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ScienceDirect
Journal of Power Sources 160 (2006) 1065–1073
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

A study of the process parameters for yttria-stabilized zirconia electrolyte films prepared by screen-printing

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Received 10 February 2006; accepted 17 February 2006
Available online 29 March 2006

Abstract

Screen-printing technology was developed to fabricate gas-tight yttria-stabilized zirconia (YSZ) electrolyte films on porous NiO–YSZ anode substrates for use in solid oxide fuel cells (SOFCs). Several key process parameters such as the starting YSZ powder, printing ink composition, printing time and sintering temperature were studied and reported in detail. SEM results revealed that the selected process parameters exerted obvious influences on the microstructure of the screen-printed YSZ films. Open-circuit voltages (OCVs) were used to evaluate the usage feasibility of screen-printed YSZ films in SOFCs. Cell performance test results showed that the above-mentioned parameters had crucial effects on the OCVs and power density of the prepared cells. Based on appropriate parameters, an OCV value of 1.081 V and a power density of 0.96 Wcm^{-2} were obtained at 800 °C using hydrogen as fuel and ambient air as oxidant.

Keywords: Solid oxide fuel cells; Screen-printing; Electrolyte films; Process parameter; Yttria-stabilized zirconia

1. Introduction

Solid oxide fuel cells (SOFCs) are considered a promising energy conversion device because of high efficiency, low pollution and fuel flexibility [1,2]. For the viewpoint of cost reduction and long-term stability, it is necessary to reduce the operating temperature. Operation of SOFCs at intermediate-temperatures (600–800 °C) has many advantages including lower degradation rate of cell components, wider material choice and cost reduction. Towards this end, reduction of the thickness of electrolyte is desirable. Up to now, significant developments have been made to make thin film electrolytes. There are a number of approaches for thin film fabrication, such as chemical vapor deposition (CVD) [3], DC magnetron sputtering [4], tape casting [5], sol–gel dip-drawing [6], spray coating [7,8], plaster casting [9] and so on. Each technique has its advantages and disadvantages. For example, CVD is an effective way to make a gas-tight and uniform thin electrolyte film below 5 μm, however, it has some drawbacks of high cost, relatively low deposition rates, and the presence of corrosive gases. Spray coating has high deposition rates, but it is difficult to obtain a thin dense electrolyte film. Very thin dense films can be fabricated by the sol–gel technique, but many coatings are necessary to get a fully dense film, and this is very time consuming.

To reduce the cost of fabrication, a screen-printing technique [10] was developed to fabricate gas-tight yttria-stabilized zirconia (YSZ) electrolyte films for anode-supported SOFCs. In this technique, YSZ powder was firstly mixed with appropriate organic vehicles to make homogeneous and stable printing inks. Then the ink was extruded through a screen onto the anode substrate by a scraping blade. Finally, the anode substrate with printed electrolyte film was dried and co-fired at high temperature to densify the YSZ film. Compared with the film deposition techniques mentioned above, the screen-printing technique is cost-effective and simple. This technique has been extensively adopted to fabricate photoconductor films [11], $BaCeO_3$-based

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doi:10.1016/j.jpowsour.2006.02.074

films [12] and ferroelectric films [13]. For fabrication of SOFCs, the technique has been used to make electrolyte films using powders of samaria-doped ceria (SDC) [14], yttria-doped ceria (YDC) [15]. Recently, Dollen and Barnett [16] prepared anode-supported YSZ film SOFCs by screen-printing technology and got a maximum power density of 1.45 Wcm^{-2} at 800 °C. In our previous report [17], the effect of the starting powder on screen-printed YSZ films was investigated. However, to the best of this author's knowledge, there are few publications on a screen-printed dense YSZ electrolyte film for SOFCs. The report related to the influences of the process parameters on microstructure and performance of screen-printed YSZ electrolyte films was also insufficient.

In this paper, screen-printing technology was developed to fabricate YSZ electrolyte films onto NiO–YSZ porous anode substrates. Several important process parameters including starting YSZ powder, printing ink composition, number of printing layers and sintering temperature were studied and reported in detail.

2. Experimental

2.1. Starting YSZ powder preparation

YSZ powder bought from Tosoh corporation (TZ-8Y, Tosoh Corporation, Tokyo, Japan) was used to prepare the printing ink. The YSZ powder was divided into two batches: the first batch was the original powder without any treatment and named YSZ-0; the second batch was ball-milled with ethanol media for different time using an agate jar (70 cm^3) and zirconia ball (1 cm in diameter). A rotation speed of 200 rpm was used during ball milling. The powder, which was ball-milled for 13 h, is named YSZ-13. Similarly, the same powders which were ball-milled for 24 h and 36 h are called YSZ-24 and YSZ-36, respectively.

