



Effect of fabrication parameters on coating properties of tubular solid oxide fuel cell electrolyte prepared by vacuum slurry coating

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ABSTRACT

The process of vacuum slurry coating for the fabrication of a dense and thin electrolyte film on a porous anode tube is investigated for application in solid oxide fuel cells. 8 mol% yttria stabilized zirconia is coated on an anode tube by vacuum slurry-coating process as a function of pre-sintering temperature of the anode tube, vacuum pressure, slurry concentration, number of coats, and immersion time. A dense electrolyte layer is formed on the anode tube after final sintering at 1400 °C. With decrease in the pre-sintering temperature of the anode tube, the grain size of the coated electrolyte layer increases and the number of surface pores in the coating layer decreases. This is attributed to a reduced difference in the respective shrinkage of the anode tube and the electrolyte layer. The thickness of the coated electrolyte layer increases with the content of solid powder in the slurry, the number of dip-coats, and the immersion time. Although vacuum pressure has no great influence on the electrolyte thickness, higher vacuum produces a denser coating layer, as confirmed by low gas permeability and a reduced number of defects in the coating layer. A single cell with the vacuum slurry coated electrolyte shows a good performance of 620 mW cm⁻² (0.7 V) at 750 °C. These experimental results indicate that the vacuum slurry-coating process is an effective method to fabricate a dense thin film on a porous anode support.

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1. Introduction

Solid oxide fuel cells (SOFCs) are one of the most efficient of energy conversion devices [1]. The main issue in present SOFC development is lowering of the operating temperature to the range of 600–800 °C. An intermediate-temperature SOFC would offer several merits such as a greater cell life-time, the possible use of metal alloy inter-connectors, easy gas-tight sealing, and low cost. One problem associated with lowering the operating temperature is an increase in ohmic loss in the 8 mol% yttria stabilized zirconia (8YSZ) electrolyte. In order to reduce this ohmic loss at medium operating temperature, methods of fabricating a thin-film electrolyte or syntheses of alternative materials with higher ionic conductivity have been investigated [2].

For fabrication of dense, thin-film electrolytes, various processes such as polarized electrochemical vapour deposition (PEVD) [3], RF

magnetron sputtering [4] and plasma spray [5] have been developed, but they are expensive in both terms of both equipment and operational costs. The dip-coating technique is well known to be simple and cost-effective for preparing a thin and dense YSZ film, and has a high flexibility in coating components with complex geometries [6]. Nevertheless, this method still has some problems in coating porous substrates; such as low green density, a large pore distribution of a green layer, and the formation of cracks during drying. It is especially difficult to obtain a dense YSZ coating layer with a thin thickness on a porous substrate using a conventional dip-coating method.

In the dip-coating process, the driving force for film formation is the capillary force of the porous substrate. The capillary force generated by the touching meniscus causes the electrolyte slurry to yield quickly a uniform coating thickness over the porous substrate. As the capillary force increases, the porous surface will effectively be coated, which will reduce the influence of surface defects in the substrate on the coating properties [7]. If the capillary force is not sufficient, the coating layer will have several defects such as uncoated areas, pores, cracks, and pinholes. To compensate for a weak capillary force, an external force such as vacuum or high pressure can be applied inside or outside the anode tube.

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Table 1
Properties of anode tube according to pre-sintering temperature.

Pre-sintering temperature (°C)	Wall thickness (mm)	Porosity (%)
1100	1.47	60.7
1200	1.32	50.3
1300	1.18	40.5

In this work, a vacuum slurry-coating process has been studied to obtain a thin and dense electrolyte layer on the porous anode tube. The vacuum is applied inside the porous tube and the electrolyte is coated on its outer surface. Pre-sintering temperature of the anode tube, vacuum pressure, immersion time, number of coats and slurry concentration are varied to determine the best conditions for formation of a dense electrolyte layer during vacuum slurry coating.

2. Experimental

The materials of the anode tube were a mixture of NiO and 8YSZ (NiO–8YSZ) powders. The anode tubes were prepared by an extrusion process [8]. The extruded tubes were dried at room temperature for 24 h by rolling and pre-sintered at 1100, 1200 and 1300 °C for 3 h. Properties of the anode tube as a function of pre-sintering temperature are shown in Table 1. The porosity of the anode tube was obtained by means of a mercury porosimeter (Autopore IV 9500, Micromeritics, USA). The surface of the pre-sintered anode tube has a rough morphology with macro-holes. The anode functional layer (AFL) was coated on the pre-sintered anode tube for surface modification and followed by a pre-firing step at 1000 °C for 3 h.

