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Enhancing Oxygen Permeation Via Multiple Types of Oxygen Transport Paths in Hepta-Bore Perovskite Hollow Fibers

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Significance The multiple types of efficient oxygen transport paths were demonstrated in high-mechanical-strength hepta-bore $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ hollow fiber membranes. These types of paths play a prominent role in enhancing oxygen permeation fluxes (17.6 mL min^{-1} cm^{-2} at 1223 K) which greatly transcend the performance of state-of-the-art $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ hollow fiber membranes, showing a good commercialization prospect. © 2017 American Institute of Chemical Engineers *AIChE J*, 00: 000–000, 2017

Keywords: oxygen permeation, oxygen transport paths, perovskite hollow fiber, hepta-bore

Power generation from fossil fuels causing large amounts of emissions (e.g., CO_2, NO_x) has generated a lot of serious environmental problems (e.g., global warming, acid rain). Currently, to mitigate these issues, oxyfuel combustion is considered as one of the most promising techniques to reduce these emissions.[1] This technique not only avoids formation of NO_x by eliminating presence of atmospheric nitrogen, and enriches CO_2 content in the flue gas to values of 96–99% to facilitate subsequent CO_2 capture, but also improves combustion flame temperature and increases combustion efficiency.[2,3] Low-cost pure oxygen production is one of the key factors restricting large-scale industrialization of this technique. Mixed ionic and electronic conducting (MIEC) (e.g., perovskite) membranes are the promising candidates for pure oxygen production with lower energy consumption and cost compared to traditional oxygen producing technology (e.g., the capital and energy-intensive cryogenic air-separation process).[2] However, for realizing MIEC membrane commercialization, the most challenge is to develop membranes with excellent oxygen permeation performance to achieve high-efficiency energy conservation and emission reduction.

As promising candidates for future industrialization, perovskite hollow fiber (HF) membranes possess large surface/volume ratios, asymmetric structure and thin walls, and thereby exhibit high oxygen permeation fluxes (Figure 1A).[4,5] Up to now, there have been many perovskite HF membranes showing high oxygen permeation fluxes (e.g., $BaCo_xFe_yZr_zO_{3-\delta}$,[6] $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.8}O_{3-\delta}$,[7,8] $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF),[9] $BaBi_{0.05}Sc_{0.1}Co_{0.85}O_{3-\delta}$,[10] $Ba_0.Sr_{0.5}Co_{0.8}Cu_{0.2}O_{3-\delta}$,[11] $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$,[12] $SrCo_{0.9}Sc_{0.1}O_{3-\delta}$,[13] $SrFe_{0.8}Nb_{0.2}O_{3-\delta}$,[14] $SrFe_{0.9}Ta_{0.1}O_{3-\delta}$,[15] $SrCo_{0.9}Nb_{0.1}F_{0.1}O_{3-\delta}$[16]). However, the oxygen permeation fluxes in vast majority of perovskite HF membranes cannot exceed the desired commercial target value (10 mL·min^{-1}·cm^{-2}) at 1173 K.[10] According to Wagener equation, it seems that reducing wall thickness can enhance its oxygen permeation flux.[17] This enhancement is theoretically limited, because when membrane thickness is far below than the characteristic membrane thickness, oxygen permeation process is controlled by surface exchange kinetics rather than bulk diffusion, and reducing thickness is not very effective to improve oxygen permeation flux.[17] Under this circumstance, further enhancing oxygen permeation flux could be achieved by membrane surface modification. For example, Leo et al. reported that oxygen permeation flux of palladium-modified BSCF HF membrane exceeded the coveted target value.[18] Unfortunately, surface modification is complicated and discommodious and often contains sophisticated apparatus. Additionally, because of thin walls with many finger or sponge-like pores, these conventional single-bore perovskite HF membranes also suffer from low mechanical strength (e.g., breaking load) restricting their commercialization. Recently, to improve the mechanical strength, new multibore HF membranes[19–22] and novel bundling strategy[23] were reported, but showing little enhanced oxygen permeation. Therefore, to the best of our knowledge, the reported perovskite HF membrane could rarely simultaneously meet these commercialization requirements in the aspects

Additional Supporting Information may be found in the online version of this article.

