

Solid Oxide Fuel Cells : Designs, Materials, and Applications

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ABSTRACT

The Solid Oxide Fuel Cell (SOFC) is an electrochemical device to convert chemical energy of a fuel into electricity at temperatures from about 600 to 1000°C. The SOFC offers certain advantages over lower temperature fuel cells, notably its ability to use CO as a fuel rather than being poisoned by it, and high grade exhaust heat for combined heat and power, or combined cycle gas turbine applications. This paper reviews the operating principle, materials for different cell and stack components, cell designs, and applications of SOFCs. Among all designs of Solid Oxide Fuel Cells (SOFCs), the most progress has been achieved with the tubular design. However, the electrical resistance of tubular SOFCs is high, and specific power output (W/cm²) and volumetric power density (W/cm³) low. Planar SOFCs, in contrast, are capable of achieving very high power densities.

Key words : Solid oxide fuel cell, Oxide electrolyte, Electrodes, Interconnection, Seals, Tubular, Planar

1. Introduction

Solid Oxide Fuel Cells (SOFCs), based on an oxide ion conducting electrolyte, offer a clean, low-pollution technology to electrochemically generate electricity at high efficiencies. These fuel cells provide many advantages over traditional energy conversion systems including high efficiency, reliability, modularity, fuel adaptability, and very low levels of SO_x and NO_x emissions. Quiet, vibration-free operation of solid oxide fuel cells also eliminates noise usually associated with conventional power generation systems. Furthermore, because of their high operation temperature (800–1000°C), some hydrocarbon fuels such as natural gas can be reformed within the cell stack eliminating the need for an expensive, external reformer. In spite of these advantages, the degree and extent of their market penetration really depends on the ability to reduce the cost of SOFC-based power systems while ensuring their long-term durability. This paper reviews the operating principle, materials and fabrication processes, designs, and applications of solid oxide fuel cells.

2. Operating Principle

A solid oxide fuel cell 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 reacts with incoming electrons from the external circuit to form oxygen ions,

which migrate to the anode 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 flow from the anode through the external circuit to the cathode.

The overall cell reaction is simply the oxidation of fuel (H₂ and/or CO) and the open circuit voltage, E^o , of the fuel cell is given by the Nernst equation:

$$E^o = \frac{RT}{4F} \ln \left\{ \frac{P_{O_2}(\text{oxidant})}{P_{O_2}(\text{fuel})} \right\} \quad (1)$$

where R is the gas constant, T is the cell temperature, F is the Faraday constant, and P_{O_2} 's are the oxygen partial pressures. Under cell operating conditions, i.e., when a current passes through it, the cell voltage (V) is given by:

$$V = E^o - IR - \eta_A - \eta_F \quad (2)$$

where I is the current passing through the cell, R is the electrical resistance of the cell, and η_A and η_F are the polarization voltage losses associated with the air electrode and the fuel electrode, respectively. To keep the IR loss low, the electrolyte is fabricated in the form of a thin film.

If the fuel is reformed natural gas, for example, the hydrogen and carbon monoxide in the fuel are converted to water and carbon dioxide. During this process, electrons are transported from the anode to the cathode through an external circuit, resulting in the generation of an electric current. In this process, a substantial fraction of the enthalpy associated with the oxidation of the fuel to water and carbon dioxide is directly converted to electrical work. Since no intermediate steps are involved in the energy conversion process, SOFCs can deliver substantially higher electrical conversion efficiencies when compared with traditional technologies such as coal-fired power plants and electrical

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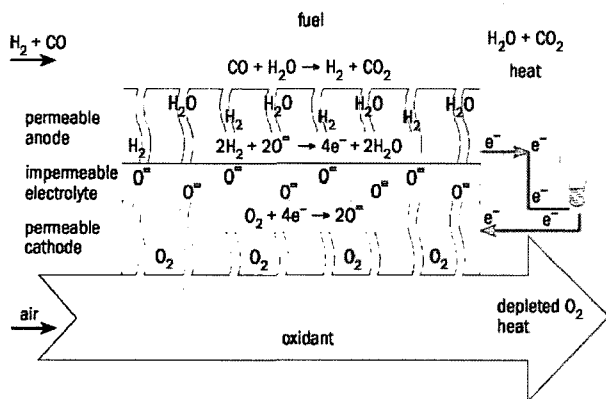


Fig. 1. Operating principle of a solid oxide fuel cell.

generators based on internal combustion engines.

Over the last two decades, SOFCs have been developed for operation primarily in the temperature range of 900 to 1000°C. Such high temperature SOFCs allow internal reforming of hydrocarbon fuels, 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. Ohmic losses from the electrolyte can be minimized either by the use of higher conductivity electrolyte materials and/or through the use of thinner electrolyte.

