Highly efficient preparation of Ce$_{0.8}$Sm$_{0.2}$O$_{2-\delta}$–SrCo$_{0.9}$Nb$_{0.1}$O$_{3-\delta}$ dual-phase four-channel hollow fiber membrane via one-step thermal processing approach

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ABSTRACT

Fabricating dual-phase hollow-fiber membranes via a one-step thermal processing (OSTP) approach is challenging, because of complex sintering kinetics and the subsequent impacts on membrane morphology, phase stability, and permeation properties. In this study, we have demonstrated that Ce$_{0.8}$Sm$_{0.2}$O$_{2-\delta}$–SrCo$_{0.9}$Nb$_{0.1}$O$_{3-\delta}$ (SDC-SCN) four-channel hollow fiber membrane can be manufactured via a single high-temperature sintering process, by using metal oxides and carbonates directly as membrane materials (sources of metal ions). It has been found that use of a low ramping rate reduces grain sizes, increases grain and forming cobalt oxide nanoparticles, a key step to promoting surface exchange process followed by enhancing oxygen permeation. While the grain boundary interface region can be limited to approximately 20–30 nm. At 1173 K oxygen permeation of the SDC-SCN four-channel hollow fiber membrane was measured at approximately 1.2 mL cm$^{-2}$ min$^{-1}$ using helium as the sweep gas. Meanwhile, the dual-phase membrane shows a good tolerance to carbon dioxide, with the oxygen permeation flux fully recovered after long-term exposure to carbon dioxide (more than 100 h). This will enable further application of the OSTP approach for preparing dual-phase multi-channel hollow fiber membranes for applications of oxyfuel combustion, catalytic membrane reactors and carbon dioxide capture.

1. Introduction

Mixed ionic-electronic conducting (MIEC) membranes, a type of high temperature oxygen perm-selective membranes enabling energy-efficient separation and various “green” chemistry opportunities, have garnered a lot of interests from industrial and academic communities over the past decades. The great selectivity to oxygen (theoretically 100%) at temperatures over 973 K allows effective separation of pure oxygen and complete rejection of other gaseous substances. After years of development, applications of MIEC oxygen-permeable membrane have been extended to areas other than air separation, such as membrane reactor for effective conversion of natural gas, hydrogen production and abatement of greenhouse gases [1–4]. Perovskite oxide (ABO$_3$) is one of the mostly studied MIEC materials. However, owing to the existence of active transition metals and alkali metals (such as Ba, Sr, Co, Cu, Fe, etc.), segregation of elements, unwanted reactions between gaseous molecules and membrane materials, and etching of membrane surface occur readily during long-term operation, which significantly restricts lifetime of membrane reactors under strongly reducing and/or corrosive atmospheres (e.g. hydrogen, carbon monoxide, hydrogen sulfide, carbon dioxide and sulfur dioxide) [5–7]. To address such issues, oxygen-permeable membranes consisting of a dual-phase material have been the focus of catalytic membrane reactor research, due to a more flexible design of membrane material and significantly improved thermal-chemical stability of the membranes. The dual-phase membranes normally consist of a perovskite oxide phase and a second fluorite oxide phase. Both oxides can conduct oxygen ions at high temperatures, forming continuous pathways for efficient transport of oxygen ions.
Meanwhile, fluoride oxides are thermal-chemically very stable, inhibiting element segregation of perovskite oxides during oxygen permeation, thus improving membrane stability [8–15].

Different from conventional approaches which normally involve multiple material processing steps and sintering, oxides and carbonates were directly utilized as precursor membrane materials for the preparation of a dual-phase four-channel hollow fiber membrane via a one-step thermal processing (OSTP) approach. A composite of 60 wt% CeO,8SmO,2O2−δ−0.4 wt%SrCO3−0.1O3δ−4 wt%SrCo3O5, Nb2O5 (SDC-SCN) was selected as the target phase of the membrane, due to its high oxygen permeability and carbon dioxide tolerance proved in our previous study [16]. Meanwhile, a multi-channel hollow fiber membrane geometry was selected due to its advantages in both oxygen permeation and mechanical robustness, when compared with alternative geometries such as disk-like membrane, tubular membrane and single-channel hollow fiber membrane [17–19].

