Pre-Combustion Carbon Dioxide Capture by a New Dual-Phase Ceramic-Carbonate Membrane Reactor

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Tasks

- Task A  Synthesis of Dual-Phase Membrane Disks
- Task B  Studying Permeation and Separation Properties of Disk Membranes
- Task C  Synthesis of Tubular Dual-Phase Membranes
- Task D  Gas Separation and Stability Study on Tubular Membranes
- Task E  Synthesis and WGS Reaction Kinetic Study of High Temperature Catalyst
- Task F  Modeling and Analysis of Dual-Phase Membrane Reactor for WGS
- Task G  Experimental Studies on WGS in Dual-Phase Membrane Reactors
- Task H  Economic Analysis
Background
High Temperature CO$_2$ Selective Membranes

- Pre-combustion CO$_2$ capture at higher temperatures (400-800$^\circ$C)

\[ \text{CH}_x + \text{H}_2\text{O} \implies \text{H}_2 + \text{CO}_2 \]

- Reforming reaction with CO$_2$ removal (600-900$^\circ$C)

\[ \text{CH}_x + \text{H}_2\text{O} \implies \text{H}_2 + \text{CO}_2 \]
Microporous membranes made from silicas, carbons and zeolites are capable of separating CO$_2$ from N$_2$ at low temperature.

Ultrathin, ion exchanged Y-type zeolites are best candidates for low temperature separation.

CO$_2$/N$_2$ selectivity decreases with increasing temperatures.
Separation Mechanism - Adsorption & Diffusion

\[ F = [\text{Solubility}] [\text{Diffusivity}] \]

**Adsorption Dominating**
- (strongly adsorbing, low temperature)

\[ \alpha_{1/2} \propto \frac{S_1}{S_2} \]

**Diffusion Dominating**
- (non-adsorbing, or high temperature)

\[ \alpha_{1/2} \propto \frac{D_1}{D_2} \]

At high temperature diffusion controlled selectivity for \( \text{CO}_2/\text{H}_2 \) is less than 1 for microporous membranes.
Concept of Dual-Phase Membrane

$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO}_3^= \rightarrow \text{CO}_2 + \text{O}^-$

Upstream
High $P_{\text{CO}_2}$

Downstream
Low $P_{\text{CO}_2}$

DUAL-PHASE MEMBRANE
Dual-Phase Membrane Characteristics

- **He permeance of support:**
  \[ \sim 10^{-6} \text{ mol/m}^2\text{·s·Pa} \]

- **After infiltration of carbonate:**
  - **He permeance:**
    \[ <10^{-10} \text{ mol/m}^2\text{·s·Pa} \]
Carbon Dioxide Permeance

- All ceramic supports infiltrated with Li/Na/K molten carbonate
- Feed CO₂ concentration of 50% (YSZ tested with 25%)
- Feed and sweep flow rates of 100 mL·min⁻¹

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<tr>
<th>Name</th>
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<td>YSZ</td>
<td>Zr₀.₉₂Y₀.₀₈O₂</td>
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<td>BYS</td>
<td>Bi₁.₅Y₀.₃Sm₀.₂O₃</td>
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<td>Ce₀.₈Sm₀.₂O₁.₉</td>
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<td>LCGFA</td>
<td>La₀.₈₅Ce₀.₁Ga₀.₃Fe₀.₆Al₀.₀₅O₃-δ</td>
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</table>

All membranes tested with 43.5/31.5/25 Li/Na/K (mol%) carbonate mixture
High Temperature Permeation Measurements
Progress and Current Status of Project
Part I: High pressure SDC carbonate disk membranes
High Pressure CO\textsubscript{2}/N\textsubscript{2} Feed Test

Feed gas composition: 50\% CO\textsubscript{2}, 50\% N\textsubscript{2}

Feed gas flow rate: 50 ml/min

Temperature: T=700 °C

Total Feed Pressure range: 1-5 atm

CO\textsubscript{2} flux increases with upstream carbon dioxide partial pressure;

The membrane exhibited good mechanical strength at high pressure.
High Pressure Syngas Feed Test

Feed gas composition:
50% CO, 35% CO\(_2\), 10% H\(_2\), 5% N\(_2\)

Feed gas flow rate:
50 ml/min

Temperature: T=700 °C

Total Feed Pressure range: 1-4 atm

CO\(_2\) flux did not change after normalized by thickness;

The membrane was stable in high pressure syngas.
Part II: Long term stability of SDC-carbonate disk membranes
SDC-Carbonate Membrane in Syngas

- SDC-carbonate permeation was measured with feed composition of 50% CO, 35% CO$_2$, 10% H$_2$, 5% N$_2$
- SDC-carbonate shows excellent stability for 35 days

SDC-carbonate permeation increased with exposure to syngas due to increase in driving force.

