Communication

Collectable Single Pure-Pd Metal Membrane with High Strength and Flexibility Prepared through Electroplating for Hydrogen Purification

Naruki Endo [1,*] **, Yumi Kaneko** [2] **, Norikazu Dezawa** [2] **, Yasuhiro Komo** [2] **and Masanobu Higuchi** [2]

1   Renewable Energy Research Center, National Institute of Advanced Industrial Science and Technology (AIST), 2-2-9 Machiikedai, Koriyama 963-0298, Japan
2   Sanno Co., Ltd., 5-8-8, Tsunashima-Higashi, Kouhoku-ku, Yokohama 223-0052, Japan
*   Correspondence: naruki.endo@aist.go.jp

Abstract: Among the various film preparation methods, electroplating is one of the simplest and most economical methods. However, it is challenging to collect a dense single Pd film through plating, owing to the accumulation of stress in the film during the process. Therefore, the characteristics of a single plated film have not been clearly identified, although pure Pd is widely used in metallic-hydrogen-purification membranes. In this study, stress concentration in film during preparation was reduced by optimizing the plating process, and a dense single flat film was successfully collected. No impurities were detected. Thus, a high-purity Pd film was prepared. Its surface texture was found to be significantly different from that of the rolled film, and several approximately 5 μm sized aggregates were observed on the surface. The plated film is reported to have mechanical properties superior to those of the rolled film, with twice the displacement and four times the breaking point strength. The hydrogen permeabilities of the plated film (5.4×10^{-9}–1.1×10^{-8} mol·m^{-1}·s^{-1}·Pa$^{-1/2}$ at 250–450 °C) were comparable to those of the rolled and reported films, indicating that the surface texture does not have a strong effect on hydrogen permeability. The results of this study promote the practical use of Pd-based membranes through electroplating.

Keywords: palladium; Pd-based membrane; electroplating; hydrogen purification

1. Introduction

Hydrogen has been gaining increased significance in the global trend toward the realization of a carbon-neutral society by 2050–2060. As most hydrogen is currently produced via reforming reactions [1], purification processes are necessary to obtain pure hydrogen with high added value. Hydrogen purification using metallic-hydrogen-separation membranes yields 100% pure hydrogen in a one-step process [2]. Thus, the practical applications of such membranes are being explored [1,2].

There are two major categories of metallic-hydrogen-purification/separation membranes, namely Pd-based [3–16] and non-Pd-based [17–20]. The former has been the subject of extensive research and development [6–16]; such membranes prepared using the rolling method are now in practical use, albeit on a small scale. However, in addition to the high price of Pd itself, the membrane preparation process becomes more expensive as the rolled membrane becomes thinner, which is a major issue. Other dry-process methods include vapor deposition, such as physical vapor deposition (PVD) [21,22] and chemical vapor deposition (CVD) [23,24]. While PVD and CVD enable strict film thickness and composition control, they are not suitable for mass production due to high equipment costs and strict depositing conditions.

There are two wet-process methods, namely electroless plating (ELP) [25–28] and electroplating [29,30]. ELP is one of the most promising methods because it can deposit on various types of supports, although it has disadvantages of complicated pretreatment and

difficult thickness control. Gade et al. prepared single pure Pd and PdCu films using ELP to evaluate the permeabilities of Pd-based films and reported that it was comparable to those of rolled films and previously reported values [31]. However, it is difficult to control ELP thickness because ELP conducts film deposition through spontaneous reaction; thus, single defect-free films of <7.2 μm could not be collected. The mechanical property of the single film has not been investigated at all.

Recently, we reported the preparation of a Pd alloy through electroplating to reduce expenses [32,33]. Electroplating offers advantages of low-cost equipment, mass-production suitability, easy control of thickness, and preparation of high-purity membranes [4,5]. In our previous studies, we plated a PdCu alloy in a one-step process and found that the plated film had higher strength and was more flexible than a rolled PdCu film [32,33]. However, the composition of PdCu alloys significantly impacted hydrogen permeability [31,34]. This makes it particularly difficult to control alloy composition during plating. However, we started our work with a PdCu alloy because the alloy has the advantage of containing more than half Cu (at%), which prevents the accumulation of stress in the film and makes it as easy to collect as a single film.