The feasibility of the OSTP approach has been demonstrated in our previous study [20], where oxides or carbonates, instead of as-prepared perovskite oxides, were directly employed in a phase-inversion process for fabrication of a single-phase perovskite hollow fiber membrane. In this OSTP, solid-state reactions converting raw chemicals (metal ion sources) into perovskite oxides and membrane densification occurred simultaneously (Fig. 1a), allowing approximately 50% reduction in time and energy required in conventional multi-step approaches [20]. To advance the OSTP approach to the preparation of dual-phase hollow fiber membranes, the biggest challenge is controlling and stabilizing crystal structures of separate oxides during the single thermal treatment, as the thermodynamics and kinetics of crystallization are commonly very different between perovskites and fluorites. As shown in Fig. 1b and c, any mismatch between crystallization (solid-state reaction) and densification (solid-state sintering) rates (i.e., (i) crystallization of perovskites; (ii) crystallization of fluorites; (iii) densification of perovskite phases; (iv) densification of fluoride phases and (v) co-densification of the two phases) leads to the formation of impurities and residues (the two phases might be physically isolated by the formation impurity particles) and impair integrity and perm-selectivity of the resultant membranes.

In addition to the more complex sintering kinetics of dual-phase membrane via OSTP, this study also focuses on the feasibility of advancing the OSTP approach to preparing four-channel hollow fiber membranes. The sintering kinetics (mainly the ramping rate) and its impacts on membrane morphology, crystal structure, phase stability and permeation properties have been systematically investigated, followed by outlining prominent potentials of utilizing the dual-phase four-channel hollow fiber membranes for applications with enriched carbon dioxide, such as catalytic membrane reactor (dry reforming and carbon dioxide dissociation) and oxyfuel combustion (O2/CO2), where sufficient oxygen permeation and chemical stability under carbon dioxide atmosphere are both important.

2. Experimental

2.1. One-step thermal processing of dual-phase hollow fiber

The 60 wt%CeO,8SmO,2O2−δ−0.4 wt%SrCO3−0.1O3δ−4 wt%SrCo3O5, Nb2O5 (analytical grade) dual-phase membrane was fabricated via the OSTP approach. Stoichiometric amounts of raw materials SrCO3, CoO2, Nb2O5, CeO2 and Sm2O3 were mixed with polyetherimide (PEI) and 1- methyl-2-pyrrolidone (NMP) via ball milling for 24 h. The spinning suspension obtained consisted of 66 wt% solids, 27 wt% NMP and 7 wt% PEI. Deionized water was used as both internal and external coagulants. The four-channel hollow fiber precursors were obtained by extruding the spinning suspension through a spinneret, the details of which have been described elsewhere [20]. Injection rate of the internal coagulant was 8 mL min−1, while the one for suspension was kept at 3 mL min−1. After the phase inversion process, hollow fiber precursors were dried at room temperature for 24 h, and before being sintered at 1563 K for 10 h in static air, with the heating and cooling rates ranging from 2 K min−1 to 5 K min−1, to obtain gas-tight SDC-SCN four-channel hollow fibers. For reference, we also prepared SDC-SCN four-channel hollow fibers via traditional two-step thermal processing approach (TSTP, including separate steps of oxides calcination and membrane sintering) where pre-prepared SDC and SCN oxide powders were used for preparing the spinning suspension.

2.2. Synthesis of SDC and SCN powders

To investigate phase structure and adsorption property of single-phase oxides, we synthesized single-phase SDC and SCN powders using traditional methods. SDC powder was synthesized by an EDTA-citric acid complex sol-gel method. The required amounts of Sm (NO3)3 and Ce(NO3)3 (analytical grade) were dissolved in an aqueous solution. EDTA and citric acid were dissolved in deionized water, and the pH of the solution was adjusted to approximately 7 by the addition of aqueous ammonia. The nitrate solution was added dropwise to the EDTA-citric acid complex solution, with the molar ratio of metal ion: citric acid: EDTA: at 1:1:2: A gel was obtained by evaporating water at 338 K under stirring, followed by pre-fire in air at 473 K to remove organic compounds, and calcination at 1073 K for 5 h under a static air atmosphere to obtain SDC powder. SCN powder was prepared by a solid-state method. The stoichiometric amounts of SrCO3, CoO2 and Nb2O5 were mixed in ethanol, and ball-milled for 24 h. After evaporating ethanol, the mixture was calcined at 1373 K for 5 h under a static air atmosphere to obtain SCN powder.

