

Fabrication of anode supports for solid oxide fuel cells using nickel carbonate as a pore former

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A method of fabricating NiO-YSZ (yttria stabilized zirconia) anode substrates was developed using a new pore former, i. e. nickel carbonate $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, which enables both the shrinkage and porosity, which must be compatible with the that of the electrolyte film and sufficient for the fuel supply and exhaust, respectively, to be easily tailored. In particular, the successful use of nickel carbonate as a pore former, instead of the previously used pore formers, such as graphite, carbon black, and polymer beads, suggests that other zirconium or nickel compound derivatives have the potential to be used as pore formers.

Key words: Solid oxide fuel cell, Anode, Pore former, Electrolyte, Nickel carbonate.

Introduction

Solid oxide fuel cells (SOFCs) have received a great deal of attention as a promising system for electrical power generation because of their high power conversion efficiency and pollution-free operation [1-4]. In particular, SOFCs based on anode supports have been under active research in the past few decades, due to their excellent performance, especially in the intermediate temperature region [1, 2]. Nickel oxide-yttria stabilized zirconia (NiO-YSZ) composite material is most frequently used as the anode in solid oxide fuel cells, because of its high electrical conductivity, high electrochemical activity for the oxidation of hydrogen, high thermodynamic stability, and compatibility with the other components of the cell [1, 5, 6].

To maximize the fuel-oxidation reaction and the resultant cell performance, the anode used as the substrate of the electrolyte film should have sufficient porosity to supply the fuel and remove the reaction products [7]. The pore channel network developed by the connected pores provides pathways for transporting the fuel to the sites of the triple phase boundary (TPB) and its oxidation products and water vapor away from these sites. The degree of concentration polarization can be minimized during the operation of the SOFC, provided that the rapid diffusion of the fuel and the reaction products occurs through the whole anode substrate [7]. The electrical conductivity of the anodes should also be high enough to transport the electrons produced by the fuel-oxidation reaction to the external current collector, in order to prevent electrical polarization [7]. Moreover, good compatibility with the other fuel cell components,

such as the matching of its sintering shrinkage and thermal expansion coefficient with those of the electrolyte, is necessary for high quality anodes of SOFCs [8-13].

Many methods have been proposed [4, 9, 14-16] to provide anode substrates with suitable porosity for gas diffusion. The most effective and popular method of forming a porous microstructure is the addition of pore formers to the NiO-YSZ composite powders [10]. Flour, rice or corn starch, graphite and spherical polymers are widely used as pore formers [10, 12, 17]. The microstructure and pore structure are also significantly influenced by the size, shape and quantity of the pore formers [18, 19]. In fact, not only the porosity, but also the sintering shrinkage, are of great importance in the successful fabrication of anode-supported electrolyte film cells and, therefore, the sintering shrinkage of the anode should be close to that of the electrolyte film, in order to decrease the stress between them upon sintering [7]. The immoderate stress caused by shrinking mismatch may produce cracks in the electrolyte film, distort the fuel cell and, in turn, diminish the cell performance [11]. Nickel carbonate $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ was used in this study as a new pore former. The anode substrate and anode functional layer prepared with the newly suggested pore former have the potential to provide appropriate porosity as well as suitable shrinkage that matches well with those of the YSZ electrolyte film.

Experimental Procedure

Commercially available YSZ containing 8 mol.% Y_2O_3 (TZ-8YS, Tosho Co., Shunan, Japan) and NiO (NiO-FP, Sumitomo Metal Mining Co., Ltd., Tokyo, Japan) powders were used for the fabrication of the NiO-YSZ anode substrate. The average particle sizes of the YSZ and NiO powders as determined by a particle size

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Table 1. Compositions of powder mixtures used for anode substrate and anode functional layer

Compositions of powder mixtures used for anode substrate:

Symbol	Methanol (g)	8 YSZ (g)	NiO (g)	Graphite (g)	PMMA (g)	$\text{NiCO}_3 \cdot 2\text{Ni(OH)}_2 \cdot 4\text{H}_2\text{O}$ (g)	Ni(OH)_2 (g)
GR13	40	44	56	12.5			
PM12	40	44	56		11.7		
NC17	40	44	39.2			16.8	
NC20	40	44	35.8			20.2	
NC21	40	44	34.7			21.3	
NC22	40	44	33.6			22.4	

Composition of powder mixture used for anode functional layer:

