Fuel Cells and their Development

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A survey of modern fuel-cell types is given, and for each type the problem and potential advantages are discussed. The long-term market penetration of fuel cells is assessed, with transport identified as a key area.

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1. Introduction

Fuel cells remain an enigma: no other technology has taken so long to advance from initial discovery to widespread application, and even today there remain real doubts about the extent to which fuel cells will penetrate the energy generation market (Blomen & Mugerwa 1993; Appleby & Foulkes 1989). The advantages of fuel cells are well rehearsed: they possess high thermodynamic efficiencies, particularly when used with hydrogen as a fuel, excellent part-load characteristics, rapid response times, low pollution emission behaviour, simplicity of mechanical engineering, good power/weight ratio and their modularity of construction makes them ideally flexible in power provision. Such advantages should have led to rapid and extensive exploitation of fuel cells in a wide variety of environments, but historically this has not happened, and we need to explore the reasons for this with some care.

To understand the problems faced by fuel cell technology, we should first investigate the generic problems inherent in fuel-cell operation. A fuel cell is a device that converts chemical free energy into electrical energy. Any chemical reaction whose overall free energy is *negative* can be used to drive a fuel cell, the maximum voltage from such a cell being given by (Brett & Brett 1993)

$$E = -\Delta G/nF, \tag{1.1}$$

where n is the number of electrons involved in each of the half-cell reactions making up the overall chemical process in the fuel cell and $F = 96\,500\ \mathrm{C\ mol^{-1}}$ is the Faraday.

A very simple realization of a fuel cell is shown in figure 1, which demonstrates the mode of operation of an alkaline fuel cell, so called because the electrolyte is aqueous KOH. The cell consists of two electrodes: at the *anode*, hydrogen is oxidized to water as

$$\mathrm{H_2 + 2OH^- = 2H_2O + 2e^-} \tag{1.2}$$

and at the *cathode*, oxygen (usually supplied as air) is reduced to hydroxide ions

$$\tfrac{1}{2}\mathrm{O_2 + H_2O + 2e^- = 2OH^-}. \tag{1.3}$$

The *nett* chemical reaction, the sum of the anode and cathode reactions, is then

$$\mathrm{H_2} + \tfrac{1}{2}\mathrm{O_2 = H_2O}, \tag{1.4}$$

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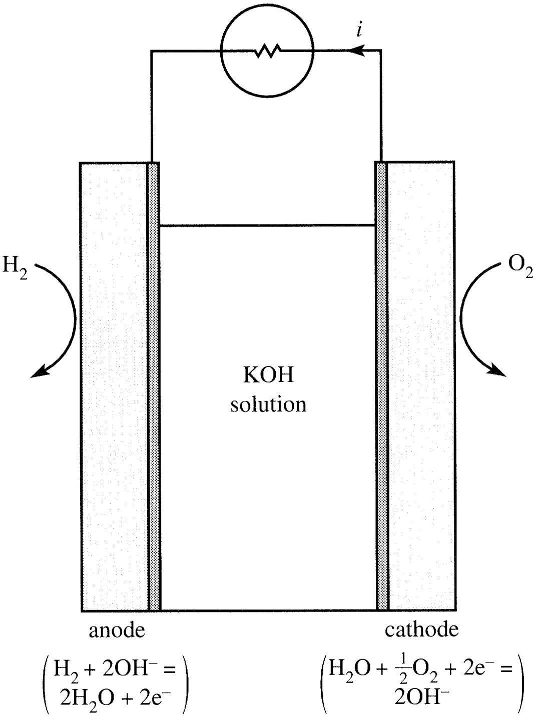

Figure 1. A schematic of an alkaline fuel cell, with the flow of current shown conventionally.

which can be seen to be the combustion of hydrogen in air. Such a reaction can, of course, be used to drive an internal combustion engine, but if electrical power is required, the *direct* conversion of the free energy associated with (1.4) in a fuel cell represents an exceedingly attractive alternative, at least in principle.

However, it will be noted that the fuel used is hydrogen, and therein lies one of the major problems for fuel cells. All attempts to drive fuel cells directly using primary fuels, such as coal oil, natural gas, etc., have failed (Blomen & Mugerwa 1993), at least with low-temperature devices such as that shown in figure 1, and either high temperatures or fuel reforming or both have proved necessary, leading to high costs associated with the use of expensive catalysts or complex engineering. These interconnected problems have bedevilled efforts to build commercially attractive fuel cell systems. Since the work of Grove, more than 150 years ago, led to the realization of the first fuel cell, hydrogen–oxygen fuel cells of steadily increasing efficiencies have been fabricated, but this enhanced performance has not been sufficient to justify the costs of isolation of H_2 from the primary fuels available. The dominance of coal in the nineteenth century led to innumerable attempts to explore the latter's electrochemistry, attempts only abandoned when it was realized that not only would the ash severely contaminate the molten KOH favoured as the electrolyte, but that this electrolyte actually reacted directly with carbon when moisture was present.

The end of the nineteenth century saw, at least in America, the rise of oil and renewed efforts to realize fuel cells based directly on hydrocarbon oxidation at the anode. Facile splitting of the non-polar C–C bond has remained beyond the reach of electrocatalysis (Lund & Baizer 1991), and the activation of the C–H bond to allow controlled electrochemical oxidation also remains an elusive goal. As we shall see below, *internal reforming* of natural gas remains a real possibility for at least one type of modern fuel cell, based on molten carbonate (see issue 9 of *Ber. BunsenGes. Phys. Chem.* **94** (1990)), but for both coal and heavy hydrocarbon fractions, reforming externally with steam remains the only option, resulting in fuel cell systems that are both technically complex and prone to the production of sulphur-containing poisons.

The emergence of natural gas as a major energy vector has altered the equation in several ways: methane can be reformed with high efficiency, and considerable ingenuity has been expended on the design of reformers that are significantly less complex than those required for heavier fuels. The innate purity of natural gas has also led to considerable advantages in terms of poisoning, allowing internal reforming as a possibility, as well as the coupling of external reformers to low-temperature fuel cells that are particularly prone to poisoning. Even more attractive is the possible use of methanol as a major fuel, since this is a liquid that can be transported easily and would be ideal for traction. Methanol is appreciably more reactive than methane, it can be reformed at temperatures of *ca.* 300 °C and is even sufficiently *electro*active for direct oxidation at the anode at temperatures in excess of *ca.* 100 °C. A *direct* methanol fuel cell, as implied by the latter possibility, would indeed be a serious competitor for traction applications, since the costs of reforming need no longer be considered (Hamnett & Troughton 1992).

