

PREPARATION OF SUPPORTED PALLADIUM MEMBRANE AND SEPARATION OF HYDROGEN

Kanna Aoki, Shuichi Yokoyama, Katsuki Kusakabe and Shigeharu Morooka[†]

Department of Chemical Science and Technology, Kyushu University, Fukuoka 812-81, Japan

(Received 10 May 1996 • accepted 26 August 1996)

Abstract – Palladium acetate was sublimed at a reduced pressure at 400°C, carried into the macropores of the porous wall of an α -alumina support tube and was decomposed there. A thin palladium membrane which was thus formed showed a hydrogen permeance of 10^{-6} mol·m⁻²·s⁻¹·Pa⁻¹ and a hydrogen/nitrogen permselectivity higher than 1000. The membrane was stable against hydrogen embrittlement even when the permeation temperature was varied between 100 and 300°C, and it was stable to sulfur or chlorine. To test the ability of this system for the separation of hydrogen and deuterium, a palladium disk was used instead of the prepared membrane since a definite membrane thickness was necessary for calculation. When H₂ and D₂ permeated through the membrane independently, the H/D permselectivity was approximately 7 at 150–200°C under a feed side pressure of 0.4 MPa and a permeate side pressure of 0.1 MPa. When a mixture of H₂ and D₂ was fed, the H/D permselectivity was reduced to 1.2–1.6.

Key words: Palladium, Hydrogen, Deuterium, CVD, Permeance

INTRODUCTION

Membranes used for gas separation are classified into two categories, porous membranes such as zeolite and amorphous silica membranes which function via interaction between molecules and pore walls, and non-porous membranes such as metal and yttria-stabilized zirconia membranes which function via dissolution-diffusion mechanism. The palladium membrane belongs to the latter class. Hydrogen molecules are dissociated into protons on the surface and diffuse into the membrane, and the protons then reassociate on the opposite side of the membrane. With the exception of hydrogen, the solubility of gases in palladium is negligible. Because of its properties, hydrogen is separated with a high selectivity [Shu et al., 1991; Itoh et al., 1992].

The high cost of palladium, however, is a problem in industrial applications, and many efforts have been devoted to the development of thin membranes for purposes of cost-effectiveness. Table 1 shows those results. Another problem with palladium membrane is the hydrogen embrittlement that is caused by the transition between the α - and β -phases at a temperature below 300°C and a pressure below 2 MPa [van Swaay et al., 1960; Knapton, 1977; Shu et al., 1991]. Since the lattice constant of the β -phase is at least 3% larger than that of the α -phase, nucleation and growth of the β -phase cause strains in the metal [Fort et al., 1975]. To overcome hydrogen embrittlement, palladium membranes are alloyed or the process is operated under conditions where no phase transition occurs.

Typical methods developed for formation of thin palladium membranes are described below.

1. Spray Pyrolysis

Spray pyrolysis is a technique which is useful for producing

fine particles of metal oxides or noble metals. A solution of metal salts is sprayed into a heated gas stream and is pyrolyzed. Li et al. [1993] applied this technique to form a palladium-silver membrane on a γ -alumina-coated α -alumina porous tube. Palladium and silver were supplied as an aqueous solution of palladium nitrate and silver nitrate. The solution was atomized by an ultrasonic vibrator into an oxygen stream and was entrained into a hydrogen-oxygen flame. Palladium nitrate was first decomposed to PdO and then reduced to palladium metal at 700°C. Silver nitrate was vaporized in the flame, and a portion of it was co-deposited on the support tube which was maintained at temperatures of 970–1070°C.

Fig. 1 shows the changes in morphology of the alloy membrane during its formation. Metal particles smaller than 1 μ m in diameter were observed in the early stage of deposition (3 min). After 10 min deposition, these particles sintered with one other to larger islands. A continuous palladium-silver alloy membrane was obtained after 100 min of deposition. The thickness of the membrane was determined to be 1.5–2 μ m from SEM observation of the fractured surface. The silver content in the alloy membrane was only 4 wt% although the silver concentration in the spray solution was 10–40 wt% of the total metal. To increase the silver content in the membrane, spray pyrolysis was repeated with a 0.1 mol·L⁻¹ silver nitrate solution, and, as a result, a Pd-Ag alloy membrane containing 24 wt% silver was obtained. The permeance of hydrogen through the alloy membrane increased with increasing temperature according to the solution-diffusion mechanism and reached 10^{-6} mol·m⁻²·s⁻¹·Pa⁻¹ at a permeation temperature of 500°C. The H₂/N₂ separation factor was 24 at the same temperature. This suggests the presence of narrow channels through which nitrogen leaked, although pinholes larger than 5 nm were not recognized by SEM observation.

2. Chemical Plating and Other Methods

[†]To whom all correspondences should be addressed.

Table 1. Properties of supported Pd and Pd-alloy membranes prepared by various methods

Investigator	Substrate	Method	P_H [kPa]	P_t [kPa]	Permeance* [mol · m ⁻² · s ⁻¹ · Pa ⁻¹]	H_2/N_2 *	Thickness [μm]
Peachey et al. [1996] ^a	tantalum foil	electron beam evaporation	105	6	1.5×10^{-6}	-	1
Jayaraman et al. [1995b] ^a	porous alumina tube	sputtering	103	0	2.5×10^{-7}	4.5	-
Morooka et al. [1995] ^a	porous alumina tube	crossflow CVD	101	0	7.0×10^{-6}	>1000	8
Athayde et al. [1994] ^a	porous ceramic disk	sputtering	712	101	1.2×10^{-8}	-	0.025-0.1
Yan et al. [1994] ^a	porous alumina tube	crossflow CVD	101	0	1.4×10^{-6}	>1000	2
Chai et al. [1994] ^a	porous alumina disk	sputtering	101	76	2.7×10^{-7}	3.3	0.25-0.5
Lee et al. [1994] ^a	porous alumina tube	sol-gel	104	101	2.8×10^{-6}	10	-
Collins et al. [1993] ^a	porous alumina tube	electroless plating	200	121	1.0×10^{-6}	650	11-20
Li et al. [1993] ^b	porous alumina disk	spray pyrolysis	101	0	1.0×10^{-6}	24	1.5-2.0
Uemiya et al. [1991] ^c	porous alumina tube	electroless plating	202	101	6.3×10^{-6}	very large	4.5-6.4

