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Comprehensive Characterization and Permeation Analysis of Thin Pd/Al_2O_3 Composite Membranes Prepared by Suction-Assisted Electroless Deposition

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ABSTRACT

In this work, suction-assisted electroless deposition technique is proposed to prepare high hydrogen permselective Pd/Al_2O_3 composite membranes. Effects of suction pressure and plating time on the surface morphology and denseness of the resulting composite membranes have been investigated. Scanning electron microscopy (SEM), electron probe microscope analysis (EPMA), x-ray diffractometry (XRD), and nitrogen permeability technique were used to characterize these membranes. Furthermore, the hydrogen permeability and selectivity of the composite membranes were also studied. The experimental result shows that the nitrogen permeability of the palladium (Pd) top layer is decreased with

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lowering the suction pressure. Under suction pressure of 3 kPa and plating time of 1 hr, a membrane with a perfectly dense 4.5 μm thick Pd layer can be obtained, whose H_2/N_2 selectivity is approaching infinite. As compared to the conventional electroless deposition, via suction assistance, the adhesion between the Pd top layer and Al_2O_3 support of the resulting membranes can be remarkably improved, and the thickness attained for complete denseness can also be reduced effectively. Based on the hydrogen permeation results, it is found that the rate-limiting step for the hydrogen permeation through the Pd top layer is controlled by the surface reaction. Furthermore, the activation energy is estimated as 18 kJ/mol. This value is in a good agreement with those reported in literature for Pd layers thinner than 10 μm.

Key Words: Pd/Al_2O_3 composite membrane; Electroless deposition; Suction; Hydrogen permeation.

INTRODUCTION

Palladium (Pd)-based membranes have been regarded as promising materials for hydrogen separation and purification processes at elevated temperature. Recently, these membranes have received much attention for their applications in membrane reactors, especially for dehydrogenation,[1] hydrogenation,[2,3] methane reforming,[4] etc. In these practical uses, characteristics of the palladium layer always play an important role on the performance of separation. Therefore, numerous investigations were focused on the fabrication of palladium-based composite membranes with thin and dense palladium layers in order to improve the performance of hydrogen permeability and selectivity.[5–12]

There are many methods used deposit a palladium layer onto a porous substrate, such as sputtering,[13] electroplating,[14,15] electroless plating,[5,7] chemical vapor deposition,[6] etc. Among them, the electroless plating technique demonstrates advantages of simple equipment, ease of operation, and relatively low cost. More important, it can acquire a high-quality deposited film. For example, Collins and Way[16] reported that the hydrogen flux of $0.71\,mol/m^2$ sec and H_2/N_2 selectivity of 650 were achieved by using the Pd/Al_2O_3 composite membrane with a 11.4 μm thick Pd layer at 823 K and the pressure difference of 670 kPa. Ilias et al.[7] demonstrated that the measured hydrogen permeability of the Pd/Al_2O_3 composite membrane with a thickness of 12 μm is found to be $0.97\,mol/m^2$ sec at the pressure difference of 240 kPa and temperature of 573 K. Huang et al.[17] prepared a Pd/Al_2O_3 composite membrane with a 15 μm thick palladium layer. The hydrogen permeability

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was measured to be 0.095 mol/m^2 sec at the pressure difference of 220 kPa and temperature of 669 K. Furthermore, this membrane exhibited gas-tight, i.e., the H_2/N_2 selectivity was infinite. However, as reported by Mardilovich et al.,[18] due to influences by roughness and pore size of the support, the thickness of palladium layer prepared by the conventional electroless deposition is required to be larger than 10 μm to obtain a perfectly dense layer. Li et al.[19] proposed an improved technique to deposit the Pd layer by electroless deposition with osmosis. They found, via osmosis-assisted deposition, the H_2/N_2 selectivity of the 10.3 μm thick Pd layer can be largely enhanced. The influences of osmosis in reducing Pd grain size and promoting the adhesion between the top layer and support were also reported by Souleimanova et al.[20] Nam et al.[13] prepared pinhole-free Pd/Ni alloy membranes deposited on a porous stainless steel (PSS) support by vacuum electrodeposition technique. With the vacuum assistance, the deposited layer became denser and the adhesion between top layer and support was remarkably enhanced. It seems a promising approach to achieve a thin and perfectly dense Pd layer by vacuum facilitated deposition. However, the further experimental results are lacking, much less information was found on the Al_2O_3 support.

The objective of this study is to deposit a thin (<10 μm) and dense palladium layer on the Al_2O_3 support by suction-assisted electroless plating. The effects of suction on the microstructure and performances of hydrogen permeability and selectivity of composite membranes were also studied.

THEORETICAL

Analysis of Gas Permeation Through a Pd/Al_2O_3 Composite Membrane

The schematic diagram for gases permeating through a Pd/Al_2O_3 composite membrane comprising a porous support and a thin Pd top layer is shown in Fig. 1. If there are a few pinholes or pores existing in the top layer, it can be considered as a porous layer, which includes dense (Pd lattice) and porous (pores and defects) portions. Then, the permeation of gases through the composite membrane can be analyzed and calculated based on the resistance model.[17] At steady-state transport, the gas flux that passes over the composite membrane is equal to that which passes through the top layer, as well as that through the porous support, i.e.,

$$J_o = J_{top} = J_{support} \tag{1}$$

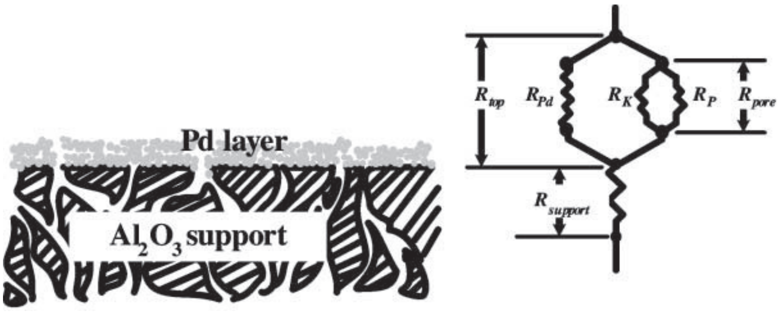

Figure 1. Schematic resistance representation for hydrogen permeating through a Pd/Al_2O_3 composite membrane.

