Oxygen permeation through perovskite membranes and the improvement of oxygen flux by surface modification

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Abstract

BSCF hollow fiber membranes possessing an asymmetric layered structure were prepared using a modified phase inversion process followed by subsequent sintering at temperatures from 1100 to 1175 °C. The fibers were characterized by SEM, and tested for air separation at ambient pressure and temperatures between 650 and 950 °C. Although the prepared hollow fibers resulted in self-supported asymmetric substrate with a very thin densified perovskite layer for mixed conduction, O2 permeation was controlled by surface O2 exchange kinetics rather than bulk diffusion. In order to improve O2 flux, surface modification was carried out by the attachment of Pt particles on the surface of the hollow fiber. The maximum O2 flux measured for pure perovskite hollow fiber was 0.0268 mol m⁻² s⁻¹ at 950 °C whilst O2 fluxes increased up to 25% after the surface modification using Pt micro-particles.

Keywords: Hollow fiber; Perovskite; Mixed conduction; O2 Permeation; Surface modification

1. Introduction

Current tonnage O2 production by cryogenic processes is very energy expensive and production cost reduction by 35% or more is required [1–4], which in turn is driving academic and industrial researchers toward membrane technology development for the last decade. Of particular attention, ion conducting ceramic membranes have attracted the attention of the research community, with over 20 laboratories worldwide conducting research on the subject. It is well known that some ceramics with defined structures like perovskite and fluorite exhibit good mixed ionic and electronic conducting properties. Dense membranes made from these ceramic materials show good O2 permeation at elevated temperatures without the need of external electrical loadings. Owning to the mixed ionic electronic conducting (MIEC) oxide’s ability to conduct O2 ions and electrons, it preferentially allows only O2 to permeate. As a result, pure O2 production can be achieved by heating such a ceramic membrane system (or called O2 generator) where air is used as a feedstock. Since the operating temperature at which the O2 flux becomes significant is in the range where many partial oxidation reactions occur, another potential use of these mixed conducting ceramic membranes would be the selective feeding (or extracting) of O2 in chemical reactors, e.g., in hydrocarbon oxidation and dehydrogenation processes [5]. Presently intensive research is focused on mixed conducting perovskite oxides. Teraoka et al. [6–8] pioneered the work on the development of high O2 permeation flux through SrCo0.8Fe0.2O3 perovskite membranes. The high permeation flux was attributed to the high concentration of O2 vacancy in the lattice due to the total substitution of La³⁺ metal ion by Sr²⁺ in the A-site of perovskite. Although this material lacked sufficient chemical and structural stability in practical operation conditions, their work encouraged a large number of researchers to explore new membranes with improved phase stability and O2 permeability by optimizing the metal oxide composition in...
ABO₃ perovskite structure. One example is the composition of Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃₋δ (BSCF), developed from SrCo₀.₈Fe₀.₂O₃₋δ by partially doping with Ba. This material exhibits the highest O₂ permeation flux, but also has favorable phase stability at high temperatures [9].

The thermodynamic driving force for O₂ transport through the mixed conducting membranes is the O₂ chemical potential gradient along the thickness of the membrane. For a certain material, the permeation flux can be increased by reducing the thickness \( l \) of the membrane. In the case that \( l \) is larger than the critical thickness \( L_c \), the O₂ permeation resistance by bulk diffusion is lower than O₂ available via surface exchange reactions. However, if \( l \) is smaller than \( L_c \), the membrane surface exchange reaction becomes the rate-limiting step. Hence, any further increase in the permeation rate can be achieved only (i) by improving the surface exchange kinetics, (ii) by coating the surface of the membrane with a more porous layer thus increasing the effective surface area, or (iii) by coating the membrane surfaces with materials of superior O₂ exchange properties [10].

In this work, mixed conducting hollow fiber membranes based on BSCF perovskite were prepared and tested for O₂ separation. O₂ fluxes through the membranes were investigated using O₂ surface exchange kinetics to study surface modification effects derived from the use of Pt particles. The present work particularly focus on the development of new perovskite ion conducting ceramic membranes.

2. Experimental

2.1. Materials

Ba(NO₃)₂, Co(NO₃)₂, Fe(NO₃)₃, and Sr(NO₃)₂ [all > 98%, Alfa Aesar], citric acid [> 99%, Ajax], ethylenediaminetetraacetic acid (EDTA) [> 99.5%, Aldrich], and platinum powder [0.15–0.45 μm, Aldrich] were used as received. Polyethersulfone (PESf) [Radel A-300, Solvay Advanced Polymers] and N-methyl-2-pyrrolidone (NMP) [EMD Chemicals Inc.] were used for preparing suspensions. Polyvinylpyrrolidone (PVP) \( [M_w = 1,300,000; \text{Alfa Aesar}] \) was used as an additive. Ag paste [China, Shanghai] was used as the high temperature sealant. Tap water was used as both the internal and the external gelation medium (nonsolvent).

