FUEL CELLS

1. Introduction

Fuel cells are electrochemical devices that convert the chemical energy of a fuel directly into electrical and thermal energy. In a typical fuel cell, hydrogen is fed to the anode (negative electrode), and oxygen (or air) is fed to the cathode (positive electrode). The electrons removed from the oxidized fuel pass round an external circuit to the cathode. The fuel cell has the theoretical capability of producing electrical energy for as long as the reactants are provided to the electrodes. In reality, degradation or malfunction of the components limits the practical operating life of fuel cells, though systems have run continuously for several years.

Besides the direct production of electricity, heat is also produced in fuel cells. This heat can be used in combined heat and power (CHP) systems, or, in some high temperature fuel cells, for the production of further electrical energy using turbines.

Although the majority of fuel cells use hydrogen as the fuel, other fuels can be used, methanol being a notable example. Also, methane can be used, though this is usually re-formed to hydrogen and carbon monoxide either within the fuel cell itself, or in a fuel reformer adjacent to the fuel cell system.

2. Basic Principles and Problems

For the operation of a fuel cell to be as effective as possible, the electrodes should have a large area, and the electrolyte between the cells should be as thin as possible. A common electrolyte for fuel cells is an acid, with mobile H^+ ions. The reactions at the anode and cathode of such a cell are shown in Figure 1. It will be seen from this figure that electrons flow from anode to cathode, and that, in this case, water forms at the cathode. Catalysts are needed at the electrodes to promote the reactions, which should proceed as readily as possible if a large current is to be obtained from a small fuel cell.

Practical fuel cells cannot be this simple. One major problem is that, as we shall see, the voltage of each cell is only 1 V or less. This means that for useful

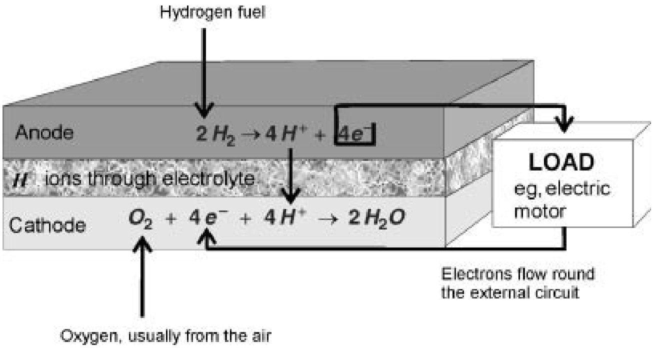

Fig. 1. Basis of fuel cell operation with acid electrolyte and hydrogen fuel.

levels of power many such cells must be connected in series. If this is to be done efficiently then each cell must be connected to the next in a way that avoids the current being taken off the edge of the electrode (as it is in Fig. 1), but over the whole surface on the electrode. The way this is usually done is to use a bipolar plate as the cell interconnect, as in Figure 2. The plate must be a good conductor of electricity, and have channels over its surface to allow the fuel to flow over the anode and the air or oxygen over the cathode. At the same time, it must make a good electrical contact with the electrodes, be as thin and light as possible, and also cheap to manufacture. A further requirement of the cell interconnects is that leakage of reactants must be prevented, which is often a very difficult feature of fuel cell stack design. The electrode material must be porous to allow the reactants to penetrate it, which means that a design as in Figure 2 would allow the hydrogen gas to be fed over the cathodes, as well as the anodes, via the porous edges of the electrodes. The same would be true of the air, which is also able to reach the anodes. In addition, fuel gas would leak out of the cell at the edges. The solution is to have seals around the edge of all electrodes, but this is not easy, as the seal must prevent gas flow round the entire edge of all the electrodes, which can number several hundred in one stack.

Fuel cells where the fuel and oxidant gases are fed in at the sides of the stack, as in Figure 2, are said to be “externally manifolded”. Many designs do not use this method, and have a solid edge to the cell interconnect, to help in preventing leaks. The reactants are fed through tubes running down the stack, with precisely placed holes that release the gases into the channels of the bipolar plates. This method, known as “internal manifolding”, makes sealing the edges of the electrodes easier, but is prone to internal leaks. Some cells use a mixture, with internal manifolding for the fuel, and external manifolding for the air fed to the cathodes.

The design and manufacture of the cell interconnect is a vitally important part of a fuel cell system, and a major contributor to the cost of a stack. Different approaches to the problem are taken for each of the different types of fuel cell, which are outlined below. Developers are trying different materials and manufacturing methods. It is not necessary for the connect to be made in one piece, and composite material bipolar plates are quite common in phosphoric acid

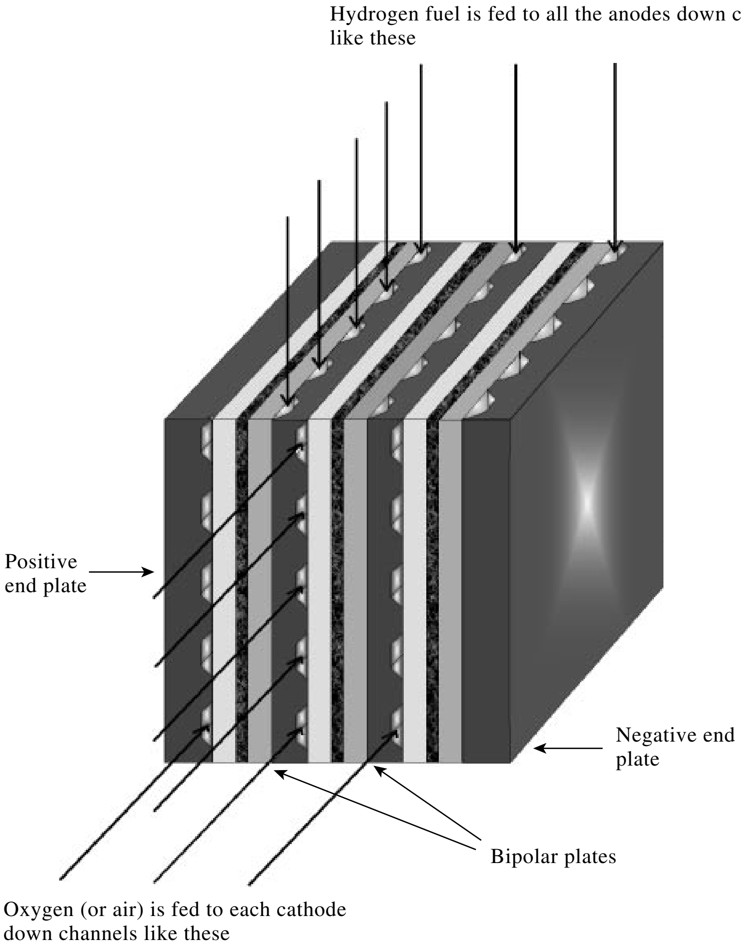

Fig. 2. Bipolar plate for connecting cells is series.

and the proton exchange membrane (PEM) fuel cells. Furthermore, there are some designs that break away from the planar-type construction of Figure 2 completely—and use totally different types of cell interconnects. The solid oxide fuel cell to be discussed in the section Solid Oxide Fuel Cell is a particularly good example of this.

Although the cells of Figure 1 use hydrogen as the fuel, it is in theory possible to use any fuel at the anode. However, there are not many other fuels that react at all readily, and very little success has been achieved with alternative fuels. Two exceptions to this rule are carbon monoxide, which is readily oxidized at temperatures above $\sim 500^\circ$C, and methanol, where promising developments have taken place recently.

Much interest is being shown in hydrogen as an energy carrier for the future—if and when this becomes a reality it will be widely available. However, at the moment hydrogen is difficult to obtain, expensive, and is difficult to store.

This lack of a hydrogen infrastructure is a major brake on the development of a market for fuel cells.

Other problems faced by fuel cells are that the catalysts used to promote the reactions may degrade and become poisoned by impurities in the reactant gas, resulting in a much shorter operating life than the envisioned application and economy requires. Another is that the inherent simplicity of the fuel cell shown in Figures 1 and 2, with no moving parts, can often be lost in a mass of extra equipment, known as "balance of plant", that is needed to make the cell function. This might include pressure regulators for the flow of fuel, pumps for the flow of air, a cooling system, a system to circulate the electrolyte if it is not solid, a chemical plant to extract hydrogen from a more conventional hydrocarbon fuel, and so on.

Finally, in this section we should mention the problem of the heat produced by fuel cells. Clearly, the conversion of chemical to electrical energy is not 100% efficient, and heat is produced. A concern of fuel cell developers has been to effectively extract this heat, and also, if possible, to design systems where the heat can be used by other systems in bottoming cycles or in combined heat and power systems.

To summarize, the efforts of fuel cell developers over recent years has been directed at these key problems:

- To improve the current produced per square centimeter (cm^2) of electrode.
- To reduce manufacturing costs.
- To simplify the problem of fuel supply.
- To extend the life of the cell.
- To maintain the inherent simplicity of the fuel cell operation in the whole system.
- To enable the best use of the heat produced by the fuel cell.

3. Different Fuel Cell Types

Many of the requirements listed above have contrary requirements of the fuel cell. For example, to have greater fuel flexibility and better use of the waste heat, the fuel cell should operate at a high temperature. However, this will probably increase manufacturing costs, and make the system more complex. The result of these competing requirements is that a number of different fuel cell types are being developed, which all play to different strengths and solve different weaknesses of fuel cells. The key feature of each type of fuel cell is, in most cases, the electrolyte that is used. One important exception to this is the "direct methanol fuel cell", which is defined by the fuel used (see Table 1).