3. Cell Materials

All SOFCs consist essentially of four components: the electrolyte, the cathode, the anode, and the interconnection. The materials for these components are selected based on suitable electrical conducting properties required of these components to perform their intended 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.¹⁻³ The most commonly used materials for the different cell components are discussed below.

3.1. Electrolyte

Solid oxide fuel cells are based on the concept of an oxide ion conducting electrolyte through which the oxide ions

migrate from the cathode side to the anode side where they oxidize the fuel (H₂, CO, etc.) to generate an electrical voltage. Oxide materials such as Yttria-Stabilized Zirconia (YSZ), rare earth doped ceria, rare earth doped bismuth oxide, and doped lanthanum gallates have been widely investigated as electrolytes.³ Of these materials, YSZ has been most successfully employed in SOFCs. The yttria dopant serves dual roles: it stabilizes the high temperature cubic phase in zirconia and also generates oxygen vacancies; the high oxide ion conductivity in YSZ is attributed to these oxygen vacancies.

Zirconia doped with about 10 mole percent yttria is generally used as the electrolyte. The conductivity of Yttria-Stabilized Zirconia (YSZ) at 1000°C is maximum (about 0.1 S·cm⁻¹) at about 10 mole percent yttria as shown by Strickler and Carlson;⁴ the activation energy is also least near this composition. The thermal expansion of 10 mole percent YSZ is about 10 × 10⁶/°C; materials for all other cell components are chosen to have thermal expansion near this value. For optimum cell performance, the YSZ electrolyte must be free of porosity so as not to allow gases to permeate from one side of the electrolyte to the other, it should be uniformly thin to minimize ohmic loss, and it should have high oxide ion conductivity with transport number for oxide ions close to unity and a transport number for electrons as close to zero as possible.

Among other electrolyte materials, lanthanum gallate based perovskite, and scandia-doped zirconia, both having higher conductivity than YSZ, have received the most attention. Ceria-based materials also have higher conductivity than YSZ; however their use as an SOFC electrolyte is limited to temperatures below about 600°C due to the onset of electronic conductivity in reducing fuel environments at higher temperatures.

3.2. Cathode

The cathode operates in an oxidizing environment of air or oxygen and has to meet the following requirements: high electronic conductivity; chemical and dimensional stability in environments encountered during cell fabrication and cell operation; thermal expansion match with other cell components; compatibility and minimum reactivity with the electrolyte and the interconnection with which it comes into contact, and high catalytic activity for oxygen molecule dissociation and oxygen reduction. 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 requirements greatly restrict the number of suitable candidate materials.

For high temperature SOFCs operating at around 1000°C, the preferred cathode material is a perovskite oxide, lanthanum manganite (LaMnO₃), which, when doped with an appropriate amount of Ca or Sr, offers adequate electrical conductivity and electrocatalytic activity, a reasonable thermal expansion match to YSZ, and stability in the SOFC cathode operating environment. Lanthanum manganite is a p-type perovskite oxide and shows reversible oxidation-

reduction behavior.^{5,6} The material can have oxygen excess or deficiency depending upon the ambient oxygen partial pressure and temperature. Although, it is stable in air and oxidizing atmospheres, it dissociates at 1000°C at oxygen pressures $\leq 10^{-14}$ atm. The electronic conductivity of lanthanum manganite is due to hopping of an electron hole between the +3 and +4 valence states of Mn. This conductivity is enhanced by doping with a divalent ion such as Ca or Sr. Furthermore, the reactivity and interdiffusion studies between doped lanthanum manganite and yttria-stabilized zirconia electrolyte have shown any interactions between these two materials up to 1000°C to be minimal.⁷

For SOFCs operating at substantially lower temperatures, such as 650–800°C, alternative cathode materials have been developed and optimized, since lanthanum manganite does not appear to be a satisfactory choice, owing (at least in part) to its low ionic conductivity and slow surface oxygen exchange kinetics. A number of alternative perovskite compositions, typically containing La on the A site, and transition metals such as Co, Fe and/or Ni on the B site, have received attention in this regard. In general, these materials offer higher oxygen 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.⁸

Minimization of cathodic polarization losses is one of the biggest challenges to be overcome in obtaining high, stable power densities from lower temperature SOFCs. Cathodic polarization exhibits high activation energy relative to the other internal power losses (e.g. electrolyte ohmic losses), and improving cathode performance is increasingly important as the SOFC operating temperature is reduced.

3.3. Anode

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. The reducing conditions present on the fuel side of an SOFC permit the use of a metal such as nickel (also cobalt or ruthenium) as the anode. However, the thermal expansion of nickel, $13.3 \times 10^{-6}/^\circ C$, is considerably larger than that of YSZ. Nickel also tends to sinter at the cell operating temperature resulting in a decrease in the anode porosity. These problems are circumvented by using a Ni/YSZ cermet for the anode. The YSZ prevents sintering of the nickel particles, decreases the effective thermal expansion coefficient bringing it closer to that of the electrolyte, and provides bet-

ter adhesion of the anode with the electrolyte. In the Ni/YSZ cermet anode, nickel 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, nickel is also highly active for the steam reforming of methane.¹⁰ This catalytic property is exploited in 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.

