*Journal of Applied Electrochemistry* **34**: 637–641, 2004.



# Production of dense yttria-stabilized zirconia thin films by dip-coating for IT-SOFC application

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Received 3 July 2003; accepted in revised form 17 December 2003

*Key words:* dip-coating, electrolyte, IT-SOFCs, thin films, yttria-stabilized zirconia (YSZ)

**Abstract**

Yttria-stabilized zirconia (YSZ) thin films were prepared by conventional and modified dip-coating techniques followed by heating to an appropriate temperature in air. Scanning electron microscopy showed that films of the thickness ranging from 20 to 30 $\mu$m were dense and crack-free. The electrical properties of the films were investigated by ac impedance spectroscopy. $La_{0.8}Sr_{0.2}MnO_3$ paste was printed on to a YSZ electrolyte/anode assembly to create single fuel cells which were tested in the temperature range 650–800 °C. The results showed that both open circuit voltage (OCV) and maximum power density values of the cells with electrolytes produced by the modified dip coating were higher than those fabricated by conventional processing. At 800 °C, the OCV reached 0.98 V and a maximum power density of 190 mW $cm^{-2}$ was attained, demonstrating that the modified dip coating process is a simple and cost-effective fabrication technique for IT-SOFCs, though further improvement is necessary.

## 1. Introduction

Intermediate temperature (400–800 °C) fuel cells have received much attention in recent years, since they combine the advantages of both high and low temperature fuel cells such as fast electrode kinetics, fuel flexibility and less degradation problems [1, 2]. The trend toward lower operating temperatures makes SOFC a leading candidate, not only for application as stationary power plants, but also to replace internal combustion engines in vehicles [3]. There are two major approaches to realize this goal: one is to search a new electrolyte with higher ionic conductivity and the other is to lower the resistance by decreasing the electrolyte thickness.

The oxygen-ion conductivity of yttria-stabilized zirconia (YSZ) is not as high as that of some other oxides such as doped ceria and doped lanthanum gallate. However, YSZ remains the preferred electrolyte due to its optimal combination of electrochemical and chemical stability and mechanical properties. One major complication is how to prepare dense YSZ layers of thickness as thin as 10 $\mu$m. To fabricate dense YSZ thin films, various techniques such as CVD [4, 5], PVD [6, 7], EVD [8, 9], sol–gel [10], spray pyrolysis [11], tape casting [12] and screen printing [13] have been used. Although gas deposition processes such as CVD and PVD have had some success, they require complex equipment and show less efficiency. The liquid precursor methods such as sol–gel and spray pyrolysis are time-, labor- and energy-intensive. Tape casting and screen-printing are considered very cost-effective and promising techniques, but these methods usually involve large shrinkage associated with the removal of polymeric binders and plasticizers in subsequent sintering steps, which reduce the quality of large area cells.

Dip-coating using ceramic particle suspensions, as a conventional ceramic formation process, is well known to be simple and cost-effective. It has attracted much attention and has demonstrated itself to be a good candidate for depositing thin electrolyte layers [14, 15]. It has the advantage of uniform coating of large areas, easy control of film thickness and inexpensive fabrication. However, in the conventional dip coating process the driving force for film formation is the capillary force of the porous substrate. Given that the powder for suspension preparation usually has a narrow particle size distribution, the green layers formed on the porous substrate are characterized by quite uniform pore distribution. This may easily result in membranes with high porosity and narrow pore size distribution after drying and heating. Therefore, the dip-coating process with ceramic suspensions has been the successful technique for ceramic separation membranes. However, it is difficult to get a dense membrane, particularly at lower sintering temperatures required by the process of co-sintering with electrode support. In order to solve this problem, the key issue is to fabricate a much denser

packing green membrane. The companies ToTo-KEPC and MHI-EPDC (Japan) have developed a new dip-coating technique for tubular type SOFCs, but the details of the method were not reported [16].

