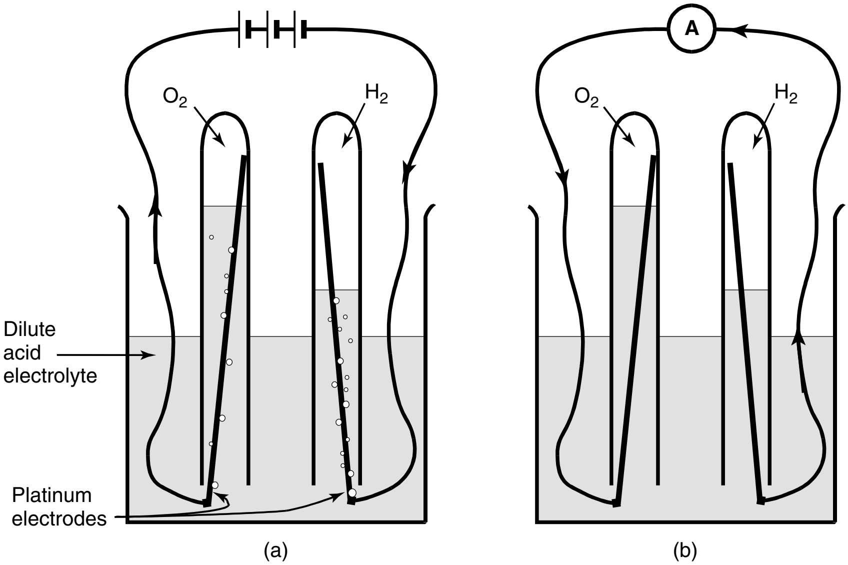
1

Introduction

1.1 Hydrogen Fuel Cells – Basic Principles

The basic operation of the hydrogen fuel cell is extremely simple. The first demonstration of a fuel cell was by lawyer and scientist William Grove in 1839, using an experiment along the lines of that shown in Figures 1.1a and 1.1b. In Figure 1.1a, water is being electrolysed into hydrogen and oxygen by passing an electric current through it. In Figure 1.1b, the power supply has been replaced with an ammeter, and a small current is



Note that the arrows represent the flow of negative electrons from – to +.

Figure 1.1 (a) The electrolysis of water. The water is separated into hydrogen and oxygen by the passage of an electric current. (b) A small current flows. The oxygen and hydrogen are recombining.

Fuel Cell Systems Explained, Second Edition James Larminie and Andrew Dicks

ISBN: 0-470-84857-X

flowing. The electrolysis is being reversed – the hydrogen and oxygen are recombining, and an electric current is being produced.

Another way of looking at the fuel cell is to say that the hydrogen fuel is being 'burnt' or combusted in the simple reaction

$$2H_2 + O_2 \rightarrow 2H_2O \qquad [1.1]$$

However, instead of heat energy being liberated, electrical energy is produced.

The experiment shown in Figures 1.1a and 1.1b makes a reasonable demonstration of the basic principle of the fuel cell, but the currents produced are very small. The main reasons for the small current are

- the low 'contact area' between the gas, the electrode, and the electrolyte – basically just a small ring where the electrode emerges from the electrolyte.
- the large distance between the electrodes – the electrolyte resists the flow of electric current.

To overcome these problems, the electrodes are usually made flat, with a thin layer of electrolyte as in Figure 1.2. The structure of the electrode is porous so that both the electrolyte from one side and the gas from the other can penetrate it. This is to give the maximum possible contact between the electrode, the electrolyte, and the gas.

However, to understand how the reaction between hydrogen and oxygen produces an electric current, and where the electrons come from, we need to consider the separate reactions taking place at each electrode. These important details vary for different types of fuel cells, but if we start with a cell based around an acid electrolyte, as used by Grove, we shall start with the simplest and still the most common type.

At the anode of an **acid electrolyte** fuel cell, the hydrogen gas ionises, releasing electrons and creating H^+ ions (or protons).

$$2H_2 \rightarrow 4H^+ + 4e^- \qquad [1.2]$$

This reaction releases energy. At the cathode, oxygen reacts with electrons taken from the electrode, and H^+ ions from the electrolyte, to form water.

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \qquad [1.3]$$

Clearly, for both these reactions to proceed continuously, electrons produced at the anode must pass through an electrical circuit to the cathode. Also, H^+ ions must pass through the electrolyte. An acid is a fluid with free H^+ ions, and so serves this purpose very well. Certain polymers can also be made to contain mobile H^+ ions. These materials are called *proton exchange membranes*, as an H^+ ion is also a proton.

Comparing equations 1.2 and 1.3 we can see that two hydrogen molecules will be needed for each oxygen molecule if the system is to be kept in balance. This is shown in Figure 1.3. It should be noted that the electrolyte must only allow H^+ ions to pass through it, and not electrons. Otherwise, the electrons would go through the electrolyte, not a round the external circuit, and all would be lost.

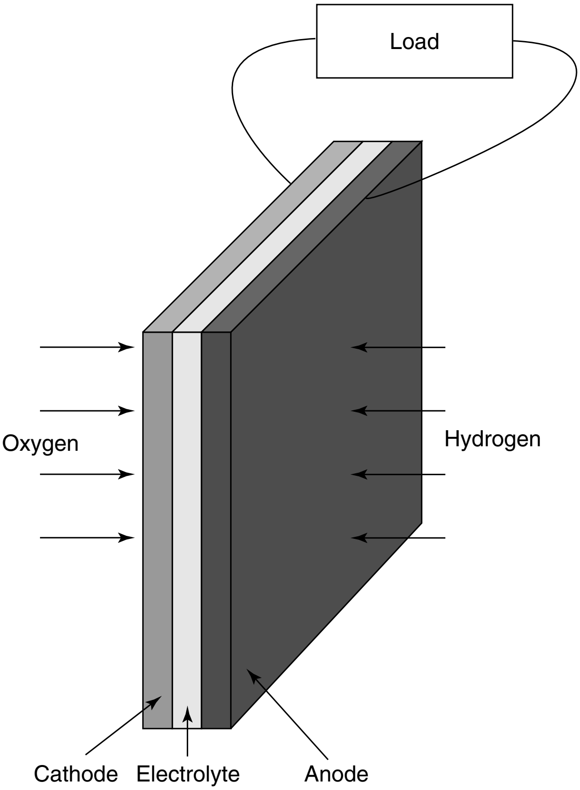


Figure 1.2 Basic cathode–electrolyte–anode construction of a fuel cell.

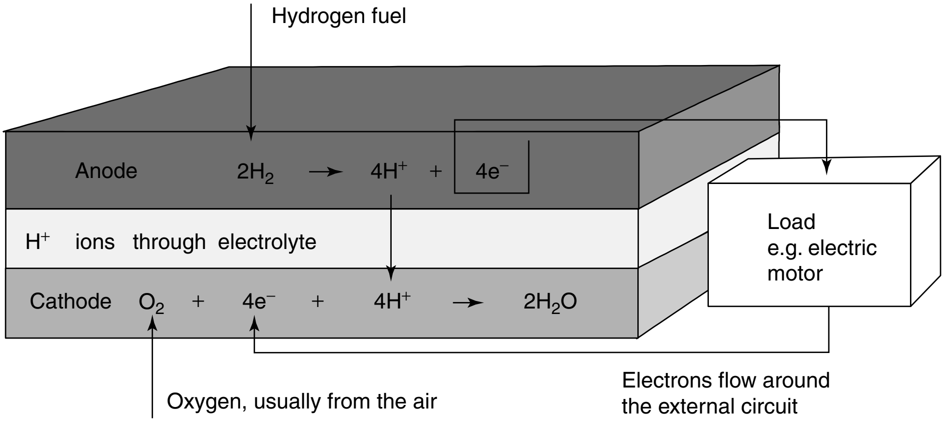


Figure 1.3 Electrode reactions and charge flow for an acid electrolyte fuel cell. Note that although the negative electrons flow from anode to cathode, the 'conventional current' flows from cathode to anode.

