Journal of Membrane Science 346 (2010) 353–360

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Oxygen permeation of BSCF membrane with varying thickness and surface coating

Won Ki Hong, Gyeong Man Choi*

Fuel Cell Research Center and Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea

ARTICLE INFO

Article history:
Received 24 March 2009
Received in revised form
29 September 2009
Accepted 30 September 2009
Available online 7 October 2009

Keywords:
Membrane
Oxygen permeability
BSCF
The characteristic membrane thickness
Coating

ABSTRACT

The oxygen permeation of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) membranes was measured between 750 and 900 °C as a function of membrane thickness with or without $La_{0.7}Sr_{0.3}CoO_3$ (LSC) coating layer under controlled P_{O_2}-gradient (Air/He). In order to see the relative effects of bulk diffusion and surface-exchange kinetics, the thickness of membrane was varied from 0.5 to 2.0 mm. The oxygen-permeation flux at 900 °C increased with LSC coating from that of uncoated membrane. For example, it increased ~1.8 times for 1 mm-thick BSCF membrane. The characteristic membrane thickness (L_C) which divides the bulk-diffusion limit and surface-exchange kinetics limit was estimated using the modified Wagner equation. The L_C values were 0.55 and 1.10 mm at 900 °C for the coated and uncoated BSCF membranes, respectively, and decreased with decreasing temperature.

1. Introduction

Mixed ion and electron conducting materials have attracted considerable attention for their applications in the fields of oxygen-permeating membranes, cathode materials for solid oxide fuel cell (SOFC), and gas sensors [1–4]. Among the oxygen-permeating membranes, perovskite-type (ABO_3) membranes exhibit the highest oxygen permeability due to their high ionic and electronic conductivity. $SrCo_{0.8}Fe_{0.2}O_3$ (SCF) is a typical perovskite material and exhibits one of the largest oxygen-permeation fluxes. However undesirable ordering that occurs in relatively reducing environment changes the perovskite into a brownmillerite-type structure [5]. $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) was developed recently by the partial substitution of Sr^{2+} in SCF with Ba^{2+} of a larger ionic radius. The structural stability of material was remarkably improved and the oxygen permeability was also enhanced [6]. Thereafter, various researches have been performed to study oxygen permeation, thermal expansion, oxygen non-stoichiometry and phase stability of BSCF [7–12]. According to the earlier publications, the oxygen permeation of BSCF membrane was often considered to be limited by bulk diffusion [11–13]. However this is doubtful since the permeation flux of BSCF membranes vary widely among researchers and thus was questioned [7,14]. In order to maximize the oxygen-permeation flux, we often reduce the membrane thickness. However, with decreasing membrane thickness, the membrane becomes more surface limiting and the flux does not always increase in proportion to the decreasing membrane thickness.

In this study, we have measured the oxygen-permeation flux of the coated and uncoated BSCF membranes as a function of membrane thickness and estimated the characteristic membrane thickness (L_C). The L_C is defined as the thickness of membrane that divides the bulk limit and surface limit [15]. It is shown for YSZ (yttria-stabilized zirconia) in reducing atmosphere at high temperature that the surface coating was very effective to enhance the permeation and the permeation measurement as a function of membrane thickness resulted in the determination of L_C value [16]. If the membrane is thicker than L_C, the oxygen-permeation flux is controlled by bulk diffusion and increases in proportion to the decreasing membrane thickness. When the membrane thickness becomes below L_C value, the contribution of the surface-exchange kinetics increases and the oxygen-permeation flux increases little with decreasing membrane thickness. The coating of membrane often enhances the surface-exchange kinetics and thus decreases L_C value. If we can reduce the L_C value, we can obtain a high permeation flux for a thin membrane.

2. Experimental procedure

BSCF powder was synthesized by a combined citrate and EDTA (ethylenediaminetetraacetic acid) complexing method [17]. EDTA (99.5%, Junsei Chemical, Japan)–ammonia (28.0–30.0%, Jun-

---

* Corresponding author.
E-mail address: gmchoi@postech.ac.kr (G.M. Choi).

