

Short communication

Fabrication and characterization of anode-supported electrolyte thin films for intermediate temperature solid oxide fuel cells

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Abstract

Anode-supported electrolyte thin films for improving the solid oxide fuel cell (SOFC) performance at intermediate temperature (IT) have been manufactured by a wet-chemical process, and their microstructures, gas permeabilities, and electrical performances have been investigated. NiO–YSZ anode supports of a flat tube type were prepared by the extrusion method, and their surfaces were modified via slurry coating of fine NiO–YSZ particles for controlling the surface roughness and the pore size. An anode-supported yttria-stabilized zirconia (YSZ) electrolyte was fabricated by dip-coating YSZ slurry (viscosity 4.5 cP, solid contents 2.7 vol.%) onto the modified anode support, then it was coated with YSZ sol (viscosity 2.5 cP), and sintered at 1400 °C. The cathode consisted of three consecutive layers of LSM–YSZ composite, strontium-doped lanthanum manganite (LSM), and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF). After each successive slurry layer was applied it was co-fired at 1200 °C. The thickness of YSZ electrolyte layers could be controlled below 15 μm, and the YSZ layers' acceptability as an electrolyte film for an SOFC was estimated from the result of the gas impermeability ranging below 2 bar. The unit cells fabricated in this work showed a good electrical performance of 550 mW cm⁻² at 850 °C. This is attributed to the reduced resistance through the thin YSZ electrolyte. © 2004 Elsevier B.V. All rights reserved.

Keywords: Surface modification; Thin YSZ electrolyte; Wet-chemical process; Nitrogen permeability; Electrical performance

1. Introduction

Solid oxide fuel cells are energy conversion devices that produce electricity via the electrochemically combining reactions of fuel and oxidant gases across an ionic-conducting ceramic. The SOFCs have attracted special interests as a method of future electric power generation because of high efficiency and pollution-free operation. Present development of SOFCs is focused on lowering the operating temperature below 800 °C. The advantages of a reduced-temperature operation for SOFCs include wider material choice, better long-term performance, system compactness, and potentially reduced fuel cell costs [1–3]. However, it does increase the electrolyte resistivity and decrease the ionic conductivity.

This can be overcome by lowering the electrolyte resistance either by using a thin Y₂O₃ stabilized ZrO₂ (YSZ) electrolyte or by using higher ionic conductive materials such as doped ceria, $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mn}_{0.2}\text{O}_3$ or $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\alpha}$ [4–9]. In addition, reducing the electrode/electrolyte interfacial polarization losses and/or increasing the electrochemical activity of electrodes needs to be considered [10–11]. As a method for manufacturing thin YSZ electrolyte, a colloidal process is a very simple and cost-effective way that proves to be less restricted by geometric limitations (e.g. shape, size, etc.). The major challenge is to build up the thin YSZ electrolyte onto the porous anode support without any defects (e.g. cracks, pin-holes, etc.) so that the system is not short-circuited by gas crossover through the electrolyte.

To achieve this aim, the characteristics of electrolyte prepared by dip-coating a thin YSZ film onto the porous NiO–YSZ anode support were investigated. The surfaces

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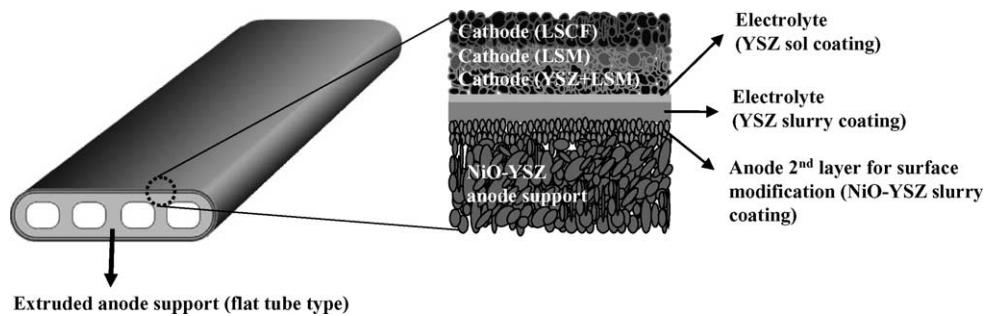


Fig. 1. Schematic diagram of anode-supported SOFC single cell.

