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Dip-coating thin yttria-stabilized zirconia films for solid oxide fuel cell applications

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Abstract

The preparation of high-quality yttria-stabilized zirconia (YSZ) electrolyte films on porous substrates is critical to the fabrication of high-performance solid-state ionic devices such as solid oxide fuel cells (SOFCs) and gas sensors. In this paper, stable, fully dispersed YSZ suspensions were prepared. Particles zeta-potential and relative viscosity of suspensions were investigated. Thin YSZ films were deposited on NiO–YSZ anode supports with the YSZ suspensions and then heated to 1400 °C in air. Dense and crack-free films were obtained with thickness in the range of 20–30 μm. $La_{0.8}Sr_{0.2}MnO_3$ (LSM) paste was printed on the YSZ electrolyte/anode to assemble single fuel cell and tested in the temperature range of 650–800 °C. The open circuit voltage (OCV) of the cells reached 0.98 V and maximum power density 190 mW/cm^2 at 800 °C, showing a reasonable performance. The deposited thin films could be considered for electrolyte application in intermediate temperature SOFCs.

Keywords: A. Suspensions; E. Fuel cells; Dip-coating; Thin films

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1. Introduction

Solid oxide fuel cells (SOFCs) have been extensively studied because of its high energy conversion efficiency, very low emissions to atmosphere and fuel flexibility (natural gas, coal gas, hydrogen, etc.) [1]. The conventional SOFCs with yttria-stabilized zirconia (YSZ) as electrolyte, which is normally in a thickness of about 200 μm, are operated at around 1000 °C in order to attain reasonable power density. The high operation temperature leads to many material problems, such as electrode sintering, interfacial diffusion between electrolyte and electrode and mechanical stress due to different thermal expansion coefficients. These problems have limited the commercialization of SOFCs. Therefore, it has been a trend to reduce the operation temperature(700–800 °C or less) [2]. In order to reduce the operating temperature while maintaining reasonable electrochemical power density, the structure with thin YSZ film electrolyte on porous anode support has been designed and developed [3], in which the key is to develop proper techniques to make dense thin electrolyte.

Various attempts have been made to prepare thin dense films using electrochemical deposition (EVD) [4], plasma spray [5], RF sputtering [6], spray pyrolysis [7], and sol–gel [8], method etc. In this paper, a dip-coating technique, which is usually employed to fabricate porous ceramic membranes, has been developed for the preparation of dense oxide film. In comparison to other fabrication methods, the dip-coating process is an easy and inexpensive method for preparing thin films, it offers a potential route for SOFCs electrolyte preparation, and makes the process very attractive and economical for potential large-scale commercial fabrication.

In this investigation, a water-soluble polyelectrolyte was used to disperse zirconia powder with nanosize particles in water. The rheological behavior of the suspensions, resulting packing efficiency and densification of films were the focus of this investigation. A single solid oxide fuel cell fabricated from the supported YSZ film electrolyte on the anode substrate and a $La_{0.8}Sr_{0.2}MnO_3$ (LSM) cathode prepared on YSZ film was tested.

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2. Materials and experimental procedure

2.1. Materials

The investigated YSZ powder produced by a chemical coprecipitation method has an average particle diameter 0.43 μm determined by laser diffraction. The powder surface area is 26.3 m^2/g characterized by Brunauer–Emmett–Teller method (BET) and the primary particle size of the powder is 30 nm measured by transmission electron microscopy (TEM) (Fig. 1). The average diameter of NiO used in this study from commercial source is 1 μm. Polyacrylic acid (homemade) is used as dispersant in this investigation. HCl, NaOH, and NaCl used in this experiment are analytical grade.

2.2. Experimental procedure

NiO–YSZ composite powders were mixed through ball-milling using ZrO_2 balls as milling media in ethanol for 24 h. The powders were then pressed into pellets (diameter 15 mm, pressure 200 MPa) and subsequently fired at 800 °C for 2 h. After fabrication, the surfaces of fired pellets were grounded using SiC 4000 paper.

