

Materials for fuel-cell technologies

Brian C. H. Steele* & Angelika Heinzl†‡

*Centre for Ion Conducting Ceramics, Department of Materials, Imperial College, London SW7 2BP, UK (e-mail: b.steele@ic.ac.uk)

†Fraunhofer Institute for Solar Energy Systems, Heidenhofstrasse 2, 79110 Freiburg, Germany

‡Present address: Fachgebiet Energietechnik, Universität Duisburg, Lotharstr. 1-21, 47057 Duisburg, Germany (e-mail: a.heinzl@uni-duisburg.de)

Fuel cells convert chemical energy directly into electrical energy with high efficiency and low emission of pollutants. However, before fuel-cell technology can gain a significant share of the electrical power market, important issues have to be addressed. These issues include optimal choice of fuel, and the development of alternative materials in the fuel-cell stack. Present fuel-cell prototypes often use materials selected more than 25 years ago. Commercialization aspects, including cost and durability, have revealed inadequacies in some of these materials. Here we summarize recent progress in the search and development of innovative alternative materials.

The successful conversion of chemical energy into electrical energy in a primitive fuel cell was first demonstrated¹ over 160 years ago. However, in spite of the attractive system efficiencies and environmental benefits associated with fuel-cell technology, it has proved difficult to develop the early scientific experiments into commercially viable industrial products. These problems have often been associated with the lack of appropriate materials or manufacturing routes that would enable the cost of electricity per kWh to compete with the existing technology, as outlined in a recent survey².

The types of fuel cells under active development are summarized in Fig. 1. The alkaline fuel cell (AFC), polymeric-electrolyte-membrane fuel cell (PEMFC) and phosphoric-acid fuel cell (PAFC) stacks essentially require relatively pure hydrogen to be supplied to the anode. Accordingly, the use of hydrocarbon or alcohol fuels requires an external fuel processor to be incorporated into the system. This item not only increases the complexity and cost of the system, but also decreases the overall efficiency as indicated in Fig. 2. In contrast, molten-carbonate fuel cells (MCFCs) and solid-oxide fuel cells (SOFCs) operating at higher temperatures have the advantage that both CO and H₂ can be electrochemically oxidized at the anode. Moreover, the fuel-processing reaction can be accomplished within the stack, which enables innovative thermal integration/management design features to provide excellent system efficiencies (~50%).

Although the introduction of a 'hydrogen economy' might seem an attractive scenario, its implementation is beset with formidable technical and economic difficulties. The cheapest technology for the large-scale production of hydrogen is the steam reforming of natural gas, which produces significant emissions of greenhouse gases³. The topic of hydrogen storage is addressed in the accompanying review by Schlapbach and Züttel (see pages 353–358); unless there is a breakthrough in the production of hydrogen and the development of new hydrogen-storage materials, the concept of a 'hydrogen economy' will remain an unlikely scenario. In this article, therefore, we assume that fuel cells have to be designed for operation on hydrocarbon or alcohol fuels to ensure that the technology is able to penetrate the relevant major markets. Otherwise fuel-cell technology will be confined to restricted niche activities where hydrogen might be a commercial option, such as city bus fleets. Clearly the choice of fuel is a

further complication in the factors influencing the commercialization of fuel cells.

Constraints on material selection

Materials selection for a commercial product involves an iterative design process that eventually becomes specific to the particular product and application. However, it is possible to make a few general statements about the selection of materials for fuel cells. The combined area-specific resistivity (ASR) of the cell components (electrolyte, anode and cathode) should be below 0.5 Ω cm² (and ideally approach 0.1 Ω cm²) to ensure high power densities, with targets of 1 kW dm⁻³ and 1 kW kg⁻¹ often mentioned for transport applications. High power densities are also important to reduce costs, as the amount of material per kW is thus minimized. These topics, and considerations of cell efficiencies, are summarized in Box 1.

The need to minimize cell resistivities has a major impact on the selection and processing of the cell components. Cost-effective fabrication of porous electrode structures was achieved for the first time only about 40 years ago. The electrolyte, gaseous reactants, electrocatalyst and current collector have to be brought into close contact within a confined spatial region termed the triple-phase-boundary interface. For the low-temperature systems, the introduction of hydrophobic polytetrafluoroethylene (PTFE or Teflon) greatly simplified the fabrication of porous, liquid-resistant gas-diffusion structures. Metal or carbon powders (or porous carbon papers) provided the electronic pathways, and to further reduce the ASR of the electrode a metallic wire mesh or screen was usually incorporated into the structure. Further improvements in performance were obtained during the 1960s by depositing small crystallites (2–5 nm) of the electrocatalyst (usually platinum or Pt alloys) onto carbon powder or paper. In retrospect, this accomplishment was probably the first manifestation of an engineered nanostructure, and it is not surprising that its implementation more than 40 years ago was so difficult.

High ionic conductivities (>1 S cm⁻¹) associated with the liquid KOH, phosphoric acid and molten carbonate electrolytes ensured that, with appropriate design strategies, the ASR values of these components can be small. Although exhibiting lower specific ionic conductivity values, the Nafion membrane used in the PEMFC system can be fabricated relatively easily as a thick film (100 μm) to produce satisfactory ASR values, provided the water content of the film is controlled under the dynamic conditions of cell operation. In contrast, it has been, and continues to be,

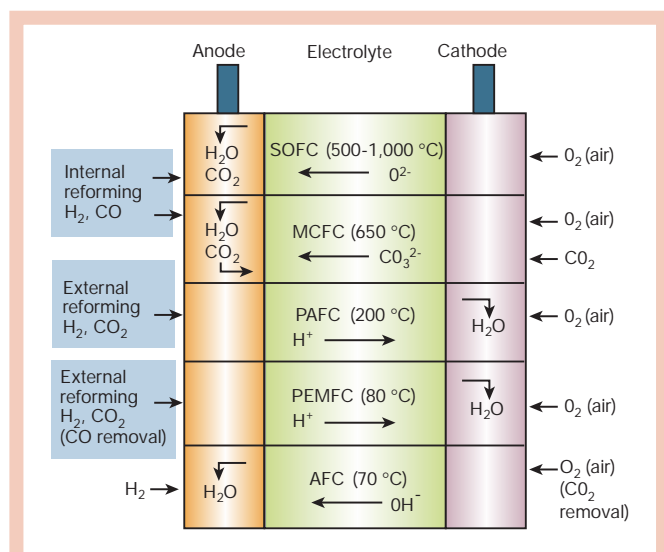


Figure 1 Summary of fuel-cell types. The oxidation reaction takes place at the anode (+) and involves the liberation of electrons (for example, $\text{O}^{2-} + \text{H}_2 = \text{H}_2\text{O} + 2\text{e}^-$ or $\text{H}_2 = 2\text{H}^+ + 2\text{e}^-$). These electrons travel round the external circuit producing electrical energy by means of the external load, and arrive at the cathode (-) to participate in the reduction reaction (for example, $1/2\text{O}_2 + 2\text{e}^- = \text{O}^{2-}$ or $1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}$). It should be noted that as well as producing electrical energy and the reaction products (for example, H_2O and CO_2), the fuel-cell reactions also produce heat. The reaction products are formed at the anode for SOFC, MCFC and AFC types, and at the cathode for PAFC and PEMFC types. This difference has implications for the design of the entire fuel-cell system, including pumps and heat exchangers. To maintain the composition of the electrolyte component in the MCFC system, CO_2 has to be recirculated from the anode exhaust to the cathode input. Additionally, the composition of the polymeric-membrane electrolyte has to be carefully controlled during operation by an appropriate 'water management' technology.

difficult to scale-up thick-film technologies to provide cost-effective ceramic solid-oxide electrolyte components with required thicknesses in the range 10–30 μm . Usually the thick-film electrolyte has to be sintered dense at temperatures approaching 1,400 °C; this requires a porous ceramic substrate, which is often the anode or cathode material. The substrate material has to be carefully selected to avoid reaction with the electrolyte, and/or thermal expansion mismatch, during the high-temperature sintering process. The incorporation of a relatively weak, brittle structural component in SOFC stacks is at present restricting the application of SOFC systems to those situations that do not demand rapid temperature fluctuations. In this respect the recent development² of sintering procedures below 1,000 °C, which should allow the use of metal substrates, represents a significant advance that will enable the development of more rugged SOFC systems.