As well as facing up to different problems, the various fuel types also try to play to the different strengths of fuel cells. The PEM fuel cell (PEMFC) capitalizes on the essential simplicity of the fuel cell. The electrolyte is a solid polymer, in which protons are mobile. The chemistry is the same as the acid electrolyte fuel cell of Figure 1. With a solid and immobile electrolyte, this type of cell is inherently very simple. These cells run at quite low temperatures, so the problem

Table 1. **Data for Different Types of Fuel Cells**

Fuel cell type	Mobile ion	Operating temperature °C	Applications and notes
alkaline fuel cell (AFC)	OH^-	50–200	used in space vehicles, eg, Apollo, shuttle
proton exchange membrane (PEM)	H^+	50–100	especially suitable for vehicles and mobile applications, but also for lower power CHP systems
direct methanol fuel cell (DMFC)	H^+	20–100	likely early applications in portable electronic equipment, but perhaps also for cars
phosphoric acid fuel cell (PAFC)	H^+	∼ 220	large numbers of 200-kW CHP systems in use
molten carbonate fuel cell (MCFC)	CO_3^{2-}	∼650	suitable for medium to large scale CHP systems, up to megawatt (MW) capacity
solid oxide fuel cell (SOFC)	O^{2-}	∼600–1000	suitable for all sizes of CHP systems, 0.5 kW to multi-MW

of slow reaction rates is addressed by using sophisticated catalysts and electrodes. Platinum is the catalyst, but developments in recent years mean that only minute amounts are used, and the cost of the platinum is a small part of the total price of a PEM fuel cell. A weakness of this type of cell is that the only suitable gaseous fuel is quite pure hydrogen.

An important variant of the PEM fuel cell is the direct methanol fuel cell (DMFC). As a fuel, methanol has many advantages over hydrogen—being a liquid it can be readily stored and transported. The main problems with the DMFC is that there is a large overvoltage at the anode, which makes the cell less efficient, and the fact that the methanol tends to diffuse through the proton conducting membrane. Nevertheless, good progress is being made to at least partially solve these problems, and they are likely to prove useful for portable electronics equipment, and possibly for transport applications in the more distant future.

Although PEM fuel cells were used on the first manned spacecraft, the alkaline fuel cell (AFC) was used on the Apollo and Shuttle Orbiter craft. The problem of slow reaction rate is overcome by using highly porous electrodes, with a platinum catalyst, and by operating at quite high pressures. These cells have been designed to operate over a fairly wide temperature range. The major disadvantage is the alkaline electrolyte, which is usually circulated around the fuel cell, making the system more complex. However, the electrolyte is very low cost.

The phosphoric acid fuel cell (PAFC) was the first to be produced in commercial quantity and enjoy widespread terrestrial use. Many 200-kW systems, manufactured by the International Fuel Cells Corporation, are installed in the United States and Europe. In addition, a number of Japanese companies have installed systems, mainly for their own domestic market. Porous electrodes, platinum catalysts, and a fairly high temperature (~220°C) are used to boost the reaction rate to a reasonable level. The hydrogen fuel problem is solved by "reforming" methane to hydrogen and carbon dioxide, but the equipment needed to do this adds considerably to the costs, complexity, and size of the fuel cell. Nevertheless, they use the inherent simplicity of a fuel cell to provide a reliable and maintenance-free power system. Some have run continuously for many years without any maintenance requiring shutdown or human intervention.

As is the way of things, each fuel cell type solves some problems, but brings new difficulties of its own. The solid oxide fuel cell (SOFC) operates in the region of 600–1000°C, which means that high reaction rates can be achieved without expensive catalysts, and that gases such as natural gas can be used directly, or "internally reformed" within the fuel cell, without the need for a separate unit. However, the ceramic materials that these cells are made from are difficult to handle, so they are expensive to manufacture, and there is still quite a large amount of extra equipment needed to make a full fuel cell system. This extra plant includes air and fuel preheaters, also the cooling system is more complex, and they are not easy to start up.

Despite operating at temperatures of up to 1000°C, the SOFC always stays in the solid state. This is not true for the molten carbonate fuel cell (MCFC), which has the interesting feature that it needs the carbon dioxide in the oxidant supply for the cathode to work. The high temperature means that a good reaction rate is achieved using a comparatively inexpensive catalyst—nickel. The nickel also forms the electrical basis of the electrode. Like the SOFC, it can use gases such as methane and coal gas directly, without an external re-former. However, this simplicity is somewhat offset by the nature of the electrolyte, a hot and corrosive mixture of lithium, potassium, and sodium carbonates.

In Figure 1, the separate reactions at the anode and the cathode of an acid fuel cell are shown, these are the reactions for both the PEMFC and the PAFC. It will be seen that in this case the water forms at the cathode, which is convenient, as the water is evaporated by the air passing over the cathode. However, if the electrolyte has a negative ion, then the water forms at the fuel anode. Figure 3

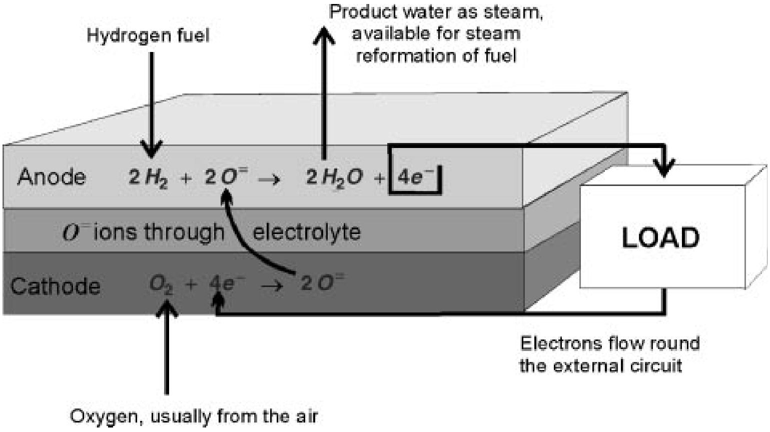

Fig. 3. Anode and cathode reactions in the SOFC.

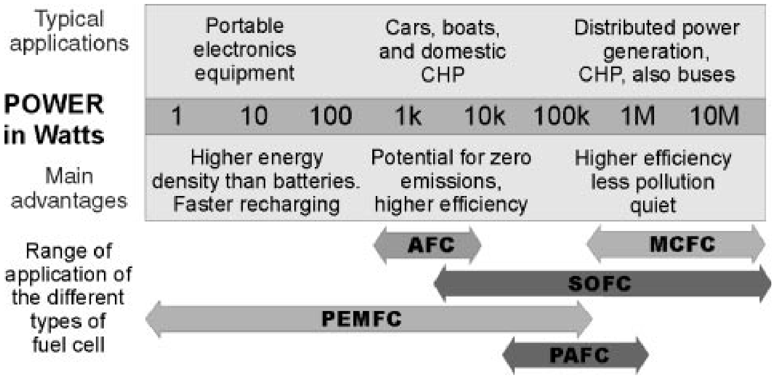

Fig. 4. Chart showing the range of applications of different types of fuel cells.

shows the separate reactions at the anode and cathode of the SOFC. In the case of the hot fuel cells such as the SOFC and the MCFC, it turns out that the formation of the water at the fuel anode is again convenient, as it means that steam is available for steam re-formation of methane within the fuel cell itself.

An important feature of fuel cells is that the different types of cell have a very wide range of application. They can be used in small portable electronics equipment (PEMFCs or DMFCs) right through to large multi-MW power stations (SOFCs and MCFCs), and everything in between. As generators of electrical power, fuel cells have a range of possible application that far exceeds any other type, which explains the very great interest being shown in these devices of late. The range of applications of the different types of cell is shown in Figure 4.

4. Fuel Cell Thermodynamics

4.1. Open Circuit Voltage. The energy driving electron transfer in electrochemical cells is the Gibbs free energy. If the overall fuel cell reaction produces a change in molar Gibbs free energy of Δg, and involves the transfer of n electrons, then the cell emf, E, in the absence of any losses is given by the formula:

$$E = \frac{-\Delta g}{nF} \tag{1}$$

Where F is the Faraday constant. In the case of the hydrogen fuel cell, for which the overall reaction is

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$

The value of Δg is -237.2 kJ/mol, when using pure reactants, at STP. The number of electrons transferred per mole of hydrogen is 2 (see Fig. 1), and this gives a value for E of 1.23 V.

Table 2. **The Parameter Δg and Maximum Electromotive Force (emf), for Hydrogen Fuel Cells Using Pure Reactants at Standard Pressure**

Form of water product	Temperatures °C	Δg, kJ/mol	Maximum emf, V
liquid	25	−237.2	1.23
gas	100	−225.3	1.17
gas	200	−220.4	1.14
gas	400	−210.3	1.09
gas	600	−199.6	1.04
gas	800	−188.6	0.98
gas	1000	−177.4	0.92

However, the value of the Gibb's free energy is not constant. It varies with temperature and pressure, as well as the purity of the reactants, in accordance with standard chemical thermodynamics. Some example values for the hydrogen fuel cell are given in Table 2. They show that the Gibb's free energy change for the reaction, and hence the open circuit voltage, declines in magnitude with increasing temperature.

As we shall see, this has important implications for the efficiency of high temperature fuel cells.

The Nernst equation describes the effect of other issues such as reactant concentration and pressure on the open circuit voltage, or maximum emf. This equation can be given in many forms. One example below shows the effect of the partial pressure of the reactant and product gases in a hydrogen fuel cell.

$$E = E^0 + \frac{RT}{2F} \ln \left(\frac{P_{H_2} + P_{O_2}^{1/2}}{P_{H_2O}} \right) \tag{2}$$

E^0 is the EMF at standard pressure, and R is the universal gas constant. This equation allows designers to calculate the benefits of increasing the pressure of a system. In practice, especially with low temperature fuel cells, the benefits of higher pressures exceed what the Nernst equation would predict because higher pressure also somewhat reduces the losses to be discussed in the following section.