Table 1
Slurry compositions for dip-coating of cell components

	Ceramic powder (g)				Dispersant, fish oil (cm ³)	Homogenizer, Triton-X 100 (cm ³)	Binder, PVA (g)	Plasticizer, dibutyl phthalate (cm ³)	Solvent (cm ³)	
	NiO	YSZ	LSM	LSCF					Toluene	IPA
Anode second layer for surface modification	53	42			2	2	10	10	168	366
Electrolyte		100			2	2	10	10	168	336
Cathode first		24	36		3.75	3.75	15	15	87.5	175
Cathode second			60		3.75	3.75	15	15	87.5	175
Cathode third				60	3.75	3.75	15	15	87.5	175

of extruded anode supports were modified via synthesizing fine NiO–YSZ functional layers for easy build up of thin and defect-free YSZ electrolyte layers. The YSZ electrolyte layers were characterized by nitrogen permeation tests and scanning electron microscopy. Lastly, their effects on the improvement of SOFC performance are also reported.

2. Experimental

A NiO–YSZ anode support was prepared by extrusion method [12], and dip-coating processes were used to prepare SOFC unit cells. As depicted in Fig. 1, a flat tube type cell was chosen for the SOFC structure because of its short current paths and its facility for cell stacking.

The slurry compositions for dip-coating of the cell components are summarized in Table 1. First, fine NiO–YSZ layer was synthesized on the anode support for the surface modification. The slurry for surface modification of the anode sup-

port was prepared by using the commercial YSZ (TZ-8YS, Tosoh Co., Japan) particles and the synthesized NiO particles. The submicron sized NiO particles were obtained via a precipitation method. Table 2 shows the coating sequence for the synthesis of the anode-supported electrolyte structure. The electrolyte layer was fabricated on the modified anode support using the YSZ slurry coating and the sol–gel method in series to form a thin and dense layer. Each coated layer was dried at 300 °C for 1 h and sintered at 1400 °C for 3 h. The cathode consisted of functionally graded layers of LSM–YSZ composite, LSM, and LSCF. The cathodes were co-fired at 1200 °C for 3 h.

The morphology and thickness of the layers were observed using scanning electronic microscopy (SEM; model S4200, Hitachi, Ltd., Japan). The pore size distribution and porosity of anode support were measured by mercury porosimetry (Model Autopore II, Micrometrics Instrument Corp., USA). The N₂ gas permeability of electrolyte layer was detected using a bubble flow meter (Model Optiflow 420, Agilent Tech-

Table 2
Coating sequences for anode-supported electrolytes

Sample no.	Anode second layer for surface modification, NiO–YSZ slurry coating (no. of coating)	Electrolyte layer	
		YSZ slurry coating (no. of coating)	YSZ sol coating (no. of coating)
Cell 1		1	
Cell 2		1	1
Cell 3	1	1	
Cell 4	1	2	
Cell 5		2	2
Cell 6	1	1	1
Cell 7	1	1	3
Cell 8	1	1	2

