Preparation of Ultrathin Palladium Membrane Using Electrophoresis of Metallic Nanoparticles

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A new procedure to prepare ultrathin membrane composed of nanoparticles was investigated. The nanoparticles were prepared in aqueous solution containing Pd^{II} ions by sonochemical reduction. Electrophoresis was used to fix the nanoparticles on a porous substrate disc. The ultrathin membrane was successfully prepared with the combination procedure, and the obtained Pd membrane showed high perm-selectivity for H_2 and 3.85 of the separation factor of H_2/N_2 at room temperature.

To supply large amount of hydrogen, production and purification are the most significant issues for widespread adoption fuel cells.[1] Improving the activity of hydrogen perm-selective membrane is crucial for realization of a hydrogen economy. In general, thinner and denser membranes show high performance for hydrogen permeation due to decreasing time through the membrane and increasing collision frequency between gas and the walls of micropores in the membrane. Pd and its alloy membranes are commercially used because they have higher permeability of hydrogen than that of the other gases.[2] However, they are expensive and difficult to make thin films less than 2 µm in thickness by conventional methods.[2,3]

In this letter, we introduce a new method for the assembly of hydrogen perm-selective membrane by electrophoretic bottom-up assembly of palladium nanoparticles on a porous substrate. The perm-selectivity of the membrane was evaluated at room temperature.

Monodisperse Pd nanoparticles were prepared from aqueous Pd^{II} solution with sonochemcal reduction.[4] Designated amounts of $Na_2[PdCl_4]\cdot 3H_2O$ were added to ultrapure water (0.1–0.4 mM) and stirred for a couple of hours. 100 mL of the solution was put in a glass vessel, polyethylene(40)glycol monostearate (PEG40-MS) was added, and the solution was purged with pure Ar for 20 min. Ultrasonic irradiation was carried out at room temperature, using a multiwave ultrasonic generator (200 kHz, 6.0 W/cm^2) equipped with a barium titanate oscillator of 65 mm in diameter. Formation of nanoparticles was monitored during ultrasonic irradiation by a UV–vis spectrophotometer. The absorption peak around 400 nm due to Pd^{II} complex decreased with increasing irradiation time, while a broad absorption band corresponding to Pd^0 nanoparticles increased. The color of the solution also changed from yellow to dark gray after 20 min of irradiation. Therefore, it was decided that the reduction of Pd^{II} had finished at 20 min of irradiation because the 400 nm absorption peak completely disappeared and that no more change of the broad absorption band occurred after further irradiation.

The prepared Pd nanoparticles were observed by high-resolution transmission electron microscopy (HR-TEM). From TEM images the average particle size was calculated to be 4.04 nm, and very narrow size distribution was also obtained. Using sonochemical reduction monodisperse ultrafine Pd nanoparticles were obtained.

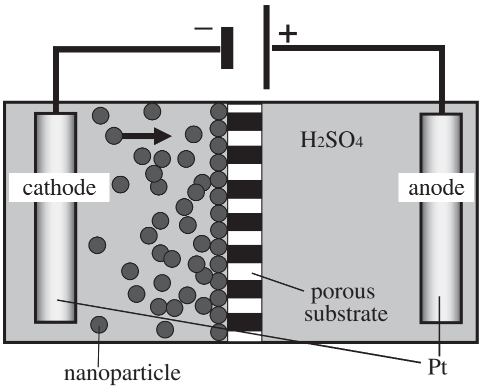

Figure 1. Schematic illustration of the experimental setup for the electrophoretic deposition.

The obtained Pd colloidal solution was very stable because no agglomeration was observed over long storage at room temperature. An electrophoresis method was applied to prepare thin layer membrane which consisted of Pd nanoparticles. Prior to the electrophoresis process, the zeta potential of Pd colloid was measured at room temperature and was −11.0 mV at pH 2.9. Figure 1 shows schematic representation of how the membrane was modified. Pd colloidal solution was put in the cathodal side in the electrophoretic bath because the Pd nanoparticles moved to the anodic side owing to negative zeta potential when the DC electric potential was applied to the solution. A commercially supplied porous alumina disc (prepared by anodic oxidation: AAO disc) was used as substrate to support Pd membrane. Before electrophoresis, many micropores on the surface of AAO disc were observed by field emission SEM observation as shown in Figure 2a. Those micropores completely disappeared after the process (Figure 2b), and the white color of the original AAO disc changed to black, meaning the Pd nanoparticles moved and stacked on the surface of the disc.[7]

