimensions 10^{-5} to 10^{-7} centimeter. The micropore structure may be obtained either by coating the inside of the macropores with a microporous layer or by incorporating the microporosity within the material from which the electrodes are fabricated. The presence of the micropore structure within the electrodes greatly increases the solid-solution area where the electrochemical reactions occur. Very large internal areas often are required if the electrochemical reactions are to be carried out at appreciable rates—that is, if appreciable currents are to be drawn from the electrochemical cells.

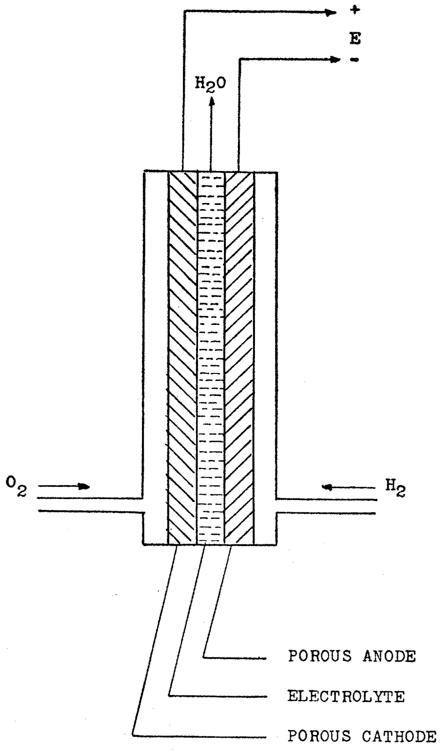

Fig. 1. Functional representation of a hydrogen-oxygen fuel cell.

Union Carbide hydrogen-oxygen cell. In the Union Carbide cell, hydrogen and oxygen (or air) are fed through porous carbon electrodes with concentrated potassium hydroxide as the electrolyte. The catalysts incorporated in the porous carbon anodes are extremely effective in catalyzing the electrochemical oxidation of hydrogen according to reaction 1, and hence, relatively little electrode polarization occurs at the hydrogen anode under operating conditions. The potential of the oxygen cathodes, however, deviates considerably from that expected for the four-electron reduction shown in reaction 3. Extensive laboratory studies (*6*) have demonstrated that the cathodic reduction in this cell involves the formation of the perhydroxyl anion (HO_2^-) as an intermediate, according to the reaction:

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \qquad (4)$$

Catalysts are incorporated in the cathodes to decompose the peroxide as fast as it is formed, according to the reaction:

$$HO_2^- \xrightarrow{\text{catalyst}} OH^- + \tfrac{1}{2}O_2 \qquad (5)$$

The oxygen liberated during the chemical decomposition of the hydrogen peroxide according to reaction 5 is utilized by the cathode in reaction 4, and hence, four equivalents of charge are obtained per mole of oxygen consumed by the cell. Thus, the over-all cathodic reaction is that given by reaction 2. The more effective the catalyst is for reaction 5, the closer the cell voltage should approach the thermodynamic value predicted on the basis of the over-all reaction for the cell (reaction 3). Much research has been, and continues to be, directed toward finding good catalysts for the peroxide-decomposition step.

Water produced as a product in reaction 3 must be removed from the electrolytic solution within the cell as it is formed. The Union Carbide hydrogen-oxygen cells are designed for operation at temperatures usually in the range of 40° to 60°C. In operation at relatively low power levels, sufficient water can be evaporated from the electrolyte directly through the porous electrodes. Unfortunately, most of this evaporation must occur through the porous carbon anode because water is produced at the anode but consumed at the cathode (see reactions 1 and 2). This necessitates the circulation of an excess of hydrogen gas past the rear of the anodes and the condensation of this water out of the hydrogen gas in a separate condenser prior to the recirculation of the hydrogen to the anode. At moderately high power levels, evaporation of the water vapor directly through the porous electrodes may be insufficient to maintain a reasonable electrolyte concentration, and it may be necessary to circulate the electrolytic solution of the cell through an external evaporator to remove water formed by the cell reaction. Thus, a significant amount of auxiliary equipment is required to operate the hydrogen-oxygen fuel cells.

Figure 2 is a photograph of a hydrogen-oxygen battery similar to one which the Union Carbide Consumer Products Company is developing under contract with the U.S. Signal Corps. The battery in Fig. 2 consists of 36 cells in series and has been designed to provide approximately 200 watts at 28 volts in operation on air as the source of oxygen. The catalyst-impregnated semihydrophobic carbon electrodes of this battery are mounted parallel to each other, in an arrangement similar to that shown functionally in Fig. 1. The hydrogen gas and the air are fed to the individual electrodes from manifolds at the ends of the battery, through a network of holes or channels in the plastic frames of the cells. Specific information is not available on terminal voltage in relation to current or the operating life of the battery in Fig. 2. Cells using similar carbon electrodes have been found capable of providing 0.90 volt at a current density (*7*) of 50 amperes per square foot in operation on pure hydrogen and oxygen, each at 1 atmosphere, at 40°C. Furthermore, operational life well in excess of 1 year has been obtained by Union Carbide with similar cells.