In rehearsing the problems of the *anode*, it would not be appropriate to lose sight of the fact that even for a hydrogen based fuel cell there are other problems that reduce both efficiency and practicability. Perhaps the most serious is the relatively poor performance of electrocatalysts on the *cathode* side. Reduction of oxygen does not take place until relatively high overpotentials (*ca.* 0.3 V) (Kinoshita 1992) and a typical current–potential curve for a fuel cell is shown in figure 2. This illustrates the very large losses at reasonable current densities (*ca.* 0.5 A cm^{-2}) associated both with the necessity to provide high overpotentials and, at higher current densities, with ohmic losses associated with the finite ionic resistivity of the internal electrolyte. At very high power loads, an additional loss associated with fuel transport is encountered; the finite solubility of hydrogen and oxygen in ionic electrolyte inevitably leads to difficulties at high enough current densities, where the cell performance declines catastrophically.

2. Types of fuel cell

(*a*) *The alkaline fuel cell*

The alkaline fuel cell is the simplest low-temperature fuel cell in concept and operation, and is shown schematically in figure 1. It operates at temperatures of *ca.* 70 °C, and even at room temperature has power levels of *ca.* 50% of those at the nominal operating temperature. Within Europe, stacks have been constructed and tested by Elenco and Siemens particularly, and considerable experience gained in operation of fuel cells in general (van der Broeck 1993).

The electrode construction is critically important in this, as in all low-temperature systems, with the primary requirements being: (*a*) good electronic conductivity to reduce ohmic losses; (*b*) adequate mechanical stability and suitable porosity; (*c*) chemical stability in the rather aggressive alkaline electrolyte; (*d*) stable electroactivity of the catalyst with time. These are quite demanding considerations, especially as the cell must operate over several years. Normally, the electrodes have been fabricated

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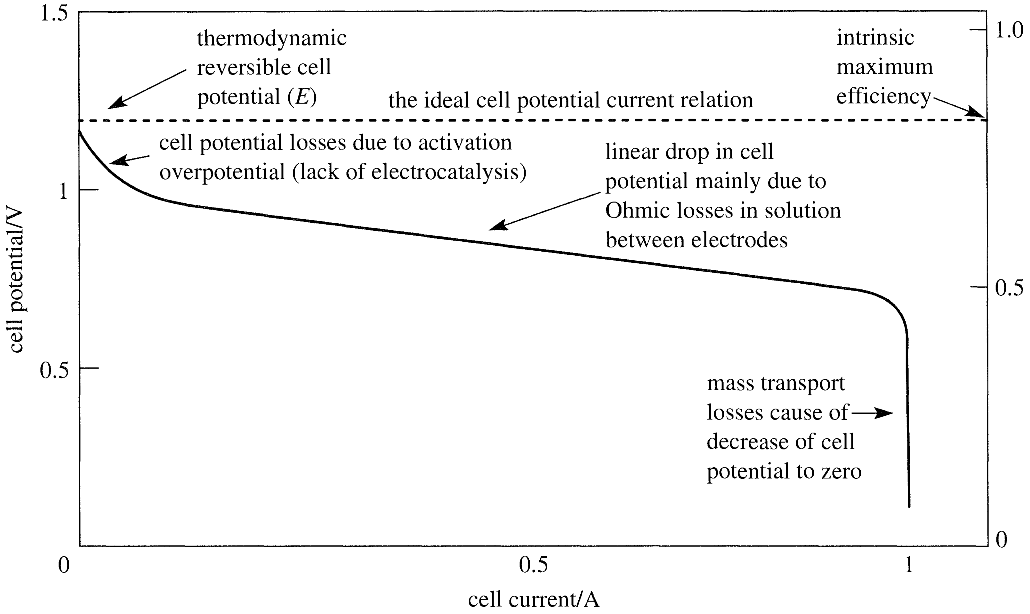


Figure 2. Typical plot of cell potential against current for fuel cells, illustrating regions of control by various types of overpotential.

from a mixture of carbon and PTFE, the latter controlling both the macroporosity of the electrode and its hydrophobicity. By using a multi-layer structure, with an outer uncatalysed but highly hydrophobic layer to allow ingress of gas without egress of electrolyte, free standing electrodes can be made. Furthermore, the cost of the current collector is relatively low in these systems, since nickel mesh can be used.

The primary cost of these electrodes lies in the catalyst particularly for the cathode. The Elenco electrodes used platinum, though with a relatively low loading ($0.6\ \mathrm{mg\ cm^{-2}}$), but an immense advantage of alkaline electrolytes is that the oxygen reduction reaction is relatively facile, and non-noble metal catalysts can be used: the Siemens electrodes, for example, used Ti-doped Raney Nickel at the anode and silver at the cathode, the latter with a rather high loading of $60\ \mathrm{mg\ cm^{-2}}$.

The primary problems associated with the alkaline fuel cell are: (*a*) operation in air is problematic owing to the presence of CO_2, which is absorbed into the alkaline electrolyte, generating the relatively insoluble K_2CO_3 which, in turn, can deposit on and foul the cathode. CO_2 must, therefore, be scrubbed from the air if it is used as the oxidant; (*b*) the poisoning of the electrodes, which is particularly severe for platinum, since the anode can be poisoned by traces of CO in the hydrogen arising from suboptimal efficiency of the reformer, or by sulphur-containing compounds derived from the primary fuel; (*c*) removal of the main combustion product, water, which would otherwise dilute the KOH and reduce performance. This is achieved in the Siemens cell by a remarkable piece of engineering, in which the electrolyte is pumped through the cell, carrying away waste heat, and is then passed through an evaporator, in which a hydrophobic diffusion membrane eliminates excess water from the electrolyte, passing it back at its normal strength into the stack. It should, however, be emphasized that the evaporator is comparable in size to the stack, giving a rather large overall system.

The alkaline fuel cell is perhaps best known for its role in the Apollo programme, for which its compact structure, high power/weight ratio and reliability made it ideal. The hydrogen and oxygen could be carried in cryogenic form, and the product, water, used in the capsule. By using high catalyst loading, the performance of the cell exceeded 70% in efficiency terms, and there has recently been a revival of interest in such cells as the basis of a *regenerative* system in which a water store can be electrolysed to hydrogen and oxygen with photovoltaics. These gases are then stored for use during the satellite's dark period, when they can be recycled through the fuel cell.

