CO₂-Tolerant SrFe_{0.8}Nb_{0.2}O_{3-δ}-Carbonate Dual-Phase Multichannel Hollow Fiber Membrane for CO₂ Capture

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ABSTRACT: Ceramic–carbonate dual-phase membranes have attracted a lot of attention because of the emission of CO₂ and environmental problems. In this study, a dense SrFe_{0.8}Nb_{0.2}O_{3-δ}-carbonate dual-phase multichannel hollow fiber membrane has been successfully prepared via a phase inversion–sintering technique and impregnation. The morphology, crystal structure, phase stability, breaking load, and CO₂ permeation flux of the as-prepared membranes were systematically investigated. The membrane not only had a higher CO₂ permeation flux but also was of good thermomechanical stability in thermal recycles. Meanwhile, the membrane can be operated stably at 973 K over 200 h without any degradation of CO₂ permeation flux. Our work demonstrates that the ceramic–carbonate dual-phase mixed-conducting multichannel hollow fiber membrane is a promising candidate for postcombustion CO₂ capture.

1. INTRODUCTION

Concerns about global warming and climate change have increased over the last decades, and the concept of sustaining manufacturing has been proposed to address the problem, which illustrates that industries should improve their energy efficiency and gradually convert their processes toward considerably more sustainable operation. With 80% of the energy consumption in the world from fossil fuels, dealing with the flue gas emitted from conventional power plants can greatly reduce emissions of CO₂ and realize the industrial sustainable development of industries. Many research works have been conducted to develop technologies for CO₂ capture and storage (CCS). Currently, there are three major strategies for CCS from power plants: precombustion, postcombustion, and oxyfuel combustion.^{1–5} Available separation processes for CO₂ capture via postcombustion, such as adsorption and cryogenic distillation, require that the temperature of the flue gas should be lowered until the processes can proceed.^{6,7} Compared with such traditional technologies, high-temperature perm-selective membranes, which can handle large and continuous-flow streams for postcombustion capture, have attracted a lot of attention because of their simplified CO₂ capture process as well as low capture cost.^{8,9} The high-temperature perm-selective membranes should meet the following requirements for industrial application: high CO₂ permeation flux, high chemical and thermal stability under a CO₂ atmosphere and reducing conditions, and high mechanical strength. Many efforts have been made to improve the performance according to these requirements.

To develop membranes that are perm-selective to CO₂ at high temperatures, the concept of a dual-phase membrane at high temperatures consisting of a metallic phase and a molten carbonate phase was reported by Lin and co-workers.¹⁰ These kinds of membranes are permeable to CO₂ with O₂ at high temperatures. However, the general metal support is easily oxidized in the atmosphere containing O₂ above 923 K, which would make the dual-phase membrane gradually lose the function of CO₂ separation. Although utilizing silver as the

metallic phase has been shown to improve CO₂ permeability, the cost of this material does not meet the demand of industrialization.¹¹ Moreover, the metal carbonate membrane permeating CO₂ and O₂ together results in the subsequent separation of CO₂ and O₂ from a gas mixture. To address this problems, Anderson and Lin¹² proposed a new ceramic–carbonate by using ionic conducting or mixed-conducting ceramics as the support, and the transporting mechanism can be denoted according to the following reaction equation:

On the feed side of the membrane, a carbonate ion is formed by the reaction of CO₂ with lattice oxygen ions in the ceramic phase, which can be transported to the molten carbonate phase by the CO₂ partial gradient. On the permeate membrane surface, CO₂ is released from the carbonate phase and oxygen ions return to the ceramic phase. The first mixed ionic and electronic conducting (MIEC) material used as the ceramic support was La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ} (LSCF), which shows a high electronic and oxygen ionic conductivity at high temperatures.^{13,14} However, the LSCF–carbonate membrane showed a drop of CO₂ permeation flux with increasing time. The reason may be that alkaline-earth metals reacting with CO₂ result in a carbonate layer on the surface of the membrane. To find a suitable material integrated with good chemical stability and permeation flux, many studies have been conducted based on this concept. The ionic conducting ceramic materials, including YSZ (Y₂O₃-stabilized ZrO₂), GDC (Gd₂O₃-doped CeO₂), SDC (Sm₂O₃-doped CeO₂), and BYS (Bi_{1.5}Y_{0.3}Sm_{0.2}O₃), have been investigated because of their excellent stability under a CO₂-containing atmosphere.^{15–19}

