Additive effect of NiO on electrochemical properties of mixed ion conductor $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$

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Perovskite-type mixed protonic and oxide ionic conductors for electrolyte material of solid oxide fuel cells were investigated, focusing on $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb) due to its high ionic conductivity and chemical stability. BZCYYb and NiO-added BZCYYb were evaluated using electrolyte-supported cell (ESC) and anode-supported cell (ASC) samples. 2 wt.% NiO was solid solute into the BZCYYb, resulting in improvement in the sinterability and thermal-expansion behavior. The addition of NiO, however, lead to the deterioration of cell performance. Compared with the ESC, power density of the ASC was much higher due to thin electrolyte, whereas its open-circuit voltage (OCV) was lower. This is due to Ni diffusion from the NiO-BZCYYb anode into the BZCYYb electrolyte during high-temperature co-sintering process at 1350°C. From the results of OCV measurements, 0–2 wt.% NiO was considered to be dissolved in the BZCYYb electrolyte of the ASC, suggesting that controlling Ni diffusion during co-sintering process is essential to achieve higher-performance ASCs using BZCYYb.

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1. Introduction

Solid oxide fuel cells (SOFCs) are promising power generation devices due to their high efficiency. Recently, SOFCs using mixed ion conductors, which can transport both protons and oxide ions, have attracted much attention for wide temperature range operation, because they have low activation energy for proton conduction compared with conventional SOFCs using oxide ion conductors such as Y_2O_3 stabilized ZrO_2 .^{1)–9)} When hydrogen (H_2) is used as fuel, mixed proton- and oxide ion-conducting SOFCs can theoretically achieve higher voltage at high fuel utilization compared with oxide ion-conducting SOFCs on the assumption that cell internal resistances of both SOFCs are the same, because of little or no dilution of H_2 at the anode side.^{10),11)} This indicates the possibility of further high efficiency by using mixed ion conductors for electrolyte. In addition, several studies have reported the possibility of use of mixed proton- and oxide ion-conducting SOFCs for high efficiency methane-fueled operation.^{11)–14)}

A perovskite-type material $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb) exhibits high mixed ionic conductivity and good chemical stability in atmospheres containing CO_2 and H_2O .¹⁵⁾ Currently, due to the resulting high power density, the majority of cell configurations are anode-supported type with thin electrolyte.^{16)–18)} Anode-supported cells (ASCs) with BZCYYb electrolyte are generally fabricated via a high temperature co-sintering process with a NiO-based anode and a BZCYYb electrolyte. Diffusion of Ni from the anode into BZCYYb electrolyte during this co-sintering process improves the sinterability of BZCYYb, resulting in a dense electrolyte layer without defects such as pinholes and cracks.^{19)–21)} However, Ni diffusion generally has a

negative effect for mixed ion conductors, namely, decrease in proton transport number, which leads to lower open-circuit voltage (OCV). Solid solution of Ni into the lattice of mixed ion conductors causes degradation of protonic conductivity due to decrease in proton concentration, resulting in a low proton transport number.²²⁾

In the present study, the electrochemical properties of BZCYYb with NiO addition were investigated to clarify positive and negative effects of NiO addition. First, using electrolyte-supported cells (ESCs), characteristics of NiO-added BZCYYb and pure BZCYYb were compared. Then, the electrochemical performance of an ASC with BZCYYb fabricated via a co-sintering process was evaluated.

2. Experimental procedures

2.1 Fabrication of ESC samples

An electrolyte disk of $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb) with 2 wt.% NiO was prepared as follows using commercial BZCYYb powder ($5.2\text{ m}^2\text{ g}^{-1}$ in specific surface area) and NiO powder ($3.0\text{ m}^2\text{ g}^{-1}$ in specific surface area). The BZCYYb and NiO powders were mixed by ball-milling with ethanol for 24 h, and then dried at 70°C for 48 h. Using the resulting NiO-mixed BZCYYb powder and also pure BZCYYb powder for comparison, 30 mm diameter disks were formed by uniaxial pressing at 20 MPa for 1 min. These disks were sintered at 1350°C for 3 h in air on Al_2O_3 plates whose upper side was covered with BZCYYb powder. After sintering, the diameter and thickness of the disks were 23 and 1.0 mm, respectively. For preparation of the cathode and anode, a Pt paste was painted on both sides of the disks, and then the disks were sintered at 950°C for 2 h in air.

