Journal of Alloys and Compounds 480 (2009) 554–557

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Dip coating technique in fabrication of cone-shaped anode-supported solid oxide fuel cells

Yaohui Bai, Jiang Liu*, Hongbo Gao, Chao Jin

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 610641, PR China

ARTICLE INFO

Article history:
Received 13 December 2008
Received in revised form 20 January 2009
Accepted 24 January 2009
Available online 6 February 2009

Keywords:
Solid oxide fuel cell
Cone-shaped
Anode-supported
Dip coating

ABSTRACT

A simple and cost-effective dip coating technique was successfully developed to fabricate NiO-YSZ anode substrates for cone-shaped anode-supported solid oxide fuel cells. A single cell, NiO-YSZ/YSZ/LSM-YSZ, was assembled and tested to demonstrate the feasibility of the technique applied. Using humidified hydrogen (75 ml/min) as fuel and ambient air as oxidant, the maximum power density of the cell was 0.78 and 1.0 W/cm^2 at 800 and 850 °C, respectively. The observed open-circuit voltages (OCV) was closed to the theoretical value and the scanning electron microscope (SEM) results revealed that the microstructures of the anode substrate and the cathode layer are porous and the electrolyte film is dense.

1. Introduction

For recent years, solid oxide fuel cell (SOFC) has been recognized as one of the most promising technologies for converting chemical energy of fuels to electrical power because of its high conversion efficiency, lower emission pollution and practical fuel flexibility [1–7]. There are two major designs of SOFCs: anode-supported and electrolyte supported types. Because the electrolytes are the thickest components of the electrolyte supported SOFCs and the general electrolyte material is 8% yttria stabilized zirconia (YSZ) whose ionic conductivity is low at low temperature, the ohmic resistance loss restricts the performance of electrolyte supported SOFCs. For decreasing the thickness of electrolyte to reduce the ohm resistance loss and lower the operation temperature, we choose to research the anode-supported type. However, tubular SOFCs are difficult to fix in series and the large ohm resistance loss occurs while the electrical current goes through the long distance of the thin cathode film. To solve these problems, we fabricated the cone-shaped cells which can be fixed in series via embedding them one by one [8,9]. The schematic diagram of SOFCs stack by the cone-shaped single fuel cells is shown in Fig. 1.

Fabrication of the anode substrate and the electrolyte film is one of the key steps. Sui and co-workers [10,11] used to fabricate the cone-shaped SOFCs with slip casting technique which is complex and time-cost. Dip coating technique is a molding method which deposits a cover layer on the mold via a dip process. It needs no expensive equipment and the cycle is short. Moreover, dip coating technique is suitable for mass production. However, in the previous researches, dip coating technique was just applied in the fabrication of thin membranes such as the electrolyte films. In this paper, the simple and cost-effective dip coating technique was successfully developed to fabricate NiO-YSZ anode substrates for cone-shaped anode-supported SOFCs. The fabricating processes were described in detail. To demonstrate the feasibility of the technique, a single cell, NiO-YSZ/YSZ/LSM-YSZ, was assembled and tested. The microstructure of cross-section of the cell after testing was examined by scanning electron microscope (SEM) analysis.

2. Experimental

2.1. Preparation of NiO-YSZ cone-shaped anode substrates and YSZ electrolyte film by dip coating

The NiO (J.T. Baker) and YSZ (TZ-8Y, TOSOH Corporation, Tokyo, Japan) powders were mixed in a weight ratio of 1:1. In addition, 10 wt.% carbon powders were added as pore former to make sufficient porosity. The mixed powders were firstly ball-milled with ethanol (A.R. Sinopharm Chemical reagent Co. Ltd.) media by planetary ball mill for 3 h using an agate jar and zirconia ball media. The rotation speed was 200 rpm. Then, triethanolamine (A.R. Fuchen Chemistry reagent plant, Tianjin, China), dibutyl phthalate (A.R. Hubei University Chemical reagent plant) and polyethylene glycol (Sinopharm Chemical reagent Co. Ltd.) were added to the agate jar properly. The slurry was ball-milled for 1 h. Polyviyl butyral (Guangda Bingfeng Chemical plant, Tianjin, China) was dissolved in the ethanol at 60 °C. Then it was added to the slurry. Finally, the anode slurry was ball-milled for 1 h.

After ball-milled, the anode slurry was poured into a container. A cone-shaped mold was inserted into the slurry vertically without attaching the bottom of the

* Corresponding author. Tel.: +86 20 22236168; fax: +86 20 22236168.
E-mail address: jiangliu@scut.edu.cn (J. Liu).

