

Solid-State Ionic Devices

by Eric D. Wachsman and Enrico Traversa

Solid-state ionic devices can be used to harness chemical energy to produce electricity in a fuel cell (SOFCs), convert one chemical species to another (both with and without application of an electric potential), separate one chemical species from another, or detect chemical species by producing an electric signal. SOFCs were described in a companion article in this issue, and in this article we focus on some of the other applications of solid-state ion conducting materials.

Solid-State Electrolytic Devices

Numerous electrolytic devices are made possible by solid-state ion conducting materials, whereby an applied electric potential is used to drive specific chemical reactions. Examples include high temperature steam electrolysis, upgrading of hydrocarbons, and pollution control (e.g., NO_x reduction).¹ Among these, ceramic oxygen generators (COG) are receiving the greatest attention for medical and aerospace applications because they can readily produce a pure oxygen gas stream from ambient air.

Compact COGs are being developed to provide a continuous supply of oxygen-enriched air for people with breathing disorders. Similarly, these devices can enrich the breathing oxygen concentration for high altitude aircrafts. More recently this technology has sparked the interest of NASA for space exploration. Because of the distance involved, if we are to travel to other planets in the future, we need to utilize available planetary resources (*in-situ* resource utilization, or ISRU) for life support and propellant production. An example is NASA's plan to send a manned mission to Mars. In order for this to be feasible this mission will require the utilization of the Mars CO_2 atmosphere to produce the propellant for the return trip and oxygen, both for breathing and the fuel oxidant. The technology envisioned to make this possible is based on a COG converting CO_2 to O_2 and CO. Experimental results demonstrating the efficacy of this technology are shown by the Faradaic oxygen production from CO_2/CO gas mixtures² in Fig. 1. This technology also has potential for mine safety, military, and emergency response applications.

Ion Transport Membranes and Membrane Reactors

Gas separation and purification is one of the most important industrial chemical processes. Major advances in

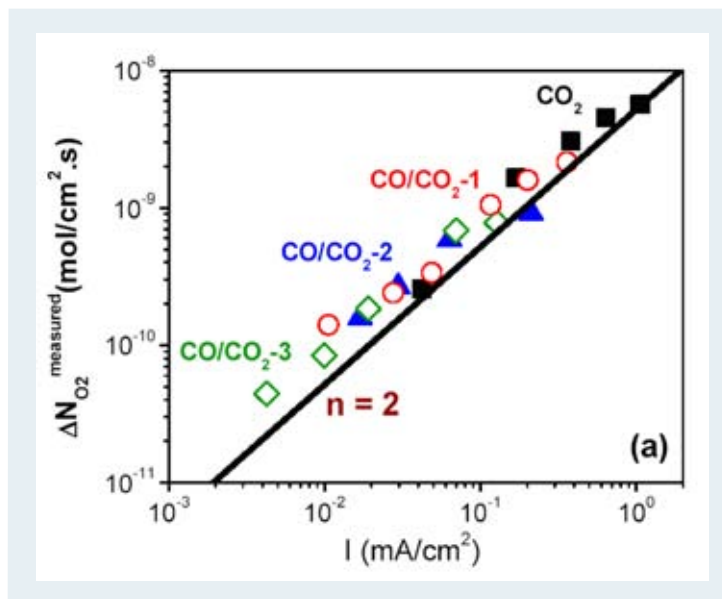


Fig. 1. Faradaic production of O_2 from CO/CO_2 gas mixtures in a ceramic oxygen generator (from Ref. 2).

gas separation technology have been achieved using membranes, either porous³ or dense (e.g., Pd alloys for H_2 separation⁴), operating under a pressure (total or partial) gradient. Among these, ion transport membranes (ITM) are receiving a lot of attention due to their unique properties and ability to integrate with other chemical processes. In fact, recent advances in ITM technology present the possibility for a dramatic reduction in the cost of producing pure O_2 , as well as converting petroleum, coal, and even biomass-derived feed stocks to H_2 and other “value added” hydrocarbons. Because of this potential, several major corporations are actively pursuing development of this technology.

ITMs are based on dense, high-temperature, ion-conducting ceramics, typically perovskite oxides. In the oxygen-ion conductors, an oxygen-ion moves from a filled (O_O^\times) to a vacant ($\text{V}_\text{O}^{\bullet\bullet}$) oxygen site through a fixed cation lattice (M_M^\times). Therefore, the actual charged solid-state ionic species involved in oxygen-ion transport are $\text{V}_\text{O}^{\bullet\bullet}$. In the proton-conducting oxides the proton is associated with an oxygen site ($\text{OH}_\text{O}^\bullet$) and hops between adjacent oxygen sites. Because oxygen and hydrogen are transported through lattice sites (vs. porous membrane diffusion), the gas separation selectivity is essentially infinite. This is a dramatic improvement in selectivity over porous gas separation membranes that employ size exclusion (the difference in size between gas molecules relative to the pore size) as the mechanism for separation.³ In addition,

ionic transport is a thermally activated process and high ionic conductivities, ~ 1 S/cm, are achieved in the 600–1000°C temperature range. While these high temperatures create several materials issues, they are compatible with typical industrial gas processing (e.g., catalytic oxidation and steam reforming) temperatures resulting in a more efficient thermal integration.

This advantage in thermal integration provides the opportunity for ITMs to be used in membrane reactors. Membrane reactors can circumvent thermodynamic equilibrium limitations by *in situ* removal of product species, thus permitting greater product yields.⁵ Not only do membrane reactors result in greater yields, but the product is already purified removing the need for downstream purification processes.

