APPLICATION OF IONIC AND ELECTRONIC CONDUCTING CERAMICS IN SOLID OXIDE FUEL CELLS

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ABSTRACT

Solid oxide fuel cells (SOFCs) offer a pollution-free technology to electrochemically generate electricity at high efficiencies. These fuel cells consist of an oxygen ion conducting electrolyte, electronic or mixed electronic/ionic conducting electrodes, and an electronic conducting interconnection. This paper reviews the ceramic materials used for the different cell components, and discusses the performance of cells fabricated using these materials. The paper also discusses the materials and processing studies that are underway to reduce the cell cost, and summarizes the recently built power generation systems that employed state-of-the-art SOFCs.

1. INTRODUCTION

High temperature solid oxide fuel cells (SOFCs) offer a clean, pollution-free technology to electrochemically generate electricity at high efficiencies. These fuel cells provide high efficiency, reliability, modularity, fuel adaptability, and very low levels of NOx and SOx 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 temperature of operation (~1000°C), these cells can be operated directly on natural gas eliminating the need for an expensive, external reformer system. These fuel cells also produce high quality exhaust heat which can be used for process heat or a bottoming electric power cycle to further increase the overall efficiency. Also, pressurized SOFCs can be successfully used as replacements for combustors in combustion turbines; such integrated SOFC-combustion turbine power systems are expected to reach efficiencies approaching 70%.

The solid oxide fuel cells consist of an oxygen ion conducting electrolyte, electronic or mixed electronic/ionic conducting electrodes, and an electronic...
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conducting interconnection. This paper reviews the ceramic materials used for the different cell components, and discusses the performance of cells fabricated using these materials. The paper also summarizes the recently built power generation systems that employed state-of-the-art SOFCs.

2. MATERIALS FOR SOFC COMPONENTS

Solid oxide fuel cells of several different designs are presently under development; these include planar, monolithic and tubular geometries. The materials being considered for cell components in these different designs are either the same or very similar in nature. The most progress to date has been achieved with the tubular geometry fuel cell. Fig. 1 illustrates the design of the Westinghouse tubular geometry cell. In this design, the cell components are deposited in the form of thin layers on a ceramic cathode tube. The materials for different cell components have been selected based on the following criteria:

(a) Suitable electrical conducting properties required of different cell components to perform their intended cell functions.

(b) Adequate chemical stability at high temperatures during cell operation as well as during cell fabrication.

(c) Minimal reactivity and interdiffusion among different cell components.

(d) Matching thermal expansion among different cell components.

In addition to above materials selection criteria, the fabrication processes have been chosen so that every sequential component fabrication process does not affect those components already fabricated onto the cathode tube. The materials and fabrication processes used for different cell components are discussed below.

Cathode (Air Electrode)

With operating temperature of around 1000°C in air or oxygen atmosphere, the material for the air electrode in solid oxide fuel cells has to meet the following requirements:

(a) High electronic conductivity.

(b) Chemical and dimensional stability in environments encountered during cell operation and during fabrication of interconnection, electrolyte and fuel electrode layers.
(c) Thermal expansion match with other cell components.

(d) Sufficient porosity and good adherence at the surface of the electrolyte.

(e) Compatibility and minimum reactivity with the electrolyte and the interconnection with which air electrode comes into contact.

To satisfy these requirements, lanthanum manganite suitably doped with alkaline and rare earth elements is used in the form of a porous tube onto which other cell components are fabricated. Lanthanum manganite is a p-type perovskite oxide and shows reversible oxidation-reduction behavior. 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 ≤10^{14} atm. The electronic conductivity of lanthanum manganite is due to small polaron hopping which is enhanced by doping with a divalent ion such as calcium or strontium. The defect chemistry, electrical conduction, and cathodic polarization behavior of doped lanthanum manganites have been studied in detail [1,2], and alkaline earth doped lanthanum manganite has been found to satisfy all the requirements to be an effective air electrode. Furthermore, the reactivity and interdiffusion studies [3,4], between doped lanthanum manganite and yttria stabilized zirconia electrolyte have shown any interactions between these two materials at 1000°C to be minimal.

