Article

Characterization of Pd₆₀Cu₄₀ Composite Membrane Prepared by a Reverse Build-Up Method for Hydrogen Purification

Yasunari Shinoda ^{1,*} , Masakazu Takeuchi ¹, Hikaru Mizukami ², Norikazu Dezawa ³, Yasuhiro Komo ³, Takuya Harada ¹, Hiroki Takasu ⁴ and Yukitaka Kato ⁴

¹ Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1, Ōokayama, Meguro-ku, Tokyo 152-8550, Japan; m5-takeuchi@nri.co.jp (M.T.); harada.t.an@m.titech.ac.jp (T.H.)

² Department of Transdisciplinary Science and Engineering, School of Environment and Society, Tokyo Institute of Technology, 2-12-1, Ōokayama, Meguro-ku, Tokyo 152-8550, Japan; mizukami.h.aa@m.titech.ac.jp

³ Sanno Co., Ltd., 5-8-8, Tsunashima-Higashi, Kouhoku-ku, Yokohama 223-0052, Japan; dezawa@sanno.co.jp (N.D.); y_komo@sanno.co.jp (Y.K.)

⁴ Laboratory for Zero-Carbon Energy, Institute of Innovative Research, Tokyo Institute of Technology (Tokyo Tech), 2-12-1, Ōokayama, Meguro-ku, Tokyo 152-8550, Japan; takasu.h.aa@m.titech.ac.jp (H.T.); kato.y.ae@m.titech.ac.jp (Y.K.)

* Correspondence: shinoda.y.ae@m.titech.ac.jp; Tel./Fax: +81-3-5734-2964

Citation: Shinoda, Y.; Takeuchi, M.; Mizukami, H.; Dezawa, N.; Komo, Y.; Harada, T.; Takasu, H.; Kato, Y. Characterization of Pd₆₀Cu₄₀ Composite Membrane Prepared by a Reverse Build-Up Method for Hydrogen Purification. *Energies* **2021**, *14*, 8262. <https://doi.org/10.3390/en14248262>

Academic Editors: Majid Bahrami and Ilya Girmik

Received: 8 November 2021

Accepted: 1 December 2021

Published: 8 December 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Abstract: A thin Pd-based H₂-permeable membrane is required to produce high-purity H₂ with high efficiency. In this study, a porous Ni-supported Pd₆₀Cu₄₀ composite H₂-permeable membrane was developed using a reverse build-up method to produce economical H₂ purification. The thickness of the Pd₆₀Cu₄₀ alloy layer produced by the improved membrane production process reached 1.0 μm; it was thinner than the layer obtained in a previous study (3.7 μm). The membrane was characterized by scanning electron microscope, inductively coupled plasma optical emission spectrometer, H₂ permeation test, and Auger microprobe analysis. The permeation tests were performed at 300–320 °C and 50–100 kPa with H₂ introduced from the primary side. The H₂ permeation flux was stable up to ~320 °C. The *n*-value was determined to be 1.0. The H₂ permeance of the membrane was 2.70 × 10^{−6} mol m^{−2} s^{−1} Pa^{−1.0} at 320 °C, after 30 h, similar to those of other 2.2-μm-thick and 3.7-μm-thick Pd₆₀Cu₄₀ composite membranes, suggesting that the adsorption and dissociation reaction processes on the PdCu alloy surface were rate-limiting. The Pd cost of the membrane was estimated to be ~1/30 of the Pd cost of the pure Pd₆₀Cu₄₀ membrane.

Keywords: hydrogen energy; hydrogen purification; membrane separation; palladium; Pd-alloy

1. Introduction

With the aim of creating a low-carbon society, the demand for H₂ as a next-generation energy carrier has increased [1]. H₂ is generally produced by methane steam reforming reactions (MSR) [2,3]. However, because the product is a mixture, H₂ must be separated and purified from the gases [4]. To obtain high-purity H₂ for industrial use, membrane separation methods are effective [5]. H₂ separation membranes composed of ceramics, polymers, and metals can selectively separate H₂ gas [6], with those made of Pd metal reportedly exhibiting excellent H₂ permeability and selectivity [7,8]. The superior H₂ permeability and selectivity of dense Pd to other materials is due to the difference in the mechanism by which H₂ permeates through membranes. Pd has high catalytic activity for H₂ dissociation [9]. Since H₂ permeates through the Pd-based membrane by the solution-diffusion mechanism [10], H₂ with higher purity can be obtained, than from other membranes [6]. Furthermore, Pd-based membranes can continuously separate H₂ gas because of their high H₂ selectivity [11]. This feature allows the reaction system to de-equilibrate the MSR reaction of Equations (1)–(3) to the formation of H₂, resulting

in an improved H₂ yield and the recovery of more H₂, facilitating effective feedstock utilization [12,13].

For these reasons, the use of Pd-based H₂-permeable membranes enables the supply of high-purity H₂ ($\geq 99.99\%$) [14,15], which is required for H₂ fuel cell vehicles (FCVs) [16]. However, it is difficult to produce high-purity H₂ using materials for membranes other than Pd, therefore, Pd-based devices have been widely developed for advanced energy applications in industry [17,18]. However, the widespread use of Pd-based devices is restricted by the high material cost of Pd [19]. To solve this problem, reducing the material cost of the membrane by alloying it with Au [20,21], Ag [22,23], Cu [24–26], and Ru [27,28] have been explored to address these issues. Among these elements, Cu, which is remarkably inexpensive, has been studied. Cu has the additional advantages of resistance to H₂S [29], higher durability in thermal cycling tests than PdAg alloys and other materials, and prevents H₂ embrittlement, which is a problem associated with pure Pd membranes [30]. In particular, the Pd₆₀Cu₄₀ wt.% (Pd₄₇Cu₅₃ at.%) alloy has the highest H₂ permeability at 350 °C among the PdCu alloys reported thus far [8,31]. For these reasons, H₂-permeable membranes of Pd₆₀Cu₄₀ alloy have been developed.

To promote the industrial feasibility of Pd-based H₂-permeable membranes, a method to reduce the Pd requirement by making the Pd alloy layer thinner has been investigated [22,32,33]. Making the Pd alloy layer thinner reduces the material cost and lowers the H₂ permeation resistance in the membrane, thus improving the performance. However, although the material cost can be reduced by thinning the Pd alloy layer, the membrane's durability is significantly reduced, hampering its industrial application as a stand-alone membrane. Therefore, Pd-based composite membranes formed on a porous support consisting of Vycor glass, ceramics, and porous stainless steel (PSS) have been developed [6]. Among these materials, composite membranes supported by tube-type porous ceramics are commonly used [34].

Conversely, ceramic supports are vulnerable to prolonged use and thermal cycling. They are also prone to delamination from the thin Pd layer [35], limiting the processing size of the membrane [36–38]. Therefore, the development of ceramic-supported composite H₂-permeable membranes is limited when considering the large area of the membranes to realize large scale H₂ production. Therefore, a composite membrane with a Ni support layer is considered in this study. The use of metal supports can solve the problem of ceramic-supported composite membranes. In addition, it is confirmed it prepares larger areas than the case of ceramic tube-type membrane reactors. Therefore, it is expected to obtain H₂ permeability and selectivity, allowing large-scale H₂ production. In particular, Ni metal has an advantage in that it can easily be formed on a Pd alloy membrane at a low cost by electroplating. Furthermore, since Ni's thermal expansion coefficient is similar to that of Pd, peeling is unlikely to occur between the Ni support layer and the Pd alloy layer.