The AFL was applied by a dip-coating process. It was made of the same material as that of the anode tube but the NiO powders in the AFL were finer than those of the tube. The AFL causes the surface of the anode tube to become smooth and also increases the three-phase boundary [8]. The slurry of the AFL was prepared by using commercial 8YSZ (TZ-8YS, Tosoh Co., Japan) particles and submicron-sized NiO (Nickel oxide, J.T. Baker, USA) particles. The latter were prepared by a ball-mill process for 24 h. The 8YSZ electrolyte layer was coated on the anode tube using the vacuum slurry-coating process. The porous anode tube was sealed at its end and connected to a vacuum system, which provided an extra force to allow particle fluid motion and resulted in a dense coated layer. The electrolyte-coated anode tube was then co-sintered at 1400 °C for 5 h. A schematic diagram of a vacuum slurry-coating process is shown in Fig. 1. The vacuum slurry coating was performed at various conditions to fabricate dense and thin electrolyte layers, as shown in Table 2.

The surface morphology and thickness of the coated layers were observed using scanning electronic microscopy (SEM, S-4700, Hitachi Ltd., Japan) and then grain sizes were evaluated with image analysis (Image-pro, Media cybernetics, USA). The gas tightness of the electrolyte layer was evaluated by a helium gas leakage test. The helium gas permeability was measured using a bubble flow meter (Alltech, USA) at 5 atm. The sintering behaviour of NiO–8YSZ composite and 8YSZ were examined using a dilatometer (DIL 402C, Netzsch GmbH, Germany) from 100 to 1400 °C with a heating rate

Table 2
Experimental conditions of vacuum slurry coating for dense electrolyte.

Items	Conditions
Vacuum pressure	160–760 Torr
Number of coats	1–3 times
Concentration of slurry	1–15 wt.% 8YSZ
Immersion times	10–30 s

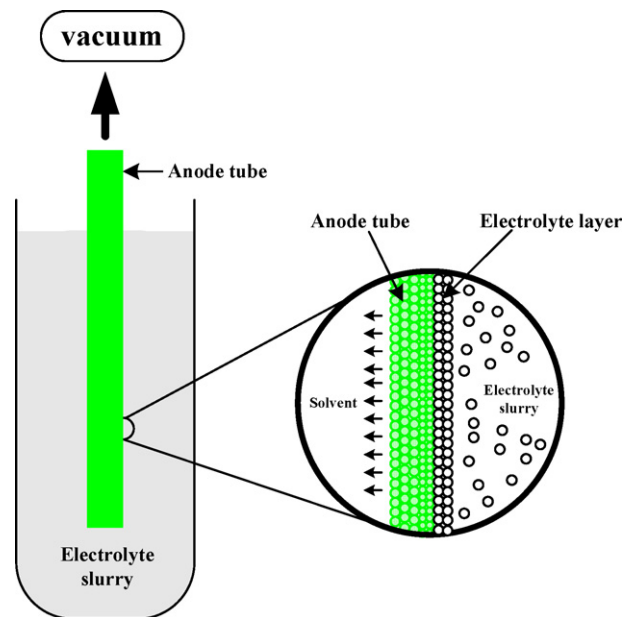


Fig. 1. Schematic diagram of vacuum slurry-coating process.

of 2 °C min⁻¹. The porosity of a fully sintered anode tube at 1400 °C was about 27%. The AFL was about 8 μm in thickness after sintering at 1400 °C for 5 h.

Cell performance was tested at various temperatures between 700 and 800 °C with a fuel gas of 5% H₂O–95% H₂ and with air as the cathode gas. The flow rates of the anode and cathode gases were 0.2 L min⁻¹ and 0.6 L min⁻¹, respectively. The cathode consisted of consecutive layers of a LSM–YSZ composite, (La_{0.6}Sr_{0.4})_{0.97}MnO_{3-δ} (LSM) and La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF). The cathode layers were co-sintered at 1200 °C for 3 h. Impedance spectra were obtained with SI1287 and SI 1260 equipment (Solartron Instruments, UK) at open-circuit voltage (OCV) with an amplitude of 30 mV at a frequency between 0.1 and 5000 Hz.