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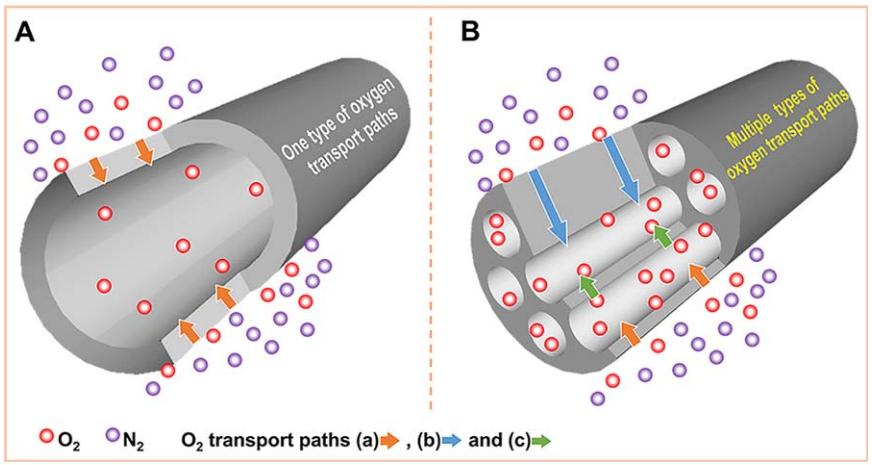

Figure 1. Schematic of oxygen permeation processes of typical conventional perovskite HF membranes with only one type of oxygen transport paths (A), and new hepta-bore perovskite HF membrane with multiple types of efficient oxygen transport paths (B).

[Color figure can be viewed at wileyonlinelibrary.com]

of permeation flux, fabrication simplicity, and mechanical strength.

For pure oxygen production applied in oxyfuel process, how to highly improve the performance of perovskite HF membranes easily, cheaply, and reliably? Here, to address these critical issues, rather than using traditional routes (e.g., developing thin low-mechanical-strength HF membranes with only one type of oxygen transport paths (i.e., (a)), Figure 1A, or modifying these HF membranes surfaces), we demonstrate a new route for enhancing oxygen permeation via multiple types of efficient oxygen transport paths (i.e., (a), (b), and (c)) in high-mechanical-strength hepta-bore BSCF HF membranes (Figure 1B).

XRD diffraction patterns (Figure 2A) show that the as-synthesized BSCF powder and the as-prepared hepta-bore BSCF HF membranes exhibit well-formed perovskite crystalline structure, in agreement with that of the reported BSCF material.[9] As shown in Figure 2B, with uniform diameter, the as-prepared hepta-bore BSCF HF membranes are usually *ca.* 35–40 cm in length, and there are no obvious distortion, cracks, or defects in these HF membranes. The cross section (Figure 2C) visually shows that the hepta-bore structure is well formed, and the outer and inner-bore diameters of these HF membranes are ~2.4 mm and ~0.6 mm, respectively. Large amounts of closely packed finger-like pores were near the outer and inner walls of the HF, and dense structures evolved from sponge-like structures in HF precursor during sintering were at the center wall (Figures 2D and 2E). The formation of this asymmetric microstructure resulted from the complicated interactions among solvent (i.e., N-methyl-2-pyrrolidone), nonsolvent (i.e., H_2O), and polymer binder (i.e., polyetherimide, PEI) during the phase inversion process.[24] Additionally, the as-prepared HFs exhibited fully densified outer and inner surfaces (Figures 2F and 2G), guaranteeing the HF was leak-free together with the sandwiched dense layer. Unlike the single-bore perovskite HF membranes with weak breaking load, the as-prepared hepta-bore BSCF HF membrane can withstand a high breaking load of about 13.5 N (see Supporting Information Table S1), which is possibly caused by the special braced structures (Figure 2C) playing a supporting role in bearing the applied force. Because the breaking load is considered as one of the prerequisites that largely determines the practicability of perovskite HF membranes, these hepta-bore HF membranes with excellent mechanical strength have a better industrialization prospect.

