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# ARTICLE

# Fabrication of palladium-copper alloy membrane for hydrogen purification using a reverse build-up method

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Aiming to develop an economical Pd alloy H<sub>2</sub>-permeable membrane, the preparation process of the reverse build-up method (RBM) primer layer was newly improved for thin Pd alloy layers. A uniform and smooth 0.5  $\mu$ m pinhole-less Pd<sub>60</sub>Cu<sub>40</sub> layer was successfully prepared. H<sub>2</sub> permeation performance and H<sub>2</sub>/He selectivity were measured using a mixture of H<sub>2</sub> and He gases. H<sub>2</sub> permeation performance and H<sub>2</sub>/He selectivity of the Pd<sub>60</sub>Cu<sub>40</sub> layer were measured at 300°C. The H<sub>2</sub> permeation performance and H<sub>2</sub>/He selectivity of the Pd<sub>60</sub>Cu<sub>40</sub> layer were measured at 300°C. This performance level was relatively high relative to other literatures on Pd alloy composite membranes. The economic efficiency of the composite membrane fabricated by RBM was compared with that of a conventional rolled Pd<sub>60</sub>Cu<sub>40</sub> membrane. The Pd requirement per unit H<sub>2</sub> permeation of the developed membrane at 300°C and 200 kPa was estimated to be approximately 1/269 times that of the rolled membrane. Thus, improved RBM was demonstrated to be a low-cost method for producing Pd-alloy membranes.

Keywords: hydrogen purification; palladium-copper alloy; membrane separation; reverse build-up method

## 1. Introduction

Technologies to produce H<sub>2</sub> from renewable and nuclear energy sources are being researched worldwide to realize a zero-carbon society [1]. H<sub>2</sub> is a clean energy carrier that does not emit CO<sub>2</sub> when used [2]. Fuel reforming is primarily used for H<sub>2</sub> production [3]. The H<sub>2</sub> produced must be separated from the gas mixture. In addition, the  $H_2$  needs to be purified for industrial use [4]. The use of H<sub>2</sub>-permeable membranes composed of dense metallic materials in H<sub>2</sub> separation and purification processes is effective [5]. H2-permeable membranes based on Pd alloys are promising candidates for H<sub>2</sub> separation and purification. However, Pd is a precious metal, and its price has risen in recent years. Therefore, reducing the Pd usage is a key subject. The most basic method to reduce Pd use is to fabricate thin membranes. Therefore, the development of Pd-based membranes with thin Pd layers has been widely investigated [6,7].

The conventional rolling method presents limitations regarding thickness in thin membrane fabrication. When rolled membranes are made thinner, the mechanical stability of the stand-alone use is reduced and pinholes generation. The reduction in mechanical stability can be overcome by using a protective film or by compositing with a support. On the other hand, pinholes that occur during membrane formation can cause impurity leakage. Therefore, the most important item in the thinning of Pd membranes is the removal of scratches and adhered particles generated during membrane formation that cause pinholes. Therefore, the minimum thickness of the rolled Pd-alloy membranes generally available on the market is approximately 20 µm [7]). In addition, the rolling method presents a problem of thin membranes in membrane fabrication requiring more processing, resulting in increased costs. In contrast to rolled membranes, composite membranes have been developed in which thinned Pd alloy layers are formed on a porous ceramic materials by a electroless plating (ELP) or other methods [8]. However, pinhole-free and uniform thin Pd membranes are not easily formed, owing to the non-smoothness and defective surface of the support. Therefore, in general, thin membranes are more likely to form pinholes during membrane fabrication [9], thus limiting their thicknesses.

Therefore, we have independently developed a reverse build-up method (RBM) [10] for thin composite membranes to achieve economical Pd-alloy membranes with significantly reduced material costs. In a previous study, we succeeded in making the Ni support layer porous and composite it with a PdCu layer of a few µm by RBM [11]. Since then, we have focused on the development of even thinner PdCu layers and cultivated techniques for economical membranes development. This method enables the reduction of the thickness of the Pdalloy layer to a few micrometers [12]. The objectives of

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this study were to fabricate an economically advantageous membrane with a thin Pd-alloy layer of thickness < 1  $\mu$ m by RBM. In this article, we describe a new composite membrane with a uniform PdCu layer of less than 1  $\mu$ m, which has rarely been reported before, and an improved RBM for its development. The composite membrane developed by improved RBM have sufficient H<sub>2</sub> permeability and has proven to be more economically advantageous than conventional rolled membrane.

