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ORIGINAL PAPER

Effect of co-sintering temperature on the performance of SOFC with YSZ electrolyte thin films fabricated by dip-coating method

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Abstract Anode-supported yttria-stabilized zirconia (YSZ) electrolyte thin films were fabricated by the dip-coating method using the simple methylethylketone/ethanol-based YSZ suspension. Influences of the sintering temperature on the performance of solid oxide fuel cells were studied. Fully dense YSZ electrolyte thin films were obtained after being sintered at 1,300 °C as well as at 1,400 or 1,500 °C through SEM observation. The open circuit voltages of the cells all reached above 1.10 V at the testing temperatures. The testing results proved that both the anode performance and the electrolyte conductivity sintered at 1,300 °C were superior to those sintered at 1,400 or 1,500 °C. Investigation on the cell voltage drop under operation condition revealed, that the sintering temperature has more significant effect on the performance of the electrodes than on the electrolyte.

Keywords YSZ thin films · Dip-coating method · Co-sintering temperature · Cell performance · Electrochemical properties

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Introduction

Solid oxide fuel cells (SOFCs) have many merits, such as low environmental pollution, flexible fuels, and high conversion efficiency and it is a promising power generation technology for the future. However, the relatively high temperature (800–1,000 °C) of SOFC causes many materials and technology issues. Currently, it is more desirable to develop intermediate temperature solid oxide fuel cells (IT-SOFC) with the typical operating temperature from 600 to 800 °C [1–4]. Yttria-stabilized zirconia (YSZ) is the most commonly used electrolyte for SOFCs because of its good merits, including high mechanical stability, high hardness, and excellent chemical stability in both oxidizing and reducing environments [5, 6]. However, operation of SOFCs at the intermediate temperature will result in a drastic increase in the electrolyte resistivity as well as the overpotential at electrodes. In order to achieve the effective performance of the IT-SOFCs, one preferable and practical method is to prepare YSZ electrolyte as thin as possible [2, 7–9].

So far, various deposition methods have been applied to fabricate dense electrolyte thin films for IT-SOFCs, including electrochemical vapor deposition [10], physical vapor deposition [9], plasma spraying [11, 12], tape casting [13], screen-printing [14], dip-coating [15] etc. Compared to other fabrication methods, dip-coating belongs to the wet-chemical process and is considered to be a simple and cost-effective membrane fabricating method. Moreover, it is unrestricted by the shape and size of anodes and has the advantages of potential large-scale commercial fabrication as well as flexible control in film thickness [15, 16]. As an effective method for fabricating dense and thin films,

researchers have studied the factors that will probably affect the electrolyte films, such as the property of the dip-coating suspension [16–19], the conditions of the anode support [16]. Dip-coating method usually applies a mixture of polymeric sol and YSZ particle suspension [5] or YSZ slurry coating followed by an additional sol modification [16] which results in the high organic content and the solid content as low as about 12 wt.% or even lower [16, 20]. However, the key challenge is still the preparation of fully dense YSZ electrolyte thin films onto porous anode supports without any defects (e.g. cracks, pinholes, etc.).

In our previous paper, we developed a simple methyl-ethylketone/ethanol (MEK/EtOH)-based YSZ suspension with the solid content as high as 30 wt.% to dip-coat green YSZ thin films onto the porous anode supports and no additional modified process was needed [21]. However, the dense YSZ electrolyte is required to be co-sintered at 1,500 °C and it was found out that higher co-sintering temperature for anode substrates and electrolyte films would deteriorated anode microstructure and resulted in the decrease of the cell output. Therefore, it is necessary to research the co-sintering process of the YSZ thin film fabricated by this method at lower temperatures.

In this paper, three sintering processes were employed to densify YSZ electrolyte films and influences of the sintering processes on the performance of the cells with dip-coated YSZ electrolyte films were studied in detail. It is indicated that both fully dense and higher conductivity dip-coated YSZ electrolyte films and excellent electrochemical active anode was obtained at 1,300 °C.

