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Advanced Anodes for High Temperature Fuel Cells

A. Atkinson
Imperial College

S. Barnett
Northwestern University

Raymond J. Gorte
University of Pennsylvania, gorte@seas.upenn.edu

J. T.S. Irvine
University of St. Andrews

A. J. McEvoy
Ecole Polytechnique Fédérale

See next page for additional authors

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Advanced Anodes for High Temperature Fuel Cells

Abstract

Fuel cells will undoubtedly find widespread use in this new millennium in the conversion of chemical to electrical energy, as they offer very high efficiencies and have unique scalability in electricity generation applications. The solid oxide fuel cell (SOFC) is one of the most exciting of these energy technologies; it is an all-ceramic device that operates at temperatures in the range 500-1000°C. The SOFC offers certain advantages over lower temperature fuel cells, notably its ability to utilise CO as a fuel rather than being poisoned and the availability of high-grade exhaust heat for combined heat and power or combined cycle gas turbine applications. Although cost is clearly the most important barrier to widespread SOFC implementation, perhaps the most important technical barriers currently being addressed relate to the electrodes, particularly the fuel electrode or anode. In terms of mitigating global warming, the ability of the SOFC to utilise commonly available fuels at high efficiency, promises an effective and early reduction in carbon dioxide emissions and hence is one of the lead new technologies to improve the environment. Herein, we discuss recent developments of SOFC fuel electrodes that will enable the better utilisation of readily available fuels.

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Author(s)

A. Atkinson, S. Barnett, Raymond J. Gorte, J. T.S. Irvine, A. J. McEvoy, M. B. Mogensen, S. Singhal, and John M. Vohs

A. Atkinson¹, S Barnett², R.J. Gorte³, J.T.S. Irvine^{4*}, A.J. McEvoy⁵, M.B. Mogensen⁶, S Singhal⁷, J. Vohs³,

¹Dept of Materials, Imperial College, London, SW7 2BP, UK

²Northwestern University, Department of Materials Science, Evanston, IL 60208, USA

³University of Pennsylvania Department of Chemical Engineering, Philadelphia, PA 19104, USA

⁴School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, UK

⁵DCICMB-FSB, Ecole Polytechnique Fédérale, CH-1015 -LPI Department, EPFL, 1015 Lausanne, Switzerland

⁶Risø National Laboratory, Materials Research Department, P.O. Box 49, Denmark

⁷Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA 99352, USA

ABSTRACT

Fuel cells will undoubtedly find widespread use in this new millennium in the conversion of chemical to electrical energy, as they offer very high efficiencies and have unique scalability in electricity generation applications. The solid oxide fuel cell (SOFC) is one of the most exciting of these energy technologies; it is an all-ceramic device that operates at temperatures in the range 500-1000°C. The SOFC offers certain advantages over lower temperature fuel cells, notably its ability to utilise CO as a fuel rather than being poisoned and the availability of high-grade exhaust heat for combined heat and power or combined cycle gas turbine applications. Although cost is clearly the most important barrier to widespread SOFC implementation, perhaps the most important technical barriers currently being addressed relate to the electrodes, particularly the fuel electrode or anode. In terms of mitigating global warming, the ability of the SOFC to utilise commonly available fuels at high efficiency, promises an effective and early reduction in carbon dioxide emissions and hence is one of the lead new technologies to improve the environment. Herein, we discuss recent developments of SOFC fuel electrodes that will enable the better utilisation of readily available fuels.

INTRODUCTION

Fuel cell technology has been much heralded in recent years as a keystone of the future energy economy. In association with the hydrogen economy, it has been strongly promoted by the governments of most of the world's leading industrialised nations. There is now a phenomenal commercial interest in fuel cell technology with new start-up companies being established and major players in the energy market turning their attention to this technology. The market scale is certainly in the billions of euros per annum. The degree and extent of market penetration and establishment really only depend on the ability to reduce the

cost of these devices whilst ensuring their long-term stability. The technology is certain to be applied; its scale will depend on the success of researchers in improving performance and cost. It is quite likely that the fuel cell's impact upon society will be revolutionary. In the long-term fuel cells are an essential component of any hydrogen or similar clean energy economy, in the short-term they promise greatly enhanced conversion efficiencies of more conventional fuels and so will deliver large reductions in CO₂ emissions.

Fuel cells can be viewed as devices for electrochemically converting chemical fuels into electricity, essentially batteries with external fuel supplies. Fuel cells offer extremely high chemical to electrical conversion efficiencies due to the absence of the Carnot limitation and further energy gains can be achieved when produced heat is utilised in combined heat and power or gas turbine applications. Furthermore the technology does not produce significant amounts of pollutants such sulphur or nitrogen oxides especially when compared to internal combustion engines.

All fuel cells consist of essentially 4 components, the electrolyte, the air electrode, the fuel electrode and the interconnect. In solid oxide fuel cells, which typically operate at temperatures in the range 800-950°C, the electrolyte is normally yttria stabilised zirconia, which offers good oxygen ion transport, whilst blocking electronic transport. The electrolyte's function is to allow the transport of oxygen ions from the electrolyte's interface with the air electrode to its interface with the fuel electrode. The function of the air electrode, which is typically a lanthanum strontium manganese oxide composite with yttria stabilised zirconia, is to facilitate the reduction of oxygen molecules to oxygen ions transporting electrons to the electrode / electrolyte interface and allowing gas diffusion to and from this interface. The function of the fuel electrode, which is the main subject of this review, is to facilitate the oxidation of the fuel and the transport of electrons from the electrolyte to the fuel electrode interface, as well as allowing diffusion of fuel gas to this interface and exhaust gases away from this interface. An appropriate microstructure for the electrode interface along with a schematic of the electrochemical processes is shown in figure 1. The other element is the interconnect, which has traditionally been lanthanum strontium chromite but in lower temperature variants attention has been focused upon corrosion resistant steels. The functions of this component are to transfer electrons between individual cells in the stack, whilst preventing gas crossover between the fuel and oxidant streams.

