Intermediate temperature solid oxide fuel cells

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High temperature solid oxide fuel cells (SOFCs), typified by developers such as Siemens Westinghouse and Rolls-Royce, operate in the temperature region of 850–1000 °C. For such systems, very high efficiencies can be achieved from integration with gas turbines for large-scale stationary applications. However, high temperature operation means that the components of the stack need to be predominantly ceramic and high temperature metal alloys are needed for many balance-of-plant components. For smaller scale applications, where integration with a heat engine is not appropriate, there is a trend to move to lower temperatures of operation, into the so-called intermediate temperature (IT) range of 500–750 °C. This expands the choice of materials and stack geometries that can be used, offering reduced system cost and, in principle, reducing the corrosion rate of stack and system components.

This review introduces the IT-SOFC and explains the advantages of operation in this temperature regime. The main advances made in materials chemistry that have made IT operation possible are described and some of the engineering issues and the new opportunities that reduced temperature operation affords are discussed.

This *tutorial review* examines the advances being made in materials and engineering that are allowing solid oxide fuel cells to operate at lower temperature. The challenges and advantages of operating in the so-called 'intermediate temperature' range of 500–750 °C are discussed and the opportunities for applications not traditionally associated with solid oxide fuel cells are highlighted. This article serves as an introduction for scientists and engineers interested in intermediate temperature solid oxide fuel cells and the challenges and opportunities of reduced temperature operation.

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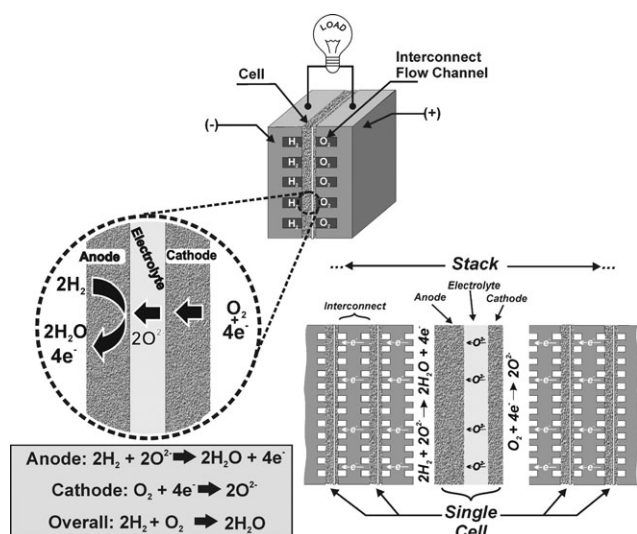
Introduction

Fuel cells are electrochemical energy conversion devices that convert chemical energy in fuel directly into electricity (and heat) without involving the process of combustion.[1] A simplistic view of a fuel cell is that it is a cross between a battery (chemical energy converted directly into electrical energy) and a heat engine (a continuously fuelled, air breathing device); this is why fuel cells are sometimes referred to as *electrochemical engines*. There is a range of different fuel cell

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Fig. 1 Summary of solid oxide fuel cell operation (with hydrogen as fuel) and assembly of cells into stacks.

technologies, each with its own materials set and suited to different applications. However, they all share the characteristics of high efficiency, no moving parts, quiet operation and low (compared to heat engines) or zero emissions at the point of use. The range of fuel cell applications, and the size of the potential markets, for such devices are enormous; areas of use include: battery replacement in small portable electronic devices, prime movers and/or auxiliary power units in vehicles, residential combined heat and power (CHP) and large-scale megawatt (MW) electrical power generation. Widespread adoption of fuel cell technology is anticipated to contribute to a reduced dependence on fossil fuels, lessen CO_2 and noxious pollutant emissions, improve security of electricity supply and enable the development of a 'hydrogen economy'.

Fig. 1 shows the generic fuel cell mode of operation for a solid oxide fuel cell (SOFC).[2] Fuel cells come in a range of architectures (planar, tubular *etc.*), but central to all is the electrolyte. This may be solid (polymer or ceramic) or liquid (aqueous or molten salt) and must have a high ionic and low electronic conductivity for efficient operation. The electrolyte in an SOFC is an oxide ion conductor; however, the electrolyte may also be a proton, carbonate or hydroxide ion conductor depending on the type of fuel cell.

On each side of the electrolyte is an electrode/electrocatalyst. Oxidant is fed to the cathode (positive electrode), which is almost always oxygen in the form of air, and fuel is supplied to the anode (negative electrode). Oxygen is reduced at the

cathode, producing oxide ions (O^{2-}) which migrate through the electrolyte and react with the fuel at the anode. If the fuel is hydrogen, water is liberated as shown in the equation in Fig. 1. The power and voltage of the fuel cell is increased by connecting individual cells in series to form a 'stack', analogous to the cells in a battery, with each cell connected to its adjacent cell using an electrically conducting interconnect which also serves to distribute reactant across the surface of the electrodes using flow channels.

There are a number of fuel cell technologies, operating over a range of temperatures from ambient to over 1000 °C and using a diverse range of materials. Fig. 2 summarises the main fuel cell varieties; note the different ion transport mechanisms in the electrolyte. Each fuel cell is named according to its electrolyte type and it is primarily the electrolyte used that determines the temperature range of operation. The 'low' temperature fuel cell technologies: alkaline fuel cells (AFCs), polymer electrolyte fuel cells (PEFCs) and phosphoric acid fuel cells (PAFCs), require relatively pure hydrogen to maintain stable performance. This is because low temperature operation necessitates the need for precious metal electrocatalysts (*i.e.* platinum) to ensure adequate electrode reaction kinetics; these catalysts are deactivated by carbon monoxide at the low operating temperatures.

If hydrocarbons (such as natural gas) are to be used as a fuel for low temperature fuel cells, a fuel processor must be used to convert the fuel into hydrogen containing very low levels of carbon monoxide. The fuel processor may be composed of a reformer reactor, shift reactor and gas clean up stage, all adding to the cost and complexity of the system and eroding the efficiency.[1]

Of the various fuel cell technologies, PEFCs (low temperature) and SOFCs (high temperature) are currently attracting most attention (and development budget). It is the SOFCs and their trend to move to lower temperature operation that is the subject of this review.

Fuel cells and temperature of operation

There is no consensus as to the optimal operating temperature of fuel cells *per se*. The preferred temperature of operation will depend to a large extent on the application. However, there is currently significant effort to raise the operating temperature of PEFCs and reduce that of SOFCs for certain applications. PEFCs lay claim to automotive applications, a power range of ~10–100 kW where stack cooling and water management are key challenges. Efforts to increase PEFC operating temperatures to as high as 200 °C using novel polymer electrolyte

Fig. 2 Summary of the different types of fuel cells, including temperature of operation and materials used.