2.2. Printing ink preparation

The printing ink contains two constituents: YSZ particles and a temporary organic vehicle. The former is the main constituent of the ink and the latter controls the rheological properties of the printing ink. The organic vehicle prepared by ourselves is a terpineol–ethylcellulose mixture which was obtained by dissolving 6 wt.% ethylcellulose (analytical reagent, A.R., Dongfeng Chemical Reagents Plant, Wenzhou, China) into 94 wt.% terpineol (A.R., Tianjin Kermel Chemical Reagents Development Centre, Tianjin, China). To investigate the effect of the starting powder on the screen-printed YSZ films, the as-prepared YSZ powder of YSZ-0, YSZ-13, YSZ-24 and YSZ-36 was mixed with the organic vehicle in an agate mortar in a weight ratio of 4:5, respectively, and ground for 2 h to get a homogeneous and stable printing ink. To study the effect of ink composition on the screen-printed YSZ films, the YSZ-13 powder was mixed with the organic vehicle in different weight ratios. The YSZ content in printing ink was varied from 17 to 45 wt.% in this study. The viscosity of as-prepared YSZ ink was tested with a NDJ-99 rotation viscometer (Chengdu instrument plant, Chengdu, China) at room temperature. The shear rate was varied from 1.5 to 60 rpm according to the instrument range and the ink viscosity.

2.3. Preparation of YSZ films and cells

NiO–YSZ anode substrates were prepared by a conventional ceramic process. The NiO and YSZ powders were mixed in a weight ratio of 1:1. To form sufficient porosity, 10 wt.% starch was added as a pore former. The mixed powders were pressed into pellets of 13 mm in diameter and 0.5 mm in thickness. The green pellets were pre-sintered at 1100 °C for 2 h to improve the mechanical properties. The sintered pellets were used as the supports of the cells. The mean porosity of the NiO–YSZ anode was about 59% as tested by a standard Archimedes method.

The as-prepared YSZ printing ink was screen printed through a terylene screen onto the NiO–YSZ anode substrates by a rubber squeegee. The mesh count of the screen is 165 wires cm^{-1} and the wire diameter is 30 μm. The screen has an opening size of 30 μm and an open area of 25%. The angle between the rubber squeegee and the screen was kept at 65–85°and the distance between the screen and the top surface of the anode substrates was 2–5 mm. The printing rate was about 5 cm s^{-1}. Different printing times were used to study the effect on the thickness of films and OCVs of the cells. After drying in air, the anode/film bilayers were sintered at 1200, 1250, 1300, 1350 or 1400 °C for 4 h at a heating rate of 5 °C min^{-1} in air to densify the YSZ films.

$La_{0.7}Sr_{0.3}MnO_3$ (LSM)–YSZ composite cathode layer was deposited onto the sintered YSZ film also by screen-printing technology. The cathode powder was composed of 60 wt.% LSM and 40 wt.% YSZ. The powder was mixed thoroughly with the ethylcellulose–terpineol vehicle to get cathode printing ink. After screen printing, the cathode was sintered at 1200 °C for 2 h in air. The cathode effective area was 0.25 cm^2.

2.4. Films microstructure and cells testing

Microstructure of the screen-printed YSZ films was examined by a scanning electron microscope (SEM) (S-570, Hitachi Ltd., Tokyo, Japan).

Cells were tested from 650 to 850 °C. Hydrogen was supplied to the anode side and the cathode side was exposed to ambient air. Hydrogen flow rate is 110 standard cubic centimeters per minute (sccm). Cells performance and electrochemical impedance spectroscopy were measured using SI 1260 impedance/gain-phase analyzer in combination with SI 1287 electrochemical interface (Solartron Instruments, Hampshire, UK). Current–voltage (*I–V*) curves were tested by linear sweep voltammetry at a scanning rate of 5 mV s^{-1}. The impedance data were collected in the frequency range of 910 kHz to 0.1 Hz with a excitation amplitude of 10 mV under open-circuit conditions. Gas tightness of the YSZ electrolyte films was evaluated by comparing open-circuit voltages (OCVs) of the cells with the OCVs predicted by the Nernst equation.

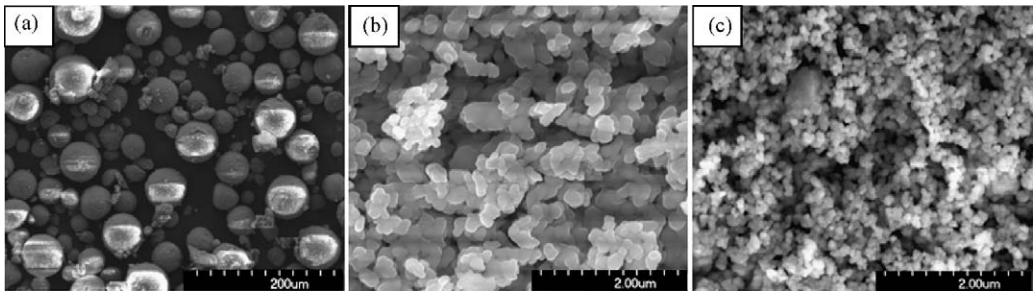

Fig. 1. Morphology of starting YSZ powder: (a) original Tosoh YSZ powder of YSZ-0, (b) ball-milled YSZ powder of YSZ-13 and (c) ball-milled YSZ powder of YSZ-36.

3. Results and discussion

3.1. On the effect of the starting YSZ powder

3.1.1. Morphology of the starting YSZ powder

Fig. 1 shows the morphology of the starting YSZ powder. As shown in Fig. 1(a), the original Tosoh YSZ powder without ball-milling consisted of spherical aggregates with a diameter of 20–60 μm. After ball-milling for 13 h, as can be seen from Fig. 1(b), the YSZ particles exhibited a spheroidal shape with a particle size of 0.2–0.6 μm. It was clear that ball-milling considerably enhanced the uniformity of the YSZ powder by partly breaking the aggregates as shown in Fig. 1(a). Fig. 1(c) shows the morphology of the YSZ-36 powder. The powder was composed of spherical granules with an average particle size of 0.2 μm. After ball milling for about 36 h, the aggregates in the original YSZ powder were thoroughly broken and the powder showed a very good uniformity.