The other main area of interest has been in military applications, where the low thermal signature, silent operation and pollution-free exhaust of the fuel cell is extremely attractive in terms of detection by common acoustic and infrared equipment. Operation of submarines under these conditions is especially important, but in principle any military vehicle could be adapted. Progress in the adaptation of alkaline fuel cells to traction more generally has been much slower, partly because the economics of using fuel cells in vehicles must ultimately address the problem of cost. The costs of internal combustion engine technology are now very low indeed, with figures of 50–100 $\$ \mathrm{kW}^{-1}$ quoted for a normal family car; current fuel-cell technology is quite remote from that figure, with the result that exploration of niche markets is essential. One such market is the powering of city buses, where environmental considerations are playing an increasingly important role. The overall costs of bus operation are quite different from those associated with private vehicles, and the depreciation of the cell plays a much smaller role in the economic assessments that have been carried out. However, the difficulties of operation with *air* as an oxidant in these applications, which would be essential if the overall weight of the system is to be minimized, have militated in favour of the solid–polymer electrolyte systems described in more detail below.

(*b*) *The phosphoric acid cell*

The difficulties associated with the use of air as an oxidant in alkaline fuel cells sparked considerable interest in the exploration of acidic media, where CO_2 would present fewer problems. The common mineral acids, however, present quite serious problems in this regard: adequate conductivities can only be attained at temperatures close to boiling, at which the thermal instability of the commoner strong oxy-acids, particularly in contact with powerful noble-metal catalysts, can lead to decomposition products that poison the electrodes. Perchloric acid was found to be explosively unstable in contact with the fuel, the hydrohalic acids are extremely corrosive, and perfluorosulphonic acids, though possessing considerable advantages such as high ionic conductivity, thermal stability, high oxygen solubility and low adsorption on the platinum catalysts, have led to electrode flooding through their high wettability on PTFE and have presented considerable concentration management problems as well as being much more expensive. The restrictions on temperature associated with these acids was particularly troublesome as the kinetics of the oxygen reduction reaction are poor in acid at low temperature, a drawback that can most easily be overcome by increasing the temperature to take advantage of the positive enthalpy of activation.

Phosphoric acid at room temperature is only slightly dissociated, showing very low conductivity even in concentrated solution, and oxygen reduction at low temperatures on platinum shows very poor kinetics owing to strong competitive adsorption

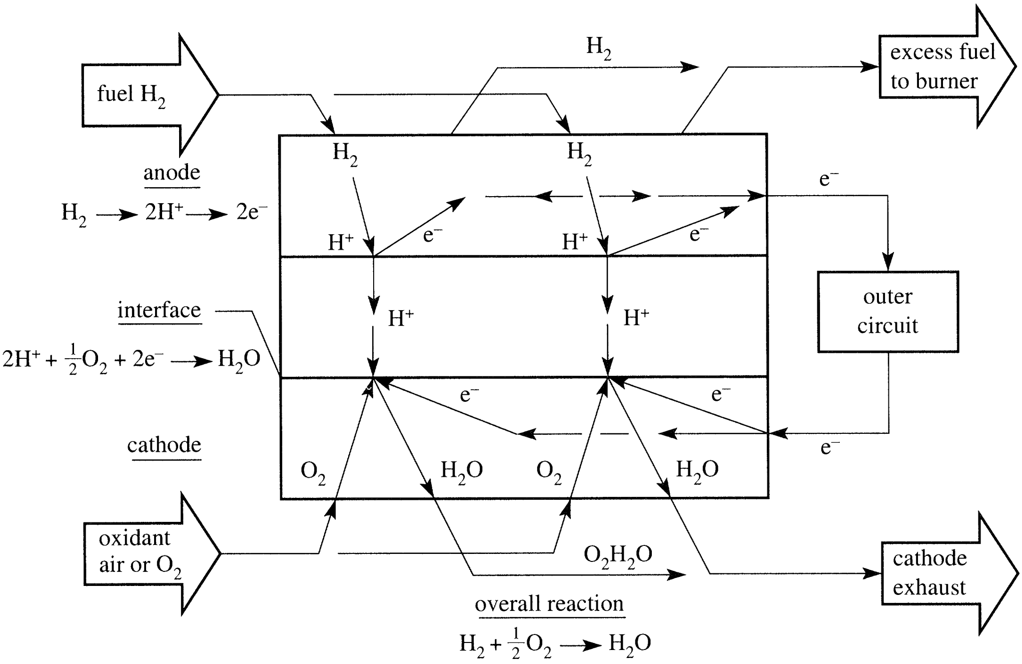


Figure 3. Principles of operation of phosphoric acid fuel cell.

of phosphate ions. However, at temperatures above *ca.* 150 °C, the pure acid is found predominantly in the polymeric state, as pyrophosphoric acid, which is a strong acid of high conductivity and the large size and low charge density of the polymeric anions leads to low chemisorption on platinum, facilitating the oxygen reduction reaction. Other advantages of phosphoric acid include: workability at high temperatures; tolerance to CO_2; low vapour pressure; high oxygen solubility; low corrosion rate and large contact angle. The result is that since its introduction in 1967, the phosphoric-acid fuel cell has undoubtedly come to dominate the low-temperature fuel cell market, and is the only commercially available fuel cell.

The basic principles of the cell are shown in figure 3, and the stack realization is shown in figure 4. The reactions taking place are: at the anode

$$H_2(g) = 2H^+ + 2e^- \tag{2.1}$$

and at the cathode

$$2H^+ + \tfrac{1}{2}O_2 + 2e^- = H_2O(g). \tag{2.2}$$

The basic design of the stack is bipolar, with separator plates used to delineate the individual cells. Within each cell, impervious graphitic carbon sheets are used for the bipolar plates, and each electrode is formed of a ribbed porous carbon-paper substrate onto which is affixed a catalyst layer composed of a high-surface-area carbon powder compacted with PTFE, which acts both as a binder and to control the hydrophobicity of the electrode. Between anode and cathode is a porous matrix formed from PTFE bonded silicon carbide impregnated with phosphoric acid that acts as the electrolyte and also as a separator to prevent the oxidant and fuel gases mixing; since there is some loss of electrolyte, means of replenishment are incorporated into the cell. The operating temperature lies between 190 and 210 °C, and active cooling systems, using air, water or dielectric liquid, are essential.