Basing on the zeta-potential value (measured by Malvern Zetasizer 3000HS, UK) of YSZ particles in the aqueous suspensions, YSZ powder, water and dispersants were mixed in proportion and ball-milled at pH 10 for 48 h. Stable, fully dispersed YSZ aqueous suspensions could be obtained. A dip-coating technique was used to form wet films onto NiO–YSZ anode supports with the YSZ suspensions. The green films and anode supports were then co-sintered at 1400°C for a couple of hours to get dense supported electrolyte layers. A flow chart of the preparation process was shown in Fig. 2.

A paste of LSM powder in an organic solvent was printed on YSZ surface of the disk. And the disk was then heated to a temperature of 1200 °C for 2 h. Pt–NiO–YSZ/YSZ/LSM–Pt single cells were assembled. Current–voltage measurements for the cells were measured at 800 °C with hydrogen on the anode and oxygen on the cathode side. Pt mesh was used for collecting the current on both electrodes. Microstructures of all the specimens were characterized by scanning electron microscopy (Hitachi X-650, Japan).

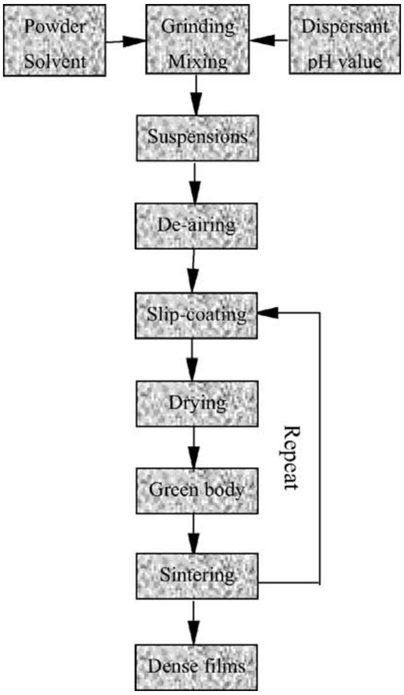

Fig. 2. Flow chart of the production of dense YSZ thin films.

3. Results and discussing

3.1. Suspensions

It is generally recognized that the denser the powder compacts, the easier to densify to high-density [9–11]. In dip-coating process, the dispersion of the particles in the suspensions is a critic factor to decide the compact density. Fully dispersed suspensions are easy to obtain high-density compacts and subsequently dense samples after sintering.

YSZ particles electrophoresis properties in aqueous solution give a direction to prepare its suspensions. Well-dispersed suspensions can be obtained with high

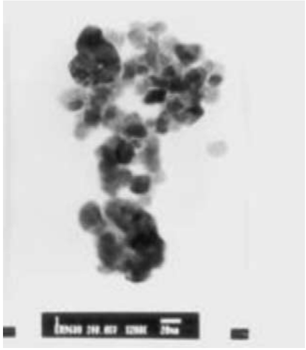

Fig. 1. TEM image of YSZ powder.

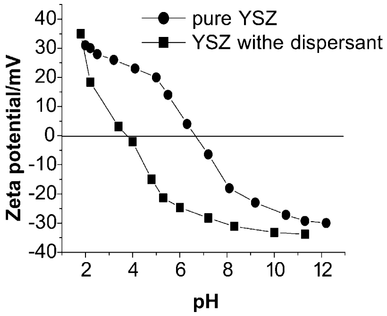

Fig. 3. Zeta-potential vs. pH of 0.01 vol.% YSZ and 0.01 vol.% YSZ+PAA suspensions.