One approach to overcoming the limitations of nickel anodes, which has met with some success, is to augment the oxidation activity of Ni/YSZ cermets through the addition of an oxide-based oxidation catalyst. For example, stable operation on dry methane has been reported at 650°C in an SOFC using an yttria-doped ceria interlayer between the YSZ electrolyte and the Ni/YSZ cermet anode.¹⁰ Ceria is a well known oxidation catalyst, and might be expected to increase 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 to suppress carbon deposition reactions that take place on nickel.

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 highly oxidizing environments and/or the ability to tolerate significant quantities of sulphur and/or hydrocarbon species in the fuel stream. To simplify SOFC system requirements, it is desirable that the anode material be stable not only while exposed to the fuel environment during operation, but also when exposed to more oxidizing conditions (i.e. air) during system start-up and shutdown. Modifications to Ni-based anodes may offer some level of sulphur tolerance, though the data remains inconclusive. Alternative materials, such as ceria or strontium titanate/ceria mixtures, have yielded some promising results, 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).⁸ Copper cermet anodes have also been proposed for intermediate-temperature (<800°C) SOFCs intended to operate directly on hydrocarbon fuels without prior reformation,⁹ 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.

3.4. Interconnection

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.⁵⁾

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's operating temperature, and strong adhesion or bond strength 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 APU, have also been developed specifically for the SOFC interconnect application. Although these alloys demonstrate improved performance over the 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. As an alternative

approach to developing new alloys, surface modification can result in enhanced performance. For example, electrically conductive perovskites and spinels can be applied onto metallic interconnects to minimize scale growth, electrical resistance and Cr volatility.⁸⁾

Long term degradation (i.e. over a period of years) of SOFC performance could occur owing to the presence of volatile Cr species from the metallic interconnects in the cathode environment. Interaction of chromium vapour species (e.g. CrO_3 , $\text{CrO}_2(\text{OH})_2$) with the cathode materials could lead to bulk reaction and/or surface deposition of Cr oxides in the vicinity of the cathode/electrolyte interface, resulting in a decrease in the cell electrical performance. While this is of concern, the impact of this phenomenon on commercial SOFC stacks is unclear. At lower operating temperatures, Cr volatility from the oxide scales grown on metallic alloy interconnects is a problem, but not all Cr-containing oxides liberate volatile Cr species at the same rate, so appropriate tailoring of the scale chemistry may be helpful. If necessary, other mitigation strategies could be employed, involving, for example, a reduction in Cr vapor pressure and flux during stack operation and/or the development of Cr-tolerant cathode materials. Possible approaches include use of suitable surface layers on alloy interconnects to reduce Cr evaporation; La-chromites, Mn-chromite and non-Cr-containing oxides such as $(\text{Mn},\text{Co})_3\text{O}_4$ can reduce Cr flux during the operation of cell or stack. Such layers could potentially be applied either in a separate fabrication step (e.g. thermal spray) or grown *in-situ* through suitable modification of the alloy bulk or surface. Another approach is the gettering of Cr vapor present in the gas phase before it makes its way to the cathode/electrolyte interface.⁸⁾

4. Cell Designs

Since 1960s, 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. Detailed examples of these designs are discussed by Singhal and Kendall³⁾ and only the two main generic designs are discussed here.

4.1. Planar SOFC Design

In the planar design, illustrated in Fig. 2 in its most generic version, the cell components are configured as thin, flat plates. The interconnection, which is ribbed on both sides, forms gas flow channels and serves as a bipolar gas separator contacting the anode and the cathode of adjoining cells. The cells are fabricated by low-cost conventional

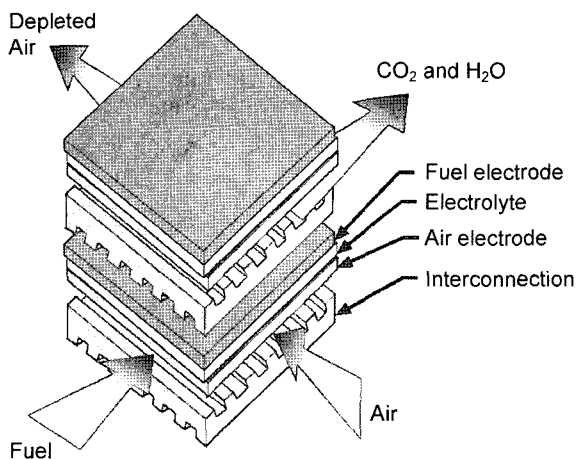


Fig. 2. Planar solid oxide fuel cell design.

ceramic processing techniques such as tape casting, tape calendaring, slurry sintering, screen printing, or by plasma spraying. Different organizations have developed several different variations of the planar design and use different manufacturing processes. Fig. 3 shows examples of planar SOFC stacks.

