

Fuel Cells

The major portion of the electric power produced in the world today is generated through some form of heat engine operated by the combustion of fossil fuels—coal, oil, or natural gas. A three-step conversion process is required: transformation of the chemical energy of the fuel into thermal energy by combustion, transformation of the thermal energy into mechanical work in a heat engine, and transformation of this work into electrical energy by means of a generator. The fact that fossil fuels are at present our most widely distributed and least expensive primary energy source is an outstanding advantage for such a conversion process. However, the over-all efficiency of conventional electric power generation is restricted by incomplete combustion, heat losses, and the inherent limitations of mechanical devices. Furthermore, even under ideal conditions, the thermodynamics of heat engines places a limitation on the attainable over-all efficiency of converting thermal energy into mechanical work. Nuclear power plants now being designed also are subject to this thermodynamic limitation, which arises because of the restriction on temperatures attainable in practice for heat source and heat sink of the engine.

The thermodynamic limitations and most of the efficiency losses in the other steps in electric power generation could be avoided if the chemical energy of the fuel were converted directly to electrical energy. The high operating efficiency of electrochemical cells is well known, and if such cells were constructed, effectively using fossil fuels in some form for the anode (oxidizing) reaction, a practical source of electrical energy might be provided independent of the steam cycle and its inherent limitations. Electrogenetic cells employing common fuels (fuel cells) or products readily derived from fossil fuels have been studied on a laboratory scale for a number of years (*1, 2*) and recent advances in improvement of their performance suggests that serious attention be given to this source of electrical energy.

Fuel cells, operating at ambient temperatures and employing fuel gases, are capable of a fuel-use efficiency of 70 to 80% compared with an efficiency of about 35% for a steam power plant operating on coal. On the basis of fuel consumed, modern electrical generating plants require from 0.7 to 0.8 pound of coal per kilowatt-hour of electricity while a fuel cell would theoretically require the equivalent of only 0.3 pound of coal per kilowatt-hour. Other advantages of fuel cells would be their high ratio of electrical energy per unit weight, their adaptability for both large or small-scale applications, and their long operating life and storage characteristics. The components of the cell

other than the fuel, are not consumed in the electrode reactions, and thus the cell could be operated indefinitely if the fuel were continually supplied.

Types of Fuel Cells

The fundamental principles of operation of a fuel cell are essentially the same as those in all galvanic cells. Basically, we are concerned with two half-cell reactions—one involving oxidation and releasing electrons, the other involving reduction and requiring electrons. The two half-cells are separated by an electrolyte barrier so that reaction can occur only by the migration of ions. Such an arrangement of two half-cells is shown in Figure 1, where the fuel oxidized is hydrogen and the material reduced is the oxygen of the air. In this case the

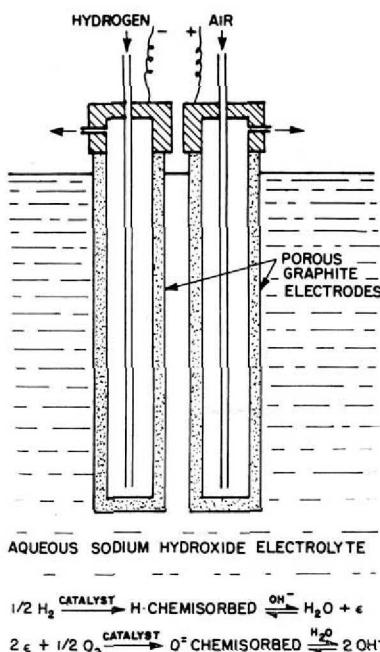


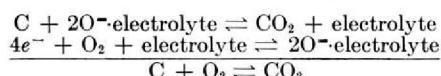
Figure 1. Fuel gas cell operated on hydrogen.

electrolyte is an aqueous solution of sodium hydroxide and the hydroxyl ions are the mobile species which serve to transport the oxidizing agent to the fuel electrode.

