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Electrochemical Capture of CO₂ from Natural Gas Using a High-Temperature Ceramic-Carbonate Membrane

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This study reports the first investigation of using a ceramic-carbonate dual-phase membrane to electrochemically separate CO₂ from a simulated natural gas. The CO₂ permeation flux density was systematically studied as a function of temperature, CO₂ partial pressure and time. As expected, the flux density was observed to increase with temperature and CO₂ partial pressure. Long-term stability test showed that flux density experienced an initial performance-improving “break-in” period followed by a slow decay. Post-test microstructural analysis suggested that a gradual loss of carbonate during the test could be the cause of the flux-time behavior observed.

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Natural gas is a cleaner burning and flexible alternative to other fossil fuels, and is widely used in power generation, residential, industrial, and transportation sectors.^{1,2} Sources of natural gas include conventional onshore and offshore wells and unconventional wells that rely on stimulation technologies to enhance natural gas recovery in the reservoir. Examples of the latter include hydraulic fracturing in shale and water removing in coal bed methane (CBM) wells.^{3,4}

The composition of natural gas varies considerably with sources, and even within a source.^{5,6} Other than minor amounts of H₂S, H₂O, N₂, He and VOC (volatile organic compounds), CO₂ concentration in a natural gas can vary from 0 to 70%, see Table I. As an acidic gas, CO₂ must be removed prior to transportation in order to protect pipelines. During the removal process, avoiding accidental CH₄ release to the atmosphere is also important since CH₄ is a heat-trapping gas 86 times more powerful than CO₂. Therefore, a safe, efficient and low-cost separation process for CO₂ removal from raw natural gas is technologically and environmentally important. The conventional means of removing CO₂ from a CO₂/CH₄ mixture is based on reversible sorbent/solvent adsorption/absorption processes. Pressure swing adsorption (PSA) using zeolite,¹² metal organic framework (MOF)^{13–15} and carbon nanotube¹⁶ are some examples of sorbents used to separate CO₂ from CH₄. Amine-based liquids such as MEA or MDEA^{17,18} are examples of solvents employed to capture CO₂ from CH₄, but often with high energy penalty and CH₄ loss.

Recently, organic and inorganic membranes have received much attention as an effective means of separating CO₂ from CH₄.^{19–24} For instance, Peters and co-workers utilized the PVAm/PVA membrane to remove CO₂ from CH₄. The CO₂ permeance reached 3.7×10^{-8} mol·s⁻¹·m⁻²·Pa⁻¹ with a selectivity of 35–40.²⁵ Xie and co-workers studied the alumina-supported cobalt-adeninate MOF membranes for CO₂/CH₄ separation, and achieved a high CO₂ permeance 4.55×10^{-6} mol·s⁻¹·m⁻²·Pa⁻¹ but with a low selectivity of 3.2.²² Venna and Carreon further reported a high CO₂ permeance of 2.4×10^{-5} mol·s⁻¹·m⁻²·Pa⁻¹ under a pressure differential of 40 KPa using a zeolite imidazolate framework (ZIF) membrane, but with a selectivity of 5.1.²⁶ As well documented in the literature, the trade-off between permeability and selectivity (or so called “Robeson Upper Bound”) is a major barrier for the aforementioned membranes to overcome.^{27,28} Furthermore, the requirement for high-pressure feed and low operating-temperature makes the organic membranes only suitable for high-pressure and low-temperature CO₂ separation from streams such as pre-combustion products where pressure of 25–30 bar and temperature of <50°C are typically present. For post-combustion

carbon capture, where near ambient-pressure and high-temperature CO₂-containing streams are present, the membrane technology is less advantageous compared to its solvent and sorbent rivals.