in which

$$J_o = F_o(P_h - P_l) \tag{2}$$
$$J_{top} = F_{top}(P_h - P_i) \tag{3}$$

and

$$J_{support} = F_{support}(P_i - P_l) \tag{4}$$

Therefore, the overall flow resistance of gases permeating through the Pd/Al_2O_3 composite membrane, R_o, is equal to the sum of resistances in the support ($R_{support}$) and the Pd top layer (R_{top}) as expressed by

$$R_o = R_{top} + R_{support} \tag{5}$$

i.e.,

$$\frac{1}{F_o} = \frac{1}{F_{top}} + \frac{1}{F_{support}} \tag{6}$$

in which J is the gas flux, and P_h and P_l represent pressures in the feed and permeate sides, respectively. The interfacial pressure, P_i, is the pressure at Pd layer–support interface. According to Eq. (5), the resistance in the Pd top layer can be estimated by subtracting the resistance in the support from that in the composite membrane. In addition, the gas permeability of the Pd layer can be obtained from Eq. (6). According to our previous work,[21] the transport behaviors of nitrogen and hydrogen through the porous Al_2O_3

support can be described by Knudsen diffusion and Poiseuille flow. Therefore, the gas permeability in the support, F_{support}, can be expressed as

$$F_{\mathrm{support}} = F_{\mathrm{oK}} + F_{\mathrm{oP}}\left(\frac{P_{\mathrm{i}} + P_{\mathrm{l}}}{2}\right) \tag{7}$$

where F_{oK} and F_{oP} are permeabilities attributed to Knudsen diffusion and Poiseuille flow, respectively. Once values of F_{oK} and F_{oP} are determined from the permeation data of the Al_2O_3 support, the value of P_{i} can be determined as below:[21]

$$P_{\mathrm{i}} = \frac{-F_{\mathrm{oK}} + (F_{\mathrm{oK}}^2 + 2F_{\mathrm{oP}}F_{\mathrm{oK}}P_{\mathrm{l}} + F_{\mathrm{oP}}^2P_{\mathrm{l}}^2 + 2F_{\mathrm{oP}}J)^{0.5}}{F_{\mathrm{oP}}} \tag{8}$$

As can be seen from Eq. (8), P_{i} is a function of J, P_{l}, and the nature of gas. When the pressure in permeate side (P_{l}) is kept constant for a certain gas, the P_{i} value can be determined by the gas flux, and is only varied with the pressure in the feed side (P_{h}).

Nitrogen Permeation Through the Pd Top Layer

In the porous Pd top layer, nitrogen can permeate merely through the porous portion via Knudsen diffusion and Poiseuille flow. Therefore, the nitrogen permeability in the Pd top layer, $F_{\mathrm{top,N_2}}$, can be calculated by Eq. (3). Also, nitrogen permeabilities contributed by Knudsen diffusion, $F_{\mathrm{oK,N_2}}$, and Poiseuille flow $F_{\mathrm{oP,N_2}}$, can be determined. Furthermore, the average pore size of the Pd top layer is estimated as[21]

$$d = 2r = 17.02\eta_{\mathrm{N_2}}\left(\frac{RT}{M}\right)^{0.5}\frac{F_{oP,N_2}}{F_{oK,N_2}} \tag{9}$$

where d represents the average pore size, M is the molecular weight, T is the Kelvin temperature, and $\eta_{\mathrm{N_2}}$ is the viscosity of nitrogen.

Hydrogen Permeation Through the Pd Top Layer

Hydrogen permeating through the Pd top layer includes two parts of transport: the porous portion via Knudsen diffusion and Poiseuille flow, and the dense portion via solution-diffusion mechanism. As shown in Fig. 1, the nitrogen permeability of the Pd top layer is the sum of nitrogen permeabilities in the dense and porous portion. In other words, the reciprocal resistance of the Pd top layer, $1/R_{\mathrm{top}}$, is the sum of reciprocal resistances in the dense portion, $1/R_{\mathrm{Pd}}$, and the porous portion, $1/R_{\mathrm{pore}}$. Therefore,

$$\frac{1}{R_{\mathrm{top}}} = \frac{1}{R_{\mathrm{Pd}}} + \frac{1}{R_{\mathrm{pore}}} \tag{10}$$

For the porous portion, hydrogen permeabilities contributed by Knudsen diffusion $F_{\mathrm{oK,H_2}}$, and Poiseuille flow, $F_{\mathrm{oP,H_2}}$, can be theoretically calculated from nitrogen permeabilities at the same temperature and transmembrane pressure, i.e.,

$$F_{\mathrm{oK,H_2}} = \sqrt{\frac{M_{\mathrm{N_2}}}{M_{\mathrm{H_2}}}} \cdot F_{\mathrm{oK,N_2}} \tag{11}$$

$$F_{\mathrm{oP,H_2}} = \frac{\eta_{\mathrm{N_2}}}{\eta_{\mathrm{H_2}}} \cdot F_{\mathrm{oP,N_2}} \tag{12}$$

Similarly, the P_{i} value for hydrogen through the composite membrane is determined from Eq. (8). When the values of $F_{\mathrm{oK,H_2}}$, $F_{\mathrm{oP,H_2}}$, and P_{i} are obtained, the hydrogen flux in the porous portion, J_{pore}, is then estimated by

$$J_{\mathrm{pore}} = \left[F_{\mathrm{oK,H_2}} + F_{\mathrm{oP,H_2}}\left(\frac{P_{\mathrm{h}} + P_{\mathrm{i}}}{2}\right)\right](P_{\mathrm{h}} - P_{\mathrm{i}}) \tag{13}$$

Subsequently, the hydrogen flux in the dense portion, J_{Pd}, can be determined by subtracting the flux in the porous portion from that in the top layer.