In general, a pure Pd film absorbs hydrogen during the plating process and becomes hard and brittle [35,36]. This makes it difficult to obtain a single flat film (see Figure 1a). Although pure Pd is the most typical metallic-hydrogen-purification membrane, there is no report on the preparation and characterization of a dense single Pd film through electroplating (<10 μm thickness). Further, the mechanical and hydrogen-permeable properties of a pure-Pd-plated film are not well understood. Moreover, for other metals, the mechanical properties change significantly, owing to hydrogen absorption during electroplating [37].
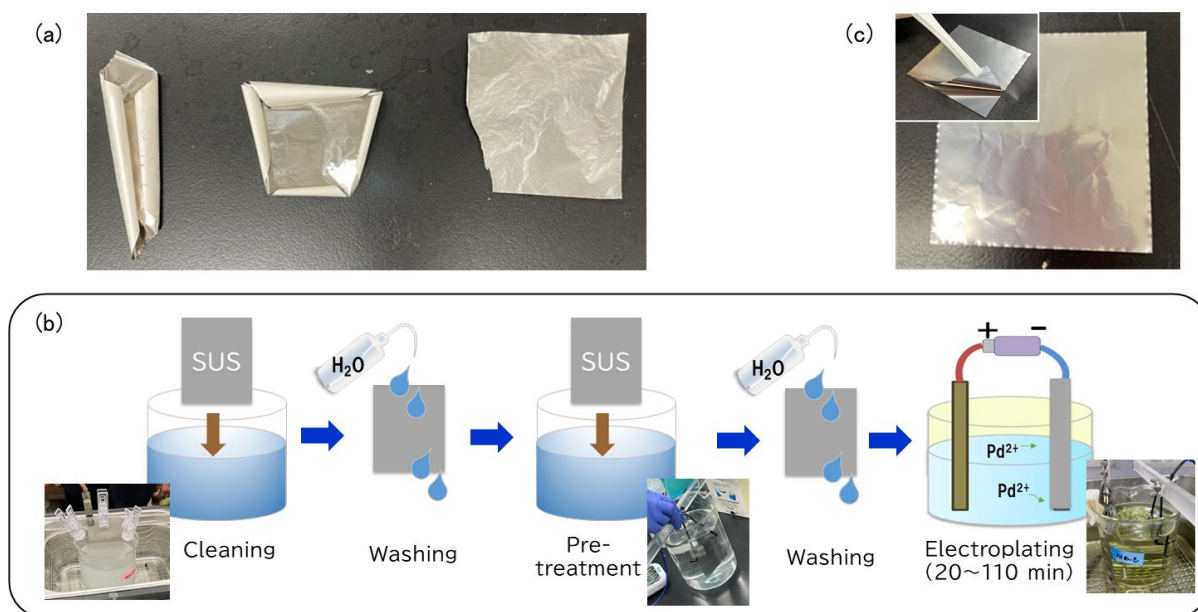

Figure 1. (**a**) Photograph of the plated Pd films prepared under conventional plating conditions. The film was neither a single flat one, due to the stress caused by hydrogen absorption during the plating process, nor was it broken when peeled from an SUS (stainless steel) substrate. (**b**) Schematic of each process involved in electroplating. No special processes were used; only general-purpose equipment was used. (**c**) Collected single flat pure-Pd-plated film. The inset depicts the process of peeling the plated film from a substrate.

In this short communication, we report the characterization of a single pure-Pd-plated film itself. This was conducted by applying the know-how of single film collection, cultivated during the PdCu one-step plating process to achieve pure Pd plating, and we succeeded in recovering dense single flat films with a thickness of 3–15 μm. Mechanical

properties of thin films, with a minimum thickness of 3 μm, and their hydrogen permeability were evaluated. The main objective is to show that a single pure Pd film prepared by electroplating has desirable properties for practical use.

2. Materials and Methods

As it is essential to prepare pure Pd films at a low cost, all the equipment used for electroplating, including the plating solution and substrates, were general-purpose products. The electroplating process is depicted in Figure 1b. An SUS304 (non-porous stainless steel) plate (60 mm × 60 mm) was used as the substrate, which was electrolytically degreased (6 V, 10–120 s) using an alkaline degreasing solution (pH 12–13). Next, the surfaces were washed first with distilled water and then with hydrochloric acid (1–6 N; by immersion for 10–120 s). Thereafter, the surfaces were washed with distilled water again and electroplated under the following conditions. PALLABRIGHT SST (Japan Pure Chemical Co., Ltd., Tokyo, Japan) was used as the Pd-plating solution. A potentiostat/galvanostat HA-151B (Hokuto Denko Co., Ltd., Tokyo, Japan) was used as the power supply for plating. The plating was performed for 20–110 min for a thickness of 3–15 μm at a current density of 0.5–2.0 A/dm^2 and a temperature of 40–65 °C. These conditions were set to achieve a Pd film with a thickness of 3–15 μm. The key here is to not clean the substrate too much so that the plated film can be removed from the substrate, but rather to plate relatively slowly, thereby preventing hydrogen absorption on the Pd film during electroplating. By doing so, as depicted in Figure 1c, stress is not accumulated in the film, and the film becomes flexible so that it can be removed as a single flat film.