4.2. Operating Fuel Cell Voltages. The equations considered above give the no-loss open circuit voltage of a fuel cell. However, the actual operating voltage of a cell is always less than this, due to irreversibilities in the system. These occur most strongly when a current is drawn from the cell, but even the open circuit fuel cell voltage is usually reduced by various effects. This finding is especially noticeable in low temperature cells such as the PEMFC and the DMFC, where very small quantities of fuel passing through the electrolyte of the cell to the cathode cause a mixed reaction, which depresses the voltage. However, it is when a current is drawn that a more important drop in voltage occurs.

The difference between the open circuit voltage and the theoretical no loss emf considered in the previous section is normally called the "overvoltage", though the terms "voltage loss", "over potential", "irreversibility" are also used, reflecting the interdisciplinary nature of fuel cells. There are three main causes of voltage loss that increase with current: activation losses, ohmic losses, and mass transport (or concentration) overvoltage.

Activation Losses. These are caused by the slowness of the reactions taking place on the surface of the electrodes. A proportion of the voltage generated is lost in driving the chemical reaction that transfers the electrons. The overvoltage can be expressed by the Tafel equation:

$$\eta_{\text{act}} = a \ln\left(\frac{i}{i_0}\right) = a \ln i - a \ln i_0 \quad \text{for} \quad i > i_0 \tag{3}$$

Where i_0 is the exchange current density, a is a constant, and i is the current density in milliamperes per square centimeter (mA/cm^2). The value of a is typically in the range 0.03–0.06. However, i_0 varies much more widely, being dependent on the temperature, catalyst used, roughness of the electrode, and the reaction. In the hydrogen fuel cell, the activation overvoltage is much greater at the air cathode than the fuel anode—indeed the activation voltage loss at the hydrogen electrode is generally reckoned as negligible provided a suitable catalyst is present.

Ohmic Losses. This overvoltage is due to the normal electrical resistance of the materials of the fuel cell, the interconnections between the cells, as well as the resistance to the flow of ions through the electrolyte. This voltage drop is proportional to the current density

$$\eta_{\text{ohm}} = i\,r \tag{4}$$

Here r is the area specific resistance in kilo ohm square centimeters (kWcm^2) if the current density i is in the usual unit of milliamperes per square centimeter (mA/cm^2).

Mass Transport (or Concentration) Overvoltage. This loss has a particular impact at higher current densities, and is the result of a drop in the concentration of the reactant gases due to their consumption at the electrode, and the finite rate of supply, combined with the increasing concentration of reaction products. The effect of product water blocking gas channels in the porous structure of the electrodes, and the presence of nitrogen when air is used as the oxidant are two particular important causes of this loss. Two approaches to the modeling of this overvoltage have commonly been used. The first is derived from the Nernst equation, and uses diffusion effects [eg, Section 3.7 in Ref. 1], giving the equation

$$\eta_{\text{trans}} = -B \ln\left(1 + \frac{i}{i_l}\right) \tag{5}$$

Where B is a constant and i_l is the limiting current corresponding to the current produced when the reactants are supplied and consumed at their fastest possible rate. This equation gives quite a good fit with observed results. However, it does not take into account the effect of reaction products, and recent work (eg, Ref. 2) involving empirical analysis of real fuel cell performance has achieved a better fit with a somewhat simpler equation:

$$\eta_{\text{trans}} = m \exp(n\, i) \tag{6}$$

Where m and n are constants that depend on many factors of fuel cell design and conditions.

If equations 3, 4, and 6 are combined, then the voltage of the fuel cell is given by the equation

$$V = E_{\text{OC}} - a \ln i - ri - m \exp(ni) \tag{7}$$

where $E_{\text{OC}}=E_{\text{O}}+a$ ln i_{O} and is the actual open circuit voltage.

The values of the constants in equation 7 vary greatly with type of fuel cell, and its temperature of operation. Some studies in the literature give example figures. Reference 2 gives the following for a high performance PEM fuel cell operating at 70°C:

$$E_{\text{OC}} = 1.05\,\text{V} \quad a = 0.03\,\text{V} \quad R = 2.45 \times 10^{-3} k\Omega\text{cm}^2$$
$$m = 2.11 \times 10^{-5}\,\text{V} \quad n = 8.0 \times 10^{-3}$$

If a graph of equation 7 is plotted for increasing current density then a curve as in Figure 5 is found, which shows the classical shape of the voltage/current curve for a fuel cell. There is an initial fairly rapid fall in voltage caused by the air cathode activation losses. A fairly linear region follows, where the ohmic losses predominate, and then at higher currents the voltage falls more quickly, as mass transport effects become more important. This characteristic curve is found for

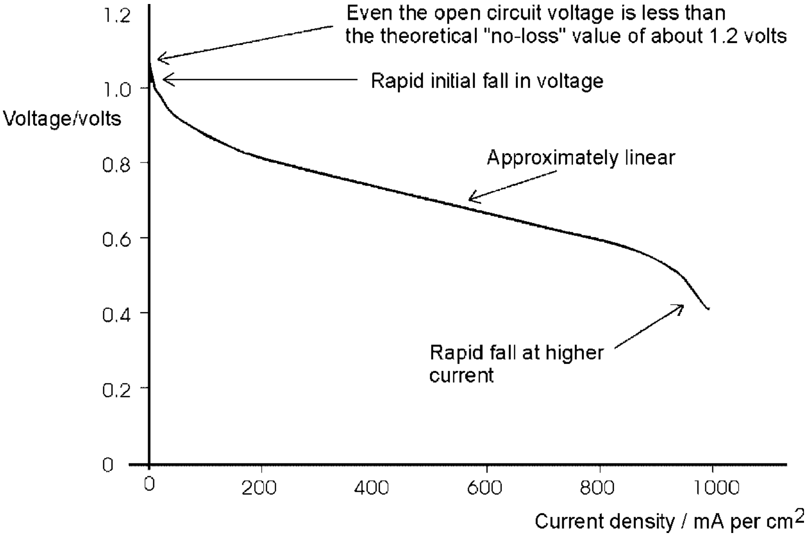

Fig. 5. Typical graph of voltage versus current density for a single fuel cell.

all low and medium temperature fuel cells. With higher temperature cells the activation overvoltage is less important, so all the early part of the curve is approximately linear, though again there is a more rapid fall of voltage at higher currents.

4.3. Fuel Cell Efficiency and Efficiency Limit. One of the most important advantages of fuel cells is that they have potentially very high efficiencies. The efficiency of a fuel cell is usually given in terms of the ratio of the electrical energy output to the specific enthalpy of the fuel used—in other words the ratio of the electrical output to the heat energy that could be obtained by burning the fuel.

$$\varepsilon_{\mathrm{fc}} = \frac{W_e}{\Delta H} \tag{8}$$

It can be shown (eg, Section 2.4 in Ref. 1) that this cell efficiency can be expressed as

$$\varepsilon_{\mathrm{fc}} = \frac{V_c}{E_0} \tag{9}$$

Where V_c is the average voltage of each single cell in the stack. Since the theoretical open circuit emf E_0 can be easily calculated, and the cell voltage easily measured or modeled, this makes the efficiency straightforward to find. However, there are also system inefficiencies to consider, of which the most important relates to fuel utilization. In most fuel cells, some of the fuel is not actually consumed, but is passed through the cell. Such venting of fuel may be done to clear trace impurities from the system. In the case of cells that use hydrogen derived from re-formed hydrocarbons, 100% fuel utilization is not possible since there is carbon dioxide and steam in the fuel gas stream, and there must still be some hydrogen left at the exit, or else the cells near the exit would have too low a fuel concentration to operate properly. So we have a more complete equation

$$\varepsilon_{\mathrm{system}} = \varepsilon_{\mathrm{fc}} \times \varepsilon_{\mathrm{util}} \tag{10}$$

where $\varepsilon_{\mathrm{util}}$ is the utilization coefficient, being the ratio of the fuel reacted in the cell to the fuel supplied.

Practical fuel cell efficiencies of ~80% have been achieved—but this was using pure hydrogen and oxygen reactants, at high pressure, in the Shuttle Orbiter fuel cells. More typical figures are ~40–45% obtained from cells running on air, though these are higher than the great majority of heat engines.

It is often stated that fuel cells are not subject to the Carnot limit that applies to heat engines, and so have an inherently higher efficiency. This statement is highly misleading, as fuel cells also have a theoretical limit to their efficiency. The Gibb's free energy harnessed by electrochemical cells such as fuel cells is the maximum possible value for the electrical work obtained from a fuel cell. So, adapting equation 8 we can say that the maximum possible efficiency of a fuel cell is given by the equation

$$\varepsilon_{\max} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \tag{11}$$

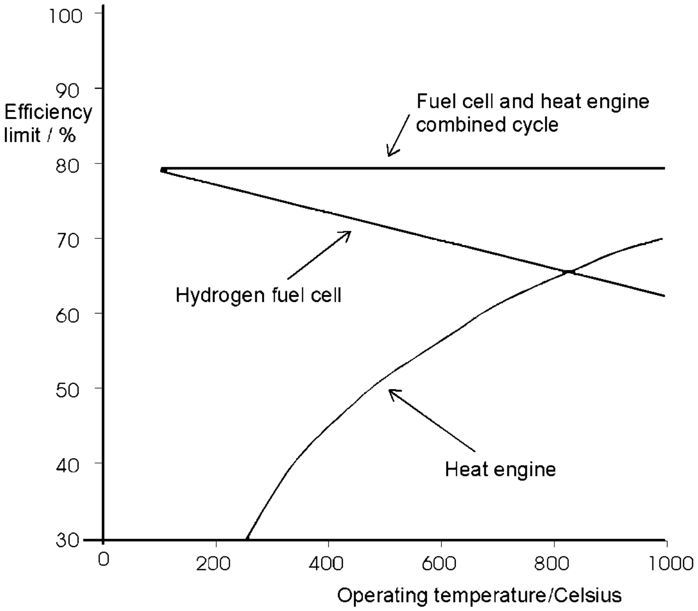

Fig. 6. Graph showing the efficiency limits for a heat engine, hydrogen fuel cell at 1 bar, and a combined cycle of fuel cell with turbine. The exit temperature for the heat engine is 100°C.

