



Further optimization of barium cerate properties via co-doping strategy for potential application as proton-conducting solid oxide fuel cell electrolyte



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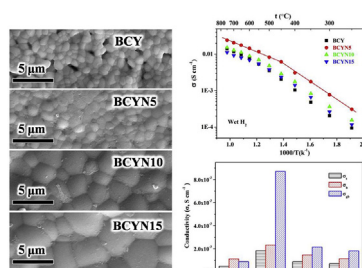
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HIGHLIGHTS

- The sinterability increased with an increase of Nd doping level.
- $\text{BaCe}_{0.8}\text{Y}_{0.15}\text{Nd}_{0.05}\text{O}_{3-\delta}$ (BCYN5) exhibited the highest conductivity.
- BCYN5 showed the decreasing grain and grain-boundary resistances.
- The fuel cell with the BCYN5 electrolyte showed a high power output.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Barium cerate
Sinterability
Electrical conductivity
Co-doping
Solid oxide fuel cells

ABSTRACT

Yttrium-doped BaCeO_3 is one of the most promising electrolyte candidates for solid oxide fuel cells because of its high ionic conductivity. Nd and Y co-doped BaCeO_3 strategy is adopted for the further optimization of Y-doped BaCeO_3 electrolyte properties. X-ray diffraction results indicate that the structure of $\text{BaCe}_{0.8}\text{Y}_{0.2-x}\text{Nd}_x\text{O}_{3-\delta}$ ($x = 0, 0.05, 0.1, 0.15$) with orthorhombic perovskite phase becomes more symmetric with increasing Nd concentration. The scanning electron microscope observation demonstrates that the densification and grain size of the sintered pellets significantly enhance with the increase of Nd doping level. Whether in dry and humid hydrogen or air, the increase of Nd dopant firstly increases the conductivities of $\text{BaCe}_{0.8}\text{Y}_{0.2-x}\text{Nd}_x\text{O}_{3-\delta}$ ($x = 0, 0.05, 0.1, 0.15$) and then decrease them after reaching the peak value at $x = 0.05$. Electrochemical impedance spectra at 350 °C can distinguish clearly the contribution of grain and grain boundary to total conductivity and the highest conductivity of $\text{BaCe}_{0.8}\text{Y}_{0.15}\text{Nd}_{0.05}\text{O}_{3-\delta}$ ascribes to the decrease in bulk and grain boundary resistances due to the synergistic effect of Nd and Y doping. The anode-supported single cell with $\text{BaCe}_{0.8}\text{Y}_{0.15}\text{Nd}_{0.05}\text{O}_{3-\delta}$ electrolyte shows an encouraging peak power density of 660 mW cm^{-2} at 700 °C, suggesting that $\text{BaCe}_{0.8}\text{Y}_{0.15}\text{Nd}_{0.05}\text{O}_{3-\delta}$ is a potential electrolyte material for the highly-efficient proton-conducting solid oxide fuel cell.

1. Introduction

Solid oxide fuel cells (SOFCs) are one of the most promising energy

conversion systems which can high-effectively convert chemical energy into electric energy with low environmental impact [1–5]. Yttria-stabilized zirconia (YSZ) is the most often used electrolyte for solid oxide