Experimental

In order to fabricate porous NiO–YSZ anode supports, NiO powders (Canadian INCO Metals, 99.9%), YSZ powders

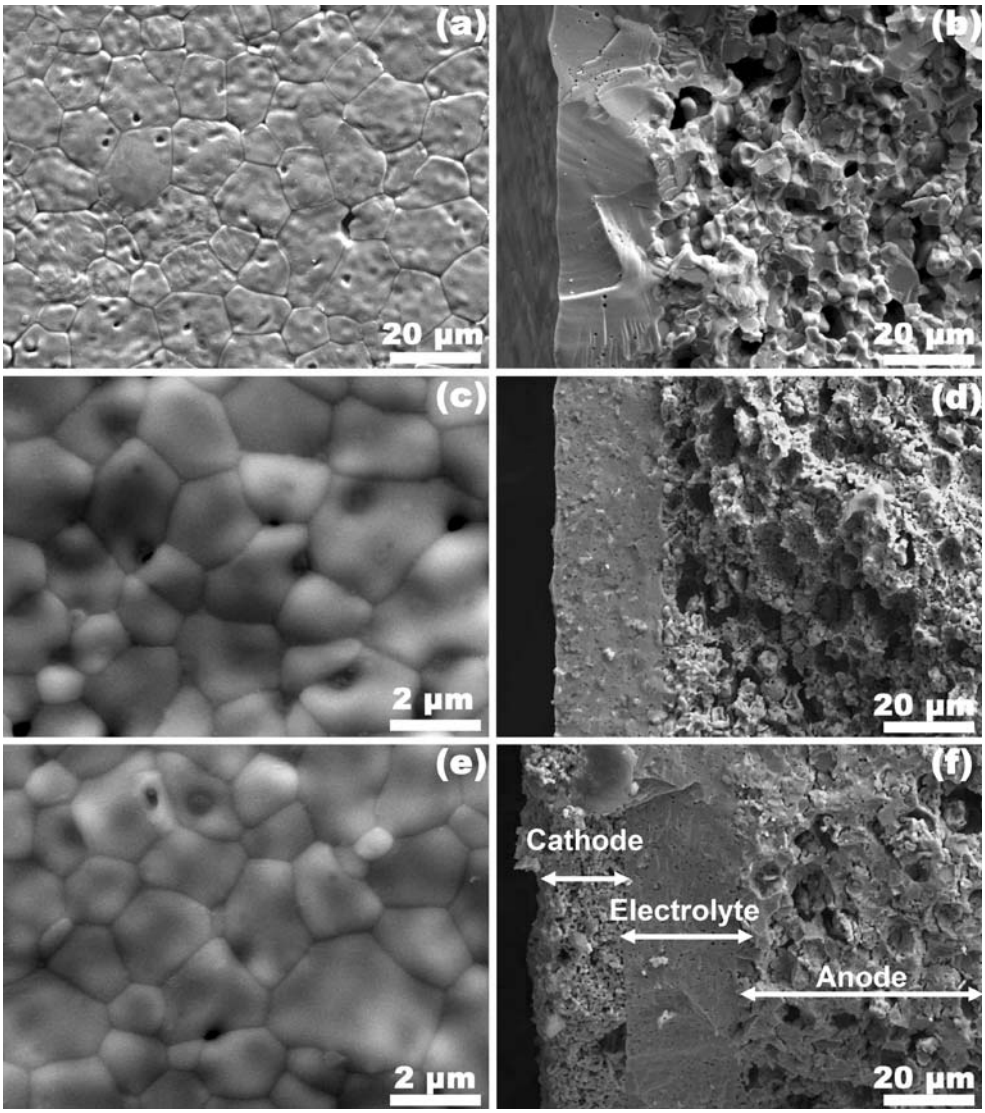

Fig. 1 SEM micrographs of the surface and cross-section for the three samples: **a**, **b** S15; **c**, **d** S14; **e**, **f** S13