Hydrogen-oxygen cells in which carbon electrodes are used have been worked on by other groups, including Davtyan (*8*) in the U.S.S.R. and Justi (*9*) in Germany. None of these other groups has developed its cells to the advanced state of the Union Carbide system.

Bacon hydrogen-oxygen cell. Bacon (*3*) and his associates at Marshalls in Cambridge, England, have developed a hydrogen-oxygen cell which uses sintered nickel electrodes in a concentrated potassium hydroxide solution and operates at temperatures from 200° to 240°F and pressures of 400 to 800 pounds per square inch. The macropores of the nickel cathodes in these cells are coated internally with a layer of microporous nickel oxide in which lithium has been incorporated as a doping agent. The macropores of the nickel anode are also coated with a microporous layer of nickel. Figure 3 shows a Bacon battery consisting of 40 cells in series, with each electrode approximately 10 inches in diameter. Operation for up to 1500 hours has been achieved with cells of the type used in this battery. The gases are supplied to the rear compartment behind each electrode through a network of channels within the frames of the cells. The Bacon cells must be preheated to at least 150°C before significant power can be drawn from the cells, but self-generated heat should be sufficient to maintain temperature during normal operation. Operation of the Bacon cells on air rather than pure oxygen does not appear feasible because of the need to compress the gases fed to the cells. As with the Union Carbide hydrogen-oxygen cells, water may be removed from the cells as vapor primarily through the anodes. The much higher operating temperatures of the Bacon cells facilitate the removal of water in this manner.

The battery shown in Fig. 3 is capable of supplying 3.2 kilowatts at 32 volts and 100 amperes, or 5.7 kilowatts at 24 volts and 240 amperes. During the past year, since the completion of this battery, Bacon and his colleagues have improved the performance of individual cell units by a considerable amount. With the introduction of these new improvements it should be possible to obtain up to twice as much power with the same size battery. The Bacon cell appears to have the highest power per unit weight or volume of any of the hydrogen-oxygen cells now available.

The Bacon cell is presently being worked on in the United States by the Patterson-Moos Research Division of the Leesona Corporation, the U.S. licensee. The work of Bacon and his associates in England, however, appears to have been discontinued at this time.

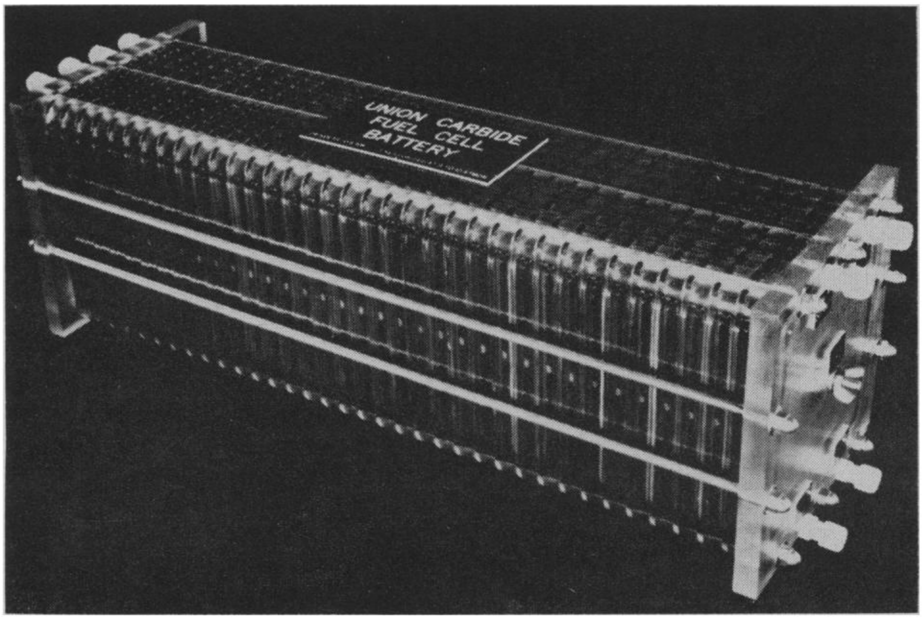

Fig. 2. The Union Carbide hydrogen-oxygen cell. [Courtesy Union Carbide Consumer Products Company]

Justi hydrogen-oxygen cell. Justi (*4, 5*) and his associates at Braunschweig, Germany, have developed a hydrogen-oxygen cell, using hydrophilic, porous silver cathodes and porous nickel anodes in a concentrated potassium hydroxide electrolyte. Justi obtains extremely high catalytic activity in his electrodes by using Raney metals in their preparation. The cells can be operated from room temperatures to temperatures in excess of 90°C at atmospheric pressure. The open-circuit voltage at room temperature is approximately 1.1 volts, while current densities of the order of 100 amperes per square foot have been obtained at terminal voltages of 0.90 volt. Single cell units have been operated for more than a year with no apparent loss in operating characteristics. At this time, information on operating characteristics is available only for relatively small laboratory units.

