JOURNAL OF MATERIALS SCIENCE **36** (2001) 1053–1068

# Material science and engineering: The enabling technology for the commercialisation of fuel cell systems

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The critical role of materials science and engineering in the development of fuel cell technology is surveyed. The inability to fabricate reliable triple-phase-boundary (tbp) structures involving electrolytes, electronic conductors, and gaseous reactants, severely restricted the progress of fuel cells until about four decades ago (∼1960). However at the start of the new millennium, commercialisation of four fuel cell types: polymeric electrolyte membrane (PEMFC), phosphoric acid (PAFC), molten carbonate (MCFC), and solid oxide (SOFC), is now being very energetically pursued. Materials selection for each type of fuel cell is briefly examined, and the predominant engineering issues related to the development of commercial products are summarised. The fabrication, reliability, and cost of the relevant materials is of paramount importance to ensure rapid market penetration. The choice of fuel and relevant infrastructure is also considered, and the crucial role of materials for energy storage (particularly hydrogen) and fuel processing, is emphasised.

## 1. Introduction

### 1.1. Preface

Although the concept of producing electrical power from a simple electrochemical cell was first demonstrated in 1839 [1], another 120 years were to elapse before Bacon [2] was able to assemble a fuel cell stack which exhibited useful power densities. Bacon's cell, as modified by Pratt & Whitney, became the on-board power system for the NASA Apollo space vehicles which enabled astronauts to land on the moon in 1969. Examination of the initial 120 years of fuel cell R&D clearly indicates how progress was limited by the non-availability of suitable materials to contain corrosive electrolytes over extended periods, and the lack of appropriate materials processing technology to produce stable porous electrodes. The present survey seeks to highlight how materials development over the past four decades has enabled fuel cell development to attain its present status with real commercial exploitation now expected in the first decade of the new millennium.

### 1.2. Fuel cell operation

The operation of a single fuel cell is depicted schematically in Fig. 1. As long as the fuel and oxidant are supplied to the anode and cathode respectively then the fuel cell will continue to supply electrical power and produce reaction products such as water and carbon dioxide. In contrast the production of electricity from another type of electrochemical power system, a battery, is constrained by the total quantity of reactants stored within the battery container. It will be noted that a three-phase interfacial region has to be established within each electrode to ensure that the electrolyte, reactants, and electronic species are in intimate contact. The fabrication and stability of this three-phase boundary (tpb) is of crucial importance to the electrochemical performance of a fuel cell, and this feature will be the subject of more detailed scrutiny later. A variety of fuel cell systems are under commercial development, and they are usually identified, see Fig. 1, by the type of electrolyte incorporated within the cell: viz: alkaline fuel cell (AFC), polymer electrolyte membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC). Examination of Fig. 1 reveals that the lower temperature systems, AFC, PEMFC, and PAFC, essentially operate on $H_2$ fuel, whereas the higher temperature systems can also electrochemically oxidise CO, which is advantageous when a hydrocarbon fuel is supplied to the fuel cell. It should also be noted that the reaction products $H_2O$ (and $CO_2$) are produced at the anode by AFC, MCFC, and SOFC cells but at the cathode by PEMFC and PAFC cells. This difference has a significant impact on the design strategies adopted for the various fuel cell systems.

The electrochemical oxidation of a fuel can, in theory, be accomplished at very high efficiencies (e.g., 83% for the $H_2/O_2$ reaction at 25 °C) compared to heat engines utilising the combustion of a fuel. Moreover high combustion temperatures result in the formation of environmental pollutants such as $NO_x$ which are

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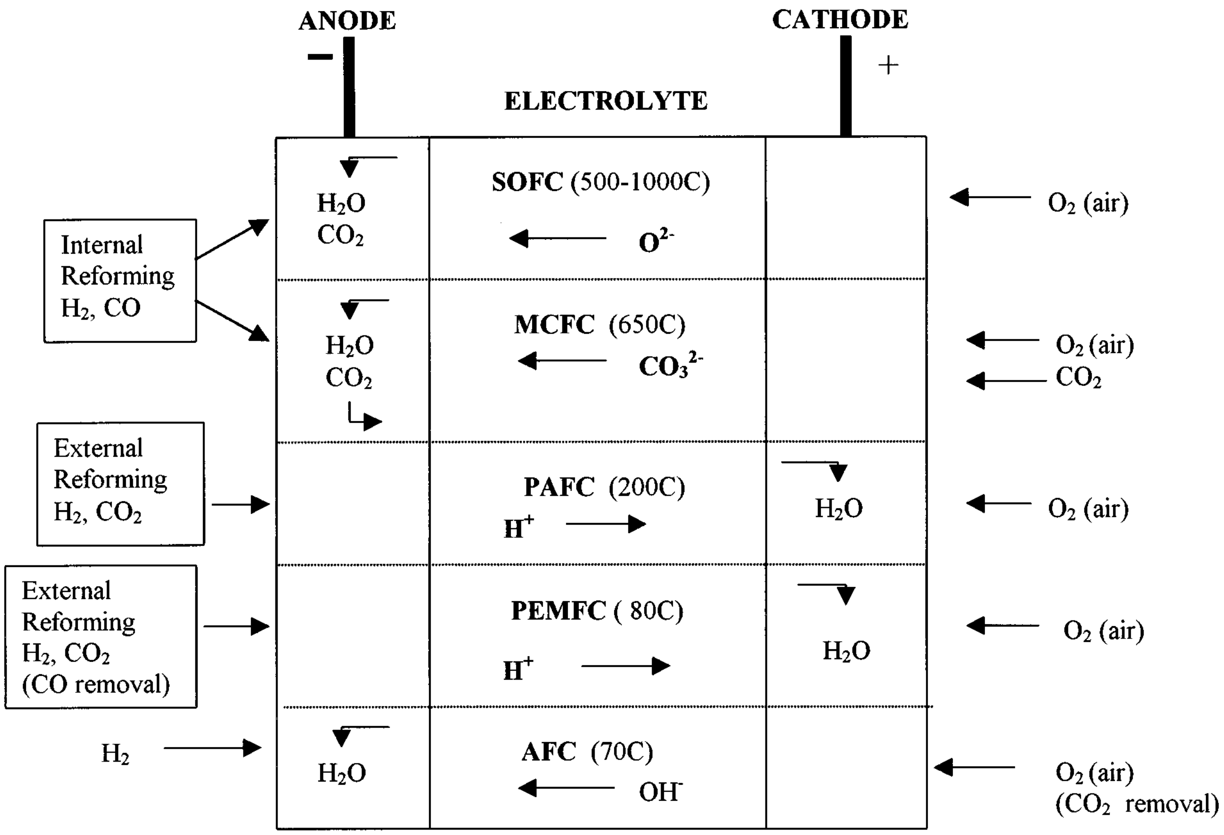


*Figure 1* Fuel cell types with typical reactants.

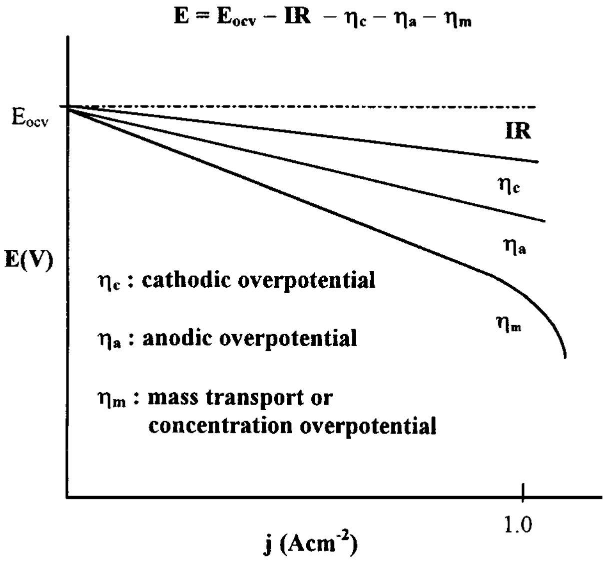


*Figure 2* Current-voltage characteristics of fuel cells.

essentially absent in the exhaust gases emitted from a fuel cell. However in practice fuel cells also experience irreversible losses due to resistive and polarisation losses, see Fig. 2, and efficiencies of fuel cell stacks rarely exceed 50–60%. The irreversible losses appear as heat, and for example a 1 kW fuel cell operating at 50% efficiency also has to dissipate 1 kW of heat. Thermal management of fuel cell stacks is thus an important design consideration requiring careful selection of cooling fluid and associated materials. In use a fuel cell is typically operated around 0.7 V, and so many individual cells are usually connected in series, see Fig. 3, using impermeable electronic conducting inter-connect or bi-polar plates, which often also distribute the reactant gases to the respective porous electrodes. Further information on fuel cell types and technology is provided by a variety of books published in the last decade [e.g. 3–7]. Useful historical surveys have been provided by Appleby [9] and Kordesch [8], and summaries of the current technological and commercial status of fuel cells are provided in the Fuel Cell Handbook issued by the US Department of Energy [10], and Proceedings of the Grove Fuel Cell Symposium [11]. Much useful information can also be downloaded from a variety of web sites [12].

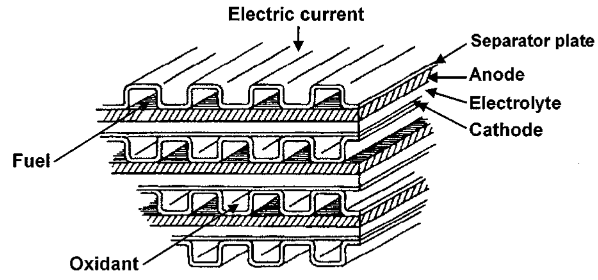


*Figure 3* Typical planar stack arrangement.