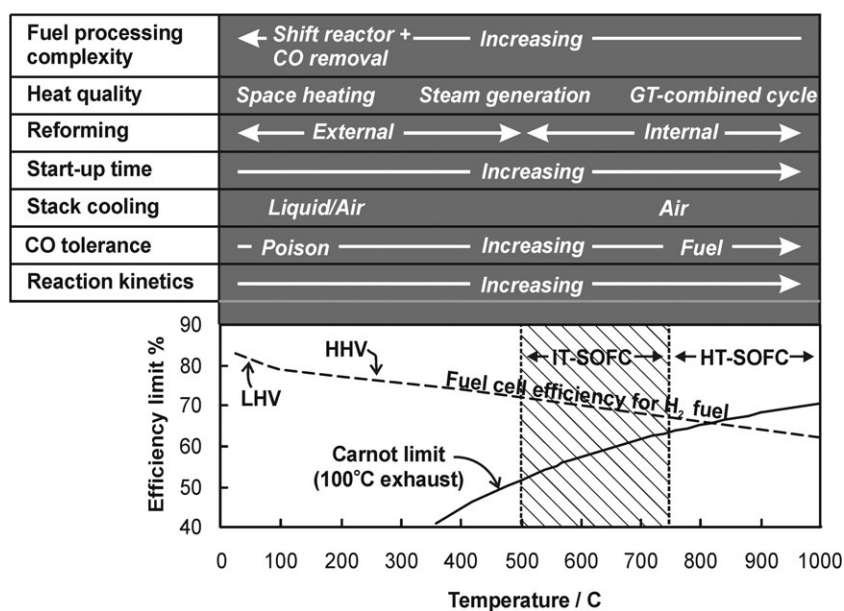| Fuel processing complexity | ◄ Shift reactor + CO removal ──── Increasing ──── |
Heat quality	Space heating Steam generation GT-combined cycle
Reforming	◄──── External ────► ◄──── Internal ────►
Start-up time	──────── Increasing ────────►
Stack cooling	Liquid/Air Air
CO tolerance	─ Poison ──── Increasing ──── Fuel ──►
Reaction kinetics	──────── Increasing ────────►

Fig. 3 Summary of the generic fuel cell issues related to temperature of operation.

materials that do not require water to be present within the electrolyte membrane will also facilitate stack cooling since heat rejection is easier from higher temperature systems, so avoiding the need for large radiators and reducing parasitic losses from cooling fans and pumps. Increased temperature also significantly reduces the poisoning effect of CO on the electrocatalyst. In contrast, the operating temperature of SOFCs is being lowered to better address small scale applications such as residential micro-CHP and auxiliary power units (APUs).

So, is there an optimum fuel cell temperature of operation for different applications? Fig. 3 summarises some of the issues related to operating temperature. There are certain trends associated with increasing operating temperature: non-precious metal electrodes may be used, since high temperature promotes the electrochemical reactions occurring at the anode and cathode; carbon monoxide (CO), which is a poison to low temperature fuel cells that use precious metal catalysts, can be used as a fuel itself; high temperature operation allows the conversion process of hydrocarbons to hydrogen to occur within the fuel cell (internal reforming) or stack, so obviating the need for external fuel processing; heat 'quality' increases—low temperature fuel cells produce heat at a temperature suitable for space heating, whereas intermediate temperature fuel cells are good for raising steam and high temperature fuel cells suitable for operating in combined cycles with a gas turbine.

The theoretical maximum efficiency limit (shown in Fig. 3 for H₂ as the fuel) is a direct function of temperature, decreasing with increasing temperature.[1] In fact, compared to the Carnot efficiency limit, the theoretical maximum efficiency of a hydrogen fuelled fuel cell at high operating temperature is less than that of an equivalent heat engine. However, in practice the irreversible losses that occur in fuel cells due to electrokinetics and ohmic resistances are lower at high temperatures, which usually more than offset the loss of

maximum efficiency determined by the thermodynamics of reaction. Also, if a high temperature fuel cell is integrated with a gas turbine in a hybrid arrangement, then overall efficiency in excess of the individual efficiencies of the fuel cell and heat engine in isolation can be achieved.

In reality, there is no 'ideal' operating temperature for fuel cells in general, the appropriate fuel cell technology to choose for a given application is a function of the required performance, lifetime, cost, fuel, size, weight, efficiency, start-up time, waste heat quality, *etc*. However, it is clear that lowering the operating temperature of SOFCs unlocks a wider range of potential applications, including some that have previously been the domain of low temperature fuel cells.

Intermediate temperature SOFCs

High temperature SOFCs (HT-SOFCs), typified by developers such as Siemens Westinghouse and Rolls-Royce operate in the temperature region of 850–1000 °C.[3] For such systems, high efficiencies can be achieved from integration with gas turbines for large-scale stationary applications. High temperature operation means that the components of the stack need to be mainly ceramic and a tubular or box section design is commonly used which results in low volumetric power density. For smaller scale applications, such as micro-CHP, APUs and small electrical generators, there is a trend to move to lower temperatures of operation, into the so-called intermediate temperature (IT) range of 500–750 °C, as defined by Steele.[4]

By lowering the temperature of operation, a wider range of materials can be used that allow cheaper fabrication, particularly in relation to interconnects and balance-of-plant (BoP) components. Lower temperature operation also affords more rapid start-up and shut-down, reduced corrosion rate of metallic components, improved durability (sintering and component inter-diffusion is accelerated at higher temperatures[5]), more robust construction through the use of compressive seals
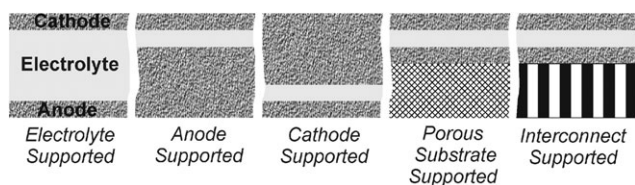
Fig. 4 Illustration of the different types of cell support architectures for SOFCs.

and metallic interconnects as well as the advantage of greatly simplified system requirements.

There are two main routes by which SOFCs can be operated at lower temperatures, while still attaining comparable performance to the higher temperature technology. The dimensional thickness of the electrolyte can be reduced, so reducing the area specific resistance of the fuel cell, and/or materials development can bring about the same result by improving the ionic conductivity of the electrolyte at lower temperatures and bring about improvements in the performance of electrodes.[6]

Since metallic interconnects and non-ceramic seals can be used at lower temperatures, IT-SOFCs are more conducive to planar stack architectures than HT-SOFCs. As can be seen in Fig. 4, a number of cell configurations exist, each classified according to the layer that mechanically supports the cell. These include individual support by each of the cell components as well as distinct structural components such as porous substrates or porous metal supports.[7] As a general indicator of the scale of these assemblies, the supporting component will typically have a thickness > 150 μm and the supported layers a thickness of 10s of microns.

An alternative approach is to use an SOFC with only one gas chamber. This design offers the possibility of reducing stack components and eliminating the need for sealing. In this configuration, referred to as a single-chamber SOFC (SC-SOFC), both the anode and cathode are exposed to the

same mixture of fuel and air. There is therefore no need for gas sealing between the anode and cathode compartments. This design has the advantage of improved mechanical and thermal properties due to its simplified structure and reduced carbon deposition due to the level of oxygen in the mixture. Effective operation relies on the anode and cathode being selective to the hydrogen oxidation reaction and oxygen reduction reaction, respectively, under which conditions the maximum open circuit voltage is achieved. In practice, neither electrode is inert to the opposing reaction, which leads to a reduction in cell potential and therefore efficiency. Recent advances in SC-SOFCs have been reviewed by Yano et al.[8]

Materials selection and processing for IT-SOFCs

Electrolyte. The properties of the electrolyte have a major impact on fuel cell performance through its contribution to the ohmic internal resistance. An ideal SOFC electrolyte should have the following characteristics: high oxide ion conductivity (typically $> 1 \times 10^{-3}$ S cm^{-1}); low electronic conductivity; good thermal and chemical stability in relation to the reactant environment and the contacting electrode materials; closely matched thermal expansion coefficient (TEC) between the electrodes and contacting components; fully dense structure to maximise conductivity and minimise reactant cross-over; simple forming properties so that very thin layers (few 10s of μm) can be fabricated; be low cost and environmentally benign. Goodenough has provided a review of oxide ion electrolytes, the materials used and conduction mechanisms.[9]