^aPd membrane, ^bPd-Ag membrane, ^cMaximum value

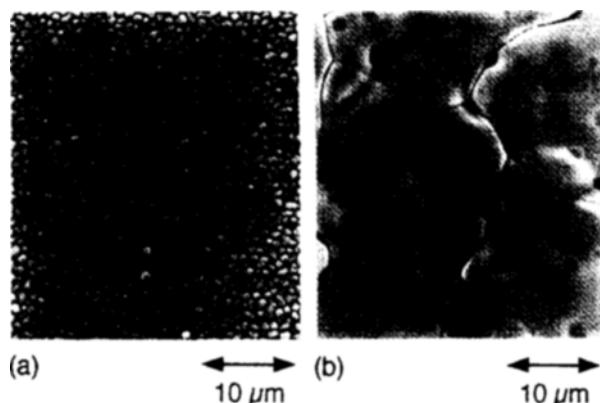


Fig. 1. Morphology of the palladium-silver membrane prepared by spray pyrolysis. Reaction period; (a) 3 min, (b) 100 min.

Uemiya et al. [1991] prepared a palladium membrane about 5 μm thick on the surface of a porous tube by a chemical plating technique. The membrane was then alloyed with a chemically plated silver layer by heating at 800°C. The hydrogen flux of this membrane was equivalent to that of a rolled palladium-silver film of the same thickness, and the concentration of nitrogen on the lower pressure side was below 0.01%. Jayaraman et al. [1995a] formed a palladium film as thin as 1 μm on a porous alumina support by a sputter deposition technique, but they reported no data on H₂ permselectivity. Usually, a membrane formed on the top surface of a porous support is mechanically fragile. Hence, Konno et al. [1988] impregnated a porous alumina film with palladium which was produced from an aqueous solution of [Pd(NH₃)₄]Cl₂. The separation factor between hydrogen and nitrogen for this membrane was about 100 at 300°C. However, wet processes require rather complicated procedures.

In this study, a dry process was developed for a supported thin palladium membrane that was stable against hydrogen embrittlement and mechanical abrasion. To realize separation of hydrogen and deuterium with the supported thin palladium membrane, permeation of these gases was evaluated using a palladium disk with a definite thickness. Then a separation model for hydrogen and deuterium was proposed.

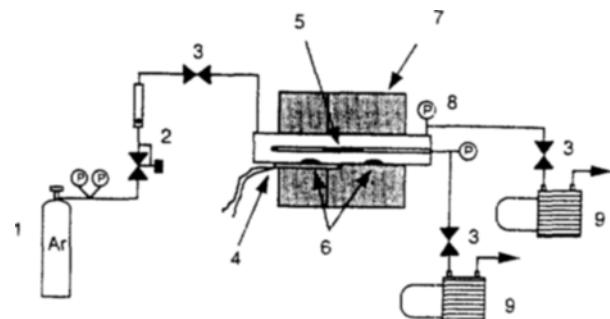


Fig. 2. Experimental set-up for CVD synthesis of the palladium membrane.

1. Gas cylinder	6. Palladium acetate
2. Mass flow controller	7. Furnace
3. Stop valve	8. Pressure gauge
4. Thermocouple	9. Vacuum pump.
5. Membrane	

EXPERIMENTAL

1. Preparation of Thin Palladium Membranes and Permeation Tests

The support tube was a porous α -alumina tube of 2.4 mm O. D. and 1.8 mm I.D., supplied by NOK, Japan. The average pore size was 150 nm, and the volume fraction of pores was approximately 45%. It was sealed with an Na₂O-B₂O₃-SiO₂ glass sealant except for the central portion of ca. 50 mm length. One end of the support tube was also closed with the sealant. The support tube was then fixed coaxially in a CVD reactor with O-rings as shown in Fig. 2. Palladium (II) acetate was used as the palladium source, and approximately 200 mg was placed in the shell side of the reactor. Argon was introduced into the shell side of the reactor as the carrier, and gas in the reactor was continuously exhausted from the outside end of the support tube with a rotary pump to a pressure of approximately 600 Pa which was necessary to sublime the reactant before the decomposition. The reactor was heated externally with an electric furnace at a rate of 3.3 K · min⁻¹ and was then maintained at 400°C for 2 h. The gas was also evacuated across the porous wall of the support from the tube side with a second vacuum pump. At the beginning of the reaction, more than 90% of the

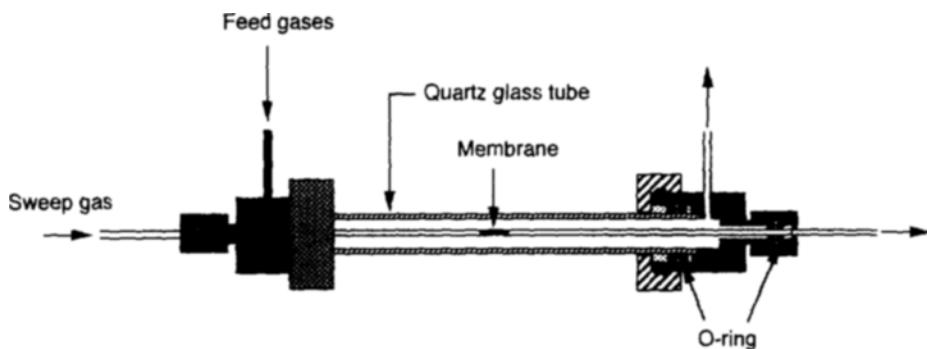


Fig. 3. Details of CVD membrane sealing.