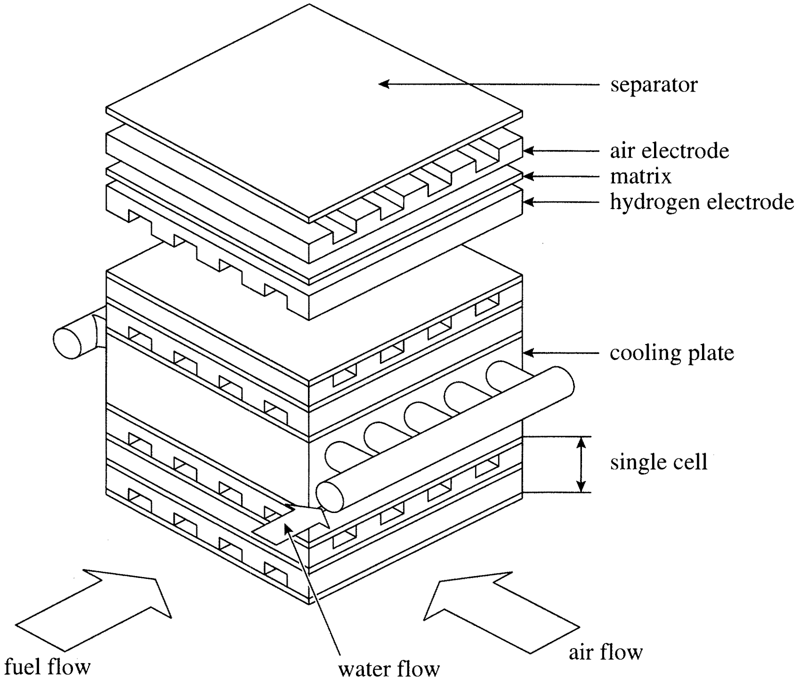


Figure 4. Model of a phosphoric acid fuel cell stack system showing the principal components and the water-colling system.

The performance of the PAFC has been carefully studied. The greatest loss of efficiency is in the stack itself: the efficiency of the stack is given by

$$\eta_{\mathrm{FC}} = \frac{\text{electrical energy generated in the cell}}{\text{hydrogen energy consumed in cell}}$$

and for the PAFC, operating under standard conditions of 150–350 mA cm^{-2} under one atmosphere pressure, with a cell voltage of 700–600 mV, $\eta_{\mathrm{FC}} \approx 0.4$–$0.5$. Other losses in the overall system include: (*a*) the fuel processing efficiency (ratio of the heating value of hydrogen supplied to the fuel cell to the heating value of natural gas to the reformer) which is normally in the range 0.8–0.85; (*b*) the inverter efficiency (ratio of the AC output power from the inverter to the DC input power from the stack), which normally is very high, *ca.* 0.96 and (*c*) the auxiliary power factor, η_{m} (defined as the ratio of the ac output to load to AC output power from the inverter) which is usually also very high, *ca.* 0.97. Combining these together yields a value of *ca.* 0.35–0.4 for the overall efficiency of a PAFC.

The primary difficulties encountered in the phosphoric acid system have been the poisoning of the platinum electrocatalyst by H_2S and CO, both of which are present in the reformed fuel. It is vital to incorporate a desulphurizer in the fuel stream to reduce the former to ppm levels, but by operating above 180 °C, the sensitivity of the platinum to CO has been much reduced, and it is possible to operate with CO levels as high as 1–2%. Even so, the demands on fuel purity do lead to considerable engineering complexity in the design of the overall system, with heat management a very significant problem. Even a simplified flow system for the fuel consists of a desulphurization stage, a steam reformer, a two stage shift converter and a separator. Incorporation of these stages into a proper heat balance system substantially reduces the flexibility of operation of the overall stack, and the PAFC has been developed mainly for stationary power applications, where operation under steady-state conditions can take place.

The commercial importance of PAFCs has led to considerable research on the cell lifetimes, which in turn are known to depend on operating conditions such as working temperatures, voltages, pressures and modes of operation, such as start-up and shut down conditions. All PAFCs are observed, however, to deteriorate with time, and this has been traced to agglomeration of the platinum catalyst particles, corrosion of the support carbon, particularly at the cathode, progressive electrode flooding and loss of acid. The oxidation of the carbon support has important implications for operation of the cell; oxidation of carbon to CO_2 is known to take place at the cathode at potentials above *ca.* 0.8 V, and experimental data do show a much higher rate of deterioration at cell voltages in excess of this value. In addition, severe transient conditions are found to be highly detrimental to performance, since uncontrolled pressure differences can build up that can lead to electrode flooding or starvation. In this regard, proper control of the reactant gases to the cell is essential, particularly under conditions of varying demand.

The development of the PAFC has taken two directions. The most important is the construction of relatively large stationary power units, such as the 11 MW system at Goi, near Tokyo in Japan, with smaller systems in the US and Europe, which have allowed technologists to study the operation of these systems under real conditions. Smaller scale local CHP systems are also under active development, with the key advantage being the lack of any efficiency penalty for partial-load operation, even under 50% load; this balance is particularly suitable for applications such as small hospitals. There has also been considerable investigation of vehicular applications, using reformed methanol as the fuel, again directed at buses as the primary commercial goal. Again, it would seem that niche markets may dictate the success of such systems in the next few years.

(*c*) *Molten carbonate fuel cell*

The necessity of using noble-metal catalysts and the sensitivity of the phosphoric acid fuel cell to significant quantities of CO are serious drawbacks; only by working at higher temperatures can the kinetics of the oxygen reduction reaction be sufficiently accelerated for the use of cheaper catalysts, and as we have already seen, high temperatures also favour the desorption of adsorbed CO. In addition, heat from higher temperature fuel cells can be used in combined cycle operation, allowing us to increase the system efficiency quite substantially, albeit at the cost of flexibility of operation. An additional advantage of high-temperature operation is improved compatibility with the operating temperature of the reformer, allowing us, at least in principle, the attractive prospect of combining the reformer with the fuel cell stack (Selman 1993).

The basic principle of operation of molten carbonate fuel cells is shown in figure 5. At the cathode, made from porous lithiated NiO ($Li_xNi_{1-x}O$: $0.022 \leqslant x \leqslant 0.04$), the reaction is

$$\tfrac{1}{2}O_2 + CO_2 + 2e^- = CO_3^{2-}. \qquad (2.3)$$

The electrolyte is a eutectic mixture of 68% Li_2CO_3/32% K_2CO_3, at a temperature of 650 °C, retained in a porous γ-$LiAlO_2$ tile. At the anode, made from a porous

