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Short communication

Solid oxide fuel cells with dense yttria-stabilized zirconia electrolyte membranes fabricated by a dry pressing process

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Abstract

Dense yttria-stabilized zirconia (YSZ) electrolyte films were successfully fabricated onto anode substrates using a modified dry pressing process. The film thickness was uniform, and could be readily controlled by the mass of the nanocrystalline YSZ powders. The electrolyte films adhered well to the anode substrates by controlling the anode composition. An anode-supported solid oxide fuel cell (SOFC) with a dense YSZ electrolyte film of 8 μm in thickness was operated at temperatures from 700 to 800 °C using humidified (3 vol% H_2O) hydrogen as fuel and air as oxidant. An open circuit voltage of 1.06 V and a maximum power density of 791 mW cm^{-2} were achieved at 800 °C. The results indicate that the gas permeation through the electrolyte film was negligible, and that good performance can be obtained by this simple and cost-effective technique which can significantly reduce the fabrication cost of SOFCs.

Keywords: Solid oxide fuel cell; Dry pressing; Electrolyte thin film; Yttria-stabilized zirconia

1. Introduction

Solid oxide fuel cells (SOFCs) offer a clean and low polluting technology to directly convert chemical energy into electrical energy at high efficiencies [1]. However, the high operating temperature of conventional electrolyte-supported cells can lead not only to a high fabrication cost for SOFCs systems, but also complex materials problems including electrode sintering, interfacial diffusion between electrolyte and electrode, and mechanical stress due to the different thermal expansion coefficients. These problems have limited the commercial development of SOFCs [2]. Lowering the operating temperature of SOFCs will reduce the fabrication cost and complexity of the stack by enabling the selection of cheaper candidate materials used as interconnects such as metal alloys [3]. Approaches to lower the operating temperature have included employing intermediate temperature electrolyte materials such as doped ceria and Sr- and Mg-doped lanthanum gallate (LSGM), or reducing the electrolyte thickness in anode-supported SOFCs. Although the use of advanced materials to replace the conventional yttria-stablized zirconia (YSZ) electrolyte is desirable, some issues associated with the stability of these materials under the harsh operation environment still exist, for example, the low mechanical strength and stability of doped ceria, and the poor chemical compatibility of LSGM with NiO anode. In fact, up to now, YSZ is still the most commonly used electrolyte material for SOFCs because of its unique properties such as high chemical and thermal stability, excellent mechanical properties and pure ionic conductivity over a wide range of conditions. The progress in fabricating anode-supported thin electrolyte films in recent years has permitted the lowering of the operating temperatures by reducing the high Ohmic resistance in SOFCs.

Various film preparation techniques have been developed for the fabrication of electrolyte membranes on porous anode substrates. These techniques include physical, chemical and electrochemical vapor deposition [4], and liquid precursor methods such as the sol–gel process [5], tape casting [6], slurry coating [7,8], spray coating [9] and filter-coating [10]. The cost to build

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the vapor deposition apparatus is high. On the other hand, most of the liquid phase-containing methods are considered to be less efficient because the coating and drying have to be repeated in order to avoid film cracks and achieve the required density or desired thickness. Moreover, many of these film preparation techniques are complex, expensive and difficult to control [4]. The dry pressing process, is a simple and cost-effective method, and has been widely used to make parts thicker than 0.5 mm, and this technique has been successfully used to prepare ceria-based electrolyte membranes as thin as 8 μm in thickness [11]. However, in the case of the YSZ, which is the most commonly used as an electrolyte material for SOFCs, as yet, there has been no literature to report the fabrication of dense YSZ electrolyte membranes thinner than 50 μm for SOFC application by a simple dry pressing technique [12]. This is in part due to the delamination or cracking in the electrolyte/anode bilayer during compressing or co-sintering, or due to the requirement to use commercial micro-size YSZ, making it very difficult to press a film thinner than 50 μm by the traditional dry pressing method.

In the present work, we report our initial results on SOFCs based on YSZ electrolyte thin films fabricated by a modified dry pressing method. The implementation of this simple and cost-effective fabrication technique possesses great potential to dramatically reduce the fabrication cost of SOFCs, thereby making SOFCs potentially economically competitive with conventional technologies. By utilization of the highly porous and low bulk density of nanocrystalline YSZ powders and an optimum anode composition, a dense YSZ electrolyte film as thin as 8 μm, which is well bonded to the anode substrate, has been fabricated by this modified dry-pressing method and has been tested in SOFCs.