## 2. Experimental

## 2.1. Membrane preparation

In this study, we improved the process of the primer layer step in the previous RBM and aimed to fabricate a uniform and flat Pd alloy layer of less than 1 µm, which was not feasible in the past. A Pd-alloy layer is generally formed on porous ceramic support in conventional composite membranes. Conversely, in the proposed method, a smooth flat Pd-alloy membrane is formed first, followed by the formation of porous metal support. We focused on the smooth flatness and uniformity of the Pd-alloy layer to develop a thin Pd-alloy membrane with high H<sub>2</sub> selectivity. A polyimide (PI) film (Kapton, Du-Pont-Toray) was first prepared and used as the primer layer in the RBM procedure. The formation of the primer laver is an important step in the membrane formation process to create a smooth. flat, thin layer. Particles smaller than a few µm adhered to the PI sheet were removed with a silicone adhesive roller. The presence of these particles is a factor that makes thin membrane formation difficult, and if the particles are not removed sufficiently, pinholes will be generated. In previous RBM studies, removal of particles adhering to the resin after spin-coating to form the primer layer was difficult because of the destruction of the primer layer and other adverse effects. Details will be described later, but by incorporating an improved method, we have succeeded in developing a thin Pd alloy layer that could not be realized before. This study used Pd alloys with relatively inexpensive Cu to reduce Pd use and expenses. Alloying Pd overcomes the low durability due to the H<sub>2</sub> embrittlement reported for pure Pd membranes [13]. In particular, the Pd<sub>60</sub>Cu<sub>40</sub> alloy has been reported to have the highest permeability among all PdCu alloys [14]. Unless stated otherwise, the PdCu described in this study is an alloy of Pd<sub>60</sub>Cu<sub>40</sub> (wt. %) composition. To improve the mechanical strength of the PdCu membrane, a porous Ni laver, which did not inhibit H<sub>2</sub> diffusion within the support layer, was subsequently layered on the PdCu. Ni was selected as the metal support material because of its relatively high durability against H<sub>2</sub> permeation and its expected temperature durability owing to its close thermal expansion coefficient with that of Pd metal [15]. The experimental details of the layers formation conditions have been described previously [11]. The following process was used to dissolve the primer layers. The PI sheet was removed using a proprietary alkaline dissolving solution.

#### 2.2. Evaluation principle

The defining equation used to evaluate the composite membrane fabricated in this study is described as follows. To investigate the H<sub>2</sub> permeation performance of the membranes, the H<sub>2</sub> flux was defined. Eq. (1) represents the experimentally calculated H<sub>2</sub> permeation flux,  $J_{\text{H2}}$  [mol m<sup>-2</sup> s<sup>-1</sup>]. Herein, it is common to evaluate their properties based on Fick's law, which states that the concentration gradient is the driving force of diffusion and is expressed as follows (Yun and Ted Oyama, 2011).

$$J_{\rm H_2} = \frac{n_{\rm H_2}}{A_{\rm eff} \cdot t} = \frac{\varphi_{\rm H_2}}{L} \left( P_{1,\rm H_2}^n - P_{2,\rm H_2}^n \right) \tag{1}$$

Here,  $n_{\rm H2}$  [mol],  $A_{\rm eff.}$  [m<sup>2</sup>], t [s],  $\varphi_{\rm H2}$  [mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-n</sup>], L [m],  $P_{1,\rm H2}$  [Pa], and  $P_{2,\rm H2}$  [Pa] are the amount of H<sub>2</sub> permeated through a membrane, effective membrane area, permeation time, H<sub>2</sub> permeability coefficient, Pd-alloy thickness, H<sub>2</sub> partial pressure on the primary side (high H<sub>2</sub> partial pressure), and that on the secondary side (low H<sub>2</sub> partial pressure, assuming 0 Pa), respectively. This relationship provides H<sub>2</sub> permeance of membrane  $\varphi_{\rm H2}/L$ [mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-n</sup>]. The H<sub>2</sub> pressure exponent is *n* (range from 0.5 to 1), also termed the *n*-value. The H<sub>2</sub> partial pressure difference ( $\Delta P_{\rm H2}$  [Pa]) is defined as the difference in H<sub>2</sub> partial pressure between the primary and secondary sides.

