Article

Performance of BaCe$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ Proton Electrolyte Materials for Solid Oxide Fuel Cells by Compositing the Transition Metal Oxide NiO

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Abstract: Since the conduction activation energy of a proton is low, proton-conducting solid oxide fuel cells (H-SOFCs) can work at low temperatures (around 600 °C), which is conductive to maintaining the long-term stability of SOFCs. Proton conductor BaCe$_{1-x}$Y$_x$O$_{3-\delta}$ is the most commonly used electrolyte material for H-SOFCs, which directly affects the performance of SOFCs. For the purpose of realizing the high-performance BaCe$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ (BCY) proton electrolyte materials for SOFC, the effect of different contents of the transition metal oxide NiO on the performance of proton electrolyte BCY was studied. Specifically, BCY-x mol% NiO (named BCY, BCY + 0.5NiO, BCY + 1NiO, BCY + 2NiO, and BCY + 3NiO, when x = 0, 0.5, 1, 2, and 3, respectively) composite electrolyte materials were prepared, and their crystal structures, morphologies, and electrochemical properties were explored. The results showed that NiO could effectively improve the density of BCY prepared at 1400 °C and enhance the proton conductivity of BCY and the performance of BCY-based SOFCs. Among them, the BCY + 2NiO electrolyte had good density and the highest proton conductivity, and the SOFC based on the BCY + 2NiO electrolyte had the best electrochemical performance, indicating that the optimal content of the NiO additive was 2 mol% in this case. The results reported in this work are conductive to the realization of high-performance proton electrolyte materials for the SOFC.

Keywords: intermediate-temperature solid oxide fuel cell; perovskite materials; proton conductor; electrolyte

1. Introduction

Intermediate temperature (600–800 °C) solid oxide fuel cells (IT-SOFC) are considered one of the most promising electricity-generation methods because of their advantages of high efficiency, low cost, and environmental protection [1–7]. SOFCs can be divided into oxygen-ion-conducting SOFCs (O-SOFCs) and proton-conducting SOFCs (H-SOFCs), according to the ion types conducted by the electrolytes [8–13]. In regard to O-SOFC, because of the high activation energy of oxygen ion conduction, O-SOFC requires a high operation temperature (800 °C), which will result in critical issues (e.g., poor long-term stability, interlayer diffusion, fabrication, and materials problems). So, the high operation temperature remains a big challenge to O-SOFC commercialization. As for H-SOFC, since the conduction activation energy of a proton is lower than that of an oxygen ion, it can work at a reduced temperature, which improves the long-term stability of the device and decreases the production cost. The proton conductor BaCe$_{1-x}$Y$_x$O$_{3-\delta}$ (BCY) is the commonly used electrolyte material for H-SOFCs [14,15]. Despite the fact that such a material has the outstanding advantage of its high proton conductivity ($10^{-2}–10^{-3}$ S cm$^{-1}$ at 600 °C) [16–18], it still has the disadvantage of being difficult to sinter. An extremely high temperature (above 1400 °C) is required for it to be sintered, which will bring adverse effects such as the evaporation of the Ba element in the material [19]. At present, an effective way to improve the sintering degree of the material is to composite transition metal oxides (e.g., ZnO, CuO, and NiO) into the material [20–22], which is attributed to the viscous flow mechanism of these sintering aids. Moreover, these sintering aids can easily diffuse to
the surface of BCY particles and form thin amorphous films around BCY particles. The amorphous films formed by these sintering aids are able to reduce the friction between BCY particles, increase the contact area of BCY particles in compact solids, promote the mass diffusivity of BCY materials, and further enhance the densification of the BCY electrolyte during the sintering process [23–25]. For example, Ming Zhang et al. reported that the sintering temperature of the dense ceramic electrolyte Ba$_x$Ce$_{0.8}$Y$_{0.2}$O$_{3-δ}$ ($x = 1, 0.98, 0.96$, and 0.94) prepared by a solid-state reaction method decreased by 573 K with the ZnO sintering aid [20]. S. Presto et al. reported that, by the addition of 0.75 wt% CuO, the relative density of BCY sintered at 1000 °C and 1100 °C was up to 96% and 98%, respectively [21]. R. Costa et al. reported that the relative density of the BCY electrolyte could reach 95% under the sintering temperature of 1250 °C for 10 h with 4 mol% NiO additive [22].

