Anode-supported SOFC with thin film of proton-conducting $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\alpha}$ by electrophoretic deposition

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Anode-supported solid oxide fuel cells with a thin layer of proton conducting $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\alpha}$ (BCY) were fabricated by electrophoretic deposition technique using an organic suspension. BCY green films were formed on a graphite-added NiO–BCY substrate. By the classification of particle size distribution by the suitable period of sedimentation yielded a crack-free green film. Sintering of the crack-free green film at 1450°C yielded a dense layer of BCY with the thickness of about $9.2 \pm 0.3 \mu\text{m}$ after sintering at 1450°C. The BCY thin film on the NiO–BCY substrate exhibited conductivity of $1.6 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at 600°C and its activation energy was 0.35 eV. The anode-supported single cell with the BCY thin film resulted in the maximum power density of $74.2 \text{ mW}\cdot\text{cm}^{-2}$ at 600°C.

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1. Introduction

Solid oxide fuel cells (SOFCs) are promising next-gen power generator, because of their high energy-conversion efficiency and fuel flexibility. Common types of SOFCs adopt an oxide ionic conductor as the solid electrolyte layer, such as 8 mol % Y_2O_3 – ZrO_2 (8YSZ). Other types of oxide ionic conductors have been also developed, e.g. 10 mol % Sc_2O_3 – ZrO (10ScSZ), $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ (GDC), and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ (LSGM8282). Some of them have even higher oxide ionic conductivity than YSZ. The oxide ionic conductors commonly have high activation energies: 8YSZ ($\sim 1 \text{ eV}^{(1)}$), 10ScSZ (0.51 – $0.67 \text{ eV}^{(2)}$), GDC (0.61 – $0.86 \text{ eV}^{(3)}$) and LSGM8282 ($0.63 \text{ eV}^{(4)}$). Therefore, high temperature of 800–900°C is usually required for a stable operation of SOFC. However, high temperature operation may reduce the long-term stability, material selectivity, and cost effectiveness. Therefore, many efforts to reduce operation temperature have been devoted.⁽⁵⁾

Nafion117, which is frequently used as a protonic conductor for polymer electrolyte membrane fuel cells, possesses lower activation energy under sufficient humidity: 0.1 – $0.4 \text{ eV}^{(6)}$. Since proton is much smaller in ionic radius than oxide ion, activation energy for proton conduction tends to be significantly small than that of oxide-ionic conduction. Iwahara et al.^(7,8) discovered a high-temperature proton-conducting oxide based on SrZrO_3 and BaCeO_3 . Electrical conductivity and chemical stability of those oxides is variable by doping the trivalent cations such as Y^{3+} .⁽⁹⁾ The activation energy of yttria-doped $\text{BaCeO}_{3-\alpha}$ (BCY) for proton conduction was reported to be around $0.5 \text{ eV}^{(10)}$; there are also reports of even lower values such as $0.35 \text{ eV}^{(11)}$ and $0.29 \text{ eV}^{(12)}$. Therefore, the electrical conductivity is essentially higher below 600°C than that of the oxide ionic conductors.⁽¹³⁾ Therefore, the proton conducting oxides are candidates for intermediate temperature SOFC (IT-SOFC), which can be operated below 600°C. Bi et al.⁽¹⁴⁾ reported on the anode-supported SOFC with $\text{BaZr}_{0.7}$ –

$\text{Y}_{0.2}\text{Pr}_{0.1}\text{O}_{3-\delta}$ film with $30 \mu\text{m}$ thick, and maximum powder density at 600°C was $163 \text{ mW}\cdot\text{cm}^{-2}$. SOFCs with proton conducting thin films have been fabricated using pulsed laser deposition,^(15,16) screen-printing,⁽¹⁷⁾ and electrophoretic deposition (EPD).⁽¹⁸⁾ The series of proton conducting oxides are generally hard to sinter. Therefore, high temperature above 1600°C is required to yield a dense phase of the oxides. In a case of anode-support cell, high temperature sintering may cause a deterioration of anode such as Ni-particle growth and excessive densification of the anode support. For this reason, lower temperature for the co-sintering process is desirable. In this study, BCY thin films were formed using EPD to reduce the sintering temperature. Uchikoshi et al.⁽¹⁹⁾ reported that densities of EPD films are nearly comparable to that of films after the Cold Isostatic Pressing treatment. In order to reduce temperature in the co-sintering process, particle size distribution of a BCY suspension was controlled by sedimentation process of the BCY suspension.