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.01.089

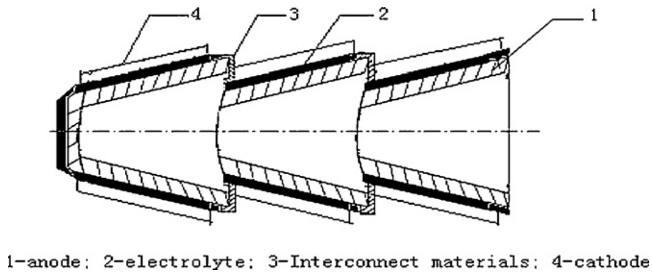

Fig. 1. Sketch map of SOFC stack by the cone-shaped single fuel cells.

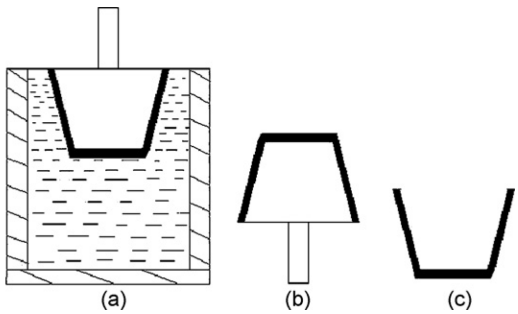

Fig. 2. Schematic diagram of dip coating technique: (a) a mould dipped into the anode slurry; (b) slurry deposited on the mould; (c) a cone-shaped anode substrate.

container. After few seconds, the cone-shaped mold was taken up and the slurry was dried in the air. Then the dip coating process was repeated for five times. After drying, the green cone-shaped anode could be taken off easily from the mold. The green anode is not easy to crack attributing to its good toughness. The wall thickness of the green anode was about 0.06 cm while it became 0.04 cm after precalcinations at 1200 °C for 2 h. The schematic diagram of dip coating technique is shown in Fig. 2. The picture of (a) the green anode substrate by dip coating technique compared with the sintered one and (b) the anode substrate stack is shown in Fig. 3.

The YSZ powder (TZ-8Y, TOSOH Corporation, Tokyo, Japan) mixed with triethanolamine, dibutyl phthalate and polyethylene glycol was firstly ball-milled with ethanol media by planetary ball mill for 1 h. Then polyviyl butyral dissolved in the ethanol at 60 °C was added to the YSZ slurry. Finally, the slurry was ball-milled for 1 h. A rotation speed of 200 rpm was used during ball milling.

After ball-milled, the electrolyte slurry was poured into a container. The cone-shaped anode was dip into the slurry without overflowing the outer wall. After few seconds, the anode was taken up and dried by a hair drier. Then the dip coating process was repeated for two more times. After that, the anode/electrolyte bi-component was co-sintered at 1400 °C for 4 h. The thickness of the YSZ film is about 19.9 μm. The compositions of the anode and electrolyte slurry are shown in Table 1.

2.2. Preparation of LSM-YSZ cathode

Cathode powder $La_{0.7}Sr_{0.3}MnO_3$ (LSM) was synthesized by citric-nitrate process. LSM powder and YSZ (TZ-8Y, TOSOH Corporation, Tokyo, Japan) powder were mixed in a weight ratio of 1:1. The mixed powder was ground for 1 h with the terpineol-ethylcellulose vehicle in an agate mortar to get the stable composite cathode paste. The terpineol-ethylcellulose vehicle was prepared by dissolving 6 wt.% methylcellulose into 94 wt.% terpineol (A.R., Tianjin Kermel Chemical Reagents Development Center, and Tianjin, China). After that, the LSM-YSZ composite cathode paste was applied on YSZ electrolyte film by brush printing and sintered at 1200 °C for 2 h. The cathode area was 0.24 cm^2.

2.3. Cell assembling and testing

Silver paste (Shanghai Research Institute of Synthetic Resins, Shanghai, China) was used as the current collector for both anode and cathode. A four-probe set-up was applied to eliminate the Ohmic loss in the silver wires. The single cone-shaped SOFC was attached to one end of an alumina tube with the anode inside by using silver paste as sealing and jointing material.