Another important component in a fuel-cell stack is the impermeable electronic conducting bipolar plate. This has the dual function of distributing the fuel and air to the anode and cathode, respectively, as well providing the electrical contact between adjacent cells. The corrosive acidic conditions prevailing in the PEMFC and PAFC systems severely restricts the choice of bipolar plate material and at present graphite is usually selected. However, alternative materials or manufacturing methods are mandatory if these systems are ever to attain the target costs. Major research and development (R&D) programmes are examining the behaviour of alternative carbon-based materials produced by injection moulding, or coated stainless steels. For the high-temperature systems (MCFC and SOFC) operating in the temperature range 500–750 °C, appropriate stainless steel compositions can be specified which seem to satisfy the technical and economic constraints. But for SOFCs operating at higher temperatures (800–1000 °C), alternative, more expensive bipolar plate materials have to be specified, which at present incur significant cost penalties.

Additional constraints influencing material selection arise from reliability and durability issues. For transport applications, minimal values of performance degradation (for example, 0.1% over 1,000 h) are required for projected operational lifetimes of 5,000 h. But for stationary applications — for example, distributed CHP (combined heat and power) systems — a similar degradation rate must extend over a period of at least 40,000 h (5 years). These different lifetime targets seem to be introducing problems for PEMFC prototype CHP systems, as the stack components were developed originally for transport applications.

A fuel-cell system also incorporates relevant balance-of-plant items such as pumps, valves, heat exchangers and piping. Although these important components comprise at least half the cost of a fuel-cell system, we will not consider them further here, except to note that for the PAFC system, many of which have now been operated for periods approaching 30,000 h, the main source of system breakdown has been balance-of-plant items. External fuel processors (reformers) are also the subject of intensive development around the world, and a variety of innovative compact reformers using diffusion-bonded printed-circuit components or micro-channel designs⁴ also illustrate the impact of materials technology on this aspect of fuel-cell systems.

For more than four decades now, reliable, efficient, fuel-cell systems incorporating AFC stacks have proved their worth in the Apollo spacecraft and space shuttles. Excellent electrode kinetics, when operating on pure hydrogen and oxygen, are an attractive feature of this system. But for terrestrial applications, the additional economic restraints, which include the need to replace hydrogen by cheaper hydrocarbon or alcohol fuels, have provided severe problems for materials selection and the associated fuel-processing technology. After 20 years development, the Elenco consortium abandoned attempts in 1996 to develop a bus powered by an AFC system. Although Zevco have purchased the technical rights, it is anticipated that market penetration of AFC systems will be small, in spite of a recent publication⁵ advocating the use of AFC systems with ammonia as the source of hydrogen fuel.

Approximately 200 PAFC co-generation units (International Fuel Cells (IFC) PC25 systems, delivering 200 kW) have been installed around the world, and have exhibited excellent reliability. However, the commercial future of this system is possibly in jeopardy as the manufacturers (IFC and Japanese companies) have been unable to reduce the capital cost sufficiently below US\$3,000 per kW_e as originally forecast^{6,7}. Most observers⁸ believe that for initial market entry the target cost per kW_e must be reduced to around US\$1,000 per kW_e , falling to below US\$500 per kW_e with volume production. Accordingly, we focus here on materials aspects of the PEMFC, MCFC and SOFC systems, which at present still appear to present opportunities to exploit their potential.

It is important to note that the materials currently being used in PEMFC, MCFC and tubular SOFC prototype demonstration units essentially remain the same as those selected at least 25 years ago^{9,10}. Although innovative fabrication and processing routes have improved the attributes (for example, lower cost and lower Pt loadings) of these materials, it is only in the past five years that system engineering and commercialization issues have highlighted the inadequacies of some of the materials originally selected. As indicated in the next two sections, it is these issues that are now driving the development of alternative materials, particularly for the PEMFC and intermediate temperature (IT)-SOFC stacks.

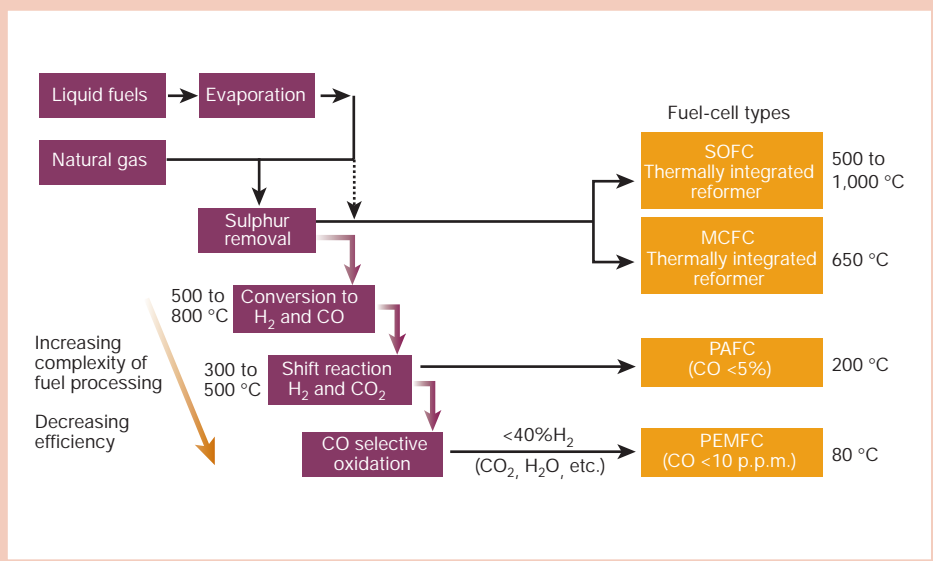
Polymeric-electrolyte-membrane fuel cells

The most important materials under development for PEMFC stacks are construction materials for the cell frames, bipolar plates, electrocatalysts for the fuel and air electrode, and the ion conducting membrane.

Depending on the fuel to be used in the PEM cell, the requirements for these materials are completely different. The simplest case is the operation with pure hydrogen and oxygen or air. Cells with high

Figure 2 Fuel-cell types and fuel processing.

