

Supporting Information

Asymmetric tubular ceramic-carbonate dual phase membrane for high temperature CO₂ separation

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1. Experimental details

1.1 Preparation of SDC and BYs powders

$\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) and $\text{Bi}_{1.5}\text{Y}_{0.3}\text{Sm}_{0.2}\text{O}_{3-\delta}$ (BYs) powders were synthesized via the citrate method from the metal nitrates.^[1] For BYs synthesis, stoichiometric amounts of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Sigma-Aldrich), $\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Sigma-Aldrich) and $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were mixed into a measured volume of dilute nitric acid solution (10 vol% HNO_3) under continuous agitation, followed by the addition of solid citric acid (mole ratio of total metal ions to citrate is 1:2) with stirring. The solution containing the complex precursor was then heated on a hot plate at 250-400 °C. Upon heating, the solution boiled and formed a gel. The gel underwent a dehydration and decomposition process, which led to a foam formation. The foam ignited to produce a soft and fluffy product. Finally, the products were calcined in air at 900 °C for 5 h to prepare BYs oxide. SDC was prepared via the same method. However, only deionized water was used for precursor preparing, and no dilute nitric acid solution was required. SDC oxide was synthesized after the calcination at 550 °C for 5h or 900 °C for 5h.

1.2 Preparation of tubular porous SDC and SDC/SDC-BYs substrates

For asymmetric **SDC/SDC-BYs substrate** synthesis: SDC-BYs slurry with the powder composition of 55 wt% SDC (calcined at 900 °C) and 45 wt% BYs, and the powder to water ratio of about 50wt%:50wt% was prepared by the ball mill at 175 rpm for 3h. A few drops of 3wt% PVA solution were added into the powder before ball mill. SDC slurry was prepared via the same method using 550 °C calcined SDC powder, and the powder to water ratio is about 15wt%:85wt%. A centrifugal casting technique was used for the preparation of ceramic tubes. As shown in [Fig. S1](#), homogeneous SDC-BYs suspension was poured into the stainless steel mould with inner diameter of 7.2 mm. This mould was fixed onto the home made machine, with this machine the mould can rotate at a very high speed. Because of the centrifugal force, the SDC powder in the suspension moved towards the wall of the mould. After centrifugation for 20 min at the rate of 4200 rpm, the liquid in the middle of the tube was poured out and the dilute SDC slurry was added. After the second centrifugation for 20 min at the rate of 4200 rpm, the liquid in the middle of the tube was poured out. The mould with tube was then dried in a humidity chamber at 40 °C with a relative humidity of 60% for 12 h. The asymmetric tube with a thin SDC inner layer and a thick SDC-BYs outer layer was obtained after sintering at 1120 °C for 12h.

For symmetric **SDC substrate** synthesis: About 50 wt% SDC (calcined at 550 °C),

50wt% water and a few drops of PVA solution were mixed and ball milled at 175 rpm for 3h to prepare homogeneous SDC slurry. The SDC slurry was poured into the stainless steel mould. After centrifugation for 20 min at the rate of 4000 rpm, the green tubes were dried and sintered at 1420°C for 12h.