In this study, a metal-supported composite H₂-permeable membrane suitable for large-scale H₂ production was developed using a reverse build-up method [39]. Conventional Pd alloy freestanding membranes are fabricated using the rolling method, but typical membrane thicknesses are greater than 20 µm, resulting in high cost and low H₂ permeability [22,26]. In addition, in the commonly used electroless plating (ELP) method of forming a Pd alloy layer on porous ceramic supports, it is not easy to control the thickness of the Pd alloy layer. It is generally known that a minimum thickness of 5 µm is required to produce a defect-free membrane [40]. As a result, the uniformity of the membrane is low, and there are problems in achieving both H₂ permeability and H₂ selectivity [6].

In contrast, in the reverse build-up method, the Pd alloy layer is deposited on a smooth surface to form a metal support, to achieve a Pd alloy layer with high smoothness and uniformity. This method allows the thickness of the Pd alloy layer to be reduced to a

few microns or less and allows the fabrication of a smooth and thinner membrane with a thickness of up to approximately 1.0 μm membrane without pinholes. In the authors' previous study [41], a $\text{Pd}_{60}\text{Cu}_{40}$ alloy layer fabricated using the reverse build-up method was successfully thinned down to 3.7 μm . In this study, a metal-supported composite H_2 -permeable membrane was developed with a $\text{Pd}_{60}\text{Cu}_{40}$ alloy layer thinned down to 1.0 μm , by improving the membrane production method. Therefore, this research has succeeded in fabricating a thin 1.0- μm $\text{Pd}_{60}\text{Cu}_{40}$ layer, which was previously impossible, by improving the process of primer layer formation. Furthermore, an investigation of the effect of thinning the Pd alloy layer on H_2 permeability and selectivity was conducted. Finally, the impact of operating this low-cost thin membrane at high temperatures was investigated and evaluated to expand its industrial applications.

2. Materials and Methods

2.1. Reverse Build-Up Method

Composite membranes were developed using the reverse build-up method based on previous studies [39,41]. One of the most critical steps in the fabrication of thin composite membranes is the formation of a primer layer. In the reverse build-up method, the surface condition of the primer layer is carried over to the $\text{Pd}_{60}\text{Cu}_{40}$ alloy layer, so the thin $\text{Pd}_{60}\text{Cu}_{40}$ alloy layer formed by sputtering in the next step, reflects the effect of surface irregularities and defects in the primer layer. Therefore, the H_2 permeability and selectivity of the composite membrane are greatly affected. Moreover, the conventional resin and spin-coating conditions are examined to form a smooth and uniform primer layer. The improved process was carried out as follows.

The cleaning method of a glass substrate was improved against the conventional method, to form a primer layer with a smoother and more uniform surface. First, a 72×52 mm substrate (Matsunami Glass Co., Ltd., Osaka, Japan) was cleaned with ethanol in an ultrasonic generator for 30 min. Then, one side of the substrate was wiped, and the substrate was installed in the spin-coater with the wiped side facing down. The surface was then dried by spinning it at 1000 rpm for 5 min to prepare the primer layer.

Next, a primer layer of the polymer was formed on the glass substrate by spin coating. The polymer solution was prepared according to the following procedure: 1 g of S-Lec BX-L butyral resin (Sekisui Chemical Co., Ltd., Osaka, Japan) was added to 25 g of toluene, and the mixture was stirred at room temperature for 6 h. Then, 25 g of ethanol was added so that the weight ratio of toluene to ethanol was 1:1, and the mixture was stirred at room temperature for 12 h. After the polymer solution was thoroughly mixed, the glass substrate was placed in a spin coater (Active Co., Ltd., Saitama, Japan). The polymer solution (5 mL) was dropped onto the glass substrate using a syringe (Terumo Co., Ltd., Tokyo, Japan) and spread evenly over the entire surface. The substrate was spun at 100 rpm for 500 s, and a primer layer was prepared on the glass substrate. The coated substrate was stored in a desiccator at room temperature and allowed to dry naturally for at least 24 h. The above procedure improved the formation of the primer layer, which is an important step in the fabrication of thin membranes by magnetron sputtering. It was then possible to form a 1.0 μm $\text{Pd}_{60}\text{Cu}_{40}$ alloy layer, which was difficult to fabricate in a previous study.

In this study, a $\text{Pd}_{60}\text{Cu}_{40}$ alloy layer was introduced as an H_2 -permeable membrane. $\text{Pd}_{60}\text{Cu}_{40}$ alloy ($\text{Pd}_{60}\text{Cu}_{40}$, 99.9 wt.%, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan) target with a diameter of 100 mm was used for high-frequency magnetron sputtering (Takao Co., Ltd., Kanagawa, Japan). The glass substrate on which the primer layer was formed by spin coating was installed in the sputtering apparatus as the cathode. Sputtering was performed at a pressure of Ar under vacuuming for 48 min.

A porous Ni support was formed by electroplating to improve the mechanical strength of the thin $\text{Pd}_{60}\text{Cu}_{40}$ alloy layer. Next, 2 L of 60% Ni sulfamate solution was prepared as an electroplating bath. In addition, 5 mL of a Ni-plating additive, based on a previous study [42], was added dropwise to the bath. The temperature of the electroplating bath, rotation speed of the magnetic stirrer, and pH of the bath were adjusted to 50 $^{\circ}\text{C}$, 800 rpm,

and <5.0 , respectively. A pure Ni plate (99%, Nilaco Co., Ltd., Tokyo, Japan) was used as the anode, and the substrate sputtered with a thin Pd₆₀Cu₄₀ alloy layer was used as the cathode. The anode and cathode plate were fixed with jigs, electricity was supplied from the power supply device (YAMABISHI Co., Ltd., Tokyo, Japan), and the current density was 0.01 A cm^{-2} for 1 h.

Finally, the primer layer was dissolved in ethanol, and the composite membrane was removed from the glass substrate to complete the process.

2.2. Sample Characterization

The composite membranes fabricated by the reverse build-up method in this study were named PCNX, where X is the thickness of the Pd₆₀Cu₄₀ alloy layer (μm). Scanning electron microscopy (SEM, Hitachi Co., Ltd., Tokyo, Japan) was used to observe the fabricated composite membranes. Cross-sectional SEM images were used to determine the thickness of each membrane layer.

PdCu alloy membrane samples were prepared to investigate the composition of the fabricated membranes. The samples were obtained by magnetron sputtering on a glass substrate directly at Ar pressure of 0.2 Pa for 24 min. The chemical composition (mg L^{-1}) of the obtained PdCu alloy membrane samples was evaluated using an inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent Technologies Co., Ltd., Cheshire, UK).

Figure 1a shows the experimental set-up used for the H₂ permeation tests. Figure 1b shows a cross-sectional view of the composite membrane fabricated in this study. The obtained composite membrane was cut into a circular shape, as shown in Figure 1c, and the diameter of the cut membrane sample was 12 mm. The sample was sandwiched between two stainless steel gaskets (316 L stainless steel VCR face seal fitting, 1/4 in Swagelok Co., Ltd., Solon, OH, USA). Thus, the membrane sample's effective surface area for H₂ permeation was the inner part of the membrane surface that was not on the gasket. The gasket had outer and inner diameters of 11.9 and 5.6 mm, respectively. The composite membrane was then installed in the test chamber of the permeation test apparatus with the surface of the Pd₆₀Cu₄₀ alloy layer on the primary side of the test chamber. The area around the composite membrane was covered with a mantle heater, and thermocouples were installed to adjust the composite membrane temperature.

