Preparation of thin and dense electroless-plated Pd membrane by controlling Pd deposition behavior

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Electroless Pd plating at different deposition temperatures was investigated to control Pd deposition behavior for preparing a much thinner Pd membrane to reduce Pd usage and achieve high hydrogen permeation flux. The deposition temperature directly influenced on the membrane thickness uniformity and defect formation. In our experimental condition, a thin Pd electroless-plated membrane with a thickness of 3 μm could be prepared at 333 K using a formic acid bath. It was found that this membrane showed no leakage of helium and high H₂ permeation flux. The rate-limiting step of Pd deposition during the electroless plating must be one of the important factors for preparing the thinner Pd plating membrane with no pinholes.

Key words: Pd membrane, electroless plating, plating deposition temperature, H₂ separation

1. INTRODUCTION

Hydrogen is considered a clean energy source with increasing the attention on global warming. Hydrogen separation membranes have been of great interest as promising materials for hydrogen production and purification in a variety of applications including membrane reactors [1,2]. Pd based membranes have been extensively studied due to their exclusive hydrogen selectivity and high permeability. However, the development of thin Pd based membrane has been necessary not only for enhancement of their membrane performance but also reducing Pd usage because of its poor resources and increasing demand in a wide variety of technologies such as catalysts for chemical industry.

To reduce the membrane thickness with mechanical strength, various porous supports such as porous glass [3], porous ceramics [4-8] and porous metals [9-12] have been frequently used, and the different methods including electroless plating [3-5,9], sputtering [8], chemical vapor deposition [6,7] and electroplating [10,11] have been developed to prepare a thin Pd membranes on porous supports. Considering practical applications, electroless plating, in particular, has strong advantages with respect to cost, simple equipment and availability of non-conductive and complex shape substrates.

Due to the easy operability of electroless plating, a lot of investigations have been focused on the preparation of a thin Pd membrane using electroless plating [13-17]. Pan et al. [13] successfully prepared a thin Pd membrane with 2-3 μm thick on a porous alumina hollow fiber and their membrane showed the H₂/N₂ separation factor over 1000. However, they employed a γ-alumina intermediate layer on the α-alumina hollow fiber and the very small pore size of the γ-alumina could achieve the thin Pd membrane with good performance. In contrast, a thin Pd membrane could be prepared on the big surface pores of a porous stainless steel tube with marked roughness by an in-situ multi-dimensional plating method [14]. Chen et al. [15] reported a modified electroless plating method named suction-assisted electroless deposition for preparing a thin Pd membrane. The prepared Pd membrane had 4.5 μm thickness and N₂ leakage was not detected. A modified electroless plating method was also reported by Tanaka et al [16]. They prepared a Pd layer within a porous γ-alumina support by a vacuum electroless plating technique. The resultant Pd membrane consisted of Pd nanoparticles encapsulated in the γ-alumina layer. Zhang et al. [17] could synthesize thin Pd membranes with 5-6 μm thick using the vacuum electroless plating technique as well. They investigated the influence of vacuum on the membrane performance.

In this study, aiming to prepare a thin and dense Pd membrane with high hydrogen permeability and reproducibility, the control of deposition behavior of Pd electroless plating was tried by adjusting the deposition temperature.

2. EXPERIMENTAL

As a porous ceramic support for thin Pd electroless-plated membranes, α-Al₂O₃ capillary tube with 6 mm O.D. (mean pore size: 0.07 μm, NORITAKE CO., LIMITED) was employed. Pd nuclei were deposited on the outer surface of the tube by sensitization and activation treatments with stannous chloride and Pd chloride solutions, respectively, with the process repeated three times. The electroless Pd plating was then performed using a formic acid electroless plating solution [18] summarized in Table I for inhibiting the formation of defects by generated gas bubbles during the plating. The deposition temperature was adjusted at 323, 333 and 343 K to control the Pd deposition rate with mechanical stirring. The Pd
deposition rate was shown in Fig. 1. Based on the deposition rate, the thickness of each Pd membranes was adjusted to be approximately 3 μm to evaluate the effect of the deposition temperature. After the electroless plating, as-prepared membranes were rinsed by water and ethanol ultrasonically.

Table I Electroless plating bath composition using formic acid [18]

<p>| | | |</p>
<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PdCl\textsubscript{2}</td>
<td>[g/l]</td>
<td>1.77</td>
</tr>
<tr>
<td>HCOOH</td>
<td>[ml/l]</td>
<td>8.52</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{8}N\textsubscript{2}·H\textsubscript{2}O</td>
<td>[ml/l]</td>
<td>7.09</td>
</tr>
<tr>
<td>pH</td>
<td>3.8</td>
<td></td>
</tr>
</tbody>
</table>

The membrane performance was evaluated by single gas permeation using helium and hydrogen. For the helium leakage test, one end of a Pd membrane was capped by epoxy resin, and helium was introduced into the inside of the membrane at 0.2 MPa abs. The helium leakage was measured by a TCD gas chromatography using nitrogen sweep flow at an ambient temperature. The hydrogen permeation tests were carried out at 673, 723 and 773 K with different pressure gradients.