2. Experimental

2.1. YSZ electrolyte films fabrication

The YSZ powders were synthesized by a glycine nitrate process. The appropriate quantities of Y^{3+} and Zr^{4+} nitrates (molar ratio 4:23 of Y^{3+}:Zr^{4+} corresponding to 8 mol% YSZ) were dissolved in deionized water, and mixed with glycine by stirring. The stoichiometric solutions were heated to vaporize water on a heating stove, and then burned to form a grey ash. The ash was calcined at 700 °C for 2 h to crystallize and produce porous and low bulk density nanocrystalline YSZ powders. The synthesis of the highly porous YSZ with an extremely low bulk density is the key to successfully prepare thin and dense YSZ electrolyte films on anode substrates. The powders of YSZ and NiO (synthesized by homogeneous precipitation) with a weight ratio of 1:1 were mixed with fluor and organic binder to form an anode precursor. The precursor was pressed in a stainless mold to flatten the surface and create some mechanical strength. The diameter of the metal mold was 13 mm, and the thickness of the green anode was 0.6 mm. Then the prepared YSZ powders were added through a screen (silk net, 250 mesh). The use of the screen can effectively make the YSZ powders evenly distributed onto the substrates. The coated YSZ powders layer was pressed together with the anode substrate and the bilayer was subsequently sintered at 1400 °C for 4 h, to form dense YSZ electrolyte films.

2.2. Cell fabrication and test

$La_{0.85}Sr_{0.15}MnO_3$ (LSM) powders were prepared by the glycine nitrate process. The LSM and YSZ (TZ-8Y, Tosoh Co.) powders with a weight ratio of 60:40 were mixed with ethyl cellulose and terpineol to form a cathode paste, applied to the YSZ film and sintered at 1200 °C for 2 h. The cathode area was 0.05 cm^2. Silver paste was screen-printed onto the electrodes for current collectors. Two silver wires were pasted onto each current collector as the current and voltage leads, respectively, thus a membrane electrode assembly (MEA) was fabricated. The MEA was sealed on one side of a ceramic tube with silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins, Shanghai, China) to complete the fabrication of a single cell. The single cell was tested from 700 to 800 °C using humidified H_2 (3 vol% H_2O) and stationary air as fuel and oxidant, respectively. The typical hydrogen flow rate was set to 100 ml min^{-1}. The current–voltage (*I–V*) characteristics of the cell were measured and the impedance spectra of the cell were recorded in the range from 0.1 Hz to 910 kHz under open-circuit conditions using the electrochemical interface: Solartron SI 1287 and the impedance analyzer SI 1260. The microstructure and morphology of the tested cell were examined with a Hitachi S-570 scanning electron microscope (SEM).

3. Results and discussion

Fig. 1 shows the microstructures of a tested cell component using the SEM. From the electrolyte surface (Fig. 1a) and the cross-section (Fig. 1b) of the cell structures, it can be seen that the YSZ electrolyte film as thin as 8 μm appears to be dense, almost without any noticeable pores. The SEM image also shows that the thin electrolyte film is adhered well to the anode substrate without any cracks or delaminations between them. The electrolyte film is dense and the film thickness can be readily controlled by the mass of the YSZ powders used. It is the extremely loose YSZ powders with a low bulk density that makes it possible to prepare such a thin YSZ film by the dry pressing process. However, it is also due to the use of the screen through which the YSZ powders can be distributed onto the anode substrate to form a green film with a uniform thickness. In particular, the addition of organic binder to the anode substrate cannot only adjust the shrinkage of the anode substrate to match that of the electrolyte film, but also make the film better bonded to the anode substrate after dry pressing and sintering.