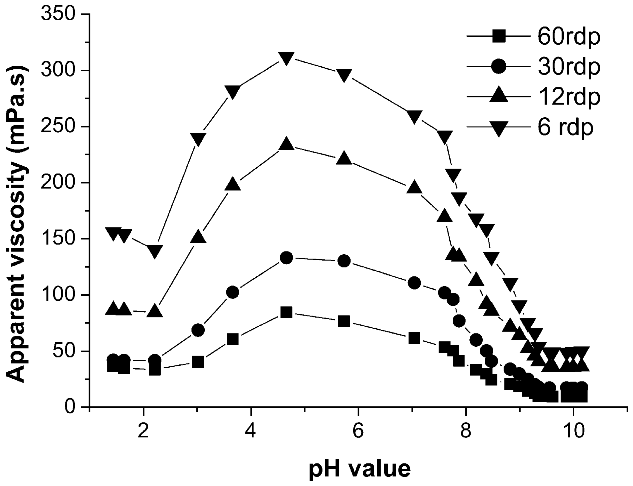

Fig. 4. The dependence of apparent viscosity on pH value.

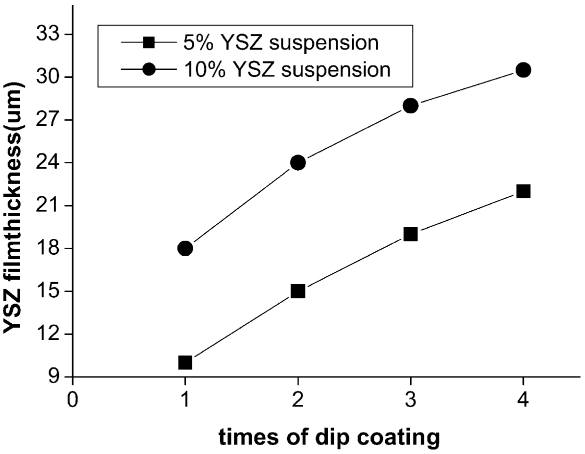

Fig. 5. YSZ thin film thickness depend on times of dip-coating.

zeta-potential value of the particles where there is sufficiently high surface charge density to generate a strong repulsion double-layer surface [12,13]. To reach this goal, polyelectrolytes are usually added to the suspensions. Which can increase the charges of YSZ particle surface and the branches of the polyelectrolyte stretching in the suspensions also impede the agglomeration of particles. The effect of pH on zeta-potential of YSZ particles in aqueous solution is shown in Fig. 3. The isoelectric point (IEP) of YSZ particles with polyelectrolyte shifts obviously from pH 6.82 to pH 4.0. This is due to the addition of the dispersant makes the particles more negatively charged. At pH below 2 and above 9, the zeta-potential reach 35 and 32, respectively. It can make us obtain stable, well-dispersed zirconia suspensions in principle.

Apparent viscosity is used to reflect the dispersion of the suspensions. Fig. 4 is the drawing of the dependence of apparent viscosity of 10% solid content suspensions on pH value. At IEP (about at pH 4), the suspensions are in strongly flocculated state as long-range van de Waals interactions between particles dominate. The viscosity of the suspensions reaches its maximum value. Two pH ranges are also characterized with lower viscosity in Fig. 4. At above pH 9, electrosteric forces make the particles apart from each other and the suspensions are in dispersed conditions. As the same, electrostatic mechanism can explain the dispersion of zirconia particles in acid condition [14–16]. In our investigation, we prepare suspensions approximately at pH 10, not in acid condition. One of the main reasons is that yttria dissolve from the powder in acid condition. Well-dispersed YSZ suspensions have guaranteed the formation of high-density YSZ green films.

3.2. The preparation and characterization of thin YSZ films

A number of factors have influence on the formation of YSZ dense thin films. Among them, the surface quality of the substrate, slip-coating process and dryness, sintering processes are most important.

Uniform pore-size distribution and smoothness of the substrate surface guarantee the preparation of high quality green YSZ film. The surface view of NiO–YSZ is shown in Fig. 7(a), there are almost no big pores in the NiO–YSZ cermet support. The average pore-size of the support is approximate 2 μm. The surface image of green YSZ film coating with 5% solid content well-dispersed slurry is shown in Fig. 7(b), the green film is uniform and smoothness. The YSZ particles almost cannot be seen from the image, this may be a thin layer of excessive polyelectrolyte in the suspension covering on the surface of green YSZ film.

