Graded porous solid oxide fuel cells fabricated by multilayer tape casting and co-firing progress

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Abstract:

Solid oxide fuel cells (SOFCs) with graded porous cathode were fabricated via a multilayer tape casting and co-firing technique, which is a low-cost and reproducible fabrication process. The effects of pore formers on the electrochemical performance of graded cathode are studied to minimize cathodic polarization resistance. Examination of the microstructures reveals that the multilayer single cell had no delamination, observable cracks, or other large defects. The cell prepared by the co-firing process exhibits low interfacial polarization resistance and high power density at the operating temperature range of 700-800 °C. This simple fabrication technique can be used for optimization of electrode microstructures and cost-effective fabrication of high-performance SOFCs.

Keywords: Graded cathode, Multilayer tape casting, Co-firing, Solid Oxide Fuel Cell

1. Introduction

Solid oxide fuel cells (SOFCs) have gained remarkable interest in recent years owing to their high efficiency, low emission, and fuel flexibility [1-3]. However, the cost of current SOFC systems is still prohibitive for many practical applications. To be

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economically competitive, both the cost of materials and the cost of fabrication for SOFC systems must be dramatically reduced [4-5]. One effective approach to cost reduction is to reduce the operating temperature of SOFCs. As a consequence, however, reduction of operating temperature considerably increased electrode polarization resistance, especially the resistance to oxygen reduction at the cathode. To address this problem, many studies have been conducted to develop new electrode materials or composite electrodes with high catalytic activity at relatively low temperatures [6]. Nevertheless, for a given electrode material, the electrode performance can be drastically altered by changing its microstructure, including pore and grain sizes, size distribution, and porosity.

Among various fabrication methods, tape casting is a well-established technique for fabricating large, thin, and flat ceramic tapes with a thickness range of 1-1000 μm . The scalability and longstanding success of the tape casting process makes it a legitimate technique for low-cost manufacturing of SOFC components, such as electrolyte membranes, anode supports, and interconnect layers[7-9]. Recently, tape casting and co-firing techniques have been applied to the fabrication of SOFC single cells and have proven to be scalable and cost-effective. A peak power density of 250 mW cm^{-2} at 900°C has been obtained in an anode-supported cell with a LSM cathode YSZ electrolyte by screen printing and co-firing[10]. Wang et al. [8] fabricated Ni/ScSz anode-supported SOFCs by a multilayer tape casting and co-sintering technique. With the use of a LSCF/GDC composite cathode sintered at 1100°C , they obtained a maximum power density of 0.85 W cm^{-2} and an area-specific polarization resistance of $0.336 \Omega \text{ cm}^2$ at 850°C . H. Moon [11] developed NiO/YSZ anode-supported SOFCs with an anode active layer via a tape casting and lamination technique. After pressing isostatically for

10 min, the half cell with the anode and electrolyte was sintered at 1350 °C for 3 h. The prepared SOFC with a LSM/YSZ cathode exhibited high power density and low cell resistance of 0.73 W cm⁻² and 0.35 Ω cm², respectively, at 700 °C.

Materials in the (La, Sr)(Co, Fe)O_{3-δ} family have been extensively investigated and utilized as a cathode for SOFC due to their high ionic and electronic conductivity and good catalytic activity for the oxygen reduction reaction[12-13]. There have been various processes used for the preparation of porous LSCF electrode such as screen printing[14], dip coating[15] and spray painting[16]. To date, most studies on LSCF cathode reported in the literatures focus on cathodes of uniform microstructures. In this communication, we report our findings on fabrication and characterization of porous La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} cathodes with graded microstructures fabricated by tape casting. The effect of the amount of pore formers on the performance of the graded cathode was determined. Meanwhile, an anode-supported SOFC cell was fabricated by tape casting and co-firing process to produce a cost-effective single cell that operates at intermediate temperatures. The power density and area specific resistance of the resulting SOFC were evaluated.