The properties of the PCN1.0 membrane fabricated in this study and the parameters used in the H₂ permeation test are listed in Table 1. The composition of the PdCu alloy (wt.%), the thickness of the PdCu alloy layer (μm) and porous Ni support layer (μm), and the total membrane thickness (μm) of the PCN1.0 membrane are shown. The effective diameter of the membrane sample matched the inner diameter of the gasket. Therefore, the effective membrane surface area of the membrane sample, determined based on the inner diameter, is shown in Table 1.

Table 1. Summary of sample characteristics.

Sample Specifications	PCN1.0
wt.% Pd:Cu	60:40
Thickness of the PdCu alloy layer (μm)	1.0
Thickness of porous Ni support layer (μm)	12
Total membrane thickness (μm)	13
Effective diameter of the membrane sample (mm)	5.6
Effective membrane surface area of the membrane sample (mm^2)	24.6

The flow rate of each gas used in the H₂ permeation test was adjusted using a mass flow controller (MFC, KOFLOC Co., Ltd., Kyoto, Japan). A mixture of 20 mL min^{-1} of H₂ and $4\text{--}20 \text{ mL min}^{-1}$ of He was supplied to the primary side, and 100 mL min^{-1} of N₂ as a sweep gas was provided to the secondary side. The H₂ and He permeated through the composite membrane, and the N₂ sweep gas was sent to a gas chromatograph

with a thermal conductivity detector (TCD-GC, SHIMADZU Co., Ltd., Kyoto, Japan) for compositional analysis.

Figure 1. Apparatus for the measurement of the H₂ permeation performance of composite membranes, (a) experimental set-up, (b) image diagram of the composite membrane, (c) photos of surfaces of Pd₆₀Cu₄₀ alloy layer and porous Ni support layer.

Measurements were made at four temperatures of 300, 305, 310, and 320 °C and five pressures of 50, 60, 70, 84, and 100 kPa for the H₂ partial pressure, $\Delta P_{H_2}^n$ (Paⁿ) to determine the pressure exponent n called the n -value, referring to a previous study [41]. The n -value explains the exponential dependence of the H₂ permeation flux on H₂ partial pressure and usually ranges from 0.50 to 1.0. Subsequently, H₂ permeation tests were performed on the PCN1.0 membrane at 320 °C. The H₂ partial pressure difference ($\Delta P_{H_2}^n$ (Paⁿ)) between the primary and secondary, is defined by Equation (4) below:

$$\Delta P_{H_2}^n = P_{H_2, \text{feed}}^n - P_{H_2, \text{perm}}^n [\text{Pa}^n] \quad (0.50 \leq n \leq 1.0) \quad (4)$$

where $P_{H_2, \text{feed}}$ [Pa] is the partial pressure of H₂ on the primary side of the chamber, $P_{H_2, \text{perm}}$ [Pa] is the partial pressure of H₂ on the secondary side of the chamber. $P_{H_2, \text{perm}}$ is significantly smaller than $P_{H_2, \text{feed}}$ and thus, it can be ignored. It is well known that the mechanism of H₂ permeation through Pd-based membranes generally follows the solution-diffusion mechanism, and the driving force is the H₂ partial pressure difference [6,43]. The steps of H₂ permeation are as follows: H₂ is adsorbed on the surface of the Pd membrane and dissociates into hydrogen atoms. The atoms then dissolve into the Pd bulk and diffuse through the bulk. Next, hydrogen atoms associate on the Pd surface and recombine into H₂. Finally, H₂ is desorbed from the surface [6,43].

The H₂ permeation flux on the secondary side of the test chamber, J_{H_2} (mol m⁻² s⁻¹), was assumed to be defined by Equation (5):

$$J_{H_2} = \frac{\varphi_{H_2}}{L} (P_{H_2, \text{feed}}^n - P_{H_2, \text{perm}}^n) [\text{mol m}^{-2} \text{s}^{-1}] \quad (5)$$

where L (μm) is the $\text{Pd}_{60}\text{Cu}_{40}$ alloy layer thickness, φ_{H_2} ($\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-n}$) is the H_2 permeability coefficient, and φ_{H_2}/L ($\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-n}$) is the H_2 permeance. The relationship between the Pd-based membrane thickness and the n -value has been reported [6]. When diffusion in Pd bulk is the rate-limiting step, the n -value is 0.5. This always follows Sievert's Law in a thick ($5 \mu\text{m} <$) Pd-based membrane, as shown in Equation (6) [44].

$$J_{\text{H}_2} = \frac{\varphi_{\text{H}_2}}{L} (P_{\text{H}_2, \text{feed}}^{0.5} - P_{\text{H}_2, \text{perm}}^{0.5}) [\text{mol m}^{-2} \text{s}^{-1}] \quad (n = 0.5) \quad (6)$$

Conversely, when the n -value is near 1.0, it matches the Pd-alloy membranes' rate-limiting surface reaction (adsorption and dissociation reaction).

The selectivity of H_2 over He, $\alpha_{\text{H}_2/\text{He}}$ (–), was calculated using Equation (7). Here, φ_{He} [$\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-n}$] is the He permeability coefficient, and n of φ_{H_2} and φ_{He} is 1.0.

$$\alpha_{\text{H}_2/\text{He}} = \frac{\varphi_{\text{H}_2}}{\varphi_{\text{He}}} \quad (n = 1.0) \quad (7)$$

The relationship between φ_{H_2} and T can be generally described by Arrhenius law. The temperature dependence of the H_2 permeability coefficient can be defined by Equation (8) [45]:

$$\varphi_{\text{H}_2} = A \exp\left(-\frac{E_a}{RT}\right) [\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-n}] \quad (8)$$

where R is the universal gas constant, $8.31 \text{ J mol}^{-1} \text{K}^{-1}$, and T is the absolute temperature (K). The activation energy, E_a (kJ mol^{-1}), and the pre-exponential factor at 300–320 °C, A , were obtained from Equation (8). Further, Equation (9) can be obtained from Equation (8). Then based on Equation (8), $\ln(\varphi_{\text{H}_2}/L)$ and the reciprocal of temperature, $1/T$ (K^{-1}), have a linear relationship.

$$\ln\left(\frac{\varphi_{\text{H}_2}}{L}\right) = -\frac{E_a}{RT} + \ln\left(\frac{A}{L}\right) \quad (9)$$

When H_2 -permeable membranes are used in combination with particulate devices such as fuel cells, they must be used at high temperatures. Finally, a high-temperature measurement was performed during the H_2 permeation test, at 320 °C, with PCN1.0, to investigate the cause of the degradation of the membrane performance at high temperatures (400 °C). It is known that metal interdiffusion progresses at high temperatures, and the membrane performance is significantly degraded [46]. A change in the performance of PCN1.0 during the high-temperature operation was observed. The surface of the PdCu alloy layer and the cross-section of PCN1.0 were analyzed after the H_2 permeation test to observe the phenomenon of metal interdiffusion using an FE Auger microprobe (JEOL Co., Ltd., Tokyo, Japan).