2. Experimental section

2.1 Sample preparations

2.1.1 Preparation of $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\alpha}$ (BCY)

The BCY powders used for the electrolyte layer were prepared by citric-nitrate method.⁽²⁰⁾ The aqueous solution of the nitrates mixture was added drop wise in the aqueous solution of citric acid with magnetic stirring. The mixed solution was evaporated at 80°C and then heated at 100°C for 4 h. The resultant yellow gel precursor was calcinated at 1100°C for 4 h, and then ball-milled in ethanol for 24 h. Crystallography of the prepared BCY powders was characterized by XRD analysis. Particle-size distributions were measured by the dynamic light scattering method (Otsuka Electronics Co., Ltd., ELSZ-2000ZS). The specific surface area of the prepared BCY powder was evaluated by the BET analysis (Microtrac Bell, Co., BELLSORP-mini) and it was $7.88 \text{ m}^2\cdot\text{g}^{-1}$. While, the BCY powder used for the anode substrate layer was prepared by the conventional solid-state reaction starting from the stoichiometric amount of BaCO_3 , CeO_2 , and Y_2O_3 . The mixed powders were pressed into pellet and calcinated at 1200°C for 10 h to yield BCY powder.

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2.1.2 Preparation of NiO-BCY powder and substrate for EPD

The NiO (Sumitomo Metal Mining Co. Ltd.; NiO-FP $d = 0.5$ μm) and the prepared BCY powders were mixed with ball-milling in ethanol for 2 h. The amount of NiO was adjusted 60 wt % in Ni metal equivalent. The dried mixed powder was pressed into pellet at 40 MPa and then calcinated at 1300°C for 4 h. The calcinated pellet was again pulverized into a fine powder of NiO-BCY with ball-milling in ethanol for 24 h. Graphite powder (Hayashi Pure Chemical) was mixed in the BCY-NiO composite powder in the weight ratio 30 wt %, and again pressed into pellet at 40 MPa. The graphite-added NiO-BCY pellets (NiO-BCY-C) were used as a substrate for BCY deposition in the EPD process.

2.2 Formation of BCY thin films

2.2.1 Suspension of BCY particles

The BCY powders prepared by the chemical route were dispersed in acetylacetone added with small amount of I_2 as a charging agent. The concentrations of BCY powder and I_2 were 8.0 and 0.33 $\text{g}\cdot\text{L}^{-1}$, respectively. The mixtures were subjected to ultrasonic agitation for 30 min to obtain a suspension. After standing the suspension for prescribed periods the supernatants of the suspension was used for the EPD process. Zeta-potential was measured for the sample prepared by diluting the above suspension by 100 times with acetylacetone, and was evaluated as +79.6 mV.

2.2.2 Formation of BCY films by EPD

BCY films were formed on the graphite-added NiO-BCY substrate (NiO-BCY-C). The substrate and stainless sheet were soaked in the suspension. The distance between the electrodes was fixed at 1.0 cm. The EPD was carried out applying a constant dc voltage of 30 $\text{V}\cdot\text{cm}^{-1}$ for 3 min. The green films were sintered at 1450°C for 4 h. During the heating process, graphite in the substrate will be oxidized to be carbon dioxide and evaporate around 500°C. Therefore, the added graphite can be also used as a pore-former.²¹⁾ Morphology and elemental mapping of the BCY films were observed with scanning electron microscope (SEM) with energy dispersive X-ray spectrometry (EDX).

2.3 Measurement of the cell properties

For the impedance and i - v measurements of the cell, Pt paste was applied on the surface of the BCY film and anode substrate as the cathode and current collector, respectively.

Both the Pt deposits were led by Pt-wire and sintered at 1000°C. The impedance measurements were performed with the two-terminal configuration in the frequency range of 0.01 Hz–15.0 MHz. For the measurement of SOFC performance, the anode and cathode sides were exposed to H_2 and air gasses passing through a water bubbler at room temperature, respectively. The flow rates of the exposed gases were 100 $\text{ml}\cdot\text{min}^{-1}$. Gas leakage test from the cell and/or inorganic sealer was conducted using He with TCD detector of gas chromatography, and no significant leakage was confirmed. The test cells were heated in the tubular furnace with temperature controller. The impedance measurements and i - v characteristics were conducted with Solartron 1260 impedance/gain phase analyzer connected with 1287A potentiostat/galvanostat.

3. Results and discussion

3.1 Particle size distributions

Particle size distribution of the as-ballmilled BCY prepared by the citrate method was measured by being dispersed in water containing hexametaphosphoric acid as a dispersant. **Figure 1**

Fig. 1. Volume fraction of BCY particles in water prepared by the citrate method. Small amount of hexametaphosphoric acid was added as a dispersant.

