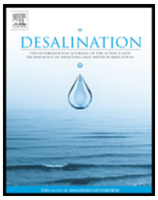
Desalination 270 (2011) 64–75

Contents lists available at ScienceDirect

Desalination

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



Oxygen permeation of $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ perovskite-type membrane: Experimental and modeling

Ali Ghadimi, Mohammad Ali Alaee, Amir Behrouzifar, Amir Atabak Asadi, Toraj Mohammadi *

Research Centre for Membrane Separation Processes, Chemical Engineering Department, Iran University of Science and Technology (IUST), Narmak, Tehran, Iran

ARTICLE INFO

Article history:
Received 24 August 2010
Received in revised form 6 November 2010
Accepted 8 November 2010
Available online 3 December 2010

Keywords:
Dense ceramic membrane
Perovskite
Mixed-conducting membrane
Mathematical modeling
Air separation

ABSTRACT

$Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{0.3-\delta}$ ($x = 0.2, 0.5, 0.8$) dense membranes were prepared by a combined EDTA and citrate complexing method. In our previous works, effects of sintering temperature, sintering dwell time and pressing pressure on microstructure and theoretical densities of the membranes were examined and finally the best corresponding values were reported as 1100 °C, 8–9 h and 200–250 MPa, respectively. In the present work, effects of temperature (650–950 °C), feed flow rate (100–200 cm³/min), sweep gas flow rate (40–80 cm³/min) and membrane thickness (4–5 mm) on oxygen permeation behavior of the $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{0.3-\delta}$ membranes were investigated. Also, a mathematical model based on Nernst–Planck equation was developed to predict oxygen permeation through the perovskite-type membranes. Both bulk diffusion and surface reactions were incorporated into the model. It was observed that surface reactions are not elementary and a correction term should be introduced into the model to compensate this effect. Also, using a dimensionless Reynolds number, effect of feed flow rate on oxygen flux was taken into account. With aids of these modifications, it was realized that, there is a reasonable agreement between predicted results and experimental data with correlation coefficient (R) of higher than 0.960 and mean squared relative error (MSRE) of lower than 0.022 for all the membranes. Oxygen vacancy bulk diffusion coefficient (D_v), surface exchange rate constants (k_f and k_r), contribution of each resistance to oxygen permeation and characteristic thickness (L_c) of the BSCF membranes were also estimated.

1. Introduction

Oxygen has many usages in different industries such as steel, chemicals and petrochemicals, etc. In many of these applications, air is used as oxygen source, but in some industries enriched air or pure oxygen is needed. Mixed-conducting membranes have the potential to produce ultrapure oxygen at large volumes, low costs and high efficiencies [1]. Many types of ceramic materials can be used as dense membranes for air separation. Among these, perovskite-type materials have been attracted more attention because of their higher oxygen flux and excellent stability.

$SrCoO_{3-\delta}$ is a significant perovskite-type parent material. Among the different phase structures of $SrCoO_{3-\delta}$, the oxide with a cubic structure has the highest conductivity. Unfortunately, this cubic phase is not stable. Therefore, substitution of either the A- or B-site, has been widely applied to stabilize the cubic lattice structure of $SrCoO_{3-\delta}$ [2–5]. Structural stability and the oxygen permeation flux of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) which was developed recently by Shao et al. was remarkably enhanced respect to $SrCoO_{3-\delta}$ and its other derivatives [6]. Thereafter, oxygen permeability, phase stability and mechanical properties of BSCF studied by several research groups [7–12]. Alaee et al. [7,8] studied the effect of Ba content and operating conditions on oxygen permeation of BSCF perovskite-type membranes. Hong et al. [9] investigated the effect of membrane thickness and introduced a $La_{0.7}Sr_{0.3}CoO_3$ (LSC) coating layer on oxygen permeation of BSCF membrane. Shen et al. [10] also studied the effects of a thin $RBaCo_2O_{5+\delta}$ (R = Pr, Nd, Sm, Gd) coating layer on oxygen permeation flux through BSCF membrane. Baumann et al. [11] investigated the influence of sintering conditions on microstructure and oxygen permeation of BSCF membrane.