2.3. Characterisations

The morphologies of hollow fiber samples were investigated using a scanning electron microscope (SEM, Hitachi S-4800, Japan) equipped with a backscattered electron (BSE) detector. A focused ion beam (FIB, FEI, Helios Nanolab 600i, United States) was employed to extract a cross-section lamella (90 nm thickness, Fig. 2) from the SDC-SCN grain boundary interface. The FIB workstation was operated at a voltage of 15 kV. The sites of interest were protected from the gallium ion beam by locally depositing a carbon layer followed by the application of a thicker platinum layer. The gallium ion beam was then used to carve out a lamella which was mounted on a transmission electron microscopy (TEM) grid and ion milled until it became electron-transparent. The as-prepared lamella was observed using high-resolution transmission electron microscopy (HRTEM, FEI, Tecnai G2 F30 S-TWIN, America) operated at an accelerating voltage of 300 kV and equipped with an energy dispersive X-ray spectrometer (EDX).

Phase structures of the samples were characterized by X-ray diffraction (XRD, Bruker, model D8 advance, Germany) in the range of 20° ≤ 2θ ≤ 80° and at a step width of 0.02°. The variation of crystal structures of the dual-phase membrane (sintered at 2 K min−1 and 1563 K for 10 h) at high temperature was characterized by an in-situ XRD instrument equipped with a high-temperature attachment (in-situ HTXRD, Philips, X’ Pert Pro). The samples were tested in air from 298 K to 1273 K with a heating rate of 2 K min−1 and each temperature point was maintained for 30 min to achieve thermal equilibrium before diffraction data collection. All diffraction patterns were collected by step scanning at increments of 0.05° in the range 20° ≤ 2θ ≤ 80°. The mechanical strength of the dual-phase hollow fiber membrane was measured by a three-point bending test performed using a tensile tester (Model CMT6203, USA) with a load cell of 5 kN.

Carbon dioxide adsorption/desorption (CO2-TPD) experiments were performed using high-temperature chemisorption instrument (MicrotractBEL, BELCAT II, Japan). Powder specimens (150 mg) were placed in a U-shaped quartz tube and preheated in flowing pure carbon dioxide (20 mL min−1) to 973 K, held for 2 h, cooled to room temperature, and re-heated to 1173 K at a rate of 10 K min−1. The effluents gases were...
Fig. 1. Schematic of the one-step thermal processing (OSTP). (a) single-phase (perovskite) membrane fabrication; dual-phase (perovskite-fluorite) membrane in the case of (b) matched and (c) mismatched reaction and ramping rates.
monitored using a mass spectrometer (Hiden Analytical, QIC-20, United Kingdom).

2.4. Oxygen permeation

The setup used to carry out the oxygen permeation experiments in the hollow fiber membrane is described in detail elsewhere [21]. The supply of various gases was controlled by mass flow controllers (Sevenstar, CS200, China). The air flow rate at the feed side (shell side) was 120 mL min\(^{-1}\), and helium flow rate at the sweep side (lumen side) was 60 mL min\(^{-1}\). The temperature around the samples was controlled by a high-temperature tubular furnace (HF-Kejing, OTF-1200X, China). The gas composition at the sweep side outlet was determined using an online gas chromatographer (Agilent, 7820A, Germany) equipped with a 5A molecular sieve column. Unlike tubular membranes and disk-like membranes, the membrane area of multi-channel hollow fiber

![Fig. 2. Cross-section of lamella at the SDC-SCN grain boundary extracted by the FIB technique. (a) Overview and (b) Close view.](image)

![Fig. 3. Microstructure and phase structure of the dual-phase hollow fiber membrane fabricated via the OSTP approach (2K min\(^{-1}\) ramping rate, 1563 K for 10 h). SEM micrographs: (a) cross-section overview; (b) in the region of the skeleton marked on a; (c) top-view of hollow fiber outermost surface, insert is the BSE micrograph. (d) XRD patterns of dual-phase SDC-SCN membrane (OSTP) and reference samples of single phase SDC (sol-gel method) and SCN (solid-state method). (e) In-situ high-temperature XRD patterns of dual-phase SCF-SCN membrane (OSTP approach).](image)
membrane for oxygen permeation flux calculation is difficult to obtain. To be consistent with the literatures [17, 22], the outermost surface area of the multi-channel hollow fiber membrane was used for calculation in this study. The possible oxygen leakage due to imperfect sealing at high temperatures was monitored through the mole fraction of nitrogen (79 mol. % in the feed side) that leaked into the sweep side. The experiments were conducted only if the nitrogen leakage was below 0.5 mol. %.

