AN ASSESSMENT AND COMPARISON OF FUEL CELLS FOR TRANSPORTATION APPLICATIONS

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AN ASSESSMENT AND COMPARISON OF FUEL CELLS FOR TRANSPORTATION APPLICATIONS

M. Krumpelt and C. C. Christianson

ABSTRACT

Fuel cells offer the potential of a clean, efficient power source for buses, cars, and other transportation applications. When the fuel cell is run on methanol, refueling would be as rapid as with gasoline-powered internal combustion engines, providing a virtually unlimited range while still maintaining the smooth and quiet acceleration that is typical for electric vehicles. The advantages and disadvantages of five types of fuel cells are reviewed and analyzed for a transportation application: alkaline, phosphoric acid, proton exchange membrane, molten carbonate, and solid oxide. The status of each technology is discussed, system designs are reviewed, and preliminary comparisons of power densities, start-up times, and dynamic response capabilities are made. To test the concept, a fuel cell/battery powered urban bus appears to be a good first step that can be realized today with phosphoric acid cells. In the longer term, the proton exchange membrane and solid oxide fuel cells appear to be superior.

I. INTRODUCTION

Experience over the past 15 years has alerted the public to our extreme dependence on imported oil. This concern and the desire for improved air quality in urban areas have led to the conclusion that we must inevitably replace the petroleum-fueled internal combustion engine used in transportation with a more advanced power source.¹

Electric-powered vehicles have been suggested as a means of reducing petroleum use in the transportation sector and of drastically reducing environmental emissions. However, for many applications, user acceptance will only be forthcoming if such a vehicle has the same virtually unlimited range (through rapid replenishment of the fuel) as present automobiles.

Powering a vehicle with batteries alone cannot achieve an acceptable extended range through rapid refueling, but a fuel cell/battery hybrid system, or ultimately a stand-alone fuel cell, could have that capability. The fuel of choice for such vehicles would be either methanol derived from coal or ethanol obtained from biomass. Both can be converted efficiently and virtually free of emissions to electricity in fuel cell systems, as will be discussed in more detail later.

Recognizing the potential of the fuel cells in transportation, the Department of Energy (DOE) entered into an initiative with the Department of Transportation (DOT) to develop an urban bus powered by a phosphoric acid fuel cell/battery hybrid system.²,³ The transit bus was selected as the test vehicle because it can easily accommodate the present fuel cell technology, and because the higher acquisition costs of fuel cell systems can be amortized over a longer service life than is possible in passenger cars. This program,
Research and Development of a Fuel Cell/Battery Powered Bus, was initiated in FY 1987 and is presently in the systems definition stage.

Phosphoric acid fuel cells (PAFC) were chosen because they are the only type of fuel cells that are sufficiently developed to be put on a vehicle in the near term. It was recognized that other types of fuel cells may be more suited for the application but are not yet sufficiently developed.

The primary motivation for developing fuel cells until now was their use in manned and unmanned space flight and, potentially, in utility power plants. Both applications require an energy conversion device that is efficient and reliable and that can provide continuous power to the electrical grid. In transportation, the power system must not only be efficient and reliable but also capable of the following:

- High power density
- Rapid start-up
- Frequent load changes
- Shock and vibration resistance

To fit into buses and cars the power density, in terms of weight and volume, must be increased substantially over state-of-the-art PAFC technology. In addition, start-up times must be reduced, and rapid load response between 100% and about 30% power must be possible. The transportation application, therefore, adds new challenges to the fuel cell development.

An additional challenge is that internal combustion engines are inexpensive by comparison. The cost of a typical engine in automobiles is only about $50/kW. The equivalent cost of fuel cell systems is much higher, although the technology is still in a developmental stage and the margin for improvement is large.

Because of the potentially enormous payoff from replacing the highly developed but nevertheless antiquated technology of the internal combustion engine (the first combustion engines were built 100 years ago) with a cleaner and more efficient device, it was the objective of this effort to qualitatively assess the merits of the various types of fuel cells for transportation application.

Before beginning the assessment, we will briefly trace the history of the fuel cell development and discuss the technology status.

II. DEVELOPMENT HISTORY AND CURRENT STATUS

The concept of converting chemical energy directly into electricity goes back to the early 1800s, when Grove showed that the electrolysis of water into hydrogen and oxygen could be reversed. Over the following 150 years, several generations of scientists became fascinated by the idea but were frustrated by their inability to overcome the technical hurdles. Not until the 1950s did Francis Bacon succeed in building a device that could generate practical amounts of power over prolonged periods. That device, the Bacon cell, had an alkaline electrolyte of 45% KOH and sintered nickel electrodes and ran on pure hydrogen and oxygen at 200-240°C. The largest unit produced 6 kW of power.
A. Alkaline Fuel Cells

Building onto the success of the Bacon cell, Pratt and Whitney Aircraft began a US government sponsored program to develop a fuel cell for the Apollo space program. By 1955 such alkaline fuel cells were routinely used in space flight, and today they are still used in the Space Shuttle. Four parallel modules of about 15 kW size provide all the electric power for the shuttle. Each module measures 38 x 35 x 101 cm, operates at 80-90°C and 60 psi (0.4 MPa), and has 32 cells. The KOH electrolyte is held in a silicon carbide matrix.

