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Preparation of Pore-fill-type Palladium–Porous Alumina Composite Membrane for Hydrogen Separation

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A method for formation of the palladium layer in a thermally stable porous substrate was studied. A composite membrane with Pd layer encapsulated in a porous α-alumina substrate (Pd/Al_2O_3(PF)) was successfully prepared by a new seeding technique and electroless plating. From SEM–EDX, the Pd layer was observed only in the porous substrate at a depth of 10 µm from the top surface. This membrane showed extremely high H_2 permselectivity ($\alpha_{H_2/N_2} > 10000$) at 773 K and good stability.

Palladium-based membranes have been extensively studied due to their hydrogen selectivity and permeability.[1,2] Early commercialization of Pd membranes involved rolled membrane plates with thicknesses of 20 µm. Many research groups have investigated reducing the amount of Pd required in these membranes, which directly affects their cost. Various preparation methods have been applied to prepare a thin Pd-based membranes, including electroplating,[3,4] electroless plating,[5,6] and chemical vapor deposition.[7]

However, the α- to β-phase transition of Pd causes hydrogen embrittlement and reduces the membrane lifespan.[8] Although thin Pd-based membranes show high permeability, thermal stress and hydrogen embrittlement greatly affect their stability. Performance of thin Pd membranes prepared on substrate surfaces is further degraded by the Pd layer peeling off, alloying with metal catalysts, and breakage caused by collision with other materials.[9] Consequently, development of a new structural H_2 separation membrane is required.

Recently, pore-fill-type Pd–γ-Al_2O_3 composite membranes have been prepared by seeding with Pd nuclei on a mesoporous support and subsequent coating with γ-alumina or boehmite as a protective layer.[10–13] However, the γ-alumina or boehmite layers are not expected to have high thermal stability due to the low phase transition temperatures.

In this work, we developed a method for direct formation of the Pd layer in a porous substrate. This method was used to successfully prepare a new pore-fill-type Pd membrane, with the Pd layer encapsulated in a commercially available tubular porous α-alumina substrate. Supported Pd metal membranes were deposited in the pores of the substrate using a counter-diffusion technique, with agarose as the gel precursor. Because α-alumina is a stable phase, this composite structure can be heat-treated and alloyed at high temperature. The Pd layer is not exposed on the top surface, which reduces susceptibility to mechanical damage like peeling. Thus, pore-fill-type membranes may be advantageous for application in separation or catalytic membrane processes.

The pore-fill-type Pd membrane (Pd/Al_2O_3(PF)) was prepared using agarose gel containing Pd salt (Pd-gel). The Pd-gel was poured into the tubular porous α-Al_2O_3 and cooled to immobilize the gel in the pores. This dispersed Pd nuclei into pores of the α-Al_2O_3 substrate. The Pd layer formed at the interface between the α-Al_2O_3 pores and Pd-gel. This method enables preparation of a Pd layer in a porous substrate.

The substrate used was a commercially available (NGK Insulators, Ltd.) microfiltration (MF) porous α-alumina tube with an asymmetric multilayer structure. The MF tubes had the following dimensions: outer diameter, 10 mm; inner diameter, 7 mm; length, 300 mm; porosity, 34%; average pore diameter of effective top layer, 0.1 µm. Thickness of intermediate layer and top layer was 80 and 25 µm, respectively. Prior to formation of the metallic working layer, the tube was ultrasonically washed with trichloroethylene and then ethanol. The outer surface of the tubes was uniformly coated with a glaze (Asahi Glass Co. AP5761D) except for the central area (4 cm length, 12.56 cm^2). Agarose L, hydrochloric acid (HCl, 35%), hydrazine monohydrate ($N_2H_4 \cdot H_2O$, 98%), tin chloride ($SnCl_2$), and palladium chloride ($PdCl_2$) were purchased from Wako Pure Chemical Industries Corporation. Paratop (Okuno Chemical Industries Co., Ltd.) was used as an electroless plating solution, which consisted of ethylenediamine palladium (Pd source), sodium formate (reductant), and deionized water.

The Pd/Al_2O_3(PF) was synthesized as shown in Figure 1. First, the Pd-gel was prepared by dissolving agarose L (1.25 g), $PdCl_2$ (25 mg), and HCl (25 µL) in 25 mL of deionized water. Then the Pd-gel was poured into the α-Al_2O_3 tube and cooled in an ice bath to immobilize it in the porous α-Al_2O_3. The tube was then dipped in hydrazine monohydrate solution (1 mL/200 mL) to reduce the Pd. After the product was washed with deionized water, primary electroless plating was carried out for 10 min at 327 K to grow Pd nuclei. After electroless plating, the Pd-gel was removed from the α-Al_2O_3 tube by calcination at 1123 K. Then, additional electroless plating was carried out for 1.5 h to densify the Pd layer.

For comparison, a conventional Pd membrane (Pd/Al_2O_3(S)) was prepared by sensitization and activation for Pd seeding by alternately dipping in $SnCl_2$ and $PdCl_2$ solutions.[14] Electroless plating was then carried out for 1.5 h at 327 K.