2.5. Carbon dioxide stability

Experiments on the stability and reversibility of the membrane exposed to carbon dioxide were performed in the setup for oxygen permeation described in Section 2.4. Air (120 mL·min⁻¹) was fed into the feed side (shell side), while carbon dioxide and helium (60 mL·min⁻¹) were alternatively fed into the sweep side (lumen side). The membrane was exposed to 100% carbon dioxide for 24, 24, 24, 24 and 100 h. After each exposure, the sweep side was switched to helium for 4 h to examine the recovery of oxygen flux.

3. Results and discussion

3.1. Morphology and phase structure

Microstructure of the dual-phase four-channel hollow fiber membrane prepared via the OSTP approach was examined by SEM. As shown in Fig. 3a, the membrane forms an asymmetrical four-channel structure. The outermost diameter of the hollow fiber is 3.05 ± 0.05 mm. The shape of the inner channel is close to an ellipse. Graphical measurements were used to obtain the circumference of the elliptical channels. The circumferences of the outermost hollow fiber and sum of the four inner channels (based on Fig. 3a) are 9.6 ± 0.3 mm and 9.8 ± 0.2 mm, respectively. This indicates that surface areas of the outermost surface and the inner surface are similar. Large amounts of closely packed finger-like pores are distributed in the bulk of hollow fiber skeleton while sponge-like pores are located near external and internal surfaces and sandwiched between layers of finger-like pores (Fig. 3b). It has been demonstrated that both the finger-like and sponge-like layers greatly affect membrane properties such as mechanical strength and oxygen permeation. The finger-like pores have very low tortuosity, which are beneficial in terms of reducing mass transfer resistance and thus increasing oxygen permeation [23, 24]. After high-temperature sintering, the sponge-like layers become gas tight, and provides the majority of mechanical strength and perm-selectivity to oxygen [25]. From the view of top surface (Fig. 3c), there is a dense surface with grains distributed homogenously. The insert in Fig. 3c presents a micrograph of the top membrane surface using BSE imaging. It shows a distinct contrast image when the light area is SDC and the dark area is SCN, indicating a uniform distribution of grain particles of the two oxides. Room-temperature XRD further confirms the formation of the two oxides via the OSTP approach. Shape and clear characteristic peaks of SDC and SCN identified in the dual-phase membrane (Fig. 3d) match well with diffraction peaks of the reference samples made of single-phase fluorite and perovskite oxides (the major diffraction angles for single phase SDC and SCN are 28.5°, 33.0°, 47.3° and 56.1°, and 32.5°, 40.1°, 46.8° and 58.2°, respectively). As shown in Fig. 3c and d, some small particles are found on the membrane surface, but not detected by XRD. This may be due to the detection limit of XRD, and the high-crystallinity masks from the SDC and SCN. Formation of impurity particles on the membrane surface will be discussed in detail later.

Effects of temperature on the chemical compatibility between perovskite and fluorite was also studied via in-situ XRD, between temperatures of 298–1273 K and at a temperature step of 200 K. As shown in Fig. 3e, diffraction peaks of both the SCN perovskite phase and SDC fluorite phase are sharp and clear, with no additional phases observed during the process of heating. Note that the diffraction peaks shift to a low angle at elevated temperatures owing to thermal expansion of oxide lattice [26]. Meanwhile, diffraction peaks of the two phases are partially overlapped at room temperature; however, the difference in thermal expansion rates at elevated temperatures leads to the separation of diffraction peaks. For example, for temperatures higher than 473 K, a split of the two-phase diffraction peaks can be observed; while at 1273 K, the overlapped peaks have been separated completely. These results indicate a good compatibility ofbulk SDC and SCN at elevated temperatures.

To further understand and characterize structural changes occurring at the grain boundary of the two oxides after OSTP, we extracted electron-transparent lamellae around the interface and examined them by TEM and EDX. Fig. 4a shows straight and smooth grain boundaries and two bulk phases (marked as I and II). HRTEM was employed to analyze the crystal evolution of materials at an atomic scale. The oxides exhibit a high crystallinity. Within each grain, continuous single-directional lattice fringes can be observed on the bulk of the left and right half sides. The marked d-spacing of 0.313 nm corresponds to the interplanar distance of the SDC [1 1 1] lattice planes, which agrees to the diffraction data of SDC (ICDD NO. is 75-0158). The marked d-spacing of 0.375 nm corresponds to the interplanar distance of the SCN [1 0 0] lattice planes [27]. The corresponding EDX was obtained around the grain boundary. Ce and Sm are mainly concentrated in area I, while elements of Sr and Co are mainly concentrated in area II, indicating that area I is the SDC phase and area II is the SCN phase. To explore cation exchanges (or solid-state reaction) between the two oxides at the grain boundary interface, elemental compositions (expressed as an atomic fraction) at various points of interest marked with numbers (in Fig. 4a) are plotted in Fig. 4b. These data indicate that the bulk of the perovskite and the fluorite in the vicinity of the grain boundary interface display similar compositions, equivalent to the composition of nominal perovskite and fluorite and as thus unaffected by the OSTP approach. In contrast, the grain boundary interface region at a width of approximately 20–30 nm experience drastic changes in composition. Sr/Co and Sm/Ce ions are found enriched on the side of SDC and SCN, respectively. Ion exchange is inevitable at the interface during high-temperature processing. However, it can be restricted to the nanometer level and the related effect on oxygen permeation can be controlled within a small range.

