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Preparation of YSZ film by gravity-electrophoretic deposition and its application in SOFC

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Abstract

A gravity-electrophoretic deposition method (GD-EPD) was developed for depositing yttria-stabilized zirconia (YSZ) films on porous NiO-YSZ anode substrates. GD-EPD was the method that deposited an additional layer of YSZ by electrophoretic deposition (EPD) technique on the YSZ film prepared by gravity deposition method (GD). The microstructure of the YSZ film, the performance and impedance spectra of fuel cell prepared by GD-EPD were investigated and compared with that of the YSZ film prepared by only GD method. The SEM photos showed that the size and quantity of the pin-holes in YSZ film has been reduced down by the subsequent EPD process after GD. The output properties of the fuel cell with YSZ film deposited by GD-EPD were obviously improved. The most apparent improvement was the fuel cell's power density of GD-EPD sample that increased seven times from 20 to 144 mW cm^{-2} at intermediate-temperature of 700 °C than that of GD ones.

Keywords: A. Films; D. ZrO_2; E. Fuel cells; Gravity-electrophoretic deposition (GD-EPD)

1. Introduction

Solid oxide fuel cells (SOFCs) have been regarded as a kind of green energy in the 21st century [1], because of its higher energy conversion efficiency, environmentally friendly and low pollutions. Conventional SOFCs based on YSZ (yttria-stabilized zirconia) electrolyte are usually operated at 1000 °C or more in order to obtain higher power densities. However, the high operating temperature makes the requirements on the materials very strict, such as thermal and chemical stability, conductivity, matching of the thermal expansion coefficient between different materials, etc. In addition, high temperature operation over a long period would incur many problems such as limited material selection and fast performance degradation of cell components [2]. These problems had limited the commercial development of SOFCs. Therefore, it is necessary to reduce the operation temperature of SOFC down to 600–800 °C, while the power density of high temperature is still maintained. One of the challenges associated with lowering the operating temperature is the resulting significant increase in the resistivity of the YSZ electrolyte [3]. An effective approach to overcome this problem is to reduce the thickness of the YSZ electrolyte.

There are many techniques applied to produce YSZ films, such as electrochemical vapor deposition (EVD) [4], chemical vapor deposition (CVD) [5], physical vapor deposition (PVD) [6], sol–gel [7], and ceramic processing methods such as slip casting [8], electrophoretic deposition (EPD) [9], centrifugal casting [10], etc. Each technique has its advantages and disadvantages. YSZ was a typical ceramic material, thus using ceramic powder processing methods to obtain YSZ film had many potential advantages at preparation technique and reducing the cost of production.

In this paper, a new ceramic powder processing method named GD-EPD has been described. In this technique, gravity deposition method (GD) was used firstly to obtain YSZ layer on porous NiO-YSZ anode substrate, and then another ceramic powder processing method called electrophoretic deposition

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(EPD) was used to make additional layer of YSZ on it. In GD, YSZ particles of larger size can be sedimentated to the surface of the substrate under the gravity of itself in YSZ suspension. In EPD, charged YSZ particles of smaller size can be driven by a dc electric field to move towards the substrate (an oppositely charge electrode), on which they ultimately deposit and form a particulate layer. The aim of the present paper is to use the GD-EPD method to prepare denser YSZ film on NiO-YSZ anode substrate for using in SOFC of intermediate-temperature.

2. Experimental

The anode materials (NiO-YSZ) were prepared by mixing YSZ powder (China building material academy, Beijing, China), NiO powder (made by ourselves) and amylums (commercial) by a weight ratio of 5:5:1. The purpose of adding amylums was to form more pores in anode. The mixture was milled in agate mortar for 1 h. Then, the mixed powder was pressed into pellets with a diameter of about 13 mm and a thickness of about 0.6 mm. The pellets were subsequently baked at 900 °C for 2 h to form the porous NiO-YSZ substrates.

