Reduced-Temperature Solid Oxide Fuel Cells Fabricated by Screen Printing

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Electrolyte films of samaria-doped ceria (SDC, $Sm_{0.2}Ce_{0.8}O_{1.9}$) are fabricated onto porous NiO-SDC substrates by a screen printing technique. A cathode layer, consisting of $Sm_{0.5}Sr_{0.5}CoO_3$ and 10 wt % SDC, is subsequently screen printed on the electrolyte to form a single cell, which is tested at temperatures from 400 to 600°C. When humidified (3% H_2O) hydrogen or methane is used as fuel and stationary air as oxidant, the maximum power densities are 188 (or 78) and 397 (or 304) mW/cm² at 500 and 600°C, respectively. Impedance analysis indicates that the performances of the solid oxide fuel cells (SOFCs) below 550°C are determined primarily by the interfacial resistance, implying that the development of catalytically active electrode materials is critical to the successful development of high-performance SOFCs to be operated at temperatures below 600°C.
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A solid oxide fuel cell (SOFC) is one of the cleanest, most efficient, and versatile technologies for chemical-to-electrical energy conversion. While existing SOFC technology has demonstrated much higher energy efficiency with minimal pollutant emission over conventional energy technologies, the cost of the current SOFC systems is still prohibitive for broad commercialization except for a small niche market. To be economically competitive, both the cost of materials and the cost of fabrication for SOFC systems must be dramatically reduced. One effective approach to cost reduction is to reduce the operating temperature. For example, if the operating temperature of SOFCs can be reduced to 400-600°C, the interconnect, heat exchangers, and structure components may be fabricated from relatively inexpensive metal components.[1,2] Accordingly, extensive efforts have recently been focused on reduced-temperature SOFCs. Doshi *et al.* reported a maximum power density of 140 mW/cm² at 500°C for a H_2/air fuel cell based on a thin film GCO ($Gd_{0.2}Ce_{0.8}O_{1.9}$) electrolyte with a Ni-GCO anode and an ANLC-1 cathode.[3] The anode-supported cell was prepared by a multiplayer tape-casting technique. The total cell resistance at 500°C was 1.3 Ω cm², of which 0.7 Ω cm² was attributed to the electrolyte and nearly 0.6 Ω cm² to the cathode, while the polarization of the anode was negligible. Barnett *et al.*[4] reported a direct electrochemical oxidation of methane in SOFCs that generated power densities up to 370, 250, and 125 mW/cm² at 650, 600, and 550°C, respectively. The electrolyte film, an 8 μm thick YSZ, was prepared on a $La_{0.8}Sr_{0.2}MnO_3$ cathode using magnetron sputtering.

To significantly reduce the cost of fabrication, we have studied screen printing for fabrication of SOFCs based on an SDC ($Sm_{0.2}Ce_{0.8}O_{1.9}$) electrolyte film, a cermet anode consisting of SDC and NiO, and a composite cathode consisting of $Sm_{0.5}Sr_{0.5}CoO_3$ and 10% SDC. Compared with the film preparation techniques mentioned earlier, screen printing is simple and cost effective.[1] It has been extensively used for the preparation of electrolytes with thickness varying from a few tens of micrometers to about 200 μm. In this article, we report our initial results on SOFCs based on SDC electrolyte fabricated using screen printing and characterized at temperatures from 400 to 600°C. The observed power densities and the interfacial resistances are impressive at these low temperatures, while the detailed electrochemical characteristics of the cells, especially the interfacial phenomena, are still under investigation.

The SDC electrolyte powder and the cathode material ($Sm_{0.5}Sr_{0.5}CoO_3$) were prepared by a glycine/nitrate process.[5-7] The anode pellets were prepared from a mixture of NiO and SDC powder at a weight ratio of NiO:SDC = 65:35. The mixed powder was pressed under 2×10^8 Pa into a pellet (10 mm diam and 0.3-0.5 mm thick). An electrolyte slurry consisting of SDC powder, methylcellulose, terpineol, and ethanol was screen printed onto the green anode pellet and subsequently fired at 1350°C in air for 5 h. The temperature was increased at a rate of 120°C/h up to the firing temperature, pausing for 60 min at 450°C to remove organics. A cathode slurry consisting of $Sm_{0.5}Sr_{0.5}CoO_3$, 10 wt % SDC, and a Heraeus binder (V006) was also applied to the electrolyte by screen printing. The cathode was fired at 950°C in air for 4 h with heating and cooling rates of 300°C/h. Shown in Fig. 1 are the microstructures of each cell component as characterized using a scanning electron microscope (SEM, Hitachi S-800). The SDC electrolyte layer (with thickness of 30 μm) is dense while both anode and cathode are porous. The porosities of the cathode and anode are 27 and 35%, respectively, as estimated from quantitative microscopy.