Other groups which have developed hydrogen-oxygen cells with porous-metal electrodes and caustic solutions

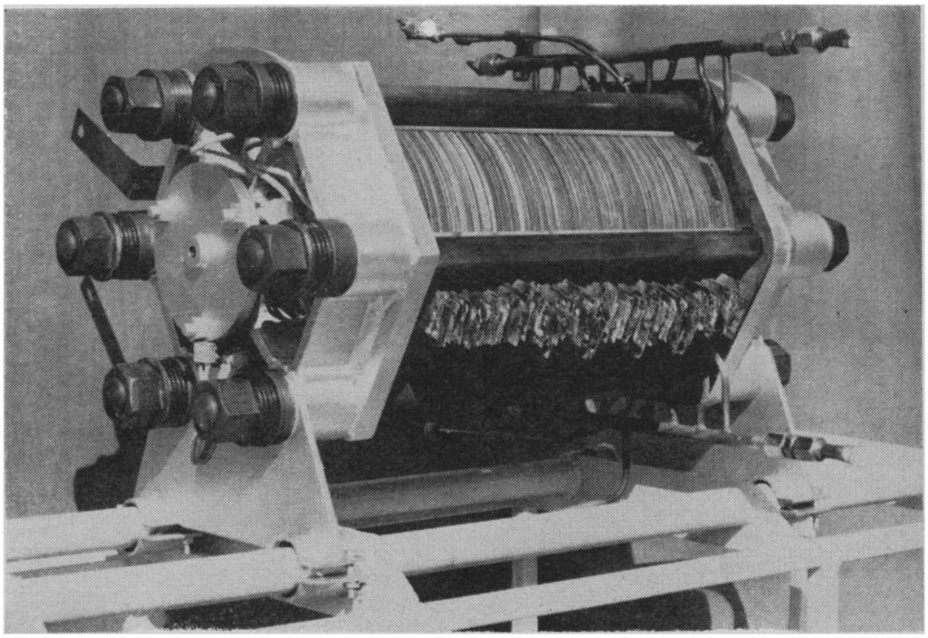

Fig. 3. The Bacon hydrogen-oxygen cell. [Courtesy F. Bacon]

include the Electric Storage Battery Company and the Allis Chalmers Manufacturing Company (*10*). In 1959 Allis Chalmers powered a tractor with such cells. The power plant consisted of 1008 individual cells with a total output of 14 kilowatts. The cells were of the type of construction shown in Fig. 1 and had a cross section of 1 square foot. Each cell provided 0.7 volt at 20 amperes per square foot at a temperature of 150°F. The original announcement concerning the fuel-cell-powered tractor indicated that the cells operated on propane or a propane-hydrogen mixture. In a recent paper (*10*) on this power plant, however, the cells were described as operating on hydrogen, with no indication that they operated on propane or any other hydrocarbon. Thus, the electrochemical oxidation of hydrogen, rather than propane, appears to have been the principal source of power for the tractor. The Allis Chalmers tractor is historically significant, however, as the first large-scale mobile machine to be powered by a fuel cell, even though the source of power appears to have been hydrogen rather than propane. The tractor recently has been transferred to the Smithsonian Institution.

General Electric ion-exchange membrane cell. This cell (*11*) differs drastically from the hydrogen-oxygen cells just described in that the electrolyte is an ion-exchange resin and not a liquid. While anionic-type resins can be used, the best results have been obtained so far with cation-exchange resins in which the conducting species is the hydronium ion (H_3O^+) and the anions are immobile. The membrane, with a thickness of 0.6 to 0.8 millimeter, is sandwiched between two porous metal electrodes containing catalysts (for example, platinum and palladium) for promoting the electrode reactions with a minimum of electrode polarization. These cells are capable of operating with either pure oxygen or air fed through the cathodes. The open-circuit voltage, on hydrogen and either pure oxygen or air at atmospheric pressure, is approximately 1.05 volts at room temperatures and drops to 0.81 volt at 20 amperes per square foot on oxygen, and 0.72 volt at 20 amperes per square foot on air. While these current densities are somewhat lower than those obtained with most present-day hydrogen-oxygen cells, this factor is offset by the thin cell construction possible with the membrane cell. Operation of these cells appears feasible at temperatures from 0° to 100°C.

The electrode reactions and the over-all cell reaction in the General Electric cell with the cation-exchange resins are as follows:

$$\text{Anode: } 2H_2 + 4H_2O \rightarrow 4H_3O^+ + 4e^- \tag{6}$$

$$\text{Cathode: } O_2 + 4H_3O^+ + 4e^- \rightarrow 6H_2O \tag{7}$$

$$\text{Cell: } 2H_2 + O_2 \rightarrow 2H_2O \tag{8}$$

While the over-all cell reaction is the same as for the other hydrogen-oxygen cells, the electrode reactions differ. In this cell, water is produced at the oxygen cathode and consumed at the hydrogen anode, in contrast to the situation for hydrogen-oxygen cells with alkaline electrolytes.