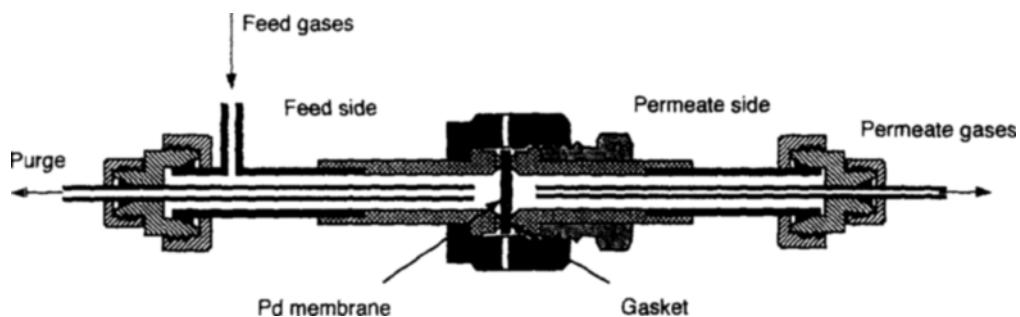


Fig. 4. Details of disk membrane sealing.

gaseous reactant was withdrawn through the porous wall of the tube. When the temperature was increased above 200°C, the palladium source was transported by the argon carrier through the porous wall, where it was decomposed there to form a palladium layer. After the palladium source was sublimed, the reactor was disassembled, and the same amount of palladium acetate was again placed in it. This procedure was repeated a maximum of four times until the evacuation pressure in the tube side reached a prescribed value. Details are reported in earlier papers [Yan et al., 1994; Morooka et al., 1995].

This membrane was used for the permeation tests. Fig. 3 shows a diagram of the membrane assembly. Hydrogen or nitrogen was introduced into the outside of the tube, and argon was introduced into the inside as the carrier. The hydrogen concentration on the inside of the tube was determined with a gas chromatograph equipped with a TCD. The flow rates inside and outside the tube were controlled with mass flow controllers and measured with soap film flow meters downstream of the pressure relief valves. To check the stability of the palladium membrane against chemical poisoning, the membrane was exposed to mixture of nitrogen and methyl disulfide (CH_3SSCH_3) or carbon tetrachloride (CCl_4) at 360°C, and the H_2 and N_2 permeances were then determined. To evaluate resistance to hydrogen embrittlement, the permeation temperature was varied between 100 and 300°C in a hydrogen atmosphere at 0.1 MPa, and hydrogen and nitrogen permeances were then measured.

2. Separation of Hydrogen and Deuterium

Permeation to hydrogen and deuterium was evaluated by using a palladium disk of 0.1 mm thickness instead of the membrane prepared by the CVD, since a definite thickness was required for mathematical modeling. To activate the surface reaction, the disk was abraded with a fine emery paper and was

electrolytically coated with palladium black using a solution of $2.37 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \text{ PdCl}_2$, $9.46 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} (\text{NH}_4)_2\text{SO}_4$ and $4.03 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ naphthalene-1,3,6-trisulfonic acid trisodium salt. The Pd disk was then sealed to a porous stainless steel disk as shown in Fig. 4. Feed rates of H_2 and D_2 and pressures on the feed and permeate sides were controlled with mass flow controllers. Concentrations of H_2 and D_2 on the feed side were kept constant by purging the gas continuously. The Pd disk was heated with an electric furnace to 500°C at a rate of $3 \text{ K} \cdot \text{min}^{-1}$ and held at this temperature for 10 min. It was then cooled to a prescribed permeation temperature of 100–450°C. Concentrations of H_2 , D_2 and HD were determined with a gas chromatograph fitted with a column of activated alumina particles impregnated with ferric oxide.

RESULTS AND DISCUSSION

1. Morphology of CVD Membranes

Fig. 5 shows micrographs of the fractured sections of the support tube before and after deposition. The fractured sections after the fourth repetition of the CVD indicates that macropores of the support are packed with palladium, which appears in the photographs as dark regions. The white grains are α -alumina particles. Sublimed palladium acetate was transferred into the support tube, adsorbed and decomposed in pores near the top surface. Fig. 6 illustrates the deposition mechanism. The amount of deposited palladium was determined by dissolving the membrane in aqua regia. The palladium-filled layer was calculated to be $4.4 \mu\text{m}$, by assuming that all pores were tightly packed with metallic palladium. However, the SEM micrographs show that the palladium deposits spread out gradually over $8 \mu\text{m}$ from the top surface.