Although selected fuels can be introduced directly into the anode compartment of the high-temperature fuel cells (SOFC and MCFC), better thermal management of the stack can usually be achieved by having separate reformer compartments that are thermally integrated within the stack to produce a mixture of fuel and syngas (H_2 and CO). For the lower-temperature fuel cells (PAFC and PEMFC), external reformers are required. Some of the fuel has to be consumed in these external reformers to maintain the operating temperature. Moreover, dilution of the H_2 fuel reduces performance of the cells, resulting in significant efficiency losses compared with operation on pure H_2 . It should be noted that the AFC stack cannot be operated on reformat fuels because of the presence of CO_2 in these gases.



power density and very low degradation are already state of the art. The main requirement for the future is to achieve reduction in the capital cost of the system by attention to materials selection and fabrication, and also by scaling-up the production volume. This target will probably cause a complete review of all the materials used up to now. The second possibility is to operate the PEM cell with a reformat fuel. In that case, inert gases and CO traces are present in the fuel. This is a challenge for the fuel electrode in particular, and a CO -tolerant catalyst is required. The most difficult option is the direct methanol fuel cell (DMFC). The methanol electrode also needs a CO -tolerant catalyst, as adsorbed CO species are formed during the electro-oxidation of methanol. In addition, the small polar methanol molecule behaves in a way similar to water and readily permeates through existing membrane materials. This behaviour leads to a loss in fuel and also to the formation of a mixed potential at the air electrode. The development of innovative membrane materials could remove this disadvantage. As the tolerance to CO by the electrocatalysts is strongly dependent on temperature, an alternative membrane with a better temperature stability is also another

important R&D target. However, an operation temperature above the boiling point of water requires a completely different type of membrane material, as no liquid water will be present under these circumstances for the hydrated protonic-conduction mechanism.

Bipolar plates

Much effort is being expended on the development of cost-effective materials for the bipolar plates. With respect to corrosion resistance, graphite materials are preferred. However, the conductivity of graphite materials is much less than that of metallic materials. Some conductivity values are: C polymers, $\sim 1 \text{ S cm}^{-1}$; graphite, 10^3 S cm^{-1} ; gold, $45,000 \times 10^3 \text{ S cm}^{-1}$; Fe alloys, $5,300 \times 10^3 \text{ S cm}^{-1}$; Ti, $2,400 \times 10^3 \text{ S cm}^{-1}$. For bipolar plates, polymer/graphite compounds are developed with at least 10 S cm^{-1} , reducing the resistivity of the bipolar plate well below the resistivity of the membrane. In addition, the fabrication costs of graphite plates incorporating gas-distribution channels are high, making such components too expensive. Moreover, as graphite materials are porous, a binder or resin has to be added to produce the necessary impermeability.

Polymeric materials can be machined more easily and cheaply by hot pressing or injection moulding. Polypropylene, for example, can be mixed with graphite to achieve sufficient electrical conductivity. Higher contents of graphite produce better electrical conductivity values, but the associated mechanical properties become more undesirable as the increased brittleness not only reduces the toughness, but also makes manufacturing more difficult and expensive. Typical carbon contents range between 50 and 80 weight%, and several groups^{11–14} are optimizing the machining processes in association with optimization of the material.

Another strategy is to use metallic bipolar plates. The gaseous flow structure can easily be fabricated in thin metal foils by pressing, but only a few metals are sufficiently corrosion-resistant in the acidic environment of the membrane. The most promising materials are stainless steels, as the other candidate metals such as titanium, niobium, tantalum and gold (including gold-plated metals) are too expensive. Stainless steels can provide satisfactory performance for several thousand hours. The steel is protected by a passive layer at the cathode side, but the anode side becomes contaminated by corrosion products^{15–18}. Stacks with metallic bipolar plates have been developed by Nuvera and by Siemens.

Electrocatalyst

The second important problem is associated with the electrocatalyst. For operation with pure hydrogen and air, platinum is the most active material. To reduce the cost, nanoparticles of platinum on a carbon

Box 1

Cell efficiencies

The overall cell efficiency η is given by the equation

$$\eta = \eta_g \eta_v \alpha$$

where η_g is the Gibbs efficiency, η_v is the voltage efficiency, and α is the fraction of fuel used.

$$\eta_g = \Delta G / \Delta H = nFE_0 / \Delta H$$

$$\eta_v = E / E_0 = (E_0 - IR_c) / E_0$$

where E_0 is the open circuit voltage, and ΔH is the heat of the overall cell reaction. Thus

$$\eta = nF(E_0 - IR_c)\alpha / \Delta H$$

R_c is the area specific resistivity of the cell components (electrolyte, anode and cathode). Note that the cell structure is often termed the membrane-electrode assembly (MEA) for PEMFC systems, and positive-electrolyte-negative (PEN) for SOFC systems.

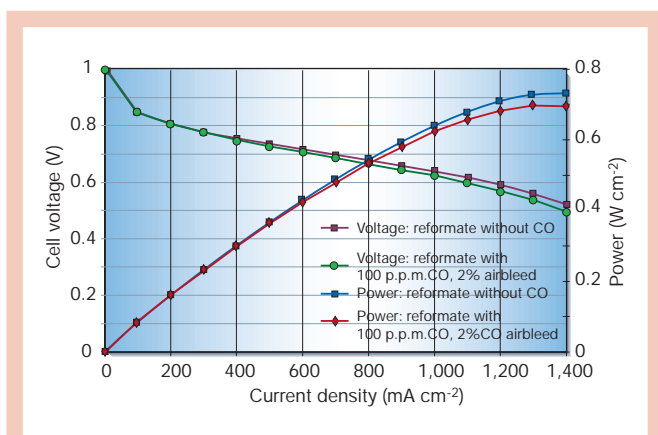


Figure 3 CO tolerance on Pt/Ru anode electrodes. Active cell area, 50 cm²; precious metal loadings, <0.4 mg cm⁻²; temperature, 80 °C; pressure, 3 bar; anode fuel reformate, 60% H₂, 25% CO₂, 15% N₂; cathode, air. (From ref. 56.)

support have been developed, and the reduction in noble-metal content without degrading the cell performance has been, and continues to be, an important R&D activity¹⁹. The platinum loading has been significantly reduced from 2 mg per square centimetre of electrode to values below 0.5 mg cm⁻² without significant impact on performance and lifetime. In the laboratory, even lower platinum loadings have been examined^{20,21}.

For fuels containing traces of CO, or methanol in the DMFC, a CO-tolerant catalyst is required. This remains one of the most challenging tasks for the successful development of commercial PEMFC systems²². For reformate electrodes as well as for methanol oxidation, the removal of adsorbed CO species is the rate-determining step. The oxidation of adsorbed CO on Pt is slow, and is facilitated by adjacent adsorbed OH species. This is the reason why Ru, with its low potential for OH-ads formation, is the most efficient component of the binary catalysts. Pt/Ru and other binary and ternary alloys with these noble metals have been investigated intensively²³, and performance values have increased significantly. The loss in performance is usually expressed in mV for a certain CO content of the fuel, and recent publications show promising results, as indicated, for example, in Fig. 3.

Membranes

Although the US General Electric Company (GE) initiated the development of PEMFCs in the 1950s, it was the introduction of Nafion by DuPont that ensured continuing interest in these systems. Initially Nafion was manufactured²⁴ for membrane cells used in the production of chlorine (chlor-alkali cells). By 1990, Ballard had overcome many of the engineering problems associated with PEMFC systems, and this had stimulated many groups in the United States and Japan to improve the properties of the original Nafion material²⁵. For example, higher ionic conductivities could be attained by selecting perfluorosulphonic acid copolymers with a short pendant group, and it was realized that gas and small-molecule permeability were other important characteristics that had to be improved.