0376-7388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2009.09.056

sei Chemical, Japan) buffer solution was first prepared with EDTA: ammonia ratio of 1:2, followed by adding appropriate amounts of $Ba(NO_3)_2$ (99 + %, Acros Organics, USA), $Sr(NO_3)_2$ (99 + %, Acros Organics), $Co(NO_3)_2{\cdot}6H_2O$(98 + %, Acros Organics), $Fe(NO_3)_3{\cdot}9H_2O$ (98.5%, Kanto Chemical, Japan) into the buffer solution under continuous stirring at 80 °C. After complete dissolution of these nitrates, a proper amount of citric acid (99.5%, Aldrich Chemical, USA) was added to form a solution with EDTA:citric acid:total metal ions in molar ratio of 1:1.5:1. The pH value of the solution was adjusted to ∼6 using the ammonia solution. The solution was subsequently evaporated at 80 °C until the formation of a dark purple gel. Finally, the gel was heated to 200 °C for 2 h, followed by heating at 800 °C for 5 h to obtain BSCF powder. The powder was die-pressed at 0.5 MPa and the diameter of die was 36 mm. The use of die with large diameter is beneficial for the permeation measurement since it maximizes the geometrical factor (surface area (*A*)/thickness (*t*)) and thus minimizes the effect of side-wall permeation as will be discussed later. The die-pressed pellet was further cold-isostatically pressed at 200 MPa for 30 s. The diameter of sample after sintering at 1120 °C for 5 h in air became ∼26 mm. The precise control of sintering temperature is important for the densification of BSCF sample without melting due possibly to the presence of liquid phase during sintering. The sintered membrane was crushed and the powder was used for characterization by X-ray diffraction (XRD) using Cu Kα radiation (MAC Science, M18XCE, Japan). The composition of sintered BSCF membrane was analyzed using Inductively Coupled Plasma Spectroscopy (ICP) analysis (ICP-AES, Iris Advantage, USA). The ICP analysis was performed at RIST, Korea.

The sintered samples in bar shape were cut for different thicknesses (0.5, 0.75, 1, 1.5, and 2.0 mm) and polished with SiC abrasive paper (#100). For the surface coating of BSCF membrane, $La_{0.7}Sr_{0.3}CoO_3$ (NexTech Materials Ltd., USA) powders were prepared in slurry form and was screen-printed on both surfaces of BSCF membrane to result in ∼20 μm-thick layer followed by sintering at 900 °C for 2 h. The coating material was chosen considering the match of thermal expansion coefficient (TEC). The TEC of BSCF ($\sim 19 \times 10^{-6}\,K^{-1}$ at 20–850 °C) [18] is close to that of $La_{0.6}Sr_{0.4}CoO_3$ ($\sim 20.5 \times 10^{-6}\,K^{-1}$ at 20–1000 °C) [19]. $La_{0.7}Sr_{0.3}CoO_3$ (LSC) has been used as an effective coating material for the La_2NiO_4-type oxygen-permeation membrane [20]. For the comparison of coating materials, BSCF slurries containing 10 wt% of carbon black as a pore former was also screen-printed to result in ∼20 μm-thick coating layer followed by sintering at 900 °C for 2 h. Since BSCF is an easy-sintering material, the coating layer easily densifies without the use of pore former. The diameter of coated area was 20 mm. The microstructure of membrane with coating layer was examined with a scanning electron microscope (Hitachi S570, Japan). The schematic diagram of setup for the oxygen-permeation measurement of BSCF was shown in Fig. 1. The polished membranes in plate form were sealed with Au-rings (I.D. = 20 mm, O.D. = 25 mm, *t* = 0.02 mm) to alumina tubes (I.D. = 20 mm, O.D. = 25 mm) on both sides. Thus the effective diameter of membrane exposed to gas was 20 mm. The setup was heated to 1040 °C and maintained for 40 min in order to soften Au-rings and insure good sealing with the heating rate of 2.0 °C/min. Gas leakage due to a possible bad sealing was detected by monitoring nitrogen concentration with gas chromatograph (HP 4890D, USA). In the test, HP3398A-program was used and the column was molecular sieve 13× having the length of 10 ft in order to analyze N_2 and O_2. Thermal conductivity detector (TCD) was used. The pre-heating for ∼30 min was required before the analysis since TCD is very weak for moisture. The typical amount of leaked nitrogen due to bad sealing was below 0.05% of sweep gas volume ($\sim 80\,cm^3/min$) at 900 °C. Thus the leakage was negligible and Au ring was found to be a good sealing material. The oxygen-permeation flux through the side-wall of BSCF sample (hereafter, side-wall permeation) was measured while maintaining the same oxygen partial-pressure (P_{O_2}) (He) on both sides of membrane. As will be discussed in detail later, the side-wall permeation was small, i.e., below 10% of main-permeation flux (across membrane) for the coated membranes thinner than 1.5 mm. The oxygen permeation was measured using gas chromatograph (HP4890D, USA) and zirconia oxygen-sensor positioned down-stream of the measurement chamber. The oxygen-permeation flux across the flat surface of membrane was measured under fixed P_{O_2} gradients (Air/He). The permeate-side (low-P_{O_2} side) was flown with He gas, and the feed side (high-P_{O_2} side) was flown with dry air (∼0.21 atm). The flow rates of both feed and permeate sides were maintained at $\sim 80\,cm^3/min$. The oxygen flux (J_{O_2}) was calculated by the following equation:

$$J_{O_2}\left[\mathrm{cm^3/cm^2\ min}\right] = \frac{J[\mathrm{cm^3/\ min}]\cdot C_{O_2}[\text{vol. fraction}]}{A[\mathrm{cm^2}]} \tag{1}$$

where *J* is the flow rate, C_{O_2} is the volume fraction of permeated oxygen quantity and *A* is the area of membrane surface exposed to the flowing gas. The *A* value was fixed as 3.14 cm^2 for the all coated or uncoated membranes in this study.

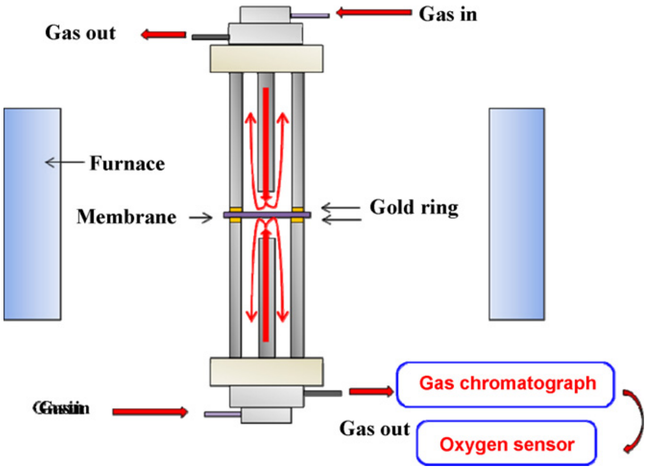

Fig. 1. Schematic diagram of experimental setup was shown for the oxygen-permeation measurement.

3. Results and discussion

Table 1 shows the composition of BSCF membrane determined by ICP analysis. The composition of powder was in good match with what we have intended to obtain (Ba:Sr:Co:Fe = 5:5:8:2). While Ba and Sr showed negligible discrepancies, Fe and Co showed ∼2% and ∼3% excesses, respectively. Fig. 2 shows XRD patterns of BSCF powder after crushing the pellet sintered at 1120 °C for 5 h in air. The single-phase BSCF was identified without any noticeable second-phase peaks. The peaks shown in Fig. 2 were indexed using a cubic lattice and were in good match with published data [7,21].

Before the discussion of the oxygen-permeation flux (J_{O_2}) of membrane, we need to estimate the leakage of the measurement setup. Both mechanical leakage (due to bad sealing, etc.) and side-wall permeation (through side of membrane) was measured at

Table 1
The composition of BSCF membrane used in this experiment was shown, determined by Inductively Coupled Plasma Spectroscopy (ICP) analysis.

	Ba	Sr	Co	Fe
Formula	0.500	0.500	0.800	0.200
ICP results	0.499	0.502	0.823	0.204

ICP analysis was performed at RIST, Korea.