Factfiles

The Institution of Engineering and Technology

Fuel **Cells**

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Summary

This Factfile describes the principles behind the operation of fuel cells and the various types of fuel cell available, and gives information on fuel cell performance, systems and applications.

Principles of Operation

A fuel cell works much like a battery. In both batteries and fuel cells two electrodes, an anode and a cathode, are separated by an electrolyte. A storage battery is a sealed unit, containing all the substances in the electrochemical oxidation-reduction reactions involved and has, therefore, a limited capacity. In contrast, a fuel cell is supplied with its reactants externally and operates continuously as long as it is supplied with fuel.

While fuel cells have been used in niche applications for many years, mainly as standby electrical power supply units, recent improvements in their cost and efficiency are leading to future uses in the much larger market of ‘zero emission’ vehicles (ZEVs). The new generation of fuel cells will probably also find other applications , such as in small (3–10 kW) combined heat and power (CHP) units.

Fuel Cell Types

The five basic types of fuel cell[1] are classified by the electrolyte that they employ,

- **low temperature** types include the alkaline fuel cell (AFC) and solid polymer fuel cell (SPFC),
- the **medium temperature** type is the phosphoric acid fuel cell (PAFC),
- the two **high temperature** types are the molten carbonate fuel cell (MCFC) and the solid oxide fuel cell (SOFC).

Oxygen from air is the oxidant (cathode fuel) in all these, but a number of fuels can be ‘burned’ at the anode. An idealised schematic diagram illustrating the structure, electron and ion flow for the various types of fuel cell is shown in **Figure 1**.

An alternative classification is based on fuels:

- **Reformate/air fuel cells**, in which the feedstock is hydrogen produced by the in-situ steam-reforming and/or partial oxidation of fuels such as methane, gasoline ($C_8H_{15.4}$) or diesel fuel ($C_{14}H_{22.5}$). The carbon monoxide (CO) also produced is tolerated in some cell types but not in others, in which case it must be removed from the reformer output prior to being fed to the anode, e.g. $2\ CH_3OH$ (methanol) + H_2O (steam) + heat → $5\ H_2 + CO + CO_2$ $CH_3(CH_2)_6CH_3$ (gasoline) + $6O_2$ (air) → $9H_2 + 4\ CO + 4\ CO_2$ + heat
- **Hydrogen/air fuel cells**, which use stored or chemically generated pure hydrogen as the anode feedstock.
- **Direct oxidation fuel cells**, in which an organic fuel is directly oxidised at the anode.

Hydrogen is a favoured anode feedstock because its electrochemical oxidation is fast and clean; however it is not a primary fuel. If it is not made by fuel reforming, as described above, it must be produced by other means, usually the electrolysis of water. This only makes sense in greenhouse gas abatement terms if the electricity comes from a non-fossil fuel source such as nuclear or a renewable energy source.

Table 1 lists some fuel cells based on these types, where the solid polymer design, SPFC, appears in the Proton Exchange Membrane Fuel Cell (PEMFC) and in the Direct Methanol Fuel Cell (DMFC). A summary of fuel cell electrochemical reactions is shown in **Table 2**.

