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Morphology, performance and stability of multi-bore capillary $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ oxygen transport membranes

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ABSTRACT

Mixed ionic-electronic conducting 3, 4, 7-bore capillary membranes made of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) were successfully prepared by the combined phase inversion/sintering technique. The membranes fabricated have asymmetric wall structures with micro-channels formed in between surfaces, and dense layers sandwiched in between the micro-channels. By changing the solvent from DMSO to NMP, changes in the morphology of the 7-bore membrane were observed, where the separation layer has reduced its effective thickness. The multi-bore membranes exhibited 3-point bending fracture loads of 10.4, 13.5, 15.4 and 11.7 N with a 3 cm testing span for the 3-bore, 4-bore, 7-bore-DMSO and 7-bore-NMP samples, respectively, which are much stronger than single-bore hollow fibre membranes. Oxygen permeation of the multi-bore membranes was measured with a sweep gas flow through lumen and the effect of operating temperature has on the performance was studied between 750 °C to 1000 °C. Oxygen fluxes measured are comparable to typical sandwich-like structured single-bore hollow fibres at temperatures below 900 °C, but are notably higher at higher temperatures owe to their thinner membrane walls. The 200-h long-term permeation test conducted on the 7-bore membrane showed a slight increase in permeation flux, but the sign of kinetic demixing/decomposition appeared on the outer surface, where the surface of the thinnest membrane walls underwent faster demixing/decomposition than the thickest walls. In summary, the results demonstrated that multi-bore configurations can achieve optimised material distribution during the fabrication, and can obtain strong mechanical property, high permeation flux for the final products whilst maintaining high membrane area to volume ratios.

1. Introduction

Oxygen production is of great importance in industrial and environmental processes. Current technologies such as the cryogenic distillation and pressure swing adsorption (PSA) are expensive and energy intensive. The search for alternate technology has led to the use of ceramic membranes for oxygen separation. Over the past 30 years, considerable efforts have focused on the use of dense ceramic membranes, especially mixed ionic-electronic conducting (MIEC) membranes capable of conducting both ions and electrons [1–4]. These MIEC membranes can theoretically produce 100% pure oxygen at elevated temperatures under oxygen partial pressure differences without the need of an external electrical circuit. As a result, these membranes offer a simplified and cost effective method for oxygen separation. Furthermore, they have attracted considerable attention for their integration with membrane reactors in reactions such as partial oxidation of methane to syngas (POM) and oxidative coupling of methane to C_2 (ethylene and/or ethane) [5–9].

The performance of MIEC membranes strongly depends on the membrane material and the membrane structure. Enormous efforts have been made to tune the chemistry of the membrane material to obtain highly permeable and stable materials, an excellent review article can be found elsewhere [3]. Besides the membrane material, membrane structure is equally important for oxygen separation, therefore vast amount of research have also been undertaken to study different membrane configurations. Disk and plate membranes have been widely used in research works because of the ease of fabrication. However, membrane of this geometry possesses low separation area to volume ratio, which makes it undesirable for large scale production. Conventional tubular membranes have a larger active area compared to that of the disc membranes, but their thick dense separation layers contribute to an increased bulk diffusion resistance, resulting in low oxygen permeation flux. So far the most advanced structural design in terms of permeation rate has been the hollow fibre configuration.

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Hollow fibre membranes have thin separating layers and exhibit high membrane area to volume ratios, resulting in higher oxygen permeation flux per unit volume compared to conventional disk and tubular membranes [10–16]. However, major drawbacks of hollow fibres are the weak mechanical stability from their small dimensions, which may jeopardize the robustness of membrane modules in high flowrate and high pressure operating conditions. In order to solve the mechanical stability issue, efforts have been made to optimize membrane configuration to achieve membranes with good mechanical property whilst maintaining good oxygen permeation flux. A bundling strategy has been proposed recently to improve the mechanical stability of hollow fibre membranes by using catalytic perovskite binders, which may not only increase the mechanical stability, but also increase the permeation flux owe to the catalytic activity of the binder [17]. However, such strategy adopts multi-step batch-by-batch fabrication process and needs extra cost for the binder material, therefore the whole fabrication cost is significantly increased. Alternatively, the requirement of one-step continuous production has led to the recent interest in fabricating multi-bore capillary membranes [18–21]. Results obtained from such configurations showed some promising results where they exhibited an improved mechanical property with good oxygen permeation flux for the 4-bore membranes. However, work in this field is still very limited and so far only 4-bore membranes were investigated on 3 different membrane materials, i.e., Nb_2O_5-doped $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCFNb), $SrFe_{0.8}Nb_{0.2}O_{3-\delta}$ (SFN) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) for oxygen separation [18–21].