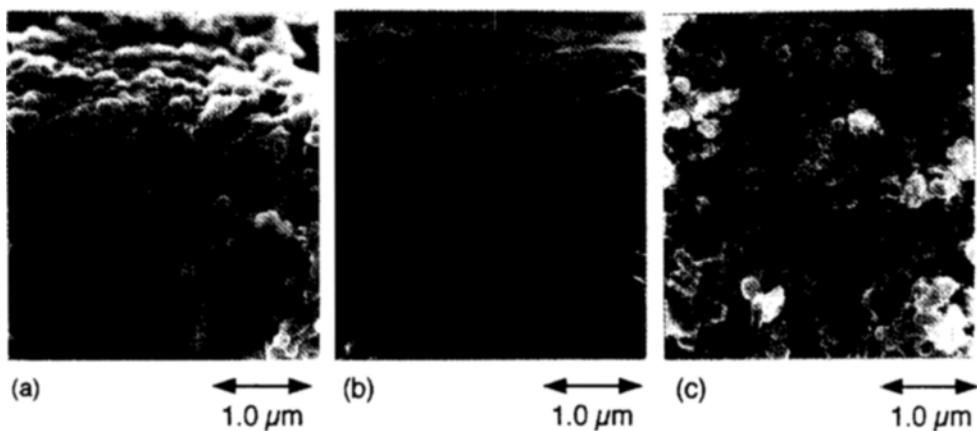


Fig. 5. Fractured surfaces of support tube and palladium membrane formed by CVD.

(a) Support tube; (b) palladium membrane near the top surface; (c) palladium membrane 20 μm below the top surface.

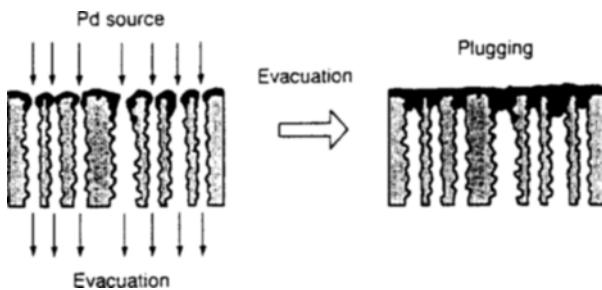


Fig. 6. Mechanism of plugging by CVD as a result of forced cross flow.

2. Hydrogen and Nitrogen Permeation

Permeance of *i*-component through a tubular membrane, k_i , is defined as follows:

$$k_i = Q_i / [2\pi r l_p (p_{hi} - p_{li})] \\ = J_i / (p_{hi} - p_{li}) \quad (1)$$

where p_{hi} and p_{li} are partial pressures of *i*-component in the feed and permeate sides, respectively. p_{hi} and p_{li} are logarithmically averaged along the tube length. The permeation of hydrogen through a dense palladium film usually involves; 1) reversible dissociative chemisorption of molecular hydrogen on the membrane surface; 2) diffusion of atomic hydrogen in the membrane; and 3) reversible associative desorption of atomic hydrogen on the other surface. When the concentration of hydrogen in a dense palladium membrane is very low and the diffusion through the metal phase is controlling, the hydrogen flux is described by the following equation [Shu et al., 1991].

$$J_{\text{H}_2} = [D / (K\delta)] (p_{\text{H}_2}^{0.5} - p_{\text{H}_2}^{0.5}) \quad (2)$$

As shown in Fig. 7, however, the hydrogen flux through the membrane prepared by the CVD process was approximately proportional to $(p_{\text{H}_2} - p_{\text{H}_2})$ and not to $(p_{\text{H}_2}^{0.5} - p_{\text{H}_2}^{0.5})$. The partial pressure of hydrogen in the shell side was varied either by dilution with argon to a mole fraction of 0.2 or by raising the total pressure to 200 kPa, while maintaining the pressure in the tube side at atmospheric, but the linear relationship was not affected. The exponent of the hydrogen partial pressure becomes

less than unity by approaching the diffusion-controlling condition with a thicker membrane.

Fig. 8 shows the effect of repeated deposition on permeation of palladium membranes. Hydrogen permeance increased with increasing permeation temperature, while nitrogen permeance was nearly unchanged. Nitrogen molecules permeate through the remaining macropores of the membrane by Knudsen diffusion mechanism, which was less affected by temperature. The separation factor of hydrogen compared to nitrogen was as low as 15 when the membrane was prepared by one-time deposition. This indicates that the plugging of macropores was not complete. When CVD reaction was repeated, nitrogen permeance decreased greatly while hydrogen permeance decreased only to a lesser extent. The selectivity of hydrogen compared to nitrogen exceeded 1000 after the fourth repetition. Hydrogen permeance remained in the order of $10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ at 300–500°C after the fourth repetition.

When CH_3SSCH_3 was introduced at a concentration of 0.2 mol%, nitrogen began to leak after 50-h operation. At a concentration of 0.02 mol%, however, the permeance of hydrogen and nitrogen remained unchanged for 100 h. When the contaminant was 0.05 mol% of CCl_4 , the permeance of nitrogen was increased from $10^{-10} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ to $10^{-9} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ after an exposure of 20 h. It then remained unchanged for 120 h. By an exposure to 2.5 mol% CCl_4 for 60 h, N_2 permeation increased to $10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$. The change in nitrogen permeance suggests that chlorine damaged the palladium membrane more extensively than sulfur, but that the membrane was quite stable against chlorine and sulfur at concentrations in the order of 0.01 mol% [Kusakabe et al., 1996]. This result differs from that obtained with a palladium-silver alloy foil, whose H_2 permeance was decreased to a trace level by poisoning with CCl_4 [Ali et al., 1994]. A palladium foil membrane was also reported to deteriorate in seconds by exposure to H_2S at 700°C [Edlund and Pledger, 1993]. The palladium membrane prepared by the CVD is finely divided in macropores of the support. Microcracks caused by poisoning are confined in the macropores and will not grow. This is a major reason of the toughness of the membrane.

