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Palladium Membrane Formed in Macropores of Support Tube by Chemical Vapor Deposition with Crossflow through a Porous Wall

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ABSTRACT

Palladium acetate vapor was sublimed at a reduced pressure and was evacuated through the porous wall of an α-alumina support tube of 1.8 mm i.d. and 2.4 mm o.d. Due to chemical vapor deposition (CVD), a thin palladium membrane was formed in macropores of the support. The membrane part was about 50 mm in length and was used without any pretreatment. The palladium membrane, prepared at a maximum CVD temperature of 400°C, showed hydrogen permeance and selectivity to nitrogen higher than 10^{-6} mol·m^{-2}·s^{-1}·Pa^{-1} and 1000 at 300–500°C, respectively. Even after the permeation temperature was repeatedly varied between 100 and 300°C in a hydrogen atmosphere, the membrane exhibited no hydrogen embrittlement. The amount of palladium deposited in pores of the support tube was 22 g/m^2 of the outer surface of the tube. The thickness of the palladium membrane calculated from this value was 4.4 μm.

Key Words. Gas separation; Inorganic membrane; Palladium membrane; Chemical vapor deposition; Porous tube

INTRODUCTION

Various types of inorganic membranes have been prepared for gas separation at high temperature (1, 2). Several research groups were successful

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in forming amorphous silica membranes with high hydrogen selectivity by the chemical vapor deposition (CVD) method (3–6). However, amorphous silica is not very strong in the high-temperature steam that is always present in reformed or synthesized gas. Low hydrogen permeance of amorphous silica is also a problem from the economic point of view. Therefore, we searched for membrane materials other than amorphous silica to meet a variety of needs.

Palladium is an interesting material for hydrogen separation since it sorbs much hydrogen (7, 8). Recently, Athayde et al. (9) formed a thin palladium membrane of about 50 nm thickness by sputtering and coating the membrane with a protective polymeric layer. The permeance of their membrane was about 2×10^{-8} $\mathrm{mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}}$ at 100°C, but the membrane was usable only below 100°C. In our previous study (10), a novel metal-organic chemical vapor deposition (MOCVD) process was developed to form a thin palladium film. By using palladium(II) acetate as the palladium source, palladium was deposited inside macropores of an α-alumina support tube, and a 10-mm long palladium membrane was obtained. The hydrogen permeance was larger than 0.1 $\mathrm{mol \cdot m^{-2} \cdot s^{-1}}$ at 300–500°C when the hydrogen pressure difference between the feed and permeate sides was about 0.1 MPa, and the selectivity of hydrogen to nitrogen was higher than 1000. Figure 1 indicates features of a membrane formed by a CVD method with a crossflow of reactants through the porous wall of a support tube (crossflow CVD, hereafter). Conventional methods

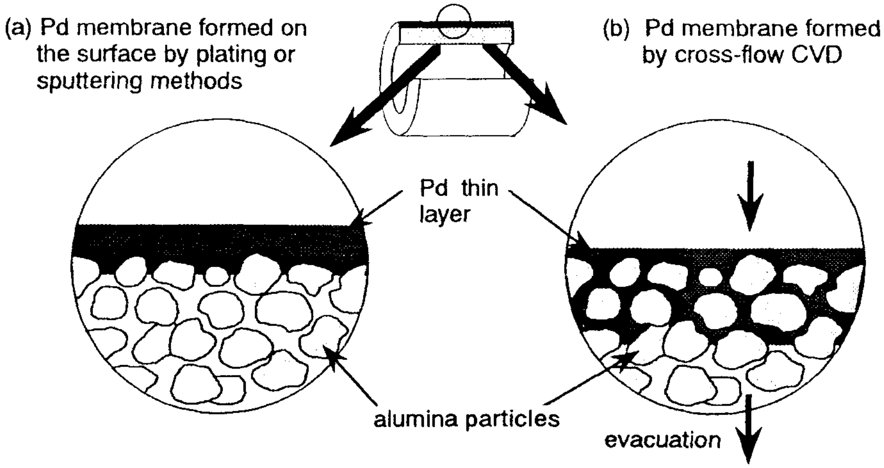


FIG. 1 Features of membranes formed in pores of support.

such as plating and sputtering form a palladium membrane on the top of the support tube, but the crossflow CVD can form a membrane in pores of the support tube. Thus the mechanical strength of the palladium membrane was greatly improved without any coating. To apply this technique to practical applications such as membrane reactors, we wanted to prepare long palladium membranes with a wide permeating area. However, the CVD reactor used in the previous study (10) was a vertical glass tube and was not suitable for this purpose. For this communication a horizontal reactor was newly designed to produce longer membranes. The present system can be easily scaled up to commercial plant size.