2.2. Preparation of the BSCF precursor powder

The BSCF precursor powder was prepared by combined EDTA–citrate complexation. For this purpose, EDTA powder (with a ratio of 29.2 g EDTA to 75 mL ammonia) was added under magnetic stirring into aqueous ammonium hydroxide (28.0–30.0%) to form a water-soluble ammonium salt. In a separate beaker stoichiometric quantities of Ba(NO₃)₂, Sr(NO₃)₂, Co(NO₃)₂, Fe(NO₃)₃, and citric acid in granular form were dissolved in distilled water. The EDTA solution was then added into the solution of the metal ions and citric acid under stirring. The molar ratios of EDTA, citric acid, and total metal ions in the final solution were 1:2:1. The final mixture was heated at 100 °C for several hours to remove excess water until a viscous gel was obtained. The resultant gel was heated in a furnace at 250 °C for 12 h to obtain a black solid mass, which was subsequently calcined at 600 °C for 12 h to form a BSCF precursor powder.

2.3. Preparation of BSCF membranes

The BSCF precursor powder 61.5 wt% was added to a polymer solution 38.5 wt% (a mixture of PESf and NMP, with a mass ratio of 4:1) and the mixture was stirred for 24 h to ensure uniform distribution of particles. The resulting suspension was subsequently degassed at room temperature and transferred to a stainless steel reservoir which was pressurized with nitrogen to 2.8 × 10⁵ Pa. Extrusion was carried out through a tube-in-orifice spinneret with orifice diameter and inner diameter 2.5 and 0.72 mm, respectively. The fibers emerging from the spinneret at 5 m min⁻¹ were passed through an air gap of 2 cm and immersed in a water bath to complete gelation. The detailed preparation procedures are described elsewhere [11]. The dried hollow fibers were heated in a furnace to 800 °C at about 3 °C min⁻¹ and maintained at this temperature for 15 h to decompose and remove the polymer. Subsequent sintering was carried out at a

![Fig. 1. Schematic of permeation cell.](image-url)
temperature from 1000 to 1175 °C for 8 h to obtain an impermeable structure. The fibers were finally cooled down to room temperature at 2 °C min⁻¹ and tested for gas tightness and air separation.

The phase structures of both precursor powder and sintered BSCF fibers were analyzed using a Shimadzu X-ray diffractometer.

2.4. Hollow fiber surface modification by Pt deposition

The immersion-induced phase inversion technique, commonly employed for the spinning of polymeric membranes, was modified to prepare the inorganic membranes in this work by extruding the mixture of polymer solution and inorganic powder followed by sintering step. A coating suspension was prepared by dispersing 0.2 g Pt particles in 20 g ethanol. BSCF hollow fibers 15 cm in length were immersed into the solution for a few seconds and then rapidly withdrawn to obtain a uniform coating on both the interior and exterior surfaces. The coated fibers were dried at room temperature for 20 min. Coating and drying were repeated a total of three times to ensure a better Pt attachment.

2.5. O₂ measurement

Fig. 1 shows a BSCF fibers connected on both sides with small-diameter quartz tubes and sealed with Ag paste. The
Ag paste seal process was repeated until an adequate seal was achieved. The permeation measurements were carried out by placing an inorganic hollow fiber directly into a tube furnace. In order to maintain constant feed composition along the fiber, an air flow of 300 mL min⁻¹ was passed near the central part of the furnace through a small quartz tube. He was used as a sweep gas in the permeate stream. The O₂ in the permeate stream was measured using a Gas Chromatograph (GC) (HP 5890II series). A washed molecular sieve 5A (6 ft × 1/8 in-0.085 in; 80/100 mesh) was used for the separation of O₂ and nitrogen. The flow rate was measured by an electronic flow meter downstream of the fiber. Gas tightness of the seals were verified by the absence of nitrogen gas in the permeate stream.