3.2. Sintering kinetics

In the OSTP approach, solid-state reactions of raw chemicals and solid-state sintering of membrane occurred simultaneously at elevated temperatures, which can thus be considered as an in-situ reactive sintering process. As discussed in Introduction, the scenario is even more complex for a heterogeneous system containing more than one phase; therefore, it is important to study the reactive sintering kinetics and its effects on microstructure and phase structure of the dual-phase hollow fiber membrane. It has been widely accepted that ramping rate is one of the most important factors determining the rates of reaction and densification [28]. Therefore, in this study, sintering kinetics were investigated by means of a stepwise ramping rate accompanied by SEM and oxygen permeation flux.

The surface morphologies of the dual-phase hollow fiber at ramping rates of 2, 3, 4, and 5 K min⁻¹ are shown in Fig. 5a. The figure clearly shows a dense surface with homogenously distributed perovskite and fluorite oxide grains. As the SEM was operated at a high accelerating voltage, the electron microscope micrographs provide a light/dark contrast between perovskite SCN (dark-colored grains) and fluorite SDC phases (light-colored grains). A large number of brighter nanoparticles are found on the surface of the SDC grains and at grain boundaries at the ramping rates of 2 and 3 K min⁻¹. Notably, these brighter nanoparticles on the SDC surfaces concentrate at the grain boundary when the ramping rate increases to 4 K min⁻¹, while impurities are barely observed at a higher ramping rate of 5 K min⁻¹. Since the nanoparticles are too small to be detected by XRD, TEM and EDX analyses were used to
identify the nanoparticles. As shown in Fig. 5b, irregular particles with the size of 200–300 nm are found on the SDC bulk surface. From EDX, the nanoparticles are identified as cobalt oxide (CoO, the stoichiometric coefficient $x$ could not be precisely confirmed by EDX). The formation of impurities is closely related to the formation enthalpy of SDC and SCN, but these have rarely been reported in literature. Lu et al. [29] provided a simple method to estimate the enthalpy of formation of complex oxides with an error of less than 1%. Based on this method, the estimated enthalpies of formation of Ce$_{0.8}$Sm$_{0.2}$O$_2$ and SrCo$_{0.9}$Nb$_{0.1}$O$_3$ are calculated as -1053.3 and -954.3 kJ/mol (298.15 K), respectively. For the convenience of calculation, the nonstoichiometric coefficient $\delta$ is set to zero. Thermodynamically, lower ramping rates (lower temperature) favor the formation of the two oxides. However, kinetically, the chemical reaction occurred by solid-state diffusion of ions, which is characterized by a slow kinetic rate. The reaction starts at the points of contact between the initial solid components and continues by ionic interdiffusion through the product phase. In this case, the degree of mixing and concentration of raw chemicals are key factors for a faster reaction [30].

As shown in Fig. 5c, a clear surface can be observed, indicating that the simultaneous solid-state reaction and sintering in the OSTP approach is the main reason for the formation of nanoparticle impurities. Ramping rates also have a significant effect on grain size. It can be seen from Fig. 5a that grain size of the two oxides increases with the increase in ramping rate. This effect is more obvious to the SCN phase, which is consistent with the analysis of the effects of the ramping rate on oxide formation. Noting that the effects of ramping rate on the phase structure and microstructure of the membrane also directly affect its mechanical strength. The breaking loads of the membrane sintered at 2, 3, 4, and 5 K min$^{-1}$ are 7.61, 7.57, 6.07, and 6.01 N, respectively. The breaking load of the dual-phase hollow fiber membrane decreases with the increase in the ramping rate, which may be due to the increase in the grain size [30]. However, this effect of ramping rate on membrane strength is unremarkable.