EXPERIMENTAL

Preparation of Membrane

A porous α-alumina tube manufactured by NOK Corporation (Japan) was used as the support. The properties of the support were: o.d., 2.4 mm; i.d., 1.8 mm; void fraction, 0.42; and average pore size, about 150 nm. The morphology of the membranes was observed with a scanning electron microscope (SEM, Hitachi S-900). Figure 2 shows the fractured surface of the as-received α-alumina tube.

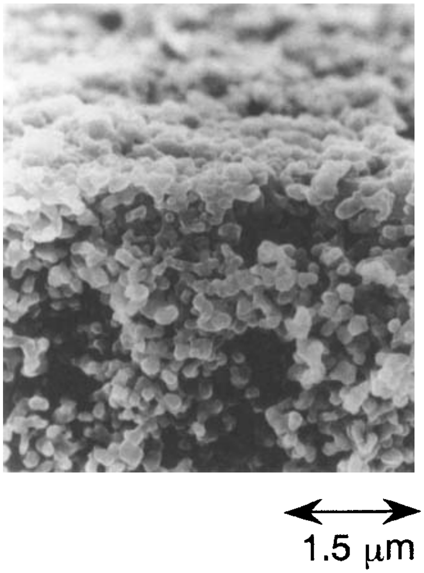


FIG. 2 SEM micrograph of fractured surface of α-alumina.

Figure 3 presents a schematic diagram of the experimental apparatus. The reactor was a horizontal quartz tube of 290 mm length and 10 mm i.d. The outer surface of the porous α-alumina tube was coated with a glass sealant except for the central part of about 50 mm length. The sealing procedure was reported elsewhere (5, 6, 10). The end of the support tube placed in the reactor was also closed with the sealant. Then the support tube was fixed coaxially in the reactor with O-rings. Gas in the reactor was continuously exhausted from the outside end of the support tube with a rotary pump. The shell side of the reactor was evacuated with another rotary pump. The pressure at each outlet was measured with Pirani gauges. The palladium source, palladium(II) acetate (reagent grade, Wako Pure Chemical Ind., Japan), was used as received. About 200 mg palladium acetate was placed in the shell side of the reactor as the palladium source. Then the pressure in the shell side was reduced to about 600 Pa, which was necessary to sublime the reactant before its decomposition at 190–240°C. The reactor was heated externally with an electric furnace to 400°C at a rate of 3.3°C/min and kept at that temperature for 2 hours. At the beginning of the reaction, more than 90% of the gaseous reactant was withdrawn through the porous wall of the tube. The reaction was repeated a maximum of four times by charging the same amount of palladium acetate.

Characterization of Membrane

The membrane prepared by MOCVD was cut apart, pulverized, and soaked in aqua regia for 4 days. Then the amount of palladium in the solution was determined with ICP-AES (Seiko I, SPS 1200). Gas perme-

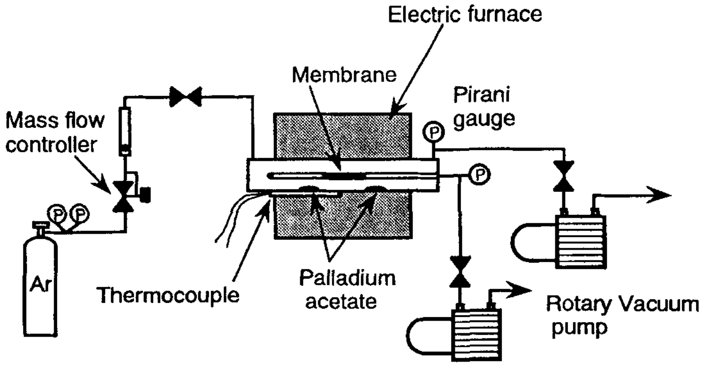


FIG. 3 Schematic diagram of horizontal-type crossflow CVD apparatus.