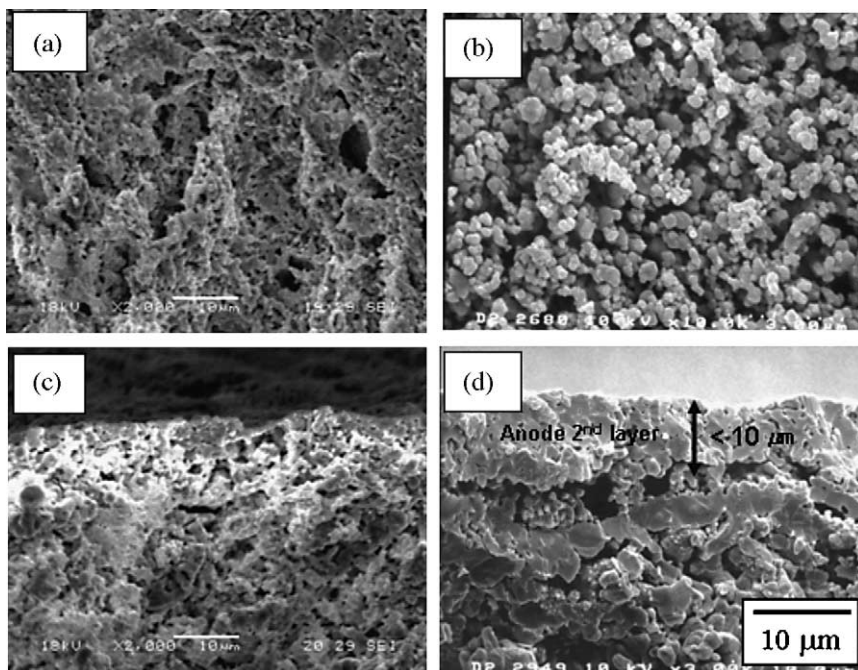


Fig. 2. SEM micrographs of anode support: (a) plan view of as-extruded anode support; (b) plan view of surface-modified anode support; (c) fracture surface of as-extruded anode support; (d) fracture surface of surface-modified anode support.

nologies, USA). The performances of a single cell were evaluated at various temperatures (700–850 °C) in reactive gases of humidified hydrogen with 3% H₂O and air (H₂/air = 1/3).

3. Results and discussion

3.1. Surface modification of NiO–YSZ anode support

Fig. 2 shows the microstructure changes of the anode supports attributed to the surface modification. After synthesiz-

ing the anode second layer with fine NiO–YSZ particles, large defects disappeared and the pores of the surface were minutely and uniformly distributed (see Fig. 2b and d). The data in Fig. 3 shows that the support has the proper pore distributions (>1 μm) and the proper functional layer pore size (0.24 μm). On the other hand, sufficient gas flow must be supplied to the reaction sites for the efficient electrical reactions, even after surface modification. Naturally, the nitrogen permeabilities slightly decreased after surface modification as

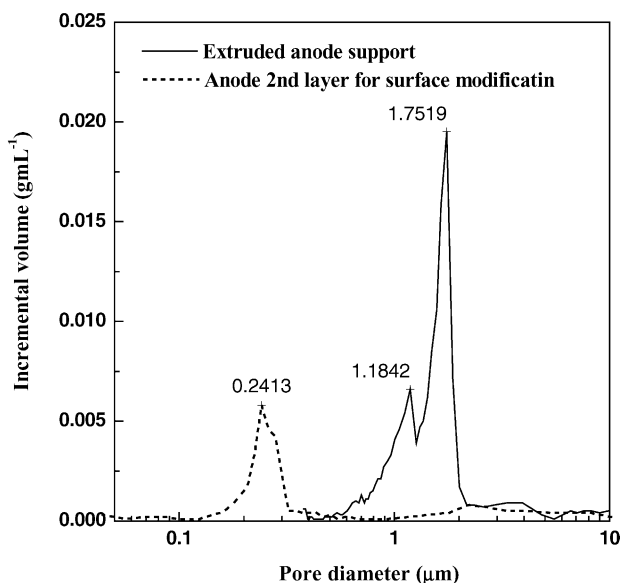


Fig. 3. Pore-size distributions of NiO–YSZ anode supports.

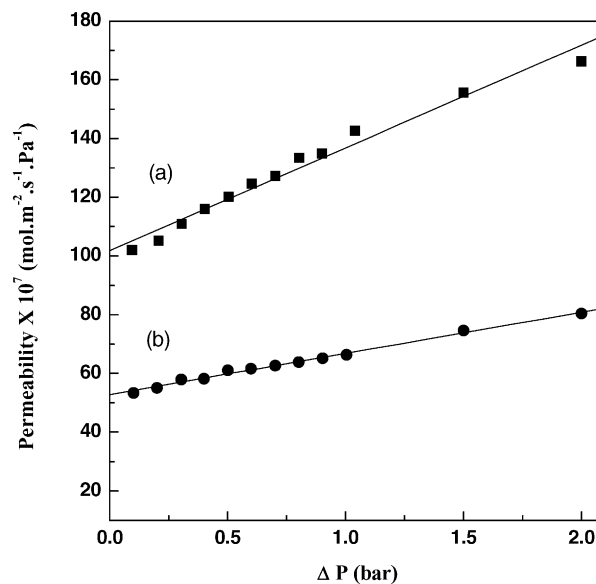


Fig. 4. N₂ Permeabilities of extruded anode support: (a) as-extruded anode support; (b) surface-modified anode support.

