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YSZ thin films deposited by spin-coating for IT-SOFCs

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Abstract

Dense and crack-free yttria stabilized zirconia (YSZ) thin films were fabricated using a spin-coating technique for intermediate temperature solid oxide fuel cells (IT-SOFCs). The film thickness was greatly affected by spinning speed and coating cycles. The morphology of the films was investigated with scanning electron microscope. With cathodes consisting of yttria-stabilized bismuth oxide and sliver, anodes of samaria-doped ceria and nickel, the supported YSZ films were characterized as electrolytes for single cells with humidified hydrogen as fuel and stationary air as oxidant. Open circuit voltage was 1.08 V at 700 °C, close to the theoretical value and power density was 535 mW/cm^2 at 750 °C and 400 mW/cm^2 at 700 °C. Impedance analysis indicates that the performances of the SOFCs are determined essentially by the interfacial resistances, suggesting that optimizing the electrode materials are especially important for IT-SOFCs.

Keywords: Solid oxide fuel cell; Thin film; Spin-coating technique; YSZ; IT-SOFC

1. Introduction

Energy conversion using solid oxide fuel cells (SOFCs) is a highly efficient and environmental friendly technology with low emissions of NO_x, dust, and noise. In addition, SOFCs offer fuel flexibility, such as hydrocarbons and nature gas [1]. SOFCs are generally operated at high temperature between 800 and 1000 °C, because the electrolyte, Y_2O_3 stabilized ZrO_2 (YSZ) has a low ionic conductivity at operating temperature below 800 °C. Such high operating temperature leads to some serious problems, such as physical and chemical degradation of SOFCs components. Therefore, it is highly desirable to develop SOFCs operating at intermediate temperature. However, as the temperature is lowered, resistive losses across the solid electrolyte increase, and so does polarization at the air and fuel electrodes. In order to settle these problems, either thinner or more conductive electrolytes are needed. A shorter path for oxygen ions will allow thin film YSZ electrolyte to have less ohmic resistance at intermediate temperature (600–800 °C) than thick films at 1000 °C. Various attempts have thus been made to develop thin film electrolytes, including electrochemical vapor deposition (EVD) [2], plasma spraying [3], RF sputtering [4], spray pyrolysis [5], and sol–gel method [6].

In this paper, YSZ film was deposited with spin-coating technique on porous green substrate consisted of nickel oxide and samaria doped ceria (SDC). Spin-coating is a technique that utilizes centrifugal forces created by a spinning substrate to spread a coating solution evenly over a surface. With this method, dense, crack-free YSZ films supported on NiO-SDC substrates were attained after sintering at 1300 °C for 5 h. The films as electrolytes for SOFCs were characterized with a single cell arrangement at temperature from 600 to 750 °C.

2. Experimental procedures

A suspension consisting of 10 wt.% YSZ and ethanol was prepared by ultrasonic dispersion of commercial YSZ (8 mol% Y_2O_3, Farmeiya Advanced Materials Co., Ltd.) powder in ethanol. The suspension was then spin-coated on a porous green NiO-SDC substrate processed by pressing a mixing powder consisting of 60 wt.% NiO and 40 wt.% SDC

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($Ce_{0.8}Sm_{0.2}O_{1.9}$) under uniaxial pressure of 250 MPa using a ϕ 15 mm die. Typically, the suspension was dripped on the center of the substrate, which was immediately spun at 2500 rpm for 30 s to form a thin, uniform YSZ layer. After the solvent in YSZ layer was dried at room temperature, another cycle was done. The layer thickness was controlled by the speed and the coating cycles. The electrolyte/electrode bilayer was then co-fired at 1300 °C for 5 h in order to achieve a dense YSZ film.

In order to characterize the electrochemical performances of the YSZ film, a composite consisting of yttria stabilized bismuth oxide ($Y_{0.25}Bi_{0.75}O_{1.5}$, YSB) and Ag powder was used as the cathode [7]. The composite powders were made into slurry with an organic binder. The slurry was subsequently painted onto the YSZ film, dried at room temperature, and fired at high temperature to form the cathode. Sliver paste (DAD-87, Shanghai Research Institution of Synthetic Resins) was painted on top of each electrode as a current collector. After baking, the sliver was well adhered to the surface of the electrodes. The single cell was fixed and sealed to zirconia tube with the sliver paste. Humidified hydrogen was used as fuel and ambient stationary air was used as oxidant. The cell tube apparatus was placed in a furnace and heated to the testing temperature, where fuel was applied. After complete reduction of NiO to Ni, the cell gave a stable open-circuit voltage over 1.0 V. The cell performance, such as *I–V*, *I–P* characteristics was then measured. Resistances of the single cell at open circuit conditions were measured using CHI604A electrochemistry analyzer in the frequency range from 0.01 Hz to 100 KHz. Surface and the cross-sectional morphologies of the films and the tested single cells were analyzed using Hitachi X-650 scanning electron microscopy (SEM).