For all currently viable fuels this function is always <1, and furthermore it falls with rising temperature. It is interesting to compare the values given by equation 11 for hydrogen (by far the most important fuel cell fuel) with the Carnot equation. This is done in Figure 6, where it can be seen that the efficiency limit for a fuel cell is actually lower than for a heat engine above ~800°C.

In practice the actual operating efficiencies of fuel cells tend to rise with temperature, because the losses mentioned previously, especially the activation overvoltage, decrease with temperature and more than compensate for the changes in the Gibb's free energy. Furthermore, the potential advantage of the high temperature fuel cell becomes even clearer if we consider the possibility of combined cycle systems. The energy that is not converted into electrical energy is in the form of heat, and is carried by the hot air, carbon dioxide, and steam that leaves the fuel cell. This hot gas stream can be used to drive a heat engine. If the operating temperature of the fuel cell is T_{fc}, then the maximum energy that could be obtained from such a heat engine, with an exhaust temperature of T_e, is

$$\mathrm{W}_m = \left(1 + \frac{T_e}{T_{\text{fc}}}\right) T_{\text{fc}} \Delta S \tag{12}$$

This work could be converted into electrical energy with an alternator. The total electrical output that could thus be obtained from a combined cycle system is

$$W_{\text{io}} = W_{\text{fc}} + W_m = \Delta G + \left(1 + \frac{T_e}{T_{\text{fc}}}\right) T_{\text{fc}} \Delta S \tag{13}$$

Thus the maximum efficiency of the combined cycle system is

$$\varepsilon_{\max} = \frac{\Delta G + \left(1 + \frac{T_e}{T_{\mathrm{fc}}}\right) T_{\mathrm{fc}} \Delta S}{\Delta H} \tag{14}$$

If this is plotted for hydrogen, then an almost straight line is obtained at ~80% efficiency, as shown in Figure 6, which is a most important result, as a fuel cell operating at ~800°C, and a turbine operating at the same temperature, can both operate at quite close to their theoretical limits. This finding means that this type of machine holds very great promise for highly efficient power generation systems. Companies, including Siemens-Westinghouse and Rolls-Royce, are actively developing such systems based on SOFC technology (see this section). Figure 12 shows the system diagram of such a system.

5. Proton Exchange Membrane Fuel Cells

5.1. Introduction. The PEMFC is being actively developed for transport, small and medium CHP systems, and for portable electronics equipment by many companies in the United States, Europe, and Japan. The most energetic developments are in the automotive sector, with nearly all the major companies having well-funded development programs. The fuel cell has the potential to enable electric cars with performance in terms of speed and range that equals that of internal combustion engine powered vehicles. Some in the industry, notably the chairman of the Ford Motor Company, have speculated that fuel cells will displace ic engines as the prime mover of vehicles in the course of this century. It is the PEMFC that will be used in such vehicles.

5.2. PEMFC Electrodes. The electrochemical activity of the PEMFC electrodes is almost universally provided by a platinum catalyst on carbon support. Successful work in recent years has seen the development of methods of finely dividing the catalyst over the supporting carbon such that excellent performance is obtained with catalyst loading as low as 0.1 mg/cm^2. The structure of the electrode is critical, as it must be porous, have a large surface area, and must allow electron flow to or from the reaction sites. In addition, it must have good ionic conduction with the electrolyte.

5.3. PEMFC Electrolyte. The standard material that has been used by workers in the field is Nafion (Du Pont), a polytetrafluoroethylene (PTFE)-based structure, which is both strong and inert in oxidizing and reducing environments. The proton conductivity is introduced by the addition of sulfonic acid branches to the structure, as in Figure 7.

The sulfonate side chains tend to cluster within the structure of the material. These regions are hydrophilic, and can hold water within the structure. The resulting liquid is acidic. Provided the hydrated regions are sufficiently large, then protons can move freely within the material. Alternative sulfonated polymers are being tried in order to reduce costs. The precise nature of the electrolyte in most PEMFCs is proprietary.

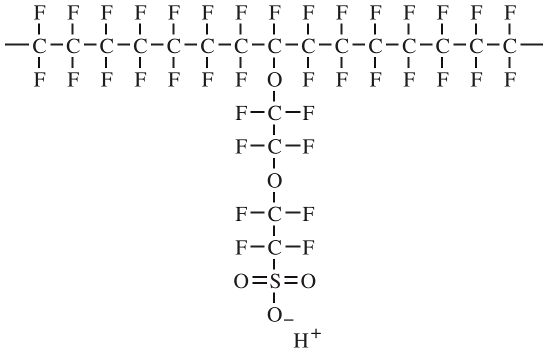

Fig. 7. An example of a sulfonated PTFE structure used as a PEMFC electrolyte.

5.4. Water Management in the PEMFC.

For the proton exchange membrane to work properly, it must be sufficiently hydrated. On the other hand, there must not be too much water or else the electrodes will become flooded, which will prevent the reactant gases permeating the electrode pores. In essence, water supply should be no problem, as water is produced as the main by-product of the fuel cell reaction. As shown in Figure 1, the water is produced at the cathode, and has to diffuse through the membrane. However, since air is circulating over the cathode, the water will evaporate. The cell designer has to ensure that the rate of circulation of air is sufficient to evaporate the water and prevent flooding, but not so great that the membrane dries out. This optimum rate of air flow will vary with current, temperature, and air humidity.

A further complication is that there is a tendency for water to be dragged from the fuel anode toward the air cathode by the protons as they move through the membrane, which exacerbates the problem of the cathode side being more hydrated than the anode. This problem is clearly worse if the current in higher, as the rate of proton movement is higher—exactly when it is most important that membrane be fully and evenly hydrated.

A full explanation of these very important issues is given in Chapter 4 of Ref. 1. Experience and theory shows that it is possible to make PEMFCs that work satisfactorily using solely their own water production (self-humidification) provided that the operating temperature is $<70^{\circ}$C. If the flow of air over the cathode is produced solely by diffusion and convection such cells are said to be “air breathing”. A correct water balance can be achieved at a range of currents because the temperature and humidity, and hence the natural rate of air circulation, will rise with current. Very few such fuel cells have powers in excess of 50 W, and their main application is for portable electronics equipment. The performance in terms of current and power density is not particularly good, but this is compensated by the lack of fans or pumps or any other ancillary equipment. In these cells, the reactant air is also the cooling air.

Somewhat larger self-humidifying PEMFCs are made with pumps carefully controlling the rate of flow of air over the cathodes. Sometimes the incoming air is made more humid by transferring water from the exit air using a membrane.

Such fuel cells have separate cooling systems—the reactant air flow is not sufficient.

However, to get the performance required in automotive applications it is not possible to rely solely on self-humidification. Most high power (>5 kW) PEMFCs operate at ~90°C—and at this temperature the drying effect of the cathode air would result in far too low a hydration level. The hydrogen fuel or incoming air, or both, need to be humidified before they enter the fuel cell, which is known as "external humidification". All practical systems use water condensed out of the hot exit air to humidify the fuel or incoming air. The equipment used is adapted from that used in the air conditioning industry.

5.5. PEMFC Operating Pressure. The optimum operating pressure of the PEMFC is a topic of some controversy. The main benefit of operating at a higher pressure is the higher cell voltage, as given in equation 2. In practice the gain is somewhat more than this equation would predict, because of a reduction in the activation overvoltage that also results from higher pressure. Typically, the voltage gain per cell by increasing the pressure from P_1 to P_2 will be

$$\Delta V_{\text{gain}} = C \ln\left(\frac{P_2}{P_1}\right) \tag{15}$$

Where C is a constant that varies from ~0.05 to 0.10 depending on the fuel cell design and its operating temperature. Set against this voltage gain, work will have to be done to pressurize the incoming air, and possibly the fuel gas too, depending on how it is stored. It can be shown page 95 in Ref. 1 that the power loss involved in compressing the air from a pressure of P_1 to P_2 can be transformed into a voltage loss (per cell) given by the formula

$$\Delta V_{\text{oss}} = 3.58 \times 10^{-4} \times \frac{T_l}{\eta} \times \left[\left(\frac{P_2}{P}\right)^{0.286} - 1\right] \tag{16}$$

Where T_1 is the inlet air temperature; η is the efficiency of the compressor system, including the driving motor, typically ~0.65–0.75, and λ is the stoichiometry of the air supply, typically ~2. The net voltage gain (or loss) is the difference between equations 15 and 16. *In most circumstances the power lost exceeds the power gained.* The exception is on larger more powerful systems involving external humidification. At higher pressure, the mass of water that needs to be added to the incoming reactant gases is less to achieve the same humidity. Also, higher pressure is needed to get the reactant gases through the long gas channels in the large fuel cells. As a result, most automotive PEMFCs operate at ~2 bar. The power consumed by the compressors needed to achieve this pressure is considerable. In most cases, the exit gases provide some of the power using a turbocharger system, but this will not provide enough. In one notable and successful PEMFC design, that of the 250 kW fuel cell engine for buses produced by Ballard in the late 1990s, the total compressor power was ~50 kW, 40 kW of this coming from an electric motor. Thus ~ of the fuel cell output power is taken up with this parasitic load—but the benefits outweigh this loss.