The major functional components of these reactors are the reaction catalysts (e.g., oxidation, steam reforming, and water gas shift) and the oxygen-ion or proton transport (or O_2 and H_2 separation, respectively) membranes, which are described below.

Oxygen-ion transport membranes — Oxygen-ion transport membranes are based on metal oxides (such as $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{M}_x\text{O}_3$ perovskite-type oxides) that exhibit both ionic and electronic (mixed) conductivity. For O_2 separation these oxides are typically p-type semiconducting oxides so that a high degree of electron-hole (h^\bullet) conduction is obtained under oxidizing conditions. Because of their significant electronic conductivity, these mixed ionic-

electronic conductors (MIEC) have an internal electrical short and the ionic species will selectively permeate through a dense film of the material under a partial pressure gradient. The potential permeation flux rates of these materials are extremely high. For example, based on the results of Teraoka, *et al.*⁶ and assuming the flux is bulk diffusion limited, calculated O₂ flux rates through a 50- μm -thick membrane of La_{0.6}Sr_{0.4}Co_{0.8}Cu_{0.2}O₃ at 600°C are 22400 L (STP) h⁻¹•m⁻² of membrane surface area under an 0.21 atm P_{O₂}-gradient. The governing equation under these conditions is the Wagner Equation (described in The Chalkboard article in this issue).

Because of the potential high O₂ flux of these materials under a simple air P_{O₂}-gradient, major industrial gas suppliers are developing ITMs to produce pure O₂ from air. By siting one of these ITM units next to a hydrocarbon processing unit, dramatic improvements in the conversion efficiency is achieved because the N₂ is removed prior to reaction of O₂ with the hydrocarbon feed stream. Due to the thermal compatibility of these membranes with, for example, catalytic oxidation processes, membrane reactors are under development to integrate the partial oxidation of hydrocarbons, such as natural gas, to syngas using an oxygen-ion transport membrane, as shown in Fig. 2. The integrated process further improves efficiency and reduces cost.

Proton transport membranes — A series of perovskite-type oxides (e.g., BaCe_{1-x}M_xO₃, where M is a metal acceptor dopant) have been shown to have high proton conductivity at elevated temperatures.^{7,8} These materials are receiving considerable attention because of their numerous applications as H⁺ electrolytes in fuel cells, hydrogen

pumps, electrolyzers, and gas sensors.⁹ BaCe_{1-x}M_xO₃-type protonic conductors have sufficient ionic conductivity to obtain comparable flux rates to the oxygen-ion conductors. However, they have insufficient electronic conductivity. The electronic conductivity is necessary to balance the transport of charge through the material. Further, it is desirable that the electronic conductivity is n-type (e⁻ conduction) so that electronic conductivity is obtained under low P_{O₂} conditions. If comparable electronic conduction can be obtained with the BaCe_xM_xO₃-type protonic conductors, they would be excellent H₂ permeation membrane materials, equivalent to palladium alloy films, but with the potential advantages of higher temperature operation (for thermal integration) and lower cost.

Because of the dramatic potential of these materials in H₂ production, several groups including Argonne National Lab, Georgia Tech, and the University of Florida, have been developing mixed protonic-electronic membrane materials. Most of the earlier work focused on developing composite membranes of the proton conducting oxide and a metal phase for electronic transport;¹⁰ however, more recent work has shown that by use of a multivalent dopant cation, n-type electronic conduction can be achieved in a single phase material.¹¹⁻¹³

Ultimately these two MIEC membranes can be combined in series, and integrated with partial oxidation, steam reforming, and water gas shift catalysts, also in series, to optimize the thermodynamics of hydrogen production. The first membrane separates O₂ from air (with infinite selectivity) and reacts any of the hydrocarbons in the feed to form CO and H₂, facilitated by an oxidation catalyst. The second membrane separates the H₂ (also with infinite selectivity) providing a pure H₂ gas stream. As the process gas stream continues through the reactor, any hydrogen that has not been separated

will tend to oxidize to H₂O. A water gas shift catalyst, with the introduction of additional H₂O, in the later part of the reactor could push the conversion to higher H₂ yields.

Exhaust Sensors

Undoubtedly, oxygen sensors (λ probes) are the most widespread and successfully implemented solid state ionic device today (Fig. 3). Comprised primarily of an oxygen-ion conducting electrolyte (yttria-stabilized zirconia) with a Pt electrode on the exhaust (sensing) side and another Pt electrode on the air (reference) side, it generates a voltage via the Nernst equation due to the difference in P_{O₂} between the two sides.

By monitoring the exhaust P_{O₂}, these sensors have been used to control the air-to-fuel ratio (λ) near stoichiometric combustion, of essentially every automobile produced during the last 30 years. While initially deployed to work with the three-way catalytic converter to reduce air pollution, they also produce the additional benefit of improved fuel efficiency. The three-way catalytic converter combined with λ probe control of the air-fuel ratio, has been the pioneering technological breakthrough to minimize pollutant emissions from automotive exhaust gases, simultaneously reducing the concentrations of both oxidizing (CO and HCs) and reducing (NO_x) exhaust pollutants.

However, regulations for vehicle pollutant emission are becoming increasingly stringent worldwide, and proposed limits cannot be met using conventional three-way catalytic converter and λ probe control. For instance, recent regulations require On-Board Diagnostic (OBD) systems to control exhaust pollutants. The current OBD systems monitor the converter efficiency through the measurement of the oxygen content up-stream and down-stream of the converter using two λ probes but does not directly monitor the actual pollutant concentrations.¹⁴ In contrast, emission control and fuel efficiency could be further improved by deployment of sensors capable of directly detecting CO/HCs and NO_x in the exhaust gas stream, in addition to O₂, to provide improved feedback for automotive engine control.