## 2. Materials selection

### 2.1. General comments

Materials selection for a commercial product involves an iterative design process which eventually becomes very specific to the particular product and application. However it is suggested that the following general technical issues usually define the preliminary selection of materials. It is, of course, recognised that cost considerations will provide further constraints on the selection of materials, and the processing routes adopted by the manufacturers.

## 2.2. Electrolyte properties

Corrosion properties dominate the selection of materials for the immobilisation and containment of liquid electrolytes. For solid electrolytes it is the proposed temperature of operation and thermodynamic stability that determines the choice of electrolyte material, and relevant processing route to fabricate this component in a thick film (10–30 $\mu$m) form. It is interesting to note that to minimise resistive losses all electrolytes in fuel cells require specific ionic conductivities greater than $10^{-2}$ S $\text{cm}^{-1}$.

## 2.3. Electrode materials

As well as being thermodynamically stable in contact with the appropriate electrolyte and electro-catalytically active, the materials selected for the electrode have to be capable of being fabricated into stable three-phase boundary structures, and these very important criteria are discussed further in Section 2.7

## 2.4. Stack configuration and assembly

The materials chosen for the stack components ie. bipolar plates, manifolds, seals, etc tend to be specific to the particular fuel cell type. Their selection is also influenced by the stack configuration: tubular, planar, internal or external manifolding. Moreover the design of the stack component has to incorporate provision for the supply and removal of reactants and products, cooling, and maintaining an invariant electrolyte composition where appropriate.

## 2.5. Balance-of-plant (BOP)

The pumps, heat exchangers, fuel processing units, ducting, etc, incorporated into a fuel cell system all involve material selection choices. Until recently this important area had tended to be neglected even though the cost of the BOP is often at least as great as the fuel cell stack. A consequence of this neglect has been that the reliability of the fuel cell plant (e.g. PAFC systems) has often been constrained by the failure of BOP units rather than the relatively novel fuel cell stack.

## 2.6. Power conditioning and control

To ensure stable electrical output to an external load requires appropriate DC/AC invertors and system control for the stack. This is another area that would benefit from more attention as fuel cell system producers usually have to specify off-the-shelf equipment that has not been specifically designed to operate with this new technology.

## 2.7. Development of stable porous three phase boundary electrode structures

In his innovative 1842 paper Grove [13] recognised that the power output of his fuel cell was limited by the small effective electrode area represented by a single meniscus on his platinum sheet. This important ‘notable surface of action’ was the region in which the electrolyte, gaseous reactants, and electro-catalytic conductor were in close contact. It is now termed the triple phase boundary (tpb) interfacial region. The early frustrations and disappointments in fuel cell technology were principally associated with problems in producing stable porous structures with ‘controlled wetting’ so that the liquid electrolyte could penetrate into a thin electro-catalytic layer but not flood the thicker gas diffusion layer. The introduction of hydrophobic PTFE (Teflon) in the 1950’s greatly simplified fabrication of a porous liquid resistant gas diffusion electrode structures. Metal or carbon powders provided the electronic pathways, and to reduce the area specific resistance (ASR) of the electrode a metallic wire mesh/screen was usually incorporated into the structure. Further improvements in performance were obtained during the 1960’s by depositing small crystallites (2–5 nm) of the electro-catalyst (usually Pt or Pt alloys) onto the dispersed carbon powder. By 1970 the basic features of modern porous gas diffusion electrodes, see Fig. 4, had been developed. In retrospect this accomplishment was probably the first manifestation of an engineered nanostructure, and it not surprising that its implementation more than thirty years ago was so difficult.

It was necessary to develop different concepts for the porous gas electrodes used in the high temperature fell cells systems, MCFC and SOFC. These will be discussed in the later sections devoted to these types.

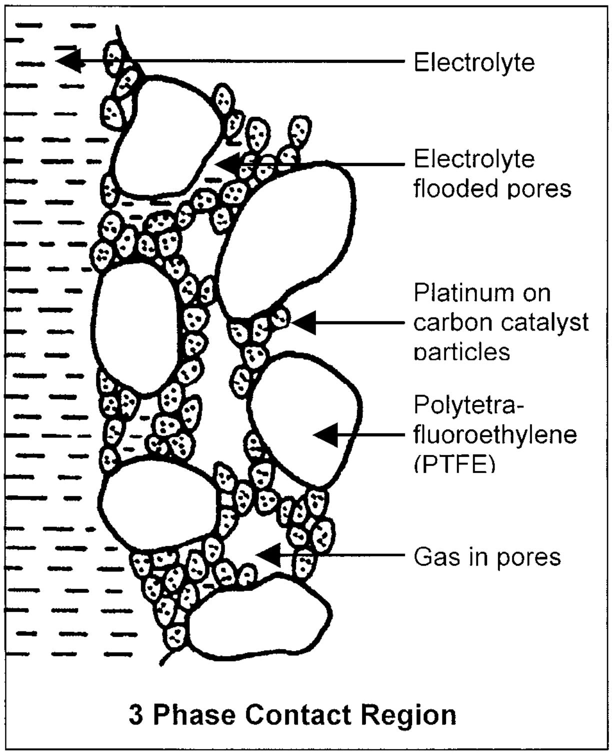


*Figure 4* Three-phase-boundary interfacial structure for liquid electrolytes.

## 2.8. Fuel choice and fuel storage

It is important to recognise that the type of fuel and its storage has important ramifications for both fuel cell technology and associated materials development. Although the lower temperature fuel cell systems exhibit excellent performance with pure $H_2$, this fuel is relatively expensive to produce, and its storage incurs large gravimetric and volumetric energy density penalties, see Fig. 5. Lightweight cylinders for compressed hydrogen (300 bar) are being developed [14], and work continues on the development of metal hydrides [15]. Controversy remains about how much hydrogen can be reversibly stored in activated carbon, particularly [16] in carbon nanotubes (fullerenes). Clearly if a novel hydrogen storage material can be developed with a reversible capacity approaching 10% by weight of hydrogen, then there would be a paradigm shift in attitudes to hydrogen fuel and the ‘hydrogen economy’. However until this occurs, fuel cells for transport will probably be provided with liquid fuels such as gasoline or methanol, whilst stationary fuel cells for CHP will be supplied with natural gas. This scenario introduces problems for the low temperature fuel cells as an external fuel processor must be incorporated into the system to produce the hydrogen, see Fig. 6. This not only increases the cost and complexity of the unit, but reduces the overall efficiency. For example, the recent CEC Mercatox project [17], concluded that using methanol with the Johnson Matthey ‘Hot Spot’ reformer and POX CO removal unit, together with a PEMFC stack would only generate system efficiencies around 30% which is below that projected for modern diesel engines.

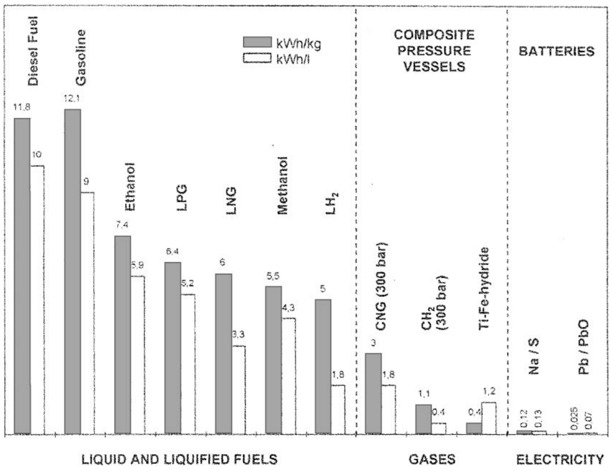


*Figure 5* Gravimetric and volumetric energy densities of selected fuels.

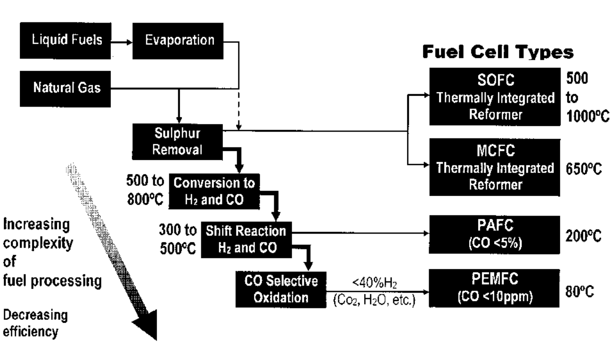


*Figure 6* Fuel cell types and influence of fuel processing.

There is much discussion regarding the most appropriate fuel infrastructure for transport applications in the future. However most observers [e.g. 18] believe that methanol and hydrogen will have a significant role as they can both be produced via a variety of pathways, many of which are compatible with sustainable/renewable energy strategies. It is appropriate therefore to also consider materials aspects of direct methanol fuel cells (DMFC). Accordingly brief comments about DMFC systems are provided in the sections devoted to PEMFC and SOFC stacks.

Finally it should be noted that materials play a major role in the production of hydrogen via steam reforming plants, novel microchannel fuel processors [19], ion conducting ceramic membrane technologies [20], and $H_2$ purification using thin Pd alloy membranes.

