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

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Project Objectives

◆ Synthesize chemically/thermally stable dual-phase ceramic-carbonate membranes with CO₂ permeance and CO₂ selectivity (with respect to H₂, CO or H₂O) larger than 5x10⁻⁷ mol/m²·s·Pa and 500;

◆ Fabricate tubular dual-phase membranes and membrane reactor modules suitable for WGS membrane reactor applications;

◆ Identify experimental conditions for WGS in the dual-phase membrane reactor that will produce the hydrogen stream with at least 93% purity and CO₂ stream with at least 95% purity.
Technology Background
Ceramic-carbonate dual-phase membrane

High temperature (>500 °C); Theoretical CO₂ selectivity 100%

Ceramic phase: oxygen ion conductor, Sm₀.₂Ce₀.₈O₁.₉₋₈ (SDC)
Molten carbonate phase: Li, Na, K carbonates
IGCC power plant with CO₂ capture

**Gasifier**
- Coal
- Steam
- Oxygen
- Cryogenic ASU

**Cooler**
- Particulate removal
- Sulfur removal

**HT WGS Reactor**

**Cooler**

**LT WGS Reactor**

**Amine absorber**

**Compressor**

**Amine**

**Compressor**

**GT**

**Electricity Power**

**H₂**

**CO₂**

**Improve:** Efficiency, Reduce: Cost, Emission

30%H₂, 40%CO, 20%H₂O, 10%CO₂
1450 °C, 50 bar
IGCC power plant with CO₂ capture

Improve: Efficiency, Reduce: Cost, Emission

Advanced membrane technology
Dual-phase membrane reactor for high temperature WGS

$CO + H_2O \rightarrow CO_2 + H_2$

WGS

$900 ^\circ C$, no catalyst is required
Advantages of dual-phase WGS membrane reactor

◆ Advantages

- High thermal and chemical stability
- High CO₂ permeability (especially under high feed pressure)
- Removal of pure CO₂
- Keep H₂ rich stream at high pressure

◆ Potential impacts

- CO conversion ➔ Reduce the cost of subsequent WGS reaction
- CO₂ removal ➔ Reduce the cost of subsequent CO₂ capture
Progress and Current Status of Project
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
Tasks A-D

- Work accomplished

- **Membrane materials**
  - $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF)
  - $\text{Bi}_{1.5}\text{Y}_{0.3}\text{Sm}_{0.2}\text{O}_{3}$ (BYS)
  - Yttria-stabilized zirconia (YSZ)
  - $\text{La}_{0.85}\text{Ce}_{0.1}\text{Ga}_{0.3}\text{Fe}_{0.65}\text{Al}_{0.05}\text{O}_{3-\delta}$ (LCGFA)
  - $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9-\delta}$ (SDC)

- **Membrane geometry**
  - Disk membrane
  - Tubular membrane
  - Symmetric thick membrane
  - Asymmetric thin membrane

- **Membrane property**
  - $\text{CO}_2$ transport property
  - Long-term stability
  - $\text{CO}_2$ permeation model
Tasks

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**High temperature water gas shift (WGS) reaction**

**Membrane**

- Ceramic: SDC
- Carbonate: Li$_2$CO$_3$/Na$_2$CO$_3$/K$_2$CO$_3$
- OD: 1.1 cm; ID: 0.8 cm; Thickness: 1.5 mm; Effective length: 2.5 cm.

**Reaction conditions**

- Temperature: 800-900 °C
- Feed, Sweep side pressure: 1 atm
- Catalyst: No
- Simulated syngas: 49.5% CO, 36% CO$_2$, 10% H$_2$ and 4.5% N$_2$
- Feed side: Syngas flow rate 10-30 mL·min$^{-1}$, N$_2$ flow rate 10 mL·min$^{-1}$, steam to CO molar ratio 1.0-3.0
- Sweep side: He flow rate 60 mL·min$^{-1}$. 
High temperature syngas WGS reaction

Schematic diagram:

- **Sweep in**
- **Membrane reactor**
- **Furnace**
- **Sweep out**
- **GC**
- **Vent**
- **Heating jacket**
- **Ice-water cold trap**
- **Syringe pump**
- **H₂O**
- **MFC**
- **He**
- **Syngas**
- **N₂**
- **Alumina disk**
- **Dual-phase membrane**
- **Ceramic Sealant**
- **Alumina tubes**
Morphology of tubular dual-phase membrane

a-c: porous supports; d-f: dual phase membrane
CO\textsubscript{2} flux as a function of temperature during the WGS reaction (a) and the Arrhenius plot (b). Syngas flow rate 20 ml/min, H\textsubscript{2}O/CO=3.0.

- 900 °C, CO\textsubscript{2} flux is about 0.36 ml·cm\textsuperscript{-2}·min\textsuperscript{-1};
- CO\textsubscript{2} permeation activation energy is 91 kJ·mol\textsuperscript{-1}.
High temperature syngas WGS performance

Effect of temperature

![Graph showing CO conversion and CO2 recovery as a function of temperature.](image)

Syngas WGS performance as a function of temperature. Syngas flow rate 20 ml/min; Residence time 1.26 s; H2O/CO=3.0.