The oxygen permeation flux was evaluated using the dual-phase four-channel hollow fiber membranes sintered at different ramping rates. As shown in Fig. 6a, the membranes sintered at different rates follow a comment trend in which the increase in temperature gradually increases the oxygen permeation flux. This is attributed to the enhanced oxygen surface exchange and bulk diffusion at elevated temperatures. It was observed that a higher ramping rate has a negative effect on membrane permeation flux. For example, at 1173 K, the permeation flux of the membrane sintered at 2, 3, 4, and 5 K min$^{-1}$ are 1.20, 1.04, 0.97, and 0.75 mL cm$^{-2}$·min$^{-1}$, respectively. They show certain competitiveness with fluorite-perovskite based dual-phase hollow fiber membranes reported in literature (Listed in Table 1). In our previous study, we found that the oxygen permeation process of SDC-SCN dual-phase membrane is controlled mainly by the surface exchange reactions when the
membrane thickness is sufficient thin (thinner than 0.5 mm) [16]. Additionally, the conductivity of SDC is 1–2 orders of magnitude lower than SCN phase and hence the oxygen permeation is limited mainly by the ionic conductivity from the fluorite phase [10]. In this case, the surface conditions of the SDC grains and three-phase boundaries (TPB, gas-solid boundary at the dual-phase grain boundary) play an important role in surface exchange kinetics and oxygen permeation of the SDC-SCN hollow fiber membrane. Meanwhile, it has been reported that large TPB and cobalt oxide can significantly promote reduction and evolution of oxygen and transfer of oxygen molecular/oxygen intermediates at membrane surface, and improves the oxygen permeation [31–35]. Therefore, a relationship between oxygen permeation and membrane surface morphologies can be established. A lower ramping rate results in a large number of cobalt oxide nanoparticles on the surface of SDC grains and larger TPB, and thus a higher oxygen permeation flux. In addition, the contribution of surface exchanges at the outmost surfaces on the oxygen permeation flux can be observed from the apparent activation energies. From Fig. 6b. The apparent activation energies of the membrane sintered at 2, 3, 4, and 5 K min⁻¹ are 85.8 ± 3.9, 90.0 ± 0.5, 90.5 ± 7.1 and 94.0 ± 3.2 kJ/mol, receptivity. The decoration of cobalt oxide decreases activation energies, due to an increased rate of surface oxygen exchange [35]. In this study, low ramping rates resulted in small grain size, increased grain boundaries (TPB), and a cobalt oxide “impurity” which jointly contribute to increase surface oxygen exchange and oxygen permeation.
3.3. Carbon dioxide adsorption/desorption

Carbon dioxide is present in many membrane processes, such as catalytic membrane reactors, oxyfuel combustion, and other carbon dioxide separation and capture processes. Interactions between membrane materials (mostly perovskite oxides) and carbon dioxide are inevitable, no matter reversible or irreversible, and impairs oxygen permeation and even membrane stability. Oxygen permeation of the

### Table 1

Oxygen permeation flux through fluorite-perovskite based dual-phase hollow fiber membranes.