![Graph showing permeation rate vs. days and temperature](image-url)
Part III: Symmetrical Tubular SDC-Carbonate Membranes & WGS Reaction Tests
**CO$_2$/N$_2$ Separation**

- **900 °C, CO$_2$ permeation flux 0.51 ml·cm$^{-2}$·min$^{-1}$, CO$_2$ permeance $0.78 \times 10^{-7}$ mol·m$^{-2}$·s$^{-1}$·Pa$^{-1}$.**

- **The CO$_2$ flux increases with increasing the feed CO$_2$ concentration, while the permeance decreases.**
Simulated syngas (50% CO, 36% CO₂, 10% H₂ and 5% N₂) was fed to the membrane

Feed side: simulated syngas flow rate 50 ml·min⁻¹; Sweep side: He flow rate 50 ml·min⁻¹.

Thickness of the membrane is about 1.5 cm.

900°C, CO₂ separation results agree well with the data from CO₂/N₂ separation.
Tests in Membrane Reactor WGS Tests

Water gas shift at high temperatures

**Type I**

\[ CO + H_2O + N_2 \rightarrow CO_2 \rightarrow H_2, N_2, H_2O \]

**Type II**

\[ CO + H_2 + CO_2 + N_2 + H_2O \rightarrow CO_2 \rightarrow H_2, N_2, H_2O \]
High Temperature WGS: Type I H$_2$O/CO Feed

- Operation temperature: 800°C
- Feed Composition: 33%CO, 66% N$_2$
  - Flow Rate: 30 ml/min
- Sweep: Helium at 60 ml/min.
- Thickness of the membrane is about 1.5 cm.

- With increasing H$_2$O/CO ratio, the CO conversion increases first and then decreases, while the CO$_2$ recovery decreases;
- the optimized H$_2$O/CO ratio is 3.
Temperature: 800°C
Feed: syngas 20 ml/min and N₂ 10 ml/min, H₂O/CO ratio 1-3.
Sweep: helium 60 ml/min.

Feed: syngas 20 ml/min, N₂ 10 ml/min and H₂O to CO ratio is 3;
Sweep: Helium 60 ml/min.
Thickness of the membrane is about 1.5 cm.
High Temperature WGS: Type II H$_2$O/Syngas Feed

Temperature: 800$^\circ$C
Feed: syngas 20 ml/min, N$_2$ 10 ml/min and H$_2$O to CO ratio is 3;
Sweep: helium 60 ml/min.

- The CO conversion and CO$_2$ recovery are stable during the 30 h test;
- The membrane is stable under the high temperature syngas WGS environment.
Part IV: Asymmetrical Thin Film Tubular SDC-Carbonate Membranes
Prepared by centrifugal casting method
The SDC layer bonded well with the SDC-BYS layer;
After infiltration the SDC layer became dense while the SDC-BYS layer was still porous.
CO₂/N₂ Separation Test

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. Thickness of the membrane is about 150 μm.

700°C, Feed side: CO₂ flow rate 5-45 ml·min⁻¹, CO₂ and N₂ total flow rate 50 ml·min⁻¹; Sweep side: He flow rate 50 ml·min⁻¹.
CO₂ Separation from Simulated Syngas

Feed side: syngas flow rate 100 ml·min⁻¹; Sweep side: He flow rate 100 ml·min⁻¹. Thickness of the membrane is about 120 mm.

Feed side: syngas flow rate 100 ml·min⁻¹; Sweep side: He flow rate 100 ml·min⁻¹.
**CO₂ Separation from Simulated Syngas**

- Asymmetrical, thin membrane has much higher permeation flux than thick membranes.

- CO₂ permeance of the membrane is stable during the operating period;

- This membrane is potential for the application in pre-combustion CO₂ capture.

Feed side: Syngas at 50 ml/min;

Sweep side: He at 50 ml/min.
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Summary

- SDC-carbonate (disk and tubular) membranes prepared showing excellent CO$_2$ selectivity, CO$_2$ permeance with syngas feed
- SDC-carbonate membrane has shown feasibility for high temperature water gas shift reaction with simulated coal-gas feed
- SDC-carbonate membranes shows long-term stability of more than one month at 700°C
- 150 μm dual-phase membrane successfully prepared on tubular support and tested in syngas conditions showing improved performance and stability