A major advantage of the membrane cell is that water removal is simple, since water tends to form as droplets on the rear surface of the cathode during operation and can be either drained off or evaporated away. In fact, care must be taken not to dehydrate the resin, since the electrical resistance of the membrane decreases drastically when the water absorbed in the membrane decreases below a critical level. In operation on air it is desirable to maintain the relative humidity of the air at least at 25 percent to prevent excessive dehydration of the membrane. Of the various fuel-cell systems developed as of this date, the membrane system appears to require the least auxiliary equipment for its operation.

General Electric is currently developing a portable 200-watt, 24-volt system for operation on air for the U.S. Navy and the Army Signal Corps. Preliminary models of this power package are scheduled for delivery this year. The battery consists of 35 cells in series connection, each cell having the dimensions 9 by 14 by ⅜ inches. The complete system (Fig. 4) is expected to weigh 55 pounds, including all auxiliaries and a sufficient chemical source of hydrogen (metal hydride reacting with water) for operation on air at 200 watts for 24 hours. With replacement of the chemical source of hydrogen gas, continuous operation for up to 2000 hours should be possible. Single-cell units of smaller size have been run continuously by General Electric for periods of almost 2 years.

Other hydrogen-oxygen cells. The General Electric Company (*12*) has also worked on the development of a redox cell in which the chemical reactions for the continuous-feed cells are regenerated from cell products external to the cell by chemical reactions with hydrogen gas and oxygen gas or air. The reactions are as follows:

Electrochemical reactions.

$$\text{Anode: } 2Ti^{3+} + 2H_2O \rightarrow 2TiO^{++} + 4H^+ + 2e^- \tag{9}$$

$$\text{Cathode: } Br_2 + 2e^- \rightarrow 2Br^- \tag{10}$$

$$\text{Cell: } 2Ti^{3+} + Br_2 + 2H_2O \rightarrow 2Br^- + 2TiO^{++} + 4H^+ \tag{11}$$

Regeneration reactions.

$$2H_2 + 4TiO^{++} + 4H^+ \rightarrow 4Ti^{3+} + 4H_2O \tag{12}$$

$$O_2 + 4Br^- + 4H^+ \rightarrow 2Br_2 + 2H_2O \tag{13}$$

Over-all reaction.

$$2H_2 + O_2 \rightarrow 2H_2O \tag{14}$$

The electrolyte of the cell is concentrated sulfuric acid plus the reactants and products indicated in reactions 9 and 10. The major advantage of the redox system is the possibility of using hydrogen containing impurities (particularly CO and CO_2) which would be harmful in the other hydrogen-oxygen cells involving alkaline electrolytes. Unfortunately, technical complications have impeded the development of this and related systems involving such redox reactions.

It is interesting to note that Rideal and Posner (*13*) in England have attempted to regenerate the anodic reactants for a redox cell through the use of coal at somewhat elevated temperatures in an arrangement similar to that described for the hydrogen-oxygen redox system of General Electric. Only a small portion of the coal could be oxidized in this manner, however.

Hydrogen-oxygen cells operating at high temperatures ($> 400°C$) with fused alkali metal carbonates have received attention both here (*14–16*) and in other countries (*17–18*) including the U.S.S.R. (*8, 19*). The reactions in these cells are as follows:

$$\text{Anode: } 2H_2 + 2CO_3^{--} \rightarrow 2H_2O + 2CO_2 + 4e^- \tag{15}$$

$$\text{Cathode: } O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{--} \tag{16}$$

$$\text{Cell: } 2H_2 + O_2 \rightarrow 2H_2O \tag{17}$$

While carbon dioxide is formed at the anode, the same amount of carbon dioxide must be introduced with the oxygen to the cathode. The transfer of anodically formed carbon dioxide to the cathode is not a simple operation.

Three types of fused carbonate hydrogen-oxygen cells are under investigation. In one type, porous metal electrodes are placed in contact with the fluid fused carbonate electrolyte in an arrangement similar to that shown in Fig. 1. In the second type, the fused carbonates are contained within a porous ceramic disk with thin porous metal electrodes attached to the opposite sides of the disk. Thermal cracking of these disks, however, is a common occurrence, and this has prompted Broers at the University of Amsterdam to propose a third method of construction involving the use of an alkali metal carbonate-magnesium oxide paste placed between two porous metal electrodes.

These high-temperature cells are capable of operating on either H_2 or H_2–CO mixtures, but their development has been delayed by such undesirable features as rapid degeneration of cell components at high temperatures, the need to supply carbon dioxide in the oxygen feed, and relatively low power output per unit weight.