The cell reactions are simple and straightforward, at least theoretically. Hydrogen reacts on the anode with hydroxide ions to form water, releasing two electrons:

\[ \text{H}_2 + 2\text{OH}^- = 2\text{H}_2\text{O} + 2e^- \]  
(1)

On the cathode hydroxide ions are regenerated from water and electrons:

\[ \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^- = 2\text{OH}^- \]  
(2)

The net reaction is the formation of water from hydrogen and oxygen.

\[ \text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O} \]  
(3)

Simultaneously, hydroxide ions migrate from the cathode through the electrolyte to the anode, and electrons flow from the anode through the electric circuit to the cathode. Schematically, such a fuel cell is illustrated in Fig. 1, showing alternating layers of anodes, electrolytes, and cathodes with flow channels for the fuel and oxidant gases. By "stacking" up individual cells as shown in the figure, the voltage of the assembly is raised to over 100 V.

The drawback of alkaline fuel cells is the need for carbon-dioxide-free fuel and oxidant. Being a strong base, the KOH electrolyte reacts with weak acids such as carbon dioxide to form potassium carbonate, neutralizing the electrolyte. Any carbon dioxide must, therefore, be removed from both the fuel and oxidant streams before they are admitted to the fuel cell. Alternatively, the electrolyte can be recirculated and purged. However, when the fuel contains as much CO₂ as reformed hydrocarbons do, the equipment and materials for handling the CO₂ become expensive. Despite its technical maturity, the alkaline fuel cell has, therefore, not found many terrestrial applications yet. A cheap and abundant source of hydrogen could change that.

B. Proton Exchange Membrane Fuel Cells

Beginning in the early 1980s, the General Electric Co. developed a new type of fuel cell using a perfluorinated ion exchange membrane as the electrolyte. The membrane was developed by DuPont and is being sold under the name of Nafion. In essence, it consists of a Teflon matrix with side chains terminating in sulfuric acid groups. Because of the acidity of the electrolyte, carbon dioxide is not absorbed. This makes it possible to run a proton exchange fuel cell on hydrogen that is derived from fossil fuels such as methane, methanol, or coal.
The electrochemistry in this fuel cell is similar to that of the alkaline cell, except that the migrating species in the electrolyte is the proton rather than the hydroxide ion. The product water is, therefore, evolving on the cathode rather than the anode.

This type of fuel cell was originally referred to as the Solid Polymer Electrolyte (SPE). Since the name has become a registered trademark for the Hamilton-Standard Division of United Technologies Corp., who bought the General Electric technology, it is today, generically called the Proton Exchange Membrane (PEM) cell.

This type of cell was used in the Gemini project, but NASA discontinued the project in favor of the alkaline cell because it had better performance.

Following the termination of the Gemini project, General Electric continued for many years to pursue other applications for the SPE technology. One was to use essentially the same cell as a water electrolyzer to make oxygen on submarines. Another effort was to electrolyze brine to make chlorine and sodium hydroxide. Although technically both efforts were very successful, the economics were not attractive. In 1985 General Electric sold the technology to Hamilton-Standard.

At about the same time General Motors began to review various types of fuel cells and concluded that the PEM was unique in that it allowed start-up from ambient temperature at partial load. Lengthy warm-up periods were not needed. General Motors considers a virtually instantaneous start-up to be vital for transportation applications and selected the PEM for further study. Los Alamos National Laboratory conducted a feasibility study of fuel cell powered buses and also concluded that PEM offered good prospects.
The PEM technology received new impetus in the past two years from the development of a new membrane by Dow Chemical. Being the largest chlorine producer in the US, Dow began the research for an alternative to Nafion in the early sixties and announced success in the middle eighties. Dow Chemical's membrane has a lower electrical resistance than Nafion, which permits the current density to be increased. Given the high cost per unit area of fluorocarbon membranes, a high current density improves the economics.

Compared to alkaline fuel cells, PEMs have the advantages of being compatible with fossil fuels. The negative consequence of having a relatively low operating temperature of only 80°C is an extreme sensitivity to carbon monoxide poisoning of the electrocatalyst. Low-temperature fuel cells need platinum to catalyze the anodic and cathodic fuel cell reactions, but carbon monoxide is preferentially adsorbed on platinum in acid electrolytes, blocking the access of hydrogen to the catalyst surface. This adsorption is inversely related to temperature. At 80°C the allowable concentration in the fuel is only a few parts per million.

