Short communication

Thin yttria-stabilized zirconia electrolyte and transition layers fabricated by particle suspension spray

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Abstract

In order to develop high performance intermediate temperature (<800 °C) solid oxide fuel cells (SOFCs) with a lower fabrication cost, a pressurized spray process of ceramic suspensions has been established to prepare both dense yttria-stabilized zirconia (YSZ) electrolyte membranes and transition anode layers on NiO + YSZ anode supports. A single cell with 10 µm thick YSZ electrolyte on a porous anode support and ∼20 µm thick cathode layer showed peak power densities of only 212 mW cm^{-2} at 700 °C and 407 mW cm^{-2} for 800 °C. While a cell with 10 µm thick YSZ electrolyte and a transition layer on the porous anode support using a ultra-fine NiO + YSZ powder showed peak power densities of 346 and 837 mW cm^{-2} at 700 and 800 °C, respectively. The dramatic improvement of cell performance was attributed to the much improved anode microstructure that was confirmed by both scanning electron microscopes (SEM) observation and impedance spectroscopy. The results have demonstrated that a pressurized spray coating is a suitable technique to fabricate high performance SOFCs and at lower cost.
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Keywords: SOFCs; Suspension spray; Dense YSZ electrolyte; Transition anode layer

1. Introduction

Solid oxide fuel cells (SOFCs) as electrochemical energy conversion devices have attracted extensive studies because of their high energy efficiency, simple operation and environmental friendliness. In recent years, anode supported thin electrolyte SOFCs have demonstrated a high power density, even at temperatures around or below 800 °C. In fabrication of anode supported SOFCs, there have been a number of techniques developed to prepare thin electrolyte layers on anode supports, such as aerosol-assisted metal-organic chemical vapor deposition (MOCVD) [1], polarized electrochemical vapor deposition (PEVD) [2], RF magnetron sputtering [3], screen printing [4], slurry coating [5] process, etc. The techniques involving gaseous process are generally of quite high cost in both equipment and operation, and of rather low efficiency, which makes them difficult to scale up for commercialization. The other conventional ceramic processing methods usually use large amounts of organic additives, which may lead to large shrinkages associated with the removal of additives on subsequent drying and sintering, and thus it is difficult to fabricate dense thin membranes with a larger area on porous supports. Conventional slurry processing remains but some problems are still to be solved, such as a low green density, a large pore distribution of the green layer and cracks during drying. A suspension spray process has been commonly considered as a low cost technique for the preparation of functional ceramic layers in SOFCs. Though there were reports to mention that some companies had employed this technique to fabricate YSZ layers, but there is no detailed description in the literatures.

To improve the microstructure and to increase triple phase boundaries (TPB) of the positive–electrolyte–negative (PEN) assembly, it is usual to deposit a transition layer on the as-prepared porous anode support by some process. In this work, we developed a pressurized suspension spray coating [6] to directly fabricate both the ultra-fine transition anode layer and the YSZ electrolyte layer on a porous anode support. Fuel cells have been assembled and tested.

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2. Experiments

2.1. Preparation of the anode support

A commercial YSZ powder with particle size of about 1 μm and NiO powder prepared by calcining analytical-grade $Ni(HCO_3)_2$ at 350 °C for 2 h were used in this study. The NiO and YSZ powders with a weight ratio of 60:40 with 20 wt% starch were mixed and milled in ethyl alcohol for 24 h. The dried mixed powders were pressed into Ø 20 mm pellets under 200 MPa and then fired at 950 °C for 2 h as the anode supports.

2.2. Preparation of anode transition layer and electrolyte membrane

The fine NiO–YSZ mixture powders were prepared by a chemical co-precipitation process with using $Ni(NO_3)_2$, $Zr(NO_3)_4$ and $Y(NO_3)_3$ as starting precursors and $(NH_4)_2CO_3$ as the precipitator. The precipitates were washed, filtered, dried and subsequently calcined at 700 °C for 2 h. A suspension of NiO–YSZ powder with a NiO content of 60 wt% was prepared by ball-milling the powder in distilled water for 3 h and then adding polyethylene glycol (PEG) as a surfactant for another 24 h. For making YSZ suspensions, a commercial YSZ powder (TZ-8Y, Tosoh. Corp., Japan) was used.

In the spray process described elsewhere [6] the suspensions are fluidized by a pressurized air-flow and became fog-droplets, which are then carried by the air flow toward onto the support to form a particulate layer. The YSZ electrolyte layer was thus prepared on a porous anode support without or with an anode transition layer that was previously deposited by the same procedure. The multi-layer green disks were subsequently co-sintered at 1400 °C for 5 h.