A metastable YSZ suspension was obtained by dispersing 1 g of YSZ powders (TZ-8Y, Tosoh Corporation, Tokyo, Japan) in 100 ml of isopropanol and sonicated with a high intensity ultrasonic probe for 10 min. Two porous NiO-YSZ anode substrates were placed on a salver and immerged into the YSZ suspension. The substrates with coatings were taken out 2 h later. Then, the coated pellets were dried in air for 12 h and co-sintered at 1000 °C for 2 h. This process was repeated for four times to get a sufficient thickness. After that, one sample was sintered at 1400 °C for 2 h, which was called 1#. The other one was reduced in hydrogen at 900 °C for 1 h and then deposited another layer of YSZ by EPD technique, then sintered at 1400 °C for 2 h, which was called 2#.

The sedimentation curve of YSZ particle in metastable suspension was measured with a FA2004 balance. In this method, a salver immerged into YSZ suspension was hanged under the balance. Then the deposited mass of YSZ particles was measured by the balance and the data were transferred into computer through RS-232-C standard interface. The thickness of the deposited film could be readily controlled via this method.

The sintering curves of YSZ electrolyte and NiO-YSZ anode substrate were investigated with a dilatometer (DIL 402C/3/G Netzsch GmbH, Germany) with air purging. In this measurement, the material powders were pressed into a small bar with a diameter of 6 mm and a height of about 8 mm, the bar was heated from room temperature to 500 °C at a rate of 5 K/min in order to burn out the amylums pore-maker smoothly and obtain uniform pores in the NiO-YSZ supporter, and from 500 to 900 °C at 10 K/min, then holding at 900 °C for 2 h, finally to 1300 °C at 10 K/min and holding at 1300 °C for 2 h. Scanning electron microscopy (SEM) photos of YSZ membranes were obtained using Hitachi S-4700 scanning electron microscope.

$La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.8}O_3$ (LSCF) powders were synthesized by solid-state reaction method [11]. Some adhesives were put in the powders to form slurry. The slurry was applied on the other side of the two samples and then fired at 300 °C for 30 min to burn out the adhesives. Finally, the two samples were sintered at 900 °C for 5 h.

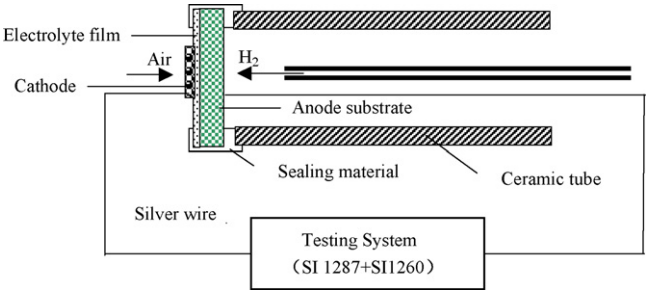


Fig. 1. Testing system of single cell.

To assemble a single fuel cell, a NiO-YSZ/YSZ/LSCF pellet was sealed onto one end of ceramic tubes (Fig. 1) as the method mentioned in reference [10]. The silver layers on both electrode surfaces made from silver paste (DAD-87, Shanghai Research Institute of Synthetic Resin, Shanghai, China) were used as current collectors to collect current on both anode and cathode. Thus, a single fuel cell was prepared and to be tested. In the process of fuel cell testing, the hydrogen was used as fuel and the oxygen in air was used as oxidant. The anode chamber was purged with nitrogen below 500 °C, and the nitrogen was changed to the fuel gas (H_2) at 500 °C. The *I–V* curves of single cell were measured with Solartron 1287 (Solartron Instruments, Hampshire, England) Electrochemical Interface at potentiodynamic mode, the potential was scanned from open circuit value to zero with a rate of 10 mV/s, potential and current data were both collected synchronously. The impedance spectra of fuel cells were measured with Solartron 1287 Electrochemical Interface combined with SI 1260 impedance/gain-phase analyzer when the cell performances were tested, the frequency range is from 910 kHz to 0.5 Hz.