Currently, electrolyte-supported, cathode-supported, anode-supported, and metallic substrate-supported planar SOFCs are under development. In electrolyte-supported cells, the thickness of the electrolyte, typically Ytria-Stabilized Zirconia (YSZ), is 50 to 150 μm , making their ohmic resistance

high, and such cells are suitable only for operation at $\sim 1000^\circ\text{C}$. In electrode-supported designs, the electrolyte thickness can be much lower, typically 5 to 20 μm , which decreases their ohmic resistance and makes them better suited for operation at lower temperatures. The anode (Ni/YSZ cermet) is selected as the supporting electrode, because it provides superior thermal and electrical conductivity, superior mechanical strength, and minimal chemical interaction with the electrolyte. Kim *et al.*¹¹ have reported power densities as high as 1.8 W/cm^2 at 800°C for such anode-supported SOFCs. At Pacific Northwest National Laboratory,¹² similar anode-supported cells have been developed using $\sim 10 \mu\text{m}$ thick tape cast YSZ electrolyte and $\sim 600 \mu\text{m}$ thick tape cast Ni/YSZ anode which are laminated together and co-sintered at about 1350°C for 1 h. Cathode consists of either Sr-doped lanthanum manganite (LSM), LSM+YSZ, or Sr-doped lanthanum ferrite (LSF), which is applied to the electrolyte by screen printing and then sintered. Cells with LSF cathode and a $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ interlayer between the LSF cathode and the YSZ electrolyte have shown a power density of up to 1 W/cm^2 (at 0.7 V) at 800°C with air as oxidant and a mixture of 97% $\text{H}_2 + 3\% \text{H}_2\text{O}$ as fuel, as illustrated in Fig. 4. The performance of these cells depends to a large extent on the microstructures of the cathode and at the cathode/electrolyte interface; optimization of cathode and interlayer materials and microstructures can provide still higher and stable performance.

Planar designs offer several potential advantages, includ-

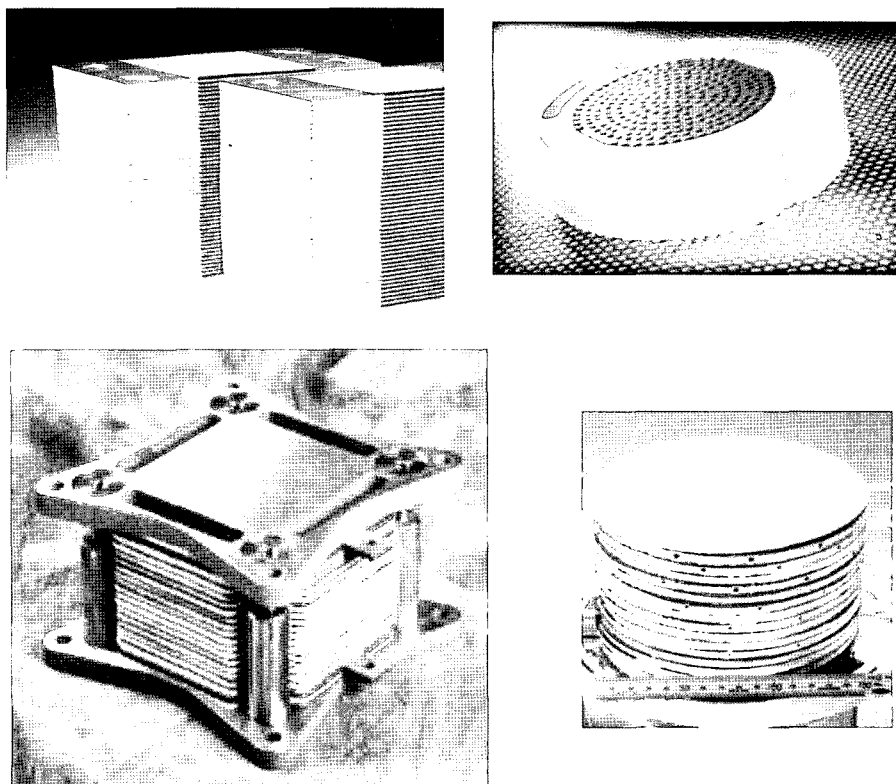


Fig. 3. Examples of planar SOFC stacks.