Another difficulty with PEMs is the need for humidification of the fuel and oxidant streams. Failure to maintain at least 400 mm Hg of H₂O pressure results in a dehydration of the membrane, which leads to catastrophic increases in electrical resistance. The best way of maintaining high enough steam pressures without overly diluting the hydrogen and oxygen is to pressurize the system.

Maintaining a high partial pressure of water in the cell is further complicated by the fact that every proton migrating across the membrane and carrying the current is surrounded by 3-8 molecules of water as a hydration shell. This water must be continuously replenished. The need to keep the membrane from dehydrating and to supply a surplus of water to the anode increases the system complexity, which will be discussed later.

C. Phosphoric Acid Fuel Cells

Phosphoric acid fuel cells (PAFCs) were developed in response to the expressed desire of the gas utilities to expand sales of natural gas by generating electricity in "on-site" power plants to be located at shopping malls, industrial complexes, etc.

The initial development of the PAFC technology took place at the Power Systems Division of United Technologies (formerly Pratt and Whitney, presently International Fuel Cells, Inc.). It led to fuel cell stacks of about one square foot of area and 100-200 individual cells operating at a current density of 150-200 mA/cm². The stacks had a nominal operating temperature of 190°C and were cooled with a steam/water mixture, which was also used in some cases for heating purposes. The fuel and air streams were at ambient pressure. The electrochemistry is virtually identical to that of the PEM.

Under sponsorship of the Electric Power Research Institute and the Department of Energy, another generation of cells was developed for operation under pressure. By pressurizing the fuel and air streams to about 700 kPa, the cell voltage and current density were improved. The cell area was enlarged to almost eight square feet. Pilot plants of 4.5 MW and, later, of 11 MW operating on natural gas were designed and built. The PAFC technology developed by IFC is now ready to be commercialized.
During the height of the energy crisis, Westinghouse Electric purchased an alternative PAFC stack design from Energy Research Corp. Instead of steam, these stacks are cooled by air. Westinghouse intended to build 7.5-MW utility power plants, but the decline of oil prices in 1987 led to cancellation of the orders.

Engelhard Corp. developed PAFCs for a forklift truck. Instead of steam or air, these PAFCs are cooled with oil to circumvent the potential corrosion caused by shunt currents through conductive coolant channels, and to maintain the advantage of the higher heat capacity of a liquid relative to a gas.4,8

Following the lead of the US, several large Japanese companies and the Japanese government became engaged in PAFC research in the eighties. Until very recently their technology was trailing that of the US companies, but progress has been rapid and this may be changing. Large fuel cell stacks are being tested and are reported to work very well.

In a transportation application, PAFCs have the disadvantage that they cannot be started from room temperature but must be preheated to above 100°C before any current can be drawn. Further, the cells must always be maintained under partial load to prevent the carbon support of the catalyst from oxidizing. The best use of PAFCs is, therefore, in steady operating modes.

As is the case with alkaline fuel cells and PEMs, the PAFC requires hydrogen fuel. Hydrocarbons and carbon monoxide must be reacted with steam in separate reforming and shift reactors. This will be discussed later.

D. Molten Carbonate Fuel Cells

The concept of the molten carbonate fuel cell (MCFC) originated in Holland in the late 1950s. Instead of aqueous solutions of either KOH or H$_3$PO$_4$, the electrolyte is a molten salt (Li$_2$CO$_3$-K$_2$CO$_3$) with a melting point of 500-600°C. The actual operating temperature of the cells is higher still, averaging about 650°C.

The chemistry of MCFCs is unique in that the hydrogen fuel reacts with a carbonate ion to form water and carbon dioxide:

\[ \text{H}_2 + \text{CO}_3^{2-} = \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^- \]  

To regenerate the carbonate ion on the cathode side, carbon dioxide has to be supplied to the cathode:

\[ \text{CO}_2 + \frac{1}{2}\text{O}_2 + 2\text{e}^- = \text{CO}_3^{2-} \]  

As will be shown later, this requirement for recycling CO$_2$ affects the system design.

Molten carbonate fuel cells are more flexible than the previously discussed cells with respect to fuels. Carbon monoxide is no longer a catalyst poison but can be used as fuel. The reason is that CO reacts in the fuel cell channels with water to form hydrogen and carbon dioxide. Moreover, even hydrocarbons such as methane can be fed directly to the MCFC when a reforming catalyst is added to the cells, as will be discussed in more detail later.4,8
The Institute of Gas Technology (IGT) was the first institution in the US to begin working on the MCFC, followed by Texas Instruments. As a result of the 1973 energy crisis, DOE initiated support of MCFC R&D in 1978 and began a major R&D effort in 1980. Two contractors won the DOE award: United Technologies and General Electric/IGT.

