3 Solid oxide fuel cells

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Abstract

Despite being first demonstrated over 160 years ago, and offering significant environmental benefits and high electrical efficiency, it is only in the last two decades that fuel cells have offered a realistic prospect of being commercially viable. The solid oxide fuel cell (SOFC) offers great promise and is presently the subject of intense research activity. Unlike other fuel cells the SOFC is a solid-state device which operates at elevated temperatures. This review discusses the particular issues facing the development of a high temperature solid-state fuel cell and the inorganic materials currently used and under investigation for such cells, together with the problems associated with operating SOFCs on practical hydrocarbon fuels.

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Solid Oxide Fuel Cells

## 1.	Introduction

Fuel cells are currently attracting tremendous interest because of their huge potential for power generation in stationary, portable and transport applications and our increasing need for sustainable energy resources [1-4]. The combination of the high efficiency with which chemical energy is converted directly into electrical energy, and the very much lower emissions of sulfur and nitrogen oxides and hydrocarbon pollutants, and significantly reduced CO_2 emissions, confers very significant environmental advantages on fuel cells over conventional power generation.

Despite the fact that the fuel cell was discovered over 160 years ago, and the high efficiencies and environmental advantages offered by fuel cells, only now are fuel cells approaching commercial reality. The major factor underlying this is the cost of fuel cell technology. However, significant advances in the development of both materials with improved properties and in manufacturing processes in the last two decades have made fuel cells a realistic proposition to compete on a commercial footing with conventional power generation.

There is now a whole range of different types of fuel cells, which have been developed, which differ in the nature of the electrolyte. However, the basic operating principle of all types of fuel cell is the same, and is shown in Fig. 1.

At the anode, a fuel such as hydrogen is oxidized into protons and electrons, whilst at the cathode, oxygen is reduced to oxide species, and these then react to form water. Depending upon the electrolyte, either protons or oxide ions are transported through an ion conducting, but electronically insulating, electrolyte, while electrons travel round an external circuit delivering electric power.
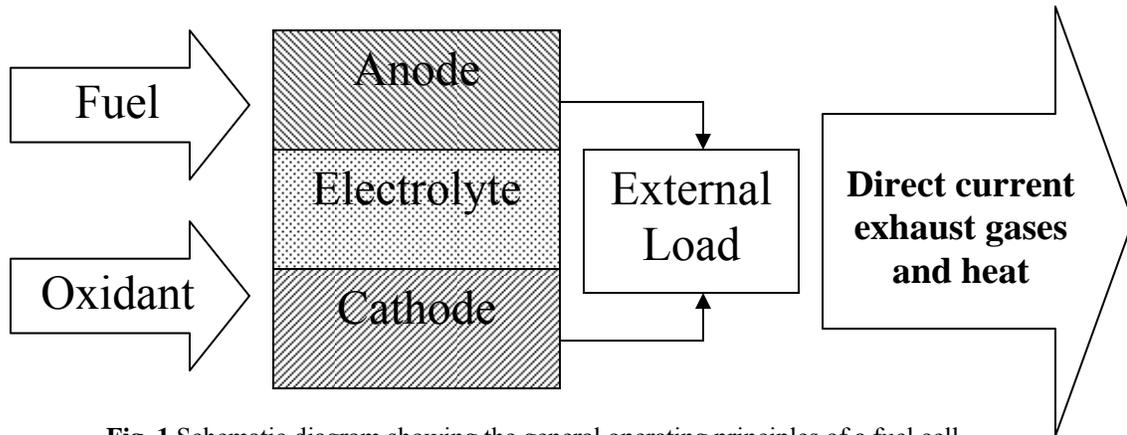

Fig. 1 Schematic diagram showing the general operating principles of a fuel cell.

There are five main types of fuel cell, summarized in Table I, which all have the same basic operating principle, namely two electrodes separated by an electrolyte. Ions move

in one direction, which depends on the electrolyte, across the electrolyte to the opposite electrode, where reaction occurs, while the electrons flow round an external circuit, producing electric power. Each type of fuel cell is characterized by the electrolyte.

Table I Characteristics of different types of fuel cells

Type	Temperature °C	Fuel	Electrolyte	Mobile ion	Efficiency (%)
PEM: polymer electrolyte membrane	70–110	H_2, CH_3OH	Sulfonated polymers (Nafion)	$(H_2O)_nH^+$	30-40
AFC: alkali fuel cell	100–250	H_2	Aqueous KOH	OH^-	35-45
PAFC: phosphoric acid fuel cell	150–250	H_2	H_3PO_4	H^+	35-42
MCFC: molten carbonate fuel cell	500–700	hydrocarbons, CO	$(Na,K)_2CO_3$	CO^{2-}_3	45-60
SOFC: solid oxide fuel cell	700–1000	hydrocarbons, CO	$(Zr,Y)O_{2-d}$	O_2^-	45-65

It is generally considered that the two types of fuel cells most likely to succeed in achieving widespread commercial application are the polymer electrolyte membrane and the solid oxide fuel cell. The most obvious difference in characteristics between the different types of fuel cell is the operating temperature, with molten carbonate and solid oxide fuel cells having elevated operating temperatures of $\sim 650°C$ and $750–1000°C$, respectively, compared to the much lower operating temperatures of around 100°C for PEM fuel cells, and around $200°C$ for phosphoric acid fuel cells. This difference in operating temperature has a number of implications for the applications for which particular fuel cell types are most suited.

2. Applications of fuel cells

The potential applications of fuel cells in society are ever increasing, driven by the different benefits which fuel cells bring to bear, such as environmental considerations (no NO_x, SO_x or hydrocarbon emissions and no or much reduced CO_2 emissions), especially in urban areas where localized pollution is a major issue, and efficiency considerations (better utilization of fossil fuels and renewable fuels, such as biogas and landfill gas). Their potentially high reliability and low maintenance coupled to their quiet operation and modular nature makes fuel cells particularly suited to localized power generation free from distributed networks, in 'high quality', uninterrupted power supplies, and in small scale and remote applications. Applications range all the way from very small scale ones requiring only a few Watts to large scale distributed power generation of hundreds of MW.

Fuel cells offer significantly higher power densities than batteries, as well as being smaller and lighter and having much longer lifetimes, so there is an increasing number of

applications emerging where only a few Watts are required, such as palm top and lap top computers, mobile phones and other portable electronic devices, and computer systems in vehicles.

The combination of their high efficiency and significantly reduced emissions of pollutants mean that fuel cell powered vehicles are a very attractive proposition, especially in heavily populated urban areas. Low temperature fuel cells, in particular PEM fuel cells, are the most suited to transport applications, because of the need for short warm up and cool down times, and because there are no problems with temperature cycling. The concept of a fuel cell powered vehicle running on hydrogen, the so called "zero emission' vehicle, is a very attractive one and is currently an area of intense activity for almost all the major motor manufacturers.

Solid oxide fuel cells are particularly suited to combined heat and power (CHP) applications, ranging from less than 1 kW to several MW, which covers individual households, larger residential units and business and industrial premises, providing all the power and hot water from a single system. Such fuel cell CHP units offer significantly greater efficiency than the current situation where electricity is distributed from a small number of centralized power stations, whilst heating is supplied by decentralized boiler units in each house. Another advantage such CHP units offer for both domestic and commercial use is the reliability in the supply, which is becoming increasingly important, especially in certain commercial applications. Finally it should also be noted that in the power range 5–100 kW the existing technology is inefficient and displays extremely poor performance when operating at part load.

Fuel cells, in particular SOFCs, offer potential for large scale distributed power generation (hundreds of MW), where the heat from the SOFC is used to drive a gas turbine to produce more electricity and increase the system efficiency to levels as high as 80%, significantly higher than any conventional electricity generation.

The modular nature of fuel cells makes them ideally suited for small scale, stand alone and remote applications, for example on gas pipelines, farms, caravans. The flexibility in the choice of fuel, and in particular the ability to operate SOFCs directly on practical hydrocarbon fuels, makes the SOFC particularly suited to such applications.

A rapidly developing market for fuel cells is in those applications where there is a real need for high quality, uninterrupted power supply. Such applications include information technology companies, airports and hospitals where there is a willingness to pay much higher prices for the guarantee of high quality, uninterrupted power to protect very valuable IT equipment or life-supporting equipment. Currently expensive surge protectors and stand by emergency generators are required. Fuel cells are also well suited to high current, low voltage applications such as power tools, wheelchairs, electric bicycles, scooters and boats. Other applications include auxiliary power units in vehicles. This review focuses on solid oxide fuel cells (SOFCs), and in particular the materials used in SOFCs, the function and properties of these materials. Some of the challenges to

be met and opportunities for SOFCs, together with some of the recent advances and developments in this rapidly developing area are reviewed.

3   Solid oxide fuel cells

3.1   Operating principle of SOFC

The operating principle of a SOFC with an oxide ion conductor is schematically shown in Fig. 2.