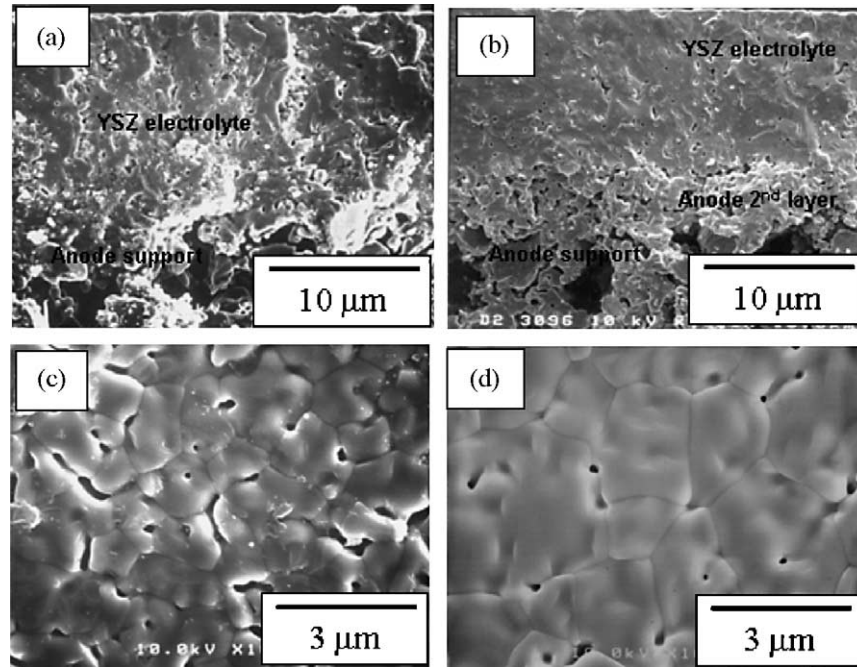


Fig. 5. SEM micrographs of anode-supported electrolytes: (a) fracture surface of cell 1; (b) fracture surface of cell 3; (c) plan view of cell 1; (d) plan view of cell 3.

can be seen in Fig. 4. However, the drop rate of the nitrogen permeabilities through the thin anode second layer was so trifling that it is acceptable for using it as gas channels. Consequently, the defects of the electrolyte were significantly eliminated by the surface modification of the support (see Fig. 5).

3.2. Characteristics of YSZ electrolyte

Thin and dense YSZ electrolyte layers are readily synthesized via the sol-gel method due to their fine structure and high reactivity compared to the conventional ceramic colloidal process. However, the YSZ sol gets into the substrate