In general, the permeation of hydrogen in the dense portion of the Pd layer, J_{Pd}, can be expressed as

$$J_{\mathrm{Pd}} = F_{\mathrm{Pd}}(P_{\mathrm{h}}^{n} - P_{\mathrm{i}}^{n}) \tag{14}$$

where F_{Pd} represents the permeability due to solution-diffusion mechanism and n is the corresponding pressure exponent, which varies from 0.5 to 1. The n value is strongly dependent on the rate-limiting step of hydrogen permeating through the Pd layer.[22] The transport mechanism of hydrogen permeating through the dense Pd layer includes the dissociative adsorption on Pd surface in the feed side (i.e., surface reaction), diffusion through the Pd layer, and associative desorption on Pd surface in the permeate side. If the diffusion of hydrogen in the Pd layer is the rate-limiting step, Sievert's law will be obeyed, and thus the n value is equal to 0.5. On the other hand, the n value approaches to unity if the rate is controlled by the surface reaction. Recently, Cirscuoli et al.[23] demonstrated the effect of Pd-layer thickness on the transport mechanism. They reported that the n value is close to unity as the thickness goes below 10 μm, because the transport rate is predominately governed by the surface reaction. Experimentally, values of F_{Pd} and n in Eq. (14) can be obtained by nonlinear regression. Furthermore, the apparent activation energy (E_a) can be determined from the slope of Arrhenius plot, as expressed by

$$E_a = -R\frac{d \ln F_{Pd}}{d(1/T)} \tag{15}$$

EXPERIMENTAL

Preparation of Pd/Al_2O_3 Composite Membranes

The Pd/Al_2O_3 composite membrane was prepared by electroless deposition technique. The porous α-Al_2O_3 disks prepared in our laboratory,[24] which are with a thickness of 2 mm, a diameter of 3 cm, and an average pore size of 0.20 μm were used as supports. Prior to the electroless deposition, a convenient activation procedure was used to preseed palladium nuclei onto the surface of Al_2O_3 supports for initiating the deposition. The activation procedure was performed by alternatively immersing the supports in acidic $SnCl_2$ solution and acidic $PdCl_2$ solution ten times.[16] In order to improve the adhesion of the Pd layer onto the Al_2O_3 support, the electroless deposition was carried out with evacuating from the back side of the Al_2O_3 support. The suction pressure of the electroless plating system was regulated by an aspirator (A-3S, Tokyo Rikakikai Co., Ltd.). As listed in Table 1, the hydrazine-based plating bath contained palladium chloride, hydrazine, Na_2EDTA, and ammonia water. The plating temperature was kept at 333 K. After the electroless deposition, the composite membrane was rinsed with deionized water and then dried for use.

Membrane Characterization

The surface morphology of the deposited film was observed by using a scanning electron microscope (SEM, JKA-840, JEOL Co.). Palladium and

Table 1. The compositions of palladium deposition bath.

$PdCl_2$ (mM)	5
Na_2EDTA (M)	0.16
NH_4OH (28%, ml)	200
N_2H_4 (1 M, ml)	5

aluminum distributions along the cross section of composite membranes were measured by means of an electron probe microanalyzer (EPMA). Also, the thickness of the palladium layer was estimated from the cross-sectional view of composite membrane by SEM observation and by weight-gained method. The crystallite size of deposited palladium grains was determined by Scherrer equation from the line broadening of Pd (111) peak measured by using a x-ray diffractometer (XRD, RX-III, Rigaku Co.) with CuK_α radiation and nickel filter.

Gas Permeation Measurements

The gas permeation measurement was carried out in a stainless permeation cell at temperatures of 573, 593, and 623 K, respectively. The effective area of the membrane for permeation was $17.31\,cm^2$. The transmembrane pressure ranged from 50 to 300 kPa, and the pressure in the permeate side was kept at ambient atmosphere. The steady-state permeation rates of gases were measured by using a soap-bubble flowmeter.

RESULTS AND DISCUSSION

Effect of Suction Pressure on Denseness of the Pd Top Layer

Nitrogen permeabilities of the Al_2O_3 support depending on average pressures are shown in Fig. 2. This is a typical illustration for gas permeating a porous medium via Knudsen diffusion and Poiseuille flow. The values, F_{oK} and F_{oP}, of the Al_2O_3 support are calculated as $4.41 \times 10^{-7}\,mol/m^2\,sec\,Pa$ and $4.62 \times 10^{-13}\,mol/m^2\,sec\,Pa^2$ at 573 K, respectively. Also, the average pore size of the Al_2O_3 support is calculated as $0.22\,\mu m$ from Eq. (9).

The dependence of nitrogen permeabilities of Pd top layers with different suction pressures on the average pressure at 573 K are illustrated in Fig. 3. As can be seen in this figure, it is found that the nitrogen permeability of the Pd top layer is slightly and linearly increased with the average pressure, $(P_h + P_i)/2$. Besides, it is decreased with the temperature. These results indicate that the permeation of nitrogen through the Pd top layer can be described by Knudsen diffusion and Poiseuille flow. Moreover, the nitrogen permeability is decreased with lowering the suction pressure. Figure 4 shows the effect of suction pressure on nitrogen permeabilities of Pd top layers