6. Direct Methanol Fuel Cells

6.1. Introduction. In principle, most fuel cell types can be used with methanol as the fuel. However, it is only with the PEM that much serious work is being done. The anode reaction is

$$CH_3OH + H_2O \longrightarrow CO_2 + 6\,H^+ + 6\,e^- \tag{17}$$

Each fully reacted methanol molecule thus produces six electrons. Since it is a liquid at operating conditions, it has a high energy density, and can be produced from natural gas or renewable biological sources. The existing gasoline infrastructure could reasonably easily be adapted to this fuel. In many respects, the direct methanol fuel cell would be an ideal system—which is why considerable research effort is directed toward making it work, although there are many problems.

Development is at early stage with these fuel cells, and issues such as the operating temperature, and even whether the methanol should be fed as a liquid or a vapor, are still issues where a standard practice has yet to evolve.

6.2. DMFC Electrodes. One major problem with the DMFC is that the oxidation reaction of equation 17 does not proceed nearly as readily as for hydrogen. There is thus a considerable overvoltage at the fuel anode. Much research has been undertaken on the mechanisms of methanol oxidation, and Ref. 3 gives a review of this work. A particularly important problem is the intermediate products of the reaction, which can include carbon monoxide. Standard practice is to alloy the platinum catalyst with ruthenium. Another change made in comparison with the hydrogen fueled PEMFC is to increase the ionomer content of the catalyst layer.

The air cathode can be the same as for the hydrogen fueled PEMFC. However, the second major problem for the DMFC is that of “fuel crossover”. Methanol diffuses through the electrolyte and reacts on the air cathode. The resulting mixed reaction greatly reduces the open circuit voltage. One way to reduce this problem is to use catalysts that promote the reduction of oxygen but not the oxidation of the methanol fuel—and considerable work is being undertaken to develop such selective catalysts.

6.3. DMFC Electrolyte. The main difference between the electrolyte in the DMFC and the hydrogen fueled PEMFC is that the optimum thickness will usually be greater, since although proton conductivity is still very important, and better when thin, the problem of fuel crossover is much greater, and a thicker membrane can help with this.

7. The Alkaline Electrolyte Fuel Cell

7.1. Introduction. The anode reaction for the alkaline fuel cell is

$$2\,H_2 + 4\,OH^- \rightarrow 4\,H_2O + 4\,e^- \tag{18}$$

The electrons thus produced pass round the external circuit to the cathode, where they react forming new OH^- ions

$$O_2 + 4\,e^- + 2\,H_2O \rightarrow 4\,OH^- \tag{19}$$

The commercial future of alkaline electrolyte fuel cells is a controversial issue. What is beyond doubt is that the AFC played a crucial role in the development of fuel cells. The pioneering and hugely important work of Bacon in the 1940s and 1950s was undertaken with AFCs. They provided the electrical power and the potable water for the spacecraft that took humans to the moon, and are still used on the Shuttle Orbiter vehicles.

The main advantage of the AFC is that the cathode overvoltage is noticeably less than that found with the acid (including PEM) fuel cells. The main disadvantage relates to terrestrial applications using air or hydrogen derived from hydrocarbons, both of which will contain carbon dioxide. The alkaline electrolyte, usually potassium carbonate, reacts with the carbon dioxide to form potassium carbonate. The main consequences are

- The reduction in OH^- concentration reduces the rate of reaction at the anode.
- The carbonate is less soluble, so will eventually precipitate out, blocking the pores of the electrodes.
- Oxygen solubility is reduced increasing the activation losses at the cathode.
- The electrolyte conductivity is reduced, increasing the ohmic losses.

These problems can be solved by extensive filtering of the gases to remove the carbon dioxide, but this adds to system complexity, cost, size and weight, and complicates servicing. The fact that the product water appears at the fuel anode is another complication, as it means the fuel gas must be circulated actively, with the product water condensed out.

Set against these problems are the facts that the electrolyte, KOH solution, is very low in cost, and that the electrodes can be made considerably more cheaply. Also, there is not the water management problem that the rival PEMFC has to deal with.

A few of small companies are actively developing AFC systems for various transport and small scale CHP applications.

7.2. AFC Electrolyte.

The KOH solution used as the electrolyte can be used in liquid form (mobile) or it can be retained in a matrix (static). The advantage of the static system is that the electrolyte is to all intents and purposes solid, and can be in any orientation. This arrangement is used in the Apollo and Shuttle fuel cell systems, which use pure hydrogen and oxygen. However, for terrestrial systems the mobile system is used, as it permits reasonably easy renewal of the electrolyte, but because much clean up of the reactant gases is attempted, carbonation will eventually occur. The circulation of the electrolyte helps to cool the cell, but it adds to system complexity and costs, as the corrosive liquid is not easy to handle.

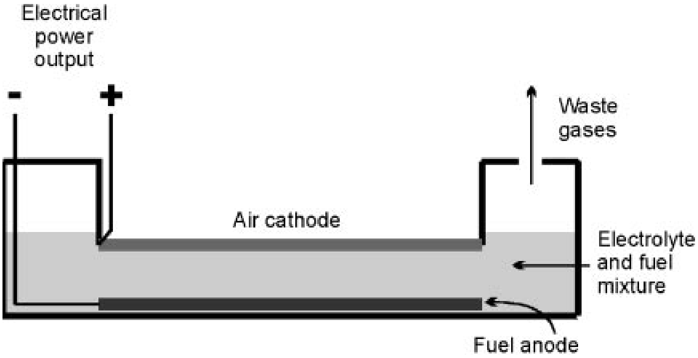

Fig. 8. An electrolyte-dissolved fuel-fuel cell, arguably the simplest of all types.

7.3. AFC Electrodes.

It is possible to make AFCs using nickel electrodes, and many notable cells, including the Bacon cell and the Apollo systems, used nickel as the anode catalyst, and nickel oxide as the cathode catalyst. However, the penalty for this was that the cell had to operate at high pressure, or temperature, or both. For example, the Apollo systems operated at 3.4 bar and 230°C. Lower temperature systems often, but by no means always, use platinum catalysts. These tend to be rolled onto a nickel mesh support, and are bound with PTFE, which, being hydrophobic, expels the product water. There is a thin PFTE layer on the gas side preventing the egress of KOH solution, but allowing the entry of reactant gases.

7.4. Electrolyte Dissolved Fuel AFCs.

An interesting variant of the AFC is that where the fuel is dissolved in the electrolyte. This makes for a very simple fuel cell system, as shown in Figure 8. The fuel will usually be in full contact with anode and cathode, and the fuel crossover problem is dealt with by having an air cathode catalyst that promotes the reduction of oxygen but NOT the oxidation of fuel. Alternatively, there can be a membrane in the electrolyte that alloys the passage of OH^- ions, but blocks the diffusion of the fuel. In any case, the fuel, solid or liquid, can be added to the electrolyte as it is consumed.

Fuels that can be used in this way include methanol, hydrazine, and sodium tetrahydridoborate ($NaBH_4$). The later is currently being actively pursed as a viable fuel cell system, and this idea was the subject of tests in the 1960s and 1970s. However, there are no commercial cells of this type in production, apart from a demonstration cell for education purposes.

8. Phosphoric Acid Fuel Cell

8.1. Introduction.

The phosphoric acid fuel cell is currently the most advanced system in terms of commercial development. Several hundred units, typically of power ~200 kW, are installed as CHP units in hospitals, government buildings, military bases, commercial premises, and even prisons. The great majority of these units are fueled with natural gas, which is steam re-formed, with the carbon monoxide converted using further shift reformation. Typically, a carbon monoxide level of 0.5% can be tolerated, which is much more easily attainable than the 10 ppm or less needed by the PEMFC.

8.2. PAFC Electrolyte. Phosphoric acid (H_3PO_4) is the only common inorganic acid that has good enough thermal, chemical, and electrochemical stability and low enough volatility above ~150°C, to be considered as an electrolyte for fuel cells. Most importantly, phosphoric acid is tolerant to CO_2 in the fuel and oxidant, unlike the alkaline fuel cell.

Phosphoric acid is a colorless viscous hygroscopic liquid. In the PAFC, it is contained by capillary action within the pores of a matrix made of silicon carbide particles held together with a small amount of PTFE. The pure 100% phosphoric acid, used in fuel cells since the early 1980s, has a freezing point of 42°C, so to avoid stresses developing due to freezing and re-thawing, PAFC stacks are usually maintained above this temperature once they have been commissioned. Although the vapor pressure is low, some acid is lost during normal fuel cell operation over long periods at high temperature. The loss depends on the operating conditions (especially gas flow velocities and current density). It is therefore necessary to replenish electrolyte during operation, or ensure that sufficient reserve of acid is in the matrix at the start of operation to last the projected lifetime. The SiC matrix comprising particles of ~1 micron is 0.1–0.2 mm thick, which is thin enough to allow reasonably low ohmic losses while having sufficient mechanical strength and the ability to prevent crossover of reactant gases from one side of the cell to the other. Under some conditions, the pressure difference between anode and cathode can rise considerably, depending on the design of the system. The SiC matrix presently used is not robust enough to stand pressure differences >100–200 mbar.

8.3. PAFC Electrodes and Catalysts. Like the PEM fuel cell, the PAFC uses gas diffusion electrodes. In the mid-1960s, the porous electrodes used in the PAFC were PTFE-bonded Pt black, and the loadings were ~9 mg Pt/cm^2 on each electrode. Since then, Pt supported on carbon has replaced Pt black as the electrocatalyst. The carbon is bonded with PTFE (~30–50 wt%) to form an electrode support structure. The carbon has important functions:

- To disperse the Pt catalyst to ensure good utilization of the catalytic metal.
- To provide micropores in the electrode for maximum gas diffusion to the catalyst and electrode–electrolyte interface.
- To increase the electrical conductivity of the catalyst.