The following properties of polymeric membranes need to be optimized for use in fuel cells: (1) high proton conduction, assured by acid ionic groups (usually SO₃H), depending on sulphonation degree and on thickness of the membrane; (2) good mechanical, chemical and thermal strength requiring the selection of a suitable polymer backbone; mechanical strength for thin membranes can frequently be improved by reinforcement; (3) low gas permeability, which is dependent on material and thickness of the membrane; (4) for DMFC applications low electro-osmotic drag coefficient to reduce methanol crossover

There is significant interaction between the desired properties of the membrane — high conductivity, low swelling, low gas and

methanol permeability, and stability — and the type of backbone polymer, the degree of sulphonation and the nano-phase separation into hydrophilic and hydrophobic domains (for example, high degrees of sulphonation usually lead to highly conductive membranes, but also to extreme swelling properties). To satisfy these requirements, different approaches have been examined: sulphonated perfluorinated materials with²⁶ and without²⁷ microporous support; sulphonated polyhydrocarbons; acid–base complexes and blends with a surplus of acid ionic groups; and inorganic–organic composite materials with improved thermal stability and better water-retaining properties.

Because of their PTFE-like backbone and relatively low equivalent weight, Nafion and related materials are a favoured option and are commonly used in fuel-cell stacks, but the costs remain high. Therefore, much effort is being applied to the development of cheaper, usually fluorine-free, membrane materials. But hydrocarbons often suffer from an insufficient thermal stability, and so more and more aromatic groups have been introduced into the polymer backbone. Polyarylenes^{28,29} seem to be the most stable molecules among the hydrocarbons. For example, poly(arylene ether sulphone)-based membranes were prepared by sulphonation of commercially available polymers such as Udel and Victrex³⁰. For high ionic conductivity, high sulphonation fractions are desirable, but high sulphonation can lead to extreme swelling even at room temperature. Thus, crosslinking of the polymer chains at the sulphonic acid groups can be included in the synthesis steps to overcome the problems of swelling. However, the long-term stability of these sulphonamide crosslinking bridges remains unproven. Alternative crosslinking methods, such as covalent crosslinking and ionic crosslinking by the introduction of polymeric bases (acid–base blend membranes), have also been examined³¹.

For operation at elevated temperatures, which is desirable for high power density DMFC systems and for reformate fuels with CO levels above 100 p.p.m., the conduction mechanism becomes the dominant issue. In the types of membranes described earlier (hydrated polymers), the proton-conduction mechanism is based on the migration of hydrated protons. Above 100 °C, pressurized operation is required to ensure the presence of liquid water. Phosphoric acid and polymers with immobilized heterocycles exhibit a conduction mechanism relying on structure diffusion³², and can be used at temperatures above the boiling point of water. As phosphoric acid in its liquid form in a porous matrix is well known from PAFC development, new ways to achieve a composite with better properties have been investigated. One polymer material for high-temperature application is polybenzimidazole (PBI), which forms adducts with inorganic acids. Initial publications from Savinell³³ described the use of PBI with phosphoric acid as membrane in fuel-cell experiments. Later developments led to acid–base blend polymers with PBI and sulphonated polyetheretherketones. Reduced methanol permeability and performance data comparable to that of Nafion 112 have been reported^{34,35}. Axiva (part of the Hoechst Celanese group) announced the manufacture of PBI-based membrane materials, but only in exclusive cooperation with partners (Plug Power and Honda).

It should be emphasized that if an alternative membrane material does emerge, considerable R&D will still be necessary to optimize and manufacture the new membrane–electrode assembly (MEA). This development has taken many years for Nafion-type MEAs, although some of the expertise gained may be able to be transferred to the new system.

Fuel cells operating at elevated temperatures

Solid-oxide fuel cells

In contrast to other fuel-cell types a SOFC stack can, in principle, be designed to operate within a wide temperature range (500–1,000 °C). It is necessary, therefore, to select the desired temperature of operation. This, in turn, is influenced by the specific application, the type of fuel and the properties of available solid electrolytes. For example,

if the SOFC stack is to be integrated with a gas turbine, then system requirements indicate that the temperature of the exhaust gas from the stack should exceed about 850 °C. The steam reformation of fuels such as diesel, petrol and propane to produce H₂ and CO gases for the anode also, at present, requires fuel processors operating in excess of 700 °C. But it is the properties of the solid electrolyte that exert the biggest influence on stack design and materials selection, as indicated earlier.

Figure 4 summarizes how the specific ionic conductivity of a selection of solid electrolytes varies with the reciprocal of temperature. By taking a typical value of 0.15 Ω cm² for the maximum ASR value, it is possible to calculate the maximum thickness allowed for a given electrolyte component. For example, a design configuration that specified a self-supported (~150 μm), yttria-stabilized zirconia (YSZ) electrolyte would require a temperature of operation greater than 950 °C. Operation at 950 °C poses major problems for planar (flat) SOFC configurations compared to tubular configurations used, for example, in the Siemens–Westinghouse arrangement. These include stability of the electrode–electrolyte interface, selection of the bipolar-plate material, and the optimal material composition and arrangement for the seals that are necessary in planar SOFC stacks. Economic solutions are still sought today.

Owing to these intrinsic problems with the high-temperature planar configuration, there was early interest in tubular designs that eliminated the high-temperature sealing problem. A variety of tubular configurations was initially examined³⁶, but the arrangement eventually adopted by Siemens–Westinghouse has so far proved the most successful. This arrangement uses a 1.5-m porous tubular cathode (La(Sr)MnO₃, or LSM). After deposition of the La(Sr)CrO₃ interconnect strip by plasma spraying, an electrochemical vapour-deposition (EVD) process is used to fabricate an impermeable, thick-film (30–40 μm) electrolyte (YSZ) layer. The cell structure is completed by using a slurry-spray process to deposit the porous Ni-YSZ anode. Although successful from a technical perspective, the EVD process is relatively expensive and efforts are underway to replace this process by an alternative, cheaper fabrication route. However, conventional ceramic routes involving the deposition of YSZ powders and subsequent sintering are constrained by the need to restrict the sintering temperature to below about 1,250 °C to ensure

insignificant reaction between the LSM cathode and electrolyte. Selection of the cathode (LSM) and anode (Ni-YSZ) compositions was established during the 1970s by Westinghouse and ABB, after examining a variety of oxide compositions for long-term compatibility with YSZ at elevated temperatures. This empirical conclusion was later explained in terms of available thermochemical data³⁷.

The Siemens–Westinghouse tubular design remains the most developed SOFC system, and has been evaluated in units generating 25 kW, 100 kW and 200 kW. More recently 200-kW units have been combined with microturbines to provide a system capable of generating electricity around 60% efficiency. Large, multi-megawatt integrated systems are predicted to produce electricity at efficiencies approaching 70%. However, these advances are more concerned with issues of system design rather than the selection and development of new materials.

Intermediate temperature solid-oxide fuel cells

The strategic programmes of large multinational companies (such as Westinghouse, GE and ABB) favoured the development of multi-megawatt, high-temperature SOFC stacks, and these priorities had a strong influence on the development of SOFC designs and materials for two decades from 1970. By 1990, however, it was beginning to be recognized that for smaller SOFC stacks not destined to be integrated with gas turbines, the operating temperature should be lowered as far as possible without compromising the electrode kinetics and internal resistance of the cell. The development of these smaller IT-SOFC stacks for distributed (embedded) CHP units, to produce stand-by power, is also being stimulated by liberalization (deregulation) of electrical supply policies. In addition, many automotive manufacturers are examining whether small SOFC stacks (3–5 kW) can be developed to supply the electrical power for auxiliary functions such as air conditioning in vehicles.