Fig. 9 shows changes in hydrogen permeance of the pal-

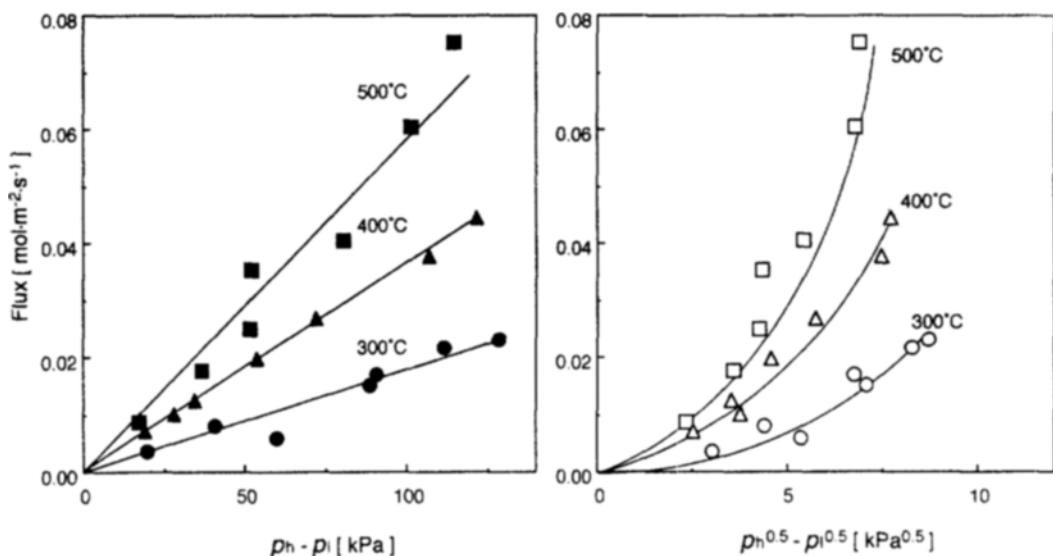


Fig. 7. Relationship between hydrogen flux and pressure differences between feed and permeate sides (after Morooka et al., 1995). Permeation temperatures are 300, 400 and 500°C. The palladium membrane was prepared by four repetitions of CVD at 400°C.

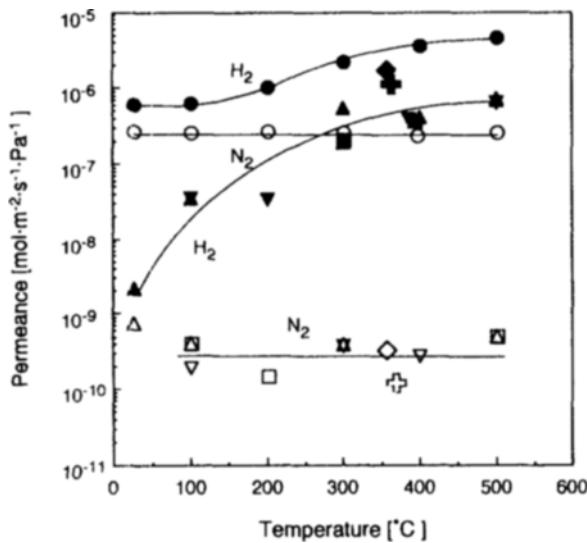


Fig. 8. Effects of permeation temperature and CVD repetition on permeances of palladium membrane.

●, H_2 permeance after single CVD; ▲, ■, ▽, ◆ and +, H_2 permeance after four repetitions of CVD for membranes prepared independently for reproducibility test. Open keys, nitrogen permeance.

ladium disk by repeating the temperature change between 100°C and 300°C at a pressure of 0.1 MPa. No nitrogen was permeated until the 13th cycle. At the 14th cycle, hydrogen permeance was increased and nitrogen began to permeate downstream of the disk, which indicates a failure in the membrane. As with the palladium membrane formed in the macropores of the support, however, there was no change in hydrogen permeance after the 35th repetition as shown in Fig. 10. Hydrogen and nitrogen permeances were measured after 5, 15, 25, and 35 temperature cycles in this case. Nitrogen permeance was increased gradually, but the H_2/N_2 separation factor was as high as 100 at 300°C after the 35th repetition.

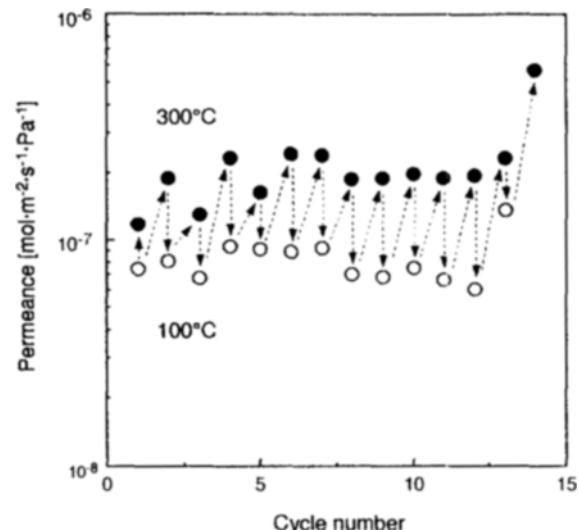


Fig. 9. Effect of temperature cycling between 100 and 300°C on H_2 permeance of palladium disk.

3. Separation of Hydrogen Isotopes

Fig. 11 shows isotherms of hydrogen-palladium [Gillespie and Galstaun, 1936; Wicke and Nernst, 1964; Holleck, 1970; Shu et al., 1991] and deuterium-palladium systems [Gillespie and Downs, 1939; Wicke and Nernst, 1964]. There are large differences in the dissociation pressures of hydrogen and deuterium hydrides.

According to Fick's law, the permeation flux of hydrogen or deuterium ions through palladium membranes is expressed as

$$J_i = (D_i / \delta) \Delta c_i \quad (3)$$

where $i=H$ or D . Δc_i is the concentration difference of H or D in a membrane on the two surfaces. The diffusivity D_i increases exponentially with increasing temperature.

