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Synthesis and Evaluation of Ni Catalysts Supported on $\text{BaCe}_{0.5}\text{Zr}_{0.3-x}\text{Y}_{0.2}\text{Ni}_x\text{O}_{3-\delta}$ with Fused-Aggregate Network Structure for the Hydrogen Electrode of Solid Oxide Electrolysis Cell

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Abstract: Nickel nanoparticles loaded on the electron–proton mixed conductor $\text{BaCe}_{0.5}\text{Zr}_{0.3-x}\text{Y}_{0.2}\text{Ni}_x\text{O}_{3-\delta}$ (Ni/BCZYN, $x = 0$ and 0.03) were synthesized for use in the hydrogen electrode of a proton-conducting solid oxide electrolysis cell (SOEC). The Ni nanoparticles, synthesized by an impregnation method, were from 45.8 nm to 84.1 nm in diameter, and were highly dispersed on the BCZYN. The BCZYN nanoparticles, fabricated by the flame oxide synthesis method, constructed a unique microstructure, the so-called “fused-aggregate network structure”. The BCZYN nanoparticles have capability of constructing a scaffold for the hydrogen electrode with both electronically conducting pathways and gas diffusion pathways. The catalytic activity on Ni/BCZYN ($x = 0$ and 0.03) catalyst layers (CLs) improved with the circumference length of the Ni nanoparticles. Moreover, the catalytic activity on the Ni/BCZYN ($x = 0.03$) CL was higher than that of the Ni/BCZYN ($x = 0$) CL. BCZYN ($x = 0.03$) possesses higher electronic conductivity than BCZYN ($x = 0$) due to the Ni doping, resulting in an enlarged effective reaction zone (ERZ). We conclude that the proton reduction reaction in the ERZ was the rate-determining step on the hydrogen electrode, and the reaction was enhanced by improving the electronic conductivity of the electron–proton mixed conductor BCZYN.

Keywords: electron–proton mixed conductor; proton conductor; hydrogen electrode; solid oxide electrolysis cell; nanostructured materials

1. Introduction

The widespread use of hydrogen in fuel cell vehicles (FCVs) and residential use is expected to reduce CO_2 generation and to lead to better distributed electric power generation. The reforming of hydrocarbons, the electrolysis of water, and the capture of byproduct gases from steel manufacturing are candidate methods of hydrogen generation. In particular, water vapor electrolysis by use of solid oxide electrolysis cells (SOECs) can generate high purity hydrogen, with their highest conversion efficiency at high temperature (700–900 °C). The SOECs can also operate reversibly as a solid oxide fuel cell (SOFC) and thus contribute to the leveling of electric power generation.

SOECs utilizing an oxide-ion conducting electrolyte can generate high purity hydrogen at the hydrogen electrode, but it is necessary to remove a slight amount of unreacted water [1]. SOECs utilizing a proton-conducting electrolyte, however, can produce high purity hydrogen directly at the hydrogen electrode [2–4]. The proton-conducting electrolytes of the SrCeO_3 and BaCeO_3 systems have high conductivity, up to 0.07 S cm^{-1} at 800°C , which is higher than those of the SrZrO_3 and BaZrO_3 systems [5–9]. However, these systems are not chemically stable in the presence of water vapor or CO_2 [9–14]. The $\text{BaCe}_{0.8-y}\text{Zr}_y\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCZY) system has relatively high proton conductivity with thermodynamic stability in the presence of water vapor and CO_2 at high temperature and is a promising candidate electrolyte for SOECs [15–18]. In particular, BCZY ($y \geq 0.3$) showed relatively high proton conductivity at 700°C , with a high proton transference number [19]. He and Rao reported a high electrolysis current density (0.83 A cm^{-2} at 1.5 V) at 700°C by use of a thin BCZY electrolyte (thickness: $30 \mu\text{m}$) [20,21]. Yoo also reported a high electrolysis current density (1.1 A cm^{-2} at 1.3 V) by use of a thin BCZY electrolyte (thickness: $10\text{--}15 \mu\text{m}$) [22].