Examples of the most appropriate solid-electrolyte composition for operation at intermediate temperatures (500–750 °C) can be identified from Fig. 4. If we once again assume that the electrolyte component should not contribute more than 0.15 Ω cm² to the total cell ASR, then for a thick-film thickness (*L*) of 15 μm, the associated specific ionic conductivity (σ) of the electrolyte should exceed 10⁻² S cm⁻¹ ($\sigma = L/ASR = 0.0015/0.15$). Examination of Fig. 4 indicates that the ionic conductivity of YSZ attains this target value around 700 °C, and for Ce_{0.9}Gd_{0.1}O_{1.95} (CGO) the relevant temperature is 500 °C. The use of thinner electrolyte films would allow the operating temperature to be lowered. But at present it seems that the minimum thickness for dense impermeable films that can be reliably mass produced using relatively cheap ceramic fabrication routes is around 10–15 μm. The use of a thick-film electrolyte requires this component to be supported on an appropriate substrate. As the substrate is the principal structural component in these cells, it is necessary to optimize the conflicting requirements of mechanical strength and gaseous permeability.

An IT-SOFC configuration that seeks to retain the specific advantages of both the tubular and planar arrangements is being developed by Rolls-Royce³⁸. This integrated planar-stack concept incorporates multi-cell assemblies connected in series and supported by a ceramic substrate, and has many similar features to the original Westinghouse tubular design³⁹.

Most development work on planar IT-SOFC systems has involved thick-film YSZ electrolytes, and so far most groups have used anode (Ni-YSZ) substrates, which allow the electrolyte powder to be sintered to a dense film around 1,400 °C. One of the problems associated with using porous, composite Ni-YSZ substrates is their relatively poor thermal-expansion compatibility with the YSZ thick film. Accordingly, several groups are examining porous substrates based on Ni-Al₂O₃ or Ni-TiO₂ compositions, with thin interfacial anodic regions incorporating Ni, YSZ and/or doped CeO₂. Although replacement of the YSZ can provide better thermal-expansion compatibility, problems still remain over the volume changes associated

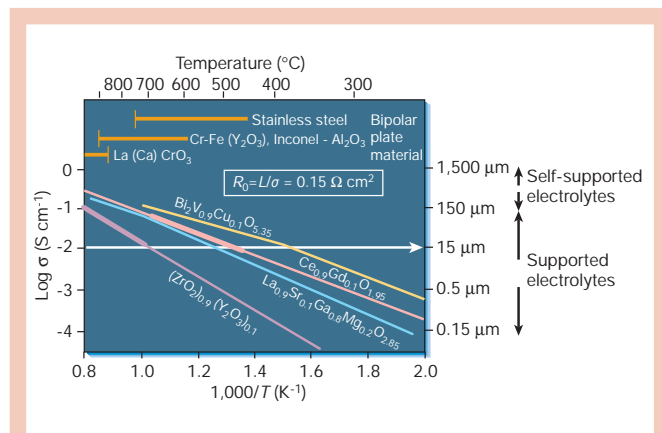


Figure 4 Specific conductivity versus reciprocal temperature for selected solid-oxide electrolytes. To ensure that the total internal resistance (that is, electrolyte + electrodes) of a fuel cell is sufficiently small, the target value for the area specific resistivity (ASR) of the electrolyte is set at 0.15 Ω cm². Films of oxide electrolytes can be reliably produced using cheap, conventional ceramic fabrication routes at thicknesses down to ~15 μm. It follows that the specific conductivity of the electrolyte must exceed 10⁻² S cm⁻¹. This is achieved at 500 °C for the electrolyte Ce_{0.9}Gd_{0.1}O_{1.95}, and at 700 °C for the electrolyte (ZrO)_{0.9}(Y₂O)_{0.1}. Although the electrolyte Bi₂V_{0.9}Cu_{0.1}O_{5.35} exhibits higher conductivities, it is not stable in the reducing environment imposed by the fuel in the anode compartment of a fuel cell.

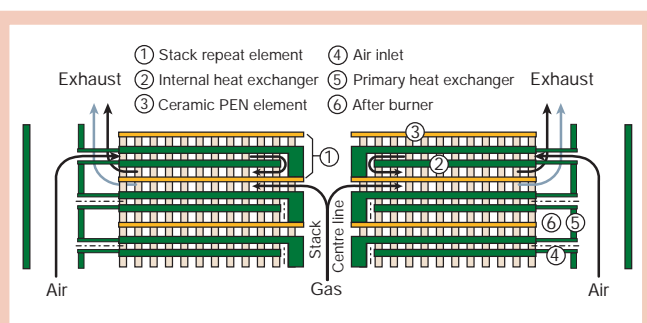


Figure 5 Schematic view of the Sulzer Hexis micro-CHP stack for residential applications. Small (1–5 kW) micro-CHP units are being beta tested for residential applications. The combination of small-scale joint production of electricity and heat is more efficient than the combination of conventional central power stations and decentralized heating equipment. Moreover, security of supply for domestic electrical equipment (for example, central heating pumps and computers) is a major advantage, and part of the emerging trend for distributed power.⁵⁷

with the reduction and oxidation of the Ni component. As the porous substrate–electrolyte films are usually co-fired in air around 1,400 °C, nickel is present as NiO, which has to be carefully reduced by the fuel during the initial heating cycle of the assembled stack. Additionally, operating procedures have to be specified to prevent the nickel re-oxidizing when SOFC stacks are cooled down in the absence of fuel flowing through the anode compartment (of note here is the use of forming gas, N_2/H_2 , to protect the Ni-YSZ anode in the Siemens–Westinghouse tubular configuration).

Most IT-SOFC developers are using metallic bipolar plates. Often a ferritic stainless steel is specified because of the low ($12.5 \times 10^{-6} K^{-1}$) thermal-expansion coefficients of these alloys. Moreover, by using compositions stabilized with Nb–Ti, excellent electronic interfacial contacts can be maintained⁴⁰ between the cell components for extended periods. Providing appropriate precautions are followed, many R&D laboratories have reported good performance values for IT-SOFC stacks incorporating the following positive–electrolyte–negative (PEN) components: anode-supported thick-film YSZ electrolytes, LSM-YSZ cathodes, and stainless steel bipolar plates.

To minimize sealing requirements, many IT-SOFC stacks have adopted a circular design in which the fuel and air are introduced by means of an appropriate manifold at the centre of the PEN structure. Arrangements are made to distribute the air and fuel gases over the cathode and anode, and the flow rates are adjusted to ensure almost complete conversion of the fuel by the time it reaches the stack periphery. Unreacted fuel and air are then combusted without large temperature changes. These design features minimize sealing problems and allow limited thermal cycling. Examples are provided by the Sulzer Hexis micro-CHP configuration designed for residential accommodation (Fig. 5), and the auxiliary power unit (APU) prototype (Fig. 6) constructed by the Delphi–BMW–Global Thermoelectric consortium for incorporation into vehicles. But at present the heating and cooling rates cannot exceed ~ 500 °C per hour, owing to the development of stresses associated with thermal-expansion mismatch, and to the brittle glass and ceramic seals. Although this restriction may not be too severe for larger CHP systems (>100 kW), it is not satisfactory for smaller systems (1–10 kW) designed for micro-CHP and APU applications. Further R&D is still required to produce more rugged IT-SOFC stacks. Commercial units can be expected in the next five years once reliability and cost requirements ($<US\$1,000$ per kW) have been effectively demonstrated.

IT-SOFC stacks incorporating alternative components

Although YSZ is still the favoured electrolyte material for SOFC stacks, selection of this material is not without problems and research

continues into the long-term evaluation of scandia-doped ZrO_2 , which can exhibit higher ionic conductivities than the traditional YSZ material.