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Recently, modeling work has reported CO₂ transport through ceramic–carbonate membranes using ionic conducting ceramic supports, which can contribute to our understanding of these kinds of membranes.^{20,21} The mixed-conducting oxide La_{0.85}Ce_{0.1}Ga_{0.3}Fe_{0.65}Al_{0.05}O_{3-δ} has been also investigated because of its high chemical stability under simulated syngas conditions and CO₂ atmosphere compared with LSCF.²²

Besides the development of advanced materials, many efforts are focused on the optimization of membrane geometries. Currently, researchers studied mainly disk-shaped thick membranes, which would increase the mass-transfer resistance. To improve the permeation flux, disk-shaped and tubular membranes of asymmetric structures have been fabricated.^{23–26} Nevertheless, there are some problems for engineering application related to these kinds of membranes, such as the lower surface/volume ratio and thick bulk transport layer. Alternatively, hollow fiber membranes with the advantages of providing a higher surface/volume ratio, easier sealing, and a thinner separating layer for less transport resistance can be applied to the dual-phase membranes. Zuo et al.^{27,28} prepared a single-channel hollow fiber with YSZ and measured a CO₂ flux of 0.22 mL·cm⁻²·min⁻¹ at 1223 K. However, the conventional single-channel mixed-conducting-carbonate dual-phase hollow fiber membranes may not meet the requirements of industrialization because of low mechanical strength.^{29–31} In our previous recent work,^{32–34} we developed a mixed-conducting multichannel hollow fiber (MCMHF) membrane with high performance that combines the advantages of multichannel tubular membrane technology and conventional hollow fibers. This configuration has good improvement of the mechanical strength, permeation flux, energy efficiency, and robustness in long-term operation.

Therefore, this work is aimed at developing a mixed-conducting-carbonate dual-phase membrane with a multichannel hollow fiber configuration for CO₂ separation. As shown in Figure 1, the optimized configuration and the transporting mechanism of the dual-phase membrane are illustrated. SrFe_{0.8}Nb_{0.2}O_{3-δ} (SFN) was selected as the mixed-conducting support for its excellent CO₂ tolerance and high

oxygen ionic conductivity.³⁵ The multichannel SFN–carbonate dual-phase hollow fiber membrane was prepared via a combined phase inversion–sintering technique and impregnation. The objective of this paper is to report the synthesis and characterization of MCMHF–carbonate dual-phase membranes, as well as CO₂ permeation from the system of CO₂/N₂ at high temperatures.

2. EXPERIMENTAL SECTION

2.1. Synthesis of a SrFe_{0.8}Nb_{0.2}O_{3-δ} (SFN) Powder. The SFN powders were synthesized by the conventional solid-state reaction technique as reported by Zhang et al.³⁶ The required stoichiometric amounts of SrCO₃ (99%), Fe₂O₃ (99%), and Nb₂O₅ (99%) were mixed and ball-milled in ethanol for 24 h and then dried at 393 K. The SFN oxide was formed after further calcination at 1573 K for 10 h in air with heating and cooling rates of 2 K·min⁻¹. The sintered SFN powders were ground and sieved (300 meshes) for preparation of the MCMHF support.

2.2. Preparation of a Porous SFN MCMHF. The black porous multichannel hollow fiber was prepared via a phase inversion–sintering technique. The spinning solution was composed of 61.54 wt % SFN powder, 30.77 wt % 1-methyl-2-pyrrolidinone (NMP), and 7.69 wt % poly(ether sulfone) (PES). The multichannel hollow fiber precursors were obtained using a tetrabore spinneret with an orifice diameter of 4.8 mm and a four-bore diameter of 1.2 mm. Deionized water was used as the external and internal coagulant. The formed precursor fibers were then put in ethanol from water to avoid destruction of the perovskite structure.³⁷ After the wet hollow fibers dried completely, the MIEC support precursors were sintered at 1573 K for 4 h to remove the polymers and to achieve sufficient mechanical strength. The preparation conditions for obtaining the porous hollow fiber precursor are summarized in Table 1.

