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Oxygen permeation and partial oxidation of methane reaction in $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ oxygen permeation membrane

Shidong Song, Peng Zhang, Minfang Han*, Subhash C. Singhal

Union Research Center of Fuel Cell, School of Chemical & Environment Engineering, China University of Mining & Technology, Beijing 100083, China

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ABSTRACT

Dense perovskite materials exhibiting mixed ionic and electronic conductivity can be used as a membrane material for the production of oxygen of very high purity and in partial oxidation of methane to syngas in membrane reactors. They represent an attractive technology which is energy- and cost-efficient in comparison with conventional technologies in those fields. Currently, one of the most promising membrane materials is $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ perovskite which possesses very high oxygen permeation flux. However, its stability is not satisfactorily high. In this work, $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ perovskite was prepared by introducing A-site deficiency into $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ and expected to enhance the stability and as well as the oxygen permeability. Under an air/helium oxygen gradient, the oxygen permeation flux of 1 mm thick $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ membrane was 1.8 ml min^{-1} cm^{-2} at 875 °C, which is slightly higher than that of $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ membrane under the similar condition. A 400 h durability test of $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ membrane for POM reaction at 875 °C showed no degradation in the measured oxygen permeation flux and methane conversion, which indicated that $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ had a significantly better stability than $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ and could be a promising material for oxygen generator.

1. Introduction

Perovskite oxides with mixed electronic and oxygen-ionic conductivity (MIEC) have attracted considerable attention owing to their versatile applications, such as in electrodes of solid oxide fuel cells (SOFCs) [1] and oxygen permeation membranes [2] which can be used for partial oxidation of methane (POM) to syngas [3]. Oxygen permeation through the dense perovskite membrane is due to transport of oxygen ions under an oxygen partial pressure gradient. Perovskites are ABO_3-type oxides in which A-site and B-site are generally occupied by Ln (Ln=rare earth elements) cations in 12-fold coordination and by transition cations in 6-fold coordination, respectively. In B-site, transition metal elements, particularly Co [4], Fe [5], Mn [6] and Ti [7], are favorable for their mixed charge valence that allows easy formation of oxygen defects. The cobalt-containing perovskite oxides, such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCFO) oxides [8], have been extensively studied because almost all of them exhibit very high oxygen permeability, which can be attributed to the weak binding energy between Co–O. In A-site, La is widely used for its appropriate ionic radius that enables easy construction of the cubic ABO_3 lattice. As trivalent La cation is replaced by divalent alkaline earth elements, such as Ca [9], Sr [8] and Ba [10] on A-site gradually, the electron holes and oxygen vacancies are generated by charge compensation, leading to an increase in the oxygen vacancy concentration. Thus, compositions highest in Sr and Co tend to offer the highest oxygen permeability. For example, with the full substitution of La by Sr cation, $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCFO) shows the highest oxygen permeability within $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ compositions [8]. However, SCFO oxides have a very limited chemical and structural stability and will transform from a perovskite with disorderly arranged oxygen vacancies to a brownmillerite with orderly arranged oxygen vacancies below 770 °C in the reducing atmosphere [11], which deteriorates oxygen ion transport. For successful applications, the oxygen permeation membrane is required to possess both high oxygen permeability and adequate stability under an oxygen partial pressure gradient at high temperatures. When it is applied in a POM membrane reactor, the membrane must withstand oxidizing atmosphere (ambient or flowing air) on its air side and highly reducing atmosphere (CH_4, H_2 and CO) on the sweep side at high temperatures. Teraoka et al. [8] systematically studied the oxygen permeation flux of $La_{0.6}A_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (A=Ba, Ca, Sr) and concluded that doping Ba cation at A-site in perovskite could achieve the highest oxygen permeation flux. Shao et al. [3,10,12] reported that $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO) perovskite had high oxygen permeability and improved stability compared with SCFO because doping

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* Corresponding author. Tel.: +86 10 62331098; fax: +86 10 62331098.
E-mail addresses: songshidong@hotmail.com (S. Song), hanminfang@sina.com (M. Han).