Among the aforementioned transition metal oxides, NiO is the most commonly used component of the SOFC anode. The addition of NiO does not complicate the composition of the BCY material, while it is beneficial to the sintering of the BCY electrolyte [26]. Although it has been reported that the sintering degree of the BCY proton electrolyte of the SOFC is improved by compositing NiO transition metal oxides, the effects of different NiO contents on the sintering degree and electrochemical properties of BCY materials and the electrochemical properties of BCY-based SOFCs have not been systematically studied. Based on this, this work studied the effects of the different NiO contents on the performance of proton electrolyte BCY and BCY-based SOFCs, to explore the optimal content of NiO.

2. Experimental

2.1. Subtopic A: Experimental and Model of SOFC Set up

BaCe$_{0.8}$Y$_{0.2}$O$_{3-δ}$-$x$ mol% NiO (named BCY, BCY + 0.5NiO, BCY + 1NiO, BCY + 2NiO, and BCY + 3NiO, when $x = 0, 0.5, 1, 2$, and 3, respectively) composite electrolyte materials were prepared in this work, among which BCY was purchased from the Nexceris, LLC, Fuelcell materials, Lewis Center, OH, USA, and NiO was prepared by the glycine-nitrate method [27]. (La$_{0.6}$Sr$_{0.4}$)$_{0.6}$Ce$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ (LSCF)-BaZr$_{0.7}$Ce$_{0.2}$Y$_{0.1}$O$_{3-δ}$ (BZCY) was the oxygen electrode material of SOFC (the mass ratio of LSCF and BZCY was 7:3), in which LSCF and BZCY was purchased from the Nexceris, LLC, Fuelcell materials, Lewis Center, OH, USA. NiO–BCY was the hydrogen electrode material of the SOFC (the mass ratio of NiO to BCY was 5:5). BCY–NiO electrolyte ceramic sheets were made by pressing BCY–NiO powder into green sheets with a diameter of 16 mm under 10 MPa and sintered at 1400 °C for 5 h. The schematic diagram of the electrolytes preparation is shown in Figure 1.

![Figure 1. Schematic diagram of the BCY-NiO electrolytes preparation.](image)

The preparation process of NiO–BCY/BCY–NiO/LSCF–BZCY structured single SOFC was as follows: firstly, the hydrogen electrode/electrolyte (NiO–BCY/BCY–NiO) structure was prepared by the CO pressing method. The hydrogen electrode powders and electrolyte powders were pressed into a double-layer green sheet with a diameter of 16 mm using the CO pressing method under a pressure of 1 MPa and then sintered at 1400 °C for 5 h. The mass of the hydrogen electrode powder was 300 mg (the mass ratio of NiO, BCY and starch was 5:5:2), and the electrolyte powder was 100 mg, respectively. Subsequently, the
LSCF–BZCY oxygen electrode was coated on the electrolyte surface by screen printing and sintered at 1000 °C for 2 h. In this way, a single SOFC was obtained. The area of the coated oxygen electrode was 0.4 cm × 0.4 cm. Silver paste was the collector and silver wire was the conductor, of the SOFC.

2.2. Subtopic B: Morphology Analysis

The crystal structures of the BCY–NiO composite electrolyte materials were determined by a Japan Rigaku-D-Max Ra X-ray diffractometer (XRD). The surface morphologies of BCY–NiO electrolyte sheets and films were characterized by an FEI Quanta FEG 250 scanning electron microscope (SEM).