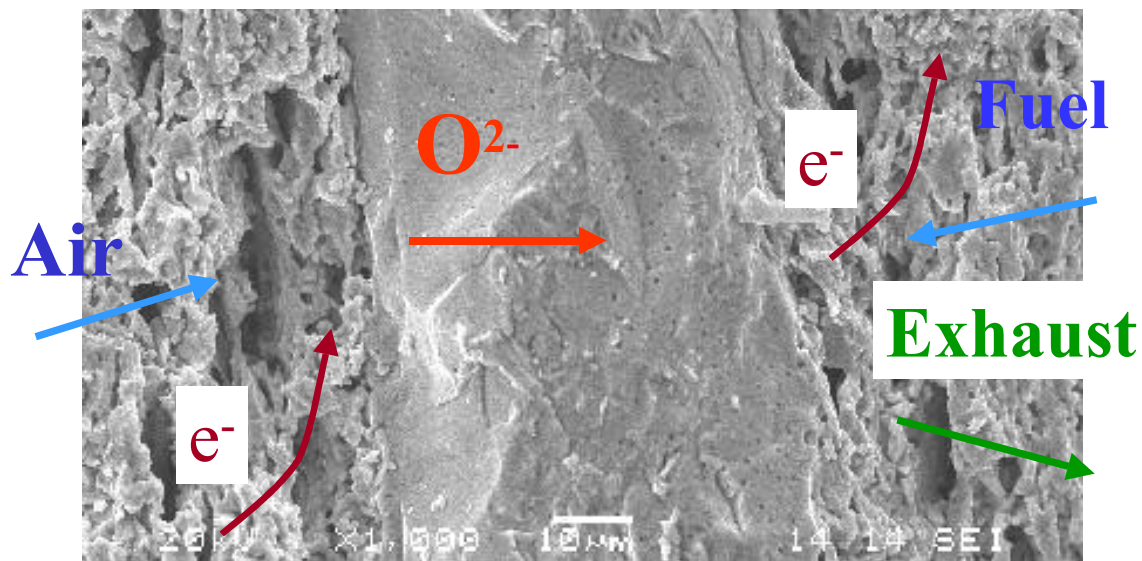


Figure 1 Schematic of processes occurring within the air electrode, electrolyte and fuel electrode and at their interfaces, superimposed upon an appropriate microstructure for such an electrode/electrolyte structure

Solid oxide have a particularly wide range of applications ranging from centralised MW scale generation through to localised applications at 100+ kW level for distributed generation to local domestic generation at the 10 of kW scale.

Just a thought: The DOE SECA program is geared towards 5 kW modules, which is the range required for APU. There are also several groups, including ours and the people at Adaptive Ceramics (University of Michigan) that are working on SOFC in the 20 W range.

There is also a wide range of other applications where cleaner energy is required, such as corrosion protection, uninterruptible power supplies, remote generation and domestic appliances. The most publicised examples are in the automobile sector where companies such as Ford and Renault are looking at high temperature fuel cells for auxiliary power generation and other companies such as Daimler Chrysler are looking at lower temperature polymer based fuel cells for complete electrical generation.

FUELS FOR FUEL CELLS

Each of the many applications for fuel cells in electricity generation has its own characteristic fuel requirements or preferred fuel. Fuels can range from hydrogen to methane to diesel to coal. On the other hand, most fuel cells can work only with fairly pure hydrogen, and those that can use other fuels still typically work best with hydrogen. This mismatch between the desired and/or available fuel and the fuel cell has limited the commercial implementation of fuel cells.

Hydrogen is the fuel normally associated with fuel cells. The first application of fuel cells was for space power – this is well matched with the fuel cell because high-purity fuel (hydrogen) and oxidant (oxygen) are utilized without regard to cost. Fuel cells are also viewed as a key element in a future hydrogen economy, not only because they can very efficiently convert hydrogen to electricity, but because they may also work well as electrolyzers for storing excess energy as hydrogen. However, until hydrogen produced from renewable energy sources is widely available, the hydrogen economy makes little sense since hydrogen is currently produced from hydrocarbons; it is more sensible to produce electricity directly from the hydrocarbon fuels. Nonetheless, reversible fuel cell/electrolyzers using hydrogen as the storage medium should be viable in the near future for matching distributed-generation electricity supply with widely varying demand levels.

Based on the widespread availability of natural gas – methane with small amounts of other hydrocarbons – most stationary fuel cell systems have been designed for this fuel. While direct introduction of either dry natural gas (direct hydrocarbon operation) or steam-natural gas mixtures (internal reforming) to SOFC anodes has been reported, in most cases partial external reforming is used. In this case, the fuel mixture arriving at the fuel cell anode is primarily methane, hydrogen, and CO. There is typically a small amount of intentionally-added sulphur-containing odorant in natural gas that can degrade anode performance if not removed, and some natural gases intrinsically contain larger amounts. Bio-derived fuels, e.g. landfill gas, are often similar to natural gas, but contain a range of impurities such as ammonia, hydrogen sulphide and halogens, usually in quite significant concentrations.

Liquid hydrocarbons, e.g. propane, are also used for a number of stationary power generation applications because of their widespread availability. Because of their high energy densities, liquid hydrocarbons are also preferred for portable and transportation applications. Propane and butane are being considered as portable generator fuels because they are readily available, inexpensive, and are the lowest molecular weight (and highest H-to-C ratio) hydrocarbons that can be easily used in liquid form. Their vapour pressures at ambient temperature are low enough so as to not require high-strength tanks, and yet high enough to avoid the need for a fuel pump. Gasoline and diesel are clearly preferred for transportation. JP-8, a kerosene-like fuel, is desired for military applications. All of these liquid fuels are characterized by a fairly broad range of molecular weights and substantial sulphur-containing impurities, which can cause anode degradation problems including coking and sulphur contamination if not removed.

Alcohols including methanol and ethanol have been widely considered for use in portable fuel cell applications because they are liquid fuels with reasonably high energy densities, are readily available from industrial processes (or renewably from biomass), and have been shown to work with polymer electrolyte membrane fuel cells and SOFCs. Dimethyl ether and ammonia are also industrially-produced fuels that

have been considered for portable applications. These fuels have the disadvantage of being relatively expensive because of processing costs, but have the advantage of being relatively pure.

There is substantial interest in environmentally-friendly utilisation of large coal reserves using fuel cells. Problems are the relatively large amounts of impurities present in many coals, including sulphur and chlorine, and the high degree of CO₂ emission from coal relative to hydrocarbons. Also, coal gasification is needed to produce a gaseous fuel that can be introduced into a fuel cell.

Clearly, there is a diverse range of fuels that could be and are likely to be used in fuel cells. For high temperature fuel cells such as the SOFC there is the important possibility of utilising these fuels without pre-processing or at least with only partial pre-processing. To achieve it is essential to appropriately select and tailor the fuel electrode components and structure.