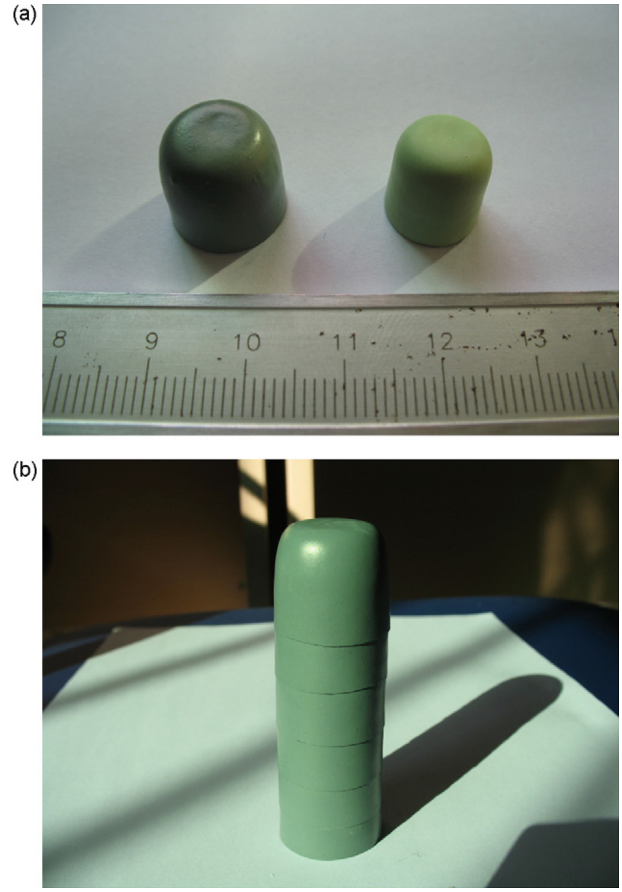

Fig. 3. Photos of (a) the green anode substrate by dip coating technique compared with the sintered one and (b) the anode substrate stack. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Hydrogen saturated with water at room temperature (3% water) was used as fuel at the anode side at a flow rate of 75 ml/min and ambient air as oxidant at the cathode side. The single cell, NiO-YSZ/YSZ/LSM-YSZ, was tested in the temperature range of 600–850 °C. The cell performance and electrochemical impedance spectroscopy were tested using CHI604B (Shanghai Chenhua Instruments Ltd., China). The current–voltage (*I–V*) curves were measured by linear sweep voltammetry at a scanning rate of 5 mV/s. The impedances were measured in the frequency range of 100 kHz–0.1 Hz with signal amplitude of 5 mV under open-circuit condition. After electrochemical test, the cell was fractured and examined using a SEM.

3. Results and discussion

3.1. Electrochemical performance of the single cone-shaped SOFC

Fig. 4 presents the comparison of experimental and theoretical open-circuit voltages (OCVs) at different testing temperatures. The theoretical OCVs values were calculated based on the Nernst equation by assuming that the oxygen partial pressure at the cathode side was 0.21 and that the hydrogen and vapor partial pressure at anode was 0.97 and 0.03, respectively. As shown in Fig. 4, at all testing temperatures, the experimental OCV values are lower than the

Table 1
Compositions of the anode/electrolyte slurries.

	Powders (g)	Triethanolamine (g)	Ethanol (g)	Dibutyl phthalate (g)	Polyethylene glycol (g)	Polyvinyl butyral (g)
Anode slurry	45	1.35	40.5	3.6	3.6	5.4
Electrolyte slurry	24.5	0.7	72	0.9	0.9	1

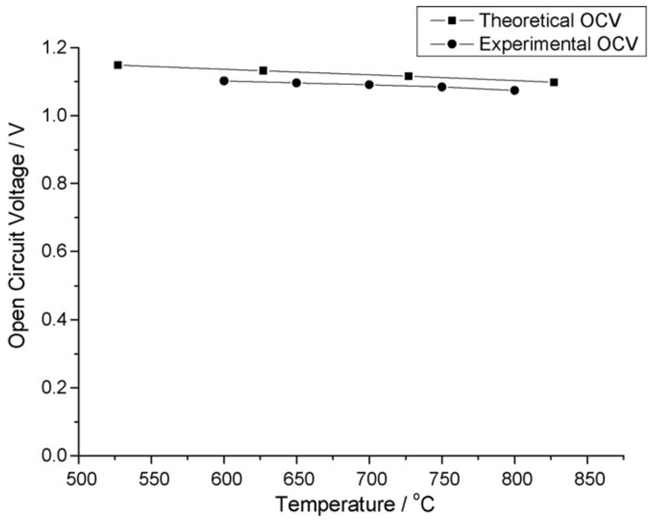

Fig. 4. Comparison of experimental and theoretical OCV at different testing temperatures.