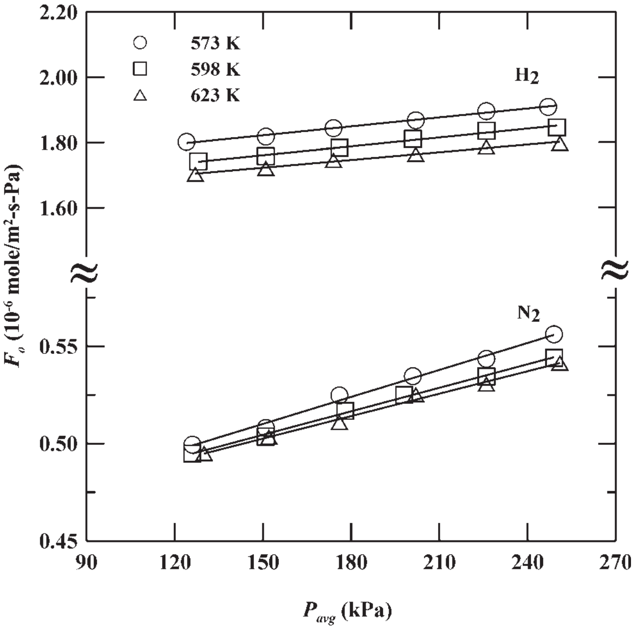

Figure 2. Dependence of gas permeabilities on the average pressure for the Al_2O_3 support.

measured at 573 K and average pressure of 300 kPa. Since a high degree of evacuation introduces more Pd grains penetrated into the pores resulting in the block of pores, moreover, it favors eliminating gas bubbles in the deposited layer, the nitrogen permeability of the Pd top layer is found to decrease with increasing degree of evacuation. For membrane Pd-6, no nitrogen leakage can be detected. Therefore, it is obvious that the Pd top layer of membrane Pd-6 is quite dense.

Surprisingly, the effect of suction pressure on the calculated average pore size of the Pd top layer does not follow the same trend as that of nitrogen permeability. On the contrary, as the suction pressure is decreased from 101 to 48 kPa, the average pore size of Pd top layers is increased from 0.02 to 0.22 μm. The increase in average pore size might reasonably result from the block of smaller pores by Pd grains. If the degree of evacuation is raised further i.e., suction pressure is decreased below 48 kPa, the pore size is sharply reduced, as can be seen for membranes Pd-5 and Pd-6. Accordingly, the assistance of suction can effectively improve the denseness of the Pd top layer.

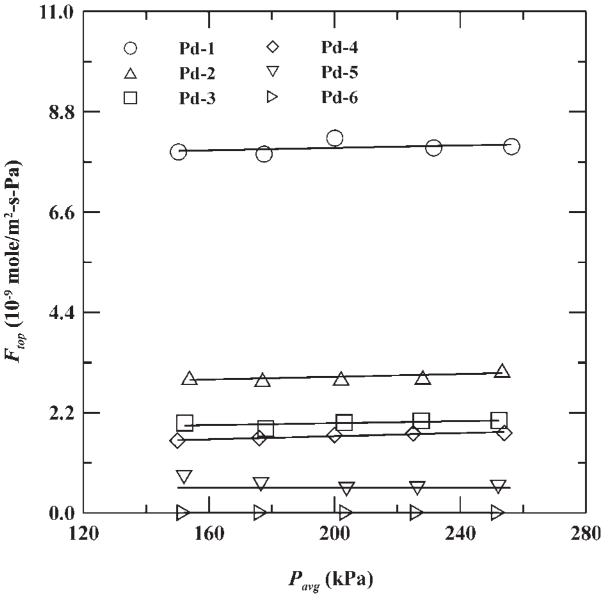

Figure 3. Effect of the nitrogen permeability of Pd top layer on the average pressures for composite membranes prepared with different suction pressures.

Effect of Plating Time on Thickness and Denseness of the Palladium (Pd) Top Layer

The dependence of plating time on the nitrogen permeability and thickness of the Pd top layer at suction pressure of 3 kPa is illustrated in Fig. 5. Here, the thickness is calculated by weight-gained method, which corresponds to the deposition rate of Pd. From Fig. 5, it reveals that the nitrogen permeability measured at 323 K and transmembrane pressure of 300 kPa is decreased with increasing the plating time, due to the reduction of porosity and the increase of film thickness. Except at the initial induction period, the deposition rate can almost remain constant. Besides, it was found that 1 hr is required to obtain a perfectly dense Pd top layer, i.e., membrane Pd-6. The thickness of the membrane Pd-6 is estimated as 8.4 μm.

Characterization of the Pd Top Layer

Surface morphologies of two composite membranes, Pd-1 and Pd-6, are compared in Fig. 6. It was found that the surface of membrane Pd-1 is loosely

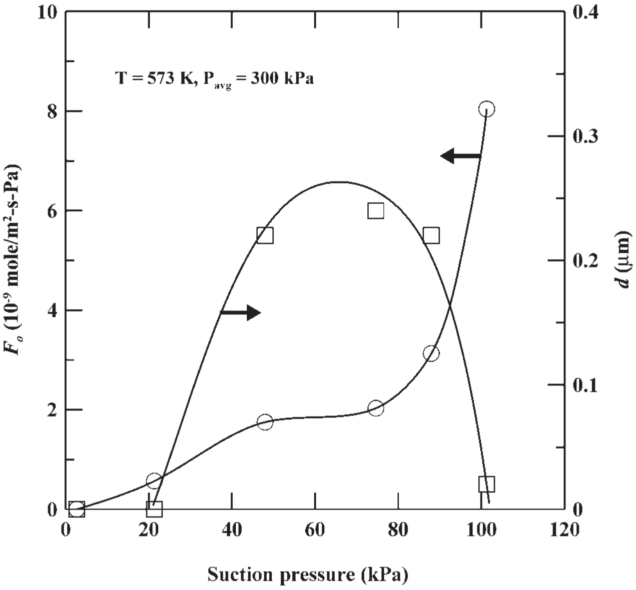

Figure 4. Effect of suction pressure on the nitrogen permeability and average pore size of the Pd top layer.

packed with grains of about 2.3 µm, while the surface of membrane Pd-6 is tightly composed of grains of about 1.3 µm. The smaller grain size for membrane Pd-6 might result from the obstructed growth by suction, especially at high degrees of evacuation. It is also obvious that the smaller grain and denser structure of the Pd top layer are obtained under an evacuated environment. Furthermore, XRD patterns of membranes Pd-6 and Pd-1 are compared as shown in Fig. 7. It was found that they have no significant differences between them. Moreover, from half-width of the Pd (111) peak, it demonstrates that both membranes have almost the same crystallite size, i.e., 35 nm. Consequently, the suction-assisted deposition changes the size of Pd grains, but does not influence the Pd crystallite size.

