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Short communication

Low temperature solid oxide fuel cells based on $Sm_{0.2}Ce_{0.8}O_{1.9}$ films fabricated by slurry spin coating

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Abstract

A simple and effective slurry spin coating approach was developed for fabricating $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) films on porous NiO-SDC anode substrates. A dense SDC film with a thickness of ~15 μm was obtained after sintering at 1400 °C for 4 h. With the same approach, the novel $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)-SDC composite cathode layer was fabricated on the film. When dry hydrogen was used as the fuel and stationary air as the oxidant, maximum power densities of the cell were 648 mW cm^{-2} at 600 °C and 869 mW cm^{-2} at 650 °C, respectively. AC impedance analysis indicated that the resistance of the cell under open-circuit conditions was essentially dominated by the interfacial resistance. The activation energies of the interfacial resistance and the ohmic resistance were 99.49 and 54.30 kJ mol^{-1}, respectively.

Keywords: SOFCs; Slurry spin coating; $Sm_{0.2}Ce_{0.8}O_{1.9}$ film; $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathode

1. Introduction

From the viewpoint of cost reduction, long-term performance stability and widening the material selection, it is desirable to investigate low temperature solid oxide fuel cells (SOFCs). However, significant obstacles for both electrolyte resistance and electrode overpotentials appear with reduction in the operating temperature [1]. To reduce the electrolyte resistance of the cell, fabrication of a thin electrolyte film as well as adopting a new intermediate temperature electrolyte material has been the subject of recent studies.

Recently, several methods for fabricating thin films on porous substrates, such as screen-printing, dry-pressing, electrophoretic and centrifugal casting have been reported [2–6]. Doped cerias are noteworthy as candidate electrolyte materials in SOFCs for their high ionic conductivities at lower temperatures [7]. Peng et al. [2] fabricated a ~15 μm $Y_{0.2}Ce_{0.8}O_{1.9}$ (YDC) film on NiO-YDC anode by a screen-printing method, and got a maximum power density of ~230 mW cm^{-2} at 600 °C with a $Sm_{0.5}Sr_{0.5}CoO_{2.75}$ (SSC) cathode. Based on a ~15 μm $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC) film by dry-pressing and with SSC cathode, Xia et al. [3] got a maximum power density of ~380 mW cm^{-2} at 600 °C. With the same dry-pressing method, Shao and Halle [6] fabricated a $Sm_{0.15}Ce_{0.85}O_{2-\delta}$ (SDC) film of ~20 μm thick, however, they got an extraordinary performance of 1010 mW cm^{-2} at 600 °C by using a high performance $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) cathode.

In this paper, a simple and effective slurry spin coating method for fabricating a $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) film of ~15 μm and a BSCF-SDC composite cathode layer of ~10 μm is reported. Compared with the traditional sol–gel [8,9] and suspension spin coating [10] methods, the slurry spin coating technology introduced here has many merits, which are advantageous to commercial development. This method avoids the complex steps of preparing a polymeric yttria stabilized zirconia (YSZ) sol for coating and the time-consuming heating and sintering procedures for many cycles [8]. The electrochemical performance of the single cell

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based on the SDC film are presented and discussed in this study.

2. Experimental

$Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) powders were prepared using a glycine-nitrate process [7] in this study. Stoichiometric amounts of $Ce(NO_3)_3{\cdot}6H_2O$ (analytical reagent, A. R.) and Sm_2O_3 (A. R.) were dissolved in the diluted HNO_3 (A. R.), to which glycine (A. R.) was added. The mixture was heated on a hot plate, evaporated to a brown-red gel, spontaneously ignited to flame, and finally converted to a pale-yellow ash. Then the ash was calcined at 800 °C for 2 h. Nickel oxide (NiO) powders were synthesized by the precipitation method, using $Ni(NO_3)_2{\cdot}6H_2O$ (A. R.) as the material and ammonia (A. R.) as the precipitant. After washing and drying, the resultant powders were subsequently calcined at 400 °C for 2 h. The anode powders were prepared by mixing NiO powders with SDC powders in a weight ratio of 65:35 [2,11], and ball-milled for 20 h with ethanol media. Then 20 wt.% flour was added as a pore former, and ball-milled for another 2 h. After drying, with a diameter of 13 mm under uniaxial pressure the anode powders were subsequently pressed into pellets, which were then calcined at 1000 °C for 2 h as substrates.