At the present time, workers at United Technologies have tested several stacks of one square foot size and 20 individual cells. They also built and operated an eight square foot stack. General Electric abandoned the technology in 1984, thus allowing Energy Research Corp. to assume a more prominent role. Also, several large Japanese companies entered the MCFC field.

The motivation for developing MCFCs is the prospect of improved economics relative to PAFCs in utility power plants. There are principally three reasons for that expectation. One is a lower cost of the fuel cells themselves, because nickel is used instead of platinum as the electrocatalyst. The second is a higher system efficiency. The third is a simpler and, therefore, less expensive system. The last two points are the direct consequence of operating the fuel cell at higher temperature, where internal resistance in the cell is lower, and where direct use of carbon monoxide and methane in the fuel cell become possible, eliminating the expense of shift and reforming reactors.

However, the MCFC technology is still struggling to overcome several technical problems. The presently used cathode material dissolves before the desirable life for utility applications of 40,000 h is reached. The electrolyte accumulates near the negative end of the stack through shunt-current-induced migration, causing starvation at the cathode, and the anodes and cathodes tend to creep under the applied load.

For transportation applications, the MCFC has two further shortcomings. One is the very limited thermal cyclability. Once the electrolyte becomes solid, it is prone to develop cracks during reheating. The second problem is a concern that the cell materials, in general, and the electrolyte matrix, in particular, may not be able to withstand the vibrations of a vehicle.

E. Solid Oxide Fuel Cells

Operating at even higher temperatures than the MCFC, the solid oxide fuel cell (SOFC) has an oxide ion conducting electrolyte of yttrium doped zirconium oxide, YxZr1-xO2. For this electrolyte to have sufficiently high conductivity, the cell must be operated at 1000°C. The electrochemistry of the SOFC resembles that of the alkaline cell, where an O2− ion is substituted for the OH−. Due to the high operating temperature, the SOFC can use virtually any hydrocarbon fuel without any fuel processing.

The early work on developing SOFCs was concentrated on finding compatible anode, electrolyte, cathode, and interconnect materials. Having succeeded in that, a cell was designed which did not require a sealing material between the electrochemically active area and the gas manifolds. This "seal less" SOFC from Westinghouse provided the basis for DOE to become involved in its development in 1983. At present, several assemblies of 256 "tubes" generating 2-3 kW of power have been tested. However, this type of cell design has a low
power density and may not be able to tolerate the vibrations of a transportation application.9

Argonne National Laboratory derived a conceptual design for a "monolithic" SOFC10 and began to develop it in 1985 for defense applications. The monolithic SOFC is based on the same materials and electrochemistry as the tubular SOFC cell, but has a self-supporting, compact structure, with wall thicknesses of only 2/1000 to 3/1000 of an inch. Because the kinetics of the cell chemistry are rapid at the high operating temperature, the current density is high in SOFCs. In single cells, 2000 mA/cm² has been demonstrated.

Although conceptually elegant, the monolithic SOFC is still in an early stage of development and manufacturability is not assured. The anode, electrolyte, cathode, and interconnect materials are made initially with organic binders. During burnout of the binder and sintering into the final geometry, cracks develop in the structure. Current research is aimed at making crack-free assemblies of 10 W size.

III. SYSTEM DESIGNS

All of the fuel cells discussed above depend to some degree on fuel processing and on external means of temperature control. If, for example, methanol is used as fuel, but the fuel cell cannot operate directly on methanol, then equipment for converting the methanol into hydrogen is needed. Or, if the fuel cell stack is operated at high power densities, then pumps and heat exchangers are needed to remove the heat from the system. Because the cost of all the peripheral components can easily exceed that of the fuel cell alone and can profoundly influence the cost competitiveness, it is absolutely essential to consider the whole system and not just the fuel cell in any actual application.

To make an assessment of the merits of the five types of fuel cells for transportation, conceptual system designs for operation on methanol fuel are given below. Before discussing the system components, we will briefly review some fundamentals of processing the fuel and of heat generation in the fuel cell.

Methanol can be converted to hydrogen by reaction with water:

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} = 3 \text{H}_2 + \text{CO}_2$$

This reaction requires that at least one mole of water is provided for every mole of methanol. This water must be free of minerals since deposits would otherwise form in the equipment.

The reaction proceeds in two steps, each requiring a different temperature and catalyst. The first step is the decomposition of methanol to hydrogen and carbon monoxide:

$$\text{CH}_3\text{OH} = \text{CO} + 2\text{H}_2$$

This reforming reaction is endothermic. A minimum temperature of 200°C is needed, but higher temperatures are preferable because the equilibrium is
driven further to the CO side and higher percentages of the methanol are converted. A catalyst is usually used to increase the reaction rates.

The second step is the shift reaction:

\[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \]  

(8)

Shifting is a slightly exothermic reaction. Temperatures of about 200°C over an iron oxide catalyst are desirable. The higher the H\textsubscript{2}O/CO ratio, the more complete is the reaction. Reforming and shifting can be combined by designing the equipment to have different temperature zones.

