

Short communication

# Anode-supported solid oxide fuel cell based on dense electrolyte membrane fabricated by filter-coating

Xianshuang Xin<sup>a,\*</sup>, Zhe Lü<sup>a</sup>, Xiqiang Huang<sup>a</sup>, Xueqing Sha<sup>a</sup>, Yaohui Zhang<sup>a</sup>, Wenhui Su<sup>a,b,c</sup>

<sup>a</sup> Center for Condensed Matter Science and Technology, Harbin Institute of Technology, Harbin 150001, PR China

<sup>b</sup> Department of Condensed Matter Physics, Jilin University, Changchun 130023, PR China

<sup>c</sup> International Center for Materials Physics, Academia Sinica, Shenyang 110015, PR China

Received 8 November 2005; received in revised form 10 December 2005; accepted 12 December 2005

Available online 24 January 2006

## Abstract

A simple and cost-effective technique, filter-coating, has been developed to fabricate dense electrolyte membranes. Eight mole percent yttria-stabilized zirconia (YSZ) electrolyte membrane as thin as 7  $\mu\text{m}$  was prepared by filter-coating on a porous substrate. The thickness of the YSZ film was uniform, and could be readily controlled by the concentration of the YSZ suspension and the rate of the suspension deposition. The YSZ electrolyte film was dense and was well bonded to the Ni-YSZ anode substrate. An anode-supported solid oxide fuel cell (SOFC) with a YSZ electrolyte film and a  $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$  (LSM) + YSZ cathode was fabricated and its performance was evaluated between 700 and 850  $^{\circ}\text{C}$  with humidified hydrogen as the fuel and ambient air as the oxidant. An open circuit voltage (OCV) of 1.09 V was observed at 800  $^{\circ}\text{C}$ , which was close to the theoretical value, and the maximum power density measured was 1050  $\text{mW cm}^{-2}$ . The results demonstrate that the dense YSZ film fabricated by filter-coating is suitable for application to SOFCs.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Solid oxide fuel cell; Filter-coating; Thin electrolyte film; Yttria-stabilized zirconia

## 1. Introduction

Solid oxide fuel cells (SOFCs) have received considerable attention for use in the direct conversion of chemical energy into electrical energy [1]. In electrolyte-supported cells, the ohmic contribution is large due to high electrolyte resistance. The high operating temperatures of conventional SOFCs can lead to complex materials problems. A lower operating temperature has been recognized worldwide as the key to low-cost SOFCs. A reduction in the temperature will therefore allow the use of a wider range of materials such as alloys, interconnectors and glass sealants. It will also lead to reductions in electrode sintering and interfacial diffusion between the electrolyte and electrode, and a reduction in the thermal stress of the active ceramic structures, leading to a longer expected lifetime of the system. To reduce the fabrication cost and increase the durability of the system components, it is desirable to reduce the operating temperature of SOFCs from 1000 to 800  $^{\circ}\text{C}$  or lower. Approaches to minimiz-

ing the resistive loss across the electrolyte when lowering the operating temperature have included replacing YSZ by alternative electrolyte materials with a higher ionic conductivity such as doped ceria or doped lanthanum gallate, or by reducing the thickness of the solid oxide electrolyte from 100 to 500  $\mu\text{m}$  in conventional electrolyte-supported cells to 5–20  $\mu\text{m}$  in anode-supported cells [2,3].

The anode (Ni/YSZ) is selected as the supporting electrode because it provides superior thermal and electrical conductivity, good mechanical strength, and minimal chemical interaction with the electrolyte during the co-sintering process. In this design, the ohmic loss is smaller than that in electrolyte-supported cells. In addition, the contribution of the electrode activation polarization is also expected to be lower, especially with the use of composite electrodes whose reaction zones spread from the interface of electrolyte and electrode to the electrodes. Thus, an anode-supported design in principle is better suited for operation at lower temperatures [4]. Anode-supported SOFCs require sufficient power densities at intermediate operating temperatures (650–800  $^{\circ}\text{C}$ ) and that the membrane materials are compatible both during fabrication and during operation. Several methods for depositing thin films onto porous substrates