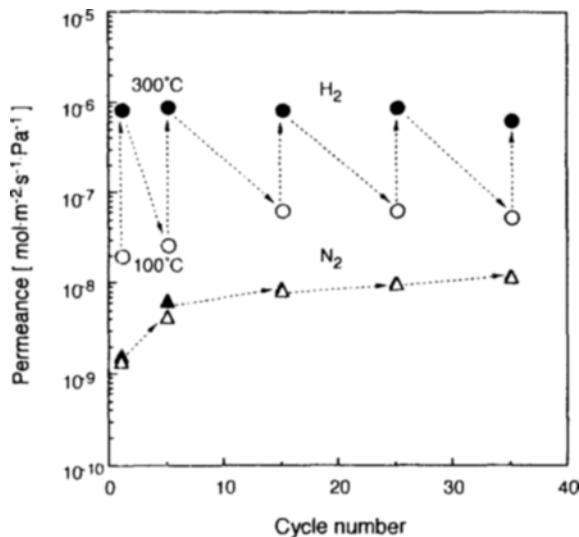


Fig. 10. Effect of temperature cycling between 100 and 300°C on H₂ and N₂ permeances of palladium membrane formed by four repetitions of CVD.

$$D_i = D_{0i} \exp(-E_i/RT) \quad (4)$$

Data of diffusivity reported in the literature are generally consistent. Nagamoto and Inoue [1985] presented the following equation for hydrogen diffusivity.

$$D_H = 2.3 \times 10^{-7} \exp(-2610/RT) \quad (5)$$

Difference in diffusivity between the α - and β -phase is negligible [Nagamoto and Inoue, 1977]. Thus, the diffusion coefficient was assumed to be constant in this study. Nishikawa et al. [1996] obtained the hydrogen/deuterium diffusivity ratio as follows.

$$D_H/D_D = 2.12 \exp(-276.6/T) \quad (6)$$

Fig. 12 illustrates two models for the distribution of H or D in a palladium film when the β - and α -phases prevail at the high and low pressure sides, respectively. The solid line represents a sorption isotherm. Model A assumes a distinct two-phase region, and

$$\Delta c_i = c_{hi} - c_{li} \quad (7)$$

Model B assumes a homogeneous distribution of α - and β -phase domains, and

$$\Delta c_i = (c_{lb} - c_{li}) + (c_{hi} - c_{hb}) \quad (8)$$

Hydrogen and deuterium fluxes were obtained using the single-component gas of $p_h=0.4$ MPa and $p_l=0.1$ MPa. Fig. 13 shows the effect of temperature on hydrogen and deuterium fluxes. The ratio of hydrogen flux to deuterium flux is approximately 7 at 150-200°C. This high theoretical permselectivity is realized under conditions where the feed and permeate sides of the membrane belong, respectively, to the β -phase and α -phase for hydrogen and both sides belong to the α -phase for deuterium. The calculation from Model A and Eqs. (3)-(7) are consistent with the experimental data collected herein.

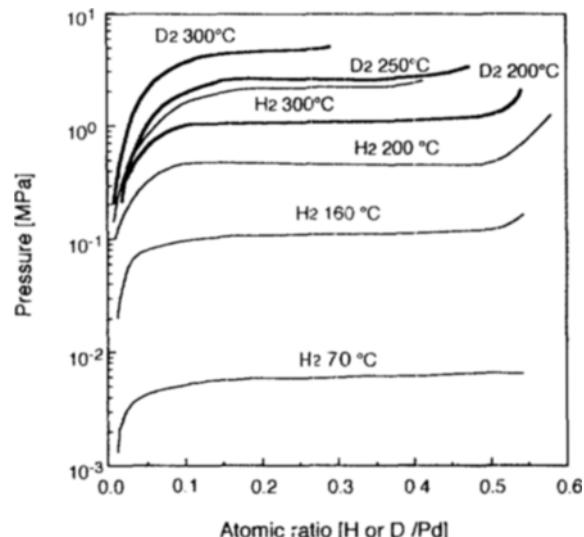


Fig. 11. Sorption isotherms of hydrogen and deuterium.

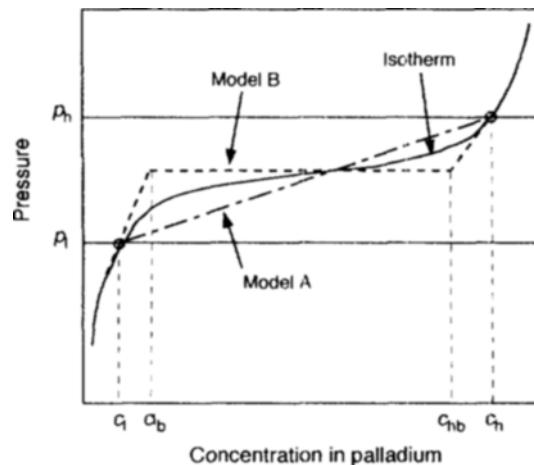


Fig. 12. Modeling of hydrogen distribution in palladium membrane.