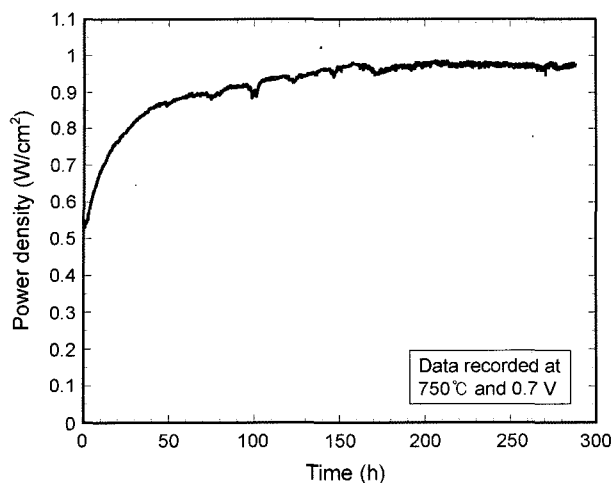


Fig. 4. Performance of an anode-supported planar SOFC at 800°C.

ing simpler and less expensive manufacturing processes and higher power densities than tubular cells described in the next section. However, planar designs need high temperature gas-tight seals between the components in the SOFC stack; such seals are not necessary with tubular cells. These seals must prevent (or at least minimize sufficiently for acceptable performance) both leakage of fuel and oxidant gases from the stack to the outside environment, and mixing of fuel and oxidant gases within the stack; leakage of fuel leads to reduced stack efficiency (as a lower fraction of the input fuel is available for conversion to electricity), while mixing of fuel and oxidant within the stack not only reduces efficiency but can also lead to degradation of the cell components owing to localized "hot spots" resulting from the heat of the combustion reactions. The seals must also offer electrical insulation to prevent shorting between cells within the stack.

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 be used in any given stack design between different components.⁸⁾ Rigid seals typically rely on a glass that softens and "glues together" the adjacent stack components during stack fabrication (at a temperature above the operating temperature), but then becomes rigid and immobile, frequently due to crystallization, when cooled to the operating temperature. Glass-based seals represent a relatively straightforward means of sealing an SOFC stack (at least initially), but the brittle nature of glasses (below the glass transition temperature) and glass-ceramics makes the seals vulnerable to crack formation (resulting from stresses related to thermal expansion mismatches with the adjacent components). As a consequence, the Coefficient of Thermal Expansion (CTE) must be similar to that of the other components. While glass compositions can be tailored to optimize their physical properties, the selection of glasses

offering appropriate thermal expansion behavior is relatively narrow, and the selection is further limited by the need for the glass to have appropriate wetting behavior and viscosity at the sealing temperature. Chemical compatibility with the stack components and the gaseous constituents of the highly oxidizing and reducing environments is another concern. Glasses tend to interact with other stack components, such as interconnects or electrodes, at SOFC operating temperatures. Interactions can occur over a short range (e.g. via direct physical contact) or over longer distances (via gaseous transport of species to or from the glass). The formation of volatile reaction products at the electrodes (due to interaction of the glass with high temperature gases) must be avoided to prevent/minimize surface contamination and poisoning of electrodes. For example, B_2O_3 tends to volatilize in both fuel and air, while SiO_2 tends to volatilize in fuel. Alkali-containing glasses are usually avoided, as volatilization of alkali species degrades cathode performance because of a coarsening of cathode grains at the cathode/electrolyte interface. Sealing glasses also tend to be very reactive toward metallic interconnect materials. These reactions can result in formation of secondary phases and/or extensive porosity, either of which can seriously degrade the strength of the seal. Interactions with the SOFC gases can also compromise the seal itself, both in terms of strength and/or hermeticity, through loss of seal material. To ensure long-term stability of the seal, it may be necessary to minimize the amount of volatile constituents and/or minimize the exposed seal-surface area.⁸⁾

While all three constituents of the primary glass-forming oxides (B_2O_3 , P_2O_5 , SiO_2) have been investigated for SOFC seals, the best results to date have been obtained using compositions based on silica. Alkali silicate glasses tend to be very reactive towards other SOFC components, though alkaline-earth aluminosilicate glasses have yielded promising results. One of the primary advantages of the latter (particularly those containing BaO) is the ability to tailor their CTE to match that of other SOFC stack components. These glasses also offer good wetting of stack components, high electrical resistivity and rapid crystallization kinetics after the viscous sealing process. As a result, successful bonding with YSZ is frequently reported, though bonding with alloy interconnects tends to be more challenging and problematic.⁸⁾

Another possible means of sealing stack components is brazing, whereby a filler metal, the liquidus of which is well below that of the materials to be joined, is heated to a point at which it is molten, is allowed to flow and fill the gap between the two joining pieces under capillary action, and then cooled to solidify the joint. Although most commercial brazes do not wet ceramic surfaces, the addition of a reactive metal, such as Ti or Zr, results in the reduction of the ceramic phase at the joining interface to give an intermediate layer that is in chemical equilibrium with both the ceramic and braze-metal phases. Once this reduced phase forms, wetting of the ceramic surface by the filler metal is

improved greatly. While active metal brazing solves the wetting issue, preferential oxidation of the active element in the braze at SOFC operating temperatures can lead to rapid deterioration of the joint. The desire to accomplish sealing in an inexpensive oxidizing environment greatly complicates the search for an appropriate joining material. Use of a reducing environment at joining temperatures of the order of 800°C or greater adds cost and can damage cathode materials, resulting in a severe loss in cell performance. This processing restriction eliminates conventional active metal brazing as a joining technique and essentially reduces the list of candidate joining materials to noble metal-based brazes.⁸⁾