Figure 1. Principle of Fuel Cell Operation

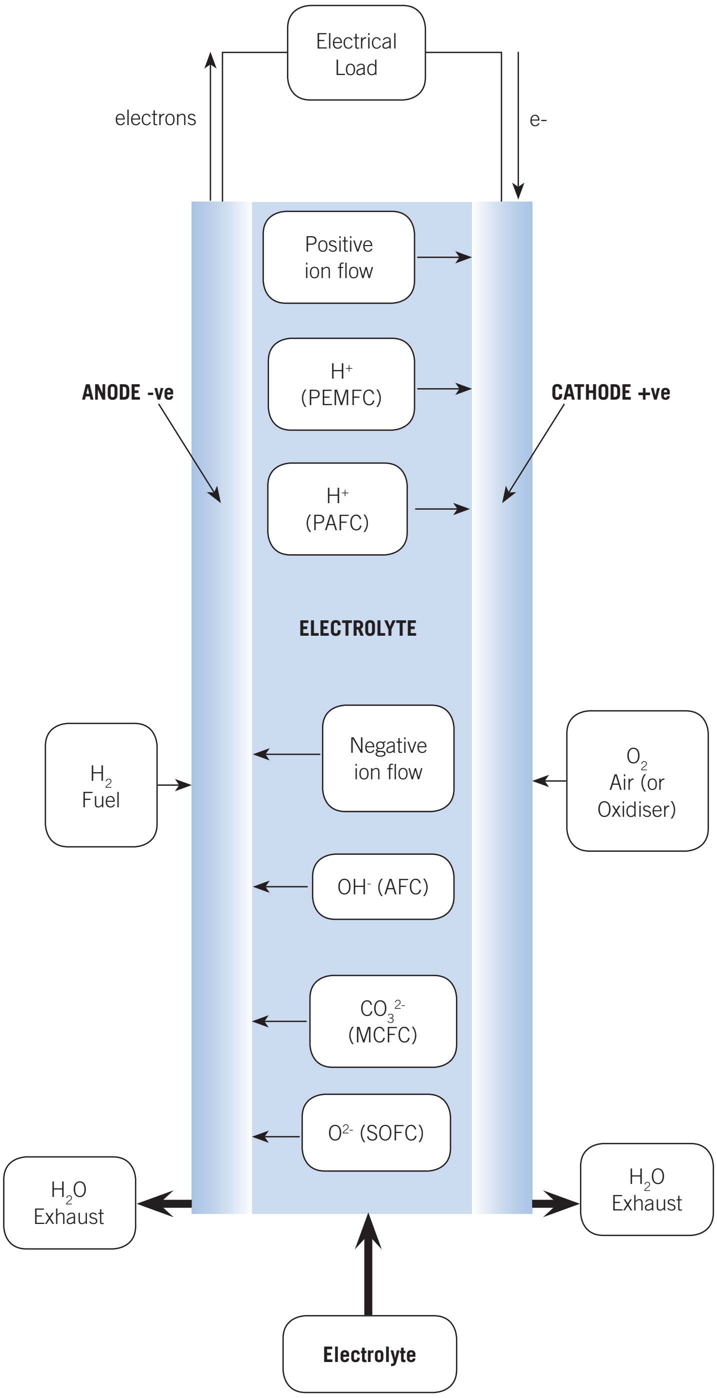


Table 1. Fuel Cell Types and Characteristics

Type	**AFC**	**PEMFC**	**DMFC**	**PAFC**	**MCFC**	**SOFC**
Electrolyte	Aqueous Potassium Hydroxide (30-40%)	Sulphonated Organic Polymer (hydrated during operation)	Sulphonated Organic Polymer (hydrated during operation)	Phosphoric Acid	Molten Lithium / Sodium / Patassium Carbonate	Yttria-stabilised Zirconia
Operating Temp. °C	60-90	70-100	90	150-220	600-700	650-1000
Charge Carrier	OH^-	H^+	H^+	H^+	CO_3^{2-}	O^{2-}
Anode	Nickel (Ni) or precious metal	Platinum (Pt)	Plantium - Ruthenium (Pt, Ru)	Platinum (Pt)	Nickel / Chromium Oxide	Nickel / Yttria-stabilised Zirconia
Cathode	Platinum (Pt) or lithiated NiO	Platinum (Pt)	Plantium - Ruthenium (Pt, Ru)	Platinum (Pt)	Nickel Oxide (NiO)	Strontium (Sr) doped Lanthanum Manganite
C-generation Heat	None	Low Quality	None	Acceptable for many applications	High	High
Electrical Efficiency %	60	40-45	30-35	40-45	50-60	50-60
Fuel Sources	H_2 Removal of CO_2 from both gas streams necessary	H_2 Reformate with less than 10ppm CO	Water / Methanol solution	H_2 Reformate	H_2, CO, Natural gas	H_2, CO, Natural gas