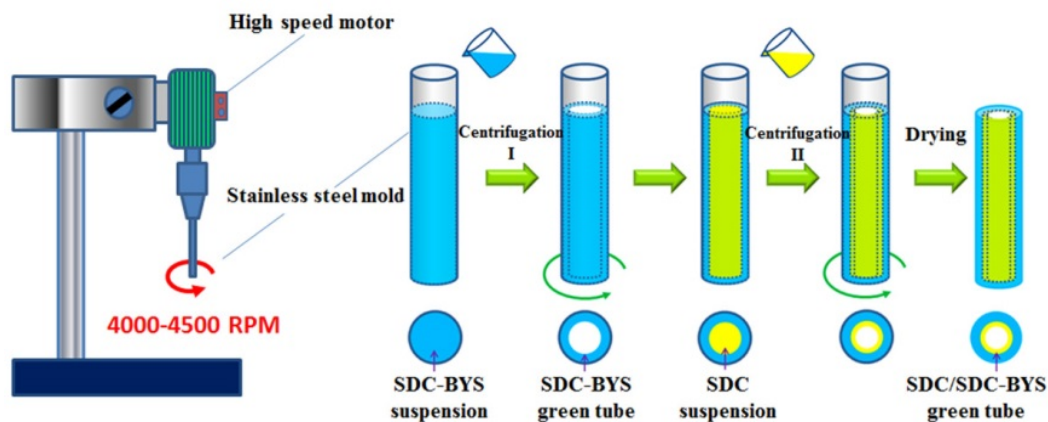


Fig. S1 Schematic diagram of the centrifugal casting method for preparing SDC/SDC-BYS tubes.

1.3 Preparation of tubular ceramic-carbonate dual-phase membranes

Asymmetric dual-phase membrane was obtained via a direct infiltration of molten carbonates into the SDC inner layer of asymmetric porous support by the method described in our previous work.^[2] Lithium (Li), sodium (Na), and potassium (K) carbonates from Fisher Scientific (Li_2CO_3 , 99.2%; Na_2CO_3 , 99.9%; K_2CO_3 , 99.8%) were mixed in the molar ratio of 42.5%: 32.5: 25 and heated to 600 °C in a box furnace. The asymmetric support was preheated in the furnace for 20 min, then vertically dipped into the molten carbonate and held for 1h to allow the molten carbonates infiltrating into the thin SDC inner-layer via the capillary force. After removing the excess carbonate on the surface and cooling down, the dual-phase membrane was prepared. Because of the carbonate non-wettable property of BYs,^[1] the SDC-BYS outer layer was still porous after infiltration.

1.4 Characterizations

The crystal phases of the samples were determined by X-ray diffraction (XRD) with Cu Ka radiation (Bruker, AXS-D8). Diffraction patterns were collected at room temperature in the range of $20 < 2\theta < 70$, with a step width of 0.05° and a scan rate of 0.2 s per step. The morphologies of the substrate and membrane were examined by scanning electron microscopy (SEM) (Philips FEI XL-30) after gold deposition. Porosity of the porous substrate was examined by the liquid nitrogen method.^[3]

The gas-tightness of the asymmetric dual-phase membranes was tested before the high temperature gas permeation. As shown in Fig. S2, the membrane was assembled into a tubular permeation cell sealed with A B glue. The N₂ was fed to the tube side and the shell side was connected to a soap bubble flowmeter. The feed pressure was 0.3MPa. If no obvious N₂ flow rate was observed on the soap bubble flowmeter in 3 h, the membrane was considered to be gas tight. Only gas tight membranes (without defects) will be used for CO₂ separation.

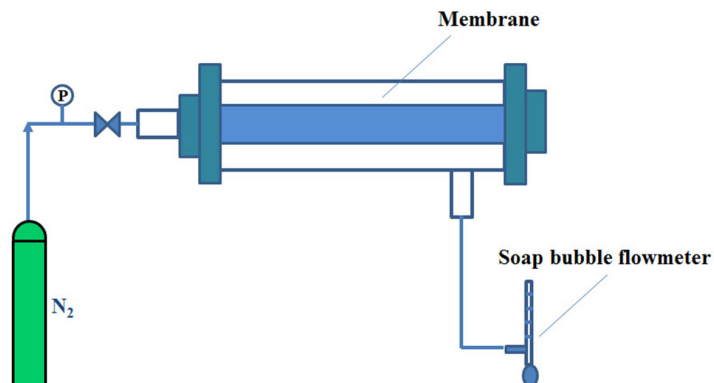


Fig. S2 Apparatus for gas tight test of the tubular dual-phase membranes at room temperature.