3.1.2. Microstructure of the YSZ films

Fig. 2 shows cross-sectional view of cells with screen-printed YSZ films prepared from different YSZ powders. As can be seen

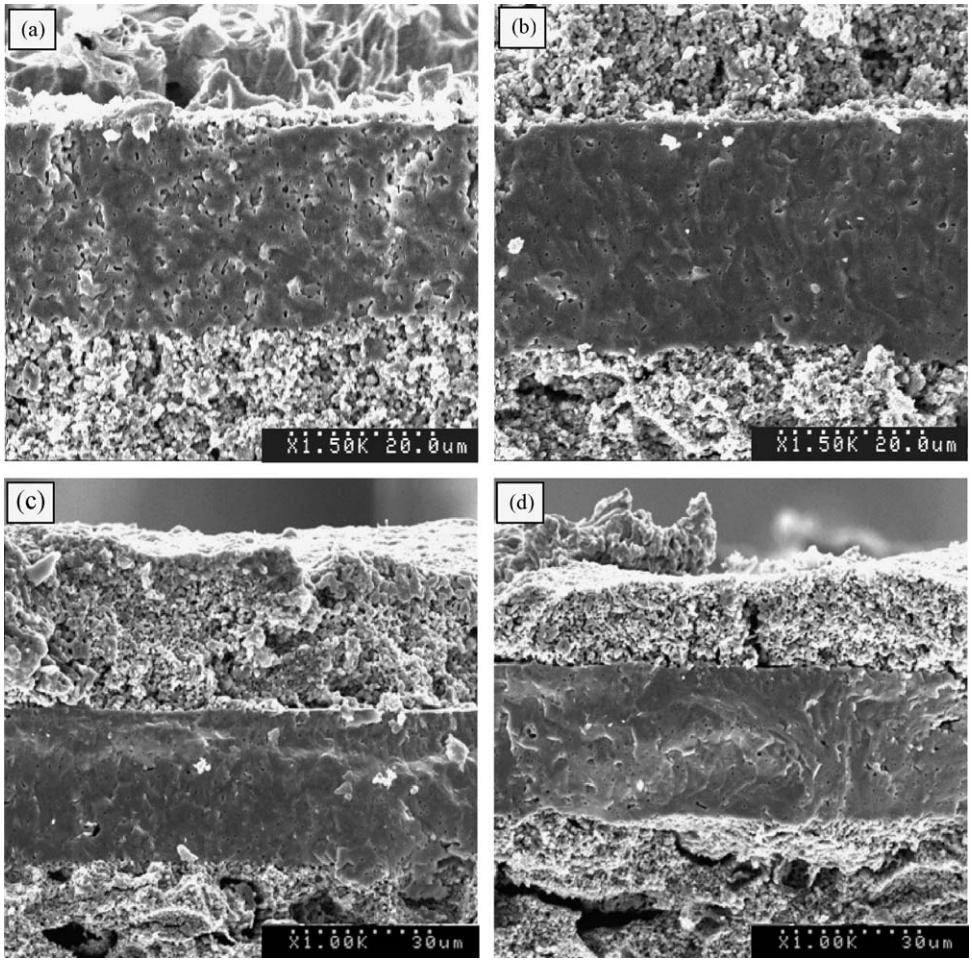

Fig. 2. Microstructure of anode-supported SOFCs with screen-printed YSZ film prepared from (a) YSZ-0 powder, (b) YSZ-13 powder, (c) YSZ-24 powder and (d) YSZ-36 powder. From bottom to top: Ni–YSZ anode, YSZ film and LSM–YSZ composite cathode.

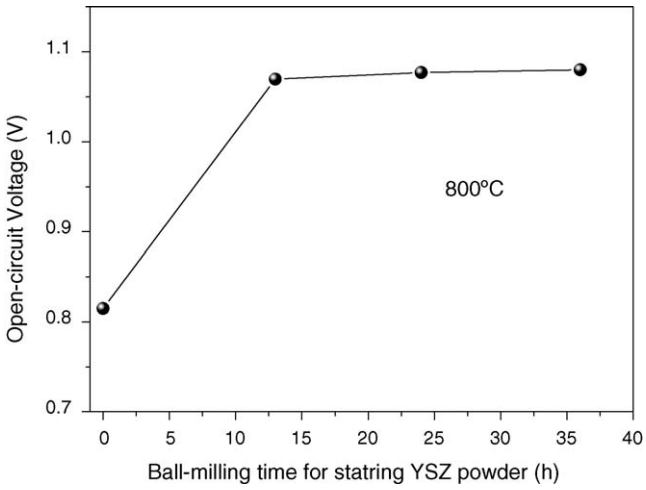

Fig. 3. Effect of ball-milling time on OCVs of the cells with screen-printed YSZ electrolyte films. The OCVs data were collected at 800 °C.