ance was determined using the flow system reported elsewhere (5, 6, 10). Hydrogen, helium, and nitrogen were introduced separately into the shell side of the membrane, and argon into the permeate side (inside) as the carrier. Flow rates through the shell and permeate sides were measured with soap-film flowmeters, and the gas composition was determined with a gas chromatography equipped with a thermal conductivity detector (Shimadzu, GC-8A). The partial pressure of permeate in the shell side was changed either by dilution with argon to a mole fraction of 0.2 or by raising the total pressure to 200 kPa. The pressure in the tube side was kept atmospheric. The permeance of the i-component through the membrane, k_i, is defined as follows:

$$k_i = Q_i/[2\pi r_p l_p(p_{H,i} - p_{L,i}) = J_i/(p_{H,i} - p_{L,i}) \quad (1)$$

where Q_i is the permeation rate of the i-component, r_p is the outer membrane radius, l_p is the membrane length, $p_{H,i}$ and $p_{L,i}$ are the partial pressures of the i-component in the shell and permeate sides, respectively, and J_i is the permeation flux of the i-component. $(p_{H,i} - p_{L,i})$ is the logarithmically averaged value of the partial pressure difference along the tube length. The separation factor of hydrogen to nitrogen is given as k_{H2}/k_{N2}.

To check the stability of the palladium membrane formed, the membrane was placed in a nitrogen flow containing methyl disulfide (CH_3SSCH_3) at 360°C for a prescribed period. The mole fraction of CH_3SSCH_3 in nitrogen was 2×10^{-4} to 3×10^{-4}. The changes in permeance and selectivity over the time period were measured.

RESULTS AND DISCUSSION

Morphology of Membrane

Figures 4(a), (b), and (c) show micrographs of top surface and fractured section of the palladium membrane prepared after the fourth repetition of the reaction. The fractured section indicates that macropores of the support were packed with palladium, represented in the photographs by the dark part. The white grains are α-alumina particles. Palladium acetate was sublimed during the temperature-raising period, and the vapor was transferred through the support tube, trapped in pores, and decomposed there. Based on SEM observations, the membrane structure did not change along the membrane length, indicating that the palladium concentration was the same everywhere in the reactor at a given time. This result indicates that a further scale-up of the reactor in the axial direction is possible without any difficulties.

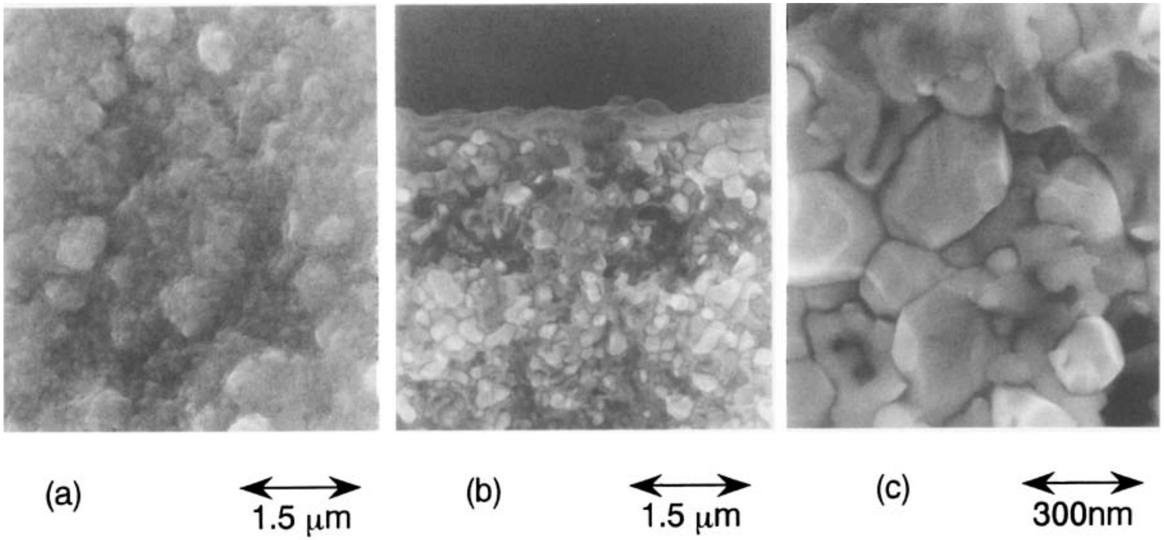


FIG. 4 SEM micrographs of (a) top surface, (b) fractured surface, and (c) high-magnification view of fractured surface of palladium membrane prepared by three repetitions of crossflow CVD.

