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Bismuth and niobium co-doped barium cobalt oxide as a promising cathode material for intermediate temperature solid oxide fuel cells

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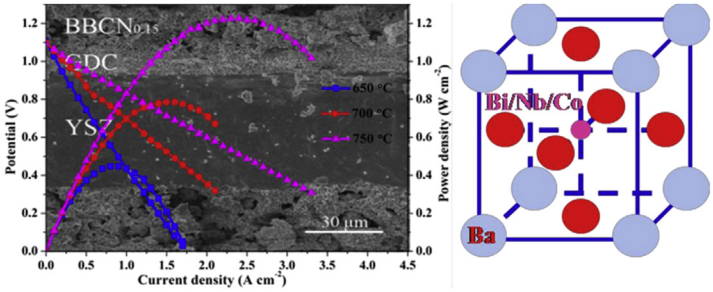
HIGHLIGHTS

- $BaBi_{0.05}Co_{0.95-y}Nb_yO_{3-\delta}$ ($0.1 \leq y \leq 0.2$) is investigated as cathode for IT-SOFCs.
- $BaBi_{0.05}Co_{0.8}Nb_{0.15}O_{3-\delta}$ presents the biggest lattice parameter 4.719 Å.
- With Nb doping, the electrical conductivities and TEC values gradually decrease.
- Maximum power density of single cell with $y = 0.15$ reaches 1.23 W cm^{-2} at 750 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

Perovskite oxides $BaBi_{0.05}Co_{0.95-y}Nb_yO_{3-\delta}$ (BBCNy, $0 \leq y \leq 0.2$) are synthesized and evaluated as potential cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFCs). Highly charged Nb^{5+} successfully stabilizes the cubic perovskite structure to room temperature with Nb substituting content $y \geq 0.1$. The phase structure, thermal expansion behavior, electrical conductivity and electrochemical performance of BBCNy with cubic phase are systematically studied. The samples exhibit excellent chemical compatibility with GDC and have sufficiently high electrical conductivities. However, the thermal expansion coefficients of BBCNy samples are nearly twice those of the most commonly used electrolyte materials YSZ and GDC, which is a major drawback for application in IT-SOFCs. The polarization resistances of BBCNy with $y = 0.10$, 0.15 and 0.20 on GDC electrolyte are 0.086, 0.079 and 0.107 Ω cm^2 at 700 °C, respectively. Even though the YSZ electrolyte membrane and GDC barrier layer are approximately 50 μm and 10 μm in thickness, the highest maximum power density (1.23 W cm^{-2}) of the single cell Ni-YSZ|YSZ|GDC|$BBCN_{0.15}$ is obtained at 750 °C. Good long-term stability of the single cell with $BBCN_{0.15}$ cathode is also demonstrated. These results demonstrate that BBCNy perovskite oxides with cubic structure are very promising cathode materials for IT-SOFCs.

1. Introduction

Solid oxide fuel cells (SOFCs) are highly efficient and environmentally friendly devices to convert chemical energy in fuels directly to electrical power as compared to traditional thermal power generation plants [1–3]. Recently, considerable efforts are focused on lowering the working temperature to an intermediate

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range of 600–800 °C [4]. Unfortunately, with lowering the operating temperature, the cathode polarization increases more rapidly than other polarizations, which is severely detrimental for performances of the fuel cells [5]. Therefore, it is critical to exploit novel cathode materials with superior catalytic activity for IT-SOFCs.

Due to the superior catalytic activity for oxygen reduction reaction (ORR) at reduced temperatures, oxygen-deficient conductors with mixed ionic and electronic conductivities have been comprehensively and thoroughly developed [6–8]. Among the large variety of mixed conducting oxides, $BaCoO_{3-\delta}$ is a promising parent component for many perovskite oxides with diverse properties [9]. On the one hand, Ba^{2+} with the large ionic radius (1.60 Å) is beneficial to create large free volume [10] and sufficient oxygen vacancy [11,12] for oxygen ions transportation in the bulk; on the other hand, the low binding energy of Ba–O can enhance the fast oxygen diffusion in the bulk and the quick oxygen exchange over the surface [13]. Therefore, the cathode materials based on $BaCoO_{3-\delta}$ should have promising performances.

Reported as an oxygen ion conductor, bismuth oxide has a high oxygen ion conductivity due to the small binding energy of Bi–O bond [14]. Niu et al. [15,16] investigated the effect of Bi replacing in A-site of $Bi_{1-x}Sr_xFeO_{3-\delta}$ and found that the electrode performance was promoted effectively. Zhou et al. [17] studied the B-site ordered double perovskite $Ba_2Bi_{0.1}Sc_{0.2}Co_{1.7}O_{6-\delta}$ and found that it showed promising performance as a cathode material for IT-SOFCs. However, Shao et al. [14] demonstrated that a low Bi doping concentration in $BaBi_xCo_{0.2}Fe_{0.8-x}O_{3-\delta}$ was favorable due to the large expansion of Bi at high temperatures resulted from the thermal reduction reaction of Bi^{5+} to Bi^{3+}. Therefore, in this work, only 5 mol% Bi will be doped in B-site of $BaCoO_{3-\delta}$. However, just doping 5 mol% Bi cannot stabilize the simple cubic perovskite structure to room temperature due to the large ionic radius mismatch between Ba and Bi/Co. To enhance the structure stability, one of the most reliable and effective strategies is to dope proper cations in B-site. Nagai et al. [18] found that Nb_2O_5 was the most effective dopant for the structure stability of $SrCoO_{3-\delta}$-based oxides. Dong et al. [5] further demonstrated the effectiveness of Nb doping in B-site for stabilizing the cubic perovskite structure of $BaFeO_3$ and found that a small amount of Nb doping further enhanced the electrochemical activity of $BaNb_{0.05}Fe_{0.95}O_{3-\delta}$. In addition, Zhou et al. [19] reported that $SrSc_{0.175}Nb_{0.025}Co_{0.8}O_{3-\delta}$ achieved extremely outstanding performance due to the presence of favorable transport paths by doping a small amount of Nb. Therefore, the substitution of Co by Nb may not only stabilize the cubic perovskite structure to room temperature, but also promote the performances of cathode materials.