Rolled Pd films (99.9% Pd, Tanaka Kikinzoku Kogyo Co., Ltd., Tokyo, Japan) were prepared using the cold rolling process. Pd ingots were rolled to thicknesses of 15 and 50 μm. We obtained rolled films of diameters 12.1 and 20 mm. However, rolled films with thicknesses of <15 μm were not available because such films are impossible to prepare.

The prepared films were characterized through scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectrometry, and X-ray diffraction (XRD). The surface morphology of all films was observed through field-emission scanning electron microscopy (FE-SEM; FEI QUANTA FEG250). The concentrations of Pd and other elements were analyzed through an EDAX AMETEK OCTAN PRO EDX spectrometer. Its lower detection limits were several wt% for light elements (Be, B, C, N, O and F) and 0.2–1 wt% for other elements. FE-SEM and EDX spectrometry were performed under vacuum at room temperature (~20 °C). The thickness of each film sample was determined from cross-sectional SEM observations. XRD was performed using a Rigaku Smartlab X-ray diffractometer with Cu Kα radiation. The scanned 2θ angles ranged from 20° to 100°.

The mechanical strength measurements were carried out using SHIMAZU EZ-TEST series EZ-SX. The sample films with 20 mm diameters were cut from a 500 mm × 500 mm Pd film. The plated and rolled films were 3.2–15.1 and 15 μm thick, respectively. The sample was held in place using a holder and pressed using a spherical jig (φ7 mm). The crosshead speed was 1 mm/min. The mechanical strength tests were measured three times for each sample of the same film thickness and the displacement against load force was measured within a measurement error of ±5%. These mechanical measurements were carried out using our proposed method [32,38,39].

The hydrogen permeation tests were performed using a conventional gas-permeation apparatus; the details of these tests are described in [32,40]. The samples used for comparison were plated Pd (3.2–10.2 μm thickness) and rolled Pd (50 μm thickness). Each sample was cut to φ12.1 mm and sealed using Cu gaskets (with outer and inner diameters of φ12.1 mm and φ5.2 mm, respectively). The diameter used to calculate hydrogen permeability was φ7.1 mm, which was the diameter of the Cu gaskets tightened by Swagelok VCR fittings. Hydrogen gas (99.9999%) was introduced on the upstream side (p_1 = 400–200 kPa), and the downstream side was kept under atmospheric pressure (p_2 = 101 kPa). Thereafter, the temperature was decreased incrementally by 50 °C from 450 °C and measured after 30 min. The hydrogen gas permeating the membranes was measured using a mass flow

meter (HORIBA MODEL SEF-E40; 50 mL/min). A helium (He) leak test was performed before/after each hydrogen permeation test, and no He flow rate was observed. This shows that each plated film was defect-free and dense.