In preparing a single cell, a slurry was made by mixing 70 wt% NSM ($Nd_{0.7}Sr_{0.3}MnO_3$, prepared by a glycine–nitrate process), 30 wt% SDC ($Ce_{0.8}Sm_{0.2}O_{1.9}$, synthesized by co-precipitation method) and an organic binder was applied on the electrolyte surface of the above multi-layers by screen-printing and then sintered at 1100 °C in air for 2 h to form a porous cathode.

The morphology and thickness of all the membranes and layers in the cell assembled were observed by scanning electron microscopes (SEM, Hitachi X-650, Japan).

2.3. Cell performance

The single cell was sealed on an alumina tube with silver paste and electrochemically tested on a self-assembled cell testing system in the temperature range of 600–800 °C. Humidified (3% H_2O) hydrogen, which can be achieved by bubbling H_2 through water at about 25 °C, was used as fuel and stationary air as oxidant. Fuel cell performances were examined with digital multimeters (GDM-8145). The ac conductivities of the cells were measured by a two-probe impedance spectroscopy (Chi604a, Shanghai, Chenhua) under open-current conditions. Measurements were made every about 50 °C interval in air over
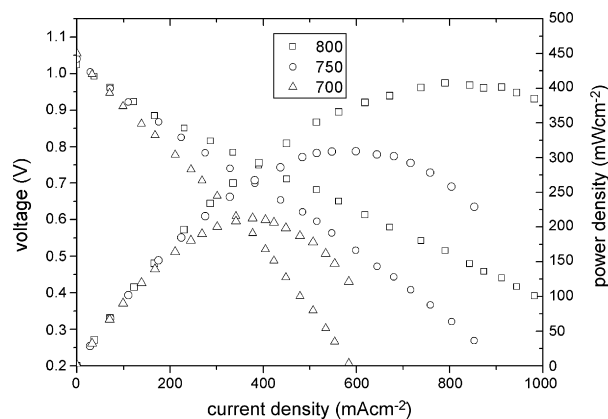

Fig. 1. The *I–V* and power density curves of the single cell without the transition anode layer measured at 700–800 °C.

the temperature range of 600–800 °C. The frequency range was 1 MHz to 1 Hz, and in some cases down to 0.1 Hz.

3. Results and discussion

Fig. 1 shows the *I–V* and power density curves of a single cell without an anode transition layer measured at 700–800 °C. As seen from the curves, the OCV is about 1.02 and 1.05 V at 800 and 700 °C, respectively, which are quite close to the theoretical values calculated according to the Nernst equation, 1.13 and 1.15 V, respectively. This indicates the electrolyte membrane was dense enough, as any leakage in the electrolyte membrane would lead to severely lowering of the OCV values. SEM photography of the fracture section (Fig. 2) illustrates the YSZ layer is completely dense and even the closed pores are almost eliminated, that is consistent with the evidence from the OCV values. It can be also noted that the *I–V* curves in Fig. 1 are bending down slightly at a certain current density for 700 and 750 °C. That implies the existence of concentration polarization associated with the anode microstructure.

The maximum power densities of the cell were 407, 309 and 212 mW cm^{-2} at the current density of 790, 598 and 377 mA cm^{-2} for 800, 750 and 700 °C, respectively. The rel-
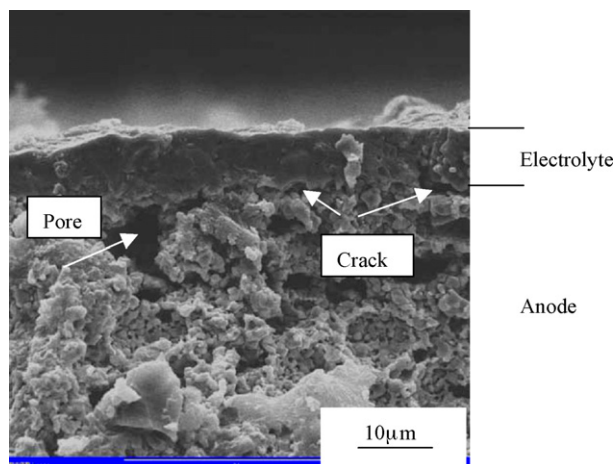

Fig. 2. Cross-section of YSZ layer sintered at 1400 °C for 5 h.

atively poor performance level is possibly from the poor interfacial conditions between the YSZ membrane and the anode as can be seen from the SEM photos in Fig. 2. The YSZ layer adheres to the substrate weakly, and cracks and other disfigurements such as big pores are present at the interface. These defects are related to the rough surface of the anode support due to the forming process and the additives of organic binder being added to create porosity. A thin and dense electrolyte layer would be hardly formed on such a non-smooth surface and it would cause microcracks and non-bonded interfaces between the electrolyte and anode support. Obviously, the poor condition of the anode/electrolyte interface would certainly reduce the length of the three-phase boundary (TPB), where the electrochemical reaction takes place.