3. Results and discussion

3.1. BSCF hollow fiber membrane preparation

Fig. 2 shows the X-ray diffraction (XRD) pattern and a scanning electron microscope (SEM) micrograph of the BSCF precursor powder calcined at 600 °C. The XRD indicates that the sample is generally amorphous due to amorphous metal oxides, though some crystallinity organization is observed at 2θ angles of 23°, 32°, and 42°. It is clear that the precursor powder was agglomerated with a particle sizes around 80 nm. It should be noted that at this temperature, the powder is not in a perovskite phase, but a mixture of some intermediate phase, metal oxides, and carbonates [12]. Fig. 3 shows the XRD pattern of the hollow fibers after being sintered at 1100 °C. The XRD spectra exhibit patterns that shows seven strong diffraction peaks with respective 2θ angles and lattice planes of 22.28 {100}, 31.72 {110}, 39.24 {111}, 45.52 {200}, 56.6 {211}, 66.36 {220}, and 75.72 {310}, which are related to the cubic perovskite phase of BSCF [9]. The calculated lattice parameter for BSCF is 0.3967 nm.

Fig. 4 shows the SEM pictures and photograph of typical BSCF hollow fiber membranes. These hollow fibers were sintered in the range of 1100–1175 °C resulting in thickness of 0.20–0.5 mm and an outer diameter of 1.4 mm (Fig. 4a), and lengths up to 30 cm (Fig. 4b). A magnified part of the hollow fiber cross section (Fig. 4c) illustrates a sponge-like structure with short finger-like structures near the outer and inner walls of the fibers. The formation of these structures is attributed to the polymer phase inversion process. The micrograph of Fig. 4d relates to the hollow fiber’s outer layer which shows complete densification (i.e. no pin holes). The outer layer was derived from the BSCF precursor powder (80 nm size in Fig. 2d) which coalesced after sintering into larger particles with a size around 2 μm. In addition, the dense outer layer was fully integrated on the porous part (i.e. as a substrate or support) of the hollow fiber as reported elsewhere [13]. As a result, the dense outer layer provides the gas tightness required for O₂ separation from air.

3.2. Evidence of surface reaction exchange step controlled O₂ permeation

O₂ permeation was tested by O₂ extraction from air. As displayed in Fig. 1, BSCF hollow fiber membrane outside surface (i.e. layer) was exposed directly to air and He as sweep gas was passed through the lumen. At high temperatures, O₂ permeate from the air side to the lumen because of the O₂ concentration (or partial pressure) gradient across the membrane. Fig. 5 shows the effect of operating temperature on the O₂ fluxes through three different hollow fibers (I, II, and III) as listed in Table 1. At He sweep flow rates around 0.23 mol m⁻² s⁻¹, the temperature dependence of the O₂ permeation flux was investigated from 600 to 950 °C. At temperatures less than 600 °C, the O₂ fluxes were very low which could lead to significant measurement errors. Appreciable high O₂ flux values were measured when the operating temperature was higher than 700 °C. Above 700 °C, the O₂ fluxes increased sharply with temperature. For example, at He sweep rate of 0.235 mol m⁻² s⁻¹, the O₂ flux through the sample II increased by one order of magnitude from 0.0027 to 0.020 mol m⁻² s⁻¹ as the temperature was raised from 750 to 950 °C. As listed in Table 1, samples I and II were sintered at the same temperature of 1100 °C, but with different fiber wall thickness whilst sample III was sintered at a higher temperature of 1175 °C. As a result, the fully densified skin layer (i.e. also the mixed conducting layer) of sample III should be thicker than that of sample I or II which were sintered at a lower temperature of 1100 °C. However, as shown in Fig. 5, at the same operating conditions, all three fibers resulted in similar O₂ fluxes. This can be explained by the analysis of gas transport through the hollow fiber membranes. O₂ permeation through an MIEC perovskite membrane from the high O₂ partial pressure side to the low O₂ partial pressure side includes the following steps in series: (i) mass transfer of gaseous O₂
from the gas stream to the membrane surface (high pressure side); (2) surface reaction between the molecular O₂ and oxygen vacancies at the membrane surface (high pressure side); (3) oxygen vacancy bulk diffusion across the membrane; (4) surface reaction between lattice oxygen and electron–hole at the membrane surface (low pressure side); and (5) mass transfer of O₂ from the membrane surface to the gas stream (low pressure side). Generally, the gas phase resistance may be negligible compared to that of bulk diffusion and exchange reactions. The results in this work may suggest in a qualitative manner that the dense layer ($l$) is thinner than the critical thickness ($L_c$). In this case, the resistance by bulk diffusion is not rate limiting and the surface exchange reaction becomes the rate-limiting step. This is the reason why the three hollow fiber samples with different thickness displayed similar O₂ permeation rate. Using a BSCF ceramic disk (with thickness 1.5 mm and membrane area 0.85 cm²), Shao et al. [9] reported O₂ flux 0.0104 mol m⁻² s⁻¹ at 950 °C using a 0.5454 mol m⁻² s⁻¹ He sweep rate. Under similar operating conditions, the O₂ flux through the hollow fiber sample I was 0.0255 mol m⁻² s⁻¹. If the assumption of the critical thickness is correct in this