Positive Cathodes and Negative Anodes

Looking at Figures 1.3 and 1.4, the reader will see that the electrons are flowing from the anode to the cathode. The **cathode** is thus the electrically **positive** terminal, since electrons flow from − to +. Many newcomers to fuel cells find this confusing. This is hardly surprising. The Concise Oxford English Dictionary defines cathode as

> "**1**. the negative electrode in an electrolyte cell or electron valve or tube, **2**. the positive terminal of a primary cell such as a battery."

Having two such opposite definitions is bound to cause confusion, but we note that the cathode is the correct name for the positive terminal of **all** primary batteries. It also helps to remember that cations are positive ions, for example, H^+ is a cation. Anions are negative ions, for example, OH^- is an anion. It is also true that the **cathode is always the electrode into which electrons flow**, and similarly the anode is always the electrode from which electrons flow. This holds true for electrolysis, cells, valves, forward biased diodes, and fuel cells.

A further possible confusion is that while negative electrons flow from minus to plus, the 'conventional positive current' flows the other way, from the positive to the negative terminal.

In an **alkaline electrolyte fuel cell** the overall reaction is the same, but the reactions at each electrode are different. In an alkali, hydroxyl (OH^-) ions are available and mobile. At the anode, these react with hydrogen, releasing energy and electrons, and producing water.

$$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^- \qquad [1.4]$$

At the cathode, oxygen reacts with electrons taken from the electrode, and water in the electrolyte, forming new OH^- ions.

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \qquad [1.5]$$

For these reactions to proceed continuously, the OH^- ions must be able to pass through the electrolyte, and there must be an electrical circuit for the electrons to go from the anode to the cathode. Also, comparing equations 1.4 and 1.5 we see that, as with the acid electrolyte, twice as much hydrogen is needed as oxygen. This is shown in Figure 1.4. Note that although water is consumed at the cathode, it is created twice as fast at the anode.

There are many different fuel cell types, with different electrolytes. The details of the anode and cathode reactions are different in each case. However, it is not appropriate to go over every example here. The most important other fuel cell chemistries are covered in Chapter 7 when we consider the solid oxide and molten carbonate fuel cells.

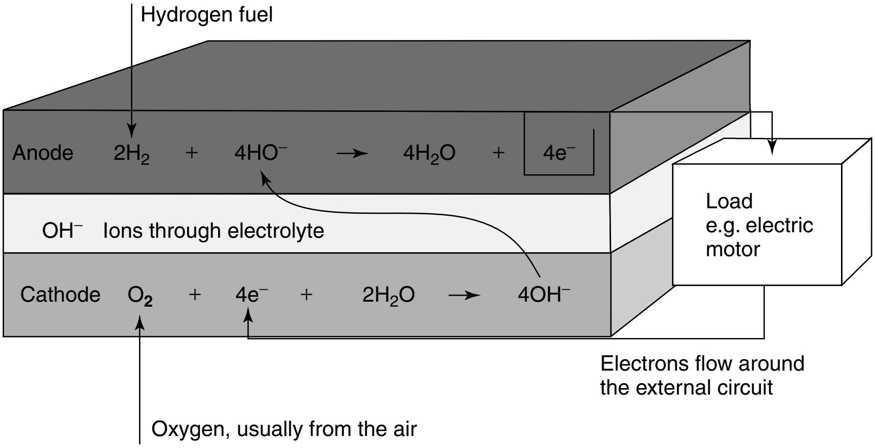


Figure 1.4 Electrode reactions and charge flow for an alkaline electrolyte fuel cell. Electrons flow from anode to cathode, but conventional positive current flows from cathode to anode.

1.2 What Limits the Current?

At the anode, hydrogen reacts, releasing energy. However, just because energy is released, it does not mean that the reaction proceeds at an unlimited rate. The reaction has the ‘classical’ energy form shown in Figure 1.5.

Although energy is released, the ‘activation energy’ must be supplied to get over the ‘energy hill’. If the probability of a molecule having enough energy is low, then the

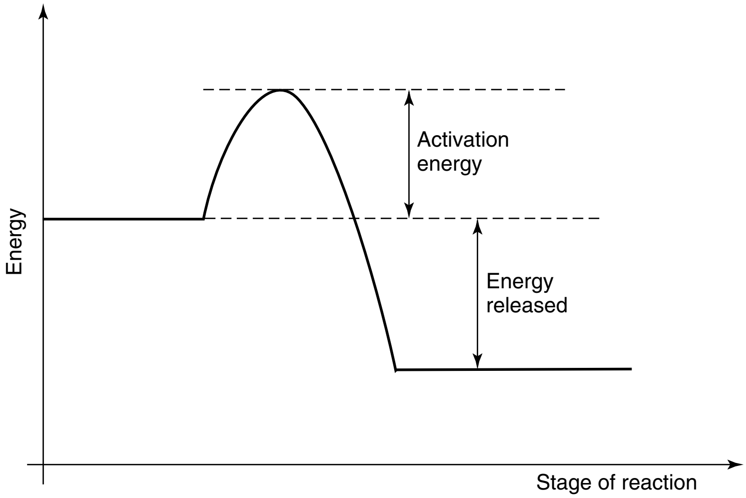


Figure 1.5 Classical energy diagram for a simple exothermic chemical reaction.

reaction will only proceed slowly. Except at very high temperatures, this is indeed the case for fuel cell reactions.

The three main ways of dealing with the slow reaction rates are

- the use of catalysts,
- raising the temperature,
- increasing the electrode area.

The first two can be applied to any chemical reaction. However, the third is special to fuel cells and is very important. If we take a reaction such as that of equation 1.4, we see that fuel gas and OH^- ions from the electrolyte are needed, as well as the necessary activation energy. Furthermore, this ‘coming together’ of H_2 fuel and OH^- ions must take place **on the surface of the electrode**, as the electrons produced must be removed.

This reaction, involving fuel or oxygen (usually a gas), with the electrolyte (solid or liquid) and the electrode, is sometimes called the *three phase contact*. The bringing together of these three things is a very important issue in fuel cell design.

Clearly, the rate at which the reaction happens will be proportional to the area of the electrode. This is very important. Indeed, electrode area is such a vital issue that the performance of a fuel cell design is often quoted in terms of the current *per* cm^2.

However, the straightforward area (length × width) is not the only issue. As has already been mentioned, the electrode is made highly porous. This has the effect of greatly increasing the effective surface area. Modern fuel cell electrodes have a microstructure that gives them surface areas that can be hundreds or even thousands of times their straightforward ‘length × width’ (See Figure 1.6.) The microstructural design and manufacture of a fuel cell electrode is thus a very important issue for practical fuel cells. In addition to these surface area considerations, the electrodes may have to incorporate a catalyst and endure high temperatures in a corrosive environment. The problems of reaction rates are dealt with in a more quantitative way in Chapter 3.

1.3 Connecting Cells in Series – the Bipolar Plate

For reasons explained in Chapters 2 and 3, the voltage of a fuel cell is quite small, about 0.7 V when drawing a useful current. This means that to produce a useful voltage many cells have to be connected in series. Such a collection of fuel cells in series is known as a ‘stack’. The most obvious way to do this is by simply connecting the edge of each anode to the cathode of the next cell, all along the line, as in Figure 1.7. (For simplicity, this diagram ignores the problem of supplying gas to the electrodes.)

The problem with this method is that the electrons have to flow across the face of the electrode to the current collection point at the edge. The electrodes might be quite good conductors, but if each cell is only operating at about 0.7 V, even a small voltage drop is important. Unless the current flows are very low, and the electrode is a particularly good conductor, or very small, this method is not used.