MATERIALS CHOICE

The materials selection for an SOFC anode is determined by a number of factors. First, the function required of it as the site for the electrochemical oxidation of the fuel associated with charge transfer to a conducting contact. Second, the environment in which it operates, at high temperature in contact not only with the fuel, including possible impurities and increasing concentrations of oxidation products, but also with the other materials, the electrolyte and contact components of the cell, and all this with stability over an adequate commercial lifetime at high efficiency. Third, the processability of the anode, which must be such that an open but well connected framework can be achieved and retained during the fabrication of the fuel cell. With regards to stability, whilst in normal operation the ambient oxygen partial pressure is low, it can vary over several orders of magnitude, and to accommodate fault conditions or even just to provide flexibility of operating parameters, the ability to recover even after brief exposure to air at high temperature would be advantageous. A further aspect of this stability is the maintenance of structural integrity over the whole temperature range to which the component is exposed, from the sintering temperature during fabrication through normal operating conditions and then, repeatedly, cycling down to ambient temperature. Compatibility with other cell component materials implies an absence of solid state contact reactions, with interdiffusion of constituent elements of those materials or formation of reaction product layers which would interfere with anode functionality. It also requires a match of properties, such as shrinkage during sintering and thermal expansivity to minimise stresses during temperature variations due to operating procedures, start-up and shut-down.

By definition of its role, it is a requirement that the anode material should be an adequate electronic conductor, and also be electrocatalytically sufficiently active to sustain a high current density with low overpotential loss. However the catalytic behaviour of anode materials should not extend to the promotion

of unwanted side reactions, hydrocarbon pyrolysis followed by deposition of vitreous carbon being an example. An intimate contact between the two solid phases, the electrolyte delivering the oxide ions and the anode on which they are electrically neutralized, is clearly essential, as is access of the fuel and removal of reaction products, these being in the gas phase. On this model the reaction is therefore sited on a "three-phase boundary" zone. Low loss operation implies that the three-phase boundary is not dimensionally limited to a planar interface of solid materials, but that it be delocalised to provide a "volumetric" reaction region in three dimensions, porous for gas diffusion and permitting both electron and ion transport. One option is to provide a single-phase electrode with mixed conductivity permitting both oxygen ion and electron mobility within the anode material. The alternative is to employ a porous composite, as in the nickel cermetes that have typically been used in SOFCs to date.

Ni Cermet Anodes

After some early investigations using single-phase anodes, nickel zirconia cermet anodes have been the dominant SOFC anode for some forty years. Single-phase materials investigated in the earliest SOFC developments included graphite, iron oxide, platinum group and transition metals (1,2). Graphite is corroded electrochemically and platinum spalls off in service, presumably due to water vapour evolution at the metal oxide interface. As for the transition metals, iron is no longer protected by the reducing activity of the fuel gas once the partial pressure of oxidation products in the anode compartment of an operating cell exceeds a critical value, and it then corrodes with formation of a red iron oxide. Cobalt is somewhat more stable, but also more costly. Nickel has a significant thermal expansion mismatch to stabilized zirconia, and at high temperatures the metal aggregates by grain growth, finally obstructing the porosity of the anode and eliminating the three-phase boundaries required for cell operation. As a consequence, all-metal anodes have not found acceptance. This was the context for the introduction of the nickel-zirconia cermet anode by Spacil (3). His 40 year old text remains a strikingly modern presentation of the anode specification, making reference to many of the concepts and procedures still current in SOFC technology and which have made this composite the current standard anode material. As the best transition metal option, he associated nickel with the stabilised zirconia ceramic material of the electrolyte to confront the two problems mentioned, the difference of thermal expansion which would mechanically stress any nickel anode – electrolyte bond, and the aggregation in service. A minimum metal proportion in the cermet is necessary for continuity of electronic conduction, while the zirconia particles may be noncontinuous. Spacil had therefore recognised that the functionality of the ceramic in the composite was essentially structural, to retain the dispersion of the metal particles and the porosity of the anode during long-term operation. Structure and elemental distribution in a typical anode cermet are imaged in Figure 2. The provision of oxide ion mobility complementary to the electronic conductivity and electrocatalytic

action of the metal is a very important secondary role of the ceramic, enhancing the electrochemical performance by the delocalisation of the electrochemically active zone already mentioned.

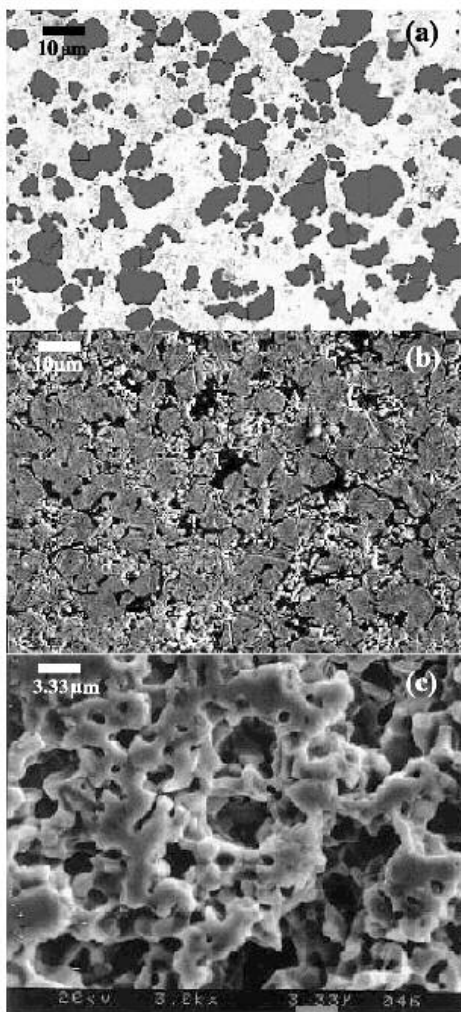


Figure 2: Image of a Ni – YSZ cermet by scanning electron microscopy with elemental mapping, showing (a) nickel distribution; (b) overall cermet morphology; and (c) zirconia structural skeleton (4).

The major disadvantage of the Ni cermet electrode arises from the promotion of competitive catalytic cracking of hydrocarbon reactions. The rapid deposition of carbon at Ni cermets means that direct oxidation of methane is not technically viable in Ni-containing solid oxide fuel cells. In order to utilise natural gas as fuel, the fuel needs to be externally or internally reformed with steam.

Catalytic Properties

The catalytic properties of the anode in a SOFC are very important in determining the overall cell performance. In the commonly used Ni/YSZ cermet anode, Ni has the dual roles of catalyst for hydrogen oxidation and electrical current conductor. In addition to being an excellent catalyst for the oxidation of hydrogen, Ni is highly active for the steam reforming of methane. This catalytic property is exploited in so called internal reforming SOFCs that can operate on fuels composed of mixtures of methane and water. In these systems the $\text{CH}_4/\text{H}_2\text{O}$ mixture reacts on the Ni anode producing a H_2 -rich synthesis gas which then undergoes electrochemical oxidation at the three phase boundary. Due to the thermodynamic limitations of the steam reforming reaction, internal reforming SOFCs generally operate at temperatures above 900°C . Some application scientists have also termed reforming that occurs within the stack but external to the SOFC as internal reforming, but this seems misleading and in-stack reforming is a more appropriate term.