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barium into SCFO could suppress the oxidation of Co and Fe cations to their higher valence states in crystal lattice thereby stabilizing the perovskite structure under reducing atmosphere. Recently, Wei et al. [13] prepared a novel BSCFO hollow-fiber membrane and reported a very high oxygen permeation flux of 3 ml $\mathrm{min}^{-1}\,\mathrm{cm}^{-2}$ at 950 °C. Unfortunately, BSCFO still lacks chemical stability in reducing atmosphere, especially in the presence of a large amount of CO_2 at high temperatures [14].

$BaCoO_3$-based perovskites have drawn a great deal of attention and been extensively investigated for their application in oxygen permeation membranes [15]. It is commonly believed that the larger size of Ba cation (1.6 Å in 12-fold coordination) than that of Sr (1.44 Å in 12-fold coordination) could enlarge the free volume in perovskite lattice and thus promote oxygen ion mobility [12]; while some further investigations point out that a high composition of Ba may deteriorate the structural stability of cubic perovskite [16]. Since high oxygen permeability is of practical importance, it is reasonable and promising to develop a good oxygen permeation material by improving the structural stability of $BaCoO_3$-based perovskites. One feasible strategy is to dope their B-sites with other transition elements to improve their stability. Luo et al. [17,18] reported $BaCo_{0.7}Fe_{0.2}Ta_{0.1}O_{3-\delta}$ (BCFT) perovskite membrane could achieve a very stable performance during a 400 h POM operation. Recently, it has been reported that introduction of Nb in the B-site of cobalt-based perovskites can also significantly improve the chemical stability and oxygen permeability [19]. Nagai et al. [20] systematically studied a variety of potential substitution cations for B-site in $Sr(Co_{0.9}X_{0.1})O_{3-\delta}$ aiming to improve its stability, where X is Ni, Cu, Zn, Cr, Fe, Al, Ga, In, Ce, Ti, Zr, Sn, V or Nb. They found that the sequence of stability upon the substituting cations is (Ni, Cu, Zn, In, Ce) < (Cr, Al, Ga, Zr, Sn, V) < Fe < Ti < Nb and the order of oxygen permeability at 900 °C is $SrCo_{0.9}Nb_{0.1}O_{3-\delta} > SrCoO_{3-\delta} \gg SrCo_{0.9}Ti_{0.1}O_{3-\delta} > SrCo_{0.9}Fe_{0.1}O_{3-\delta}$, which indicated that the doping of high valence Nb cation in the B-site contributes to both good chemical stability and high oxygen permeability. Harada et al. [21,22] first reported $Ba_{1.0}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ oxide (BCFNO) as an oxygen permeation membrane for POM to syngas. BCFNO membrane exhibited a remarkably high performance with an oxygen permeation flux of more than 20 ml $\mathrm{min}^{-1}\,\mathrm{cm}^{-2}$ and maintained a 300 h consecutive operation. Normally, good MIECs with high oxygen permeability at elevated temperatures, such as $LaMnO_3$ [23], LSCFO [24] and BSCFO [25], should perform well as cathodes of SOFCs due to the similar requirements for surface oxygen exchange reaction and bulk diffusion processes at cathodes and the air side of oxygen permeation membranes. Recently, BCFNO has been investigated as cathodes in SOFCs and the maximum power density of 618 mW cm^{-2} at 800 °C [26] and 569 mW cm^{-2} at 700 °C [27] has been achieved, which indicates a similar high electrochemical activity for BCFNO and BSCFO. Activity of BSCFO, one of the most promising cathode materials for SOFCs, can be further increased by introducing A-site deficiency in BSCFO lattice, which can create additional oxygen vacancies, facilitate oxygen exchange reaction and promote oxygen ion diffusion within the cathode material [28]. Therefore, A-site deficient BCFNO, $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ has been systematically evaluated as cathode for SOFCs as well [29,30]. The effect of A-site nonstoichiometry on the cell performance of $Ba_{1-x}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ has been reported in our prior work [31], and the maximum power density of SOFCs using A-site deficient $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ as the cathode on a ceria-based electrolyte reached 1062 mW cm^{-2} at 600 °C. Subsequently, we systematically evaluated $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ as oxygen electrode material for LSGM-electrolyte supported SOFCs and solid oxide electrolysis cells (SOECs) and obtained high performances [1,29–31].