3. Results and Discussion

3.1. Sample Characterization

Figure 2 shows the SEM images of the prepared PCN1.0 membrane, being: (a) surface of the $\text{Pd}_{60}\text{Cu}_{40}$ alloy layer, (b) surface of the porous Ni layer, and (c) cross-section of PCN1.0. As shown in Figure 2a, no noticeable scratches or pinholes were observed on the $\text{Pd}_{60}\text{Cu}_{40}$ alloy surface layer. From Figure 2c, the thickness of the developed PCN1.0 membrane was determined to be 1.0 μm for the $\text{Pd}_{60}\text{Cu}_{40}$ alloy layer and 12 μm for the porous Ni support layer. Using the reverse build-up method, a composite membrane with a thin $\text{Pd}_{60}\text{Cu}_{40}$ alloy layer was successfully developed.

Figure 2. SEM images of PCN1.0: (a) the surface of the Pd₆₀Cu₄₀ alloy layer, (b) the surface of the porous Ni support layer, (c) the cross-section of the composite membrane after fabrication.

The composition of the Pd₆₀Cu₄₀ alloy layer formed by magnetron sputtering was analyzed using ICP-OES. The elemental ratio (at.%) and the weight ratio (wt.%) of Pd and Cu, respectively, were determined using the ICP-OES analytical results. The analytical and calculation results are presented in Table 2. The results confirmed that the Pd₆₀Cu₄₀ alloy membrane formed by magnetron sputtering consisted of Pd₆₀Cu₄₀ wt.% (Pd₄₇Cu₅₃ at.%), and that there was no change in the Pd₆₀Cu₄₀ alloy ratio during the membrane deposition process by magnetron sputtering.

Table 2. Results of ICP-OES analysis and calculated ratio after sputtering.

Concentrations	Analyte Elements	
	Pd	Cu
Analyzed concentration (mg L ^{−1})	28.51	18.89
Calculated atomic ratio (at.%)	47.06	52.94
Calculated weight ratio (wt.%)	60.15	39.85
Sputtering target weight ratio (wt.%)	60	40

3.2. Evaluation of H₂ Permeation Measurement

The obtained PCN1.0 membrane was tested for H₂ permeation at $\Delta P_{H_2} = 50, 60, 70, 84, \text{ and } 100 \text{ kPa}$ at 300, 305, 310, and 320 °C. The n -value can be obtained by measuring the H₂ permeation flux, J_{H_2} at different P_{H_2} values, and feed. Figure 3 shows the results of J_{H_2} versus ΔP_{H_2} for $n = 0.5, 0.6, 0.7, 0.8, 0.9, \text{ and } 1.0$, at 320 °C. The pressure dependence of J_{H_2} was investigated to determine the n -value of the PCN1.0 membrane. The coefficient of determination R^2 was closest to 1 and showed a linear form when $n = 1.0$. The n -value of 1.0 was also typical for the other thin membranes reported in other studies [19,32], confirming that this result of $n = 1.0$ was appropriate. The other results at 300, 305, and 310 °C also showed a shape similar to that shown in Figure 3, with the graph at $n = 1.0$ having the best linear match.

Figure 4 shows the H₂ permeance ($n = 1.0$) calculated based on Equation (5), ϕ_{H_2}/L , and H₂/He selectivity calculated based on Equation (7), $\alpha_{H_2/He}$, as a function of time after reaching 320 °C. A few hours after the start of the test, the values of ϕ_{H_2}/L and $\alpha_{H_2/He}$ were stable. After 30 h, ϕ_{H_2}/L and $\alpha_{H_2/He}$ were $2.70 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1.0}$ and 377, respectively, indicating high H₂ permeability and selectivity. The values of $\alpha_{H_2/He}$ were similar to those reported in other studies [47]. It was suggested that the effect of membrane pinholes was negligible.

Figure 3. H₂ permeation flux through PCN1.0 at 320 °C as a function of the transmembrane pressure difference, (a) $n = 0.5$, 0.6, 0.7, (b) $n = 0.8$, 0.9, 1.0.

Figure 4. H₂ permeance, ϕ_{H_2}/L and H₂/He selectivity, $\alpha_{H_2/He}$ as a function of time for PCN1.0 subjected to H₂ permeation at 320 °C.

Figure 5 shows the relationship between the inverse of temperature, $1/T$ (K), and $\ln(\phi_{H_2}/L)$ based on Equation (9).

From the results of the Arrhenius plot shown in Figure 5, the activation energy, E_a , and pre-exponential factor at 300–320 °C, A , were determined. The value of E_a was calculated to be 9.43 kJ mol⁻¹. The value of E_a was similar to that of other thin membranes studied [22].

Table 3 compares the H₂ permeability and selectivity of the thin membranes reported in other studies. The PCN1.0 membrane prepared in this study demonstrated high H₂ permeance, H₂ permeability coefficient, and H₂/He selectivity at 320 °C.

Figure 5. Arrhenius plot of the H_2 permeability coefficient, φ_{H_2} ($n = 1.0$) of PCN1.0 vs. inverse temperature, $1/T$; test temperature ranges from 300 to 320 °C. From the slope of the best fit line, E_a was calculated to be 9.43 kJ mol $^{-1}$.

Table 3. Comparison of PCN1.0 with literature values.

Selective Layer	Thickness of Selective Layer	Thickness of Supported Layer	T	ΔP	H_2 Permeability Coefficient	H_2 Permeance	H_2/N_2 Selectivity	n	Ref.
Materials	μm	μm	$^{\circ}C$	kPa	$mol\ m^{-1}\ s^{-1}\ Pa^{-n}$	$mol\ m^{-2}\ s^{-1}\ Pa^{-n}$			
Pd/ γ - Al_2O_3 with Pd	1	Alumina	450	100		1.06×10^{-5}	23	1	[48]
Pd/ γ - Al_2O_3 with Pd	1	Alumina	400	75		6.7×10^{-7}	23	1	
Pd/ γ - Al_2O_3	1	Alumina	300			2×10^{-7}	>200 (H_2/He)	1	[49]
Pd	1	Alumina	450	68		2.06×10^{-6}	780	1	[50]
Pd-Ni alloy	1	Alumina	450	68		2.06×10^{-6}	317	1	
PdNi $_{0.2-0.3}$ /Ni powder	1	Stainless steel	450	68		2.21×10^{-6}	>400	1	
PdNi $_{0.2-0.3}$ (at.%)	1–2	PSS/Ni	450		5.90×10^{-9}			0.5	
Pd $_{99.7}$ Nb $_{0.3}$ (at.%)	1–2	PSS/Ni	450		2.8×10^{-9}			0.5	
Pd	1	Alumina	350	100		3.3×10^{-6}		1	[51]
Pd	1	Ni microstructured support grid	350	100		3.6×10^{-6}		1	[46]
Pd $_{77}$ Ag $_{23}$ (wt.%)	1.4	microchannel	300			1.70×10^{-10}	5700–390	0.5	[52]
Pd $_{77}$ Ag $_{23}$ (wt.%)	1.2	YSZ-doped Al_2O_3 hollow fiber	450	100	5.81×10^{-12}		1583	1	[53]
Pd	1.2	YSZ-doped Al_2O_6 hollow fiber	450	100	3.55×10^{-12}		2600	1	

Table 3. Cont.