Table 2. Summary of Fuel Cell Electrochemical Reactions

Type	**Fuel to Anode**	**Product of catalytic reaction**	**Ion in electrolyte**	**Product of catalytic reaction**	**Fuel to Cathode**
AFC	$2H_2$ →	H^+ ↓ $4H_2O + 4e^-$	$4OH^-$ ←	$4OH^-$	O_2 ← $+2H_2O + 4e^-$
PEMFC	$2H_2$ →	$4H^+$ ↓ $+4e^-$	$4H^+$ →	↓ $2H_2O$	O_2 ← $+4e^-$
DMFC	CH_3OH → $+H_2O$	$6H^+$ ↓ $CO_2+ +6e^-$	$6H^+$ →	↓ $3H_2O$	$3/2\ O_2$ ← $+6e^-$
PAFC	$2H_2$ →	H^+ ↓ $+4e^-$	$4H^+$ →	↓ $2H_2O$	O_2 ← $+4e^-$
MCFC	$2H_2$ → in hydro-carbon fuel	↓ $2H_2O$ $+2CO_2 +4e^-$	$2CO_3^{2-}$ ←	$2CO_3^{2-}$	O_2 ← $+2\ CO_2 +4e^-$
SOFC	$2H_2$ → in hydro-carbon fuel	H^+ ↓ $2H_2O +4e^-$	$2O^{2-}$ ←	$2O^{2-}$	O_2 ← $+4e^-$

Fuel Cell Performance

Thermodynamic Efficiency η_{th}

The amount of energy available for useful work, arising from the energy changes of the electrochemical reaction occurring in a fuel cell under standard conditions of temperature and pressure, is governed by the Gibbs Free Energy equation:

$$\Delta G = \Delta H - T\Delta S$$

where ΔG is the Gibbs Free Energy or standard free energy of formation available for work, ΔH is the standard enthalpy of formation, T is the absolute temperature of 298.15K and ΔS is the entropy change for the reaction.

For a hydrogen-oxygen reaction

$$H_2\ (\text{gas}) + \tfrac{1}{2}\, O_2\ (\text{gas}) \rightarrow H_2O$$

the thermodynamic values from tables are:

$\Delta G = 237.13$ kJ/mol and $\Delta H = 285.13$ kJ/mol
for water as a liquid; and

$\Delta G = 228.57$ kJ/mol and $\Delta H = 241.82$ kJ/mol
for water as a gas.

The maximum theoretical thermodynamic efficiency, η_{th}, is the ratio of the Gibbs Free Energy to the standard enthalpy of formation:

$$\eta_{th} = \frac{\Delta G}{\Delta H} \times 100$$

$$= 83.0\%\ (\text{liquid})\ \text{to}\ 94.5\%(\text{gas})$$

Electrical Efficiency, η_{elec}

The electrical efficiency (η_{elec}) is defined as the ratio of the maximum of the electrical work done ($W_{elec.max}$) on an electrical load at a measured terminal voltage to the standard enthalpy of formation.

$$\eta_{elec} = \frac{W_{elec.max}}{\Delta H} \times 100$$

This efficiency is the common measure of cell efficiency. In practice because of internal resistance of the cells it is considerably less than the thermodynamic efficiency.

Cell Voltage

Electrons generated at the site of oxidation (the anode) of a cell are “pushed” towards the cathode by an electromotive force, or EMF. This force is due to the difference in electric potential energy of an electron at the two electrodes. The quantity of electric work done is proportional to the number of electrons (the quantity of electric charge) moved and the magnitude of the potential difference.

Work = (charge) x (potential energy difference)

When the fuel cell reactants and products are present as pure solids or in concentrations of 1.0mole, or as gases at 1.0bar, the measured cell potential (potential energy difference) in volts is the standard potential (E^0) - all values being given at 25°C (298K). The standard potential E^0 is a quantitative measure of the maximum cell potential ie open-circuit voltage.

For the hydrogen-oxygen fuel cell involving the transfer of two electrons per molecule of water formed:

$$2H^+ + O^{2-} \rightarrow H2O$$

for water as a liquid $E^0 = 1.23$ volts
and for water as a gas $E^0 = 1.18$ volts

This is the voltage for a single cell. Practical fuel cells are built from an interconnected assembly of such single cells into ‘stacks’ to provide the desired voltage and power output.