3. Results and discussion

3.1. Effect of pre-sintered anode tube on sintering property of coated electrolyte

The sintering curves of the NiO–8YSZ composite and 8YSZ pellets are presented in Fig. 2. The pellets of NiO–8YSZ compos-

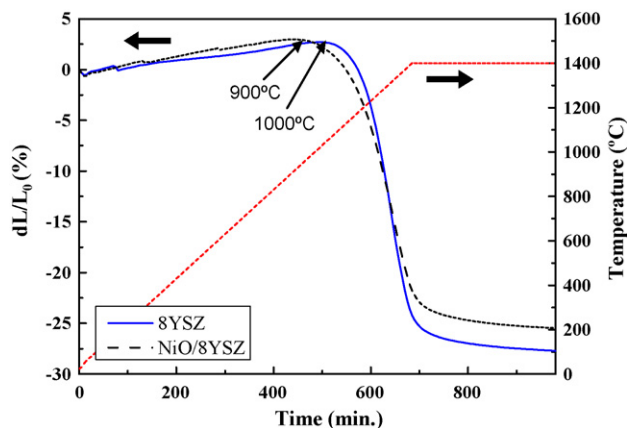


Fig. 2. Sintering curves for 8YSZ and NiO/8YSZ composite pellets between 100 and 1400 °C.

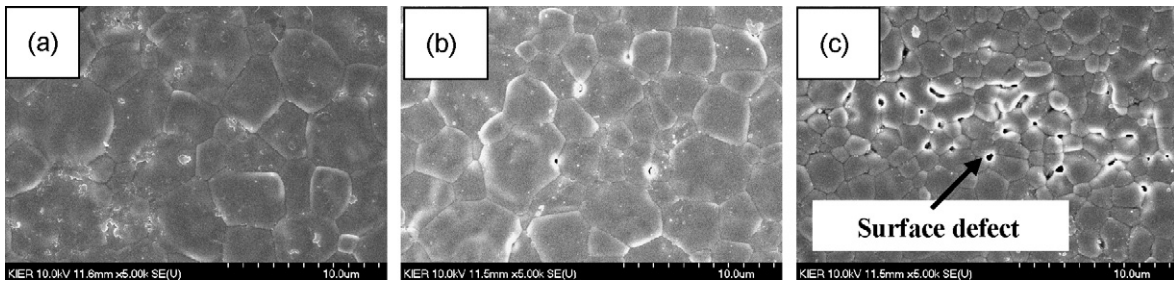


Fig. 3. Surface morphology of coated electrolyte layer after final sintering at 1400 °C for 5 h as function of pre-sintering temperature of anode substrate tube: (a) 1100 °C, (b) 1200 °C, and (c) 1300 °C.

ite and 8YSZ start shrinking at 1000 and 1100 °C, respectively. The shrinkage rates are 25.5% in NiO-YSZ and 27.7% in 8YSZ at 1400 °C. As the shrinkage rate of the anode tube is less than that of the 8YSZ layer [9], the 8YSZ layer is under tensile stress if the anode tube and the electrolyte are co-sintered [10]. The tensile stress inhibits the sintering of the electrolyte during co-sintering. The shrinkage difference between the anode tube and the electrolyte can be controlled by pre-sintering the anode tube. In other words, the shrinkage difference will decrease when the anode tube is pre-sintered at a temperature in the positive shrinkage region and then the electrolyte is co-sintered.

The surface morphology of the coated electrolyte was evaluated as a function of pre-sintering temperature of the anode tube, as shown in Fig. 3. The results are summarized in Table 3. As the pre-sintering temperature is decreased, the grain size of the electrolyte layer increases, but its surface pores decrease. A dense electrolyte layer is formed when it is coated on the pre-

Table 3

Shrinkage ratio of anode tube and average grain size of coated electrolyte as function of pre-sintering temperature after sintering at 1400 °C for 5 h.

Pre-sintering temperature (°C)	1100	1200	1300
Shrinkage ratio of anode tube ^a (%)	24.7	22.0	13.3
Average grain size (μm)	3.9	2.8	1.6

^a Shrinkage ratio of anode tube = 100 × (sample length at pre-sintering temperature – sample length at 1400 °C)/sample length at pre-sintering temperature.

sintered anode tube at 1100 °C and is sintered finally at 1400 °C. As the pre-sintering temperature decreases, the shrinkage of the anode tube after the final sintering increases and approaches that of the electrolyte. From the data in Table 3 and Fig. 3, in order to obtain a dense electrolyte layer, it is clear that the shrinkage difference between the pre-sintered anode tube and the coating electrolyte should be small, which is consistent with the results of Bao et al. [9]. The pre-sintered anode tube at 1000 °C is not easy to handle because of its low mechanical strength, but the