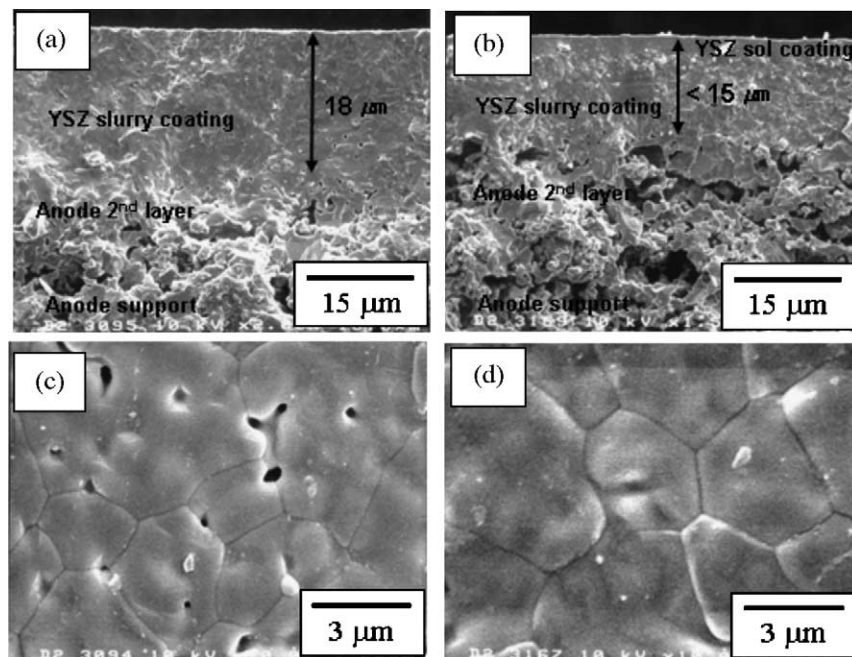


Fig. 6. SEM micrographs of anode-supported electrolytes: (a) fracture surface of cell 4; (b) fracture surface of cell 8; (c) plan view of cell 4; (d) plan view of cell 8.

by capillary action when the solution comes in contact with porous surfaces. YSZ electrolyte layers are thus desirable to be synthesized by both the slurry dip-coating process and the sol-gel synthesis. Fig. 6 shows cross-sectional and plan view images of YSZ electrolyte layers. When the electrolyte layers were built up by a repeated slurry-coating process (see Fig. 6a and c) pin-holes still remained, and the thickness of the layer increased in proportion to the dipping times. The defects could be removed by sol-gel coating. In this work, a fully dense electrolyte layer (see Fig. 6b and d) could be obtained by slurry coating (one time) and repeated sol-gel coating (two times) and the thickness of YSZ electrolyte layers could be controlled below 15 μm .

The effects of coating layers onto the nitrogen permeabilities of anode-supported electrolytes at room temperature are given in Fig. 7. Gas permeability tests are usually applied to estimate the characteristics of membranes. From the comparative results of cell 2 with cell 6, the flatness of the support could be a decisive factor in the formation of a defect-free electrolyte layer. The N_2 permeability decreased with the number of slurry coatings as can be seen in cell 3 and cell 4. However, the thickness of the electrolyte also increased considerably with the coating times and gas tight electrolyte layers could not be obtained just by repeated YSZ slurry coating. Therefore, the sol-gel synthesis was introduced in order to produce the thin and fully dense YSZ electrolyte layer. Consequently, the YSZ layer (cell 8) was estimated to be acceptable as an electrolyte film for SOFC from the result of the gas impermeability in the range below 2 bar.

3.3. Single cell performance

Fig. 7 shows a comparison of cell performance with anode-supported electrolytes prepared by the different coat-

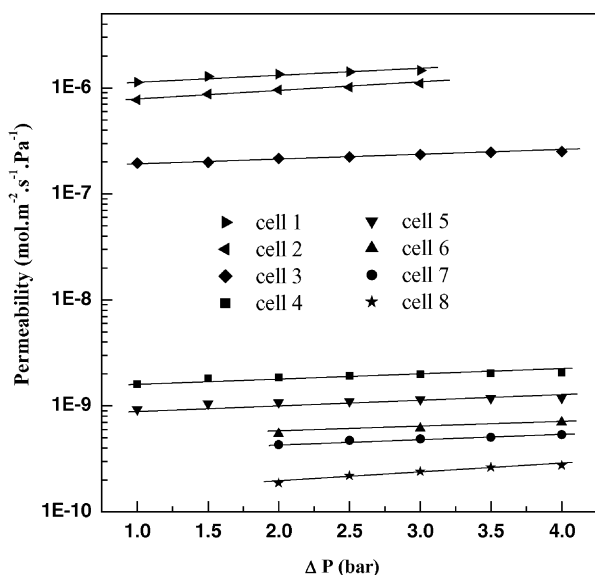


Fig. 7. N_2 permeabilities of anode-supported electrolytes.

