Development of Innovative Gas Separation Membranes through Sub-Nanoscale Materials Control - Development of Novel Carbon Membranes

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Background

CO₂/N₂, CO₂/H₂ Separation performance of carbon membrane

CO₂/N₂: Separation factor: 6.8-101 ¹)
High CO₂/N₂ separation performance

CO₂/H₂: Separation factor: 5.5 ²)

CO₂ selective permeation due to
selective adsorption on the pore surface
Affinity to CO₂ ↑ → Separation performance ↑

Problem: Decline of separation performance under humidified conditions

Separation target: Humidified gas
(WGS gas, flue gas)

Humidity $\uparrow$  \quad \rightarrow \quad$ Permeance $\downarrow$
Separation factor $\downarrow$

Cause: H$_2$O adsorption and blockage

Previous approach: Hydrophobic layer coating \(^3\)

Our approach

Incorporate CO$_2$ affinity materials in the pores

$\rightarrow$ Enhanced CO$_2$ permeation using adsorbed H$_2$O in the pores

Novel Carbon Membranes with enhanced CO₂ affinity

**Approach**

Incorporate CO₂ affinity materials in the pores → Enhanced CO₂ permeation under humidified conditions
Materials

Porous support: tubular porous $\alpha$-alumina membrane

(Noritake Co., Japan, pore diameter: 150nm (symmetric), Outer-diameter: 10mm)

Precursor: Cardo polyimide (PI-BTCOOME)

Solvent: 1-Methyl-2-pyrrolidinone (NMP)

$\text{CO}_2$ affinity materials:
(1) Alkali metal carbonate
(2) DL-2,3-Diaminopropionic acid hydrochloride (DAPA)

Membrane preparation procedure

Method A (Blend)

- Preparation of precursor solution
- Dip coating (Outer-surface)
- Drying
- Carbonization
- Product

Method B (Post-treatment)

- 7wt% precursor/NMP solution, 1 min
- 60 °C, >8h
- $\text{N}_2$ atmosphere
- Heating rate: 5°C/min
- 600 °C, 3h
Method A:
Blend CO₂ affinity materials in precursor solution

Method B:
Post-treatment of CO₂ affinity materials after preparation of carbon membranes
Water vapor sorption using carbon films with/without $\text{Cs}_2\text{CO}_3$ (Method A)

$\begin{align*}
\text{Sorbed amount} \ [\text{g-H}_2\text{O/g-carbon}] \\
\hline
\text{Cs}_2\text{CO}_3 (0) & \bullet \\
\text{Cs}_2\text{CO}_3 (0.5) & \triangle \\
\text{Cs}_2\text{CO}_3 (1) & \square \\
\end{align*}$

Cs$_2$CO$_3$ (x):
Precursor solution:
PI-BTCOOCH$_2$/($\text{Cs}_2\text{CO}_3$/$\text{H}_2\text{O}$/NMP = x/(10-x)/90wt%) (7/93 wt%)

$\rightarrow$ Increase in $\text{H}_2\text{O}$ adsorption at low humidity
More hydrophilic pores
Effect of Cs$_2$CO$_3$ post-treatment on separation performance

<table>
<thead>
<tr>
<th>With/without Cs$_2$CO$_3$</th>
<th>Method</th>
<th>Relative humidity [RH%]</th>
<th>( Q_{\text{CO}_2} ) ([\text{m}^3 \text{m}^{-2} \text{s}^{-1} \text{Pa}^{-1}])</th>
<th>( Q_{\text{N}_2} ) ([\text{m}^3 \text{m}^{-2} \text{s}^{-1} \text{Pa}^{-1}])</th>
<th>Separation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without Cs$_2$CO$_3$</td>
<td>N/A</td>
<td>0</td>
<td>( 8.9 \times 10^{-10} )</td>
<td>( 4.0 \times 10^{-11} )</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>N/A</td>
<td>100</td>
<td>( 3.6 \times 10^{-10} )</td>
<td>( 3.0 \times 10^{-11} )</td>
<td>12</td>
</tr>
<tr>
<td>Cs$_2$CO$_3$</td>
<td>Method A</td>
<td>100</td>
<td>( 3.0 \times 10^{-10} )</td>
<td>( 2.8 \times 10^{-10} )</td>
<td>1</td>
</tr>
<tr>
<td>Cs$_2$CO$_3$</td>
<td>Method B</td>
<td>100</td>
<td>( 1.2 \times 10^{-9} )</td>
<td>( 2.6 \times 10^{-11} )</td>
<td>46</td>
</tr>
</tbody>
</table>