2.3. Subtopic C: Electrical Performance Analysis

The impedance spectra of the BCY–NiO electrolytes were measured using the electrochemical workstation CHI 760E (Shanghai Chenhua Instrument Corporation, Shanghai, China) over a frequency range of 10^{-1}–10^{6} Hz and a signal amplitude of 50 mV in the water-vapor atmosphere in a temperature range of 550–700 °C. The current density-voltage characteristic curves of the SOFCs with dry hydrogen as the fuel and air as the oxidant were studied by a linear voltage sweep at a scanning rate of 9 mV s^{-1} at the above-mentioned electrochemical workstation.

3. Results and Discussion

3.1. Morphological Analysis on BCY–NiO Powders

Figure 2a shows the XRD patterns of BCY–NiO powder samples calcined at 1400 °C for 5 h. It should be noted that all of the main peaks of BCY–NiO correspond to the perovskite phase, indicating that the addition of NiO does not change the crystal structure of BCY. To study the effect of NiO on the BCY lattice structure, the Rietveld refinement is performed on the BCY–NiO samples, as shown in Figure 2b–f. The XRD Rietveld refinement results of the BCY–NiO samples are listed in the Supplementary Table S1, and the lattice volume of the BCY–NiO composite in the Supplementary Table S1 has been shown as a column diagram in Figure 3. It can be seen that the lattice constant of BCY decreases slightly by compositing NiO, which is due to the partial Ni^{2+} (0.069 nm) in substitution for Ce^{4+} (0.097 nm) [28,29]. The slight change of the BCY lattice constant indicates the low solubility of Ni in BCY (the Ni solubility limit was lower than 0.4 mol% [22]). The NiO peaks in the XRD cannot be observed; one reason may be that NiO is amorphous and mainly exists at the grain boundaries of the composites. The other reason may be that the content of NiO in the composite material is relatively low, which is below the detection limit of the instrument.
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Figure 2. (a) XRD patterns of BCY–NiO powder samples calcined at 1400 °C for 5 h; (b–f) XRD Rietveld refinement results of BCY–NiO powder samples.

Figure 3. Column diagram of the lattice volume of BCY–NiO composites.

3.2. SEM Microstructure Analysis and Conductivity Tests on BCY–NiO Electrolytes

Figure 4a–e show the SEMs of BCY–NiO ceramic electrolyte sheets, respectively. It can be seen that the BCY electrolyte sheet is not dense and porous, which indicates that 1400 °C is unsuitable for sintering the BCY electrolyte sheet. However, the BCY + 0.5NiO, BCY + 1NiO, BCY + 2NiO, and BCY + 3NiO ceramic electrolyte sheets prepared at 1400 °C
are dense. The density of the BCY-NiO ceramic electrolyte sheets is measured by the Archimedes method. The relative densities of the BCY, BCY + 0.5NiO, BCY + 1NiO, BCY + 2NiO, and BCY + 3NiO ceramic electrolyte sheets are 77%, 89%, 94%, 93%, and 94%, respectively. It can be seen that the dense BCY ceramic electrolyte sheet can be obtained by compositing NiO at a sintering temperature of 1400 ℃. Due to the viscous flow mechanism of the NiO sintering aid, NiO addition can enhance the densification of the BCY electrolyte during the sintering process. Because the 0.5% mol NiO content is too low, the BCY electrolyte density cannot be significantly enhanced. The NiO content of 1% mol, 2% mol, and 3% mol is enough to enhance the density of the BCY electrolytes. The relative density of the BCY + 1NiO, BCY + 2NiO, and BCY + 3NiO ceramic electrolyte sheets can be compared with the that of BCY + 4 mol% NiO electrolyte (95% relative density value) [22]. Notably, the grain size of BCY increases with the addition of NiO, demonstrating that the viscous flow nature of the sintering aid NiO is conducive to the growth of BCY grains [23,30,31].

Figure 4. (a–e) SEM images of BCY–NiO ceramic electrolyte sheets.