The voltages and power densities of the cell with YSZ electrolyte film of 8 μm in thickness as a function of current density at different measuring temperatures are shown in Fig. 2. The open circuit voltage (OCV) is 1.06 V, which is close to the theoretical value of 1.105 V at 800 °C, indicating that the thin electrolyte film prepared by the modified dry pressing process is dense and impermeable. The maximum power densities are 295, 511 and 791 mW cm^{-2} at 700, 750 and 800 °C, respectively, illustrating that good performance can be obtained for

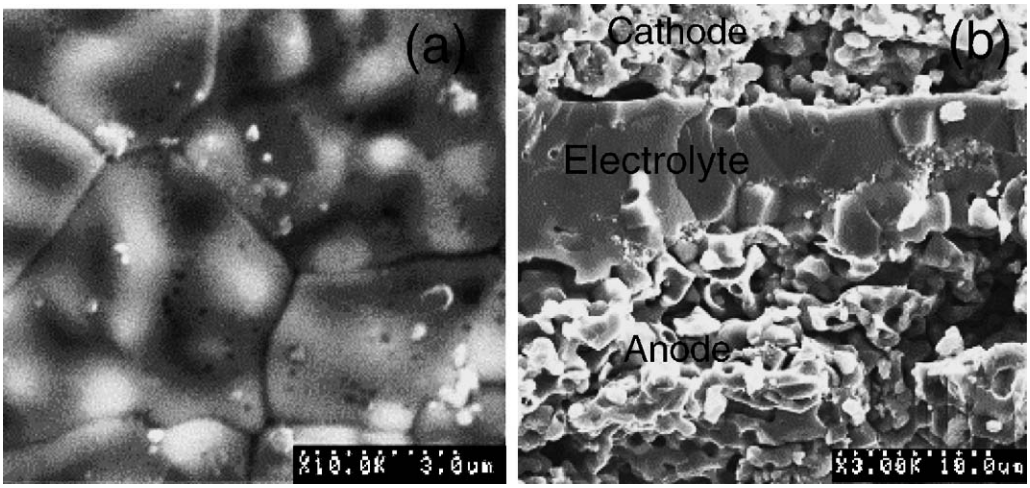

Fig. 1. (a) Surface micrograph of the YSZ electrolyte and (b) cross-sectional micrograph of the post-test cell with an 8 μm YSZ electrolyte film, a Ni–YSZ anode and a LSM–YSZ cathode.

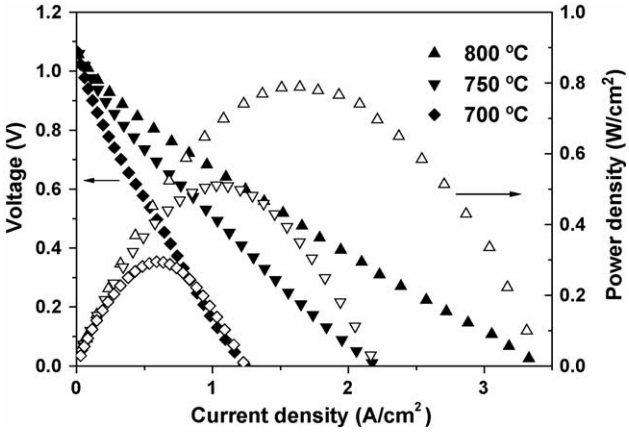

Fig. 2. Cell voltage and power density as a function of current density for a fuel cell with a YSZ electrolyte film of 8 μm in thickness.

SOFC application using thin YSZ electrolyte films fabricated by this simple and cost-effective technique.

Fig. 3 shows the typical impedance spectra in the open circuit condition at measuring temperatures from 700 to 800 °C. The high-frequency (HF) intercept with the real axis gives Ohmic losses (R_o), and the difference between the high-frequency and low-frequency (LF) intercepts with the real axis in the cell represents the sum of the electrode polarization resistances (R_e). The electrode polarization resistance, which is higher than the Ohmic polarization resistance (Table 1), accounts for about 94% of the total cell resistance ($R_o + R_e$) at respective operating temperatures. The Ohmic polarization resistance (0.040 Ω cm^2) of this cell is lower than that (0.10 Ω cm^2) reported by De Souza et al. [13] at 800 °C whose film thickness was 10 μm, indicating that a desirable performance of electrolyte film was achieved. On the other hand, the electrode polarization resistance of 0.57 Ω cm^2 in the tested cell is eight times higher than the value (0.067 Ω cm^2) in the same literature. The results indicate that the electrode polarization is dominant, and the Ohmic polarization is negligible in this single cell. Further optimization of the electrode microstructure to reduce the electrode polarization resistance may further enhance the cell performance.