3. Results and discussion

3.1. Sintering shrinkage characteristic of YSZ electrolyte and NiO-YSZ anode

Fig. 2 shows the sintering curves of YSZ electrolyte and NiO-YSZ anode. A typical sintering curve usually includes two

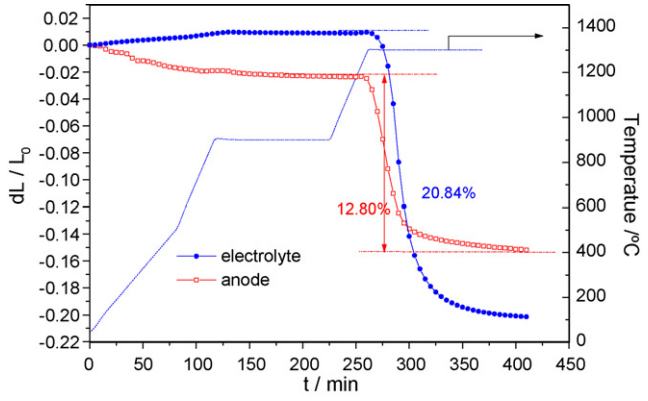


Fig. 2. Sintering curve and shrinkage of different samples.

segments. One segment is expanding, the other is shrinking. At lower temperature, the sample expands with temperature increasing and shows positive thermal expansion coefficient (TEC), over a certain temperature, TEC changes to negative and the shrinkage begin. According to the sintering curves, such parameters, e.g., TEC, starting shrinkage temperature, shrinkage rate and the total shrinkage ratio (sintering step) can be obtained easily. From Fig. 2, it can be seen that the starting shrinkage temperature was almost the same but the total shrinkage ratio of YSZ electrolyte was larger than that of NiO-YSZ anode. This mismatch would produce stress during co-sintering process and some cracks in electrolyte film might be formed. So the co-sintering process should be controlled carefully.

3.2. Sedimentation curve of YSZ particles

Fig. 3 shows the sedimentation curve of YSZ particles in YSZ suspension. The sediment mass increased rapidly in the first 10 min, corresponding to the sedimentation of bigger YSZ particles, then the sedimentation rate became slow, corresponding to the sedimentation of smaller YSZ particles. According to the data of sedimentation curve the mass of deposited YSZ particles could be estimated, then the thickness of the film could be calculated according to Eq. (1).

$$h = \frac{m}{(\rho_P - \rho_L)A}\frac{1}{D} \quad (1)$$

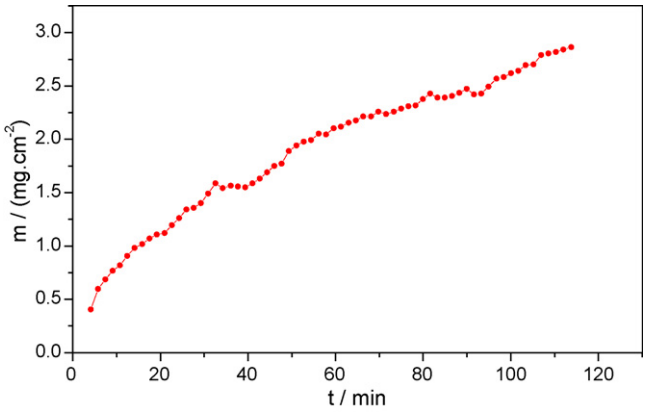
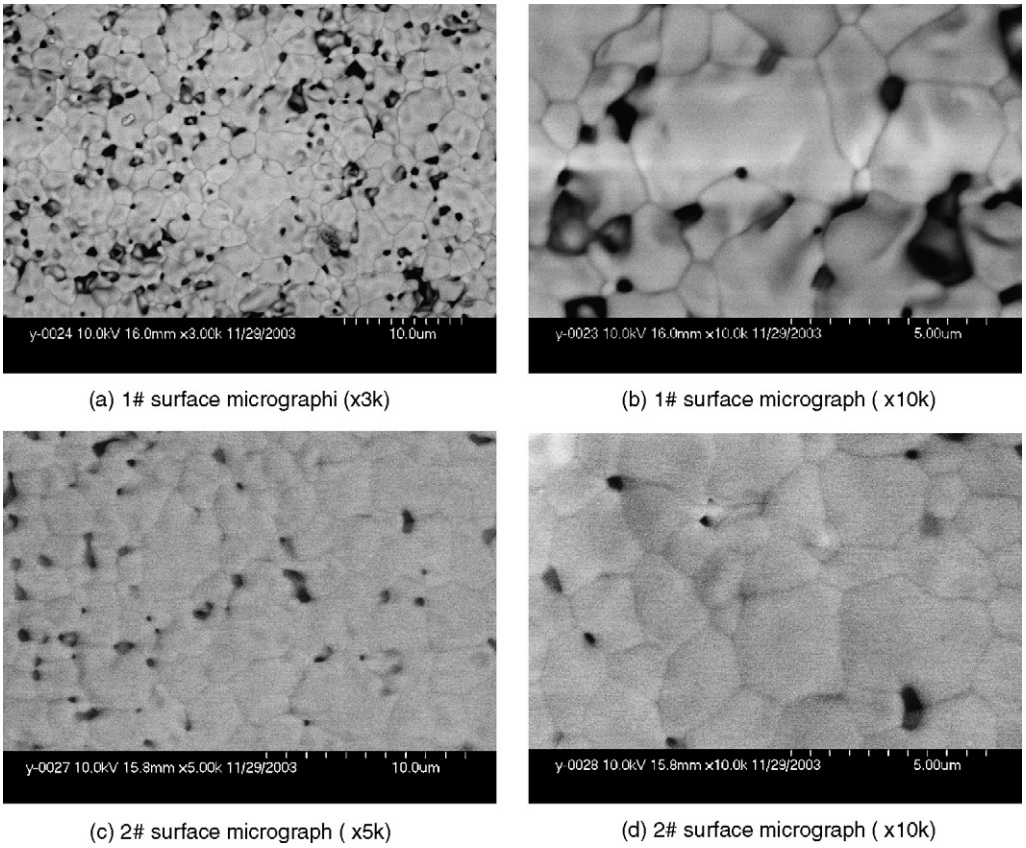