To study the effect of NiO on the electrochemical properties of the BCY electrolytes, the impedance spectra of the BCY–NiO ceramic electrolyte sheets are measured in a water-vapor atmosphere in the temperature range from 550 ℃ to 700 ℃. The impedance spectra of the BCY–NiO ceramic electrolyte sheets at 650 ℃ is shown in Figure 5. The ohmic resistances of BCY, BCY + 0.5NiO, BCY + 1NiO, BCY + 2NiO, and BCY + 3NiO ceramic electrolyte sheets are calculated to be 3.40 Ω cm², 2.91 Ω cm², 3.02 Ω cm², 2.50 Ω cm² and 2.79 Ω cm², respectively. The corresponding conductivities are 0.029 S cm⁻¹, 0.034 S cm⁻¹, 0.033 S cm⁻¹, 0.04 S cm⁻¹ and 0.036 S cm⁻¹, respectively. Arrhenius plots of the conductivity of the BCY–NiO composite electrolytes in the temperature range from 550 ℃ to 700 ℃ are shown in Figure 6. The activation energy value of the BCY, BCY + 0.5NiO, BCY + 1NiO, BCY + 2NiO, and BCY + 3NiO electrolytes are calculated to be 1.08 eV, 1.13 eV, 1.19 eV, 1.11 eV, and 1.10 eV, respectively. The best case is BCY in our case. Its activation energy is 1.08 eV. It should be noted that the activation energy of BCY was increased by adding the NiO. The possible reason is that more oxygen ions participate in the conduction by adding the NiO. Since the conduction activation energy of oxygen ion is higher than that of the proton ion, the BCY–NiO electrolytes have higher activation energy than the BCY electrolyte. The proton conductivity of BCY is significantly improved by compositing NiO.
transformation metal oxides NiO can not only improve the sintering degree of electrolytes but also enhance proton transport at electrolyte grain boundaries by reducing the grain boundary blocking effect caused by the siliceous layers and space charge effects. However, too many transformation metal oxides will also hinder the transport of proton at the grain boundary, which may be due to the decrease in the grain-to-grain contact area induced by the increase in the transformation metal oxides content [23–25,30,31]. The BCY + 2NiO ceramic electrolyte sheet has the highest proton conductivity, indicating that the optimal content of the NiO additive is 2 mol% in this case. We have compared the conductivity of the BCY + 2NiO electrolyte with that of the BCY electrolytes reported by other groups, which is shown in the Supplementary Table S2. It should be noted that the conductivity of the BCY + 2NiO electrolyte in our case can be comparable to that of these BCY electrolytes [21,32–34]. It should be noted that the conductivity of BCY + 2NiO sintered at 1400 °C is higher than that of the BCY electrolytes sintering at higher temperatures, indicating that adding NiO can enhance the conductivity and reduce the sintering temperature of the BCY electrolytes. It is also found that the conductivity of BCY + 2NiO is comparable to that of BCY + 1.5%wt CuO sintered at 1100 °C. However, due to the low melting point of CuO (around 1000 °C) [35,36], CuO in the BCY electrolyte may melt and penetrate into the cathode and anode of the SOFC during SOFC fabrication, which may affect the electrodes and electrolytes performance. So, the BCY + CuO electrolyte may not be suitable for the SOFC.

![Impedance spectra of BCY–NiO ceramic electrolyte sheets measured in water-vapor atmosphere at 650 °C.](image)

**Figure 5.** Impedance spectra of BCY–NiO ceramic electrolyte sheets measured in water-vapor atmosphere at 650 °C.

![Arrhenius plots of the conductivity of BCY–NiO composite electrolytes in the temperature range from 550 °C to 700 °C.](image)

**Figure 6.** Arrhenius plots of the conductivity of BCY–NiO composite electrolytes in the temperature range from 550 °C to 700 °C.

Figure 7 represents the surface SEMs of NiO–BCY/BCY–NiO structures. Obviously, the surface of the BCY film is porous and not dense, so it is unsuitable as the electrolyte layer of the SOFC. The BCY + 0.5NiO, BCY + 1NiO, BCY + 2NiO, and BCY + 3NiO electrolyte layers are relatively dense, which ensures the airtightness of the electrolytes in the SOFCs.
From Figure 7, it can be noted that the BCY + 2NiO film has a higher density than the other composites, which indicates that the 2% mol NiO is most beneficial to reduce the friction between BCY particles, increase the contact area of BCY particles in compact solids, promote the mass diffusivity of BCY materials, and further enhance the densification of BCY film during the sintering process in our case.