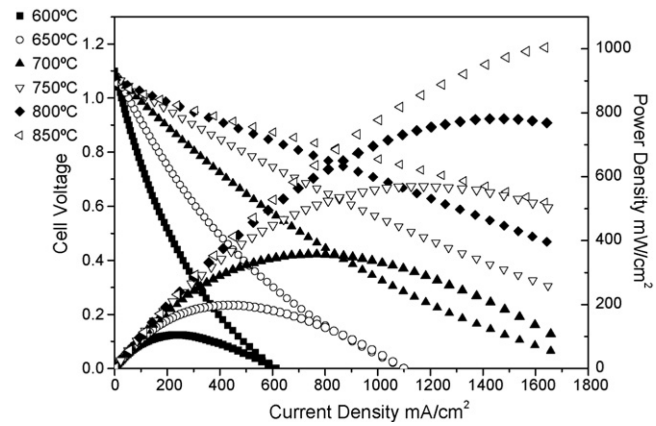

Fig. 5. Voltage and power density versus current density of a cone-shaped SOFC operated on humidified hydrogen (3% water).

theoretical values. As can be seen from Fig. 7, the YSZ film is quite dense and crack-free in cross-section. So, the gas leakage through the YSZ film is insignificant. The difference between experimental OCV values and theoretical ones may come from the gas leakage across the silver paste sealing. Therefore, further research for the sealing material is necessary in the future.

Fig. 5 shows the performance of the single cone-shaped SOFC from 600 to 850 °C, using humidified hydrogen (75 ml/min) as fuel and ambient air as oxidant. The maximum power densities of the cell were 0.78 and 1.0 W/cm^2 at 800 and 850 °C, respectively. At lower temperature (600–700 °C), the *I*–*V* curves were concave up, indicating that activation polarization which occurs by electrode/electrolyte interface polarization resistance dominated in the overall resistance.

The impedance spectra of the single cone-shaped SOFC under open-circuit condition tested at different temperatures are shown in Fig. 6. For the whole cell impedance, the intercepts of the real axis at high-frequency corresponded to the cell ohmic resistance while the arcs at low-frequency were the overall electrodes polarization resistance including both anode and cathode polarization resistance. Impedance spectra showed that the ohmic resistance is small and the polarization resistance dominated in the overall resistance. Therefore, further improvement of electrode activity and electrode/electrolyte interface for anode-supported SOFCs is very necessary in future study.

3.2. Microstructure of the single cell

Fig. 7 shows the microstructures of cross-section of the cone-shaped anode-supported single cell after testing (above) and

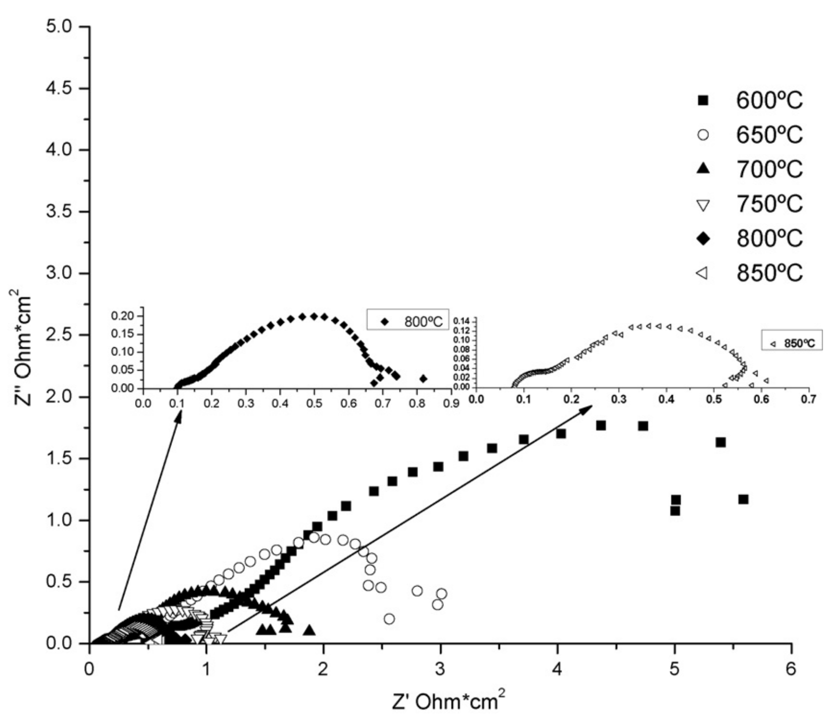

Fig. 6. Electrochemical impedance spectra measured from 600 to 850 °C.