The cross-sectional views of membranes prepared without suction (Pd-1) and with suction pressure of 3 kPa (Pd-6) are illustrated in Fig. 8. As can be found, the thickness of membrane Pd-1 is about 6 µm, and that of membrane Pd-6 is about 4.5 µm. The thickness of membrane Pd-6 determined from SEM observations is smaller than that obtained from the weight-gained method. This result can be confirmed again from EPMA analysis. Figure 8 indicates that some Pd grains are introduced into porous Al_2O_3 support, especially for membrane Pd-6. With the suction-aided method, the adhesion between Pd

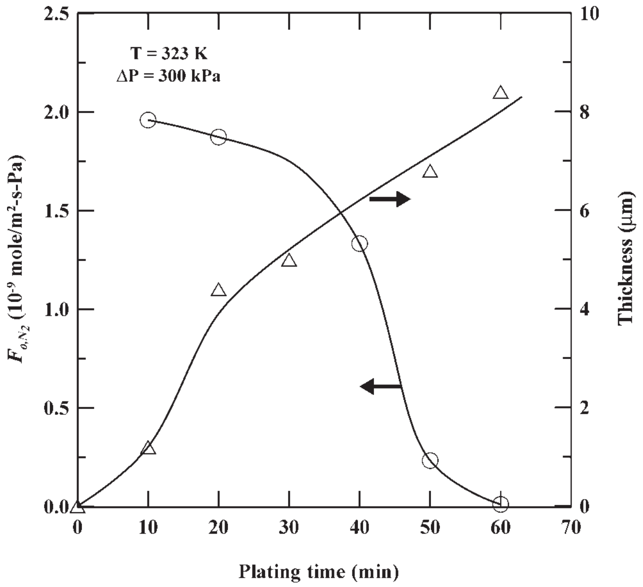

Figure 5. Effects of the plating time on the nitrogen permeability and thickness of the Pd top layer (suction pressure: 3 kPa).

layer and Al_2O_3 support for membrane Pd-6 is better than that for membrane Pd-1. In other words, the adhesion at Pd/Al_2O_3 interface can be remarkably improved by suction. It is worthy to mention, the thickness of the Pd layer for membrane Pd-6 is approaching the commercialized requirement, i.e., 5 μm.[18]

Hydrogen Permeability and Selectivity

Hydrogen Permeation Through Al_2O_3 Supports

Figure 2 shows hydrogen permeabilities of Al_2O_3 supports as a function of the average pressure at 573, 598, and 623 K, respectively. Since the hydrogen permeability is increased linearly with the average pressure and decreased with the temperature, it indicates that the hydrogen transport mechanism can be described by Knudsen diffusion and Poiseuille flow. Furthermore, the H_2/N_2 selectivity is defined as the permeability ratio of the hydrogen to the nitrogen under the same transmembrane pressure. At transmembrane pressure of 300 kPa and temperature of 623 K, the H_2/N_2 selectivity of the Al_2O_3 support is 3.38, which is smaller than that value obtained via Knudsen mechanism, i.e., 3.74.

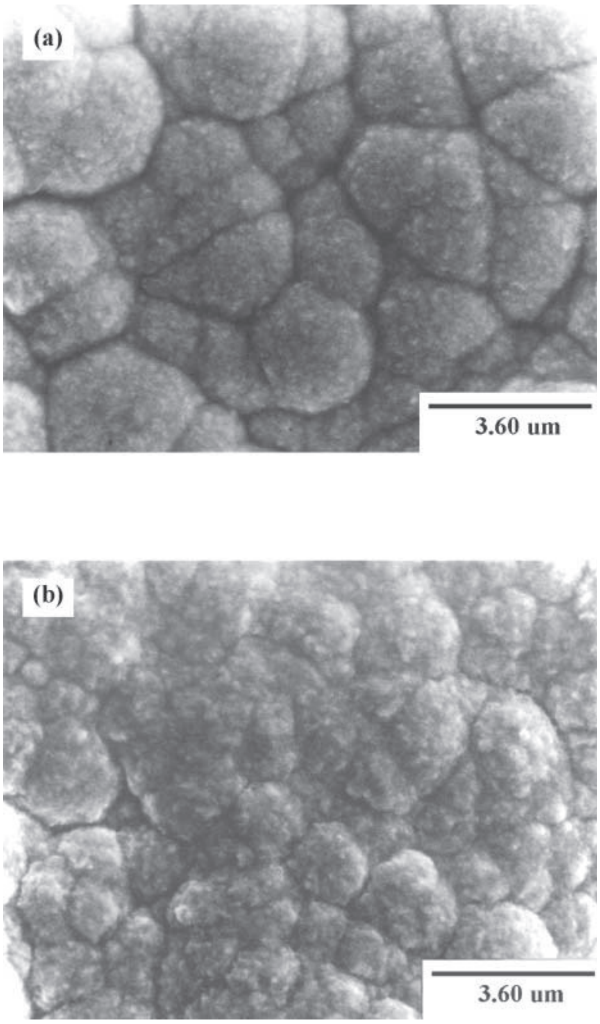

Figure 6. Surface morphologies of composite membranes (a) Pd-1 and (b) Pd-6 (plating time: 1 hr).

Hydrogen Permeation Through the Pd Top Layer

In order to realize permeability and selectivity of Pd/Al_2O_3 composite membranes prepared via suction-assisted deposition, membranes Pd-6 and Pd-1 are employed for comparison.