3. RESULTS AND DISCUSSION

Fig. 2 shows the SEM images of the electroless-plated Pd membrane surfaces prepared at different deposition temperatures. No large pinholes could be observed on all membranes. The surface morphology at 323 and 333 K were very similar, but only the Pd grain size at 343 K was relatively small. The nucleation of Pd in the plating solution seemed to be occurred at 343 K because of low thermal stability of this plating bath. Hence, the Pd nuclei generated during the electroless plating must be involved within the Pd membrane at 343 K, resulting in this smaller grain size of the Pd membrane.

The cross sectional area was observed as well and the Pd infiltration into the porous Al\textsubscript{2}O\textsubscript{3} supports was analyzed by EDX. The SEM-EDX images were shown in Fig. 3. Although all the membranes could be prepared with a thickness of approximately 3 μm, their thickness uniformity was with an order of 323 > 333 > 343 K from the standard deviation shown in Table II. The thickness uniformity should be governed by the reaction rate and diffusion rate of Pd ions in the plating solutions and good uniformity could be achieved when the deposition rate of Pd ions was much slower than their diffusion rate. The deposition temperature can be considered to influence the deposition rate rather than the diffusion rate because the plating solution was mechanically stirred with relatively high rate. Therefore, the better uniformity of the membrane could be achieved at the lower deposition temperature. In such a case, the infiltration of a Pd layer into the porous support is possible to be easily occurred. However, there were not clearly identified in our experimental results (Fig. 3). Since the formation of a Pd/alumina composite layer with no defects is expected to achieve much thinner membrane thickness, further investigations on the plating condition should be required.

![Fig. 1 Pd deposition rate of the formic acid plating bath at different deposition temperature](image)

![Fig. 2 SEM images of Pd membrane surface prepared at different deposition temperatures](image)

![Fig. 3 EDX analysis of the cross sectional area over plated Pd membranes prepared at different deposition temperatures](image)

Table II Pd membrane performance plated at different deposition temperature

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>343</th>
<th>333</th>
<th>323</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness [μm]</td>
<td>2.73</td>
<td>2.69</td>
<td>2.70</td>
</tr>
<tr>
<td>SD [μm]\textsuperscript{a}</td>
<td>0.479</td>
<td>0.359</td>
<td>0.319</td>
</tr>
<tr>
<td>Deposition rate ([μm \text{ min}^{-1}])\textsuperscript{b}</td>
<td>0.135</td>
<td>0.098</td>
<td>0.057</td>
</tr>
<tr>
<td>Number of leaks ([\text{cm}^{-2}])</td>
<td>5.48</td>
<td>1.59</td>
<td>0</td>
</tr>
<tr>
<td>Leakage ([\text{ml min}^{-1} \text{ cm}^{-2}])</td>
<td>0.165</td>
<td>0.088</td>
<td>N.D.\textsuperscript{c}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Standard deviation of Pd membrane thickness  
\textsuperscript{b}Based on the membrane thickness at 15 min  
\textsuperscript{c}Below the detection limit
The results of the He leakage test were summarized in Table II, and the appearance of leakage on the surface of the Pd membranes were shown in Fig. 4. With the decrease of the deposition temperature from 343 to 333 K, He leakage was reduced only by half although the number of leaks decreased less than one third. This indicates that the remaining leaks of the membrane prepared at 333 K must be derived from relatively large pores and/or defects of the porous support, of which the size was larger than its mean pore diameter. However, these remaining pinholes could be completely plugged by further decrease of the deposition temperature to 323 K, because its He leakage could not be detected by a TCD gas chromatography as well as no leaks was not observed visually.

![Image of plated Pd membranes prepared at different deposition temperatures](image)

**Fig. 4** He leak through plated Pd membranes prepared at different deposition temperatures

The schematic image of the Pd growth mechanism was shown in Fig. 5. At high deposition temperature, Pd nuclei adsorbed on the top of the outer surface of the support would be preferentially reacted and grown in a direction perpendicular to the support surface, because the reaction rate of Pd ions would be much faster than their diffusion rate. In other words, the growth rate in a vertical direction was much faster than that in a horizontal direction to the surface of the support. In addition, at higher deposition temperature, the nucleation in the solution would be occurred and this causes nonuniform growth of Pd membranes. Therefore, some large pores of the support were difficult to be plugged when the thin Pd layer was prepared. In contrast, when the diffusion-controlled growth of Pd layer can be achieved by decreasing the deposition temperature, Pd nuclei grow isotropically. A much thinner Pd membrane, thus, could be prepared.