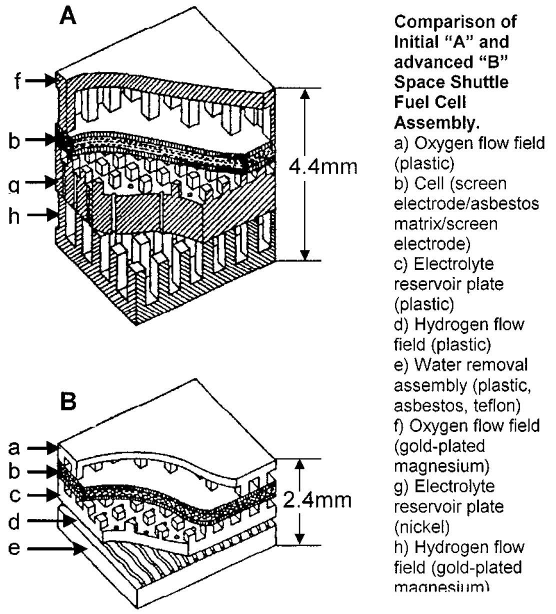
## 3. Alkaline fuel cell (AFC)

The AFC system had an important role in the historical development of fuel cells. Bacon [21] used this system to construct the first practical fuel cell in which he obtained 230 mA/cm$^2$ at 0.8 V towards the end of 1953. This had increased to 400 mA/cm$^2$ by 1959 which was the year when the technology was licensed to Pratt & Whitney (P&W). P&W (United Technologies) subsequently modified and developed the system for the Apollo space modules which allowed the NASA astronauts to land on the moon in 1969. Today the AFC system powers the Space Shuttle, and its reliability has been successfully demonstrated on many missions over the past twenty years.

As the solubility of molecular oxygen is higher in alkaline electrolytes compared to acid electrolytes the overall rate of oxygen reduction is higher, and the use of non-noble metal electro-catalysts such as Ni is feasible. However the strong KOH solutions at high temperatures ($\sim$200C) and high pressures (e.g. 40 atm) as originally used by Bacon had to be treated with respect. In later years P&W engineers were to claim [22], with only a modicum of exaggeration, that if a screwdriver were to be dropped into a vessel containing the hot electrolyte, it would dissolve before hitting the bottom!

A major disadvantage of AFC systems is that the KOH electrolyte reacts with $CO_2$ impurities present in air or impure hydrogen derived from hydrocarbon and alcohol fuels. Although there are claims [23] that performance degradation associated with this reaction can be negligible with suitable electrodes over significant operational times, it is apparent that most developers have terminated development of AFC systems in favour of PEMFC systems. However the availability of pure cryogenic oxygen and hydrogen for space meant that the AFC system became the workhorse of the NASA programmes.

There are two principle design configurations for the AFC system. The one eventually employed by P&W for the space shuttle uses an immobilised (matrix) configuration in which the KOH solution is contained in a butyl-bonded potassium titanate fibre matrix which



**Comparison of Initial "A" and advanced "B" Space Shuttle Fuel Cell Assembly.**
a) Oxygen flow field (plastic)
b) Cell (screen electrode/asbestos matrix/screen electrode)
c) Electrolyte reservoir plate (plastic)
d) Hydrogen flow field (plastic)
e) Water removal assembly (plastic, asbestos, teflon)
f) Oxygen flow field (gold-plated magnesium)
g) Electrolyte reservoir plate (nickel)
h) Hydrogen flow field (gold-plated magnesium)

*Figure 7* Evolution of AFC cell arrangement for Space Shuttle.

replaced the original asbestos separator. A schematic diagram of the AFC cell which operates at 92 °C and 0.40–0.44 Pa is shown in Fig. 7. It will be noted that relatively expensive materials are specified for the cell, which reflects the fact that power/weight (∼300 W/kg), and energy/volume issues are paramount, with cost considerations a second issue. The water produced in the anodic half-cell reaction ($H_2 + 2OH^- \Rightarrow 2H_2O + 2e^-$) is removed by vapour transfer into the hydrogen gas. After separation in a centrifuge the water droplets are collected and used as potable water for the astronauts. Thermal management is via the electroformed nickel bi-polar plates which are contact with the cooling liquid every 4th cell. Ni is used for tubing and Ni plated steel for pumps etc.

The other AFC design configuration uses a circulating electrolyte which also provides the mechanism for water control and thermal management. This arrangement was used by Siemens for modules destined to be used in submarines, and by ELENCO for AFC systems to be used in transport (buses). For the electric vehicle applications costs had to be minimised and ELENCO adopted a monopolar plate design with edge current collection. The anodes and cathodes were multi-layer gas diffusion electrodes. After more than 20 years development the ELENCO project was terminated in 1995. The technology has been licensed by ZEVCO for selected niche markets including a London taxi. A recent survey on AFC applications has been provided by Kordesch *et al.* [24].

## 4. Polymer electrolyte membrane fuel cell (PEMFC)

The recognition, that for most applications in the foreseeable future fuel cells would be supplied with hydrocarbon fuels, stimulated investigations into the acid electrolyte systems, PEMFC and PAFC, that are tolerant to the $CO_2$ usually present in the impure hydrogen derived from fossil fuels.

The General Electric Company initiated development of solid polymer electrolyte fuel cells in the 1950's for the Gemini space capsules. Although high Pt loadings were used with the polystyrene sulphonate ion exchange membrane incorporated in these systems the power densities were relatively low (∼50 mW/cm$^2$). These, and other stability problems, meant that the AFC system was the preferred option for the Apollo space programme. However the introduction of the superior perfluorinated sulphonic acid polymer, Nafion, in the 1960's ensured that development of polymeric electrolyte fuel cells continued. Unfortunately Pt loadings were still too high in 1970, and investigations into PEMFC systems languished for more than a decade until Ballard (Canada) began work in 1984 under a contract from the Canadian Defence Department. By the mid 1990's Ballard had overcome many of the engineering problems associated with this system, and were able to demonstrate impressive power densities (1.5 W/cm$^2$) with low Pt (0.5 mg/cm$^2$) loadings in 1 kW stacks [25]. The high power densities and operation at relatively low temperatures (∼80C) means that the PEMFC system is particularly appropriate for electric vehicles, and very large development and demonstration projects have been initiated by automobile manufacturers around the world. It is hoped that these programmes can lead to significant reductions in the cost of the PEMFC components, and innovative strategies to accommodate the requirement that the $H_2$ supplied to the cell should contain less than 10 ppm CO. There is also increasing interest in PEMFC systems as a replacement for batteries for portable applications such as mobile telephones, laptop computers, and the electronic equipment carried by military personnel. For example [26] a small PEMFC in combination with a lithium aluminium hydride storage capsule can provide 400 Wh/kg, which is far in excess of that provide by battery systems.

Before discussing the materials requirements in detail it is useful to summarise a typical PEMFC stack design such as that is depicted in Fig. 8.

Graphite bi-polar plates are pressed against the membrane-electrode assembly (MEA). These plates have a manifold of grooves to distribute the reactant gases to the electrodes, and must incorporate any special design features specified for the water and thermal

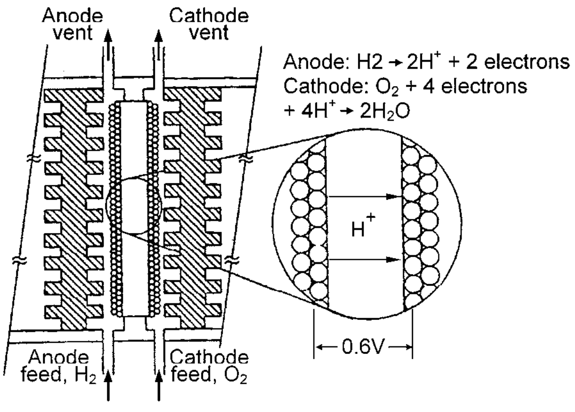


*Figure 8* Schematic diagram of PEMFC.

management. It should be noted that the $H_2O$ reaction product is rejected at the cathode where it is usually removed by using an excess flow of oxidant gas. However water management is still a critical issue in the operation of PEMFC stacks. The ionic conductivity is highest when the membranes are fully saturated. However during operation water is also transported through the cell as the proton may be considered as being hydrated $H(H_2O)_n^+$ with values of $n$ typically between 1 and 2. However this effect is mitigated by back diffusion of $H_2O$ from the cathode, and possible diffusion of any $H_2O$ in the fuel stream through the anode. Without adequate water management, an imbalance will occur between water production and evaporation within the cell.

Adverse effects include dilution of reactant gases by water vapour, flooding of the electrodes, and dehydration of the solid polymer membrane. The adherence of the membrane to the electrode will also be adversely affected if dehydration occurs. Clearly water management is very important in the design and operation of PEFMC, and Ballard claim that their automated systems satisfy this requirement in a cost effective manner [27].

Although machined graphite bi-polar plates provide a technical solution for this component the associated high fabrication costs indicate that an alternative cheaper material must be developed if PEMFC systems are to have a high market penetration particularly for transport applications. Moulded/pressed graphite, plated metals (e.g. stainless steel, aluminium), conductive polymeric materials, etc, are being examined as possible replacements for graphite, together with proprietary compositions developed by Ballard.

The gas diffusion electrodes incorporate a porous carbon cloth support with a hydrophobic coating. Onto this are deposited fine powdered carbon loaded with nanosized Pt crystallites (2–5 nm), and this structure is bonded to the electrolyte membrane by using a soluble form of the Nafion polymer. Processing improvements have steadily increased the performance of these electrodes such that Pt loadings as low as 0.4 mg $Pt/cm^2$ can now be specified. This corresponds to around 1.5 g Pt/kW which satisfies the relevant economic targets.

Although Nafion based membranes are the preferred electrolytes for PEMFC systems today, this material exhibits certain undesirable features in addition to its high cost. When hydrogen rich gases derived from hydrocarbon or alcohol fuels are used, the sensitivity of the anodic electro-catalysts to traces of CO ($<10$ ppm) remains a major problem which could be ameliorated by raising the temperature of operation. Increasing attention is also being given to the direct electrochemical oxidation of methanol which would also benefit from operation at higher temperatures to reduce the concentration of deleterious adsorbed species. Moreover the methanol permeability of Nafion is too high for many technological applications. Limits to the maximum operational temperature and methanol cross-over at present introduce severe constraints for systems incorporating Nafion, and so it is not surprising that investigators are examining alternative polymeric electrolyte materials. These include sulphonated polyetherketones (PEEK), radiation grafted co-polymers [28]. A recent survey [29] summarises the theoretical basis for the development of novel membrane materials, and Fig. 9 indicates the major differences between Nafion and sulphonated PEEK which are responsible for the lower performance characteristics of the PEEK based membrane. Another approach to increase the operating temperature is to try to develop composite polymeric/ceramic materials [30].

