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ScienceDirect
Journal of Power Sources 160 (2006) 436–438
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

Development of yttria-stabilized zirconia thin films via slurry spin coating for intermediate-to-low temperature solid oxide fuel cells

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Received 11 December 2005; received in revised form 16 January 2006; accepted 25 January 2006
Available online 3 March 2006

Abstract

Yttria-stabilized zirconia (YSZ) thin films were successfully fabricated on porous NiO–YSZ anode substrates via a slurry spin coating method. With ~34-μm-thick $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC)-impregnated $La_{0.7}Sr_{0.3}MnO_3$ (LSM) cathodes, a single cell based on a ~9-μm-thick YSZ film exhibited a good performance at intermediate-to-low temperature. The cell produced an open-circuit voltage (OCV) of ~1.08 V, and maximum power densities of ~0.42 and ~0.70 W cm^{-2} at 650 °C, while the cathode was exposed to the stationary air and blown with 100 mL min^{-1} oxygen airflow, respectively. Enhanced cell performance with oxygen airflow was attributed to the improved cathode performance. By separating the total voltage drop into ohmic and non-ohmic contributions, it could be concluded that the cell performance was primarily determined by the polarization of the electrodes. It is believed that by optimizing the film fabrication process and improving the cathode performance, intermediate-to-low temperature solid oxide fuel cells (SOFCs) based on supported YSZ electrolyte thin films could be put into practice in not far future.
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Keywords: Solid oxide fuel cells (SOFCs); Slurry spin coating; Yttria-stabilized zirconia thin film; Impregnation; Oxygen airflow

1. Introduction

Up to now, yttria-stabilized zirconia (YSZ) has been used as the most successful electrolyte for solid oxide fuel cells (SOFCs) due to its pure ion conductivity, good chemical compatibility and excellent mechanical properties [1]. However, the conductivity of YSZ is not high enough for SOFCs operating in intermediate-to-low temperatures (500–650 °C). It is thus desirable to fabricate YSZ electrolyte films with a thickness of only a few microns.

As a method for manufacturing a thin YSZ electrolyte film, a colloidal process is a very simple and cost-effective way that proves to be less restricted by geometric limitations [2]. As a consequence, slurry coating [2–4], spin coating [5–6], dip coating [7], tape casting [1], etc., have been widely used for SOFCs. To form a suitable slurry composition, many organic additives have to be proportionally added and ball-milled with the electrolyte powders. In order to avoid cracks during drying, very careful drying or baking and sintering processes have to be adopted, which need to be repeated several times.

Recently, a new method of slurry spin coating has been developed for fabricating $Sm_{0.2}Ce_{0.8}O_{1.9}$ thin films in our laboratory [8]. Slurry spin coating is a good combination of slurry coating and spin coating techniques, and the slurry is simply prepared by mixing electrolyte powders with ethyl cellulose and terpineol. It requires no strict baking and cooling rates during processing, and thus is efficient and fast. In this work, we present the development of fabricating YSZ thin films by this slurry spin coating technique. Electrochemical characteristics of the single cell based on a ~9-μm-thick YSZ film at 500–650 °C were performed and discussed.

2. Experimental

NiO was synthesized by the precipitation method [8]. NiO, YSZ (TZ-8YS, Tosoh Corp.) and flour were mixed in the weight

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doi:10.1016/j.jpowsour.2006.01.079

ratio of 5:5:2, and ball-milled with ethanol media. After drying, the green powders were uniaxially pressed into pellets with a diameter of 13 mm, which were subsequently calcined at 1100 °C for 2 h to increase the mechanical strength of the anode substrates.

YSZ powders were mixed with ethyl cellulose (chemical reagent) and terpineol (analytical reagent, A.R.) to prepare the electrolyte slurry, which was then spin coated on an anode substrate for three layers at 6000 rpm for 60 s. Each layer was baked at 400 °C for 10 min with an average heating rate of ~15 °C min^{-1} and a cooling rate of 20–40 °C min^{-1}. Finally, the bilayer was co-sintered at 1400 °C for 4 h.

$La_{0.7}Sr_{0.3}MnO_3$ (LSM) powders were synthesized by the Pechini method, and the resultant powders were subsequently calcined at 1000 °C for 2 h. $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC)-impregnated LSM cathodes [9] were prepared. LSM and activated carbon (A.R.) mixture was deposited on the sintered YSZ films, followed by sintering at 1100 °C for 2 h. The sintered cathodes were then impregnated by the synthesized $Sm_{0.2}Ce_{0.8}(NO_3)_x$ solution, and calcined at 850 °C for 1 h. The impregnation–calcination cycle was repeated for three times. The active area of the cathode was 0.28 cm^2.