Carbon Cells. Since our fossil fuels are predominantly carbonaceous in nature, a cell in which carbon is used directly as the fuel electrode would appear advantageous. For example, in such a cell coal could be used as the anode where it would be oxidized to carbon dioxide in the half-cell reaction. Cells of this type have been constructed (*3, 4*), and a schematic representation of such a cell is shown in Figure 2. In

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this cell the half-cell reactions ideally² are:



Baur reports (4) that open circuit potentials of 0.83 volt can be obtained which under a current drain of 7 amperes per cubic foot of cell volume fall to 0.65 volt.

Unfortunately fuel cells utilizing carbon directly as the anode have several disadvantages. The oxidation

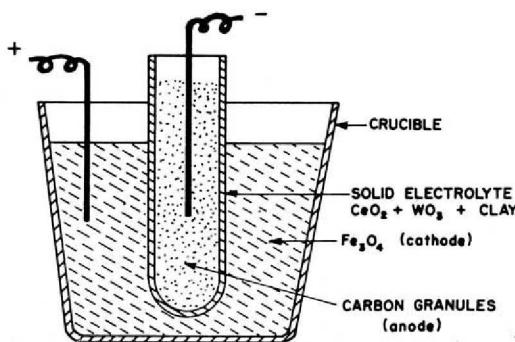


Figure 2. Direct carbon fuel cell after Baur (2).

of the carbon by the electrolyte species proceeds only at a negligible rate at room temperature. Thus, to obtain a reaction rate sufficient to permit reasonable current drain, the cell must be operated at high temperatures (around 800 to 1000°C). Operation of a fuel cell at temperatures greater than the temperature of its surroundings results in heat losses which represent a loss in efficiency. In addition, at temperatures where a high reaction rate is obtained, much of the fuel electrode would be consumed by carbon dioxide (the product of the electrode reaction) through the reaction:



This represents an additional loss in efficiency of fuel utilization since the latter reaction does not contribute to the electrical energy of the cell. These limitations on the efficiency of cells directly employing solid carbonaceous fuels added to the difficulties encountered in high temperature operations make the direct carbon cell unattractive for commercial development.

Gas Cells. An alternative to the direct use of solid fuels is to use fuel gases—such as hydrogen or carbon monoxide—obtained either from the gasification of coal with steam or by the reforming of oil or natural gas. In a cell using a gas as fuel, oxidation of the gas must take place on the surface of a conductor since the gas itself cannot form a conducting electrode. Oxidation of fuel gases by the electrolyte species can usually be achieved at moderate temperatures by the use of proper catalysts, and in most cases no side reactions occur. Thus by employing fuel gases in a galvanic cell, the limitations imposed in the direct use of solid carbonaceous fuels are avoided. In the fuel gas cell shown in Figure 1, the gases, hydrogen and air, diffuse into the porous graphite electrodes which are impregnated with catalysts such as Fe-Co-Ni-group metals on the hydrogen side and Cu-Ag-Au-group oxides at the air electrode. The gases react with the electrolyte species on the surface of the catalysts according to the half-cell

² In practice carbon monoxide also is found to be a product of the electrode reaction.

reactions shown. The graphite electrodes serve as conductors of the electrons flowing in the circuit, and a slight positive gas pressure prevents the electrolyte from flooding the electrodes. Several variations of fuel gas cells have been developed (5, 6, 7) employing both aqueous and molten salt electrolytes. Generally, alkali electrolytes are used in the hydrogen cells and carbonate electrolytes in those cells employing carbon monoxide.