The H<sub>2</sub>/He selectivity  $\alpha_{\text{H2/He}}$  was calculated using Eq. (2).

$$\alpha_{\rm H_2/He} = \frac{\varphi_{\rm H_2}}{\varphi_{\rm He}} \tag{2}$$

Here,  $\varphi_{\text{He}}$  [mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-n</sup>] is the He permeability coefficient, and the *n*-value is 1. The evaluation equation for the kinetic analysis is described as follows. The Arrhenius law can describe the relationship between  $\varphi_{\text{H2}}$ and the reciprocal of temperature 1/T [K<sup>-1</sup>]. Thus, the membrane temperature dependence on  $\varphi_{\text{H2}}$  can be explained using Eq. (3).

$$\varphi_{\rm H_2} = A \cdot \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

Here,  $E_a$  [kJ mol<sup>-1</sup>] is the activation energy, A is the preexponential factor, and R [J K<sup>-1</sup> mol<sup>-1</sup>] is the gas constant (8.31 J K<sup>-1</sup> mol<sup>-1</sup>).  $E_a$  and A were calculated by plotting Eq. (3) organized in logarithms.

## 2.3. Membrane characterization

Scanning electron microscopy (SEM, JCM-7000 NeoScope, JEOL Ltd.) was used to observe the fabricated membranes. The layer surfaces and membrane crosssections were observed in several parts. The thicknesses of the PdCu and Ni layers were determined from the SEM observations of the cross-sections. The composition of the PdCu layer was determined from the results measured by electron dispersive X-ray analysis (EDX, JCM-7000



Figure 1. SEM images of a composite membrane. The surfaces of the (a) PdCu layer, (b) porous Ni support layer, and (c), (d) a crosssection of the composite membrane after fabrication.

NeoScope, JEOL). EDX was measured at a randomly selected point on the surface of the PdCu layer. The composition of Pd and Cu in the PdCu layer was quantitatively analyzed using these results.

The H<sub>2</sub> permeability and selectivity of the developed composite membrane were investigated. Details of the experimental setup are as in a previous study [12]. A mixture of H<sub>2</sub> and He gases was supplied at a rate of 100 mL min<sup>-1</sup> to the membrane on the primary side. He gas was selected to detect pinholes and cracks in the membrane and adjust the H2 partial pressure. N2 was used as a sweep gas and flowed at 200 mL min<sup>-1</sup> on the secondary side. Based on a previous study [11], the measurements were performed at 300, 305, 310, and 315°C temperatures. The H<sub>2</sub> partial pressure was controlled at 50, 60, 70, 80, 90, and 100 kPa, by adjusting the He flow rate. The measurements were performed at each temperature and pressure. Finally, a pressure resistance test of the developed membrane was conducted. First, the H<sub>2</sub> permeation flux and H<sub>2</sub>/He selectivity were measured at 80 kPa while the membrane was maintained at 300°C. Subsequently, the He flow was stopped. The H<sub>2</sub> permeation flux at each pressure was then measured by increasing the pressure from 100 kPa in increments of 20 kPa. After the H<sub>2</sub> permeation flux at 200 kPa was measured, the high-pressure system was shut down, and He was resupplied to measure the H<sub>2</sub> permeation flux and H<sub>2</sub>/He selectivity at 80 kPa.