Oxygen flux through perovskite membranes is a function of many parameters. The most important is the membrane composition, e.g. the $BaCoO_3$ and $SrCoO_3$ exhibit oxygen conduction, but the $BaCeO_3$ and $SrCeO_3$ are proton conductors [13]. Preparation methods also affect permeation behavior and phase stability of the membranes. Temperature, membrane thickness, upstream oxygen concentration, feed and permeate side pressures, feed and sweep gas flow rates, feed impurities even at very low concentrations and membrane age also affect oxygen permeation characteristic of the membranes. Experimental studies of these factors need huge time and money. Here an accurate and simple model can be very useful.

Many researchers attempt to model oxygen permeation through perovskite membranes. Kim et al. [14] derived two expressions for oxygen permeation through tubular perovskite membranes in surface reaction limited and diffusion limited regimes. Their model

---

* Corresponding author. Tel.: +98 21 77240496; fax: +98 21 77240495.
E-mail address: torajmohammadi@iust.ac.ir (T. Mohammadi).

0011-9164/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2010.11.022

was able to deduce the ambipolar diffusion coefficient and the surface exchange rate coefficient from the dependence of oxygen permeation on oxygen pressure gradient. Oxygen permeation through $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ and $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ were fitted accurately using their model. Li et al. [15] developed a mathematical model in consideration of membrane bulk diffusion and surface reaction to simulate the performance of disk-shaped dense $La_{0.2}Sr_{0.8}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membranes for oxygen permeation. Also, characteristic thickness of the LSCF membrane was estimated to be 1.8 mm using modeling and experimental study. Xu and Thomson [16] developed an explicit oxygen permeation model for ion-conducting membranes with a high ratio of electronic to ionic conductivity. Their model took into account both bulk diffusion resistance and surface exchange kinetics. They used their model to predict oxygen permeation through $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ over a wide range of temperatures and oxygen partial pressures. Yang and Lin [17] derived an explicit semi-empirical equation for oxygen nonstoichiometry of perovskite-type ceramics from the results of a point defect model and coupled that equation with oxygen permeation equation to predict oxygen permeation current density through $La_{0.1}Sr_{0.9}Co_{0.5}Fe_{0.5}O_{3-\delta}$ and $La_{0.1}Sr_{0.9}Co_{0.9}Fe_{0.1}O_{3-\delta}$ ceramic membranes. Tan et al. [18–20] developed a mathematical model for a hollow-fiber $La_{0.6}Sr_{0.4}Co_{0.2}F_{0.8}O_{3-\delta}$ membrane module for air separation and studied performance of the module at various operating conditions, operating modes and flow patterns, both experimentally and theoretically.

These models were successfully used to study oxygen permeation through perovskite-type membranes. However, in all of these models, surface reactions of oxygen oxidation and reduction were considered elementary, and in most of them effects of flow rates were not considered.

In this research, citrate-EDTA complexing method was employed to synthesis $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{0.3-\delta}$ ($x=0.2$, 0.5, 0.8) perovskite membranes. Effects of sintering temperature, sintering dwell time and pressing pressure on density and structure of the membranes were studied and the best value of each parameter to obtain dense and stable membranes were reported [21–23]. In this work, oxygen permeation of the $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes were studied experimentally and theoretically. Influence of temperature and feed and sweep gas flow rates on permeation of oxygen through 9 membranes which have three different compositions and three different thicknesses were investigated. Finally, a mathematical model which relates oxygen permeation flux to temperature, oxygen partial pressure in upstream and downstream, membrane thickness and feed flow rate was developed. In this model, surface reactions were supposed to be non-elementary. With the aid of these improvements, the mathematical model predictions showed an excellent agreement with the experimental data. Constant values of the model for each membrane were acquired using nonlinear regression. Also, characteristic thickness of the membranes and contribution of different resistances to oxygen permeation were calculated.