\* Corresponding author. Tel.: +86 451 86418420; fax: +86 451 86412828.  
E-mail address: [xinxianshuang@sohu.com](mailto:xinxianshuang@sohu.com) (X. Xin).

have been reported [5]. In the past several years, much progress has been made in the development of intermediate temperature SOFCs based on thin YSZ electrolytes films [6,7]. Numerous authors have reported higher power densities at reduced temperatures through the use of anode-supported electrolyte films [8–10]. The requirement for significant cost reduction, as well as robustness and high density of the membranes, has prompted the exploration of alternative membrane preparing techniques in which the fabrication is easier and simple.

In this work, we developed a simple and cost-effective approach to fabricating thin YSZ electrolyte films for SOFCs by using a filter-coating method. A filter-coating suspension made of powders in a solvent has been used. By the filter-coating process, dense films of 5–20  $\mu\text{m}$  in thickness could be prepared on the porous anode substrates, and good cell performance can be achieved for low temperature SOFC operation.

## 2. Experimental

### 2.1. YSZ electrolyte films fabrication

Eight mole percent yttria-stabilized zirconia (YSZ, Building Material Academy of China) and NiO (synthesized by homogeneous precipitation [11]) powders were used to prepare Ni/YSZ cermet anode substrates. The powders of YSZ and NiO (50 and 50 wt.%) were weighed and mixed with flour as a pore former in ethanol by ball milling for 12 h, and then dried to form an anode precursor. The precursor was subsequently pressed at 200 MPa under uniaxial pressure to form a disc (13 mm in diameter and  $\sim 1.5$  mm in thickness). The green anode disc was then baked to reduce the extent of shrinkage and increase the mechanical strength of the anode substrate.

The filter-coating setup is shown schematically in Fig. 1. The anode substrates were affixed to the bottom of the funnel and were near to the filter paper, and then immersed into the YSZ suspension, as shown in Fig. 1a. The suspension consisted of  $6\text{ g l}^{-1}$  of YSZ powders (TZ-8Y, Tosoh Co.) with an average diameter of  $0.35\ \mu\text{m}$ , and suspended in isopropanol by mixing with a suitable polyvinyl butyral (PVB) binder. The addition of the binder can increase the strength of the green film, making the electrolyte films free from possible cracks during drying and

sintering. With the suspension coming down and the solvent filtered out through the filter paper, a thin filter cake was left behind on the anode substrate and filter paper (Fig. 1b). Both the suspension concentration and the filter rate determine the thickness and the quality of the green films. High filter rates make the control of the deposit thickness and the densification of the green films very difficult and are thus to be avoided. The process in some respects resembles vacuum infiltration [12] and vacuum slip casting [13], but the suspension is much less concentrated compared to the two techniques. Moreover, the suspension of the filter-coating is filtered out naturally and there is no vacuum apparatus necessary. The coated Ni/YSZ cermet substrate was dried and fired at  $1400\ ^\circ\text{C}$  for 4 h, and then dense YSZ electrolyte films were formed.

### 2.2. Single cell fabrication and test

$\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$  (LSM) powders were prepared by the glycine nitrate process. The LSM and YSZ (TZ-8Y, Tosoh Co.) powders in a mass ratio of 60:40 were mixed with ethyl cellulose and terpineol to form a cathode paste, applied onto YSZ film supported by NiO-YSZ substrate, and sintered at  $1200\ ^\circ\text{C}$  for 2 h. Silver paste was then screen-printed onto the electrodes, and the binder was burned out. A single cell was tested from 700 to  $850\ ^\circ\text{C}$  using an in-house test station for evaluating the performance of SOFCs with humidified  $\text{H}_2$  (3 vol.%  $\text{H}_2\text{O}$ ) as fuel and ambient air as oxidant. The current–voltage ( $I$ – $V$ ) characteristics of the cell were measured and the impedance spectra of the cells were recorded in the range 0.1–910 kHz under open circuit conditions using the electrochemical interface Solartron SI 1287 and impedance analyzer SI 1260, respectively. The microstructure and morphology of the cell structure were examined by a Hitachi S-570 scanning electron microscope (SEM).