The ICP measurement of palladium revealed that about 22 g palladium was deposited per square meter of the outer surface of the support tube. The volumetric fraction of pores was 0.42 for the support tube used in the present study. Thus the palladium-filled layer is 4.4 μm thick if all pores are tightly packed with metallic palladium which has a density of 12 $\mathrm{Mg \cdot m^{-3}}$. The SEM micrographs of the fractured section show that the palladium deposits (dark part) spreads out over about 8 μm from the top surface, suggesting that macropores of the support tube in the dark part were not completely filled with palladium. Its packing density decreased gradually with increasing depth from the top surface.

Gas Permeation

Figure 5 shows the effect of repeated deposition on permeation of palladium membranes. Hydrogen permeance increased with increasing permeation temperature, while nitrogen permeance remained almost unchanged. The separation factor of hydrogen compared to nitrogen was as

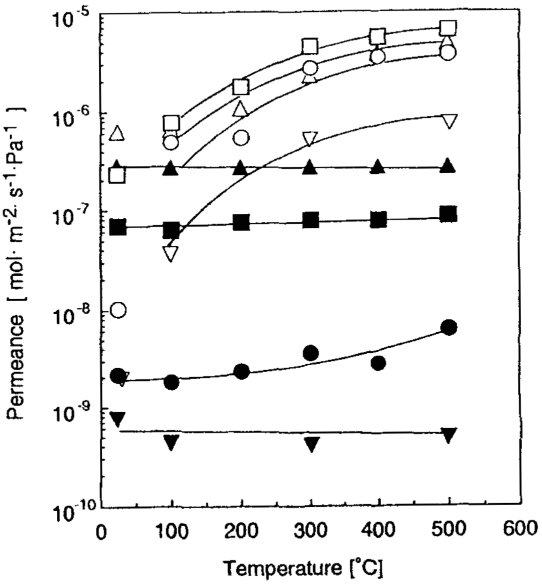


FIG. 5 Effect of permeation temperature and CVD repetitions on hydrogen and nitrogen permeances of palladium membrane. Repetition of CVD: (△ and ▲) first, (□ and ■) second, (○ and ●) third, (▽ and ▼) fourth. Open keys, hydrogen permeance; filled keys, nitrogen permeance.

low as 15 when the membrane was prepared by one-time deposition. This indicates that the plugging of macropores was not completed. When the CVD reaction was repeated, nitrogen permeance decreased greatly while hydrogen permeance was not decreased as much. The selectivity of hydrogen compared to nitrogen exceeded 1000 after the fourth repetition. The hydrogen permeance was still on the order of 10^{-6} mol·m^{-2}·s^{-1}·Pa^{-1} at 300–500°C after the fourth repetition. This value is equivalent to that of Yan et al. (10) and Uemiya et al. (11, 12). The permeance of the membrane at 100°C was 3×10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1} and was comparable to that of the membrane formed by Athayde et al. (9). The hydrogen permeance of the membrane formed after the third coating was 5×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} at 100°C and was one order of magnitude higher than that of Athayde et al.

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

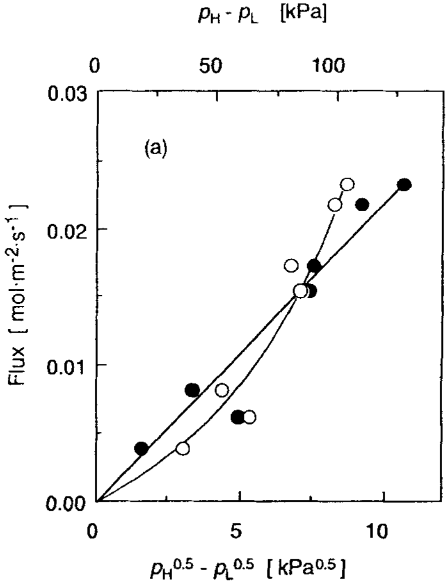
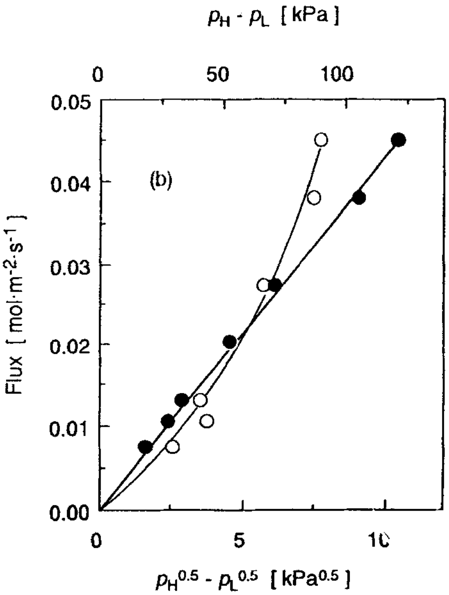