When an external load is applied to the cell, oxygen is reduced at the porous air electrode to produce oxide ions. These ions migrate through the solid electrolyte to the fuel electrode, and they react with the fuel, H_2 or CO, to produce H_2O or CO_2. Alternatively, a proton conducting solid electrolyte can be used, where H_2 is oxidized to produce protons that subsequently react with oxygen to form water. In some cases, CH_4 can be oxidized directly on the anode to form CO_2 and H_2O. The open-circuit voltage, E_o, of the cell can be calculated from the free energy change, ΔG, of the electrochemical reaction or from the partial pressure of the oxygen $P_{o(c)}$ at the cathode and $P_o(a)$ at the anode:

$$E_o = -\Delta G/nF = (RT/nF) \ln P_{o(c)}/P_{o(a)} \qquad (1)$$

In this equation, R is the gas constant, T the absolute temperature, F the Faraday constant, and n the electron equivalent of oxygen (n = 4). The cell voltage at 1000°C is about 1 V for the SOFC with pure hydrogen and air. The cell voltage drops as current is drained due to polarization. The total polarization of a cell, η, is the sum of three terms: anode polarization, η_a, cathode polarization, η_c, and resistance polarization, η_r.

$$\eta = \eta_a + \eta_c + \eta_r \qquad (2)$$

The polarization depends on the electrode materials, the electrolyte, the cell design, and the operating temperature.
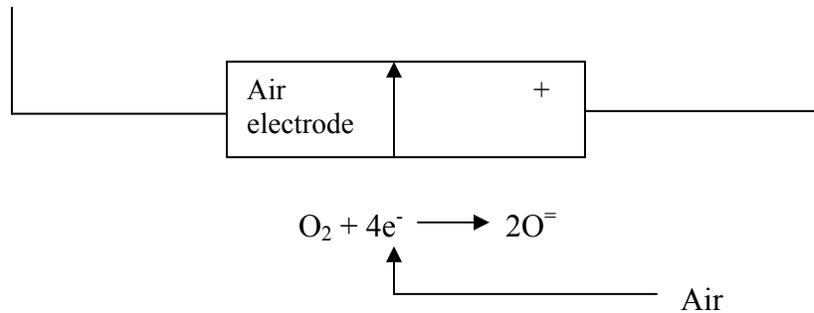
Air electrode | +

$$O_2 + 4e^- \longrightarrow 2O^=$$

Air
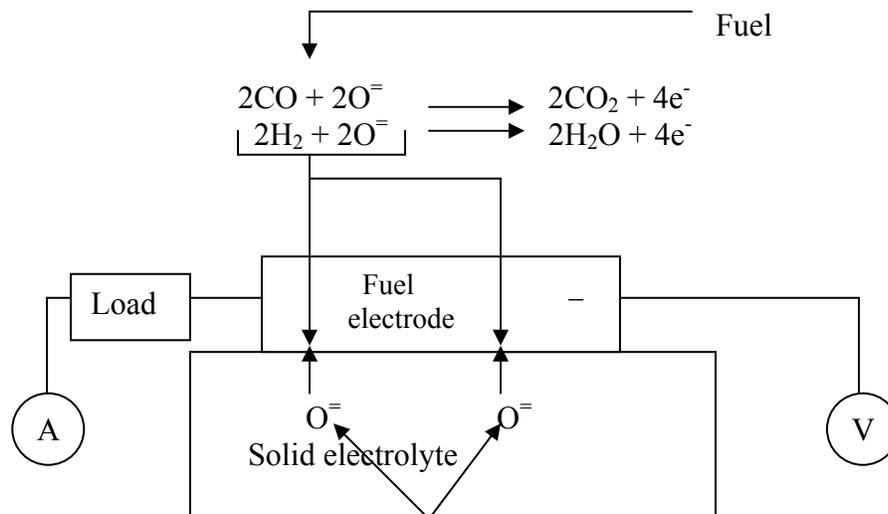
Fig. 2. Principle of operation of SOFC

3.2   Historical background of solid oxide fuel cells

The solid oxide fuel cell was first conceived following the discovery of solid oxide electrolytes in 1899 by Nernst [5]. Nernst reported that the conductivity of pure metal oxides rose only very slowly with temperature and remained only relatively low, whereas mixtures of metal oxides can possess dramatically higher conductivities. He noted that this result was in complete agreement with the known behaviour of liquid electrolytes, comparing the behaviour to that of aqueous salt solutions, which have very high conductivity, whereas the conductivities of pure water and pure common salt are both very low. Many mixed oxides which exhibit high conductivity at elevated temperatures were quickly identified, including the particularly favourable composition 85% zirconium oxide and 15% yttrium oxide, patented by Nernst in 1899. In this patent, Nernst suggested that zirconium oxide, stabilized with 15% yttrium oxide could be used as a glowing filament in lamps, the Nernst 'glower'. The Nernst lamp suffered from a number of practical disadvantages, and interest disappeared with the introduction of the first tungsten filament lamps in 1905. Nernst was convinced that his glowers were ionic conductors, and he proposed that in zirconia the oxidic additions were dissociated to some extent and were able to provide the necessary charge carriers.

In 1905 Haber filed the first patent on fuel cells with a solid electrolyte, using glass and porcelain as the electrolyte materials, depending on the temperature of operation, and platinum and gold as the electrode materials [6]. In 1916 Baur and Treadwell filed a patent on fuel cells with metal oxides as the electrodes and ceramic solids with salt melts in the pores as the electrolyte.

It was not until 1935 that Schottky suggested that yttria stabilized zirconia could be used as a solid fuel cell electrolyte. In 1943 Wagner recognized the existence of vacancies in the anion sublattice of mixed oxide solid solutions and hence explained the conduction mechanism of the Nernst glowers, namely that they are oxide ion conductors [6]. In 1937 Baur came to the conclusion, after many unsuccessful experiments with various types of liquid electrolytes that the solid oxide fuel cell had to be completely dry. Baur and Preis subsequently went on to demonstrate the solid oxide (or ceramic) fuel cell with an yttria-stabilized zirconia electrolyte, successfully running their cell at 1000°C [6]. Unfortunately the high operating temperature and the reducing nature of the fuel gas led

to serious materials problems and despite a very significant search by Baur and other researchers for suitable materials, this was unsuccessful. This effectively hindered the development of the solid oxide fuel cell until the 1960s.

After 1960 various factors resulted in renewed interest in fuel cell technology, whilst advances in the preparation and production of ceramic materials led to a resurgence of interest in solid oxide fuel cells. In the early 1960s a rapidly increasing number of patents were filed relating to the development of SOFC technology. One of the problems with SOFCs at this time was their poor efficiency, as they had thick electrolyte layers and suffered from high losses because of their internal resistance. Continued advances in preparation and production methods through the 1970s led to the development of considerably thinner electrolytes, which gave a significant improvement in performance. In the last two decades numerous designs of SOFCs have been investigated, including various tubular and planar designs.

4   SOFC Materials

A solid oxide fuel cell consists of two porous electrodes, which are separated by a dense electrolyte capable of oxygen ion conduction. The material of choice for different cell components is governed by the following criteria;

(a) Different cell components should have the requisite electrical conduction properties for proper cell functioning.
(b) The cell materials should have adequate chemical and structural stability particularly at high temperature both during cell fabrication as well as during cell operation.
(c) The different cell components should have minimum reactivity and interdiffusion among them.
(d) The thermal expansion behavior of different components should have close and proper matching in order to avoid thermal stress.

Finally the fabrication process should be so chosen that every component could be fabricated without much difficulty.

4.1   Electrolyte materials

In an SOFC, the electrolyte is a solid oxide that forms an O^{2-} charge carrier separating the oxidative and reductive half reactions. In high temperature planar designs, the electrolyte can also function as the support during fabrication. Electrolytes can be categorized as single or bilayer, the latter combining materials to enhance performance. Design requirements for the electrolyte are [7-11]:

- ionically conductive (should be characterized by oxygen ion transport numbers close to 1);
- electronically insulating;
- chemically stable at high temperatures;

- chemically stable in reducing and oxidizing environments;
- gas tight/free of porosity;
- production as a uniformly thin layer (to minimize ohmic losses);
- thermal expansion that matches electrodes;
- uses inexpensive materials.

Table II provides the list of different electrolyte materials. Singhal and Kendall [7] note that stabilized zirconia and ceria possessing the fluorite structure has been the most favored SOFC electrolytes with perovskites, brownmillerites, and hexagonal structured oxides as more recent alternatives. Among the candidate materials, zirconia is a relatively cheap base material and is by far the most popular for SOFC electrolyte material. Among the available electrolyte materials, operating temperature is very important to electrolyte performance. This more recently means that low/intermediate temperature planar cells are anode supported because of the electrolyte needs to be comparably thin [1]. At higher temperatures, the electrolyte can be as thick as 150–250 μm because of higher ionic conductivities [1].