In principle, the use of ceria-based electrolytes such as CGO should allow the cell operating temperature to be lowered to around 500 °C (see Fig. 4). But perceived problems associated with PEN structures incorporating ceria-based electrolytes have restricted investment in this technology. It is well known that, at elevated temperatures, Ce^{4+} ions can be reduced to Ce^{3+} under the fuel-rich conditions prevailing in the anode compartment. The associated electronic conductivity (and deleterious lattice expansion) produces an internal short circuit in the PEN structure, which can significantly degrade the efficiency and performance of cells. However, if the operating temperature is lowered to around 500 °C, then the electronic conductivity is small, and can be neglected under typical operating conditions of the cell^{41,42}.

Another significant difficulty that has restricted exploitation of the attractive properties of CGO at 500 °C has been the need to develop alternative cathode compositions that function effectively at lower temperatures. Recent developments in this area have been surveyed by Ralph *et al.*⁴³, and there are indications⁴⁴ that appropriate materials for composite cathodes can be fabricated which exhibit small over-potentials at 500 °C (for example, 0.15 V at $1 A cm^{-2}$). Composite anodes such as Ni-CGO also provide adequate performance at 500 °C for simulated syngas fuels, indicating that IT-SOFC stacks at 500 °C are now a viable option.

Operation at intermediate temperatures is stimulating R&D effort into alternative anode compositions to replace the established Ni-YSZ anode. One strategy⁴⁵ is to develop electronic conducting oxides that are redox stable, to avoid the use of Ni. This metal can catalyse carbon deposition under certain operating conditions, and also forms NiO, which is accompanied by a deleterious volume expansion, when the anode compartment becomes too oxidizing. Another approach is concerned with the identification of alternative anodes that allow the direct anodic oxidation of hydrocarbons. The claims made in recent publications^{46,47} remain controversial⁴⁸, but there is little doubt that this topic will remain a fruitful area for further investigations.

Operation at 500 °C allows the use of compliant high-temperature gaskets in place of rigid, brittle glass or ceramic seals, thus permitting greater design flexibility for the stack configuration. At Imperial College, London, researchers have taken advantage of the fact that the thermal-expansion coefficient of CGO and ferritic stainless steel are virtually identical ($12.5 \times 10^{-6} K^{-1}$), so that the thick-film PEN structure can be supported on a porous stainless steel foil. These metal-supported PEN structures are robust, and should withstand the rapid temperature cycles expected during operation of small IT-SOFC stacks.

Another electrolyte, doped $LaGaO_3$ (LSGM), is also attracting much attention for IT-SOFC applications. Although its conductivity is slightly smaller (see Fig. 4) than CGO at 500 °C, its ionic domain is wider and it could be more appropriate to use this electrolyte at temperatures around 600 °C, where the reduction of Ce^{4+} in CGO becomes significant. It has been difficult to fabricate pure single-phase ceramic electrolytes, and second phases such as $SrLaGa_5O_7$ and $La_4Ga_2O_9$ are often detected in the grain boundaries. Whether these phases are responsible for the enhanced reactivity of LSGM, or whether it is an intrinsic property of LSGM, are questions that require urgent. Moreover, the preferred composition, $La_{0.9}S_{0.1}Ga_{0.8}M_{0.2}O_3$, does not seem to be stable at lower temperatures (P. Majewski, personal communication). Although research continues into the synthesis of alternative oxygen-ion conducting electrolytes, it has proved difficult to prepare alternative materials with an appropriate combination of properties that can displace the traditional fluorite compositions involving ZrO_2 and CeO_2 .

Experiments involving single-compartment SOFC fuel cells have been reported. In this configuration a mixture of the fuel and air flows

over both electrodes of a ceramic cell. One electrode incorporates an electrocatalyst optimized for the reduction of oxygen, whereas the second electrode is designed to catalyse the fuel oxidation. This configuration eliminates the need for cell sealing and excellent current–voltage (I – V) characteristics have been reported⁴⁹. But the published data need to be interpreted with caution as it seems that the electrodes also catalyse the external oxidation of the fuel. The heat generated by these surface reactions can significantly raise the temperature of small samples, so that the reported data probably refer to I – V values around 100 °C higher than those stated. Parasitic chemical oxidation of the fuel will of course significantly reduce the overall system efficiency, and technological exploitation of this configuration seems unlikely.

Very high performances have been claimed⁵⁰ at 500 °C using composite electrolytes incorporating CGO and molten salts. But the long-term stability of such mixtures in a fuel-cell environment must be doubtful and these claims require further independent scrutiny.

Investigations also continue into ceramic proton conductors. The composition $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$, for example, can exhibit a protonic conductivity that approaches the oxygen-ion conductivity of CGO at 500 °C (that is, 10^{-2} S cm^{-1})^{51,52}. But solid-state fuel cells incorporating ceramic proton conductors will not be able to electrochemically oxidize CO, and do not, at present, appear to offer any advantages over the oxygen-ion conducting electrolytes in this temperature region. Interesting results have also been reported⁵³ for the solid acid CsHSO_4 at 160 °C. Ceramic protonic conductors are more likely to be exploited in chemical engineering applications requiring the separation and generation of hydrogen.

Molten-carbonate fuel cells

Although the materials (Table 1) used for MCFC stack components have essentially remained unchanged² over the past 25 years, significant developments in fabrication technology were introduced during the 1980s. Cost-effective tape-casting techniques now allow the immobilized electrolyte matrix to be manufactured up to a size of 1 m². These manufacturing advances were important as the power

Table 1 Materials used in the MCFC stack

Anode	Ni-Cr
Cathode	NiO (Li doped)
Electrolyte	Li/Na/KCO ₃ (60/20/20)
Matrix*	γ -LiAlO ₂ + Al ₂ O ₃
Bipolar plate	Stainless steel 310
Wet seal	Aluminized stainless steel

*For electrolyte immobilization.

density of MCFC systems operating at 650 °C is relatively low ($\sim 150\text{ mW cm}^{-2}$), requiring large cell areas to be fabricated. The requirement to recirculate CO₂ from the anode exhaust to the cathode to maintain the composition of the carbonate electrolyte also complicates the balance-of-plant equipment. It follows that the MCFC is only likely to be commercialized only at sizes greater than 100 kW, and originally MCFC plants were conceived as large (multi-megawatt scale), centralized coal-fired power stations.

To develop user confidence it was considered that large plants should be demonstrated as soon as possible, and this led to the construction in the United States of the 1.8-MW Santa Clara system by Energy Research Corporation. Although commissioned in April 1996, evaluation of the plant had to be curtailed owing to problems with the material selected for the stack external manifold. It is now believed that a more appropriate strategy is to develop smaller MCFC systems ($\sim 250\text{ kW}$) for distributed CHP applications using natural gas. An example of this approach is provided by the 300-kW 'Hot Module' unit, developed by MTU Friedrichshafen (a subsidiary of DaimlerChrysler AG), and it is encouraging to note that the first demonstration module has already been operated successfully for more than 1 year (8,000 h) at an electrical efficiency of 47%. Because of the corrosive nature of the molten salt Li/Na/KCO₃ electrolyte, lifetime issues have always been of concern for the MCFC system. However, a recent appraisal⁵⁴ suggests that most components should attain the target value of 40,000 h, except possibly the coating used to protect the anode structure, which remains the focus of further materials development.

Operating procedures for MCFC systems are influenced by limitations associated with two of the components. In cooling down the hot stack in the absence of a fuel supply, it is necessary to protect the Ni-Cr anode from oxidation by the introduction of an inert gas into the anode compartment. More serious, however, is the inability of the immobilized electrolyte matrix to withstand more than 3 to 5 thermal cycles through the melting point of the molten salt electrolyte. Thus, during stand-by situations the temperature of the MCFC stack must be maintained high enough to prevent solidification of the molten salt electrolyte. Clearly both the MCFC and SOFC systems will initially be competing for the same sub-megawatt CHP market sector. It is expected that both will operate at similar electrical efficiencies, and so the cost of the installed plant will determine which technology eventually has the largest market penetration. It is also interesting to note that both fuel-cell types require procedures to prevent redox reactions damaging the anode, and to restrict thermal cycling of the plant during abnormal operating situations.