As in all other energy conversion devices, fuel cells generate some heat, but unlike internal combustion engines, the amount of the heat can vary with operating conditions. When operated at very low current densities, fuel cells can theoretically operate at the equilibrium potential corresponding to the free energy of the reaction. In this case, no heat would be generated, and the conversion efficiency (eff) would be:

\[ \text{eff} = \frac{nF\epsilon^0}{\Delta H^\circ} = 1 - \frac{T\Delta S}{\Delta H^\circ} \]  

(9)

where \( n \) is the number of electrons transferred in the reaction, \( F \) is the Faraday constant, \( \epsilon^0 \) is the equilibrium potential, \( \Delta H^\circ \) is the standard reaction enthalpy, \( T \) is the temperature, and \( \Delta S \) is the reaction entropy. For the formation of water, the \( T\Delta S \) term is small, leading to theoretical efficiencies close to 90%. In practical cells, the actual operating potential is considerably lower than the equilibrium potential due to ohmic losses and electrode overpotentials. The amount of heat generated in the cell is then given by:

\[ \Delta H = [nF(\epsilon^0 - \epsilon) - T\Delta S] U \]  

(10)

where \( \epsilon^0 \) is the equilibrium potential, \( \epsilon \) is the actual cell operating potential, and \( U \) is the utilization of fuel (\( U \) is typically 85% but can be lower). The operating potential of most fuel cells ranges from 0.6 to 0.8 V, depending on current density. However, the open circuit potential depends on the operating temperature of the cell. It is about 1.4 V at ambient temperature and decreases to less than one volt at 1000°C. As a consequence, up to 50% of the heat of combustion may need to be removed as heat. More heat needs to be removed from the cells operating at low temperatures than the ones at high temperature. The ability to remove that heat limits the size and power density of the cells.

A. Alkaline Fuel Cell

System designs for alkaline fuel cells operating on methanol are not readily available because removing the carbon dioxide from the reformed fuel or the electrolyte appears to be impractical. Alkaline fuel cells may have a role in transportation whenever hydrogen fuel is available in tanks, but it is difficult to see how they would be practical with alcohols.

B. Phosphoric Acid Fuel Cell

A flow diagram showing the main components of a PAFC power source in a forklift truck is given in Fig. 2. Engelhard Corp. has been developing the
system for several years and is about to commercialize it. A similar design but larger is being considered for the fuel cell powered bus mentioned in the introduction.\textsuperscript{11}

The system functions as follows. Under steady-state operating conditions, methanol and purified water are mixed and pumped from the respective storage tanks to the vaporizer, where the mixture is evaporated with heat coming from the fuel cell. Mineral oil of about 190°C is used as the heat transfer medium.

Leaving the evaporator, the evaporated methanol/water mixture is passed through a reforming reactor where both react to form hydrogen and carbon dioxide as shown in Eq. 6. Reaction conditions are chosen to drive the equilibrium to where only 0.5% CO is left in the fuel stream, because the fuel cell catalyst cannot tolerate more. The fuel stream consisting of hydrogen, carbon dioxide, water vapor, a small amount of unreacted methanol, and 0.5% CO is fed to the anode side of the fuel cell, where about 80% of the hydrogen is converted to electricity. The depleted fuel stream is routed to the burner, where remaining fuel is burned, providing the heat for the reform reactor.

Separate from the fuel stream, air is passed through the cathode side to complete the electrochemical reaction.

To start up the PAFC system, the oil circulating through the fuel cell is heated in an auxiliary burner until the fuel cell has reached a temperature near 130°C. Simultaneously, methanol is pumped through the reformer and fuel cell without reacting and then burned in the reformer burner until thermal equilibrium is reached. When starting from ambient temperatures, the start-up can take over an hour, but start-up from standby temperatures will only take minutes.
In a transportation application, the electric power coming from the fuel cell would drive electric motors, which would be connected to a drive train, transmission, and finally to the wheels. At the present stage of development, it will be necessary to also use batteries in parallel with the fuel cells, because the dynamic response of the fuel cell system is not fast enough. Electrically, fuel cells can respond quickly to the changes in the amount of power being required by the vehicle, but when the current is increased or decreased, the fuel processing rate has to be changed correspondingly, and the heat removal rate from the cell has to be adjusted. In principle, these rate changes should be manageable, but at present it is preferable to run the system at constant conditions.

For the fuel cell/battery hybrid bus program of DOE/DOT, it was decided to add enough battery capacity to the system for absorbing the peaks and troughs of the drive cycle, and to concentrate the development effort on the technology of interfacing the fuel cells with the batteries and the motor controller. In addition, effort is being devoted to developing the drive train and transmission for the hybrid bus.

For a broader transportation application, the dynamic response of fuel processing, i.e., the reformer, would need to be improved. Further, the power density of the system as a whole is still too low, the cost is too high, and the start-up is too slow.