Table II List of different electrolyte materials

Systems	Acronym	Formula
Zirconia electrolytes	YSZ	$(ZrO_2)_{1-x}(Y_2O_3)_x$ ($x\sim0.08$–0.1)
	SSZ	$(ZrO_2)_x(Sc_2O_3)_{1-x}$ ($x\sim0.8$)
	CaSZ	$Zr_{0.85}Ca_{0.15}O_{1.85}$
Ceria electrolytes	GDC	$Ce_xGd_{1-x}O_y$ ($x\sim0.8$, $y\sim1.8$)
	SDC	$Ce_xSm_{1-x}O_y$ ($x\sim0.8$, $y\sim1.9$)
	YDC	$Ce_xY_{1-x}O_y$ ($x\sim0.8$, $y\sim1.96$)
	CDC	$Ce_xCa_{(1-x)}O_y$ ($x\sim0.9$, $y\sim1.8$)
Lanthanum electrolytes	LSGM	$La_xSr_{1-x}Ga_yMg_{1-y}O_3$ ($x\sim0.9$, $y\sim0.8$)
	LSGMC	$La_xSr_{1-x}Ga_yMg_{1-y-z}Co_zO_3$ ($x\sim0.8$, $y\sim0.8$, $z\sim0.085$)
	LSGMF	$La_xSr_{1-x}Ga_yMg_{1-y-z}Fe_zO_3$ ($x\sim0.8$, $y\sim0.5$, $z\sim0.4$)
	LSGMCF	$La_{0.8}Sr_{0.2}Ga_{0.32}Mg_{0.08}Co_{0.2}Fe_{0.4}O_3$
	LaAlO$_3$-based	$La_{1-x}Ca_xAlO_3$ ($x = 0.0027$–0.008)
		$La_{1-x}Ba_xAlO_3$ ($x = 0.1$)
Others	BCY	$BaCe_xY_{1-x}O_3$ ($x\sim0.25$)
	YSHa	$(HfO_2)_{1-x}(Y_2O_3)_x$ ($x\sim0.08$–0.1)
	YSTh	$(ThO_2)_{1-x}(Y_2O_3)_x$ ($x\sim0.08$–0.1)
Bismuth oxide-based		$(Bi_2O_3)_x(Nb_2O_5)_{1-x}$ ($x\sim0.25$)
Pyrochlorores-based		YZr_2O_7, $Gd_2Ti_2O_7$
Barium brownmillerites		$BaZrO_3$, $Ba_2In_2O_5$, $Ba_3In_xAO_y$ (A = Ti, Zr, Ce, Hf), $Ba_3Sc_2ZrO_8$
Strontium brownmillerites		$Sr_2ScAl_xA_yO_z$ (A =Mg, Zn), Sr_2ScAlO_5, $Sr_3In_2HfO_8$

Table III presents approximate conductivities for select electrolyte materials. Among the materials included and for 600–800°C, YSB and LSGMC provide the greatest average conductivity. For 800–1000°C, LSGMC and GDC provide the greatest average conductivity.

Badwal and Foger [9] note that with operating temperatures ranging from 800 to 1000°C, zirconia has good thermal and mechanical shock resistance when doped with yttria,

scandia, samarium, and magnesium as Y_2O_3, Sc_2O_3, Sm_2O_3, and MgO. Among the zirconia electrolyte materials, YSZ is the most used SOFC electrolyte. YSZ is characterized by good chemical and mechanical stability with high quality raw materials available [2]. Most common is approximately 8.5% yittria (called CZP [2,9]). Also, although characterized by lower ion conductivity, 3% yttria (called 3YTZ [2]) has been used because of its higher mechanical stability. Many times 5–20% alumina is added to enhance the mechanical properties, the sintered density, and the electrical properties [12]. In spite of its popularity, Ralph et al. [13] suggests it is doubtful YSZ will operate well at temperatures below 700°C because of decreased ionic conductivity. Also, although it can be produced at thicknesses of 1 μm, reliability can be low when the electrolyte is made extremely thin [14].

Table III Approximate and example conductivities (S cm−1) for select electrolyte materials a

Solid electrolytes		600°C	700°C	800°C	900°C	1000°C
Zirconia electrolytes	YSZ	2.82E−03	8.29E−03	2.00E−02	4.13E−02	7.64−02
	SSZ	2.51E−02	5.38E−02	1.00E−01	1.67E−01	2.58E−01
	CaSZ	1.78E−04	8.69E−04	3.16E−03	9.23E−03	2.28E−02
Ceria electrolytes	GDC	2.82E−02	7.30E−02	1.58E−01	3.01E−01	5.18E−01
	YDC	1.00E−02	2.01E−02	3.55E−02	5.68E−02	8.46E−02
	CDC	5.01E−03	1.30E−02	2.82E−02	5.36E−02	9.21E−02
Lanthanum electrolytes	LSGM	3.16E−02	7.69E−02	1.58E−01	2.89E−01	4.79E−01
	LSGMC	5.62E−02	1.20E−01	2.24E−01	3.74E−01	5.77E−01
Other electrolytes	YSB	1.00E−01	1.89E−01	3.16E−01		2.02E−01
	YSTh	5.62E−05	3.12E−04	1.26E−03	4.00E−03	1.06E−02

a Data approximated from [22] and will be dependent upon the electrolyte microstructure, doping, and fabrication/sintering processes.

Another zirconia electrolyte, SSZ, is quite promising and Badwal and Foger [9] note that 8–9% SSZ has been used because of its mechanical stability and an ionic conductivity much higher than YSZ. However, SSZ has issues associated with phase transition, aging, and cost. Specifically, although 8–12% scandia doping has been shown to give optimal oxide conductivity at higher temperatures, scandia has a phase transition around 600–700°C when doping is over 8%. Also, 7–9% doping has been seen to degrade faster than dopants over 9% [16]. Hirano et al. [17] found that annealing causes a decreased conductivity at 1000◦C and adding Gd_2O_3, Y_2O_3, CeO_2, and Al_2O_3 helps suppress the phase transition. They also found that adding 1% Bi_2O_3 helped stabilize the SSZ and lowered the sintering temperature. However, Badwal and Foger [9] note that SSZ is costly (due to the high cost of scandium) and because the conductivity has been shown to deteriorate over time.

As an alternative to zirconia, ceria electrolytes have high oxygen conductivity when doped with gadolina, samaria, yittria, and calcium (as GDC, SDC, YDC, and CDC). Although these alternatives have been shown to be more stable than zirconia electrolytes [12], they become unstable at low oxygen partial pressures as well as above 700°C due to increasing electrical conductivity causing cells to short circuit [3].

Among the four ceria materials, GDC, SDC, and YDC are the most promising and have been shown to outperform CDC, which has not been recently used. Of concern for these materials is reaction with YSZ above 1300°C with the use of interlayers being an important option despite interfacial resistance issues below 600°C [18]. Specifically, GDC can be used as a compliment interlayer to YSZ to protect against unfavorable anode and cathode reactions. For example, Tsoga et al. [19] found a 1 μm layer of $Ce_{0.43}Ar_{0.43}Gd_{0.1}Y_{0.04}O_{1.93}$ helped suppress the diffusion problems using cobalt-containing cathodes and YSZ at sintering temperatures. In this case, the resistance of a GDC variant interlayer was much less than when the YSZ electrolyte was allowed to react with the cathode. As another option, Balazs and Glass [20] found GDC, SDC, and YDC electrolytes to have the highest conductivity of all the rare-earth oxides (except promethium which was not measured) when doped with cerium oxide because they tend to not react with many other SOFC materials.

Among the four preferred ceria electrolyte materials,GDC has shown higher ionic conductivity than YSZ [10,21,22] with thermal expansion properties nearly identical to ferretic stainless steel interconnects [23] and compatibility with most cathode materials. However, GDC has issues linked to stability and cost. Specifically, GDC has mixed electronic/ionic conductivity at low oxygen partial pressures and is not as mechanically stable as YSZ [2]. Addition of praseodymium oxide can help the stability. Also, gadolinium is relatively expensive which hampers the economic feasibility of GDC [24]. SDC shows high ionic conductivity for operation below 700°C [25,26]. For example, Zhu et al. found a high performance of 0.25 Wcm^{-2} below 400°C for SDC/carbonate electrolytes [27]. Since SDC is relatively compatible with nickel, many times it is used in combination with SDC/Ni anodes. In fact, Xia et al. [18] demonstrated this design with performances as high as 397 $mWcm^{-2}$ at 600°C. Also, SDC has outperformed YDC for similarly prepared cells and temperatures between 500 and 600°C [28].

Finally, YDC-salt electrolytes have been shown to significantly outperform pure YDC electrolytes and YSZ/YDC bilayered electrolytes by a factor of 7 and 3, respectively, at 600°C [24]. Salts used were NaCl, LiOH, NaOH, and LiCl with weight percentages varying between 10 and 25%. Zhu et al. [24] also note that "pure YDC in intermediate temperatures is not successful due to its poor chemical stability compared to ceria". YDC also has the advantage of being the least expensive electrolyte between YDC, SDC and GDC. Similar to SDC, a YDC electrolyte is well used when paired with a YDC/Ni anode. In fact, Peng et al. [28] used this design and achieved performance as high as 360 $mWcm^{-2}$ at 650°C.

Lanthanum gallate electrolytes provide an alternative to zirconia and ceria materials. The most commonly cited are LSGM and LSGMC. Specifically, several studies have shown LSGM to have an ionic conductivity higher than YSZ [22,29,30] although Yan et al. [31] did note equivalent ionic conductivity to YSZ at 1000°C. Also, Maric et al. [32] state that an LSGM electrolyte paired with a Ni/SDC anode has the best chance of success at 700–800°C. This combination was also explored by Inagaki et al. [33] who found comparable performance at 800°C to a YSZ electrolyte – YSZ/Ni anode – LSM/YSZ cathode combination at 1000°C.

Problematic issues with LSGM relate to gallium evaporation at low oxygen partial pressures and reducing atmospheres [2,34], long-term mechanical stability with a high creep rate when compared to YSZ [13,31], difficulties in producing thin films [35], and cost [9]. Although LSGM has been demonstrated to perform better than YSZ of equal thickness, LSGM has difficulties being made as thin as YSZ. This means that very thin YSZ can outperform a thick LSGM cell [31] at intermediate/high temperatures noting that Yan et al. [31] were able to make a thin (15 μm) LSGM electrolyte using wet processes. Finally, LSGM also can form unwanted second phases at lower temperatures such as $SrLaGaO_7$ and $La_4Ga_2O_9$ in electrolyte boundaries [23].