2. Experimental process

2.1 Cathode Preparation

La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} powders with varying particle sizes were prepared by citrate method [15] and gelcasting technique [17], respectively. The LSCF powders synthesized by the citrate method (S.A. 14.38 m²·g⁻¹) and gelcasting (S.A. 8.07 m²·g⁻¹) were used for active layer (inner layer) and central layer, respectively. For current collector (top layer), commercial La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} powders (S.A. 1.36 m²·g⁻¹, Inframat Advanced

Materials) were applied. Two pore formers were selected: graphite (Alfa Aesar) and corn starch (Sigma-Aldrich). The graphite and the starch were applied for inner layer and top layer and the amounts were from 5wt% to 20wt% and from 25wt% to 40wt%, respectively. For central layer, 15vol% of graphite and 15vol% of starch were added to the LSCF slips. In a first step, the LSCF powders and pore formers were ball milled for 12h with dispersant in a mixture of xylene and ethanol to form a stable slurry. In a second step, two plasticizers and a commercial bonder were added to confer adequate flexibility and strength to the tapes, and left for further milling for another 12h. The resulting homogeneous slurry was then cast under doctor blade. The inner layer was cast first on the carrier film and allowed to dry in air for several minutes, then the central layer and the top layer were prepared similarly. The thickness of each layer is 20 μ m. After drying overnight at room temperature, the three layer green tape was cut into disks with diameter of 15mm. For comparison, 60 μ m thick single-layer LSCF cathodes of uniform microstructure were also fabricated using the same method.

2.2 Fabrication of symmetric cell and anode supported cell

In order to characterize the electrochemically behavior of these cathodes with different microstructures, electrolyte-supported symmetric cells with a configuration of LSCF | SDC | YSZ | SDC | LSCF were used. The YSZ electrolyte membranes were fabricated from 8mol% Y_2O_3 -doped ZrO_2 (Tosoh, Japan) using tape casting and sintering at 1400 °C for 5h. To avoid the reaction between LSCF cathode and YSZ electrolyte, a $Sm_{0.2}Ce_{0.8}O_{1.95}$ (SDC) buffer layer was applied by drop coating SDC slurry on both sides of the YSZ pellets. The slurry was a mixture of the SDC powder and additives dispersed in an organic solvent. Then the LSCF green tapes were bonded to the buffer layer. After

dried at 80 °C for 1 h, the symmetric cells were heated in a furnace at a rate of 3 °C /min up to 1080 °C.

The button cell in this study had Ni-YSZ anode supports, Ni-YSZ active layer, YSZ electrolyte, SDC buffer layer and graded LSCF cathodes (shown in Fig.1). Electrolyte thin film and anode were prepared by co-tape casting, which were the same as described in cathode preparation. The YSZ film was cast first, then followed by the anode active layer and anode support. After drying overnight at room temperature, the multilayer green tapes were detached and co-fired at 1400°C for 5h in air. After that, the graded LSCF cathode was bonded to the YSZ electrolyte using SDC as buffer layer (similar to the symmetric cell fabrication) and subsequently sintered at 1100 °C for 2h.

2.3 Electrochemical and microstructural characterization

Electrochemical Impedance spectroscopy at open circuit voltage was carried out using a frequency response analyzer (Solartron 1255) in the air at temperatures ranging from 650-800 °C. The frequency was from 10MHz to 0.01Hz and the AC amplitude was 5 mV. All data were collected in 30min after the desired temperature reached. The data was corrected for electrode area, and divided by two (symmetric cell) to obtain the actual interfacial polarization resistance of each electrolyte/electrode interface. The button cell was tested at 700-800 °C in a home-developed cell testing system with humidified hydrogen (3vol% H₂O) as fuel and stationary air as oxidant. The electrochemical performance of cell was recorded with an electrochemistry workstation (CHI 660). The microstructure and morphology of the samples after testing were examined using a scanning electron microscopy (SEM, Hitachi S-4800).

