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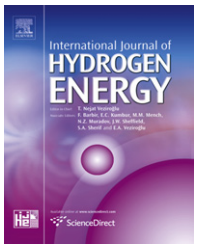

Bismuth doping effects on the structure, electrical conductivity and oxygen permeability of $Ba_{0.6}Sr_{0.4}Co_{0.7}Fe_{0.3}O_{3-\delta}$ ceramic membranes

Jianying Yang [a], *Hailei Zhao* [a,b,*], *Xiaotong Liu* [a], *Yongna Shen* [a], *Lihua Xu* [a]

[a] *School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China*
[b] *Beijing Key Lab. of New Energy Materials and Technology, Beijing 100083, China*

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ABSTRACT

A series of $Ba_{0.6}Sr_{0.4}Co_{0.7}Fe_{0.3-x}Bi_xO_{3-\delta}$ (BSCFB, $x = 0$–0.2) ceramic membranes were prepared by solid state reaction method. The doping effects on the phase structure, structural stability, electrical conductivity and oxygen permeability were investigated. Little amount of Bi ($x = 0$–0.08) can maintain the cubic perovskite structure of BSCFB materials while more Bi ($x > 0.08$) will result in the generation of other impurities. Even in the Bi solid solution range, Bi doping is unfavorable for the enhancement of structural stability of BSCFB membranes. The electrical conductivity decreases with Bi doping level, while the oxygen permeability of BSCF membrane can be increased remarkably with little amount of Bi doping ($x = 0.05$). More Bi leads to the structure deterioration of membrane surface under oxygen permeation condition, resulting in a severe decrease in oxygen permeability. Considering the overall performance, a low Bi doping amount such as $x = 0.05$ is favored for the membrane applications.

1. Introduction

The fast development of modern society brings great convenience and prosperity to human being but at the expense of the huge consumption rate of energy. The severe emission of greenhouse gases and the worn out of fossil fuel make it urgent to explore new clean energy sources. Meanwhile, hydrogen is expected to play a significant role in the future energy system [1] because it can provide viable, sustainable options for meeting the world's energy requirements [2]. Among the diversified methods of producing hydrogen, the partial oxidation of methane (POM) in a reaction device equipped with mixed ionic and electronic conducting (MIEC) membrane is regarded an efficient and low cost technology [3] and thus has attracted much attention. The MIEC membranes can combine the separation of oxygen from air and the catalytic oxidation in a single process serving not only as sustainable oxygen sources but also barriers to N_2 to avoid the generation of NO_x pollutants [4]. Furthermore, the intermediate temperature needed for oxygen permeation of membranes can be attained by the heat generated by the POM reaction itself [5] thus being energy-saving. MIEC membrane is one of the most crucial parts of this POM technology. From the perspective of application, the membrane must possess sufficient oxygen permeability and sustainable structural stability to withstand harsh conditions [6].

* *Corresponding author*. University of Science and Technology Beijing, School of Materials Science and Engineering, 30 Xueyuan Rd., Haidian District, Beijing 100083, China. Tel./fax: +86 10 82376837.
E-mail address: hlzhao@ustb.edu.cn (H. Zhao).

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Since Teraoka [7] first reported the high oxygen permeation flux of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCFO) membrane, many researches have been made based on this kind of materials. Shao [6,8] first reported that the doping of barium into SCFO, namely $Ba_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$ (BSCF) could suppress the oxidation of Co^{3+} and Fe^{3+} to higher valence states of Co^{4+} and Fe^{4+} in the lattice, and stabilize the perovskite structure under lower oxygen partial pressures. Higher oxygen permeation rates were also achieved from this doping strategy. Then, the BSCF material system was widely explored and regarded as promising MIEC materials for both oxygen permeation devices and IT-SOFCs [9–13].

Bismuth is an interesting element because bismuth oxides show high oxygen ionic conductivity [14] and many works have been reported that Bi doping could improve the oxygen permeability of oxide membranes. Li [15] investigated the effect of Bi doping at the A-site of $Sr_{10-n/2}Bi_nFe_{20}O_m$ and $Sr_{1-x}Bi_xFeO_3$, and found that the oxygen flux increased with the increasing bismuth content in both oxides. Shao reported that the increasing bismuth content in $BaBi_xCo_{0.2}Fe_{0.8-x}O_{3-\delta}$ resulted in an increasing oxygen flux, where Shao also indicated that a low bismuth content was favored due to the large expansion coefficient of the material accompanied by the valence change from Bi^{5+} to Bi^{3+} at high temperature [16]. Sunarso investigated the structure and oxygen permeability of barium bismuth oxides [17]; barium bismuth iron oxides [18] and Bi doped $BaSc_{0.1}Co_{0.9}O_{3-\delta}$ [19,20]. The proper introduction of bismuth could result in the significant improvement of the oxygen permeability while maintaining the stability of the cubic perovskite membranes.