The existence and function of a variety of efficient oxygen transport paths in the as-prepared hepta-bore BSCF HF membranes were proved by a series of experiments and analysis as follows. Normally, as is well known, according the mechanism of oxygen permeation in perovskite membranes, oxygen partial pressure gradient is the driving force for oxygen transport.[17] In this case of hepta-bore BSCF HF membrane whose shell and lumen sides were selected as the feed and sweep sides, respectively (Figure 1B), when the oxygen partial pressure gradient of both sides appeared, oxygen would inevitably transport from feed side to peripheral and center bores, indicating that the efficient oxygen transport paths (a) and (b) exist in these BSCF HF membranes. Assuming that there was no oxygen transport path (c) in the membrane, that is, there was no oxygen transport behavior between peripheral bores and center bore, the total oxygen permeation is contributed by paths (a) and (b). To find out whether the assumption is reasonable or not, we measured the oxygen permeation of the three membrane samples (see Supporting Information for the details about operating conditions): (i) hepta-bore HF whose center bore was plugged and sealed (Figure 3A (i)); (ii) hepta-bore HF whose peripheral bores were plugged and sealed (Figure 3A (ii)); and (iii) hepta-bore HF without any treatment (Figure 3A (iii)). For sample (i), due to the thin wall, the oxygen permeation flux produced by path (a) was 9.1 mL min^{-1} cm^{-2} at 1173 K, which compares favorably with previously reported BSCF HF membranes with PEI as polymer binder (Figure 3B).[18,25] For sample (ii), although the wall was relatively thick, the oxygen permeation flux produced by path (b) was detectable and fairish. For sample (iii), a remarkable oxygen permeation flux achieved 14.8 mL min^{-1} cm^{-2} at 1173 K,

