

Electronic Supplementary Information

1. MECC working principle

When the membrane is used for the separate the CO_2 from the flue gas, CO_2 and O_2 react at the triple phase boundaries of metal, carbonate and gas on feed-side surface of the membrane: $\text{CO}_2 + 1/2\text{O}_2 + 2\text{e}^- = \text{CO}_3^{2-}$; at the permeate side a reverse reaction occurs: $\text{CO}_3^{2-} = \text{CO}_2 + 1/2\text{O}_2 + 2\text{e}^-$. In the bulk, the CO_3^{2-} transport through the molten carbonate phase while being charge compensated by electrons transport in the silver phase. Fig. S1 shows the overall permeation process.

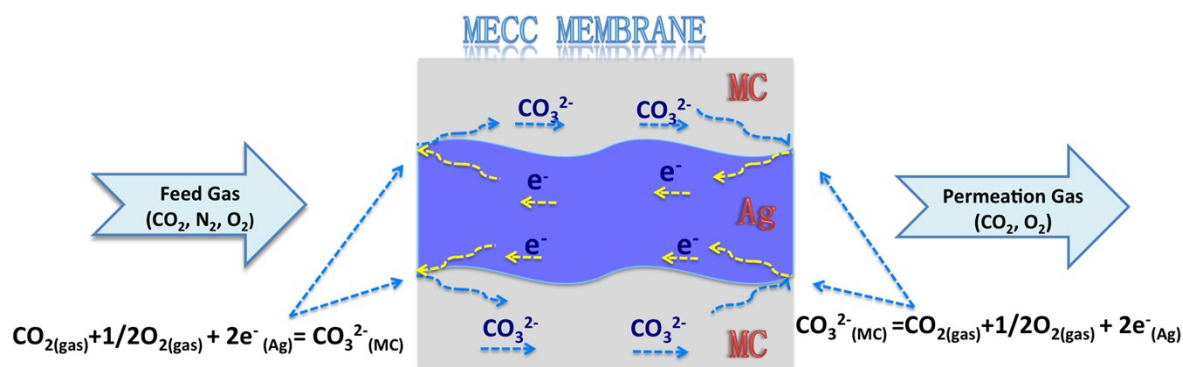


Fig. S1 Working principle of MECC membrane with a flue gas as the feeding gas.

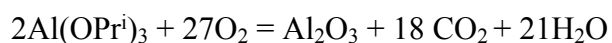
2. Fabrication of silver porous matrix

Silver powder (1-2 micron, 99% metal basis, Alfa Aesar) was used as raw material of matrix. Carbon black was the pore former. Silver powder and the pore former were intimately mixed by ball milling in ethanol with a volume ratio of 1:1. After drying

the mixture in the oven, the powders were then pressed into pellets (Ø20 mm) under 70 MPa. The pellets were finally sintered at 650°C for 2 hours. After sintering, the silver pellets were porous with a diameter shrunk to 16 mm.

3. Chemical vapor deposition of Al₂O₃

Aluminum isopropoxide was employed as the precursor for CVD process to deposit Al₂O₃²¹. Chemical oxidation reaction of the precursor can be written as:



As shown in Fig. S2, silver substrate was leaning against the reactant gases. The solid precursor was spread over a ceramic wool made of high-purity Al₂O₃ and heated at 300-310°C. N₂ was used as the carrier gas for the sublimated precursor to the surface of the substrate where the oxidizer air was simultaneously fed. The substrate temperature was controlled at 350-360°C. It was found that approximately 1µm Al₂O₃ can be grown over a 1-h period by this method.

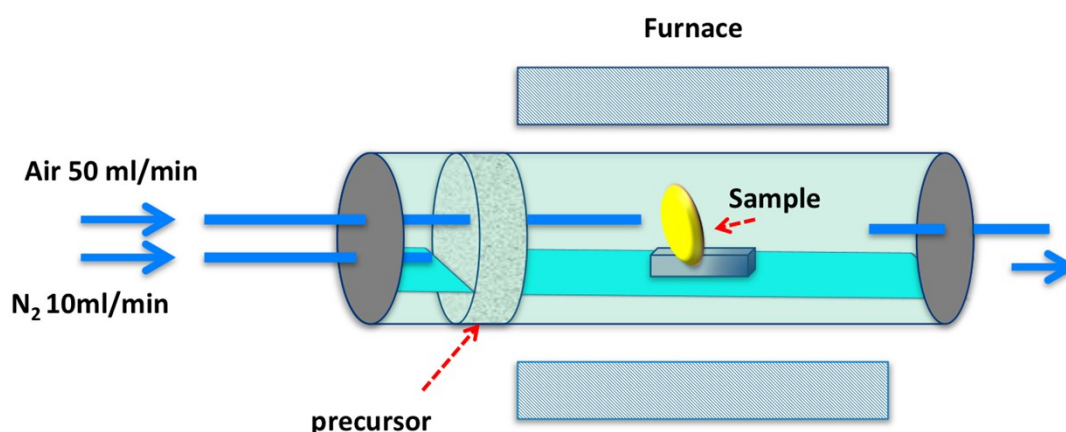


Fig. S2 A schematic of the CVD reactor used in this study.