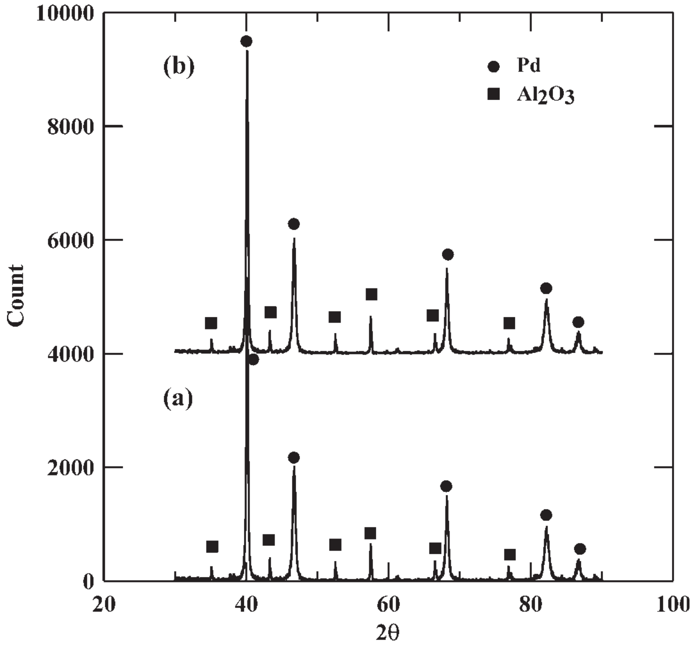

Figure 7. X-ray diffraction patterns of composite membranes (a) Pd-1 and (b) Pd-6 (plating time: 1 hr).

Figure 9 shows the calculated hydrogen flux in the dense portion of the top layer for membrane Pd-1, J_{Pd}, as a function of the pressure difference across the Pd top layer, $P_{\mathrm{h}} - P_{\mathrm{i}}$. It demonstrates that the hydrogen flux is increased linearly with the pressure difference. Since the value n equal to 1 is deviated from that of Sievert's law, the rate of hydrogen permeating through the dense Pd portion of membrane Pd-1 is controlled by the surface reaction. Furthermore, for membrane Pd-1, there is about 98% of hydrogen passing through the dense portion of the top layer, as listed in Table 2. The selectivity of hydrogen to nitrogen at 623 K is estimated as 213.

For membrane Pd-6, hydrogen fluxes in the dense portion of the top layer at 573, 593, and 623 K are illustrated in Fig. 10. From this Fig. 10, it is found that the hydrogen fluxes are increased linearly with increasing pressure difference. Also, they are increased with an increase of temperature. Since the value of n is also equal to 1, the permeation of hydrogen is controlled by the surface reaction. The result is consistent with that reported by Ward and Dao,[22] who demonstrated that the surface reaction was the rate-limiting step for hydrogen permeating through a thin (<10 μm) Pd layer. As can be seen in Table 2, since

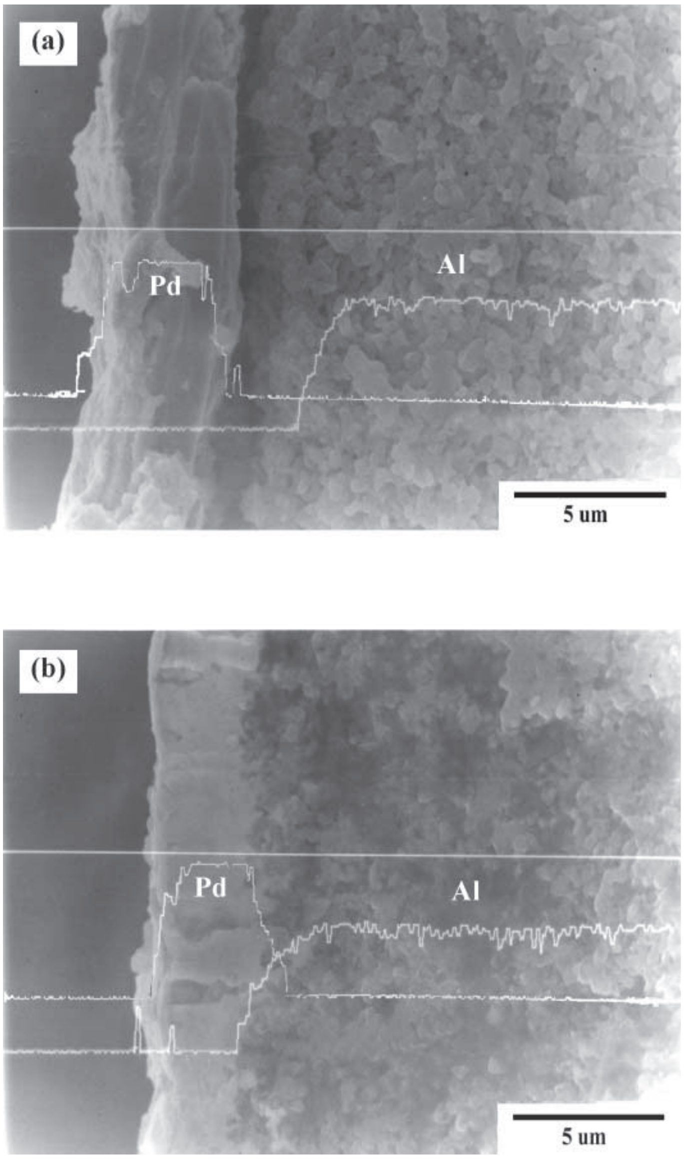

Figure 8. X-ray line scanning photographs of cross section of the composite membranes (a) Pd-1 and (b) Pd-6.