By using carbon to disperse the platinum, a dramatic reduction in Pt loading has also been achieved over the last two decades—the loadings are currently ~0.10 mg Pt/cm^2 in the anode and ~0.50 mg Pt/cm^2 in the cathode. The low Pt loadings that can now be achieved result in part from the small crystallite sizes (down to ~2 nm) and high surface areas (up to 100 m^2/g).

The PTFE binds the carbon black particles together to form an integral (but porous) structure, which is supported on a porous carbon paper substrate. The carbon paper serves as a structural support for the electrocatalyst layer, as well as acting as the current collector. A typical carbon paper used in PAFCs has an initial porosity of ~90%, which is reduced to ~60% by impregnation with 40 wt% PTFE. This wet proof carbon paper contains macropores of 3–50 micron diameter (median pore diameter of ~12.5 micron) and micropores with a median pore diameter of about 3.4 nm for gas permeability. The composite structure consisting of a carbon black/PTFE layer on carbon paper substrate forms a stable, three-phase interface, with electrolyte on one side (electrocatalyst side) and the reactant gas on the other side of the carbon paper.

Lifetimes of 40,000 h are now expected, but electrode performance does decay with time, which is due primarily to the sintering (or agglomeration) of Pt catalyst particles and the obstruction of gases through the porous structure caused by electrolyte flooding. During operation, the platinum particles have the tendency to migrate to the surface of the carbon and agglomerate into larger particles, thereby decreasing the active surface area. The rate of this sintering phenomenon depends mainly on the operating temperature. An unusual difficulty is that corrosion of carbon becomes a problem at high cell voltages (above ~0.8 V). For practical applications, low current densities, with cell voltages above 0.8 V, and hot idling at open circuit potential are therefore best avoided.

8.4. PAFC Stack Cooling. Cooling can be done by either liquid (water/steam or a dielectric fluid) or gas (air) coolants that are routed through cooling channels or pipes located in the cell stack, usually about every fifth cell. Liquid cooling requires complex manifolds and connections, but better heat removal is achieved than with air cooling. The advantage of gas cooling is its simplicity, reliability, and relatively low cost. However, the size of the cell is limited, and the air cooling passages are much larger than those needed for liquid cooling. Therefore water cooling is the most popular method.

Water cooling can be done with either boiling water or pressurized water. Boiling water cooling uses the latent heat of vaporization of water to remove the heat from the cells. Since the average temperature of the cells is ~180–200°C, this means that the temperature of the cooling water is ~150–180°C. Quite uniform temperatures in the stack can be achieved using boiling water cooling, leading to increased cell efficiency. If pressurized water is used as the cooling medium, the heat is only removed from the stack by the heat capacity of the cooling water, so the cooling is not so efficient as with boiling water. Nevertheless pressurized water gives a better overall performance than using oil (dielectric) cooling or air cooling, though these may be preferred for smaller systems.

8.5. PAFC Operating Pressure. Cell performance for any fuel cell is a function of pressure, temperature, reactant gas composition, and utilization. As with the PEMFC, the gains are somewhat higher than equation 2 above would predict. Quoting experimental data collected over some period, Hischenhofer and co-workers (4) suggest the formula

$$\Delta V = 63.5 \ln\left(\frac{P_2}{P_1}\right) \tag{20}$$

is a reasonable approximation for a pressure range of 1 bar $< P <$ 10 bar. However, there are costs involved in raising the pressure, particularly the work that needs to be done to compress the reactant air, as in equation 16. Consequently, PAFCs are almost universally operated at only a very little above atmospheric pressure.

We have also seen above that an increase in temperature should result in a fall in cell voltage. In practice, the kinetics for the reduction of oxygen on platinum improve as the cell temperature increases, which more than compensates for this. Again, quoting experimental data collected over some period, Hirschenhofer and co-workers (4) suggest that at a mid-range operating load ($\sim$250 mA/cm^2), the voltage gain (ΔV_T) with increasing temperature of pure hydrogen and air is given by

$$\Delta V_T = 1.15\ \Delta T\ \mathrm{mV} \tag{21}$$

However, raising the temperature also increases the rate of unhelpful reactions, such as electrolyte evaporation and corrosion, and so most PAFCs operate at $\sim$220°C.

8.6. Effects of Fuel and Oxidant Utilization. Fuel and oxidant utilizations are important operating parameters for fuel cells such as the PAFC where the fuel is a reformed hydrocarbon. The carbon dioxide and unreacted hydrocarbons (eg, methane) are electrochemically inert and act as diluents. If the fuel utilization is too high, the cells near the exit of the fuel gas flow will suffer from large mass flow overvoltages. The same applies on the cathode side, the use of air with $\sim$21% oxygen means that the rate of flow must be sufficient to maintain suitable oxygen concentrations throughout the stack. Low utilizations therefore, particularly oxygen utilization, yield high performance. As mentioned in the section Fuel Cell Efficiency and Efficiency Limit, the drawback of low utilization is lower efficiency and the choice of operating utilizations requires a careful balance of all system and stack aspects. State-of-the-art PAFC systems employ utilizations of typically 85 and 50% for the fuel and oxidant, respectively.

8.7. Effects of Carbon Monoxide and Sulfur. As with the platinum anode catalyst in the PEM fuel cell, the anode of the PAFC may be poisoned by carbon monoxide in the fuel gas. The CO occupies catalyst sites. Such CO is produced by steam re-forming and for the PAFC the level that the anode can tolerate is dependent on the temperature of the cell. The higher the temperature, the greater the tolerance for CO. The absorption of CO on the anode electrocatalyst is reversible and CO will be desorbed if the temperature is raised. Any CO has some effect on the PAFC performance, but the effect is not nearly so important as in the PEMFC. At a working temperature >190°C a CO level of up to 1% is acceptable, but some quote a level of 0.5% as the target.

Sulfur in the fuel stream, usually present as H_2S, will similarly poison the anode of a PAFC. State-of-the-art PAFC stacks are able to tolerate $\sim$50 ppm of sulfur in the fuel. Sulfur poisoning does not affect the cathode, and poisoned anodes can be reactivated by increasing the temperature or by polarization at high potentials

9. Molten Carbonate Fuel Cell

9.1. Introduction. The electrolyte of the molten carbonate fuel cell is a molten mixture of alkali metal carbonates—usually a binary mixture of lithium and potassium, or lithium and sodium carbonates, which is retained in a ceramic

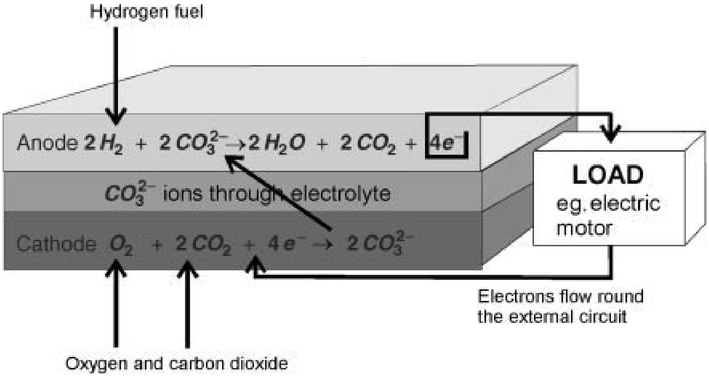

Fig. 9. The anode and cathode reaction for a molten carbonate fuel cell using hydrogen fuel. Note that the product water is at the anode, and that both carbon dioxide and oxygen need to be supplied to the cathode.

matrix of $LiAlO_2$. At the high operating temperatures (typically 600−700°C) the alkali carbonates form a highly conductive molten salt, with carbonate $CO_3{}^{2-}$ ions providing ionic conduction. This is shown schematically in Figure 9 which also shows the anode and cathode reactions. Note that unlike all of the common fuel cells, carbon dioxide needs to be supplied to the cathode as well as oxygen, and this becomes converted to carbonate ions, which provide the means of ion transfer between the cathode and the anode. At the anode, the carbonate ions are converted back into CO_2. There is therefore a net transfer of CO_2 from cathode to anode; 1 mol of CO_2 is transferred along with two Faradays of charge or 2 mol of electrons. The overall reaction of the MCFC is therefore

$$H_2 + \frac{1}{2}\,O_2 + CO_2\,(\text{cathode}) \rightarrow H_2O + CO_2\,(\text{anode}) \tag{22}$$

9.2. Carbon Dioxide Supply for the MCFC. The problem of supplying CO_2 to the cathode is usually solved using the CO_2 generated at the cell anodes. This CO_2 is recycled externally to the cathodes where it is consumed and might at first seem an added complication, and a disadvantage for this type of cell, but this can be done by feeding the anode exhaust gas to a combustor (burner), which converts the unused hydrogen or fuel gas into water and CO_2. The exhaust gas from the combustor is then mixed with fresh air and fed to the cathode inlet, as is shown in Figure 10. This process is no more complex than for other “hot” fuel cells, as the process also serves to preheat the reactant air, burn the unused fuel, and bring the waste heat into one stream for use in a bottoming cycle or for other purposes.

9.3. Fueling the MCFC. An important advantage of the MCFC compared to the PAFC and PEMFC is the abilities to directly electrochemically convert carbon monoxide and internally re-form hydrocarbon fuels.

The steam re-formation of fuels such as methane is dealt with elsewhere, but in most state-of-the-art MCFC this is done internally to the fuel cells.