![Image of Pd growth mechanism](image)

**Fig. 5** Growth mechanism of Pd nuclei by different rate controlling steps

![Graph showing hydrogen flux with pressure gradient](image)

**Fig. 6** Pressure dependence of hydrogen flux for Pd membrane prepared at 323 K

Fig. 6 shows the hydrogen flux with the pressure gradient through the Pd membrane prepared at 323 K. The hydrogen flux was almost proportional to the difference in the square root of hydrogen pressure. This is consistent with Sieverts' law [19] for a defect-free Pd membrane with the solution-diffusion mechanism. The hydrogen flux was as high as 0.32 mol m⁻² s⁻¹ at 773 K. Table III summarizes the comparable results for the Pd membranes prepared by various electroless plating methods in the reported literatures. The hydrogen flux

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Method</th>
<th>( t ) [( \mu m )]</th>
<th>( T ) [K]</th>
<th>( H_2 ) flux [mol m⁻² s⁻¹]</th>
<th>( E_a ) [kJ mol⁻¹]</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>Pd/PG</td>
<td>ELP</td>
<td>13</td>
<td>773</td>
<td>0.09</td>
<td>10.7</td>
<td>14</td>
</tr>
<tr>
<td>Pd/PSS</td>
<td>MD-ELP</td>
<td>6</td>
<td>773</td>
<td>0.26</td>
<td>16.7</td>
<td>3</td>
</tr>
<tr>
<td>Pd/CeO₂/PSS</td>
<td>ELP+CVD</td>
<td>6</td>
<td>773</td>
<td>0.23</td>
<td>17.3</td>
<td>20</td>
</tr>
<tr>
<td>Pd/ZrO₂/PSS</td>
<td>ELP</td>
<td>10</td>
<td>773</td>
<td>0.08</td>
<td>7.1</td>
<td>21</td>
</tr>
<tr>
<td>Pd/HF</td>
<td>ELP</td>
<td>5</td>
<td>773</td>
<td>0.33</td>
<td>21.3</td>
<td>22</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>ELP</td>
<td>7</td>
<td>673</td>
<td>0.13</td>
<td>8.8</td>
<td>1</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>VELP</td>
<td>5</td>
<td>773</td>
<td>0.28</td>
<td>7.0</td>
<td>17</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>ELP</td>
<td>3</td>
<td>773</td>
<td>0.32</td>
<td>6.8</td>
<td>This work</td>
</tr>
</tbody>
</table>

\( ^a \) PG: porous glass, PSS: porous stainless steel, HF: Al₂O₃ hollow fiber
\( ^b \) ELP: electroless plating, MD-ELP: multi-dimensional electroless plating, CVD: chemical vapor deposition, VELP: vacuum electroless plating.
\( ^c \) membrane thickness, \( ^d \) hydrogen pressure gradient = 100 kPa, \( ^e \) activation energy.
\( ^f \) hydrogen pressure gradient = 40 kPa
over our prepared membrane was slightly higher than the previous reports, but its permeability was in the rage from 12.9 to 15.0 nmol m\(^{-1}\) s\(^{-1}\) Pa\(^{-0.5}\). This permeability is in good agreement with those reported by other groups, for instance 7-14 \[23\], 13.6 \[24\], and 4-15.8 nmol m\(^{-1}\) s\(^{-1}\) Pa\(^{-0.5}\) [25]). This clearly indicates the high hydrogen flux was derived from much thinner membrane thickness. However, the durability of this membrane remains unclear although no deterioration of its membrane performance was observed during the hydrogen permeation test. Hence, further investigation of the membrane stability will be necessary because the deterioration of the membrane performance caused by hydrogen embrittlement and thermal stress would be easily occurred with decreasing the membrane thickness.

An Arrhenius plot of hydrogen permeance was shown in Fig. 7. The activation energy is calculated to be 6.8 kJ/mol. It is also in agreement with the previous reports in the rage of 5-21 kJ/mol for the thin Pd membranes [3,14,17,26]. However, the activation energy in our membrane was relatively low since the Pd membranes with high selectivity generally show the activation energy of 10-15 kJ/mol. This low activation energy seems to be related to its microscopic structure, i.e., membrane thickness, small grains of the membrane, as well as the substrate resistance and experimental conditions.

![Arrhenius relation of hydrogen permeability with temperature through Pd membrane prepared at 323 K](image)

**Fig. 7** Arrhenius relation of hydrogen permeability with temperature through Pd membrane prepared at 323 K

4. CONCLUSION

A thin and dense Pd electroless-plated membrane could be successfully prepared by controlling the Pd deposition behavior. The membrane performance was drastically improved by decreasing the deposition temperature. The lower deposition rate of Pd ions than the diffusion rate might derive the thin Pd membrane with no defect because of its isotropic growth of Pd nuclei on the substrate surface. A much thinner Pd plated membrane is expected to be achieved by further improvement of the membrane preparation conditions, for instance, a nucleation method.

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**REFERENCES**


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