### 4.1. Direct methanol fuel cell (DMFC)

A useful historical survey of the development of DMFC systems has recently been provided by McNicol *et al.* [31]. Most of the original work was conducted with sulphuric acid electrolytes, but more recently attention has focussed on stacks incorporating the Nafion polymer electrolyte membrane. A report [32] from the Los Alamos National Laboratory (LANL) summarises recent progress with this system, and indicates the adoption of different strategies for DMFC development depending on whether the application is for portable electronic equipment, or for electric vehicles. A major problem with the Nafion membrane is its permeability to methanol which lowers the effective fuel utilisation, and degrades the performance of the cathode. To reduce the severity of this problem the cells designed for portable power were operated around 60C at 0.45 V with relatively high catalyst (PtRu) loadings (1 $mg/cm^2$). Projected power densities of 300 W/l were claimed for this arrangement. For electric vehicles the operational temperature was increased to 100C. A dilute fuel was used to reduce methanol crossover which introduced major challenges in water management as 2.5–3 $H_2O/H^+$ were transported to the cathode and had to be returned to the anode. Process design appeared to overcome most of the difficulties and the authors claim that 1 kW/l should be achievable with their configuration. This is comparable to values reported for PEMFC stacks using $H_2$, with the added benefit of using a liquid fuel. The work on DMFC systems clearly demonstrates again the need for an alternative polymeric electrolyte to Nafion with minimal methanol permeability, and higher temperature operation.

## 5. Phosphoric acid fuel cell (PAFC)

The other $CO_2$ tolerant low temperature cell is the PAFC system operating at 200C. Although a number of US companies carried out R&D activities into this system almost all the development work is now focused on the International Fuel Cells (United Technologies/Pratt & Witney) 200 kW PC25C unit which normally operates around 1 atm pressure. PAFC Systems are also being developed by Fuji Electric Corporation, Toshiba Corporation and Mitsubishi Electric Corporation in Japan. The largest plant operated delivered 11 MW of grid quality AC power. In 1990 a joint venture, ONSI, was established between International Fuel Cells (IFC) and Toshiba, with a minority participation (recently terminated) by Ansaldo (Italy) to manufacture and market

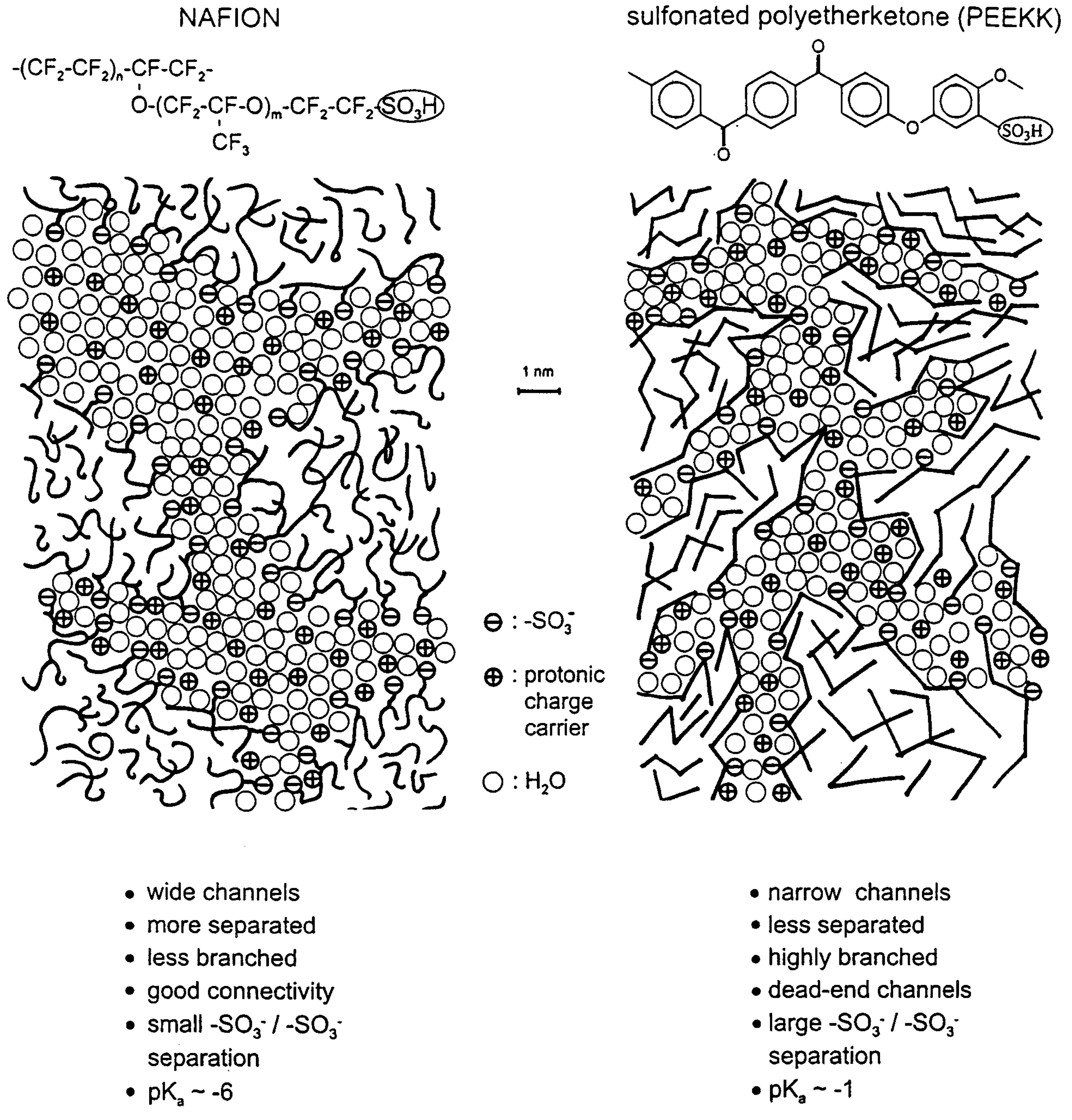


*Figure 9* Schematic representation of the microstructures of NAFION and a sulphonated polyetherketone depicting the less pronounced hydrophobic/hydrophilic separation of the latter compared to the first.

PAFC units worldwide. At present (Spring, 2000) almost 200 of the ONSI PC25 units have been installed world-wide and a report by Whitaker [33] in 1997 summarised the main features of this extensive demonstration programme. Some of the early models have now been in service for over 25,000 hrs with over 95% availability, and one unit established a world record for any power plant by running for 9500 hrs continuously at full rated load. A later report [34] has provided details of the performance of 30 PC25 units installed at a variety of US defence sites with climatic variations ranging from desert to arctic conditions. Despite the rugged conditions the generators continue to perform well after small agreed modifications to the balance of plant.

Although the 200 kW PC25 PAFC units have demonstrated impressive reliability and satisfied relevant technical specifications, penetration of the distributed CHP market has been disappointing. Partly this is due to cost issues. In spite of \$1000/kW subsidies by the US and Japanese governments the capital cost (~\$2500/kW) is still too high. Moreover with external fuel processing the overall electrical efficiency is at best 40% (LHV), and so savings on fuel running costs are insufficient with the current low price of natural gas and oil. As will be discussed later materials costs are still a significant factor in the economics of PAFC systems.

The materials incorporated into the PC25 stacks have remained unchanged over the past 25 years. The electrolyte is 100% $H_3PO_4$ immobilised in a PTFE-bonded SiC matrix. The gas diffusion electrodes consist of PTFE-bonded nanosized Pt crystallites dispersed on carbon (Vulcan XC-72) supported on a carbon paper substrate. A significant reduction in the anode Pt loading has occurred from 0.25 mgPt/cm$^2$ (1975) to

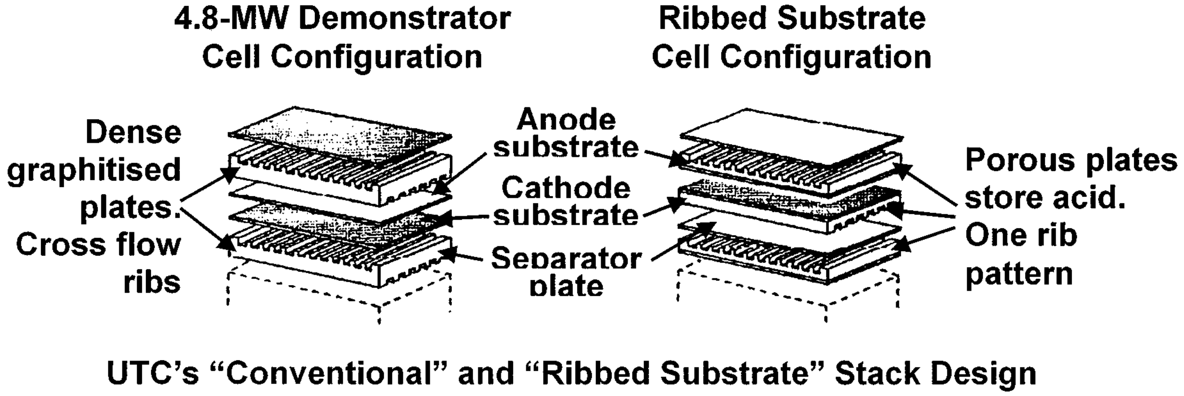


*Figure 10* Evolution of PAFC stack configuration.