A much better method of cell interconnection is to use a ‘bipolar plate’. This makes connections all over the surface of one cathode and the anode of the next cell (hence ‘bipolar’); at the same time, the bipolar plate serves as a means of feeding oxygen to the

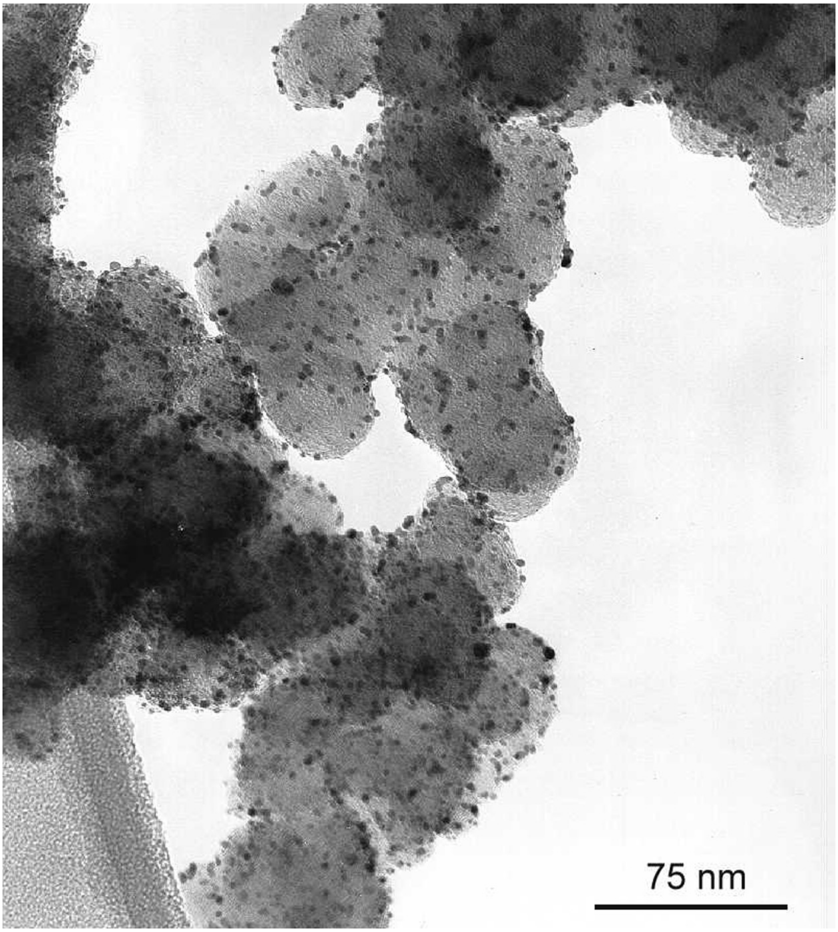


Figure 1.6 TEM image of fuel cell catalyst. The black specks are the catalyst particles finely divided over a carbon support. The structure clearly has a large surface area. (Reproduced by kind permission of Johnson Matthey Plc.)

cathode and fuel gas to the anode. Although a good electrical connection must be made between the two electrodes, the two gas supplies must be strictly separated.

The method of connecting to a single cell, all over the electrode surfaces, while at the same time feeding hydrogen to the anode and oxygen to the cathode, is shown in Figure 1.8. The grooved plates are made of a good conductor such as graphite, or stainless steel.

To connect several cells in series, ‘bipolar plates’ are made. These plates – or cell interconnects – have channels cut in them so that the gases can flow over the face of the electrodes. At the same time, they are made in such a way that they make a good electrical contact with the surface of each alternate electrode. A simple design of a bipolar plate is shown in Figure 1.9.

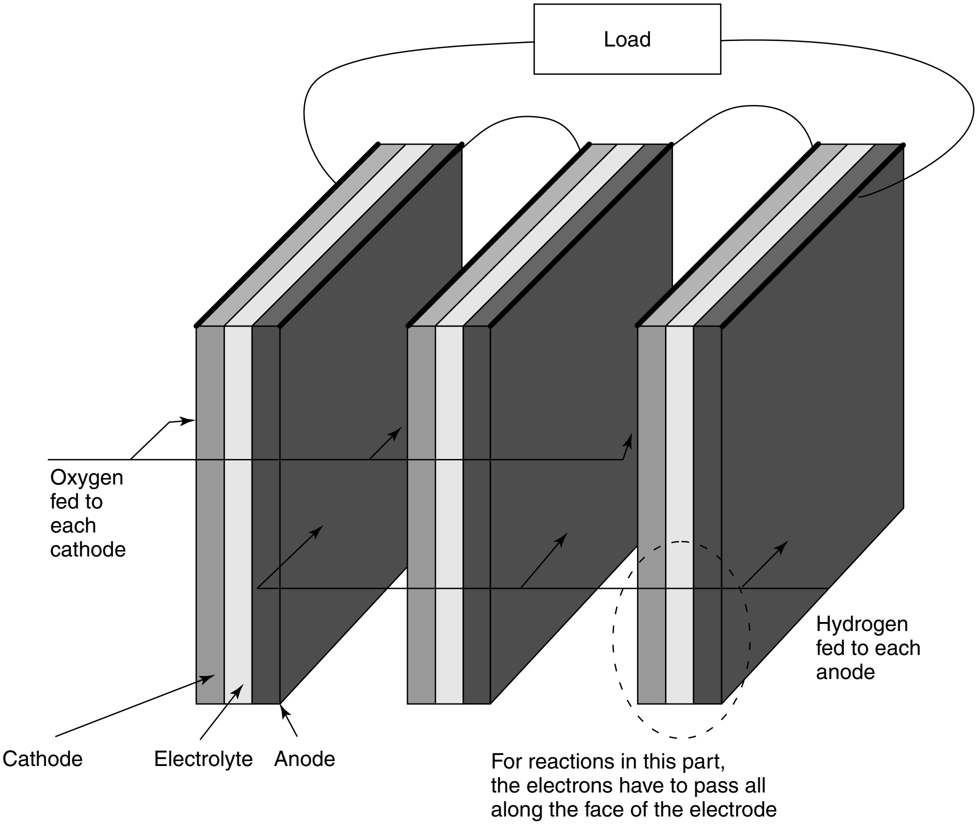


Figure 1.7 Simple edge connection of three cells in series.

To connect several cells in series, anode/electrolyte/cathode assemblies (as in Figure 1.2) need to be prepared. These are then 'stacked' together as shown in Figure 1.10. This 'stack' has vertical channels for feeding hydrogen over the anodes and horizontal channels for feeding oxygen (or air) over the cathodes. The result is a solid block in which the electric current passes efficiently, more or less straight through the cells rather than over the surface of each electrode one after the other. The electrodes are also well supported, and the whole structure is strong and robust. However, the design of the bipolar plate is not simple. If the electrical contact is to be optimised, the contact points should be as large as possible, but this would mitigate the good gas flow over the electrodes. If the contact points have to be small, at least they should be frequent. However, this makes the plate more complex, difficult, and expensive to manufacture, as well as fragile. Ideally the bipolar plate should be as thin as possible, to minimise electrical resistance and to make the fuel cells stack small. However, this makes the channels for the gas flow narrow, which means it is more difficult to pump the gas round the cell. This sometimes has to be done at a high rate, especially when using air instead of pure oxygen on the cathode. In the case of low-temperature fuel cells, the circulating air has to evaporate and carry away the product water. In addition, there usually have to be further channels through the bipolar plate to carry a cooling fluid. Some of the further complications for the bipolar plate are considered in the next section.