Use of mixed lanthanides instead of pure lanthanum in the cathode material to reduce cell cost has also yielded encouraging results. Over 90% of the weight of a tubular SOFC is that of the doped lanthanum manganite air electrode tube. Presently, the air electrode material is synthesized using high purity component oxides such as La₂O₃ and MnO₂. Over 70% reduction in the cost of air electrode raw materials is possible if mixed lanthanides are used instead of pure lanthanum compounds to synthesize the air electrode powder. These mixed lanthanides contain Nd, Pr, Ce and Sm in addition to La. Cells have now been fabricated using air electrode powder synthesized using mixed lanthanides. Fig. 2 compares the performance of a cell fabricated using mixed lanthanides for the air electrode to that of a cell fabricated using pure lanthanum oxide instead. The performance of the cell with air electrode fabricated using mixed lanthanides at 400 mA/cm² is only about 8% lower, primarily due to slightly higher resistivity of the mixed lanthanides air electrode and non-optimized cell fabrication conditions. Further adjustments in the composition of the air electrode material synthesized using mixed lanthanides are expected to result in lower air electrode resistivity and a cell performance equivalent to that of cells using high purity air electrode material. The substitution of mixed lanthanides for lanthanum in air electrodes results in a major reduction in the cost of raw materials used in the manufacture of tubular SOFCs.


**Electrolyte**

Solid oxide fuel cells are based on the concept of an oxygen ion conducting electrolyte through which the oxygen ions migrate from the air electrode (cathode) side to the fuel electrode (anode) side where they oxidize the fuel (H₂, CO, etc.) to generate an electrical voltage. Fluorite structure oxides for use as an electrolyte have been extensively investigated and reviewed [5-7]. Yttria stabilized zirconia (YSZ) is the most widely used electrolyte. This material exhibits cubic fluorite structure in which yttrium (Y³⁺) substitutes for the zirconium (Zr⁴⁺) cations generating oxygen vacancies. The high ionic conductivity of yttria stabilized zirconia is attributed to these oxygen ion vacancies along with low activation energy for oxygen ion migration. Other materials based on Er₂O₃ or Y₂O₃ stabilized Bi₂O₃ [8,9] and ceria stabilized with gadolinia [10] exhibit even higher conductivity than YSZ at the same temperature; however, these oxides are unstable and suffer from electronic conduction in the reducing fuel environment limiting their usefulness in practical SOFCs. Recently, alkaline earth (Mg, Sr, etc.) doped lanthanum gallate (LaGaO₃) has been identified as an excellent oxygen ion conductor with a conductivity about the same or better than YSZ at 800°C [11-13]. However, its application in practical SOFCs must await further development of compatible anode and cathode materials to obtain high performance.

In the Westinghouse tubular SOFCs, zirconia doped with about 10 mole percent yttria is 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 [14]; the activation energy is also least near this composition. The thermal expansion of 10 mole percent YSZ is about 10 x 10⁻⁶/°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 oxygen ion conductivity with transport number for oxygen ions close to unity and a transport number for electrons as close to zero as possible. Electrolyte with these desired properties is deposited in the form of about 40 μm thick layer by an electrochemical vapor deposition process (EVD) [15,16]. Deposition of the YSZ electrolyte film by a non-EVD technique, such as colloidal/electrophoretic deposition followed by sintering, is currently being investigated to reduce cell cost.