NH	40	44					56
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analyzer (LS 13 320, Porous Material Inc., Brea, CA, USA) were 0.2 and 0.3 μm , respectively. Poly(methyl methacrylate) (PMMA) (LDX-50, Sunjin Chem. Co., Ltd., Ansan, Korea), graphite (F50, Kuraray Co., Ltd., Tokyo, Japan) and nickel carbonate ($\text{NiCO}_3 \cdot 2\text{Ni(OH)}_2 \cdot 4\text{H}_2\text{O}$) (Junsei Chemical, Tokyo, Japan) powders were used as the pore formers. The average particle size of the PMMA spheres was determined to be 5 μm by the manufacturer. The powder mixtures for the anode substrate were prepared according to the compositions indicated in Table 1. Each powder mixture was ball milled in a polyethylene bottle for 24 h with a methyl alcohol medium. The slurry of powder mixtures was dried at 50 °C overnight and then ground in an agate mortar to form powders for pressing.

These powders were pressed into disks 20 mm in diameter at a pressure of 12.7 MPa. The powder compacts then were pre-sintered at 1050 °C for 30 minutes to obtain sufficient mechanical strength for handling. This pre-sintering was conducted at a heating rate of 0.5 °C/minute up to 600 °C and then 5 °C/minute from 600 °C to 1050 °C, for the complete burning-out of the organic additives and PMMA. After measuring the dimensions and weights of the pre-sintered compacts, they were sintered by heating them at a rate of 5 °C/minute to 1400 °C and holding them at this temperature for 3 h. The dimensions and weights of the sintered compacts were also measured and then they were heat-treated at 950 °C for 5 h in argon gas containing 5 vol.% hydrogen for the purpose of reducing the NiO in the sintered compacts to Ni. Then, the dimensions and weights of the reduced disks were measured again. These measurements were conducted to determine the linear shrinkage that occurred during each heat-treatment process and the resultant porosity of the disk.

The porosity of the reduced disks (anode substrates) was measured by the Archimedes method. The gas permeability of the reduced anodes was determined using a capillary flow meter (CFP-1500 AEL, Porous Material Inc., Ithaca, NY, USA), and the electrical conductivity was measured by the 4-point probe

method (CMT-SR1000N, Chang Min Co., Ltd., Sungnam, Korea) using a DC power supply (UP-3005D, Unicorn Tech Co., Ltd., Anyang, Korea) and a digital multimeter (Model 2000 6-1/2-Digit DMM, Keithley Instruments Inc., Cleveland, OH, USA). The mechanical strength of the anodes was also determined using a bi-axial method (ISO6872 : 2008E, AG 500E, Shimadzu Co., Kyoto, Japan) and their microstructures were observed by scanning electron microscopy (SEM, S-4200, Hitachi High-technologies Co., Ltd., Tokyo, Japan). The anode functional layer and YSZ electrolyte films were deposited on the pre-sintered anode substrates by the slurry dip coating technique [20] and co-sintered at 1400 °C for 3 h in air. The detailed procedures used for fabricating the functional layer and the electrolyte film on the anode substrate are described in the next section.

Results and Discussion

The porosity of the anode substrate in fuel cells affects their performance and, hence, from this perspective, should be as high as possible. However, the mechanical strength and electrical conductivity of the substrate should also be considered in the fabrication of fuel cells [7]. These factors decrease with increasing porosity, which is not desirable for the cell performance and, hence, a porosity of around 40 vol.% is usually regarded as most appropriate [21]. Besides, the matching of the sintering shrinkage between the anode substrate and electrolyte film is very important for the formation of an electrolyte film on the anode substrate [2]. Since the sintering shrinkage of YSZ was determined to be 22% [7], the shrinkage of the anode substrate should be controlled to be close to this value.

Fig. 1 shows the variation of the porosity after the reduction treatment and sintering shrinkage of the anode substrate with the amount of pore former added to the powder mixture (56 wt.% NiO-44 wt.% YSZ). The first two characters in the upper abscissa denote the sort of pore former that was used (e.g., GR = graphite, PM = PMMA, NC = nickel carbonate,

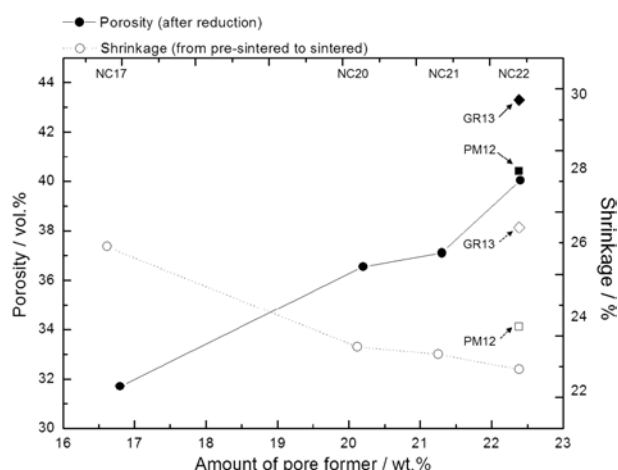


Fig. 1. Variations of the porosity and sintering shrinkage of the anode substrate with the amount of pore former added to the powder mixture (56-x wt.% NiO-x wt.% $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ -44 wt.% YSZ).