3. Results and Discussion

Electroplated Pd could be easily delaminated from the substrate by cutting it around the edges (see Figure 1c), yielding a 60 mm × 60 mm film. The surface observation results obtained through FE-SEM are presented in Figure 2a–c. The SEM images of the surfaces of the pure-Pd-plated film before and after the hydrogen-permeation test are presented in (a) and (b), respectively. The SEM image of the rolled film is depicted in Figure 2c for comparison; the image is before performing the test because there was almost no change in its microstructure before and after the hydrogen-permeation test. The surface texture after plating, depicted in Figure 2a, indicates an aggregate structure with a thickness of approximately 3–5 μm and a rough surface. This structure has a cauliflower-like texture, which is similar to that reported in previously published papers [31,35]. After the test (Figure 2b), the surface structure was altered due to the high temperature, and the grain boundaries of the aggregates became more distinct; therefore, the surface roughness increased. In contrast, the rolled film had rolled lines and no aggregates, which were seen in the plated film, and its surface structure was smoother than that of the plated film (see Figure 2a–c).
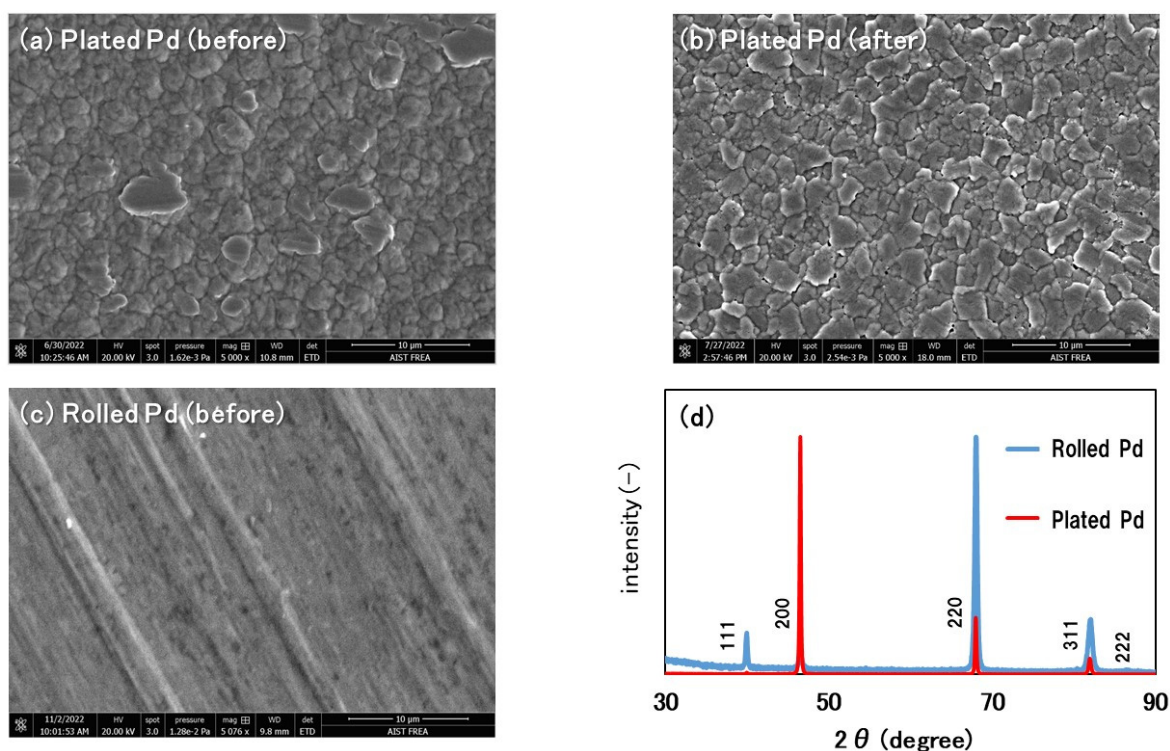

Figure 2. SEM images of the surfaces of the pure-Pd-plated film (**a**) before and (**b**) after the hydrogen-permeation tests; (**c**) rolled film. (**a**,**c**) Depiction of the as-plated and as-rolled states. (**d**) XRD profiles of the plated (red line) and rolled (blue line) Pd films before the hydrogen-permeation tests. Both samples had different peak intensities due to grain orientation, but they had the same FCC structure. The 111 peak of the plated film is very low but appears at the same angle as the rolled film.

Figure 2d presents the XRD results for the plated and rolled films. Both samples are depicted after preparation. Although the peak intensities of both samples are different due to the orientation of the crystal grains during each preparation process, the peak positions for both are identical, indicating an FCC structure. No peaks indicating any other structure were observed, and the lattice parameter obtained from this result was

$a = 3.8910 \pm 0.0002$ Å, which is a slightly larger value than previously reported for pure Pd because of hydrogen absorption [41]. Compositional analysis through EDX was also performed. The spectrum obtained for the plated film was the same as that obtained for the rolled film, and no elements except Pd were detected. From these results, it can be concluded that a single pure Pd film can be plated.