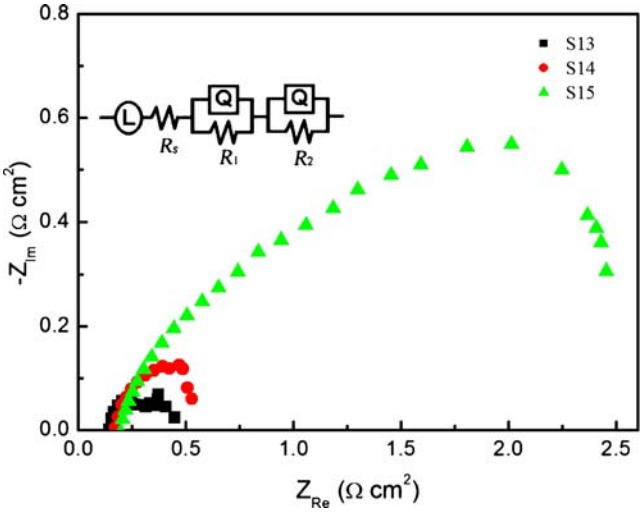

Fig. 2 Impedance spectra and equivalent circuit for the cells operated at 800 °C with the electrolyte sintered at different temperatures under open-circuit (fitting parameters see Table 1)

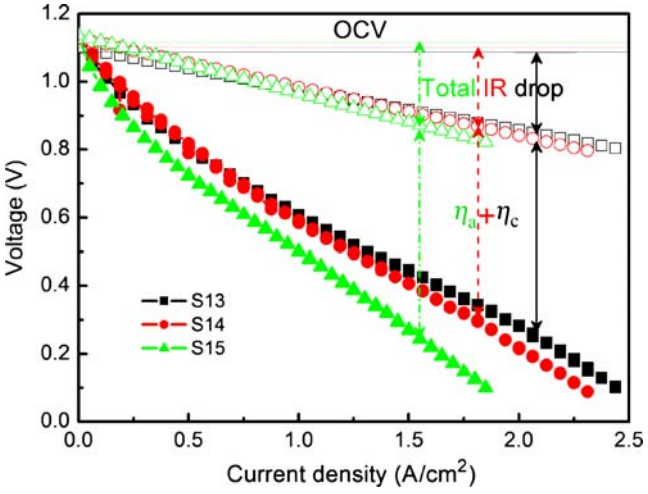

Fig. 3 Separation of ohmic drops and electrode polarization losses of the cells at 800 °C

(TZ-8Y, Tosoh, Japan) and flour as pore-former were dispersed in ethanol in a weight ratio of 54:36:10. Then the mixture was ball-milled for 48 h. After drying, the mixed powders were uniaxially pressed into pellets with a diameter of 20 mm, which were subsequently calcined at 1,000 °C for 2 h to guarantee the strength of the anode supports.

YSZ electrolyte films were fabricated by dip-coating YSZ suspension onto the as-prepared NiO–YSZ anode supports. YSZ powders with an average particle size of 0.2 μm were used as raw materials and the YSZ suspension for dip-coating was prepared as follows: YSZ powders and 2.5 mass% dispersant triethanolamine were dispersed in the MEK/EtOH composite solvent and ball-milled for 24 h and then the binder poly-vinyl-butyl and plasticizer polyethylene glycol and diethyl-o-phthalate were added, another 24 h ball-milling was needed to obtain the stably dispersed suspension with a solid content as high as 30 wt.%.