2.2 Fabrication of ASC sample

The same NiO and BZCYYb powders at a weight ratio of 60:40 with pore former were used for the anode substrate material

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prepared as follows. A mixture of these materials was pressed at 20 MPa for 1 min and sintered at 900°C for 1 h in air. A BZCYYb suspension was prepared by ball-milling BZCYYb powder in ethanol and toluene mixture solvent with a small amount of polyvinyl butyral binder, amine-based dispersant, and plasticizer for 48 h. The BZCYYb suspension was deposited on the pre-sintered anode substrate by a spin-coating technique. Then, the anode substrate with BZCYYb was co-sintered at 1350°C for 3 h in air. A cathode paste was prepared by mixing $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) powder and the BZCYYb powder at a weight ratio of 70:30 in α -terpineol solvent with ethyl cellulose, dispersant, and plasticizer. The cathode was prepared by screen-printing the cathode paste on a BZCYYb electrolyte layer and sintered at 1050°C for 1 h in air. The effective area and approximate thickness of the cathode were 0.283 cm² and 50 μm , respectively. In all sintering processes, the samples were placed on an Al_2O_3 plate whose upper side was covered with BZCYYb powder.

2.3 Characterization and measurements

The crystal structures of BZCYYb and NiO-added BZCYYb were characterized using X-ray diffraction (XRD, SmartLab, Rigaku) at room temperature with Cu K α radiation. The step size was 0.01° and the scan speed was 10° min⁻¹. To prepare powders for XRD analysis, the disks were ground into powder using a mortar and a pestle. The open porosity of the disks was determined by the Archimedes method. Thermal-expansion analysis was carried out using a thermomechanical analyzer (TMA, TMA8310, Rigaku) under ambient air atmosphere. For TMA, square column samples of BZCYYb and NiO-added BZCYYb with approximate dimensions of 3 × 3 × 20 mm³ were prepared via the same pressing and sintering procedures as the disks. The temperature range was room temperature to 1000°C and the rates of both heating and cooling were 5°C min⁻¹. The morphology of the ESC and ASC samples was observed using scanning electron microscopy (SEM, JSM-5600, JEOL).

Electrochemical measurements were performed for the ESC and ASC samples. Cell performance was evaluated by current density–voltage (i – V) measurements and electrochemical impedance spectroscopy (EIS) using 3% humidified H₂ to the anode and 3% humidified air to the cathode. In EIS, the frequency range was 1 MHz to 0.1 Hz and the amplitude of applied voltage was 10 mV.

3. Results and discussion

3.1 Comparison in characteristics between pure BZCYYb and NiO-added BZCYYb

Figure 1 shows the XRD patterns with Cu K α radiation for the BZCYYb and NiO-added BZCYYb powder samples sintered at 1350°C for 3 h in air. Both powders clearly exhibited peaks corresponding to the perovskite structure of BZCYYb. A large amount of transition metal additives such as Ni in BZCYYb causes a segregation at the grain-boundary of BZCYYb.²¹⁾ In our samples, peaks of NiO, whose main peaks are usually $2\theta = 37.3$ and 43.3°, were not observed even for NiO-added BZCYYb. Also, the crystal system of NiO-added BZCYYb was a cubic perovskite structure, whereas that of BZCYYb was an orthorhombic perovskite structure where additional and split peaks were observed. These results suggest that 2 wt.% NiO was fully solid solute in the crystal structure of BZCYYb.

Figure 2 shows SEM images of the surface of the BZCYYb and NiO-added BZCYYb disks. Here, both of these disks were sintered at 1350°C for 3 h in air. Although mixed ion conductors involving BZCYYb generally exhibit poor sinterability, these

Fig. 1. XRD patterns for BZCYYb and 2 wt.% NiO-added BZCYYb powders sintered at 1350°C for 3 h in air.

Fig. 2. SEM images of surface of BZCYYb and 2 wt.% NiO-added BZCYYb disks sintered at 1350°C for 3 h in air.