Compliant seals, which attempt to simultaneously perform the sealing function and prevent thermal stress generation between adjacent components, can allow for the use of stack components with considerable thermal expansion mismatch. Glasses with a T_g below the stack operating temperature can provide some measure of stress relief due to viscous flow, but it is difficult to tailor a glass viscosity low enough for stress relief but not so low as to allow for glass migration from the seal area. The problem is the relatively large ΔT s encountered within the stack; glass viscosity can change significantly over a 50–100°C temperature range, so that a glass with the optimum viscosity near the cell inlets may be far too fluid near the cell outlets.⁸⁾

Compressive seals, which typically utilize materials such as sheet-structure silicates to act as a gasket between components, can help to improve the stack's tolerance to thermal expansion mismatch between the various stack components. A compliant high-temperature material is placed between the two sealing surfaces and compressed, using a load frame external to the stack, to accomplish sealing. Because the seal conforms to both sealing surfaces and is under constant compression during use, it forms a dynamic structure that reduces the need for CTE matching. It is also possible for the sealing surfaces to slide past one another without disrupting the hermeticity of the seal. The primary challenge associated with this technology is the need for a compliant high temperature sealing material that functions adequately as a reliable compressive seal. A number of materials have been considered for compressive seals, including mica, nickel and copper. Each has been found to have limitations when used in a simple gasket configuration, ranging from oxidation in the case of the metals to relatively high leak rates in the case of the mica. The route to enhanced performance could lie with new hybrid and composite seal approaches, in which mica is combined with other materials.⁹⁾

Successful development of sealing materials and concepts for planar SOFCs is probably the most important issue for the long-term performance stability and life-time of planar SOFC stacks and hence for their eventual commercialization at competitive costs.

Sizeable cost reductions are possible with the planar design cells through a concept called "mass customization"

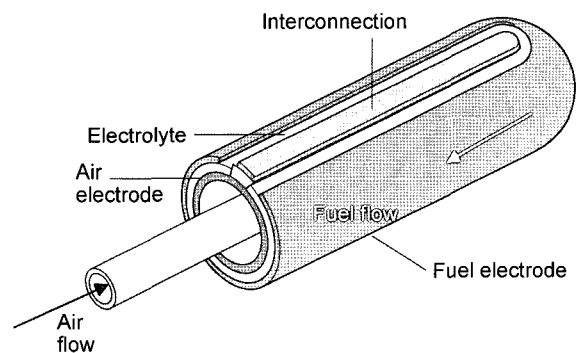


Fig. 5. Tubular solid oxide fuel cell design.¹⁴⁾

that is being pursued in the U.S. Department of Energy's Solid State Energy Conversion Alliance (SECA).¹³⁾ This concept involves the development of a 3 to 10 kW size core SOFC module, that can be mass produced and then combined for different size applications in stationary power generation, transportation, and military market sectors, thus eliminating the need to produce custom-designed and inherently more expensive fuel cell stacks to meet a specific power rating. Very high power densities of anode-supported planar SOFCs make them very attractive for use in the core SOFC module.

4.2. Tubular SOFC Design

In the tubular SOFC, as illustrated by the Siemens Westinghouse design shown in Fig. 5,¹⁴⁾ the cell components are deposited in the form of thin layers on a doped lanthanum manganite cathode tube.^{1,2)} The cathode tube (2.2 cm diameter, 2.2 mm wall thickness, about 180 cm length) is fabricated by extrusion followed by sintering to obtain about 30–35% porosity. Up until recently, a dense YSZ electrolyte (about 40 μm thick) and a porous Ni-YSZ anode (about 100–150 μm thick) layers were deposited on this cathode tube by electrochemical vapor deposition.¹⁵⁾ However, since the electrochemical vapor deposition process is complex and capital-cost intensive, both of these layers are now deposited by atmospheric plasma spraying in order to reduce cost.¹⁴⁾ The doped lanthanum chromite interconnection, in the form of about 85 μm thick strip along the length of the cathode tube, is also deposited by atmospheric plasma spraying followed by densification sintering to obtain a gas-tight layer.¹⁶⁾