The electrodes of the SOEC are gas diffusion electrodes, wherein it is required to construct electronically conducting pathways, gas diffusion pathways, and high surface area in the catalyst layers (CLs), with large triple phase boundary (TPB) in order to reduce the overpotential. In the case of oxide-ion conducting SOECs, composites of Ni and the oxide-ion conducting electrolyte are typically used as the hydrogen electrode. Watanabe and coworkers have demonstrated high electrode performance for nanometer-sized Ni dispersed on mixed oxide-ionic and electronic conducting (MOEC) oxides with both a large TPB and large effective reaction zone (ERZ) [23–27]. The design concepts of the electrode are (1) application of materials with a highly conductive MOEC oxide as a porous electrode, (2) enlargement of the ERZ by controlling the microstructure of the porous electrode using MOEC oxides, where oxide-ions, electrons, and reactant gases can have maximum contact, and (3) activation of the reaction by highly dispersed electrocatalysts on the surface of the porous electrode using MOEC oxides. Moreover, Uchida and co-workers also proposed the concept of the double-layer (DL) electrode of CL/current collecting layer (CCL) for the oxide-ion conducting SOEC to enhance the performance of the hydrogen electrodes [28]. The performance of the DL electrode for a oxide-ion conducting SOEC improved with the high dispersion of Ni-based catalysts, the amount of the Ni catalysts in the CL, the volume fraction of μm -sized Ni in the CCL and the porosity and thickness of each layer [29].

In the case of the proton-conducting SOECs, composites of Ni and proton-conducting electrolytes are also typically used as the hydrogen electrode [20–22,30]. In the present study, we have sought to apply the DL electrode (CL: nanometer-sized Ni dispersed on porous mixed proton-electron conducting (MPEC) oxide; CCL: composite of Ni and MPEC oxide) to the proton-conducting SOEC, based on the electrode design concept described above, as shown in Figure 1. The CCL of μm -sized Ni-MPEC oxide cermet is formed on top of the CL to supply a highly electronically conductive layer, with high gas-diffusion rate from the separator (interconnect) to the CL, and an intimate contact between the separator and the CL. The slight amount of Ni doping in the proton-conducting oxide enhanced the electronic conductivity in the oxide [31–34], which was one of the most promising MPEC oxides for applications based on the above concept.

Furthermore, rutile-structured oxide nanoparticles with a fused-aggregate network structure were developed, whose microstructure was similar to that of carbon black and had the ability to provide effective gas diffusion pathways, electron transport pathways and high surface area [35–41]. We expected that nanoparticles with the fused-aggregate network structure would also be well suited for these design concepts for the CLs of a hydrogen electrode in a proton-conducting SOEC.

Figure 1. Schematic image of double layer (DL) electrode for proton-conducting solid oxide electrolysis cells (SOEC).

In the present study, we have focused on the hydrogen electrode for the proton-conducting SOEC.

At first, we sought to synthesize a perovskite-structured MPEC oxide of $\text{BaCe}_{0.5}\text{Zr}_{0.3-x}\text{Y}_{0.2}\text{Ni}_x\text{O}_{3-\delta}$ (Ni/BCZYN, $x = 0$ and 0.03) with fused-aggregate network structure by the flame oxide-synthesis method and to fabricate the hydrogen electrode with highly dispersed Ni nanoparticles loaded on the MPEC oxide CLs with Ni-MPEC oxide cermet CCLs. Next, we evaluated the performance of the hydrogen electrode based on these electrode design concepts.