Very recently, we as well as other groups have developed a new type of membranes based on electrochemical principles. The membrane is composed of an oxide-ion conducting ceramic and carbonate-ion conducting carbonate phase, forming a mixed oxide-ion and carbon-ion conductor (MOCC). The membranes have been demonstrated with high-flux and high-selectivity in separating CO₂ from a mixture of CO₂/N₂ (for example, CO₂ flux = 0.13 ml·cm⁻² min⁻¹ with a membrane thickness of 1.32 mm at 650°C) and CO₂/H₂/N₂ (for example, CO₂ flux = 1.84 ml·cm⁻² min⁻¹ with a membrane thickness of 1.2 mm at 700°C).^{29–34} Here we report that MOCC membranes can also separate CO₂ from CH₄ with high-flux and selectivity even under the ambient pressure. The oxide-ion conducting ceramic matrix used in this study was a samarium doped ceria (SDC), within which a carbonate-ion conducting eutectic mixture of Li₂CO₃-Na₂CO₃ was held. A schematic illustrating the overall CO₂ permeation process through a MOCC membrane with CH₄/CO₂ as the feeding gas and helium as the sweeping gas is shown in Fig. 1. The driving force for the CO₂ separation is the chemical potential (partial pressure) of CO₂ existing across the MOCC membrane. At the CH₄-CO₂/MOCC interface, CO₂ reacts with O²⁻ to form CO₃²⁻. The formed CO₃²⁻ then transports through the molten carbonate phase toward the MOCC/He/Helium interface where a reverse reaction occurs to release CO₂ and O²⁻;^{29–31} O²⁻ then migrates in an opposite direction through the oxide-ion matrix to charge compensate the flux of CO₃²⁻. Evidently, only CO₂ can transport across the membrane as long as there is no physical leakage, yielding exclusive selectivity for CO₂ separation. Therefore, the “Robeson Upper Boundary” is no longer applicable to electrochemical membranes like MOCC.

Table I. Variations of CO₂ concentration in natural gas.^{7–11}

Natural gas type	CO ₂ concentration (%)
Ordinary natural gas	0–70
Shale gas	0–12
Gas hydrates	0–1
Coal bed	30–55
Biogas from organic waste	30–45
Biogas form landfill	30–60
Biogas from sewage digester	30–45

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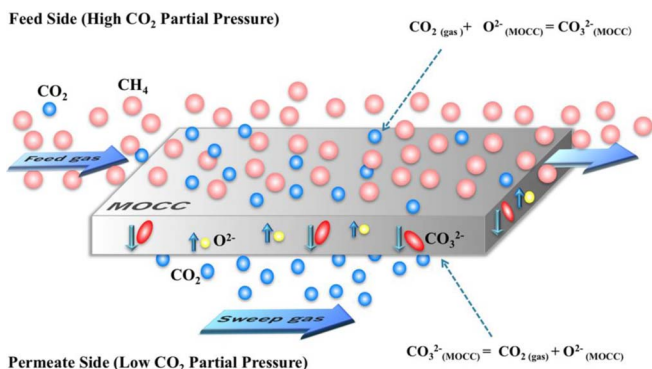


Figure 1. Schematic illustration of working principle of MOCC membranes for CO₂/CH₄ separation.

Experimental

Fabrication of MOCC membranes.— The fabrication of MOCC membranes includes two steps. The first step is the making of porous ceramic SDC matrix. To maximize the homogeneity and minimize the size of the pores, a “co-precipitation” and “sacrificial template” technique was employed.²⁹ The porosity of the SDC matrix fabricated for this study was controlled to be 0.4. Thus fabricated porous matrix was then infiltrated at 650°C with eutectic molten carbonates of Li₂CO₃ and Na₂CO₃ in a molar ratio of 52:48, forming a dense MOCC membrane.³⁰ Details about the procedure can be found in our previous work.^{30,31}

CO₂ permeation measurement.— The CO₂ permeation measurements on MOCC membranes were performed using a homemade test station and established test protocol, both of which can also be found in our previous work.^{29–31} The button cell membranes used to evaluate the permeation flux have a diameter of 17 mm, thickness of 1.2 mm, and effective area of 0.921 cm². The effect of temperature on CO₂ flux was studied in the temperature range of 600–700°C with a simulated natural gas containing 75%CH₄, 15%CO₂ and 10%N₂ as the feeding gas; N₂ was used as the tracer gas to indicate and quantify any leakage. The effect of CO₂ partial pressure on CO₂ flux was investigated by varying mass flow rates of the constituents in the feeding gas. In doing so, the flow rates of CO₂ was varied from 15–50 ml·min⁻¹ while N₂ flow rate was fixed at 20 ml·min⁻¹; CH₄ served as the balance to keep the total flow rate at 120 ml·min⁻¹. The actual flow rates of CO₂, CH₄ and N₂ used for this study are listed in Table II. While changing the partial pressure of oxygen in the feed gas can impact on the resultant CO₂ flux as was previously demonstrated [30], the variation of CH₄ concentrations would not affect the partial pressure of oxygen in the feed gas as both CH₄ and N₂ are considered inert. The long-term stability of MOCC in a simulated natural gas containing 15% CO₂ was also evaluated at 650°C. The microstructure of the membrane after the long-term operation was further examined by scanning electron microscope (SEM) to understand the root cause of the degradation.