0.1 mgPt/cm$^2$ (2000), but the cathode loading remains relatively high at 0.5 mgPt/cm$^2$. The gas distribution plates consist of two ribbed porous graphite substrates which also serve as electrolyte reservoirs, together with another dense impermeable graphite sheet which functions as the bi-polar separator plate, see Fig. 10. These graphite components are relatively expensive to manufacture and also restrict the operational window of the cells. Although it was demonstrated that selected carbon and graphite materials, which are thermodynamically unstable in phosphoric acid at 200C, were sufficiently kinetically stable to be used in PAFC stacks with projected lifetimes of 40,000 hrs, it has been necessary to recognise the limitations of these carbon based materials. For example the performance of the PAFC system can be enhanced by operating under pressure (3–8 atm), but this is offset by increased degradation rates of the graphite and carbon components. Carbon corrosion and Pt dissolution also become issues at cell voltages above 0.8 V, and so it is essential to avoid operating the stack at low current densities near open-circuit potential. Although provision can be made for protecting the cathode structure when the stack is idling, by replacing air by inactive nitrogen, this incurs a cost penalty for small and medium sized PAFC systems.

It will certainly be interesting to monitor how the PAFC and PEMFC systems compete in the future for the distributed CHP market.

TABLE I Lifetime estimation (37) for components in DIR MCFC development stack

| Component | State-of-Art | Endurance (hr) |
|---|---|---|
| Anode | Ni-Cr | 40,000 |
| Cathode | NiO (Li) | 40,000 |
| Matrix | $\gamma$-LiAlO2 + Al2O3 | 40,000 (no thermal cycling) |
| Electrolyte | Li/Na/K: 60/20/20 | 25,000–40,000 |
| Catalyst | BG Technology | 6,000–40,000 |
| Separator | 310 S stainless steel | 40,000 (fuel side?) |
| Anode coating | Ni clad layer | 10,000–15,000 |
| Wet-seal | aluminised metal | 40,000 |

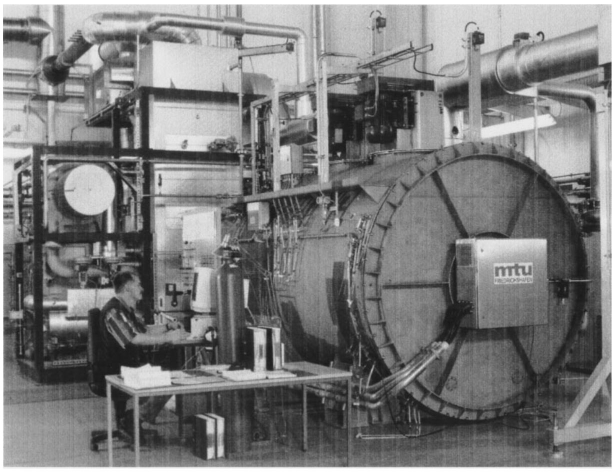


*Figure 11* ARGE MCFC 'Hot Module' under test at the Ruhrgas plant in Dorsten.

## 6. Molten carbonate fuel cell (MCFC)

The pioneering work of Broers [35] in the Netherlands stimulated interest in this system, and a historical perspective of MCFC development upto the mid 1980's has been provided by Selman [36]. The materials used for MCFC stack components have essentially remained unchanged over the past 25 years and are listed in Table I. A major development in the early 1980's was the introduction of more cost effective tape-casting techniques to fabricate the immobilised electrolyte matrix, and cell areas over 1 m$^2$ have now been successfully manufactured and tested.

MCFC systems were originally conceived as large (GW scale) centralised coal fired power stations. To develop user confidence it was considered that large MCFC plants should be demonstrated as soon as possible, and this led to the construction of the 1.8 MW Santa Clara (USA) system by Energy Research Corp which went on stream in April 1996. However testing of this plant had to be curtailed due to problems associated with the insulating properties of the material selected for the external manifold. It is now believed that a more appropriate strategy is to develop initially smaller MCFC systems ($\sim$250 kW) for distributed CHP applications using natural gas. An example of this approach is provided by the Hot Module MCFC project organised by the European Direct Fuel Cell Consortium (ARGE) which is co-ordinated by MTU (Germany). The compact pressurised stack fabricated by this group is illustrated in Fig. 11. In addition to the activities in the USA and Europe, Hitachi, IHH, and Mitsubishi Electric Corp, are also very active in scaling up MCFC

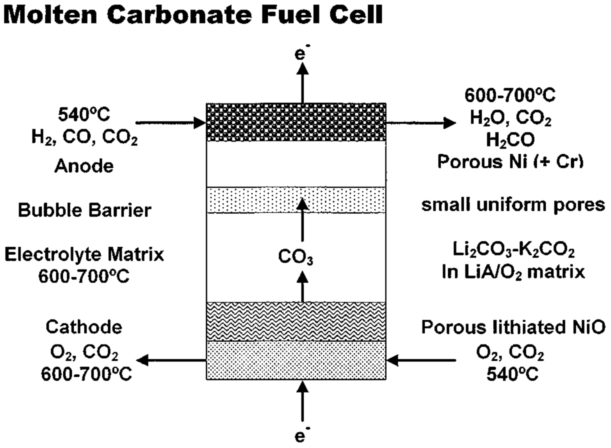


*Figure 12* Schematic diagram of MCFC.

technology in Japan. An analysis of MCFC lifetime limiting issues has recently been given by Huijsmans *et al.* [37]. All the critical endurance problems relate to materials and projections suggest (Table I) that most of the components could survive the target period of 40,000 hrs. Exceptions include the catalyst and anode coating, and uncertainties remain about corrosion on the fuel side of the bi-polar (separator) plate. It is disappointing that after 25 years development these uncertainties remain, and they will probably not be resolved until a 100 kW demonstration system has been operated for at least 25,000 hrs.

For the low temperature fuel cell systems PTFE serves as a binder and hydrophobic phase to maintain the integrity of the electrode structure, and to establish a stable ‘tpb’ interface. A different approach has to be adopted for MCFC stacks in that a ‘fixed-volume capillary equilibrium concept’ is used to control electrolyte distribution. By correct adjustment of the pore diameters in the electrolyte matrix and electrodes, an appropriate distribution of the electrolyte can be achieved as indicated in Fig. 12. At thermodynamic equilibrium, the diameters of the largest flooded pores in the porous components are related by the expression:

$$\gamma_c \cos\theta_c/d_c = \gamma_e \cos\theta_e/d_e = \gamma_a \cos\theta_a/d_a$$

where $\gamma$ is the interfacial tension, $\theta$ is the contact angle of the electrolyte, $d$ the pore diameter, and the subscripts indicate the porous components (cathode, electrolyte matrix, and anode). Electrolyte management, that is, control over the optimal distribution of molten carbonate is critical for achieving high performance and endurance for MCFC systems. However various processes, including corrosion reactions, voltage driven migration, creepage and vapourisation of the molten salt, all tend to contribute to the redistribution of the electrolyte, and subsequent degradation of stack performance and longevity.

## 7. Solid oxide fuel cell (SOFC)

### 7.1. High temperature SOFC

Over the past four decades the development of solid oxide fuel cell (SOFC) technology has been very influenced by the strategic priorities of large multi-national companies manufacturing electrical generation plant. These companies were initially interested in multi-MW SOFC systems that could be integrated with coal gasification plants (e.g. Westinghouse), or used to generate hydrogen by electrolysis of steam (e.g. General Electric, Brown Boveri, Dornier, etc). For both these applications, technical and economic considerations required that the SOFC stacks be operated around 1000C. The expertise associated with these earlier projects is now being exploited by Siemens-Westinghouse, MHI (Japan), and Z-TEK (USA), to develop large SOFC stacks integrated with gas turbines to produce electrical efficiencies around 70%. These combined systems still require the SOFC stack to be operated in excess of 850C to ensure low kWh energy costs.

Historical perspectives of SOFC development have been provided by Mobius [38] and Minh [39], and it is evident that by the early 1970’s the compositions of the materials to be used in the very high temperature (HT) versions of SOFC stacks had been identified. Of particular importance was the selection of SrO doped $LaMnO_3$ for the cathode material. Although other materials such as $La(Sr)Fe(Co)O_{3-x}$ exhibited superior electro-catalytic behaviour, they were incompatible with the chosen yttria stabilised zirconia (YSZ) electrolyte. It should be noted that the procedures to fabricate the HT-SOFC units often required temperatures upto 1300C, and it was essential that the components exposed to these high temperatures were thermodynamically and mechanically (e.g.: similar thermal expansion coefficients) compatible. A useful survey of the thermodynamic properties of zirconia based ceramics by Yokokawa [40] provides an interesting theoretical basis for the original empirical development of SOFC components.