2. Results and Discussion

2.1. Characterization of Samples

The X-ray powder diffraction (XRD) profiles of the BCZYN ($x = 0$ and 0.03) with fused-aggregate network structure, CCLs of submicrometer-sized $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCZY(CCL)) and electrolyte $\text{BaCe}_{0.1}\text{Zr}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCZY(EL)) are shown in Figure 2(a) and (b). All of the phases were determined to be the pseudo-cubic perovskite structure, with no impurity phases. The crystallite sizes of BCZYN ($x = 0$ and 0.03), BCZY(CCL) and BCZY(EL), which were determined by applying the Scherrer equation to the XRD peak of the (110) plane, were 28.9 nm (BCZYN ($x = 0$)), 22.7 nm (BCZYN ($x = 0.03$)), 38.3 nm (BCZY(CCL)), and 29.7 nm (BCZY(EL)). The transmission electron microscopy (TEM) images of BCZYN ($x = 0$ and 0.03) nanoparticles are shown in the inset of Figure 2(a). The nanoparticles were partially fused with nearest neighbors and constructed chain-like microstructures, the fused-aggregate network structure referred to earlier [35–41]. The XRD profiles of Ni/BCZYN ($x = 0$ and 0.03) CLs sintered at $1000\text{ }^\circ\text{C}$ in 4% hydrogen atmosphere (N_2 balance) are also displayed in Figure 2(c). All of the peaks were determined to be assigned to the pseudo-cubic BCZYN ($x = 0$ and 0.03) phases and Ni metal ($2\theta = 44.50^\circ, 51.85^\circ, 76.37^\circ$) without any impurity phases. The Arrhenius plots of the electrical conductivity of the highly sintered samples of BCZYN ($x = 0$ and 0.03) in 4% hydrogen atmosphere (Ar balance) are shown in Figure 2(d). The Arrhenius plots of the electrical conductivity of the highly sintered samples of BCZYN ($x = 0.03$) was higher than that of BCZYN ($x = 0$) over the whole measurement range. For example, the electrical conductivities of BCZYN ($x = 0.03$) and BCZYN ($x = 0$) at $700\text{ }^\circ\text{C}$ were 0.015 S cm^{-1} ($\log [\sigma/\text{S cm}^{-1}] = -1.82$) and 0.005 S cm^{-1} ($\log [\sigma/\text{S cm}^{-1}] = -2.30$), respectively. The enhancement of the electrical conductivity by Ni doping is crucial to improve the electrochemical activity.

Figure 2. X-ray powder diffraction (XRD) patterns and transmission electron microscopy (TEM) images of $\text{BaCe}_{0.5}\text{Zr}_{0.3-x}\text{Y}_{0.2}\text{Ni}_x\text{O}_{3-\delta}$ (BCZYN, $x = 0$ and 0.03) with fused-aggregate network structure (a), $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCZY(CCL)) and $\text{BaCe}_{0.1}\text{Zr}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCZY(EL)) sintered at 1650°C , 10 h (b), Ni/BCZYN ($x = 0$ and 0.03) catalyst layers (CLs) sintered at 1000°C in 4% hydrogen atmosphere (c), and the arrhenius plots of electrical conductivity of BCZYN ($x = 0$ and 0.03) in 4% hydrogen atmosphere (Ar balance) (d).

The scaffold was obtained by the co-sintering procedure at 1050°C , which was a much lower temperature than previous reports, with no impurity phases, particularly metallic Ni [20–22]. As seen in the cross-sectional images, the BCZYN scaffolds ($x = 0$ and 0.03) on BCZY(EL) (Figure 3a) also maintained the structure with open pores, both primary pores (<100 nm in diameter) and secondary pores (>100 nm), surrounded by the aggregates. The pore/volume ratio of each scaffold was ca. 60%, from the estimation of weight and volume.