The Pd/Al_2O_3(S) membrane had a metallic luster while the Pd/Al_2O_3(PF) did not (Figure 2). This suggested that the Pd layer was formed on the surface of the Al_2O_3 substrate for Pd/Al_2O_3(S) but not for Pd/Al_2O_3(PF).

Figure 3 shows the laser microscopic observations for cross sections of Pd/Al_2O_3(PF) and Pd/Al_2O_3(S). A Pd layer was observed only within the porous α-Al_2O_3 substrate for Pd/Al_2O_3(PF) (Figure 3a). While the Pd layer of Pd/Al_2O_3(S) was formed on the top surface of the α-Al_2O_3 substrate (Figure 3b). SEM–EDX images (Figure 4) of the Pd/Al_2O_3(PF) membrane showed the Pd layer was located 10 µm from the top surface of the porous α-Al_2O_3 substrate. The apparent thickness of the Pd

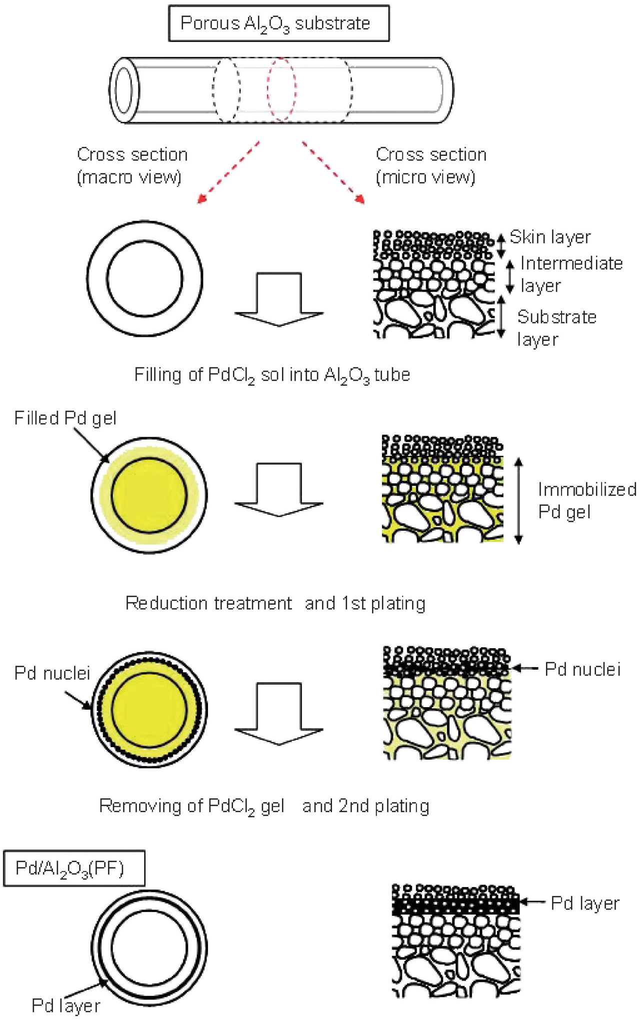

Figure 1. Synthesis of Pd/Al$_2$O$_3$(PF).

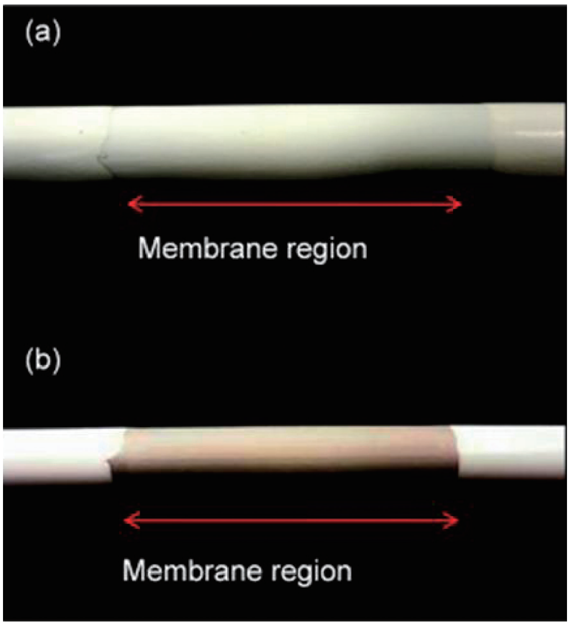

Figure 2. Images of obtained membranes (a) Pd/Al$_2$O$_3$(PF) and (b) Pd/Al$_2$O$_3$(S).