The thin and uniform green YSZ electrolyte films were obtained by dip-coating the YSZ suspension onto the porous anode supports and this same process was carried out twice for two purposes: one is to guarantee the strength of the electrolyte and the other is to prevent pin holes occurred on the electrolyte film surface during the drying and sintering process, which is called self-repairing mechanism [19]. Each layer was dried at room temperature for 1 h so that the solvent of the green layer could volatilize. No heating process was needed. After drying at room temperature for 24 h, YSZ films and anode supports were co-sintered at 1,500 °C for 5 h, 1,400 °C for 5 h, and 1,300 °C for 20 h, respectively to densify the films and these three samples were named S15, S14, and S13. For S14, a step of 1,200 °C for 2 h was added in the sintering procedure before reaching 1,400 °C comparing with that of S15. The three-step sintering process was carried out for S13 and this sample was firstly sintered at 1,200 °C for 2 h, then the temperature was raised at a rate of 1 °C/min to 1,400 °C followed by a direct temperature decrease from 1,400 °C to 1,300 °C. In order to ensure the sufficiency of grain boundary diffusion, a relatively long time such as 20 h is needed at 1,300 °C. The densification of YSZ film under lower temperature can be explained by the similar principle reported in [22].

$La_{0.8}Sr_{0.2}MnO_3$ (LSM)/YSZ powders in three different ratios were mixed with terpineol to form different cathode paste. The three kinds of paste were then screen printed onto the sintered YSZ films one after the other to form a graded cathode. Subsequently, the cell disks were sintered at 1,200 °C for 2 h.

All the single cells were tested with two-probe method in a tubular furnace in the temperature range from 750 to 850 °C. The humidified hydrogen with a flow rate of 50 sccm was used as the fuel and ambient air as the oxidant, respectively. The cell performance was measured by Arbin fuel cell testing

Table 1 Fitting parameters for the cells with the electrolyte sintered at different temperatures under open-circuit

The three samples	σ_s (S/cm)	R_s (Ω·cm^2)	R_p (Ω·cm^2)	$R_s/(R_s+R_p)$ (%)
S13	0.022	0.122	0.335	26.6
S14	0.019	0.144	0.428	25.1
S15	0.016	0.170	2.636	6.06

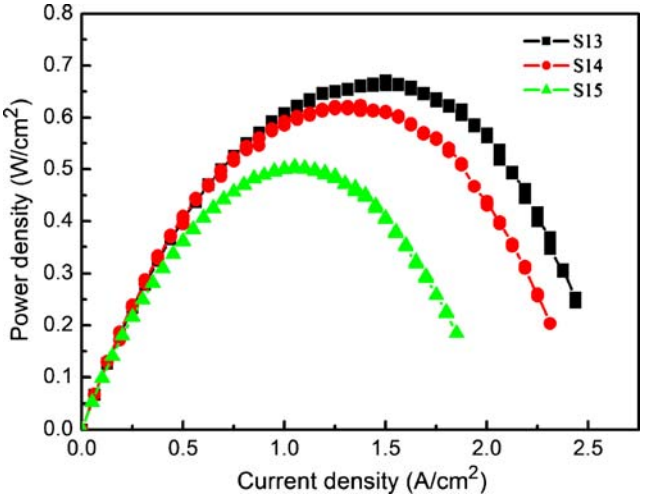

Fig. 4 The electrochemical performance of the cells under 800 °C with the electrolyte sintered at different temperatures

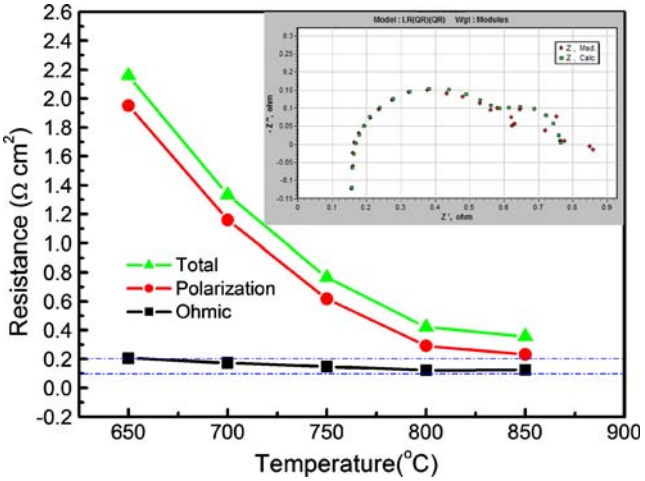

Fig. 6 Impedance spectra of a single cell for the sample S13 as measured at 750 °C (*inset*) and the total cell resistances, polarization resistance, and ohmic resistance obtained from impedance spectra at different temperatures