Hydrocarbon-consuming fuel cells. Potentially by far the most important fuel cells are those consuming hydrocarbons such as natural gas or oil. Unfortunately the electrochemical oxidation of hydrocarbons is much more difficult to accomplish than the electrochemical oxidation of hydrogen.

Fused alkali metal carbonate cells have been operated on hydrocarbons such as propane (*16, 17*) and gasoline (*19*) at temperatures above 500°C. Such operation usually has been obtained only for a few days and, in many cases, a few hours before the failure of cell components, primarily because of the high temperatures. Satisfactory gaskets are yet to be found. The development of practical, high-temperature cells operating on readily available hydrocarbons appears to be at least 10 years in the future.

Through electrochemical oxidation of a hydrocarbon in an aqueous cell at moderately low temperatures, complications associated with high-temperature operation would be avoided. The Esso Research and Engineering Company (*20*) has reported the development of a small laboratory cell which can operate on ethane, propane, or ethylene with a concentrated aqueous potassium hydroxide electrolyte and a porous oxygen cathode at temperatures of 65° to 200°C. With ethane, the electron yield has been found to be 13.8 electrons per molecule consumed as compared with the theoretical value of 14.

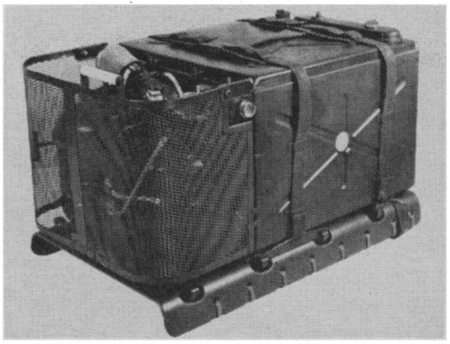

Fig. 4. The General Electric ion-exchange membrane cell. [Courtesy General Electric Company]

The products of the oxidation of the ethane are carbon dioxide (97 mole-percent) and formate (3 mole-percent). Intermittent operation for up to 500 hours has been obtained without any indication of electrode deterioration. Only low current densities (7 amp/ft^2) can be drawn from the cell at reasonable voltages in sustained operation, according to information released by Esso (*20*). Nevertheless, the electrochemical oxidation of hydrocarbons at low temperatures in the Esso cell is a major step toward the final development of practical hydrocarbon-consuming fuel cells.

A complication associated with the use of alkaline electrolytes for cells involving the oxidation of organic compounds is the accumulation of carbonates within the solution. After a brief period of operation, the concentration of the carbonates increases to the point where they precipitate out of solution. Thus, it is necessary to replace the alkaline electrolyte or to remove chemically the carbonates from the electrolytic solution; neither of these steps appears practical from an economic standpoint. The carbon dioxide formed as a product in the oxidation of organic compounds would not accumulate within the solution in the cell if the solution were acid. Considerable question, however, exists as to whether the hydrocarbon anodes or the oxygen cathodes can be operated at appreciable current densities in other than highly alkaline solutions. Another suggestion has been to use a carbonate-bicarbonate electrolyte at temperatures close to the boiling point of the electrolyte. Under these conditions, the carbon dioxide could also be removed from the solution as a gas. With this electrolyte, however, the cells are likely to be limited to relatively low power densities because of kinetic factors and complications associated with mass transport in the solution (*21*).

Alcohol-consuming cells. Many industrial and academic groups both in the United States and in Europe have been working on fuel cells that consume alcohols—particularly methanol. Alcohols can be oxidized electrochemically all the way to carbon dioxide with sufficiently catalytically active electrodes. Most of the alcohol-consuming cells use porous metal oxygen cathodes and operate with concentrated potassium hydroxide as the electrolyte, at 40° to 100°C. In operation on ethylene glycol, Spengler and Gruneberger (*5*) of Ruhrchemie AG (Germany) have reported obtaining 200 amperes per square foot at a cell voltage of 0.75 volt at 80°C, in sustained operation.

The Allis Chalmers Manufacturing Company (*10*) has developed a methanol–hydrogen-peroxide-consuming cell which they have been selling in the form of a demonstration kit (the only fuel cell commercially produced today). This cell uses silver-plated nickel electrodes for the cathodic reaction, involving the reduction of hydrogen peroxide, and platinum-plated nickel for the anodic reaction, involving the oxidation of methanol in a concentrated potassium hydroxide solution. The voltage is quite low (0.3 volt at 60 amp/ft^2), and much of the hydrogen peroxide reacts directly with the methanol without providing useful electrical energy. This cell is recommended for high school students who wish to construct fuel cells because it avoids the use of the relatively complicated porous electrode systems which are required for gaseous reactants.

None of the alcohol-consuming cells presently available appear to have any substantial commercial or military significance, since the carbon dioxide formed as a cell product accumulates within the highly alkaline electrolytic solutions in the form of carbonate, with resulting complications much the same as with the hydrocarbon-consuming aqueous cells. Cells operating with carbon-dioxide-rejecting electrolytes are yet to be developed.