For optimizing the SOFC anode performance, it is most important to ensure that the anode microstructure minimizes the polarization loss during operation. The polarization is strongly dependent on the microstructural factors of the anode, such as particle size, spatial distribution and the interconnectivity of each constituent phase. In order to improve the microstructure of the anode supports, a transition layer with much finer particles has been commonly considered to apply on the as prepared anode supports. Fang et al. [7] in this laboratory prepared a high dispersed and ultra-fine NiO–SDC mixture powder prepared by using carbonate co-precipitation. In this work, the ultra-fine NiO–YSZ powder was synthesized by this method for the spray suspension to smooth the anode support surface. Fig. 3 shows the surface morphology of a sample. It is clear that the particles are well dispersed and deposited on the support uniformity with no big pores on the surface. This surface microstructure with two phases would benefit to develop a dense electrolyte layer and establish a better connection between anode and electrolyte. Fig. 4 shows the I–V and power density curves of a single cell with such a transition anode layer tested at
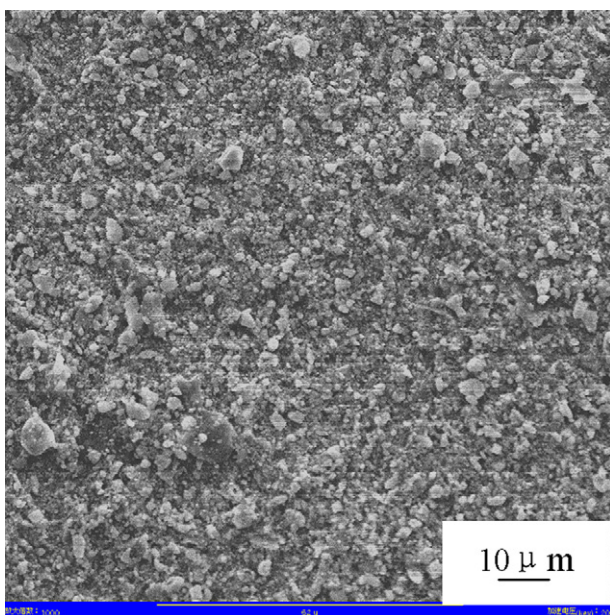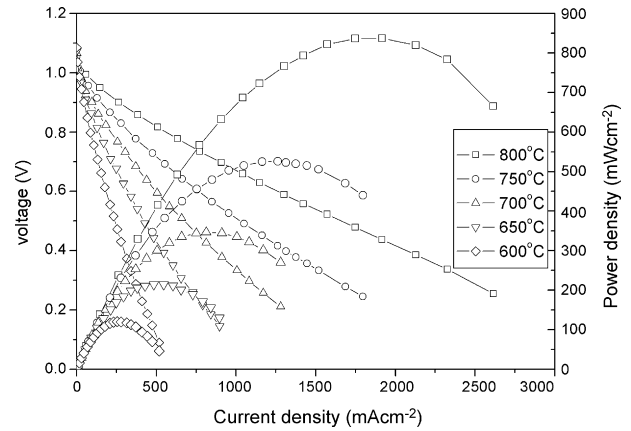

Fig. 4. The I–V and power density curves of the single cell with a transition anode layer measured at 600–800 °C.