Polarisation

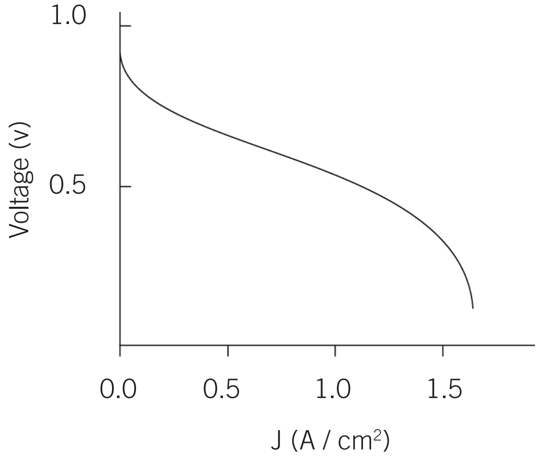
When the cell is under load, the efficiency and terminal voltage decrease because of a number of factors, including polarisation effects and interconnection losses between cells in the fuel cell stack. Polarisation effects in a cell arise for a number of reasons.

- The diffusion of ions through the electrolyte results in the building up of concentration gradients thereby decreasing the rate of transport. The relationship between concentration over-voltages and electric current is approximately linear up to a limiting value, above which the over-voltages build up rapidly (Mobility Inhibition/ Concentration Polarisation).
- To achieve a self-sustaining reaction the hydrogen and oxygen must attach to the surface of the cathode and this process takes time and limits current flow.
- Ohmic resistance arising from the transport of charged particles through the electrolyte.

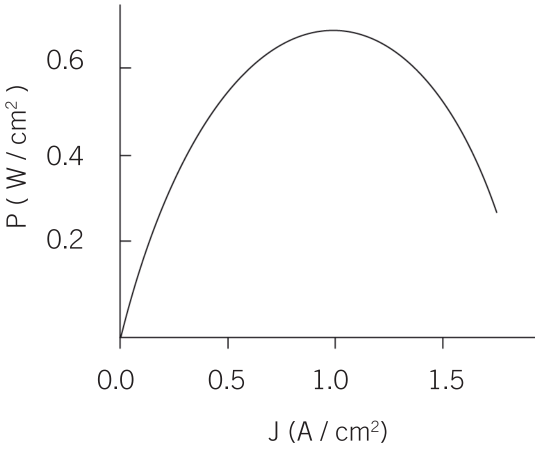
Figure 2 illustrates the performance characteristics of a Proton Exchange Membrane Fuel Cell. **Figure 2(a)** shows the voltage as a function of current density. The effects of polarisation can be seen in **Figure 2(b)** which shows the power density as a function of the current density. The power losses due to polarisation cause the curve to depart from and exist below the ideal power-current straight line relationship. As the current density increases from zero the activation power losses, initially ohmic losses at the maximum power point, and finally the mobility inhibition losses causing power shutdown, determine the location of the curve. Finally, **Figure 2(c)** shows efficiency as a function of power density. Note that unlike internal combustion engines, the efficiency increases with decreasing load.

Figure 2. Fuel Cell Performance

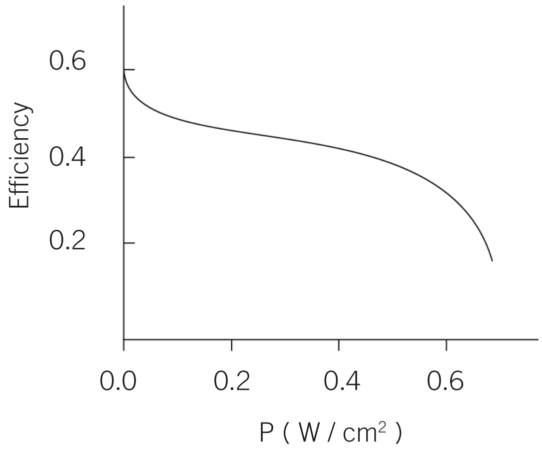
(a) Performance Curve



(b) Power Density



(c) Efficiency



Fuel Cell Systems

Fuel Processing

In practice hydrogen always occurs in combination with other elements. It is necessary, therefore, to produce it either by electrolysis in the case of water or by separation in a reformer if a hydrocarbon fuel is used as a primary source. The largest quantity of hydrogen is produced by the catalytic steam reformation of hydrocarbons. This process uses methane, CH4, as the primary starting material. Methane reacts with steam at high temperature to give carbon monoxide and hydrogen:

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

A fuel cell system which includes a fuel reformer can utilise, in principle, the hydrogen from any hydrocarbon fuel from natural gas to methanol. The two primary types of reformers being developed for transportation are steam reformers and partial oxidation reformers. Steam reformers have higher efficiency but partial oxidation reformers are simpler.

A high temperature fuel cell can use the carbon monoxide as a fuel, but for lower temperature cells the carbon monoxide is unacceptable and must be removed from the reformer gas stream. This can be achieved by a further reaction with steam, known as the water-gas shift reaction, the process producing more hydrogen:

$$CO + H_2O \rightarrow H_2 + CO_2$$

or removed by preferential oxidation reactors or by separation membranes.

If the primary fuel contains sulphur a desulphurisation process must be included prior to the reformer.

Water Management

As an exhaust product, water is seen as providing a potentially important added benefit in fuel cell operation in future, given concerns about the adequate local supplies of pure water for human consumption and industrial purposes. In the alkaline fuel cells used aboard the space shuttle for example, in seven days the fuel cells consume 680 kg of hydrogen and produce 864 litres of drinking water. In MCFC and SOFC cells this water is produced in the form of high temperature steam, the water concentration needing to be controlled in these cells to avoid electrode carbon deposition. Within SPFC cells water flow has to be controlled to facilitate ion transportation, all of which illustrates that water management is an essential part of the design of a fuel cell plant.

Temperature Control

A preheating stage, particularly for high temperature fuel cells, may be required for start-up. Heat exchangers are required to ensure the reactants enter the cells at appropriate temperatures for operation, again a particularly important requirement for high temperature cells. The flow rate of the oxidant generally controls the stack temperature.

Power Conditioning

Fuel cell output is in the form of direct current (DC); the voltage depending on the stack size. For most purposes alternating currents (AC) at higher voltages are required, therefore fuel cell output is transformed from DC to AC by means of standard power electronics in an inverter and thence to a higher voltage by means of a transformer.

Figure 3 shows these sub-systems in schematic form, in a flow diagram of a solid oxide fuel cell-based combined heat and power scheme for an office building.