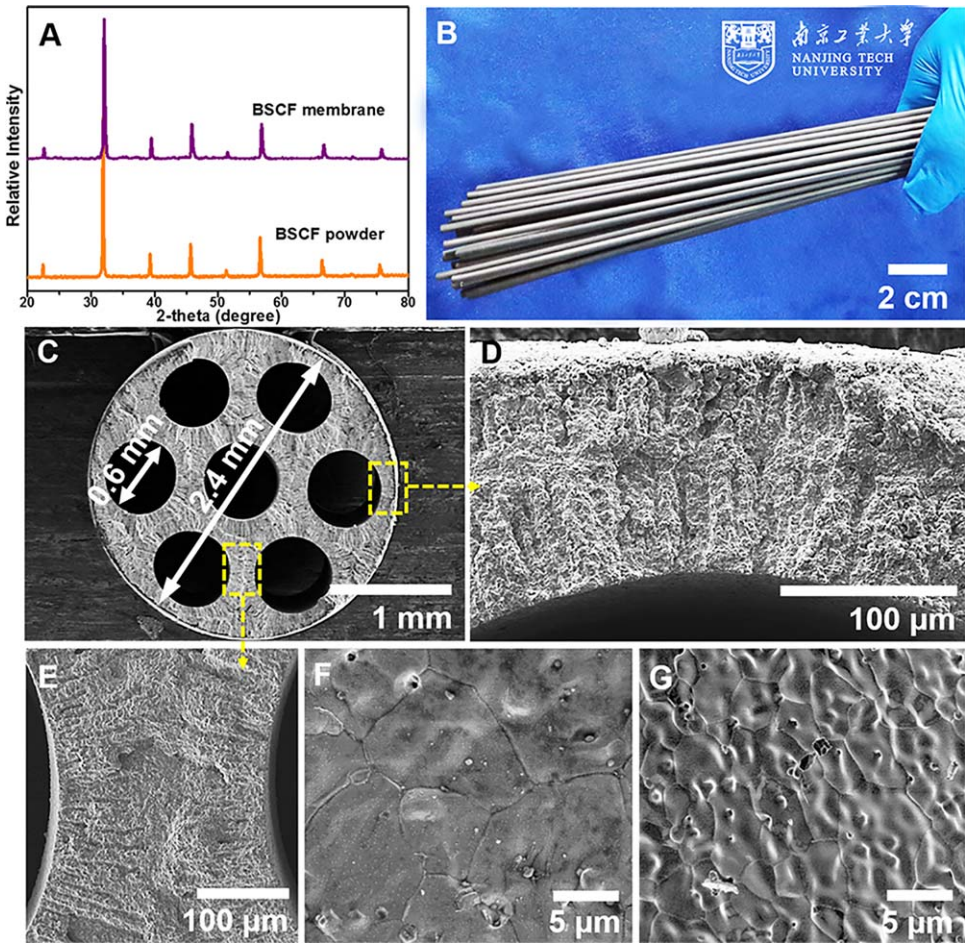

Figure 2. Crystal phase structure (A) and morphology of the as-prepared hepta-bore HF membranes: digital photograph (B), cross section (C), wall structure (D) and (E), outer surface (F), inner surface (G).

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which was obviously higher than the total oxygen permeation contributed by paths (a) and (b) (Figure 3B). These results reveal that the assumption is unreasonable and path (c) exists in the membrane. The path (c), probably resulted from oxygen partial pressure difference in center and peripheral bores, led to that the total oxygen permeation fluxes of samples (i) and (ii) were lower than those of sample (iii). Accordingly, this difference in oxygen permeation fluxes could be considered as path (c)-produced oxygen permeation fluxes, and oxygen permeation fluxes in sample (i) and sample (ii) could correspond to path (a) and (b), respectively (Figure 3A). Overall, these paths, successfully demonstrated, have noticeable contributions to oxygen permeation fluxes of the BSCF hepta-bore HF membranes at elevated temperatures (Figure 3C).

To further demonstrate the prominent role of these paths in highly enhancing oxygen permeation performance, we investigated and summarized oxygen permeation fluxes of these two types of BSCF HF membranes with PEI as the polymer binder (Figure 3B): the membranes with only one oxygen transport path such as tetra-bore HFs, hexa-bore HFs (i.e., sample (ii)); and the membranes with multiple types of oxygen transport paths (i.e., hepta-bore HFs). Probably attributed to similar wall thickness (see Supporting Information Table S2, Figure S1) and surface morphology (see Supporting Information Figure S1), BSCF HF membranes with only one type of oxygen transport paths exhibited similar oxygen permeation fluxes of about 2–10 mL min^{-1} cm^{-2} in the temperature range of 1023–1223 K, which were not only almost the same as those of the state-of the-art single-bore BSCF membranes (Figure 3B),[18,25] but also nearly equal to those produced by path (a) of the hepta-bore HF membranes. This phenomenon indicated that these different BSCF HF membranes (i.e., single-bore, tetra-bore, and hexa-bore) with only one type of oxygen transport paths possessed similar oxygen permeation fluxes. The possible reason behind this result was that the wall thickness of these membranes was smaller than the critical thickness and reducing membrane wall thickness no longer obviously enhanced oxygen permeation fluxes of these membranes.[17] As shown in Figure 3B, by comparison, our hepta-bore BSCF HF membrane with multiple types of oxygen transport paths exhibits much higher oxygen permeation fluxes of 11.5–17.6 mL min^{-1} cm^{-2} in the temperature range of 1123–1223 K, transcending the performance of these state-of-the-art BSCF HF membranes with only one type of oxygen transport paths and greatly exceeding the desired target (10 mL min^{-1} cm^{-2} at 1173 K) for commercial applications. Amount of