Figure 3. (a) Typical secondary electron microscopy (SEM) image of Ni/BCZYN ($x = 0$) hydrogen electrode. The Ni/BCZYN ($x = 0$, Ni 10 vol %) CLs was on the electrolyte of BCZY(EL) and was covered on top by the current collecting layer of Ni-BCZY composite CCLs. (b) Typical scanning transmission electron microscopy equipped with an energy dispersive X-ray analyzer (STEM-EDX) image of Ni/BCZYN ($x = 0$, Ni 10 vol %) electrode. The blue images denote the Ce element in BCZYN ($x = 0$) scaffold. The red images indicate the Ni element in the Ni nanoparticle catalysts.

Typical elemental mapping images of the Ni nanoparticle catalysts supported on BCZYN ($x = 0$) are shown in Figure 3b. The blue and red images indicate the contents of Ce and Ni, respectively, corresponding to the BCZYN ($x = 0$) and Ni nanoparticles. The particle sizes of Ni in the CLs are listed in Table 1. The Ni particles were dispersed highly on the BCZYN ($x = 0$) scaffold with particle sizes from 48.3 nm to 84.1 nm. The circumference length of triple phase boundary (TPB) around the Ni particles on the scaffold is defined by the Formula (1) [42]:

$$\text{Circumference length of TPB} = m_{\text{Ni}} \frac{\pi d_{\text{Ni}}}{\frac{4}{3} \pi \left(\frac{d_{\text{Ni}}}{2} \right)^3 \rho} = \frac{6m_{\text{Ni}}}{d_{\text{Ni}}^2 \rho} \quad (1)$$

where m_{Ni} , d_{Ni} and ρ are the loading amount of Ni (g cm^{-2}), Ni particle size (cm), and Ni density (8.908 g cm^{-3}), respectively. The circumference length of TPB of the catalysts are also summarized in Table 1. The circumference length of TPB increased gradually with increasing Ni loading amount. Only on the Ni (30 vol %) on BCZYN ($x = 0$) were the particles aggregated with nearest neighbors, resulting in the 84.1 nm particle size, which led to a decreased circumference length of TPB. Further investigations are needed to elucidate the reason why the Ni particles (30 vol %) aggregated with nearest neighbors on BCZYN ($x = 0$).

Table 1. Ni particle size and circumference length of triple phase boundary (TPB) of Ni/BCZYN ($x = 0$ and 0.03).

x	Ni Loading Amount/vol %	Ni Particle Size/nm	Circumference Length of TPB/ 10^7 cm cm^{-2} (Electrode Area)
0	10	48.3 ± 15.4	0.857
	15	45.8 ± 20.6	1.49
	20	55.3 ± 21.2	1.45
	30	84.1 ± 47.3	0.444
0.03	10	49.9 ± 19.3	0.792
	15	52.9 ± 18.4	1.12
	20	58.2 ± 22.5	1.31
	30	58.7 ± 21.3	2.21

2.2. Performances of Ni/BCZYN CLs

IR-free polarization curves for the hydrogen electrode by use of Ni/BCZYN ($x = 0$ and 0.03) CLs with CCLs at 700°C are shown in Figure 4a and b, respectively. The curves exhibit highly symmetrical behavior about the origin for the hydrogen evolution reaction and proton generation reaction on all of the Ni/BCZYN ($x = 0$ and 0.03) CLs with CCLs. For example, the current densities at overpotentials (η) of 0.1 V and -0.1 V on 20 vol % Ni/BCZYN ($x = 0$) CL with CCL were 0.013 A cm^{-2} and -0.014 A cm^{-2} , respectively. These symmetrical curves of current density vs. η indicate that the hydrogen evolution and proton generation on these CLs occur reversibly. The low ohmic resistance, reversible performance and low η on all of the Ni/BCZYN ($x = 0$ and 0.03) CLs with CCLs are highly desirable for the reversible operation of the SOEC/SOFC [43]. The η for our 20 vol % of Ni dispersed BCZYN ($x = 0.03$) CL was also confirmed to be at approximately the same level as that for a Ni-BCZY composite (NiO:BCZY = 65:35 wt %) [20,21]. The reported hydrogen electrode included a higher amount of Ni than that of our hydrogen electrode. We expect that the electrocatalytic activity of our hydrogen electrode would be improved further by increasing the electrical conductivity. The Ni doping in BCZYN described in the present work is one of the possible methods to increase the electrical conductivity, but the limit of Ni doping content in BCZYN synthesized by the flame oxide synthesis method was $x = 0.03$. In continuing work, we will evaluate the electrochemical activity of a hydrogen electrode in which Ni particles are added to Ni/BCZYN CLs in order to further enhance the conductivity.