NH = nickel hydroxide) and the following digits are the amount of pore former that was replacing NiO in the powder mixture. As would be expected, the porosity increases with an increase in the amount of pore former (nickel carbonate). The sintering shrinkage, however, decreased with an increase in the amount of nickel carbonate added, and reached around 22%, which is close to the sintering shrinkage of the YSZ electrolyte film. When the amount of nickel carbonate added was 22.4 wt.% (NC22), the porosity and sintering shrinkage reached 40.0 vol.% and 22.5%, respectively.

Figs. 2(a) and (b) show the microstructures of the anode substrate fabricated by adding up to 11.7 wt.% of the PMMA spheres. Spherical pores with a diameter of about 5 μm are homogeneously distributed throughout the anode substrate and are connected to each other to form a pore network channel. The microstructures of the anode substrate fabricated by adding up to 12.5 wt.% of graphite are also shown in Figs. 2(c) and (d). Plate-like shaped pores with a diameter of about 2-5 μm are distributed throughout the anode substrate and are also connected to each other to form a pore network channel. The microstructure between the pores, however, is rather dense, as can be seen in the figures, and this is believed not to facilitate the occurrence of electrochemical reactions at the triple phase boundaries [7]. To improve the microstructure by creating micro-pores between the pores, the pore former was replaced by nickel carbonate. Due to the volumetric change arising from the phase transformation from $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ to NiO during sintering, micro-pores developed at the sites of the nickel carbonate particles. As shown in Figs. 2(e) and (f), the microstructure in the anode substrate to which nickel carbonate was added was more uniform and microporous than that of the anode substrate in which PMMA or graphite was used alone as the pore former (Figs. 2(a)-(d)). On the other hand, the sintering

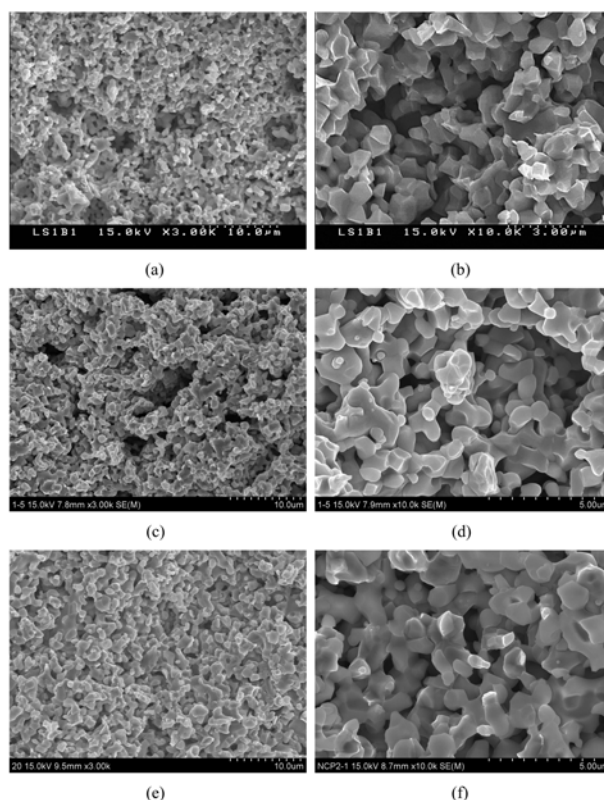


Fig. 2. SEM micrographs showing the microstructures of the anode substrate fabricated by adding (a) and (b) 11.7 wt.% PMMA (PM12), (c) and (d) 12.5 wt.% graphite (GR13) and (e) and (f) 22.4 wt.% $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (NC22).

shrinkage of the anode substrate must be close to that of the electrolyte film (22%), as mentioned above. Therefore, the porosity (40.0 vol.%), sintering shrinkage (22.5%), and resultant microstructure of this anode substrate material (NC22) are considered to satisfy the requirements for high-performance anodes quite well.