The cell tube is closed at one end. For cell operation, oxidant (air or oxygen) is introduced through an alumina injector tube positioned inside the cell. The oxidant is discharged near the closed end of the cell and flows through the annular space formed by the cell and the coaxial injector tube. Fuel flows on the outside of the cell from the closed end and is electrochemically oxidized while flowing to the open end of the cell generating electricity. At the open end of the cell, the oxygen-depleted air exits the cell and is combusted with the partially depleted fuel. Typically, 50 to 90 percent of the fuel is utilized in the electrochemical cell reaction. Part of the depleted fuel is recirculated in the fuel stream and the

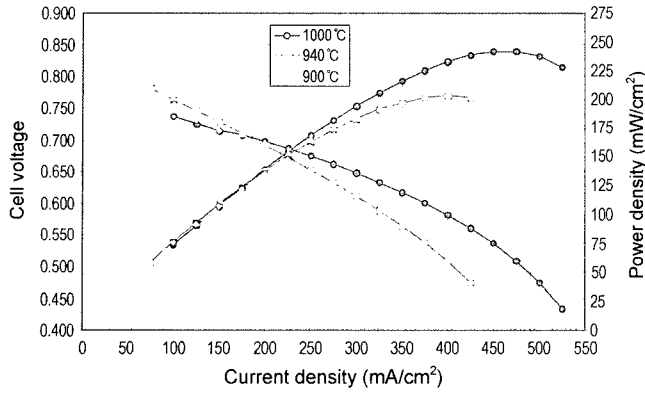


Fig. 6. Voltage-current density and power-current density plots of a tubular SOFC.³⁾

rest combusted to preheat incoming air and/or fuel. The exhaust gas from the fuel cell is at 600 to 900°C depending on the operating conditions.

The voltage-current and power-current characteristics of a 2.2 cm diameter, 150 cm active length cell at 800, 900, and 1000°C with 89% H₂ + 11% H₂O fuel (85% fuel utilization) and air as oxidant (4 stoichs) are shown in Fig. 6. Such tubular cells have a power density at 1000°C of about 0.2 W/cm². To construct an electric generator, individual cells are connected in both electrical parallel and series to form a semi-rigid bundle that becomes the basic building block of a generator. Nickel felt, consisting of long sinter-bonded nickel metal fibers, is used to provide soft, mechanically compliant, low electrical resistance connections between the cells. This material bonds to the nickel particles in the anode and the nickel plating on the interconnection for the series connection, and to the two adjacent cell anodes for the parallel connection. A three-in-parallel by eight-in-series cell bundle is shown in Fig. 7. Such cell bundles are arrayed in series to build voltage and form generator modules.

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

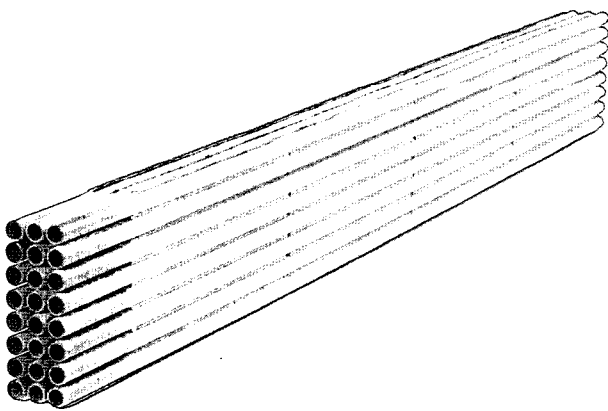


Fig. 7. A three-in-parallel by eight-in-series tubular cell bundle.¹⁾

(several years). However, their areal power density is much lower (about 0.2 W/cm²) compared to planar cells (up to 2 W/cm² for single cells and at least 0.5 W/cm² 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 are under development.^{14,17)} 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. Fig. 8 shows several of such designs being developed by Siemens Westinghouse. The performance of these new design cells, compared in Fig. 9, is much higher than that of cylindrical tubular cells, but still lower than that of anode-supported planar cells.¹⁷⁾

5. SOFC Applications and Systems

Using planar SOFCs, stationary power generation systems of from 1 kW to 25 kW size have been fabricated and

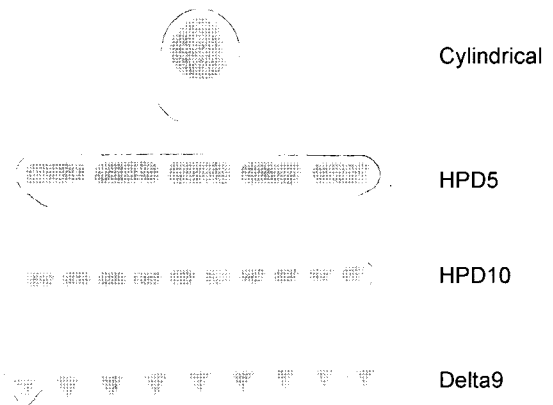


Fig. 8. Alternate tubular geometry cells being developed by Siemens Westinghouse.¹⁷⁾