Further, the mechanical strength of the prepared pure Pd film was investigated. The results of the measurement are presented in Figure 3a. The horizontal and vertical axes represent the displacement (mm) and load force (N), respectively. The plated films were 3.2–15.1 μm thick, and the rolled film was 15 μm. The peaks in the curves indicate the points of film breakage. The results for the plated films indicate that the thicker the film, the larger the displacement and the higher the load at the points of film breakage. The displacement of the 15 μm thick rolled film was smaller than that of the 5.5 μm thick plated film, and the breaking point of the rolled film appeared between 9.5 and 5.5 μm. Figure 3b presents the plots of the film thickness (μm) on the horizontal axis and breaking load force (N) on the vertical axis. The plots indicate that the breaking load increases with an increase in film thickness. The breaking load of the rolled film is equivalent to that of the 7.5 μm thick plated film; this indicates that the plated film with half the thickness has the same strength as that of the rolled film. Comparing both films with the same thickness of 15 μm, it can be seen that the breaking load for the plated film is approximately four times higher than that of the rolled film. These results indicate that the plated films are stronger and more flexible than the rolled films.
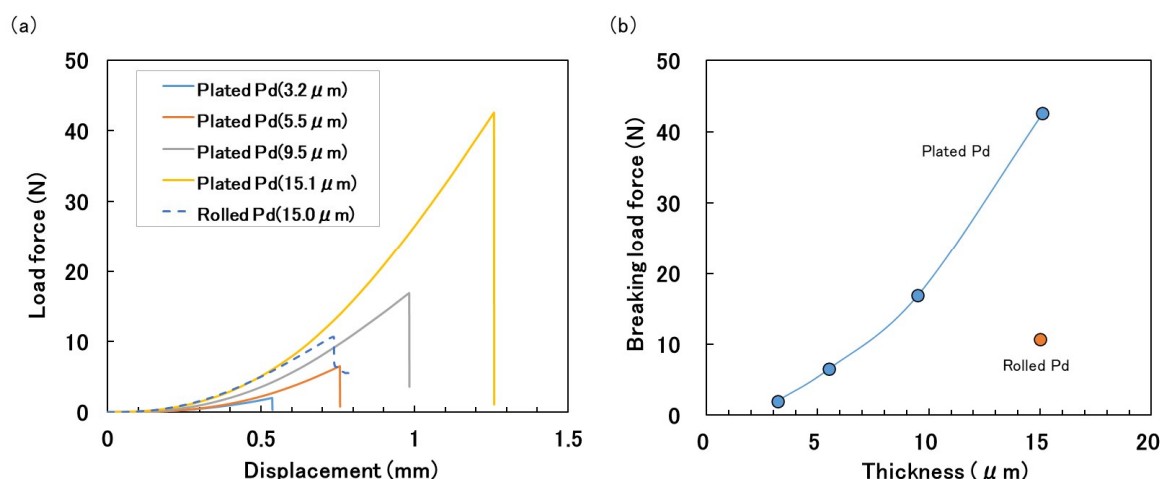

Figure 3. (**a**) Plots of load force (N) vs. displacement (mm) for the as-plated Pd films (3.2–15.1 μm thickness) and as-rolled one (15 μm thickness). (**b**) Plots of breaking load force (in N) vs. thickness (μm) of the plated and rolled pure Pd films.

The plated film is more flexible than the rolled film because the latter unavoidably undergoes work hardening, during which point defects and dislocations are introduced into the film during the rolling process [32]. In the former case, it is considered that our plating process restricts the absorption of hydrogen to the maximum extent possible, such that stress does not accumulate easily in the film and film ductility is maintained. In contrast, the plated films demonstrate a much higher breaking strength than the rolled film because pure Pd prepared through plating is generally known to have higher hardness than bulk Pd [35,36]. The high strength and flexibility of the plated film indicate that the amount of used Pd can be reduced, and material handling can be simplified when rolled film is replaced by plated film. These are significant advantages in practical applications.

The results of the hydrogen-permeation tests are presented in Figure 4a,b. The vertical axes in both figures represent the permeated hydrogen flow rate, whereas the horizontal axes in (a) and (b) represent the film thickness and reciprocal of the film thickness (1/thickness), respectively. For each film thickness, the permeated hydrogen flow rate was higher at

higher temperatures; the thinner the film, the larger the difference in flow rate. Compared with the permeated hydrogen flow rate at the same temperature, the flow rate for the film with 1/2 or 1/3 thickness increased by almost two or three times. Figure 4b indicates that the plots for all temperatures are approximately on a straight line passing through the origin. This indicates that hydrogen permeation through the plated films with thicknesses of approximately 3–10 μm was mostly diffusion limitation. This also implies that the quality of the films with different thicknesses was similar. It is generally understood that hydrogen permeation changes from diffusion limitation to surface molecular dissociation limitation at a thickness of $\leq$5 μm [4]; however, our pure Pd film indicated a diffusion limitation even at a thickness of 3.2 μm. We are currently evaluating thinner films to preliminarily observe that flow dependence tends to deviate from linearity at thicknesses of approximately 1.5–2.0 μm.
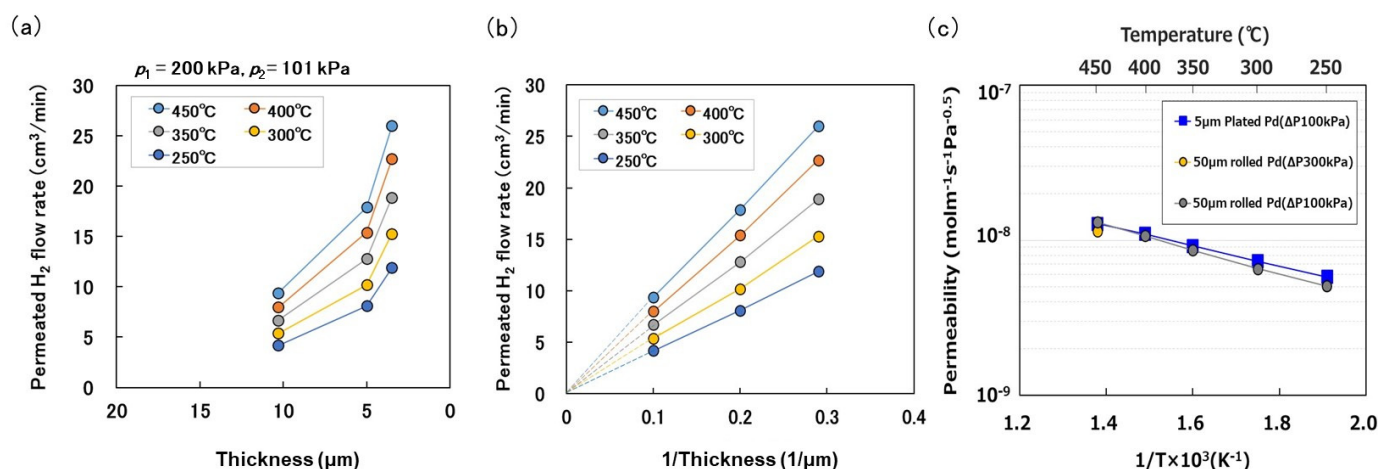