The advantages of using the new pore former, nickel carbonate $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, include the fact that its surface characteristics are likely to be similar to those of the oxide powders used for the anode substrate materials and that, in contrast to those of graphite, the particles of the new pore former are nonporous. Furthermore, this pore former additive is based on the same element as one of the ingredients constituting the anode substrate material, Ni, and transforms into nickel oxide during sintering. This concept for choosing the pore former could be extended to the use of other nickel and/or zirconium compound derivatives, such as nickel hydroxide, zirconium carbonate, etc. [7].

Fig. 3 shows the variations of (a) the electrical conductivity at room temperature and (b) the bi-axial strength of the anode substrates with the amount of pore former. Both the electrical conductivity and bi-axial strength decrease monotonically with an increasing amount of nickel carbonate, which is attributed to the increase in porosity afforded by the addition of nickel carbonate, as noted in Fig. 1. Similar behaviors of the

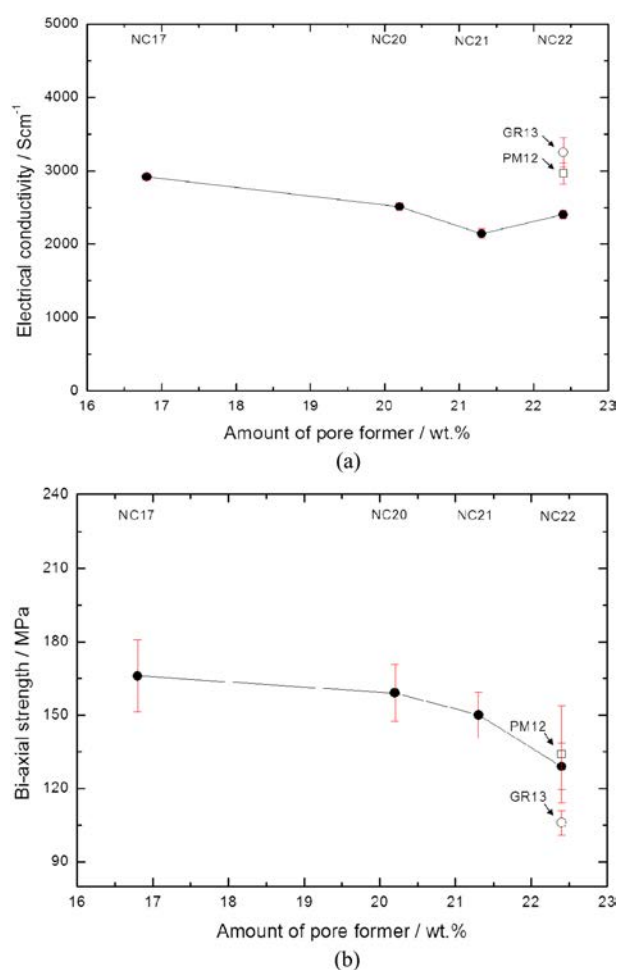


Fig. 3. Variations of (a) electrical conductivity at room temperature and (b) bi-axial strength of the anode substrates with the amount of pore former.

electrical conductivity and mechanical strength were also observed for the anode substrate to which PMMA was added, but the latter is likely to be slightly superior to the former.

The large-size pores formed at the PMMA or graphite particle sites during sintering are believed to contribute to the gas phase transport. However, the micro-pores in the microstructure formed by the addition of the micro-pore former (nickel carbonate) and also formed during the reduction process, would greatly increase the length of triple phase boundaries (TPBs), which is crucial for the cell performance [1]. The small size pores provided by the addition of the micro-pore former are therefore considered to greatly enhance the cell performance. The electrical conductivity and mechanical strength of the nickel carbonate added anode substrate (NC22) were determined to be 2403 S/cm and 129 MPa, respectively, which are much higher than those reported for Ni-YSZ composite anode substrates having the same level of porosity [22, 23]. Furthermore, the gas permeability was also measured to be $0.077 \text{ cm}^2/(\text{cm H}_2\text{O min})$, which is higher than the normally reported value [24].