equipment (USA). The electrochemical impedance behavior was studied with Parstat M2273 (Princeton Applied Research). The frequency used was from 100 kHz to 100 mHz with the amplitude of the sinusoidal signal 10 mV. The impedance measurement was conducted under open circuit and the measured spectra were fitted to the equivalent circuit by using the nonlinear least square fitting software, ZSimpWin. The YSZ grain size and the microstructure of YSZ electrolyte films were characterized by scanning electron microscopy (FEI Sirion, Netherlands).

Results and discussion

Fig. 1 shows the surface morphology of the YSZ films sintered at different temperatures and the cross-sectional microstructure of the tested cells. As can be seen from Fig. 1a, c, e, fully dense dip-coated YSZ thin films can be obtained under all the three sintering processes and there are no open holes or obvious defects in the films. The average crystal grain size for the sample S13 or S14 is about 2.5 μm, which is obviously smaller than that of S15. From Fig. 1b, d, f, it is clearly observed that the two-layer YSZ film is about 27 μm in thickness, uniformly continuous and well adhered to the porous Ni–YSZ anode supports. No open pores exist. However, the anode support of S15 presents the over-sintering phenomenon which result in Ni aggregation in the anode, see Fig. 1b.

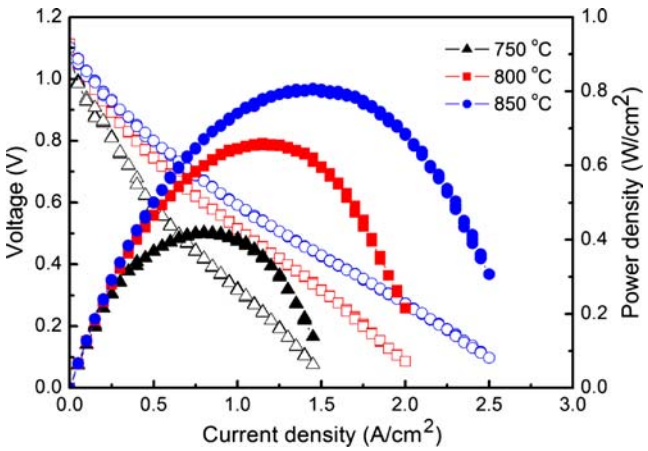

Fig. 5 The typical cell performance with the electrolyte sintered at 1,300 °C

The impedance spectra and equivalent circuits for the cells operated at 800 °C with the electrolyte sintered at different temperatures under open circuit are presented in Fig. 2. In these spectra, the intercepts with the real axis at high frequency (HF) denote the overall electrolyte resistance (R_s) of the cell, those at low frequency (LF) show the total cell resistance, and the difference between the high- and low-frequency intercepts represents the total interfacial polarization resistance (R_p) of the cell, which is the sum of R_1 and R_2 (see insert in Fig. 2).

As shown in Fig. 2, both R_s and R_p increase with the increase of the sintering temperature for YSZ electrolyte films, whereas the ratio of $R_s/(R_s+R_p)$ decreases. The calculated values are shown in Table 1. The conductivities (σ_s) of YSZ electrolyte films S15, S14, and S13 are 0.016, 0.019, and 0.022 S/cm, respectively, indicating that the conductivity of sample S13 is almost the same as that of dense YSZ bulk, reported by M. Hattori et al. [23]. This conform to the investigation in the literature [22], the smaller the YSZ grain size, the higher the conductivity of YSZ electrolyte especially at medium or low temperature.