Although Ni is an excellent hydrogen oxidation and methane steam reforming catalyst it also catalyses the formation of carbon filaments from hydrocarbons under reducing conditions. The mechanism involves carbon formation on the Ni surface, carbon dissolution into the bulk Ni, and precipitation of graphitic carbon from some facet of the Ni particle after it becomes supersaturated in carbon [5]. Unless sufficient amounts of steam are present along with the hydrocarbon in order to remove carbon from the Ni surface at a rate faster than that of carbon dissolution and precipitation, the anode will be destroyed. While thermodynamic calculations are often used to predict the conditions under which carbon formation is favoured [6], carbon fibres can be formed even when carbon is not thermodynamically predicted. This is particularly true in the presence of higher hydrocarbons, since these molecules form carbon on the Ni surface more rapidly than steam can remove it. As a result, even when using methane as the fuel relatively high steam-to-carbon ratios are needed in order to suppress this deleterious reaction. Unfortunately, due to the high catalytic activity of Ni for hydrocarbon cracking, this approach does not work for higher hydrocarbons and it is generally not possible to operate Ni-based anodes on higher hydrocarbon-based fuels, without pre-reforming with steam or oxygen.

One approach to overcoming the limitations of Ni anodes, which has met with some success, is to augment the oxidation activity of Ni/YSZ cermets via the addition of an oxide-based oxidation catalyst. For example stable operation on dry methane at 650°C in an SOFC using an yttria-doped ceria interlayer between the YSZ electrolyte and the Ni/YSZ cermet anode [7]. Ceria is a well-known oxidation catalyst and increases the activity of the anode for the electrochemical oxidation of methane. This approach still requires, however, that the operating temperature be maintained below 700°C , in order to suppress carbon deposition reactions, which take place on Ni.

Most research aimed at overcoming the limitations of Ni-based anodes has focused on the development of alternative anode materials that are catalytically active for the oxidation of methane or higher hydrocarbons and inactive for cracking reactions that can lead to carbon deposition. This latter criterion is a difficult one and rules out most transition metals with the possible exception of Cu, Ag, and Au. While these metals make good current collectors they are not highly active oxidation catalysts. Since many metal oxides are excellent oxidation catalysts and are not active for catalytic cracking, most of the work in this area has focused on the development of electronic or mixed electronic-ionic conducting, ceramic anodes. As discussed below, these materials were generally chosen based on their electronic and ionic conductivities rather than their catalytic properties. Although stable performance while operating on hydrocarbons, principally methane, has been achieved in SOFCs which use many of these materials as anodes, it is likely that their catalytic properties are not optimal. The use of composite ceramic anodes has been suggested as one avenue for optimising both the transport (ionic and electronic) and catalytic properties of ceramic anodes.

Although catalytic anodes that allow for the operation of SOFCs directly on hydrocarbons have been developed, the performance of these anodes (e.g. maximum current density) is still not at the level obtained in state of the art SOFCs with Ni/YSZ anodes operating on hydrogen. Thus there is still much room for improvement in the catalytic properties of SOFC anodes designed to directly utilise hydrocarbons. Understanding the mechanisms of the surface reactions that occur on the anode near the three-phase boundary is likely to be key to further advances in this area. Unfortunately, fundamental insight into these reaction mechanisms is rather limited. For systems that directly utilise hydrocarbon fuels, the mechanism of the surface oxidation reactions is undoubtedly highly complex and involves multiple elementary steps and reaction intermediates. At the very least it would be useful to identify the rate limiting step or steps in the reaction mechanism. Even for Ni/YSZ cermet anodes, the mechanism for hydrogen oxidation reactions is not completely understood. For example it has been shown that the rate of this reaction is dependent on water partial pressure with higher pressures resulting in higher reaction rates [8]. The mechanism by which water affects this reaction is currently under discussion, with the speculation that the zirconia surface is hydroxylated.

There is clearly a need for fundamental studies of the mechanisms of the catalytic reactions that occur near the three-phase boundary in the anode of a solid oxide fuel cell. Many *in situ* spectroscopic probes such as Raman and infrared spectroscopy are routinely used in catalysis research to characterize surface intermediates and reaction mechanisms. It is very difficult, however, to apply these techniques to an operating SOFC anode. Nonetheless some inroads are being made in this area. For example, Liu and co-workers [9] are pioneering the application of infrared emission spectroscopy to characterize working SOFC anodes. Although these studies are in the early stages, preliminary results appear very promising.

Development of models of anodes that allow other spectroscopic probes such as photoelectron spectroscopy and detailed kinetic measurements to be made are also needed in order to advance research in this area.

Other Cermets

In order to find alternative anodes with lower susceptibility to hydrocarbon cracking, alternative cermets to nickel yttria zirconia have been sought. Interest has largely focused on ceria replacing zirconia and copper replacing nickel. One approach is to alloy copper with nickel, for instance Bernardo et al [10] added copper to nickel to reduce the catalytic activity of nickel for hydrocarbon cracking. The influence of adding nickel to $(\text{Ce,Zr})\text{O}_2$ or $(\text{Ce,Y,Zr})\text{O}_2$ to form a cermet was also studied [11] and cerium oxide is reported as a promising support. In a series of publications, Gorte et al [12,13] reported that noble metals (Pd, Pt, Rh) had much higher specific rates for water gas shift, steam reforming and carbon dioxide reforming of methane when supported on cerium oxide than when supported on silica or alumina. Ramirez-Cabrera et al [14] studied gadolinium-doped ceria, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) as an anode material at 900°C in 5% CH_4 with steam/methane ratios between 0 and 5.5. This material revealed itself to be resistant to carbon deposition, although the reaction rate was controlled by slow methane adsorption. Marina et al [15] studied the same catalyst for methane oxidation and it was demonstrated that ceria has a low activity for methane oxidation but a high resistance to carbon deposition. It was proposed to add a catalyst (Ni, Rh, Ru) to break the C-H bond more easily.