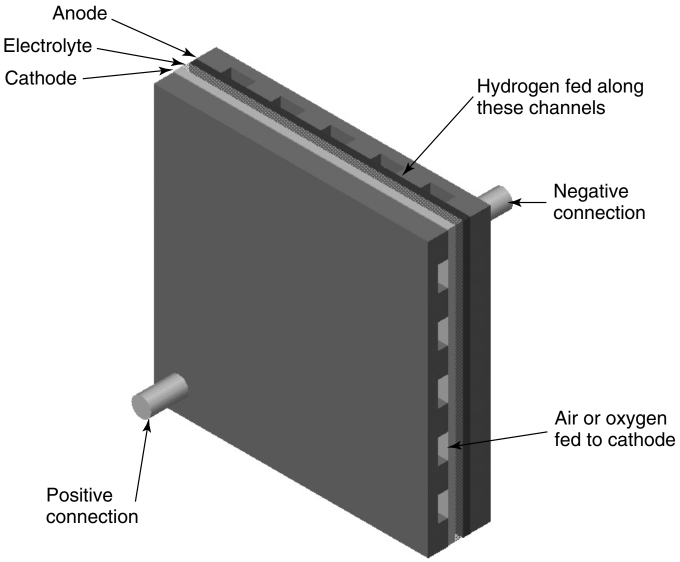


Figure 1.8 Single cell, with end plates for taking current from all over the face of the electrodes, and also supplying gas to the whole electrode.

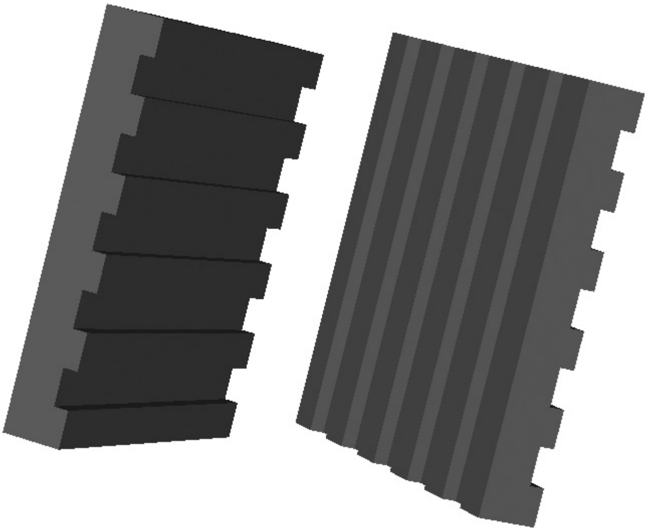


Figure 1.9 Two bipolar plates of very simple design. There are horizontal grooves on one side and vertical grooves on the other.

1.4 Gas Supply and Cooling

The arrangement shown in Figure 1.10 has been simplified to show the basic principle of the bipolar plate. However, the problem of gas supply and of preventing leaks means that in reality the design is somewhat more complex.

Because the electrodes must be porous (to allow the gas in), they would allow the gas to leak out of their edges. The result is that the edges of the electrodes must be sealed. Sometimes this is done by making the electrolyte somewhat larger than one or both of the electrodes and fitting a sealing gasket around each electrode, as shown in Figure 1.11. Such assemblies can then be made into a stack, as in Figures 1.10 and 1.12.

The fuel and oxygen can then be supplied to the electrodes using the manifolds as shown disassembled in Figure 1.12 and assembled in Figure 1.13. Because of the seals around the edge of the electrodes, the hydrogen should only come into contact with the anodes as it is fed vertically through the fuel cell stack. Similarly, the oxygen (or air) fed horizontally through the stack should only contact the cathodes, and not even the edges of the anodes. Such would not be the case in Figure 1.10.

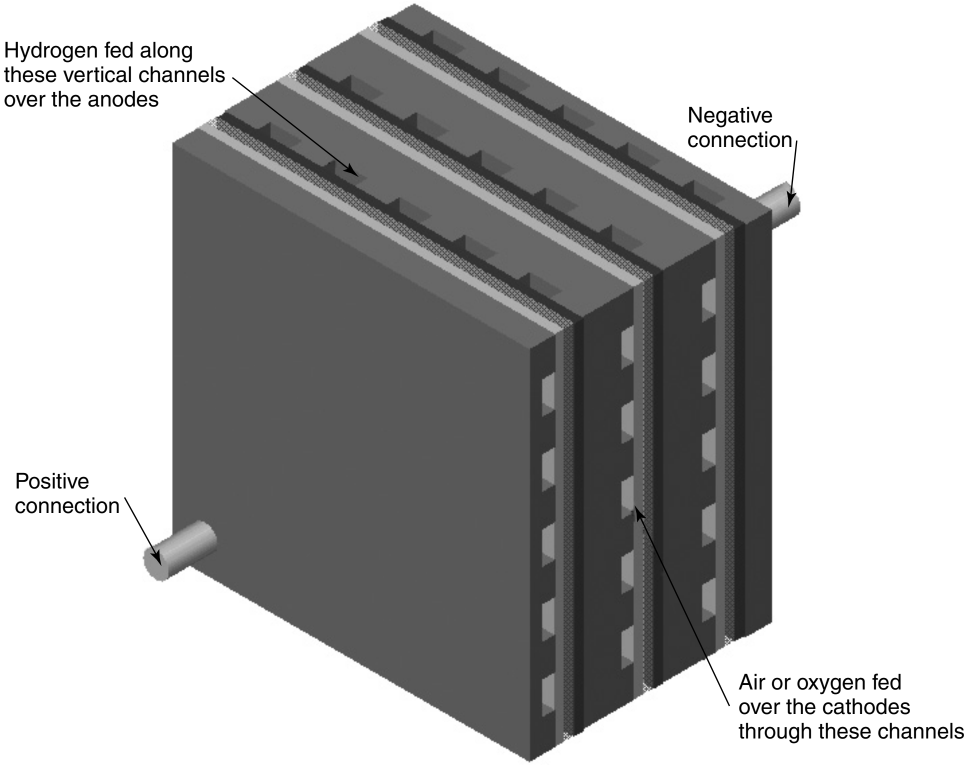


Figure 1.10 A three-cell stack showing how bipolar plates connect the anode of one cell to the cathode of its neighbour.

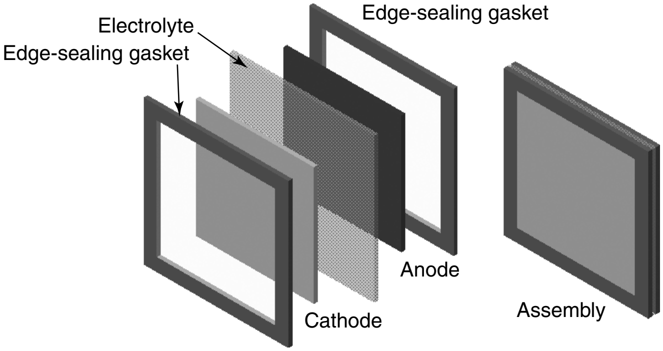


Figure 1.11 The construction of anode/electrolyte/cathode assemblies with edge seals. These prevent the gases leaking in or out through the edges of the porous electrodes.

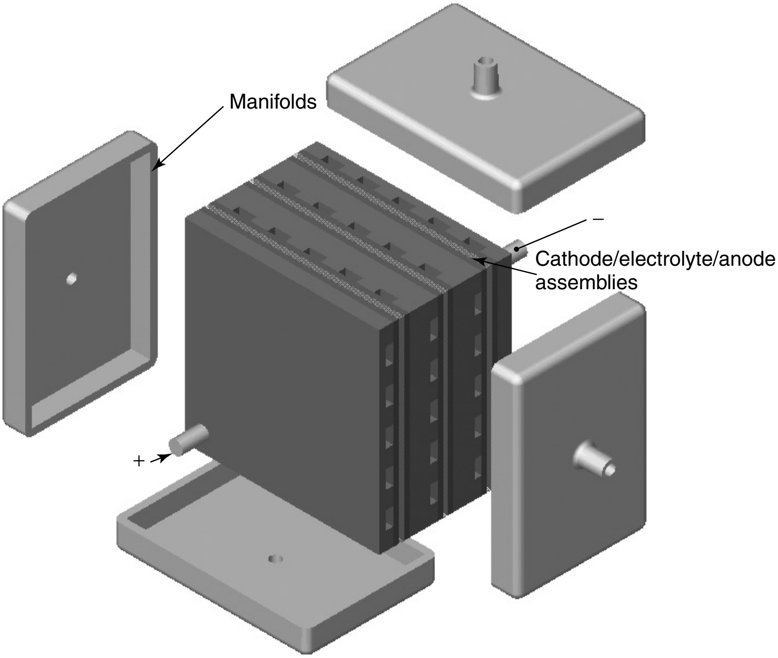


Figure 1.12 Three-cell stack, with external manifolds. Unlike Figure 1.10, the electrodes now have edge seals.

