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# Improvement of oxygen permeation in perovskite hollow fibre membranes by the enhanced surface exchange kinetics

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ABSTRACT

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) perovskite hollow fibre membranes with an asymmetric structure were fabricated by the phase inversion–sintering technique. The oxygen permeation flux is increased noticeably due to the porous inner surface. Additional coating of a porous perovskite layer as a promoter on the inner and/or outer surfaces of the LSCF hollow fibres further promotes the oxygen permeation due to the acceleration of the surface exchange kinetics. Several typical perovskites such as $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCFe), $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), $SrCo_{0.9}Sc_{0.1}O_{3-\delta}$ (SCSc), $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ (SCNb) as well as LSCF itself were used as the promoters. The permeation results indicate that the oxygen permeation flux of the LSCF hollow fibre membranes has been further improved remarkably by the surface-coating modification. The enhancing effect of the $SrCoO_{3-\delta}$ (SC)-based perovskites on oxygen permeation follows the order of SCSc > BSCF > SCNb ~ SCFe > LSCF. This coating strategy can be applied to evaluate the catalytic activity of the perovskites to surface exchange reactions for the preparation of oxygen permeable membranes. Coating of the perovskites on the downstream membrane surface exhibits better enhancement than on the upstream membrane surface, but coating on both membrane surfaces may promote the oxygen permeation to the largest extent. By combing the individual advantages of different perovskite oxides, the resultant composite membranes may be of high permeability, high mechanical strength and high stability.

## 1. Introduction

Mixed ionic-electronic conducting (MIEC) ceramic membranes have received considerable attention in the last two decades due to their potential applications in the production of pure oxygen and partial oxidation of hydrocarbons [1–3]. The MIEC membrane technology exhibits a number of important advantages for air separation over the polymer-based membranes and the industrial-scale state-of-the-art methods such as pressure swing adsorption (PSA) and cryogenic distillation, including high energy-efficiency, simplified operation and remarkably reduced costs. For example, the oxygen production cost by the MIEC membrane process can be theoretically reduced by around 35% compared to the cryogenic distillation or PSA methods [3]. In the MIEC membrane reactor, oxidation of hydrocarbons is integrated with the air separation in a single step. As a result, abundant air from atmosphere can be used as oxidant without the need of nitrogen removal, making the system much simplified. However, the MIEC membranes must have sufficiently high structural/chemical stability and sustainable mechanical integrity in addition to the high oxygen permeability, e.g., 5–10 $cm^3$(STP) $cm^{-2}$ $min^{-1}$ for a commercially viable process [4], before this technology can be put into practical applications.

So far most of the MIEC membranes are made from perovskite oxides with a general formula of $ABO_3$ because a variety of elements can be accommodated in the crystal lattice and oxygen vacancies can be produced by partial substitution of the A- and/or B-site cations with lower or higher valence cations. The performances of these perovskite membranes in terms of oxygen permeability and stability are highly dependent on their compositions. For example, the perovskite containing cobalt such as $SrCoO_{3-\delta}$ (SC)-based ones usually have the highest oxygen permeability since the strontium at A-site induces the formation of oxygen vacancies while the cobalt ions at B-site, which have small binding energy with oxygen, facilitate fast diffusion of oxygen within the oxide bulk and fast oxygen surface exchange

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kinetics [5–8]. But such composite membranes also exhibit low structural/chemical stability due to the high thermal expansion, abrupt phase transition at a certain temperature as well as the interaction with gas species such as carbon dioxide [9,10]. In order to improve the membrane stability, many efforts have recently been focused on the development of cobalt-free membranes [11–13]. Doping of metal ions with high valence state such as $La^{3+}$ in the A-site of the SC-based perovskites can improve the mechanical stability of the membranes, but the oxygen permeability is also subsequently reduced because of the decrease in oxygen vacancy concentration [14]. In fact, it is hard to find a single composite membrane to have high oxygen permeability, high structural and phase stability, and high mechanical strength at the same time.

In addition to the search for novel advanced membrane materials with high performances, research efforts are also directed towards optimization of the membrane architecture both for permeability and kinetic stability reasons [15]. Shaping the membranes in the hollow fibre geometry offers many advantages over the planar and tubular ones such as higher surface area/volume ratio and facile high-temperature sealing. Furthermore, the phase inversion-induced hollow fibre membranes have a thin wall thickness typically between 0.1 and 0.4 mm, and usually possess an asymmetric structure consisting of a very thin effective separation layer integrated with porous substrate [16–20]. Therefore, the oxygen permeation rate in the hollow fibre membranes can be much higher than that in the planar or tubular ones. For such hollow fibre membranes, the relative limiting effect of the surface exchange kinetics on membrane performances can be significant [21,22], or even may reduce the advantages of the hollow fibre configuration.