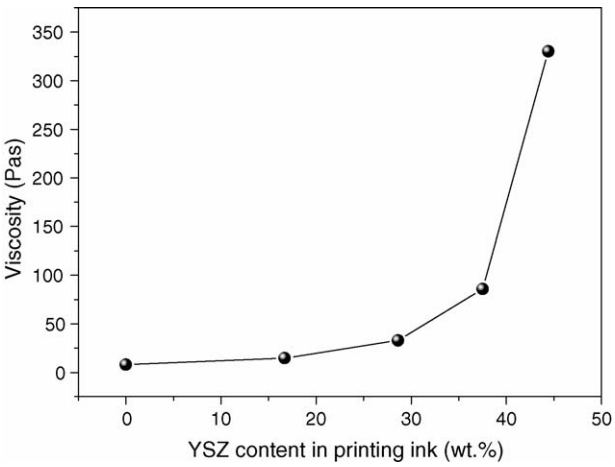

Fig. 4. Effect of YSZ content on viscosity of printing ink.

from Fig. 2(a), the YSZ film prepared with the YSZ-0 powder and without ball-milling was very porous in cross-section. These open pores will lower the OCV of the cell because of the gas leakage through the electrolyte films. On the other hand, Fig. 2(b–d) shows that the compactness of the YSZ film can be significantly improved by using the ball-milled YSZ powder. It is clear that the compactness of screen-printed YSZ films were obviously influenced by the properties of starting YSZ powder. As shown in Fig. 1, the ball-milling can break the aggregates and enhance the uniformity of the powder. The YSZ powder with a good uniformity helps to obtain a homogeneous printing ink, which helps to enhance the pack density of the screen-printing films [17].

3.1.3. Open-circuit voltages (OCVs)

Fig. 3 shows the effect of ball-milling time on OCVs of the cells with screen-printed YSZ electrolyte films. The OCVs plotted in Fig. 3 were obtained from the cells shown in Fig. 2. The cell shown in Fig. 2(a) provides a low OCV of 0.815 V at 800 °C. This OCV is obviously lower than a calculated Nernst value of 1.10 V. The cells shown in Fig. 2(b–d) can obtain a OCV of about 1.08 V, which implies gas leakage across YSZ films is insignificant.

3.2. On the effect of the printing ink composition

3.2.1. Viscosity of the ink

The effect of YSZ content on the viscosity of the printing ink was tested and the results were plotted in Fig. 4. All of the viscosity data were collected at room temperature (25 °C). The terpineol–ethylcellulose organic vehicle has a viscosity of 7.9 Pa s. The viscosity increases with increasing YSZ content as shown in Fig. 4.

3.2.2. Microstructure of YSZ films

The viscosity and rheology of the printing ink are very important for screen-printing technology. The viscosity of ink can be controlled by adjusting the ratio of the YSZ powder to the organic vehicle. If the YSZ content in the ink is too low, a porous film is observed because of the volatilization of the organic vehicle during sintering of the film. If the YSZ content is too

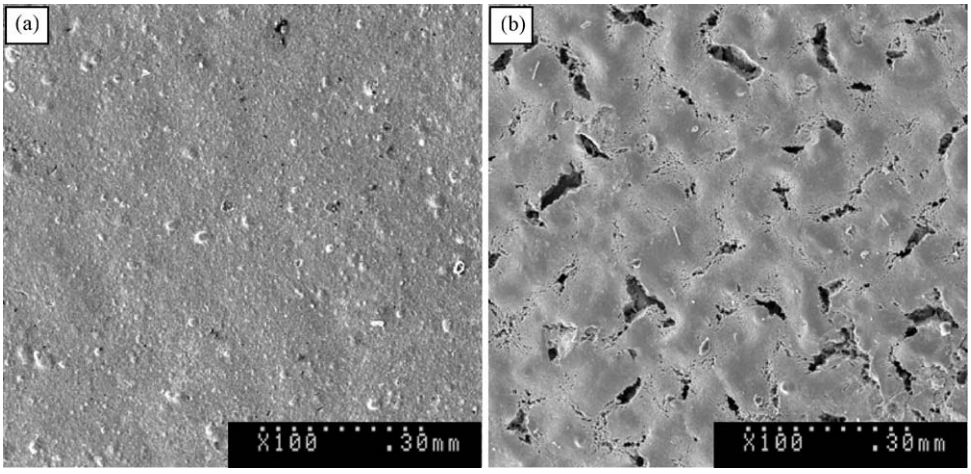

Fig. 5. Effect of printing ink composition on screen-printed YSZ films.