Table 1. Preparation Parameters for the SFN MCMHF Supports

parameter	value
composition of the spinning suspension (wt %)	
SFN powder	61.54
NMP	30.77
PES	7.69
spinning temperature (K)	298
injection rate of internal coagulant (mL·min ⁻¹)	16
injection rate of of suspension (mL·min ⁻¹)	12
air gap (cm)	10
sintering temperature (K)	1573
sintering time (h)	4

Figure 1. Schematic configuration of an asymmetric SFN–carbonate MCMHF dual-phase membrane and transport of ions and permeation of CO₂ through the membrane.

2.3. Preparation of a SFN–Carbonate Dual-Phase Hollow Fiber Membrane. The preparation of a SFN–carbonate dual-phase membrane was achieved by the direct infiltration of molten carbonates into the porous hollow fiber support. The carbonate powders Li₂CO₃ (99.99%), Na₂CO₃ (99.8%), and K₂CO₃ (99%) mixed in a 42.5/32.5/25 mol % ratio were placed in a furnace and heated to 823 K. The mixture of Li/Na/K carbonates was chosen because of their lower melting point and higher carbonate ion conductivity.³⁸ The porous MCMHF support preheated at 823 K for 1 h was then immersed in the carbonate mixture for 1 h to ensure complete infiltration via capillary force. The membrane was cooled to room temperature at a rate of 2 K·min⁻¹. Redundant carbonate was removed with SiC paper.

2.4. Characterization. The crystal phases of the as-prepared SFN powder, MCMHF support, and dual-phase membrane were characterized by X-ray diffraction (XRD; Bruker, model D8 Advance) using Cu Kα radiation. The XRD patterns were collected at room temperature by step scanning at an increment of 0.05° in the range of 20° ≤ 2θ ≤ 80°. The microstructure and morphology of the hollow fiber membranes were observed via scanning electron microscopy

(SEM; Hitachi S-4800, Japan). The composition of the support and the distribution of carbonate were verified by energy-dispersive X-ray spectroscopy (EDX; Hitachi S-4800, Japan). The mechanical strength of the hollow fibers was measured through a three-point bending test performed using a tensile instrument (model CMT6203) provided with a load cell for 5 kN. The samples of hollow fibers were fixed in the sample holder with a spec gauge length of 30 mm. The crosshead speed was set at $0.02 \text{ cm} \cdot \text{min}^{-1}$. The load (F_m) needed to break the hollow fiber was recorded for each sample.

2.5. Measurements of CO_2 Permeation. As shown in Figure 2, the CO_2 permeation test in this study was carried out in a homemade

Figure 2. Schematic diagram of the SFN-carbonate dual-phase MCMHF membrane module for the CO_2 permeation test.

unit, which is similar to the dense MCMHF oxygen permeation membrane.^{34,39} A dual-phase membrane with a length of 30 mm was sealed with two dense Al_2O_3 ceramic tubes. The hollow fiber was housed with a quartz tube. The sealing was completed with the high-temperature sealing method in our experiment. The gas mixture of CO_2 and N_2 was introduced to the feed side at $100 \text{ mL} \cdot \text{min}^{-1}$ and helium to the downstream as a sweep gas at $100 \text{ mL} \cdot \text{min}^{-1}$ during the heating and permeation measurements. The inlet gas flow rates were controlled by mass flow controllers (model D07-19B, Beijing Jianzhong Machine Factory, China). Both sides of the membrane were maintained at atmospheric pressure (0.1 MPa). A programmable temperature controller (model AI-708 PA, Xiamen Yudian Automation Technology Co., Ltd.) monitored the temperature surrounding the membrane. The gas composition in the sweep gas was measured by online gas chromatography (GC; model GC-8A, Shimadzu, Japan), and helium was the carrier gas. The amount of N_2 detected in the sweep gas during permeation measurements determined a CO_2 leak through the seal. Corrected CO_2 flux was worked out by subtracting the CO_2 associated with the leak. The Knudsen diffusion mechanism was assumed to explain the gas leakage through the membrane or the seal. Leaking N_2 flux was less than 0.5% of the total amount of CO_2 measured. At each condition, we repeated the measurement at least three times in around 30 min intervals and took their average as the flux value. All of the values of the gas flow rates in this study were calculated at the conditions of the standard temperature and pressure (STP). The area of the MCMHF membrane is simply defined as the membrane outer surface area due to the complex structure of the MCMHF membrane in this work.