Fig. 3. Sedimentation curve of YSZ particles.

In this equation, h is the thickness of the deposited film, m is the deposited mass measured by balance, ρ_P is the density of YSZ particles, ρ_L is the density of solvent, D is a factor related with the relative density of the film, and A is the area of the substrate. If we presumed the film is dense enough, D equals 1. Then the thickness of YSZ film deposited for 2 h is about 5.5 μm. So, the thickness of YSZ film should be about 22 μm by repeating this process for four times.

3.3. Results of SEM

Fig. 4(a) and (b) show the scanning electron micrographs of 1# sample. It can be seen that the surface of YSZ film prepared



(a) 1# surface micrographi (x3k)

(b) 1# surface micrograph (x10k)

(c) 2# surface micrograph (x5k)

(d) 2# surface micrograph (x10k)

Fig. 4. Scanning electron micrographs of YSZ membranes.

only by GD technique was sintered well. The particles of submicron were agglomerated to grains with size of several microns and sintered together. In this sample, the grain boundaries were clear enough to be distinguished. However, there still exist some holes, the sizes of which were less than 1 μm. The shape and size of these holes were not uniform. These holes were probably formed during the sedimentation process and they may affect the electrical conductivity of electrolyte and the open voltage (OCV) of the fuel cell.

Fig. 4(c) and (d) show the scanning electron micrographs of 2# sample. It is obvious that the size and the amount of the holes in 2# sample were less than that of 1# sample. In addition, the grain boundaries of 2# sample were not as clear as that of 1#. It proved that another YSZ layer by EPD technique on the YSZ surface prepared by GD and sintering for longer time can improve the performance of YSZ film. We can expect this membrane provide a better property of conductivity and OCV of fuel cell.

3.4. Properties of fuel cells

Fig. 5(a) shows the performance of the fuel cell made from 1# sample. The maximum open circuit voltage was 0.98 V at 620 °C. It was less than the theoretical one (about 1.23 V). This difference should be attributed to the open and gas-permeable holes existing in the YSZ electrolyte film. A small amount of fuel gas might leak out through these holes and cause the cathode potential dropping down. In addition, the shrinkage of YSZ film and NiO-YSZ anode substrate was not coincident during co-sintering (Fig. 2), it could produce very large stress between the film and the substrate to form a few micron cracks which would influence the performances of the fuel cell, not only the open circuit voltage, but also the current density and the power density. The current density and power density of this fuel cell were 0.54 A/cm^2 and 105 mW/cm^2 at 800 °C, 0.27 A/cm^2 and 57 mW/cm^2 at 750 °C, 0.09 A/cm^2 and 20 mW/cm^2 at 700 °C, respectively.