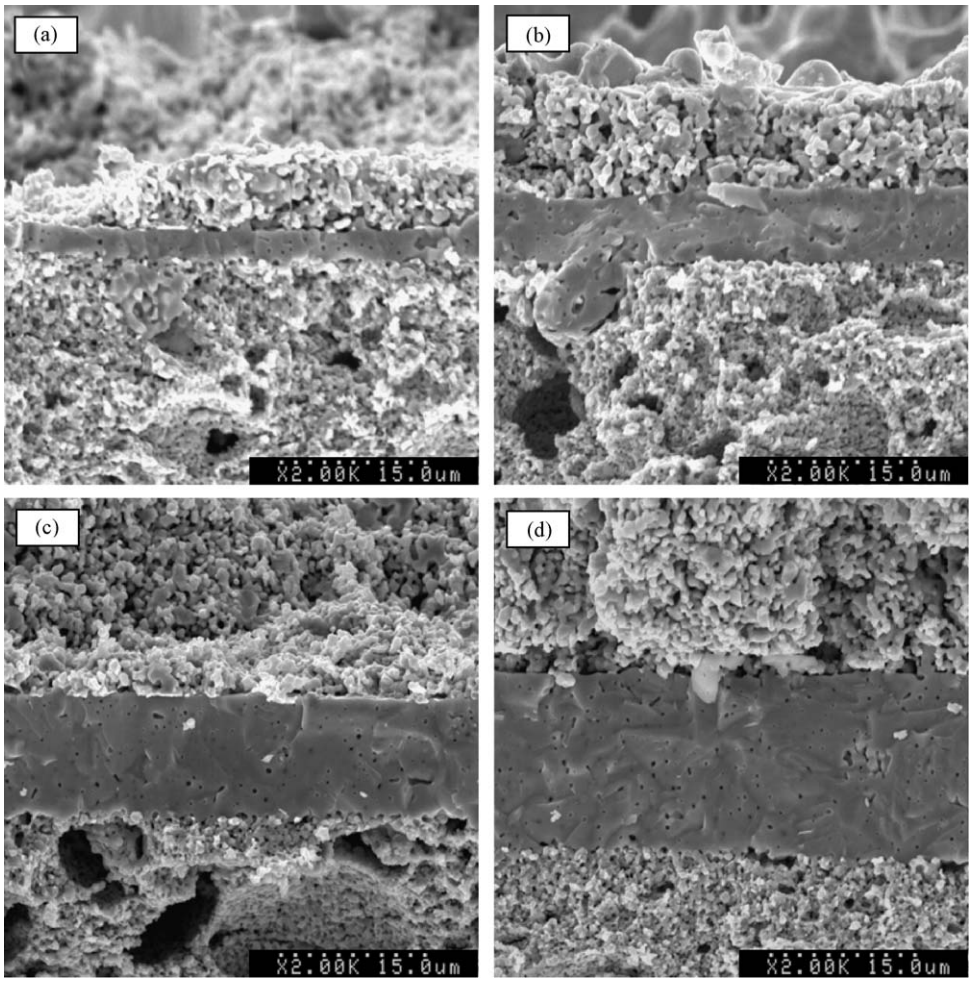

Fig. 6. Microstructure of anode-supported SOFCs with different layers of YSZ films: (a) single printing, (b) three-layer printing, (c) five-layer printing and (d) seven-layer printing. From bottom to top: Ni–YSZ anode, YSZ film and LSM–YSZ composite cathode.

high, on the other hand, cracks and incomplete ink coverage occur because of the poor rheology of the ink [16,18]. Fig. 5 shows the effect of ink composition on the microstructure of screen-printed YSZ films. The YSZ film shown in Fig. 5(a) was prepared from the ink with an optimized YSZ content of 40 wt.%. There are no cracks in the surface of the sintered YSZ film. Fig. 5(b) shows a film prepared from an ink comprising 70 wt.% of YSZ. Many large cracks can be seen in surface of the film. Furthermore, rectangular traces made by screen can be clearly seen, implying that the printing ink has a poor rheology during screen printing. A typical YSZ content in ink for successful printing is 30–45 wt.% in this study.

3.3. On effect of the printing times

3.3.1. Microstructure of the YSZ films

Fig. 6 shows the microstructure of cells with different layers of screen-printed YSZ films from one to seven layers. It can be seen that the thickness of the YSZ films increases with increasing printing times. The thinnest YSZ film prepared by screen-printing is about 2 μm in this study as shown in Fig. 6(a).

3.3.2. Open-circuit voltages (OCVs)

The experimental OCVs obtained from the YSZ films with different printing times are plotted in Fig. 7. The theoretical OCVs derived from the Nernst equation are also plotted for comparison. The single and three-layer printing YSZ films provide OCVs of lower than 1.0 V from 650 to 850 °C. When

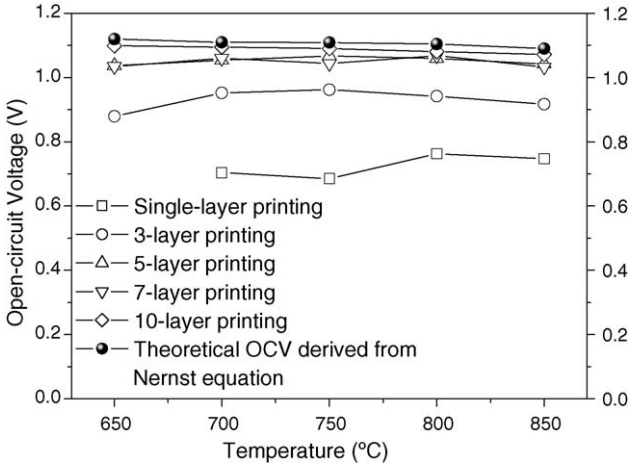

Fig. 7. Effect of printing layers on open-circuit voltage of the cells.