Selective Layer	Thickness of Selective Layer	Thickness of Supported Layer	<i>T</i>	ΔP	H ₂ Permeability Coefficient	H ₂ Permeance	H ₂ /N ₂ Selectivity	<i>n</i>	Ref.
Pd	1.3	hollow-fiber α -alumina	460	105		$8.0\text{--}40.0 \times 10^{-7}$	160–5500	1	[54]
PdAg	1	ZrO ₂	400	100		8.00×10^{-6}	500	1	[55]
Pd ₆₀ Cu ₄₀ (wt.%)	1.5	Al ₂ O ₃	350	100	5.7×10^{-9}	3.81×10^{-3}	93	0.5	[56]
Pd	1	anodized alumina	400	101		7.40×10^{-8}	200	1	[57]
Pd ₆₀ Cu ₄₀ (wt.%)	1.0	Porous Ni	320	84	2.70×10^{-12}	2.70×10^{-6}	377 (H ₂ /He)	1	This study
Pd ₆₀ Cu ₄₀ (wt.%)	1.0	Porous Ni	320	84	7.83×10^{-10}	7.83×10^{-4}	377 (H ₂ /He)	0.5	This study

Next, the H₂ permeation performance and membrane thickness of the PCN1.0, PCN2.2, and PCN3.7 membranes were developed using the reverse build-up method and pure Pd₆₀Cu₄₀ alloy membranes prepared by the conventional rolling method were compared (Table 4).

Table 4. Comparison of H₂ permeation of PCN1.0, PCN2.2, and PCN3.7 membranes.

<i>T</i> = 320 °C, ΔP_{H_2} = 84 kPa <i>n</i> = 1.0	This Study PCN3.7	This Study PCN2.2	This Study PCN1.0	Reference Pd ₆₀ Cu ₄₀ [58,59]
Layer thickness (μm)	Pd ₆₀ Cu ₄₀ : 3.7 Porous Ni: 13	Pd ₆₀ Cu ₄₀ : 2.2 Porous Ni: 15	Pd ₆₀ Cu ₄₀ : 1.0 Porous Ni: 12	Pd ₆₀ Cu ₄₀ : 25.4
H ₂ permeation flux, <i>J</i> _{H2} (mol m ^{−2} s ^{−1})	2.22×10^{-1}	2.24×10^{-1}	2.27×10^{-1}	1.93×10^{-1}
H ₂ permeability coefficient, φ_{H_2} (mol m ^{−1} s ^{−1} Pa ^{−<i>n</i>})	9.65×10^{-12}	5.87×10^{-12}	2.70×10^{-12}	5.84×10^{-11}
H ₂ permeance, φ_{H_2}/L (mol m ^{−2} s ^{−1} Pa ^{−<i>n</i>})	2.64×10^{-6}	2.67×10^{-6}	2.70×10^{-6}	2.29×10^{-6}

The H₂ permeance of a pure Pd₆₀Cu₄₀ (thickness: 25.4 μm) alloy membrane at 320 °C was determined using the values of H₂ permeance at temperatures of ~320 °C in the literature [58,59]. Additionally, the H₂ permeation flux was calculated by multiplying that value by the pressure value reported in the literature. Furthermore, the H₂ permeance at 320 °C and ΔP_{H_2} = 84 kPa was calculated by dividing the flux value by the H₂ partial pressure difference of 84 kPa, which was the experimental condition used in this study. It was confirmed that the H₂ permeation flux value was improved by 18% compared with the PCN1.0 membrane and the pure Pd₆₀Cu₄₀ alloy membrane. Because the Pd₆₀Cu₄₀ alloy layer thickness was reduced to 1.0/25.4, the overall reduction in Pd usage by ~1/30 was achieved.

Comparison of the PCN1.0, PCN2.2, and PCN3.7 membranes revealed that the H₂ permeance values were almost unchanged, suggesting that the adsorption and dissociation reaction processes on the PdCu alloy surface were rate-limiting. Therefore, it is suggested that these PCN membranes have nearly the exact value of H₂ permeance due to the pronounced rate-limiting condition of the surface reaction. Consequently, it was confirmed that the performance of the Pd alloy itself can be evaluated in terms of surface reaction by thinning down to ~1 μm, as in this study.

3.3. Analysis of the Membrane after H₂ Permeation Test

The H₂ permeation flux and H₂/He selectivity of the PCN1.0 were stable at 320 °C. Therefore, it was investigated whether the membrane could be operated at a high tempera-

ture (400 °C). Figure 6 illustrates the change in H₂ permeation flux and H₂/He selectivity with time when the H₂ permeation test was continued at 320 °C for 25 h continuously, then increased to 400 °C after one hour and then decreased back to 320 °C.

Figure 6. Results of H₂ permeability coefficient, ϕ_{H_2} , and H₂/He selectivity, $\alpha_{H_2/He}$ as a function of time for PCN1.0 subjected to H₂ permeation at 320 and 400 °C. The magnified view from 25 to 27 h is shown on the right. The yellow area indicates the time when the temperature was increased to 400 °C.

When the temperature was raised to 400 °C, the performance increased immediately but quickly deteriorated, and the H₂ permeation flux decreased by approximately 40% compared with that before the temperature was raised. The performance did not return to normal when the temperature was increased to 320 °C again, suggesting that the membrane had degraded. The main reason for the degradation of performance after high-temperature measurement was thought to be either the change in the crystal structure or the intermetallic diffusion. However, since the crystal structure did not change from the reported phase diagram [19], the cause of the degradation was concluded to be intermetallic diffusion. Therefore, the surface of the PdCu alloy layer of the PCN1.0 membrane after the measurement in Figure 6 was analyzed.

Figure 7 shows the SEM images of the surface of the PdCu alloy layer analyzed by Auger microprobe and the results of Auger profiles. The i, ii, and iii points were randomly selected and analyzed on the surface of the PdCu alloy layer before the H₂ permeation test. The points iv, v, and vi were randomly selected on the surface of the PdCu alloy layer after the H₂ permeation test.

Ni was not detected on the PdCu alloy surface before the H₂ permeation test. However, Ni was observed on the surface of the PdCu alloy layer after the permeation test, and the concentration ratio of Pd significantly decreased (Figure 7d). Furthermore, on the PdCu alloy surface after the H₂ permeation test, similar Ni ratios were detected at all three locations (iv v, vi), suggesting that the diffusion of Ni into the PdCu layer occurred throughout the entire PdCu alloy layer (Figure 7d).

Next, the ratio of each atom in the PCN1.0 cross-section to the depth direction was investigated with respect to the PdCu alloy surface. Figure 8 shows the Auger microprobe analysis results of PCN1.0 before and after the H₂ permeation test at 320–400 °C. From the cross-sectional SEM image, the zero point in the depth direction was determined to be the surface of the PdCu alloy layer.

Figure 7. SEM images and Auger microprobe analysis results of the PdCu alloy surface before and after the H₂ permeation test. SEM image of the surface of PdCu alloy layer: (a) before the test, (b) after the test. Auger microprobe analysis result of the surface of PdCu alloy layer: (c) before the test, (d) after the test.