FIG. 6 Relationship between hydrogen flux and pressure difference. Membrane was prepared by four-time repetitions of crossflow CVD. Hydrogen partial pressure in the feed side was changed in the range of 20 to 200 kPa. Pressure difference: open keys ($p^{0.5}_{H,H_2} - p^{0.5}_{L,H_2}$); filled keys ($p_{H,H_2} - p_{L,H_2}$). Permeation temperature: (a) 300°C, (b) 400°C, (c) 500°C.



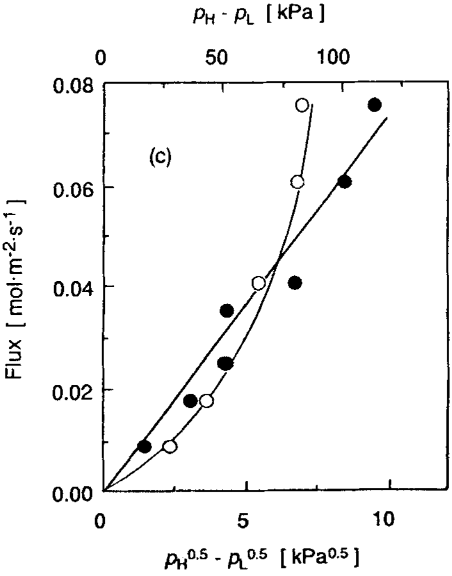


FIG. 6 Continued

other surface. If the rate-determining step for hydrogen permeation is diffusion in the palladium film, the hydrogen flux, J_{H2}, is described by

$$J_{H2} = [D/(K\delta)](p_{H,H2}^{0.5} - p_{L,H2}^{0.5}) \tag{2}$$

where D is the diffusivity of hydrogen atom in palladium, K is Sievert's constant, δ is the membrane thickness, and $p_{H,H2}$ and $p_{L,H2}$ are the hydrogen partial pressures in the shell and permeate sides. As shown in Figs. 6(a), (b), and (c), the hydrogen flux through the membrane prepared by the four-time repetition was nearly proportional to the difference in hydrogen partial pressure between the feed and permeate sides when permeation temperature was higher than 200°C. The partial pressure of hydrogen in the shell side, $p_{H,H2}$, was changed over a range of 20 to 200 kPa, but the linear relationship shown in Figs. 6(a)–(c) was not affected. The membrane formed by Athayde et al. (9) was about 50 nm in thickness and was also proportional to ($p_{H,H2} - p_{L,H2}$). However, our conclusion is valid in the pressure range tested, and the exponent of the hydrogen partial pressures will become smaller than unity at higher pressures and with thicker membranes.

As indicated Fig. 5, a small amount of nitrogen always leaked through the prepared membrane. This suggests that the palladium membrane formed was not a completely dense foil, and that hydrogen was partially transported by migration through boundaries of palladium grains packed in macropores. Yan et al. (10) found the same tendency with their palladium membranes. This membrane structure suggests that the membrane may be easily poisoned by sulfur. Actually, Ali et al. (13) found that a silver/palladium alloy foil of 0.2 mm thickness was poisoned when it was exposed to hydrogen containing 1630 ppm CH_3SSCH_3 at 400°C. The hydrogen permeance was decreased to 12% of the original value after exposure to this mixture for 1 hour. Their membrane was regenerated by repeated oxidation–reduction at 360–440°C for 2–3 days.