In a binary mixture of H₂ and D₂, the palladium membrane catalyzes exchange reactions between adsorbed H₂ and D₂. From Eq. (1), the permselectivity of H to D, α_{HD} , is defined by

$$\alpha_{HD} = [J_H/(p_{hH} - p_{lH})]/[J_D/(p_{hD} - p_{lD})] \quad (9)$$

where $p_h=2p_{lH}+p_{hD}$, and $p_l=2p_{lD}+p_{hD}$. Under a steady-state operation, permeation flux is calculated from the flow rate of carrier gas introduced into the permeate side and the partial pressure of permeate. The selectivity is then given as

$$\alpha_{HD} = [p_{hH}/(p_{hH} - p_{lH})]/[p_{hD}/(p_{hD} - p_{lD})] \quad (10)$$

Suzuki and Kimura [1984] investigated permeances of H₂ and D₂ through a palladium-silver alloy in H₂-He, D₂-He and H₂-D₂ systems, and concluded that the theoretical separation factor calculated from H₂-He and D₂-He agreed with the H₂-D₂ system. However, their calculations neglected the formation of HD in the permeate side. Mitsuishi et al. [1983] investigated permeances of H₂, HD and D₂ through a Pd-Ag-Au alloy tube (Pd:Ag:Au=75:20:5 in mass) in H₂-Ar, D₂-Ar and H₂-D₂-Ar sys-

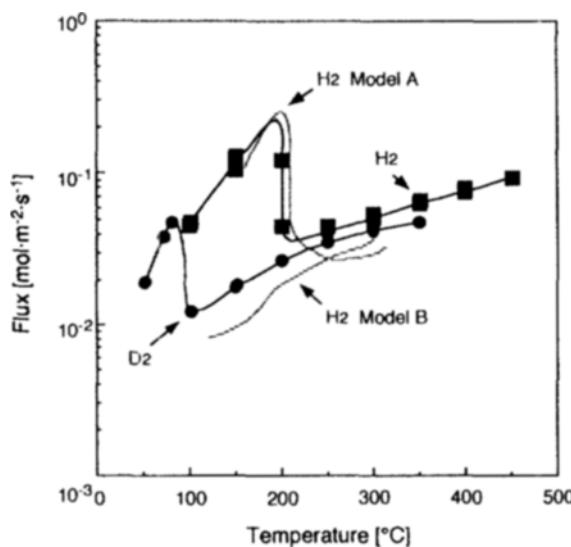


Fig. 13. H_2 and D_2 fluxes versus permeation temperature. $p_h=0.4$ MPa, $p_p=0.1$ MPa.

tems. In this study, the formation of HD in the permeate side was taken into account, and they reported that the permeation rates for the mixture agreed with the theoretical predictions. Under their experimental conditions, the α -phase prevailed, and the separation factor was 1.19.

In the present experiment, the total pressures in the feed and permeate sides were maintained at 0.7 MPa and 0.1 MPa, respectively. The temperature was maintained at 150°C, and the H:D composition in the feed side was varied. The selectivity was 1.64 when a mixture of H:D=3:22 was fed. This value was decreased to 1.2 when the H_2 fraction in the feed was increased. The H:D dependency of the separation factor suggests that the β -phase, induced by hydrogen, affects the permeation of deuterium. If the CVD palladium membrane is applied to separation of hydrogen isotopes, the permeance will be much increased because of the thinness of the CVD membrane.

CONCLUSIONS

A high-performance palladium membrane was prepared by a crossflow CVD method in macropores of an α -alumina support tube. Hydrogen permeance and selectivity to nitrogen were higher than 10^{-6} mol·m⁻²·s⁻¹·Pa⁻¹ and 1000, respectively. The membrane was resistant to hydrogen embrittlement and sulfur and chlorine poisoning. When the H_2/D_2 selectivity was calculated from permeances of H_2 and D_2 determined separately with a feed of H_2 or D_2 , the value was as high as 7 at a 150–200°C under a feed pressure of 0.4 MPa and a permeate pressure of 0.1 MPa. The selectivity was decreased to 1.2–1.6 when a mixture of H_2 and D_2 was fed.

ACKNOWLEDGEMENTS

This study was supported by the Ministry of Education, Science, Sports and Culture, the New Energy and Industrial Technology Development Organization (NEDO) and the Research Institute of Innovative Technology for the Earth (RITE). The

authors deeply appreciate the valuable advice of professor Masaumi Nishikawa, Department of Nuclear Engineering, Kyushu University. The α -alumina support tubes were kindly supplied by NOK Corporation, Japan.

NOMENCLATURE

Δc_i	: concentration difference of i-component between high and low pressure sides [mol·m⁻³]
D_i	: diffusivity in palladium [m²·s⁻¹]
D_0	: pre-exponential term of Eq. (4) [m²·s⁻¹]
E_i	: activation energy for diffusion [J·mol⁻¹]
J_i	: permeation flux of i-component [mol·m⁻²·s⁻¹]
K	: Sievert's constant [m³·Pa⁰⁵·mol⁻¹]
k_i	: permeance of i-component [mol·m⁻²·s⁻¹·Pa⁻¹]
l_p	: membrane length [m]
p_{hi} , p_{pi}	: partial pressures of i-component in the shell and permeate sides, respectively [Pa]
Q_i	: permeation rate of i-component [mol·s⁻¹]
R	: gas constant [J·mol⁻¹·K⁻¹]
r_p	: outer membrane radius [m]
T	: temperature [K]

Greek Letters

α_{ij}	: selectivity of i-component to j-component
δ	: membrane thickness [m]