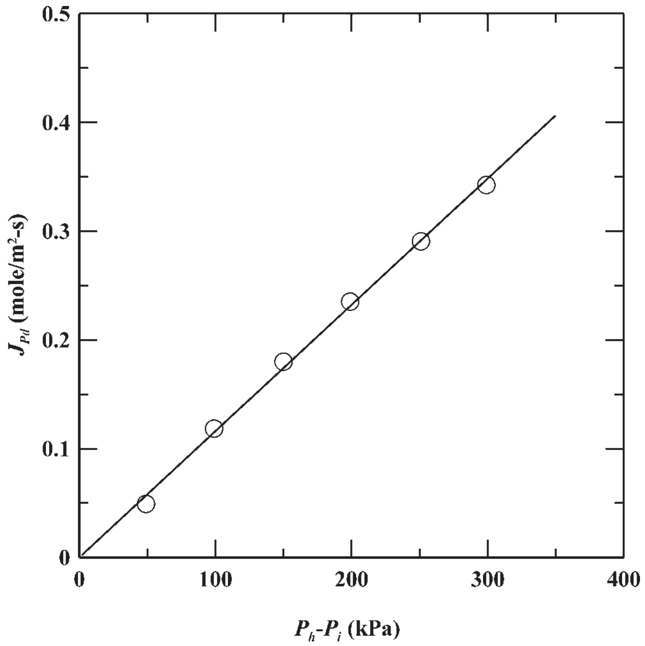

Figure 9. Dependence of the hydrogen flux in the dense portion of the Pd top layer on $P_h - P_i$ for the composite membrane Pd-1.

the membrane Pd-6 is impermeable to nitrogen, the selectivity of hydrogen to nitrogen is approaching infinite. This is strong evidence that the top layer of membrane Pd-6 is perfectly dense and pinhole-free. Comparing the result of hydrogen permeation for membrane Pd-6 with those reported in literature,[5–7,16–19] which can be found in Table 3, membrane Pd-6 exhibits excellent hydrogen permselectivity, and moreover, with the thinnest Pd layer, i.e., 4.5 μm. Consequently, the suction-assisted deposition can reduce the thickness of Pd layer required for complete denseness and enhance the hydrogen permselectivity.

Activation Energy of Hydrogen Permeation

The effect of temperature on the hydrogen permeability through the Pd top layer for membrane Pd-6 is shown in Fig. 11. According to the linear relationship of Arrhenius plot, the apparent activation energy E_a is estimated as 18.4 kJ/mol. Comparing the result with those reported by

Table 2. Hydrogen permeabilities and selectivities of Pd top layers and the Al_2O_3 support.

Membranes	Temperature (K)	F_{oK,H_2} (mol/m^2 sec Pa)	F_{oP,H_2} (mol/m^2 sec Pa^2)	F_{Pd} (mol/m^2 sec Pa^n)	n	J_{Pd} (%)	α
Pd-1	623	1.86×10^{-8}	6.30×10^{-16}	1.16×10^{-6}	1	98	213
Pd-6	573	—	—	9.92×10^{-8}	1	100	∞
	598	—	—	1.18×10^{-7}	1	100	∞
	623	—	—	1.38×10^{-7}	1	100	∞
Al_2O_3	573	1.67×10^{-6}	9.60×10^{-13}	—	—	—	3.51
	598	1.62×10^{-6}	9.20×10^{-13}	—	—	—	3.55
	623	1.61×10^{-6}	7.73×10^{-13}	—	—	—	3.38

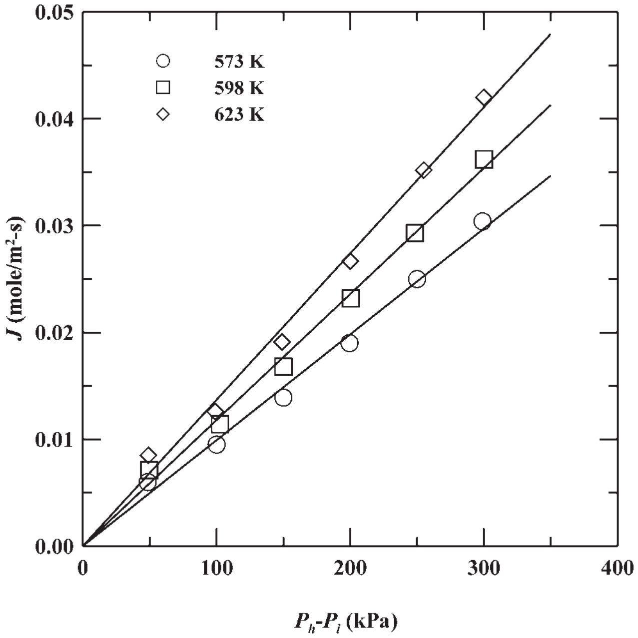

Figure 10. Dependence of the hydrogen flux in the Pd top layer on average pressure for the composite membrane Pd-6.

other investigators in Table 3, most of the E_a values are in the range of 10.7–18.4 kJ/mol, regardless of the support materials and deposition techniques. To further correlate E_a values with the thickness of Pd layer, as illustrated in Fig. 12, it shows that E_a values are about 14.6 kJ/mol for Pd layers with thickness larger than 10 µm. However, on the other hand, the E_a value is up to 38 kJ/mol as the thickness of Pd layer is decreased to 0.5 µm. It is therefore concluded that the difference in the apparent activation energy of hydrogen permeation is due to the change in rate-determining step caused by the thickness of Pd layer.

CONCLUSIONS

High hydrogen permselective Pd/Al_2O_3 composite membranes were prepared by suction-assisted electroless deposition. The nitrogen permeation results show that the nitrogen permeability of the Pd top layer is decreased

Table 3. Hydrogen selectivities and activation energies of deposited palladium layer.