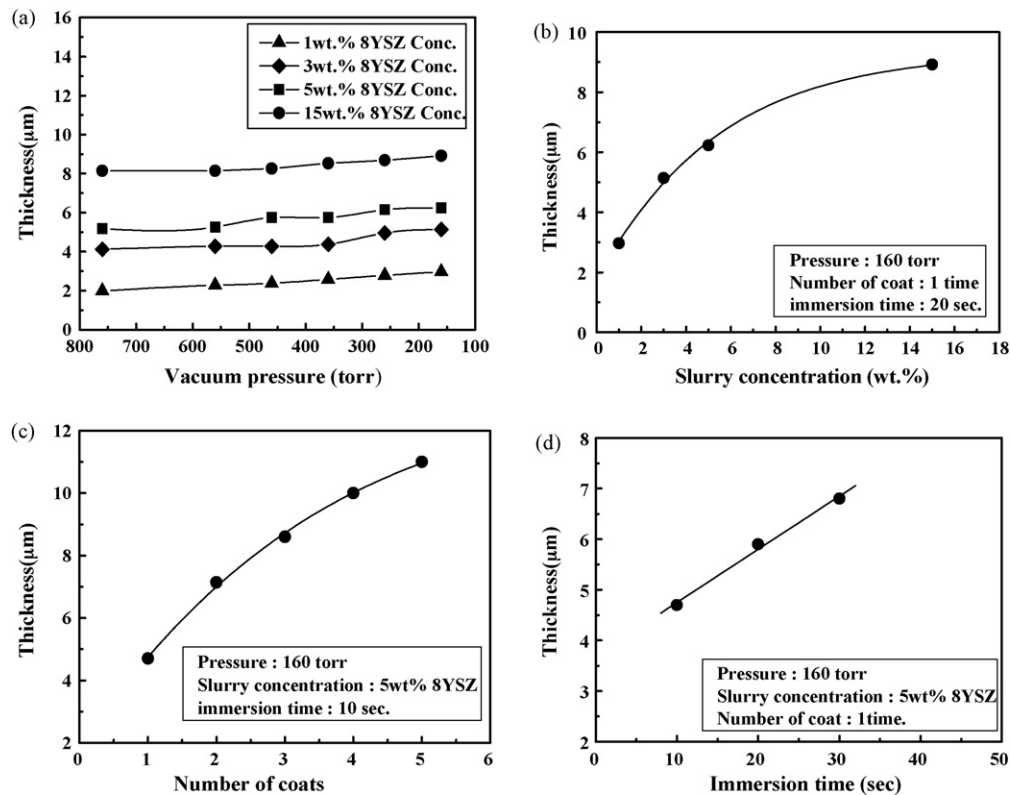


Fig. 4. Dependence of electrolyte thickness on fabrication parameter in vacuum slurry coating. (a) vacuum pressure, (b) slurry concentration, (c) number of coats, and (d) immersion time.

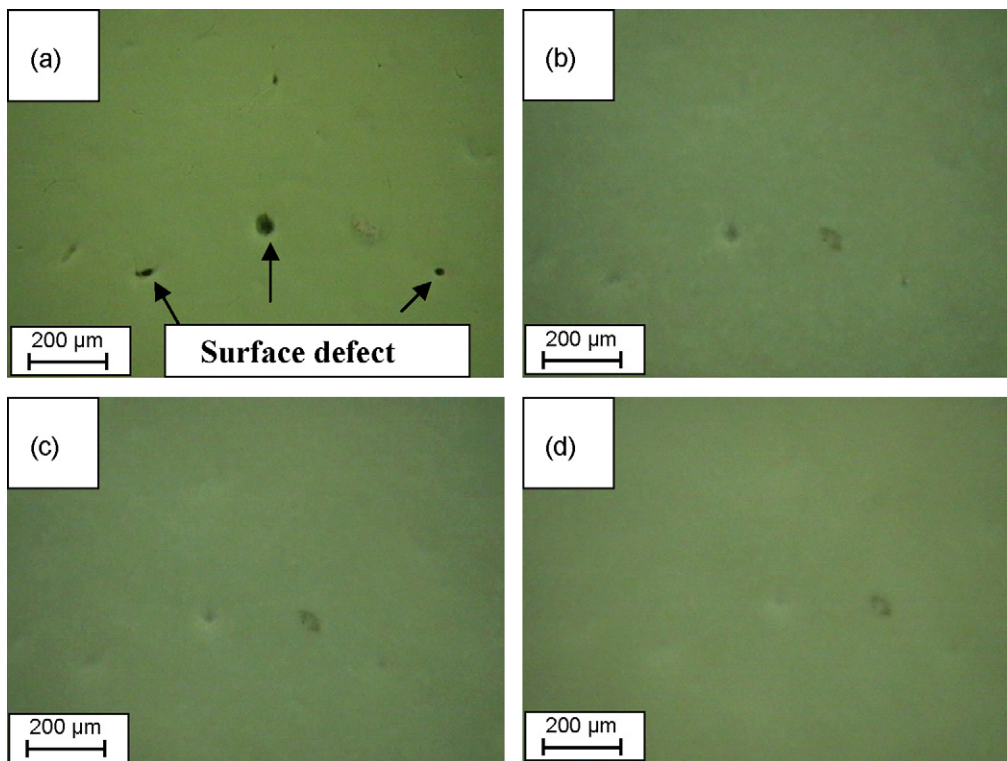


Fig. 5. Surface morphology of dried coating layer as function of immersion time: (a) 0 s, (b) 10 s, (c) 20 s and (d) 30 s. Slurry concentration: 3 wt.% 8YSZ; vacuum pressure: 160 Torr; number of coating: 1 time.

pre-sintered tube at 1100 °C has strong mechanical strength. From the shrinkage difference and mechanical strength, the optimum pre-sintering temperature of the anode tube is suggested to be 1100 °C.