Results and Discussion

The effect of temperature.— The Arrhenius plot of CO₂ flux density, J_{CO₂}, measured with a simulated natural gas containing 15%CO₂

Table II. Mass flow rates (mL·min⁻¹) of CO₂, CH₄ and N₂ used to make different CO₂ concentrations of the feeding gas.

	Gas1	Gas2	Gas3	Gas4	Gas5	Gas6	Gas7	Gas8
CO ₂	15	20	25	30	35	40	45	50
CH ₄	85	80	75	70	65	60	55	50
N ₂	20	20	20	20	20	20	20	20

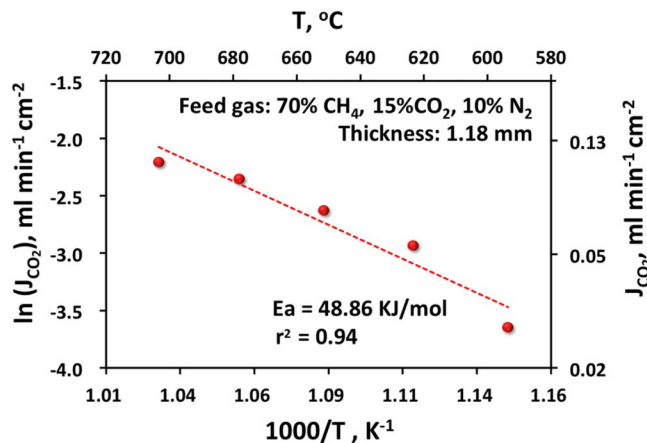


Figure 2. Arrhenius plots of CO₂ flux density in a simulated natural gas containing 15% CO₂.

as the feeding gas is shown in Fig. 2. As expected, J_{CO₂} increases with temperature, indicating that the permeation of CO₂ is a thermally activated process. The slope of the straight-line (ln(J_{CO₂}) vs 1000/T) yields an activation energy of E_a = 48.86 kJ mol⁻¹. This value is lower than that of SDC,³² a rate-limiting phase previously identified for the CO₂ transport in MOCC.³⁰ One possible reason for the lowered E_a is the electronic conduction induced by the reduction of Ce⁴⁺ at low partial pressure of oxygen (P_{O₂}) exposed to the membrane. Overall, at 700°C, J_{CO₂} reaches 0.11 ml·min⁻¹·cm⁻², a moderately high flux-density for the membrane thickness and operating temperature tested.

The effect of CO₂ partial pressure.— For the same sample, the J_{CO₂} was also measured as a function of the gradient of CO₂ partial pressure at 650°C; the result is shown in Fig. 3. A linear relationship is clearly observed, suggesting that a modified Wagner equation previously established for the CO₂ transport could also be applicable to this study:³⁰

$$J_{CO_2} \approx -\frac{\varepsilon}{\tau} \frac{RT}{4F^2L} (1 - \varphi) (\sigma_{O^{2-}}) \ln \frac{P'_{CO_2}}{P''_{CO_2}}$$

Here ε and τ are the porosity and tortuosity of the porous SDC matrix, respectively; φ is the volume fraction of carbonate phase; $\sigma_{O^{2-}}$ is the conductivity of O²⁻, P'_{CO₂} is the higher CO₂ partial pressure at

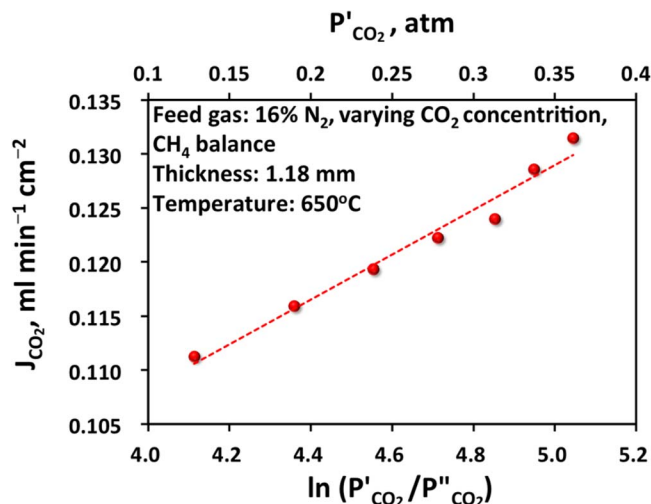


Figure 3. CO₂ flux density as function of logarithm of CO₂ partial pressure across the membrane.