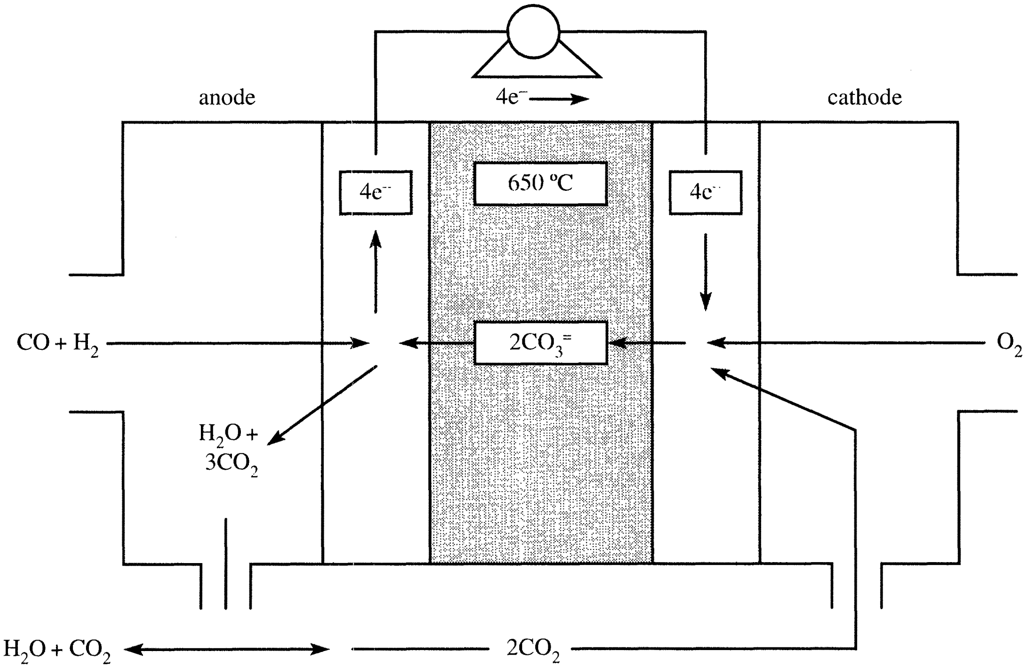


Figure 5. Schematic diagram of a molten carbonate fuel cell.

Ni–10 wt%–Cr alloy (the Cr preventing sintering), the reaction is

$$H_2 + CO_3^{2-} = H_2O + CO_2 + 2e^-. \tag{2.4}$$

In a practical cell, the CO_2 produced at the anode must be transferred to the cathode, which can be carried out either by burning the spent anode stream with excess air and mixing the result with the cathode inlet stream after removal of water vapour or by directly separating CO_2 at the anode exhaust point. A major advantage of this cell is that CO, far from being a problem, can actually serve as the fuel, probably through the water–gas shift reaction,

$$CO + H_2O = CO_2 + H_2, \tag{2.5}$$

which at 650 °C equilibrates very rapidly on Ni.

We have seen that at least in principle, the reformer and stack temperatures are sufficiently comparable for the two to be combined, and three configurations have been suggested: (*a*) indirect reforming, in which a conventional reformer is provided operating separately from the stack; (*b*) direct internal reforming, in which the reformer catalyst pellets are incorporated into each anode gas inlet channel, and therefore operate at 650 °C, a temperature maintained by direct heating of the anode compartment; (*c*) indirect internal reforming, in which the reformation takes place in separate catalyst chambers installed in a stack between a set of cells so that waste heat from the fuel cell stack is supplied to help maintain the reformer temperature during the endothermic reformation process. The most elegant solution is (*b*), which is also the most cost-effective solution, but contamination from electrolyte vapour in the anode space leads to rapid degradation of the catalyst performance (Ishida 1990).

The overall performance figures for the MCFC reflect the fact that the E^0 value for reaction (1.4) above is reduced from the room temperature value with a nett value of 1.02 V at 650 °C. The cell current drops almost linearly with increasing current; at ambient pressures, state-of-the-art cells show a voltage of 0.70–0.75 V at 150–160 mA cm^{-2}, though this can be appreciably enhanced with pressure.

Problems with the MCFC are: (*a*) the oxygen reduction reaction remains relatively slow, and its mechanism depends critically on the electrolyte, with the initial reduction product being either peroxide in Li-rich mixtures or *super*oxide in K-rich electrolytes, with both present at the eutectic composition; (*b*) dissolution of NiO leads to serious problems since the Ni(II) can migrate to the anode where, at the low potentials, it deposits as the metal. The deposition of metal grains in the pores of the tile can lead, eventually to the formation of electronically conducting pathways through the electrolyte, effectively short-circuiting the cell. The dissolution of Ni is related to the partial pressure of CO_2, and may involve the reaction:

$$\mathrm{NiO} + \mathrm{CO_2} = \mathrm{Ni^{2+}} + \mathrm{CO_3^{2-}}. \tag{2.6}$$

(*c*) Water must be present in the feed gas to avoid carbon deposition through the Boudouard reaction:

$$2\mathrm{CO} = \mathrm{CO_2} + \mathrm{C}. \tag{2.7}$$

(*d*) Electrolyte management is a key problem in the MCFC; the control of the three-phase boundary relies on controlling the extent to which the molten carbonate is drawn out of the tile at the cell operating temperature by capillary action. By careful choice of pore size in electrode and tile, and by partially pre-filling the porous electrodes themselves, an initially optimum distribution of electrolyte can be assured, but throughout the lifetime of the cell, a slow but steady loss of electrolyte has been found, that leads to gradual performance decay. This decay may, however, become catastrophic if loss of electrolyte from the tile leads to the tile becoming permeable to the fuel gases; gas crossover is usually accompanied by intense local hotspots and rapid loss of performance, and it is therefore essential that a liquid layer is maintained at all times.

(*d*) *Solid-oxide fuel cell*

At a sufficiently high temperature, all kinetic limitations at the cathode will disappear, and it also becomes possible to use solid ceramic oxide-ion conductors that show very high conductivities above *ca.* 900 °C (Murugesamoothi *et al.* 1993; Bruce 1995).

The principle of operation of these cells is shown in figure 6. The electrolyte is typically ZrO_2 with 8–10 mol% Y_2O_3; the latter not only stabilizes the fluorite structure, preventing transition at lower temperatures to the baddeleyite phase with resultant shattering of the ceramic, but confers a substantial ionic conductivity through the presence of mobile O^{2-} ions. Research has been carried out into improved electrolytes, which must: (*a*) show high oxygen ion conductivity and minimum electronic conductivity; (*b*) good chemical stability with respect to the electrodes and inlet gases; (*c*) have a high density to inhibit fuel crossover; (*d*) have a thermal expansion compatible with other components. Materials such as Bi_2O_3 and doped-CeO_2 do show higher oxide-ion conductivity at lower temperatures than stabilized zirconia, but are more easily reduced to electronic conductors at the anode.