Fig. 5 shows how the specific ionic conductivity of different solid oxide electrolytes varies with temperature (conductivity data from Wincewicz and Cooper and references therein[10]). Note that these are representative values of conductivity for each of the electrolytes, actual values will depend on the microstructure, exact level of doping, fabrication and sintering processes. The oxide ion transport mechanism in ceramic
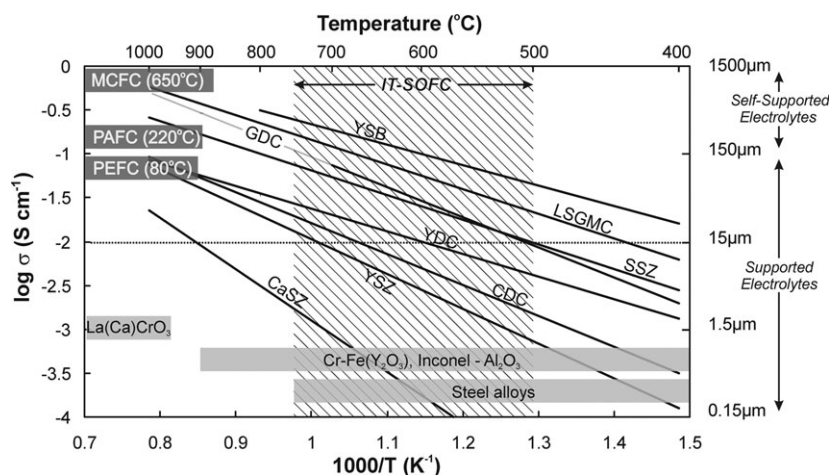
Fig. 5 Specific ionic conductivity as a function of reciprocal temperature including conductivity of selected solid oxide fuel cell electrolytes and operational range of different interconnect materials. Conductivity data from Wincewicz and Cooper and references therein.[10] Note that the exact conductivity will depend on the electrolyte microstructure, doping level and fabrication process. YSB [$(Bi_2O_3)_{0.75}(Y_2O_3)_{0.25}$]; LSGMC ($La_xSr_{1-x}Ga_yMg_{1-y-z}Co_zO_3$; $x \approx 0.8$, $y \approx 0.8$, $z \approx 0.085$); CGO ($Ce_{0.9}Gd_{0.1}O_{1.95}$); SSZ [$(ZrO_2)_{0.8}(Sc_2O_3)_{0.2}$]; YDC ($Ce_{0.8}Y_{0.2}O_{1.96}$); CDC ($Ce_{0.9}Ca_{0.1}O_{1.8}$); YSZ [$(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$]; CaSZ ($Zr_{0.85}Ca_{0.15}O_{1.85}$). The conductivity range of electrolytes used in MCFC, PAFC and PEFC are included for comparison.

electrolytes is thermally activated and the conductivity is a strong function of temperature. Ionic conductivity exhibits an Arrhenius-like dependence on temperature, which is the reason for the graph being plotted as the logarithm of conductivity vs. reciprocal of temperature.

Steele used the following approach to determine the trade-off between electrolyte conductivity and thickness in order to give a suitable power density (with respect to cell area).[4,11] It is assumed that adequate performance is obtained from an SOFC provided the electrolyte's area specific resistance (ASR) is less than 0.15 Ω cm^2. If the thinnest dense impermeable electrolyte layer that can be reliably produced using low cost processing routes is 15 μm, then the specific ionic conductivity required to achieve the target ASR is (σ = thickness/ASR)10^{-2} S cm^{-1} (log σ = −2). So, gadolinium doped ceria (CGO) for example, would attain the required ASR at a temperature of above ∼500 °C, whereas yttria stabilised zirconia (YSZ) would require over 700 °C. If the cell is to be electrolyte supported, calling for a thickness of at least 150 μm, then a YSZ electrolyte would require an operating temperature >950 °C.

The thickness of the electrolyte that can be tolerated on this basis dictates the supporting configuration of the cell. Even for electrolytes with superior low temperature conductivity, electrolyte supported geometries lead to high ohmic resistance in the IT regime of operation and therefore configurations other than electrolyte supported tend to be the route taken for IT-SOFCs.

Zirconia (ZrO$_2$) based materials have been studied extensively as electrolytes for SOFCs.[12] By doping with lower oxidation state (aliovalent) cations such as Y^{3+}, zirconia is stabilised in its cubic form. The addition of aliovalent cations also has the effect of producing oxygen vacancies, so increasing the oxide ion conductivity. Yttria stabilised zirconia (YSZ) is the most widely used electrolyte for SOFCs and boasts good chemical and physical stability as well as a wide operating range of temperature and pO$_2$, without suffering from electronic conductivity. Addition of ∼8 mol% of yttria i.e. (ZrO$_2$)$_{0.92}$(Y$_2$O$_3$)$_{0.08}$ (8YSZ—the number prefix representing the dopant mol percentage composition) leads to the highest oxide ion conductivity, although higher levels (i.e. 10 YSZ) produce a better stabilised cubic phase. A range of dopant cations have been investigated including Y^{3+}, Eu^{3+}, Gd^{3+}, Yb^{3+}, Er^{3+}, Dy^{3+}, Sc^{3+} Ca^{2+} and Mg^{2+}. Scandia stabilised zirconia (SSZ) gives the highest conductivity, as can be seen in Fig. 5. Although Sc$_2$O$_3$ is more expensive than Y$_2$O$_3$. The quantity used in a thin supported electrolyte is small and hence there is currently much interest in this electrolyte.

Although YSZ has a lower ionic conductivity than many of the materials being developed for IT operation, suitable conductance can be achieved by fabricating the electrolyte film with a thickness of 10 μm or less. The challenge is then to produce a homogenous, leak free layer on a porous substrate by a process that is amenable to volume manufacture.

Doped ceria is considered to be a promising electrolyte for IT operation.[6,13] Ceria (CeO$_2$) has a fluorite structure and oxygen vacancies are introduced by substituting Ce^{4+} with divalent alkaline earth or trivalent rare earth ions.[14] The oxide ion conductivity is a function of temperature, dopant concentration and type, the maximum ionic conductivity occurring at ∼10–20 mol% for most dopants. It is generally found, and is the case for ceria and zirconia based electrolytes, that the highest oxygen ion conductivity is observed when the aliovalent doping cation is closest to the ionic radius of the host cation. In the case of Zr^{4+} it is Sc^{3+} and in the case of Ce^{4+} it is Sm^{3+} or Gd^{3+}. Gadolinium doped ceria Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (10CGO), is the most extensively studied ceria based electrolyte.[15]

Ceria based electrolytes suffer from the partial reduction of Ce^{4+} to Ce^{3+} when exposed to a combination of low (1 × 10^{-19} atm) pO$_2$ and high (>600 °C) temperature, the reduction process taking place at the anode side of the fuel cell and affecting a significant volume fraction of the electrolyte. The consequence of this chemical reaction is that (i) there is a volume expansion of the lattice which can result in mechanical failure of the electrolyte; and (ii) electronic (n-type) conductivity is introduced that reduces performance due to electronic leakage currents between the anode and cathode. The mechanism of reduction and mixed ionic electronic conduction of ceria based electrolytes has been studied and reviewed in depth.[14,16]