- 900 °C, CO conversion and CO2 recovery are 26.1% and 18.7%, respectively, in membrane reactor (MR); CO conversion of traditional reactor (TR) is much lower.
High temperature syngas WGS performance

- Effect of $\text{H}_2\text{O}$ (steam)/CO ratio

Syngas WGS performance as a function of steam to CO ratio at 900 °C. Syngas flow rate 20 ml/min.
High temperature syngas WGS performance

- Effect of syngas flow rate

Syngas WGS performance as a function of syngas flow rate at 900 °C. \( \text{H}_2\text{O}/\text{CO}=3.0 \). Residence time from 2.16 s to 0.89 s.
High temperature syngas WGS performance

- **Long-term stability**

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0-30 h</td>
</tr>
<tr>
<td>2</td>
<td>30-58 h</td>
</tr>
<tr>
<td>3</td>
<td>58-84 h</td>
</tr>
<tr>
<td>4</td>
<td>84-112 h</td>
</tr>
</tbody>
</table>


- 900 °C, CO conversion and CO₂ recovery and CO₂ flux maintain at around 26.2%, 18.4% and 0.36 mL·cm⁻²·min⁻¹, respectively, for more than 110h.
Modeling

- New CO₂ permeation equation

\[ J_{CO_2} = k \cdot \frac{RT}{4F^2L} \cdot \ln\left(\frac{P'_{CO_2}}{P''_{CO_2}}\right) \]

\[ J_{CO_2} = k' \cdot \frac{RT}{4F^2L} \cdot (P'_{CO_2}^n - P''_{CO_2}^n) \]

Lin and co-workers, J. Membr. Sci. 467(2014) 244.
Modeling

- Kinetic equation for WGS reaction without catalyst

\[ \gamma = F k_f [CO]^{0.5} [H_2O] (1 - \frac{[CO_2][H_2]}{K_{eq}[CO][H_2O]}) \]

**F**: a correction factor used to account for the catalytic activity of membrane materials;

**k_f**: forward reaction rate constant based on the study of Bustamante et al.;

\[ k_f = k_o e^{-Ea/RT} \]

**K_{eq}**: temperature-dependent WGS equilibrium constant.

Iyoha O., H₂ production in palladium & palladium-copper membrane reactors at 1173K in the presence of H₂S, PhD thesis, University of Pittsburgh, (2007);
Comparison of Experimental and Modeling Results

- Reliability of the modeling

![Graph showing comparison of CO conversion and CO2 recovery with experimental and simulated data across different temperatures.]

- Simulated CO conversion
- Simulated CO2 recovery
- Experimental-CO conversion
- Experimental-CO2 recovery
Simulation Conditions

◆ Membrane

SDC/Carbonate tubular membrane;
OD: 1.1cm; ID: 0.8cm; Thickness: 1.5 mm; Effective length: 2.5cm.

◆ Reaction conditions

Temperature: 900 °C;
Feed pressure: 1, 10, 20, 30, 40 atm;
Sweep side pressure: 1 atm;
Catalyst: No;
Syngas: 56.5% CO, 8.2% CO₂, 35.3% H₂;
Feed side: Syngas flow rate 10-40 mL·min⁻¹, steam to CO molar ratio 1.0-4.0;
Sweep side: He flow rate 60 mL·min⁻¹.

20 atm; Steam to CO ratio of 3; Syngas flow rate 25 mL/min; Residence time 1.12 s.
Modeling Results

*Effect of feed pressure*

900 °C; Steam to CO ratio of 3; Syngas flow rate 25 mL/min.
Modeling Results

- Effect of Steam to CO ratio

900 °C; 20 atm; Syngas flow rate 25 mL/min.
Effect of syngas flow rate

900 °C; 20 atm; Steam to CO ratio of 3; Residence time from 2.8 s to 0.7 s.

Syngas flow rate 10 mL·min⁻¹: CO conversion, CO₂ recovery and H₂ concentration are 72%, 90% and 78%, respectively.
Modeling Results

- Schematic of multi-stage membrane reactor

Gasifier Syngas → WGS Membrane Reactor → Compressor → CO₂ storage

Steam flows through the system as indicated.
Modeling Results

- Multi-stage membrane reactor

900 °C; 20 atm; syngas flow rate 20 mL/min; Steam to CO ratio of 3.
Modeling Results

- Multi-stage membrane reactor

900 °C; syngas flow rate 20 mL/min; Steam to CO ratio of 3.

93% (objective)
Summary

- In the membrane reactor, the removal of CO₂ by membrane promotes the conversion of CO, facilitating the H₂ production and CO₂ capture.
- Syngas WGS reaction was successfully operated in the tubular membrane reactors. SDC-carbonate membranes showed good CO₂ flux and high thermal and chemical stability.
- Experimental conditions for WGS membrane reactor to produce 93% hydrogen stream were identified by modeling analysis.
- SDC-carbonate dual phase membranes are promising for high temperature CO₂ separation in industrial processes, such as IGCC.