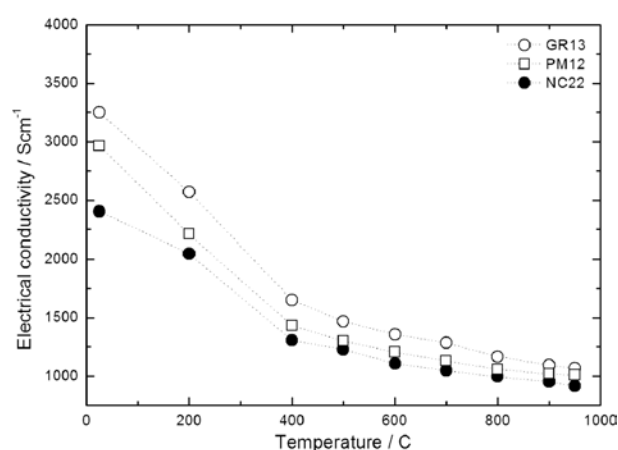
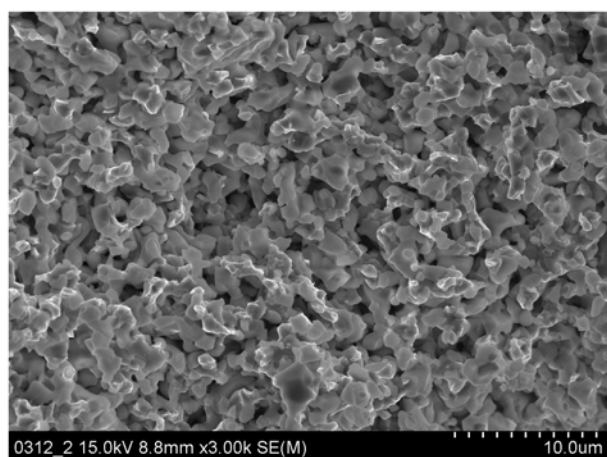


Fig. 4. Electrical conductivities of the anode substrates (e.g., GR13, PM12 and NC22) prepared in this study plotted as a function of temperature.

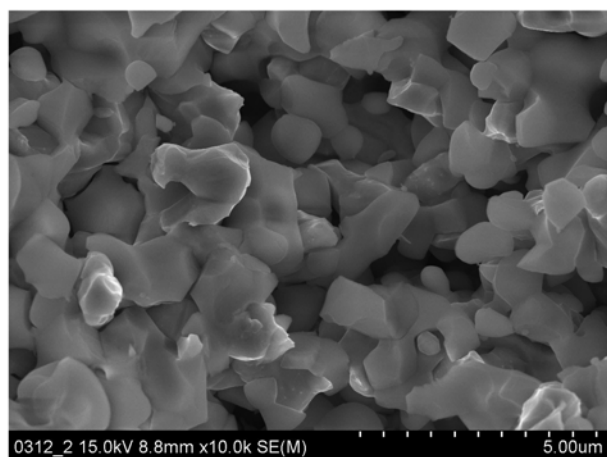
The anode must have sufficiently high electrical conductivity for electron flow in a reducing environment at its operating temperature. The electrical conductivities of the Ni-YSZ anode substrates prepared in this study are plotted as a function of temperature in Fig. 4. Their electrical conductivities of more than 10^3 S/cm at their normal operating temperature, e.g., 750°C , are higher than the literature values measured for anode substrate materials with the same level of porosity [23]. Their conduction behaviors follow typical metallic behavior, where the conductivity decreases with increasing temperature, indicating that the conduction occurs through the Ni connections. The GR12, PM13, and NC22 samples could be used as the anode of an SOFC, since their electrical conductivities are sufficiently high and their strength and porosity are in the acceptable range.

On the other hand, lowering the operation temperature of solid oxide fuel cells may allow a significant cost reduction by extending the materials available for constituting SOFC systems [25-27], and this can be achieved by reducing the thickness of the electrolyte film layer developed on the anode substrate. The interfacial resistance between the electrolyte and the anode substrate, however, becomes dominant at intermediate temperatures and has an effect on the performance of the cell. Multi-layer anode structures, such as those consisting of an anode functional layer formed on the anode substrate, have therefore been proposed [25, 26, 28]. By constructing the anode functional layer with a finer microstructure and making use of the resultant increase of the triple phase boundary length, the activation polarization due to the interface resistance can be minimized [25, 26, 28, 29].