The arrangement of Figures 1.12 and 1.13 is used in some systems. It is called *external manifolding*. It has the advantage of simplicity. However, it has two major disadvantages. The first is that it is difficult to cool the system. Fuel cells are far from 100% efficient, and considerable quantities of heat energy as well as electrical power are generated. (Chapter 3

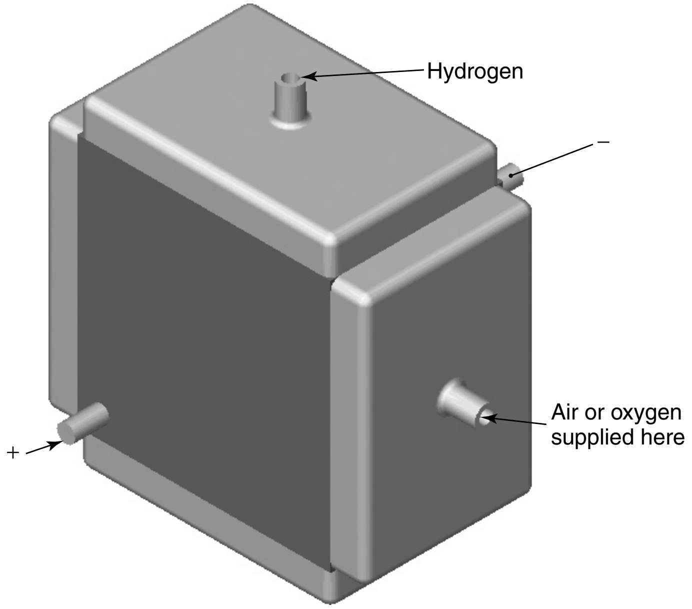


Figure 1.13 The external manifolds are fitted to the fuel cell stack. Note that no provision has been made for cooling – see Section 1.4.

gives the reasons.) It is clear from Figures 1.12 and 1.13 that it would be hard to supply a cooling fluid running through the cells. In practice, this type of cell has to be cooled by the reactant air passing over the cathodes. This means air has to be supplied at a higher rate than demanded by the cell chemistry; sometimes this is sufficient to cool the cell, but it is a waste of energy. The second disadvantage is that the gasket round the edge of the electrodes is not evenly pressed down – at the point where there is a channel, the gasket is not pressed firmly onto the electrode. This results in an increased probability of leakage of the reactant gases.

A more common arrangement requires a more complex bipolar plate and is shown in Figure 1.14. The plates are made larger relative to the electrodes and have extra channels running through the stack that feed the fuel and oxygen to the electrodes. Carefully placed holes feed the reactants into the channels that run over the surface of the electrodes. This type of arrangement is called *internal manifolding*. It results in a fuel cell stack that has the appearance of the solid block with the reactant gases fed in at the ends where the positive and negative connections are also made.

Such a fuel cell stack is shown under test in Figure 1.15. The end plate is quite complex, with several connections. The stack is a solid block. Electrical connections have been made to each of the approximately 60 cells in the stack for testing purposes. The typical form of a fuel cell as a solid block with connections at each end is also illustrated in Figure 4.1.

The bipolar plate with internal manifolding can be cooled in various ways. The simplest way is to make narrow channels up through the plates and to drive cooling air or

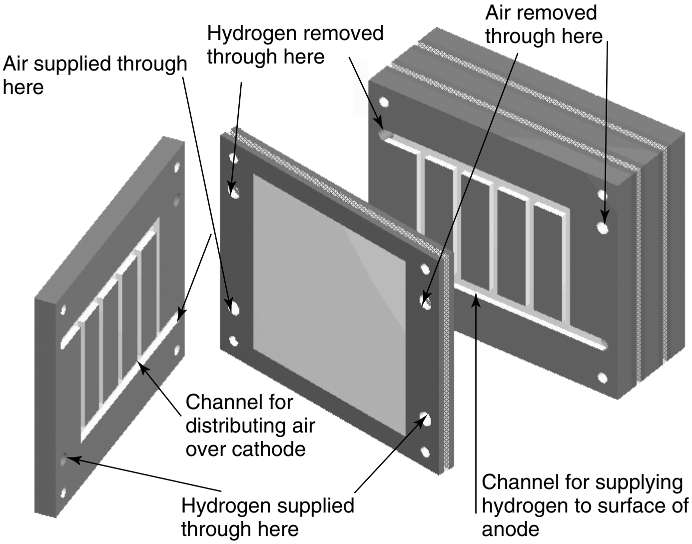


Figure 1.14 Internal manifolding. A more complex bipolar plate allows reactant gases to be fed to electrodes through internal tubes. (Picture by kind permission of Ballard Power Systems.)

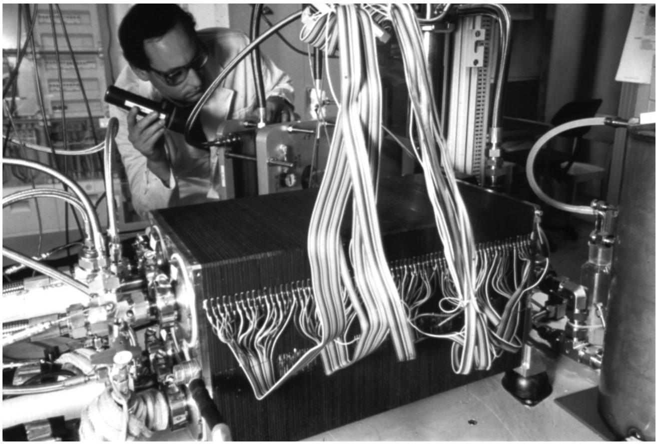


Figure 1.15 Photograph of a fuel cell stack under test. The voltage of each of the approximately 60 cells in the stack is being measured. Note the carefully engineered end plates. (Photograph reproduced by kind permission of Ballard Power Systems.)

water through them. Such an approach is used in several systems shown in Chapter 4. Alternatively, channels can be provided along the length of the cell, and there is provision for this in the system shown in Figure 1.14. The preferred cooling method varies greatly with the different fuel cell types, and is addressed in Chapters 4 to 7.

It should now be clear that the bipolar plate is usually quite a complex item in a fuel cell stack. In addition to being a fairly complex item to make, the question of its material is often difficult. Graphite, for example, is often used, but this is difficult to work with and is brittle. Stainless steel can also be used, but this will corrode in some types of fuel cells. Ceramic materials have been used in the very high temperature fuel cells. The bipolar plate nearly always makes a major contribution to the cost of a fuel cell.

Anyone who has made fuel cells knows that **leaks** are a major problem. If the path of hydrogen through a stack using internal manifolding (as in Figure 1.14) is imagined, the possibilities for the gas to escape are many. The gas must reach the edge of every porous electrode – so the entire edge of every electrode is a possible escape route, both under and over the edge gasket. Other likely trouble spots are the joints between each and every bipolar plate. In addition, if there is the smallest hole in any of the electrolytes, a serious leak is certain. In Chapters 4 to 7, when the different fuel cell types are described in more detail, attention is given to the different ways in which this problem is solved.