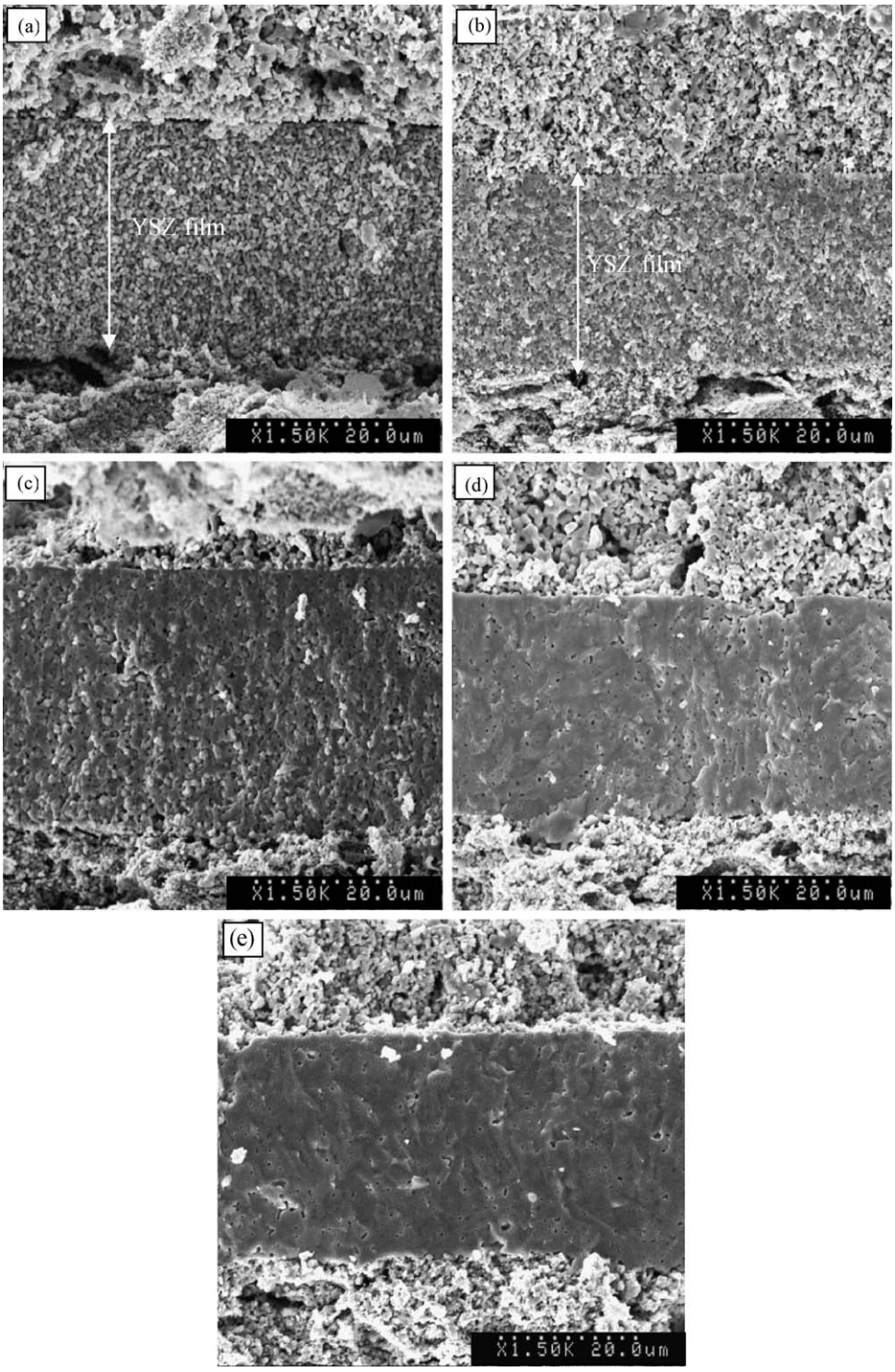

Fig. 8. Cross-sectional microstructure of SOFCs with screen-printed YSZ films sintered at different temperatures: (a) 1200 °C, (b) 1250 °C, (c) 1300 °C, (d) 1350 °C and (e) 1400 °C.

the printing times increases to five or above, OCVs of higher than 1.0 V were obtained. Near theoretical OCVs were observed from the 10-layer printing of the YSZ film. The OCVs results of Fig. 7 suggest that, based on our experimental condition, at least five-layers of printing is necessary to get high OCVs for successful operation of SOFCs.

3.4. On the sintering temperature of the YSZ films

3.4.1. Microstructure of the YSZ films

Figs. 8 and 9 show the cross-sectional and surface microstructural features of the screen-printed YSZ films sintered at different temperatures. The densification of the screen-printed YSZ