3.2. Effect of vacuum coating parameters

The electrolyte must be sufficiently dense to prevent the gas leakage and thin enough to reduce the ohmic resistance. The dependence of the electrolyte thickness on the vacuum coating parameters is shown in Fig. 4. The electrolyte thickness depends strongly on 8YSZ concentration, number of coats, and immersion time. On the other hand, the effect of vacuum pressure on the electrolyte thickness is small. During vacuum slurry coating in Fig. 1, the vacuum is applied inside the porous anode tube, which is dipped in the electrolyte slurry. The electrolyte slurry was coated on outer surface of the porous anode tube and then the solvent in the slurry was extracted across the porous tube. The applied vac-

uum enhances the extraction of the solvent and thus leads to the compactness of the coating layer.

The results shown in Fig. 5, illustrate the dried surface morphology of the electrolyte-coated anode tube. The anode tube is covered gradually with electrolyte as the immersion time increases during vacuum slurry coating. The surface defects of the anode tube are completely covered by an electrolyte layer after 30 s of immersion time. Moreover, the closed pores inside the electrolyte layer are reduced with increasing immersion time, as shown in Fig. 6. In the vacuum slurry-coating process, the applied vacuum removes gas pores inside the electrolyte layer and thus a long immersion time is more effective to obtain a dense layer. The dried surface of the coated electrolyte as a function of slurry concentration is shown in Fig. 7. The surface defects of the electrolyte layer decrease with increasing 8YSZ concentration, but surface defects of the electrolyte still exist even at high concentration.

The gas leak rate of the electrolyte layer on the anode tube coated with vacuum slurry is given in Fig. 8. The rate decreased

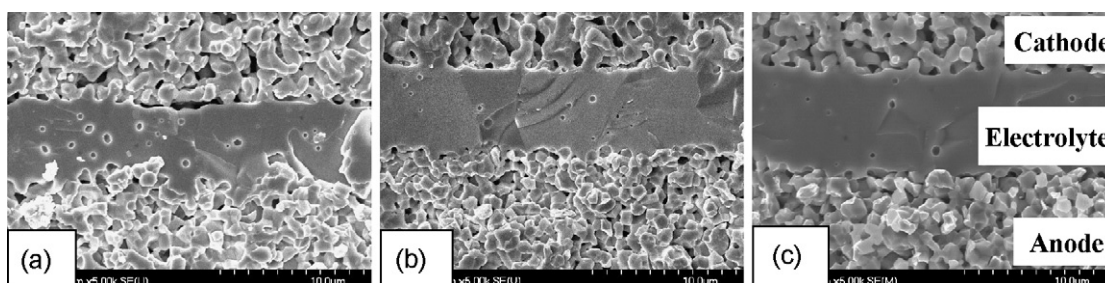


Fig. 6. SEM micrographs of coating layer as function of immersion time: (a) 10 s, (b) 20 s and (c) 30 s. Slurry concentration: 5 wt.% 8YSZ; vacuum pressure: 160 Torr; number of coating: 1 time.