Our previous study has shown successful preparation of 3, 7, 19-bore porous capillary membranes made of alumina using the combined phase-inversion and sintering method [22], and they showed not only much improved mechanical property, but also enhanced water permeation flux compared with their single-bore hollow fibre counterparts. Furthermore, both fracture load and permeation flux increased when the number of bores increased. It would be interesting to investigate the effects of different configuration MIEC multi-bore membranes have on their mechanical and permeation performances, as the knowledge from porous membranes may differ from dense membranes due to different transport mechanisms. In this study, multi-bore $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) MIEC capillary membranes with 3, 4 and 7 bores are prepared and studied. LSCF is selected as the membrane material because it possesses both good permeability and good chemical stability [23–27], furthermore, widely available literature regarding LSCF single-bore hollow fibre membranes makes it easy for comparisons. We show here that different from conventional ram extrusion, by adjusting fabrication parameters in the phase-inversion process, the morphology of multi-bore membranes can be notably altered. The mechanical property and oxygen permeation flux for the multi-bore LSCF membranes are studied, and the long-term 200 h test on stability and kinetic demixing/decomposition are also investigated with the 7-bore membrane.

2. Experimental

2.1. Materials

Commercially available $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) ceramic powder with surface area of 10.2 $m^2\,g^{-1}$ was used as the membrane material (Fuel Cell Materials, Columbus, Ohio). The polymer binder used was Polyethersulfone (PESf) (RadelA-300, Solvay Advanced Polymers GmbH, Dusseldorf, Germany). Arlacel P135 (Uniquema, Wilton, UK) was used as the dispersant and dimethyl sulfoxide (DMSO, VWR) or N-Methyl-2-pyrrolidone (NMP, VWR) was selected as the solvent. The internal and external coagulants used were deionised water.

Table 1
Ceramic suspension compositions and spinning parameters.

Suspension compositions	LSCF (wt%)	67.0			
	DMSO or NMP (wt%)	25.8			
	PESf (wt%)	6.7			
	Dispersant (wt%)	0.5			
Spinning parameters		3-bore	4-bore	7-bore DMSO	NMP
	Dope extrusion rate ($cm^3\,min^{-1}$)	9	9	8	9
	Bore liquid (water) rate ($cm^3\,min^{-1}$)	12	14	14	18
	Air gap (cm)	0	0	0	1

2.2. Multi-bore capillary membrane fabrication

The LSCF multi-bore capillary membranes were fabricated using the combined phase inversion/sintering method and the compositions of ceramic suspension are listed in Table 1. The ceramic suspension was mixed thoroughly by ball milling prior to removing air bubbles using the vacuum system, and then spun through a specially designed spinneret to obtain the multi-bore capillary membrane precursors. In this study, triple, tetra and seven-bore spinnerets were used, whose geometric configurations are shown in Fig. 1. For the 3-bore and 4-bore membranes, DMSO was used as the solvent for the ceramic suspension; for the 7-bore membranes, two types of suspension were used, in which DMSO or NMP was the solvent, and the obtained membrane will be named as 7-bore-DMSO and 7-bore-NMP in the following sections, respectively. The spinning parameters used to obtain the multi-bore capillary membranes are also summarised in Table 1. After drying, the precursors were then heated to 600 °C at a rate of 2 °C min^{-1} and then stayed at this temperature for 2 h to remove the polymer binder, followed by sintering at 1350 °C for 5 h with a heating rate of 3 °C min^{-1}. Finally, the furnace was cooled at a rate of 3 °C min^{-1} to room temperature.

2.3. Oxygen permeation test

The shell side of the membrane was exposed to ambient air and the sweep gas argon was fed through the capillary bores creating the oxygen partial pressure difference for oxygen permeation. The flowrate of the sweep gas was maintained at 100 $cm^3\,min^{-1}$ throughout the experiment. The oxygen permeated was carried by the sweep gas and measured by gas chromatography (GC, Varian 3900). The oxygen permeation flux was calculated using the below equation:

$$J_{O_2}=\frac{V_{Ar}\,y_{o_2}}{A_o\,(100-y_{02})} \quad (1)$$

where J_{O_2} is the oxygen permeation flux, V_{Ar} is the volumetric flowrate of the argon sweep gas, A_o is the outer membrane surface area, y_{02} is the percentage oxygen concentration detected by the GC. The data were collected within a time window of 30 min after the temperature became stable, and a stable flux with an error less than 2% is reported within 2 h.

2.4. Characterisation

Morphologies of the multi-bore capillary membranes were studied using the Gemini LEO 1525 field emission gun scanning electron microscope (SEM). The mechanical property was evaluated using the three-point bending method by an Instron materials testing system (Model 5544) with a 5 kN load cell, the samples were positioned with a span of 30 mm onto the sample holder. A minimum of 5 samples were tested and the average value with an error less than 15% is reported.