In this paper we present the preliminary results for producing dense YSZ thin films on porous Ni-YSZ anode supports for IT-SOFCs by a modified dip-coating technique. The idea has two aspects: preparing the suspension of mixed powders with different particle sizes in order to get a denser green compact and to apply an external force during the dip-coating process.

## 2. Experimental

### 2.1. *Preparation of thin films*

NiO/YSZ anode cermet substrates were prepared by a conventional ceramic process from NiO and YSZ powders with 50% weight of NiO. The NiO powder had a grain size between 1 and 2 $\mu$m and the YSZ powder had a grain size of less than 2 $\mu$m from commercial sources. NiO and YSZ powders were mixed thoroughly by ball milling in alcohol and then dried. The disks of $\sim$1.5 mm thickness and 15 mm diameter were uni-axially pressed and calcined at 800 °C for 2 h.

### 2.2. *Preparation of stable YSZ suspensions*

The precursor YSZ powder was a powder mixture of at least two kinds of YSZ powders, one was commercially available with sub-micrometer particle size and another one was prepared by a chemical process with nanometer particle size [17]. The suspensions were prepared by mixing the YSZ powder (with a wide particle size distribution) with a dispersant and a binder.

### 2.3. *Dip-coating under an external pressure gradient*

Differing from the conventional dip-coating, where only the capillary force plays a role in the membrane formation, we modified the process by applying a pressure gradient across the wet compact layer of suspended particles. The set-up is shown schematically in Figure 1. The porous NiO/YSZ anode disk was sealed to a ceramic or glass tube and connected to a vacuum system, which provided the extra force to allow particle fluid motion and resulting in a denser membrane. The green membranes and anode supports were then co-sintered at different temperatures for 2 h to attain dense supported electrolyte layers.

### 2.4. *Characterization of the thin films*

The microstructures of the resulting YSZ layers were observed by scanning electron microscopy (Hitachi X-650, Japan). Conductivity measurements for the films were performed using AC impedance (CH1600A Series, Shanghai, China) under a controlled atmosphere of argon. A paste of LSM powder in an organic solvent was printed on the YSZ surface 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 performed

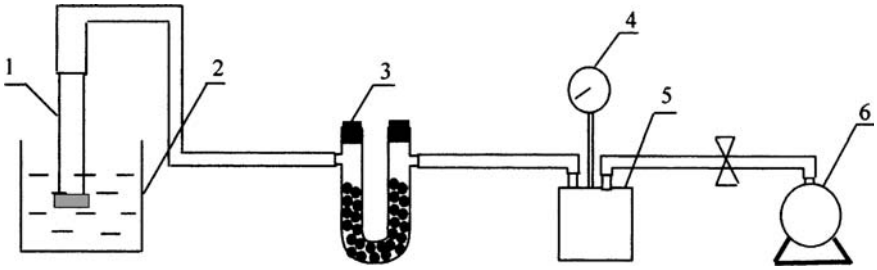


*Fig. 1.* Equipment for modified dip-coating technique. (1) Specimen holder, (2) suspension, (3) desiccator, (4) manometer, (5) bumper, (6) pump.

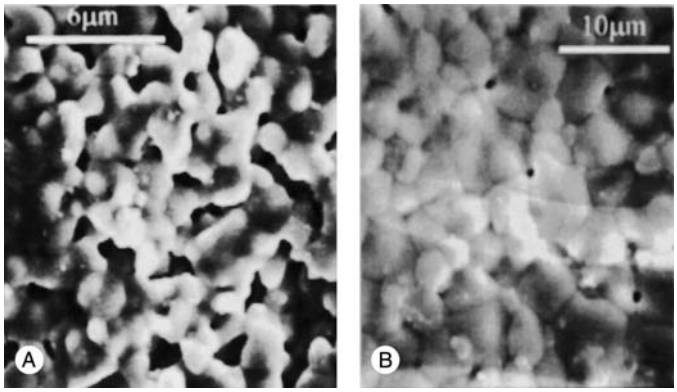


*Fig. 2.* Thin films surface micrograph by conventional (A) and modified dip-coating techniques (B).