Fig. 3. Thermal-expansion behaviors of BZCYYb and 2 wt.% NiO-added BZCYYb samples under ambient air atmosphere.

images reveal that both disks could be densified by using the very fine starting powders here. The open porosity measured by the Archimedes method was lower than 2 vol.% for both BZCYYb and NiO-added BZCYYb disks. In general, the open porosity is required to be lower than 5 vol.% for use as an electrolyte. The grain size of the NiO-added BZCYYb disk was larger than that of the BZCYYb disk because NiO worked as a sintering aid. These results indicate that both disks can be used for electrolyte material in electrochemical measurements without gas cross-leak.

Figure 3 shows the thermal-expansion behaviors of BZCYYb and NiO-added BZCYYb as a function of temperature for heating and cooling operations at the rate of 5°C min⁻¹ under ambient air atmosphere. The BZCYYb exhibited anomalous expansion behavior between 500 and 800°C during both heating and cooling operations. Also, the curves had a hysteresis loop. This

Fig. 4. i - V characteristics for ESC with either BZCYYb or NiO-added BZCYYb electrolytes at 800°C using 3% humidified H_2 and 3% humidified air.

behavior might be related to different proton concentration between BZCYYb and NiO-added BZCYYb. Yamaguchi et al.²³⁾ reported that the degree of hysteretic behavior of a mixed ion conductor Yb-doped BaCeO₃ (BCYb) depended on the amount of doped Yb, the cooling and heating rates, and humidified condition, and thus they concluded that the anomalous expansion was due to water incorporation. In the BCYb case, proton concentration increased with increasing the amount of Yb up to 0.2 of the B-site of BCYb. Okuyama et al.²²⁾ reported that Ni solid solution decreased the proton concentration of BaZr_{0.2}Ce_{0.6}Y_{0.2}O_{3-δ} (BZCY) because the partial oxygen vacancies produced by the Ni ion substitution on the cation site of BZCY could not take part in the hydration. In our study, the observed anomalous expansion of BZCYYb was considered to be related to the proton concentration in the lattice similar to the cases of BCYb and BZCY. Here, the TMA was measured under ambient air which contained a little amount of water. The water incorporation in cooling operation could therefore occur. For NiO-added BZCYYb, the anomalous expansion was improved to a relatively linear behavior even though a slight hysteresis loop still remained, suggesting that Ni addition decreased the proton concentration of BZCYYb.

Figure 4 shows the i - V characteristics evaluated at 800°C for the ESCs with either BZCYYb or NiO-added BZCYYb disks as electrolyte and Pt electrodes as cathode and anode. The electrochemical performance of the cell with the BZCYYb electrolyte was higher than that with NiO-added BZCYYb electrolyte, namely, 4 times higher maximum power density. Also, the cell with the BZCYYb electrolyte showed the OCV of 1.010 V, that was corresponding to 92% value of the theoretical OCV (1.102 V), even at a high temperature of 800°C, where the mobility of electron holes generally increases and proton concentration decreases due to dehydration from the lattice.^{22),23)} The area-specific resistance (ASR) of the cell with the BZCYYb electrolyte was 2.72 Ω cm², which was estimated from the gradient of the i - V characteristics between 0 and 50 mA cm⁻². Then, we estimated the conductivity of the BZCYYb electrolyte assuming that contribution of Pt electrode polarization for the ASR was negligible because the used BZCYYb electrolyte was thick (1 mm) and the catalytic activity of Pt for electrochemical reaction such as oxygen reduction is very high. The resulting conductivity of 0.037 S cm⁻¹ was appropriate value for barium zirconate-cerate type mixed ion conductors,²⁴⁾⁻²⁷⁾ although that was slightly lower than the previously reported BZCYYb conductivity.¹⁵⁾ For the cell with NiO-

Fig. 5. SEM images of cross-section of ASC with BZCYYb electrolyte fabricated via co-sintering process.

added BZCYYb, the measured OCV (0.787 V) was much lower than the theoretical OCV (1.102 V) due to decreased proton transport number by the NiO addition. Also, the estimated conductivity of the NiO-added BZCYYb electrolyte by the same method as the BZCYYb case was 0.012 S cm⁻¹, which was much lower value than that of the BZCYYb electrolyte. Although NiO addition effectively improved the sinterability and thermal-expansion behavior of BZCYYb, excessive addition would lead to low proton transport number and low protonic conductivity that degrade cell performance.