A recent strategy to improve fuel efficiency (and thus reduce overall emissions) is to operate the engine under lean-burn combustion. However, the high oxygen concentration hinders the NO_x reduction reaction in the catalytic converter, making necessary the implementation of a transient NO_x storage process. When the engine is operated in lean conditions CO and HCs are rapidly oxidized and NO_x is adsorbed on the catalyst surface. Then the engine operation is shifted to rich-

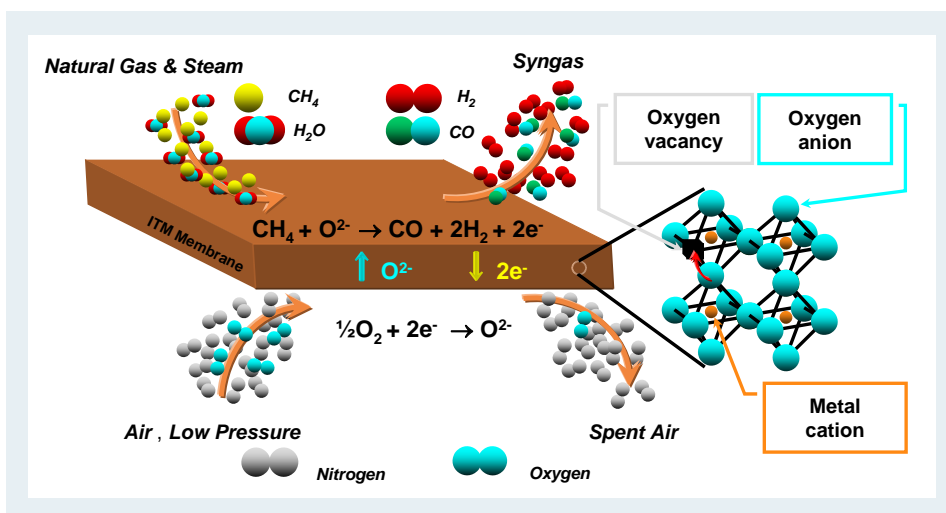


Fig. 2. ITM Syngas technology being developed by Air Products.

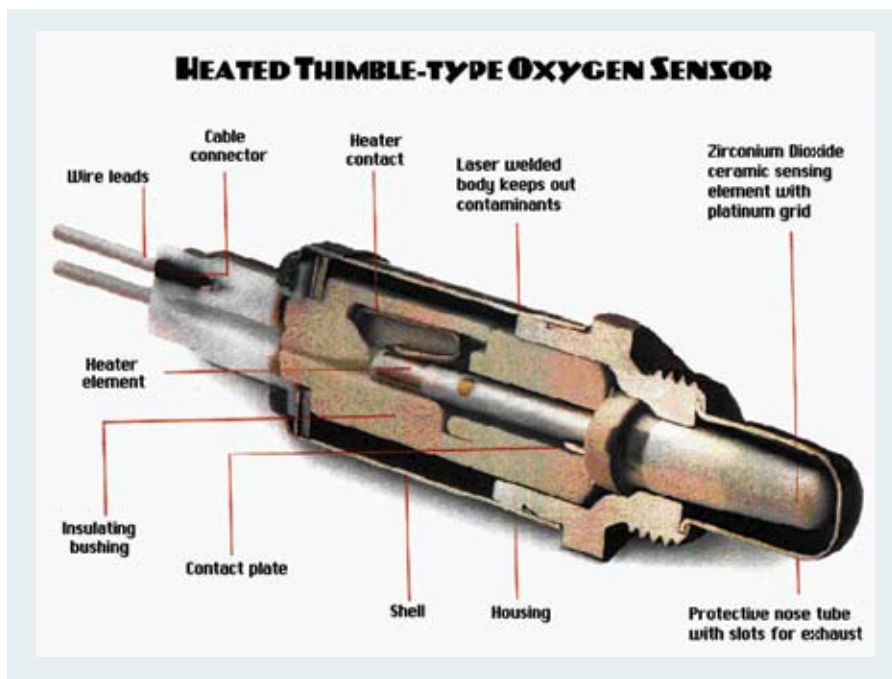


Fig. 3. Cross-section of an oxygen sensor.

burn conditions for a few seconds and the adsorbed NO_x is reacted with the temporarily higher CO and HC concentrations. After this catalyst regeneration, the engine is returned to lean-burn operation. Proper operation of this method requires the availability of a sensor to measure NO_x conversion as well as slip from the spent catalyst.¹⁵

Development of solid-state sensors, similar to the λ probe, that can directly measure CO/HCs and NO_x , has been an area of tremendous research effort. However, in contrast to the λ probe these sensors are based on a non-Nernstian potential mechanism, typically with both electrodes in the same gas stream. They are comprised of the same YSZ electrolyte and a metallic electrode (e.g., Pt), but the other electrode is typically an oxide electrode and the difference in potential generated between the two electrodes results in a non-Nernstian potential that is sensitive to the gaseous species of interest (CO, HCs, or NO_x). These sensors seem to be the most promising to meet all of the requirements needed for exhaust gas monitoring.¹⁶ From a manufacturing point of view, these sensors are only a modification of the λ probe, by substitution of one of the Pt electrodes with an oxide, and can therefore easily be implemented into mass production and practical use.