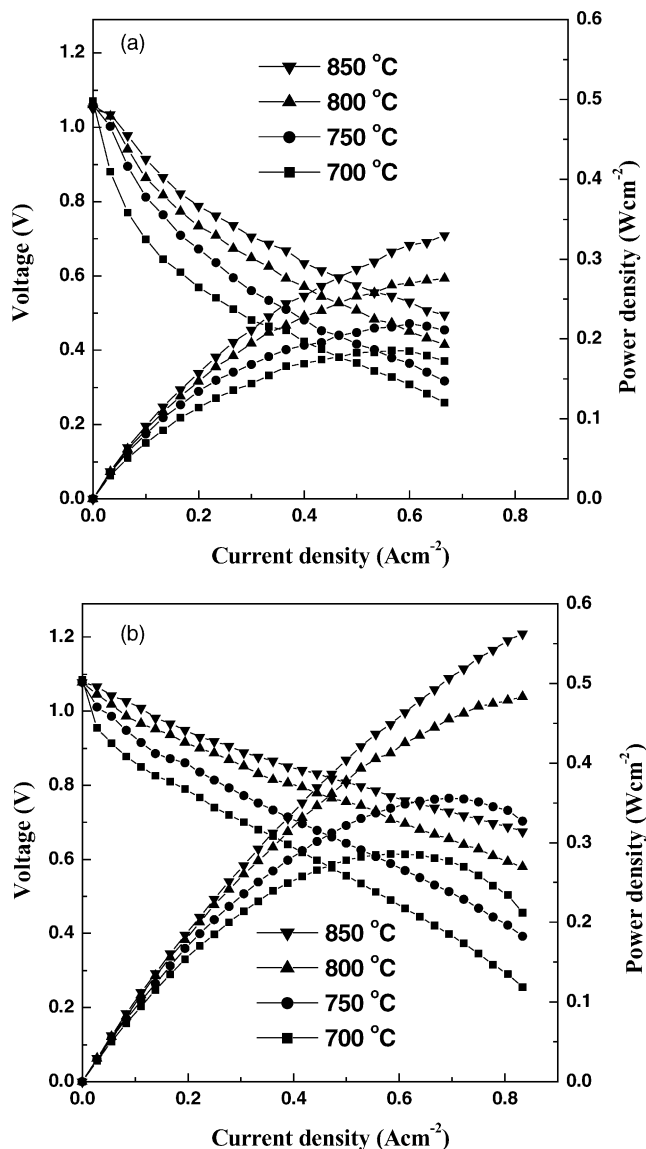


Fig. 8. Performance curves of the anode-supported single cell at various temperatures in reactive gases of humidified hydrogen with 3% H_2O and air ($\text{H}_2/\text{air} = 1/3$): (a) single cell using cell 4; (b) single cell using cell 8.

ing processes using cell 4 and cell 8, respectively. In both cells, the open circuit voltages keep a stable value in the range of 1.06–1.08 V with increasing temperature. In Fig. 8a, the IR drop due to the electrical resistance through the electrolyte is so large that the maximum power density is below 0.35 mW cm^{-2} at 850°C . However, the unit cells test in Fig. 8b show a good electrical performance of 0.56 mW cm^{-2} at 850°C and the power density at 700°C still reaches about 0.3 mW cm^{-2} . This is attributed to the reduced resistance through the thin and gas tight YSZ electrolyte. From this point of view, the thin sol-gel coating of YSZ electrolyte layers is a suitable technique for intermediate temperature application of SOFCs.

4. Conclusions

Anode-supported electrolyte thin films have been manufactured by the wet-chemical process. NiO–YSZ anode supports were prepared by the extrusion method and their surfaces were modified via slurry coating of fine NiO–YSZ particles. Anode-supported YSZ electrolytes were fabricated by dip-coating YSZ slurry and YSZ sol–gel coating. The thickness of YSZ electrolyte layers could be controlled below 15 μm and the YSZ layers were estimated to be acceptable as an electrolyte film for SOFC from the result of the gas impermeability in the range below 2 bar. The unit cells fabricated in this work showed a good electrical performance of 550 mW cm^{-2} at 850°C and the power density at 700°C still reached about 0.3 mW cm^{-2} attributed to the reduced resistance through the thin YSZ electrolyte. The results of this study indicate that the IR-drop due to the electrical resistance through the electrolyte can be controlled via synthesizing the thin and dense electrolyte membrane.

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