3.2 Electrochemical performance of ASC with BZCYYb electrolyte

In evaluation of NiO-added BZCYYb, an excessive NiO addition apparently affected proton transport number, resulting in the low OCV value (Fig. 4). Next we fabricated an ASC with BZCYYb via a high temperature co-sintering process of 1350°C and investigated the effect of Ni diffusion from a Ni-based anode into a BZCYYb electrolyte layer. Figure 5 shows cross-sectional SEM images of the ASC. Because the SEM observation was carried out after electrochemical measurements at high temperatures using humidified H_2 fuel, the anode was already reduced from NiO to Ni. A dense BZCYYb electrolyte layer approximately 10 μm thick was formed on the porous Ni-BZCYYb anode. Although the electrolyte layer had a few closed pores, it was successfully densified without significant defects. Also, the electrolyte thickness of 10 μm is generally sufficient to prevent gas cross-leak in ASCs. For example, our previous study actually achieved almost complete gas tightness by a BZCYYb layer even with 5 μm thickness.²¹⁾

Figures 6 and 7 show the i - V characteristics and impedance spectra for the ASC feeding 3% humidified H_2 to the anode and 3% humidified air to the cathode in the temperature range of 600 to 800°C. Due to its thin electrolyte layer, the power density of the ASC (Fig. 6) was much higher than that of the ESC with BZCYYb electrolyte (Fig. 4). This was evident from the ohmic resistance, which was determined by the intercept on the real axis at the higher frequency side of the impedance spectra in Fig. 7. In addition, at these high temperatures, the LSCF-BZCYYb cathode and Ni-BZCYYb anode might have higher activity than the Pt cathode and anode. However, in terms of OCV, the ASC (0.892 V) was inferior to the ESC (1.010 V). Assuming no gas leakage, the lower OCV of the ASC was due to a decrease in ionic transport number of the electrolyte. In the present study, the BZCYYb electrolyte and NiO-BZCYYb anode underwent co-sintering at 1350°C. During this process, a slight amount of Ni was considered to be diffused into the BZCYYb electrolyte, resulting in the decrease in proton transport number.

The measured OCV of each cell and theoretical OCV were compared. In the case of mixed ion conductors, the theoretical OCV can be calculated by the Nernst equation with proton and

Fig. 6. i - V characteristics for ASC with thin BZCYYb electrolyte ($10\ \mu\text{m}$ thick) using 3% humidified H_2 and 3% humidified air.

Fig. 7. Impedance spectra for ASC with thin BZCYYb electrolyte ($10\ \mu\text{m}$ thick) using 3% humidified H_2 and 3% humidified air under OCV condition.

Fig. 8. OCVs of ASC and ESCs with either BZCYYb or 2 wt.% NiO-added BZCYYb disks.

oxide ion transport numbers.¹¹⁾ In this study, each of proton and oxide ion transport numbers of the used electrolytes was not measured, and thus the theoretical OCV was calculated assuming that the ionic transport number was unity. As shown in Fig. 8, the OCV of the ASC was lower than that of the ESC with BZCYYb disk but was higher than that of the ESC with 2 wt.% NiO-added BZCYYb disk. This indicates that the amount of diffused NiO should be 0–2 wt.%. Although just a little amount of NiO precipitates might be located at the grain boundaries of BZCYYb,²⁸⁾ the diffused Ni was considered to be mostly dissolved in the lattice of BZCYYb from the XRD results (Fig. 1). Our results suggest that controlling Ni diffusion during co-sintering is crucial to achieve high OCV in ASCs, particularly in high temperature operation.

4. Conclusions

The high temperature properties of BZCYYb and NiO-added BZCYYb were investigated using ESC and ASC samples. XRD results showed that 2 wt.% NiO was fully solid solute in the lattice of BZCYYb. Although the addition of NiO to BZCYYb effectively improved the sinterability and thermal-expansion behavior, it decreased the electrochemical performance. In particular, OCV was significantly lowered. Due to low ohmic resistance, the ASC exhibited much higher power density compared with the ESC with BZCYYb. The OCV of the ASC was lower, however, even with using BZCYYb suspension without NiO to prepare the electrolyte layer, because Ni diffused from the NiO-BZCYYb anode into the BZCYYb electrolyte layer during the high temperature co-sintering process. Comparison in OCVs among the ESC and ASC samples suggested that 0–2 wt.% NiO was considered to be solid solute in the BZCYYb electrolyte of the ASC. These results suggest that controlling Ni diffusion during co-sintering is essential to achieve higher performance ASCs using BZCYYb.