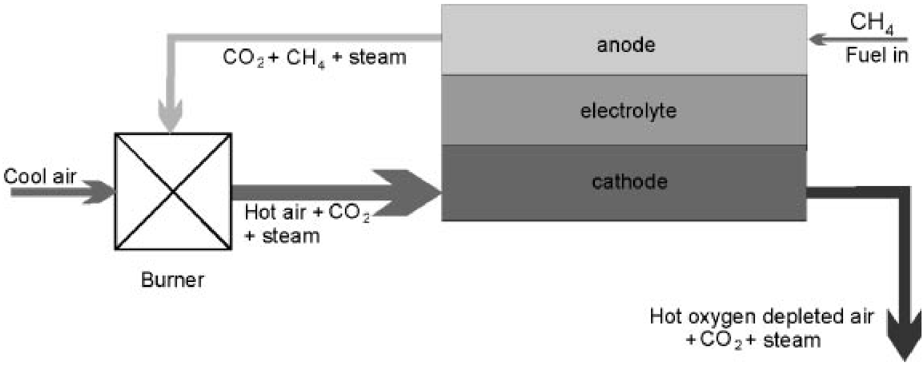

Fig. 10. Adding CO_2 to the cathode gas steam need not add to the overall system complexity.

(Such systems are sometimes called "direct fuel cells".) The basic reaction is

$$CH_4 + H_2O \rightarrow 3\,H_2 + CO \tag{23}$$

This reaction is endothermic, and the energy input required helps cool the cell. The steam required will be available around the anode, as can be seen from Figure 10. In principle, this is a very simple system, though in practice it is not so easy to achieve. One problem is starting the system, another is carbon formation.

The carbon monoxide thus produced can be used by the MCFC as fuel, the anode reaction being

$$2\,CO + 2\,CO_3^{2-} \rightarrow 4\,CO_2 + 4\,e^- \tag{24}$$

The cathode reaction being as with hydrogen. The emf of the carbon monoxide fuel cell is calculated in exactly the same way as for the hydrogen fuel cell, using equation 1. It so happens that at 650°C, the operating temperature of the MCFC, the values for hydrogen and carbon monoxide are remarkably similar, as is shown in Table 3. Thus there is no problem of mixed reaction affecting the cell voltage.

However, since plenty of steam is present in the system, it is possible that the electrochemical oxidation of the CO would probably proceed via the water–gas shift reaction, a fast reaction that occurs on the nickel anode electrocatalyst. The shift reaction converts CO and steam to hydrogen, which then oxidizes

Table 3. **Values of and Δg_f and E for Hydrogen and Carbon Monoxide Fuel Cells at 650°C**

Fuel	$\frac{\Delta g_f}{\text{kJ/mol}}$	E/V
H_2	−197	1.02
CO	−201	1.04

rapidly on the anode. The two reactions (direct oxidation of CO, or shift reaction then the oxidation of H_2), are entirely equivalent.

9.4. Electrolyte. State-of-the-art MCFC electrolytes contain typically 60 wt% carbonate constrained in a matrix of 40 wt% $LiOAlO_2$. The γ form of $LiOAlO_2$ is the most stable in the MCFC electrolyte and is used in the form of fibres of <1-micron diameter. Other materials (eg, larger size particles of $LiOAlO_2$) may be added and many details are proprietary. The matrix is made using tape-casting methods commonly employed in the ceramics and electronics industry. The process involves dispersing the ceramic materials in a "solvent". This solvent contains dissolved binders, plasticizers, and additives to achieve the desired viscosity and rheology of the resulting mixture. This material is then cast in the form of a thin film over a moving smooth surface, and the required thickness is obtained by shearing with an adjustable blade device. After drying, this material is then heated further in air and any binder is burnt out at 250–300°C. The semistiff structure is then assembled into the stack structure. Tape casting of the electrolyte and other components provides a means of producing large area components. The methods can also be applied to the cathode and anode materials and fabrication of stacks of electrode area up to 1 m^2 is now easily achieved.

The ohmic resistance of the MCFC electrolyte, and especially the ceramic matrix, has an important and large effect on the operating voltage, compared with most other fuel cells. Under typical MCFC operating conditions the electrolyte typically accounts for 70% of the ohmic losses. The most important way to reduce the resistance of the electrolyte is to make it thinner. However, there is a tradeoff between low resistance and long term stability, which is aided by thicker materials.

9.5. MCFC Anodes. MCFC anodes are made of a porous sintered Ni–Cr/Ni–Al alloy. These are usually made with a thickness of 0.4–0.8 mm with a porosity of between 55 and 75%. Fabrication is by hot pressing finely divided powder, or by tape casting a slurry of the powdered material, which is subsequently sintered. Chromium (usually 10–20%) is added to the basic nickel component to reduce the sintering of the nickel during cell operation. This sintering can be a major problem in the MCFC anode, leading to growth in pore sizes, loss of surface area, and mechanical deformation under compressive load in the stack. This can result in performance decay in the MCFC, through redistribution of carbonate from the electrolyte. Unfortunately, the chromium added to anodes also reacts with lithium from the electrolyte with time, thereby exacerbating the loss of electrolyte. This can be overcome to some extent by the addition of aluminium, which improves both creep resistance in the anode, and electrolyte loss. Although Ni–Cr/Ni–Al alloy anodes have achieved commercially acceptable stability, the cost is relatively high and developers are investigating alternative materials. Partial substitution of the nickel with copper, for example, can go some way to reducing the materials costs. The anode of the MCFC needs to provide more than just electrocatalytic activity. Because the anode reaction is relatively fast at MCFC temperatures, a high surface area is not required, compared with the cathode. Partial flooding of anode with molten carbonate is therefore acceptable, and is used to good effect to act as a reservoir for carbonate. The partial flooding of the anode also provides a means for replenishing carbonate in a stack during prolonged use.

9.6. MCFC Cathodes. Cathodes are currently made from lithiated nickel oxide, with a thickness of between 0.5 and 1.0 mm. One of the major problems with the MCFC is that the nickel oxide cathode material has a small but significant solubility in molten carbonates. Through dissolution, some nickel ions are formed in the electrolyte. These then tend to diffuse into the electrolyte towards the anode. As the nickel ions move toward the chemically reducing conditions at the anode (hydrogen is present from the fuel gas), so metallic nickel can precipitate out in the electrolyte. This precipitation of nickel can cause internal short-circuits of the fuel cell with subsequent loss of power. It has been found that this problem is reduced if the more basic, rather than acidic, carbonates are used in the electrolyte. Operating at atmospheric pressure and keeping the CO_2 partial pressure in the cathode compartment low also helps this problem, as does using a relatively thick electrolyte matrix.

9.7. MCFC Bipolar Plates. The bipolar plates for the MCFC are usually fabricated from thin sheets of stainless steel. The anode side of the plate is coated with nickel, which is stable in the reducing environment of the anode. It provides a conducting path for current collection and is not wetted by electrolyte that may migrate out of the anode. Gas tight sealing of the cell is achieved by allowing the electrolyte from the matrix to contact the bipolar plate at the edge of each cell outside the electrochemically active area. To avoid corrosion of the stainless steel in this “wet seal” area, the bipolar plate is coated with a thin layer of aluminium, which provides a protective layer of $LiAlO_2$ after reaction of Al with Li_2CO_3. There are many designs of bipolar plate, depending on whether the gases are externally or internally manifolded. Some designs of bipolar plate have been developed especially for internal re-forming, with a re-forming catalyst incorporated within the anode gas flow field.

9.8. MCFC Operating Temperature and Pressure. We have already seen (eq. 2) that increasing the pressure results in an increase in cell voltage. Furthermore equation 2 indicates that the benefit should be higher at the higher temperatures. On the other hand, equation 16 gives the cost of running at higher pressure in terms of the power needed to compress the reactant air. In the MCFC, there are also other costs of running at higher pressure. These include that fact that higher pressure inhibits steam reformation (eq. 23), and also promotes harmful side reactions such as carbon deposition and nickel oxide dissolution at the cathode. For these reasons MFFCs are only very rarely pressurized.

All MCFCs operate at close to 650°C. The melting point must obviously be reached. Above this temperature the main benefit is a reduction in cathode overvoltage, but against this must be set the adverse affects of Gibb’s free energy changes, and the increase in the rate of undesirable processes such as electrolyte evaporation and material corrosion. The result is that 650°C is generally regarded as an optimum operating temperature.

10. Solid Oxide Fuel Cell

10.1. Introduction. The SOFC is a completely solid-state device that uses an oxide ion-conducting ceramic material as the electrolyte. It is therefore simpler in concept than all of the other fuel cell systems described as only two phases (gas and solid) are required. The electrolyte management issues that arise with the PAFC and MCFC do not occur and the high operating temperatures mean that precious metal electrocatalysts are not needed. As with the MCFC, both hydrogen and carbon monoxide can act as fuels in the SOFC.

The SOFC is similar to the MCFC in that a negatively charged ion (O^{2-}) is transferred from the cathode through the electrolyte to the anode. The product water is formed at the anode. Most SOFCs are based on an electrolyte of zirconia stabilized with the addition of a small percentage of yttria (Y_2O_3). Above a temperature of ~700°C, stabilized zirconia possesses an adequate level of a oxygen ion (O^{2-}) conductivity, and therefore the SOFC typically operates between ~700 and 1100°C. This is the highest operating temperature of all fuel cells, which presents both challenges for the construction and durability, and also opportunities, eg, in combined cycle (bottoming cycle) applications.