Conclusions

Probable applications of fuel cells in the next decade together with a selection of critical materials issues are summarized in Table 2. It is recognized that the capital costs (US\$3,000–10,000 per kW) of prototype fuel-cell systems are too high. Although volume production can be expected to reduce these costs, it may be difficult to attain sufficient market share to justify the investment for mass production while competing against established technology. Although significant niche markets exist, such as the PEMFC system for city buses, many observers believe that a more appropriate strategy is to target those sectors of the market (for example, 1–10 kW generation) where the existing technology is inefficient and displays extremely poor

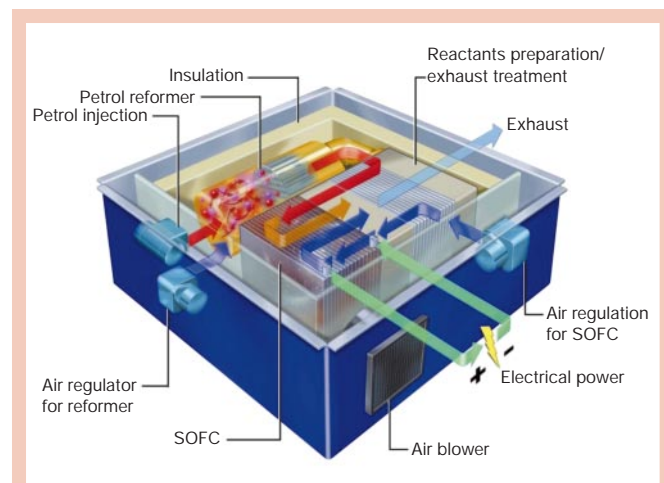


Figure 6 Schematic view of the Delphi–BMW–Global Thermoelectric auxiliary power unit (APU). Depending upon the functions installed in a vehicle, it has been suggested that at least 10% of the output of an internal combustion engine has been used to provide electrical energy. With the introduction of electromagnetic valve trains and smart piezoelectric suspensions this fraction is expected to increase significantly. Furthermore, to maintain air conditioning and refrigeration (in lorries, for example), internal combustion IC engines have to be kept idling even when the vehicle is stationary. Under these low-load conditions the engine is very inefficient and makes significant contributions to environmental pollution. The use of a fuel-cell APU would make a significant contribution to improving air quality and reducing emissions of greenhouse gases.⁵⁸

Table 2 Summary of future R&D requirements for fuel-cell materials

Application	Size (kW)	Fuel cell	Fuel	Critical materials issues
Power systems for portable electronic devices	0.001–0.05	PEMFC DMFC	H ₂ CH ₃ OH	Membranes exhibiting less permeability to CH ₃ OH, H ₂ O
Micro-CHP	1–10	PEMFC SOFC	CH ₄ LPG CH ₄ LPG	Novel PEN structures CO-tolerant anodes, novel membranes, bipolar plates More robust thick-film PENs operating at 500–700 °C
APU, UPS, remote locations, scooters	1–10	SOFC	LPG Petrol	More robust thick-film PENs operating at 500–700 °C; rapid start-up
Distributed CHP	50–250	PEMFC MCFC SOFC	CH ₄ CH ₄ CH ₄	CO-tolerant anodes, novel membranes, bipolar plates Better thermal cycling characteristics Cheaper fabrication processes; redox-resistant anodes
City buses	200	PEMFC	H ₂	Cheaper components
Large power units	10 ³ –10 ⁴	SOFC/GT	CH ₄	Cheaper fabrication processes for tubular SOFC system

Abbreviations: UPS, uninterruptible power systems; LPG, liquid petroleum gas; GT, gas turbine. Other abbreviations defined in the text.

part-load performance. This, for example, is the strategy adopted recently by the US Department of Energy for the Solid State Energy Conversion Alliance, which aims to mass produce 5-kW SOFC modular stacks with a target cost of US\$400 per kW. Once this small-scale technology has demonstrated its reliability, and met cost targets, then larger units based on the same technology can be expected to penetrate other sectors of the stationary power and transport market.

Another area receiving increased attention is the development of fuel-cell power sources for a variety of portable electronic devices. As batteries struggle to keep up with the specific power demands of mobile devices, innovative DMFC designs⁵⁵, fabricated using techniques developed for the semiconductor industry, promise energy densities that are between three and five times better than current lithium-ion batteries. The high profit margins and relatively low power demands (~1 W for transmission) associated with cellular telephones, for example, could provide a useful market entry for these small fuel cells, particularly for hybrid systems. □

- Grove, W. R. On voltaic series and the combination of gases by platinum. *Phil. Mag. Ser. 3* **14**, 127–130 (1839).
- Steele, B. C. H. Material science and engineering: the enabling technology for the commercialisation of fuel cell systems. *J. Mater. Sci.* **36**, 1053–1068 (2001).
- Bauen, A. & Hart, J. Assessment of the environmental benefits of transport and stationary fuel cells. *J. Power Sources* **86**, 482–494 (2000).
- Dicks, A. L. & Larminie, J. in *Proc. Fuel Cell 2000* (ed. Blomen, L.) 357–367 (European Fuel Cell Forum, Oberrohrdorf, Switzerland, 2000).
- Kordesch, K. et al. Alkaline fuel cells applications. *J. Power Sources* **86**, 162–165 (2000).
- Anahara, R. Total development of fuel cells in Japan. *J. Power Sources* **49**, xi–xiv (1994).
- Whitaker, J. Investment in volume building: the 'virtuous cycle' in PAFC. *J. Power Sources* **71**, 71–74 (1998).
- MacKerron, G. Financial considerations of exploiting fuel cell technology. *J. Power Sources* **86**, 28–33 (2000).
- Kordesch, K. & Simader, G. *Fuel Cells and their Applications* (VCH, Weinheim, Germany, 1996).
- Larminie, J. & Dicks, A. *Fuel Cell Systems Explained* (Wiley, Bognor Regis, 2000).
- Borup, R. L. & Vanderborgh, N. E. Design and testing criteria for bipolar plate materials for PEM fuel cell applications. *Mater. Res. Soc. Symp. Proc.* **393**, 151–155 (1995).
- Barbir, F., Joy, G. C. & Weinberg, D. J. in *Proc. Fuel Cell Seminar 2000* 483–486 (Courtesy Associates, Washington DC, 2000).
- Scholta, J., Rohland, B., Trapp, V. & Focken, U. Investigations on novel low-cost graphite composite bipolar plates. *J. Power Sources* **84**, 231–234 (1999).
- Mahlendorf, F., Niemzig, O. & Kreuz, C. in *Proc. Fuel Cell Seminar 2000* 138–140 (Courtesy Associates, Washington DC, 2000).
- Mallant, R., Koene, F., Verhoeve, C. & Ruiter, A. in *1994 Fuel Cell Seminar* 503–506 (Courtesy Associates, Washington DC, 1994).