2. Experimental

2.1. Synthesis of the membranes

BSCF powders were synthesized using the citrate-EDTA complexing method. After mixing stoichiometric amounts of the metallic nitrates (Ba(NO) , Sr(NO) , Co(NO) ·6H O, Fe(NO) ·9H O) and evaporating the solvent under heating and stirring, the formed gel was dried at 120–150 °C overnight to make a primary powder, which was calcined at 950 °C for 5 h to obtain a secondary powder with final composition. The secondary powder was pressed into disks in a stainless steel mould (21 mm in diameter) under a hydraulic pressure of 200–250 MPa. These green disks were sintered in a furnace at temperatures of 1100 °C for 8–9 h with heating and cooling rates of 1–3 °C/min. Detail information regarding preparation of the BSCF ceramic powders can be found in literature [21–23].

2.2. Experimental design

A full factorial design of experiments was applied to investigate the effects of the membrane thickness, temperature, feed flow rate and sweep gas flow rate for three membranes; $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ ($x=0.2$, 0.5, 0.8). Each parameter was examined at three levels and $3^4=81$ experiments were conducted for each membrane. The parameters and their corresponding levels are presented in Table 1. Each run was repeated twice and if in any run, a major difference was observed, that run was performed for the third time to ensure the accuracy of data. Excellent agreements between repeated and initial runs were observed in most cases.

2.3. Oxygen permeation measurements

Oxygen permeation fluxes through the membranes were measured using the permeation apparatus as shown in Fig. 1. In this work, a simple temperature resistance stainless steel shell-and-tube permeation module was used as permeator for oxygen permeation measurements. The disk-shaped membrane module is shown in Fig. 2. The disk membrane between two stainless tubes was sealed with ceramic fibers reinforced with high temperature cement glue (heat resistance to 1200 °C).

The membrane module was mounted in a tubular furnace and the operating temperature was measured by a thermocouple. A microprocessor temperature controller (Model BATEC PC 21, Amjad Company, Iran) was used to control the temperature within ±1 °C of the set points. Flow rates of the inlet gases were controlled by mass flow controllers (Models 8085 Brooks, Company). Air was introduced into the upstream side of the membrane. Helium, as sweep gas for the permeating oxygen, was fed to the downstream side of the membrane. Both upstream and downstream sides were maintained at atmospheric pressure. The effluent streams were analyzed by gas chromatography (Teif Gostar Company, Iran) which was equipped with a 2 m 5 Å molecular sieves operated at 24 °C with helium as carrier gas.

The amount of leakage through pores or cracks due to the sealing problem was almost constant in the entire temperature range studied. The leaked oxygen was usually less than 0.1% of the total oxygen, and in most cases, no nitrogen leakage was detected. It is reasonable to assume that the leaking of nitrogen and oxygen through the pores or cracks is in accordance with the Knudsen diffusion mechanism, so the fluxes of leaked N_2 and O_2 have a simple relationship and the permeation fluxes were calculated using Eq. (1):

$$J_{O_2} = \left(C_{O_2} - C_{N_2} \times \frac{0.21}{0.79} \times \sqrt{\frac{28}{32}} \right) \times \frac{F}{S} \tag{1}$$

where C_{O_2} and C_{N_2} are the measured concentrations of oxygen and nitrogen in the permeation side; respectively, F is flow rate of the sweep gas and S is the membrane area.

Table 1
The experimental parameters and their levels for oxygen permeation measurements.

Parameter	Levels	Dimension
Membrane thickness	4.0, 4.5 and 5.0	mm
Temperature	650, 800 and 950	°C
Feed flow rate	100, 150 and 200	cm³/min
Sweep gas flow rate	40, 60 and 80	cm³/min