C. Proton Exchange Membrane Fuel Cell

A flow diagram for a PEM system is shown in Fig. 3. In general, the layout is similar to the PAFC system, but the following additional components are needed:

- A preoxidizer between the reformer and the fuel cell to remove CO
- A turbocompressor
- A water recovery system

![Fig. 3. Schematic of Proton Exchange Membrane Fuel Cell System](image-url)
The preoxidizer is needed to reduce the 0.5% carbon monoxide coming from the reforming reactor to only a few parts per million, because the PEM has a much lower tolerance for CO than does the PAFC. This extreme sensitivity to CO is the consequence of a cell operating temperature of only 80°C (versus 190°C for PAFC). At the lower temperature, carbon monoxide is adsorbed to a much greater extent on the surface of the platinum electrocatalyst, blocking the reaction sites for hydrogen and rendering it inactive. In the preoxidizer, carbon monoxide is oxidized with a precisely controlled amount of air, while most of the hydrogen is unaffected.

The turbocompressor serves the purpose of raising the air pressure to at least 3 atm (0.3 MPa), but perhaps as high as 10 atm (1 MPa). Although there is still some debate whether pressurization is needed, it is probably the best solution to prevent the membranes from dehydrating. Turbocompressors in sizes suited for transportation systems are not presently available but can be developed using turbocharger technology from cars and trucks.

Because of the continuous flux of water across the membrane, as discussed earlier, it is necessary to inject more water into the fuel stream than required for reforming. At the rather low operating temperature of the PEM, it is difficult but not impossible to use the heat generated in the fuel cell for evaporating that water. By designing the fuel cell stack to include a humidification section, some of this water can be supplied. Alternatively, it has to be evaporated by burning fuel.

It may also be necessary to recover water from the air stream and recycle it to the evaporator to avoid the need for large water tanks.

Starting up the PEM system is easier than the PAFC because the fuel cell can be operated at ambient temperature and does not need to be preheated. However, it will also be necessary to bring the reformer to its normal operating conditions before hydrogen will become available. Start-up times for the system will, therefore, be longer than for the fuel cell.

D. Molten Carbonate Fuel Cell

Molten carbonate fuel cell systems have been developed for natural gas fuel and for coal. It is straightforward to conceptualize a methanol based system from the reported results on the two other fuels. Such a conceptual system is shown in Fig. 4.

Fuel and water are evaporated in an evaporator that is heated with the depleted fuel coming from the fuel cell. The methanol/water mixture will be hotter than in the PAFC and PEM systems because it will be fed directly to the fuel cell, whose operating temperature is 650°C. To prevent undercooling the cell, the fuel mixture should be about 500°C upon entering the cell.

Because of the higher operating temperature of the cell, the methanol will be reformed internally. Such internally reforming MCFCs would contain the reforming catalyst in the flow channels of the cell, instead of in a separate reform reactor. The advantage is not only a cost saving of the reform reactor, but also a significant increase in the performance of the fuel cell system. The reason is a perfect synergism between the fuel cell chemistry and the reform reactions.
As discussed earlier, the reform reaction is endothermic, but the cell reaction is exothermic. Reforming the methanol in the cell will, therefore, remove heat from the cell and decrease the cooling requirements. Further, the reform reaction consumes water, but the cell reaction generates water. Reforming in the cell will, therefore, decrease the amount of water that needs to be supplied and will drive the reaction to completion. Finally, the response of the system to changes in load will be much quicker in an internally reforming system, because the heat being generated by an increased load will not have to be transported to a separate reactor but will be available immediately for reforming more fuel. Such internally reforming MCFCs are being developed for methane fuel but may need to to be modified for methanol.

Leaving the fuel cell, the depleted fuel is completely oxidized in a catalytic burner, which provides heat to the evaporator. A portion of the exhaust gas is recycled to the air intake, as discussed earlier, to supply carbon dioxide to the cathode.

The MCFC system does not have a separate coolant, unlike the PAFC and PEM systems. Instead, the reactant air is used to remove the excess heat from the cell. However, the air must be preheated to about 600°C in an air heater before it can be admitted to the cell.

Because of the relatively high operating temperature of the cell, a thermal enclosure will be required to keep it fairly hot at all times. A separate burner that is thermostatically controlled could be used to maintain the temperature. Preliminary estimates of the fuel consumption in such a burner indicate that roughly 10% more methanol would be needed to maintain the MCFC on hot standby all the time.

To start up an MCFC system from hot standby will only take a few minutes. Start-up from ambient temperatures will take several hours and may be harmful to the cells because the electrolyte tends to develop cracks when the molten salt solidifies.
An advantage of the MCFC system over any of the previously discussed ones is an anticipated excellent dynamic response, due primarily to the internal reforming capability.