## 3. Results and discussion

#### 3.1. Membrane characterization

The results of the SEM observations are presented as follows. Figure 1 shows the results for the fabricated membrane. Figure 1 (a) shows PdCu, (b) shows the Ni surface, and (c) (d) shows the cross-section of the composite membrane. It was also confirmed that the Ni layer surface was porous, with pores of a few micrometers. From the composite membrane's cross-sectional SEM image, the developed membrane's thicknesses were observed. Cross-sectional SEM observation of the resulting composite membrane revealed the boundary between layers in an image at a magnification of 10.000x (Figure 1 (d)). The observations revealed that a  $0.5 \,\mu m$  PdCu layer was successfully formed. The thicknesses of the PdCu and porous Ni support layers were determined to be 0.5 µm and 9.8 µm, respectively. The developed composite membrane was named PI-PCNX, where X denotes the thickness of

Table 1. EDX composition of PI-PCN0.5 membrane afterfabrication of PdCu layer.

	wt.%	at.%
Pd	$60.37\pm0.31$	$47.64\pm0.25$
Cu	$39.63 \pm 0.52$	$52.36\pm0.68$



Figure 2.  $H_2$  permeation flux to the  $H_2$  partial pressure difference for the PI-PCN 0.5 membrane when measured at different temperatures (300–315°C).

the PdCu layer  $[\mu m]$ . Thus, the membrane obtained in this study was called PI-PCN0.5.

EDX then analyzed the PdCu alloy layer. As shown in **Table 1**, the Pd and Cu concentrations on the surface were around 60 wt.% and 40 wt.%, respectively. The Pd: Cu composition of the surface of the alloy layer resulted from the sputtering process used to fabricate the membrane in RBM, which directly reflected the composition of the target ingot. It is also consistent with the result determined as  $Pd_{60}Cu_{40}$  wt.% by ICP analysis in a previous study [12].

Next, a kinetic analysis of the developed PI-PCN0.5 membrane was performed. The *n*-value, which is an important parameter for investigating the rate-limiting process of  $H_2$  permeation, was calculated. The results of the measurements at different temperatures and pressures are shown in **Figure 2**. In our previous studies [11,12], it was confirmed that the  $H_2$  permeation performance decreased owing to metal interdiffusion when measurements were made at temperatures higher than 320°C, or for long-term periods. Therefore, in this study, measurements were started immediately after the temperature was increased to avoid performance degradation. The *n*-values for the most linear relationship between flux and  $H_2$  partial pressure

difference were determined at several temperatures from  $300-315^{\circ}$ C. The most linear agreement was observed when the *n*-value was equal to 1 for all measured temperatures. A positive correlation with the temperature was also observed for the same measured H<sub>2</sub> partial pressure difference. This temperature dependence was confirmed at all measured pressures ranging from 50–100 kPa. Furthermore, high H<sub>2</sub>/He selectivity values greater than  $\sim 300 (> 99.9\%)$  were stable in all measurements during this experiment. Therefore, it was assumed that the effect of He leakage through the pinhole was negligible. The *n*-values of 1 for all measured temperatures suggest that the surface reaction of the membrane is rate-limiting [9] for the H<sub>2</sub>-permeable membrane developed.

Based on Eq. (3) and the results shown in Figure 2, the activation energy  $E_a$  [kJ mol<sup>-1</sup>] was calculated from the Arrhenius plot. The Arrhenius plot results are shown in **Figure 3**. The  $E_a$  value of PI-PCN0.5 was estimated to be 18.1 kJ mol<sup>-1</sup>. This positive  $E_a$  value demonstrates that the H<sub>2</sub> permeability coefficient increased with temperature. It is known that the range of activation energies for Pd-based membranes is approximately 5.4–38 kJ mol<sup>-1</sup> [16], and the analysis results in this study were also in this range. There are few reports on calculating activation energies for Pd alloy composite membranes of less than a few micrometers. For composite membranes formed by a typical ELP, even if the PdCu layer is successfully thinned, the uniformity and smoothness issues of the layer could make accurate kinetic analysis difficult. Since the Arrhenius plot of this



Figure 3. Arrhenius plots of the H<sub>2</sub> permeability of the PI-PCN0.5 membrane at temperatures from 300-315 °C (*n* = 1).

PI-PCN0.5 shows good linear agreement and is close to the literature values of activation energy measured in a temperature range close to that of the present study using PdCu alloys [17], it is concluded that the current results are reasonable. Considering the PdCu composition and the temperature range of the measurements in this study, it is expected to be a bcc structure with high hydrogen permeability by the PdCu phase diagram [18]. Future work should also consider the correlation between the structural analysis of crystals and activation energies.