Multiply dip-coating processes are important to eliminate the influence of the surface defects of the supports and obtained higher density compact. But the green films thickness also increases with the dip-coating times increasing. Fig. 5 is the drawing of the film thickness dependence on dip-coating times with different concentration of suspension. Nonlinear relationship between film thickness and dip-coating times is observed. As dip-coating times increases, the thickness of the film by one time coating decreases. Decreasing pore-size in top layer has resulted in this phenomenon. Using

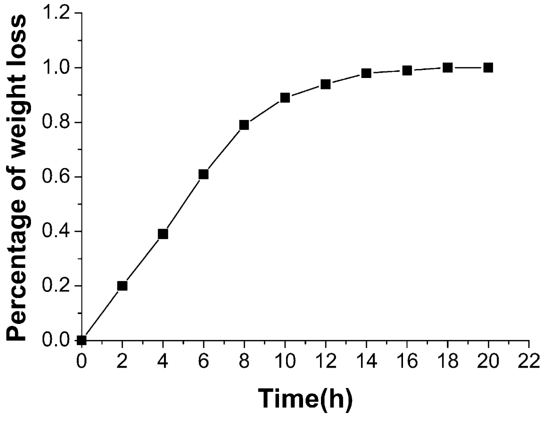

Fig. 6. Percentage of weight loss of green film vs. time.

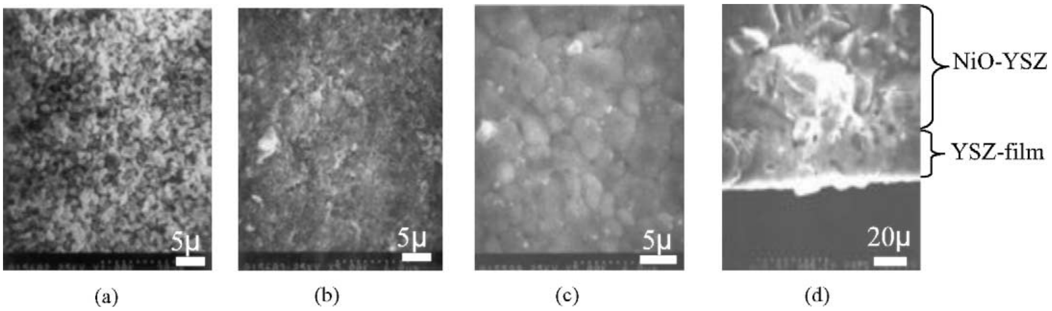

Fig. 7. Surface and cross-sectional microstructures of samples. (a) Substrate, (b) green film, (c) YSZ film after sintering, (d) cross-section of YSZ film.

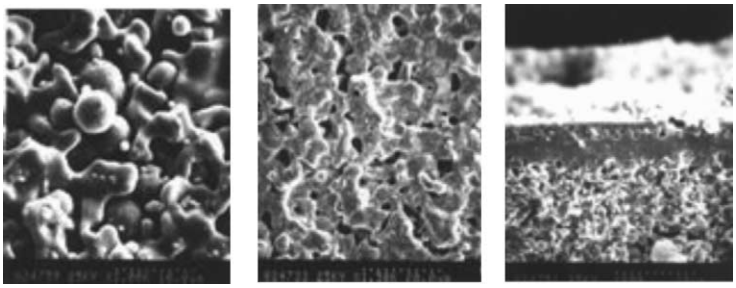

Fig. 8. Anode, cathode, and sandwich structure of the cell.

suspensions with 10 and 5% solid content, after four times coating, the films reached approximately 32 and 22 μm thickness, respectively. It is enough to obtained dense YSZ film after sintering.