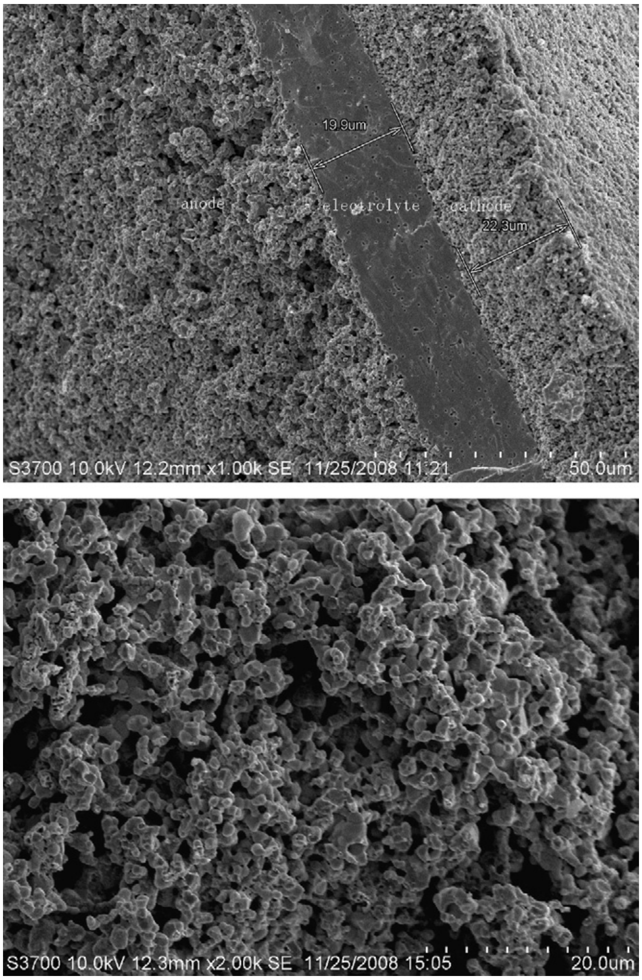

Fig. 7. SEM micrograph of (above) cross-section of a single cell after testing and (below) cross-section of anode.

reduced anode (below). From the figures, we can see that the microstructure of the anode fabricated by dip coating is porous and uniform. It demonstrates that dip coating technique is available to fabricate the anode substrate of SOFC. The dense YSZ electrolyte film is well adhered to the porous anode substrate, the thickness of the electrolyte membrane is ~19.9 μm and the cathode layer is ~23.3 μm.

4. Conclusions

In this paper, simple and cost-effective dip coating technique was successfully developed to fabricate the NiO-YSZ anode substrate and YSZ electrolyte film for the cone-shaped anode-supported single SOFCs. The single cell, NiO-YSZ/YSZ/LSM-YSZ, exhibited a good performance in the intermediate temperature. The observed OCVs implied that the YSZ film was reasonably dense. The results of the impedance spectra showed that the fuel cell performance was restricted by the electrode polarization resistance while the YSZ electrolyte resistance was negligible. SEM result reveals that the microstructure of the anode was porous and the YSZ film was dense. All the factors above indicate that dip coating technique is effective and feasible for fabricating NiO-YSZ anode substrates and YSZ electrolyte films for the cone-shaped anode-supported SOFCs.

Acknowledgements

Financial support from the National “863” program of China (grant no. 200AA05Z136), the Department of Science and Technology of Guangdong Province (grant no. B15-B2051290) and Department of Education of Guangdong Province (grant no. B15-N9060210) are gratefully acknowledged.

References

[1] N.Q. Minh, J. Am. Ceram. Soc. 76 (1993) 563–588.
[2] Y. Zhang, S. Zha, M. Liu, Adv. Mater. 17 (2005) 487–491.
[3] S.C. Singhal, Solid State Ionics 135 (2000) 305–313.
[4] G.A. Tompsett, C. Finnerty, K. Kendall, T. Alston, N.M. Sammes, J. Power Sources 86 (2000) 376–382.
[5] B.C.H. Steele, Nature 400 (1999) 619–621.
[6] M. Doriya, Solid State Ionics 152 (2002) 383–392.
[7] H. Tu, U. Stimming, J. Power Sources 127 (2004) 284–293.
[8] J. Sui, J. Liu, J. Chin. Ceram. Soc. 34 (2006) 1461–1465.
[9] J. Liu, CN Patent 200510101487, 3 (2005).
[10] J. Sui, J. Liu, J. Am. Ceram. Soc. 91 (2008) 1335–1337.
[11] Y.H. hang, J. Liu, J. Yin, W.S. Yuan, J. Sui, Int. J. Applied Appl. Ceram. Technol. 5 (6) (2008) 568–573.