In contrast to the reported inactivity of acceptor-doped ceria, undoped ceria has been reported to be quite an effective oxidation catalyst, this can be attributed to the presence of oxygen vacancies making the doped material more difficult to reduce and hence a less effective catalyst. Ceria is a well-known oxidation catalyst and increases the activity of the anode for the electrochemical oxidation of methane. This approach still requires, however, that the operating temperature be maintained below 700°C , in order to suppress carbon deposition reactions, which take place on Ni. Another approach being used in the development of cermet anodes that allow the use of fairly dry hydrocarbon is to use a relatively inert metal such as Cu for electrical conductivity and a metal oxide to provide catalytic activity and ionic conductivity. Examples of this type of composite anode include Cu/CeO₂/YSZ [16] and Cu/YZT (titania doped yttria zirconia) [17]. The Cu/CeO₂/YSZ anode system is particularly interesting and has been shown to be effective for the direct utilization of a variety of hydrocarbon fuels including butane and decane and highly resistant to deactivation via carbon deposition [18]. The role of Cu in these anodes appears to be exclusively current conduction while ceria primarily acts as an oxidation catalyst. It has been shown that SOFCs that have anodes that contain only Cu and YSZ exhibit very poor performance

while operating on hydrocarbons. The addition of ceria to the anode, however, produces a marked increase in performance while operating on both hydrogen and hydrocarbons. It is important to note that SOFCs with Cu/CeO₂/YSZ anodes always exhibit even higher current densities while operating on hydrogen compared to hydrocarbons. This indicates that catalysis plays a critical role and suggests that enhancements in the catalytic activity of the anode are still needed in order to optimize performance using hydrocarbon fuels.

Alternative Anode Materials

The basic properties of the “standard” Ni/zirconia or Ni/ceria cermets are well established and for these materials the requirement is to optimise their properties through control of microstructure and minor additives. The situation is different for oxide anodes where the requirement is still at the stage of identifying suitable candidates. Oxides are under investigation as single phase anodes, single phase anode current collectors and components of composites for either of these functions. In addition to electrochemical performance, the candidate materials need to display other characteristic properties, some being essential and some desirable. These properties include: electronic conductivity; oxygen diffusivity (ionic conductivity); oxygen surface exchange; chemical stability and compatibility; compatible thermal expansion; mechanical strength and dimensional stability under redox cycling. For application as a current collector, electrochemical activity is not required and therefore oxygen diffusivity and surface exchange properties are not relevant. In this section we briefly review what is known about these properties for leading candidate materials and identify areas where further work is required. The materials of interest at this stage are ceria (doped and undoped) and transition metal perovskite and fluorite-related structures. From the point of view of chemical stability under reducing conditions, oxides containing large amounts of Co and Ni are probably not viable and so the emphasis is on Fe, Mn, Cr and Ti as transition metal ions that can be used to give electronic conductivity. The relevant properties of some typical candidate oxide anode materials are summarised in Table 1.

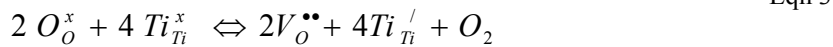
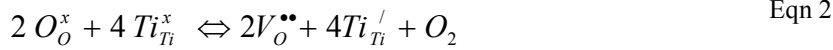
The target for electronic conductivity for anode materials is often set to be 100 S cm⁻¹, but the actual requirement depends on the cell design and particularly the length of the current path to the current collection locations. Thus this could be relaxed to as low as 1 S cm⁻¹ for a well-distributed current collection. Similarly, if the material were used as a porous support and current collector with thickness of 0.5 mm it would also need a conductivity greater than approximately 1 S cm⁻¹ to maintain losses below 0.1 ohm cm². Since these are targets for porous structures, the actual requirement for the intrinsic materials properties, i.e. in dense form, would need to be about 1 order of magnitude greater.

A suitable benchmark material is the perovskite $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$, which has been thoroughly investigated as an interconnect material for SOFCs [19] and is also a potential anode material for SOFCs due to the relatively good stability in both reducing and oxidising atmospheres at high temperatures [20]. The acceptor doping gives high p-type conductivity in air but, as with all p-type materials, this decreases under reducing conditions. Addition of reducible transition metals such as Ti can introduce significant n-type contribution at low $p(\text{O}_2)$ s but the dilution of Cr on the B-site generally has a greater effect [21], substitution of mid-transition metals such as Mn or Fe does not have such a dilution effect, indicating some complementarity of electronic function and affords an extension of the p-type domain to lower $p(\text{O}_2)$ s, although conductivities are still below 10 Scm^{-1} under reducing conditions [22]. It is interesting to note that whilst n-type electronic conductivity would seem the more natural form of electronic defect under fuel conditions, p-type conduction, if it can be retained to low partial oxygen pressures offers a significant advantage, in that conductivity will increase under load.

The reported polarization resistance using chromite perovskites is generally too high for efficient SOFC operation, although significant improvements have been achieved using low level doping of the B-site. With 3% replacement of Cr by V methane cracking seems to be avoided, although the polarisation resistance is still of the order $10 \Omega\text{cm}^2$ at 900°C [23]. The introduction of other transition elements into the B-site of $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{M}_y\text{O}_3$ ($\text{M} = \text{Mn, Fe, Co, Ni}$) has been shown to improve the catalytic properties for methane reforming [24]. Of these various dopants, nickel seems to be the most successful and the lowest polarisation resistances have been reported for 10% Ni-substituted lanthanum chromite [25]; however, other workers have found nickel exsolution from 10% Ni-doped lanthanum chromites in fuel conditions [26]. Certainly nickel oxides would not be stable in fuel atmospheres, and although the nickel may be stabilised by the lattice in higher oxidation state, there will always be the suspicion that the activity of nickel doped perovskites is due to surface exsolution of nickel metal, and hence raise questions about long term stability. A particularly successful approach has been to create perovskites with dual B-site occupancy, such as those based upon lanthanum chromium manganite [22]. This approach has very successfully combined the good oxidation catalysis properties of lanthanum manganite with the stability and conductivity of the chromite, without compromising any of these good properties by dilution.