Fig. 2. Volume fractions of BCY particles in I_2 -added acetylacetone observed after standing the suspension for 0, 60, 120, and 180 min.

showed the volume distribution of the BCY particles. The BCY exhibited bimodal distribution which has two peaks at 172 and 766 nm. By using the as-ballmilled BCY powder, BCY films were formed on the anode substrate by EPD. Though deposition was achieved for the BCY powder, cracks were observed on the surface of the BCY green films. We judged appearance of the cracks is caused by the inhomogeneity in the particle size distribution. In order to obtain a monomodal size distribution, the BCY particles were classified by sedimentation in the acetylacetone suspension for different periods. Preliminarily, time course of particle size distribution was measured in the optical cell set in the cell holder of the particle size analyzer. During the entire measurement the cell was kept in the cell holder. The laser probe of the analyzer is illuminated only to the center part of the suspension, hence the supernatant. **Figure 2** shows the change in the volume distribution of the BCY particles with time. The suspension initially exhibited bimodal distribution with the weak peak at around 230 nm and the strong peak in the range of 10^4 nm. The peak in higher distribution was not observed in the water dispersion, and it will be assigned to highly aggregated particles. Such the distribution was disappeared after 60 min, and the suspension

Fig. 3. SEM pictures of the surface of the BCY green films prepared using the supernatant of the suspension after standing for (a) 0, (b) 60, and (c) 120 min.

became monomodal distribution. By this time the aggregated particles precipitated on the bottom of the measurement cell which is not illuminated by laser probe. The aggregated particle again appeared at 120 min. Therefore, we judged that the suspension was in the monomodal distribution between 60 and 120 min.

3.2 Morphology control by EPD

Figure 3 shows the surface SEM images of the BCY green films prepared using the suspension sedimented for 0, 90 and 180 min. The film prepared after the 90 min sedimentation was homogeneous and had no cracks. On the other hand, those prepared after 0 and 180 min sedimentation exhibited crack formation, and other part of the films were fairly dense. It should be noted that those cracks were not repaired even after the sintering process. The monomodal distribution after the sedimentation can be one of reasons for formation of the crack-free film. Formation and propagation of cracks on a wet-processed film is mainly caused by tensile stress during drying process, and starts from defects in the film.²²⁾ The particle size inhomogeneity seen in Fig. 2 may produce such the defect in the deposition. Modifying other condition such as solvent, evaporation speed control and use of a binder may suppress the crack formation. In this study, we selected the 90 min sedimentation as a crack-free condition. Then, the crack-free green film was sintered at 1450°C for 4 h. To avoid barium evaporation at high temperature, the BCY deposited Ni-BCY-graphite was covered with BCY power during the firing. **Figure 4** shows the SEM images of the cross-section and surface of the BCY film after the sintering. A dense BCY layer was observed in the surface picture in Fig. 4(b). From the EDX analysis of the cross-section Ba- and Ce-enriched layer can be assigned to the deposited BCY layer, and its thickness was evaluated as $9.2 \pm 0.3 \mu\text{m}$. We tentatively conclude that the densification at low temperature such as 1450°C is due to effects of EPD and shrinkage of the substrate during the sintering. In fact surface shrinkage of the 30 wt% graphite contained NiO-BCY was 30.4% by sintering at 1450°C. It should be noted that Ni particles are significantly coarsened to 2–6 μm after the sintering even by the low temperature sintering: the size of the NiO particle is originally 0.5 μm . Crystalline segregations with the size of 0.6–1.4 μm were observed in the surface picture. The segregations were not detected by XRD, but Y-enriched spots were observed in the cross-sectional Y-mapping in Fig. 4(f). We assigned the segregations to Y_2O_3 crystal depositions. In fact the Y_2O_3 segregation has been also reported in the sintered analogs,²³⁾ and the segregation can be suppressed by atmospheric control of P_{Ba} and P_{O_2} . In this study, perfect suppression of the segregation was not achieved even by burying the samples in BCY powder during sintering.

3.3 Electrical properties

Dense BCY film with thickness of about 9.2 μm was formed on the NiO-BCY substrate by sintering at 1450°C. Electrical

Fig. 4. SEM pictures and EDX mappings of the BCY film on the NiO-BCY sintered at 1450°C after the EPD process.