Figure 4. (**a**) Dependence of the permeated hydrogen flow rate on film thickness at various temperatures. (**b**) Dependence on the thickness (1/thickness) of permeated hydrogen flow rate at each film thickness. (**c**) Temperature dependence of the hydrogen permeabilities of plated Pd (5 μm thickness) and rolled Pd (50 μm thickness) at 250–450 °C. The experimental conditions are indicated in the figure.

The temperature dependence of hydrogen permeability of the plated film (5 μm thickness) is depicted in Figure 4c, along with the results for the rolled film (50 μm thickness) for comparison. Hydrogen permeability gradually decreased with a decrease in temperature. A similar result was obtained for the rolled film, although the plated film exhibited a slightly higher value, suggesting the contribution of increased surface roughness. The hydrogen permeability of the plated film was the same for a thickness of 10 μm (not shown in Figure 4c). These permeability values were comparable to the values reported in the literature [42]. The results obtained indicate that although the surface structures of the plated and rolled films were significantly different (see Figure 2a–c), their effect on hydrogen permeability was not so strong. This is significant knowledge pertaining to the development of Pd-based hydrogen-permeable membranes through electroplating in the future.

4. Conclusions

In this communication, pure Pd film was deposited through electroplating and successfully recovered as a dense single flat film. The collected film exhibited an FCC crystal structure, did not contain any impurities, and comprised highly pure Pd. Unlike conventional Pd films, the plated film prepared in this study demonstrated low stress accumulation; the displacement and breaking strength were twice and four times higher, respectively, than those of the rolled films. Although the surface texture of the plated film was significantly different from that of the rolled film, the hydrogen permeability of the former was

comparable to that of the latter and previously reported films. Such plated films can be prepared easily and at a low cost; they also demonstrate excellent mechanical properties. Therefore, the Pd-plated film is favorable for practical applications. Detailed investigations of the plating process and relationship between its microstructure and mechanical strength are currently underway.

Author Contributions: N.E. conceived the experimental design. N.E. and N.D. co-wrote the paper and analyzed the data. Y.K. (Yumi Kaneko) and N.D. performed the electroplating. N.D. measured the mechanical properties and hydrogen permeability. Y.K. (Yasuhiro Komo) and M.H. conceived and contributed to the overall project planning. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: The data obtained in this study are referenced in the main body of the paper and are available from the corresponding author upon reasonable request.

