Available online at www.sciencedirect.com
ScienceDirect
Journal of Power Sources 163 (2007) 957–959
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

YSZ films fabricated by a spin smoothing technique and its application in solid oxide fuel cell

Jiaming Wang [a,*], Zhe Lü [a], Xiqiang Huang [a], Kongfa Chen [a], Na Ai [a], Jinyan Hu [a], Wenhui Su [a,b,c]

[a] *Center for Condensed Matter Science and Technology, Harbin Institute of Technology, Harbin 150001, China*
[b] *Department of Condensed Matter Physics, Jilin University, Changchun 130022, China*
[c] *International Center for Material Physics, Academia, Shenyang 110015, China*

Received 10 July 2006; received in revised form 19 September 2006; accepted 20 September 2006
Available online 16 November 2006

Abstract

A dense single-layer YSZ film has been successfully fabricated by a spin smoothing method. Followed by a simplified slurry coating, an additional spin smoothing process was conducted to obtain a thinner and smoother film. By employment of high-viscosity slurry including high YSZ content, the film has a suitable thickness by a single coating cycle. With $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC)-impregnated $La_{0.7}Sr_{0.3}MnO_3$ (LSM) cathode and porous NiO–YSZ anode, single solid oxide fuel cell (SOFC) based on an 8-μm-thick YSZ film was obtained. Open-circuit voltage (OCV) of the cell was 1.04 V at 800 °C, and maximum power densities were 676, 965 and 1420 mW cm^{-2} at 700, 750 and 800 °C, respectively, using H_2 at a flow rate of 40 mL min^{-1} as fuel and ambient air as oxidant. The power density could be increased to 1648 mW cm^{-2} at 800 °C when the flow rate of H_2 was enhanced to 200 mL min^{-1}.

Keywords: Solid oxide fuel cells (SOFCs); Spin smoothing; YSZ thin film

1. Introduction

Reducing the operation temperature of solid oxide fuel cells (SOFCs) down to 600–800 °C can get several benefits such as cost reduction and long-term life [1,2]. One efficient method to achieve this objective is to fabricate thin and high-quality electrolyte films. Slurry coating [3–5], spin coating [6,7], spray coating [8], tape casting [9], CVD [10], screen-printing [11,12] were several successful methods reported in fabricating electrolyte films. Although high-quality thin-film yttria stabilized zirconia (YSZ) electrolytes have been obtained, most of them need a complex fabrication process such as careful drying, baking and many coating cycles which were done to get perfect films with suitable thickness [12–14].

Will et al. [13] described fabrication process of YSZ electrolyte film via sol–gel. After coating, the samples were dried at room temperature, which might cost a long time and was disadvantageous to commercial development. After drying, the samples were heat-treated at 600 °C. The coating, drying and heat-treating processes need to be repeated. Kim et al. [14] deposited YSZ films with up to six spinning cycles to adjust the film thickness; each cycle contained a process of coating, 12 h room temperature drying and heating with certain heating/cooling rate. In our previous work [15,16], a process of 10-min baking at 400 °C with a heating rate of 10 °C min^{-1} and a cooling rate of 20–40 °C min^{-1} for three to five cycles was needed in fabricating the YSZ electrolyte film by slurry spin coating. It has simplified the fabrication process evidently. However, three or more layers were still needed in order to repair the pores or pinholes in the previous layers, and the process of baking was somewhat time-consuming.

In this study, the YSZ films were fabricated by a spin smoothing technique and the samples were directly baked at about 80 °C for 10 min without heating or cooling process for only a single cycle. Obviously, the method of spin smoothing is very simple and efficient. Spin smoothing is a good combination of slurry coating and spin coating techniques. It is a technique that utilizes centrifugal forces created by spinning substrate to smooth

* Corresponding author. Tel.: +86 451 86418420; fax: +86 451 86412828.
E-mail address: chenyu@hit.edu.cn (J. Wang).

0378-7753/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2006.09.064

a thick and rough film. The thick and rough film was obtained by painting on the anode substrate using a brush. In this paper, the process of spin smoothing has been described, and high-quality thin electrolyte film has been subsequently fabricated. Electrochemical characteristics of the single cell based on such a YSZ electrolyte film at 700–800 °C were performed and discussed.