- Zawodzinski, C., Mahlon, S. & Gottesfeld, S. in *1996 Fuel Cell Seminar* 659–662 (Courtesy Associates, Washington DC, 1996).
- Makkus, R. C., Janssen, A. H. H., de Bruijn, F. A. & Mallant, R. K. A. Use of stainless steel for cost competitive bipolar plates in the SPFC. *J. Power Sources* **86**, 274–282 (2000).
- Davies, D. P., Adcock, P. L., Turpin, M. & Rowen, S. J. Stainless steel as a bi-polar plate material for solid polymer fuel cells. *J. Power Sources* **86**, 237–242 (2000).
- Starz, K. A., Auer, A., Lehmann, Th. & Zuber, R. Characterization of platinum-based electrocatalysts for mobile PEMFC applications. *J. Power Sources* **84**, 167–172 (1999).
- Wilson, M. S., Valerio, J. & Gottesfeld, S. Low platinum loading electrodes for polymer electrolyte fuel cells fabricated using thermoplastic ionomers. *Electrochim. Acta* **3**, 355–363 (1995).
- Uchida, M., Fukuoka, Y., Sugawara, Y., Ohara, H. & Ohta, A. Improved preparation process of very low-platinum-loading electrodes for polymer electrolyte fuel cells. *J. Electrochem. Soc.* **145**, 3708–3713 (1998).
- Gottesfeld, S. et al. in *Fuel Cell Seminar 2000* 799–802 (Courtesy Associates, Washington DC, 2000).
- McNicol, B. D., Rand, D. A. J. & Williams, K. R. Direct methanol-air fuel cells for road transport. *J. Power Sources* **83**, 15–31 (1999).
- Grot, W., Perfluorinated cation exchange polymers. *Chemie-Ing.-Techn.* **MS260/75** (1975).
- Eisman, G. A. in *Proc. Vol. 86-13* 156–171 (Electrochemical Society, New Jersey, 1986).
- Kolde, J. A., Bahar, B., Wilson, M. S., Zawodzinski, T. A. & Gottesfeld, S. Advanced composite fuel cell membranes. *J. Electrochem. Soc.* **95**, 193–201 (1995).
- Wakizoe, M. & Watanabe, A. in *2000 Fuel Cell Seminar* 27–30 (Courtesy Associates, Washington DC, 2000).
- Huang, R. Y. M. & Kim, J. J. *J. Appl. Polym. Sci.* **89**, 4017, 4029 (1984).
- Zerfuß, T. Thesis, Univ. Freiburg (1998).
- Nolte, R., Ledjeff, K., Bauer, M. & Mühlaupt, R. Partially sulphonated poly(arylene ether sulfone)—a versatile proton conducting membrane material for modern energy conversion technologies. *J. Membr. Sci.* **83**, 211–220 (1993).
- Kerres, J. A. Development of ionomer membranes for fuel cells. *J. Membr. Sci.* **185**, 3–27 (2001).
- Kreuer, K. D. On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. *J. Membr. Sci.* **185**, 29–39 (2001).
- Savinell, R. F. et al. A polymer electrolyte for operation at temperatures upto 200C. *J. Electrochem. Soc.* **141**, L46–L48 (1994).
- Hasiotis, C. et al. Development and characterization of acid-doped polybenzimidazole/sulfonated polysulfone blend polymer electrolytes for fuel cells. *J. Electrochem. Soc.* **148**, A513–A519 (2001).
- Kerres, J., Ullrich, A., Meier, F. & Haring, T. Synthesis and characterization of novel acid-base polymer blends for application in membrane fuel cells. *Solid State Ionics* **125**, 243–249 (1999).
- Minh, N. Q. & Takahashi, T. *Science and Technology of Ceramic Fuel Cells* (Elsevier, Amsterdam, 1995).
- Yokokawa, H. Phase diagrams and thermodynamic properties of zirconia based ceramics. *Key Eng. Mater.* **154/155**, 37–74 (1998).
- Day, M. J. in *4th European SOFC Forum* (ed. McEvoy, A. J.) 133–140 (European Fuel Cell Forum, Oberrohrdorf, Switzerland, 2000).
- Sverdrup, E. F., Warde, C. J. & Eback, R. L. Design of high temperature solid-electrolyte fuel-cell batteries for maximum power output per unit volume. *Energy Convers.* **13**, 129–141 (1973).
- Dulieu, D. et al. in *3rd European SOFC Forum* (ed. Stevens, P.) 447–458 (European Fuel Cell Forum, Oberrohrdorf, Switzerland, 1998).
- Steele, B. C. H. Appraisal of Ce_{1-x}Gd_xO_{2-y/2} electrolytes for IT-SOFC operation at 500C. *Solid State Ionics* **129**, 95–110 (2000).
- Xia, C., Chen, F. & Liu, M. Reduced temperature SOFC fabricated by screen printing. *Electrochem. Solid State Lett.* **4**, A52–A54 (2001).
- Ralph, J. M., Schoeler, A. C. & Krumpelt, M. Materials for lower temperature SOFC. *J. Mater. Sci.* **36**, 1161–1172 (2001).
- Doshi, R. et al. Development of SOFCs that operate at 500C. *J. Electrochem. Soc.* **146**, 1273–1278 (1999).
- Irving, J. T. et al. in *4th European SOFC Forum* (ed. McEvoy, A. J.) 471–477 (European Fuel Cell Forum, Oberrohrdorf, Switzerland, 2000).
- Murray, E. P. & Tsai, T. A direct-methane fuel cell with a ceria based anode. *Nature* **400**, 649–651 (1999).
- Park, S., Craciun, R., Radu, V. & Gorte, R. J. Direct oxidation of hydrocarbons in a SOFC. 1. Methane oxidation. *J. Electrochem. Soc.* **146**, 3603–3606 (1999).
- Primdahl, S. & Mogensen, M. Exchange current densities in mixed conducting SOFC anodes. (Abstr. BS-PO-24, International Society for Solid State Ionics 2001, 8–13 July 2001, Cairns, Australia.) *Solid State Ionics* (in the press).
- Hibino, T. et al. A low operating temperature SOFC in hydrocarbon-air mixtures. *Science* **288**, 2031–2033 (2000).
- Zhu, B. Advantages of intermediate temperature SOFC for traction applications. *J. Power Sources* **93**, 82–86 (2001).
- Kreuer, K. D. On the development of proton conducting materials for technological applications. *Solid State Ionics* **97**, 1–15 (1997).
- Bohn, H. G. & Schober, T. Electrical conductivity of the high temperature proton conductor BaZr_{0.9}Y_{0.1}O_{2.95}. *J. Am. Ceram. Soc.* **83**, 768–772 (2000).
- Haile, S. M., Boysen, D. A., Chisholm, C. R. I. & Merle, R. B. Solid acids as fuel cell electrolytes. *Nature* **410**, 910–913 (2001).
- Huijismans, J. P. P. et al. An analysis of endurance issues for MCFC. *J. Power Sources* **86**, 117–121 (2000).
- Hockaday, R. et al. in *Proc. Fuel Cell 2000* (ed. Blomen, L.) 37–44 (European Fuel Cell Forum, Oberrohrdorf, Switzerland, 2000).
- Starz, K. A., Ruth, K., Vogt, M. & Zuber, R. in *Proc. Int. Symp. Fuel Cells for Vehicles 20-22 November 2000*, 210–215 (Nagoya, Japan, 2000).
- Diethelm, R., Batawi, E. & Honegger, K. in *Proc. Fuel Cell 2000* (ed. Blomen, L.) 203–211 (European Fuel Cell Forum, Oberrohrdorf, Switzerland, 2000).
- Fizelman, J., Botti, J., Tachtler, J. & Wolfgang, S. SOFC auxiliary power unit: a paradigm shift in electric supply for transportation. *Automotive Eng. Int.* **108** (Delphi Suppl.), 14–20 (2000).