Figure 4. Polarization curves of Ni/BCZYN ($x = 0$), (a) and Ni/BCZYN ($x = 0.03$), (b) hydrogen electrode at various Ni loading amount.

Moreover, the η of the Ni/BCZYN ($x = 0.03$) CLs were lower than those of the Ni/BCZYN ($x = 0$) CLs at the same Ni loading amount. In order to elucidate the improvement of the performance of the hydrogen electrode in detail, the current densities at $\eta = -0.1$ V as a function of circumference length of TPB are summarized in Figure 5. The current densities at $\eta = -0.1$ V for the Ni/BCZYN ($x = 0$) CLs increased with circumference length of TPB and saturated above circumference length of TPB = 1.0×10^7 cm cm⁻² (electrode area). However, the current densities using the Ni/BCZYN ($x = 0.03$) CLs were higher than those using the Ni/BCZYN ($x = 0.03$) CLs at the same circumference length of TPB values. The proton reduction reaction to hydrogen is the rate-determining step in the hydrogen evolution reaction [43]. The slight amount of Ni doping in the BCZY phase enhances the electronic conductivity while maintaining the proton conductivity [31–34], which led to the enhancement of the current densities obtained using the Ni/BCZYN ($x = 0.03$) CLs. Moreover, in earlier papers, Ni dispersed on mixed conductors was found to lead to enhancement of the ERZ around the Ni catalyst particles with increasing electronic conductivity [24–26]. We consider that the enhancement of the hydrogen electrode activity on the Ni/BCZYN ($x = 0.03$) CLs is strongly related to the improvement of the electronic conductivity of BCZYN and the enhancement of the ERZ.

Figure 5. Current density at $\eta = -0.1$ V as a function of circumference length of triple phase boundary (TPB) at 700 °C.

Ni/BCZYN ($x = 0$) and Ni/BCZYN ($x = 0.03$) showed no significant difference in current density at 10 vol % Ni loading. The electrical conductivity of the pure electrode material of BCZYN ($x = 0.03$) was higher than that of BCZYN ($x = 0$) as shown in Figure 2d. The electrical conductivity of the pure electrode material was measured using the sintered dense samples. However, the current density in Figure 5 was measured from the nanoparticles of BCZYN ($x = 0$ and 0.03). In our previous research, we reported that the electrical conductivity and electrochemical activity of the catalysts on the nanoparticles increased significantly over a threshold amount of metal loading. For example, in the case of Pt loaded on Nb doped SnO_2 , these values increased abruptly over a Pt loading amount of 7 wt %. We also proved that the reason why the electrochemical activity increased in this way over the threshold amount of metal loading was that there was a diminution of the effect of an insulating depletion layer on the nanoparticle surface [37,41]. We supposed that, under the Ni loading amount of 10 vol %, the insulating depletion layer on the BCZYN nanoparticle surface disturbed the reaction on the hydrogen electrode, and thus, the current density for Ni/BCZYN ($x = 0.03$) did not show a significant difference compared to that for Ni/BCZYN ($x = 0$).