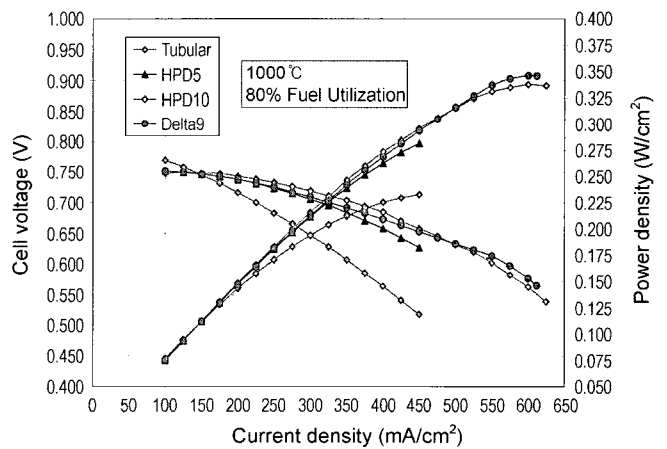


Fig. 9. Comparative performance of cylindrical and alternate tubular geometry cells.¹⁷⁾

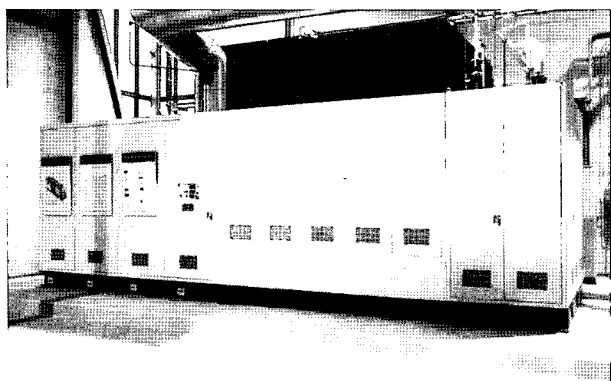


Fig. 10. Siemens Westinghouse's 100 kW size atmospheric pressure CHP system.²²⁾

tested by several organizations. Over 100 1-kW size Combined Heat and Power (CHP) units for residential application have been field tested by Sulzer Hexis¹⁸⁻²⁰⁾; however, their cost and performance degradation remains high and stack lifetime is too short. A 25 kW size system was fabricated by Ceramic Fuel Cells Ltd.²¹⁾; other organizations have also fabricated small cell stacks and systems and tested them for up to a few thousand hours. However, such tests have shown only limited stack lifetimes, primarily because of the problems with the glass seals that were employed to isolate air from the fuel in making the stacks. More recently, with improved sealing materials and sealing concepts, planar SOFC prototype systems in the 1 to 5 kW sizes have been developed and are being tested by various organizations with greater success.

Siemens Westinghouse fabricated a 100 kW atmospheric power generation system using tubular (cylindrical) SOFCs, as shown in Fig. 10.²²⁾ The SOFC stack in this system consisted of 1152 cells (2.2 cm diameter and 150 cm active length) arranged in 12 bundle rows; each row was composed of four cell bundles, with each bundle comprising 24 cells. 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 h. After replacing some cells, the system has now been installed and is operating in Italy, again with very stable performance. Siemens Westinghouse's efforts are now focused on reducing the cost of such SOFC power systems.

Fuel Cell Technologies Ltd. has fabricated and field tested over a dozen 5 kW size CHP units, each about the size of a refrigerator. These early units employed Siemens Westinghouse tubular cells and gave excellent performance and performance stability on a variety of hydrocarbon fuels. However, at present, their cost is high. The later units are expected to use higher power density alternate tubular

geometry cells to drive down the cost.³⁾

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 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 all the CO 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 is developing a 5 kW APU using anode-supported planar SOFCs, to provide electrical power needs of an automobile without the need for operating the vehicle engine.^{23,24)} This unit is intended to operate on gasoline, which is reformed through 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. Since the testing of an initial 5 kW proof-of-concept unit in 2001, Delphi has reduced the mass and volume in successive generation units to meet the stringent automotive requirements. The critical issues of start up time and tolerance to thermal cycling are presently being worked on.

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 applications, ability for rapid start up and thermal cycling needs to be developed.

6. Summary

The Solid Oxide Fuel Cell (SOFC) is an electrochemical device to convert chemical energy of a fuel into electricity at temperatures from about 600 to 1000°C. SOFCs provide a highly efficient, low-pollution power generation technology. SOFCs also offer certain other advantages over lower temperature fuel cells, notably their ability to use CO as a fuel rather than being poisoned by it, and high grade exhaust heat for combined heat and power, or combined cycle gas turbine applications. This paper has reviewed the operating principle, materials, designs, and applications of such SOFCs. The most progress has been achieved with the tubular design SOFCs; however, the electrical resistance of tubular SOFCs is high, and specific power output (W/cm²)