Other lanthanum electrolytes include LSGMC, LSGMF, LSGMCF, and $LaAlO_3$-based materials. Specifically, the doped lanthanum gallate electrolytes have shown increased performance over LSGM. Ishihara et al. [14] showed that the addition of cobalt (as LSGMC), iron (as LSGMF), and cobalt and iron (as LSGMCF) can increase ionic conductivity such that for the cobalt options, if the cobalt is kept in small amounts, the ionic conductivity can increase without increasing the electrical conductivity. Issues with these electrolytes include cobalt diffusion and excessive thermal expansion (for LSGMCF). Specifically for LSGMC, Ishihara et al. [14] demonstrated compatibility with LSCF cathodes postulating that this was because cobalt diffusion was reduced. In another study, adding magnesium oxide to LSGMC was found to improve the mechanical strength with very little decrease in electrical conductivity [36]. Finally, Singhal and Kendall [7] discuss $LaAlO_3$ electrolytes as possibly attractive at low and intermediate temperatures despite conductivities lower than YSZ. In addition, Yasuda et al. [37] found the addition of 2 wt.% Al_2O_3 to LSGM increased the mechanical strength with no effect on ionic conductivity and thermal expansion at $800^{\circ}C$.

Other electrolytes include BCY, bismuth, thoria, hafnia, and pychlorores options, as well as barium and strontium brownmillerites. Specifically, BCY has demonstrated higher ion conductivity than YSZ below $800^{\circ}C$ and SDC below $600^{\circ}C$. It has potential at temperatures below $600^{\circ}C$ because it outperformed SDC and YSZ electrolytes with a NiO/SDC anode and SSC cathode [38]. Bi_2O_3 has been stabilized with the addition of metal oxides of yittria, gadolina, and tantalum as Y_2O_3, Gd_2O_3, Ta_2O_5, and others [9]. Although doped bismuth oxides have shown nearly 10 times the ionic conductivity of zirconia, they are not very stable in reducing environments on the cathode side. Although the addition of yttrium to bismuth oxide (BYO) has high ionic conductivity and is stable [39], more research is needed on these materials. Concerning bismuth electrolytes, Badwal and Foger [9] note "that it is highly unlikely that such systems will be used as electrolytes in solid oxide fuel cells without the use of a protective coating of a more inert material such as zirconia". Additionally, electrolytes made from metal oxide stabilized Thoria (as ThO_2) or stabilized Hafnia (HfO_2) have shown ionic conductivities much lower than the zirconia options.

Finally, Singhal and Kendal [7] discuss pychlorores and brownmillerite options. Pychlorores options including gadolinium titanate ($Gd_2Ti_2O_7$) and yittrium zirconate (YZr_2O_7) are only suitable in limited oxygen partial pressure ranges. Brownmillerites offer high oxide ion conductivities with $BaZrO_3$ materials doped with yttrium having

shown high conductivity and chemical stability but are extremely difficult to process into dense electrolyte layers [29].

As described above, in addition to operating temperature impacts on performance, electrolyte compatibility with other SOFC components is also very important to applicability. Examples are presented in Table IV for YSZ, LSGMC, LSGMF, and LSGMCF.

Table IV Prominent electrolyte material incompatibilities

Electrolyte	Incompatibilities	Forms	Solution	References
YSZ	LSCF, LSM LaMO$_3$-based (M =Mg, Mn, Fe, Co) Doped ceria above 1300°C LnSrO$_3$-based (Ln =Pr, Nd, Gd)	SrZrO$_3$ La$_2$Zr$_2$O$_7$ Y$_2$Ce - Y$_{.15}$Zr Ln$_2$Zr$_2$O$_7$, SrZrO$_3$	Interlayer of GDC, keep below 1200°C Interlayer of GDC or SDC, keep below 1200°C (1000°C if M=Co) Keep cell below 1300°C Sinter at 1000°C for 100 h	[1] [34,37–39] [43,44] [45,50]
LSGMC, LSGMF, and LSGMCF	Ni O Itself or LSM (inconclusive) LSC	Nickel diffusion SrGaO$_3$, La$_4$SrO$_7$, LaSrGaO$_4$, LaSrGa$_3$O$_7$, SrLaGa$_3$O$_7$,La4Ga$_2$O$_9$ Cobalt diffusion	Interlayer of GDC of SDC Control Sr/Mg ratios Protective Interlayer	[1,31,30,47] [34,23] [48]

4.2   Anode materials

In an SOFC, the anode or the "fuel electrode" is the site where fuel is reduced within each cell. In planar designs, the anode can also function as the support during fabrication. Almost always it is the last layer deposited on tubular designs and is not a support [1]. Anode performances are the least emphasized SOFC component when it comes to temperature. This is most likely for two reasons: (1) nickel, the most popular anode material, has shown good performance at all temperature ranges, and (2) anode research is orientated towards catalytic breakdown of hydrocarbon fuels. SOFC anodes are usually made into a cermet to match the thermal expansion of the electrolyte being used to avoid high sintering rates and grain growth/shrinkage [9]. Design requirements for the anode are [9–11,30,49–50]:

- electrically conductive;
- high electrocatalytic activity;
- avoid coke deposition;
- large triple phase boundary;
- stable in a reducing environment;
- can be made thin enough to avoid mass transfer losses, but thick enough to provide area and distribute current;
- able to provide mechanical support to electrolyte and cathode if the cell is anode supported;
- thermal expansion coefficient similar neighboring cell component;

- chemically compatible with neighboring cell component;
- has a fine particle size;
- able to provide direct internal reforming (if applicable);
- tolerant to sulfur in fuels (if applicable);
- able to withstand low vapor pressures (will not cause unwanted reactions);
- uses relatively inexpensive materials.

Among the anode materials listed in Table V, nickel is the most common anode material because it is relatively inexpensive and fulfills most of the anode design requirements. The nickel is usually found in concentrations of 40–60% in the anode cermet to match the thermal expansion of YSZ and must be above the percolation threshold of 30%. To facilitate mass transfer anodes typically have porosities of 20–40% [51].

Table V List of different anode materials

Systems	Materials
Nickel Materials	NiO/YSZ
	NiO/SSZ
	NiO/GDC
	NiO/SDC
	NiO/YDC
Copper Materials	$CuO_2/CeO_2/YSZ$
	CuO_2/YSZ
	Cu/YZT
	$CuO_2/CeO_2/SDC$
Lanthanum Materials	$La_{1-x}Sr_xCrO_3$
	$La_{1-x}Sr_xCr_{1-y}M_yO_3$
	LST
	LAC
Other Materials	CeO_2/GDC
	TiO_2/YSZ
Cobalt based	
Platinum based	
Ru/YSZ	

Despite their popularity, nickel anodes are characterized by a number of problems. Notable are incompatibility with certain electrolytes [23,13] and certain fuels [13,50,52]. Specifically, nickel anodes have been shown to exhibit possible unfavorable reactions with lanthanum electrolytes [23,13,53]. In the case of LSGM, protective layers made from CeO_2, GDC, or SDC [47,1,30,47,54] have been used. Further, nickel anodes are difficult to run on dry methane and higher hydrocarbons because of the formation of carbon fibers above $700^\circ C$ [50]. For use of these fuels, there must be sufficient steam for a water gas reaction; for example there must be a steam/methane ratio greater than 2 or 3 [52,50]. Also, whereas Ralph et al. [13] note that the sulfur content of fuels must be below 10 ppm, Singhal and Kendall [7] suggest nickel at high temperatures are sensitive

to sulfur concentrations as low as 0.1 ppm. Another issue with nickel anodes is structural damage when thermal cycled repeatedly during stack heating and cooling [55].

Among the nickel anodes, NiO/YSZ is the most popular although it has shown reduced thermal expansion mismatches, controlled grain growth, and an increased triple phase boundary area [31]. NiO/SSZ cermet anodes have been used by Ukai et al. [56] showing a lower overpotential than NiO/YSZ when operating on H_2/H_2O fuel at $800°C$ and better stability than NiO/YSZ. NiO/GDC has shown improved electronic and ionic conductivity, catalytic activity, long-term stability, and suppression of carbon formation with methane as a fuel at lowsteam to carbon ratios [57–59]. Also, Marina et al. [60] found promising results with a 50:50 volume percentage NiO/SDC anode to establish good connections at an optimum sintering temperature of 1250–1300°C [30,60]. Finally, Peng et al. [28] found promising results with NiO/YDC anodes utilizing a 65:35 volume percentage at temperatures below $650°C$.

Although alloying copper with nickel has shown reduce carbon formation, the focus of research in alternative anodes has been on replacing the nickel with copper [61]. Copper cermets are less expensive than nickel anodes and have demonstrated better resistance to hydrocarbon coking and YSZ anode cermet densification [50]. Gorte et al. [50], Craciun et al. [52], and Kiratzis et al. [62] describe $Cu/CeO_2/YSZ$, Cu/YSZ, and Cu/YZT anodes. Craciun et al. showed that a copper impregnated YSZ anode gave good performance which was increased with the impregnation of CeO_2 because the CeO_2 provided ionic and electronic conductivity [50] and if needed, catalytic activity for hydrocarbon oxidation [63]. Craciun et al. also found the optimal weight percentage of copper was 40% copper which performed nearly equal to nickel. Also, Lu et al. [26] found that a $Cu/CeO_2/SDC$ anode and a relatively thick SDC electrolyte (at 380 μm) ran stable when operating on dry C_4H_{10} between 600 and $700°C$.