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

References

1. Shu, J.; Grandjean, B.P.A.; Van Neste, A.V.; Kaliaguine, S. Catalytic Palladium-Based Membrane Reactors: A Review. *Can. J. Chem. Eng.* **1991**, *69*, 1036–1060. [CrossRef]
2. Basile, A.; Gallucci, F.; Tosti, S. Synthesis, Characterization, and Applications of Palladium Membranes. *Membr. Sci. Technol.* **2008**, *13*, 255–323. [CrossRef]
3. Paglieri, S.N.; Way, J.D. Innovations in Palladium Membrane Research. *Sep. Purif. Methods* **2002**, *31*, 1–169. [CrossRef]
4. Yun, S.; Ted Oyama, S.T. Correlations in Palladium Membranes for Hydrogen Separation: A Review. *J. Membr. Sci.* **2011**, *375*, 28–45. [CrossRef]
5. Conde, J.J.; Maroño, M.; Sánchez-Hervás, J.M. Pd-Based Membranes for Hydrogen Separation: Review of Alloying Elements and Their Influence on Membrane Properties. *Sep. Purif. Rev.* **2017**, *46*, 152–177. [CrossRef]
6. Zhang, Y.; Komaki, M.; Nishimura, C. Morphological Study of Supported Thin Pd and Pd–25Ag Membranes upon Hydrogen Permeation. *J. Membr. Sci.* **2005**, *246*, 173–180. [CrossRef]
7. Kikuchi, E. Membrane Reactor Application to Hydrogen Production. *Catal. Today* **2000**, *56*, 97–101. [CrossRef]
8. Sonwane, C.G.; Wilcox, J.; Ma, Y.H. Solubility of Hydrogen in PdAg and PdAu Binary Alloys Using Density Functional Theory. *J. Phys. Chem. B* **2006**, *110*, 24549–24558. [CrossRef]
9. Shi, L.; Goldbach, A.; Zeng, G.; Xu, H. Preparation and Performance of Thin-Layered PdAu/Ceramic Composite Membranes. *Int. J. Hydrogen Energy* **2010**, *35*, 4201–4208. [CrossRef]
10. Zeng, G.; Goldbach, A.; Shi, L.; Xu, H. On Alloying and Low-Temperature Stability of Thin, Supported PdAg Membranes. *Int. J. Hydrogen Energy* **2012**, *37*, 6012–6019. [CrossRef]
11. Millet, P.; Ngameni, R.; Decaux, C.; Grigoriev, S.A. Hydrogen Sorption by $Pd_{77}Ag_{23}$ Metallic Membranes. Role of Hydrogen Content, Temperature and Sample Microstructure. *Int. J. Hydrogen Energy* **2011**, *36*, 4262–4269. [CrossRef]
12. Montesinos, H.; Julián, I.; Herguido, J.; Menéndez, M. Effect of the Presence of Light Hydrocarbon Mixtures on Hydrogen Permeance through Pd–Ag Alloyed Membranes. *Int. J. Hydrogen Energy* **2015**, *40*, 3462–3471. [CrossRef]
13. Kamakoti, P.; Morreale, B.D.; Ciocco, M.V.; Howard, B.H.; Killmeyer, R.P.; Cugini, A.V.; Sholl, D.S. Prediction of Hydrogen Flux through Sulfur-Tolerant Binary Alloy Membranes. *Science* **2005**, *307*, 569–573. [CrossRef]
14. Decaux, C.; Ngameni, R.; Solas, D.; Grigoriev, S.; Millet, P. Time and Frequency Domain Analysis of Hydrogen Permeation across PdCu Metallic Membranes for Hydrogen Purification. *Int. J. Hydrogen Energy* **2010**, *35*, 4883–4892. [CrossRef]
15. Zhang, K.; Way, J.D. Palladium-Copper Membranes for Hydrogen Separation. *Sep. Purif. Technol.* **2017**, *186*, 39–44. [CrossRef]
16. Zhao, C.; Goldbach, A.; Xu, H. Low-Temperature Stability of Body-Centered Cubic PdCu Membranes. *J. Membr. Sci.* **2017**, *542*, 60–67. [CrossRef]
17. Phair, J.W.; Donelson, R. Developments and Design of Novel (Non-palladium-Based) Metal Membranes for Hydrogen Separation. *Ind. Eng. Chem. Res.* **2006**, *45*, 5657–5674. [CrossRef]
18. Dolan, M.D. Non-Pd BCC Alloy Membranes for Industrial Hydrogen Separation. *J. Membr. Sci.* **2010**, *362*, 12–28. [CrossRef]
19. Dolan, M.D.; Song, G.; Liang, D.; Kellam, M.E.; Chandra, D.; Lamb, J.H. Hydrogen Transport through $V_{85}Ni_{10}M_5$ Alloy Membranes. *J. Membr. Sci.* **2011**, *373*, 14–19. [CrossRef]
20. Buxbaum, R.E.; Marker, T.L. Hydrogen Transport through Non-porous Membranes of Palladium-Coated Niobium, Tantalum and Vanadium. *J. Membr. Sci.* **1993**, *85*, 29–38. [CrossRef]