## 3. Results and discussion

The current–voltage and current–power density characteristics of the single cell at temperatures between 700 and  $850\ ^\circ\text{C}$  are shown in Fig. 2. The open circuit voltage (OCV) obtained at  $800\ ^\circ\text{C}$  is 1.09 V. The OCV of a fuel cell is related to the

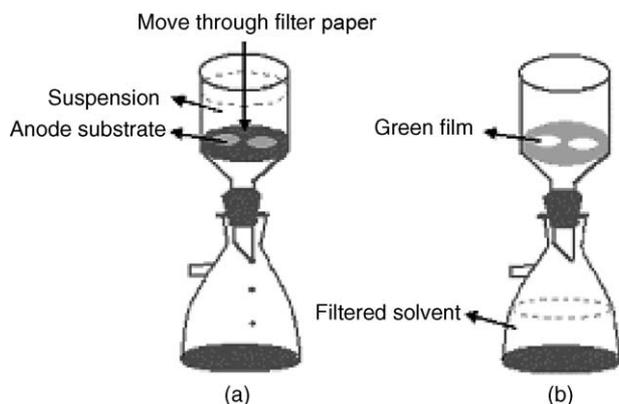


Fig. 1. Schematic for YSZ filter-coating: (a) before filter-coating and (b) after filter-coating.

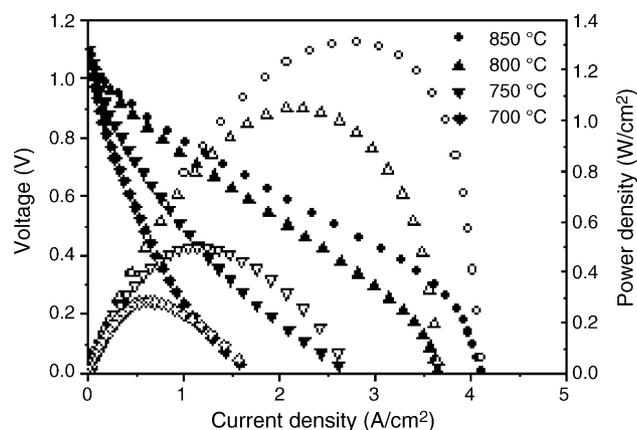


Fig. 2. Cell voltage and power density as a function of current density for a fuel cell with an anode-supported YSZ electrolyte film of  $7\ \mu\text{m}$  in thickness.

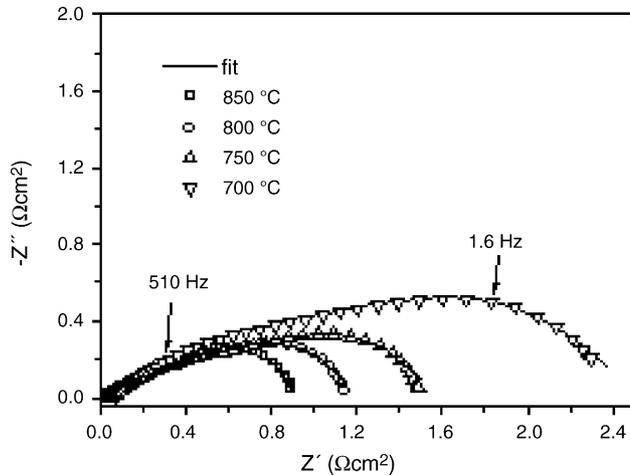


Fig. 3. Impedance spectra of a single cell measured under open circuit conditions at different temperatures.

density of the electrolyte as well as the operating conditions. At fixed operating conditions, the OCV value only depends on the density of the electrolyte. Pores and cracks in the electrolyte film will lead to an OCV value lower than the theoretical value. Therefore, the value of the OCV can be used as an indication of the quality of electrolyte film and the sealing of the cell. The cell OCV is close to the theoretical value of 1.105 V at 800 °C, which indicates negligible gas permeation through the YSZ film, implying that the film prepared by the filter-coating process is quite dense. Maximum power densities are 286, 500, 1050 and 1309  $\text{mW cm}^{-2}$  at 700, 750, 800 and 850 °C, respectively. The results illustrate that the extraordinary performance is achievable at reduced temperatures for SOFCs using thin YSZ electrolyte films fabricated by filter-coating.