2. Experimental

NiO was synthesized by a glycine-nitrate process. YSZ (TZ-8Y, Tosoh, Japan), NiO and flour in a weight ratio of 5:5:1.7 were mixed in an agate mortar and ground for 3 h. Flour was used as a pore former to enhance the porosity of the Ni–YSZ anode. The mixture was then uniaxially pressed into pellets of 13 mm diameter under a pressure of 200 MPa and precalcined at 1000 °C for 2 h in air to ensure adequate strength for anode substrates.

The slurry was prepared by mixing YSZ powder (TZ-8Y, Tosoh, Japan) with ethyl cellulose (chemical reagent, C.R.) and terpineol (analytical reagent, A.R.) in a weight ratio of 40:3.3:56.7. The ingredients were ground together in an agate mortar for 2 h. The viscosity of the slurry was ~380 Pa s.

Thick and rough slurry film was obtained by painting the slurry on the anode substrate using a brush. The film was very thick and uneven in thickness. Then it was spin smoothed on a spinner at a rotating speed of 10 krpm for 60 s to form a thin, uniform YSZ film. The whole fabrication contains only one spinning cycle. After a 10-min baking at 80 °C without heating or cooling process, the smoothed YSZ film and anode substrate was co-sintered at 1400 °C for 4 h with an average heating rate of 2.6 °C min^{-1}.

$La_{0.7}Sr_{0.3}MnO_3$ (LSM) and activated carbon (A.R.) mixture with binder in a weight ratio of 26.2:2.6:71.2 was deposited on the YSZ film and sintered at 1100 °C for 4 h. The sintered cathode was then impregnated by a $Sm_{0.2}Ce_{0.8}(NO_3)_x$ solution [17] and calcined at 850 °C for 1 h. The weight ratio of SDC was 30–60 wt.%.

Silver paste (DAD-87, Shanghai Research Institute of Synthetic Resin, China) was used to fix and seal the fuel cell to an alumina tube, which was used as a fuel cell testing implement. The fuel cell was tested by a four-probe method in a furnace at temperature ranging from 700 to 800 °C; flowing H_2 at 40 or 200 mL min^{-1} and ambient air were used as fuel and oxidant, respectively. Cell performances and electrochemical impedance spectra were measured by an electrochemical interface (Solartron SI 1287) in combination with an impedance analyzer (Solartron SI 1260). The impedance spectra were collected in the frequency ranging from 91 kHz to 0.1 Hz under open-circuit conditions. The microstructure and morphology of the tested cell were examined with a JEOL JSM6480LV scanning electron microscope (SEM).

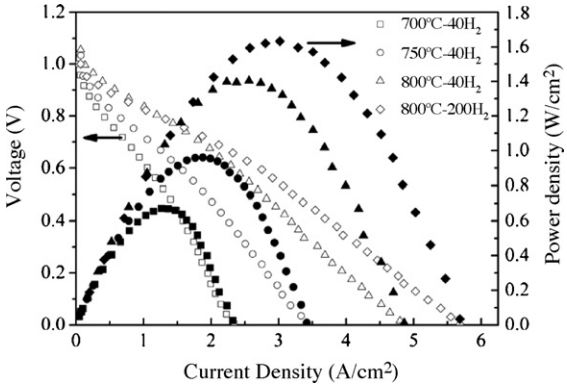

Fig. 2. Voltage and power density for the cell.

3. Results and discussion

Shown in Fig. 1 are SEM images for the surface and cross-section of a YSZ electrolyte film on Ni–YSZ substrate after cell testing. Only a few small closed pores were observed in Fig. 1a and b, and it could be seen that the thin YSZ electrolyte film was uniformly continuous, and adhered well to the porous anode substrate. The electrolyte film thickness was about 8 μm. In sol–gel method, repetitive coating was done to adjust the film thickness [7]. In spin smoothing method, in order to obtain a film with an appropriate thickness for a single cycle, high-viscosity slurry with high YSZ content must be used. Without painting, the rheology of the slurry would be too low to be spin coated. Thus, the step of painting was indispensable. After painting, the film was spin smoothed. The further smoothing process has two effects: one was to spin out the excessive slurry to form thin film and the other was to make the YSZ film uniform and even in thickness.