Donor doping on the A-site is difficult for 3,3 perovskites, but has been very successful for 2,4 perovskites. Conventional donor doping leaves the A sites filled so that the A:B ratio remains stoichiometric at 1:1. However, a better strategy has been to maintain constant total A-site charge so that the material is approximately compensated by vacancies on the A-sites ($\text{A}:\text{B}$ ratio < 1). The Schottky equilibrium between these A-site vacancies and oxygen vacancies, eqn 1, means that it becomes easier to create electronic carriers by reduction, eqn 2. Conversely the introduction of oxygen vacancies, eg eqn 3, means that increasing oxygen vacancy concentration must make it more difficult to create electronic

carriers by reduction at a given $p(O_2)$. Thus A-site deficient strontium titanates exhibit relatively high conductivity under fuel conditions [27, 28]. The standard donor doping method, replacing Sr by La has also proved very successful recently, especially in combination with ceria[29]. Effectively these compositions are oxygen hyper-stoichiometric, except when prepared under very reducing conditions and it has recently been suggested that such lanthanum strontium titanates contain extended defects analogous to the oxygen shear planes observed in lanthanum titanate, $La_2Ti_2O_7$. Nonetheless, such materials offer very high conductivities[30]. Rutile structures such as NbO_2 or Nb_2TiO_6 offer very high electronic conductivity under fuel conditions, but with very low thermal expansion coefficient [31]. Although initial studies demonstrated good compatibility with zirconia electrolytes [31], later work has shown poor compatibility with ceria electrolytes.



All these materials seem to meet the essential requirement of chemical compatibility with YSZ. However, data on other relevant properties are rather sparse. $Sr_{0.86}Y_{0.08}TiO_3$, $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$, $La_{0.8}Sr_{0.2}Fe_{0.8}Cr_{0.2}O_3$ and $La_{0.8}Sr_{0.2}Cr_{0.95}Ru_{0.05}O_3$ all have acceptable thermal expansion match to YSZ under reducing conditions, but heavier Sr doping for some of these leads to anomalous expansion coefficients and unacceptably large dimensional changes on redox cycling. Better understanding of the factors that contribute to these dimensional changes would be valuable.

Very little is known about the oxygen diffusivity (ionic conductivity) and surface exchange of oxygen under reducing conditions in any of these materials. Such studies have proved valuable in understanding the behaviour of cathodes and now need to be applied to anode materials. So far only $La_{1-x}Sr_xFe_{0.8}Cr_{0.2}O_3$ has been studied in this way.

Table 1 Summary of properties of some potential oxide anodes at 800°C under reducing conditions (p_{O_2} approximately 10^{-20} atm)

Material	Electronic conductivity ($S\ cm^{-1}$) ¹	Ionic conductivity ($S\ cm^{-1}$)	Oxygen diffusivity ($cm^2\ s^{-1}$)	Redox stability ²	Polarisation Resistance ₃	CTE ($ppm\ K^{-1}$)
CeO ₂ [32]	0.5-1[33]	0.1-0.2[33]	1E-6[34]	XX	**	12
Zr _{1-x-y} Ti _x Y _y O ₂ [35]	0.1	1E-2	?	**	*	10
La _{0.8} Sr _{0.2} Cr _{0.95} Ru _{0.05} O ₃ [36]	0.6	low	?	*	**	10
La _{0.8} Sr _{0.2} Fe _{0.8} Cr _{0.2} O ₃ [37]	0.5	?	1E-8	*	**	12
La _{0.25} Sr _{0.75} Cr _{0.5} Mn _{0.5} O ₃ [22]	3	?	?	**	***	10
Sr _{0.86} Y _{0.08} TiO ₃ [28]	80	low	?	***	*	11-12
La _{0.33} Sr _{0.66} TiO _{3.166} [29,30]	40	low	?	***	*, *** ⁴	10
Nb ₂ TiO ₇ [31]	200	Very low	?	X	-	1-2
Gd ₂ Ti(Mo,Mn)O ₇ [38,39]	0.1	reasonable	?	XXX	*	?

¹ Should only be considered as a rough guide as factors such as partial pressure of oxygen, density and microstructure are not standardised.

² *** - excellent to XXX very poor

³ These values are strongly dependent upon microstructure and will vary between different laboratories, as an indication values are ,***< $0.1\ \Omega cm^{-2}$, *** $0.1 - 0.3\ \Omega cm^{-2}$, ** $0.3-1\ \Omega cm^{-2}$, * $1 - 10\ \Omega cm^{-2}$

⁴ high performance for composite with ceria

Direct Conversion

A subject that is receiving increased attention is the development of new anode materials for direct conversion of hydrocarbon fuels without first reforming those fuels to CO and H₂. Elimination of the reforming step would decrease system complexity and avoid the necessity of diluting fuels with steam. For higher hydrocarbons, there are also energy losses associated with the need to partially oxidize the fuel. In principle, an SOFC can operate on any combustible fuel that is capable of reacting with oxide ions coming through the electrolyte. In practice, the high operating temperatures in the presence of hydrocarbons can lead to carbon formation, e.g. as discussed above for Ni based anodes.

Three strategies for direct conversion of are possible. The first strategy [**Error! Bookmark not defined.**], utilises conventional Ni-cermet anodes but modifies the operating conditions of the fuel cell. For methane at intermediate temperatures, the rate of carbon deposition may be slow enough so that oxygen anions diffusing through the electrolyte and steam generated by oxidation of methane will remove carbon as it is deposited.

A second strategy to avoid reforming involves replacing Ni cermets with composites containing Cu and ceria. Cu is relatively inert towards the carbon-formation reactions that occur on Ni, and stable operation has been observed with even large hydrocarbons over Cu-based anodes [16]. Gas-phase pyrolysis reactions can still lead to tar formation on Cu cermets; however, the compounds that form on Cu tend to be poly-aromatics, like naphthalene and anthracene, rather than graphite. It has been suggested that the poly-aromatic compounds enhance anode performance by providing additional electronic conductivity in the anode [40], figure 3.

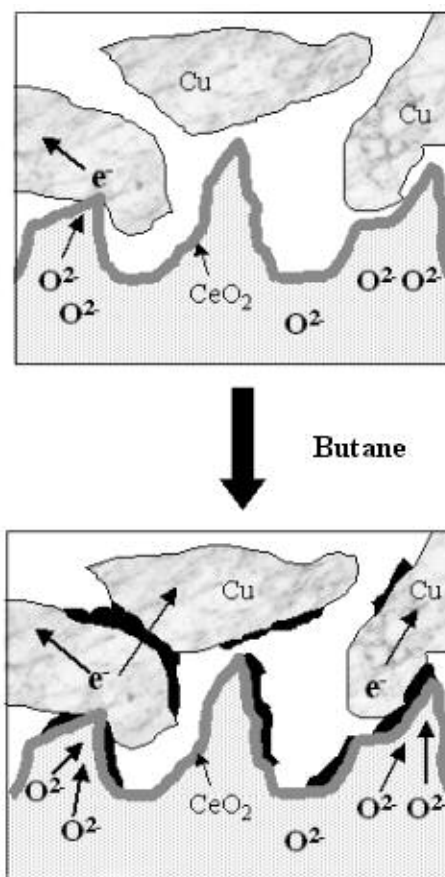


Figure 3 Schematic diagram of Cu/CeO₂ YSZ (or SDC) microstructure showing enhanced current collection following tar deposition after initial exposure to butane under operating conditions.