The sodium amalgam-oxygen cell. Sodium metal is ordinarily far too reactive for use directly as an electrode in an aqueous electrolyte. Liquid sodium amalgam, however, is much less reactive and has been used successfully in continuous-feed cells (*22*) with an oxygen cathode in a concentrated sodium hydroxide solution at temperatures from 20° to 80°C. The reactions are as follows:

$$\text{Amalgamation: } 4\text{Na} + 4x\text{Hg} \rightarrow 4\text{Na(Hg)}_x \quad (18)$$

$$\text{Anode: } 4\text{Na(Hg)}_x \rightarrow 4\text{Na}^+ + 4x\text{Hg} + 4e^- \quad (19)$$

$$\text{Cathode: } O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (20)$$

$$\text{Over-all: } 4\text{Na} + O_2 + 2H_2O \rightarrow 4\text{NaOH} \quad (21)$$

The liquid sodium amalgam is allowed to flow down the surface of a vertical steel plate in an arrangement of the type shown in Fig. 5. The oxygen cathode may consist of either a porous carbon electrode or a porous metal electrode, similar to those used in the hydrogen-oxygen cells. In contrast to all of the other systems described previously, this cell makes its own electrolyte. In addition to sodium and oxygen, however, water is required as a reactant. Sea water has been used directly, and successfully, without the removal of any of the mineral constituents prior to its introduction into the cell. The sodium hydroxide produced by the cell reaction can either be discarded directly or used for other chemical processes.

The sodium amalgam-oxygen cell provides a considerably higher voltage (for example, 1.50 volts at 150 amp/ft^2) than any of the other continuous-feed cells described in this article and is capable of operating at power densities approaching those of the Bacon cell. Furthermore, only three-fifths as much oxygen is required per unit energy output as with hydrogen-oxygen cells—a decided advantage in applications where atmospheric oxygen is not available. The sodium amalgam-oxygen cell is also capable of operating at reasonable current densities on air.

The production of electrical power with this system is expensive (of the order of $0.25 per kilowatt-hour) because of the use of sodium. Furthermore, the auxiliary equipment required for the operation of the system is relatively complicated. Some consideration is being given to the use of the sodium amalgam-oxygen cell for military applications. In addition, a possible application exists in the alkali-chlorine industry. At the present time, large quantities of sodium amalgam produced during the electrolysis of brine are allowed to react with water to produce caustic without providing any electrical energy. The use of the sodium amalgam cell makes it possible to produce caustic from sodium amalgam while obtaining electrical energy.

The sodium amalgam-oxygen system was originally developed at Western Reserve University (*22*) in 1955 and has been subsequently worked on by the Union Carbide Corporation and the M. W. Kellogg Company under contract with the U.S. Government.

Biochemical fuel cells. Several groups including the U.S. Geological Survey and Joseph Kay and Company, Inc., are reported (*23*) to be working on biochemical systems as sources of electrical energy in the form of fuel cells. The biochemical fuel cell under development by Fred Sisler of the Geological Survey consists of two sections containing inert electrodes. In the anodic section, in sea water, is a mixture of organic matter (the fuel) and bacteria (a source of enzymes for the catalytic electrochemical oxidation of the fuel). The cathodic section consists of an oxygen cathode. No information is available as to the projected operating characteristics for a cell of this type. The idea of such a fuel cell, however, is quite intriguing since it may provide a means for deriving energy from waste organic matter which cannot be utilized effectively by any other means (for example, corn cobs, sawdust, and even sewage).

Applications

Many applications exist for a reliable, low-cost fuel cell operating on a practical fuel such as oil or natural gas. While definite progress is being made toward the development of such cells, they are not likely to become available in less than 10 years. Of particular significance is the potential use of fuel cells operating on hydrocarbons, or possibly methanol, in automobiles, trucks, and locomotives. If such applications do become widespread, the effect on various industries within the United States would be extreme. The benefits, other than economic, to be derived from such developments include freedom from noise and probably from the obnoxious exhaust gases associated with conventional engines.

Development of central power plants operating with fuel cells as the main source of power appears unlikely for some time to come because of economic factors. The conversion of the low-voltage direct-current power provided by fuel cells to the high-voltage alternating-current power required for distribution is likely to prove expensive in terms of initial investment for the foreseeable future. Furthermore, in the United States fuel cells operating on hydrocarbon fuels are not likely to be competitive economically with more conventional, turbogenerating equipment operating on low-cost coal, even though the efficiency is higher for the fuel-cell system. No fuel cells currently under development appear capable of operating directly on coal.

The only type of fuel cell which is likely to become readily available for nonmilitary use during the next five years is the hydrogen-oxygen cell. Applications for these cells are quite limited because of the relative impracticality of hydrogen as a fuel in many applications. This gas is awkward to store, either cryogenically or as a compressed gas.