The cell was sealed on one end of an alumina tube, and then tested with a four-probe method. The anode side was fed with 3 vol.% H_2O humidified hydrogen and the cathode side was exposed to the ambient air or blown with 100 mL min^{-1} oxygen airflow. Electrochemical characteristics were performed with an electrochemical interface Solartron SI 1287 and an impedance analyzer SI 1260. As for the impedance spectra measurements, the frequency range was from 0.1 Hz to 91 kHz. The operating temperature was varied from 500 to 650 °C. Morphologies of the cell after electrochemical test were characterized by a scanning electron microscope, Hitachi S-570.

3. Results and discussion

Fig. 1 shows the cross-sectional view of a cell with a three-layered YSZ film and SDC-impregnated LSM cathodes after electrochemical test. The YSZ layer is well adhered to the porous anode substrate, seems dense, uniform and without cracks and pores. The film is ~9-μm thick, with an average thickness of 3 μm for each coating. The cathode layer is ~34-μm thick, has some big pores in it and seems somewhat dense, indicating the formation of a continuous and porous network of SDC phase within the LSM structure [10]. The Ni-YSZ anode shows a porous microstructure, and the pores are not so uniformly distributed. Obviously, YSZ film could be densified at the high sintering temperature of 1400 °C for 4 h, which consequently had a great influence on the porosity of the anode substrate. Calcined at 1100 °C for 2 h, the NiO–YSZ substrate had ~43% porosity, which was subsequently reduced to ~11% after sintering at 1400 °C for 4 h. And the porosity was eventually adjusted to ~35% after the reduction of NiO.

Fig. 2 shows the output performance of the cell shown in Fig. 1, and the cathode was exposed to the ambient air during test. The cell exhibits an open-circuit voltage (OCV) of ~1.08 V at 650 °C, indicating that the film is dense enough to prevent gas

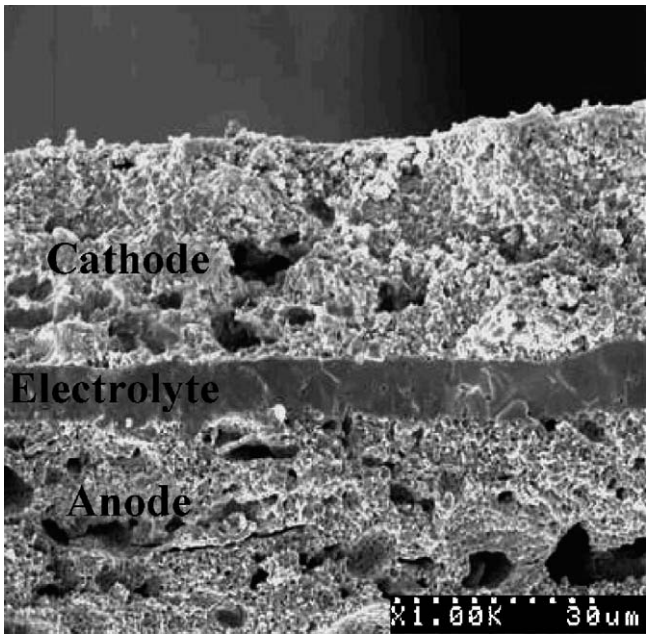

Fig. 1. Cross-sectional image of the cell after electrochemical test.

leakage through it. The maximum power densities are ~0.42, 0.30, 0.18 and 0.09 W cm^{-2} at 650, 600, 550 and 500 °C, respectively. This result is comparable with that of the low temperature SOFCs based on a Gd-doped ceria (GDC) film via dry pressing by Xia and Liu (0.38 and 0.14 W cm^{-2} at 600 and 500 °C, respectively) [11]. Moreover, the *I–V* curves show nearly linear or positive curvatures at 650 °C and below, implying that the Ni-YSZ anode support possesses desirable porosity at the operating temperature range.

With 100 mL min^{-1} oxygen airflow blown at the cathode side, the enhanced cell performance is shown in Fig. 3. The maximum power densities are ~0.70, 0.46, 0.25, 0.12 W cm^{-2} at 650, 600, 550 and 500 °C, respectively. And the maximum power density increases by ~67% at 650 °C compared with the result in Fig. 2. Great improvement of the cell performance is attributed to the enhancement of the cathode performance, which indicates that the cell performance is governed by mass trans-

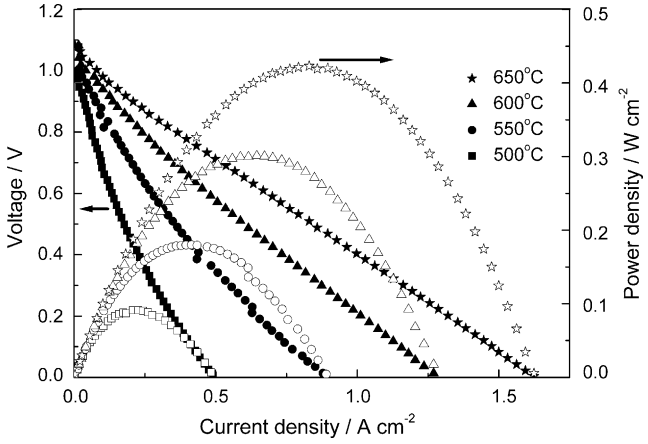

Fig. 2. Performance of the cell with stationary air at the cathode side.