Fig. 4. SEM micrographs of (a) of the prepared gas-tight BSCF hollow fiber membrane, SEM images of the BSCF hollow fiber membranes sintered at 1100 °C (b–f) (b): cross-section; (c): magnified cross-section; (d): external surface; (e): layered porous structure (viewed from the arrow head direction in (c).
work, then there was a need to further investigate this issue. 
As a test of our hypothesis, membrane surface modification was carried out by incorporating Pt catalysts, with a view to promote O₂ exchange rates at the membrane surfaces and facilitate dissociation of molecular oxygen and recombination of oxygen ion.

### 3.3. O₂ flux improvement by surface modification with Pt particle deposition

Fig. 6 shows the SEM pictures of Pt particles physically deposited on the hollow fiber membrane surfaces though the Pt attachment was not uniform and particles tended to agglomerate on the surface. Fig. 7 compares the O₂ fluxes of the membranes with (sample IV in Table 1) and without Pt particles (sample I in Table 1) in the same temperature range and at the same He sweep flow rate. It is observed that O₂ fluxes through sample IV shows similar trend as a function of the operating temperature. However, when the operating temperature was higher than 800 °C, sample IV exhibited appreciable higher O₂ fluxes. For example, at 900 °C, the measured O₂ flux of sample IV was 0.016 mol m⁻² s⁻¹, 15% higher than that of sample I. Fig. 8 shows the effect of He sweep rates on the O₂ fluxes of hollow fiber samples I, III, and IV at operating temperature of 950 °C. The O₂ fluxes increased with the He sweep rate due to the permeate side low O₂ pressure. For example, increasing the He flow rate from 0.167 to 0.458 mol m⁻² s⁻¹ lowered the average O₂ partial pressure from 0.047 to 0.026 atm and improved the O₂ flux through sample I from 0.0172 to 0.0248 mol m⁻² s⁻¹. No saturation

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**Table 1**

| Hollow fiber samples | Prep. temp. (°C) | Surface modification with Pt particles | Fiber dimension (mm) | OD | ID | L |
|----------------------|-----------------|----------------------------------------|---------------------|----|----|---|
| I                    | 1100            | No                                     | 1.33                | 0.83| 70 |
| II                   | 1100            | No                                     | 1.40                | 0.10| 72 |
| III                  | 1175            | No                                     | 1.47                | 0.97| 70 |
| IV                   | 1100            | Yes                                    | 1.34                | 0.84| 70 |

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**Fig. 5.** Effect of operating temperature on the O₂ fluxes through three different fibers (I, II, and III were prepared at: 1100, 1100, and 1175 °C, respectively).

**Fig. 6.** SEM pictures of the Pt particles deposited on the BSCF hollow fiber membrane surfaces: (a) external surface; (b) internal surface.
of O₂ flux was observed during the variation of the He flow rates. Comparing all O₂ permeation fluxes, again sample IV was the best performer. Particularly, at He sweep rates higher than 0.150 mol m⁻² s⁻¹, O₂ flux through sample IV is 22% higher than that through other samples without Pt particle attachment at similar operating conditions. The increase of O₂ flux is due to the catalytic effect of Pt particles on the reaction taking place between gas phase O₂ and the perovskite oxide membrane surfaces.

4. Conclusions

Gas-tight BSCF hollow fiber membranes showing an asymmetric porous layered structure with a top dense layer were prepared using a modified phase inversion and sintering technique and tested for air separation. The O₂ fluxes through several hollow fibers with different thickness were compared indicating strong evidence of surface reaction kinetics as the rate-limiting step. The O₂ flux increased with temperature and with the He sweep flow rate displaying dependence on the permeate side O₂ pressure. The maximum O₂ flux measured for pure perovskite hollow fiber was 0.0268 mol m⁻² s⁻¹ at 950 °C and He sweep rate of 0.547 mol m⁻² s⁻¹. After simple surface modification by Pt micro-particles, the hollow fiber improved the O₂ flux by 15–25% depending on the operating conditions.

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