Fig. 6 shows how the performance of a 10CGO based fuel cell is affected by electronic leakage current as a function of temperature. Using a model developed by Godickemeier et al.[17] and applied by Steele,[13] the presence of partial short circuiting electronic currents due to the mixed conducting properties of CGO can be estimated. Representative ASRs for both the anode and cathode are taken to be 0.5 Ω cm^2 and independent of temperature, and an electrolyte thickness of 15 μm is chosen as typical for an electrode or metal supported cell; the fuel composition is 50% H$_2$, 3% H$_2$O with N$_2$ balance. Increasing temperature promotes the reduction of Ce^{4+} and leads to higher electronic leakage current and lower open circuit voltage (OCV). Since cell voltage is a direct measure of fuel cell efficiency,[1] it can be concluded that leakage current can become a significant source of efficiency loss. However, when the cell is put under electrical load, the electronic current is reduced (i.e. the oxide ion transport number increases) as can be seen in Fig. 6(b), this is because Ce^{4+} reduction is suppressed by anode polarisation. Under practical operating cell voltages of ∼0.65 V, the loss in efficiency is negligible for operation at less than 600 °C, but is significant at (or above) 650 °C. It is for this reason that the operation of SOFCs with a CGO electrolyte is considered most effective in the 500–600 °C temperature range.

Work by Ishihara et al.[18] has shown that Sr and Mg-doped LaGaO$_3$ (LSMG) exhibits high ionic conductivity (comparable to that of CGO) and low electronic conductivity even at low pO$_2$ levels. This class of material potentially offers adequate performance as low as 400 °C.[19] However, LSGM is substantially more expensive than ceria based electrolytes, and durability problems have been reported with electrode materials.

The electrolyte materials discussed so far are all oxide ion conductors, however, proton conducting ceramics also exist which are being investigated for IT-SOFC applications. Since the size of a proton is much smaller than that of an oxide ion, higher conduction at lower temperature is envisaged. Iwahara et al. observed appreciable proton conductivity at high temperatures (∼1 × 10^{-2} S cm^{-1} at 1000 °C) in BaCeO$_3$-based oxides which is improved by doping with rare earth cations on
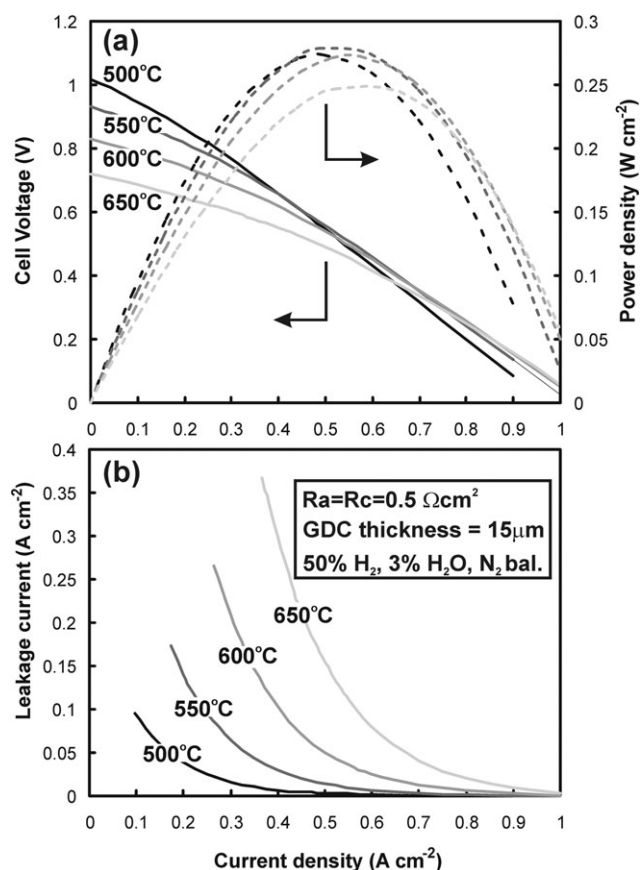
Fig. 6 (a) Model prediction of the polarisation and power profile for a CGO based fuel cell at temperatures from 500–650 °C; (b) electronic leakage current with electronic current density and temperature. R_a and R_c are the area specific resistances of the anode and cathode, respectively.

the Ce site.[20] Other barium based perovskite-type structures such as $BaZr_{0.9}Y_{0.1}O_{2.95}$ for example have shown protonic conductivity approaching that of the best oxide ion conductors at the low temperature end of IT-SOFC operation; however, the chemical stability of these materials is not suitable for long term fuel cell operation, particularly with regard to exposure to CO_2 and therefore not considered practical at present. Proton conducting systems also have the disadvantage that CO cannot be oxidised by loss of a proton. Ishihara has reviewed proton conducting ceramics for IT-SOFCs.[19]

Relatively few structure types have been identified as potential oxide ion conducting electrolytes, as is demonstrated by the preceding discussion of the fluorite and perovskite based systems. More recently, fast ion conductivity has been reported in two novel systems: apatite based $Ln_{10}(XO_4)_6O_{2\pm y}$ systems[21] and the $La_2Mo_2O_9$ based materials.[22] In the apatite type materials significant ionic conductivity has been reported in systems where the lanthanide is either La, Pr or Nd and X = Ge or Si. A number of substitutions on both cation sites have been reported with significant effects on the oxide ion conductivity, with three orders of magnitude difference reported for substitution with Bi and Ga on the La and Si sites, respectively.[21] In one study a conductivity as high as 0.05 S

cm^{-1} at 800 °C for the $La_9Ba(SiO_4)_6O_{2.5}$ composition was reported.[23] It is also of interest to note that these materials have a novel interstitial conduction pathway, as revealed by atomistic simulation, and a degree of anisotropy. Each of these features offers opportunities to develop new devices with enhanced performance.

An alternative material, $La_2Mo_2O_9$, was reported as having oxide ion conductivity as competitive as YSZ, CGO and LSGM. There are some concerns over the stability of the material, but the synthesis of this and related compositions requires relatively low temperatures and hence in the longer term may be seen as an advantage in producing devices with reduced processing temperatures.

Of course, these new materials are not likely to replace the conventional electrolytes in the near future, but as has been seen with the ceria based systems, with substantial dedication and control of the chemistry and morphology of the ceramic, successful devices may be prepared in the medium to long term. As is common with all solid oxide fuel cell materials, developers have to address concerns over durability, compatibility and synthesis conditions before technologically relevant cells can be produced. Initial studies have however demonstrated successful operation of a fuel cell based on a $La_{9.6}Si_{5.7}Mg_{0.3}O_{26.1}$ electrolyte and operating at between 600 and 800 °C.[24]

Anodes. The anode must perform electro-oxidation of fuel by catalysing the reaction and facilitating fuel access and product removal, it must also have sufficient electronic conductivity (typically 100 S cm^{-1}, although this depends on the cell design) to efficiently transport electrons to the current collector.[25] Most anodes are porous cermets (a composite of ceramic and metal), the microstructure of which is optimised to have a fully percolated metallic component which allows conduction of electrons through the structure, while optimising the amount of active three phase boundary (TPB). The TPB is the interface at which the electronic and ionic conducting phases co-exist with the open pore containing fuel and where reaction takes place in most cermets.[26] Optimisation of the microstructure to maximise the effective TPB length is a major research effort in such cermets. However, the use of mixed ionic and electronic conducting (MIEC) ceramic materials is also being investigated so that the TPB can be extended from a 1-dimensional interface to a 2-dimensional area.