Cracks are most frequently occurred when films are dried. High humidity and low temperature slower the evaporation of solvent, that allow YSZ grains stack naturally and form high dense green films. In this study, the relative humidity is controlled at 90% and the temperature at 25 °C in drying process. Fig. 6 gives the dependence of percentage of weight loss of green films on time. The critical point of drying process is about at 8 h. After 8 h, the interface of the gas/liquid began to enter green film, the rate of weight loss decreased gradually. The weight losses of the green films almost do not change as time after 18 h. Sintering procedure is also strictly controlled. The green films are heated at a rate of 1 °C/min and kept for a period at 500 °C. Fig. 7(c) and (d) show respectively the surface and cross-section of an YSZ layer that has been deposited on a porous NiO–YSZ anode supports after sintering. These micrographs indicate that the thickness of the deposited layer is uniform, approximate 30 μm. This layer is free from pores and cracks within the scale of SEM observation. At the same time, the connection between YSZ film and anode are satisfactory, no crack can be observed on the interfaces.

3.3. Electrochemical properties of YSZ thin films

Shown in Fig. 8 are the cross-sectional SEM micrographs of each cell component. The thin YSZ layer is about 30 μm; some isolated defects such as small voids are observed under SEM investigation. However, no cross-film cracks or pinholes are observed. The cathode layer, consisting of sub-micron grains, has an average thickness of 30 μm and a porosity of about 30%. The thickness of the porous anode varies from 0.5 to 0.7 mm whereas the porosity of the anode is about 25%.

Shown in Fig. 9 is Arrhenius plot of $\log \sigma T$ versus $1/T$. The calculated conduction activation energy of the YSZ thin films was obtained at the temperature between 600 and 800 °C, $E_a = 1.12$ eV, which is similar with the bulk materials $E_a = 1.14$ eV. At 800 and 750 °C, the conductivities of the thin film reach 0.0098–0.004 S/cm, respectively.

Fig. 10 presents the I–V curves and power outputs of Pt–LSM/YSZ/Ni–YSZ–Pt single cell with H_2 as fuel and O_2 as oxidant. The cell open circuit voltage (OCV) reaches 0.98 V at 800 °C, a little lower than theoretic value. The poor sealing at high temperature and few pinholes (although

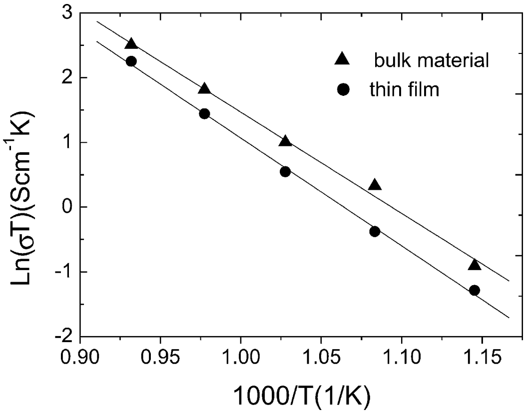

Fig. 9. Arrhenius plot of $\log \sigma T$ vs. $1/T$ of the developed YSZ films.

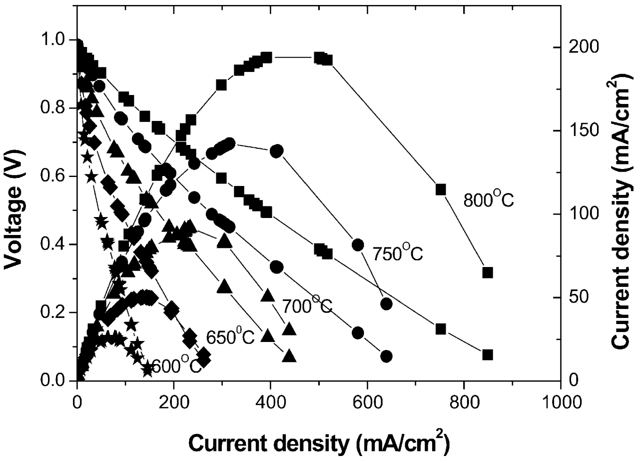

Fig. 10. I–V curves and power outputs of Pt–LSM/YSZ/Ni–YSZ–Pt single cell.

not seen from the SEM) in the film may be the reasons for the lower OCV. At 800 °C, the maximum power density of 190 mW/cm^2 is obtained, showing a reasonable performance. But the lower porosities of electrodes have greatly influences on the cell performances. Thus, the further work should be done to improve the process in order to increase anode porosity and improving the microstructure. A higher power density would be expected.