High temperature CO₂ permeation tests were carried out on a home-made permeation set-up as shown in Fig. S3. The asymmetric dual-phase membrane with the effective permeation area of about 4 cm² was sealed using ceramic sealant and assembled onto the set-up. The system was heated to 900 °C with a heating rate of 1 °C·min⁻¹ and held for 2 h to form the bonding and ensure the good sealing. CO₂ and N₂ were introduced to the outer side of the membrane tube. He with the flow rate of 50 ml·min⁻¹ was used as the sweeping gas and introduced to the tube side. Gas leakage, if present, could be detected by monitoring the N₂ concentration in the effluent from the permeate side. The CO₂ leakage from sealing is below 1% of the detected CO₂ from sweeping out stream for all tests. Both sides of the membrane were maintained at atmospheric pressure. CO₂ permeation was tested from 900 °C to 700 °C for asymmetric membrane and 900 °C to 800 °C for symmetric membrane with a cooling rate of 1 °C·min⁻¹. The feed out and sweeping out streams were analyzed by GC (Agilent, 6890 N). For each condition, the data were tested three times with about 30 min intervals and the average values were used. The errors of the data are within 10%.

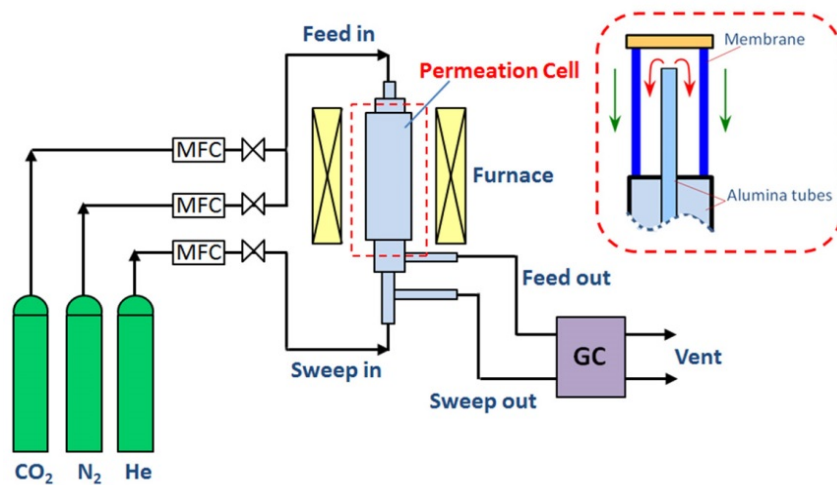


Fig. S3 Schematic diagram of the set-up for high temperature CO₂ separation test.

Reference

- [1] Bo Lu, Y.S. Lin, *J. Membr. Sci.*, 2013, **444**, 402.
- [2] S.J. Chung, J.H. Park, D. Li, J.I. Ida, I. Kumakiri, Y.S. Lin, *Ind. Eng. Chem. Res.*, 2005, **44**, 7999.
- [3] K.G. Harry, A. Johnson, *J. Archaeol. Sci.*, 2004, **31**, 1567.

2. Arrhenius plot of CO₂ permeance

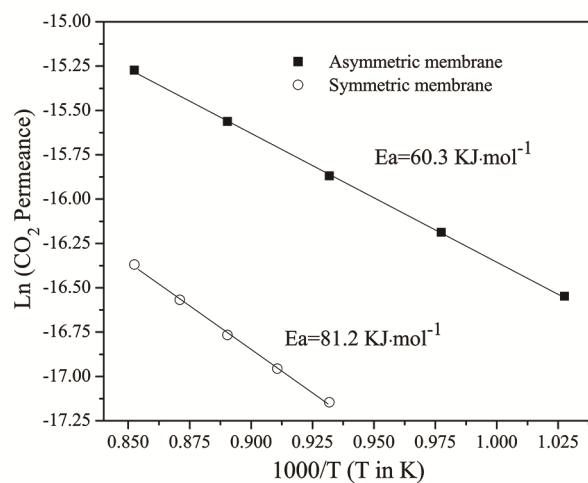


Fig. S4 Arrhenius plot of the thin and bulk tubular dual-phase membranes. Feed side: CO₂ flow rate 25 ml·min⁻¹, N₂ flow rate 25 ml·min⁻¹; Sweep side: He flow rate 50 ml·min⁻¹.