3. RESULTS AND DISCUSSION

3.1. Chemical Stability of the SFN Powder. Figure 3a shows the XRD patterns of the fresh SFN powders sintered at

Figure 3. XRD patterns of the SFN samples: (a) fresh powder; (b) powder sintered in pure CO_2 at 973 K for 24 h; (c) powder sintered in 5% H_2/Ar at 973 K for 24 h.

1573 K for 10 h, and we can see that the fresh SFN powders have a well-formed perovskite crystalline structure. The SFN powder should possess enough structural stability under a CO_2 -containing atmosphere as well as reducing conditions in order to serve as an alternative MIEC material for postcombustion CO_2 capture. As shown in Figure 3b,c, the SFN powders exposed to a pure CO_2 atmosphere for 24 h and 5% H_2/Ar for 24 h still maintain the main perovskite structure, and no impurity phase is formed under the CO_2 and reducing conditions. The results are all consistent with those reported by Zhu et al.,³⁴ which shows that SFN is a good MIEC material for O_2 separation at high temperatures. Therefore, SFN can be a promising material as the support of the dual-phase membrane for transporting oxygen ions.

3.2. Morphology and Phase Structure of the Support and Dual-Phase Membrane. The combined phase inversion and sintering process has been employed to fabricate MIEC hollow fiber membranes for O_2 separation.^{31,40–45} Hollow fibers with asymmetric structure would reduce the mass-transfer resistance, which can also be used as the MIEC porous support of the dual-phase membrane for CO_2 separation. The physical properties of the hollow fiber can be varied by the weight ratios of the SFN powder, NMP, and PES, the kinds of internal and external coagulant, the flow rates of the internal coagulant, the air gap, and the sintering conditions. In order to fabricate the porous asymmetric hollow fiber support, a well-distributed spinning suspension consisting of SFN, NMP, and PES in the mass ratio of 8:4:1 was prepared, then being extruded through a tube-in-orifice spinneret. The SFN precursor was sintered at 1573 K for 4 h to form the porous support. As can be seen in Figure 4a, the SFN MCMHF sintered at 1573 K maintained a perovskite crystalline and no secondary phase. Figure 5 depicts the SEM images of the porous support. From the cross section in Figure 5a, we can see the spongelike structure, the fingerlike structure, and small porous channels of the porous support. The outer and inner diameters of the porous hollow fiber are about 2.7 and 0.8 mm, respectively. It is worth noting that the spongelike structure no longer exists and the large fingerlike pores extend from the inner to outside surface in the thinner-wall parts of the dual-phase MCMHF membrane. The existing spongelike pores in the thicker-wall parts can improve the mechanical strength of the hollow fibers. As shown from the

Figure 4. XRD patterns of (a) the SFN porous support, (b) the fresh SFN-carbonate dual-phase MCMHF membrane, (c) the SFN-carbonate dual-phase MCMHF membrane used, and (d) the carbonates (black diamonds stand for the peaks of the carbonates).

Figure 5. SEM patterns of the porous SFN support: (a) cross section; (b) wall of the hollow fiber; (c) high magnification of the cross section near the outer surface; (d) inner surface; (e) outer surface of the thick wall; (f) outer surface of the thin wall.

outside and inner surfaces in Figure 5d–f, the support has enough pores for impregnation of the carbonate phases. The formation of such MCMHF wall structures is relevant to the exchange between the solvent and nonsolvent during the phase inversion process. In detail, the denser inner and outer surfaces may be due to fast exchange between the solvent and nonsolvent, while the fingerlike and spongelike structures may be attributed to slow exchange between the solvent and nonsolvent. The fingerlike structure throughout the entire thinner wall may be attributed to the increasing air gap and flow rate of the internal coagulant.⁴⁶