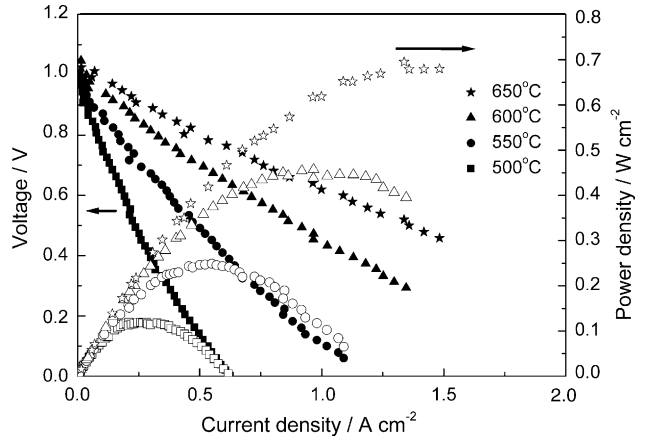

Fig. 3. Performance of the cell with 100 mL min^{-1} oxygen blown at the cathode side.

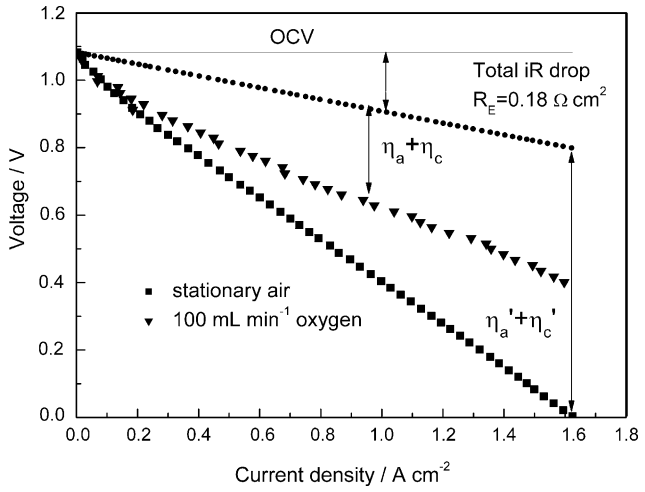

Fig. 4. Separation of ohmic drop and electrode polarization of the cell at 650 °C.

fer process as well as interfacial electrochemical reaction and ohmic polarization [12].

Fig. 4 shows the voltage drops versus current density of the cell. Total iR drop of the cell was drawn based on the ohmic resistance (∼0.18 Ω cm^2) at 650 °C, which is derived from the impedance spectra under open-circuit conditions. The total voltage drop thus could be divided into ohmic and non-ohmic contributions. It is clear that the polarization of the electrodes ($\eta_a + \eta_c$) with the oxygen airflow at the cathode side is smaller than the polarization of the electrodes ($\eta'_a + \eta'_c$) when the cathode was exposed to the air. It can be seen that the cell performance is primarily determined by the polarization of the electrodes, the percentage of which is decreasing with the increase of current density though, as described in Table 1. By optimizing the microstructure of the LSM electrodes and the impregnation process, it should be possible to improve the performance of the ion-impregnated LSM cathodes [9], and consequently put the intermediate-to-low temperature SOFCs based on supported YSZ electrolyte thin films into practice in not far future.

Table 1
Percentage of the polarization of electrodes vs. current density at 650 °C

Current density (A cm^{-2})	Percentage of $\eta_a + \eta_c$ (%)	Percentage of $\eta'_a + \eta'_c$ (%)
0.5	69	76
1.0	62	74
1.5	59	74

4. Conclusions

In this paper, development of NiO–YSZ anode-supported YSZ thin films via the slurry spin coating method is reported. By using the effective 34-μm-thick SDC-impregnated LSM cathodes, the cell based on a 9-μm-thick dense YSZ film exhibited a good performance at intermediate-to-low temperatures. The cell produced an OCV of ∼1.08 V at 650 °C, and produced maximum power densities of 0.42 and 0.70 W cm^{-2} at 650 °C, with the cathode side exposed to stationary air and blown with 100 mL min^{-1} oxygen airflow, respectively. The enhancement of the cell performance with oxygen airflow was due to improvement of the cathode performance. The cell performance was primarily governed by the polarization of the electrodes. It is believed that by optimizing the film fabrication process and improving the cathode performance, intermediate-to-low temperature SOFCs based on supported YSZ electrolyte thin films could be put into practice in the future.

Acknowledgement

The authors gratefully acknowledge financial supports from the Ministry of Science and Technology of China under Contract no. 2001AA323090.

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