4. Conclusions

Powder colloid processing is an appropriate method for preparing well-dispersed aqueous YSZ suspensions. After strictly controlling dip-coating technique, quite dense YSZ thin films in thickness of around 30 μm on NiO–YSZ anode supports were obtained with the fully dispersed suspension. Based on the films/anode bi-layer, Pt–LSM/YSZ/Ni–YSZ–Pt single cells were fabricated and tested. The single cells' OCV reached 0.98 V and power outputs of the cells reached 190 mW/cm^2 at 800 °C. These results gave us an idea that high quality YSZ thin films had been prepared.

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References

[1] N.Q. Ninh, Ceramic fuel cell, J. Am. Ceram. Soc. 76 (1993) 563.

[2] S. de Souza, S.J. Visco, L.C. De Jonghe, Thin-film solid oxide fuel cell with high performance at low-temperature, Solid State Ionics 98 (1997) 57–61.

[3] B.C.H. Steele, State-of-the-art SOFC ceramic materials, in: Proceedings of First European Solid Oxide Fuel Cell Forum, vol. 1, Oberrohrdorf, Switzerland, 1994, pp. 375–398.

[4] I. Minoru, M. Atsushi, Growth rate of yttria-stabilized zirconia thin films formed by electrochemical vapour-deposition using NiO as an oxygen source: II. Effect of the porosity of NiO substrate, Solid State Ionics 104 (1997) 303–310.

[5] G. Chiodelli, A. Magistris, M. Scagliotti, F. Parmagiani, J. Mater. Sci. 23 (1988) 1159.

[6] A. Setogchi, M. Sawano, K. Eguchi, H. Arai, Electrical properties of plasma-sprayed yttria-stabilized zirconia films, Solid State Ionics 40/41 (1990) 502.

[7] W. Naoki, Y. Makoto, RF-magnetron-sputtered heteroepitaxial YSZ and CeO_2/YSZ/Si (0 0 1) thin films with improved capacitance–voltage characteristics, Thin Solid Films 441 (2002) 268–273.

[8] T.W. Kueper, S.J. Visco, L.C. De Jonghe, Application of the stabilized zirconia thin film prepared by spray pyrolysis method to SOFC, Solid State Ionics 52 (1992) 251.

[9] J.M.F. Ferrera, H.M.M. Diz, Pressure slip casting of bimodal silicon carbide powder suspensions, Ceram. Int. 25 (1999) 491–495.

[10] D.-M. Liu, W.J. Tseng, Influence of debinding rate, solid loading and binder formulation on the green microstructure and sintering behavior of ceramic injection mouldings, Ceram. Int. 24 (1998) 471–481.

[11] A. Roosen, H.K. Bowen, Influence of various consolidation techniques on the green microstructure and sintering behavior of alumina powders, J. Am. Ceram. Soc. 71 (11) (1988) 970–977.

[12] J. Wang, L. Gao, Surface and electrokinetic properties of Y-TZP suspensions stabilized by polyelectrolytes, Ceram. Int. 26 (2000) 187–191.

[13] M. Ziomek-Moroz, W. Kemp, D.H. Sturgis, Role of particle dissolution in the stability of binary yttria–silica colloidal suspensions, J. Am. Ceram. Soc. 79 (1996) 1223–1227.

[14] F. Shojai, A.B.A. Pettersson, T. Mäntylä, J.B. Rosenholm, Electrostatic and electrosteric stabilization of aqueous slips of 3Y-ZrO_2 powder, J. Eur. Ceram. Soc. 20 (2000) 277–283.

[15] F. Tang, X. Huang, Y. Zhang, J. Guo, Effect of dispersants on surface chemical properties of nano-zirconia suspensions, Ceram. Int. 26 (2000) 93–97.

[16] B.J. Briscoe, A.U. Khan, P.F. Luckham, Stabilizing zirconia aqueous suspensions using commercial polyvalent electrolyte solutions, J. Eur. Ceram. Soc. 18 (1998) 2169–2173.