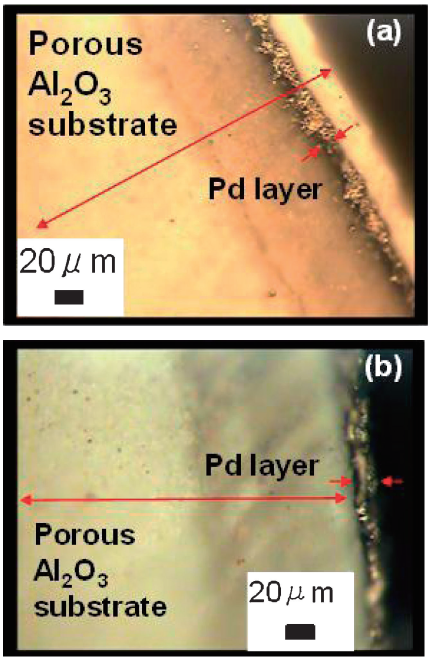

Figure 3. Laser microscopic observations of (a) Pd/Al$_2$O$_3$(PF) and (b) Pd/Al$_2$O$_3$(S).

layer was approximately 8–10 μm. These results confirmed that electroless plating caused Pd layer growth at the surface of Pd nuclei in the area of the α-Al$_2$O$_3$ substrate where they were dispersed by the Pd-gel.

Because the Pd layer was only formed in pores of α-Al$_2$O$_3$ substrate (porosity, 34%), the amount of Pd was calculated to be 3.4–4.2 mg cm^{-3}. This value corresponds to a 2.2–2.8-μm thick conventional Pd membrane. This meant the amount of Pd used to fabricate Pd/Al$_2$O$_3$(PF) was reduced to only 34% that required for the same thickness of conventional membrane.

Gas permeability measurements of the membranes were carried out using a differential pressure gas permeability device. Flow rates of permeated gas were measured by soap-film flow meter. Gas compositions were analyzed by GC-3200 TCD (GL Science Co.). The feed side of the membrane was kept at 50 kPa, and the permeate side was evacuated by a vacuum pump. Evaluation of the H$_2$ separation properties of Pd/Al$_2$O$_3$(PF) was carried out using a mixture of H$_2$/N$_2$ gas (50/50).

The hydrogen separation performance of Pd/Al$_2$O$_3$(PF) membrane at 473–773 K is shown in Figure 5. Pd/Al$_2$O$_3$(PF) exhibited high H$_2$ permeance (1.2×10^{-6} mol m^{-2} s^{-1} Pa^{-1}) and extremely high H$_2$ permselectivity ($\alpha_{H_2/N_2} > 10000$) at 773 K. These values are almost the same level as those reported previously for Pd/Al$_2$O$_3$(S),[15] even though Pd/Al$_2$O$_3$(PF) has no surface Pd layer. In addition, although the selectivity decreased at lower temperatures, the separation performance was stable and completely restored when the temperature was increased up to 773 K even after 150 h.

In conclusion, we successfully developed a method for direct formation of a Pd layer in a porous substrate. The Pd layer

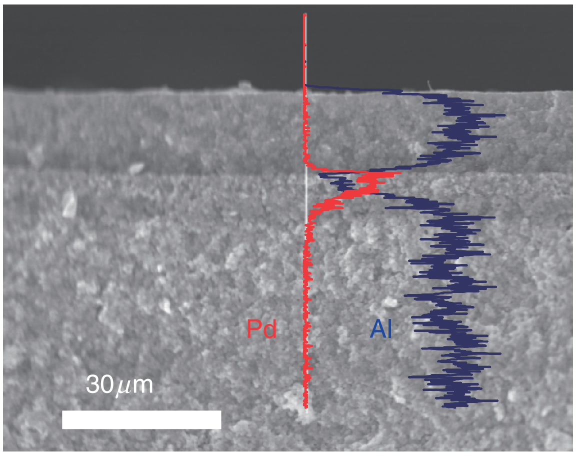

Figure 4. SEM–EDX image of a cross sectional area of Pd/Al_2O_3(PF).

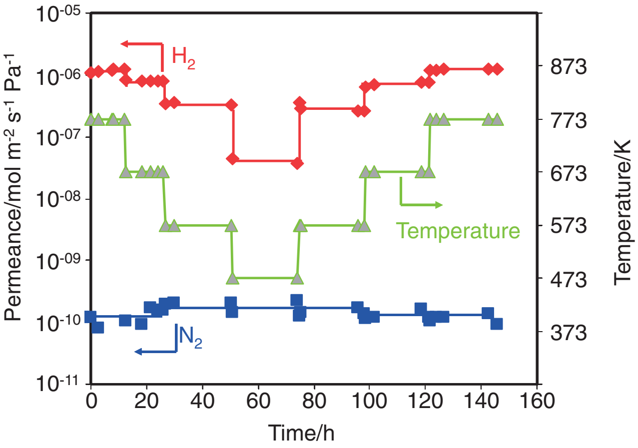

Figure 5. H_2 and N_2 permeance versus time for Pd/Al_2O_3(PF). $H_2/N_2 = 50/50$, $\Delta P = 150$ kPa.

encapsulated in the porous α-alumina substrate allowed efficient hydrogen separation. The Pd layer could be grown only within the porous alumina substrate through the selective formation of Pd nuclei using agarose gel. The Pd layer grew on the Pd nuclei within the area they were dispersed in the substrate. High hydrogen selectivity could be achieved for >100 h at 773 K. Results indicated that use of the composite structure provided membrane stability and also reduced the amount of Pd required for membrane preparation.

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