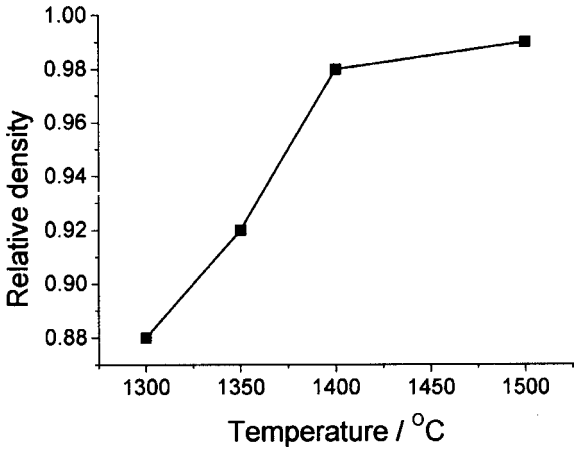


*Fig. 3.* The film relative density vs temperature.

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.

## 3. Results and discussion

### 3.1. *Preparation of the YSZ thin films*

Figure 2 shows typical micrographs of YSZ films created by conventional and modified dip-coating techniques. It can be seen that the YSZ layer obtained by the modified dip-coating technique is much denser than that by the conventional process. Smaller particles fill the pores in the membrane formed by large particles, resulting in a denser green compact and also function as sintering agent to lower the sintering temperature. In addition, the modified dip-coating technique can be well controlled and exhibits good process reproducibility.

Figure 3 gives the relative density of the films obtained at different sintering temperatures. At 1300 °C, the film density is only 88% and there are some small pores, as seen from Figure 4(A). The density reaches 95 and 97% at 1400 and 1500 °C, respectively. There are almost no pores observed in the films. The cross-sectional view (Figure 4(B) and (C)) indicates that the YSZ layer adhered very well to the anode substrate. However, higher sintering temperatures result in lower anode porosity, which increases the anodic polarization [18]. In this work, we have selected 1400 °C as the sintering temperature.

### 3.2. *Electrical properties of the films*

The electrical properties of dense films were investigated by ac impedance spectroscopy. The Arrhennius plot of log $\sigma T$ vs $1/T$ is shown in Figure 5. The calculated activation energy of the YSZ thin films obtained over