3. Results and discussion

3.1. Film thickness

The film thickness was affected by the spinning rate and coating cycles. With the same solution, lower spinning rate usually resulted in thicker films. For example, a 3-μm-thick film was fabricated for 12-cycle coating at spinning rate of 4000 rpm, meanwhile, 1000 rpm spinning rate resulted in a 20-μm-thick film. In this work, spinning rate is typically set to be 2500 rpm, at which a 10 μm thick dense YSZ film could be deposited for 20-cycle coating.

Shown in Fig. 1 is the influence of coating cycle on the film thickness. The film thickness increases with coating cycle as expected. A single-coated film was not uniform or continuous. The average thickness of a double-coated film was about 1.0 μm. It increased to be about 4.0 μm for 10-cycle coating, and 10 μm for 20-cycle coating.

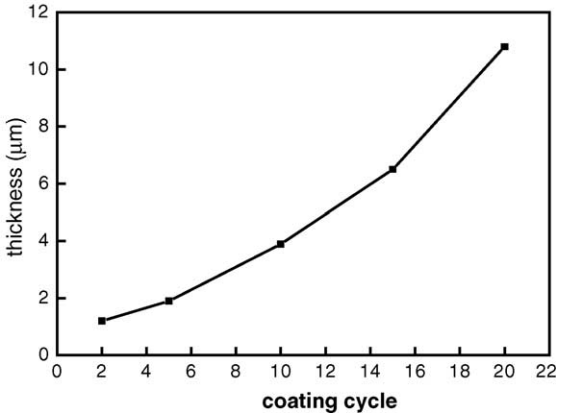

Fig. 1. Film thickness as a function of coating cycles. The spinning rate was 2500 rpm.

3.2. Microstructures of the films

The YSZ film was fabricated on the green NiO-SDC substrate by spin-coating and co-firing processes. In order to avoid cracking of the electrolyte film due to possible stresses induced by the co-firing process, shrinkages of the substrate and electrolyte film were carefully matched [8]. Shown in Fig. 2 is SEM microview for the surface and cross-section of an YSZ film supported on Ni-SDC, which was formed by reducing NiO-SDC with hydrogen at 750 °C. As shown in Fig. 2a, no pin-holes or cracks were observed on the surfaces. The average grain size was approximately 1 μm. Small grain size is believed to achieve better mechanical strength for a very thin ceramic film [9]. Cross sectional view of the film is shown in Fig. 2b, where a dense, thin and uniform electrolyte film is observed to adhere well to the porous substrate. Thin film with very few closed sub-micron pores was fabricated by sintering at 1300 °C for 5 h without using any sintering aid. This is achieved by optimizing the YSZ suspension and also the coating technique to form a uniform and high packed green film.

3.3. Cell performance

Shown in Fig. 3 is the cross-sectional view of a single cell with an YSZ film supported on a NiO-SDC anode, and with YSB-Ag cathode. It can be seen that the YSZ film is about 10-μm-thick, pore-free and well-adhered to the NiO-SDC fuel electrode, indicating that the suspension dispersion process has produced an thin-film electrolyte with high quality.

Shown in Fig. 4 is the dependence of cell voltage and power density on current density for a single cell consisting of Ni-SDC anode, YSZ electrolyte, and YSB-Ag cathode. Humidified hydrogen (3% H_2O) was used as fuel and stationary air as oxidant. Power density of 535 mW/cm^2 was generated at 750 °C. The open circuit voltage is 1.08 V at 700 °C. This value is close to the theoretical one, which

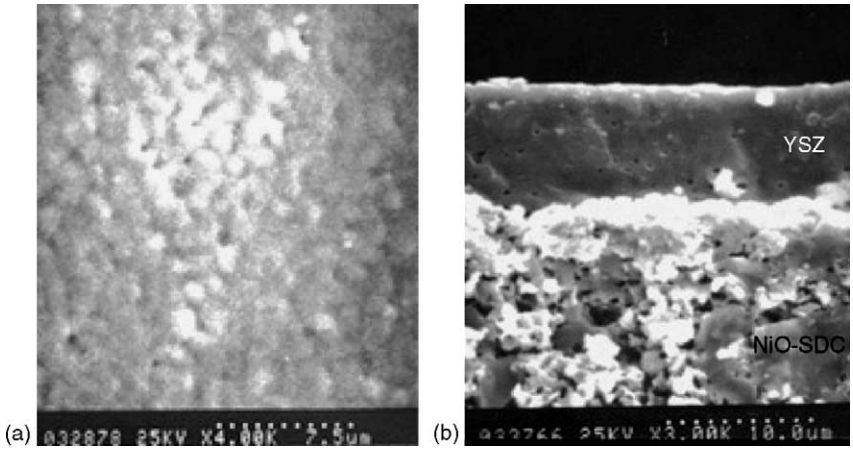

Fig. 2. SEM micrograghs for the surface (a) and cross section (b) of an YSZ film sintered at 1300 °C.

indicates that the thin film of YSZ deposited onto the porous Ni-SDC is dense enough to prevent gas leakage through the electrolyte. However, the anode-supported cell showed a little voltage drop at high current density. The reason might be the mass transport limitation through the thick anode substrate. For an anode-supported SOFC, concentration polarization loss in the anode can be a crucial problem because fresh fuel and electrochemical reaction products have to diffuse through a thick anode substrate in the opposite direction between the flow field and the anode/electrolyte interface. Compared to anode-supported cell, the self-supported cell can be free of concentration polarization. Therefore the performance will be further improved by reducing the thickness and by microstructure design such as functional graded structure [10].