Indeed, several groups worldwide including Kyushu University, Los Alamos National Lab, the University of Rome "Tor Vergata," and the University of Florida,¹⁷⁻²⁷ have been developing this type of sensors, both for NO_x and CO/HC detection, though with slightly different strategies: namely, some of the groups are developing sensors where the metallic electrode is exposed to

reference air and the oxide electrode to the exhaust gas environment, while other groups are exposing both electrodes to the atmosphere to be detected. A large number of oxides are being tested either for reducing or for oxidizing gas detection. The selection of the oxide is guided by its sensitivity and capability to detect very low concentration, selectivity towards specific gasses, stability at high temperatures, and response time. It has been also found that the

microstructure of the oxide electrode, in terms of morphology and grain size, can significantly affect the sensor response,²⁸ and therefore care should be paid to the electrode fabrication process. Most sensors have been tested in the laboratory, though some reports show tests performed in more practical conditions, such as in real engine exhaust environments.^{29,30}

Solid-state sensors for CO, HCs, and NO_x have been reviewed in recent papers.³¹⁻³³ An example of recent literature results is that of a Pt/YSZ/ Nb_2O_5 sensor, using Nb_2O_5 and Pt electrodes on tape-cast YSZ.³⁴ The EMF response of this sensor to different concentrations of propylene in air, in the temperature range 500-700°C, is shown in Fig. 4. As is typical for these types of sensors, increasing the temperature results in a more stable and faster response, but the amplitude of the EMF decreases. Under exposure to 1000 ppm of propylene in air, the EMF value of Pt/YSZ/ Nb_2O_5 at 700°C was -110 mV, still a remarkably large value for that high of a temperature. In addition, the results for the Pt/YSZ/ Nb_2O_5 sensor were found reproducible and stable: after several days of measurements, the same EMF results were obtained. The cross sensitivity was checked by performing the measurements under exposure to different saturated and unsaturated hydrocarbons, CO and NO_2 in the temperature range 500-700°C. At all the investigated temperatures, the sensor responded best to propylene. For all the gases, a linear dependence of the EMF response was observed. These results indicate that this sensor is a

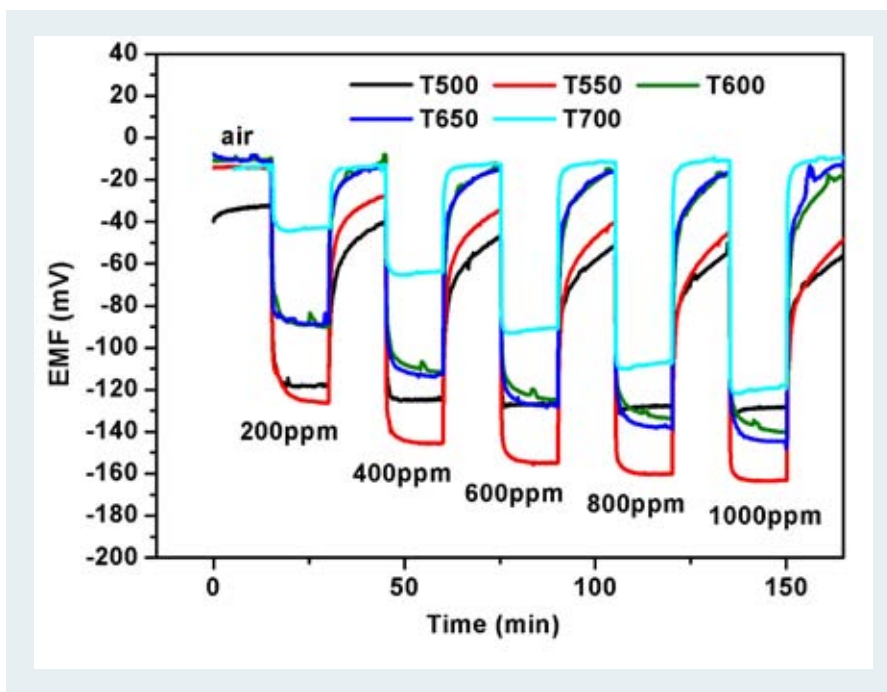


Fig. 4. EMF response versus time of Pt/YSZ/ Nb_2O_5 sensor to different concentrations of propylene in air in the temperature range 500-700°C (from Ref. 34).

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potential candidate for monitoring and controlling HCs in automotive exhaust gases.

Summary

Tremendous progress has been made in understanding the defect chemistry and transport in solid-state ion conductors. These materials are attracting increasing attention for a variety of applications, most notable among these being fuel cells for power generation, production of chemicals, oxygen generation for life support systems, and high temperature electrochemical sensors. Oxygen sensors are already a widespread commercial success and many of the other solid-state ionic devices hold similar promise as their performance is improved and cost is brought down through further technical advances and mass production. ■

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Solid Oxide Fuel Cells

by Subhash C. Singhal

Solid oxide fuel cells (SOFCs) offer a clean, low-pollution technology to electrochemically generate electricity at high efficiencies; since their efficiencies are not limited by the Carnot cycle of a heat engine.¹⁻³ These fuel cells provide many advantages over traditional energy conversion systems including high efficiency, reliability, modularity, fuel adaptability, and very low levels of NO_x and SO_x emissions. Quiet, vibration-free operation of SOFCs also eliminates noise usually associated with conventional power generation systems. Up until about six years ago, SOFCs were being developed for operation primarily in the temperature range of 900 to 1000°C; in addition to the capability of internally reforming hydrocarbon fuels (e.g., natural gas), such high temperature SOFCs provide high quality exhaust heat for cogeneration, and when pressurized, can be integrated with a gas turbine to further increase the overall efficiency of the power system. However, reduction of the SOFC operating temperature by 200°C or more allows use of a broader set of materials, is less-demanding on the seals and the balance-of-plant components, simplifies thermal management, aids in faster start up and cool down, and results in less degradation of cell and stack components. Because of these advantages, activity in the development of SOFCs capable of operating in the temperature range of 650 to 800°C has increased dramatically in the last few years. However, at lower temperatures, electrolyte conductivity and electrode kinetics decrease significantly; to overcome these drawbacks, alternative cell materials and designs are being extensively investigated.