The cell impedance spectra under open circuit conditions at different operating temperatures are presented in Fig. 3. The impedance spectra are typically characterized by a larger arc in low-frequency range and a much smaller one in the high-frequency range. The high-frequency intercept with the real axis gives the ohmic loss, and the sum of the electrode polarization resistance is the difference between the high-frequency and low-frequency intercepts with the real axis in the cell. The ohmic resistances ( $R_o$ ) are 0.079, 0.054, 0.038 and 0.030  $\Omega \text{ cm}^2$  and the electrode polarization resistances ( $R_e$ ) are 2.49, 1.55, 1.18 and 0.91  $\Omega \text{ cm}^2$  at 700, 750, 800 and 850 °C, respectively. The electrode polarization resistance accounts for about 97% of the total cell resistance ( $R_o + R_e$ ) at each operating temperature. The results indicate that the electrode polarization is dominant and the ohmic polarization is negligible in the anode-supported SOFCs. Based on the YSZ ionic conductivity of  $\sim 0.04 \text{ S cm}^{-1}$  at 800 °C [8], the ohmic resistance of the 7  $\mu\text{m}$  YSZ electrolyte is estimated to be 0.018  $\Omega \text{ cm}^2$ . The difference (0.012  $\Omega \text{ cm}^2$ ) in ohmic resistance is probably due to the ohmic resistance which includes terms not only from the electrolyte, but also the electrodes and current collectors, and their interfaces in the system. Further optimization of the electrode microstructure and electrode/electrolyte interface to reduce the total cell resistance could further boost the cell performance.

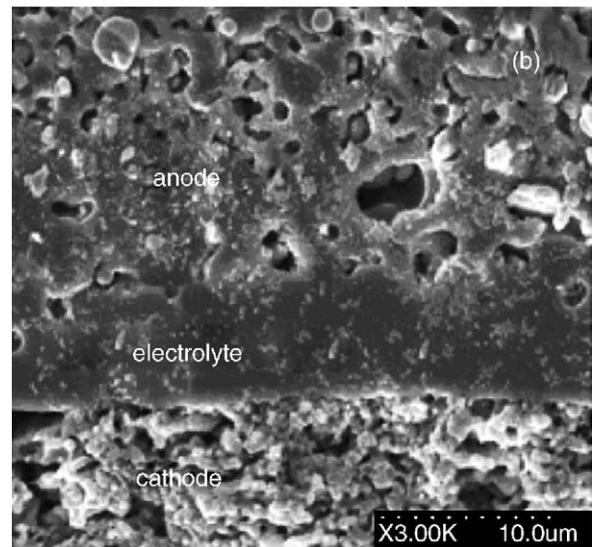
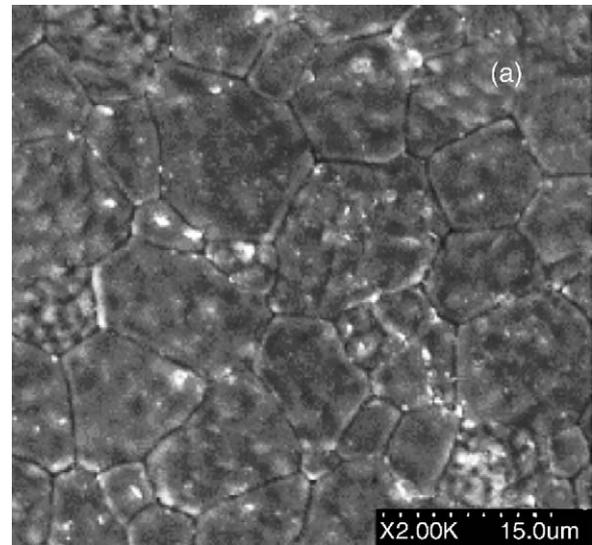


Fig. 4. (a) Surface micrograph of the YSZ electrolyte and (b) cross-sectional micrograph of the post-test cell with a Ni-YSZ anode-supported 7  $\mu\text{m}$  YSZ electrolyte film and a LSM-YSZ cathode.