It appears that Cu primarily provides electronic conductivity to the anode and is otherwise catalytically inert. This is confirmed by data showing that Au-ceria-SDC (samaria-doped ceria) composites exhibit a similar performance to that of Cu-ceria-SDC anodes, as Au would not be expected to add catalytic activity [41]. It is proposed that the function of ceria is primarily that of an oxidation catalyst, although mixed electronic-ionic conductivity (MEIC) could also enhance anode performance. In general, finely dispersed ceria seems more active than doped ceria ceramics, thus the redox oxygen exchange ability of ceria at fuel conditions might be considered as a key factor.

The third strategy for developing SOFC that can operate directly on hydrocarbon fuels involves anodes made from electronically conductive ceramics, since these are also tolerant towards carbon formation. Reasonable performance can be achieved with direct utilisation of methane

using an anode made from La-doped strontium titanate [29,30]; however, the addition of ceria to this doped SrTiO₃ enhanced the performance significantly [29]. Reasonable performance in methane can also be obtained with anodes made from Gd-doped ceria [42]. Barnett has also reported stable power generation with methane and propane fuels on an anode based on Mn-doped LaCrO₃ with YSZ and 5% Ni [43]. The addition of Ni, in amounts small enough to avoid carbon formation, was found to enhance the performance of the LaCrO₃ anodes. Similar good performance has been achieved using Ni [44] and Ru [45] substituted lanthanum chromites and most recently the split B-site perovskite (La,Sr)Mn_{0.5}Cr_{0.5}O₃ that provides both very good performance and good chemical stability [22].

An important issue for direct utilization of hydrocarbons in all of the strategies is the question of mechanism, since this relates directly to the potential of the electrons that are produced in the cell. While it has been demonstrated that there is a balance between the production rate for the total oxidation products and the generation of current [16], the cell potentials that have been reported with hydrocarbon fuels are much lower than would be predicted by direct, electrochemical oxidation of the hydrocarbons in a single step. It seems clear that at the very least the direct utilisation processes involve an initial activation step, perhaps just involving the breaking of one carbon-hydrogen bond. Indeed, the appearance of tars on Cu/CeO₂ composites utilising hydrocarbons [40] certainly indicates that some pyrolysis reactions may help initiate the hydrocarbon oxidation process in these systems. The efficient oxidation of produced CO or carbon at ceria may well be the key to the effectiveness of these materials in direct utilisation of hydrocarbons, since ceria itself is viewed as being only a moderately good catalyst [16]. Conversely much of the effort on direct utilisation has focused on reforming activity, especially for transition metal doping of lanthanum chromite based materials. It is worthwhile remembering that one of the main oxidation products is steam, so reforming can still occur even with dry fuel sources. This has led to the concept of gradual internal reforming, figure 4, which effectively provides a direct utilisation mechanism [46]. Preliminary investigations of the activity of the chromium manganite perovskite reported by Tao [22] indicate poor reforming and good oxidation activity, so this material may act in a similar manner to ceria and so its catalytic properties seem more closely related to a manganite than a chromite. The various processes that can contribute in combination to effectively achieve direct utilisation are presented in figure 5.

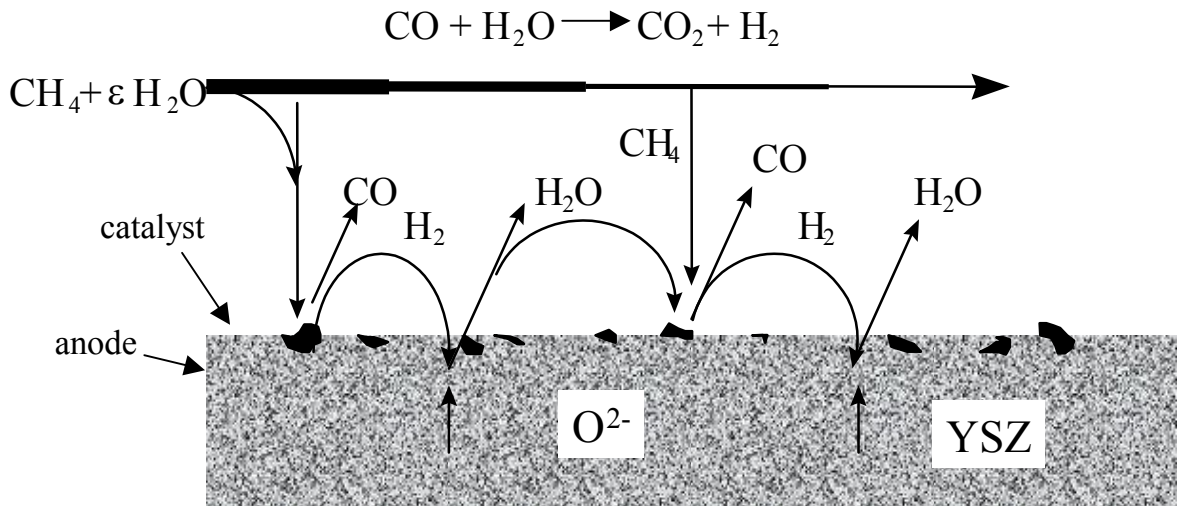


Figure 4: Schematic diagram illustrating series of processes that lead to the gradual internal methane reforming [46]