However, the work on $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ for oxygen permeation membrane is rare. To the best of our knowledge, no investigation on $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ for partial oxidation of methane to syngas has been reported yet. In this work, $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ was prepared by solid state reaction process for oxygen permeation membrane and further investigated for POM to syngas in a planar reactor with NiO/MgO solid solution as the reforming catalyst. The oxygen permeation flux, methane conversion, CO selectivity and a 400 h durability test at 875 °C were systematically studied.

2. Experimental methods

2.1. Preparation of $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ samples and NiO/MgO solid solution catalyst

The $Ba_{0.9}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ oxide was named as BCFN9721 according to the content ratio of cations. BCFN9721 was prepared by the conventional solid state reaction process. Stoichiometric amounts of $BaCO_3$, Fe_2O_3, Co_3O_4, and Nb_2O_5 were mixed by ball milling in ethyl alcohol medium for 48 h. Calcination of the precursor powders was performed at 1000 °C in air for 24 h. Then the synthesized oxide was ball milled again for 24 h. After that, the finely ground oxide powder was pressed into green pellets (20 mm in diameter) and bars (42 mm × 5.7 mm × 3.1 mm), respectively, under a uniaxial pressure at 200 MPa. These green samples were further sintered at 1150 °C in air for 6 h at a heating rate of 3 °C min^{-1}. The densities of the sintered samples were determined by Archimedes method and only those samples with relative densities higher than 95% were used for characterizations. The sintered pellets were applied as oxygen permeation membrane for permeation studies and bar samples for conductivity measurements.

NiO/MgO solid solution catalyst was prepared by impregnation method. MgO powder was immersed in $Ni(NO_3)_2\cdot 6H_2O$ aqueous solution and stirred thoroughly by magnetic stirring for 15 h. After drying on a hotplate at 80 °C, a light green precipitate was obtained. This was heated in air at 110 °C for 10 h. The resulting dry powder was further calcined in air at 800 °C for 5 h in order to get nickel–magnesia solid solution. Finally, the as-prepared catalyst was first pressed into tablets and then these tablets were pulverized into 20–40 mesh size powder. Before test, this catalyst powder was reduced in 10% H_2/90% Ar for 2 h at 875 °C.

2.2. Physico-chemical characterization

The crystallographic phases of the before- and the after-test BCFN9721 oxygen permeation membranes were verified using XRD analysis on a high power X-ray diffractometer (Rigaku D/MAX 2500) and a PANalytical X'pert PRO diffractometer using Cu-K_α radiationon, respectively. The morphology and element composition of the membrane before and after POM reaction were investigated by scanning electron microscopy (SEM) using a ZEISS-EVO 18 Special Edition instrument alongside EDS (BRUKER X-FLASH DETECTOR 5010). The electrical conductivity was measured by four-terminal DC method on sintered BCFN9721 bar in air at ascending temperatures ranging from 200 °C to 900 °C, with an interval of 50 °C and a dwell of 15 min at each temperature before the conductivities were measured to allow the system to equilibrate. The BET specific surface areas of NiO/MgO solid solution before and after POM reaction were measured by Quadrasorb SI-MP. For the alkaline-earth metal based perovskites are liable to form carbonates in the presence of CO_2 at high temperature, thermogravimetric (TG) analysis was performed on both BCFN9721 and BCFNO samples using a model HENVEN HCT-2 TGA instrument (Beijing Hengjiu Co., Ltd.) under 5% CO_2 (with