A high pressure fuel gas cell which uses hydrogen as a fuel and which gives excellent current drain characteristics has been investigated by Bacon (8) at Cambridge University. This cell employs an aqueous hydroxide electrolyte and operates at a temperature of about 250°C with pressures up to 800 psi. The open circuit potential of the cell is 1.05 volts and current densities of 150 amperes per square foot of apparent electrode area at a potential of 0.9 volt can be developed. Although the Bacon cell represents one of the more promising cells being studied, there are still some obstacles to be overcome. As far as has been reported, no attempt has been made to use impure hydrogen as a fuel (for example, hydrogen obtained from the gasification of coal). The Patterson-Moos Division of the Universal Winding Company in the United States is currently engaged in the construction of fuel cell units of kilowatt size based on Bacon's original design. These cells employ porous nickel metal electrodes for the hydrogen half-cell reactions and lithium doped nickel oxide electrodes on the oxygen side. Power ratios of 60 watts per pound or 7 watts per cubic inch of cell volume are claimed.

A high temperature cell being investigated by the Pittsburgh Consolidation Coal Company by E. Gorin and H. L. Recht represents another approach to the development of fuel gas cells. This cell operates at temperatures of the order of 400 to 800°C using molten salts as electrolytes and such fuel gases as carbon monoxide and methane. Cells of this type offer one method for the direct use of light hydrocarbons. The hydrocarbons can be cracked directly in the cell to hydrogen and carbon and the carbon removed by including a small amount of carbon dioxide in the fuel gas stream. Reasonable current drain characteristics are obtained at the higher temperatures. Sintered iron electrodes are found to give good results when carbon monoxide is used as a fuel gas and lithium doped nickel oxide with a porosity of 30 to 40% and a mean pore size of 12 to 30 microns is used as the air (oxygen) electrode. The electrolyte, which generally is a carbonate eutectic, is contained in a porous magnesium oxide matrix.

Redox Cell. A third type of fuel cell has been proposed (9) which makes indirect use of the fuel as a reducing agent. An example of this type of cell, usually referred to as a redox cell, is illustrated in Figure 3. The electrolyte solutions, which are separated by a membrane impermeable to the active ions, contain ions that undergo oxidation and reduction in the cell. The electrolyte solutions are regenerated by using a carbonaceous fuel for reduction and air for oxidation. While there are no thermodynamic restrictions on the efficiency of this type of cell, in practice the regeneration of the electrolyte solutions offers many difficulties. Various metal ions in addition to the tin(IV) ion (used for illustration in Figure 3) can be reduced by coal in

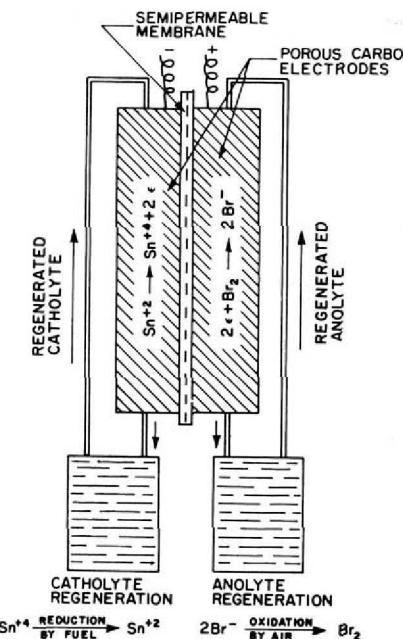


Figure 3. Redox fuel cell after Posner (7).

acid solution by autoclaving at moderate temperatures (circa 200°C). However, only a portion of the coal is active in the reduction which results in a very low fuel-use efficiency for the over-all process. The autoxidation of the bromide ion in acid solution by air proceeds satisfactorily when catalyzed by nitrogen dioxide.

Thermodynamics

Under thermodynamically reversible conditions the theoretical potential developed by a galvanic cell, ε° , is given by the equation,

$$-\Delta F^\circ = n\mathfrak{F}\varepsilon^\circ$$

where ΔF° is the difference in the free energy between the products and reactants in their standard states, n is the number of electrons involved in the cell reaction on a molecular basis, and \mathfrak{F} is the Faraday Constant. The change in free energy, and hence the potential of the cell, can be determined at any other temperature if the enthalpy change for the reaction and heat capacities of the products and reactants are known. Since these data are commonly available, the theoretical potential of a cell can be calculated as a function of temperature for various fuels. In Figure 4 the results of such calculations are shown in a graph where the cell potential in volts is plotted against temperature. Typical reactions for the three types of cells described have been selected.