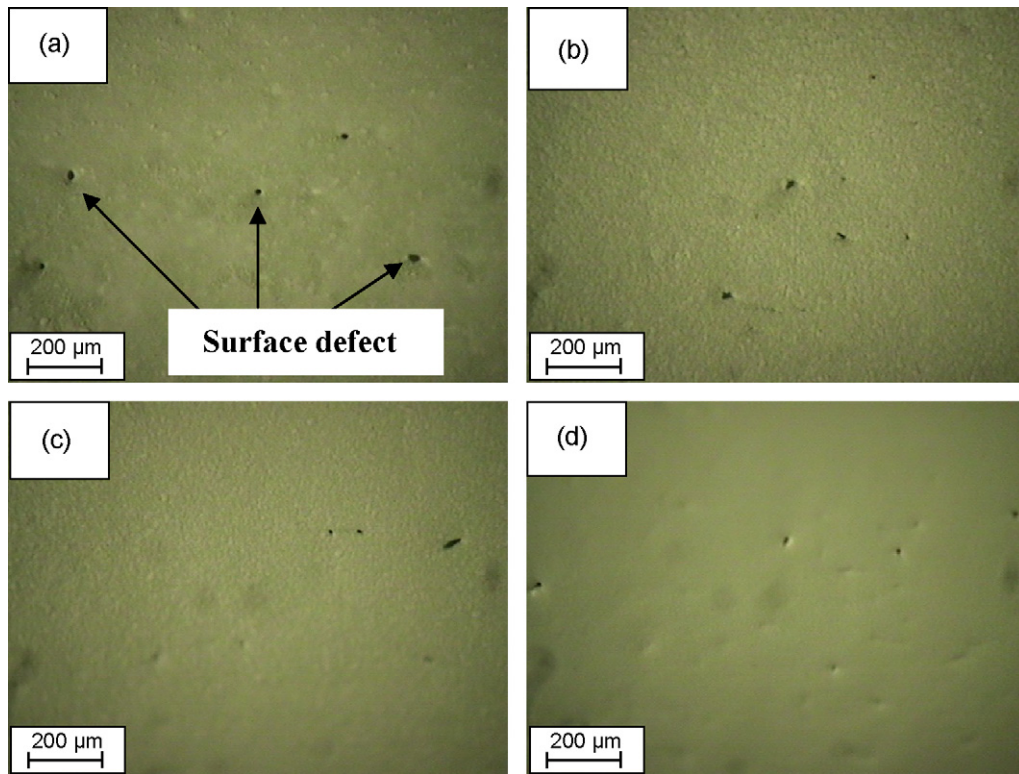


Fig. 7. Microphotographs of green coating layer as function of slurry concentration: (a) 1 wt.%, (b) 3 wt.%, (c) 5 wt.% and (d) 15 wt.%. Vacuum pressure: 160 Torr; number of coats: 1 time; immersion time: 10 s.

rapidly with increasing vacuum pressure. This behaviour indicates that the vacuum pressure has a great effect on the gas tightness of an electrolyte layer. The cross-section of the coated electrolyte layer as a function of the vacuum pressure is presented in Fig. 9. The porosity inside the electrolyte layer decreases as the vacuum pressure increases. Also the pores at the electrode|electrolyte interface disappear at high vacuum and an adherent interface is formed. Fig. 10 gives the mending defects in this work and its model [11] and shows that the surface defects of the substrate are filled during electrostatic powder coating. Bao et al. [11] suggested that as the particles fill up the surface defect (Fig. 10(c)) or bridge over the defect (Fig. 10(a)), the surface state of the substrate will effectively be modified, which will reduce the surface defects in the substrate on a dense film during fabrication. Similarly, if a sufficient vacuum

is used as an external force, instead of an electrostatic force, and is applied at the surface of the anode tube, the electrolyte particles in the slurry will fill up defects on the surface of the anode tube (Fig. 10(c)).

Du and Sammes [12] reported that an optimized vacuum pressure is needed to fabricate the dense electrolyte layer in the vacuum slurry coating because their vacuum coating process produced thick electrolyte layers of 10–50 μm depending on the vacuum coating conditions. The cracking was also generated during the drying step due to shrinkage when the electrolyte layer was thickly coated [12]. On the other hand, the vacuum coating in this work produces thin electrolytes below 10 μm , and the dependence of electrolyte thickness on vacuum pressure is not high. Additionally, the electrolyte does not crack during the drying step of the coated layer even at high vacuum. These coating properties, such as cracking and thickness, are attributed to the difference in the used slurries; an organic based-slurry is in this work while Du and Sammes [12] used an aqueous based-slurry. Therefore, it is concluded that the higher vacuum in this work is effective in filling the surface defects of the anode substrate and thus in making a dense electrolyte layer.

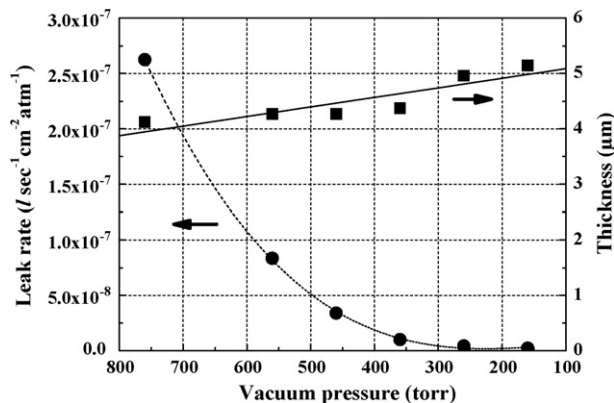


Fig. 8. Gas leak rate of electrolyte-coated anode tube prepared from various pressure conditions in vacuum slurry coating method (3 wt.% 8YSZ conc.; number of coats: 1 time; immersion time: 30 s).