An SOFC essentially consists of two porous electrodes separated by a dense, oxide ion conducting electrolyte. The operating principle of such a cell is illustrated in Fig. 1. Oxygen supplied at the cathode (air electrode) reacts with incoming electrons from the external circuit to form oxide ions, which migrate to the anode (fuel electrode) through the oxide ion conducting electrolyte. At the anode, oxide ions combine with H₂ (and/or CO) in the fuel to form H₂O (and/or CO₂), liberating electrons. Electrons (electricity) flow from the anode through the external circuit to the cathode. The materials for the cell components are selected based on suitable electrical conducting properties required of these components to perform their intended

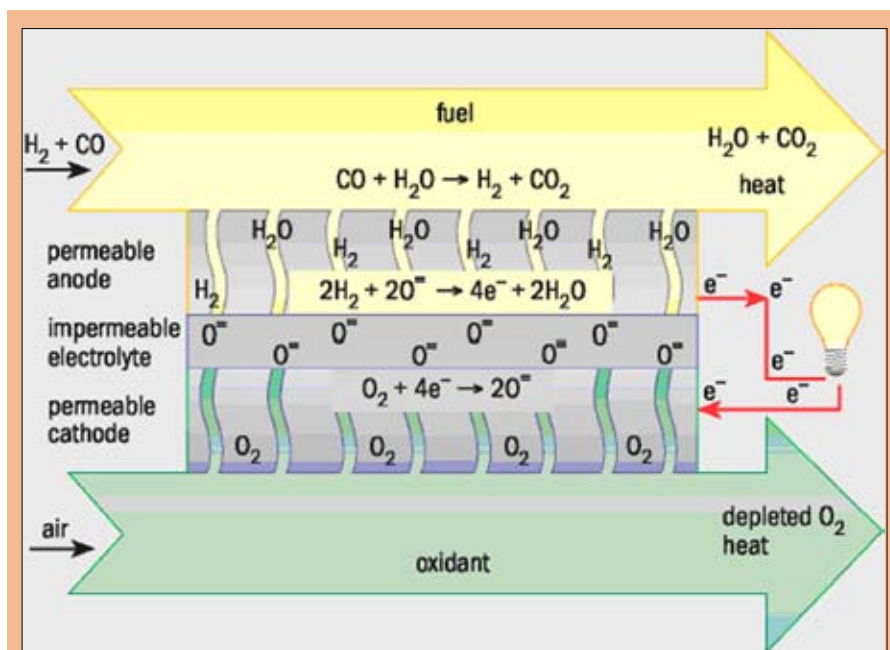


FIG. 1. Operating principle of a solid oxide fuel cell.

cell functions; adequate chemical and structural stability at high temperatures encountered during cell operation as well as during cell fabrication; minimal reactivity and interdiffusion among different components; and matching thermal expansion among different components.

Materials and Cell Designs

Yttria-doped zirconia (YSZ) remains the most widely used material for the electrolyte in SOFCs because of its sufficient ionic conductivity, chemical stability, and mechanical strength. The only drawback of stabilized ZrO₂ is the low ionic conductivity in the lower cell operation temperature regime (below about 750°C). Two solutions that have been tried to resolve this problem are to decrease the thickness of the YSZ electrolyte and to find other acceptors to replace Y. Scandia-doped zirconia has higher conductivity than YSZ but high cost of scandium and detrimental ageing effects in scandia-doped ZrO₂ make it less attractive in commercializing SOFCs. Gadolinium- or samarium-doped CeO₂ materials possess higher oxide ion conductivity (e.g., Ce_{0.9}Gd_{0.1}O_{1.95}: 0.025 Ω⁻¹·cm⁻¹ at 600°C) compared to zirconia based materials (< 0.005 Ω⁻¹·cm⁻¹). However, CeO₂ based materials, under reducing conditions at high temperatures, exhibit significant

electronic conductivity and dimensional change due to the formation of oxygen vacancies and the associated reaction of Ce⁴⁺ to Ce³⁺. Operation at temperatures below about 600°C overcomes this problem, and ceria based materials are successfully being used as electrolyte in SOFCs by Ceres Power Limited (UK). In addition to the traditionally used fluorite structure oxides such as zirconia and ceria, perovskite structure (ABO₃) also offers an opportunity to develop oxide ion conducting electrolytes by selectively substituting either the A or B ion by isovalent or aliovalent cations. (La,Sr)(Mg,Ga)O₃ (LSMG)^{4,5} has attracted attention as an electrolyte since its discovery. LSMG electrolytes, however, have two drawbacks: uncertain cost of gallium, and uncertain chemical and mechanical stability of LSMG. In spite of these drawbacks, Mitsubishi Materials Corporation (Japan) is using LSMG as the electrolyte in its SOFCs and has successfully built and tested up to 10 kW size SOFC power systems.