Using a cermet often improves matching in TECs between the electrolyte and the current collector and such cermets are used as the structural support in anode supported IT-SOFCs. The most commonly used cermet material is Ni-YSZ. Atkinson et al. have reviewed the recent advances in anode technology for SOFCs which includes development of single phase oxides with MIEC properties such as ceria and transition metal perovskites.[27]

Substantial work has been done to replace zirconia with ceria, and Ni with Cu. Nickel is an excellent electrocatalyst for the oxidation of hydrogen, unfortunately it also promotes the formation of carbon from hydrocarbon fuel.[2] Copper is being explored as a replacement since it does not significantly catalyse the carbon formation reaction, the copper simply

acting as an electron conducting matrix with ceria performing the electro-oxidation catalyst role.[28,29]

Lowering the temperature of operation means that it is easier to use materials together that have a mismatch in TEC without compromising the mechanical integrity of the electrode during temperature transients. It also means that Cu, which is highly mobile at HT-SOFC temperatures, can be used without suffering degradation caused by sintering.

There is growing interest in the use of ceramic anodes as alternatives to cermets.[27] Using an anode that is not Ni-based avoids the problem of coke formation when operating on hydrocarbon fuels, intolerance to sulfur impurities and large volume changes associated with redox cycling. Both oxygen stoichiometric and substoichiometric perovskites have been investigated.[30] Recently lanthanum-substituted strontium titanate (La-SrTiO$_3$) with nominal oxygen overstoichiometry has been studied and shown to have very high electronic conductivity and methane oxidation catalytic activity.[31]

Cathodes. Cathodes in SOFCs carry out several roles within the cell: reduction of molecular oxygen, transport of charged species to the electrolyte and distribution of the electrical current associated with the oxygen reduction reaction. At high operating temperatures the kinetics associated with cathode reactions are sufficiently rapid that cell losses are relatively minor. Decreasing operating temperature, however, increases the polarisation losses of the cell as the kinetics associated with the oxygen reduction reaction and charge transport are much slower at these low temperatures. Development of alternative cathode compositions that function effectively at lower temperatures is therefore an important step in the realisation of technologically viable IT-SOFCs.[32]

In high temperature SOFCs operating at temperatures in excess of 800 °C, cathodes operate in a traditional three phase boundary mechanism (gas, electrode and electrolyte). These cells therefore feature a largely electronic conductor as the cathode (or electronic component in a composite with the electrolyte material), typically a perovskite (ABO$_3$) structured material. A typical choice is (La,Sr)MnO$_{3\pm d}$ (LSM). This material works well with the YSZ based electrolytes, but care is required in the production of the cells as reaction between the materials to form La$_2$Zr$_2$O$_7$ insulating phases at high temperatures can result in cell degradation. Further enhancements in cathode performance can be achieved through the use of composite materials, and YSZ/LSM composites have been extensively investigated.

On reducing the temperature of cell operation to the intermediate range there are significant challenges presented in materials selection. Key processes in the cathode such as the reduction of oxygen and its incorporation and transport to the electrolyte mean that LSM is no longer effective. Materials with increased oxygen transport properties (oxygen reduction, surface exchange and diffusion) are required leading to the use of MIECs, and (La,Sr)CoO$_3$ has been identified as possessing perhaps the best transport properties in terms of both ionic and electronic conductivity. However, this material has a high apparent TEC and is difficult to use with electrolytes such as CGO. Substituting iron for cobalt to give La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-d}$ (LSCF) results in a compound with

fast ion transport, good oxygen reduction kinetics, lower TEC and acceptable electronic conduction. However, to produce a suitably active cathode it has again been found advantageous to develop composites with the electrolyte material. For these materials the phase fraction of electrolyte to cathode is critical as there is clearly a percolation threshold for both components.

Performance of intermediate temperature cathodes is still an area of intense development activity and there are a number of new materials that have been proposed. These include perovskite-type materials [(Sm,Sr)CoO$_3$, (Ba,Sr)(Co,Fe)O$_{3-d}$], layered perovskite-related structures (La$_{n+1}$Ni$_n$O$_{3n+1}$) and double perovskites (GdBaCoO$_{5+d}$), all of which have shown encouraging performance at lower temperatures.[33]

Interconnects. The interconnect (also called bipolar plate) in planar fuel cells performs the vital role of separating the fuel from air, collecting the current from the electrodes, conducting the electrical current between each layer of the stack, distributing reactant gas evenly across the face of each electrode and providing mechanical support to the cell and stack structure.[34] The component should have: high electrical conductivity; low contact resistance with the electrodes; good thermal conductivity (efficient removal of heat from the electrodes is vital in maintaining an even temperature distribution); adequate chemical and thermal stability; very low permeability to reactant gases; good mechanical strength; corrosion resistance; thin and lightweight construction; easy manufacturability and low cost. These requirements are a challenge for any class of material and are made more difficult due to the temperature of operation. Fig. 5 shows the temperature range of operation for the three main classes of interconnect material—ceramics, high performance alloys and ferritic stainless steels.

For HT-SOFCs, the interconnect must be either a ceramic or a special high-Cr or -Ni alloy; both options can make the interconnect the most expensive component of the stack on a materials value basis. The most popular ceramic option is based on the perovskite structured LaCrO$_3$ which is typically doped with Sr or Ca in order to reduce its sintering temperature and increase conductivity.

Metallic interconnects are more robust and can withstand rapid temperature change associated with fast start-up, they also make it easier to incorporate internal structure into the stack such as internal manifolding, flow-field geometries or sealing wells. Examples include the chromium based alloy Ducrolloy from Plansee (Cr-5Fe-1Y$_2$O$_3$) and the nickel based alloy Inconel 600 containing between 14–16 wt%Cr and 6–9 wt%Fe. In large part, it is the ability of metallic interconnects to form conducting chromia (Cr$_2$O$_3$) containing scales at the surface upon oxidation which protects the metal from further corrosion. However, Cr containing alloys have the disadvantage that volatile chromium compounds (CrO$_3$ or CrO$_2$(OH)$_2$) can form which accelerate degradation of the interconnect, and more importantly degrade cell performance by forming phases at the surface of electrodes, and particularly the cathode, which blocks the TPB reaction sites. Coating interconnects significantly retards corrosion and vaporisation of

chromium species. Coating materials include La(Ni,Fe)O$_3$, (La,Sr/Ca)CrO$_3$, (La,Sr/Ca)MnO$_3$, (Y,Ca)MnO$_3$ and CeO$_2$.[35]

IT-SOFC operation allows relatively low cost ferritic (low TEC) stainless steel alloys to be used. These steels also owe their corrosion resistance to the formation of chromia at the surface; however, at these temperatures Cr vaporisation is not as extreme as for HT-SOFCs, although still a notable source of performance deactivation. Ferritic steel has the advantage of high strength, machinability, closely matched TEC with the electrolyte material (i.e. both ferritic stainless steel and CGO have a TEC of 12.5 × 10^{-6} K) and low cost. Ferritic stainless steel has also been used as the mechanical support for IT-SOFCs as described later. The range of metallic alloys that have been investigated for SOFC interconnects is substantial and has been reviewed previously.[35]

Seals. Seals are necessary to stop fuel and air mixing within a fuel cell as well as avoiding leakage from the edges of cells; in certain circumstances they also act to help bond the stack together. Seals come in two main varieties: (i) bonded seals, which do not require a load during operation and (ii) compressive seals, which require a load to be applied during operation. In either case, the seal should be an electrical insulator that is chemically compatible with the gaseous environment and materials in which they are in contact, and have a thermal expansion coefficient that is compatible with the adjacent components. The last requirement is particularly important for achieving fast start-up and shut-down rates since thermally induced stresses are greatest in seals during rapid temperature transients.