Fig. 5(b) shows the performance of the fuel cell made from 2# sample. The current density and power density were 1.33 A/cm^2 and 270 mW/cm^2 at 800 °C, 1.12 A/cm^2 and 245 mW/cm^2 at 750 °C, 0.73 A/cm^2 and 144 mW/cm^2 at 700 °C, respectively. It can be seen that the performances of 2# sample are better than that of 1#. The improvements could be attributed to the additional layer in 2# sample. In GD process, most of the deposited particles were the bigger ones. Although the process was repeated for four times, there were still a few holes and some flaws of micron size in the membrane. In contrast, the EPD process could deposit smaller particles with submicron size onto the substrate, so that the holes might be filled with these small ones. In fact, the smaller particles with positive charge tend to move to the region with higher electrical conductance. Since the electrical conductance in the holes and flaws filled with suspension should be higher than other regions (sintered YSZ membrane), the holes and flaws may be filled firstly. So the film prepared by combination of GD and EPD becomes denser and exhibits better performance.

Fig. 6(a) and (b) show the impedance spectra of 1# and 2# sample during the cell test. From the figures, we could see obviously that the resistance of the electrolyte decreased in both samples when the operating temperature increased.

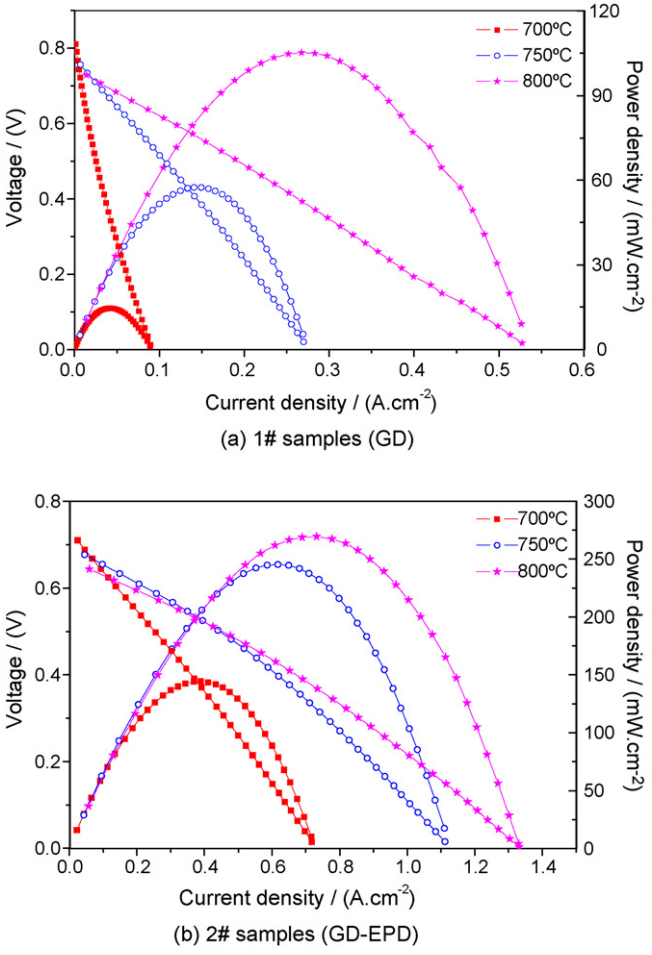


Fig. 5. Cell test results at various temperatures.