<table>
<thead>
<tr>
<th>Membrane compositions</th>
<th>Geometry</th>
<th>Temp.</th>
<th>Flow rate of sweep gas’ mL min⁻¹ (Sweep gas)</th>
<th>Oxygen flux mL min⁻¹ cm⁻²</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₁₋ₓYₓSmₓO₃₋ₓLaₓSr₂₋ₓMnxO₃₋₅</td>
<td>Single-channel hollow fiber</td>
<td>1123 K</td>
<td>100 (Helium)</td>
<td>0.52</td>
<td>[36]</td>
</tr>
<tr>
<td>Zrₓ₄₋ₓYₓSmₓO₃₋ₓLaₓSr₂₋ₓMnxO₃₋₅</td>
<td>Single-channel hollow fiber</td>
<td>1223 K</td>
<td>30 (Helium)</td>
<td>0.282</td>
<td>[37]</td>
</tr>
<tr>
<td>Zrₓ₄₋ₓYₓSmₓO₃₋ₓLaₓSr₂₋ₓFeₓO₃₋₅</td>
<td>Single-channel hollow fiber</td>
<td>1223 K</td>
<td>30 (Helium)</td>
<td>0.16</td>
<td>[38]</td>
</tr>
<tr>
<td>Ceₓ₂₋ₓSmₓO₃₋ₓLaₓSr₂₋ₓFeₓO₃₋₅</td>
<td>Single-channel hollow fiber</td>
<td>1223 K</td>
<td>30 (Helium)</td>
<td>0.50</td>
<td>[39]</td>
</tr>
<tr>
<td>Ceₓ₂₋ₓSmₓO₃₋ₓLaₓSr₂₋ₓCrₓO₃₋₅</td>
<td>Single-channel hollow fiber</td>
<td>1223 K</td>
<td>30 (Helium)</td>
<td>0.31</td>
<td>[40]</td>
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<tr>
<td>Ceₓ₂₋ₓSmₓO₃₋ₓLaₓSr₂₋ₓMnxO₃₋₅</td>
<td>Single-channel hollow fiber</td>
<td>1223 K</td>
<td>30 (Helium)</td>
<td>0.43</td>
<td>[41]</td>
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<tr>
<td>Ceₓ₂₋ₓSmₓO₃₋ₓLaₓSr₂₋ₓAlₓFeₓO₃₋₅</td>
<td>Single-channel hollow fiber</td>
<td>1223 K</td>
<td>100 (Helium)</td>
<td>1.026</td>
<td>[42]</td>
</tr>
<tr>
<td>Prₓ₀.₁₋ₓGdₓ₀.₁₋ₓCeₓO₂₋₅₋ₓCoFe₂O₄⁻ᵇ</td>
<td>Single-channel hollow fiber</td>
<td>1273 K</td>
<td>150 (Helium)</td>
<td>0.54</td>
<td>[43]</td>
</tr>
<tr>
<td>Ceₓ₂₋ₓSmₓO₃₋ₓLaₓSr₂₋ₓNiO₃₋₅⁺</td>
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<td>1223 K</td>
<td>100 (Helium)</td>
<td>1.47</td>
<td>[44]</td>
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<tr>
<td>Ceₓ₂₋ₓSmₓO₃₋ₓLaₓSr₂₋ₓSrCoₓ₋ₓNbₓO₃₋₅</td>
<td>Four-channel hollow fiber</td>
<td>1173 K</td>
<td>60 (Helium)</td>
<td>1.20</td>
<td>This work</td>
</tr>
</tbody>
</table>

a Feed gas is atmospheric air.
b Spinel structure.
c Ruddlesden-Popper type perovskite structure.

Fig. 7. Effect of carbon dioxide on the dual-phase hollow fiber membrane fabricated via the OSTP approach (2K min⁻¹ ramping rate, 1563 K for 10 h). (a) Oxygen permeation flux at 1173 K with different concentrations of carbon dioxide at the sweep side; (b) high-temperature expansion in air and pure carbon dioxide atmosphere; (c) reversibility of the oxygen permeation fluxes at 1173 K as a function of time while periodically changing the sweep gases. (in Cycle 1–5 the sweep side of membrane was exposed to flowing carbon dioxide for 24, 24, 24, 24, and 100 h, respectively); (d) CO₂-TPD profiles of SCN, SDC, and SDC-SCN powder samples.
dual-phase hollow fiber membrane was investigated using different concentrations of carbon dioxide at the sweep side (air was at the feed side). Notably, it has been reported that the present of carbon dioxide at the feed side (air side) decreases the oxygen permeation, however the impact of carbon dioxide on the oxygen permeation is inferior to that applied at the sweep side [44]. Therefore, mainly the effects of carbon dioxide at the sweep were discussed. The concentration of carbon dioxide at the sweep side ranged from 0% to 100% with a stepwise concentration of 20%. As shown in Fig. 7a, in the presence of carbon dioxide, the oxygen permeation flux decreases with an increase in the carbon dioxide concentration at the sweep side. In particular, for a sweep with 100% carbon dioxide, the oxygen permeation flux is almost zero. Such a sudden cessation of oxygen flux has been widely reported for pervoskite membranes and is considered mainly due to the interaction of carbon dioxide and membrane materials [44,45]. Lin et al. [46] systematically studied the behavior of carbon dioxide adsorption and reaction on pervoskite oxides. The carbon dioxide adsorption process for dense particles can be illustrated by the shrinking-core model, where carbonation reactions of carbon dioxide with membrane materials occurred at the surface of the dense perovskite oxide and produced a porous product layer on the unreacted perovskite core. Both carbon dioxide and oxygen can transport out of or into the porous carbonate layers. The solid carbonates (which are non-oxygen-permeable) on the membrane surface have the negative effect of blocking active sites for oxygen permeation. The blockage is further strengthened with more concentrated carbon dioxide (more coverage by carbonates on the membrane surface). The blockage of oxygen permeation from carbon dioxide can be revealed by studying the expansion behavior of the membrane at elevated temperatures, as the lattice expansion is associated with the oxygen exchange between the gas and solid. As shown in Fig. 7b, the expansion curve obtained in carbon dioxide linearly increases with the temperature, which is attributed to the atomic vibrations of the lattice during the heating process. However, deviations of the linear change (i.e., slope changes at 600–800 (I), 800–1000 (II) and >1000 K (III)) were observed in the membrane expansion curve obtained in air. This is mainly caused by the loss of a large amount of lattice oxygen, commonly known as chemical expansion [26]. Obviously, the carbon dioxide adsorbed on the membrane surfaces hinders oxygen transfer from the solid to gas phase.

