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High performance oxygen permeable membranes with Nb-doped $BaBi_{0.05}Co_{0.95}O_{3-\delta}$ perovskite oxides

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ABSTRACT

$BaBi_{0.05}Co_{0.95-x}Nb_xO_{3-\delta}$ (x=0–0.2) and $BaBi_{0.1}Co_{0.8}Nb_{0.1}O_{3-\delta}$ were synthesized via solid state reaction method and fabricated into disk-shaped membranes. The surface morphology, phase structure, oxygen nonstoichiometry and oxygen permeability of the perovskite membranes were investigated by SEM, XRD, TGA techniques and oxygen permeation studies. The experimental result indicates Nb-doping can significantly enhance the oxygen permeability compared to the un-doped disk membrane. Among all compositions, $BaBi_{0.05}Co_{0.8}Nb_{0.15}O_{3-\delta}$ showed the highest oxygen flux, reaching 2.92 ml cm^{-2} min^{-1} with 1.3 mm thickness membrane at 900 °C, coupled with the lowest activation energy, which is 44.17 kJ mol^{-1} at 750–900 °C and 74.59 kJ mol^{-1} at 600–750 °C. However, further increasing Nb-doping amount leads to a decrease in the oxygen permeability. Interestingly, the order of tendency towards increasing of oxygen nonstoichiometry with increasing temperature exactly corresponds to the order of oxygen permeation flux of various samples.

1. Introduction

Dense ceramic membrane made from mixed ionic and electronic conductors (MIEC) have attracted intense research interest in the past decade owing to their potential applications in air separation and partial oxidation of hydrocarbons to value-added products [1–6]. Perovskite materials with the general formula $ABO_{3-\delta}$ have been intensively researched due to their high ionic/electronic conductivity and stability [7–10]. However, for industrial application of oxygen permeable membranes, the oxygen permeability must be considerably improved. For this purpose, the development of new perovskite materials with high permeation property has been a top priority [11].

So far, a series of new perovskite materials have been found by partial substitution of the A-site or B-site cations in the typical ABO_3 perovskite [12–18]. Teraoka et al. [19] has researched on the oxygen permeability of $La_{0.6}A_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (A=Ba, Ca, Sr) and thereafter concluded that the perovskite material shows the highest oxygen permeation flux when Ba substitutes for A-site. Moreover, Ishihara [20] obtained the result of $BaCoO_3 > Ba_{0.6}La_{0.4}CoO_{3-\delta} > Ba_{0.1}La_{0.9}CoO_{3-\delta}$ for oxygen permeability, which means higher Ba-doping concentration possibly results in higher oxygen permeability. Also, Shao et al. [21] reported a significant increase of oxygen permeability by partial substitution of Ba in the A-site of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$. It is generally accepted that substitution of Ba in the A-site of perovskite could improve the oxygen permeation rate. In other words, when the A-site of perovskite is fully occupied by Ba, the material has the potential of attaining high oxygen permeability.

Therefore the $BaCoO_3$ system seems to be a good choice for attaining a high oxygen permeability material. However, the ionic radius of Ba is too large to form the stable cubic phase in $BaCoO_3$ which has exceeded the tolerance factor (t) [22]. For a stable cubic perovskite structure, the cation which has an ionic radius smaller than Ba^{2+} and larger than Co^{2+} is preferred to substitute in the B-site of this perovskite.

Recently, Bi-doping on the $BaSc_{0.1}Co_{0.9}O_{3-\delta}$ perovskite material has been shown to cause a noticeable improvement on oxygen permeability and phase stability [23]. When the Bi-doping composition was 0.05 and 0.1 in the B-site cations, the oxygen permeability significantly improved. However, in this perovskite material, the raw material Sc $(NO_3)_3$ or Sc_2O_3 is very expensive (Table 1S). In order to significantly reduce the cost of the perovskite material, niobium is considered as the best choice for doping in the B-site of the perovkite material. The reason is that Nb-doping in the B-site of perovskite can result in a noticeable oxygen permeability [11,24] and the price of niobium is much cheaper in comparison with scandium (Sc_2O_3 is 16 times more expensive than Nb_2O_5 as listed in Table 1S). Substitution of niobium was carried out in order to attain high-performance oxygen-permeable membrane material with lower production cost.

In this work, Nb was substituted for scandium and Nb-doping composition was studied for the series of $BaBi_{0.05}Co_{0.95-x}Nb_xO_{3-\delta}$

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perovskite. The most important contribution of this work lies in the optimization of Nb-doping concentration for deriving a high oxygen permeability perovskite material. This is very critical for industrial application of perovskite ceramic membrane for oxygen separation.

2. Experimental section

2.1. Synthesis and preparation

$BaBi_{0.05}Co_{0.95-x}Nb_xO_{3-\delta}$ (x=0–0.2) and $BaBi_{0.1}Co_{0.8}Nb_{0.1}O_{3-\delta}$ perovskite powders were synthesized via solid state reaction method. Stoichiometric amounts $BaCO_3$ (99%, Sigma–Aldrich), $Co(NO_3)_2\cdot 6H_2O$ (98%, Sigma–Aldrich), $Bi(NO_3)_3\cdot 5H_2O$ (98%, Sigma–Aldrich) and Nb_2O_5 (99.99%, Sigma–Aldrich) were weighed and mixed. The mixtures were then ball-milled with ethanol in a planetary mill (PM 200, Retsch) at 400 rpm for 6 h. The mixed powders were subsequently calcined at 850 °C for 10 h. After calcination, the powders were ball-milled again at 300 rpm for 2 h. The as-obtained powders were then pressed into disk membranes in a stainless mold (14 mm in diameter) under a hydraulic pressure about 5 ton. The disks were finally sintered at 1050 °C and 1100 °C for 7 h.