**Anode (Fuel Electrode)**

The fuel electrode of a solid oxide fuel cell must be electronically conducting, stable in the reducing environment of the fuel, and must have interconnected porosity to allow the passage of the fuel to the electrolyte surface. Due to the reducing atmosphere of the fuel gas, a metal such as nickel (or cobalt, ruthenium, etc.) can be
used for SOFC anodes. However, the thermal expansion coefficient of nickel is considerably larger than that of the YSZ electrolyte; this large thermal expansion mismatch can cause delamination of the anode from the electrolyte surface. Also, nickel can sinter at the cell operating temperature resulting in a decrease in anode porosity. To circumvent these problems, a skeleton of YSZ is formed around the nickel particles. This skeleton of YSZ supports the nickel particles, inhibits sintering of the nickel particles during cell operation, provides adherence to the electrolyte, and also provides an anode thermal expansion coefficient closer to that of the electrolyte. Such nickel/YSZ anodes show very low diffusion and activation polarization losses during cell operation. Such anodes have also been shown to possess sufficient catalytic activity at 1000°C to reform natural gas and other hydrocarbons in situ. Mixed ionic/electronic conducting solid solutions of YSZ with ceria or titania have also been suggested for use as SOFC anodes [17-19].

In Westinghouse tubular cells, a 100-150 μm thick layer of nickel/YSZ is applied over the electrolyte by a two-step process. In the first step, nickel powder slurry is applied over the electrolyte. In the second step, YSZ is grown around the nickel particles by the same EVD process as used for depositing the electrolyte. Deposition of a Ni-YSZ slurry over the electrolyte followed by sintering has also yielded anodes that are equivalent in performance to those fabricated by the EVD process; use of this non-EVD process will result in a substantial reduction in the cost of manufacturing SOFCs.

**Interconnection**

Interconnection, in the form of about 9 mm wide strip along the cell length, serves as the electric contact to the air electrode and also protects the air electrode material from the reducing environment of the fuel on the fuel electrode side. The requirements of the interconnection are the most severe of all cell components and include:

(a) Nearly 100 percent electronic conductivity.

(b) Stability in both oxidizing and reducing atmospheres at the cell operating temperature since it is exposed to air (or oxygen) on one side and fuel on the other.

(c) Low permeability for oxygen and hydrogen to minimize direct combination of oxidant and fuel during cell operation.

(d) A thermal expansion close to that of the air electrode and the electrolyte.
(e) Non-reactivity with the air electrode, electrolyte and the electric contact material (e.g., nickel).

To satisfy these requirements, doped lanthanum chromite is used as the interconnection material. 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 $10^{-8}$ atm. The conductivity is enhanced as lower valence ions (e.g., Ca, Mg, Sr, etc.) are substituted on either the La$^{3+}$ or Cr$^{3+}$ sites. The defect chemistry, oxidation-reduction behavior, and the thermal expansion behavior of these chromites have been extensively studied [1,20].

For the Westinghouse tubular SOFC, the interconnection is deposited in the form of about 85 µm thick, 9 mm wide strip along the air electrode tube length by plasma spraying [21].

3. CELL PERFORMANCE

A large number of cells with plasma sprayed interconnections have been electrically tested for over 13,000 h. These cells have shown the ability to perform for extended periods of time under a variety of operating conditions with little performance degradation. The voltage-current characteristics of 1.56 cm diameter, 50 cm active length cells at 900, 950, and 1000°C, with 89% H$_2$ + 11% H$_2$O fuel (85% fuel utilization) and air as oxidant (4 stoichs) are shown in Fig. 3.

These SOFCs have also shown the ability to thermally cycle to room temperature over 100 times without any mechanical damage or performance loss as shown in Fig. 4. This ability to sustain thermal cycles is essential for any SOFC generator to be commercially viable. In addition to the ability to sustain large number of thermal cycles, the cells can be cycled with a rapid temperature ramp rate making SOFC generators suitable for rapid start-up or restart following a power interruption. The thermal cycles in Fig. 4 are for temperature ramps from ambient temperature to 1000°C within 5 h or less.