Our previous work revealed that $Ba_{0.6}Sr_{0.4}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ is a potential oxygen permeation membrane with good structural stability against reducing atmosphere and acceptable oxygen permeability [5]. In this study, Bi was employed to dope $Ba_{0.6}Sr_{0.4}Co_{0.7}Fe_{0.3}O_{3-\delta}$ with the aim of enhancing the oxygen permeability. A series of $Ba_{0.6}Sr_{0.4}Co_{0.7}Fe_{0.3-x}Bi_xO_{3-\delta}$ (BSCFB) membranes were synthesized and their lattice structure, electrical conductivity, oxygen permeability and structural stability were investigated.

2. Experimental

2.1. Synthesis and preparation

Bi doped $Ba_{0.6}Sr_{0.4}Co_{0.7}Fe_{0.3}O_{3-\delta}$ powders were prepared by the conventional solid state reaction method. $BaCO_3$, $SrCO_3$, $Co(CH_3COO)_2{\cdot}4H_2O$, Fe_2O_3 and Bi_2O_3 (all in A.R. grade) were weighed according to the stoichiometric formula $Ba_{0.6}Sr_{0.4}Co_{0.7}Fe_{0.3-x}Bi_xO_{3-\delta}$ (BSCFB, $x = 0$, 0.05, 0.08, 0.12, 0.2) and mixed by planet ball milling in the ethyl alcohol medium for 4 h with ZrO_2 balls. After drying, the powders were screened through a 140-mesh screen and then calcined at 900 °C for 10 h with both heating and cooling rates of 3 °C/min. The calcined powders were finely grounded with an agate mortar and screened through a 140-mesh screen again, followed by pressing under a uniaxial pressure with stainless steel molds to prepare green disks and bars. The green disks and bars were sintered in air at different temperatures for 10 h with both heating and cooling rates of 3 °C/min to achieve dense samples for various characterizations.

2.2. Characterization

The lattice structure of the densified membranes was evaluated by X-ray Diffraction (XRD, RIGAKU D/MAX-A Diffractometer) using Cu Kα radiation at room temperature. The scanning electronic microscope (SEM, LEO-1450) was employed to observe the morphology of microstructure of the membranes. The structural stability of BSCFB membranes was examined in flowing Ar for 10 h and 5% H_2/Ar for 0.5 h at 900 °C with a flowing rate of 60 ml/min. The electrical conductivity was measured by four-terminal DC method from 200 to 900 °C in different atmospheres at a heating rate of 5 °C/min. The data were recorded in an interval of 50 °C after equilibrium at each temperature to reach the stable state.

2.3. Oxygen permeation measurement

Disk-shaped membranes were subjected to an oxygen permeation measuring system. The tested membranes were finely polished to 1.2 mm thick and sealed between a quartz tube and an alumina tube with silver rings between. No nitrogen leakage was guaranteed for oxygen permeation measurements. Air was fed from a gas cylinder to the oxygen rich side at a flow rate of 90 ml/min [STP], while helium was applied as sweeping gas at a flow rate of 60 ml/min. The gas flow rates were controlled by the mass flow controller. Gas chromatography was used to analyze the oxygen content in the sweeping gas and the oxygen permeation flux was calculated by Eq. (1):

$$J_{O_2}\left(\mathrm{ml\ cm^{-2}\ min^{-1}}\right) = \frac{C_{O_2} \times F}{S \times \left(1 - C_{O_2}\right)} \quad (1)$$

where C_{O_2} is the measured concentration of oxygen in the sweeping gas; F is the fixed flow rate of helium and S is the effective membrane surface area (cm^2) for permeation. Tests were performed upon cooling from 900 to 820 °C at a cooling rate of 1 °C/min and a 10 min was held to reach a stable permeation flux for each test point.

3. Results and discussion

3.1. Lattice structure and structural stability

The structure of the sintered membranes was evaluated by XRD and the results are shown in Fig. 1. For samples with low Bi doping level ($x = 0$, 0.05, 0.08), pure cubic perovskite structure was formed and the XRD peaks shifted to smaller angle with increasing Bi doping amount, indicating the gradual lattice expansion. This is attributed to the bigger radius of Bi ion than that of Co and Fe ions at B-site (Co^{3+}: 0.61 Å, CN = 6, HS; Fe^{3+}: 0.645 Å, CN = 6, HS) [21]. According to Bhalla [22], the perovskite structure with a general formula of ABO_3 correlates to large sized A cation (1.10–1.80 Å) and medium sized B cation (0.62–1.00 Å). Bi has ionic radius of 1.03 and 0.76 Å for Bi^{3+} and Bi^{5+} in a six-coordination, respectively [21], so it is reasonable to say that Bi was doped into B-site of BSCF with