The cheapest source of hydrogen presently available is the reaction of coal or hydrocarbons such as natural gas with water. Hydrogen produced in this way, however, usually contains significant amounts of carbon monoxide and carbon dioxide unless somewhat expensive steps are taken to remove these chemicals. With the exception of the General Electric ion-exchange membrane cells, all of the hydrogen-oxygen cells in advanced stages of development have alkaline electrolytes and hence require hydrogen relatively free of carbon monoxide and carbon dioxide to avoid the accumulation of carbonates within the electrolytic solution. While the General Electric membrane cell does not accumulate carbonates, some question exists as to whether the precious metal catalysts in this cell will be progressively poisoned by impurities such as sulfides and carbon monoxide.

Nonmilitary applications for hydrogen-oxygen cells appear to be limited. These cells may find some application as sources of power in such devices as lift trucks and mine locomotives where fumes associated with conventional combustion engines cannot be tolerated and where compressed hydrogen cylinders may be satisfactory as a source of hydrogen for the cells. These hydrogen cylinders could be recharged relatively easily with hydrogen produced chemically or electrochemically. Hydrogen-oxygen cells may also be of significance for power generation in instances where low-cost, relatively pure

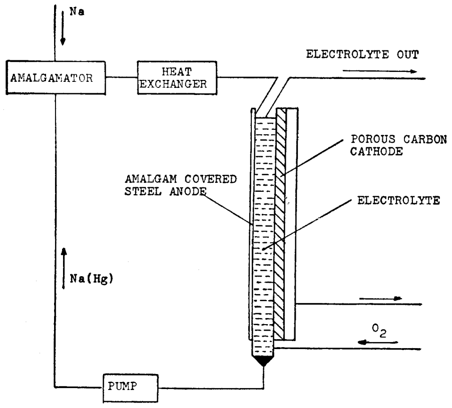

Fig. 5. Schematic drawing of the sodium amalgam-oxygen (*22*).

hydrogen is produced as a by-product of other chemical processes.

A number of military applications are being contemplated for fuel cells at the present time, and this accounts to a considerable degree for the large amount of research and development work in progress on fuel cells in the United States relative to the activity in other countries. These particular applications range from use of the cells in small portable power packs capable of being carried by a single person to use in large power plants for submarine propulsion. Some consideration has been given to the use of hydrogen-oxygen cells for auxiliary power in space vehicles. The hydrogen and oxygen would either be carried cryogenically or produced chemically by reactions involving chemicals of low molecular weight. The practicality of such applications remains to be evaluated.

Closed-cycle operations. Fuel cells are being considered for use as components in various types of closed-cycle systems. In these cycles the cell reactants are regenerated from the cell products. The various methods for regenerating cell reactants may be classified as follows: (i) chemical, (ii) electrochemical, (iii) photochemical, (iv) radiochemical, and (v) thermal. The General Electric redox system is an example of a closed-cycle system involving chemical regeneration.

Electrochemical regeneration is of interest as a means of storing electrical energy. Consideration (*5, 24*) is being given to the use of hydrogen-oxygen cells in such a closed cycle. Water would be electrolyzed in a high-pressure electrolyzer during times of excess electrical power, and the hydrogen gas would then be stored either in tanks or in porous rock strata such as are available in areas of the world where there are exhausted natural-gas wells. When power is subsequently required, the hydrogen would be consumed in hydrogen-oxygen cells. Oxygen can either be stored or obtained from air. The electrolysis operation and the subsequent power generation probably cannot be accomplished with the same cells, although attempts to do this are being made. The efficiency of such an energy storage system is likely to be less than 60 percent because of the relatively large difference between the voltage required to electrolyze water and the voltage of the operating hydrogen-oxygen cells. Such energy storage systems might be of particular interest in applications where the availability of hydroelectric power varies considerably on a seasonal basis because of variations in rainfall, and where the capacity of water-storage reservoirs is inadequate.

The closed cycle involving photochemical regeneration is illustrated by a system in which hydrogen and oxygen required for a low-temperature hydrogen-oxygen fuel cell are produced photochemically by means of solar energy from water derived from the cell. The dissociation of the water with sunlight is relatively inefficient, even with the best known catalyst added to the water to promote photochemical dissociation. The U.S. Government is currently sponsoring the study (*25, 26*) of various photochemical regeneration systems for possible space-vehicle applications. One of the more promising cycles involves the photodissociation of nitrosyl chloride to yield $NO + Cl_2$, which would then be fed to a continuous-feed cell operating on these gases (*25*).