Figure 7. (a–e) SEM images of surfaces of NiO–BCY/BCY–NiO structures.

3.3. Full Cell Electrochemical Characterization

Figure 8 shows the current density-voltage and the corresponding current density-power density curves of the BCY–NiO-based SOFCs at 650 °C. The maximum power densities of the cells based on BCY, BCY + 0.5NiO, BCY + 1NiO, BCY + 2NiO, and BCY + 3NiO are 69.4, 94.8, 74.9, 121.4, and 73.4 mW/cm², respectively. The curve of the test-temperature-dependent power density of the SOFCs based on the BCY–NiO composite electrolytes is provided in the Supplementary Figure S1. It is obvious that the power density of the BCY + 2NiO-based SOFC is the highest among the BCY–NiO-based SOFCs. In Figure 6, it can be seen that the BCY + 2NiO ceramic electrolyte sheet has the highest proton conductivity among the BCY–NiO electrolytes. The proton conductivity of the electrolyte directly affects the power density of its SOFC, so the SOFC based on the BCY + 2NiO electrolyte has the highest power density. It can be concluded that the BCY + 2NiO-based SOFC has the best performance, and the optimum addition of NiO is 2 mol% in this case.

Figure 8. Current-density voltage and the corresponding current-density–power-density curves of the BCY–NiO-based SOFCs at 650 °C.
The performance of the SOFC is decided by the electrode polarization resistance and ohmic resistance. The ohmic resistance of the SOFC includes the ohmic resistance of the electrolyte and the contact resistance of the electrolyte/electrode. The SOFC based on BCY + 2NiO has the best performance due to the highest proton conductivity of BCY + 2NiO among the BCY-NiO electrolytes. The SOFC based on BCY + 0.5NiO shows better performance than that based on BCY + 3NiO, possibly due to the lower contact resistance of the electrolyte/electrode. We compared the power density of the SOFC based on BCY + 2NiO electrolyte in our case with that reported by other groups, which is shown in the Table 1. It should be noted that the SOFC based on the BCY + 2NiO electrolyte in our case has outstanding performance, which is due to the co-pressure method of SOFC fabrication and the high conduction of the BCY + 2NiO electrolyte.

| Samples       | Sintering Temperature (°C) | Power Density (mW cm$^{-2}$) | Ref. |
|---------------|---------------------------|------------------------------|------|
| BaCe$_{0.8}$Y$_{0.2}$O$_{2.9}$ (BCY20) | 600                        | 68                           | [33] |
| BCY20         | 650                        | 103                          | [33] |
| BCY20         | 750                        | 104                          | [37] |
| BCY20         | 600                        | 74                           | [38] |
| BCY + 2 NiO   | 600                        | 87                           | This work |
| BCY + 2 NiO   | 650                        | 121                          | This work |

4. Conclusions

This work systematically studied the effects of different NiO contents on the sintering degree and electrochemical properties of BCY materials, as well as the electrochemical properties of BCY-based SOFCs. The results show that NiO can effectively improve the density of BCY prepared at 1400 °C and enhance the proton conductivity of BCY and the performance of BCY-based SOFCs. Among them, the BCY + 2NiO electrolyte has the highest density and the highest proton conductivity, and the SOFC based on the BCY + 2NiO electrolyte has the best electrochemical performance. This illustrates that the optimal content of the NiO additive in this case is 2 mol%.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings12111692/s1. Table S1. XRD Rietveld refinement result of BCY-NiO samples; Table S2. Comparison of the conductivity of the BCY electrolytes at 600 °C; Figure S1. The curve of the test-temperature-dependent power density of the SOFCs based on the BCY-NiO composite electrolytes

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