Figs. 5(a) and (b) show the microstructure of the anode functional layer fabricated by replacing NiO with nickel hydroxide $\text{Ni}(\text{OH})_2$. Pores with a size of about $1 \mu\text{m}$ were homogeneously distributed throughout the functional layer and were connected to each other



(a)



(b)

Fig. 5. SEM micrographs showing the microstructures of the anode functional layer fabricated by adding 56 wt.% Ni(OH)₂.

to form a pore network channel. Based on the fact that the porosity of the functional layer prepared without replacing NiO by Ni(OH)₂ was determined to be 24.5 vol.% after a reduction treatment, the net contribution of the total replacement of NiO by Ni(OH)₂ to the porosity is estimated to be 14.1 vol.%. Note that the porosity of the functional layer prepared with 56 wt.% Ni(OH)₂-44 wt.% YSZ after reduction was 38.6 vol.%. Such an anode functional layer with a finer microstructure is believed to provide more electrochemically active surfaces (triple phase boundaries) and thus improve the cell performance.

To fabricate the functional layer on the anode substrate pre-sintered at 1150 °C for 1 h, a dip coating slurry was prepared by replacing NiO with nickel hydroxide Ni(OH)₂, with a composition of 56.0 wt.% Ni(OH)₂-44 wt.% YSZ. The powder mixture used for the function layer was ball-milled for 24 h with zirconia balls in a liquid medium consisting of methyl alcohol containing 4 wt.% of DISPERBYK 110 (BYK-Chemie Co., Wesel, Germany) as a dispersant. After adding 8 wt.% of polyvinyl butyral resin binder (Butvar B-98, Solutia Inc., St. Louis, MO, USA) and

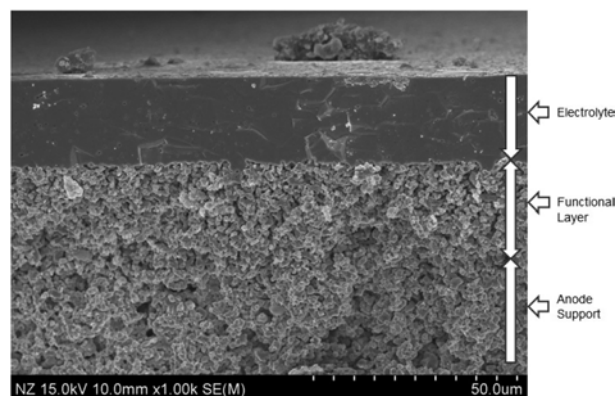


Fig. 6. SEM micrograph showing the microstructure of the anode functional layer and electrolyte film coated anode substrate.

4 wt.% of DOP (Diocetyl phthalate, 99.0%, Samchun Pure Chem. Co., Ltd., Pyongtack, Korea) plasticizer, the slurry was further ball-milled for 5 h. The solid loading of the dip coating slurry was then controlled to be 8 wt.%. The functional layer was formed on the pre-sintered anode substrate using a dip coating machine by conducting a coating process two times, in which the substrate is held in the slurry for 30 seconds in each case. The anode substrate, on which the functional layer was coated, was dried at 50 °C for 1 h and heat-treated at 1150 °C for 1 h, and then an electrolyte film layer was also formed on the heat-treated functional layer by the same dip coating process. For this process, the slurry used for the electrolyte film coating was prepared by the same process as that of the slurry used for the functional layer coating. The functional layer-coated anode substrate was dipped twice into the slurry for 30 seconds using the dip coating machine and then dried at 50 °C for 1 h. The anode substrate on which the functional layer and electrolyte film were coated was sintered at 1400 °C for 3 h.

Fig. 6 shows the cross section of the electrolyte film/anode functional layer/anode substrate structure, which was sintered at 1400 °C for 3 h and reduced at 950 °C for 5 h by Ar gas containing 5% H₂. The electrolyte film layer was about 20-μm thick and was fully densified without any defects, as shown in the figure. The key challenge was still the fabrication of fully dense YSZ electrolyte thin films onto porous anode supports without any defects (e.g. cracks, pinholes, etc.) [20]. The functional layer smooths the surface roughness of the anode substrate, which is rather rough due to the presence of relatively large pores in its interior, and improves the roughness of the surface on which the electrolyte will sit. This improved surface roughness may reduce the possibility of defect formation in the electrolyte film. Furthermore, the functional layer has a fine and homogeneous pore structure and is tightly bonded with the electrolyte and substrate.

Conclusions

The porosity of an anode substrate to which 22.4 wt.% nickel carbonate pore former was added was 40.0 vol.% after a reduction treatment. It is expected that the small pores produced by the nickel carbonate will increase the length of the TPB. The sintering shrinkage of the anode substrate was 22.5%, which matches well with that of YSZ (22%). Nickel hydroxide as a fine pore former is also successful in creating an appropriate amount (38.6 vol.%) of pores with a suitable size ($\sim 1\ \mu\text{m}$) in an anode functional layer fabricated on an anode substrate.

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