Table III. Performance comparison among different membranes for CO₂/CH₄ separation.

Membranes	Permeance × Thickness mol·s ⁻¹ ·m ⁻¹ ·Pa ⁻¹	Selectivity (CO ₂ /CH ₄)	Ref.
PVAm/PVA	7.4 × 10 ⁻¹³	35–45	25
Cobalt-adeninate MOF	2.2–5.9 × 10 ⁻¹¹	3.2–3.8	22
ZIF	1.4–2.2 × 10 ⁻¹⁰	4–7	26
MOCC	6.4–7.7 × 10 ⁻¹¹	>100	This study

the feeding side and P''_{CO_2} is the lower CO₂ partial pressure at the sweeping side; L is the thickness of the membrane; F, R and T have their usual meanings.

From the slope σ_{O_2} is estimated to be 41.5 S/m according to $-\frac{\varepsilon}{\tau} \frac{RT}{4F^2L} (1 - \varphi) (\sigma_{O_2})$ with $\varepsilon \approx \varphi = 0.4$, $\tau \approx 11.3$,³⁰ $L = 0.00118$ m, $R = 8.314$ J·mol⁻¹·K⁻¹ and $F = 96485$ C·mol⁻¹; this value is much greater than σ_{O_2} (923 K) = 3.1 S·m⁻¹ reported for air.^{34,35} The higher σ_{O_2} may be attributed to the presence of electron conduction in SDC when exposed to low-P_{O₂} atmosphere or simply oversimplification of the Wagner equation.

The highest CO₂ flux reached 0.13 ml·min⁻¹·cm⁻² at 650°C and $P_{CO_2} = 0.375$ atm. It is worth mentioning that J_{CO_2} shown in Fig. 3 is higher than in Fig. 2, e.g., 0.11 ml·min⁻¹·cm⁻² at 650°C in Fig. 3 vs 0.11 ml·min⁻¹·cm⁻² at 700°C in Fig. 2. We attribute it to the performance improving “break-in” behavior occurring during the flux-temperature measurement period that produced Fig. 2. The following long-term stability study further supports this assertion by showing an early-stage performance improvement “break-in” behavior.

The performance of MOCC is also compared in Table III with other types of membranes. Note that the flux-density obtained in this study has to be converted to permeance with the consideration of membrane thickness and pressure differential in order to compare with other membranes on the same basis. The selectivity of CO₂/CH₄ was determined from the concentration of N₂ in the sweeping gas leaked through the membrane. Within the N₂ concentration (<0.03%) detected in the sweeping helium, the selectivity of CO₂ is calculated to be >100. Evidently, the electrochemical MOCC membrane is advantageous over

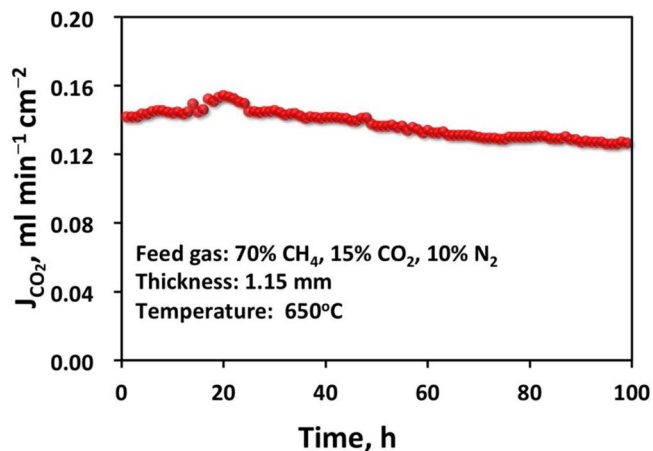


Figure 4. CO₂ flux stability measured with a simulated natural gas containing 15%CO₂ at 650°C.

other size-exclusion membranes in permeance and selectivity, and is virtually unlimited by the “Robeson Upper Bound”.^{27,28}