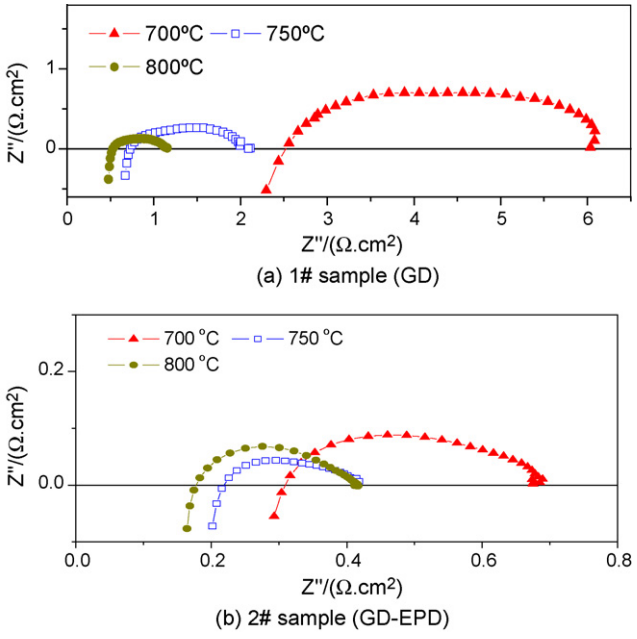


Fig. 6. Impedance spectra and equivalent circuit of fuel cell.

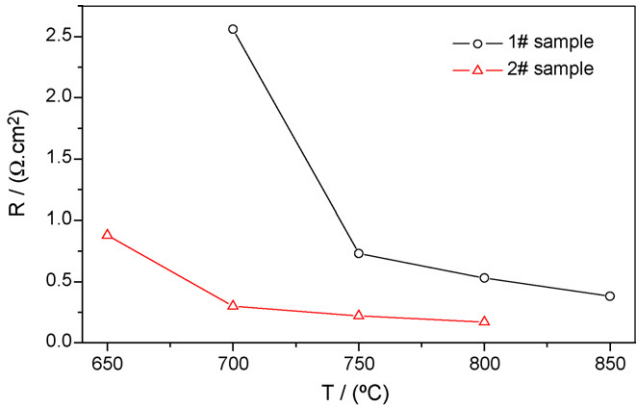


Fig. 7. Area specific resistance of YSZ film vs. operating temperature of two samples.

Correspondingly, the performance of the two samples got better. According to the comparison result of impedances of the two cells at different operating temperature, the improvement of the additional YSZ layer prepared by EPD is evident. The total resistance reduced from about 8 Ω cm^2 of 1# cell down to 0.66 Ω cm^2 of 2# cell and the output power density raised seven times from 20 to 144 mW/cm^2 at 700 °C.

In Fig. 6, the spectra are not ideal semicircles and show highly depressed and skewed because two primary factors may influence the impedance spectra of fuel cell. Firstly, the reason for highly depressed semicircle is that the interfaces between electrolyte film and electrodes are rough and the impedance spectra show the feature of a parallel circuit of constant phase element (CPE) and resistance. Secondly, the skewed semicircle at high frequency region is the combining contribution of the wire's inductance (about 0.7 μH) and the YSZ electrolyte's capacitance (about 10^{-8} F magnitude). In some impedance spectroscopy, the low frequency end is also skew to low impedance direction because of temperature fluctuation.

In the impedance spectra, the intercepts at the high frequency end mainly represent the resistance of YSZ electrolyte and a small contact resistance of Ag current collector on electrode. Neglecting the small contact resistance, the area specific resistance (ASR) of YSZ electrolyte film versus the working temperature of the two samples are obtained and shown in Fig. 7. It can be seen that the area specific resistance of 2# sample at any temperature is less than that of 1#. However, it should be noticed that the value of the area specific resistance of 2# at 750 and 800 °C were almost the same. This phenomenon should be attributed to the reducing of NiO to Ni and subsequent sintering of anode. In the sintering process, the small Ni particles might gather together to form larger ones and the electrochemical properties of the anode might become worse during the temperature increased from 750 to 800 °C. This problem might influence the stability of fuel cell during a long operating period. So, more research about the anode should be carried out in order to avoid this problem.

4. Conclusion

The present results show the GD-EPD technique can be used to prepare denser YSZ film on porous NiO-YSZ anode substrate. By the GD process repeated four times, a YSZ film of certain thickness can be obtained but there were still some holes or flaws of micron size in it. The subsequent EPD process could repair relative large holes or flaws (micron size). The fuel cell prepared by GD-EPD (GD-EPD cell) shows a better performance than the one prepared by GD (GD cell) especially at lower temperature of 700 °C, e.g., the power density of the GD-EPD cell was 144 mW/cm^2 and that of the GD cell was only 20 mW/cm^2. The method combining the GD and EPD is a simpler, easier and lower cost one for preparing the YSZ film.

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