For lanthanum anodes, Atkinson et al. [61] suggest $La_{1-x}Sr_xCrO_3$ as an alternative with good stability and $La_{1-x}Sr_xCr_{1-y}M_yO_3$ (with M= Mn, Fe, Co, Ni) as an option with improved catalytic properties. Also, Marina et al. [55] found LST ($La_{0.3}Sr_{0.7}TiO_3$) to have good electrical and electrocatalytic properties when sintered in hydrogen at $1650°C$ with a thermal expansion similar to YSZ [55]. They also suggest LST will most likely resist structural degradations due to thermal cycling better than a Ni O/YSZ anode. Sfeir [41] found LAC (LaACrO with A= Sr, Mg, Ca) to inhibit coking but to provide low overall electrocatalytic activity under a pure methane feed. However, the future of perovskite anode materials is likely little because of their high expense and because the anode overpotential is usually small compared to other cell components, money is more likely to be spent on more effective cathode materials.

In addition to nickel, copper, and lanthanum materials, SOFC anodes have been based on ceria, titanium, cobalt, platinum, and ruthenium. Specifically, Marina et al. [60] found good performance with a CeO_2/GDC anode, providing 470 mWcm^{-2} at $1000°C$. Their anode, with 40–50% cerium atoms, is substituted with gadolinium or a similar rare-earth cation and showed a reasonable compromise between conductivities and dimensional stability. Also, a titanium anode, TiO2/YSZ, was explored by Mori et al. [64]. Although

the TiO_2/YSZ anode provided an increase in mechanical strength, electrical conductivity decreased with titanium content. The titanium also lowered the firing temperature but decreased the thermal expansion coefficient of the anode cermet. Also, ruthenium anodes described by Ralph et al. [13] demonstrated low overpotential losses and high resistance to carbon deposition and grain growth but are toxic and relatively expensive. Finally, cobalt, iron, and platinum anodes are more expensive and do not show substantial performance improvements over nickel anodes [9].

A recent review article presented by Atkinson et al. [61] describes the implications of anode material choices for SOFCs including a review of fuel related issues and is recommended for further information.

4.3   Cathode materials

The cathode or the "air or oxygen electrode" is the site where oxygen is reduced to oxide ions within each cell. The cathode usually functions as the support during fabrication of tubular cells. In lower temperature SOFCs, the cathode is often the limiting resistance of the SOFC cell because of its large overpotential: usually much larger than anode overpotentials. This is because large activation and concentration polarizations develop at low temperatures. Design requirements for the cathode are [10,11,50]:

- high electronic conductivity;
- chemically compatible with neighboring cell component (usually the electrolyte);
- can be made thin and porous (thin enough to avoid mass transfer losses, but thick enough to provide area and distribute current);
- stable in an oxidizing environment;
- large triple phase boundary;
- catalyze the dissociation of oxygen;
- high ionic conductivity;
- adhesion to electrolyte surface;
- thermal expansion coefficient similar to other SOFC materials;
- relatively simple fabrication;
- uses relatively inexpensive materials.

Cathode material performance is very dependent on temperature (but less so when compared to the electrolyte), grain size, microstructure, and the formation or deposition process. List of different cathode materials are presented in Table VI. Among those listed LSM, LSF, and SSC are leading cathode materials. Specifically, LSM and LSF are the proven lanthanum options. First, LSM is the most popular cathode material for high temperature SOFCs because of its stability with zirconia electrolytes. For LSM, the perovskite $LaMnO_3$ (ABO_3) is doped both at the A and B sites by cations. Calcium (at 10–30 mol%) and strontium (at 10–20 mol%) are generally doped at the A site [9]. If the strontium concentrations are too low, a decrease has been seen in electric conductivity. Also, LSM is often mixed with YSZ to extend the triple phase boundary, reaction sites and significantly reduce electrode polarization [65]. LSM has also been mixed with platinum to increase oxygen reduction rates [9].

Table VI   Example cathode materials

Systems	Acronym	Representative chemical formulas
Lanthanum cathodes	LSM	$La_xSr_{(1-x)}MnO_3$ (x~0.8)
	LSF	$La_xSr_{(1-x)}FeO_3$ (x~0.8)
	LSC	$La_xSr_{(1-x)}CoO_3$ (x~0.6–0.8)
	LSCF	$La_{(1-x)}Sr_xFe_yCo_{(1-y)}O_3$ (x~0.4, y~0.2)
	LSMC	$La_xSr_{(1-x)}Mn_yCo_{(1-y)}O_3$ (x~0.8)
	LSMCr	$(La_xSr_{1-x})_{.91}Mn_yCr_{(1-y)}O_3$ (x~0.7, y~0.95)
	LCM	$La_xCa_{(1-x)}MnO_3$ (x~0.5)
	LSCu	$La_{(1-x)}Sr_xCuO_{2.5}$ (x~0.2)
	LSFN	$La_xSr_{(1-x)}Fe_yNi_{(1-y)}O_3$ (x = 0.8, y = 0.8)
	LNF	$LaNi_{(1-x)}Fe_xO_3$ (x~0.4)
	LSCN	$La_xSr_{(1-x)}Co_yNi_{(1-y)}O_3$ (x~0.6, y~0.98)
	LBC	$La_xBa_{(1-x)}CoO_3$ (x~0.4)
	LNC	$LaNi_{(1-x)}Co_xO_3$ (x~0.4)
	LSAF	$La_xSr_{(1-x)}Al_yFe_{(1-y)}O_3$ (x~0.8, y~0.2)
	LSCNCu	$La_xSr_{(1-x)}Co_yNi_{(1-y-z)}Cu_zO_3$ (x~0.8, y~0.8, z~0.05)
	LSFNCu	$La_xSr_{(1-x)}Fe_yNi_{(1-y-z)}Cu_zO_3$ (x~0.8, y~0.8, z~0.05)
	LNO	$LaNiO_3$
Gadolinium cathodes	GSC	$Gd_xSr_{(1-x)}CoO_3$ (x~0.8)
	GSM	$Gd_{(1-x)}Sr_xMnO_3$ (x~0.3–0.6)
Yttria cathodes	YSCF	$Y_{(1-x)}Sr_xCo_yFe_{(1-y)}O_3$ (y = 0.7, x~0.3–0.8)
	YCCF	$Y_{(1-x)}Ca_xCo_yFe_{(1-y)}O_3$ (x = 0.2, y~0.1–0.7)
	YBCu	$YBa_2Cu_3O_7$
Strontium cathodes	SSC	$Sm_xSr_{(1-x)}CoO_3$ (x~0.5)
	NSC	$Nd_xSr_{(1-x)}CoO_3$ (x~0.8)
	BSCCu	$Bi_2Sr_2CaCu_2O_8$
Praseodymium cathodes	PSM	$Pr_xSr_{(1-x)}MnO_3$ (x~0.65)
	PCM	$Pr_xCa_{(1-x)}MnO_3$ (x~0.7)
	PBC	$Pr_xBa_{(1-x)}CoO_3$ (x~0.5)

For LSM and other lanthanum-based cathodes, compatibility with YSZ electrolytes is particularly important. Specifically, LSM reacts with YSZ at temperatures above 1300°C [13,66]. Similarly, YSZ electrolytes are only compatible with LSM if the temperature stays below 1200°C [34] and the strontium content is below 30% [13]. Yoon et al. [65] saw improved performance with an SDC coating on LSM. For an LSM/YSZ cathode, Hart et al. [66] investigated an LSM/GDC composite layer at the electrolyte-cathode interface which showed higher performance at lower temperatures. As a result of these issues, LSM has been paired with GDC (or other ceria-based interlayers) for lower temperature fuel cells [67].

Despite its lower electrical conductivity [68], LSF is one of the best candidates to replace LSM between 650 and 800°C [13]. Researchers at PNNL and ANNL have focused their interests on LSF cathodes over cobalt (as LSCF), nickel, and manganese B-site cations to improve chemical and longterm stability and power density [40]. Lanthanum deficient LSF had significantly lower electrical impedance than stoichiometric LSF (i.e., $La_{0.8}Sr_{0.25}FeO_3$ performed better than $La_{0.8}Sr_{0.2}FeO_3$). Also, for lower temperature

SOFCs, LSF has shown better properties than LSM due to the overpotential of LSM. For example, the LSM overpotential at 1000°C is 1 Ωcm^{-2} but increases to 2000 Ωcm^{-2} at 500°C [69]. Already Delphi has used LSF in their power units breaking the trend of LSM commercial cathodes.

The remaining lanthanum cathode materials have shown varying success in conductivity and stability improvements over LSM and LSF. Specifically, LSC is a candidate for lower temperature stacks with a higher conductivity than LSM and one of the better power densities when coupled with an LSGM electrolyte [1,70]. However, some researchers suggest LSC is preferred with ceria electrolytes or with a protective layer of ceria due to large thermal expansion problems and reactivity with zirconia [9,10]. In general, LSC's long-term stability is hampered by cobalt diffusion and phase separation (at 750°C) and has problems with peeling after sintering [1,32,44,48,70].

LSCF is one of the better performers with GDC because of its stability [70] and thermal expansion compatibility [21]. Again, LSCF reacts with zirconia when fired but a protective layer of YDC can help offset this problem [1,71]. Like LSC, LSCF does not react with cerium electrolytes and has a similar thermal expansion coefficient which gives it excellent potential at lower temperatures [70]. Also, LSCF has shown higher activation energies than LSC such that its resistance increases rapidly as temperature decreases; LSCF also has a more compatible thermal expansion coefficient than LSC [13,72].