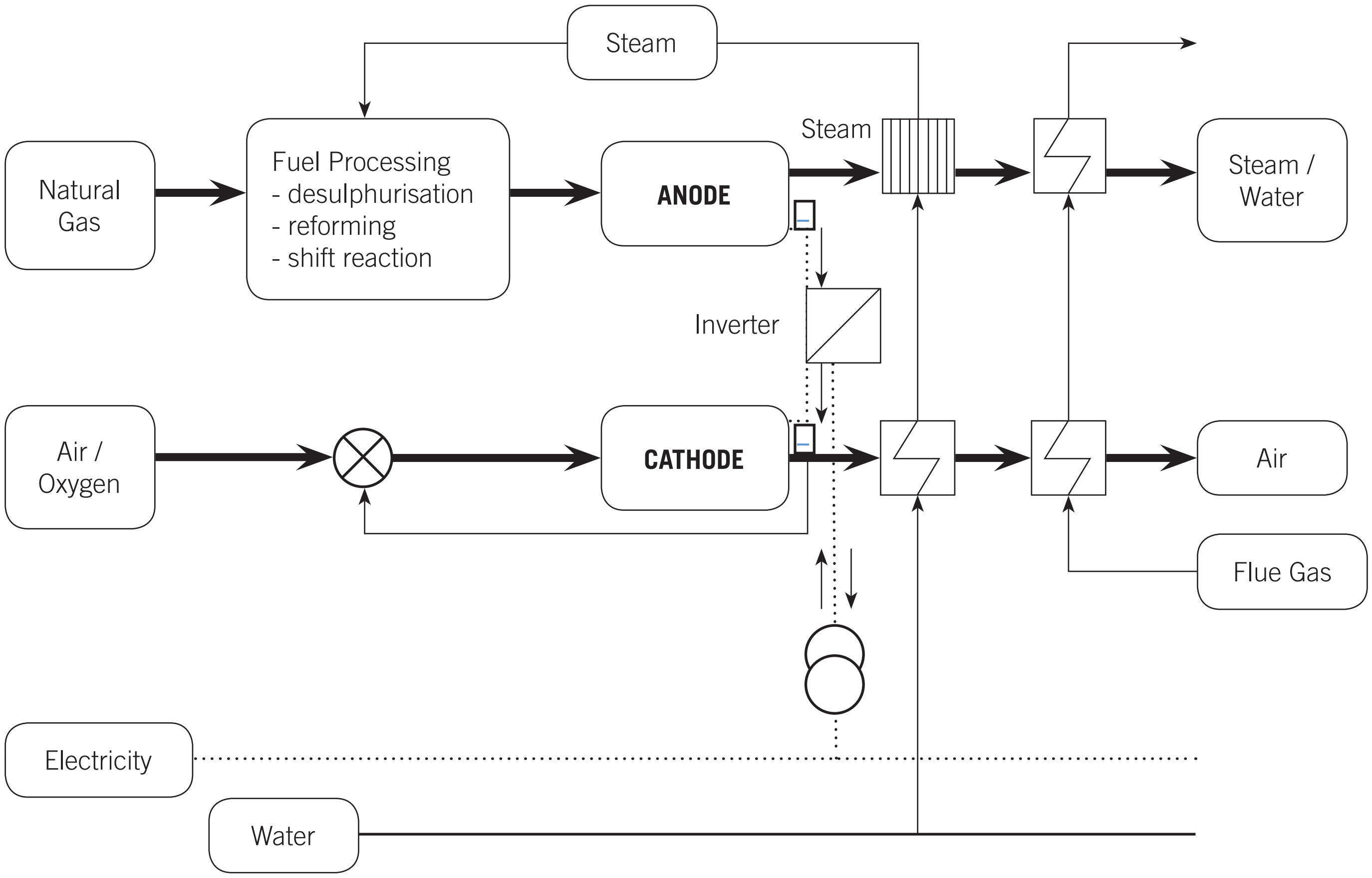
Applications

Fuel cells have the potential to be deployed in a wide range of applications. These can be divided into stationary, transportation and portable categories.

Stationary Applications

Stationary applications focus on the production of electricity in particular situations. The core application is the local supply of electricity where low noise, vibration and gaseous emissions are required. This application can be enhanced by also capturing any waste heat from the fuel cell so that heating and cooling can also be provided. This has the potential to increase the energy conversion efficiency from some 40 per cent (electricity only) to over 80 percent. Stationary fuel cells can also be used to enhance the reliability of electricity supply. By ensuring continuity of supply in the event of grid failure, supply reliability to critical loads can be significantly enhanced. Finally, stationary fuel cells can be used to make best use of waste gases that are a byproduct of certain industrial processes, including waste gas from landfill sites.

Figure 3. Flow Diagram of Solid Oxide Fuel Cell System in a Combined Heat and Power Scheme



Transportation Applications

The environmental pressure to find an alternative to the internal combustion (IC) engine has resulted in significant investment in transport applications and real progress has been made.

The attractions of the fuel cell vehicle over battery powered equivalents is that much greater energy can be stored on board and refuelling can also be carried out more quickly. However the efficiency from source to wheel is significantly lower than with battery-powered vehicles, recuperating braking energy can be more difficult and the working life of fuel cells in the uncontrolled environment of the private transport market is unproven. While some engineers believe that the fuel cell vehicle is the technology most likely to offer a genuine alternative to the IC vehicle, others place their faith in battery power. Prototype fuel cell cars, buses, trains and scooters are being tested and may result in products that are commercially viable and environmentally preferable to the alternatives - the challenge then will be to develop suitable refuelling and maintenance infrastructures for the technology.