Bonded seals tend to be glass (e.g. silicates, borosilicates, boroaluminosilicates etc.) or glass–ceramic materials. These materials are inherently brittle and prone to cracking if the thermal expansion coefficient is not carefully matched to the adjacent components. In order to operate as an effective seal, the fuel cell must operate above the glass transition temperature T_g. For most glasses, T_g is above ∼625 °C, so precluding the use of bonded seals below this temperature.

Use of compliant compressive seals means that there is much more scope for allowing differences in TEC, which provides more degrees of freedom in material selection/stack design. One approach is to use metal gaskets such as gold, however, establishing the correct balance between strength and ductility is difficult and the materials are expensive. An alternative is to use mica-based sealants. These inorganic compounds, which include materials such as muscovite [KAl$_2$(AlSi$_3$O$_{10}$)(F,OH)$_2$], phlogopite [KMg$_3$(AlSi$_3$O$_{10}$)(OH)$_2$] or vermiculite (MgFe,Al)$_3$(Al,Si$_4$O$_{10}$)(OH)$_2$ such as the commercially available Thermiculite 815™ which incorporates a stainless steel inlay. Although mica-based seals can operate in the HT-SOFC temperature regime, their compliant nature requires constant force to be applied throughout the course of operation. Active compression, using tie bolts for example, is much less of an issue for IT-SOFCs where metallic structural components can be used, however, above 650 °C bolts may still creep.

Arguably the most difficult engineering challenge in developing planar SOFC stacks involves ensuring gas tight operation. The IT-SOFC regime of operation reduces the stresses within the stack and opens the way to a broader range of materials. A comprehensive review of sealants for SOFCs has been compiled by Fergus.[36]

Balance-of-plant. Balance-of-plant (BoP) is the term used to describe the components that support the operation of the fuel cell stack. This includes the piping, heat exchangers, burners, blowers etc. Since the off-gas leaving a fuel cell is at the same temperature at the stack itself, the BoP components that come into contact with the gas stream need to be able to operate at the same temperature. By avoiding high temperature off-gas from the fuel cell, expensive steel alloys such as Inconel can be replaced with conventional austenitic stainless steel, with a significant saving in cost.

Fueling IT-SOFCs.

$$C_xH_y + xH_2O \leftrightarrow xCO + (x + y/2)H_2 \quad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (2)$$
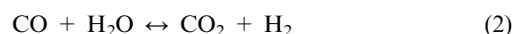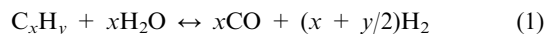
Hydrogen is the best fuel for all fuel cell types in terms of electrochemical performance and material durability, this also holds for SOFCs. However, given the lack of a supply infrastructure and difficulties in storing hydrogen, the ability of SOFCs to operate at high efficiency on hydrocarbon fuels is seen as a major advantage over low temperature technologies, consequently, hydrocarbons are considered as the preferred fuel for SOFCs. Natural gas (primarily methane) is seen as an ideal fuel due to its abundance, existing distribution infrastructure (particularly in Western Europe) and low cost. Lighter (shorter chain) hydrocarbons are also easier to reform than heavier ones.

Issues relating to fuelling of fuel cells are highly dependent on the temperature of operation and electrode materials used. Lowering the temperature from the HT to IT regime has an impact on the efficiency of internal reforming, the propensity of carbon formation to occur and the extent to which impurities such as sulfur interact with the anode.

The steam reforming (oxygenolysis) of hydrocarbons is a well established process used on an industrial scale for the production of hydrogen. The reaction is shown in eqn (1) and results in the formation of a mixture of CO and H$_2$ (syngas). Further reaction via the water gas shift (WGS) reaction [eqn (2)] converts CO and steam into more H$_2$. During internal reforming, these two reactions occur simultaneously, the equilibrium composition of the gas dictated by temperature and pressure.

The CO and H$_2$ produced are subsequently electrochemically oxidised by the O^{2-} ions at the anode [eqn (3) and (4)].

$$CO + O^{2-} \leftrightarrow CO_2 + 2e^- \quad (3)$$

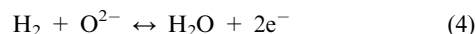$$H_2 + O^{2-} \leftrightarrow H_2O + 2e^- \quad (4)$$

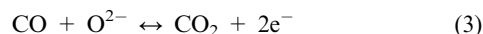Fig. 7 shows the thermodynamically predicted composition of a system supplied with methane over a range of temperatures for three different steam-to-carbon (S/C) ratios. Although the thermodynamically predicted composition may not be realised for lower temperatures due to kinetic limitations, at higher temperatures, relevant to IT-SOFC operation, kinetics are fast and the predictions are a reasonable indicator of the actual
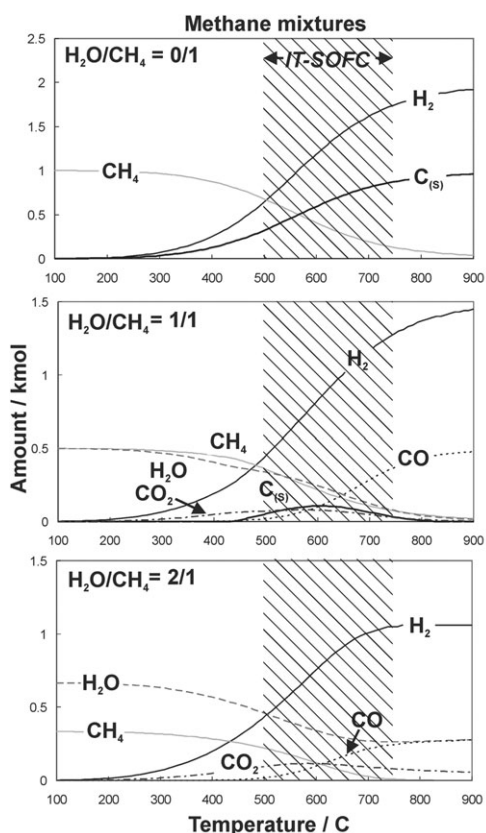
Fig. 7 Thermodynamic predictions of the equilibrium composition for methane fed at different temperatures and steam-to-carbon ratios. The combined $CH_4 + H_2O$ input amount is 1 kmol in each case.

fuel composition. The amount of solid phase carbon expected to form is also shown.

Notice that in the HT region, the various reactions go to completion and the fuel composition is relatively stable with temperature. In contrast, in the IT region of operation, the fuel composition is highly sensitive to temperature, a relatively small change in operating temperature having a significant effect on fuel composition.

It can be seen from the thermodynamically predicted fuel composition with temperature diagram that temperature and steam content have a strong effect on the formation of carbon.