Long-term flux stability.— The long-term stability of the membrane with a simulated natural gas containing 15% CO₂ as the feeding gas is shown in Fig. 4. Note that this was a new membrane performing better than the one producing Figs. 2 and 3. The better performance is likely attributed to a thinner membrane and better control of membrane synthesis. In addition, an increase in J_{CO_2} during the first 20 hours is noted, followed by a slow degradation. The initial flux increase was probably due to a gradual loss of carbonate, which may make the effective thickness of the membrane gradually smaller with time.^{29–31} Overall, the degradation rate is relatively small; the flux density remains >0.12 ml·min⁻¹·cm⁻² even after 100 hours. Our most recent study has shown that the loss of carbonate can be mitigated by modifying the surface of oxide matrix with Al₂O₃ as the latter has a full wettability with molten carbonates and thus increases membrane’s ability to immobilize molten carbonates inside the porous ceramic skeleton.^{33,36}

The microstructures of the membrane at various locations before and after the long-term test are shown in Fig. 5. In particular, the

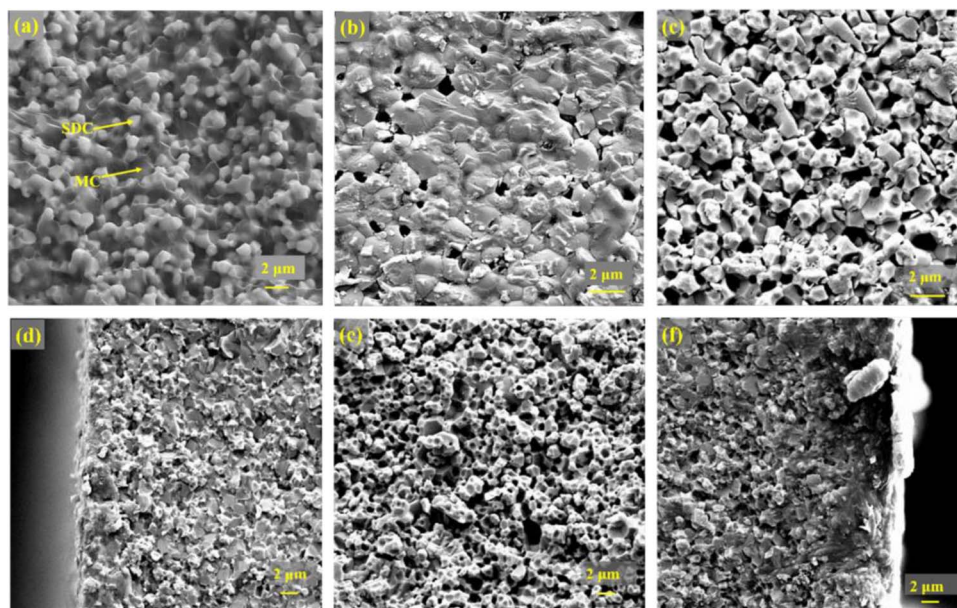


Figure 5. SEM images of membrane (a) cross sectional view before test; (b)–(f) are after 100-h test: (b) sweep side of the membrane; (c) feed side of the membrane; (d) cross section near the sweep side; (e) center of the cross section; (f) cross section near the feed side.

surface and sub-surface regions of the sweeping-gas side located at the bottom of the cell, Fig. 5b and 5d, are heavily covered by carbonate, implying a downward movement of carbonate during the test. The surface and sub-surface regions of the feeding-gas side located at the top of the cell are shown in Fig. 5c and 5f with porosity and partially filled carbonate, respectively, indirectly supporting the downward movement of carbonate. What is a surprise is the large amount of porosity observed in the mid-section of the membrane, Fig. 5e. Such as a “sandwich-like” structure seems to suggest that carbonate at the mid-section moved faster than the top layer toward the sweeping-gas side during operation. In future research, we will further investigate fundamentals of the phenomenon and develop approaches to mitigating the movement of carbonate within ceramic porous structures.

Conclusions

The electrochemical SDC-carbonate MOCC membrane has been successfully demonstrated for CO₂ separation from a simulated natural gas containing 12.5 to 37.5% CO₂ with high flux density and selectivity. The CO₂ flux density increases with temperature and CO₂ concentration in the feeding gas. The maximum flux density of CO₂ reaches 0.133 ml·min⁻¹·cm⁻² at 650°C and CO₂ concentration of 37.5%. Furthermore, the flux remains > 0.12 ml·min⁻¹·cm⁻² during a 100-h stability test at the same temperature. The gradual loss of carbonate during the operation is thought to be the reason for the initial increase and later decrease in flux density.

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