A variety of configurations and processing routes have been investigated to fabricate HT-SOFC stacks. At present the largest (200 kW) SOFC prototype stacks have been assembled by Siemens-Westinghouse (S-W). This sealless tubular design was introduced in 1980. Originally the HT-SOFC components were supported on a porous CaO stabilised zirconia tube, but this was replaced by a porous tubular $La(Sr)MnO_3$ (cathode) substrate. More recently [41] an alternative cathode substrate cross-section has been investigated to provide higher power densities and improved strength. The evolution of the S-W tubular design, and arrangement of the stack modules is shown in Fig. 13. Initially the cell construction was completed by depositing thick films of the interconnect $LaCr(Mg)O_3$, electrolyte YSZ, and anode Ni-YSZ, using electrochemical vapour deposition (EVD). This allowed good quality dense YSZ (35 $\mu$m thick) and $LaCr(Mg)O_3$ components to be produced. Moreover formation of the porous composite Ni-YSZ anode by EVD produced an excellent stable microstructure with two interpenetrating contiguous networks of ionic and electronic pathways. The technical benefits of this processing technology have been demonstrated by operating single tubular cells for almost 80,000 hrs. However the capital and labour costs associated with EVD are too expensive, and S-W have already replaced the EVD processing of the interconnect $[La(Ca)CrO_3]$

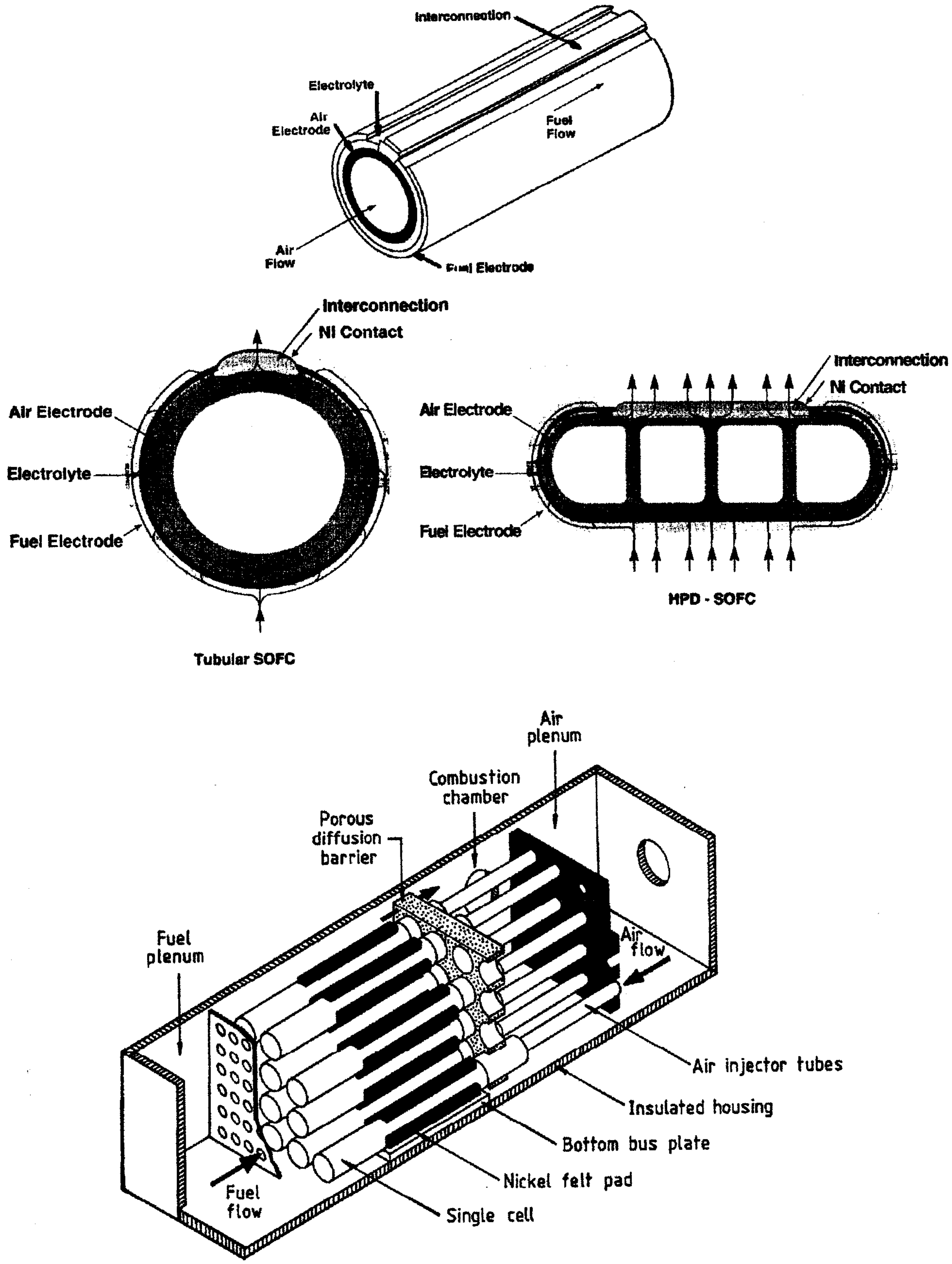


*Figure 13* Evolution of Siemens-Westinghouse tubular configuration.

and anode by cheaper plasma and liquid spraying technologies. Whether these alternative technologies can produce components with such excellent stable lifetime characteristics will not become apparent for several years. However S-W still continue with their investigations to develop cheaper alternative methods to deposit the YSZ electrolyte.

The status of the S-W demonstration programme has been summarised by George [42]. A 100 kW CHP unit continues to operate in the Netherlands, and a 200 kW pressurised (3 bar) SOFC/50 kW micro-turbine system is scheduled to be installed at the University of Irvine (California) test site in the Spring of 2000. A contract has also been agreed with Norsk-Hydro/Norsk Shell for another 250 kW P-SOFC/GT system to be installed in Norway. After these and other demonstration trials, S-W hope to enter the market with 1 MW P-SOFC/GT CHP systems. Whilst the combined SOFC/GT units should eventually be able to generate electricity with efficiencies upto 70%, recent studies [43–45] have suggested that similar electrical efficiencies could be realised by having a cascade of SOFC fuel cells, or by combining SOFC and PEMFC systems. As it should be easier to operate a combination of fuel cells rather than integrating a fuel cell with rotating power equipment it is probable that these innovative concepts will be tested in the future.

## 7.2. Intermediate temperature (IT) SOFC

It has been gradually recognised over the past decade 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 intermediate temperature (IT-SOFC) stacks for distributed (embedded) CHP units is being stimulated by electrical supply liberalisation (deregulation) 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.

Selection of the most appropriate solid electrolyte composition for intermediate temperature operation (500–750C) can usefully be discussed with reference to Fig. 14. If it is assumed that the electrolyte component should not contribute more than 0.15 $\Omega cm^2$ to the total cell area specific resistivity (ASR), then for a thick film thickness (L) of 15 microns ($15 \times 10^{-4}$ cm) the associated specific ionic conductivity ($\sigma$) value of the electrolyte should exceed $10^{-2}$ S $cm^{-1}$ ($\sigma = L/ASR = 0.0015/0.15$). Examination of Fig. 14 indicates that the ionic conductivity of yttria stabilized zirconia (YSZ) attains this target value around 700C, and for $Ce_{0.9}Gd_{0.1}O_{1.95}$(CGO) the relevant temperature is 500C. The use of thinner electrolyte films would allow the operating temperature to be lowered. However at present it appears that the minimum thickness for dense impermeable films that can be reliably mass produced using relatively cheap ceramic fabrication routes is around 10–15 microns.

Steele [46] has recently surveyed the status of IT-SOFC technology. Most developers are using an anode supported planar SOFC configuration designed to operate around 750C. The cell components are fabricated from similar materials used in the HT-SOFC systems, but the bi-polar plate is usually fabricated from a ferritic stainless steel. The LaCr(Mg)$O_3$ and La(Ca)$CrO_3$ interconnect materials used in all ceramic HT-SOFC systems are difficult to fabricate by conventional routes, and can also exhibit ‘chemical expansion’ [47, 48] and structural failure, when exposed to the large chemical potential gradients imposed by the cathodic and anodic gaseous environments. Siemens investigated a planar array configuration operating around 900C, and incorporating a high temperature Cr-Fe (95/5) alloy stabilised with 1%$Y_2O_3$ dispersion. However this system

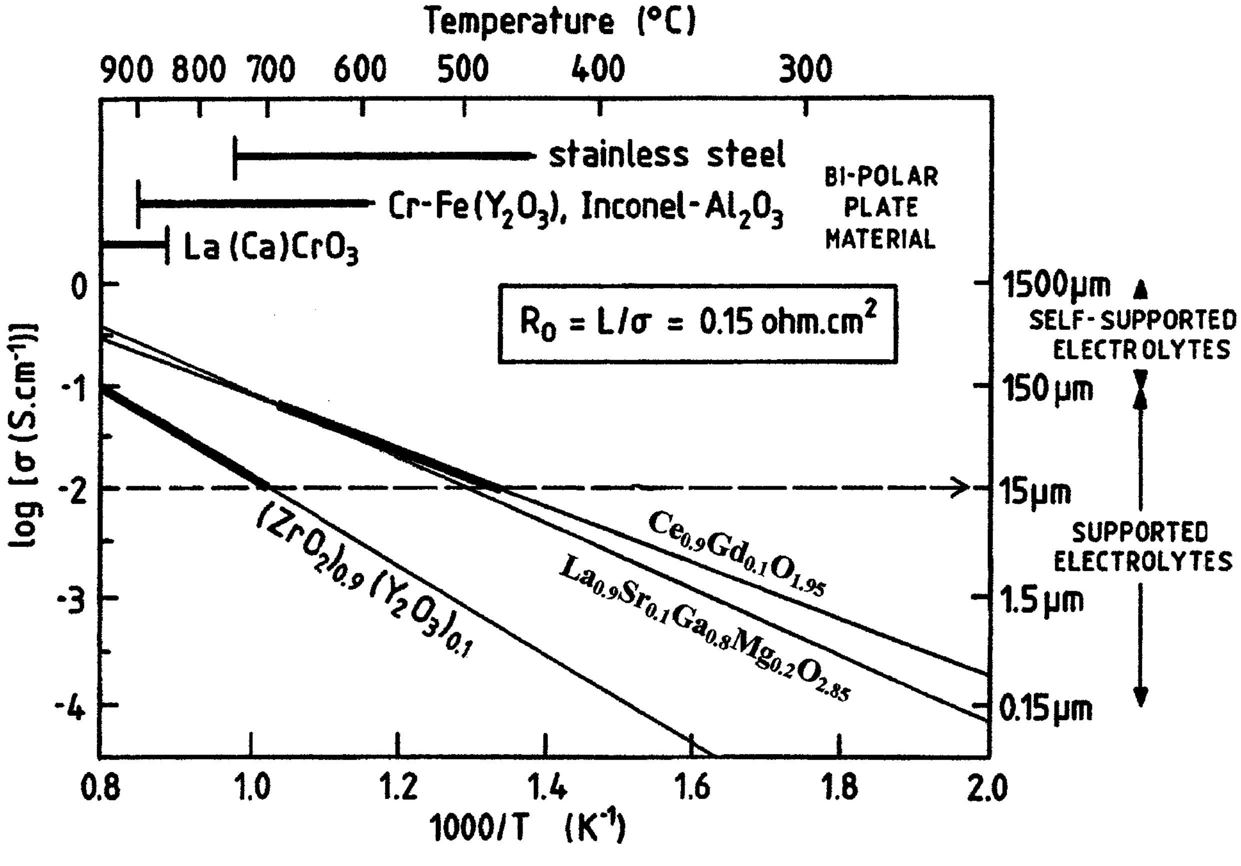


*Figure 14* Specific ionic conductivity values as a function of reciprocal temperature for selected solid electrolytes.