Gas separation conditions:
Temp.: 40 °C, Feed gas: CO$_2$/N$_2$ (5/95 vol/vol),
Feed pressure: 0.1 MPa, Permeate pressure: ca. 0 MPa

Separation performance was enhanced by Method B.
Effect of alkali metal carbonate post-treatment on separation performance (Method B)

<table>
<thead>
<tr>
<th>Alkali metal carbonate</th>
<th>$Q_{CO2}$ [m$^3$m$^{-2}$s$^{-1}$Pa$^{-1}$]</th>
<th>$Q_{N2}$ [m$^3$m$^{-2}$s$^{-1}$Pa$^{-1}$]</th>
<th>Separation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$CO$_3$</td>
<td>7.2 x 10$^{-10}$</td>
<td>1.7 x 10$^{-11}$</td>
<td>42</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>4.5 x 10$^{-10}$</td>
<td>1.0 x 10$^{-11}$</td>
<td>43</td>
</tr>
<tr>
<td>Rb$_2$CO$_3$</td>
<td>1.5 x 10$^{-9}$</td>
<td>2.9 x 10$^{-11}$</td>
<td>48</td>
</tr>
<tr>
<td>Cs$_2$CO$_3$</td>
<td>1.2 x 10$^{-9}$</td>
<td>2.6 x 10$^{-11}$</td>
<td>46</td>
</tr>
<tr>
<td>Cs$_2$CO$_3$ + DAPA</td>
<td>1.6 x 10$^{-9}$</td>
<td>2.6 x 10$^{-11}$</td>
<td>57</td>
</tr>
</tbody>
</table>

Gas separation conditions: Temp.: 40 °C, Feed gas: CO$_2$/N$_2$ (5/95 vol/vol), Humidity: ca. 100RH%, Feed pressure: 0.1 MPa, Permeate pressure: ca. 0 MPa
Effect of humidity on separation performance

Carbon membrane with Cs$_2$CO$_3$+ DAPA post-treatment

Gas separation conditions: Temp.: 40 °C, Feed gas: CO$_2$/N$_2$ (5/95 vol/vol), Feed pressure: 0.1 MPa, Permeate pressure: ca. 0 MPa

Constant separation performance at 60-100RH%
Novel carbon membranes with enhanced CO$_2$ affinity for CO$_2$ separation under humidified conditions were developed.

**Method A (Blend CO$_2$ affinity materials with precursor solution)**
- Sorbed H$_2$O increased as the amount of alkali metal carbonate increased at low relative humidity.
- Prepared membrane did not show good separation performance, probably due to defect formation.

**Method B (Post-treatment)**
- Separation performance was enhanced. Effect of CO$_2$ affinity materials were confirmed.
- Treated membrane showed constant separation performances at 60-100RH%.
Future plan

(1) Improve separation performance
   (Increase $Q_{CO_2}$ and $\alpha$)

   - Control membrane thickness
   - Optimize carbonization condition
   - Screen $CO_2$ affinity materials

(2) Separation performance under high pressure

   - Control membrane structure for high pressure

Goal:
\[
Q_{CO_2} > 1 \times 10^{-9} \ [m^3 (STP) \ m^{-2} \ s^{-1} \ Pa^{-1}]
\]
\[
\alpha > 100
\]
at 4 MPa.