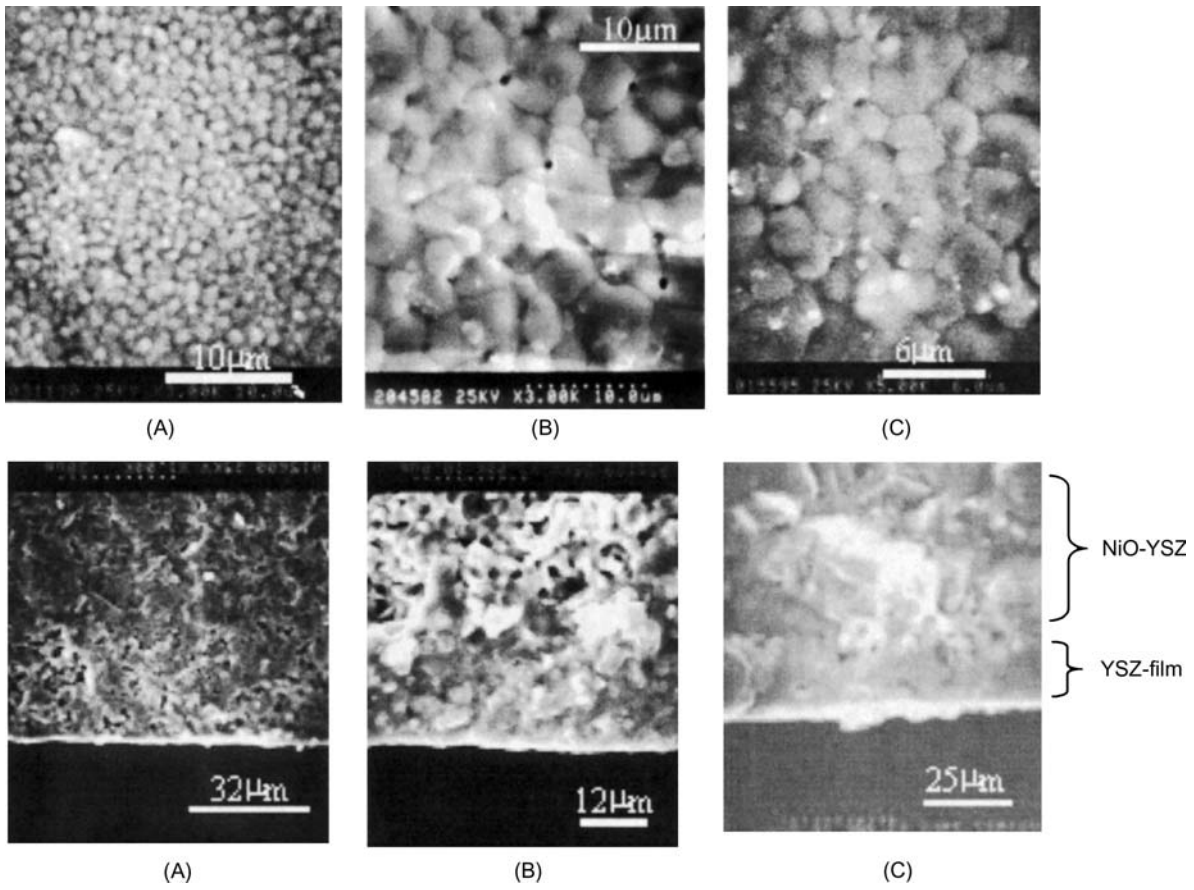


*Fig. 4.* The surface and cross-sectional micrograph of YSZ thin films by modified dip-coating sintering at different temperature (A) 1350 °C, (B) 1400 °C, (C) 1500 °C.

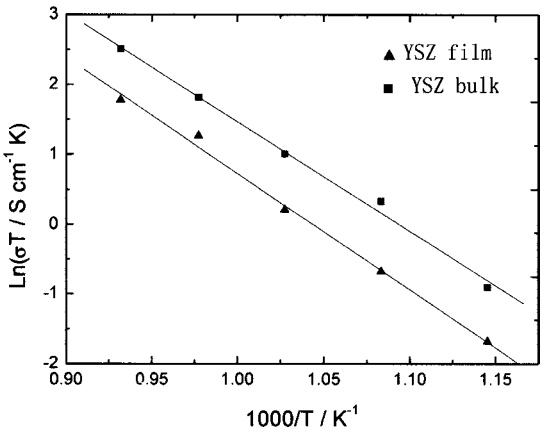


*Fig. 5.* Arrhenius plot of ln $\sigma$T vs $1/T$.

the temperature range 600–800 °C was Ea = 1.12 eV, which is similar to that for bulk materials, Ea = 1.14 eV [19, 20]. At 800 and 750 °C, the conductivities of the thin film reach 0.0098 and 0.004 S $cm^{-1}$, respectively. Those values agree with data for YSZ films obtained by plasma-sprayed and sputtering deposition techniques [19, 20].

### 3.3. *Cell performance*

Figure 6 shows the cross-sectional SEM micrographs of each cell component. The thin YSZ layer is about 30 $\mu$m and some isolated small voids are observed. However, no cross-film cracks or pinholes are observed. The LSM cathode layer, consisting of sub-micron grains, has an average thickness of 30 $\mu$m and a porosity of about 30%. The thickness of the porous anode varies from 0.5 to 0.7 mm and has a porosity of about 25%.

