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Cobalt-free niobium-doped barium ferrite as potential materials of dense ceramic membranes for oxygen separation

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ABSTRACT

Cobalt-free perovskite-type oxides with the nominal composition of $BaNb_yFe_{1-y}O_{3-\delta}$ ($y=0.025$–0.20) are synthesized and evaluated as materials used in ceramic membranes for oxygen separation. The effects of Nb-doping on the crystal structure, surface morphology, electrical conductivity, chemical bulk diffusion and surface exchange, and oxygen permeability of the oxides are systematically investigated using XRD, SEM, four-probe DC conductivity, electrical conductivity relaxation technique, and oxygen permeation studies. A small amount of Nb-doping induces a sharp increase in electrical conductivity. A further increase in the Nb-doping amount, however, lowers the electrical conductivity as a result of the blocking effect of Nb^{5+} on electronic conduction. A small amount of Nb-doping has less impact on the sintering capability. From the oxygen permeation test, it was found that Nb-doping could significantly enhance the oxygen permeability, especially below 750 °C. Among all of the compositions, $BaNb_{0.05}Fe_{0.95}O_{3-\delta}$ shows the highest oxygen permeation fluxes, reaching 1.35 and 0.61 mL cm^{-2} min^{-1} for a membrane with a thickness of 1.0 mm at 900 and 700 °C, respectively. Furthermore, the membrane is rate-controlled mainly by bulk diffusion, indicating the potential to further improve the oxygen permeation flux via a thinner membrane.

1. Introduction

Some composite oxides possess mixed oxygen-ion and electronic conductivity at an elevated temperature [1–3]. After being fabricated into dense ceramics (planar or tubular shapes) and with the presence of a steady oxygen gradient across the ceramics, oxygen in the oxygen-rich side atmosphere adsorb onto the ceramic surface and migrate through the ceramic to the other surface, where the oxygen is finally released into the oxygen-lean side atmosphere. This phenomenon suggests that such ceramics can perform as permeating membranes for the continuous oxygen separation from air; this ceramic membranes separation technology has some obvious advantages: 100% oxygen selectivity, assuming full densification of the membrane; simplicity and continuity in operation with size flexibility; a substantial reduction in capital cost for both plant construction and daily operation; and the capability of causing a coupling reaction [4–7].

Suitable materials for ceramic oxygen permeating membranes should meet several requirements in terms of high oxygen permeability, good stability, easy fabrication and so on. In the past, cobalt-based composite oxides, mainly in perovskite lattice structures, have been extensively investigated as materials for ceramic oxygen permeating membranes because of their high oxygen-ion and electronic conductivity and their high oxygen surface exchange kinetics, which originate from the high reducibility and high catalytic activity of cobalt ions [2,8–19]. However, the cobalt ions can be easily over reduced under highly reducing conditions (i.e., a coupling reaction was presented), thus causing the collapse of the perovskite structure and the failure of the membrane for oxygen separation. The easy change in valence state of the cobalt ion also induces a large chemical expansion, which is detrimental for the long-term operational stability of the membrane. Recently, to overcome these drawbacks, cobalt-free conducting membranes, specifically iron-based perovskite oxides such as $La_{0.3}Sr_{0.7}Fe_{1-x}Ga_xO_{3-\delta}$ [20], $BaCe_xFe_{1-x}O_{3-\delta}$ [21–23], $Ba_{0.95}La_{0.05}FeO_{3-\delta}$ [24–26], $Ba_{0.5}Sr_{0.5}Zn_{0.2}Fe_{0.8}O_{3-\delta}$ [27], and $SrFe_{0.7}Al_{0.3}O_{3-\delta}$ [28], have received increasing attention.

To maximize oxygen permeability, assuming no defect association, a higher concentration of oxygen vacancy in the oxide lattice

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is preferred because oxygen vacancy is typically the charge carrier of the oxygen ions [29]. Oxygen vacancies can be created through a doping strategy. Using this consideration, $BaFeO_{3-\delta}$ oxide, in which the total amount of A-site cation is replaced with the low valance state cation of Ba^{2+}, possesses a very high oxygen vacancy concentration. However, the oxygen vacancy in $BaFeO_{3-\delta}$ is normally ordered, resulting in very low oxygen permeability at a temperature lower than the appearance of the thermally induced phase transition [30–34]. Recently, we attempted to stabilize the oxygen-disordered cubic perovskite lattice structure of $BaFeO_{3-\delta}$ at lower temperatures by the partial substitution of its A-site (Ba^{2+}) or B-site (Fe^{3+}) using other cations [26,35]. In particular, we developed a new oxide with the composition of $BaNb_{0.05}Fe_{0.95}O_{3-\delta}$ from the partial substitution of B-site cations in $BaFeO_{3-\delta}$ with niobium, which showed promising electrochemical performance at an intermediate temperature when acting as an oxygen reduction electrode of solid oxide fuel cells (SOFCs) [35]. There is no direct correlation between oxygen permeability and cathodic performance of mixed conducting oxides. Active cathode materials used for SOFCs only sometimes also show good oxygen permeability when acting as oxygen separation membranes. To the best of our knowledge, the information regarding the effect of niobium doping concentration on the oxygen permeation properties (sintering behavior, oxygen permeability, and rate determination step) in air separation is still lacking in the open literature.