The anode requirements are: effective oxidation catalyst; high electronic conductivity; stability in the reducing environment; thermal expansion compatible with

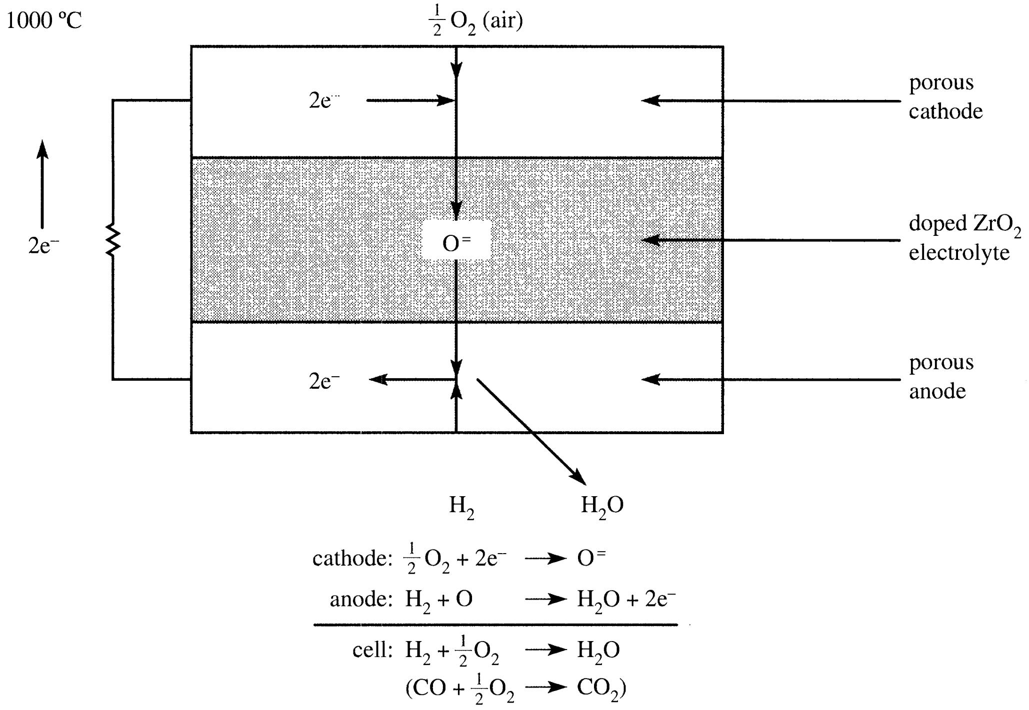


Figure 6. Principles of operation of a high-temperature solid-oxide electrolyte fuel cell.

the electrolyte and other fuel cell components; a physical structure offering low fuel transport resistance; chemical and mechanical stability; and tolerance to sulphur contaminants. The anode most closely satisfying these requirements is a porous *ca.* 35% $Ni–ZrO_2/Y_2O_3$ cermet with good electronic conductivity. Unlike conventional electrodes, there is no necessity for a well defined three-phase boundary, since oxidation of the fuel gas can take place over the entire electrode surface in this mixed electronic/ionic conductor. The anode reaction is

$$H_2 + O^{2-} = H_2O + 2e^-. \tag{2.8}$$

The cathode must (i) exhibit good electrocatalytic activity for O_2 reduction; (ii) show good electronic conductivity since it must serve as the current collector. The combination of high temperature and an oxidizing atmosphere lead to severe materials problems at the cathode, which must be stable over very wide ranges of oxygen pressure, involatile, not show any destructive phase changes, should adhere strongly to the electrolyte over a very wide temperature range, possessing, therefore, a coefficient of expansion essentially identical to ZrO_2, and should form a junction with the zirconia of very low resistance. The cathode material most closely satisfying these requirements is porous perovskite manganite of the form $La_{1-x}Sr_xMnO_3$ ($0.10 < x < 0.15$), which shows a transition from small polaron to metallic conduction near 1000 °C. It also exhibits mixed ionic/electronic conduction, again allowing reduction of the oxygen to take place over the entire surface. The cathode reaction is

$$\tfrac{1}{2}O_2 + 2e^- = O^{2-}. \tag{2.9}$$

Realization of the cell in practical terms is through three competing designs, a planar

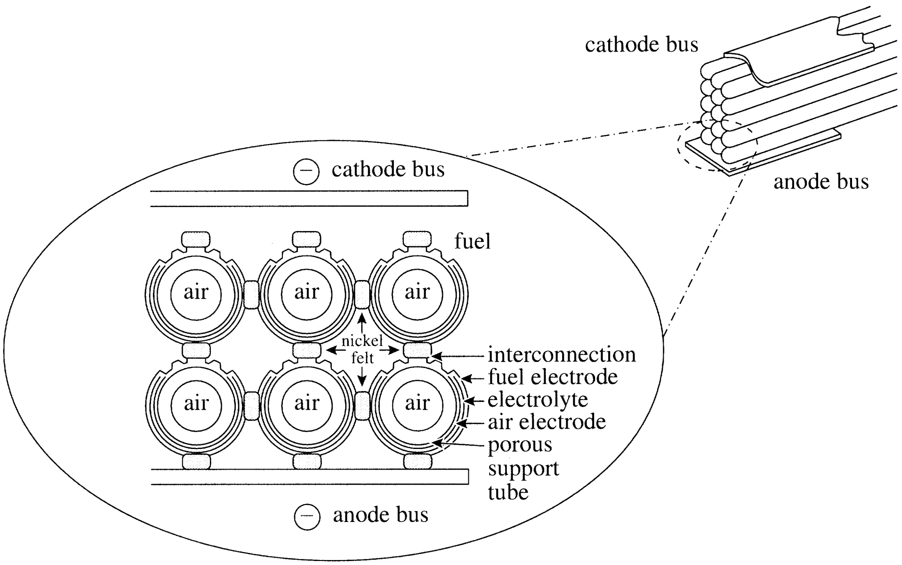


Figure 7. Schematic diagram showing the Westinghouse tubular solid-oxide fuel cell system in its ‘bundle’ configuration.

geometry, similar to conventional designs, a tubular design shown in figure 7, and a monolithic design. All these designs, however, still need to overcome quite serious interconnect and fabrication technology problems.

Although the SOFC clearly possesses a number of advantages, there remain some severe problems:

(*a*) The thermodynamic cell voltage is only 0.9 V, at 1000 °C, though because there are essentially no kinetic limitations on the cathode or anode reactions, reasonable current densities can be obtained at voltages of 0.75 V.

(*b*) The materials problems, particularly those related to thermal expansion and stability to mechanical damage are proving extremely difficult to solve.

The intolerance of SOFCs to repeated shutdown–startup cycles, which is related to the problem of compatibility of thermal expansion, suggests that the most likely type of application envisaged for SOFCs is that of stationary power generation under steady-state conditions. Westinghouse, in particular, have constructed 25 kW and 100 kW systems, and there is strong interest in both the US and Australia in developing this technology to commercialization.

(*e*) *Solid-polymer fuel cells*

Related to the solid-oxide-based fuel cells above, which are dependent on oxide-ion conducting electrolytes, it should be possible to find analogous fuel cells based on solid *proton* conductors. In fact, high-temperature solid proton conductors appear not to exist; at these elevated temperatures, all hydrated oxides tend to lose water and if conduction takes place at all, it will be through the metal or the oxide ion. However, at low temperatures (below *ca.* 150 °C), there are several types of solid-proton conductor, both inorganic and organic, that can be used in so-called solid-polymer-electrolyte or SPE fuel cells (Watkins 1993).

