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High performance yttrium-doped BSCF hollow fibre membranes

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ABSTRACT

Oxygen production from BSCF ($Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$) and yttrium-doped BSCF ($Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.175}Y_{0.025}O_{3-\delta}$) hollow fibres was investigated, and the role of yttrium in the crystal structure was further explored using high-temperature X-ray diffraction. Yttrium substitution acted to increase the oxygen flux significantly, from 4.9 to 7.0 ml cm^{-2} min^{-1} at 900 °C for the BSCF and the BSCFY membranes, respectively. Permeation was particularly enhanced at lower temperatures, between 66% and 92% over the range 650–800 °C. The lattice expansion determined from high temperature X-ray diffraction measurements in air was similar for both compositions, suggesting that the higher oxygen fluxes obtained for BSCFY hollow fibres could be attributed to the higher non-stoichiometry due to yttrium addition to the BSCF crystal structure. In addition, the improvement of oxygen fluxes for small wall thickness (~0.3 mm) hollow fibres operating below the critical length (i.e. limited surface kinetics regime) indicates that yttrium has enhanced the surface exchange rates. XRD patterns showed split peaks around 2θ 31° and 56° above 200 °C, likely corresponding to a coexisting hexagonal perovskite phase. This peak-splitting was more pronounced for BSCFY, suggesting that the kinetics of the hexagonal phase formation may be faster for the yttrium-doped perovskite. The lattice volume of BSCFY expanded more than BSCF when exposed to nitrogen at 900 °C, confirming a higher release of oxygen and enhanced oxygen non-stoichiometry.

1. Introduction

Pure oxygen is required for many industrial operations, in particular for emerging clean-coal technologies such as oxyfuel combustion and coal gasification. Oxygen for these processes is commonly produced by cryogenic air separation, and although being a highly reliable and proven method, it imposes significant financial and energy costs that could hinder the viability of these technologies in the production of clean energy [1]. An alternative technology is air separation using mixed ionic and electronic conducting (MIEC) membranes, which can be stand-alone systems for oxygen production, or be incorporated into an industrial process as a membrane reactor. In the presence of an oxygen partial pressure gradient, these dense ceramic membranes conduct oxygen ions, typically at temperatures above ~600 °C [2].

One class of MIEC membranes undergoing intensive investigation are perovskites. These materials have an ideal crystal structure of ABO_3, where A is typically a rare earth, alkaline or alkaline earth metal, and B is typically a transition metal [3]. At high temperatures, oxygen molecules (O_2) dissociate at the surface, and are transported through the bulk material via oxygen vacancies, before re-associating at the other side of the membrane. Stoichiometric perovskites have limited oxygen vacancies (and hence oxygen flux), therefore substitution of other metals for A and/or B is performed to distort the crystal structure and create additional oxygen vacancies [2–4]. This approach has been systematically carried out for several compositions, reflected by the optimisation of the most investigated perovskite compounds: $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) [5,6] and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) [7–11]. Using these compositions, a variety of engineered membrane shapes have been adopted as designs, including flat surfaces [12,13], tubes [14–16], capillaries [17,18] and hollow fibre geometries [19–21].

Hollow fibre architectures are interesting for membrane technology due to possibility of producing high surface areas with a facile technique. Inorganic hollow fibre spinning technology was adapted from the wet–dry spinning process which is used to produce polymeric hollow fibres [22,23]. A polymer is dissolved in a solvent, extruded through a die using pressure, then contacted with a coagulant on the inside and outside of the fibre, causing the solvent to diffuse out of the mixture, and the polymer to coagulate, resulting in a solid body. The solidification process during coagulation is known as phase inversion. For the production of inorganic hollow fibres, the polymer is used as a binder for ceramic powders rather than being used as the membrane material. Depending on the nature of the polymer–solvent–nonsolvent system, different morphologies can be obtained, ranging from almost completely dense hollow fibres [18] to completely porous

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substrates [22,24,25]. After production of the 'green' or un-sintered hollow fibre, the binder is decomposed by heat treatment, leaving behind the ceramic powders. This results in a reduction in fibre size, though the geometry of the fibre is retained. Further sintering of the fibre at high temperatures (generally >1000 °C), results in the densification of the membrane. This process was first reported in the open literature for the production of porous alumina hollow fibres [23], but has since been adapted for dense perovskite membranes [19,26,27], porous zirconia [24,28], steel [29] and nickel hollow fibres [30].

A major advantage to using hollow fibres is that the small wall thickness (100–500 μm) is highly beneficial to oxygen fluxes through most MIEC membranes. When the bulk diffusion step is the rate-limiting step for oxygen transport (as is the case for most perovskite materials), oxygen permeation is inversely proportional to the membrane thickness. When the thickness is reduced below the critical thickness, denoted L_c, surface exchange reactions begin to limit oxygen permeation, hindering improvements brought about by thickness reductions. Nevertheless, dramatic improvements in oxygen fluxes have been achieved through the fabrication of hollow fibres, rather than thick disc membranes. For BSCF, fluxes of 1.4 ml min^{-1} cm^{-2} were reported for a 1.8 mm disc at 950 °C by Shao et al. [11]. Production of hollow fibres with wall thickness of 0.45 mm and using binders containing sulphur, and tested under a modest O_2 partial pressure gradient (<21 kPa), achieved a flux of 5.1 ml min^{-1} cm^{-2} at 950 °C [20], while fluxes as high as 9.5 ml min^{-1} cm^{-2} were achieved through the use of a sulphur-free binder [27]. Hence, the binder also affects the perovskite structure, as contamination from the sulphur present in several commonly employed binders produce non-ionic domains which hinder oxygen permeation.