A feature of the SOFC is that the dominant design, that of Siemens-Westinghouse, is not of the planar type used by all other fuel cell technologies, and also by some developers of SOFC. The tube concept is shown in Figure 11. In the Siemens-Westinghouse design the tubes are 1.5 m long, and have a diameter

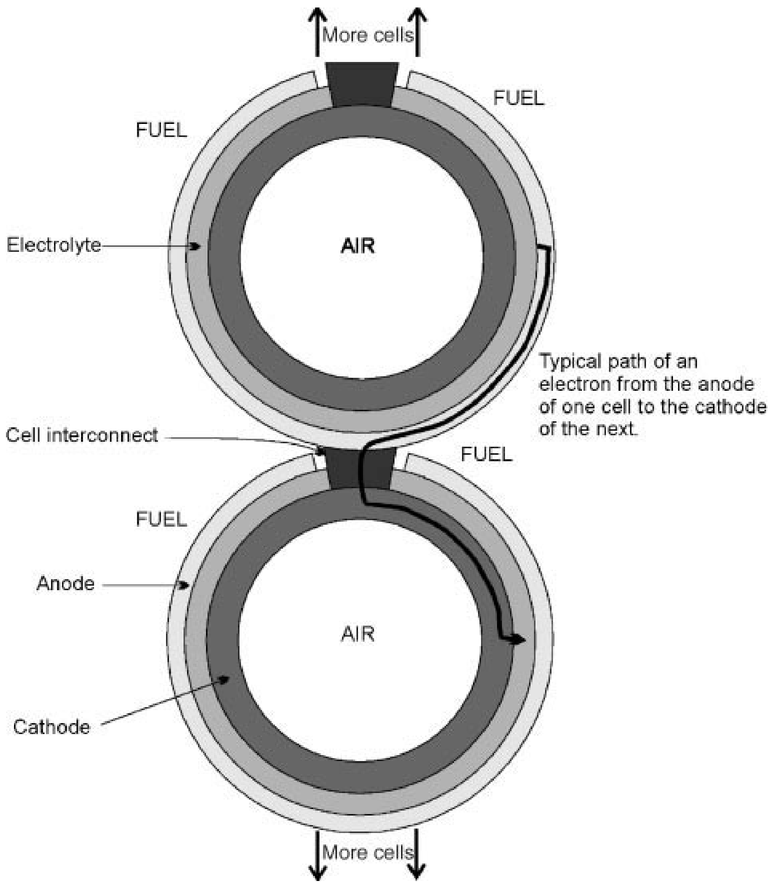

Fig. 11. Tubular SOFC construction.

of 2.2 cm and have one end closed. They are grouped in stacks of 24 cells, with each cell having an operating power of ~200 W. The genius of the tubular design is that the problem of leaks is almost entirely solved, as there are no edges where leaks can happen. The main disadvantage is that the ohmic losses are increased because of the long current path through the cell.

Since the product water forms at the fuel anode, steam is readily available for internally re-forming fuels such as methane. In the Siemens-Westinghouse system, this is accomplished using a certain amount of prereformation that is achieved using partially used fuel, containing steam, which is recirculated through the fuel cell.

10.2. SOFC Electrolyte. Zirconia doped with 8–10 mol % yttria (YSZ) is still the standard electrolyte for the high temperature SOFC, although several others have been investigated including Bi_2O_3, CeO_2, Ta_2O_5 and $LaGaO_3$. Zirconia is highly stable in both the reducing and oxidizing environments, which are to be found at the anode and cathode of the fuel cell, respectively. The ionic conductivity of YSZ (0.02 S/cm at 800°C and 0.1 S/cm at 1000°C) is comparable with that of liquid electrolytes, and it can be made very thin (25–50 micron) ensuring that the ohmic loss in the SOFC is comparable with other fuel cell types. A small amount of alumina may be added to the YSZ to improve its mechanical stability, and tetragonal phase zirconia has also been added to YSZ to strengthen the electrolyte structure so that thinner materials can be made.

Thin electrolyte structures of ~40-micron thickness can be fabricated by Electrochemical Vapor Deposition (EVD), as well as by tape casting and other ceramic processing techniques. The EVD process was pioneered by Siemens-Westinghouse to produce thin layers of refractory oxides suitable for the electrolyte, anode, and interconnection in these tubular SOFC design. However, it is now only used for fabrication of the electrolyte. In this technique, the starting material is a tube of cathode material. The appropriate metal chloride vapor to form the electrolyte is introduced on one side of the tube surface, and an oxygen–steam mixture on the other side. The gas environments on both sides of the tube act to form two galvanic couples. The net result is the formation of a dense and uniform metal oxide layer on the tube in which the deposition rate is controlled by the diffusion rate of ionic species and the concentration of electronic charge carriers.

10.3. SOFC Electrodes. The anode of state-of-the-art SOFCs is a cermet made of metallic nickel and a yttria stabilized zirconia skeleton. The zirconia serves to inhibit sintering of the metal particles and provides a thermal expansion coefficient comparable to that of the electrolyte. The anode has a high porosity (20–40%) so that mass transport of reactant and product gases is not inhibited. There is some ohmic polarization loss at the interface between the anode and the electrolyte and several developers are investigating bilayer anodes in an attempt to reduce this.

The cathode is also a porous structure that must allow rapid mass transport of reactant gases. Strontium doped lanthanum manganite, a p-type semiconductor, is most commonly used for the cathode material. Although adequate for most SOFCs, other materials may be used, particularly attractive being p-type conducting perovskite structures, which exhibit mixed ionic and electronic conductivity.

10.4. SOFC Cell Interconnects. Metals can be used as the interconnect (or bipolar plate in planar systems), but these tend to be expensive Inconel type stainless steels, particularly for stacks that need to operate at 800–1000°C. An advantage for the low temperature SOFC is that cheaper materials may be used, such as austenitic steels. An alternative, and one that is favored for the tubular design, is the use of a ceramic material for the interconnect, lanthanum chromite being the preferred choice. The electronic conductivity of this material is enhanced when some of the lanthanum is substituted by magnesium or other alkaline earth elements. Unfortunately, the material needs to be sintered to quite high temperatures (1625°C) to produce a dense phase, which exposes one of the major problems with the SOFC, that of fabrication. All of the cell components need to be compatible with respect to chemical stability and mechanical compliance (similar thermal expansion coefficients). The various layers need also to be deposited in such a way that good adherence is achieved without degrading the material due to the use of too high a sintering temperature. Many of the methods of fabrication are proprietary and considerable research is being carried out in this field.

10.5. SOFC Operating Pressure and Temperature. The improvement in cell voltage obtained by a rise in pressure follows the Nersnt equation quite accurately, as the activation overvoltages are not large in the SOFC, and so any effect of pressure is small. Equation 2 can be reduced to

$$\Delta V = 0.027 \ln\left(\frac{P_2}{P_1}\right) \tag{25}$$

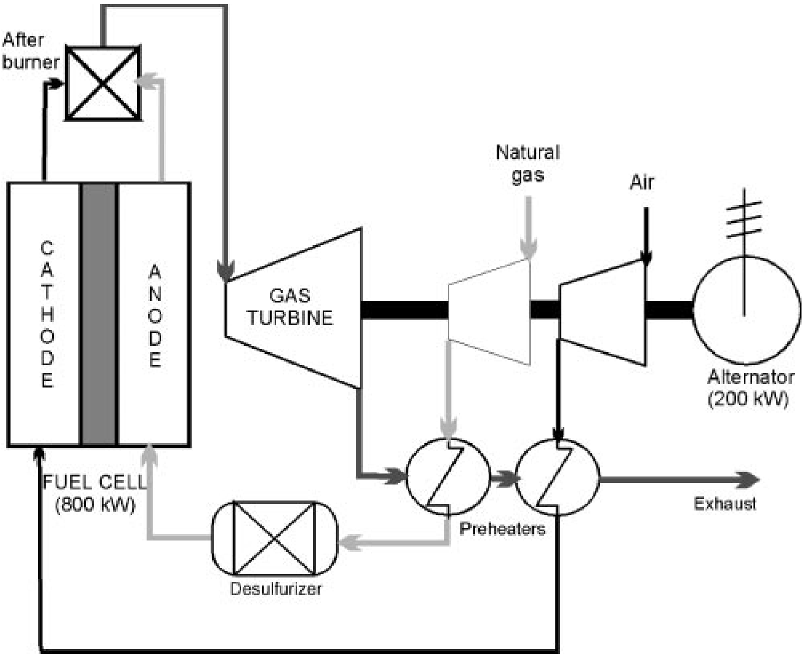

Fig. 12. SOFC and gas turbine combined cycle system.

for most SOFCs. The increase in performance does not warrant the extra power consumed in compressing the reactant gases when the SOFC is being used purely to generate electrical power and heat. However, the benefits are more significant when used in combined cycle systems such as Figure 12, and in such systems the operating pressure is usually ~3 bar.

The temperature of an SOFC has a very marked affect on its performance, though the details will vary greatly between cell types and materials used. The predominant effect is that higher temperatures increases the conductivity of the materials, and this reduces the ohmic losses within the cell. Ohmic losses are the most important type of loss in the SOFC.

For SOFC-combined cycle systems, it is beneficial to keep the operating temperature of the SOFC high. For other applications, such as CHP, and possible transport applications, it is an advantage to operate at lower temperatures, as the higher temperatures bring material and construction difficulties. Unfortunately, the performance decreases substantially for SOFCs as the temperature is lowered. For this reason, the operating temperature for SOFCs is currently ~1000°C. The main advantage of operating at lower temperatures is the possibility of using cheaper construction materials and methods. Making electrolytes and electrodes that work well at lower temperatures is a major focus of current SOFC research.

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GENERAL REFERENCES

Reference 1 provides a clear explanation of all the technology related to fuel cell systems for people from a technical, but not necessarily chemical, background.

Reference 4 provides a wealth of detail on the performance of real fuel cell systems, especially the effects of time, temperature, pressure, impurities, etc, which is based on the published performance of real fuel cells. It appears to be updated roughly every two years.

Reference 6 Contains an unsurpassed list of references in the field of fuel cell science.

Fuel Cells—from Fundamentals to Systems and *The Journal of Power Sources* are good journal references.

Hydrogen and Fuel Cell Letter is a long established newsletter.

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