21. Jayaraman, V.; Lin, Y.S. Synthesis and Hydrogen Permeation Properties of Ultrathin Palladium-Silver Alloy Membranes. *J. Membr. Sci.* **1995**, *104*, 251–262. [CrossRef]
22. McCool, B.; Xomeritakis, G.; Lin, Y.S. Composition Control and Hydrogen Permeation Characteristics of Sputter Deposited Palladium-Silver Membranes. *J. Membr. Sci.* **1999**, *161*, 67–76. [CrossRef]
23. Xomeritakis, G.; Lin, Y.S. Fabrication of a Thin Palladium Membrane Supported in a Porous Ceramic Substrate by Chemical Vapor Deposition. *J. Membr. Sci.* **1996**, *120*, 261–272. [CrossRef]
24. Kikuchi, E.; Nemoto, Y.; Kajiwara, M.; Uemiya, S.; Kojima, T. Steam Reforming of Methane in Membrane Reactors: Comparison of Electroless-Plating and CVD Membranes and Catalyst Packing Modes. *Catal. Today* **2000**, *56*, 75–81. [CrossRef]
25. Huang, Y.; Li, X.; Fan, Y.; Xu, N. Palladium-Based Composite Membranes: Principle, Preparation and Characterization. *Prog. Chem.* **2006**, *18*, 230–237.
26. Thoen, P.M.; Roa, F.; Way, J.D. High Flux Palladium–Copper Composite Membranes for Hydrogen Separations. *Desalination* **2006**, *193*, 224–229. [CrossRef]
27. Tosti, S. Supported and Laminated Pd-Based Metallic Membranes. *Int. J. Hydrogen Energy* **2003**, *28*, 1445–1454. [CrossRef]
28. 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]
29. Tong, J.; Shirai, R.; Kashima, Y.; Matsumura, Y. Preparation of a Pinhole-Free Pd–Ag Membrane on a Porous Metal Support for Pure Hydrogen Separation. *J. Membr. Sci.* **2005**, *260*, 84–89. [CrossRef]
30. Bryden, K.J.; Ying, J.Y. Electrodeposition Synthesis and Hydrogen Absorption Properties of Nanostructured Palladium–Iron Alloys. *Nanostruct. Mater.* **1997**, *9*, 485–488. [CrossRef]
31. Gade, S.K.; Thoen, P.M.; Way, J.D. Unsupported Palladium Alloy Foil Membranes Fabricated by Electroless Plating. *J. Membr. Sci.* **2008**, *316*, 112–118. [CrossRef]
32. Endo, N.; Furukawa, Y.; Goshome, K.; Yaegashi, S.; Mashiko, K.-i.; 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]
33. Kato, Y.; Maeda, T.; Endo, N.; Yaegashi, S.; Furukawa, Y.; Dezawa, N. Hydrogen Permeable Membranes and Their Preparation Methods. Japan Patent P6695929, 24 April 2020. (In Japanese).
34. Knapton, A.G. Palladium Alloys for Hydrogen Diffusion Membranes. *Platin. Met. Rev.* **1977**, *21*, 44–50.
35. Raub, C.J. Electroplating of Palladium for Electrical Contacts. *Platin. Met. Rev.* **1982**, *26*, 158–166.
36. Yasumura, K. Palladium and Palladium Alloy Bath. *J. Surf. Finish. Soc. Jpn.* **2004**, *55*, 640–645. [CrossRef]
37. Snavely, C.A. A Theory for the Mechanism of Chromium Plating; A Theory for the Physical Characteristics of Chromium Plate. *J. Electrochem. Soc.* **1947**, *92*, 537. [CrossRef]
38. Yaegashi, S.; Endo, N.; Kumakawa, M.; Suzuki, S.; Maeda, T. Method and Apparatus for Evaluating Flexibility of Sheet-Type Testing Materials. Japan Patent P6265196, 24 January 2018.
39. Endo, N.; Yaegashi, S.; Maehata, T.; Kumakawa, M.; Suzuki, S.; Mashiko, K.-i.; Maeda, T. High Thermal Stability and Flexibility of Thin Porous Ni Metal Support Prepared by Electroplating Deposition for Pd Alloy Membranes. *Mater. Trans.* **2017**, *58*, 1093–1096. [CrossRef]
40. Nishimura, C.; Komaki, M.; Amano, M. Hydrogen Permeation Characteristics of Vanadium-Nickel Alloys. *Mater. Trans. JIM* **1991**, *32*, 501–507. [CrossRef]
41. Arblaster, J.W. Crystallographic Properties of Palladium. *Platin. Met. Rev.* **2012**, *56*, 181–189. [CrossRef]
42. Amano, M.; Nishimura, C.; Komaki, M. Effect of High Concentration CO and CO_2 on Hydrogen Permeation through the Palladium Membrane. *Mater. Trans. JIM* **1990**, *31*, 404–408. [CrossRef]