The ability of recovering from carbon dioxide exposure and carbon dioxide tolerance were further investigated by periodically exposing the sweep side of the membrane to carbon dioxide and helium. The membrane was exposed to 100% carbon dioxide for 24, 24, 24, 24, and 100 h. After each exposure, the sweep side was switched to helium for 4 h to examine the recovery of oxygen permeation. As shown in Fig. 7c, the membrane has a low oxygen flux when it was exposed to 100% carbon dioxide, confirming the blockage of oxygen permeation by carbon dioxide. When carbon dioxide was removed from the sweep side, the membrane displays an immediate oxygen recovery and the recovered oxygen flux fluctuates to approximately 1.13 mL cm⁻² min⁻¹, and is very close to the original value of 1.20 mL cm⁻² min⁻¹. The membrane in each of the first four cycles (Cycle 1–4) was exposed to carbon dioxide for 24 h and then further extended to 100 h in Cycle 5. The dual-phase membrane shows good carbon dioxide tolerance and flux resilience, and the oxygen flux can be restored to 1.2 mL cm⁻² min⁻¹. The resilience from carbon dioxide exposure indicates that carbon dioxide adsorption and carbonation are reversible. To confirm this, CO₂-TPD experiments were performed on a dual-phase membrane (single-phase SDC and SFC were used as reference). As shown in Fig. 7d, pervoskite oxide and fluorate oxide exhibit different carbon dioxide adsorption/desorption behavior. Desorption peaks appear at approximately 600–800 (I), 800–1000 (II) and >1000 K (III) for the SFC oxide samples. This phenomenon is consistent with the membrane expansion behavior in carbon dioxide shown in Fig. 6b. These results indicate a strong interaction between carbon dioxide and metal oxides. Peaks were derived from the chemisorption of carbon dioxide on the SDC surface [47] and the decomposition of metal carbonates or metal oxides (e.g., cobalt carbonate, strontium carbonate or cobalt oxide) [48–50]. Very weakly eluted carbon dioxide was detected in the SDC sample, indicating an inert feature of SDC to carbon dioxide. Therefore, the existence of SDC in the dual-phase membrane can effectively reduce the adsorption and carbonation reactions, which result in carbon dioxide desorption peaks with lower intensity. Note that the temperatures of carbon dioxide desorption and carbonate decompositions are lower than the membrane operation temperature (1173 K), demonstrating the recovery capability of the membrane (in Fig. 7c) at the current operating temperature.

4. Conclusions

Ce₀.₈Sm₀.₂O₂₋₉SrCe₀.₉Nb₁O₃₋₆ (SDC-SCN) dual-phase four-channel hollow fiber membranes were successfully fabricated via a one-step thermal processing (OSTP) by directly using metal oxides and carbonates as metal ion sources and with only one high-temperature sintering throughout membrane fabrication. The as-prepared four-channel hollow fiber shows a typical asymmetric structure and dense surface with homogenously distributed pervoskite and fluorate oxide grains. Ion exchange was observed at the SDC/SCN grain boundaries after OSTP, which can be limited to the nanometer level (less than 30 nm). It was demonstrated that the membrane morphology, phase structure and permeation properties are closely related to the ramping rate in OSTP, which affects both the solid-state reaction and solid-state sintering. A low ramping rate (2 K min⁻¹) results in a dual-phase hollow fiber membrane with a smaller grain size, increased grain boundaries, and decoration by cobalt oxide nanoparticles, and with a higher oxygen permeation rate of 1.20 mL cm⁻² min⁻¹ at 1173 K. The existence of SDC in the dual-phase membrane can effectively suppress the adsorption and carbonation reactions between carbon dioxide and metal oxides. The dual-phase four-channel hollow fiber membrane shows good carbon dioxide tolerance and flux recovery ability after long-term carbon dioxide exposure (more than 100 h), which demonstrates that the oxygen flux can be restored to 1.2 mL cm⁻² min⁻¹.

Author statement


Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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