Westinghouse in conjunction with Ontario Hydro has also tested SOFCs at pressures up to 15 atmospheres on both hydrogen and natural gas fuels. Fig. 5 shows the comparative power-current density curves at 1, 3, 5, 10 and 15 atm for a 2.2 cm diameter, 150 cm active length cell at 1000°C. Operation at elevated pressures yields a higher cell power at any current density due to increased Nernst potential and reduced cathode polarization, and thereby permits higher stack efficiency and greater power output. With pressurized operation, SOFCs can be successfully used as replacements for combustors in combustion turbines; such integrated SOFC-combustion turbine power systems are expected to reach efficiencies approaching...
70%, and thus result in reduced fuel consumption cost and reduced capital cost per unit power output [22].

4. SOFC POWER GENERATION SYSTEMS

Recently, two 25 kW systems, each consisting of 576 50-cm active length cathode supported cells (with EVD electrolyte, EVD fuel electrode, and plasma sprayed interconnection), were built and tested. One system was operated at the Southern California Edison Company's Highgrove Generating Station in Grand Terrace (near San Bernardino), California, under a program with the U.S. Department of Defense's Advanced Research Projects Agency (ARPA). In addition to the SOFC generator, this system also consisted of a logistic fuel processor, located external to the SOFC stack, enabling the system to operate on either natural gas or on reformate from a logistic fuel (DF-2 diesel or JP-8 jet turbine fuel). This system was successfully operated for 5,582 h before the project completion; 766 h on jet turbine fuel, 1,555 h on diesel fuel, and 3,261 h on natural gas. During this time, the system endured five thermal cycles to room temperature, produced up to 27 kW on each of the three fuels, and showed no evidence of performance degradation.

The other system, built for a consortium of Osaka Gas and Tokyo Gas, completed 13,194 h of successful operation on desulfurized natural gas with approximately 0.1% per 1000 h of performance degradation. During this period, the unit achieved 25 kW of power output and endured ten thermal cycles to ambient temperature.

A 100 kW SOFC power generation system is presently being built for a consortium of Dutch and Danish utilities (EDB/ELSAM). The system will be installed and operated at Duiven (near Arnhem), The Netherlands, at a district heating system owned by NUON, one of the group of five Dutch gas and electricity distribution utilities which belong to the EDB consortium. The system employs 1,152 state-of-the-art cells with plasma sprayed interconnections (2.2 cm diameter, 150 cm active length); these cells are prototypic of the cells that are planned to be used in MW-class commercial SOFC generators. The system will deliver 100 kW net ac to the grid at an overall thermal efficiency of 47% (ac/LHV) and recover 26% of the fuel energy in hot water yielding a total fuel effectiveness (at 100 kW ac) of 73%. The maximum power output of the system is 160 kW net ac; at maximum power, the fuel effectiveness of the system will approach 80%.

All the systems described above have been or will be operated at 1 atm pressure. Plans to design, build, and test integrated pressurized SOFC-combustion turbine power generation systems in the 250 kW to integer MW sizes are presently being finalized.
5. SUMMARY

High temperature SOFCs successfully employ a variety of ionic, electronic, and mixed ionic/electronic conducting ceramics to provide a highly efficient, pollution-free power generation technology. Their performance has been confirmed by successful operation of power generation systems employing such cells of up to 25 kW size. In addition, significant cost reductions have been achieved by adopting non-EVD processes in cell production; further reductions in materials and processing costs will be realized when the programs currently underway are proven successful and are implemented in cell manufacturing.

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REFERENCES


![Diagram of a Tubular Solid Oxide Fuel Cell Design](image)

**Fig. 1.** Tubular solid oxide fuel cell design.
Fig. 2. Effect of air electrode material purity on the voltage-current characteristics of the cell at 1000°C.

Fig. 3. Voltage-current characteristics at different temperatures.
Fig. 4. Thermal cycling capability of Westinghouse SOFCs.

Fig. 5. Effect of pressure on cell power at 1000°C.