exhibited rapid performance degradation due to the deposition of $Cr_2O_3$ at the cathode/electrolyte interface. It was shown [49] that the Cr was transported by hexavalent Cr gaseous species, $CrO_2(OH)_2$ and $CrO_3$, which were subsequently reduced at the electrolyte interface effectively blocking the electro-catalytic sites. Reducing the temperature and introducing coatings on the metallic bi-polar plate provided an effective remedy.

IT-SOFC stack developers usually specify a ferritic stainless steel because of the low ($12.5 \times 10^{-6}$ $K^{-1}$) thermal expansion coefficients of these alloys. Moreover by using Ni-Ti stabilised compositions excellent electronic interfacial contacts can be maintained (50) between the cell components for extended periods. There remains some uncertainty about the long term effects of chromium evaporation from the stainless steel (17–18wt% Cr) in the temperature range 700–800C, and degradation processes associated with the high $P_{H2O}$ and $P_{CO2}$ values of the anode exhaust gases at high fuel utilisation. This latter problem has also been the focus of significant activity in MCFC systems which incorporate austenitic stainless steel bi-polar plates. Providing appropriate precautions are followed then many R&D laboratories have reported [51, 52] good performance values, see Fig. 15, for IT-SOFC stacks incorporating the following PEN components: anode (NI-YSZ)

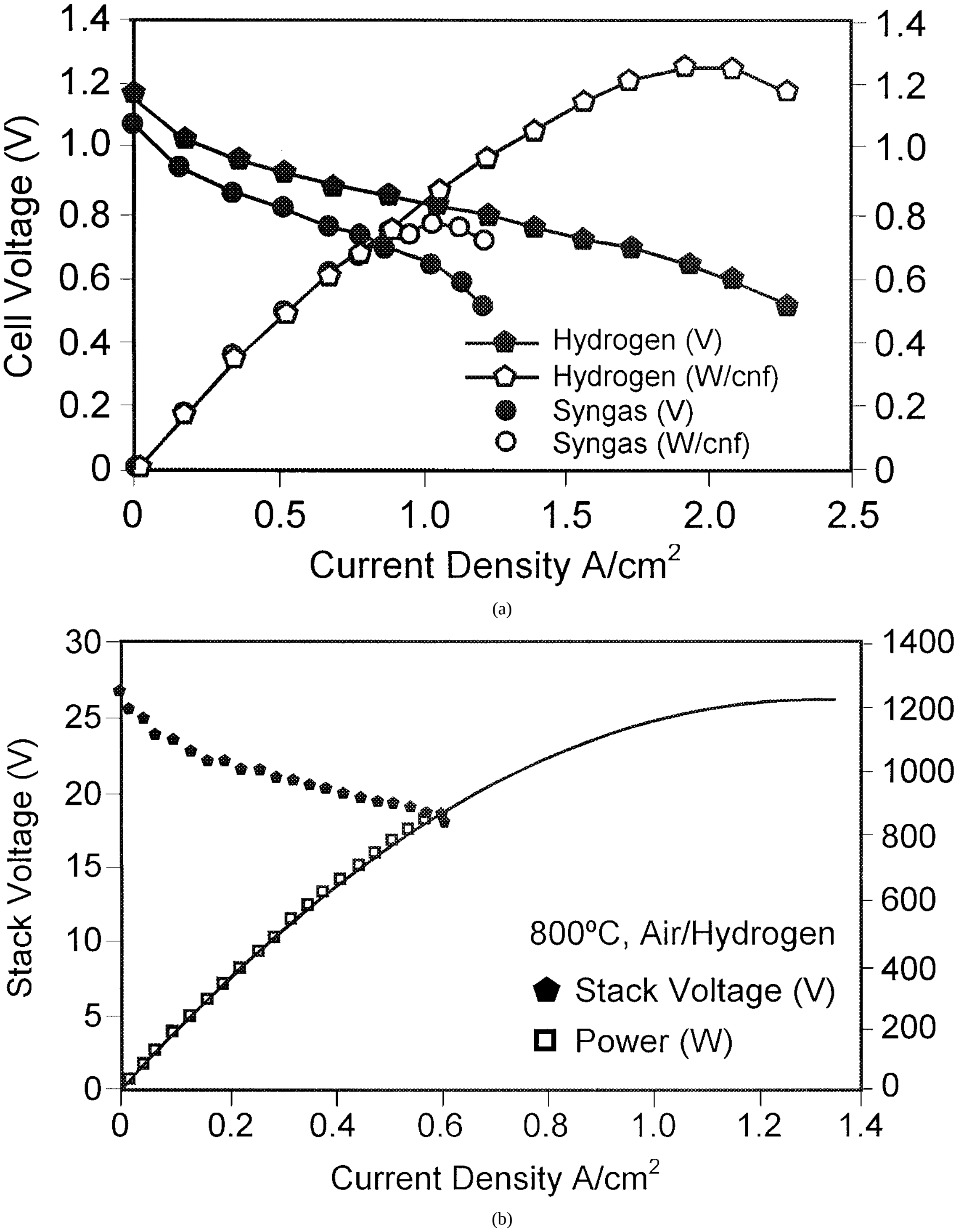


*Figure 15* (a) Performance of single anode-supported cells at 800C using either hydrogen or syngas fuel. Projections of these data indicate power densities greater than 1 kW/kg and 1 kW/l (Honeywell/Allied Signal in SOFC VI, ref. 51); (b) Performance of 26-cell stack: crossflow configuration with 10 × 10 cm PENS (Honeywell/Allied Signal in SOFC VI, ref. 51).

supported thick film YSZ electrolytes, LSM-YSZ cathodes, and stainless steel bi-polar plates.

Stack configurations for IT-SOFC systems reflect to some extent the market strategy of the relevant company. For example, the largest IT-SOFC R&D activity ($\sim$125 staff) is currently being undertaken by Ceramic Fuel Cells Pty in Australia. This company intends to produce IT-SOFC systems in 100–200 Kw sizes for distributed CHP applications, and has adopted an internal manifold planar layer incorporating a multi-PEN/stainless steel array (cf original Siemens design). The individual layers are assembled into a stack using sheet steel interconnects and glass/ceramic seals. This company hope to demonstrate a 25 kW stack around Easter, 2000. The proliferation of glass/ceramic seals suggests that the assembled stack will have to be carefully heated to the operating temperature ($\sim$750C), and always maintained at elevated temperatures ($>$650C) irrespective of the external load demand. Another company, SOFCO, also appears to be targeting the medium size CHP market with planar self supported (180 microns thick) YSZ PEN structures, which require an operating temperature in excess of 800C.

In contrast, many other developers (e.g. Honeywell/Allied Signal, Sulzer, TMI, Thermoelectric, etc) envisage early market entry with small stack sizes (typically 1–5 kW) for such applications as power sources for remote locations, portable power for defence requirements, micro-CHP (e.g. residential), and electrical power for auxiliary functions in vehicles. For these applications stacks will have to be compact, rugged, and able to withstand relatively rapid temperature cycles. Most developers, therefore, have adopted a circular design, see Fig. 16, in which the fuel and air are introduced via an appropriate manifold at the centre of the PEN structure. Arrangements are made to distribute the air and fuel gases uniformly 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 increases. Finally a simple canister enclosure around the stack collects the reacted gases as a sealless manifold. Clearly the gas flows have to be carefully controlled to ensure that significant quantities of fuel are not burnt which would produce excessive temperature excursions. These design features minimise sealing problems, and many thermal cycles have been successfully demonstrated [51, 52].

Sulzer have pioneered the use of 1 kW SOFC stacks for residential CHP applications using natural gas, and studies by the Gas Research Institute (SOFC VI) indicate that SOFC units, with their ability to oxidise both $H_2$ and CO, are more attractive than PEMFC stacks for this application when hydrocarbon fuels are used. With support from DARPA, Honeywell/Allied Signal have demonstrated a 26 cell 0.86 kW stack (peak power 1.2 kW) operating at 800C. This unit will provide the basis of a 500W portable battery charger system operating on logistic fuels such as JP-8 and diesel fuel This unit will have a volume of 43 × 28 × 23 cm and weight of 7 kg. Similar developments have also been reported by TMI. Selected car companies (e.g., BMW, Toshiba, Renault-Nissan) are also developing IT-SOFC stacks for auxiliary functions (e.g.: air conditioning) and intend to integrate a gasoline reformer within the SOFC stack. Clearly there is much activity related to the development of small IT-SOFC systems with some prototype units already being tested in the market. Commercial units can be expected in the next five years once reliability and cost requirements (<$1000/kW) have been effectively demonstrated.