Portable Applications

The energy density of a fuel cell package also makes them attractive for portable power applications where a grid supply is not available. Small portable power units are already available and it could soon be common place for small consumer electronics devices to be powered by a fuel cell system.

Stationary Power Fuel Cell Types

Various fuel cell types have been identified for large-scale stationary power generation, viz. PAFC, MCFC and SOFC and, more recently, PEMFC.

- **Phosphoric Acid Fuel Cells (PAFC)**
  PAFC's have been developed to the first stages of commercialisation. Turnkey 200 kW plants are available and hundreds have been installed in Europe, USA and Japan. With an operating temperature around 200°C there is potential for hot water supply as well as electricity depending on the matching of the heat and electricity load profiles. Electrical efficiencies can exceed 40%.
- **Molten Carbonate Fuel Cells (MCFC's)**
  MCFC'S offer higher fuel-to-electricity conversion efficiencies of up to 60%. At operating temperatures of around 650°C the waste heat produced can be used in conventional combined cycle plant for the generation of more electricity via steam turbines thus raising the overall combined station efficiency. An important requirement of MCFC's is that operation is not affected by carbon monoxide or carbon dioxide in the fuel gas. At 650°C the carbonate salts of the electrolyte are in a liquid state allowing ion transport. At the anode the carbonate ions react with the hydrogen fuel to produce electrons for the external circuit, carbon dioxide and water; the cathode is supplied with oxygen and carbon dioxide and it is important that the correct amount of carbon dioxide is supplied and re-circulated in order to replenish the electrolyte.
- **Solid Oxide Fuel Cells (SOFC's)**
  SOFC's are solid state devices operating at temperatures up to 1000°C with a potentially wider choice of fuels without having to manage liquid electrolytes. Current is conducted by the passage of oxygen ions through a solid electrolyte. At the cathode oxygen is reduced to form oxygen ions; at the anode the transported oxygen ions react with the gaseous fuel to produce electrons for the external circuit and water. Generally fuel flow is used to regulate electrical output and air flow controls the temperature. SOFC's must operate at high temperatures to enable diffusion of oxygen ions through the electrolyte made possible by reason of oxygen vacancies in the electrolyte crystalline structure. With conventional designs the anode is a composite of nickel and yttria-stabilised zirconia (YSZ). This composite is an electron conductor (due to nickel) and also an ionic conductor (due to YSZ). Nickel, however, catalyses the formation of graphite from hydrocarbons, thus carbon formation with nickel based anodes is unavoidable for the wider range of hydrocarbon fuels available. Research suggests that anodes made from a composite of copper and ceria, or samaria-doped ceria, may remove this barrier in the future. Electrical efficiency is up to 60% and, again when used with combined cycle plant, higher overall station efficiencies can be obtained. These cells may be able to reform hydrocarbon fuels internally with no pumps required to circulate hot electrolyte and although still at a relative early stage of development they are regarded as most promising for generating electricity from hydrocarbon fuels.

Advantages of Stationary Fuel Cells
Given the cost reductions in time associated with maturing technologies allowing fuel cells to be competitive with conventional generation plant, these stationary fuel cells fully developed and deployed within the electricity supply industry will have significant impacts and advantages compared with conventional generating plant, viz.

- Emission reduction (NOx, SOx, CO, hydrocarbons)
- Fossil fuel saving through higher efficiencies if used to replace older conventional fossil fuel plant - although modern 60% efficient Combined Cycle Gas Turbine (CCGT) stations are more efficient than either PEMFC or PAFC
- Thermal recovery of high grade heat for CHP schemes
- Planning flexibility in plant size without loss of efficiency
- High reliability
- Quietness of operationSuitability for embedded generation
- in either high demand or remote areas

MCFC and SOFC plants are expected to be commercially available in the coming years, initially with 20MW capacity and fuelled by natural gas.

Automotive Fuel Cell Types

Both alkaline and phosphoric acid fuel cells have been used in demonstration vehicles, but alkaline cells have an intolerance to carbon dioxide, the electrolytes reacting with the carbon dioxide, and the phosphoric acid cells are too bulky for mobile purposes.

The major technology for transportation purposes has emerged as the low temperature solid polymer fuel cell (SPFC) and, in particular, the proton exchange membrane fuel cell (PEMFC).