3. Results and discussion

Figure 2 shows the interfacial resistances of the symmetrical cells with the structurally graded LSCF cathodes under open circuit conditions at 650–800 °C. Both the content of graphite for the inner layer and that of corn starch for the outer layer have significant impact on interfacial resistances. At corn starch content of 25 wt% to 40 wt%, the trends in electrochemical performances show that an increase in the amount of pore former (graphite) for the inner layer reduces the polarization when up to 10 wt% graphite is used as a pore former. The LSCF cathode that contained ≥ 15 wt% graphite showed decreased performance relative to the 10 wt% graphite cathode. In general, cathode reaction in SOFCs occurs within a limited active region in a layer approximately 5–10 μm thick adjacent to the cathode/electrolyte interface. Within the cathode active region, the chemical reaction occurs at the triple phase boundaries (TPBs) of the oxidant gas. Therefore, the inner layer with 10 wt% graphite can offer the highest surface area and the longest TPB for catalytic reactions. Meanwhile, the interfacial resistances of the graded cathode decreased proportionally with the decrease in content of pore former (corn starch) for the outer layer. The lowest interfacial resistances were achieved at a starch content of 35 wt% (green line). Furthermore, the increase of starch content resulted in an increase of the resistance. The relatively high porosity of the outer layer allows for rapid transport of oxygen molecules. However, such high porosity also reduces the contact areas between individual LSCF particles, thereby resulting in increased interfacial resistance.

Figure 3 shows the trend of activation energies with graphite when 35 wt% starch was used as pore former for the outer layer. From the linear fitting, an activation energy of 1.65 eV was obtained for graded cathode with 20 wt% graphite, which decreased to 1.43 and 1.45 eV for the cathode with 10 and 5 wt% graphite, respectively. The activation

energies of the graded LSCF are also in agreement with those reported for the LSCF cathode at temperature range of 600-800 °C [18, 19]. When compared with the graded cathode containing 20 wt% graphite, the cathode with 10 wt% graphite exhibited much lower polarization resistances, reaching about 0.053, 0.11, 0.27, and 0.65 $\Omega \text{ cm}^2$ at 800, 750, 700, and 650 °C, respectively. Comparison between Fig. 2 and Fig. 3 indicated that the graded LSCF cathode with 10 wt% graphite and 35 wt% corn starch had the highest cathodic performance.

Figure 4 shows the typical spectra of graded and single layer LSCF electrode on YSZ measured under open circuit conditions at 750 °C. In order to separate the contributions of the two arcs, an equivalent circuit with two distributed element, similar to that reported in ref. [20] and ref. [21], has been used to fit the data. In this model, R_s represents the intercept of the impedance spectra at high frequency with the real axis; R_1 and R_2 refer to the high- and low frequency resistance, respectively. The graded LSCF had R_1 and R_2 equal to 102 $\text{m}\Omega \cdot \text{cm}^2$ and 8 $\text{m}\Omega \cdot \text{cm}^2$ at 750 °C, respectively, as compared to 152 $\text{m}\Omega \cdot \text{cm}^2$ and 31 $\text{m}\Omega \cdot \text{cm}^2$ at the same temperature for single cathode. It is reported that the high frequency arc related to the transfer of oxide ions across the electrode/electrolyte interface and the low frequency was attributed to surface exchange reactions and gaseous diffusion [22]. This supports the view that both charge transfer reactions and the oxygen mass transport were enhanced for graded porous cathode.

Figure 5 shows the cross-section SEM image of a co-fired single cell with LSCF graded cathode. Figure 5a indicates that the dense YSZ electrolyte film is approximately 15 μm and thoroughly adheres to the porous anode substrate. To enhance cell performance, an anode active layer (~10 μm thick) having fine microstructure was used

at the anode–electrolyte interface. The cells of these layers had no delamination, observable cracks, or other large defects. The three-layer LSCF cathodes with thickness of approximately 50 μm are graded in both porosity and grain size (Fig. 5b). The inner layer has the lowest porosity and finest grains ($\sim 0.5\ \mu\text{m}$ diameter), followed by the mid-layer with slightly larger grain size ($\sim 1\ \mu\text{m}$ diameter) and relatively coarser microstructure, and then the outer layer, which has the largest grains ($\sim 1.5\ \mu\text{m}$ diameter) and highest porosity. The large interconnected pores in the top layer allow rapid transport of oxygen molecules, whereas the considerably long TPB in the inner layer facilitates catalytic reactions.