The single cell was sealed on an alumina tube support with silver paste (Heraeus, C8710). The cell was horizontally mounted into an electric furnace. Electrochemical characterizations were performed at ambient pressure at temperatures from 400 to 600°C. Fuel cell performances were measured with an EG&G potentiostat/galvanostat (model 273A) interfaced with model 270/250 Research Electrochemistry software. Humidified (3% H_2O) hydrogen or methane was used as fuel and stationary air was used as oxidant. The impedances of the cell under open-circuit conditions were measured with an EG&G lock-in amplifier (model 5210) and an EG&G potentiostat/galvanostat (model 273A) interfaced with model 398 electrochemical impedance software.
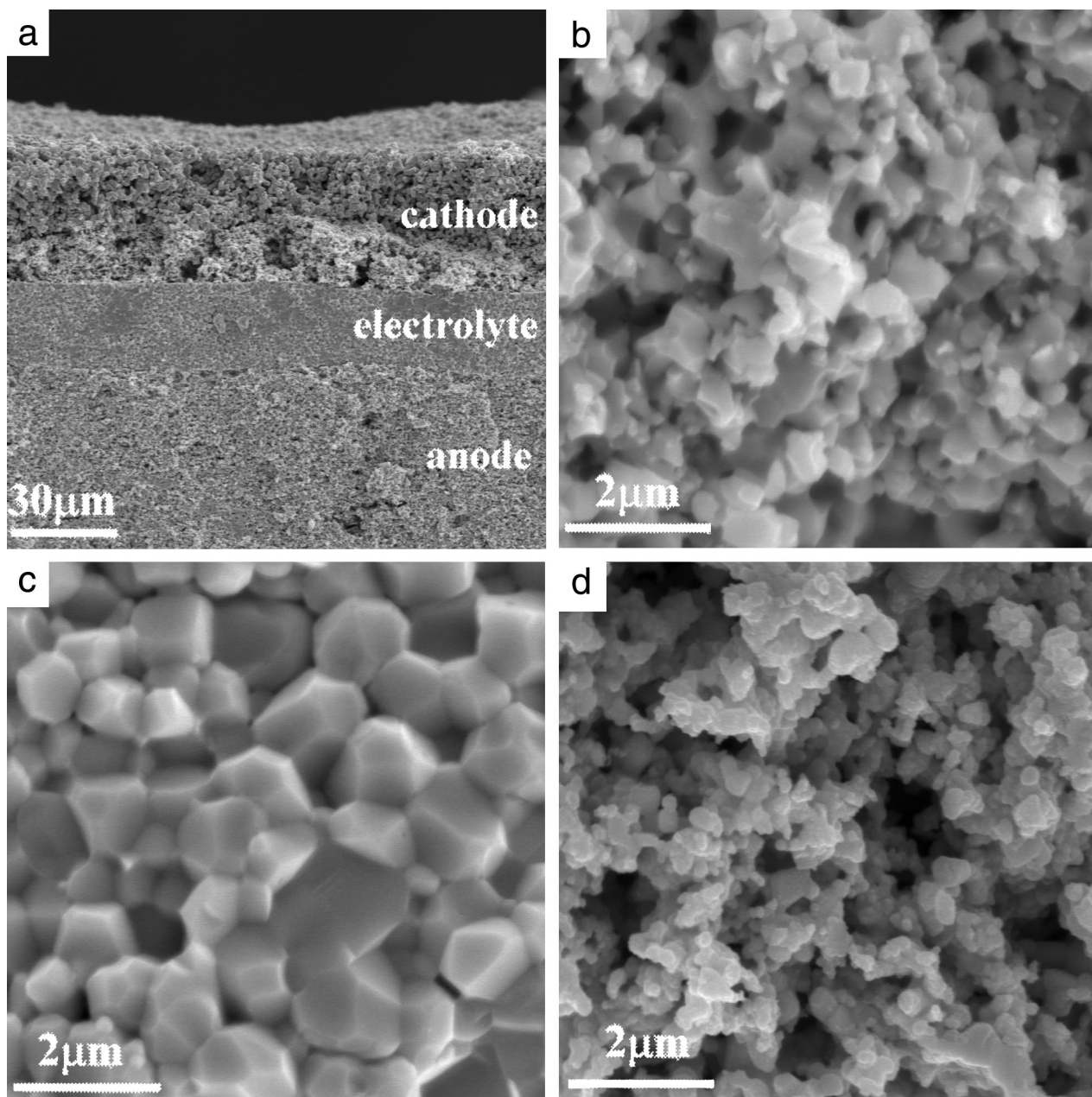
Shown in Fig. 2 are the I-V curves and the corresponding power densities for an SOFC tested at temperatures from 400 to 600°C with humidified hydrogen as fuel. Each datum point was recorded about 30 min after the cell reached the steady state. As shown in Fig. 2, an open-circuit voltage (OCV) of 1.02 V was observed at 400°C indicating that the electronic condition in SDC is insignificant. The maximum power densities were 128, 188, 240, and 397 mW/cm² at 450, 500, 550, and 600°C, respectively. Although fuel cells based on SDC electrolyte that were 0.25-0.50 mm thick have been tested at temperatures above 600°C,[8] the performance of the SOFCs below 600°C is not available in the literature. The observed current and power densities at low temperatures (400-600°C) of the fuel cells fabricated by screen printing represent significant progress in low-temperature SOFCs.