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fuel cells, because of its high ionic conductivities at a temperature higher than 800 °C, excellent chemical stability and good mechanical strength. However, the conductivity of YSZ decreases rapidly as the temperature decreases, which make it unsuitable for intermediate temperature SOFCs [6,7]. Nowadays, much effort has been made to decrease the operating temperature of SOFCs down to intermediate-to-low temperature range (500–700 °C). The electrolyte materials with high ionic conductivity are the crucial factor for the development of intermediate-to-low SOFCs, as the high electrolyte conductivity can significantly reduce the ohmic resistance of the cell and thus provide the satisfactory cell performance. Both rare-earth-doped CeO₂ (DCO, oxygen ionic conductor) and BaCeO₃ (protonic conductor) possess high ionic conductivity at intermediate-to-low temperatures and exhibit excellent SOFC performance [8,9]. Unfortunately, the partial internal short circuit of DCO that results from Ce⁴⁺/Ce³⁺ redox reaction under SOFC operation conditions significantly reduces the open circuit voltages (OCVs) of DCO-based SOFCs, which dramatically drop the working efficiency of the fuel cell and hamper its applications at high operating voltages [10–12]. Compared with oxygen-ion conducting electrolytes (YSZ and DCO), BaCeO₃-based electrolytes exhibit high proton conductivity with lower transfer activation energy and evade the internal short circuit in DCO electrolytes [13]. Hence, BaCeO₃-based electrolytes have the potential for the application in high-performance intermediate-to-low SOFCs. Improving and optimizing the properties of doped BaCeO₃ materials can further stimulate the development of SOFCs operated at a lower temperature.

For BaCeO₃ proton conductors, the proton transfer depends on the proton defects, which are carried out by oxygen vacancy introduced by the doping of trivalent rare-earth cations at B-site [14–16]. The electrical conductivities of barium cerate materials are determined by two main factors: trivalent doping element and its concentration. Many studies on electrical conductivities of trivalent-rare-earth ion-doped BaCeO₃ materials have been carried out, demonstrating that the bulk, grain boundary and total conductivities are strongly relative to the dopants with different ionic radius [17–19]. The effect of doping concentration also has been investigated and confirmed by many researchers, e.g. Zhao et al. [20] determined the relationship between electrical conduction behavior and Sm-doping level in BaCe_{1-x}Sm_xO_{3-δ} proton conductors.

The co-doping method as an optimizing strategy on electrolyte conductivity has been proposed and verified in CeO₂, BaCeO₃ and BaZrO₃ material systems. For Sm_{0.2}Nd_xCe_{0.75}O_{1.9-x/2} (x = 0–0.20) and Ce_{0.8}Sm_{0.2-x}Ca_xO_{2-δ} co-doping electrolytes, the optimal chemical compositions respectively are Sm_{0.2}Nd_{0.05}Ce_{0.75}O_{1.9-x/2} and Ce_{0.8}Sm_{0.05}Ca_{0.15}O_{2-δ}, corresponding to the maximum conductivity values [21,22]. BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-δ} and BaCe_{0.8}Sm_{0.1}Y_{0.1}O_{3-δ} displays the highest electrical conductivity in serial compositions of BaZr_{0.1}Ce_{0.7}Y_{0.2-x}Yb_xO_{3-δ} and BaCe_{0.8}Sm_xY_{0.2-x}O_{3-δ}, respectively [8,23]. Sun et al. [24] reported that the sintering capability of BaZr_{0.8}Y_{0.2-x}In_xO_{3-δ} enhanced with the increase of In doping level and BaZr_{0.8}Y_{0.15}In_{0.05}O_{3-δ} exhibited the highest total electrical conductivity.

In term of high proton conductivity, many studies have proposed that Y and Nd are two promising dopants for BaCeO₃-based electrolyte [18,25,26]. According to previous reports, Nd dopant can effectively promote the electrolyte sinterability [17,27]. Different from some transition metal oxides used as sintering aids, Nd incorporation into BaCeO₃ does not introduce the electronic conductivity and impair the electrolyte mechanical strength [28,29]. The variation of sinterability can change the grain boundary density and thus result in the impact on electrolyte conductivity. More important, the synergistic effect maybe appears in Nd and Y co-doping BaCeO₃ system. Based the above facts, Nd and Y co-doped barium cerate was well studied to further optimize Y substituted BaCeO₃ electrolyte and investigate the synergistic effect of Nd and Y substitution on phase structure, sinterability and electrical conductivity. Although Lee et al. [30] and Su et al. [31] have studied the Nd and Y co-doped barium cerate, only the electrical conductivity in

air was investigated and their results contradicted each other. The highest conductivity corresponding to BaCe_{0.8}Y_{0.1}Nd_{0.1}O_{3-δ} and BaCe_{0.8}Y_{0.15}Nd_{0.05}O_{3-δ} was reported by Lee et al. and by Su et al., respectively. Besides, the effect of Nd doping on sinterability and the conductivity in hydrogen as well as the electrochemical performance as SOFC electrolyte also have not been reported.

