



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Facile fabrication and improved carbon dioxide tolerance of a novel bilayer-structured ceramic oxygen permeating membrane

Zhenbao Zhang^a, Dengjie Chen^a, Yubo Chen^{a,c}, Yong Hao^b, Moses O. Tade^c, Zongping Shao^{a,c,d,*}

^a State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry & Chemical Engineering, Nanjing Tech University, Nanjing 210009, China

^b Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100190, China

^c Department of Chemical Engineering, Curtin University, Perth WA 6458, Australia

^d College of Energy, Nanjing Tech University, Nanjing 210009, China

ARTICLE INFO

Article history:

Received 5 April 2014

Received in revised form

1 July 2014

Accepted 11 August 2014

Available online 27 August 2014

Keywords:

Bilayer

Ceramic membrane

Oxygen permeation

Permeation flux

CO₂ poisoning

ABSTRACT

An asymmetrical Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF)/Pr_{0.5}Ce_{0.5}O_{2-δ} (PrCe) bilayer-structured ceramic membrane is fabricated by a facile technique involving dry pressing of BSCF substrate, wet spraying of PrCe thin film layer (~10 μm) and co-sintering of the bilayer structures. The phase reaction, sintering behavior and oxygen permeability of the membrane are systematically investigated using XRD, ESEM, EDX and oxygen permeation studies. The CO₂ poisoning resistance of the layer materials is characterized by FTIR and CO₂-TPD experiments. The large shrinkage of BSCF substrate and the diffusion of compositional elements from BSCF substrate into the PrCe layer promote the densification of PrCe layer at a temperature as low as 1100 °C. The as-fabricated bilayer membrane exhibits not only high oxygen permeation flux, reaching 1.6 mL cm⁻² min⁻¹ at 850 °C, but also favorable permeation stability even after the introduction of 10% CO₂ into helium sweep gas. After the continuous operation at 850 °C under the CO₂-containing atmosphere for 800 min, the permeation flux remains stable at around 1.35 mL cm⁻² min⁻¹. The facile fabrication and superiority of the bilayer-structured membrane in resistance towards CO₂ poisoning thus provides a new way for the development of ceramic membranes for oxygen separation.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

With increasing concerns from the public and government about greenhouse effect and environmental pollution associated with low-efficient and excessive use of fossil fuels, the search for innovative energy conversion technologies that can lead to reduced emissions of carbon dioxide and improved fuel efficiency has been paid great importance. The conventional way for power generation from fossil fuels is based on a combustion technique with air as the oxidant. The direct mix of air and fuels at elevated temperature, however, could not only lead to the formation of NO_x and SO_x pollutants but also introduce difficulty for subsequent CO₂ sequestration owing to the diluting effect of nitrogen. By applying pure oxygen as the oxidant, improved combustion efficiency and reduced SO_x/NO_x emissions may be reached; in addition, the subsequent CO₂ sequestration is also greatly facilitated. Thus, the

new concept of oxyfuel power process has attracted considerable attention recently. However the cost associated with the conventional oxygen production based on cryogenic distillation, which mainly determines the practical applicability of this new technology, is too high and energy intensive [1–3]. New ways for economical production of oxygen are urgently needed to realize the attractive oxyfuel power process.

Some ceramic membranes made from mixed oxygen-ion and electronic conducting oxides allow the selective permeation of oxygen at elevated temperature if an oxygen partial pressure gradient is presented across the membranes [4–6]. By integrating them into the oxyfuel power process or coupling with oxidative reactions, reduced emissions, reduced cost, or increased selectivity of targeted products may be realized. During the past decades, considerable efforts have been paid into the development of such mixed conducting membranes. The ideal ones should meet the criteria of high oxygen permeation flux, good thermo-mechanical and chemical stability, cheap materials and low fabrication cost. Up to now, there are mainly two types of mixed conducting oxides that have been investigated as materials for oxygen permeating membranes, i.e. fluorite-type oxides like doped ceria and doped

* Corresponding author at: State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry & Chemical Engineering, Nanjing Tech University, Nanjing 210009, China.

Bi_2O_3 [7–9], and perovskite-type oxides like $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF), $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC), $\text{SrSc}_{0.2}\text{Co}_{0.8}\text{O}_{3-\delta}$ (SScC), and BSCF [10–13]. However, it is difficult to meet all above requirements for a membrane made from a single-phase oxide. For example, the fluorite-type oxides usually showed good chemical stability against reducing atmosphere and impurity gases such as CO_2 but low oxygen permeability due to their relatively low ionic and electronic conductivity and poor surface oxygen exchange kinetics [14–17]. Perovskite-type oxides typically possessed much higher oxygen-ion and electronic conductivity than fluorite oxides; thus much higher oxygen permeability for the membranes made from perovskite oxides was usually demonstrated; however, those perovskite-type materials with high oxygen permeability are always alkaline earth metal element contained, which are prone to be poisoned by CO_2 in the surrounding atmosphere. For example, the introduction of CO_2 into the permeating or feed side atmospheres of the BSCF membrane caused a sharp decrease in the oxygen permeation flux or even total failure of the membrane for oxygen separation [18].

Recently, a new composite membrane with the combination of fluorite-type oxide and perovskite-type oxide in a bilayer morphological structure was proposed for application in solid oxide fuel cells for power generation and also ceramic membrane for oxygen separation [19,20]. The fluorite oxide was in a thin-film configuration which performed as a protective layer for the perovskite oxide substrate membrane, while the thick perovskite oxide membrane provided mechanical support for the fluorite thin-film layer. The small thickness ensured a low resistance for oxygen transportation within the fluorite oxide layer, while the bilayer membrane structure effectively avoided the direct contact of perovskite membrane with environmental gas at the sweeping side; as a result, high oxygen permeation flux, favorable thermochemical stability and good resistance towards chemical attack could be reached simultaneously.