3.3. Cell performance

The open-circuit voltage (OCV) of a fuel cell is related to the gas permeability of the electrolyte as well as the operating conditions. The performance of single cells prepared by vacuum slurry coating and by conventional dip-coating without vacuum is presented in Fig. 11. The single cell with vacuum-coated electrolyte shows a higher OCV of 1.11 V and also a good performance of 620 mW cm^{-2} at 0.7 V. The Nernst loss that originates from gas crossover is small due to the low gas permeability of the single cell. Fig. 12 shows impedance spectra of the single cell. The

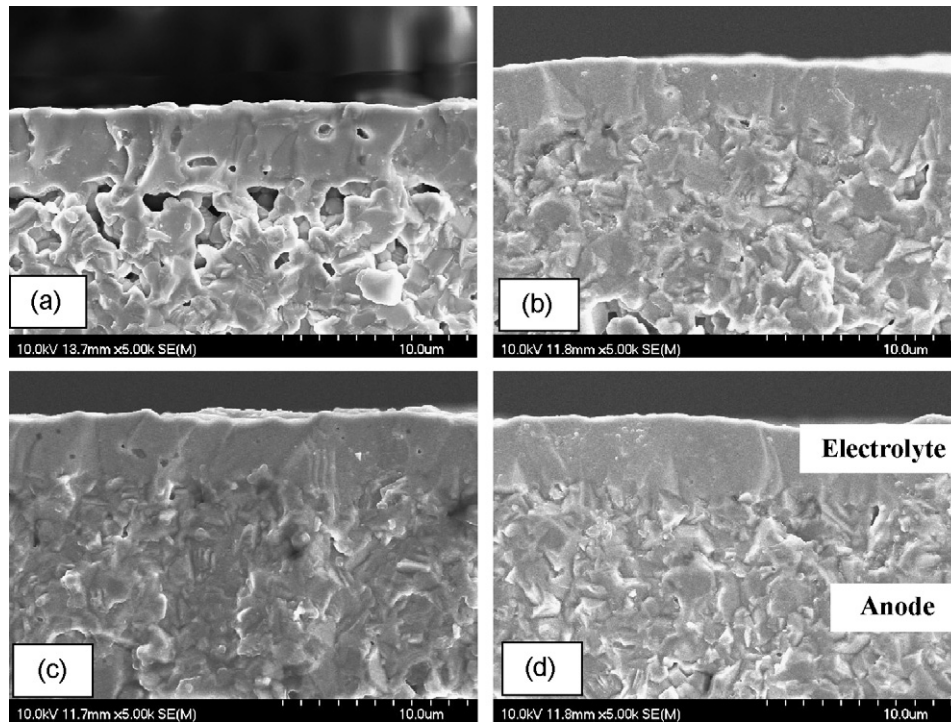
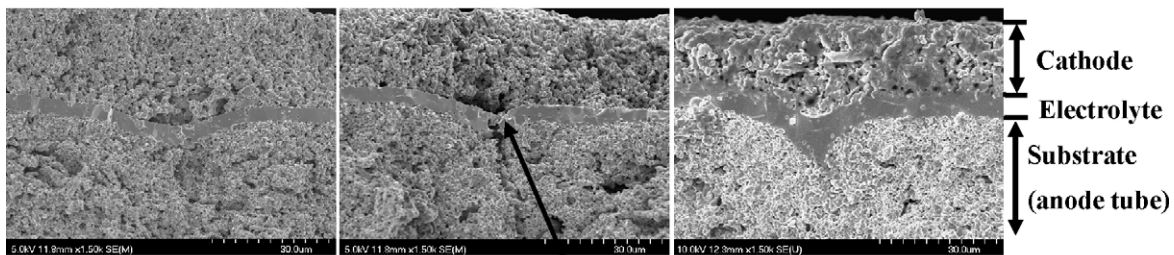


Fig. 9. Cross-sections of electrolyte layer prepared from vacuum slurry-coating process as function of vacuum pressure: (a) 760 Torr, (b) 560 Torr, (c) 360 Torr, and (d) 160 Torr. Slurry content: 3 wt.% 8YSZ; final sintering temperature: 1400 °C for 5 h.

impedance curve consists of two semi-circles of charge transfer at high frequency and mass transfer at low frequency [13]. The vacuum slurry-coated cell has a low ohmic resistance and polarization resistance compared with the conventional no vacuum dip-coated cell. The electrode polarization resistance decreases by a large amount when a vacuum slurry coated electrolyte is used for making the single cell. This is attributed to an improved compatibility at the interface between the anode and the electrolyte because of good adherence and reduced porosity. The electrode interfacial resistance is known to reduce with increasing contact between an

electrode and an electrolyte [14], and thus the good adherence between anode and electrolyte enhances the electrode performance. These impedance results are consistent with those of cell performance. On the other hand, the ohmic resistance decreases slightly after vacuum coating. The ohmic resistance depends on the electrolyte thickness and density, as well as the contact resistance. After vacuum coating, the electrolyte thickness and density increase but the contact resistance between anode and electrolyte decreases, which is considered to decrease slightly the ohmic resistance.