The potential expected from a single fuel cell is shown in Figure 4 to be of the order of one volt depending on the fuel oxidized and the temperature. Of course, higher voltages can be obtained by putting a number of cells in series. It is seen from Figure 4 that there is little to be gained thermodynamically by the use of high temperatures. Thus, if the electrode reactions had favorable rates at low temperatures and if diffusion were not a controlling factor, there would be no advantage in using high temperature cells based on considerations of the over-all reactions.

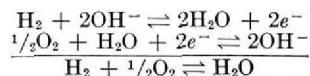
The influence of pressure on fuel cell potential can be calculated from the change in free energy of the cell re-

actions with pressure. The effect of pressure will be most pronounced in fuel gas cells where the reactants are both gases, and in this case can be expressed in the form:

$$\varepsilon_P = \varepsilon^\circ + \Delta m \frac{RT}{n\mathfrak{F}} \ln P$$

for the conversion of gaseous reactants at pressure P into products in their standard states. In the above equation ε_P is the cell potential at the pressure considered and Δm is the change in the number of moles in the gas phase. The effect of pressure on the potential of the fuel cell is illustrated in Figure 5 for the four reactions given in Figure 4. As was the case with increased temperature, little appears to be gained thermodynamically by operating fuel cells at higher pressures; however, the kinetics of the electrode reactions and diffusion processes are generally more favorable at higher temperatures and pressures.

So far only the over-all electrode reactions for fuel-cells have been discussed. There is, however, another aspect to the problem that appears to have been overlooked by previous investigators—that is, actual fuel cell electrode reactions do not necessarily correspond to the reversible over-all reactions from which theoretical potentials are calculated. For example, the oxidation of hydrogen in a reversible fuel cell would give a standard-state potential of 1.23 volts³ at 25°C for the half-cell reactions:



³ This value is based on liquid water at 25°C as the standard state for the product; however, in practice the product is in equilibrium with the aqueous hydroxide electrolyte and the actual potential is greater than 1.23 volts. Under current drain a peroxide mechanism is operative and the above standard state potential does not apply.

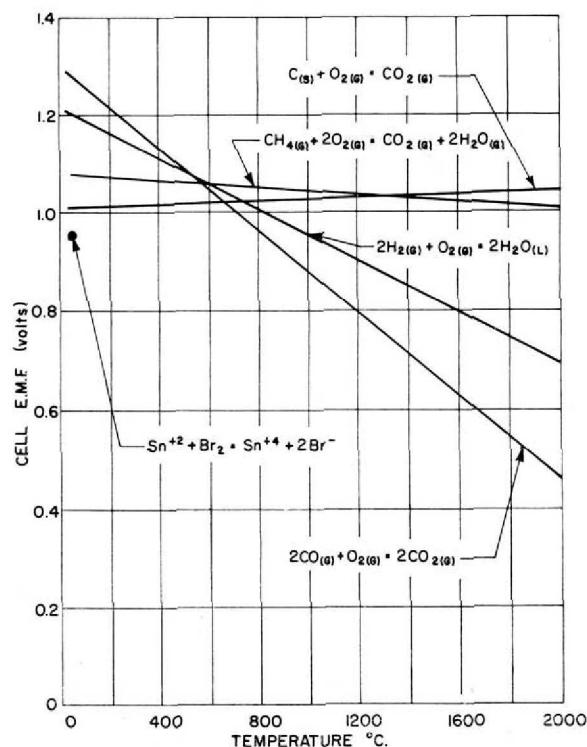


Figure 4. Temperature dependency of fuel cell reactions.