600–800 °C. The peak power densities are 837, 526, 346, 214 and 120 mW cm^{-2} at 800, 750, 700, 650 and 600 °C with the current density of 1917, 1262, 812, 483 and 254 mA cm^{-2}, respectively. Obviously, the cell performance was dramatically improved compared with the cell without the transition anode layer. It is well known that a fine particle size, large surface area, adequate porosity and a sufficient Ni content in the anode are essential to achieve high anode performance. It has been shown that optimization of the anode microstructure by using ultra-fine NiO + YSZ two phases powder, would increase the length of TPB, and hence improve the anodic performance. Fig. 5 shows the fracture microstructure of anode (Ni + YSZ) supported electrolyte (YSZ) film with a transition layer (Ni + YSZ) and cathode ($Nd_{0.7}Sr_{0.3}MnO_3$ + SDC) film. The thickness of the YSZ layer is about 10 μm which equaled to the thickness of the cell without a transition layer described above, indicating that the much improved cell performance does not come from the difference of the electrolyte thickness. Fig. 6 is a magnified SEM micrograph of the interface between the Ni/YSZ active anode layer and the YSZ electrolyte. We cannot find a distinct interfacial boundary between the YSZ electrolyte and the anode. The fine particles of well-dispersed Ni + YSZ penetrate
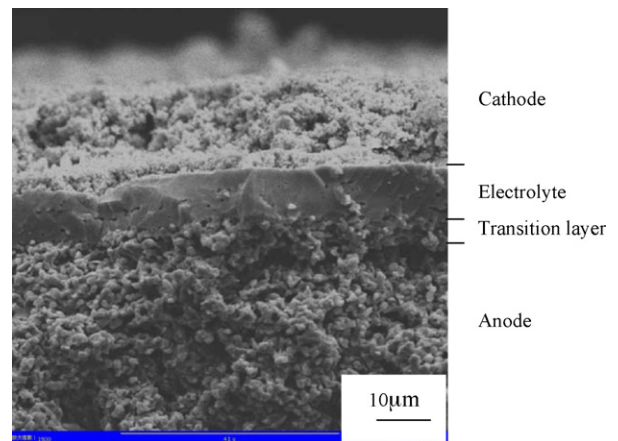

Fig. 3. The surface morphology of NiO–YSZ powder layer fabricated by pressurized spray coating.

Fig. 5. The overview of the microstructure of anode (NiO + YSZ) supported electrolyte (YSZ) film with transition layer (NiO + YSZ) and cathode ($Nd_{0.7}Sr_{0.3}MnO_3$ + SDC) film.
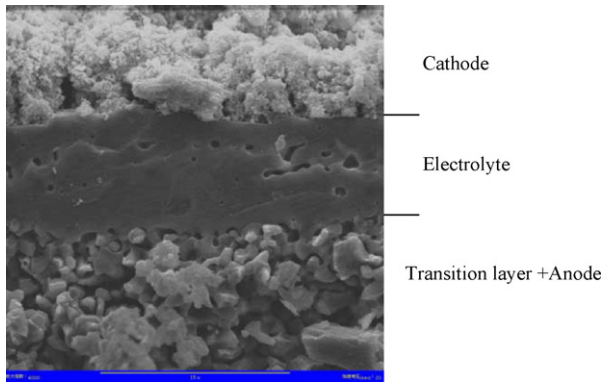
Fig. 6. The magnified SEM micrographs of the interface between Ni/YSZ transition anode layer and YSZ electrolyte.

the pores and cracks of the support and certainly improve the smoothness to enable the formation of a dense YSZ top layer. As described above, the active anode powder synthesized by chemical co-precipitation was deposited on the anode support uniformly and the two phases (NiO and YSZ) distribute homogeneously, this will enlarge the TPB region where the charge transfer reactions occur and enhance the interface combination between the electrolyte and anode support, which are certainly the reasons for the much improved cell performance [8].
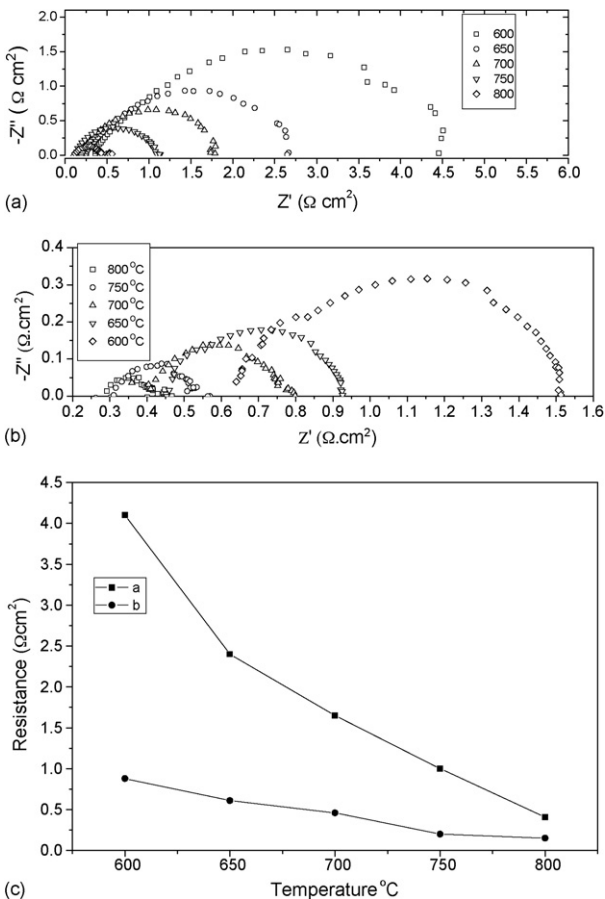

Fig. 7. The comparisons of impedance spectra of the cells with (b) and without (a) transition anode layer under open-current conditions at different temperature, and the total interfacial resistances determined from the impedance spectra (c).