Operating dry (i.e. with no initially added steam), carbon formation becomes progressively worse with increasing temperature, whereas an S/C of 2 or more results in complete suppression of carbon. Between these bounds (S/C = 1), carbon formation is predicted to be greatest in the IT range. In practice, an S/C ratio of between 2 and 3 is used to safely avoid carbon deposition; however, excessive addition of steam can lower the system efficiency due to fuel dilution and the energy required to raise the steam. The lowest temperature at which an SOFC can effectively achieve internal reforming is contentious. The reforming reaction will occur at an appreciable rate over an appropriate catalyst given an ample supply of steam at temperatures above ~500 °C. Direct coupling of the reforming reaction to the anode of the IT-SOFC then allows oxidation of the hydrogen rich reformate at the anode, shifting the equilibrium of the reforming reaction such that a high

conversion of hydrocarbon fuels can be achieved, even at operating temperatures down to 500 °C. Furthermore, since the reforming reaction is strongly endothermic ($\Delta H = +206$ kJ mol^{-1}) cooling of the cell will occur, lowering the requirement for additional air cooling, reducing the parasitic air blower load, and increasing net system efficiency. A small external pre-reformer may also be needed to convert higher hydrocarbons to methane before fuel enters the stack.

SOFC performance can be degraded by interaction of various contaminants in the fuel. Sulfur is a particular 'poison' of nickel-containing anodes even at very low (ppm) concentrations.[37] Desulfurisers are therefore commonly used to remove sulfur, though this adds to the complexity, cost and maintenance burden of the system. The interaction of sulfur (typically in the form of H_2S) with the anode is complex. Increasing temperature tends to lessen the degrading effect of sulfur on performance. However, steam and hydrogen content, oxide ion flux to the anode surface and the metallic and electrolyte material composition all have an effect.

Applications of IT-SOFCs

Lowering the temperature of operation opens up a new realm of applications for SOFCs. While HT-SOFCs dominate development for applications in the 100s of kW to MW power range, using combined cycle technology that is most efficient with a fuel cell of >850 °C, the IT-SOFC particularly suits a power range of ~1 kW to a few 10s of kW, with the majority of applications being in the sub-10 kW range. Singhal has reviewed the range of potential applications for SOFCs and describes the concept of 'mass customization' being adopted by the US Department of Energy's Solid State Energy Conversion Alliance (SECA).[38] This approach aims to achieve significant cost reductions by concentrating on the production of sub-10 kW SOFC modules that can be mass produced and then combined to suit the required size and application.

There is significant military interest in the technology for various applications including submarine power, unmanned aerial and underwater vehicles, base camp 'tent city' power and soldiers' personal power supplies etc. The ability of the technology to operate directly on logistic fuels (e.g. JP-8) is particularly attractive. A typical soldier carries 12.6 kg of batteries for communication, navigation and illumination, the life of the batteries dictating the length of the mission in many cases. IT-SOFCs therefore offer the potential for extended mission length.

Faster start-up and shut-down time, and more rugged construction due to compliant seals and metallic interconnects, make IT-SOFCs a viable technology for mobile applications. IT-SOFCs have been demonstrated for use as APUs and traction power in vehicles,[39] sometimes hybridised with battery technology.[40]

IT-SOFCs are also being considered for applications such as remote telecommunications, power for isolated communities in developing countries, regenerative fuel cells (fuel cells that can also function as electrolysers to produce hydrogen), genset replacements and truck APUs.

However, it is the small scale CHP market where the IT-SOFC is seen to be particularly well suited. Operating on

Table 1 Summary of IT-SOFC developers and technology used

Developer	Design	Temp./°C	Electrolyte	Anode	Cathode	Interconnect
Ceres power	Metal supported planar	500–650	CGO	Ni-CGO	LSCF-CGO	Ferritic steel
CFCL	Anode supported planar	750	YSZ	Ni-YSZ	LSM	Coated ferritic steel
Delphi	Anode supported planar	750	YSZ	Ni-YSZ	LSCF	Coated ferritic steel
Kyocera	Anode supported flat tubular	750	YSZ	Ni-YSZ	LSCF[a]	Metallic[a]
Mitsubishi materials	Electrolyte supported planar	600–800	LSGMC	Ni-SDC	SSC	Ferritic steel[a]
Topsoe fuel cells	Anode supported planar	750–850	YSZ	Ni-YSZ	Ni-LSM	Coated ferritic steel
Versa power	Anode supported planar	750	YSZ	Ni-YSZ	LSM-YSZ	Uncoated ferritic steel

[a] These entries are assumed since details are undisclosed. YSZ—yttria stabilised zirconia; LSM—strontium doped lanthanum manganite; LSCF—strontium cobalt doped lanthanum ferrite; LSGMC—lanthanum gallate; SSC—samaria strontium cobalt oxide; SDC—samaria doped ceria.

natural gas, and with a heat-to-power ratio around unity, IT-SOFCs are being developed for residential scale CHP, and are seen as having the potential for significant market penetration.[41,42] The micro-generation market is being created from the paradigm shift in the power generation industry, which is putting increasing emphasis on distributed generation and combined heat and power, the liberalisation of the energy market being a key driver in this transformation.

The performance and cost requirements for IT-SOFCs will largely depend on the specific application. A micro-CHP unit will require in excess of 40 000 h of operation at a near constant load with few start/stop cycles, whereas a prime mover for a vehicle will require 5000 h of operation but be subjected to dynamic load variation and large numbers of start/stop cycles. As a general indication of targets for IT-SOFC technology, the following are reasonable values (but not universal across all applications): stack cost $<\$400$–$800$ kW_e^{-1}; net system electrical efficiency 35–50% [lower heating value (LHV)]; stack energy density >0.5 kWe^{-1}; stack power density >0.25–0.5 W cm^{-2}; stack fuel utilisation $>80\%$; stack degradation rate $<0.5\%$ per 1000 h.

The future of fuel cells and the emergence of a 'hydrogen economy' are often viewed as intimately associated. Significant advancements in hydrogen storage technologies and huge investment in hydrogen distribution infrastructure is necessary in order to realise a hydrogen economy. In order for fuel cells not to be bound by the uncertain future of 'hydrogen', fuel cells need to be able to operate effectively on alternative fuels such as natural gas, alcohols, biofuels, LPG, military logistic fuels *etc*. The IT-SOFC offers an attractive fuel cell option that is much more fuel flexible than low temperature fuel cells, is suitable for a wide range of applications, and which can also be used in any future hydrogen economy should one emerge.

Technological examples of IT-SOFCs

There are a number of commercial developers of IT-SOFCs worldwide and Table 1 summarises some of these. A popular approach is to adopt an anode supported design with thin YSZ electrolyte and ferritic stainless steel interconnects for operation at the top end of the IT-SOFC temperature range (or slightly above). Versa Power Systems (Canada) have adopted this approach for example. Their technology operates at the top end of the IT-SOFC temperature range, above 700 °C. Illustrative stack performance values of >300 m W cm^{-2} (0.76 V, 725 °C) on 35% internally reformed natural gas put

this technology at the threshold of the US DoE 2012 goal for SOFC commercial power generation. Versa have recently completed SECA (Solid State Energy Conversion Alliance) performance and endurance tests on a 3–10 kW$_e$ system for operation over 3700 h. Factory cost estimates matched the US DoE's targets, showing such systems could be manufactured on a cost basis which competes with incumbent power generation technologies.

At the other end of the IT-SOFC temperature range, Ceres Power (UK) use a perforated (porous) ferritic stainless steel foil support onto which the anode, electrolyte and cathode are deposited. The high ionic conductivity of CGO and the thin electrolyte construction (10–30 μm) allows operation at temperatures of 500–600 °C. The combination of low temperature operation, compliant compression seals, ferritic steel supported design with matched TEC to the thin film anode, cathode and electrolyte make this design very robust. Ceres Power have recently demonstrated a 1 kW$_e$ system for residential micro-CHP running on natural gas which is compact enough to be wall-mounted.