4. Fabrication of MECC membrane

The final MECC membrane was prepared by infiltration of a molten carbonate into the coated porous silver matrix. The coated porous silver matrix was immersed into a binary eutectic molten carbonate ($\text{Li}_2\text{CO}_3:\text{Na}_2\text{CO}_3 = 52:48$ in mole ratio) at 650°C for 2h. Then, temperature was cooled down to approximately 500°C , just above the melting point of the molten carbonate, and the sample was slowly pulled out of the carbonate, and placed on a substrate in the furnace. After the furnace was cooled down to the room temperature, the sample was taken out and polished by a sandpaper to remove any residual molten carbonate left on both surfaces of the membrane.

5. Permeation flux measurement

The schematic of membrane reactor configuration is shown in Fig. S3. The button-type MECC membrane was first sealed to a supporting alumina tube with a commercial silver paste as the sealant. A short alumina tube was then bonded to the top surface of the sample to ensure the feed gas can fully expose the membrane surface. During the test, the reactor was subject to isothermal condition with the membrane kept in the constant-temperature zone of the furnace. A thermal couple was attached to the side of the cell to indicate the true temperature. The simulated flue gas (15% CO_2 , 10% O_2 and 75% N_2) was used as the feed gas at a flow rate of 100 ml min^{-1} . A high purity helium was used as the sweep gas at a flow rate of 50 ml min^{-1} .

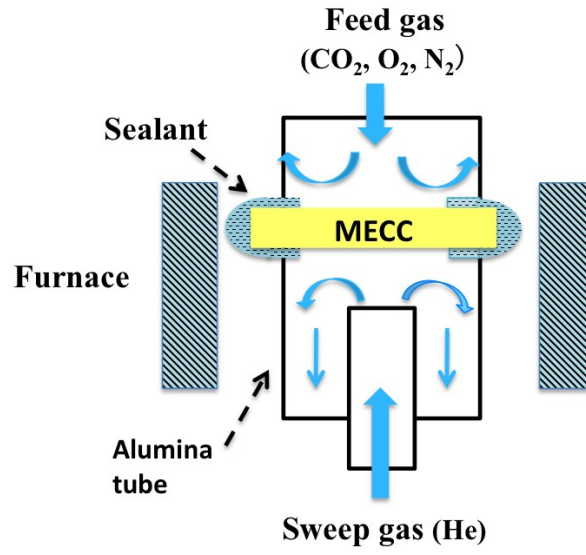


Fig. S3 A schematic of permeation cell setup

6. Flux calculation

The total flux densities of CO₂, O₂ and N₂ (leakage) were calculated using the following equations:

$$J_{N_2,leakage} = \frac{C_{N_2}}{(1 - C_{CO_2} - C_{N_2} - C_{O_2})} \times \frac{Q}{A}$$

$$J_{CO_2,total} = \frac{C_{CO_2}}{(1 - C_{CO_2} - C_{N_2} - C_{O_2})} \times \frac{Q}{A}$$

$$J_{O_2,total} = \frac{C_{O_2}}{(1 - C_{CO_2} - C_{N_2} - C_{O_2})} \times \frac{Q}{A}$$

$J_{N_2,leakage}$ is the flux density of N₂. It is also the leakage rate of the N₂. $J_{CO_2, total}$ and $J_{O_2, total}$ are the total flux densities of CO₂ and O₂, respectively; C_{N_2} , C_{O_2} and C_{CO_2} are the measured concentrations of N₂, CO₂ and O₂ in the sweep gas, respectively; Q (ml min⁻¹) is the flow rate of the helium (sweep gas); S is the effective area of the membrane.

The final flux densities of CO₂ and O₂ were corrected using the following equations:

$$J_{CO_2} = J_{CO_2, total} - \frac{C_{CO_2}'}{C_{N_2}'} J_{N_2, leakage}$$

$$J_{O_2} = J_{O_2, total} - \frac{C_{O_2}'}{C_{N_2}'} J_{N_2, leakage}$$

J_{CO_2} and J_{O_2} are the final reported flux densities, respectively. C'_{CO_2} , C'_{O_2} and C'_{N_2} are the corrected concentrations of CO_2 , O_2 and N_2 in feed gas, respectively.