1.5 Fuel Cell Types

Leaving aside practical issues such as manufacturing and materials costs, the two fundamental technical problems with fuel cells are

- the slow reaction rate, leading to low currents and power, discussed briefly in Section 1.2, and
- that hydrogen is not a readily available fuel.

To solve these problems, many different fuel cell types have been tried. The different fuel cell types are usually distinguished by the electrolyte that is used, though there are always other important differences as well. The situation now is that six classes of fuel cell have emerged as viable systems for the present and near future. Basic information about these systems is given in Table 1.1.

In addition to facing different problems, the various fuel types also try to play to the strengths of fuel cells in different ways. The **proton exchange membrane** (**PEM**) **fuel cell** capitalises 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 1.3. With a solid and immobile electrolyte, this type of cell is inherently very simple.

These cells run at quite low temperatures, so the problem 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. The problem of hydrogen supply is not really addressed – quite pure hydrogen **must** be used, though various ways of supplying this are possible, as is discussed in Chapter 8.

One theoretically very attractive solution to the hydrogen supply problem is to use methanol[1] as a fuel instead. This can be done in the PEM fuel cell, and such cells are

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[1] A fairly readily available liquid fuel, formula CH_3OH.

Table 1.1 Data for different types of fuel cell

Fuel cell type	Mobile ion	Operating temperature	Applications and notes
Alkaline (AFC)	OH^-	50–200°C	Used in space vehicles, e.g. Apollo, Shuttle.
Proton exchange membrane (PEMFC)	H^+	30–100°C	Vehicles and mobile applications, and for lower power CHP systems
Direct methanol (DMFC)	H^+	20–90°C	Suitable for portable electronic systems of low power, running for long times
Phosphoric acid (PAFC)	H^+	~220°C	Large numbers of 200-kW CHP systems in use.
Molten carbonate (MCFC)	$CO_3{}^{2-}$	~650°C	Suitable for medium- to large-scale CHP systems, up to MW capacity
Solid oxide (SOFC)	O^{2-}	500–1000°C	Suitable for all sizes of CHP systems, 2 kW to multi-MW.

called *direct methanol fuel cells*. 'Direct' because they use the methanol as the fuel, as it is in liquid form, as opposed to extracting the hydrogen from the methanol using one of the methods described in Chapter 8. Unfortunately, these cells have very low powers, but nevertheless, even at low power, there are many potential applications in the rapidly growing area of portable electronics equipment. Such cells, in the foreseeable future at least, are going to be of very low power, and used in applications requiring slow and steady consumption of electricity over long periods.

Although PEM fuel cells were used on the first manned spacecraft, the **alkaline fuel cell** 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 sometimes by operating at quite high pressures. Although some historically important alkaline fuel cells have operated at about 200°C, they more usually operate below 100°C. Alkaline fuel cells are discussed in Chapter 6, where their main problem is described – that the air and fuel supplies must be free from CO_2, or else pure oxygen and hydrogen must be used.

The **phosphoric acid fuel cell (PAFC)** was the first to be produced in commercial quantities and enjoys widespread terrestrial use. Many 200-kW systems, manufactured by the International Fuel Cells Corporation (now trading as UTC Fuel Cells Inc.), are installed in the USA and Europe, as well as systems produced by Japanese companies. Porous electrodes, platinum catalysts, and a fairly high temperature (~220°C) are used to boost the reaction rate to a reasonable level. The problem of fuelling with hydrogen is solved by 'reforming' natural gas (predominantly methane) to hydrogen and carbon dioxide, but the equipment needed to do this adds considerably to the cost, complexity, and size of the fuel cell system. Nevertheless, PAFC systems use the inherent simplicity of a fuel cell to provide an extraordinarily reliable and maintenance-free power system. Several PAFC systems have run continuously for periods of one year or more with little maintenance requiring shutdown or human intervention. (See Figure 1.16.)

Figure 1.16 Phosphoric acid fuel cell. In addition to providing 200 kW of electricity, it also provides about 200 kW of heat energy in the form of steam. Such units are called *combined heat and power* or *CHP systems*. (Reproduced by kind permission of ONSI Corporation.)

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 to 1000°C. This 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. This fuel cell type thus addresses all the problems and takes full advantage of the inherent simplicity of the fuel cell concept. Nevertheless, 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 pre-heaters; 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 air to work. The high temperature means that a good reaction rate is achieved by 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 (H_2 and CO) directly, without an external reformer. However, this simplicity is somewhat offset by the nature of the electrolyte, a hot and corrosive mixture of lithium, potassium, and sodium carbonates.

1.6 Other Cells – Some Fuel Cells, Some Not

In addition to the major fuel cell types described above, there are other fuel cells that are mentioned in scientific journals from time to time, and also cells that are described as 'fuel cells', but are not really so.

A fuel cell is usually defined as an electrochemical device that converts a supplied fuel to electrical energy (and heat) continuously, so long as reactants are supplied to its electrodes. The implication is that neither the electrodes nor the electrolyte are consumed by the operation of the cell. Of course, in all fuel cells the electrodes and electrolytes are degraded and subject to ‘wear and tear’ in use, but they are not entirely consumed in the way that happens with two of the three types of cells briefly described below, both of which are sometimes described as ‘fuel cells’.

1.6.1 Biological fuel cells

One type of genuine fuel cell that does hold promise in the very long term is the biological fuel cell. These would normally use an organic fuel, such as methanol or ethanol. However, the distinctive ‘biological’ aspect is that enzymes, rather than conventional ‘chemical’ catalysts such as platinum, promote the electrode reactions. Such cells replicate nature in the way that energy is derived from organic fuels. However, this type of cell is not yet anywhere near commercial application, and is not yet suitable for detailed consideration in an application-oriented book such as this.

The biological fuel cell should be distinguished from biological methods for generating hydrogen, which is then used in an ordinary fuel cell. This is discussed in Chapter 8.

1.6.2 Metal/air cells

The most common type of cell in this category is the zinc air battery, though aluminium/air and magnesium/air cells have been commercially produced. In all cases the basis of operation is the same. Such cells are sometimes called *zinc fuel cells*.

At the negative electrode, the metal reacts with an alkaline electrolyte to form the metal oxide or hydroxide. For example, in the case of zinc the reaction is

$$\mathrm{Zn} + 2\mathrm{OH}^- \rightarrow \mathrm{ZnO} + \mathrm{H_2O} + 2\mathrm{e}^-$$

The electrons thus released pass around the external electric circuit to the air cathode where they are available for the reaction between water and oxygen to form more hydroxyl ions. *The cathode reaction is exactly the same as for the alkaline fuel cell shown in Figure* 1.4. The metal oxide or hydroxide should remain dissolved in the electrolyte. Cells that use a salt-water electrolyte work reasonably well when they use aluminium or magnesium as the ‘fuel’.

Such cells have a very good energy density. Zinc/air batteries are very widely used in applications that require long running times at low currents, such as hearing aids. Several companies are also developing higher power units for applications such as electric vehicles. This is because they can also be ‘refuelled’ by adding more metal to the anode – which is why they are sometimes called *fuel cells*. The fact that the cathode reaction is exactly the same as for a fuel cell, and that the same electrodes can be used, is another reason. However, the electrolyte also has to be renewed to remove the metal oxide. Thus, they consume both the anode and the electrolyte, and cannot really be described as fuel cells. They are mechanically rechargeable primary batteries.

1.6.3 Redox flow cells or regenerative fuel cells

Another type of cell sometimes called a *fuel cell* is the redox flow cell (Vincent and Scrosati, 1997). In this type of cell, the reactants are removed from the electrodes during charging and are stored in tanks. The capacity of such cells can thus be very large. They are discharged by resupplying the reactants to the electrodes. Because the operation of the cell involves supply of chemicals to the electrodes, these devices are sometimes called *fuel cells*. However, this is a misnomer, as will become clear.