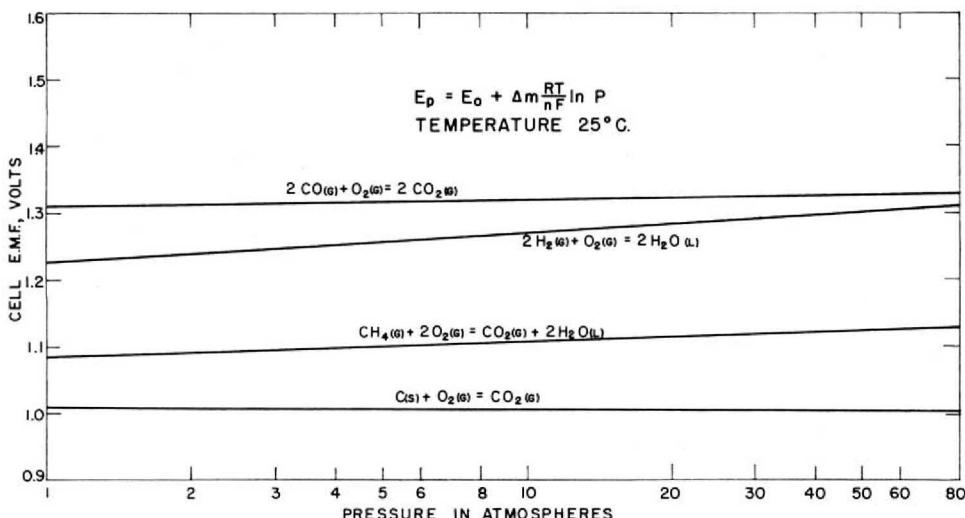
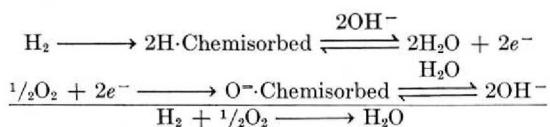


Figure 5. Pressure dependency of fuel cell reactions.

However, in an actual fuel cell the half-cell reactions cannot be expressed as simply as above since the gases (hydrogen and oxygen in the above illustration) are chemisorbed on the surface of the catalysts at their respective electrodes and should be represented as follows:



These latter equations imply that the equilibrium reaction which determines the potential of the cell is actually the equilibrium between the chemisorbed gases and the electrolyte and not between the free gases and the electrolyte. The chemisorption of the reactant gases is not a reversible process for the purpose considered here in that the heat of chemisorption is dissipated before reaction occurs, thus the greater the magnitude of the heat of chemisorption, the further the cell potential will be from that expected theoretically. This point is illustrated further in Figure 6 where the course of the reaction at the hydrogen electrode is represented. The open circuit (equilibrium conditions) potential of the cell would be expected to remain constant regardless of the catalyst employed if the free energy change corresponded to the over-all reaction. This is found not to be the case, but rather the cell potential varies directly with the heat of chemisorption of hydrogen on the catalyst. This means that since the open circuit potential is governed by the energy state of the chemisorbed hydrogen, the equilibrium reaction must be between the chemisorbed hydrogen and the electrolyte. Thus, the fuel cell electrode catalyst serves a dual purpose—it can enhance the open circuit potential of the cell as well as the kinetics of the cell reactions.

An example of the use of catalysts shows their enormous influence on fuel cell characteristics. If the fuel cell illustrated in Figure 1 is operated with only the porous graphite electrodes, an open circuit potential of about 0.1 volt is developed, and the potential rapidly falls to an immeasurably low value under current drain. When the porous graphite electrode on the hydrogen side of the cell is impregnated with palladium (extremely small amounts are adequate),

the open circuit potential increases to about 0.8 volt. The potential at a current density of three amperes per square foot of actual electrode area is about 0.6 volt (the actual surface area of an electrode may be several times the apparent or geometric area, hence this value may correspond to 30 or more amperes per square foot of geometric area). Now, if in addition the electrode on the oxygen side of the cell is impregnated with silver-silver oxide, the open circuit potential increases further to 1.15 volts, a value close to the theoretical value of 1.23 volts, and the potential under current drain is again greatly enhanced.