Appropriate selection of the materials for the respective layers is critical to obtain a defect-free asymmetrical bilayer-structured membrane with favorable thermochemical stability and oxygen permeability. The two materials should have good match in thermal expansion coefficients (TECs) and minimized unfavorable interfacial phase reaction. Since the fluorite phase usually has much lower oxygen permeability because of the poor electronic conductivity while the perovskite phase has larger TEC, higher electronic conductivity and higher TEC are preferred for the fluorite phase in the bilayer membrane. Serra et al. used a spray pyrolysis technique to successfully deposit a crack-free dense thin layer of $\text{Ce}_x\text{Gd}_{1-x}\text{O}_{2-\delta}$ (CGO) onto a pre-sintered LSCF thick membrane as a CO_2 protective layer [20]. However, the spray pyrolysis process, which requires special apparatus, is difficult for scale up. In addition, LSCF had relatively low oxygen permeability while CGO possessed very small electronic conductivity [21,22], resulting in relatively low oxygen permeation flux of the membrane [20].

In this study, we reported a new asymmetrical BSCF/PrCe bilayer-structured composite membrane for oxygen separation and a facile way for its fabrication. BSCF has the highest oxygen permeability among the various available mixed conducting perovskite oxides while PrO_2 -doped ceria shows much higher electronic conductivity than other doped ceria materials [23,24]. It suggests that both high oxygen permeation flux and favorable CO_2 poisoning resistance may be realized through the development of BSCF/PrCe asymmetrical bilayer membrane. However, the deposition of a dense fluorite coating layer over BSCF was typically difficult by the conventional fabrication process since normally a calcination temperature of 1400 °C or higher was required for the densification of fluorite oxide, while BSCF will be melted at a

temperature higher than 1100 °C [25,26]. Here we fabricated the bilayer-structured membrane based on dry press of the substrate and wet powder spray of the thin film layer in combination with a subsequent low temperature co-sintering process (1100 °C). The large shrinkage of BSCF substrate during the sintering at reduced temperature and the diffusion of compositional elements from BSCF into the PrCe layer promoted the densification of the PrCe thin film layer. The as-obtained membrane was conducted for oxygen permeation test and CO_2 poisoning effect evaluation. Significant improvement in CO_2 resistance was demonstrated, and the causes for the increased permeation flux and improved stability were discussed.

2. Experimental section

2.1. Preparation of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and $\text{Pr}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ oxide powders

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) powder was synthesized by a combined EDTA-citrate complexing sol-gel process [27]. Metal nitrates of $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$, all in analytic grades, were used as the raw materials for metal sources. For a typical synthesis, the required amounts of above metal ions according to the nominal mole ratio in BSCF were mixed into an aqueous solution, followed by the addition of EDTA and citric acid to act as complexing agents at a mole ratio of 1:1:2 for total metal ions:EDTA: citric acid. The pH value of the solution was adjusted to around 6 with the addition of $\text{NH}_3 \cdot \text{H}_2\text{O}$. A gel was obtained by heating the solution at 90 °C under stirring, which was pre-fired at 250 °C and further calcined at 1000 °C for 5 h under air atmosphere to obtain a composite oxide with desired composition and lattice structure. $\text{Pr}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$ (PrCe) powder was prepared using the same procedure, but calcined at a higher temperature of 1100 °C for 5 h.

2.2. Fabrication of asymmetrical BSCF/PrCe bilayer membrane

The PrCe slurry for wet spray deposition was prepared by dispersing PrCe powder in a premixed solution of isopropyl alcohol, ethylene glycol and glycerol, followed by high-energy ball milling at 500 rpm for 30 min (Pulverisette 6). Green disk-shape BSCF substrate membrane was prepared by dry pressing of BSCF powder using a stainless steel mold (15.0 mm in diameter) under hydraulic pressure of approximately 1.5×10^8 Pa. After the dry pressing, proper amount of PrCe slurry was wet spray deposited onto one surface of the green BSCF disk to form a bilayer structure. The bilayer-structured green membrane was sintered at 1100 °C in air for 5 h to allow the densification of both layers.

2.3. Characterization

Phase structures of the as-synthesized powders were examined by X-ray diffraction (XRD) with a Bruker D8 Advance diffractometer in the 2θ range between 10° and 90°. The XRD patterns were refined using X'pert Highscore Plus software (PANalytical). The microstructure of the sintered BSCF/PrCe bilayer membrane was examined by environmental scanning electron microscopy (ESEM, QUANTA-2000). Accurate elemental composition of PrCe and BSCF in the BSCF/PrCe membrane was determined by wavelength-dispersive X-ray spectroscopy (WDS, XRF ARL- 9800) and the energy dispersive X-ray spectroscopy (EDX, EDAX GENESIS 2000) elemental mapping was used to clarify the elemental distribution. The resistance of BSCF and PrCe oxides to CO_2 was characterized by XRD, Fourier transform infrared spectroscopy (FT-IR, AVATAR-360) and CO_2 -temperature programmed desorption

Download English Version:

<https://daneshyari.com/en/article/633241>

Download Persian Version:

<https://daneshyari.com/article/633241>

[Daneshyari.com](https://daneshyari.com)