2.2. Characterization

The surface morphology of disk membranes was ascertained by Scanning Electron Microscope (SEM, Jeol, JSM-6701F). The samples were degassed under vacuum condition to remove impurities. Platinum coating (about 10 nm thickness) was carried out at 20 mA for 40 s. The crystal phase structure of precursor powders and sintered disk membranes were determined by X-ray diffraction (XRD, Shimadzu XRD-6000 power diffract meter) with Cu Kα radiation. The disk membranes were ground into fine powders prior to the XRD measurements. Continuous scan mode was used to collect 2θ data from 20° to 80° with a 0.02° sampling pitch and a $2^\circ\ min^{-1}$ scan rate. The experiments were operated in room temperature and air atmosphere. The weight losses of the samples were examined by the Thermal Gravity Analysis (TGA, Shimadzu DTG 50), referenced with an Al_2O_3 pan, in the temperature range from room temperature to 900 °C. In order to achieve thermodynamic equilibration, a relatively slow heating rate of $3\ ^\circ C\ min^{-1}$ was used [25]. This measurement was operated under air atmosphere.

2.3. Oxygen permeation measurement

Oxygen permeation properties of various membranes were investigated in an oxygen permeation apparatus shown in Fig. 1 Silver paste was used as sealant to fix the disk membrane onto the quartz tube. The effective inner surface area was controlled in order to achieve approximately same area for the various membranes tests. The silver paste sealing was heated at 150 °C for 1 h. Subsequently, helium gas was used as a sweep gas in order to check the gas tightness of whole apparatus at room temperature. The outlet gas flows into a Gas Chromatography (GC 6890N, Agilent) and analyzed by a TCD detector using a Hayesep D 100/120 column. This sealing and testing procedure was repeated until the system was determined to be completely gas tight. However, at the high temperature, a small leakage from air still existed in the permeate gas steam. Although the amount of leaked oxygen is much less than permeated oxygen, it has to be deducted for the calculation of oxygen permeation flux

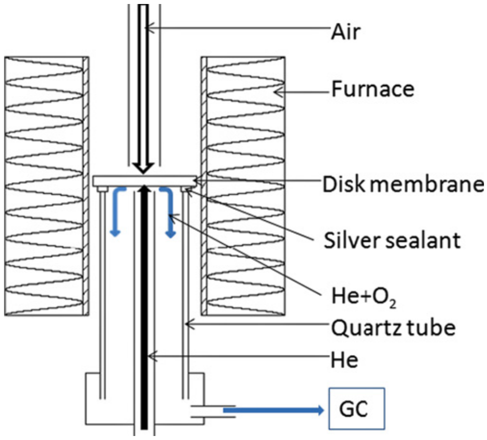

Fig. 1. Schematic drawing of the oxygen permeability measurement apparatus.

Table 1
Sintering condition.

Sample	Sintering temperature (°C)	Sintering time (h)
$BaBi_{0.05}Co_{0.95}O_{3-\delta}$	1050	7
$BaBi_{0.05}Co_{0.9}Nb_{0.05}O_{3-\delta}$	1100	7
$BaBi_{0.05}Co_{0.85}Nb_{0.1}O_{3-\delta}$	1100	7
$BaBi_{0.1}Co_{0.8}Nb_{0.1}O_{3-\delta}$	1100	7
$BaBi_{0.05}Co_{0.8}Nb_{0.15}O_{3-\delta}$	1100	7
$BaBi_{0.05}Co_{0.75}Nb_{0.2}O_{3-\delta}$	1100	7

$$J_{O_2}=V\left(x_{O_2}-\frac{21}{78}x_{N_2}\right)/A \qquad (1)$$

where J_{O_2} is oxygen permeation flux ($ml\ cm^{-2}\ min^{-1}$), V is the flow rate of permeate gas stream ($ml\ min^{-1}$), x_{O_2} and x_{N_2} are the percentages of oxygen and nitrogen in the effluent, and A is the effective membrane area (cm^2). All the values of oxygen permeation flux in this work were normalized into standard temperatures and pressure conditions.

During the oxygen permeability measurement, the upper side of the membrane was supplied with air as feed gas with a flow rate of $150\ ml\ min^{-1}$. The lower side of the membrane was supplied with helium as a sweep gas with a flow rate of $100\ ml\ min^{-1}$. The gas flow rate was controlled by mass flow controllers (5850E, Brooks) and calibrated by the bubble flow meter. The permeate stream containing a mixture of the permeated oxygen and helium were analyzed by the GC. The permeation stream flow rate was also measured by a bubble flow meter.

3. Results and discussion

3.1. Compositions and conditions

Table 1 lists the compositions and sintering condition of the disk membranes. Since the sintering condition has a significant influence on the oxygen permeability of the membrane [26,27], all the disk membranes were sintered at the same temperature (1100 °C) for the permeation tests with the exception of $BaBi_{0.05}Co_{0.95}O_{3-\delta}$ membrane which was sintered at lower temperature (1050 °C) due to its lower melting point. Since the thickness of disk membrane is the key factor influencing oxygen permeation, the thickness of all the disk membranes was maintained at 1.3 mm.