The dual-phase membrane was prepared by impregnating the MIEC support with Li/Na/K carbonates at 823 K for 1 h. For a dual-phase membrane, the MIEC phase should not react with the carbonate phase, and the reaction between the two phases would lead to a decrease of the CO₂ flux.¹² Figure 4b shows the XRD patterns of the porous support impregnated with Li/Na/K carbonates. As shown, the MIEC support still well-maintains the perovskite phase, and the peaks marked by black diamonds stand for the carbonates. The results indicate that the SFN and

carbonate are compatible with each other during infiltration. As shown in Figure 6, the dual-phase membrane is compact

Figure 6. SEM patterns of the SFN-carbonate dual-phase MCMHF membrane: (a) cross section; (b) wall of hollow fiber; (c) high magnification of the cross section; (d) inner surface; (e) outer surface; (f) EDX of potassium in the cross section.

without defects from the cross section, inner surface, and outside surface. This demonstrates that carbonates have been well-impregnated into the MIEC support. Meanwhile, EDX was applied to investigate the distribution and impregnation of carbonates. Figure 6f depicts the distribution of potassium in the cross section. Therefore, we can conclude that the carbonate phases have been impregnated in the pore channels because it is a mixture of Li/Na/K carbonates. Parts d and e of Figure 6 depict the outer and inner surfaces of the dual-phase membrane, respectively. We can see that melting carbonates have permeated into the pores and covered the surface of the membrane. The mechanical properties of the ceramic hollow fiber should be considered for industrial application. The structure of the fabricated porous support may have a great impact on the breaking load. The breaking loads of the porous support and the MCMHF dual-phase membrane measured with a length of 30 mm were about 6.8 and 7.8 N, respectively. We can find that the mechanical strength of the support immersed with carbonate has been enhanced because of carbonate phases permeating into the pores of the support.

3.3. High-Temperature CO₂ Permeation. Generally, the effect of operating conditions such as the temperature and CO₂ feed concentration will greatly affect the CO₂ permeation flux. We systematically investigated the performance of the SFN-carbonate dual-phase membrane based on the effect of the operating conditions.

3.3.1. Effect of the Temperature. Before the CO₂ permeation experiment was carried out, the dual-phase membrane was characterized by the N₂ gastight test. The two sides of the membrane were maintained at atmospheric pressure (0.1 MPa), and the permeation of N₂ was not detected at the other side of the membrane. This means that the dual-phase membrane prepared by this method is gastight enough for the CO₂ permeation test.

Figure 7 shows the CO₂ flux for the SFN–carbonate dual-phase membrane as a function of the temperature. The feed gas

Figure 7. Effect of the temperature on the CO₂ permeation flux of the SFN–carbonate membrane (feed side, CO₂ flow rate of 50 mL·min^{−1} and N₂ flow rate of 50 mL·min^{−1}; sweep side, helium flow rate of 100 mL·min^{−1}) and Arrhenius plots.

mixture flow rate of CO₂ and N₂ (1:1 in volume) is 100 mL·min^{−1}, and the flow rate of helium on the sweep side is 100 mL·min^{−1}. As shown, the CO₂ permeation flux increases with increasing temperature from 773 to 1123 K. At 1123 K, the CO₂ flux of SFN is 0.64 mL·min^{−1}·cm^{−2}, which is 8 times that of the CO₂ permeation flux at 773 K. This is because the increasing operating temperature may accelerate the surface reactions and bulk diffusion rates of oxygen ion/carbonate ions.²⁷ Arrhenius plots of the permeance data are also given in Figure 7, and the calculated activation energy for CO₂ permeation through the SFN–carbonate dual-phase membrane is 44.84 kJ·mol^{−1}, which is low compared to the oxide-ion conduction in SFN reported previously.³⁵ The difference in the activation energy may be caused by the different microstructures of the MCMHF support. Table 2 compares the permeation properties of different dual-phase membranes, and we can see that a higher oxygen ionic conductivity will lead to a larger CO₂ permeation flux.