Suppression of the surface exchange limitations can be basically achieved by increasing the membrane surface area or by coating the membrane surface with a porous material demonstrating superior oxygen exchange properties. For example, the previous study in our group indicated that the surface etching of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) hollow fibre membranes by 98% $H_2SO_4$ led to reduced effective thickness and increased effective surface area of the membrane simultaneously, resulting in an improvement factor of 18.6 in oxygen permeation flux at 800 °C and 20 mL min$^{-1}$ sweeping rate, i.e., from 0.0241 mL cm$^{-2}$ min$^{-1}$ for the original membrane to 0.451 mL cm$^{-2}$ min$^{-1}$ for the etched membrane [23]. It is noted that the flux improvement decreases with increasing temperature because the relative limiting effect of the bulk diffusion gradually becomes more noticeable as the temperature is increased. However, the surface etching also damages the mechanical strength of the hollow fibre membranes. In contrast, coating a porous layer on the membrane surfaces may not compromise the mechanical strength of the hollow fibres since the membranes' microstructure is not changed. Application of a porous layer of the same material as the membrane is able to enhance the oxygen permeation [24–27]. It is attributed to the enlargement of the contact boundary between the membrane and the gas phase, thus to provide a total increase in membrane surface area and, correspondingly, the number of sites for the oxygen exchange reactions. Other options include the application of noble metals such as Ag and Pt [24,28–30] and the metal oxides with high catalytic activity in the electrochemical reactions involving oxygen [30–34]. When using noble metals, it may be limited by their high prices and low compatibility with ceramics. Comparatively, perovskite oxides can be applied more easily to the oxygen permeable membrane surfaces due to the similar properties. Furthermore, the perovskites with both high oxygen ionic and electronic conductivity exhibit high catalytic activity to the oxygen exchange reactions.

In this study, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) perovskite hollow fibre membranes were fabricated by the phase inversion–sintering technique. A series of typical perovskites such as $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCFe), $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), $SrCo_{0.9}Sc_{0.1}O_{3-\delta}$ (SCSc), $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ (SCNb), which are usually good oxygen permeable membrane materials with high oxygen permeability but low mechanical strength, have been used as the coating catalysts to enhance the oxygen permeation in the LSCF hollow fibre membranes. It aims at fabricating the oxygen permeable hollow fibre membranes with high permeability, high mechanical strength and high stability by combing the individual advantages of different perovskite oxides.

## 2. Experimental

### 2.1. Fabrication of perovskite powders

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) was used as the membrane material, and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), $SrCo_{0.2}Fe_{0.8}O_{3-\delta}$ (SCFe), $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ (SCNb), $SrCo_{0.9}Sc_{0.1}O_{3-\delta}$ (SCSc) pervsokites were used as the catalyst materials. All these composite oxide powders were prepared through the sol–gel method described in details elsewhere [19,22]. For spinning the LSCF hollow fibre membranes, the LSCF powder precursor was calcined at 800 °C for 3 h followed by ball-milling for 48 h and sieving through a sifter of 200-mesh or 24 μm sieve-pore diameter. For other perovskite oxides, the powder precursors were calcined at 1000 °C for 2 h to remove the residual carbon and to form the desired structure.

### 2.2. Fabrication of LSCF hollow fibre membranes

The LSCF hollow fibre membranes were made from the calcined and ball-milled powders by the phase inversion and sintering technique. The detailed preparation procedures were described in our pervious publications and many other literatures [16–22]. In this study, the spinning solution consists of 63.26 wt% LSCF calcined powders, 5.08 wt% polyethersulfone (PESf) [(Radel A-300), Ameco Performance, USA] as the polymer binder, 29.45 wt% 1-methyl-2-pyrrolidinone (NMP) [AR Grade, >99.8%, Kermel Chem Inc, Tianjin, China] as the solvent and 2.21% polyvinylpyrrolidone (PVP-K30 from Fluka, $M_w$=40,000) as the additive. A spinneret with the orifice diameter/inner diameter of 3.0/1.5 mm was used for spinning hollow fibre precursors. DI water and tap water were used as the internal and the external coagulants, respectively. After drying and straightening, the hollow fibre precursors were sintered at 1400 °C for 4 h to form dense hollow fibre membranes. The gas-tight property of the hollow fibres for subsequent surface coating and oxygen permeation were measured by a nitrogen gas permeation test [35].

### 2.3. Surface coating

A slurry was prepared by mixing the calcined perovskite powder in ethanol followed by ball milling with zirconia balls in an agate bottle for 24 h. PVP-K30 (30 mg/g perovskite) and polyvinyl butyral (Hunan Sanli Chemical Co. LTD, 40 mg/g perovskite) were used as additives. The slurry was brushed onto the outer surface or was perfused into the lumen of the hollow fibres so as to deposit the perovskite on the inner surface. The deposition process was repeated so as to produce thicker perovskite layers. Post-heat treatment was conducted using a programmed temperature ramp of 5 °C min$^{-1}$ to 600 °C, held for 1 h, then 2 °C min$^{-1}$ to 1050 °C, held for 2 h and then 2 °C min$^{-1}$ to room temperature to remove the organic additives and sinter the coating layer onto the membrane surfaces.