The radiochemical closed cycles are similar to those involving photochemical regeneration, except that the source of radiation is a radioisotope or nuclear reactor. Rosenblum and English of the National Aeronautics and Space Administration (*27*) have considered the use of a hydrogen-oxygen fuel cell with the reactant gases produced by the decomposition of water with a radioisotope such as the alpha emitter polonium-210 ($t_{1/2} = 138$ days) for space-vehicle applications. In the proposed system, water is first dissociated to yield H_2 and H_2O_2. The H_2 gas is liberated readily from the water in view of its low solubility, while the H_2O_2 in solution is passed into a separate vessel in which it is catalytically decomposed to yield O_2. The H_2 and O_2 are then fed into the fuel cell. The electrolytic solution from the fuel cell is subsequently passed through a radiator to dissipate heat and is then recycled to the radiation chamber. This particular system does not appear to be competitive on a power-per-unit-weight basis with other power sources, such as a solar battery, in space-vehicle applications.

The Union Carbide Corporation is developing a closed-cycle system in which the electrochemical cells operate on H_2 (anodic reactant) and Fe^{3+} (cathodic reactant) generated by the irradiation of oxygen-free acidified ferrous sulfate solution with alpha-rays.

Several types of thermal closed cycles (*28*) involving fuel cells have been proposed for the generation of electrical energy from heat derived from a thermal source such as a nuclear reactor. The most important of these is a cycle in which the reactants for the fuel cell are obtained by heating the products of the cell reaction to a temperature sufficient to produce dissociation. The upper limit for the theoretical thermal efficiency of such a system is set by the Carnot cycle equation (Eq. 1). Advantages which are anticipated for such thermal electrochemical converters are, (i) relatively high efficiency for the conversion of thermal to electrical energy, (ii) a minimum of machinery, particularly of machinery operating in high-temperature environments, and (iii) ultimate simplicity.

Several specific systems have been proposed for the simple thermal dissociation cycle. The one that is receiving the most effort is the Li-H_2 system, originally proposed by the Mines Safety Appliance Research Corporation (*29*). The reactions are as follows:

Anode: $2Li \rightarrow 2Li^+ + 2e^-$

Cathode: $H_2 + 2e^- \rightarrow 2H^-$

Cell: $2Li + H_2 \rightarrow 2LiH$

Regeneration: $2LiH \rightarrow 2Li + H_2\uparrow$

The electrochemical cell is operated at a temperature of approximately 450°C with a fused LiF–LiCl eutectic as the electrolyte. The regeneration of the lithium hydride is accomplished at a temperature of approximately 1000°C. The theoretical upper limit (Carnot) for the efficiency cannot exceed 50 percent; the actual efficiency is likely to be much less. The U.S. Government is currently sponsoring research on this system for possible space-vehicle applications.

Many technical problems, primarily relating to the high operating temperatures, must be overcome before such systems find application.

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INSTRUMENTS AND TECHNIQUES

The Cambridge Electron Accelerator

This 6-billion-volt machine will be the world's highest energy electron synchrotron.

M. Stanley Livingston and William A. Shurcliff

By the autumn of 1961, if all goes well, the family of great accelerators will be joined by a new member: the Cambridge Electron Accelerator (CEA). The newcomer differs from the mammoth *proton* accelerators at CERN and Brookhaven in that it will produce high-energy *electrons*. The electron is the lightest of all charged particles and can be accelerated to especially high velocity. In the Cambridge machine the electrons will reach a speed virtually indistinguishable from that of light itself—a speed of 0.999,999,996 *c* (*c* is the velocity of light). A more meaningful measure is the electron energy, which will be 6 billion electron volts (6 Bev)—five times higher than that available from any existing electron accelerator. Another interesting property is the electron mass, which will be increased to nearly 12,000 times the rest mass, or to a value six times greater than the mass of a proton. (*Ponderizer* might be a more descriptive name than *accelerator.*)

This machine will also produce higher intensities than other multi-Bev accelerators. Thanks to the fast cyclic repetition rate of 60 cycles per second, the number of 6-Bev electrons produced per second will be about 6×10^{12}, equivalent to an average current of 1 microampere. Since the product of current and voltage is power, the average power in the electron beam will be 6 kilowatts. With such high electron energy and beam intensity available, experimenters will be able to explore a new range of phenomena in particle physics.

The CEA is jointly sponsored by Massachusetts Institute of Technology and Harvard University and is supported by the U.S. Atomic Energy Commission. Unlike other large accelerators, built in large open areas at the national laboratories, the CEA is located in the heart of a university, in close proximity to the Harvard physics buildings and libraries (Fig. 1). Thus it will be readily available to the faculties and students. Senior staff members of the CEA hold appointments from the universities and cooperate in the research and teaching programs. As one of the major accelerator research facilities of the country, the CEA will be available for use by qualified visiting scientists from other institutions here and abroad.

The operating policies are guided by a joint M.I.T.–Harvard committee composed of administrative and scientific representatives of the two institutions. Detailed planning began in April 1956. Site excavation was started in November 1957, with a ceremony involving a twin-handled shovel jointly wielded by President Julius A. Stratton of M.I.T. and President Nathan M. Pusey of Harvard. A laboratory staff has been assembled, with representatives from many countries. A laboratory report (*1*) summarizes the basic design principles and gives the names of many of the persons who have contributed.

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