The Preparation Characteristics of Hydrogen Permselective Membrane for Higher Performance in IS Process of Nuclear Hydrogen Production

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Introduction

- Hydrogen → The attractive fuel for the secondary energy carrier system
  - Being renewable as the energy resources.
  - Having the potential to be storable, transportable, and environmentally prior.
- If non-fossil energies such as solar or nuclear energies are used for water-splitting methods for hydrogen production, no carbon dioxide will be discharged out.
- The IS process is one of the thermochemical water splitting processes using iodine-sulfur as reaction agents through the nuclear energy.
Introducing to Membrane System for IS Process

- The application of the membrane technology in thermochemical water-splitting IS process
  - High Efficiency
  - High Performance in Separation
  - Simplification of the Process System

The objective of this work is to study the characteristics of the silica membrane preparation and the hydrogen permeselectivity of the membrane reactor used for HI decomposition in the thermochemical water splitting IS process.
Introduction

Chemical Reactions in IS Cycle

\[
16\text{H}_2\text{O} + 9\text{I}_2 + \text{SO}_2 \rightarrow (2\text{HI} + 8\text{I}_2 + 10\text{H}_2\text{O}) + (\text{H}_2\text{SO}_4 + 4\text{H}_2\text{O}) \\
\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2 \\
2\text{HI} \rightarrow \text{H}_2 + \text{I}_2
\]

Fig. Energy flow in thermochemical water-splitting by IS process.
**IS process and HI Decomposition**

- **Bunsen reaction (exothermic)**
  \[ xI_2 + SO_2 + 2H_2O = 2HI_x + H_2SO_4 \]

- **SO_2**
- **H_2SO_4**
- **H_2O**

- **HI decomposition**
  \[ 2HI = H_2 + I_2 \]

- **Vaporization**
- **Nuclear heat**

- **Distillation**
- **Membrane Reactor**

- **Acid Separation**

- **Water (H_2O)**

- **Oxygen (0.5O_2)**

- **Hydrogen (H_2)**

- **H_2SO_4 decomposition (endothermic)**

- **Temperature (°C)**: 0, 200, 400, 600, 800, 1000
The Role of Membrane Reactor in IS Cycle

- Bunsen Reaction
- Separation (H$_2$SO$_4$/HI-I$_2$-H$_2$O)
- HI Purification & Concentration (HI-I$_2$-H$_2$O)
- HI Reconcentration
- HI Decomposition & H$_2$ Separation
- Membrane Reactor
- Hydrogen (H$_2$)
- H$_2$SO$_4$ Process
**Experimentals**

**Alumina Tube Pre-preparation**

Alumina support tube: OD 5.5 mm, ID 3.5 mm, length 300mm  
pore size 0.1 µm, porosity 35% from Nano Pore Materials, Korea

Si coating portion  
Alumina tube  
Aron Ceramic D  
Glass paste sealing portion

Ethyl cellulose (EC) → Erlenmeyer flask → α-Terpineol  
Water bath (60°C, 24hr)  
SiO2-BaO-CaO-sealent → Ethanol  
Ballmill 24h  
Glass paste

Fig. The preparation of the glass sealing and glass paste for alumina support.
Membrane Preparation by Sol-Gel Method

Table. The combination of metal alkoxide solution for sol-gel coating

<table>
<thead>
<tr>
<th>Metal Alkoxide</th>
<th>Si(OC₂H₅)₄</th>
<th>Zr(OC₃H₇)₄</th>
<th>Y(CH₃COO)₃·4H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(OC₂H₅)₄</td>
<td>70</td>
<td>29.1</td>
<td>0.9</td>
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</table>

Fig. Procedure for a silica membrane preparation by sol-gel method.

- Alumina Substrate Tube
- Silica Sol Coating: Dipping time 15 min, Pulling speed 4 mm/min, 5~20 times
- Hydrolysis: Relative humidity 95%, Temp. 50°C, 30 min
- Silica Membrane
- Thermal Treatment: Temp. 550°C, 30 min
- Drying: Temp. 150°C, 60 min
Thermal Chemical Vapor Deposition (CVD) Apparatus

Cooling route
Permeation route
CVD route

Fig. Schematic diagram of thermal CVD apparatus for membrane preparation.
Tube array of Multi-tube bundle CVD treatment

- Flow rate of carrier gas (N₂) was controlled from 6.0x10⁻² to 10.0x10⁻² m/s.
- CVD temperature was controlled at 600~700°C.

Fig. The expected structure of a silica membrane.
Fig. Schematic diagram of hydrogen permselective membrane permeation apparatus.

◆ Gas permeation experiments were carried out at 303~773K by using single gas systems of hydrogen, helium, and nitrogen, etc.
Results & Discussions – Sol-Gel Preparation

Membrane Flow Model Analysis

Fig. The total flow compared with surface and Knudsen flow.

- Total flow is composed of surface flow and Knudsen flow.
- The total flow has change affected with surface flow and Knudsen flow.
Results & Discussions – Sol-Gel Preparation

Flow Model Analysis for Sol-Gel Preparation Membrane

![Graph showing examination of surface and Knudsen flow.](image)

Fig. Examination of surface and Knudsen flow.