The presence of the open pores obviously decreases the OCV. The OCV is close to theoretical, if there are no open pores in the electrolyte layer. Fig. 2 shows the performance of the fuel

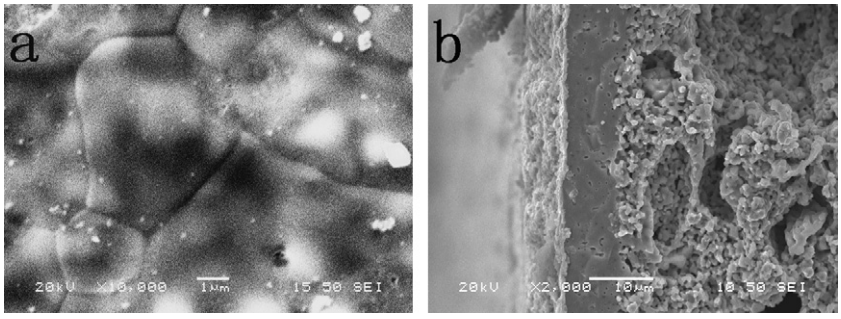

Fig. 1. SEM images of the electrolyte films: (a) surface and (b) cross-section.

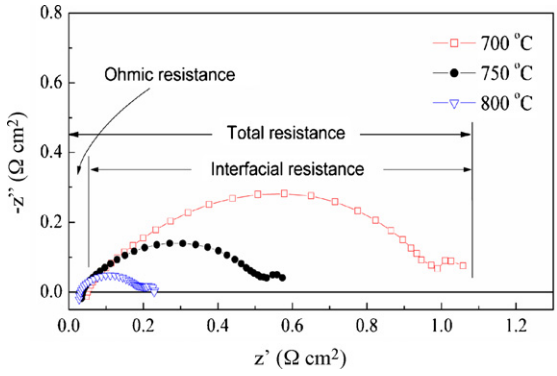

Fig. 3. Impedance spectra of the cell at open circuit.

cell with YSZ film via spin smoothing. The open-circuit voltage (OCV) of the SOFC was 1.04 V at 800 °C, which was close to the theoretical one. It indicated the film was dense and little gas leakage existed. Zhang et al. had investigated the effect of printing layers on the OCV of fuel cell [12], and the OCV of fuel cell with 7-μm-thick film prepared by three-time printing was still lower than 1 V. The printing ink that was used in [12] was similar to that we used. It can be concluded that the spin smoothing technique was better.

The power densities of the cell were 676, 965 and 1420 mW cm^{-2} at 700, 750 and 800 °C, respectively, using flowing H_2 at 40 mL min^{-1} as fuel and ambient air as oxidant. These results are higher than some SOFC results of single-layer YSZ film fabricated by other ceramic methods, such as dry pressing [18] and filter-coating [19]. This enhancement should be attributed to the usage of SDC-impregnated LSM cathode. The power density at 800 °C could be increased to 1648 mW cm^{-2} by increasing the flow rate of H_2 up to 200 mL min^{-1}. This improvement of the cell performance was attributed to the reduction of concentration polarization in Ni–YSZ anode under high current density.

Fig. 3 shows the impedance spectra of the cell at open-circuit condition ranging from 700 to 800 °C. The intercepts with real axis in high-frequency (HF) region give ohmic losses, and the intercepts with real axis in low-frequency region give total resistance. As shown, the higher testing temperature the smaller ohmic, interfacial and total resistance. The ratio of the interfacial resistance to the total resistance increased with reduction of the operating temperatures, from 86.1% at 800 °C, 93.4% at 750 °C to 95.3% at 700 °C. So at intermediate temperature, the interfacial resistance is more significant and the quality of electrode has more effect on the performance of the cell [6]. How to reduce the interfacial resistance and further improve the quality of the electrode should be studied in future.