Figures 7 and 8 show the *I–V* curves and power outputs of the Pt–LSM/YSZ/Ni–YSZ–Pt single cell with $H_2$–3%$H_2O$ as fuel and $O_2$ as oxidant. The OCV of the cell fabricated from film by conventional dip-coating reaches only 0.90 V at 800 °C, which indicates the lower density of the thin film. But cells with film produced by the modified dip-coating technique OCV reach 0.98 V. Even though the experimental value is a little lower than the theoretic value, poor sealing at high temperature and


*Fig. 6.* Anode, cathode and sandwich structure of the cell.

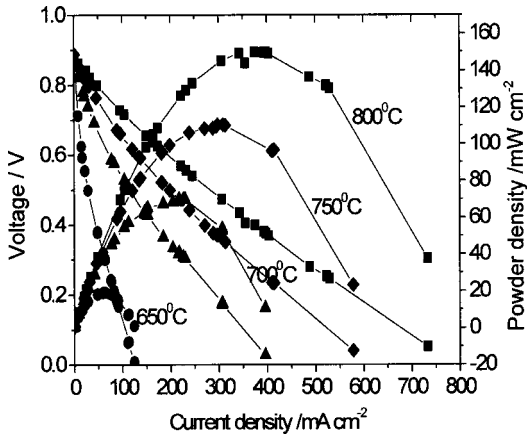


*Fig. 7.* *I–V* and *I–P* curves of Pt–LSM/YSZ/Ni–YSZ–Pt single cells (YSZ thin films by conventional dip-coating technique).

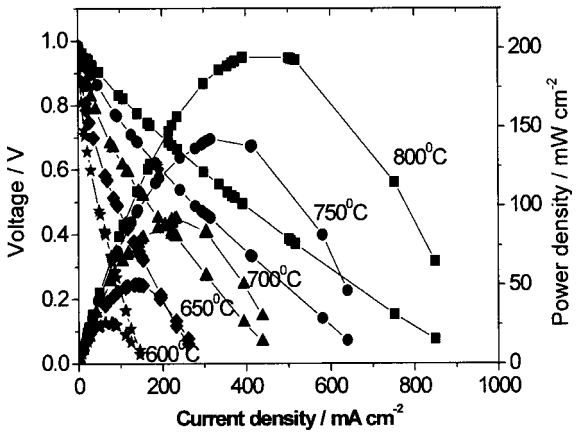


*Fig. 8.* *I–V* and *I–P* curves of Pt–LSM/YSZ/Ni–YSZ–Pt single cells (YSZ thin films by modified dip-coating technique).

a few pinholes (not seen from the SEM) in the film may be the reasons for lower OCV. At 800 °C, a maximum power density of 150 and 190 mW $cm^{-2}$ were obtained for the conventional and modified techniques, respectively, which shows a reasonable performance. The lower porosity of the electrode has greatly influenced the cell performance. Further work is necessary to improve the process and eliminate the residual pores in the electrolyte, as well as the anode microstructure.

## 4. Conclusions

This work has demonstrated that the modified dip-coating process may be a cost-effective technique for producing fairly dense YSZ thin films. Quite dense YSZ thin films of around 30 $\mu$m in thickness were obtained on NiO/YSZ anode supports. The conductivity of the YSZ layer is close to that of the bulk materials. Based on YSZ/anode bi-layers, a Pt–LSM/YSZ/Ni–YSZ–Pt single cell was assembled and tested. The cell showed an OCV of 0.98 V and a maximum power output of 190 mW $cm^{-2}$ at 800 °C.

## Acknowledgement

This work was supported by the Chinese National Science Foundation under contract No. 20071029, 2001AA323090 and MSTC under contract No. G200026409.

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