To obtain highly dispersed electrolyte powders, SDC powders were ball-milled with ethanol media for 20 h to break up the agglomerations in the green powders. The ball-milled SDC powders were mixed with ethyl cellulose (chemical reagent) and terpineol (A. R.) to form an electrolyte slurry in a mortar. A multilayer SDC film was prepared on the anode substrate using a slurry spin coating technique. To avoid cracks or pores in the film induced by evaporation of the organics during the following co-sintering process, each layer of the film was baked at 400 °C for 10 min with a heating rate of 10 °C min^{-1} before spin coating the next layer. Repetitive coating was performed to adjust the film thickness, and defects of the former layer could be repaired by the latter ones. After five cycles of coating, a bilayer of SDC film/NiO-SDC anode was co-sintered at 1400 °C for 4 h.

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), a new kind of cathode material, was synthesized by the EDTA-Pechini method [12], and subsequently calcined at 950 °C for 5 h. The BSCF powders were then mixed with SDC powders in a weight ratio of 7:3 to form the composite cathode powders. A slurry containing the composite cathode powders, ethyl cellulose and terpineol, was spin coated on the SDC film to form the cathode layer, followed by sintering at 1050 °C for 4 h.

The substrate–electrolyte bilayer was attached and sealed on one end of an alumina tube by applying a silver paste (DAD-87, Shanghai Research Institute of Synthetic Resin, China) to form a single cell, which was tested with a four-probe method from 450 to 650 °C. Dry hydrogen was used as the fuel and the cathode was exposed to the ambient air. The output performances and AC impedance spectra of the cell were measured with an electrochemical interface Solartron SI 1287 and impedance analyzer SI 1260, respectively, and the frequency range was from 0.01 Hz to 910 kHz. A scanning electron microscope, Hitachi S-570, was used to reveal the microstructure of the cell.

3. Results and discussion

Fig. 1 shows a cross-sectional SEM image of the Ag/BSCF-SDC/SDC/Ni-SDC fuel cell structure after electrochemical testing. It is observed that the SDC film is well adhered to the porous anode substrate, seems uniformly continuous, and has some closed pores though. The thickness of the five layers SDC film is ~15 μm and the cathode is ~10 μm. Xu et al. [10] fabricated a 10 μm thick YSZ film via 20-cycle spin coating. Kim et al. [8] deposited YSZ thin films on YDC substrates using sol–gel coating method. They reported that after drying at room temperature for 12 h, each layer of the sample was heat-treated at 600 °C for 2 h with a heating rate of 0.5 °C min^{-1}, then cooled to room temperature at a rate of 2 °C min^{-1}. The drying/heating process seems time-consuming. In our study, the sample was directly baked at 400 °C for 10 min with a heating rate of 10 °C min^{-1} and a cooling rate of 20–40 °C min^{-1} for five cycles, which is faster and more effective.

Fig. 2 shows the *I–V* and *I–P* characteristics of the cell, as shown in Fig. 1. The open-circuit voltage (OCV) decreases with the increase in the operating temperature. Maximum power densities of the cell are 103, 225, 388, 648 and 869 mW cm^{-2} at 450, 500, 550, 600 and 650 °C, respectively. The excellent performance of the single cell illustrates that slurry spin coating technology is an effective way to fabricate anode supported SDC thin films.