We have previously shown oxygen permeation improvements of up to 160% for the substitution of yttrium for iron in BSCF to form $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2-x}Y_xO_{3-\delta}$ [31], with the optimum composition being at $x = \sim 0.025$, henceforth denoted BSCFY. The improvements attained by yttrium doping were attributed to the increase in both lattice parameters and concentration of oxygen vacancies, which are largely related to bulk ionic diffusion. In this work, we are interested in the effect of yttrium doping for thin hollow fibre membranes. Hence, we fabricated hollow fibres of BSCF and the optimum BSCFY composition and further investigated the effects of yttrium doping on oxygen permeation performance. We also studied the evolution of the crystal structure at high temperatures to further elucidate the mechanism behind the enhancement of oxygen permeation due to yttrium doping.

2. Experimental methods

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.175}Y_{0.025}O_{3-\delta}$ (BSCFY) precursor powders were prepared via the EDTA-citrate method as reported previously [31] and calcined at 450 °C. The powders were milled with ethanol in a McCrone microniser for 15 min, resulting in a particle size distribution d_{50} of 7 μm. The slurry was dried at 80 °C to evaporate the ethanol. Hollow fibres were prepared using the conventional wet–dry fibre spinning technique with the use of a sulphur-free polymer [19,27,32,33]. The precursor powder was mixed with poly(etherimide) (PEI) [Sabic Innovative Plastics, Australia] and N-methyl-2-pyrrolidone (NMP) [99%, Sigma–Aldrich] in the ratio 7:1:4 by mass. 0.5–1 wt% of poly(vinylpyrrolidone) (PVP) [average molecular weight 40,000 g/mol, Sigma–Aldrich] was added to adjust the viscosity and assist with dispersion. The solution was degassed under vacuum, and then extruded through a tube-in-orifice spinneret with an inner diameter of 0.8 mm and an orifice diameter of 2.5 mm and contacted with deionised water which was passed through the hollow fibre lumen. The extrudate passed through a 10 cm air gap before entering a bath containing de-ionised water. The extrudate was left in the bath overnight to complete the coagulation process. The extrudate was dried in air and cut into short lengths, which were sintered for 8 h in air at 1100 °C.

X-ray diffraction (XRD) analysis was used to determine the crystal structure of the materials, which were sintered at 1100 °C and milled by hand. XRD was performed using a Bruker D8 Advance machine, using Cu Kα radiation for diffraction angles $10° \leq 2\theta \leq 105°$. High temperature XRD was performed using a Bruker D8 with a heating attachment. A thin film of perovskite powder was dispersed onto a Pt tape which acted as both the substrate and heating element. A thermocouple was welded to the underside of the Pt tape and used to monitor and control the temperature. Diffraction scans were performed at temperature of 30, 200, 400, 600, 800 and 1000 °C between 10° and 90° 2θ (Cu Kα), both heating and cooling cycles in static air. The heating and cooling rates of the platinum foil (and hence powder) were very fast (estimated to be 50 °C/s) since this could be controlled by changing the electrical current passing through the foil. The system was observed to equilibrate very quickly (as observed in the diffraction patterns), and the system was held at each temperature for 1 h before making the measurements reported in this paper. Further tests to investigate stability in reducing atmospheres were undertaken where the powder was heated to 900 °C, measured in static air, then exposed to a flow of N_2 ($P_{O_2} \sim 10^{-5}$ atm) for 5 h. The Pt peaks were used as an internal reference to confirm the test temperature and correct the data for the small changes in height resulting from the thermal expansion of the substrate during testing. A linear thermal expansion coefficient for Pt of 8.8×10^{-6} K^{-1} was used [34]. The surface morphology of the hollow fibres were investigated via field emission scanning electron microscopy (SEM) using a JEOL JSM-6610 at an accelerating voltage of 5 kV.

The membranes were tested in the oxygen permeation apparatus shown schematically in Fig. 1. The membrane was sealed to the quartz tubes using four coats of silver paste, and the furnace heated to 120 °C for 20 min between coats to evaporate the solvent. The furnace was then heated to 950 °C for 1 h to form the seal, before cooling to 900 °C for testing. The inner side of the membrane was exposed to a sweep gas flow of argon [>99.999 mol%, Coregas] supplied via a mass flow controller. The outer side was exposed to convective atmospheric air through the furnace. Permeation measurement was performed at intervals of 50 °C (with a ramp rate of 5 °C min^{-1}) at argon flow rates of 50–200 ml min^{-1}. The total permeate flow rates (argon plus the permeate flow) were measured using a bubble flow meter. The permeate stream was analysed by a gas chromatograph (Shimadzu GC-2014, 3 Å molecular sieve column) in which argon was used as a sweep gas. In this work we report oxygen fluxes associated with ionic diffusion only, by deducting any molecular oxygen flux caused by small air leaks, generally at the membrane-seal interface. Hence, the pure ionic oxygen transport through the membrane in given by the oxygen flux in Eq. (1), where J_{O_2} is the oxygen flux (ml min^{-1} cm^{-2}) which corresponds to the ionic transport of oxygen, χ is the molar fraction of the gas, F is the flow rate of permeate stream (ml min^{-1}) and A is the membrane area (cm^2).

$$J_{O_2} = \left(x_{O_2} - \frac{21}{79} x_{N_2} \right) \cdot \frac{F}{A} \qquad (1)$$

3. Results and discussion

Representative SEM micrographs of the hollow fibres are shown in Fig. 2. The outer and inner diameters were 1010 and 465 μm (respectively) for the BSCF hollow fibre (Fig. 2a), and 1225 and