3. Materials and Methods

3.1. Sample Preparation

BCZYN ($x = 0$ and 0.03) nanoparticle powders with a fused-aggregate network structure were prepared by the flame oxide synthesis method [35–41]. Briefly, reagent grade Ba, Ce, Zr, Y, and Ni 2-ethylhexanoates (Nihon Kagaku Sangyo Co. Ltd., Tokyo, Japan) were mixed in desired ratios with terpene oil as starting materials. The BCZYN ($x = 0$ and 0.03) powders were obtained by spraying the starting materials into the flame of a mixture of propane and oxygen. The BCZY(CCL) and BCZY(EL) were prepared by the solid state reaction method. Starting materials of BaCO_3 (purity 99.9%, Kanto Chemical Co. Inc., Tokyo, Japan), CeO_2 (purity 99.9%, Rare Metallic Co., Tokyo, Japan), ZrO_2 (purity 99.9%, Tosoh Co., Ltd., Tokyo, Japan), Y_2O_3 (purity 99.9%, Kanto Chemical Co. Inc., Tokyo, Japan) were mixed in desired ratios with ethanol by ball milling (300 rpm, P-6, Fritsch Co., Ltd., Idar-Oberstein, Germany) for 3 h, were calcined at 1500 °C in air for 10 h, and were separated by sieving (#400 mesh). Then, the sieved powders were pressed under isostatic pressure (200 MPa) into a columnar shape (diameter 13 mm, thickness 1.0 mm), and sintered again at 1650 °C for 10 h with the use of BCZY(CCL) and BCZY(EL) powder beds to prevent the barium evaporation from the respective pressed samples [7]. The sintered densities of these disks (diameter 13 mm, thickness 0.6 mm) were over 95%. The obtained BCZY(CCL) sintered disk was crushed and reground with isopropanol by ball milling (300 rpm) for 3 h to a sub-micrometer-sized powder ($\leq 0.3 \mu\text{m}$) in order to prepare the Ni-BCZY(CCL) CCL.

3.2. Single Cell Fabrication

Porous scaffolds of BCZYN ($x = 0$ and 0.03) powders were synthesized onto the BCZY(EL) sintered disk. In order to maintain the porosity of the BCZYN ($x = 0$ and 0.03) scaffold, carbon black (SB220, Asahi Carbon, Co., Ltd., Niigata, Japan) was added as a pore-former to the CL pastes, which were screen-printed on the BCZY(EL) sintered disk and heat-treated at 1000 °C for 4 h in N_2 . Commercial NiO powder (Kanto Chemical Co., Inc., Tokyo, Japan), BCZY(CCL) powder and carbon black pore former were mixed with 60 vol % water by ball-milling to produce the CCL pastes. The latter were screen printed on the CL scaffold by tape-casting and were co-sintered at 1050 °C for 4 h in N_2 . A paste of Pt-BCZY (Pt:BCZY(CCL) = 80:20 (vol %)) with the additive polymethyl methacrylate (PMMA) as a pore former was also screen printed on the opposite side of the BCZY(EL) to form a Pt-BCZY composite counter electrode.

Ni nanoparticle catalysts were loaded on the BCZYN ($x = 0$ and 0.03) scaffold by use of an impregnation method [24]. Briefly, 2 M nickel nitrate solution was impregnated into the BCZYN ($x = 0$ and 0.03) scaffold through the CCL, followed by heat-treatment at 400 °C for 30 min to form NiO nanoparticles. The Ni loading amounts in the CLs were adjusted at values from 10 vol % to 30 vol %.

The CLs obtained were reduced in dry hydrogen at the cell temperature ($T_{\text{cell}} = 700\text{ }^{\circ}\text{C}$) for 1 h prior to the performance evaluation as Ni/BCZYN.