3.3.2. Effect of the CO₂ Partial Pressure. For a ceramic–carbonate membrane at a given temperature, a higher CO₂ partial pressure gradient in the feed side results in a large driving force for CO₂ permeation. Figure 8 shows the CO₂ permeation flux at 973 K as a function of the logarithm of CO₂ partial pressure. The CO₂ partial pressure in the feed gas was varied from 0.1 to 0.5 atm, while the feed and sweep flow rates were maintained at 100 mL·min^{−1}. Rui et al. reported a model

Figure 8. Effect of the CO₂ partial pressure gradient on the CO₂ permeation flux of the SFN–carbonate membrane (feed- and sweep-side flow rate of 100 mL·min^{−1}, feed CO₂ = 0.1–0.5 atm, and *T* = 973 K).

for CO₂ permeation through ceramic–carbonate membranes at high temperatures based on the driving forces provided by the MIEC ceramic and carbonate phases.^{20,21} The CO₂ permeation flux through a bulk dual-phase membrane can be described as the following equation:

$$J_{\text{CO}_2} = \int_{P_{\text{CO}_2}''}^{P_{\text{CO}_2}' } \frac{kRT}{4F^2L} d \ln P_{\text{CO}_2} \quad (2)$$

where *k* is a permeance coefficient (or referred to as total conductance) defined by

$$k = \frac{(\varepsilon/\tau)_p \sigma_c (\varepsilon/\tau)_s \sigma_i}{(\varepsilon/\tau)_p \sigma_{c+} (\varepsilon/\tau)_s \sigma_i} \quad (3)$$

R is the ideal gas constant, *T* is the system temperature, *F* is Faraday's constant, *L* is the thickness of the membrane, and *P'* and *P''* are the CO₂ partial pressures in the feed and sweep gases, respectively. ε and τ represent the porosity and tortuosity of the membrane. *p* and *s* are subscripts used to identify the volume fraction to tortuosity ratio of the support porosity and solid phases, respectively, while σ_c and σ_i represent the carbonate conductivity and oxygen ionic conductivity of the ceramic phases, respectively. The CO₂ permeation flux is controlled by the oxygen ionic conductivity because the carbonate ion conductivity is much larger than the oxygen ion conductivity.^{12,50} Plots of the flux data in Figure 8 show that *J*_{CO₂} is proportional to ln(*P*_{CO₂}'/*P*_{CO₂}'') at 973 K, which is consistent with the model.

3.3.3. Thermal Cycling Performance of the MCMHF Membrane. For industrial application of CO₂ capture in the

Table 2. Comparison of CO₂ Fluxes through Different Dual-Phase Membranes

geometry	ceramic material	thickness (μm)	CO ₂ flux (×10 ^{−3} mol·m ^{−2} ·s ^{−1})	temperature (K)	<i>E</i> _a (kJ·mol ^{−1})	ref
disk	La _{0.6} Sr _{0.4} Co _{0.8} Fe _{0.2} O _{3-δ}	375	0.37	973	89.9	12
disk	Bi _{1.5} Y _{0.3} SmO _{3-δ}	~50	0.55	923	113	50
disk	Ce _{0.8} Sm _{0.2} O _{1.9}	1200	1.16	923	74.3	47
disk	Ce _{0.8} Sm _{0.2} O _{1.9}	1200	8.32	923	77.2	47
disk	Ce _{0.9} Gd _{0.1} O _{1.95}	200–400	0.25	923	77 ± 6	48
disk	Y _{0.16} Zr _{0.84} O _{2-δ}	200–400	0.35	923	84 ± 14	48
disk	Y _{0.16} Zr _{0.84} O _{2-δ}	~10	3.9	923	106	49
tube	SDC/SDC-BYS	150	10.66	1173	60.3	23
hollow fiber	YSZ	500	1.5	1173	50.66	27
hollow fiber	La _{0.6} Sr _{0.4} Co _{0.8} Fe _{0.2} O _{3-δ}	~300	6.81	1173	56.8	28
MCMHF	SrFe _{0.8} Nb _{0.2} O _{3-δ}	~220	2.3	973	44.84	this work

postcombustion process, the thermal cycling performance of the membrane is vital because the practical operation process usually contains repeated heating and cooling processes. Figure 9 shows the thermal cycling performance of the SFN–