resistance of the BCY thin film attached Ni-BCY substrate was evaluated by the a.c. impedance measurement with the both sides of the electrodes being exposed in wet H_2 atmosphere. For the measurement, Pt counter electrode was painted on the surface of the BCY film using Pt-paste and sintered at 1000°C. **Figure 5** shows the Nyquist plots of the test cell observed at different temperatures. The Nyquist plots consisted of ohmic component and a set of several capacitive semi-circles. Both of them were variable with temperature. The semi-circles are attributable to polarization resistances arising from different hydrogen reaction steps on Ni-BCY substrate and Pt counter electrode. **Figure 6** shows temperature dependences of the area specific resistances of the ohmic (R_{ohm}) and polarization components (R_{pol}) evaluated from the Nyquist plots in Fig. 5. The values of R_{pol} were calculated from width of the two intercepts of the semi-circles and the Z' -axis. Both of them exhibited the Arrhenius behaviors. From the slope of the linear fitting curves, activation energies were estimated as 0.32 eV for R_{ohm} and 0.70 eV for R_{pol} . R_{ohm} and R_{pol} are close to each other at 600°C, but contribution from R_{pol} increased with reducing temperature. The activation energy for R_{ohm} is rather close to that reported by Maide et al.¹¹⁾ for the BCY membrane prepared by the dry pressing of the nanopowder (0.35 eV). Therefore, we assigned the ohmic resistance is from the BCY film. The area specific resistance of the BCY film was evaluated as $0.58 \Omega \cdot \text{cm}^2$. Using the averaged thickness of the BCY film (9.2 μm) derives the conductivity of the BCY film as $1.6 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at 600°C. This value is compatible to those reported for the BCY sintered pellets: $6 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ (wet 5% H_2/Ar at 600°C).²⁴⁾ While, the polarization resistance is 0.97

Fig. 5. Nyquist plots of the two-terminal cell of the BCY attached Ni-BCY recorded in wet H_2 atmosphere at (a) 500, 550 and 600°C, and at (b) 350, 400, 450°C.

Fig. 6. Temperature dependences of ohmic (R_{ohm}), polarization resistances (R_{pol}) of the BCY attached Ni-BCY substrate evaluated from the Nyquist plot in Fig. 5.

$\Omega \cdot cm^2$ at 600°C, which can be assigned to the sum of the interfacial resistance between the BCY film and electrodes.

Figure 7 shows i-v and i-p characteristics of the cell operated at 500, 550 and 600°C. The open circuit voltage at 600°C was 0.941 V. This value is slightly lower than the theoretical one, which can be due to the slightly low transport number of proton conduction (0.93 at 600°C) as well as the humidification. The maximum power density at 600°C was $74.2 mW \cdot cm^{-2}$ at a current density of $163.0 mA \cdot cm^{-2}$. The cell performance was not satisfactorily good. For example, Zunic et al.¹⁸⁾ reported a maximum power density of $242 mW \cdot cm^{-2}$ at 600°C in the anode-supported cell with BCY electrolyte film with a thickness of 9.5 μm . The ohmic and polarization resistance of their cell at 600°C are reported as 1.02 and $0.82 \Omega \cdot cm^2$, respectively. **Figure 8** shows the Nyquist plots of the cell under OCV condition. The

Fig. 7. The i-v and i-p characteristics of the single cell measured in wet H_2 at 500, 550 and 600°C.

Fig. 8. Nyquist plots of the two-terminal cell of the BCY attached Ni-BCY recorded under OCV condition at 500, 550 and 600°C.

Fig. 9. Temperature dependences of ohmic (R_{ohm}), polarization resistances (R_{pol}) of the BCY attached Ni-BCY substrate evaluated from the Nyquist plot under OCV condition shown in Fig. 8.

area specific ohmic and polarization resistances at 600°C are 1.75 and $3.08 \Omega \cdot cm^2$, respectively. Both the resistance values are larger than those in Ref. 18. Especially, difference of the polarization resistances is more remarkable. From the Arrhenius plot in **Fig. 9** activation energies of R_{ohm} and R_{pol} were evaluated to 0.33 and 0.98 eV, respectively. Compared to the case in wet H_2 atmosphere (Fig. 6), the activation energy of R_{ohm} is very close. On the other hand that of R_{pol} is much larger, indicating different process having large activation energy. The large value of R_{pol} under OCV would be due to the oxygen reaction process on the Pt cathode. Replacing the Pt cathode by the ordinary used mate-

rial such as LSCF or some composites may further enhance the cell performance.

4. Conclusion

BCY thin films with a thickness of $9.2 \pm 0.3 \mu\text{m}$ were formed by the EPD on Ni-BCY substrate. Classification of the BCY particles into a monomodal size distribution was achieved by the sedimentation in organic suspension, and using the supernatant of the suspension gave a crack-free green by the EPD. A crack-free and dense BCY film with a thickness of $9.2 \mu\text{m}$ was successfully obtained after sintering at 1450°C . The sintered BCY thin film possessed a rather good conductivity, and the anode-supported SOFC exhibited the maximum power density of $74.2 \text{ mW}\cdot\text{cm}^{-2}$ at 600°C .

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