The oxidant gas is air or oxygen at the SOFC cathode, and the electrochemical reduction of O₂ requires a series of elementary reactions and involves the transfer of multiple electrons. The SOFC cathode must meet the requirements of high catalytic activity for oxygen molecule dissociation and oxygen reduction, high electronic conductivity, chemical and dimensional stability

in environments encountered during cell fabrication and cell operation, thermal expansion match with other cell components, and compatibility and minimum reactivity with the electrolyte and the interconnection. Finally, the cathode must have a stable, porous microstructure so that gaseous oxygen can readily diffuse through the cathode to the cathode/electrolyte interface. These stringent electrochemical and mechanical requirements greatly restrict the number of suitable candidate materials. Conducting perovskites are the preferred cathode materials. Lanthanum manganite (LaMnO_3), which, when substituted with low-valence elements such as Ca or Sr, has good p-type electronic conduction due to the formation of large amount of Mn^{4+} . Moreover, doped LaMnO_3 possesses adequate electrocatalytic activity, a reasonable thermal expansion match to YSZ, and stability in the SOFC cathode operating environment. For SOFCs operating at substantially lower temperatures, such as 650–800°C, alternative cathode materials, typically containing transition metals such as Co, Fe, and/or Ni on the B site, have been developed and optimized for better performance. In general, these materials offer higher oxide ion diffusion rates and exhibit faster oxygen reduction kinetics at the cathode/electrolyte interface compared with lanthanum manganite. However, the thermal expansion coefficient of cobaltites is much higher than that of the YSZ electrolyte, and the electrical conductivities of ferrites and nickelites are low. Nevertheless, promising results have been reported using these materials, though in many cases the improved cathodic performance is found to decrease during the cell lifetime as a result of chemical or microstructural instability. Minimization of cathodic polarization losses is one of the biggest challenges to be overcome in obtaining high, stable power densities from lower temperature SOFCs. Perovskite type oxides, particularly $(\text{La}, \text{Sr})\text{MO}_3$ ($M = \text{Co}, \text{Fe}, \text{and/or Ni}$), are very reactive toward YSZ. Therefore, a thin layer, generally of a CeO_2 based material, is used to reduce the chemical reaction between the cathode and YSZ. Microstructure also plays a major role in the cathode polarization; this is particularly true when a composite cathode (e.g. Sr-doped $\text{LaMnO}_3 + \text{YSZ}$), which shows a better performance compared to a single composition cathode, is used. Tanner et al.⁶ have shown that polarization resistance depends upon the grain size of the ionic conductor in the composite electrode and the volume fraction of porosity.

The anode must be an excellent catalyst for the oxidation of fuel (H_2, CO), stable in the reducing environment of

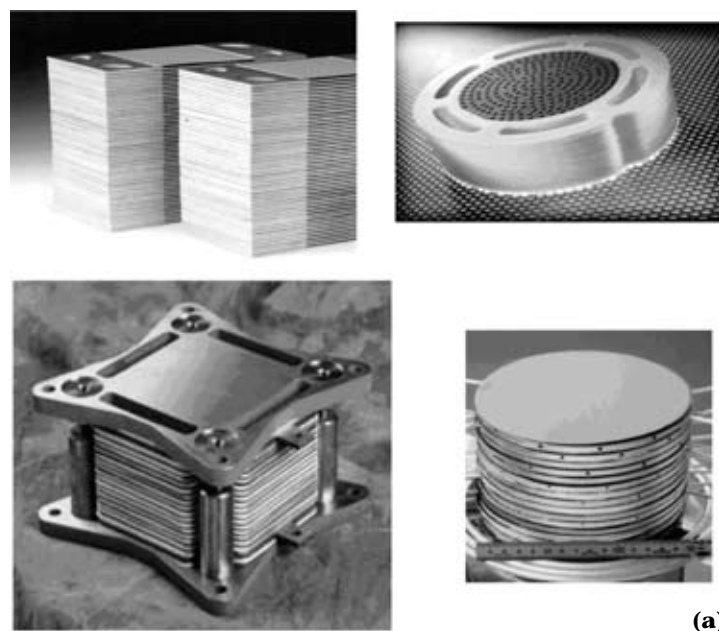
the fuel, electronically conducting, and must have sufficient porosity to allow the transport of the fuel to and the transport of the products of fuel oxidation away from the electrolyte/anode interface where the fuel oxidation reaction takes place.⁷ The other requirements include matching of its thermal expansion coefficient with that of the electrolyte and interconnect; integrity of porosity for gas permeation; chemical stability with the electrolyte and interconnect; and applicability to use with versatile fuels and impurities. In addition, cost effectiveness is always a factor for commercialization. Ni-YSZ cermets are the most commonly used anode materials for SOFCs. Ni is an excellent catalyst for fuel oxidation; however, it possesses a high thermal expansion coefficient ($13.4 \times 10^{-6}/^\circ\text{C}$), and exhibits coarsening of microstructure due to metal aggregation through grain growth at cell operation temperatures. YSZ in the anode constrains Ni aggregation and prevents sintering of the nickel particles, decreases the effective thermal expansion coefficient bringing it closer to that of the electrolyte, and provides better adhesion of the anode with the electrolyte. In the Ni/YSZ cermet anode, nickel has dual roles of the catalyst for hydrogen oxidation and the electrical current conductor. In addition, it is also highly active for the steam reforming of methane. This catalytic property is exploited in the so-called internal reforming SOFCs that can operate on fuels composed of mixtures of methane and water. Although nickel is an excellent hydrogen oxidation and methane-steam-reforming catalyst, it also catalyzes the formation of carbon from hydrocarbons under reducing conditions. Unless sufficient amounts of steam are present along with the hydrocarbon to remove carbon from the nickel surface, the anode may be destroyed. As a result, even when using methane as the fuel, relatively high steam-to-carbon ratios are needed to suppress this deleterious reaction. Unfortunately, due to the high catalytic activity of nickel for hydrocarbon cracking, this approach does not work for higher hydrocarbons, and it is generally not possible to operate nickel-based anodes on higher hydrocarbon-containing fuels without pre-reforming with steam or oxygen. In spite of this drawback, Ni-YSZ cermet remains the most commonly utilized anode material for SOFCs and is satisfactory for cells operating on clean, reformed fuel. However, advanced SOFC designs place additional constraints on the anode, such as tolerance of oxidizing environments and/or the ability to tolerate significant quantities of sulphur and/or hydrocarbon species in the fuel stream. Alternative materials, such as ceria or strontium titanate/ceria mixtures, have yielded some promising results in these designs, but the benefits obtained in terms of