Mending defect developed in this work



Mending defect model [11]

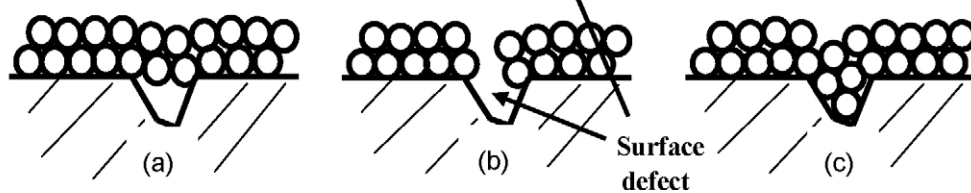


Fig. 10. Mending defect and its model [11] of electrolyte layer prepared from vacuum slurry-coating process according to vacuum pressure: (a) no vacuum, (b) low vacuum, and (c) high vacuum.

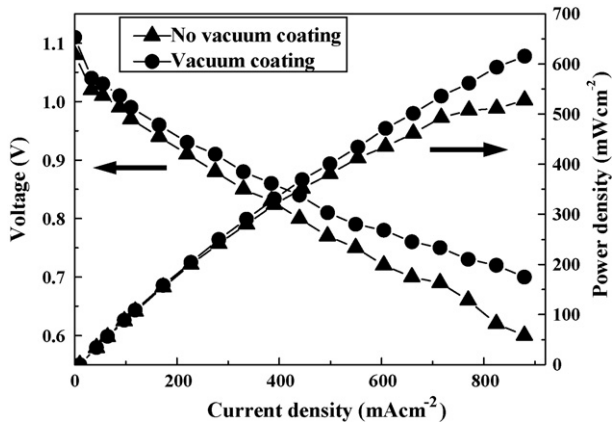


Fig. 11. Performance of single cells with vacuum and no vacuum slurry coated electrolyte at 750 °C (fuel: 3% humidified hydrogen; oxidant: air). Conditions of electrolyte coating: 3 wt.% 8YSZ concentration, immersion time of 30 s, coating of 1 time, vacuum pressure of 160 Torr.

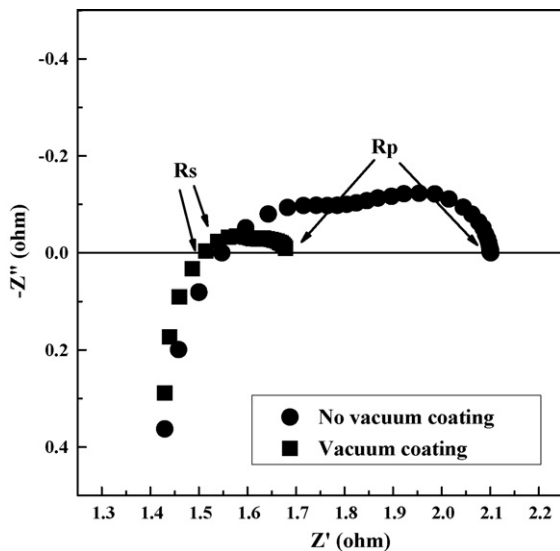


Fig. 12. Nyquist plots of single cell with electrolyte layer manufactured by vacuum slurry coating method and from no vacuum dip-coating method (R_s : ohmic resistance, R_p : electrode polarization resistance).

4. Conclusions

The vacuum slurry-coating process is an effective technique for producing thin and dense 8YSZ electrolyte layers. Dense 8YSZ thin films have been fabricated on a porous anode tube of NiO/YSZ. The coating properties of the electrolyte depend on the fabrication parameters. The pre-sintering temperature of the anode substrate tube has a great influence on the sinterability of the coated electrolyte. A dense electrolyte layer is obtained at a low pre-sintering temperature of 1100 °C and a vacuum pressure of 160 Torr. In vacuum slurry coating, the high vacuum reduces the surface defects of the coated electrolyte layer. The electrolyte thickness depends largely on the slurry concentration, the immersion time, and number of the coats. The performance of a single cell with a vacuum-coated electrolyte shows good performance, which is consistent with the impedance results.

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