Membranes	Method	Membrane thickness (μm)	Temperature (K)	Selectivity	n	E_a (kJ/mol)	Investigators
Pd/PG	Electroless plating	13	673–773	∞	—	10.7	Uemiya et al.[5]
Pd/Al$_2$O$_3$	Chemical vapor deposition	0.5	523–723	150	—	38	Xomeritakis and Lin[6]
Pd/Al$_2$O$_3$	Electroless plating	17	723–913	380	0.622	14.45	Collins and Way[16]
Pd/Al$_2$O$_3$	Electroless plating	12	373–573	—	0.501	13	Ilias et al.[7]
Pd/Al$_2$O$_3$	Electroless plating	10.3	593–850	∞	0.65	12.3	Li et al.[19]
Pd/Al$_2$O$_3$	Electroless plating	15	600–669	∞	0.5	12.7	Huang et al.[17]
Pd/Al$_2$O$_3$	Electroless plating	4.5	573–623	∞	1	18.4	This work
Pd/PSS	Electroless plating	20	623–743	5,000	0.5	16.38	Mardilovich et al.[18]

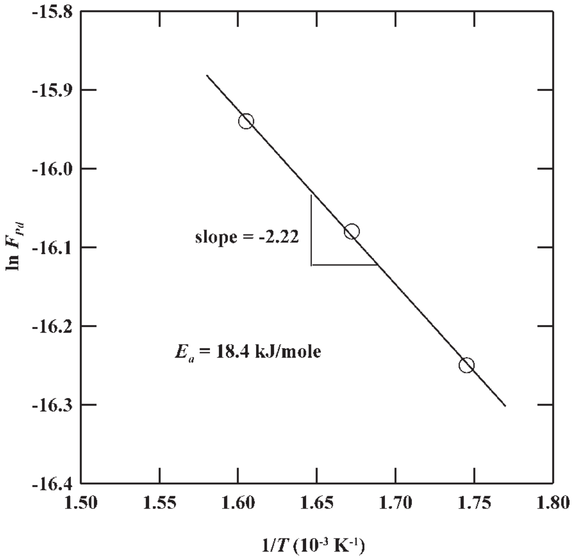

Figure 11. Arrhenius plot of the hydrogen permeability vs. reciprocal temperature for the composite membrane Pd-6.

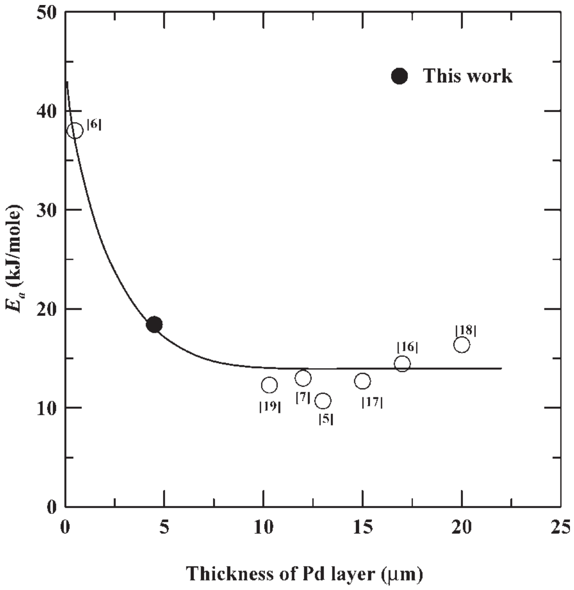

Figure 12. The dependence of activation energy on the thickness of Pd layer.

with lowering the suction pressure, due to the enhancement of denseness of the Pd layer. Furthermore, 1 hr is required for plating to obtain a perfectly dense 4.5 μm thick Pd top layer prepared with a suction pressure of 3 kPa. From SEM observations, it was found that, via suction-assisted deposition, the adhesion between the Pd top layer and Al_2O_3 support of the composite membranes can be remarkably improved. Moreover, the thickness for completely dense layer can be effectively reduced.

According to the hydrogen permeation results, the hydrogen permeability of the perfectly dense Pd layer is $1.38 \times 10^{-7}\,\mathrm{mol/m^2\,s\,Pa}$ at 623 K, and the H_2/N_2 selectivity is approaching infinite. These reveal that the resulting composite membranes demonstrate promising potential for commercialized applicability. Furthermore, the rate-limiting step for hydrogen gas permeating through the Pd layer is controlled by the surface reaction. It is comprehensible that the thickness of the Pd layer is relatively small. Based on the Arrhenius plot, the activation energy is estimated as 18 kJ/mol. This value exhibits a good agreement with those reported for a Pd layer thinner than 10 μm.

NOMENCLATURE

d	Pore diameter of the membrane (μm)
E_a	Apparent activation energy (kJ/mol)
F_o	Overall gas permeability ($\mathrm{mol/m^2\,sec^1\,Pa^1}$)
F_{top}	Gas permeability of the top layer ($\mathrm{mol\,m^2\,sec^1\,Pa^1}$)
$F_{support}$	Gas permeability of the support ($\mathrm{mol/m^2\,sec\,Pa}$)
F_{oK}	Gas permeability due to Knudsen diffusion ($\mathrm{mol/m^2\,sec\,Pa}$)
F_{oP}	Gas permeability due to Poiseuille flow ($\mathrm{mol/m^2\,sec\,Pa^2}$)
F_{Pd}	Gas permeability due to solution-diffusion mechanism ($\mathrm{mol/m^2\,sec\,Pa}$)
J_o	Overall gas flux ($\mathrm{mol/m^2\,sec}$)
J_{pore}	Gas flux in the porous portion ($\mathrm{mol/m^2/sec}$)
J_{top}	Gas flux in the top layer ($\mathrm{mol/m^2\,sec}$)
$J_{support}$	Gas flux in the support ($\mathrm{mol/m^2\,sec}$)
M	Molecular weight of gas (g/mol)
n	Pressure exponent
P_h	The feed side pressure (Pa)
P_i	The interfacial pressure (Pa)
P_l	The permeate side pressure (Pa)
R	Gas constant ($\mathrm{J/mol\,K^1}$)
R_o	Overall flow resistance ($\mathrm{m^2\,sec\,Pa/mol}$)
R_{pore}	Resistance in the porous portion ($\mathrm{m^2\,sec\,Pa/mol}$)
R_{top}	Resistance in the top layer ($\mathrm{m^2\,sec\,Pa/mol}$)

R_{support}	Resistance in the support (m^2 sec Pa/mol)
r	Pore radius of the membrane (μm)
T	Temperature (K)

Greek Symbol

η	viscosity of gas (Pa sec)

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