Applications and Fuel Sources

Of the three general types of fuel cells described (direct carbon cells, fuel gas cells, and redox cells), the fuel gas cell is the only one presently being considered for commercial development. Fuel gas cells, while offering several distinct advantages over other types of fuel cells, suffer the limitation that at present only hydrogen and carbon monoxide can be used effectively as fuel sources (cells claiming to use hydrocarbons

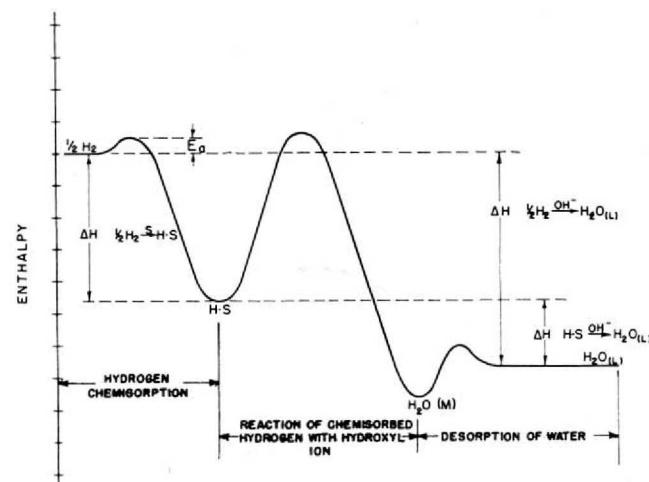


Figure 6. Course of the reaction at the hydrogen electrode.

generally depend on cracking of the hydrocarbon to produce hydrogen). Thus, the extent to which fuel cells will be used as large scale power sources in the near future will depend on the availability and cost of these gases as well as on progress made in further technological development of competing conventional and nuclear power sources.

In many small scale power applications, fuel cells can effectively compete with conventional storage batteries. The advantages offered by fuel cells are lower operating costs, the ability to be stored indefinitely, and long operating life. Such applications may include power sources for warehouse fork lifts and tractors,

mobile electronic devices, and stand-by power sources for hospital operating rooms and other service centers. A fuel gas cell manufactured by the National Carbon Company has been successfully tested as a power source for the Army's "Silent Sentry" mobile radar unit, and a small bank of these cells were operating lamps at the United States exhibit at the Brussels World Fair. In other applications requiring small amounts of electricity, such as railroad signal devices and telephone relay stations, fuel cells probably could furnish power more reliably and less expensively than present utility rates when maintenance and other costs are included. Thus, there would appear to be many practical applications and a ready market for small power output fuel cells.

The fuel gas for small scale applications would be hydrogen. Commercial tank hydrogen probably would be used in those cases where the storage weight ratio of compressed gases could be tolerated (ratio of weight of storage container to weight of fuel gas, which may be as large as 100 to 1 for compressed hydrogen). In those applications which require very low storage weight ratios, metal hydrides, lithium hydride in particular, would provide a convenient source of hydrogen. A little over eight grams of lithium hydride will yield about one cubic foot of hydrogen at STP, enough to produce over 50 watt-hours of electricity.

In order to realize the advantages of fuel cells for large scale electric power applications, the fuel costs for the cell should not greatly exceed those of fuels that would be used in the operation of conventional heat engines. Unfortunately, the cost of hydrogen or carbon monoxide per kilowatt-hour when used in a fuel cell is generally greater than the cost of the equivalent amount of coal used in a steam power plant, even though much less of the fuel gases are used because of the greater efficiency of the fuel cell.