To further verify the action of the transition anode layer to improve the interfacial charge transfer behavior, a comparison of the impedance spectra of the cells with (b) and without (a) active anode layer under open-current conditions at different temperatures as shown in Fig. 7. In these spectra, the intercept with the real axis at low frequencies represents the total resistance of the cell and the value of the intercept at high frequency is the electrolyte resistance, while the difference of the two values corresponds to the sum of the resistance of the two interfaces: the cathode–electrolyte interface (Rc) and the anode–electrolyte interface (Ra) [9]. Fig. 7c presents the total interfacial resistances determined from the impedance spectra for the two cells. The values of the cell with active anode layer were 0.88, 0.61, 0.46, 0.20 and 0.15 Ω cm^2 at 600, 650 700 750 and 800 °C, respectively, which were much lower than that of the cell without active anode layer of 4.10, 2.40, 1.65, 1.00 and 0.41 Ω cm^2 at corresponding temperatures. It also can be seen that the activation polarization is observed at low current densities in the *I–V* curves shown in Fig. 4, which was not found in Fig. 1. This behavior can be mainly attributed to the cathode polarization, because of the poor interface condition between the electrolyte and cathode shown in Fig. 5. There were some big pores and microcracks in the interface, which reduced the performance of the cell. This situation may also occur in the cell without a transition layer, but the poor anode should be the dominant factor in poor cell performance. It is believed that much improvement in the cell performance can be expected when the cathode–electrolyte microstructure is further optimized.

4. Conclusion

A pressurized suspension spray technique has been established to deposit both an ultra-thin anode transition layer and a dense YSZ electrolyte membrane on a porous anode support. The open circuit voltages of the cells which consisted of the above double layer and Nd$_{0.7}$Sr$_{0.3}$MnO$_3$/SDC as the cathode are quite close to the theoretical OCV values, indicating a highly dense YSZ electrolyte.

The cells with YSZ electrolyte directly deposited on the anode support showed a rather low power density due to the very poor interface between the anode and electrolyte. When a transition anode layer was deposited on the as prepared anode using a very fine powder of two phase mixture NiO + YSZ, the cell performance was dramatically improved, and the peak power densities reached 346 and 837 mW cm^{-2} at 700 and 800 °C, respectively.

SEM observations revealed that the transitional layer eliminated the rough surface of the anode and made a much better coherency between the electrolyte and anode, hence creating longer TPB lines and so better electrochemical performance. The total interfacial resistance of the cell with a transition anode layer measured by impedance spectroscopy was three to five times lower than that of the cell without active anode layer, which is consistent with the result from SEM observations. These results have illustrated that a pressurized spray coating is a simple and potentially commercial prospective method for preparing the key components of SOFCs.

Acknowledgement

References

[1] H.Z. Song, H.B. Wang, S.W. Zha, D.K. Peng, G.Y. Meng, Solid State Ionics 156 (3–4) (2003) 249–254.
[2] M.A. Haldane, T.H. Etsell, Mater. Sci. Eng. B 121 (1–2) (2005) 120–125.
[3] Y. Yoo, J. Power Sources 160 (1) (2006) 202–206.
[4] Y.H. Zhang, X.Q. Huang, Z. Lu, Z.Q. Liu, X.D. Ge, J.H. Xu, X.S. Xin, X.Q. Sha, W.H. Su, J. Power Sources 160 (2) (2006) 1065–1073.
[5] R. Muccillo, E.N.S. Muccillo, F.C. Fonseca, Y.V. França, T.C. Porfirio, D.Z. de Florio, M.A.C. Berton, C.M. Garcia, J. Power Sources 156 (2) (2006) 455–460.
[6] R.Q. Yan, G.B. Zhong, Q.L. Ma, X.Q. Liu, G.Y. Meng, J. Membr. Sci., in review.
[7] X.H. Fang, G.Y. Zhu, C.R. Xia, G.Y. Meng, Solid State Ionics 168 (1–2) (2004) 31–36.
[8] M. Mamak, N. Coombs, G.A. Ozin, Chem. Commun. (2002) 2300.
[9] C.R. Xia, M.L. Liu, Solid State Ionics 144 (2001) 249–255.