2. Experimental

2.1. Powders synthesis

BaCe_{0.8}Y_{0.2-x}Nd_xO_{3-δ} (BCYN, x = 0, 0.05, 0.1, 0.15) powders were synthesized via a citrate-nitrate combustion process and designated as BCY, BCYN5, BCYN10 and BCYN15 according to Nd doping level. Firstly, proper amount of Nd₂O₃, Y₂O₃, Ba(CH₃COO)₂ and Ce(NO₃)₃·6H₂O according to the stoichiometric ratio of BCYN were dissolved into a diluted nitric acid solution. Next, the citric acid as complex agent was added in a molar ratio of 1:1.5 (metal ions: citric acid) and then the pH value was adjusted to about 7 with ammonia. The solution formed sol under stirring at 60 °C and then was transferred to an evaporating dish. The sol was heated again until it was ignited. The resulted gray ash after combustion was calcined at 1100 °C for 3 h in air. SmBaCo₂O_{5+δ} (SBC) and Ce_{0.8}Sm_{0.2}O_{2-δ} (SDC) powders used as cathode, and NiO-BCYN5 (weight ratio 6:4) composite powders used as anode functional layer were synthesized using the similar procedure mentioned above, respectively. The calcining temperature was 1000 °C for SBC, 600 °C for SDC and 1000 °C for NiO-BCYN5, respectively. The anode powders were prepared by mixing NiO from the decomposition of NiCO₃·2Ni(OH)₂·4H₂O, BCYN5 and starch in a weight ratio of 3:2:1.

2.2. Sample preparation

BCYN powders were grinded for 24 h in a roller grinding machine using alcohol as the solvent and zirconia ball as the milling media, and then dried at 100 °C in oven. The dry BCYN powders were pressed under 200 MPa and 350 MPa into pellets with a diameter of about 15 mm or rectangular bars with 25 mm × 7 mm × 4 mm dimension, and then sintered at 1400 °C for 5 h in air. The obtained high-density pellets and bars were used to determine the electrical conductivity and thermal expansion coefficient, respectively.

Anode-supported half cells with BCYN5 electrolyte were prepared through a co-pressing and co-firing process. The supports were fabricated by pressing the anode powders under 70 MPa of pressure. Next, the functional layer were co-pressed on supports under 70 MPa using NiO-BCYN5 composite powders. Finally, loose BCYN5 powders were uniformly distributed over the functional layer, co-pressed at 150 MPa and subsequently sintered at 1350 °C for 5 h, obtaining half cells. SBC-SDC (weight ratio is 7:3) composite cathode was brush-painted on the electrolyte membrane surface of half cell and fired at 1000 °C for 3 h in air to form a porous cathode layer with an area of 0.237 cm². Finally, single cells with button geometry were successfully prepared for electrochemical measurement.

2.3. Characterization

The phase structure of the as-prepared powders was identified via X-ray diffraction (XRD) using CuK₁ radiation with λ = 0.15418 nm wavelength on a SHIMADZU XRD-6100 type diffractometer. The working voltage is 40 kV, the tube current 30 mA, the scanning range 20–80° and scanning speed 6° min⁻¹. The Unitcell and Powder X software were used to calculate the cell parameters. Scanning electron microscope (SEM, Zeiss EVO MA15) was employed to observe the surface and cross-sectional morphologies of the sintered pellets. The well-developed and defects-free 50 grains were selected in SEM images and the horizontal size of each grain was measured using Nano Measurer software. The grain size distribution and the average value for 50 grains were worked

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