Conventional gasification of coal has been suggested (10) as a source of fuel gases for fuel gas cells. However, present gasifiers cannot produce fuel gases at a sufficiently low cost to permit a fuel cell station operating on this fuel source to compete with a coal fired steam power plant. An improved gasifier design which would

substantially lower the cost of fuel gases from this source would appear to offer the only possibility of converting coal into electrical energy via the fuel cell at a competitive cost with conventional power generation.

Underground gasification experiments have been conducted with some success in this country, in Russia, and in England. The fuel gases obtained are of low heating value, limiting their industrial use. However, such gases probably could be used effectively in fuel gas cells. The tests conducted in the United States indicate, at present, that underground gasification cannot successfully compete with the higher performance of conventional gasifiers. Thus, although not feasible at present, underground gasification of coal may in the future provide fuel gases for fuel cell stations.

Fuel cells can most easily provide low voltage direct current and would be ideal power sources for electro-metallurgical industries such as an aluminium refining plant. An aluminium plant located in the southwest might find fuel gas cells operating on reformed natural gas an economical power source. The natural gas could be reformed with steam over a nickel catalyst to yield about 2700 cubic feet of hydrogen per thousand cubic feet of methane. Based on a cost for natural gas of \$0.20 per thousand feet at the well-head and including carbon dioxide removal from the reformed gas, a fuel cell station could produce electrical energy (5 volts dc at 1000 amperes) for a fuel cost of approximately four mills per kilowatt-hour.

Other potential fuel sources may be found in the oil industries refining plants, which produce considerable hydrogen in cracking and reforming operations, and in nuclear power plants. Water cooled nuclear reactors produce hydrogen and oxygen by the radiolysis of water—the amount depending on the operating conditions of the reactor. These gases might be separated by a diffusion process, taking advantage of the low molecular weight of hydrogen. Fuel cells, operated on the gases produced by radiolysis in nuclear power plants and stored during "off-hours," could provide a supplementary source of power during peak loads. Table 1 summarizes several fuel gas sources and comments on their applicability for various applications.

Table 1. Fuel Gas Sources

Fuel Gas	Source of fuel gas	Cell applications	Remarks
Hydrogen	Metal hydrides, in particular lithium hydride	Missiles and portable electronic equipment	High fuel cost, favorable weight ratio <i>ca.</i> 4#/kw-hr for entire cell including liquid oxygen or peroxide storage
Hydrogen	Commercial tank hydrogen	Lift trucks and tractors, signal equipment, stand-by power sources	Moderate fuel cost, high weight ratio <i>ca.</i> 14#/kw-hr for entire cell including compressed oxygen storage
Hydrogen and carbon monoxide	Conventional gasification of coal	Large scale power sources	Impure gases (CO_2 and sulfur compounds), fuel cost using Koppers gasifier and oxygen <i>ca.</i> 9 mills/kw-hr
Hydrogen and carbon monoxide	Underground gasification of coal	Large scale power sources	Impure gases, less favorable economically in U.S. than conventional gasification
Hydrogen	Oil refineries (hydrogen produced in cracking and reforming operations)	Moderate sized power sources	Limited application because of restricted nature of fuel source, costs depend on other markets for this source of hydrogen
Hydrogen	Reforming of natural gas	Large scale power sources	Appears favorable in U.S. Southwest, fuel costs <i>ca.</i> 4 mills/kw-hr
Hydrogen	Electrolysis of water	Storage of electrical energy	Suggested as a method to relieve peak load problems, not of commercial interest at present
Hydrogen	Radiolysis and photolysis of water	Conversion of other energy forms into electrical energy	No information available

In summary, fuel cells should find many immediate applications as small power sources; however, the use of fuel cells for large scale power sources will depend on the economics of fuel gas supply, capital investment costs which are unknown at present, and future developments in fuel cells and competing nuclear and conventional electrical power plants. At present, large scale applications appear to be limited to those unique situations that require direct current in areas of high electrical costs but with low cost sources of fuel gases.

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