REFERENCES

- Ali, J. K., Newson, E. J. and Rippin, D. W. T., "Deactivation and Regeneration of Pd-Ag Membranes for Dehydrogenation Reactions", *J. Memb. Sci.*, **89**, 171 (1994).
- Athayde, A. L., Baker, R. W. and Nguyen, P., "Metal Composite Membranes for Hydrogen Separation", *J. Memb. Sci.*, **94**, 299 (1994).
- Chai, M., Yamashita, Y., Machida, M., Eguchi, K. and Arai, H., "Preparation and Characterization of Metal-Dispersed Alumina Membranes for Selective Separation of Hydrogen", *J. Memb. Sci.*, **97**, 199 (1994).
- Collins, J. P. and Way, J. D., "Preparation and Characterization of a Composite Palladium-Ceramic Membrane", *Ind. Eng. Chem. Res.*, **32**, 3006 (1993).
- Edlund, D. J. and Pledger, W. A., "Thermolysis of Hydrogen Sulfide in a Metal-Membrane Reactor", *J. Memb. Sci.*, **77**, 255 (1993).
- Fort, D., Farr, J. P. G. and Harris, I. R., "A Comparison of Palladium-Silver and Palladium-Yttrium Alloys as Hydrogen Separation Membranes", *J. Less-Common Met.*, **39**, 293 (1975).
- Gillespie, L. J. and Downs, W. R., "The Palladium-Deuterium Equilibrium", *J. Am. Chem. Soc.*, **61**, 2496 (1939).
- Gillespie, L. J. and Galstaun, L. S., "The Palladium Hydrogen Equilibrium and New Palladium Hydrides", *J. Amer. Chem. Soc.*, **58**, 2565 (1936).
- Holleck, G. L., "Diffusion and Solubility of Hydrogen in Palladium and Palladium-Silver Alloys", *J. Phys. Chem.*, **74**, 503 (1970).
- Itoh, N., Xu, W.-C. and Haraya, K., "Basic Experimental Study

on Palladium Membrane Reactors", *J. Memb. Sci.*, **66**, 149 (1992).

Jayaraman, V., Lin, Y. S., Pakala, M. and Lin, R. Y., "Fabrication of Ultrathin Metallic Membranes on Ceramic Supports by Sputter Deposition", *J. Memb. Sci.*, **99**, 89 (1995a).

Jayaraman, V. and Lin, Y. S., "Synthesis and Hydrogen Permeation Properties of Ultrathin Palladium-Silver Alloy Membranes", *J. Memb. Sci.*, **104**, 251 (1995b).

Knapton, A. G., "Palladium Alloys for Hydrogen Diffusion Membranes", *Platinum Met. Rev.*, **21**, 44 (1977).

Konno, M., Shindo, M., Sugawara, S. and Saito, S., "A Composite Palladium and Porous Aluminum Oxide Membrane for Hydrogen Gas Separation", *J. Memb. Sci.*, **37**, 193 (1988).

Kusakabe, K., Yokoyama, S., Morooka, S., Hayashi, J.-I. and Nagata, H., "Development of Supported Thin Palladium Membrane and Application to Enhancement of Propane Aromatization on Ga-Silicate Catalyst", *Chem. Eng. Sci.*, **51**, 3027 (1996).

Lee, S.-J., Yang, S.-M. and Park, S. B., "Synthesis of Palladium Impregnated Alumina Membrane for Hydrogen Separation", *J. Memb. Sci.*, **96**, 223 (1994).

Li, Z. Y., Maeda, H., Kusakabe, K., Morooka, S., Anzai, H. and Akiyama, S., "Preparation of Palladium-Silver Alloy Membranes for Hydrogen Separation by the Spray Pyrolysis Method", *J. Memb. Sci.*, **78**, 247 (1993).

Mitsuishi, N., Yuki, T. and Ichihara, I., "Characteristics of the Permeation of Hydrogen-Inert Gas Mixtures through a Palladium Alloy Tube Wall", *J. Less-Common Met.*, **89**, 415 (1983).

Morooka, S., Yan, S., Yokoyama, S. and Kusakabe, K., "Palladium Membrane Formed in Macropores of Support Tube by Chemical Vapor Deposition with Crossflow through a Porous Wall", *Sep. Sci. Technol.*, **30**, 2877 (1995).

Nagamoto, H. and Inoue, H., "A Reactor with Catalytic Membrane Permeated by Hydrogen", *Chem. Eng. Commun.*, **34**, 315 (1985).

Nagamoto, H. and Inoue, H., "Sorption and Desorption of Hydrogen on Palladium Sheet", *Nihon Kagaku Kaishi (in Japanese)*, **9**, 1264 (1977).

Nishikawa, M. et al., to be published (1996).

Peache, N. M., Snow, R. C. and Dye, R. C., "Composite Pd/Ta Metal Membranes for Hydrogen Separation", *J. Memb. Sci.*, **111**, 123 (1996).

Shu, J., Grandjean, B. P. A., Van Neste, A. and Kaliaguine, S., "Catalytic Palladium-based Membrane Reactors: A Review", *Can. J. Chem. Eng.*, **69**, 1036 (1991).

Suzuki, Y. and Kimura, S., "Separation and Concentration of Hydrogen Isotopes by Palladium-Alloy Membrane (1)", *J. Nucl. Sci. Technol.*, **26**, 802 (1984).

Uemiya, S., Matsuda, T. and Kikuchi, E., "Hydrogen Permeable Palladium-Silver Alloy Membrane Supported on Porous Ceramics", *J. Memb. Sci.*, **56**, 315 (1991).

van Swaay, M. and Birchenall, C. E., "Permeability and Diffusion of Hydrogen through Palladium", *Trans. Metall. Soc. AIME*, **218**(April), 285 (1960).

Wicke, Von E. and Nernst, G. H., "Zustandsdiagramm und Thermodynamisches Verhalten der Systeme Pd/H₂ und Pd/D₂ bei Normalen Temperaturen; H/D-Trenneffekte", *Ber. Bunsenges. Physik. Chem.*, **68**, 224 (1964).

Yan, S., Maeda, H., Kusakabe, K. and Morooka, S., "Thin Palladium Membrane Formed in Support Pores by Metal-Organic Chemical Vapor Deposition Method and Application to Hydrogen Separation", *Ind. Eng. Chem. Res.*, **33**, 616 (1994).