AC impedances of the cell under open-circuit condition are plotted in Fig. 3a. The total resistances, interfacial resistances and ohmic resistances as determined from the impedance spectra at different temperatures are shown in Fig. 3b. Each type of the resistance above decreases with the increase of the temperature. Further analysis of the curves shows that the total resistance of the cell is determined primarily by the interfacial resistance. The ratio of the interfacial resistance to the total resistance increases with reduction of the operating temperatures, from 65.5% at 650 °C to 86.5% at 500 °C. It implies that

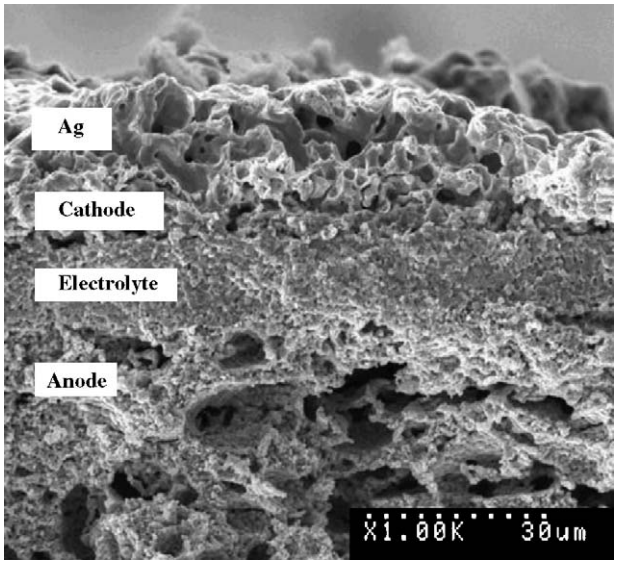

Fig. 1. SEM cross-sectional image of the cell after electrochemical testing.

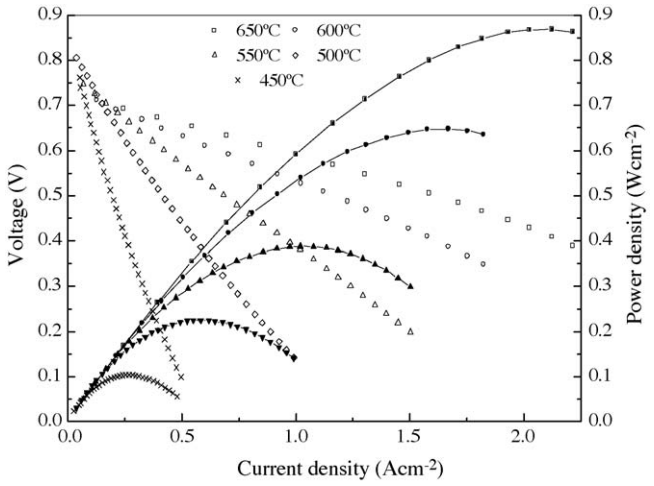

Fig. 2. Performance of the single cell from 450 to 650 °C.

the performance of the cell is critically limited by the interfacial resistance. According to previous studies [13,14], the interfacial resistance is dominated by the cathode–electrolyte interface and the resistance of the anode–electrolyte is negligible. So