A schematic diagram of this type of cell is shown in figure 8: the electrolyte itself is a polymeric membrane proton conductor and anode and cathode are, in the simplest

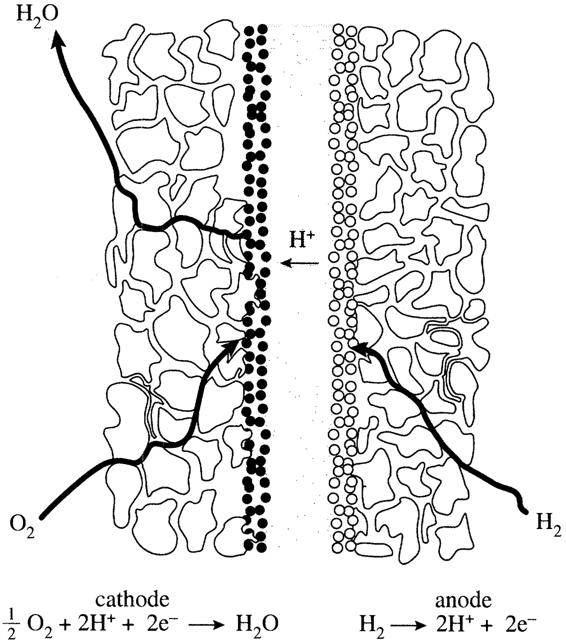


Figure 8. Schematic of operation of a solid-polymer-electrolyte H_2/O_2 fuel cell.

designs, formed either directly from metal particles or from catalysed carbon particles bound to the membrane. The current collectors are porous carbon or graphite plates, and the cell reactions are, at the anode

$$H_2 = 2H^+ + 2e^- \tag{2.10}$$

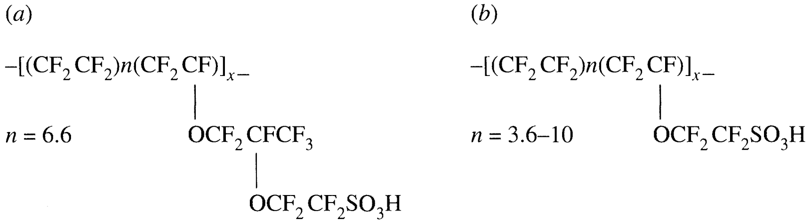
and at the cathode

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- = H_2O. \tag{2.11}$$

The low operating temperatures dictate the use of noble metal catalysts, with particular problems being experienced at the cathode.

Critical to the success of the SPEFC is the electrolyte, and the revival of interest in this configuration is due to the success of Du Pont and latterly Dow Chemical Co. in developing perfluorinated sulphonic acid polymers. These consist of a PTFE backbone to which are bonded pendant sulphonic acid groups, as shown in figure 9. These materials have the secondary advantage of being dispersible in certain organic solvents, such as ethanol, allowing membrane fabrication at a variety of thicknesses, and also allowing for the use of this sol as a binder for the catalysed carbon particles, thereby greatly increasing the utilization of the electrode by conversion to a mixed conductor.

The performance of such cells, particularly under a few bar pressure, is quite remarkable, as shown in figure 10, where power densities in excess of 1 W cm^{-2} are seen. These high performances should not, however, disguise the fact that if application of the SPEFC to transport is considered, particularly if methanol is used as the fuel and a reformer used, there are several additional sources of loss. Operation of the fuel cell at 5 bar leads to an air compressor loss of *ca.* 12% of stack output, and reformer losses of 10–15% based on the heating value of the input methanol fuel are



(a) $-[(CF_2CF_2)n(CF_2CF)]_x-$ with side chain OCF_2CFCF_3, $OCF_2CF_2SO_3H$

(b) $-[(CF_2CF_2)n(CF_2CF)]_x-$ with side chain $OCF_2CF_2SO_3H$

Figure 9. Comparison of Du Pont's Nafion and Dow perfluorosulphonate ionomer membrane.

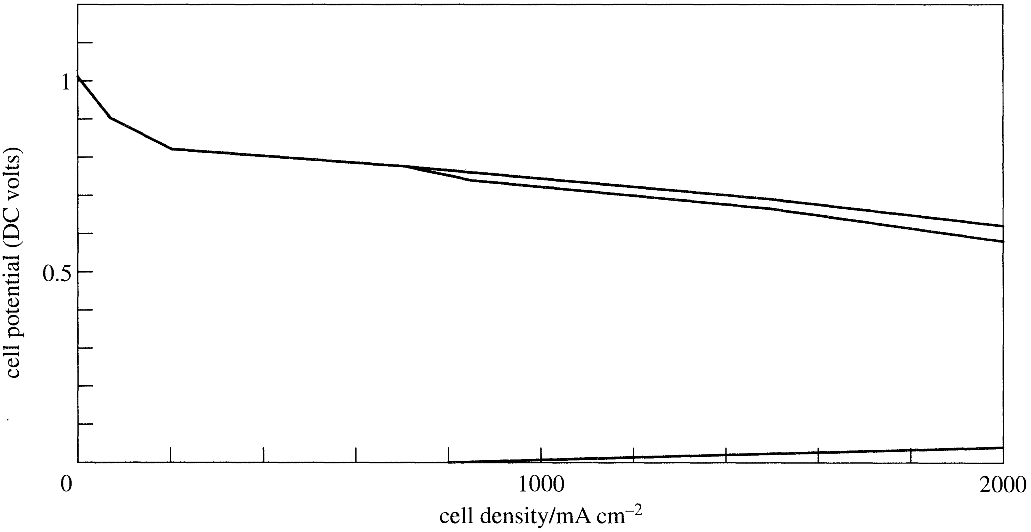


Figure 10. Cell and half-cell potentials vs current density for a single cell with Dow membrane (thickness : 125 μm) and Pt-sputtered Prototech electrodes (Pt-loading 0.45 mg cm^{-2}) operating at 95 °C with H_2/O_2 at 4–5 atm.

expected. Further losses to ancillary units, and in power converters, etc., can lead to overall power efficiencies from methanol chemical energy to wheels of *ca.* 15%.

In contrast, moreover, to the high temperature cells above, the SPEFC shows very considerable sensitivity to contaminants in the fuel gas, and in particular CO must be reduced to well below 10 ppm to avoid deterioration in the anode performance. This type of purity can only be achieved by using multi-stage reformers, and considerable effort has recently been expended on developing promoted platinum catalysts that are less sensitive to residual CO.