Recently, Wang et al. [20] studied Nb-doped $BaBi_{0.05}Co_{0.95}O_{3-\delta}$ as oxygen permeable membranes and excellent oxygen permeation performance was found for $BaBi_{0.05}Co_{0.8}Nb_{0.15}O_{3-\delta}$, which was comparable to that of the state-of-the-art $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane. However, to the best of our knowledge, its performance as a cathode material for IT-SOFCs is still unreported so far.

In this work, Nb-doped $BaBi_{0.05}Co_{0.95}O_{3-\delta}$ perovskite oxides, i.e. $BaBi_{0.05}Co_{0.95-y}Nb_yO_{3-\delta}$, are synthesized as cathode materials for IT-SOFCs. The crystal structure, oxygen vacancy concentration, thermal expansion behavior, electrical conductivity and electrochemical performance of $BaBi_{0.05}Co_{0.95-y}Nb_yO_{3-\delta}$ are systematically evaluated as a function of Nb doping content.

2. Experimental

2.1. Powder synthesis and cell fabrication

$BaBi_{0.05}Co_{0.95-y}Nb_yO_{3-\delta}$ (BBCNy, y = 0.0–0.2) powders were synthesized by a conventional solid state reaction method [20]. Analytical grade $BaCO_3$ (Aladdin, China), Bi_2O_3 (Aladdin, China), Co_3O_4 (Aladdin, China) and Nb_2O_5 (Aladdin, China) were used as the raw materials. Stoichiometric amounts of the raw materials were weighted and well mixed by high-energy ball milling at 300 rpm for 12 h using ethanol as the liquid medium. After drying, the primary powder was pressed into a pellet and pre-calcined at 900 °C for 10 h in air. Then, the pellet was ground thoroughly and subsequently pressed into a membrane and sintered at 1100 °C for 10 h in air. The as-obtained sample was ball-milled for 6 h to decrease the average particle size.

Two-electrode symmetric cells with GDC pellets as the substrate were fabricated for impedance studies. The dense electrolyte pellets were prepared by dry pressing at 30 MPa for 10 min with the commercial $Ce_{0.9}Gd_{0.1}O_{1.9}$ (GDC10-N, Fuel Cell Materials, USA) and subsequently sintered at 1500 °C for 10 h in air. The synthesized cathode powder with an average grain size of 4 μm (see Fig. S1 in supporting information) was dispersed in a pre-mixed solution (6 wt% ethyl cellulose in terpineol solution) to prepare the cathode slurry, which was then screen-printed onto both sides of a GDC pellet in a symmetric configuration and subsequently sintered at 950 °C for 2 h in air. To fabricate complete electrochemical cells, NiO-YSZ (NiO, High Purity Chemicals, Japan; YSZ, Tosoh, Japan) anode supporting electrode and YSZ electrolyte was fabricated by the co-tape casting and co-firing technique which was reported in our previous work [21]. GDC was used as the barrier layer prepared by screen-printing and then sinter at 1300 °C for 2 h to prevent the chemical reaction between BBCNy cathodes and YSZ electrolyte during high temperature operations. The cathode slurry was screen-printed onto the barrier layer and calcined at 950 °C for 2 h in air. The diluted silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins, China) and filamentary silver were used as the current collector and conductor for symmetric cells and single cells, respectively.

2.2. Characterizations

The crystal structures of BBCNy samples were identified by X-ray diffraction (XRD, PANalytical X'Pert PRO X-ray diffractometer) with Cu Kα radiation (λ = 1.5418 Å) over the 2θ range of 20–80° with an interval of 0.02°. The obtained XRD data was analysed by Rietveld method with GSAS-EXPGUI software [22] and Powder4 was used for data preparation. The Pm-3m cubic perovskite structure was employed as the initial model for BBCNy (y = 0.10–0.20) samples, where Ba was located at (0, 0, 0) site, Bi/Co/Nb at (0.5, 0.5, 0.5) site, and O at (0.5, 0.5, 0) site, respectively. During the refinement process, lattice parameters, oxygen occupation, peak shape (Pseudo-Voigt function), background and viso parameter were refined.

The oxygen nonstoichiometry of BBCNy powders at room temperature was measured by iodometric titration method. Approximately 1 g of KI powder and 0.05 g of the sample were dissolved in about 5 mL HCl solution (~6 mol L^{-1}). The $Na_2S_2O_3$ solution, whose concentration was titrated by a standard $K_2Cr_2O_7$ solution, was used for the titration. About 2 mL starch solution was added into the solution as a titration indicator before the titration terminal point. At the titration terminal point, the colour of the solution abruptly changed from blue to yellow.

The chemical compatibility between BBCNy cathodes and GDC electrolyte is examined by XRD. In a 1:1 weight ratio, the mixture of $BBCN_{0.15}$ and GDC was sintered at 950 °C for 10 h in air. Then XRD was used to detect the phase reaction result.

Thermal expansion coefficient (TEC) was measured in air using a Netzsch DIL 402PC dilatometer from 30 to 900 °C at a heating rate of 5 °C min^{-1}. The electrical conductivity was measured in air by the four-terminal technique using a Keithley 2400 multimeter with an