Fig. 4a and b shows the SEM micrographs of the cross-section and the electrolyte surface in the cell structure. It is important to note that the thin YSZ electrolyte film appears fully dense, without any noticeable pores (Fig. 4a). The SEM image also shows that no cracking or delamination is observed, and the thin electrolyte film is well adhered to the anode substrate (Fig. 4b). A uniform and dense electrolyte film fabricated by filter-coating can lead to not only a pronounced increase in the open circuit voltage, but also to a significant decrease in both ohmic and polarization resistances. Results indicate that the filter-coating process can be used to produce high quality electrolyte membranes.

#### 4. Conclusions

A simple and cost-effective thin film deposition technique was developed to successfully fabricate a dense ceramic membrane on a porous anode substrate by a filter-coating process.

The quality of the deposited film depended on the filtering rate and the suspension concentration. An SOFC based on a YSZ electrolyte film of about 7  $\mu\text{m}$  in thickness was tested from 700 to 850 °C with humidified hydrogen as fuel. An open circuit voltage of about 1.1 V was observed at all tested temperatures, which was close to the theoretical value, implying that the membrane was dense and the gas permeability of the membrane was insignificant. The electrode polarization resistance dominated the total cell resistance, illustrating that optimization of the electrode microstructure would further improve the cell performance. Maximum power densities of 286, 500, 1050 and 1309  $\text{mW cm}^{-2}$  were achieved at 700, 750, 800 and 850 °C, respectively. The results demonstrate that the filter-coating technique is a suitable thin film process to fabricate dense and high quality membranes for application to SOFCs.

### Acknowledgments

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

### References

- [1] N.Q. Ninh, *J. Am. Ceram. Soc.* 76 (1993) 563–588.
- [2] C.R. Xia, F.L. Chen, M.L. Liu, *Electrochem. Solid State Lett.* 4 (2001) A52–A54.
- [3] S.M. Haile, *Acta Mater.* 51 (2003) 5981–6000.
- [4] S.C. Singhal, *Solid State Ionics* 152–153 (2002) 405–410.
- [5] J. Will, A. Mitterdorfer, C. Kleinogel, D. Perednis, L.J. Gauckler, *Solid State Ionics* 131 (2000) 79–96.
- [6] J.H. Kim, R.H. Song, K.S. Song, S.H. Hyun, D.R. Shin, H. Yokokawa, *J. Power Sources* 122 (2003) 138–143.
- [7] J.W. Kim, A. Virkar, K.-Z. Fung, K. Mehta, S.C. Singhal, *J. Electrochem. Soc.* 146 (1999) 69–78.
- [8] S. De Souza, S.J. Visco, L.C. De Jonghe, *J. Electrochem. Soc.* 144 (1997) L35–L37.
- [9] Y. Jiang, A.V. Virkar, F. Zhao, *J. Electrochem. Soc.* 148 (2001) A1091–A1099.
- [10] Y.J. Leng, S.H. Chan, K.A. Khor, S.P. Jiang, P. Cheang, *J. Power Sources* 117 (2003) 26–34.
- [11] X.S. Xin, B.B. Zhou, S.C. Lv, W.H. Su, *Acta Phys. Sin.* 54 (2005) 1859–1862.
- [12] R.N. Basu, G. Blass, H.P. Buchkremer, D. Stöver, F. Tietz, E. Wessel, I.C. Vinke, *J. Eur. Ceram. Soc.* 25 (2005) 463–471.
- [13] Y.B. Matus, L.C. De Jonghe, C.P. Jacobson, S.J. Visco, *Solid State Ionics* 176 (2005) 443–449.