Conclusions

Advances in the chemistry and processing of materials are allowing the operating temperature of SOFCs to be lowered into the so-called intermediate temperature region of 500–750 °C. Maintaining the ability to operate on hydrocarbon fuels, either directly or with a minimum of fuel processing, and producing high-quality heat, the IT-SOFC opens up a new range of applications and opportunities for solid oxide fuel cells. IT-SOFCs have the potential to be the fuel cell technology with the simplest overall system and are a contender to be the first fuel cell technology to reach mass market.

As with all fuel cells, cost must be reduced to compete in the market with incumbent technology. Use of less, and lower cost, material is necessary; moving to lower temperature operation represents a significant step in this direction. Technical challenges still to be addressed are largely focussed on demonstrating commercially meaningful levels of cell, stack and systems durability, under realistic operating conditions for a range of applications. This is being supported by fundamental studies to improve our understanding of processes such as electrode sintering, anode–fuel interaction, electrocatalyst poisoning, and the mechanical properties of electrolytes and support structures.

Acknowledgements

References

1. J. C. Larminie and A. Dicks, *Fuel Cell Systems Explained*, John Wiley and Sons Ltd, New York, 2nd edn, 2003.
2. R. M. Ormerod, *Chem. Soc. Rev.*, 2003, **32**, 17.
3. S. C. Singhal and K. Kendall, *High-Temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications*, Elsevier Science, Oxford, UK, 2003.
4. B. C. H. Steele, *J. Mater. Sci.*, 2001, **36**, 1053.
5. S. P. Jiang and S. H. Chan, *J. Mater. Sci.*, 2004, **39**, 4405.
6. B. C. H. Steele, *Solid State Ionics*, 2000, **134**, 3.
7. M. Q. Minh, *Solid State Ionics*, 2004, **174**, 271.
8. M. Yano, A. Tomita, M. Sano and T. Hibino, *Solid State Ionics*, 2007, **177**, 3351.
9. J. B. Goodenough, *Annu. Rev. Mater. Res.*, 2003, **33**, 91.
10. K. C. Wincewicz and J. S. Cooper, *J. Power Sources*, 2005, **140**, 280.
11. B. C. H. Steele, *Solid State Ionics*, 1995, **75**, 157.
12. T. Kawada and J. Mizusaki, in *Handbook of Fuel Cells—Fundamantals, Technology and Applications*, ed. W Vielstich, H. A. Gasteiger and A Lamm, John Wiley & Sons, New Jersey, USA, 2003, vol. 4, pp. 987–1001.
13. B. C. H. Steele, *Solid State Ionics*, 2000, **129**, 95.
14. M. Mogensen, N. M. Sammes and G. A. Tompsett, *Solid State Ionics*, 2000, **129**, 63.
15. V. V. Kharton, F. M. Figueiedo, L. Navarro, E. N. Naumovich, A. V. Kovalevsky, A. A. Yaremchenko, A. P. Viskup, A. Carneiro, F. M. B. Marques and J. R. Frade, *J. Mater. Sci.*, 2001, **36**, 1105.
16. S. Wang, H. Inaba, H. Tagawa, M. Dokiya and T. Hashimoto, *Solid State Ionics*, 1998, **107**, 73.
17. M. Godickemeier, K. Sasaki, L. J. Gauckler and I. Riess, *Solid State Ionics*, 1996, **86**, 691.
18. T. Ishihara, H. Matsuda and Y. Takata, *J. Am. Chem. Soc.*, 1994, **116**, 3801.
19. T. Ishihara, in *Handbook of Fuel Cells—Fundamantals, Technology and Applications*, ed. W Vielstich, H. A. Gasteigerand A Lamm, John Wiley & Sons, New Jersey, USA, 2003, vol. 4, pp. 1109–1122.
20. H. Iwahara, H. Uchida, K. Ono and K. Ogaki, *J. Electrochem. Soc.*, 1988, **135**, 529; H. Iwahara, *Solid State Ionics*, 1988, **28**, 573.
21. E. Kendrick, M. S. Islam and P. R. Slater, *J. Mater. Chem.*, 2007, **17**, 3104.
22. P. Lacorre, F. Goutenoire, O. Bohnke, R. Retoux and Y. Laligant, *Nature*, 2000, **404**, 856.
23. J. E. H. Sansom, J. R. Tolchard, M. S. Islam, D. Apperley and P. R. Slater, *J. Mater. Chem.*, 2006, **16**, 1410.
24. H. Yoshioka and S. Tanase, *Solid State Ionics*, 2005, **176**, 2395.
25. S. P. Jiang and S. H. Chan, *J. Mater. Sci.*, 2004, **39**, 4405.
26. N. P. Brandon and D. J. Brett, *Philos. Trans. R. Soc. London, Ser. A*, 2006, **364**, 147.
27. A. Atkinson, S. Barnett, R. J. Gorte, J. T. S. Irvine, A. J. Mcevoy, M. Mogensen, S. C. Singhal and J. Vohs, *Nat. Mater.*, 2004, **3**, 17.
28. D. J. L. Brett, A. Atkinson, D. Cumming, E. Ramirez-Cabrera, R. Rudkin and N. P. Brandon, *Chem. Eng. Sci.*, 2005, **60**, 5649.
29. S. McIntosh and R. J. Gorte, *Chem. Rev.*, 2004, **104**, 4845.
30. S. Tao and J. T. S. Irvine, *Nat. Mater.*, 2003, **2**, 320.
31. J. C. Ruiz-Morales, J. Canales-Vázquez, C. Savaniu, D. Marrero-López, W. Zhou and J. T. S. Irvine, *Nature*, 2006, **439**, 568.
32. J. M. Ralph, A. C. Schoeler and M. Krumpelt, *J. Mater. Sci.*, 2001, **36**, 1161–1172.
33. S. J. Skinner, *Int. J. Inorg. Mater.*, 2001, **3**, 113.
34. K. Hilpert, W. J. Quadakkers and L. Singheiser, in *Handbook of Fuel Cells—Fundamantals Technology and Applications*, ed. W Vielstich, H. A. Gasteiger and A Lamm, John Wiley & Sons, New Jersey, USA, 2003, vol. 4, pp. 1037–1054.
35. J. W. Fergus, *Mater. Sci. Eng.*, 2005, **397**, 271.
36. J. W. Fergus, *J. Power Sources*, 2005, **147**, 46.
37. M. Gong, X. Liu, J. Trembly and C. Johnson, *J. Power Sources*, 2007, **168**, 289.
38. S. C. Singhal, *Solid State Ionics*, 2002, **152**, 405.
39. N. P. Brandon, in *Fuel Cells for Automotive Applications*, ed. R. H. Thring, Professional Engineering Publishing, London, 2004, pp. 31–41.
40. D. J. L. Brett, P. Aguiar, N. P. Brandon, R. Bull, R. C. Galloway, G. W. Hayes, K. Lillie, C. Mellors, C. Smith and A. R. Tilley, *J. Power Sources*, 2006, **157**, 782; D. J. L. Brett, P. Aguiar and N. P. Brandon, *J. Power Sources*, 2006, **163**, 514.
41. H. I. Onowviona and V. I. Ugursal, *Renewable Sustainable Energy Rev.*, 2006, **10**, 389.
42. A. D. Hawkes, P. Aguiar, C. A. Hernandez-Aramburo, M. A. Leach, N. P. Brandon, T. C. Green and C. S. Adjiman, *J. Power Sources*, 2006, **156**, 321.