sulphur, hydrocarbon and/or redox tolerance are counterbalanced by other limitations (such as the difficulty of integrating such materials with existing cell and stack fabrication processes and materials). Copper cermet anodes have also been proposed for intermediate-temperature (< 800°C) SOFCs intended to operate directly on hydrocarbon fuels without prior reformation,⁷ but the lack of catalytic activity for oxidation of fuel in copper and sintering of copper at the cell operating temperatures have limited their use in practical SOFCs. Ceramic anodes such as doped perovskites, $(\text{La}, \text{Sr})\text{TiO}_3$, $(\text{La}, \text{Sr})\text{CrO}_3$, with addition of CeO_2 have also been investigated as anodes,⁷ but they suffer from higher electronic resistance.

Since a single cell only produces voltage less than 1 V and power around 1 W/cm², many cells are electrically connected together in a cell stack to obtain higher voltage and power. To connect multiple cells together, an interconnection is used in SOFC stacks. The requirements of the interconnection are the most severe of all cell components and include: nearly 100 percent electronic conductivity; stability in both oxidizing and reducing atmospheres at the cell operating temperature since it is exposed to air (or oxygen) on the cathode side and fuel on the anode side; low permeability for oxygen and hydrogen to minimize direct combination of oxidant and fuel during cell operation; a thermal expansion coefficient close to that of the cathode and the electrolyte; and non-reactivity with other cell materials. To satisfy these requirements, doped lanthanum chromite is used as the interconnection for cells intended for operation at about 1000°C. Lanthanum chromite is a p-type conductor; its conductivity is due to small polaron hopping from room temperature to 1400°C at oxygen pressures as low as 10^{-18} atm. The conductivity is enhanced as lower valence ions (e.g., Ca, Mg, Sr, etc.) are substituted on either the La^{3+} or the Cr^{3+} sites.⁸ In cells intended for operation at lower temperatures (< 800°C), it is possible to use oxidation-resistant metallic materials for the interconnection. Compared to lanthanum chromite ceramic interconnects, metallic alloys offer advantages such as improved manufacturability, significantly lower raw material and fabrication costs, and higher electrical and thermal conductivity. But to be useful for the interconnect application, the metallic alloys must satisfy additional requirements, including resistance to surface oxidation and corrosion in a dual atmosphere (simultaneous exposure to oxidizing and reducing atmospheres), thermal expansion matching to other stack components (particularly for stacks using a rigid

seal design), chemical compatibility with other materials in contact with the interconnect, such as seals and cell materials, high electrical conductivity not only through the bulk material but also in *in-situ*-formed oxide scales, mechanical reliability and durability at the cell operating temperature, and strong adhesion between the as-formed oxide scale and the underlying alloy substrate. Ferritic stainless steels are the most promising candidates, owing to the fact that some alloys in this family offer a protective and conductive Cr-based oxide scale, appropriate thermal expansion behavior, ease of manufacturing and low cost. Several new ferritic stainless steels, such as Crofer22 (Plansee, Austria) and ZMG232 (Hitachi Metals, Japan), have been developed specifically for SOFC interconnects. Although these alloys demonstrate improved performance over traditional compositions, several critical issues remain; among these are chromia scale evaporation and subsequent poisoning of cathodes; scale electrical resistivity in the long term; corrosion and spalling under interconnect exposure conditions; and compatibility with the adjacent components such as seals and electrical contact layers. To overcome some of these problems, surface coatings, for example from electrically conductive perovskites and spinels, can be applied onto metallic interconnects to minimize scale growth, electrical resistance and Cr volatility.

In terms of stack design, most development has focused on planar and tubular design cells, each of these designs having a number of interesting variants; for example, the planar SOFC may be in the form of a circular disk fed with fuel from the central axis, or it may be in the form of a square plate fed from the edges. The tubular SOFC may be of a large diameter (> 15 mm), or of much smaller diameter (< 5 mm), the so-called microtubular cells. Also, the tubes may be flat and joined together to give higher power density and easily printable surfaces for depositing the electrode layers. Figure 2a illustrates typical planar cell stacks and Fig. 2b a tubular cell bundle. One of the inherent advantages of tubular cell bundles is that the air and the fuel are naturally isolated because the tubes are closed at one end. However, in the case of planar cell stacks, an effective seal must be provided to isolate air from the fuel. The seal must have a thermal expansion match to the fuel cell components, must be electrically insulating and must be thermochemically stable under the operational conditions of the stack. Also, the seal should exhibit no deleterious interfacial reactions with other cell components, should be stable under both the high temperature oxidizing and reducing operational conditions, should be created at a low enough temperature to avoid damaging cell



(a)



(b)

Fig. 2. Illustration of planar cell stacks (a) and a tubular cell bundle (b).

components (under 850°C for some materials), and should not migrate or flow from the designated sealing region during sealing or cell operation. In addition, the sealing system should be able to withstand thermal cycling between the cell operation temperature and room temperature. A number of different sealing approaches are under development, including rigid, bonded seals (e.g., glass-ceramics and brazes), compliant seals (e.g. viscous glasses) and compressive seals (e.g., mica-based composites); multiple sealants may also be used in any given stack design between different cell components. Successful development of sealing materials and concepts for planar SOFCs is probably the most important issue for the long-term performance stability and lifetime of planar SOFC stacks and hence for their eventual commercialization at competitive costs.