Improvements have been demonstrated using other lanthanum cathodes but not always without introducing other issues usually in addition to incompatibility with zirconia. Specifically, LSMC has shown increased ion and electrical conductivity over LSM although problems have been demonstrated related to thermal expansion coefficient mismatch with YSZ and the formation of second phases at high cobalt contents [2,9,68]. LSCN has illustrated good performance with GDC although resistance has been found to increase rapidly at temperatures below 800°C [13] and its long-term stability has been questioned [44]. LSFN is a low temperature candidate found to be stable up to 1400°C when the iron chemical subscript value is higher than 0.5 [13,73]. Also, Murata and Shimotsu [74] found that when LSMCr was combined with YSZ, performance reached 1.5 Wcm^{-2} at 1000°C with hydrogen and oxygen. Chiba et al. [75] explored the use of LNF in the cathode and found a better thermal expansion compatibility with YSZ than that of LSM. They also found LNF to exhibit three times the electronic conductivity as LSM at 800°C. LNO has shown a relatively low areal resistance on YSZ but relatively high on GDC [13]. Ishihara et al. [15] found LBC to have a comparable performance to SSC at 800°C and outperform SSC at 600°C with an LSGM electrolyte despite the formation of $BaCO_3$ in an atmosphere with greater than 10% CO_2. LCM has been found stable at high temperatures, has a thermal expansion coefficient compatible with YSZ, and resists $La_2Zr_2O_7$ generation better than LSM [40,76]. Finally and notably, LSCu was found to have no reaction with YSZ with excellent electronic conductivities and small cathode polarization which were more than eight times lower than LSM in similar conditions [63].

No improvements were found related to the use of LNC, LSAF, LSCNCu, and LSFNCu. Specifically, Hrovat et al. [77] found LNC to have a more damaging reaction with YSZ than most perovskites. Also, LSAF has shown a lower electrical ionic and electrical conductivity than LSF [78] and LSCNCu and LSFNCu had relatively large areal resistances on YSZ electrolytes [13]. No performance information was found for LNF and LSCN.

In addition, the use of praseodymium instead of lanthanum in SOFC cathodes has shown decreased cathode overpotentials and enabled higher catalytic activities [79]. Specifically, PCM has demonstrated higher electrical conductivity, lower cathode potential, low-reactivity withYSZand a more similar thermal expansion to YSZ. PSM was found to react to form $Pr_2Zr_2O_7$ or SrZrO [80]. PBC has demonstrated potential in low temperature conditions with a BCY electrolyte [38]. Kostogloudis et al. [79] found that of the praseodymium dopants paired with an LSGM electrolyte, cobalt diffused the greatest, followed by iron and then manganese. Another problem in LSGM/praseodymium cathode interface was the formation of an LSGM second phase, LaSrGa3O7 [79].

Strontium cathodes include SSC, NSC, and BSCCu. Specifically, SSC has shown a higher ionic conductivity than LSM, similar performance to LSCF, exchange parameters higher than LSC and LSM [81,82], and to be particularly compatible with GDC and LSGM [14]. A drawback of SSC is that it does not perform as well as GSC and NSC and reacts with YSZ and SSZ (at >900°C) [81,82]. SSC also has an extremely large areal resistance with YSZ, limiting its applicability at high temperatures [13]. Also, samarium is very expensive and SSC is "not desirable from the cost point of view" [15]. NSC has shown similar resistance properties to GSC with a GDC electrolyte and has potential in lower temperature applications. BSCCu showed good resistance properties on GDC and has potential on lower temperature fuel cells [13].

Gadolina materials include GSC and GSM. GSC is promising for lower temperature SOFCs because it has one of the smallest chances of an unfavorable reaction with GDC [13]. GSC has shown an overpotential at 800°C nearly one order of magnitude below that of LSM at 1000 °C [46]. It has been shown that as the strontium contents increase, GSC reacts more vigorously with YSZ to form $SrZrO_3$. If the strontium content is eliminated, the $SrZrO_3$ reaction is avoided but at temperatures above 1000°C the formation of $Gd_2Zr_2O_7$ becomes a problem [46]. Despite these issues, Ralph et al. [13] speak of GSC as "a promising new cathode material for use with GDC" because of its very low areal resistance at temperatures as low as 700 °C. A second gadolina cathode is GSM which does not react with GDC but does react with YSZ [68]. The coefficient of thermal expansion better matches YSZ and GDC than that of LSC and increases with increasing Sr contents [68].

Yittria cathodes include YSCF, YCCF, and YBCu. YSCF shows potential in intermediate temperature range (~800°C) SOFCs with SDC. YSCF has a lower overpotential than LSC (despite an unfavorable reaction with YSZ) but a higher overpotential than LSCF [25]. YCCF has demonstrated better oxygen reduction when compared to LSM although it

reacted unfavorably with YSZ [83]. Finally, YBCu has shown low activation energy with potential in low temperature fuel cells, however, no subsequent studies were found [13].

Recently Shao et al. (84) also presented $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ as a novel cathode material for ITSOFCs. With thin film samarium doped ceria (SDC) as the electrolyte, single cells exhibited considerable high current densities at lower temperatures. So far only $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ composition has been studied for SOFC applications (85-89), the other compositions in the BSCF system have not been reported. From the point of view of SOFC applications, except for good electrochemical performances, a satisfactory cathode material must also meet other requirements such as thermal expansion match with other components. Besides, the electrical conductivity, other basic parameters needs to be investigated.

4.4   Interconnect materials

In an SOFC, the interconnect is the electric link to the cathode and protects the electrolyte from the reducing reaction. Design requirements for the interconnect are [9,90,91]:

- high temperature oxidation and reduction resistance (simultaneous fuel and oxidant gas exposure);
- stable under multiple chemical gas streams;
- very high electrical conductivity;
- high density with "no open porosity";
- strong and high creep resistances for planar configurations;
- good thermal conductivity;
- phase stability under temperature range;
- resistant to sulfur poisoning, oxidation and carburization;
- low materials and fabrication cost;
- matching thermal expansion to other cell components.

Research in both tubular and planar designs that seeks to reduce operating temperatures look to cut interconnect costs. Specifically, the goal is to use cheap and established metallic interconnects below 900°C instead of the more expensive chromium perovskite materials or metallic interconnects with perovskite-coatings. Perovskites are necessary to give ample oxidation resistance above 900°C. This is particularly important in planar systems using far more interconnect material per unit of power delivered.

Among the ceramic materials used in SOFCs, doped lanthanum chromate ($LaCrO_3$) is the most common option. The doped elements of lanthanum chromate can include cobalt, iron, nickel, magnesium, copper, strontium, calcium, and vanadium [84]. Many times noble metals such as gold, palladium, silver, and platinum are added although these lanthanum chromite composites have shown volatility at temperatures above 800°C that might be detrimental during long-term operation [1,2]. In general, problems with lanthanum chromate interconnects are related to high cost, sintering difficulties, and warping. The warping issue is related to a tendency to partially reduce at the interface

between the fuel gas and interconnect causing the component to warp and the peripheral seal to break [85].

Yang et al. [91] divided metallic alloys into five groups: chromium alloys, ferritic stainless steels, austenitic stainless steel, iron super alloys, and nickel super alloys. Metallic interconnects both with and without coatings have been used. When compared to the use of ceramic materials, metallic interconnects are stronger, easier to form, have higher thermal and electrical conductivities, and negligible ionic conductivities but a thermal expansion coefficient that tends to be higher than most other cell components [34]. Also, ceramics are superior at high temperatures because of oxidation of the metallic interconnects on the cathode side. This oxide layer, usually made of chromium, has a poor conductivity and is "prone to cracking and spalling during long-term operation" [13].

Summaries of interconnect materials have been published by Zhu and Deevi [90,92] and Yang et al. [91]. Both ceramic and metallic materials are discussed in detail and these references are recommended for further information.

4.5   Seals

In planar SOFCs, seals attach the cell to the interconnect and/or metal frames as well as seal all possible leakage points. Design requirements for the seals are [9]:

- electrically insulating;
- low cost;
- thermal expansion compatibility with other cell components;
- chemically and physically stable at high temperatures;
- gastight;
- chemically compatible with other components;
- provide high mechanical bonding strength.

Seals can be classified into three categories: rigid bonded seals, compressive seals, and compliant-bonded seals. Specifically, rigid-bonded seals are the most common and are usually made from glass (pyrex) or glass-ceramic materials [13]. Currently the best candidates are SiO_2 glasses, SrO La_2O_3 Al_2O_3 L_2O_3 SiO_2 glasses. Lahl et al. [94] found aluminosilicate base glass sealants with BaO and CaO to be unsuitable for SOFC use and found MgO with varying alumina or TiO_2 content a better possibility. In their evaluation of seals, Stevenson et al. note that glasses can be tailored thermal expansion characteristics, allow hermetic sealing, and are inexpensive and easy to fabricate. However, glasses are brittle, allow only a few compatible options for thermal expansion, and are characterized by detrimental chemical interactions.

Compressive and compliant, bonded seals are less common. Compressive seals are generally mica composites with the advantage of being potentially easy to fabricate, usually from the avoidance of the viscous/sealing step. However, there are not a wide variety of these seals and they do not perform well in thermal cycling which can lead to de-coupling of adjacent stack components and possible gas leakage. Finally, Steele et al.

suggest no materials in the compliant, bonded category although it is considered an area that does have promise for sealants.