- **Proton Exchange Membrane Fuel Cells (PEMFC)**
  PEMFC's comprise a thin ion conducting membrane between two platinum coated electrodes and afford a comparatively high power density. The fuel is hydrogen which is supplied to the anode where hydrogen ions and free electrons are generated. It is necessary to control the management of the water in the membrane which is essential for the hydrogen ion transportation, the water tending to follow the hydrogen ions to the cathode, also at the anode to ensure the correct hydrogen interaction with the platinum catalyst and to prevent dehydration. Platinum catalysts are tolerant to carbon dioxide but not to carbon monoxide. Although progress is being made in alleviating this problem, an approximate guide is that quantities greater than 10 ppm for a platinum catalyst or at most 100 ppm for a platinum/ruthenium catalyst result in a degradation of performance. This change in output is illustrated in **Table 3**. The output of a PEMFC can be altered quickly to match varying load demand, thus making it suitable for automotive purposes where quick start-up is required. Stacks of cells are capable of producing 1 kW/litre or 0.7 kW/kg, equivalent to about 28 kW/cubic foot.
- **Direct Methanol Fuel Cell (DMFC)**
  In order to avoid the necessity of either storing the hydrogen on board a vehicle or reforming it from

another fuel, a solid polymer fuel cell working directly from methanol has been developed. An aqueous, low concentration 3% methanol solution is used with the methanol and water reacting at the anode to produce carbon dioxide as well as hydrogen ions and free electrons as before. The key to this process is the use of a 50:50 platinum-ruthenium alloy catalyst on the carbon electrodes. This technology is less advanced and the efficiency and power are generally lower than those of the PEMFC, but this is compensated for by the absence of a hydrogen tank or a fuel reformer. As with all fuel cells deriving hydrogen from fossil fuel, the cell emits carbon dioxide, but compared with internal combustion engines, its higher efficiency, particularly under part load, ensures less carbon dioxide being produced. In addition, again as with all fuel cells, because there is no combustion there is an absence of NOx emissions. The hydrocarbon-fuelled cell has considerable potential for the auto industries. It avoids the high cost of hydrogen and the low specific energy density of hydrogen when compressed. Liquid fuels have not only a much higher specific energy density, but also the benefits of an established distribution system supported by the necessary forecourt engineering knowledge. The range of hydrocarbon fuels which can be used as sources of hydrogen include not only methanol but also natural gas and gasoline. Solid polymer fuel cells using such fuel sources are currently being tested by a number of major automobile manufacturers in the development of proprietary ‘zero-emission’ engines.

- **Intermediate Temperature Solid Oxide Fuel Cell (ITSOFC)** More recently solid oxide fuel cells operating at 500 - 700^{o}C have been suggested with possible use in transport applications. Such cells using methanol fuel have been demonstrated. Advantages include the absence of high temperature fuel reforming and also of catalyst poisoning by carbon monoxide, which is used here as a fuel.

Table 3. PEMFC Output with Carbon Dioxide/Monoxide present in the Hydrogen Fuel Gas

Fuel Gas	**Voltage V**	**Current Density mA/cm2**	**Power W**
H2	0.17	430	100
H2, 25% CO2	0.68	430	96
H2, 25% CO2, 0.3% CO	0.71	215	50

Endnotes

1. The US industry consortium Fuel Cells 2000 website provides a useful guide to fuel cell technology. http://www.fuelcells.org

Further Information

On-line resources

- Fuel Cell Europe http://www.fuelcelleurope.org
- How stuff works http://auto.howstuffworks.com/fuel-efficiency/alternative-fuels/fuel-cell.htm
- Fuel Cells 2000 http://www.fuelcells.org
- UK Government policy and R&D support http://www.decc.gov.uk/en/content/cms/meeting_energy/h2_fuel_cells/h2_fuel_cells.aspx
- The Fuel Cells and Hydrogen Joint Undertaking (FCH JU) is a public private partnership supporting research, technological development and demonstration (RTD) activities in fuel cell and hydrogen energy technologies in Europe. http://www.fch-ju.eu/

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