Figure 6 shows the current–voltage (I–V) and current–power densities (I–P) curves of an anode-supported SOFC with the optimum grade LSCF cathode. The values were measured at 700–800 $^{\circ}\text{C}$, in which hydrogen and ambient air were used as fuel and oxidant, respectively. The open circle voltage of the cell under the operating conditions is $\sim 1.07\ \text{V}$ at 750 $^{\circ}\text{C}$, which is close to the theoretical value calculated from the Nernst equation. This finding indicates that the YSZ electrolyte is sufficiently dense without any cross cracks or pinholes. The peak power density reached 378, 622, and 1001 $\text{mW}\cdot\text{cm}^{-2}$ at 700, 750, and 800 $^{\circ}\text{C}$, respectively. The power density at 800 $^{\circ}\text{C}$ is more than twofold that for a similar cell Ni/Ni-YSZ/YSZ/LSCF fabricated by a deposition and co-sintering process in a previous report[23]. These power outputs are also higher than that of the same cell with LSM-SSZ cathode, specifically, 800, 550, and 370 $\text{mW}\cdot\text{cm}^{-2}$ at the corresponding temperatures[24]. Le et al. [25] and Myung et al.[26] reported power densities of 856 and 650 $\text{mW}\cdot\text{cm}^{-2}$ in humidified H_2 at 800 $^{\circ}\text{C}$ for NiO-YSZ anode-

supported cells with LSM-YSZ cathodes fabricated by co-tape casting and co-firing technique, respectively.

Figure 7 shows the impedance spectra of the single cell measured at 700, 750 and 800°C under open circuit condition. The intercepts of the impedance arcs on the real axis at high frequencies correspond to the ohmic resistance, which mainly comes from the electrolyte and lead wires, while the overall size of the impedance loop is attributed to the polarization resistance of the electrodes. As the operating temperature was increased from 700 to 800°C, the polarization resistances of the cell were reduced from 0.57 to 0.38 Ωcm^2 while the ohmic resistance decreased from 0.53 to 0.23 Ωcm^2 . As expected, both the ohmic loss and the polarization decreased with increasing temperature, due to the increased ionic conductivity of the electrolyte and faster electrode kinetics.

4. Conclusions

NiO-YSZ anode-supported SOFCs with graded porous cathodes were fabricated via a low-cost multilayer tape casting and co-firing technique. Based on interfacial resistance characterization, the three-layer LSCF cathode with 10 wt% graphite for inner-layer and 35 wt% corn starch for outer-layer had the highest cathodic performance. Compared with the single-layer LSCF cathode, both charge transfer reactions and the oxygen mass transport were enhanced for the graded porous cathode. The maximum power densities of the prepared button cell reached 378, 622, and 1001 $\text{mW}\cdot\text{cm}^{-2}$ at 700, 750, and 800 °C, respectively. The polarization resistances of the cell were estimated to be 0.38, 0.43, and 0.57 cm^2 at the corresponding temperatures.

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Fig.1. Flow chart of the manufacturing procedure for unit cell.

Fig.2. Effect of pore former content on electrochemical performance of LSCF cathodes: (a) 5wt% graphite; (b) 10wt% graphite and (c) 15wt% graphite.

Fig.3. Arrhenius curve for different graphite content.

Fig. 4. AC impedance spectra of graded cathode, compared to the response from the single cathode at 750 °C.

Fig.5. (a)SEM micrograph of cross-sections of a single cell; (b)Cross-sectional fracture surface of the graded LSCF cathode and grain morphology.

Fig.6. I-V and I-P curves of cells with graded LSCF cathodes at different temperatures.

Fig.7 Impedance spectra of a single cell with graded LSCF cathode measured under open circuit conditions at different temperatures.