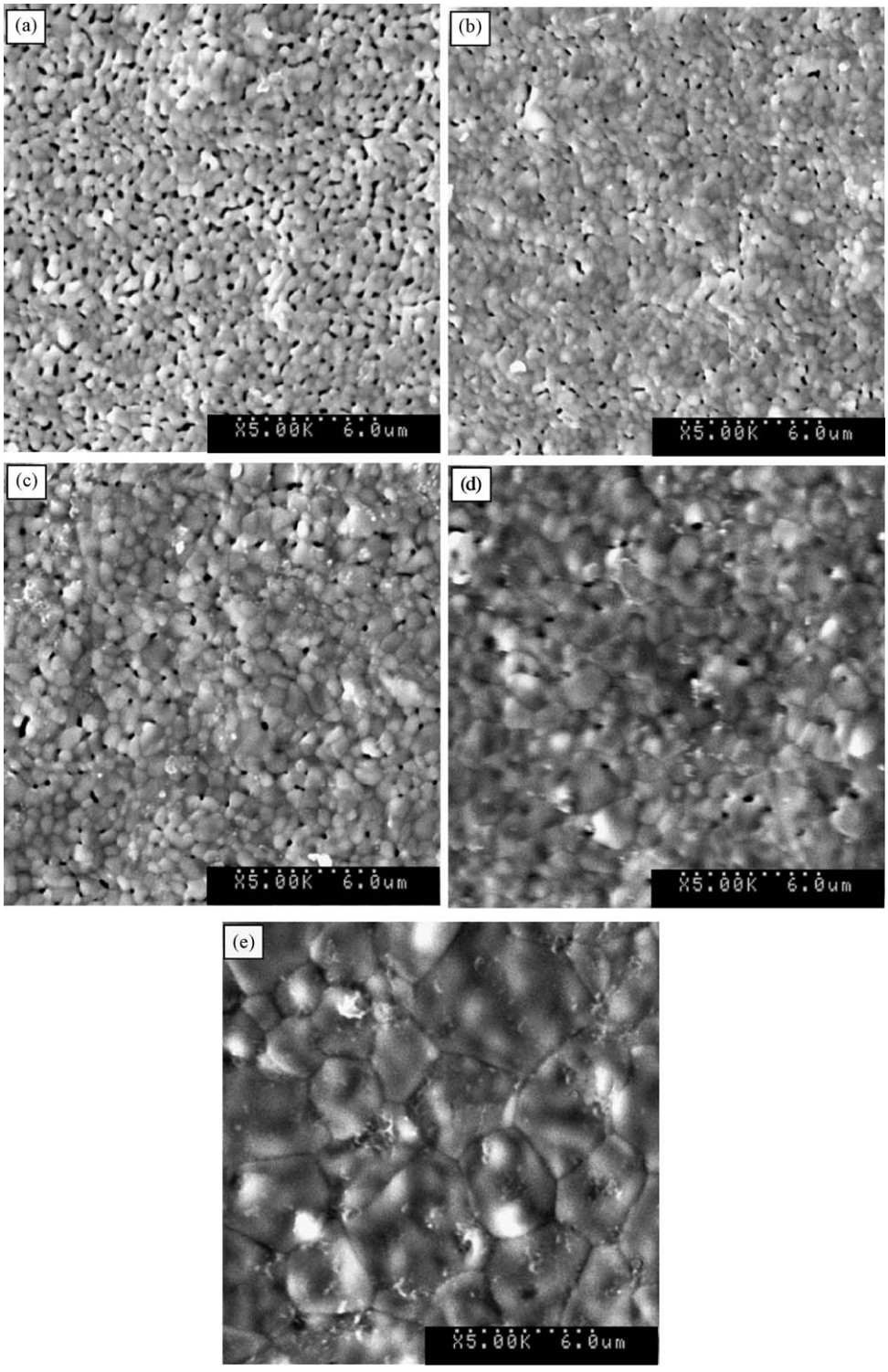

Fig. 9. Surface microstructure of screen-printed YSZ films sintered at different temperatures: (a) 1200 °C, (b) 1250 °C, (c) 1300 °C, (d) 1350 °C and (e) 1400 °C.

films was enhanced by elevation of the sintering temperatures. The YSZ films sintered at 1200 and 1250 °C show an obviously incomplete sintering as can be seen from Fig. 8(a and b). The films sintered at 1400 °C show a complete sintering with limited blind pinholes in cross-section and no cracks in surface. Although the films sintered at 1300 and 1350 °C show somewhat incomplete sintering, OCVs of higher than 1.0 V can be obtained from these films (see Fig. 10).

3.4.2. Open-circuit voltages (OCVs)

Fig. 10 shows the effect of the sintering temperature on OCVs of the cells with screen-printed YSZ films. The YSZ films sin-

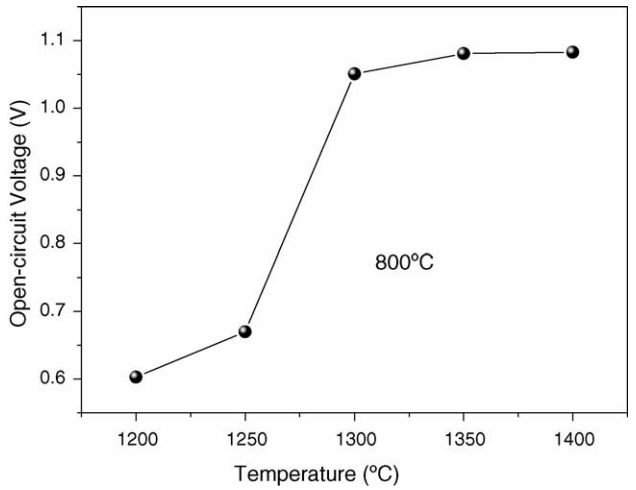

Fig. 10. Effect of sintering temperature on OCVs of the cells with screen-printed YSZ films. All of the OCVs data were collected at 800 °C.