Shown in Fig. 5a is impedance spectra of the cell measured under open circuit condition and Fig. 5b is the total cell resistance, the interfacial resistance, and electrolyte resistance as determined from the impedance spectra. The intercept with the real axis at high frequencies represents the resistance of the YSZ film whereas the diameter of the depressed semicircle corresponds the impedance of the two interfaces: the cathode-electrolyte interface and the anode-electrolyte interface. The interfacial resistance includes the contact resistance between the electrode and the electrolyte as well as the resistance to the electrochemical processes such as charge transfer and mass transfer. The electrolyte and interfacial resistances decrease with temperature. However, the impedance of the interface increased much faster than the impedance of the bulk electrolyte as temperature was reduced, indicating that the activation energy for interfacial transport process is much greater than that for the bulk transport within the electrolyte. As a result, the interfacial impedance becomes more significant at intermediate temperature. This implies that the performance of thin film YSZ-based fuel cells to be operated at intermediate temperatures depends critically on the interfacial resistances.

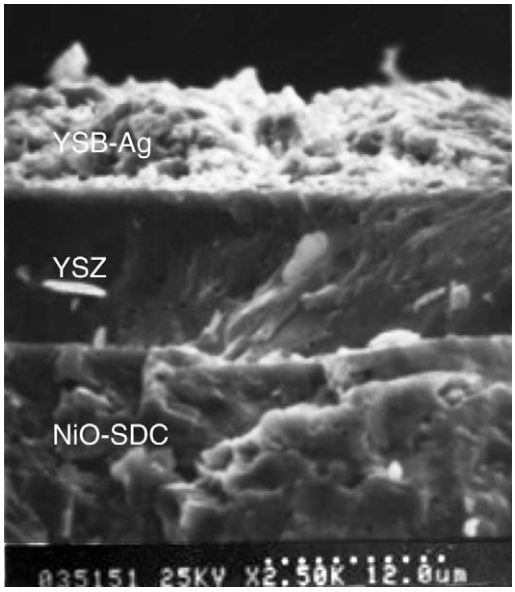

Fig. 3. SEM micrograph for a cross-sectional view of a NiO-SDC/YSZ/YSB-Ag cell.

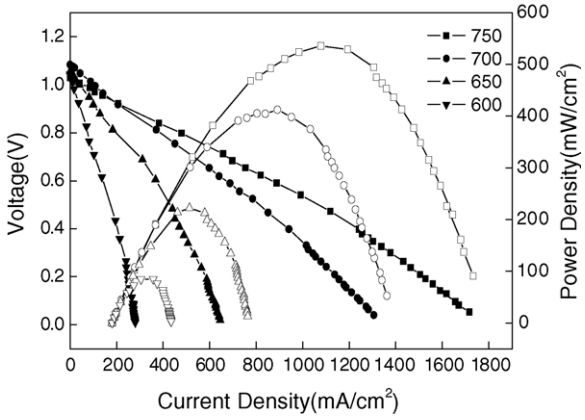

Fig. 4. Cell voltage and power density as function of current densities for a NiO-SDC/YSZ/YSB-Ag cell tested between 600 and 750 °C with humidified hydrogen as fuel and stationary air as oxidant.

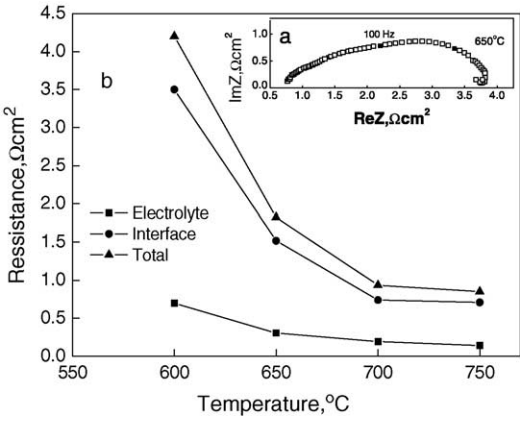

Fig. 5. (a) Impedance spectra of a single cell as measured at 650 °C and (b) the total cell resistances, interfacial resistances, and electrolyte resistances obtained from impedance spectra at different temperature.

4. Conclusion

In this paper, we presented and discussed results on anode-supported SOFCs with thin YSZ films fabricated by a spin-coating technique. The thickness of YSZ films was controlled by the spinning speed and the coating cycles. Porous anode substrates were coated with the suspension of YSZ powder and the resulting bilayers were co-fired to yield fully dense, crack free YSZ films, which was demonstrated by the achieved open circuit voltage that was close to the theoretical value. Power density of 535 mW/cm^2 were attained at 750 °C with a Ni-SDC/YSZ/YSB-Ag fuel cell. Impedance measurements at open cell conditions showed that the cell performances were essentially determined by the interfacial resistances. Therefore, the performance will be further improved by reducing the interfacial resistance.

Acknowledgement

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