Figure 3a shows the impedance spectra of a single cell with humidified hydrogen as fuel, while in Fig. 3b the interfacial polar-
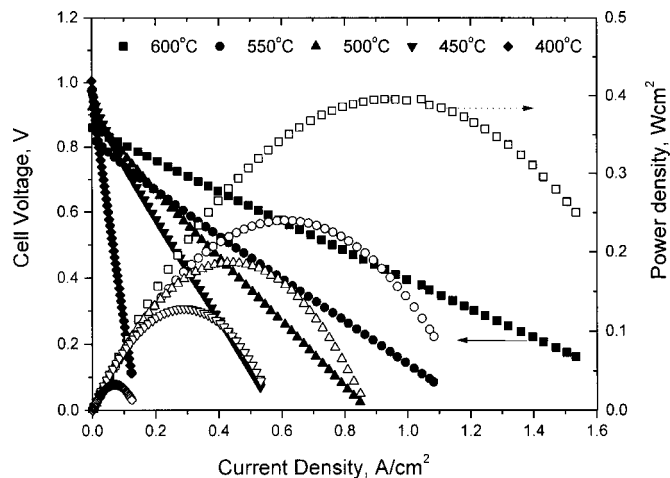
Figure 1. Cross-sectional view (SEM graphs) of (a) a single cell, (b) the porous Ni-SDC anode, (c) the dense SDC electrolyte, and (d) the porous $Sm_{0.5}Sr_{0.5}CoO_3$ + 10 wt % SDC cathode.

ization resistance and electrolyte resistance as determined from the impedance spectra are shown. At temperatures below 550°C, the interfacial resistance is much greater than the resistance of the electrolyte. The ratio of interfacial resistance to electrolyte resistance increased dramatically as the operating temperature was reduced, implying that the performance of the SOFCs to be operated at low temperatures depends critically on the interfacial resistance. Accordingly, the development of catalytically active electrodes and interfaces is critical to successful development of SOFCs to be operated at low temperatures (<600°C). Mesoporous mixed-conducting electrodes and nanostructured interfaces may significantly improve the performance of low-temperature SOFCs.

