Two-step fabrication of $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ asymmetric oxygen permeable membrane by dip coating

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ABSTRACT

Asymmetric membranes for high temperature oxygen separation with identical materials for dense layers and porous supports have been extensively reported in recent years. This paper presents a versatile method for manufacturing such asymmetric membrane, including pre-sintering, dip coating and co-firing. The porous support was elaborated through trial of different pore-forming agents and the amount. The thickness of top layer was controlled by adjusting the concentration of slurries. Several test approaches were employed to detect the detailed parameters of porous supports, such as SEM, mercury intrusion porosimetry and nitrogen permeation measurement. High performance support with excellent permeability and sufficient mechanical strength (43.84 MPa) was fabricated successfully. A stable pore structure with open porosity of 33.26% was achieved. The prepared asymmetric membrane with thickness of 20 μm for dense layer was subjected to oxygen permeation test and the result reached as high as 4.51 ml (STP) cm^{-2} min^{-1}. The results suggest that the oxygen permeability was limited by both bulk diffusion and surface exchange kinetics.

1. Introduction

For the last few decades, mixed ionic-electronic conductors (MIECs) with perovskite-type structure have attracted considerable attention due to their high performance in a wide range of applications. Among them, oxygen-permeable membranes used for oxygen separation have attracted attention increasingly due to their 100% oxygen permeation selectivity at elevated temperatures. Such a solution could reduce the cost of oxygen production and energy consumption significantly compared to the traditional method of oxygen production [1–3]. The earliest oxygen-permeable membrane was reported by Teraoka et al., who found that the $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ sintered membrane showed a high oxygen permeation flux [4]. Afterwards, a number of perovskite-type oxides that showed high performance in both oxygen permeability and stability have been reported. Among the large number of membrane material candidates, $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ (BCFN) is one of the most promising membrane materials that shows a high oxygen permeability (1.51 ml (STP) cm^{-2} min^{-1} at 850 °C for 1 mm thickness) and excellent stability under reducing atmosphere in oxygen permeation process [5,6]. However, with regard to industrial use, the oxygen permeation flux is still not high enough, especially for oxygen production.

To the membrane with a certain composition of material, its oxygen permeability is determined by surface morphology [7–14] and membrane thickness [1,15]. The oxygen permeation flux is inversely proportional to the membrane thickness when oxygen transfer is limited by bulk diffusion, as demonstrated by the Wagner equation:

$$J_{O_2} = \frac{RT\sigma_i\sigma_e}{16F^2L(\sigma_i+\sigma_e)} \ln \frac{P_{O_2,high}}{P_{O_2,low}} \tag{1}$$

where J_{O_2} is the oxygen permeation flux; R, the gas constant; T, the temperature; σ_i and σ_e are respectively the ionic and electronic conductivity; F, the Faraday constant; L, the membrane thickness and $P_{O_2,high}$ and $P_{O_2,low}$ are oxygen partial pressures at oxygen feed side and sweep side, respectively.

Consequently, decreasing the membrane thickness is an effective way of enhancing the permeation rate. However, further reducing the membrane thickness results in low mechanical strength for symmetric membranes. To solve this problem, an asymmetric-structured membrane, i.e., a thin dense membrane supported by a thick porous layer, was first proposed by Teraoka et al. [16] in 1989. This structure allows the oxygen to physically diffuse through the three-dimensional network structured porous support layer and to electrochemically permeate through the dense layer, as shown in Fig. 1.

Since then, a large amount of asymmetric membranes have been reported, as listed in Table 1. The early versions of asymmetric

membranes widely utilized dense layer and porous support with totally different compositions, which easily lead to warping or cracks due to differences in shrinkage behavior and thermal expansion coefficient during co-firing and oxygen permeation process. Thus, various measures were used to diminish the disadvantages, such as modifying the shrinkage difference by doping other materials or using particles with different sizes between porous and dense layer. To simplify the fabrication of asymmetric system, support and dense layer made of identical or similar components, which can ensure similar thermal and chemical performance, was proposed and extensively employed for the last decade.

Generally, the porous support should satisfy the following conditions: (I) sufficient mechanical strength; (II) similar shrinkage behavior to the dense layer during sintering; (III) good chemical compatibility with dense layer; (IV) similar thermal and chemical expansion parameters of the support and dense layer; (V) stable pore microstructure with a narrow pore size distribution; and (VI) low resistance to the gas flow.
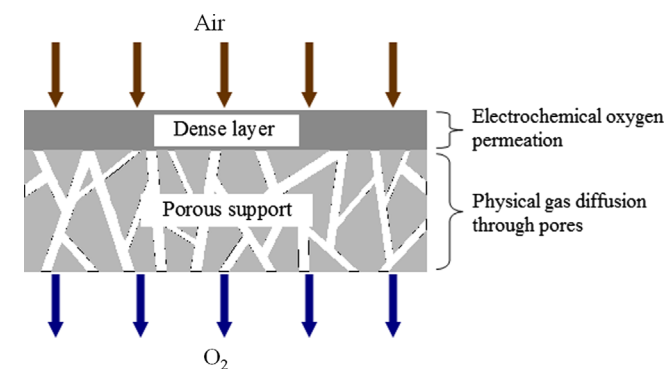

Fig. 1. Schematic view of the dense/porous asymmetric-structured membrane.