- This may be thought that the kinetic diameter of nitrogen (3.64 angstrom) is larger than that of hydrogen (2.86 angstrom) and nitrogen cannot penetrate through the non-porous layer of the membrane.
Results & Discussions – Sol-Gel Preparation

Permeation Results for Sol-Gel Preparation Membrane

Fig. The relationship of permeability on operating temperature.

➢ The activation energies of hydrogen in the operating temperature range were ca. 5 kJ/mol.
Results & Discussion – Thermal CVD Preparation

Single tube preparation

Fig. The pressure change of permeate side in CVD reactor during CVD treatment at 600°C.

Fig. The permeance change of permeate side with and deposition time in CVD reactor at 600°C.

Fig. Permeance with temperature change in silica membrane prepared at 600°C for 7hr.
Results & Discussion – Thermal CVD Preparation

Single tube preparation

Fig. The pressure change of permeate side in CVD reactor with carrier velocity during CVD treatment at 600°C.

Fig. The permeance change of He with flow velocity of carrier gas during CVD treatment at 600°C.

Fig. The permeance change of N₂ with flow velocity of carrier gas during CVD treatment at 600°C.
Results & Discussion – Thermal CVD Preparation

Scanning Electronic Microscope (SEM) Analysis

Fig. Cross-section view.

Fig. Surface view.
Energy Dispersive X-Ray (EDX) Analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
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<tbody>
<tr>
<td>O K</td>
<td>46.66</td>
<td>60.24</td>
</tr>
<tr>
<td>Al K</td>
<td>17.28</td>
<td>13.23</td>
</tr>
<tr>
<td>Si K</td>
<td>36.06</td>
<td>26.52</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td></td>
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</tbody>
</table>
Results & Discussion – Thermal CVD Preparation

Single tube preparation

Table 1. Reaction condition of CVD and permeances of gases. (at 600°C)

<table>
<thead>
<tr>
<th>Membrane number</th>
<th>Flow rate of N₂ gas [ml/min]</th>
<th>Deposition time [min]</th>
<th>Permeance [mol/Pa·m²·s] × 10⁻⁸ (at 450°C)</th>
<th>Selectivity (H₂/N₂) at 450°C</th>
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<tbody>
<tr>
<td>M600-1</td>
<td>1500</td>
<td>350</td>
<td>22.6</td>
<td>10.09</td>
</tr>
<tr>
<td>M600-2</td>
<td>1500</td>
<td>500</td>
<td>7.57</td>
<td>12.02</td>
</tr>
<tr>
<td>M600-3</td>
<td>1500</td>
<td>600</td>
<td>4.76</td>
<td>17</td>
</tr>
</tbody>
</table>

Fig. The changes of permeance with temperature in silica membrane prepared at 600°C.
Results & Discussion – Thermal CVD Preparation

Single tube preparation

Fig. The changes of permeance with temperature in silica membrane prepared at 700°C.

Table 2. Reaction condition of CVD and permeances of gases. (at 700°C)

<table>
<thead>
<tr>
<th>Membrane number</th>
<th>Flow rate of N₂ gas [ml/min]</th>
<th>Deposition time [min]</th>
<th>Permeance [mol/Pa.m².s] × 10⁻⁹ (at 450°C)</th>
<th>Selectivity (H₂/N₂) at 450°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>M700-2</td>
<td>1500</td>
<td>180</td>
<td>53.4</td>
<td>34</td>
</tr>
<tr>
<td>M700-3</td>
<td>1900</td>
<td>180</td>
<td>53.4</td>
<td>34</td>
</tr>
</tbody>
</table>
Results & Discussion – Thermal CVD Preparation

Single tube preparation

Fig. The permeance change of N$_2$ with flow velocity of carrier gas during CVD treatment at 600$^\circ$C.

Fig. The permeance changes of He and N$_2$ with deposition time during CVD treatment.

Fig. The permeance change of N$_2$ with temperature of carrier gas during CVD treatment at 600$^\circ$C.
Results & Discussion – Thermal CVD Preparation

Multi-tube preparation

Fig. The permeance changes of He and N₂ with deposition time during 3-tube CVD treatment.
Results & Discussion – Thermal CVD Preparation

Comparison of permeance in 1- and 3-tube treatment

Fig. The comparison of 1- and 3-tube treatment on pressure changes of permeate side in CVD reactor during CVD treatment.

Fig. The comparison of 1- and 3-tube treatment on permeance changes of N$_2$ in CVD reactor during CVD treatment.
Conclusions

- The permeation characteristics of hydrogen and nitrogen belong to the Knudsen flow pattern, but water is different.

- The hydrogen permeation was dominated by the activated diffusion, and the activation energy of hydrogen was ca. 5kJ/mol.

- In the preparation through thermal CVD method, the size of deposited silica particle was obtained near 11.0 nm and the thickness of deposited layer was about 2 µm. Then, the selectivity of H₂ on N₂ was 26.3 at 450°C, and the permeance of H₂ was 6x10⁻⁸ mol/Pa.m².s.
Acknowledgements

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Thanks for Your Attention!