To test the stability of the membrane formed in the present study, it was exposed to nitrogen containing 2×10^{-4} to 3×10^{-4} mole fraction CH_3SSCH_3 at 360°C for 10–24 hours. The permeate side was always purged with argon at atmospheric pressure. Then the gas in the shell side was changed to pure nitrogen at atmospheric pressure, the membrane was purged for 20 minutes, and the nitrogen permeance was determined at the same temperature. Next the nitrogen was replaced by hydrogen, the membrane was purged for 20 minutes, and the hydrogen permeance was measured. Figure 7 reveals that the permeance for hydrogen and nitrogen was not changed after the sixth repetition. This indicates that the membrane was resistant to sulfur or was regenerated by keeping it in hydrogen at 360°C for 20 minutes.

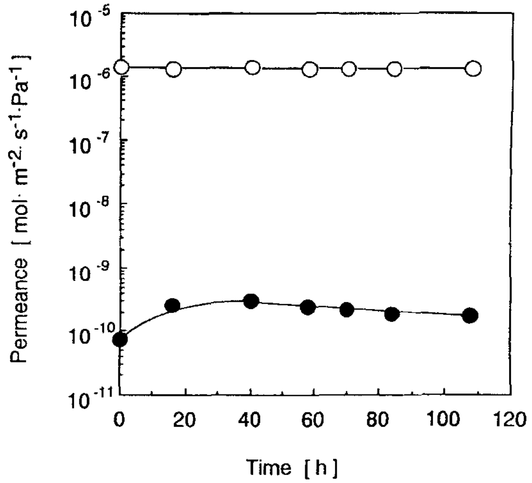


FIG. 7 Effect of exposure in sulfur-containing atmosphere on permeation of hydrogen and nitrogen. Membrane was prepared by four-time repetitions of crossflow CVD. $p_{H,H2}$ = 100 kPa, $p_{L,H2} < 60$ kPa, permeation temperature = 500°C, mole fraction of CH_3SSCH_3 in nitrogen = 2×10^{-4} to 3×10^{-4}, poisoning temperature = permeation temperature = 360°C. Time period needed for permeation test was not included.

Repeating Permeation

A hydrogen–palladium system consists of α- and β-phases below the critical temperature and pressure (8). Adsorption and desorption of hydrogen in the two-phase region results in mechanical failure of the membrane. Normally, palladium is alloyed with silver, and the two-phase region is depressed below the ambient temperature. To test the stability of the membrane against hydrogen embrittlement, the permeation temperature was varied between 100 and 300°C in a hydrogen atmosphere at 0.1 MPa. Each change of temperature was maintained for 8 to 20 hours, and the hydrogen and nitrogen permeances were measured. Figure 8 reveals that the membrane prepared by four-time depositions did not deteriorate after thermal cycling. The separation factor was higher than 1000 at 300°C. As described above, a palladium membrane formed in macropores of the support. Small cavities among palladium grains and between grains and pore walls allow expansion and contraction of the metal lattice due to phase transition.

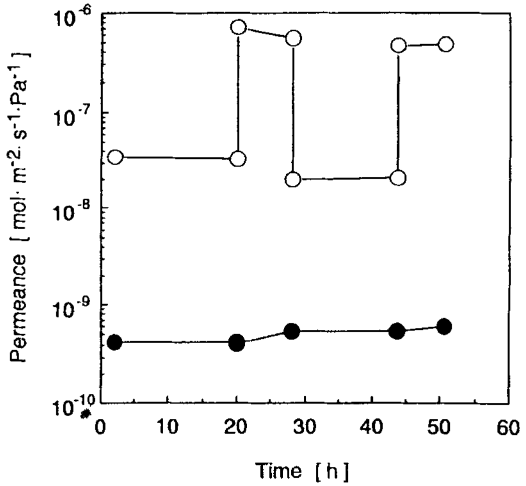


FIG. 8 Effect of temperature recycling between 100 and 300°C on hydrogen and nitrogen permeances of palladium membrane prepared by three-time repetitions of crossflow CVD. Permeation temperature = 500°C, $p_{H,H2}$ = 100 kPa, $p_{L,H2}$ < 60 kPa.

CONCLUSIONS

Palladium membranes were prepared by a crossflow CVD method in macropores of an α-alumina support tube in a horizontal-type reactor. Hydrogen permeance and selectivity to nitrogen were respectively higher than 10^{-6} $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ and 1000. The hydrogen permeance was proportional to the difference in the hydrogen pressure between the feed and permeate sides. The membrane was resistant against hydrogen embrittlement and sulfur poisoning.

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