3.3. Characterization of Sample, CL and CCL

The crystalline phases of the samples were characterized by XRD (RINT-TTR 3, Rigaku Co., Tokyo, Japan). The chemical compositions of Ni, BCZYN ($x = 0$ and 0.03), BCZY(CCL), BCZY(EL) were evaluated by inductively coupled plasma-mass spectroscopy (ICP-MS, 7700CX, Agilent Technologies, Inc., Santa Clara, CA, USA). The electrical conductivity for BCZYN ($x = 0$ and 0.03) was measured as a function of temperature in 4% hydrogen atmosphere (Ar balance) by the direct current (DC) four-probe method. Each sample for electrical conductivity measurement was sintered to densify it at $1650\text{ }^{\circ}\text{C}$ in a powder bed. The microstructure of the CL and Ni particle size were characterized by STEM (HD2700, Hitachi High-Technologies Co., Tokyo, Japan) equipped with EDX (Xflash[®], Bruker AXS GmbH, Karlsruhe, Germany). The observation samples for the STEM were prepared with a focused ion beam system (FIB, FB2200, Hitachi High-Technologies Co., Tokyo, Japan).

3.4. Electrochemical Measurement

The set-up for the test cell was described in Shimura and coworkers report [44]. The test cell was sealed with a gold ring. The area-specific ohmic resistance and steady-state IR-free polarization characteristics of the hydrogen electrodes were evaluated at $T_{\text{cell}} = 700\text{ }^{\circ}\text{C}$ by the current interruption method in a three-electrode configuration with humidified hydrogen (H_2 flow rate = $30\text{ cm}^3\text{ min}^{-1}$), while supplying dry 4% hydrogen (balance nitrogen) at $30\text{ cm}^3\text{ min}^{-1}$ to the counter electrode. A current-off pulse of 100 ms was applied from a current-pulse generator (NPGS101-2A, Nikko Keisoku Ltd., Atsugi, Japan), and the resulting potential responses were recorded with a storage oscilloscope (VC-6045, Hitachi Co., Tokyo, Japan). The proton transference number was evaluated by use of an electromotive force measurement from $600\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$ with a test cell supplied with pure hydrogen/4% hydrogen (balance nitrogen). The electromotive force of the cell by use of the BCZY(EL) agreed well with theoretical values from $600\text{ }^{\circ}\text{C}$ to $700\text{ }^{\circ}\text{C}$. The proton transference number of BCZY(EL) was confirmed to be unity in the measurement temperature range from $600\text{ }^{\circ}\text{C}$ to $700\text{ }^{\circ}\text{C}$.

All of the IR-free current-potential polarization curves were obtained at steady-state, after the test cells were conditioned by repeated galvanostatic load cycles at $T_{\text{cell}} = 700\text{ }^{\circ}\text{C}$. The current density (j) was increased from 0 to -0.035 A cm^{-2} as the hydrogen generation condition. Then, j was decreased from -0.035 A cm^{-2} to zero. The next inverse trapezoid current-time protocol was carried out between 0 and 0.035 A cm^{-2} . We also checked the ohmic resistance of the test cell in the whole current density range in order to confirm that the IR loss of the test cell displayed a completely linear relationship of current density at $T_{\text{cell}} = 700\text{ }^{\circ}\text{C}$.

4. Conclusions

Ni/BCZYN CLs ($x = 0$ and 0.03) were fabricated as hydrogen electrodes of a proton-conducting SOEC. The BCZYN particles were synthesized by the flame oxide-synthesis method and had the unique fused-aggregate network structure. The unique microstructure has the ability to construct both electronically conducting pathways and gas diffusion pathways in the CLs and is considered to be well suited as a scaffold for a gas diffusion electrode such as the hydrogen electrode in an SOEC. Highly dispersed Ni nanoparticles (particle size $> 50\text{ nm}$) were loaded on the BCZYN scaffold by the impregnation method. The performances of the Ni/BCZYN ($x = 0.03$) CLs increased monotonically with circumference length of TPB, defined by the circumference length of Ni on BCZYN ($x = 0.03$). The slight amount of Ni doping in the BCZYN scaffold was found to be crucial in improving the electronic conductivity while maintaining the proton conductivity, thereby enhancing the ERZ and improving the catalytic activity of the Ni/BCZYN CLs. Therefore, the Ni/BCZYN CLs can be considered to be a prime candidate for use in proton-conducting SOECs.

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