The single biggest advantage of tubular cells over planar cells is that they do not require any high temperature

seals to isolate oxidant from the fuel, and this makes performance of tubular cell stacks very stable over long periods of times (several years). However, their areal power density is much lower (about 0.2 W/cm^2) compared to planar cells (up to 2 W/cm^2 for single cells and at least 0.5 W/cm^2 for stacks) and manufacturing costs higher. The volumetric power density is also lower for tubular cells than for planar cells. To increase the power density and reduce the physical size and cost of tubular SOFC stacks, alternate tubular geometry cells, as illustrated in Fig. 3, are under development by Siemens.⁹ Such alternate geometry cells combine all the advantages of the tubular SOFCs, such as not requiring high temperature seals, while providing higher areal and volumetric power densities. The performance of these new design cells is higher than that of cylindrical tubular cells, but still lower than that of anode-supported planar cells.

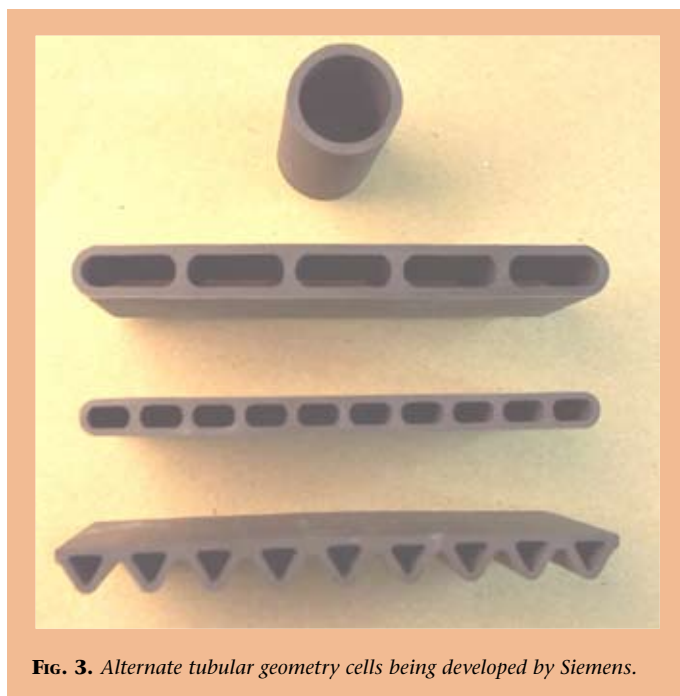


Fig. 3. Alternate tubular geometry cells being developed by Siemens.

Applications

Using planar SOFCs, stationary power generation systems of from 1 kW to 25 kW size have been fabricated and tested by several organizations. Several hundred 1-kW size combined heat and power (CHP) units for residential application were field tested by Sulzer Hexis; however, their cost and performance degradation was high and stack lifetime too short. With improved sealing materials and sealing concepts, planar SOFC prototype systems in the 1 to 5 kW sizes have recently been developed and are being tested by various organizations with greater success. Using tubular (cylindrical) SOFCs, Siemens/Westinghouse fabricated a 100 kW atmospheric power generation system.¹⁰ The system was successfully operated for two years in the Netherlands on desulfurized natural gas without any detectable performance degradation. It provided up to 108 kW of ac electricity at an efficiency of 46% to the Dutch grid and approximately 85 kW of hot water for the local district heating system. At the conclusion of the operation in The Netherlands, the system was moved to a German utility site in Essen, Germany, where it operated successfully for another 4,000 hours. After replacing some cells, the system was then installed and operated in Italy, for over two years, again with very stable performance. Siemens/Westinghouse tubular cells have also been used to fabricate and field test over a dozen 5 kW size CHP units, each about the size of a refrigerator. These units gave excellent performance and performance stability on a variety of hydrocarbon fuels. However, at present, their cost is high; future such units are expected to use higher power density alternate tubular geometry cells to drive down the cost.

Another application of SOFC systems is in the transportation sector. The polymer electrolyte membrane (PEM) fuel cell is generally regarded as the fuel cell of choice for transportation applications. PEM fuel cells require pure H₂, with no CO, as the fuel to operate successfully. However, presently no H₂ infrastructure exists, and on-board reformer systems to produce H₂ from existing fuel base (gasoline, diesel) are technically challenging, complex, and expensive. Furthermore, it is difficult to eliminate the CO entirely from the reformate stream. In contrast, SOFCs can use CO along with H₂ as fuel, and their higher operating temperature and availability of water on the anode side makes on-cell or in-stack reformation of hydrocarbon fuels feasible. Also, no noble metal catalysts are used in SOFCs reducing cost of the cells. The initial application of SOFCs in the transportation sector will be for on-board auxiliary power units (APUs). Such APUs, operating on existing fuel base, will supply the ever-increasing electrical power demands of luxury automobiles, recreational vehicles, and heavy-duty trucks. Delphi Corporation has developed a 5 kW APU using anode-supported planar SOFCs.¹¹ This unit is intended to operate on gasoline or diesel, which is reformed through catalytic partial oxidation. The building blocks of such an APU consist of an SOFC stack, fuel reformation system, waste energy recovery system, thermal management system, process air supply system, control system, and power electronics and energy storage (battery) system. Delphi has reduced the mass and volume in successive generation APU units to meet the stringent automotive requirements; the remaining issues of start up time and tolerance to thermal cycling are presently being worked on.

Summary

The challenge in successfully commercializing SOFCs offering high power densities and long term durability requires reduction of costs associated with the cells and the balance-of-plant. Additionally, for transportation APU applications, ability for rapid start up and thermal cycling needs to be developed. ■

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