4. Conclusion

In this paper, the spin smoothing technique has been reported. Since this method can reduce the coating-drying cycles down to single time and only needs an easy drying process, it is very simple and efficient. An 8-μm-thick dense and thin YSZ electrolyte film has been fabricated by this method using thick slurry. OCV of the fuel cell was 1.04 V at 800 °C; maximum power densities were 676, 965 and 1420 mW cm^{-2} at 700, 750 and 800 °C, respectively, using a H_2 airflow at 40 mL min^{-1} as fuel and ambient air as oxidant. The power density at 800 °C could be increased to 1648 mW cm^{-2} by increasing the flow rate of H_2 up to 200 mL min^{-1}. From the analysis of the impedance spectra of the cell at open-circuit condition, it came to realize that the total resistance and cell performance were essentially determined by the interfacial resistance.

Acknowledgements

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

References

[1] L.G.J. de Haart, K. Mayer, U. Stimming, I.C. Vinke, J. Power Sources 71 (1998) 302–305.
[2] T.L. Nguyen, T. Honda, T. Kato, Y. Iimura, K. Kato, A. Negishi, K. Nozaki, M. Shiono, A. Kobayashi, K. Hosoda, Z. Cai, M. Kokiya, J. Electrochem. Soc. 151 (2004) A1230–A1235.
[3] S.D. Kim, S.H. Hyun, J. Moon, J.-H. Kim, R.H. Song, J. Power Sources 139 (2005) 67–72.
[4] Z. Cai, T.N. Lan, S. Wang, M. Dokiya, Solid State Ionics 152–153 (2002) 583–590.
[5] S.P. Yoon, J. Han, S.W. Nam, T.-H. Lim, I.-H. Oh, S.-A. Hong, Y.-S. Yoo, H.C. Lim, J. Power Sources 106 (2002) 160–166.
[6] X.Y. Xu, C.R.X.S.G. Huang, D.K. Peng, Ceram. Int. 31 (2005) 1061–1064.
[7] S.-G. Kim, S.P. Yoon, S.W. Nam, S.-H. Hyun, S.-A. Hong, J. Power Sources 110 (2002) 222–228.
[8] P. Charpentier, P. Fragnaud, D.M. Schleich, E. Gehain, Solid State Ionics 135 (2000) 373–380.
[9] L.P. Meier, L. Urech, L.J. Gauckler, J. Eur. Ceram. Soc. 24 (2004) 3753–3758.
[10] K.W. Chour, J. Chen, R. Xu, Thin Solid Films 304 (1997) 106–112.
[11] P.V. Dollen, S. Barnett, J. Am. Ceram. Soc. 88 (2005) 3361–3368.
[12] Y.H. Zhang, X.Q. Huang, Z. Lü, Z.G. Liu, X.D. Ge, J.H. Xu, X.S. Xin, X.Q. Sha, W.H. Su, J. Power Sources 160 (2006) 1065–1073.
[13] J. Will, A. Mitterdorfer, C. Kleinlogel, D. Perednis, L.J. Gauckler, Solid State Ionics 131 (2000) 79–96.
[14] S.-G. Kim, S.P. Yoon, S.W. Nam, S.-H. Hyun, S.-A. Hong, J. Power Sources 110 (2002) 222–228.
[15] N. Ai, Z. Lü, K.F. Chen, X.Q. Huang, B. Wei, Y.H. Zhang, S.Y. Li, X.S. Xin, X.Q. Sha, W.H. Su, J. Power Sources 159 (2006) 637–640.
[16] K.F. Chen, Z. Lü, N. Ai, X.Q. Huang, Y.H. Zhang, X.S. Xin, R.B. Zhu, W.H. Su, J. Power Sources 160 (2006) 436–438.
[17] S.P. Jiang, Y.J. Leng, S.H. Chan, K.A. Khor, Electrochem. Solid-State Lett. 6 (2003) A67–A70.
[18] X.S. Xin, Z. Lü, X.Q. Huang, X.Q. Sha, Y.H. Zhang, W.H. Su, J. Power Sources 159 (2006) 1158–1161.
[19] X.S. Xin, Z. Lü, X.Q. Huang, X.Q. Sha, Y.H. Zhang, K.F. Chen, N. Ai, R.B. Zhu, W.H. Su, J. Power Sources 160 (2006) 1221–1224.