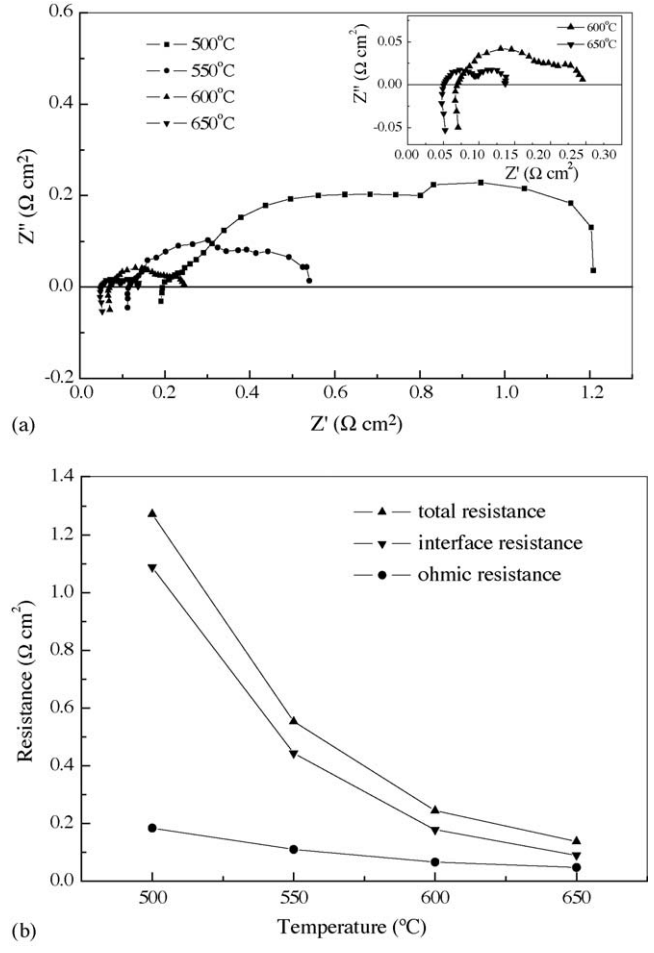

Fig. 3. (a) The impedance spectra of the cell measured under open-circuit condition and (b) the total cell resistances, interfacial resistances and ohmic resistances as determined from the impedance spectra.

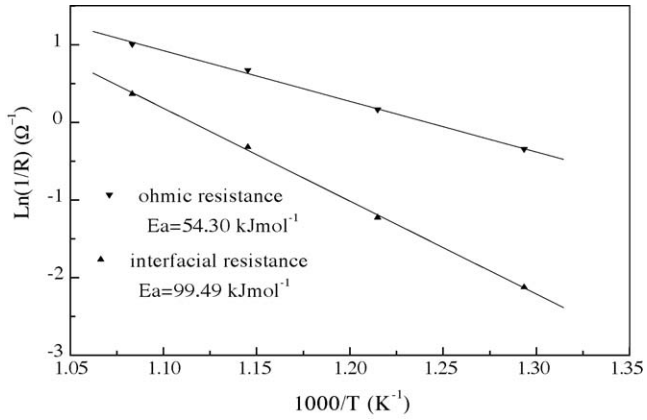

Fig. 4. Conductivity plots of the ohmic resistance and interfacial resistance.

reduction of the cathode–electrolyte interfacial resistance is significant for improving the performance of the cell in the further studies.

Fig. 4 shows the conductivity plots of the ohmic resistances and interfacial resistances. The activation energies of interfacial resistance and ohmic resistance obtained from the slope of the fitted line of the conductivity plots are 99.49 and 54.30 kJ mol^{-1}, respectively. Peng et al. [15] reported the activation energy of the SDC pellet was 75.17 kJ mol^{-1}, which is higher than the result in this study. The ohmic resistance mainly consists of the bulk resistance and the grain boundary resistance of the electrolyte. And the fabrication technology and sintering conditions have an effect on the boundary resistance [16]. Leng et al. [11] reported the activation energy of the interfacial resistance for a cell LSCF-GDC/GDC film (∼10 μm)/Ni-GDC was 115 kJ mol^{-1}, higher than that of the interfacial resistance in this study, which implies the superiority of the new BSCF-SDC cathode.

It is believed that by further reducing the cathode–electrolyte interfacial resistance and perfection of the slurry spin coating technology, better performance of the cells based on thinner and denser SDC films would be obtained in future studies.

4. Conclusion

Dense SDC thin films on NiO-SDC anode substrates were successfully fabricated by a slurry spin coating technology. Using a BSCF-SDC composite cathode, the cell with a ∼15 μm SDC electrolyte film achieved excellent performance. Maximum power densities of the cell were 103, 225, 388, 648 and 869 mW cm^{-2} at 450, 500, 550, 600 and 650 °C, respectively. Analysis of the impedance spectra showed that the cell impedance under open-circuit condition was dominated by the interfacial resistance. According to the conductivity plots, the activation energies of interfacial resistance and ohmic resistance were 99.49 and 54.30 kJ mol^{-1}, respectively. In summary, slurry spin coating technology is simple and effective, and it should be a promising approach for the fabrication of anode supported thin electrolyte films of SOFCs.

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