5   Fuels and fuel processing in SOFCs

The elevated operating temperature of SOFCs, combined with their ability to utilize carbon monoxide as a fuel and their greater resistance to poisoning by impurities in the fuel, it is possible to operate the cell directly on hydrocarbon fuels without the need for a separate complex external fuel processor to reform the hydrocarbon fuel into hydrogen and carbon dioxide, removing all traces of CO. Instead the fuel can be catalytically converted to H_2 and CO within the SOFC stack, which is internally reformed. The ability to internally reform practical hydrocarbon fuels within the SOFC, together with the ability to utilize CO and increased tolerance to other impurities in the fuel, is a significant advantage of SOFCs over low temperature fuel cells, and is essential if SOFCs are to become economic, since it both significantly increases the system efficiency by recuperating waste heat from the stack into the fuel supply, whilst at the same time substantially reducing the complexity of the system, by elimination of the external reformer and associated heating arrangements and by reduction in the stack cooling air requirements and associated equipment. Thus internally reforming SOFCs offer significantly higher system efficiencies and reduced complexity compared to lower temperature fuel cell variants.

The most common fuel for the SOFC, especially for stationary applications, is natural gas, which is cheap, abundant and readily available, with a supply infrastructure already in existence in many places. Natural gas can be internally reformed within the SOFC at temperatures as low as 600°C, which means that even lower temperature SOFCs can be operated on natural gas without the need for a complex external fuel reformer. However, in certain applications, especially remote and small-scale, stand-alone ones, bottled gas, such as propane and butane, offer significant practical advantages. The SOFC represents a real viable alternative to conventional power generation methods in remote areas with no natural gas supply, where diesel is generally used, which are both inefficient and highly polluting.

The choice of fuel is partly governed by the operating temperature. For intermediate temperature SOFCs operating at temperatures as low as 500°C, methanol is considered the most likely fuel. Intermediate temperature SOFCs operating directly on methanol offer some potential for transport applications, though the problems associated with slow start-up times and temperature cycling, still have to be overcome. There is also considerable interest in the longer term in the possibility of using higher hydrocarbons, such as petrol and diesel, in internally reforming SOFCs.

Recently, the possibility of using waste biogas, generated from vegetable matter, and landfill gas, both totally renewable fuels, directly in SOFCs has been demonstrated [96]. SOFCs can also be operated on the output from coal gasification systems. The sulfur content of these gases poisons the anode in particular, and the internal reforming catalyst, causing loss of performance and eventual cell deactivation. Thus the sulfur has to be

removed from the gas prior to entering the SOFC, though this is comparatively straightforward. Although the efficiencies of SOFCs operating on biogas, landfill gas or the output from coal gasification systems are lower than for SOFCs operating on natural gas, they do offer significantly cleaner and more efficient power generation compared to alternative means of energy generation currently utilized for these gases.
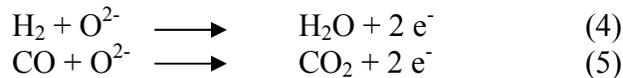
5.1   Internal reforming

In principle therefore SOFC technology is simpler, more flexible and more efficient than other fuel cell variants, with potentially significant cost benefits. However, there are several major problems associated with internal reforming in SOFCs which can lead to deactivation and a loss of cell performance, and hence result in poor durability.

A particular problem is carbon deposition resulting from hydrocarbon pyrolysis [eqn. (3)], especially on the nickel cermet anode, as well as on other active components within the SOFC, which leads to deactivation and poor durability.

$$CH_4 \longrightarrow C + 2\,H_2 \qquad\qquad (3)$$
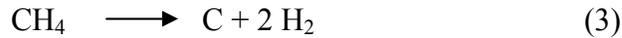
Hydrocarbon steam reforming is a strongly endothermic reaction. This can give rise to potential instabilities in the coupling between the slow exothermic fuel cell reactions [eqns. (4) and (5)] and the rapid endothermic reforming reaction.

$$H_2 + O^{2-} \longrightarrow H_2O + 2\,e^- \qquad (4)$$
$$CO + O^{2-} \longrightarrow CO_2 + 2\,e^- \qquad (5)$$

In addition self-sustained internal reforming is precluded during start-up from cold and operation at low power levels, where electrochemical losses are insufficient to meet both the heat loss from the stack and the endothermic requirements of hydrocarbon reforming. There is therefore considerable effort being devoted to developing stable internal reforming approaches for the full range of possible SOFC operating conditions, from start-up and zero power, through operation at low power loads, to operation at full load.

Internal reforming of the fuel is achieved either indirectly using a separate catalyst within the SOFC, or directly on the nickel anode. Direct reforming of the fuel on the anode offers the simplest and most cost-effective solution, and in principle provides the greatest system efficiency with least loss of energy. In direct reforming the anode must fulfill three roles, firstly as a reforming catalyst, catalyzing the conversion of hydrocarbons to hydrogen and CO, secondly as an electrocatalyst responsible for the electrochemical oxidation of H_2 and CO to water and CO_2, respectively, and finally as an electrically conducting electrode. High efficiency results from utilizing the heat from the exothermic electrochemical reaction to reform the hydrocarbon fuel, this being a strongly endothermic reaction. However, one of the major problems with direct reforming is that it gives rise to a sharp cooling effect at the cell inlet, generating inhomogeneous temperature distributions and a steep temperature gradient along the length of the anode, which is very difficult to control and can result in cracking of the anode and electrolyte

materials. Significant reductions in operating temperature of the SOFC due to the endothermic reforming reaction have been reported. Various approaches are being investigated to give greater control of the reforming reaction to minimize the temperature gradient. This includes the possibility of developing mass transfer controlled steam reforming catalysts with reduced activity.

Another particular problem with direct reforming is the susceptibility of the nickel anode to catalyze the pyrolysis of methane [eqn. (3)], which results in carbon deposition, and leads to rapid deactivation of the cell. The high metal content of the anode precludes the use of precious metals, such as rhodium or platinum, which are more resistant to carbon deposition. Much research is currently being carried out to develop nickel-based anodes which are active for hydrocarbon reforming but are more resistant to carbon deposition. Approaches include the incorporation of small amounts of dopants such as gold, molybdenum and copper into the nickel anode, and the addition of ceria to nickel/zirconia Cermets [97]. Another problem with reforming directly on the anode which has been reported is that it can cause sintering of the anode particles, resulting in a reduction in the catalytic activity of the anode and a loss of cell performance.

In indirect internal reforming a separate catalyst, which reforms the hydrocarbon fuel to synthesis gas, is integrated within the SOFC upstream of the anode. The heat from the exothermic fuel cell reaction is still utilized. Although indirect internal reforming is less efficient and less straightforward than direct reforming it is still significantly more efficient, simpler and more cost-effective than using an external reformer. The major advantage of indirect reforming over direct reforming is that it is much easier to manage and control from a thermodynamic standpoint. One approach involves the development of mass transfer controlled steam reforming catalysts with reduced activity. It is also easier to develop dispersed catalysts which do not promote carbon formation to the same extent as the nickel anode. Consequently the SOFCs currently being developed generally use a separate catalyst within the SOFC stack, upstream of the anode to indirectly reform the majority of the hydrocarbon fuel, with some residual reforming occurring directly on the anode.

The most common oxidant for reforming the hydrocarbon fuel is steam, which is added to the hydrocarbon feed, which is subsequently converted to CO and H_2 via steam reforming. This is shown in eqn. (6) for methane:

$$CH_4 + H_2O \longrightarrow CO + 3\,H_2 \qquad (6)$$

Depending on the temperature and the steam to methane ratio, the water gas shift reaction [eqn. (7)] can also occur, whereby some of the CO is converted to CO2, with production of one mole of hydrogen for every mole of CO converted.

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (7)$$

The H_2 and CO are then electrochemically oxidized to H_2O and CO_2 [eqns. (4) and (5)] at the anode by oxygen ions electrochemically pumped through the solid electrolyte, from

the cathode, with the production of electricity and heat. However, as described above, in addition to the reforming reactions, there is also the possibility of hydrocarbon pyrolysis occurring [eqn. (3)], which leads to carbon deposition on either the internal reforming catalyst or the nickel anode. Nickel in particular is well known for its propensity to promote this reaction [97-99].

Carbon deposition can also occur *via* the disproportionation of CO (the Boudouard reaction) [eqn. (8)], and by reduction of CO by H [eqn. (9)].

$$2\,CO \longrightarrow C + CO_2 \tag{8}$$
$$CO + H_2 \longrightarrow C + H_2O \tag{9}$$

The build up of carbon (coking) on either the internal reforming catalyst or the anode, or indeed anywhere else in the SOFC, is a critical problem to be avoided, or at least minimized, since over time this will lead to a loss of reforming activity and blocking of active sites, and a loss of cell performance and poor durability. The phenomenon of carbon deposition on steam reforming catalysts has been extensively studied [99].

Natural gas is the most likely fuel for the SOFC. Natural gas, although predominantly methane, contains significant proportions of higher hydrocarbons. It is well known that higher hydrocarbons are more reactive and show a greater propensity towards carbon deposition than methane, and in reality it is the presence of these higher hydrocarbons in natural gas that represents the most likely source of deleterious carbon build-up in SOFCs.

In addition to containing higher hydrocarbons, sulfurcontaining compounds, such as dimethyl sulfide, diethyl sulfide, ethyl mercaptan, tert-butyl mercaptan and tetrahydrothiophene, are added to natural gas as odorants at the level of ~ 5 ppm. Although at the elevated operating temperature of SOFCs the nickel anodes, and any internal reforming catalyst, show some tolerance to sulfur, generally the majority of the sulfur is removed from the natural gas prior to entering the SOFC to prevent poisoning of the anode and reforming catalyst. The tolerance of the anode and reforming catalyst to sulfur becomes progressively less as the operating temperature of the SOFC is lowered.