The high power density of SPEFCs makes them extremely attractive for traction applications, where the size and weight of the fuel cell should be as small as possible. Ballard have recently designed and constructed a bus that uses compressed hydrogen in cylinders as the fuel, and have been testing this in city driving in Vancouver.

(*f*) *The direct methanol fuel cell*

All the cells previously described have been based on hydrogen as a fuel, but as the Ballard bus shows, transport of this fuel clearly requires a considerable weight penalty. The alternative, which is to use methanol as a fuel and use a reformer, is both costly and fraught with engineering difficulties. Highly desirable would be a fuel cell that could *directly* oxidize methanol at the anode, but retained the high

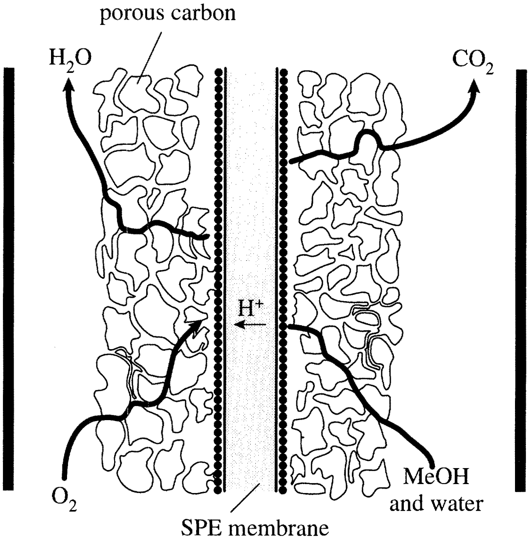


Figure 11. Solid-polymer-electrolyte fuel cell configuration for the direct methanol fuel cell.

power/weight ratio of the SPEFC described above. Such a fuel cell is now under active development in Europe and the USA, and the principles are shown in figure 11 (Hamnett & Troughton 1992). The anode reaction is

$$CH_3OH + H_2O = CO_2 + 6H^+ + 6e^- \tag{2.12}$$

and the cathode reaction is

$$\tfrac{3}{2}O_2 + 6H^+ + 6e^- = 3H_2O. \tag{2.13}$$

Methanol possesses a number of advantages as a fuel: it is a liquid, and therefore easily transported and stored; it is cheap and plentiful, and the only products of combustion are CO_2 and H_2O. The advantages of a direct methanol fuel cell are: changes in power demand can be accommodated simply by alteration in supply of the methanol feed; the fuel cell operates at temperatures below *ca.* 150 °C so there is no production of NO_x and methanol is stable in contact with the acidic membrane.

The basic problems currently faced by the direct methanol fuel cell are: (*a*) the anode reaction has poor electrode kinetics, particularly at lower temperatures, making it highly desirable to identify improved catalysts and to work at as high a temperature as possible; (*b*) the cathode reaction, the reduction of oxygen, is also slow, though the problems are not so serious as with aqueous mineral acid electrolytes. Nevertheless, the overall power density of the direct methanol fuel cells is much lower than the 600+ mW cm^{-2} envisaged for the hydrogen-fuelled SPEFC; (*c*) perhaps of greatest concern at the moment is the permeability of the current perfluorosulphonic acid membranes to methanol, allowing considerable fuel crossover. This leads both to degradation of performance, since a mixed potential develops at the cathode, and to deterioration of fuel utilization. Methanol vapour also appears in the cathode exhaust, from which it would have to be removed.

In spite of these difficulties, the DMFC-SPE does have the capability of being very cheap and potentially very competitive with the internal combustion engine, particularly in niche city driving applications, where the low pollution and relatively high efficiency at low load are attractive features. Performances from modern single

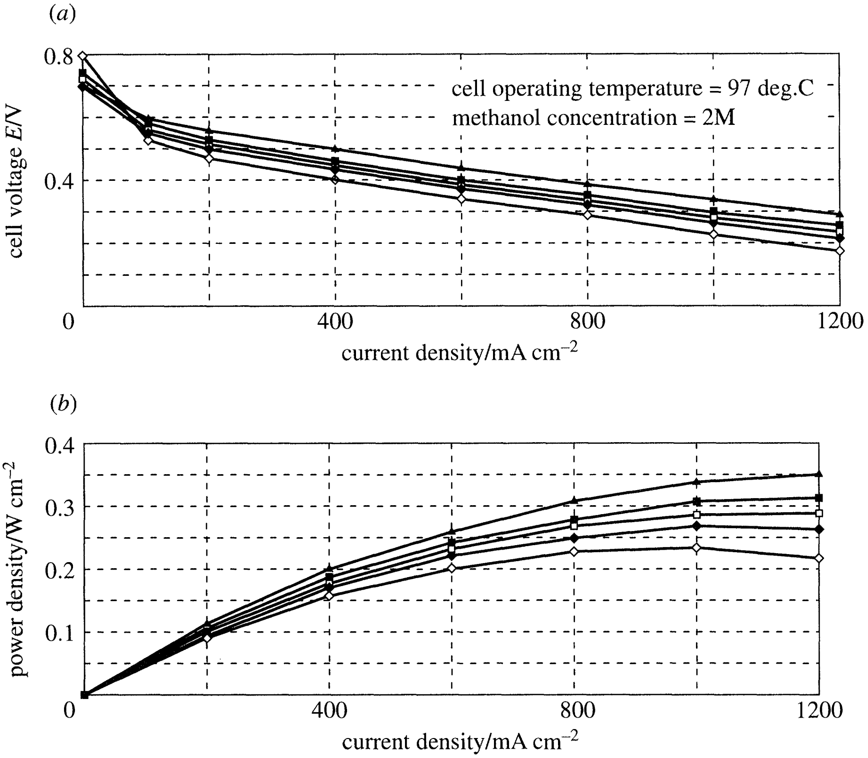


Figure 12. (*a*) Effect of oxygen pressure on the cell performance for a DMFC operating at 97 °C with a vapour feed of 2M methanol; (*b*) effect of oxygen pressure on the power output of the cell in (*a*).

cells are highly encouraging: an example is shown from our own work in figure 12, and it can be seen that in oxygen, power densities of up to 0.35 W cm^{-2} are possible; in air a power density of 0.2 W cm^{-2} has been attained with a pressure of 5 bar.

3. Conclusions

Fuel cells remain at the threshold of significant application. Severe reductions in costs are essential if stationary power applications are to be realized, and a considerable increase in lifetime would also be highly desirable. For traction applications, which are likely to be driven as much by environmental considerations as cost, the outlook is brighter, but there remains much developmental work to do. Nonetheless, the overall picture is a positive one: the extraordinary progress over the past few years has placed fuel cells firmly on the agenda of energy foresight panels the world over, and I have little doubt that we shall start to see significant encroachment, at least in niche markets, in the next decade.

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