This type of cell is used to make very large capacity rechargeable batteries and may be used by electricity utilities to balance peaks in supply and demand. There are a number of different chemistries that can be used. Cells based on vanadium have been made (Shibata and Sato, 1999), as have zinc/bromine systems (Lex and Jonshagen, 1999). This type of system is perhaps best exemplified in the so-called Regenesys™ fuel cell (Zito, 1997 or Price et al., 1999).

The operating principles of the Regenesys™ system is shown in Figure 1.17. Two fluids ('fuels') are involved. When fully charged, a solution of sodium sulphide (Na_2S_2) in water is fed to the negative electrode, and a sodium tribromide ($NaBr_3$) solution is fed to the positive electrode. The reaction at the negative electrode is

$$2Na_2S_2 \rightarrow Na_2S_4 + 2Na^+ + 2e^-$$

The electrons flow around the external circuit, and the sodium ions pass through the membrane to the positive electrolyte. Here the reaction is

$$NaBr_3 + 2Na^+ + 2e^- \rightarrow 3NaBr$$

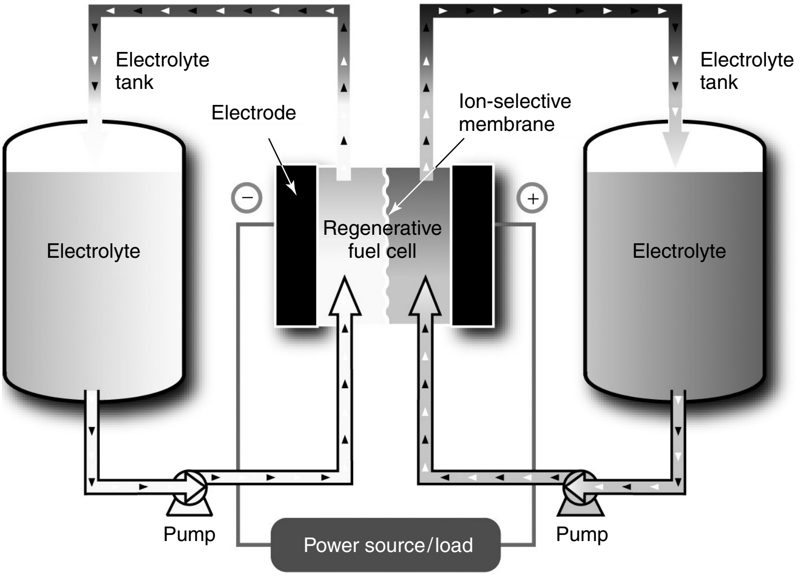

Figure 1.17 Diagram showing the principle of operation of a redox flow cell. See text for explanation. (Reproduced by kind permission of Regenesys Technology Ltd.)

Figure 1.18 Picture of the 100-MWh electrical energy storage facility being installed in Cambridgeshire, England. The storage tanks for the electrolyte solutions (‘fuel’) can be clearly seen. (Reproduced by kind permission of Regenesys Technology Ltd.)

So, as the system discharges, the sodium sulphide solution gradually changes to sodium polysulphide, and the sodium tribromide solution changes to sodium bromide. Figure 1.18 shows such a system under construction in Cambridgeshire, England. The two tanks to hold the solutions can be seen, together with a building that will hold the cells. This particular system has a storage capacity of 100 MWh, which is equivalent to the energy held in about 240,000 typical lead acid car batteries, and is believed to be the largest electrochemical electrical energy storage system in the world.

The rationale for calling this system a *fuel cell* is presumably that the electrodes are simply a surface where reactions take place and are not consumed. Furthermore, the electrodes are fed an energy-containing liquid. However, the electrolyte most certainly changes during operation, and the system cannot work indefinitely. Also, the electrolyte solutions are not fuels in any conventional sense. Indeed, this is a rather unusual and very high capacity rechargeable battery. Exactly the same arguments apply to the other cells of this type.

1.7 Other Parts of a Fuel Cell System

The core of a fuel cell power system is the electrodes, the electrolyte, and the bipolar plate that we have already considered. However, other parts frequently make up a large proportion of the engineering of the fuel cell system. These ‘extras’ are sometimes called the *balance of plant* (BOP). In the higher-temperature fuel cells used in CHP systems, the fuel cell stack often appears to be quite a small and insignificant part of the whole system, as is shown in Figure 1.19. The extra components required depend greatly on the

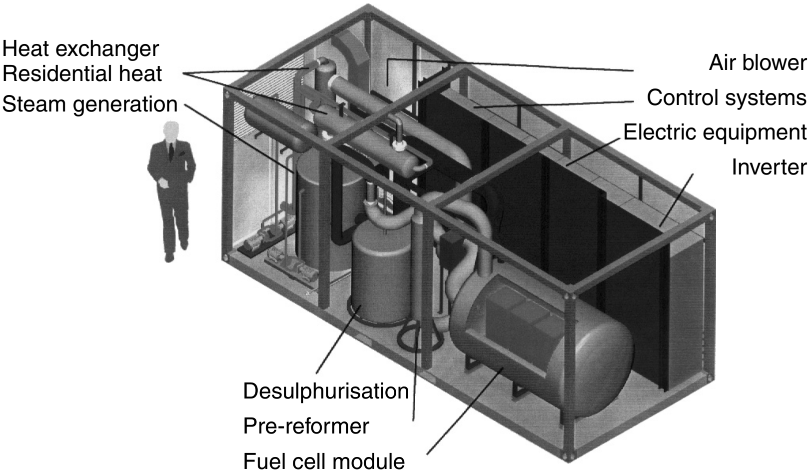

Figure 1.19 Design of a 100-kW fuel cell–based combined heat and power system. (Reproduced by kind permission of Siemens Power Generation.)

type of fuel cell, and crucially on the fuel used. These vitally important subsystem issues are described in much more detail in Chapters 8 to 10, but a summary is given here.

On all but the smallest fuel cells the air and fuel will need to be circulated through the stack using ***pumps*** or ***blowers***. Often ***compressors*** will be used, which will sometimes be accompanied by the use of ***intercoolers***, as in internal combustion engines.[2]

The direct current (DC) output of a fuel cell stack will rarely be suitable for direct connection to an electrical load, and so some kind of ***power conditioning*** is nearly always needed. This may be as simple as a voltage regulator, or a ***DC/DC converter***. In CHP systems, a DC to AC *inverter* is needed, which is a significant part of the cost of the whole system.[3] ***Electric motors***, which drive the pumps, blowers, and compressors mentioned above, will nearly always be a vital part of a fuel cell system. Frequently also, the electrical power generated will be destined for an electric motor – for example, in motor vehicles.

The supply and storage of hydrogen is a very critical problem for fuel cells. ***Fuel storage*** will clearly be a part of many systems. If the fuel cell does not use hydrogen, then some form of ***fuel processing system*** will be needed. These are often very large and complex, for example, when obtaining hydrogen from petrol in a car. In many cases ***desulphurisation*** of the fuel will be necessary. These vitally important subsystems will be discussed in detail in Chapter 8.

Various ***control valves***, as well as ***pressure regulators***, will usually be needed. In most cases a ***controller*** will be needed to coordinate the parts of the system. A special problem the controller has to deal with is the start-up and shutdown of the fuel cell system, as this can be a complex process, especially for high-temperature cells.

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[2] These components are discussed in some detail in Chapter 9.

[3] Electrical subsystems are covered in Chapter 10.