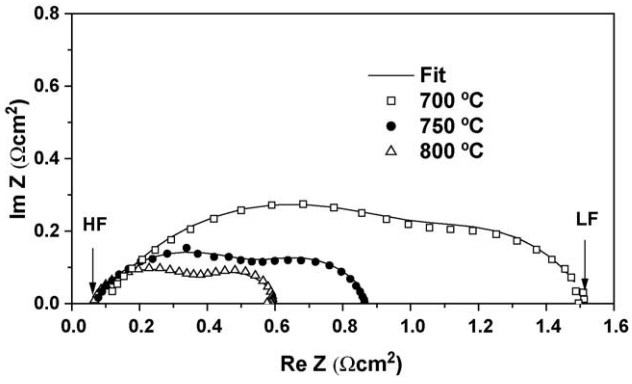

Fig. 3. Impedance spectra of a single cell measured under open circuit condition at different temperatures.

Table 1
The Ohmic polarization resistance (R_o), the electrode polarization resistance (R_e) and the total cell resistance ($R_o + R_e$) for a SOFC with a YSZ electrolyte film of 8 μm in thickness at different operating temperatures

Temperature (°C)	R_o (Ω cm^2)	R_e (Ω cm^2)	$R_o + R_e$ (Ω cm^2)	$R_e/(R_o + R_e)$ (%)
800	0.040	0.57	0.61	93.44
750	0.049	0.83	0.88	94.31
700	0.083	1.44	1.52	94.74

4. Conclusions

A simple, reproducible and cost-effective modified dry pressing technique has been developed to successfully fabricate dense YSZ electrolyte films on anode substrates. The thickness of the YSZ film was uniform, and was readily controlled by the amount of loose nanocrystalline YSZ powders. The YSZ electrolyte thin films adhered well to the anode substrates and no delamination or cracking was observed. The OCV of the cell

with YSZ electrolyte film of 8 μm in thickness was 1.06 V at 800 °C, which was very close to the theoretical value. Maximum power densities of 295, 511 and 791 mW cm^{-2} were achieved at 700, 750 and 800 °C, respectively. The results demonstrate that good cell performance has been obtained, and the use of this simple film fabricating technique may significantly reduce the fabrication cost of SOFCs.

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References

[1] S.C. Singhal, Solid State Ionics 152–153 (2002) 405–410.
[2] S.M. Haile, Acta Mater. 51 (2003) 5981–6000.
[3] K. Huang, M. Feng, J.B. Goodenough, J. Am. Ceram. Soc. 81 (1998) 357–362.
[4] J. Will, A. Mitterdorfer, C. Kleinlogel, D. Perednis, L.J. Gauckler, Solid State Ionics 131 (2000) 79–96.
[5] S.-G. Kim, S.P. Yoon, S.W. Nam, S.-H. Hyan, S.-A. Hong, J. Power Sources 110 (2002) 222–228.
[6] J. Liu, W. Liu, Z. Lu, L. Pei, L. Jia, L.Y. He, W.H. Su, Solid State Ionics 118 (1999) 67–72.
[7] J.W. Kim, A.V. Virkar, K.-Z. Fung, K. Mehta, S.C. Singhal, J. Electrochem. Soc. 146 (1999) 69–78.
[8] Y. Jiang, A.V. Virkar, F. Zhao, J. Electrochem. Soc. 148 (2001) A1091–A1099.
[9] Y.J. Leng, S.H. Chan, K.A. Khor, S.P. Jiang, P. Cheang, J. Power Sources 117 (2003) 26–34.
[10] X.S. Xin, Z. Lü, X.Q. Huang, X.Q. Sha, Y.H. Zhang, W.H. Su, J. Power Sources 159 (2006) 1158–1161.
[11] C.R. Xia, M.L. Liu, J. Am. Ceram. Soc. 84 (2001) 1903–1905.
[12] K.Y. Liu, Z. Lü, L. Jia, K.F. Chen, B. Wei, S.Y. Li, W.H. Su, Chin. J. Power Sources 11 (2005) 737–740.
[13] S. De Souza, S.J. Visco, L.C. De Jonghe, J. Electrochem. Soc. 144 (1997) L35–L37.