As shown in Table 1, the cell polarization resistance increased quickly with increasing the sintering temperature. The polarization resistance value for the sample of S15 is 2.6365 $\Omega \cdot cm^2$. It can be explained that co-sintering anode substrates and electrolyte films at a high temperature like 1,500 °C would result in over-sintering, agglomeration, and coarsening as shown in Fig. 1.

In order to further investigate the electrochemical properties of the cells under operation condition, the voltage drop versus current density of the cells at 800 °C was measured, as shown in Fig. 3. The total voltage drop thus could be divided into ohmic and non-ohmic contributions. It is clear that the IR drops of the cells for the samples of YSZ S13, S14, and S15 was approximate. However, the polarization losses of the electrodes ($\eta_a+\eta_c$, where η_a is anode polarization loss, η_c is cathode polarization loss) of all cells is higher than the IR drops and the ratio between IR drops and polarization losses is decreasing with the increase of current density. This indicated that the cell performance is primarily determined by the polarization of the electrodes, especially at high outputting current density. It can be deduced that sintering temperature has a more significant effect on the performance of electrodes than that of electrolyte.

At the testing temperature of 800 °C, the open circuit voltages (OCVs) of the cells for the samples S13, S14, and S15 are 1.11, 1.13, and 1.14 V, respectively, which are all very close to the cell theoretical voltage. The negligible difference between the OCV values also indicates that a sintering temperature at 1,300 °C could realize the full densification of dip-coated YSZ electrolyte films as well as 1,400 or 1,500 °C. The discharge curves of these cells are shown in Fig. 4; the maximum power density of the cell for the sample S13 is 671 mW/cm^2, which is about 48 mW/cm^2 higher than that of S14 and 166 mW/cm^2 higher than that of S15. Since the cathodes applied in this work are identical, thus we can assume that the electrochemical performances of the cathodes for the cells are the same. This result implied that the outstanding electrochemical performance of S13 may be contributed to the good anode microstructure obtained at lower sintering temperature.

Figure 5 shows the typical cell performance with the electrolyte sintered at 1,300 °C. The OCV values are all higher than 1.10 V at the testing temperature range from 750 to 850 °C. Such high OCV values certify that high-quality YSZ electrolyte films could be obtained by sintering the dip-coated YSZ films at the temperature as low as 1,300 °C. The maximum power densities at 750, 800, and 850 °C are 419, 657, and 800 mW/cm^2, respectively, indicating that the cell with YSZ electrolyte sintered at 1,300 °C could realize excellent power output.

The total resistance, polarization resistance, and ohmic resistance calculated from the impedance spectra of the cell for the sample S13 are shown in Fig. 6. The ohmic and polarization decrease with increasing operation temperature. However, the polarization resistance increased much faster than the ohmic resistance as temperature was decreased, indicating that the cell resistance was still determined by the polarization resistance at lower temperature. Therefore, the cell performance can be improved through changing the electrode structure to enhance its catalytic activity. In addition, the cell performance was mixed controlled by electrodes polarization resistance and ohmic resistance at high temperature. So, further decreasing the thickness of YSZ film is another effective approach to improve the cell performance.

Conclusions

Dense YSZ electrolyte thin films have been fabricated by a simple dip-coating method with a low sintering temperature of 1,300 °C. A crack-free and thin YSZ electrolyte films with 27 μm in thickness is fabricated, which is uniformly continuous and well adherent to the porous anode supports. The OCV values of the cells sintered at different temperatures are all higher than 1.10 V at 800 °C. Low-temperature sintering process improves the performance of anode and electrolyte, and promises a better cell performance. The conductivity of YSZ electrolyte film sintered at 1,300 °C is 0.022 S/cm, and the maximum power density of the cell can reach 671 mW/cm^2 at 800 °C. The cell performance could be enhanced by further reducing the electrolyte thickness or improving the anode and cathode performance, which will be studied in future research.

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