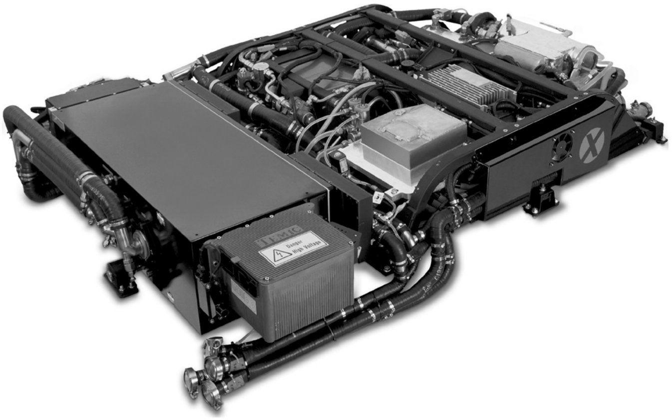

Figure 1.20 The 75-kW (approx.) fuel cell system for a prototype Mercedes Benz A-class car. (Photograph reproduced by kind permission of Ballard Power Systems.)

For all but the smallest fuel cells a ***cooling system*** will be needed. In the case of CHP systems, this will usually be called a *heat exchanger*, as the idea is not to lose the heat but to use it somewhere else. Sometimes, in the case of the higher-temperature cells, some of the heat generated in the fuel cell will be used in fuel and/or air ***pre-heaters***. In the case of the PEM fuel cell, to be described in detail in Chapter 4, there is often the need to ***humidify*** one or both of the reactant gases.

This very important idea of the balance of plant is illustrated in Figures 1.19 and 1.20. In Figure 1.19, we see that the fuel cell module is, in terms of size, a small part of the overall system, which is dominated by the fuel and heat processing systems. This will nearly always be the case for combined heat and power systems running on ordinary fuels such as natural gas. Figure 1.20 is the fuel cell engine from a car. It uses hydrogen fuel, and the waste heat is only used to warm the car interior. The fuel cell stack is the rectangular block to the left of the picture. The rest of the unit (pumps, humidifier, power electronics, compressor) is much less bulky than that of Figure 1.19, but still takes up over half the volume of the whole system.

1.8 Figures Used to Compare Systems

When comparing fuel cells with each other, and with other electric power generators, certain standard key figures are used. For comparing fuel cell electrodes and electrolytes, the key figure is the current per unit area, always known as the current density. This is usually given in $mA\,cm^{-2}$ though some Americans use $A\,ft^{-2}$. (Both figures are in fact quite similar: $1.0\,\mathrm{mA\ cm^{-2}} = 0.8\,\mathrm{A\ ft^{-2}}$.)

This figure should be given at a specific operating voltage, typically about 0.6 or 0.7 V. These two numbers can then be multiplied to give the power per unit area, typically given in $mW\,cm^{-2}$.

A note of warning should be given here. Electrodes frequently do not ‘scale up’ properly. That is, if the area is doubled, the current will often *not* double. The reasons for this are varied and often not well understood, but relate to issues such as the even delivery of reactants and removal of products from all over the face of the electrode.

Bipolar plates will be used to connect many cells in series. To the fuel cell stack will be added the ‘balance of plant’ components mentioned in Section 1.7. This will give a system of a certain power, mass, and volume. These figures give the key figures of merit for comparing electrical generators – specific power and power density.

$$\text{Power Density} = \frac{\text{Power}}{\text{Volume}}$$

The most common unit is kW m^{-3}, though kW L^{-1} is also used.

The measure of power per unit mass is called the *specific power*

$$\text{Specific Power} = \frac{\text{Power}}{\text{Mass}}$$

The straightforward SI unit of $W\,kg^{-1}$ is used for specific power.

The cost of a fuel cell system is obviously vital, and this is usually quoted in *US dollars per kilowatt*, for ease of comparison.

The lifetime of a fuel cell is rather difficult to specify. Standard engineering measures such as MTBF (mean time between failures) do not really apply well, as a fuel cell’s performance always gradually deteriorates, and their power drops fairly steadily with time as the electrodes and electrolyte age. This is sometimes given as the ‘*percentage deterioration per hour*’. The gradual decline in voltage is also sometimes given in units of millivolts per 1000 hours. Formally, the life of a fuel cell is over when it can no longer deliver the rated power, that is, when a ‘10-kW fuel cell’ can no longer deliver 10 kW. When new, the system may have been capable of, say, 25% more than the rated power −12.5 kW in this case.

The final figure of key importance is the efficiency, though as is explained in the next chapter, this is not at all a straightforward figure to give, and any information needs to be treated with caution.

In the automotive industry, the two key figures are the cost per kilowatt and the power density. In round figures, current internal combustion engine technology is about 1 kW L^{-1} and \$10 per kW. Such a system should last about 4000 h (i.e. about 1 h use each day for over 10 years). For combined heat and power systems the cost is still important, but a much higher figure of \$1000 per kW is the target. The cost is raised by the extra heat exchanger and mains grid connection systems, which are also needed by rival technologies, and because the system must withstand much more constant usage −40,000 h use would be a minimum.

1.9 Advantages and Applications

The most important disadvantage of fuel cells at the present time is the same for all types – the cost. However, there are varied advantages, which feature more or less strongly for different types and lead to different applications (Figure 1.21). These include the following:

- *Efficiency*. As is explained in the following chapter, fuel cells are generally more efficient than combustion engines whether piston or turbine based. A further feature of this is that small systems can be just as efficient as large ones. This is very important in the case of the small local power generating systems needed for combined heat and power systems.
- *Simplicity*. The essentials of a fuel cell are very simple, with few if any moving parts. This can lead to highly reliable and long-lasting systems.
- *Low emissions*. The by-product of the main fuel cell reaction, when hydrogen is the fuel, is pure water, which means a fuel cell can be essentially 'zero emission'. This is their main advantage when used in vehicles, as there is a requirement to reduce vehicle emissions, and even eliminate them within cities. However, it should be noted that, at present, emissions of CO_2 are nearly always involved in the production of hydrogen that is needed as the fuel.
- *Silence*. Fuel cells are very quiet, even those with extensive extra fuel processing equipment. This is very important in both portable power applications and for local power generation in combined heat and power schemes.

The fact that hydrogen is the preferred fuel in fuel cells is, in the main, one of their principal disadvantages. However, there are those who hold that this is a major advantage. It is envisaged that as fossil fuels run out, hydrogen will become the major world fuel and energy vector. It would be generated, for example, by massive arrays of solar cells electrolysing water. This may be true, but is unlikely to come to pass within the lifetime of this book.

The advantages of fuel cells impact particularly strongly on **combined heat and power** systems (for both large- and small-scale applications), and on **mobile power systems**,

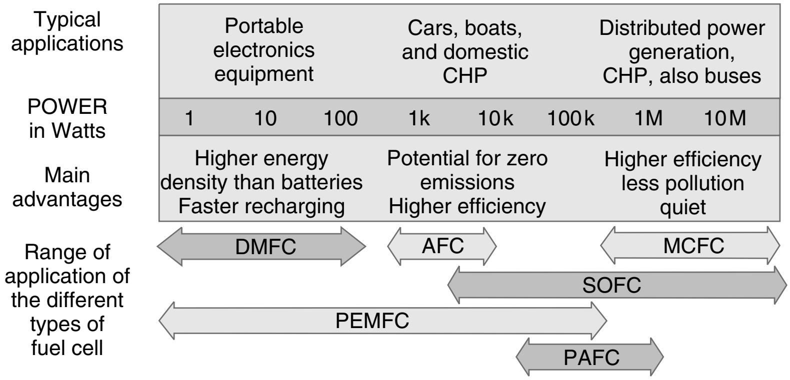

Figure 1.21 Chart to summarize the applications and main advantages of fuel cells of different types, and in different applications.

especially for **vehicles** and electronic equipment such as **portable computers, mobile telephones, and military communications equipment**. These areas are the major fields in which fuel cells are being used. Several example applications are given in the chapters in which the specific fuel cell types are described – especially Chapters 4 to 7. A key point is the wide range of applications of fuel cell power, from systems of a few watts up to megawatts. In this respect, fuel cells are quite unique as energy converters – their range of application far exceeds all other types.

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