E. Solid Oxide Fuel Cell

A schematic flow sheet of the solid oxide fuel cell system is shown in Fig. 5. It resembles the MCFC flow sheet (Fig. 4) in that this system also incorporates a fuel evaporator and an air heater, in addition to the fuel cell stack. In the SOFC system, however, because of the high stack temperature, the spent fuel has enough sensible heat to provide the heat of vaporization for the incoming fresh fuel. The chemical energy content of the spent fuel stream (along with the sensible heat in the spent air stream) is used to preheat the incoming fresh air.

As in the MCFC system, the heat generated within the stack is removed by the reactant air. Since the SOFC stack is ceramic, it is expected that the temperature gradients within the stack will have to be limited to avoid excessive thermal stresses in it. One way of reducing the temperature rise of the air flowing through the stack is to recycle part of the exhaust air back to the inlet, as shown in Fig. 5. Conceivably, this can be accomplished using an air ejector. This exhaust air recycle to limit thermal stresses in the stack causes a small decrease in efficiency because of (1) the increased pressure drop through the stack, (2) inefficiencies in the ejector at off-design (fluctuating load) operating conditions, and (3) a lower net oxygen activity in the cathode gas.

As with the MCFC system, the high-temperature components of the SOFC system must be kept in a thermal enclosure. Compressed multifoil vacuum insulations have been developed for use with advanced high-temperature batteries; it is expected that such an insulation could be adapted for use with the SOFC system. Under full or partial load operation, the heat generated within the stack is sufficient to maintain the stack at the nominal operating temperature of 1000°C, but when no useful power is being drawn, the
system would tend to cool down. To avoid long start-up times, it is desirable
to put the system in a standby mode (~800°C) rather than to turn it off and
let it cool down to room temperature. The standby conditions are maintained
by burning the fuel at a rate sufficient to balance the heat loss from the
system. Preliminary analysis of a SOFC system at standby conditions indicates
a heat loss rate of less than 200 W from a 60 kW_e power module. At 85%
combustion efficiency, a 200 W heat loss corresponds to a methanol combustion
rate of ~1 kg/day.

The SOFC standby conditions are defined to permit some electrical power
draw instantly. As the reject heat begins to raise the stack temperature,
power can be drawn at successively higher levels; this, in turn, increases the
rate of stack heat-up. Thus, the stack should be able to deliver full rated
power in a matter of minutes after start-up from standby conditions. Start-up
from ambient temperature will possibly take several hours; the heat-up must be
gradual enough to avoid excessive thermal stresses in the SOFC stack.

The SOFC system should provide excellent dynamic response due to its
internal fuel reform capability. Advantages of SOFC over MCFC include the
absence of a liquid electrolyte, a potentially smaller thermal enclosure for
the same power rating, and potentially higher transient power capability.

The concern with the SOFC technology is the rather high operating
temperature, which may lead to material fatigue and to difficulties of
controlling the temperatures in dynamic operating conditions. Also, extended
stand-by periods of several days would lead to a significant fuel consumption.

IV. ASSESSMENT

The operating conditions and development status of the five fuel cells
are summarized in Table 1; Table 2 gives the performance characteristics of
the five fuel cell systems.

<table>
<thead>
<tr>
<th>Type of Fuel Cell</th>
<th>Operating Temp., °C</th>
<th>Fuel Compatibility</th>
<th>Coolant</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH</td>
<td>25-100</td>
<td>pure H_2</td>
<td>water</td>
<td>15-kW modules in use</td>
</tr>
<tr>
<td>PEM</td>
<td>80</td>
<td>dilute H_2 with &lt;1 ppm CO</td>
<td>water</td>
<td>1 kW being tested</td>
</tr>
<tr>
<td>PAFC</td>
<td>200</td>
<td>dilute H_2 with &lt;0.5% CO</td>
<td>steam, oil, or air</td>
<td>100-kW tested</td>
</tr>
<tr>
<td>MCFC</td>
<td>650</td>
<td>H_2, CO</td>
<td>air</td>
<td>20 kW tested</td>
</tr>
<tr>
<td>SOFC</td>
<td>1000</td>
<td>H_2, CO, CH_4, CH_3OH</td>
<td>air</td>
<td>tubular cells of 3 kW tested, monolith in laboratory stage</td>
</tr>
</tbody>
</table>
Table 2. Performance Characteristics of Fuel Cell Systems