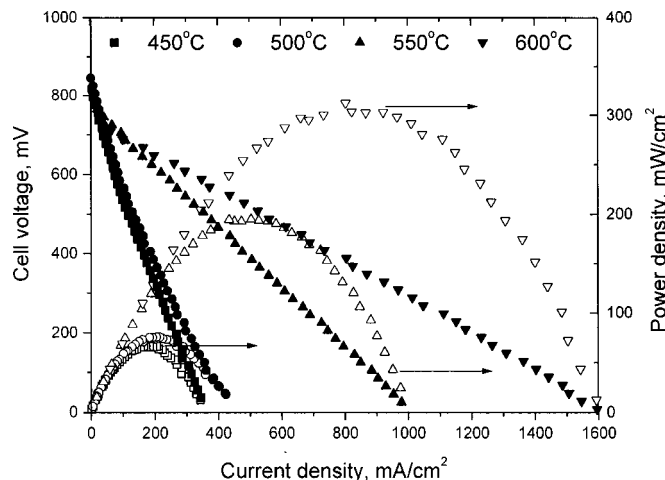It is noted that the interfacial polarization resistance was 1.0 Ω cm^2 at 500°C, about two-thirds the cell resistance, but reduced to 0.07 Ω cm^2 at 600°C, only about one-sixth of the total cell resistance. This implies that the cell performance at temperatures above 600°C can be significantly improved by reducing the thickness of the electrolyte, at these temperatures both the cathode ($Sm_{0.5}Sr_{0.5}CoO_3$ and 10 wt % SDC) and the anode (NiO and 35 wt % SDC) are sufficiently active. For example, the cell performance at 600°C may be increased by 100% by reducing the electrolyte thickness from 30 to 10 μm because the total cell resistance may be reduced from 0.48 to 0.24 Ω cm^2.
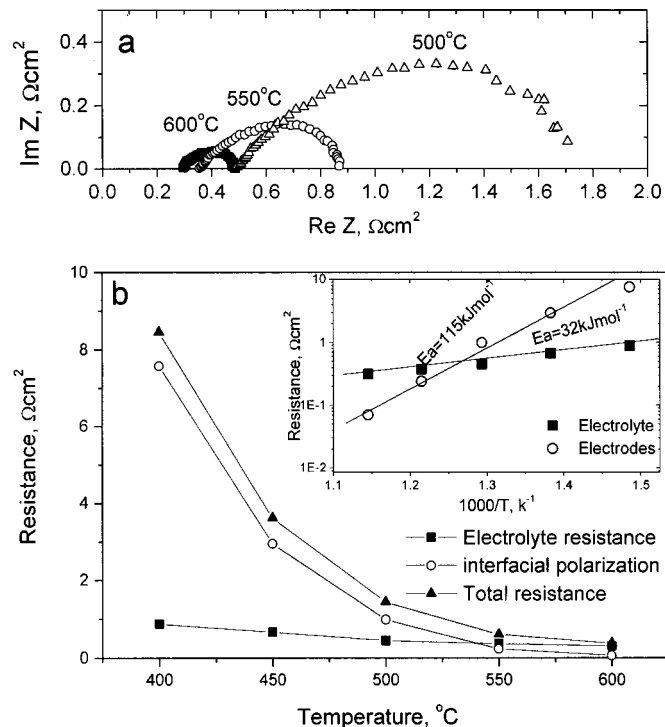
When humidified methane was used as fuel, the maximum power densities were 78, 195, and 304 mW/cm^2 at 500, 550, and 600°C, respectively, as is shown in Fig. 4. The power density at 600°C (304 mW/cm^2) observed in this work is higher than those

Figure 2. Cell voltages (solid symbols) and power densities (open symbols) as a function of current densities for an SOFC with humidified (3% H_2O) hydrogen as fuel at temperatures from 400 to 600°C.

Figure 4. Cell voltages (solid symbols) and power densities (open symbols) as a function of current densities for an SOFC with humidified (3% H_2O) methane as fuel at temperatures from 450 to 600°C.

Figure 3. (a) Impedance spectra of an SOFC (Ni-SDC/SDC/$Sm_{0.5}Sr_{0.5}CoO_3$) as measured under open-circuit conditions when humidified H_2 was used as fuel and air as oxidant at 500, 550, and 600°C. (b) Electrolyte resistance, interfacial polarization resistance, and total cell resistance as determined from the impedance spectra shown in (a).

obtained with SOFCs based on thin film (8 μm thick) YSZ prepared by magnetron sputtering (250 mW/cm²).[4]

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