Consequently there is much interest in developing optimized catalyst and anode formulations, and establishing appropriate operating conditions, for internally reforming SOFCs that avoid carbon deposition and which show some tolerance to sulfur. This is particularly important if some of the fuel processing is occurring directly on the anode.
As water is formed as the product of the electrochemical oxidation of hydrogen [eqn. (4)] at the anode, this water can be recirculated and re-introduced into the hydrocarbon fuel feed, rather than continuously adding water to the system. Carbon dioxide, formed by electrochemical oxidation of carbon monoxide [eqn. (5)], is present in the exit gas leaving the anode, so if the exit gas is recirculated, in addition to steam, CO_2 will be present in the fuel supply at the cell inlet. It is well known that CO_2 can act as an oxidant for hydrocarbons [dry reforming, eqn. (10)] [100]. Therefore, in addition to the steam, the

CO_2 can also reform the methane, though it also represents a possible source of carbon deposition.

$$CH4 + CO_2 \longrightarrow 2\, CO + 2\, H_2 \qquad (10)$$

In an SOFC where the exit gas is recirculated, the steam (and CO_2)/natural gas ratio is governed by the ratio of the exit gas that is recirculated.

In certain applications, especially in small-scale devices being developed for stand-alone or remote applications, oxygen, or simply air in many cases, is used as the oxidant rather than steam, because of the cost and complexity associated with using large quantities of steam, which makes its use less favourable in small-scale applications. Using oxygen, or air, is much simpler and cheaper in terms of system configuration and manufacture. However, it does lead to an inherent efficiency due to the large energy loss in oxidizing the hydrocarbon. Further, in order to maximize the power output from the SOFC it is necessary for the internal reforming catalyst or the anode to be selective for the partial oxidation of the hydrocarbon [eqn. (11)].

$$CH_4 + 1\!/2\, O_2 \longrightarrow CO + 2\, H_2 \qquad (11)$$

The catalytic partial oxidation of hydrocarbons has been studied over many years by many researchers. A particular problem is to develop a catalyst and operating regime where high selectivity to the partial oxidation products is obtained, whilst avoiding carbon deposition on the catalyst via eqn. (3) [101]. Clearly carbon deposition is very undesirable. However, if an excess of oxygen is used then there will be a tendency for full oxidation to CO_2 and H_2O to occur [eqn. (12)].

$$CH_4 + 2\, O_2 \longrightarrow CO_2 + 2\, H_2O \qquad (10)$$
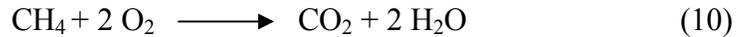
CO_2 and H_2O cannot be electrochemically oxidized, so there is a further loss of efficiency compared to using steam as the oxidant.

Although for most SOFCs under normal operation steam (and CO_2) will be used to internally reform the natural gas, selfsustained internal reforming is precluded during start-up from cold and operation at low power levels because of the strongly endothermic nature of steam (and CO_2) reforming. Partial oxidation of hydrocarbons, being exothermic, offers the potential for start-up and self-sustaining operation of internally reforming SOFCs running on natural gas or other hydrocarbon fuels at low power. Thus it is likely that a combination of partial oxidation and steam reforming (autothermal reforming) will be used as the basis for operation from zero power through low power loads to operation at full load at zero and selfsustaining low power operation partial oxidation will be used, and at high load, *i.e.* normal operation, exclusively steam (and CO_2) reforming will be used.

5.2 Direct hydrocarbon oxidation and chemical cogeneration

In principle SOFCs can operate on natural gas or other hydrocarbon fuels without the addition of any oxidant to the fuel, instead directly oxidizing the hydrocarbon at the anode using the electrochemically pumped oxygen ions from the solid electrolyte. The hydrocarbon can either be partially oxidized to carbon monoxide and hydrogen [eqn. (13)], or fully oxidized to CO_2 and water eqn. (14), or undergo a mixture of partial and total oxidation.

$$CH_4 + O^{2-} \longrightarrow CO + 2\,H_2 + 2\,e^- \qquad (13)$$
$$CH_4 + 4\,O^{2-} \longrightarrow CO_2 + 2\,H_2O + 8\,e^- \qquad (14)$$
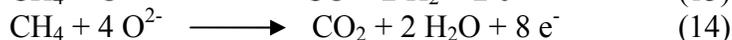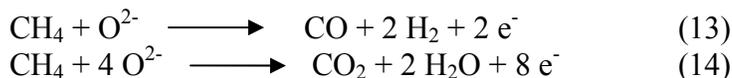
The possibility of directly oxidizing hydrocarbon fuels on the SOFC anode without any added oxidant is an extremely attractive one. This is especially true if the hydrocarbon is partially oxidized to CO and H_2 [eqn. (13)], rather than fully oxidised [eqn. (14)], since this results in the production of useful chemicals, namely synthesis gas, in addition to electricity and heat. In effect the SOFC can be thought of acting as an electrocatalytic reactor. The major problem with direct oxidation of the hydrocarbon fuel at the anode is the marked tendency towards carbon formation *via* methane decomposition [eqn. (3)]. It is extremely difficult to avoid carbon deposition in the absence of a co-fed oxidant. However, some recent studies have reported anodes which show considerable promise for the direct oxidation of hydrocarbons [102-103]. These anodes can be used may present problems for their widespread application, whilst their long term durability must be established. Nevertheless this is an area attracting much current interest.

The concept of using an SOFC for chemical cogeneration has attracted much interest, [104] offering the possibility of achieving higher product selectivity using electrochemically pumped oxygen ions compared to gas phase oxygen, whilst at the same time using air rather than pure oxygen as the oxidant, which would bring a significant cost benefit. In addition to synthesis gas, it has also been shown that oxidative coupling of methane to ethene and ethane can be carried out in an SOFC electrocatalytic reactor [eqns. (15)–(17)].

$$2\,CH_4 + O^{2-} \longrightarrow C_2H_6 + H_2O + 2\,e^- \qquad (15)$$
$$2\,CH_4 + 2\,O^{2-} \longrightarrow C_2H_4 + 2\,H_2O + 4\,e^- \qquad (16)$$
$$C_2H_6 \longrightarrow C_2H_4 + H_2 \qquad (17)$$

5.3 Utilising renewable fuels in SOFCs

It has recently been demonstrated that SOFCs can be run directly on biogas and landfill gas [96]. Biogas is predominantly a mixture of methane and carbon dioxide, the composition of which varies both with location and over time, which presents major difficulties in its use. At CO_2 levels which are too high for conventional power generation systems, SOFCs could, in theory, still extract the power available from the methane content of biogas. Furthermore, as CO_2 is inherently present in biogas in addition to methane, in principle biogas may be used directly in the SOFC without the addition of either steam or oxygen. SOFCs have been run on biogas over a wide compositional range

of methane and CO_2, with internal dry reforming of the methane by the CO2 in the biogas [eqn. (10)] [96].

For any practical application using biogas, the high sulfur content of biogas requires an efficient means of sulfur removal from the biogas prior to it entering the SOFC. Biogas can also contain other impurities, such as halides, which can potentially poison the anode and any reforming catalyst, causing deactivation of the SOFC.

6 Concluding remarks

Solid oxide fuel cells offer tremendous potential for clean, efficient and economic energy generation, especially for combined heat and power and small-scale stand-alone and remote applications. The ability to operate SOFCs directly on a range of practical hydrocarbon fuels, internally reforming the fuel and utilizing the high quality heat by-product, to give high system efficiencies and reduced system complexity, coupled to their ability to utilize carbon monoxide and their greater tolerance to impurities in the fuel, represent significant advantages of the SOFC over low temperature fuel cells.

Significant advances in the preparation and processing of inorganic materials over the last two decades, together with the development of new advanced materials with superior structural, electrical and catalytic properties, mean that SOFCs can be expected to become a commercial reality within the next few years. Such SOFCs will most commonly be operated on natural gas, but with bottled gas being the fuel of choice in certain applications, internally reforming the fuel within the fuel cell. Initial applications are most likely to be combined heat and power systems in the range 1–100 kW, small-scale and remote, stand-alone applications, and applications where there is a requirement for high quality, uninterrupted power supplies, such as in information technology companies, hospitals and airports, and thus a premium for the guarantee of uninterrupted power. Eventually it is hoped that SOFCs will break through into large-scale distributed power generation.

Future challenges involve the development of direct reforming SOFCs, operating on hydrocarbon feeds, without the need for a separate reforming catalyst upstream of the anode. In this context developing anodes capable of stable direct reforming of methane under operating conditions is essential. Another challenge is the development of SOFCs operating at lower temperatures, either by the development of ultra-thin dense, impermeable zirconia electrolyte films, or by the use of alternative solid electrolytes to yttria-stabilised zirconia, such as gadolinia-doped ceria or lanthanum gallate based structures. Lowering the operating temperatures of the SOFC would bring very significant cost benefits in terms of the scope of interconnect, manifold and sealing materials which can be used.

A particularly challenging objective is the development of SOFCs operating on pure hydrocarbon feeds without any oxidant being added to the fuel inlet, instead directly oxidizing the hydrocarbon at the anode using electrochemically pumped oxygen ions formed at the cathode. The major challenge here is the development of anodes which are stable towards carbon formation from hydrocarbon pyrolysis under these conditions.

Recent studies have shown considerable promise in this area, including the use of electrically conducting oxide materials in place of conventional nickel based anodes. Such an SOFC is an extremely attractive proposition, especially if partial oxidation of the hydrocarbon to synthesis gas can be coupled to electricity production, using the SOFC as an electrocatalytic reactor.

Another intriguing possibility, which has recently been demonstrated, is utilizing renewable fuels such as biogas, generated from vegetable matter, and landfill gas, directly in SOFCs.

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