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References

- 1) H. Iwahara, T. Yajima, T. Hibino, K. Ozaki and H. Suzuki, *Solid State Ionics*, **61**, 65–69 (1993).
- 2) H. Iwahara, T. Yajima, T. Hibino and H. Ushida, *J. Electrochem. Soc.*, **140**, 1687–1691 (1993).
- 3) H. G. Bohn and T. Schober, *J. Am. Ceram. Soc.*, **83**, 768–772 (2000).
- 4) M. Laidoudi, I. A. Talib and R. Omar, *J. Phys. D Appl. Phys.*, **35**, 397–401 (2002).
- 5) S. M. Haile, *Acta Mater.*, **51**, 5981–6000 (2003).
- 6) K. D. Kreuer, *Annu. Rev. Mater. Res.*, **33**, 333–359 (2003).
- 7) P. Babilo, T. Uda and S. M. Haile, *J. Mater. Res.*, **22**, 1322–1330 (2007).
- 8) K. Nomura and H. Kageyama, *Solid State Ionics*, **178**, 661–665 (2007).
- 9) E. Fabbri, D. Pergolesi, S. Licoccia and E. Traversa, *Solid State Ionics*, **181**, 1043–1051 (2010).
- 10) H. Iwahara, T. Esaka, H. Uchida and N. Maeda, *Solid State Ionics*, **3/4**, 359–363 (1981).
- 11) H. Shimada, X. Li, A. Hagiwara and M. Ihara, *J. Electrochem. Soc.*, **160**, F597–F607 (2013).
- 12) W. G. Coors, *J. Power Sources*, **118**, 150–156 (2003).
- 13) S. Hamakawa, K. Sato, T. Inoue, M. Nishioka, K. Kobayashi and F. Mizukami, *Catal. Today*, **117**, 297–303 (2006).
- 14) Y. Matsuzaki, Y. Tachikawa, T. Somekawa, T. Hatae, H. Matsumoto, S. Taniguchi and K. Sasaki, *Sci. Rep.*, **5**, 12640 (2015).
- 15) L. Yang, S. Wang, K. Blinn, M. Liu, Z. Liu, Z. Cheng and M. Liu, *Science*, **326**, 126–129 (2009).
- 16) D. Pergolesi, E. Fabbri and E. Traversa, *Electrochem. Commun.*, **12**, 977–980 (2010).
- 17) F. Zhao, C. Jin, C. Yang, S. Wang and F. Chen, *J. Power Sources*, **196**, 688–691 (2011).
- 18) N. Nasani, D. Ramasamy, S. Mikhalev, A. V. Kovalevsky and D. P. Fagg, *J. Power Sources*, **278**, 582–589 (2015).
- 19) S. Nikodemski, J. Tong and R. O'Hayre, *Solid State Ionics*, **253**, 201–210 (2013).
- 20) C. Duan, J. Tong, M. Shang, S. Nikodemski, M. Sanders, S. Ricote, A. Almansoori and R. O'Hayre, *Science*, **349**, 1321–1326 (2015).
- 21) T. Yamaguchi, H. Shimada, U. Honda, H. Kishimoto, T. Ishiyama, K. Hamamoto, H. Sumi, T. Suzuki and Y. Fujishiro, *Solid State Ionics*, **288**, 347–350 (2016).

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- 22) Y. Okuyama, N. Ebihara, K. Okuyama and Y. Mizutani, *ECS Trans.*, **68**, 2545–2553 (2015).
- 23) S. Yamaguchi and N. Yamada, *Solid State Ionics*, **162–163**, 23–29 (2003).
- 24) Z. Zhong, *Solid State Ionics*, **178**, 213–220 (2007).
- 25) M. A. Azimova and S. McIntosh, *Solid State Ionics*, **180**, 160–167 (2009).
- 26) Z. Shi, W. Sun and W. Liu, *J. Power Sources*, **245**, 953–957 (2014).
- 27) M. Amsif, D. Marrero-López, J. C. Ruiz-Morales, S. N. Savvin and P. Núñez, *J. Eur. Ceram. Soc.*, **34**, 1553–1562 (2014).
- 28) R. Costa, N. Grünbaum, M.-H. Berger, L. Dessemond and A. Thorel, *Solid State Ionics*, **180**, 891–895 (2009).