One of the most crucial factors of preparation of porous support is the choosing of types of pore-forming agents. During the past few decades, a variety of pore-forming agents were employed, as shown in Table 1. Normally, there are three kinds of pore-forming agents: polymers, inorganic carbon and inorganic salts. Polymers such as corn starch decompose at relatively low temperature when heating in air, while inorganic carbon like graphite and carbon black have a higher decomposition temperature. Some inorganic salts usually possess much higher decomposition temperature than the first two, but some residues may remain in pores after decomposing. In general, the intrinsic difference between pore-forming agents lies in their decomposition temperature, which may lead to various properties of porous supports.

The present work concentrated on the fabrication of a crack-free asymmetric membrane based on BCFN material, which was exploited on both porous support and dense layer. The spherical graphite particles, decomposing at a relatively high temperature under oxidizing atmosphere, were employed as the pore-forming agent. The impact of amount of graphite and its decomposition temperature on the properties of porous support was discussed. A two-step procedure including dry pressing and dip coating was applied to produce asymmetric membrane. This versatile process can be easily transplanted to the fabrication of tubular asymmetric membrane.

2. Experimental

2.1. Fabrication of porous support

The $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ powders used to produce asymmetric membrane were obtained by the method mentioned in our previous work [30]. The average particle size is 1.8 μm. The particle size distributions are shown in Fig. 2. The same BCFN powders were used in coating slurry. The graphite was chosen as

Table 1
Data compilation for asymmetric membranes.

Membrane	Thickness (μm/mm)	Pore-forming agent	Porosity (%)	Average pore size (μm)	Reference
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$	200/1.5	Inorganic matter	–	0.5	[17]
$La_{0.2}Sr_{0.8}CoO_{3-\delta}/MgO$	20/2.5	Carbon black: 4–12 wt%	28–44	0.7–2.4	[18]
$SrFeCo_{0.5}O_x$	190/0.9	Ethyl cellulose and carbon fiber	26	–	[19]
$SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$–$0.4MgO/MgO$–$0.4SCFZ$	200/1.0	Active carbon: 25–35 wt%	–	0.8	[20]
$La_{0.6}Sr_{0.4}Fe_{0.9}Ga_{0.1}O_{3-\delta}$	120/0.82	Corn starch: 40 vol%	28	1.9	[21]
$Sr_{0.77}Fe_{0.54}Al_{0.46}O_{2.54-\delta}/La_{0.5}Sr_{0.5}FeO_{3-\delta}$	500/1.4	Graphite: 2 wt%	–	–	[22]
$La_{0.8}Sr_{0.2}Fe_{0.7}Ga_{0.3}O_{3-\delta}/La_{0.8}Sr_{0.2}FeO_{3-\delta}$	120/1.0	Corn starch	34	4.6	[23]
$(SrFeO_{3-\delta})_{0.7}(SrAl_2O_4)_{0.3}$	120/0.42	Corn starch: 40–50 wt%	20	2–4	[24]
$La_{0.6}Ca_{0.4}CoO_3$	10/1.2	No pore-forming agent	–	1.9	[25]
$CaTi_{0.9}Fe_{0.1}O_{3-\delta}$	30/0.5	Corn starch: 44 vol%	–	–	[26]
$Ca_{0.8}Sr_{0.2}Ti_{0.7}Fe_{0.3}O_{3-\delta}$	35/0.5	Carbon black: 20 wt%	48	–	[27]
$La_{0.8}Sr_{0.2}Fe_{0.7}Ga_{0.3}O_{3-\delta}/La_{0.8}Sr_{0.2}FeO_{3-\delta}$	80/1.0	Corn starch: 45 vol%	34	2.5	[28]
$Ba_{0.95}La_{0.05}FeO_{3-\delta}$	46/1.4	No pore-forming agent	–	1.5	[29]

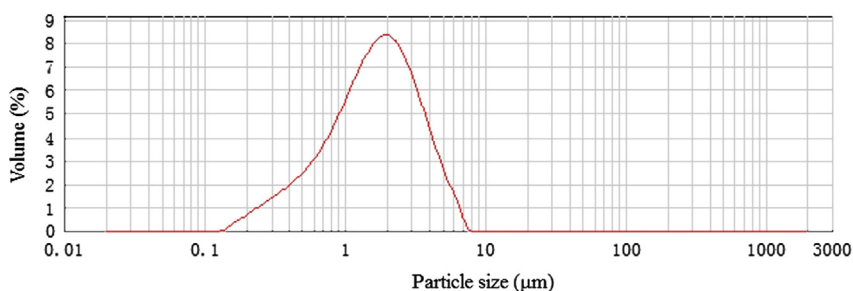*Note*: The parameters before and behind "/" refer to dense layer and porous layer, respectively.

Fig. 2. Particle size distribution of BCFN powders.