<table>
<thead>
<tr>
<th>Type of Fuel Cell System</th>
<th>Current Density, ( \text{mA/cm}^2 )</th>
<th>Power Density, ( \text{kW/ft} )</th>
<th>Start-up Time, ( \text{min} )</th>
<th>Dynamic Response</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Single Cell Stack Stack System Standby Cold</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KOH</td>
<td>5000 1000</td>
<td>10 ? 1</td>
<td>-- fast</td>
<td></td>
</tr>
<tr>
<td>PAFC</td>
<td>500 240</td>
<td>3 0.5 15 300</td>
<td>slow</td>
<td></td>
</tr>
<tr>
<td>PEM</td>
<td>4000 2000</td>
<td>20 1.5 1 5</td>
<td>slow</td>
<td></td>
</tr>
<tr>
<td>MCFC</td>
<td>400 250</td>
<td>6 1.4 15 500</td>
<td>fast</td>
<td></td>
</tr>
<tr>
<td>SOFC</td>
<td>2000 ?</td>
<td>20 2.3 1 100</td>
<td>fast</td>
<td></td>
</tr>
</tbody>
</table>

The first observation to be made is that the lower the operating temperature of the fuel cell, the more critical becomes the preparation of the fuel. At 80-100°C, the hydrogen must be virtually free of carbon monoxide, while at 1000°C almost any hydrocarbon fuel can be used directly. As a consequence, the fuel processing is more complex and, hence, more costly for alkaline cells, PEMs, and even PAFCs than for MCFCs and SOFCs.

The operating temperature also affects the method of cooling. Alkaline cells, PEMs, and PAFCs are cooled with water, although the PAFC can also be cooled with mineral oil or air. All three types of cells have cooling plates alternating at certain intervals with the fuel cell plates. The heat being removed from the cell is used for evaporating the methanol and the water, but when the fuel cell temperature is low, a large portion can only be rejected from the system. As a result, the overall fuel efficiency of such systems becomes low.

The MCFCs and SOFCs are cooled with air. There are no separate cooling plates; instead, excess air is used to remove the heat. However, the simpler cooling method of the MCFC and SOFC is offset by a need to preheat the air, which means extra heat exchangers.

Whether there is an advantage to any of the five cells related to the method of cooling is too difficult to determine from a simple qualitative discussion of the systems, but will require a more detailed engineering analysis.

A second observation to be made from Table 1 is that the development status would favor alkaline cells, PAFCs, and MCFCs, while PEMs and the monolithic SOFC are in earlier stages of development.

From Table 2, it may be observed that, while current densities of 400 to 500 \( \text{mA/cm}^2 \) have been obtained in PAFCs and MCFCs in single-cell tests, much higher current densities of 2000 to 4000 \( \text{mA/cm}^2 \) have been reported for SOFC and PEM single cells. However, such high current densities in single cells should not be interpreted as being representative of the technology, because scaleup of these two types of cells is in an earlier stage.
At high current densities, the amount of heat being generated per unit area is very high, and it is very difficult to provide enough cooling in a stack to avoid formation of "hot spots." This localized overheating at certain points in the cell assembly limits the attainable current density in PAFC and MCFC stacks and can also be expected to limit the current density in PEM and SOFC stacks. Until reasonably sized stacks have been tested, the current density remains uncertain.

To compare and evaluate the power densities, we have assumed that PEM and SOFC stacks will attain current densities of 750 mA/cm², which is still a high current density for an electrochemical device. Volumetric power densities of the fuel cells were then calculated, based on the published dimensions of stacks, and are reported in Table 2. Volumetric power densities of the entire systems were estimated by adding the volumes of the other components such as reform reactors, heat exchangers, etc., and then adding another 100% of empty space. It appears that the power density of a PEM system would be higher than that of a PAFC, but not by as much as the stack densities suggest.

In addition to power density, the start-up time and dynamic response of fuel cell systems need to be improved, as mentioned in Sec. I. Starting a fuel cell system involves bringing the cell and other system components close to their specified operating temperatures and operating conditions. Only the PEM and PAFC systems can be started up from ambient temperatures, but the fuel processing equipment will take more time before it will be ready to supply hydrogen to the cells. It may, therefore, be necessary to keep fuel cell systems in a standby mode, which will need to be defined for each type of cell. A PAFC system can be brought to full power from the standby mode in a few minutes, but it will take close to an hour for a cold start. In a very qualitative manner, one can estimate that a PEM system can be brought to full power in just minutes, because the cell is easier to start. The MCFC and SOFC systems will take hours to be operational in a cold start, but if maintained at the appropriate standby conditions, they can deliver at least small amounts of useful power instantly, warming up rapidly to full load capability in minutes. Some very preliminary estimates are listed in Table 2 to illustrate the relation between standby and cold start-up times.

It is too early to quantify the dynamic response, but qualitatively there can be no doubt that external reformers will severely limit the system response. Any system with internal reforming capability will clearly be preferable. Both MCFC and SOFCs have that capability. The MCFC may, nevertheless, not be a good candidate for transportation because of the very limited thermal cyclability. Once the molten salt solidifies, it is very difficult to reheat the stack without causing severe damage. Such a system may be too delicate for use by the public.

In conclusion, the PEM and SOFC appear to offer the best prospects for a transportation application, but both will need to be improved considerably.
REFERENCES