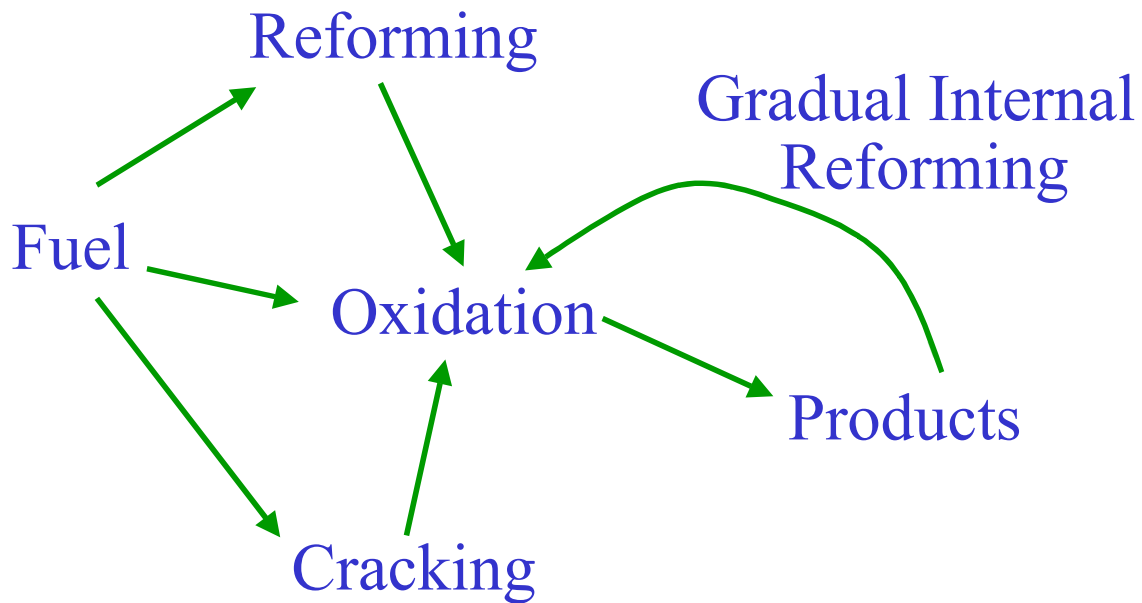


Figure 5 Diagram showing the contributing processes that can give rise to the direct utilisation of hydrocarbon fuels in solid oxide fuel cells

Microstructural Compromise

So far the discussion has related largely to the compositional nature of of candidate anodes; however, the microstructure of the electrode is at least as important as its composition. The

optimisation of durable efficient nickel cermet anodes in recent decades has relied greatly on empirical improvement of materials specifications to control cermet morphology. With modern submicron active ceramic powder, the sintering temperature can be significantly decreased, to 1400°C or lower and lower metal contents can be achieved. Associated with the reduced thermal expansivity of the cermet due to the increased ceramic content, stresses during fabrication, reduction and operation are minimized, eliminating microfissuring which contributes to electrode ageing [47]. Nickel oxide of grain size around 1 μ is now used, while the ceramic component may be bidispersed, containing a proportion of coarse powder with grains of 25 μ or larger to form the anode structural skeleton and inhibit the nickel aggregation, mixed with active submicron fine powder to promote sintering. These procedures are applied to the conventional electrolyte-supported configuration where the stabilized zirconia substrate, 150 μ or thicker, also provides the overall structural integrity of the cell. Much recent development has extended the function of the material used for the electrochemical anode to become also the load and stress-bearing support for an electrolyte now no thicker than 10 μ . This permits lowering the operating temperature to perhaps 650°C whilst providing adequate cell performance. Under these conditions materials specifications throughout the system are relaxed, with lower cost metallic structural and interconnect components, and with diminished thermomechanical stresses and reactions between materials, thereby significantly improving durability. The structural cermet, now up to 1 mm. thick, provides not only the anode functionality, but can also serve as a reaction volume for fuel processing, such as internal reforming. However the lower temperatures significantly diminish the thermal activation of the oxidation reactions, implying increased polarization and giving added importance to considerations of electrocatalysis at the anode [48]. This makes a graded anode structure advisable, with a high porosity large grain substrate bearing a finer-structured electrocatalytically active functional layer to contact with the electrolyte.

An important distinction between Cu-cermet and Ni-cermet anodes is in the required synthesis conditions. Cu-YSZ cermets prepared by calcining mixtures of CuO and YSZ, the method conventionally used to prepare Ni cermets, are unstable in reducing atmospheres above 650°C, indeed, Cu seems a remarkably mobile species [49]. It is necessary to calcine the CuO-YSZ mixtures at relatively low temperatures in order to avoid melting of the CuO, making it less easy to achieve a well connected, YSZ skeleton; however the easy migration of the Cu phase makes such composites seem untenable with respect to long term stability. The success of the Cu/CeO₂ system [16] is therefore quite extraordinary and can only be ascribed to a very advantageous microstructure. In this system a porous skeleton is first obtained by ceramic methods and then the

Cu and ceria are added in subsequent, low-temperature steps. The thermal stability is certainly very much improved upon that of more conventionally prepared systems with stable operation reported up to 800°C [16]. Such systems also offer remarkably high conductivities considering the low copper contents, e.g. ~10% by weight. These considerations can only mean that the Cu forms an intimate near continuous thin network within the retaining skeleton. Some carbon deposition is found to enhance conduction bridging some of the links between the Cu network [40]. The success of this system ably demonstrates the importance of controlled interfacial and microstructural engineering. Indeed it must be realised that the anode electrolyte microstructure is the dominant feature governing fuel electrode activity. Therefore care must always be taken in ranking new materials in terms of activity without appropriately considering microstructure.

Summary and recommendations for research on materials properties

Major advances in SOFC anode development have been achieved in recent years and there is good encouragement that new fuel electrode formulations for second generation commercial fuel cells can be found. Such new anodes will offer improved redox tolerance and better resistance to coking in hydrocarbon fuels. Two key strategies have been identified, based on oxidation catalysts such as ceria or lanthanum chromium manganite or reforming catalysts such as nickel or ruthenium doped lanthanum chromite. Additionally the function of electronic conductivity in the anode current collector has also been addressed in oxides such as those based upon strontium titanate. Although no single material fulfils all the current collection, electrochemical and catalytic performance indicators required for a supported electrode design to the extent that nickel zirconia cermets do, a number of systems individually meeting these criteria have been attained. Clearly new composites are possible to fulfil the roles of both the active electrode layer and the current collecting part.

Further research is required to optimise these materials (composition and microstructure); particularly to maximise electronic conductivity without sacrificing essential chemical stability under reducing conditions. Detailed studies are required on the most promising materials to establish and understand dimensional stability on redox cycling and long-term operation and how this can be improved without compromising electrical conductivity. Studies of oxygen diffusion, ionic conductivity and surface exchange in reducing environments are required on the most promising materials in order to improve understanding of their electro-catalytic properties. Particular care is necessary to allow reproducibility of results between laboratories and especially

to ensure that meaningful experiments are performed before their results are presented. Understanding of crystal structure, point defect populations and electronic structure need to be improved at a fundamental level and related to the key properties mentioned above in order to guide the search for new materials. More basic work to probe the mechanistic details of fuel utilisation reactions needs to be undertaken. These details are extremely important to rational design of more efficient anodes and thus high-performance SOFCs powered by practical fuels. Practical studies in real fuels need to be expanded, especially addressing issues such as sulphur tolerance and ability to utilise biofuels. The search for totally new oxide materials with even better properties should continue, because even the best ones only just meet the requirements. Most importantly this should include the highest possible electronic conductivity since such a material would also serve as a current collector.

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