The gas permeance properties of obtained Pd membranes strongly depend on the initial concentration of Pd^{II}. The permeance of hydrogen (nitrogen) decreased from 1.53×10^{-4} (6.09×10^{-5}) to 7.03×10^{-6} (1.83×10^{-4}) with increasing initial Pd^{II} concentrations ranging from 0 to 0.4 mM. Especially, in the case of 1.0 mM, no permeances for hydrogen and nitrogen were observed. On the contrary, the separation factor increased from 2.51 to 3.85 with increasing concentrations. The reason that the properties depended on the Pd concentration was the

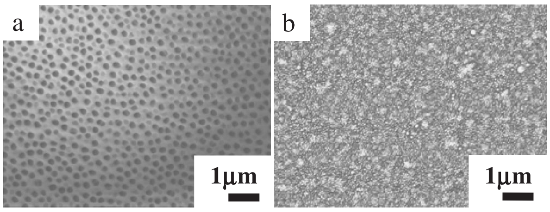

Figure 2. FE-SEM photographs of surface of membranes before (a) and after (b) electrophoresis (Initial Pd concentration: 0.4 mM, Electrophoresis condition: 500 V, 3 min).

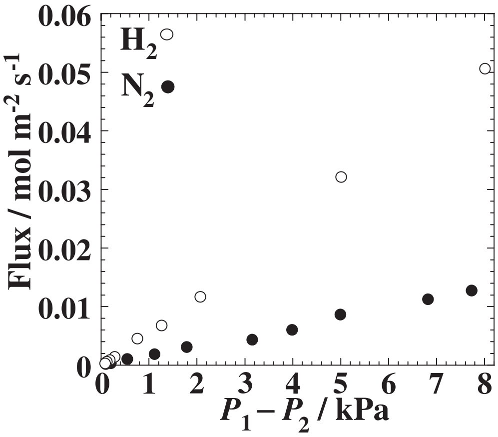

Figure 3. Permeation results of membranes which were prepared using 0.4 mM Pd colloidal solution. Hydrogen (○) and nitrogen (●) flux through the membranes as a function of the difference of the each gas partial pressures.

difference of nanoparticle concentrations in colloidal solution. Therefore, it is thought that the nanoparticles in a concentrated solution are stacked tightly on the substrate surface and became a thick membrane. Hurlbert and Konecny[5] reported that diffusion of hydrogen was the rate-determining step for thick Pd membrane (>20 μm). They claimed that the hydrogen flux was proportional to the square root of hydrogen pressure. To determine the permeation mechanism gas flux is plotted as a function of the difference of partial pressure in permeation experiments as shown in Figure 3. The gas flux is approximately proportional to the difference of partial pressure but not in the square root of it. This indicates that the surface reaction become rate-limiting in hydrogen transport and is not caused by dissolution into bulk Pd but migration through meso or micropores in the membrane.[2a] However, the separation factor has to be larger than 3.85, obtained in this work, if surface reactions occur in the permeation process. To discuss furthermore, the diameter of micropores between Pd nanoparticles is calculated and is 0.6 nm assuming that the membrane consists of spherical particles 4 nm in diameter. From HR-TEM observation, the membrane consisted of spherical particles 4 nm in average diameter.[7] The path diameter is larger than the molecular size of hydrogen, 0.289 nm,[6] but smaller than the mean free-path, 70 nm. From this point of view, it is concluded that the gas permeation in this membrane followed the Knudsen diffusion.[1,2b] Finally, the permeance of our membranes has never changed after repeating gas permeation experiments over 10 times. Hence, we suggest that these membranes have a resistance against hydrogen embrittlement.

In summary, we developed a new preparation procedure which could make very thin hydrogen perm-selective membranes. The procedure consisted of two preparation steps, one was the preparation of nanoparticles by ultrasonic irradiation, and the other was deposition of the particles on a substrate by electrophoresis. The hydrogen permeance rate and hydrogen–nitrogen separation factor of the obtained membrane showed very high performance at room temperature. Detailed diffusion mechanism analysis and optimization of electrophoretic conditions are underway. However, it is expected that this new method has potential to spread widely and to make many kinds of ultrathin perm-selective membrane easily.

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7 Supporting Information is available electrically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.