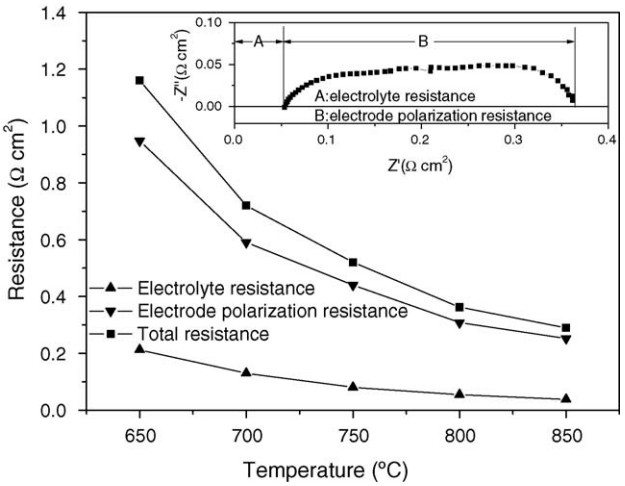

Fig. 12. Separation of electrolyte resistance and electrode polarization resistance for the cell shown in Fig. 11 from 650 to 850 °C.

tered at 1200, 1250, 1300, 1350 and 1400 °C provide OCVs of 0.6, 0.67, 1.051, 1.081 and 1.083 V, respectively. To obtain OCVs of higher than 1.0 V, the lowest sintering temperature for screen-printed YSZ films were about 1300 °C from this study.

3.5. Performance of the prepared cells

Fig. 11 shows a typical cell performance in our study. The maximum power densities at 650, 700, 750, 800 and 850 °C are 0.22, 0.43, 0.67, 0.96 and 1.36 W cm^{-2}, respectively, using hydrogen as fuel and ambient air as oxidant. The cell provides good performance at intermediate temperature. The 15-μm thick YSZ electrolyte film for the cell was sintered at 1300 °C for 4 h. A sintering temperature of 1300 °C is lower than the typical sintering temperature (1400 °C) for densification of zirconia-based electrolyte films, showing a potential advantage of energy conservation.

Fig. 12 shows the electrode polarization resistance and the electrolyte resistance for the cell shown in Fig. 11. The insert is a typical impedance of the cell tested at 800 °C. The electrode polarization resistance occupies about 82–87% of the total cell resistance from 650 to 850 °C while this ratio for the YSZ electrolyte film resistance is only about 18–13%. This result reveals that, based on the optimized electrode material, electrode microstructure and electrode/electrolyte interface, better performances can be obtained by screen-printing technology.

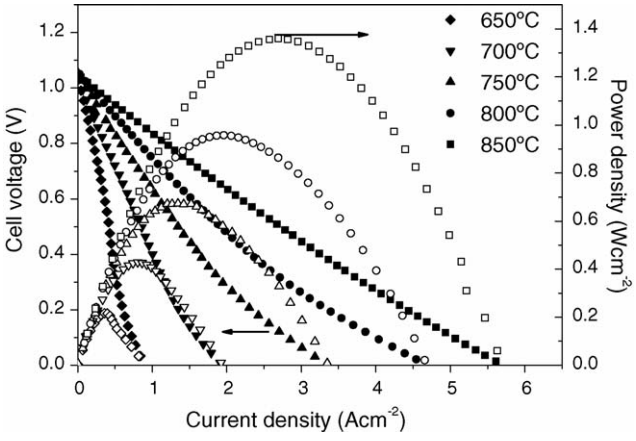

Fig. 11. Typical *I–V–P* curve of fuel cell (Ni–YSZ/YSZ/LSM–YSZ) fabricated by screen-printing. The 15-μm thick YSZ electrolyte film was sintered at 1300 °C for 4 h and the LSM–YSZ composite cathode was sintered at 1200 °C for 2 h. Hydrogen and ambient air was used as fuel and oxidant, respectively.

4. Conclusions

Four important process parameters including the starting YSZ powder, printing ink composition, printing times and sintering temperature were investigated in detail and the following conclusions can be drawn: (a) the starting YSZ powder exerts a crucial influence on the microstructure of the screen-printed YSZ electrolyte films. The films prepared from the YSZ powder with high aggregates are very porous while the films made from the YSZ powder having a good uniformity are dense and gas-tight; (b) to obtain crack-free YSZ films, the printing ink composition should be optimized. An ink composed of too high a ratio of YSZ solids results in cracks because of the poor rheology of the ink. A typical YSZ content in ink for successful printing was 30–45 wt.%; (c) after a single printing, the thinnest YSZ films of 2-μm thick can be obtained by screen-printing. At least a five-layer printing is necessary to get OCVs of higher than 1.0 V for successful operation of SOFCs; (d) the densification of the screen-printed YSZ films can be enhanced by elevation of the sintering temperatures. OCVs of 1.051 V at 800 °C were observed based on screen-printed YSZ films sintered at 1300 °C for 4 h. A sintering temperature of 1300 °C is lower than the typical sintering temperature (about 1400 °C) for densification of zirconia-based electrolyte films. A typical cell based on a 15-μm thick YSZ film sintered at 1300 °C provided the maximum power densities of 0.22, 0.43, 0.67, 0.96 and 1.36 W cm^{-2} at 650, 700, 750, 800 and 850 °C, respectively, using hydrogen as fuel and ambient air as oxidant. The performance of the cell prepared by screen-printing is basically limited by the resistance of the electrode polarization. Improvement of the electrode activ-

ity is necessary to further improve the performance of SOFCs fabricated by screen-printing technology.

Acknowledgment

Financial support from the National Natural Science Foundation of China (grant no. 10504005) is gratefully acknowledged.

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