Figure 8. Auger microprobe results of the PCN1.0 membrane. Cross-sectional SEM images of PCN1.0 membrane (a) before the H₂ permeation test (b) after the test (“+” indicates the analyzed point); and (c) concentrations of three elements, Pd, Cu, and Ni, before and after the test are shown in membrane depth (μm).

Comparing the results before and after the H₂ permeation test in the PdCu alloy layer, the ratio of Pd and Cu decreased after the H₂ permeation test, and the balance of Ni increased (Figure 8c). In addition, Ni diffused near the PdCu alloy surface and was uniformly distributed

at the layer interface (Figure 8c). Intermetallic interdiffusion between the layers occurred before and after the H₂ permeation tests of the PCN1.0 membrane at 400 °C for one hour. In future work, an intermediate layer as a diffusion barrier layer [60–62] will be inserted between the PdCu alloy and the Ni layers to address membrane degradation at high temperatures.

4. Conclusions

To achieve high-efficiency and high-purity H₂ at a low cost, a thinner (1.0 µm) Pd₆₀Cu₄₀ composite H₂-permeable membrane was successfully developed using the reverse build-up method, by improving the smoothness of the primer layer in the formation process. H₂ permeation tests were performed at 300–320 °C and 50–100 kPa. The *n*-value was determined to be 1.0. As a result, it was suggested that the surface reaction was rate-limiting. The H₂ permeance of the membrane was $2.70 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1.0}$ at 320 °C after 30 h. This value was similar to that of other 2.2-µm-thick and 3.7-µm-thick Pd₆₀Cu₄₀ composite membranes, suggesting that the adsorption and dissociation reaction processes on the PdCu alloy surface were rate-limiting. The Pd cost of the PCN1.0 was calculated to be ~1/30 of the Pd cost of the pure Pd₆₀Cu₄₀ alloy membrane. It was concluded that this method can be used to fabricate an H₂-permeable membrane at a low cost for H₂ purification.

Author Contributions: Formal analysis, Y.S.; investigation, M.T. and H.M.; writing—original draft, Y.S.; writing—review and editing, N.D., Y.K. (Yasuhiro Komo), T.H., H.T. and Y.K. (Yukitaka Kato); supervision, Y.K. (Yukitaka Kato). All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors thank Katsumi Yoshida and Anna Gubarevich at the Laboratory for Zero-Carbon Energy, Institute of Innovative Research, Tokyo Institute of Technology, for their support in obtaining the SEM images. The authors also thank the Division of Materials Analysis, Ōokayama, Open Facility Center, Tokyo Institute of Technology, for material analytical data measurement.

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

<i>A</i>	Pre-exponential factor at 300–320 °C (-)
Au	Gold
Ar	Argon
Cu	Copper
<i>E_a</i>	Activation energy (kJ mol ⁻¹)
H ₂	Hydrogen
He	Helium
<i>J_{H2}</i>	H ₂ permeation flux on the secondary side of the test chamber (mol m ⁻² s ⁻¹)
<i>L</i>	Pd ₆₀ Cu ₄₀ layer thickness (µm)
<i>n</i>	H ₂ pressure exponent (-) ($0.50 \leq n \leq 1.0$)
N ₂	Nitrogen
Ni	Nickel
<i>P_{H2,feed}</i>	Partial pressure of H ₂ on the primary side of the chamber (Pa)
<i>P_{H2,perm}</i>	Partial pressure of H ₂ on the secondary side of the chamber (Pa)

Pd	Palladium
PdAg	Palladium-silver
PdCu	Palladium-copper
R	Universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
R^2	Coefficient of determination (-)
Ru	Ruthenium
S	H_2 -permeable membrane area (m^2)
T	Absolute temperature (K)
$\alpha_{\text{H}_2/\text{He}}$	H_2/He selectivity (-)
φ_{H_2}	H_2 permeability coefficient ($\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-n}$) ($0.50 \leq n \leq 1.0$)
φ_{He}	He permeability coefficient ($\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-n}$) ($n = 1.0$)
φ_{H_2}/L	H_2 permeance ($\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-n}$) ($0.50 \leq n \leq 1.0$)

References

1. Itoh, N.; Kikuchi, Y.; Furusawa, T.; Sato, T. Tube-wall catalytic membrane reactor for hydrogen production by low-temperature ammonia decomposition. *Int. J. Hydrogen Energy* **2021**, *46*, 20257–20265. [\[CrossRef\]](#)
2. Anzelmo, B.; Wilcox, J.; Liguori, S. Natural gas steam reforming reaction at low temperature and pressure conditions for hydrogen production via Pd/PSS membrane reactor. *J. Memb. Sci.* **2017**, *522*, 343–350. [\[CrossRef\]](#)
3. Abbas, H.F.; Wan Daud, W.M.A. Hydrogen production by methane decomposition: A review. *Int. J. Hydrogen Energy* **2010**, *35*, 1160–1190. [\[CrossRef\]](#)
4. Qyyum, M.A.; Chaniago, Y.D.; Ali, W.; Saulat, H.; Lee, M. Membrane-assisted removal of hydrogen and nitrogen from synthetic natural gas for energy-efficient liquefaction. *Energies* **2020**, *13*, 5023. [\[CrossRef\]](#)
5. Endo, N.; Dezawa, N.; Komo, Y.; Maeda, T. One-step electroplating of palladium–copper alloy layers on a vanadium membrane for hydrogen separation: Quick, easy, and low-cost preparation. *Int. J. Hydrogen Energy* **2021**, *46*, 32570–32576. [\[CrossRef\]](#)
6. Yun, S.; Ted Oyama, S. Correlations in palladium membranes for hydrogen separation: A review. *J. Memb. Sci.* **2011**, *375*, 28–45. [\[CrossRef\]](#)
7. Kian, K.; Woodall, C.M.; Wilcox, J.; Liguori, S. Performance of Pd-based membranes and effects of various gas mixtures on H_2 permeation. *Environments* **2018**, *5*, 128. [\[CrossRef\]](#)
8. Alique, D.; Martinez-Diaz, D.; Sanz, R.; Calles, J.A. Review of supported pd-based membranes preparation by electroless plating for ultra-pure hydrogen production. *Membranes* **2018**, *8*, 5. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Paglieri, S.N.; Way, J.D. Innovations in palladium membrane research. *Sep. Purif. Methods* **2002**, *31*, 1–169. [\[CrossRef\]](#)
10. Dittmeyer, R.; Höllein, V.; Daub, K. Membrane reactors for hydrogenation and dehydrogenation processes based on supported palladium. *J. Mol. Catal. A Chem.* **2001**, *173*, 135–184. [\[CrossRef\]](#)
11. Tong, J.; Su, C.; Kuraoka, K.; Suda, H.; Matsumura, Y. Preparation of thin Pd membrane on CeO_2 -modified porous metal by a combined method of electroless plating and chemical vapor deposition. *J. Memb. Sci.* **2006**, *269*, 101–108. [\[CrossRef\]](#)
12. Gryaznov, V.M. Hydrogen Permeable Palladium Membrane Catalysts. *Platin. Met. Rev.* **1986**, *30*, 68–72.
13. Castro-Dominguez, B.; Mardilovich, I.P.; Ma, L.C.; Ma, R.; Dixon, A.G.; Kazantzis, N.K.; Ma, Y.H. Integration of methane steam reforming and water gas shift reaction in a Pd/Au/Pd-based catalytic membrane reactor for process intensification. *Membranes* **2016**, *6*, 44. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Gallucci, F.; Medrano, J.A.; Fernandez, E.; Melendez, J.; Van Sint Annaland, M.; Pacheco-Tanaka, D.A. Advances on high temperature Pd-based membranes and membrane reactors for hydrogen purification and production. *J. Membr. Sci. Res.* **2017**, *3*, 142–156. [\[CrossRef\]](#)
15. Basile, A. Hydrogen production using Pd-based membrane reactors for fuel cells. *Top. Catal.* **2008**, *51*, 107–122. [\[CrossRef\]](#)
16. Baloyi, L.N.; North, B.C.; Langmi, H.W.; Bladergroen, B.J.; Ojumu, T.V. The production of hydrogen through the use of a 77 wt% Pd 23 wt% Ag membrane water gas shift reactor. *S. Afr. J. Chem. Eng.* **2016**, *22*, 44–54. [\[CrossRef\]](#)
17. Miller, H.A.; Ruggeri, J.; Marchionni, A.; Bellini, M.; Pagliaro, M.V.; Bartoli, C.; Pucci, A.; Passaglia, E.; Vizza, F. Improving the energy efficiency of direct formate fuel cells with a Pd/C- CeO_2 anode catalyst and anion exchange ionomer in the catalyst layer. *Energies* **2018**, *11*, 369. [\[CrossRef\]](#)
18. Byun, M.Y.; Kim, J.S.; Baek, J.H.; Park, D.W.; Lee, M.S. Liquid-phase hydrogenation of maleic acid over Pd/ Al_2O_3 catalysts prepared via deposition–precipitation method. *Energies* **2019**, *12*, 284. [\[CrossRef\]](#)
19. Sun, G.B.; Hidajat, K.; Kawi, S. Ultra thin Pd membrane on $\alpha\text{-Al}_2\text{O}_3$ hollow fiber by electroless plating: High permeance and selectivity. *J. Memb. Sci.* **2006**, *284*, 110–119. [\[CrossRef\]](#)
20. Gao, F.; Wang, Y.; Goodman, D.W. CO oxidation over AuPd(100) from ultrahigh vacuum to near-atmospheric pressures: The critical role of contiguous Pd atoms. *J. Am. Chem. Soc.* **2009**, *131*, 5734–5735. [\[CrossRef\]](#)
21. Sonwane, C.G.; Wilcox, J.; Yi, H.M. Solubility of hydrogen in PdAg and PdAu binary alloys using density functional theory. *J. Phys. Chem. B* **2006**, *110*, 24549–24558. [\[CrossRef\]](#)
22. Melendez, J.; Fernandez, E.; Gallucci, F.; van Sint Annaland, M.; Arias, P.L.; Pacheco Tanaka, D.A. Preparation and characterization of ceramic supported ultra-thin ($\sim 1 \mu\text{m}$) Pd-Ag membranes. *J. Memb. Sci.* **2017**, *528*, 12–23. [\[CrossRef\]](#)