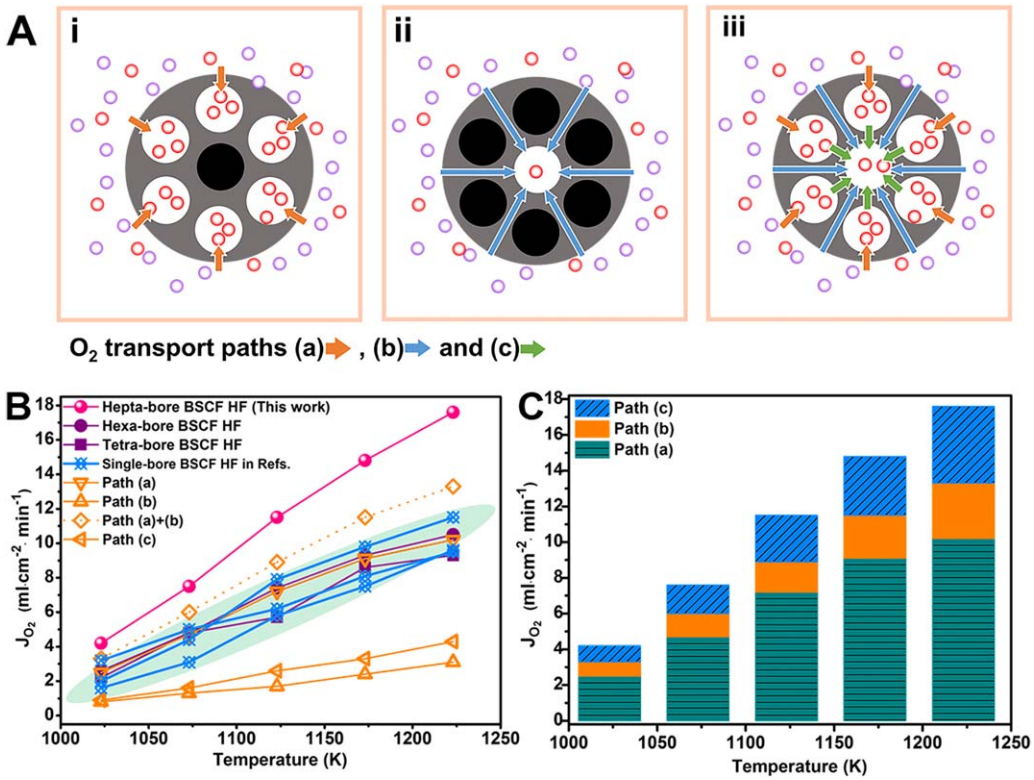

Figure 3. (A) Schematic of the proposed oxygen permeation process of the three hepta-bore HF membrane samples: (i) the membranes whose center bore was plugged and sealed (helium flow rate was 154 mL min^{-1}), (ii) the membranes whose peripheral bores were plugged and sealed (helium flow rate was 26 mL min^{-1}), and (iii) the membranes without any treatment (helium flow rate was 180 mL min^{-1}). (B) Oxygen permeation fluxes (±6%) produced by different oxygen transport paths in our hepta-bore BSCF HF membranes, and comparison of oxygen permeation performance (±6%) of different BSCF HF membranes. (C) Contributions (±6%) of multiple types of oxygen transport paths to the total oxygen permeation fluxes of the hepta-bore BSCF HF membranes at elevated temperatures.

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efficient oxygen transport paths, the only distinct difference of these two kinds of HF membranes, most likely resulted in the quite different oxygen permeation fluxes. Therefore, it could be considered that the vastly enhanced oxygen permeation fluxes of the hepta-bore BSCF HF membrane were created by these efficient oxygen transport paths.

In summary, we have successfully demonstrated that these actual multiple types of efficient oxygen transport paths in hepta-bore perovskite HF membranes (with excellent mechanical strength) play a prominent role in significantly enhancing oxygen permeation performance. At elevated temperatures, the as-prepared hepta-bore BSCF HF membranes feature extraordinary performance for oxygen permeation, which greatly transcends the performance of state-of-the-art BSCF HF membranes and clearly exceeds the coveted goal of commercialization, offering great potential for practical oxygen production. These novel findings could also potentially open the door to exploring high-performance oxygen-permeable membranes for application in energy and environmental fields.

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