### 7.3. Ceria based electrolytes

The use of ceria based electrolytes such as $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO) should in principle allow the cell operating temperature to be lowered to around 500C, see Fig. 14. However 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

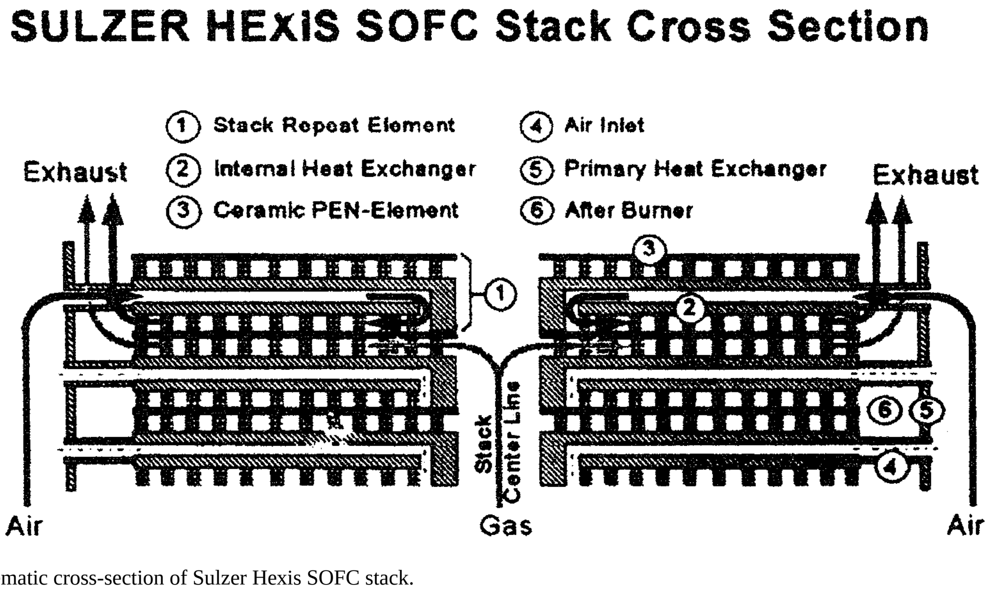
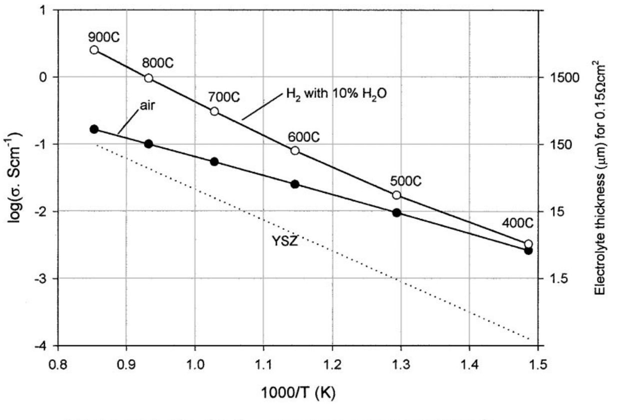


*Figure 16* Schematic cross-section of Sulzer Hexis SOFC stack.



Conductivity (σ) of $Ce_{0.9}Gd_{0.1}O_{1.95-x}$ in air and $H_2$ saturated with 10%$H_2O$
The required electrolyte thickness to achieve an ASR of 0.15Ωcm$^2$ is also plotted

*Figure 17* Specific conductivity of $Ce_{0.9}Gd_{0.1}O_{1.95}$ in air and 10% humidified hydrogen as a function of temperature.

lattice expansion) produces an internal short circuit in the PEN structure which can significantly degrade the efficiency and performance of cells incorporating ceria based electrolytes. However as emphasised by the author [53] if the operating temperature is lowered to around 500C then the electronic conductivity contribution is small and can be neglected under typical cell operating conditions. The increased ionic domain at lower temperatures is evident in the adjoining diagram, see Fig. 17. A more serious difficulty that has restricted exploitation of the attractive properties of CGO at 500C has been the need to develop alternative cathode compositions that function effectively at this temperature. Fortunately recent developments [53, 54] indicate that appropriate composite cathode materials can be fabricated which exhibit small overpotentials at 500C (e.g.: 0.15 V at 1 Acm$^{-2}$). Composite anodes such as Ni-CGO also provide adequate performance at 500C for simulated syngas fuels so that IT-SOFC stacks at 500C now appears to be a viable option. Imperial College, for example, are beginning to scale-up their technology in this area to enable the performance of small stacks to be evaluated.

Operation at 500C allows the use of compliant high temperature gaskets in place of rigid brittle glass/ceramic seals thus permitting greater design flexibility for the stack configuration. At Imperial College we also take 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. Fabrication routes have also been developed which ensure that the processing procedures do not exceed the annealing temperature (1000C) of the stainless steel. These metal supported PEN structures are very robust, and should withstand the rapid temperature cycles expected during operation of small IT-SOFC stacks.

It is envisaged that the IT-SOFC (500C) stacks will initially be supplied with humidified methanol fuel, and so can be considered as a direct methanol fuel cell (DMFC) for use in electric vehicles as suggested six years ago (55). It is probable that the thermal capacity of such stacks will be less then that associated with the fuel processing unit of a PEMFC system, and so start-up times should not be excessive. Studies have also indicated [56] that cool-down times can be extended to over 24 hours if necessary by the use of appropriate insulating technology. Another interesting development concerns the observations [57, 58] that direct electrochemical oxidation of humidified methane is possible at intermediate temperatures with anodes incorporating $CeO_2$. Lower temperature operation reduces the decomposition rate of $CH_4$ into hydrogen and carbon, and allows the direct electrochemical oxidation reaction to proceed at rates which are technologically interesting. Obviously IT-SOFC stacks operating at 500C offer some exciting possibilities, and it is important that 1 kW stacks be demonstrated as soon as possible.

## 7.4. Alternative solid electrolytes

Another electrolyte, doped $LaGaO_3$ (LSGM), is also attracting much attention for IT-SOFC applications. Although its conductivity is slightly smaller, see Fig. 14, than CGO at 500C its ionic domain is wider and it could be more appropriate to use this electrolyte at temperatures around 600C, where the reduction of $Ce^{4+}$ in CGO is becoming significant. However conflicting reports about the behaviour of this material in PEN assemblies need to be resolved before significant investment for scale-up activities can be justified. Reaction of doped $LaGaO_3$ with established electrode materials such as LSM and Ni-YSZ has been reported, vapourisation of GaO(g) at high temperatures under the reducing conditions established by anode gases has been observed [59], and rapid diffusion of transition metal cations along grain boundaries has been measured [60]. It has been difficult to fabricate pure single phase $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ ceramic electrolytes, and second phases such as $SrLaGa_3O_7$ and $La_4Ga_2O_9$ are often detected in the grain boundaries. Whether these phases are responsible for the enhanced reactivity of doped $LaGaO_3$, or whether it is an intrinsic property of doped $LaGaO_3$, are questions that remain to be answered.

New oxygen ion conductors continue to be reported, e.g. doped $La_{10}Si(Ge)_6O_{27}$ [61], and $La_2Mo_2O_9$ [62], but it is unlikely that these compositions will displace the well established fluorite ceramic electrolytes, YSZ, CGO. However further examination of $Re_{10}Si_6O_{27}$ compositions may indicate that this phase is responsible for the high grain boundary conductivity often reported [53] in impure rare-earth (Re) doped ceria electrolytes.

Finally it should be noted that selected ceramic proton conductors, e.g. $BaZr_{0.9}Y_{0.1}O_{2.95}$ [63] can also exhibit ionic conductivity values approaching those of CGO at 500C (i.e.: $10^{-2}$ S cm$^{-1}$). However ceramic fuel cells incorporating these materials will not be able to electrochemically oxidise CO, and do not appear to offer any advantages over the oxygen ion conducting electrolytes in this temperature region.

In this context the recent publication by Hibino *et al.* [64] is noteworthy. Using a single compartment fuel cell configuration these investigators reported high power densities (0.4 Wcm$^{-2}$) at 500C for a cell incorporating a 150 micron thick $Ce_{0.8}Sm_{0.2}O_{1.9}$ (CSO) electrolyte. Examination of the relevant current–voltage curves indicate specific ionic conductivity values for CSO at least 5 times higher than those anticipated [53] for oxygen ion conductivity in this material. As the whole cell was immersed in a gaseous environment containing significant water vapour partial pressures then it is possible that the predominant conducting species are protons. High hydrogen solubility in $Ce_{1.8}Re_{0.2}O_{1.9}$ electrolytes has already been reported by Sakai *et al.* [65], and so the development of stable fluorite based protonic conducting electrolytes capable of operating in the temperature range 300–500C requires further investigation. If confirmed, then a major stimulus will be given to direct methanol fuel cell technology which will have a significant impact on electric power generation for distributed CHP and transport applications.

## 8. Conclusions

Materials science and engineering has provided the enabling technology that has allowed fuel cells to progress to the present state of prototype manufacture. To ensure that fuel cell products attain commercial penetration of the relevant electrical power market selected materials related issues of reliability and cost still require addressing. However the future for at least three types of fuel cells: PEMFC, SOFC, and direct methanol systems (DMFC), appears very promising. Fuel cell technology, therefore, should make very important contributions to the reduction of environmental pollutants, to the conservation of valuable hydrocarbon fuels, and the development of sustainable energy sources.

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*Received 23 May*
*and accepted 18 July 2000*