Finally, the performance of this membrane produced by the improved RBM was compared to other PdCu alloy composite membranes. **Table 2** compares the experimental conditions, experimentally calculated permeation and selective performance, and thickness of the PdCu layer of the PI-PCN0.5 membrane obtained by improved RBM with PdCu membranes fabricated at other performances. H<sub>2</sub> permeance of the membrane was  $9.89 \times 10^{-6}$  mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup> under 300 °C and 90 kPa. This performance compares favorably with values of other PdCu alloy membranes reported in previous literature, as shown in Table 2. However, an exact comparison is difficult due to the different measurement temperatures and pressures.

Due to the relatively low temperature at which the measurements in this study were performed, improvements to achieve stable measurements at higher temperatures are a topic for future challenge. There is a possible improvement could be achieved by introducing an intermediate barrier layer between the layers to prevent interdiffusion of Pd, Cu and Ni. In addition, although we cannot reveal any results for measurements at temperatures less than 300 °C from our data, it is considered that the progression of interdiffusion is slowed down and the performance degradation is suppressed. Future measurements at lower operating temperatures for RBM membranes would provide additional insights. Since the operating temperature of the membranes can be suppressed, we plan to indicate an operational temperature range, such as the lower limit of the available temperature.

### 3.2. Evaluation of economic performance

This section evaluates the economic performance by estimating the Pd requirement per unit H<sub>2</sub> permeation for the developed membrane compared to that of the conventional

Pd wt.%	Support	Preparation method	<i>L</i> [μm]	T [K]	$\Delta P_{\rm H2}$ [kPa]	$arphi_{ m H2}/L$ [mol m <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup> ]	$\alpha_{ m H2/N2}$	Ref.
94	Vycor	Electroless plating	19	673	194	$2.04 \times 10^{-7}$	-	(Uemiya et al.) [19]
59	Self	Electroless plating	16.7	673	120	$1.01 \times 10^{-6}$	105	(Gade et al.) [20]
95	$Al_2O_3$	Electroless plating	7	753	100	$2.29  imes 10^{-6}$	900	(Zhang et al.) [21]
60	$Al_2O_3$	Electroless plating	5.5	673	100	$6.90 \times 10^{-6}$	4565	(Zhao et al.) [22]
92	$Al_2O_3$	Electroless plating	5	753	100	$2.80  imes 10^{-6}$	1000	(Zhang et al.) [21]
60	$Al_2O_3$	Electroless plating	4.6	673	100	$8.90 \times 10^{-7}$	4126	(Zhao et al.) [22]
59	$Al_2O_3$	Electroless plating	4	783	350	$5.43 \times 10^{-7}$	5000	(Pan et al.) [23]
63	Porous SUS	Vacuum electrodeposition	2	623	69	$4.83 \times 10^{-6}$	-	(Nam et al.) [24]
60	$Al_2O_3$	Electroless plating	1.5	623	100	$4.99  imes 10^{-6}$	93	(Roa and Way) [25]
60	Porous Ni	RF Magnetron sputtering	0.5	573	90	$9.89  imes 10^{-6}$	1497(He)	This work

Table 2. Characteristic comparison between PI-PCN0.5 membrane and PdCu composite membranes from literatures.

rolled PdCu membrane. First, we investigated the pressure resistance performance of the developed membrane. Pressure resistance is vital for the practical application of membranes. Pd-alloy membranes should be operated under high pressures because, based on Eq. (3), the H<sub>2</sub> partial pressure difference value increases with increasing H<sub>2</sub> permeation flux. Therefore, we first investigated the operational permeation performance of PI-PCN0.5 by conducting H<sub>2</sub> permeation tests under high pressure. The results of the pressure resistance test of the PI-PCN0.5 are shown in Figure 4. The graph's horizontal axis represents the H<sub>2</sub> partial pressure difference  $\Delta P_{\text{H2}}$  [Pa]. The left-side vertical axis, shown in red, is the H<sub>2</sub> permeation flux  $J_{H2}$ [mol  $m^{-2} s^{-1}$ ], and the right-side vertical axis, shown in blue, is the H<sub>2</sub>/He selectivity  $\alpha_{\text{H2/He}}$ . As shown in Fig. 4, there was no significant increase in  $J_{\rm H2}$  or significant decrease in  $\alpha_{H2/He}$  before and after the operation of the high-pressure system. Therefore, a pressure resistance performance of up to 200 kPa was confirmed. Many H<sub>2</sub> permeation tests near atmospheric pressure have been reported for Pd-alloy composite membranes thinned down to a few micrometers in previous studies [26,27]. In this study, pressure resistance was confirmed for a 0.5-µm-thick PdCu composite membrane, demonstrating the superiority of the pressure resistance performance.