23. Kurokawa, H.; Yakabe, H.; Yasuda, I.; Peters, T.; Bredesen, R. Inhibition effect of CO on hydrogen permeability of Pd-Ag membrane applied in a microchannel module configuration. *Int. J. Hydrogen Energy* **2014**, *39*, 17201–17209. [\[CrossRef\]](#)
24. Endo, N.; Furukawa, Y.; Goshome, K.; Yaegashi, S.; Mashiko, K.; Tetsuhiko, M. Characterization of mechanical strength and hydrogen permeability of a PdCu alloy film prepared by one-step electroplating for hydrogen separation and membrane reactors. *Int. J. Hydrogen Energy* **2019**, *44*, 8290–8297. [\[CrossRef\]](#)
25. O'Brien, C.P.; Miller, J.B.; Morreale, B.D.; Gellman, A.J. The kinetics of H₂-D₂ exchange over Pd, Cu, and PdCu surfaces. *J. Phys. Chem. C* **2011**, *115*, 24221–24230. [\[CrossRef\]](#)
26. Nayeibossadri, S.; Speight, J.; Book, D. Effects of low Ag additions on the hydrogen permeability of Pd-Cu-Ag hydrogen separation membranes. *J. Memb. Sci.* **2014**, *451*, 216–225. [\[CrossRef\]](#)
27. Liu, J.; Bellini, S.; de Nooijer, N.C.A.; Sun, Y.; Pacheco Tanaka, D.A.; Tang, C.; Li, H.; Gallucci, F.; Caravella, A. Hydrogen permeation and stability in ultra-thin Pd-Ru supported membranes. *Int. J. Hydrogen Energy* **2020**, *45*, 7455–7467. [\[CrossRef\]](#)
28. Ryi, S.K.; Li, A.; Lim, C.J.; Grace, J.R. Novel non-alloy Ru/Pd composite membrane fabricated by electroless plating for hydrogen separation. *Int. J. Hydrogen Energy* **2011**, *36*, 9335–9340. [\[CrossRef\]](#)
29. Nayeibossadri, S.; Speight, J.D.; Book, D. A novel Pd-Cu-Zr hydrogen separation membrane with a high tolerance to sulphur poisoning. *Chem. Commun.* **2015**, *51*, 15842–15845. [\[CrossRef\]](#)
30. Yoshida, K.; Morigami, H. Thermal properties of diamond/copper composite material. *Microelectron. Reliab.* **2004**, *44*, 303–308. [\[CrossRef\]](#)
31. Al-Mufachi, N.A.; Steinberger-Wilckens, R. X-ray diffraction study on the effects of hydrogen on Pd60Cu40 wt% foil membranes. *J. Memb. Sci.* **2018**, *545*, 266–274. [\[CrossRef\]](#)
32. Yun, S.; Ko, J.H.; Oyama, S.T. Ultrathin palladium membranes prepared by a novel electric field assisted activation. *J. Memb. Sci.* **2011**, *369*, 482–489. [\[CrossRef\]](#)
33. Yang, J.Y.; Nishimura, C.; Komaki, M. Hydrogen Permeation of Pd60Cu40/V-15Ni Composite Membrane under Mixing Gases of H₂+H₂S. *Trans. Mater. Res. Soc. Jpn.* **2007**, *978*, 975–978. [\[CrossRef\]](#)
34. Chen, W.H.; Escalante, J.; Chi, Y.H.; Lin, Y.L. Hydrogen permeation enhancement in a Pd membrane tube system under various vacuum degrees. *Int. J. Hydrogen Energy* **2020**, *45*, 7401–7411. [\[CrossRef\]](#)
35. Acha, E.; Requies, J.; Barrio, V.L.; Cambra, J.F.; Güemez, M.B.; Arias, P.L.; van Delft, Y.C. PdCu membrane applied to hydrogen production from methane. *J. Memb. Sci.* **2012**, *415–416*, 66–74. [\[CrossRef\]](#)
36. Jayaraman, V.; Lin, Y.S.; Pakala, M.; Lin, R.Y.; Wei, L.; Yu, J.; Hu, X.; Huang, Y. Fabrication of ultrathin metallic membranes on ceramic supports by sputter deposition. *J. Memb. Sci.* **1995**, *99*, 89–100. [\[CrossRef\]](#)
37. Wei, L.; Yu, J.; Hu, X.; Huang, Y. Fabrication of H₂-permeable palladium membranes based on pencil-coated porous stainless steel substrate. *Int. J. Hydrogen Energy* **2012**, *37*, 13007–13012. [\[CrossRef\]](#)
38. Kato, Y.; Yaegashi, S.; Watanabe, T.; Hatsuda, H.; Ryu, J. Metal Compositized Hydrogen Permeation Membrane and Its Production Method. Japan Patent 6014920, 23 February 2017.
39. Kato, Y.; Inoue, K.; Urasaki, M.; Tanaka, S.; Ninomiya, H.; Minagawa, T.; Ryu, J. Hydrogen permeability of composite hydrogen permeation membrane using a reverse buildup method. *Heat Transf. Eng.* **2013**, *34*, 917–924. [\[CrossRef\]](#)
40. Tong, J.; Su, L.; Haraya, K.; Suda, H. Thin and defect-free Pd-based composite membrane without any interlayer and substrate penetration by a combined organic and inorganic process. *Chem. Commun.* **2006**, *10*, 1142–1144. [\[CrossRef\]](#)
41. Shinoda, Y.; Takeuchi, M.; Dezawa, N.; Komo, Y.; Harada, T.; Takasu, H.; Kato, Y. Development of a H₂-permeable Pd60Cu40-based composite membrane using a reverse build-up method. *Int. J. Hydrogen Energy* **2021**, *46*, 36291–36300. [\[CrossRef\]](#)
42. Yaegashi, S.; Watanabe, T.; Kato, Y.; Hatsuda, H.; Ryu, J. Metal Compositized Hydrogen Permeation Membrane and Its Production Method. Japan Patent 6056023, 26 May 2016.
43. Zhang, X.; Xiong, G.; Yang, W. A modified electroless plating technique for thin dense palladium composite membranes with enhanced stability. *J. Memb. Sci.* **2008**, *314*, 226–237. [\[CrossRef\]](#)
44. Dunbar, Z.W. Hydrogen purification of synthetic water gas shift gases using microstructured palladium membranes. *J. Power Sources* **2015**, *297*, 525–533. [\[CrossRef\]](#)
45. Ryi, S.K.; Park, J.S.; Kim, S.H.; Cho, S.H.; Kim, D.W.; Um, K.Y. Characterization of Pd-Cu-Ni ternary alloy membrane prepared by magnetron sputtering and Cu-reflow on porous nickel support for hydrogen separation. *Sep. Purif. Technol.* **2006**, *50*, 82–91. [\[CrossRef\]](#)
46. Dunbar, Z.W.; Lee, I.C. Effects of elevated temperatures and contaminated hydrogen gas mixtures on novel ultrathin palladium composite membranes. *Int. J. Hydrogen Energy* **2017**, *42*, 29310–29319. [\[CrossRef\]](#)
47. McCool, B.; Xomeritakis, G.; Lin, Y.S. Composition control and hydrogen permeation characteristics of sputter deposited palladium-silver membranes. *J. Memb. Sci.* **1999**, *161*, 67–76. [\[CrossRef\]](#)
48. Zhao, H.B.; Pflanz, K.; Gu, J.H.; Li, A.W.; Stroh, N.; Brunner, H.; Xiong, G.X. Preparation of palladium composite membranes by modified electroless plating procedure. *J. Memb. Sci.* **1998**, *142*, 147–157. [\[CrossRef\]](#)
49. Xomeritakis, G.; Lin, Y.S. CVD Synthesis and Gas Permeation Properties of Thin Palladium/Alumina Membranes. *AIChE J.* **1998**, *44*, 174–183. [\[CrossRef\]](#)
50. Jun, C.S.; Lee, K.H. Palladium and palladium alloy composite membranes prepared by metal-organic chemical vapor deposition method (cold-wall). *J. Memb. Sci.* **2000**, *176*, 121–130. [\[CrossRef\]](#)