Herein, a systematic investigation into the influence of the partial substitution of Fe in $BaFeO_{3-\delta}$ with Nb on the crystal structure, electrical conductivity, microstructure and oxygen permeability of the related membranes has been conducted. The rate-determination steps for oxygen permeation through a $BaNb_{0.05}Fe_{0.95}O_{3-\delta}$ ceramic membrane were specifically studied to obtain a more in-depth understanding of its oxygen permeation behavior.

2. Experimental

2.1. Powder synthesis and membrane fabrication

In this study, Nb-doped $BaFeO_{3-\delta}$ composite oxides with the nominal composition of $BaNb_yFe_{1-y}O_{3-\delta}$, where y was 0.0, 0.025, 0.05, 0.075, 0.10 or 0.20, were synthesized by a mechano-activation assisted solid-state reaction method. In a typical synthesis, proper amounts of $BaCO_3$, Nb_2O_5 and Fe_2O_3 (all in analytic grades) were weighed and ground using a high-energy ball mill (FRITSCH pulverisette 6) in acetone liquid medium at a rotation speed of 400 rpm for 1 h. The as-obtained slurry was dried and calcined at 1000 °C in air for 10 h with a heating rate of 5 °C min^{-1}. The as-obtained primary product was further ground by hand for 1 h, and it was calcined again at 1200 °C in static air for 10 h to yield the products for later use.

To fabricate ceramic membranes, the powders calcined at 1200 °C were further processed using high-energy ball milling for 1 h to improve the sintering capability by decreasing the particle size. The powders were then pressed into disk-shape membranes using a stainless steel mold (15 mm in diameter) under approximately 1.5×10^8 Pa of hydraulic pressure. The resulting green pellets were sintered at 1300 °C for 5 h under an air atmosphere at a heating rate of 2 °C min^{-1}. The relative density of these sintered membranes was measured using Archimedes′ liquid displacement method with distilled water as the liquid medium. The membrane gas-tightness was also examined via the detection of nitrogen leakage in the oxygen lean side atmosphere using gas chromatography (Varian CP 3800).

2.2. Basic characterization

The phase structures of the as-synthesized powders were studied using an X-ray diffractometer (Rigaku Smartlab equipped with Cu Kα radiation). The experimental diffraction patterns were collected at room temperature by step scanning at the 2θ range of 10–90°. The General Structure Analysis System (GSAS) program was applied to analyze the diffraction patterns. The morphology of the membranes was observed using environmental scanning electron microscopy (ESEM, QUANTA-2000).

The electrical conductivities of the various samples under both air ($P_{O_2} = 0.21$ atm) and argon atmospheres ($P_{O_2} = 10^{-5}$ atm) were measured using a four-probe DC method on the sintered bars with dimensions of approximately 2 mm × 5 mm × 12 mm, which were sintered at the same temperature as the ceramic membranes used for oxygen permeation. The measurements were performed over a temperature range of 900–300 °C, at an interval of 10 °C. A constant current was applied to the two current wires, and the voltage response on the two voltage wires was recorded using a Keithley 2420 source meter interfaced with the computer for data acquisition using the Labview program. After reaching steady state, the current was increased from 1 μA until the voltage exceeded 1.0 V. The conductivity can be calculated based on the following equation:

$$\sigma = \frac{L}{A} \times K \qquad (1)$$

where L is the length of the two voltage contacts, A is the cross-sectional area of the bar-shaped samples and K is the slope of the curve of current versus voltage. Electrical conductivity relaxation (ECR) was used to determine the chemical bulk diffusion coefficient (D_{chem}) and surface exchange coefficient (k_{chem}), whose detailed experiment is in the supplementary information.

2.3. Oxygen permeation measurement

The oxygen permeation properties of the membranes were tested using the gas chromatography (GC) method in a homemade high-temperature oxygen permeation test station [12]. Both surfaces of the sintered disk membranes were carefully polished with 1000 mesh SiC paper until the desired thickness was achieved. The polished membrane was then sealed onto the top of Al_2O_3 tubes using concentrated silver paste. During the test, ambient air was used as the oxygen-rich side atmosphere, and helium was fed into the oxygen lean-side as the sweeping gas at a flow rate of 100 mL min^{-1} [STP]. The oxygen permeation measurement was performed using a temperature range of 900–700 °C with an interval of 25 °C. The permeated oxygen was carried by the helium sweeping gas to a gas chromatograph equipped with a 5 Å molecular sieve capillary column for in-situ oxygen concentration analysis. Because of the potential minor gas leakage through the sealing area, small amounts of nitrogen were often detected in the effluent gas by the gas chromatograph. The effect of leakages can be eliminated using the following equation to calculate the oxygen permeation flux:

$$J_{O_2}(mL\,cm^{-2}\,min^{-1}, STP) = \left[C_O - C_N \times \frac{0.21}{0.79} \times \left(\frac{28}{32}\right)^{1/2}\right] \times \frac{f}{S} \qquad (2)$$

where C_O and C_N are the measured gas-phase concentrations of oxygen and nitrogen in the sweeping gas, f is the flow rate of the exit gas on the sweep side (mL min^{-1}), and S is the effective surface area exposed to the sweeping gas (cm^2).