Figure 9. Thermal cycling performance of the SFN–carbonate dual-phase MCMHF membrane between 873 and 1073 K (feed side, CO_2 flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$ and N_2 flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$; sweep side, helium flow rate of $100 \text{ mL}\cdot\text{min}^{-1}$).

carbonate dual-phase MCMHF membrane. The heating and cooling rates of the dual-phase membrane were maintained at $1 \text{ K}\cdot\text{min}^{-1}$, respectively, and the required temperature points (873, 973, and 1073 K) were kept for 1 h to stabilize the CO_2 permeation flux. As shown, the thermal cycle process was repeated four times, and no degradation of the CO_2 permeation flux was observed. This thermal cycling performance demonstrates that the SFN–carbonate dual-phase MCMHF membrane possesses good thermomechanical stability in the repeated heating and cooling processes.

3.3.4. Long-Term Stability. Figure 10 shows the long-term stability of the membrane exposed to the gas mixture of CO_2

Figure 10. Time dependence of the CO_2 permeation flux of the SFN–carbonate membrane (feed side, CO_2 flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$ and N_2 flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$; sweep side, helium flow rate of $100 \text{ mL}\cdot\text{min}^{-1}$, $T = 973 \text{ K}$).

and N_2 at 973 K as a function of the exposure time to experimental conditions. The flow rates of CO_2 and N_2 on the feed side are 50 and $50 \text{ mL}\cdot\text{min}^{-1}$, respectively. The flow rate of helium on the sweep side is $100 \text{ mL}\cdot\text{min}^{-1}$. It can be seen that the CO_2 permeation stability of the SFN–carbonate membrane exposed to atmospheric pressure (0.1 MPa) was examined under steady-state conditions for 200 h, and no obvious flux degradation was observed. The permeation flux remained at

$0.31 \text{ mL}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$ at 973 K. Figure 11 shows the SEM patterns of the membrane after a long-term high-temperature

Figure 11. SEM patterns of the SFN–carbonate dual-phase MCMHF membrane after a long-term CO_2 permeation test: (a) cross section; (b) inner surface; (c) outer surface; (d) EDX of potassium in the cross section.

test; we can find that the membrane is still compact without defects. Figure 11d shows the distribution of potassium in the cross section, and we can find that carbonates are still in the pores of the MCMHF. As can be seen from the inner and outer surfaces in Figure 11b,c, the distribution of carbonates becomes uniform compared with the fresh membrane. Parts b and c of Figure 4 compare the XRD patterns of the fresh and used membranes. We can find that all are consistent with the SFN and carbonate characteristic peaks. These results indicate that the membrane maintains good stability during the CO_2 permeation test. There are two reasons for the good stability of the membrane. One is that the surface of the dual-phase membrane was covered with a layer of carbonate, which would prevent the MIEC support from reacting with carbonate. Second, the SFN material has been applied to fabricate the oxygen permeation membrane because of its good CO_2 tolerance, which would contribute to the long-term test of the membrane in the CO_2/N_2 gas mixture at high temperatures.

4. CONCLUSIONS

A dense SFN–carbonate dual-phase MCMHF membrane was successfully prepared by a combined phase inversion–sintering technique and direct impregnation. SFN and carbonate phases are chemically compatible, and the as-fabricated membrane is dense without defects. The maximum CO_2 permeation flux was $0.64 \text{ mL}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$ at 1123 K, and the long-term stability test of the SFN–carbonate dual-phase membrane showed that the CO_2 permeation flux remained at $0.31 \text{ mL}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$ at 973 K over 200 h. These results illustrate that the dual-phase MCMHF membranes can possess several advantages. First, the multichannel hollow fiber can improve the mechanical strength of the membrane, which contributes to industrial application. Second, because of the good stability of the SFN material under an atmosphere of CO_2 and reducing conditions, the dual-phase membrane can be operated at high temperatures for a long time. Third, this kind of MCMHF membrane can handle large, continuous-flow streams. Our work indicates that the SFN–carbonate dual-phase membrane is a promising candidate for CO_2 capture via the postcombustion process in the industrial application.

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Notes

The authors declare no competing financial interest.

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