Finally, the economic and permeation performance benefits of thin membranes were examined. The results in Figure 4 show that for the developed PI-PCN0.5 membrane, a maximum value of 1.44 mol  $m^{-2} s^{-1}$  was measured at 200 kPa and 300°C. Therefore, we estimated the Pd requirement per unit H<sub>2</sub> permeation for PI-PCN0.5 and a conventional rolled Pd<sub>60</sub>Cu<sub>40</sub> membrane (25.4 µm thickness) at 300°C and 200 kPa. **Table 3** compares PI-PCN0.5 and the PdCu that the conventional rolling method prepared. The H<sub>2</sub> permeation flux of the PI-PCN0.5 membrane was



Figure 4.  $H_2$  flux and  $H_2$ /He selectivity of the PI-PCN0.5 membrane tested for pressure-resistant  $H_2$  permeation at 300°C.

higher than that of the rolled PdCu. Thus, it is estimated that PI-PCN0.5 can reduce the Pd requirement per unit  $H_2$  permeation by up to approximately 1/269 (3.72 × 10<sup>-3</sup>) times, assuming that the rolled PdCu is 1.00. Therefore, the composite membrane prepared using RBM was more economical than conventional rolled membranes.

## 4. Conclusion

An economical composite H<sub>2</sub>-permeable membrane was developed using improved RBM for large-scale H<sub>2</sub> separation and purification. The generation of pinholes during membrane formation, which had been a problem when the membrane was made thinner, was overcome by improving the primer layer process. SEM observations showed that thinned PdCu layer was smooth and flat with no noticeable scratches. Based on the cross-sectional SEM observation of the composite membrane, the thicknesses of the PdCu and porous Ni support layers were determined to be 0.5 µm and 9.8 µm, respectively. The results of EDX analysis of the PdCu surface show that the ratio of Pd to Cu is around 60:40 wt.%. Although the PdCu layer to 0.5 µm, which is the smallest, it was still high compared to other literatures on Pd-alloy composite membranes. From the results of the kinetic analysis, the *n*-value was determined to be 1, suggesting that the surface reaction is the ratelimiting step in H<sub>2</sub> permeation. The value of activation energy was calculated to be 18.1 kJ mol<sup>-1</sup>. The H<sub>2</sub> permeation performance of the membrane under high pressure was tested, and a H<sub>2</sub> permeation performance of up to 200 kPa was obtained. The economics of the composite membrane were discussed and compared with those of the conventional rolled Pd<sub>60</sub>Cu<sub>40</sub> membrane (25.4 µm thickness). The Pd requirement per unit H<sub>2</sub> permeation of the developed membrane at 300 °C and 200 kPa was estimated to be approximately 1/269 times that of the rolled PdCu. Thus, improved RBM was demonstrated to be a low-cost method for producing Pd-alloy membranes.

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Table 3. Comparison of the PI-PCN0.5 membrane and the conventional rolled Pd<sub>60</sub>Cu<sub>40</sub> membrane.

$T = 300 \text{ °C}, \Delta P_{\text{H2}} = 200 \text{ kPa}$	PI-PCN0.5 (This study)	Conventional rolled Pd <sub>60</sub> Cu <sub>40</sub> [28]	
The thickness of the Pd <sub>60</sub> Cu <sub>40</sub> layer [µm]	0.5	25.4	
The thickness of the porous Ni layer [µm]	9.8	-	
Permeation flux, $J_{\rm H2}$ [mol m <sup>-2</sup> s <sup>-1</sup> ]	$1.44 \times 10^{-0} * a$	$2.72  imes 10^{-1} * b$	
Pd requirement per unit H <sub>2</sub> permeation	$3.72 \times 10^{-3}$	1.00 (assuming)	

*a*\* Measurement value at 300°C and 200 kPa.

b\* Values calculated at 300°C and 200 kPa regarding literature values.

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