51. Itoh, N.; Akiha, T.; Sato, T. Preparation of thin palladium composite membrane tube by a CVD technique and its hydrogen permselectivity. *Catal. Today* **2005**, *104*, 231–237. [[CrossRef](#)]
52. Mejdell, A.L.; Jøndahl, M.; Peters, T.A.; Bredesen, R.; Venvik, H.J. Experimental investigation of a microchannel membrane configuration with a 1.4 μm Pd/Ag23 wt.% membrane-Effects of flow and pressure. *J. Memb. Sci.* **2009**, *327*, 6–10. [[CrossRef](#)]
53. Maneerung, T.; Hidajat, K.; Kawi, S. Ultra-thin ($<1\ \mu\text{m}$) internally-coated Pd-Ag alloy hollow fiber membrane with superior thermal stability and durability for high temperature H_2 separation. *J. Memb. Sci.* **2014**, *452*, 127–142. [[CrossRef](#)]
54. Li, Z.Y.; Maeda, H.; Kusakabe, K.; Morooka, S.; Anzai, H.; Akiyama, S. Preparation of palladium-silver alloy membranes for hydrogen separation by the spray pyrolysis method. *J. Memb. Sci.* **1993**, *78*, 247–254. [[CrossRef](#)]
55. Fernandez, E.; Sanchez-Garcia, J.A.; Melendez, J.; Spallina, V.; van Sint Annaland, M.; Gallucci, F.; Pacheco Tanaka, D.A.; Prema, R. Development of highly permeable ultra-thin Pd-based supported membranes. *Chem. Eng. J.* **2016**, *305*, 149–155. [[CrossRef](#)]
56. Roa, F.; Way, J.D. Influence of Alloy Composition and Membrane Fabrication on the Pressure Dependence of the Hydrogen Flux of Palladium-Copper Membranes. *Ind. Eng. Chem. Res.* **2003**, *42*, 5827–5835. [[CrossRef](#)]
57. Seshimo, M.; Hirai, T.; Rahman, M.M.; Ozawa, M.; Sone, M.; Sakurai, M.; Higo, Y.; Kameyama, H. Functionally graded Pd/ γ -alumina composite membrane fabricated by electroless plating with emulsion of supercritical CO_2 . *J. Memb. Sci.* **2009**, *342*, 321–326. [[CrossRef](#)]
58. McKinley, D.L. Metal Alloy for Hydrogen Separation and Purification. U.S. Patent 3,350,845, 7 November 1967.
59. McKinley, D.L. Method for Hydrogen Separation and Purification. U.S. Patent 3,439,474, 22 April 1969.
60. Ma, Y.H.; Akis, B.C.; Ayturk, M.E.; Guazzone, F.; Engwall, E.E.; Mardilovich, I.P. Characterization of intermetallic diffusion barrier and alloy formation for Pd/Cu and Pd/Ag porous stainless steel composite membranes. *Ind. Eng. Chem. Res.* **2004**, *43*, 2936–2945. [[CrossRef](#)]
61. Samingprai, S.; Tantayanon, S.; Ma, Y.H. Chromium oxide intermetallic diffusion barrier for palladium membrane supported on porous stainless steel. *J. Memb. Sci.* **2010**, *347*, 8–16. [[CrossRef](#)]
62. Zhang, K.; Gao, H.; Rui, Z.; Liu, P.; Li, Y.; Lin, Y.S. High-temperature stability of palladium membranes on porous metal supports with different intermediate layers. *Ind. Eng. Chem. Res.* **2009**, *48*, 1880–1886. [[CrossRef](#)]