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Pore-filled palladium-glass composite membranes for hydrogen separation by novel electroless plating technique

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A thin Pd film possesses the ability to exclusively allow H_2 permeation. This property, which is based on the solution-diffusion transport mechanism, has inspired intensive recent efforts to develop the production of cost-effective palladium membranes for industrial applications. The separation and purification of H_2 is required in a number of technological processes [1]. For most industrial processes it is required to minimize cost and to improve permeation; and by decreasing the Pd film thickness it has been found that it is possible to reduce both the material costs and to increase the flux of H_2. However by doing so the mechanical strength of the Pd is reduced preventing the use of Pd films in industrial processes. Because of the weak structural strength of Pd films, a number of studies have therefore been carried out to investigate if the deposition of thin Pd films on mechanically stable porous substrates can increase the stability of the film. Examples of theses are electroless plating, electroplating, chemical vapor deposition and sputtering deposition [2]. From these studies it was successfully demonstrated that such composite membranes have both higher H_2 permeance and better mechanical properties than unsupported Pd films. However, a complicated substrate activation process, and problems relating to Pd consumption and concerns about the durability of the Pd film remains to be addressed. Of these the main problems are the weak interfacial adhesion of the Pd film to the substrate at high temperature, chemical resistance involving carbon deposition and resistance to sulfur poisoning [3].

The present study attempts to address the problem of adhesion failure in Pd films prepared over porous glass. We try to make a pore-filled Pd-glass composite membrane which could avoid the adhesion failure, the α-β phase transition of H_2-Pd system in temperature cycling and use of an excess of Pd. The method chosen was to apply vapor deposition with the additional aid of evacuation for substrate seeding, followed by ultrasonic irradiation under vacuum to aid Pd deposition into the pores of the porous glass (substrate) during electroless plating. The advantages of applying vapor deposition for substrate seeding are a general simplification of the deposition process and a reduction in the use of Pd during the usual seeding method; in the standard process, the substrates are normally activated by repetitively dipping the substrate into two activation solutions of Sn^{2+} and Pd^{2+} about 10 times in succession [4]. Gas permeation experiments indicate that the new method yields a Pd-glass composite membrane with high H_2/N_2 permeation selectivity and good thermal stability at temperatures up to 723 K. Also N_2 adsorption results indicate that the amount of Pd required for making the membranes are very low.

Tubular porous glass membranes (mean pore diameter of 4 nm; O.D. 5 mm; I.D. 4 mm; length ca. 6 cm) were used as the substrates. One end of the tubular substrate was sealed and the other end connected to nonporous quartz tube by melting. To deposit Pd into the pores of the glass substrate an electroless plating procedure was used. This procedure consisted of two sequential processes comprising first of substrate activation and then Pd electroless plating with ultrasonic irradiation. During substrate activation, vapor deposition of Pd was employed to incorporate metallic Pd into the pores of the glass substrates. This was accomplished using Bis(hexafluoroacetylacetonato) Palladium [Pd(hfacac)$_2$]. Fig. 1 shows the schematic diagram of the apparatus used for vapor deposition. The tubular substrate was located at the center of an electric tubular furnace, and the inside of the substrate evacuated using a vacuum pump to deposit the Pd(hfacac)$_2$ preferentially near or inside the pores. After the desired amount of Pd(hfacac)$_2$ was impregnated by vapor deposition at 323 K, it was decomposed in a H_2 flow at 523 K. After activation of the substrate, Pd electroless plating was initiated by immersing about 8 cm^2 of the activated substrate in a 50 ml "half-bath" for 16 h. During this electroless plating process, the inside of the substrate was evacuated. For the first two hours, ultrasonic irradiation was applied to this system by the use of a commercial ultrasonic cleaning bath (Frequency: 50 kHz, Power: 80 W). The bath was maintained at 298 K by cooling water to minimize the possibility of ultrasonic heating. The composition of the plating half-bath was 1.33 g/L $PdCl_2$, 20.1 g/L $Na_2EDTA \cdot 2H_2O$, 99 ml/L NH_3(28%) and 2.8 ml/L N_2H_4(1 mol/L) and its composition was half of the normal bath previously reported [4].

For comparison two types of Pd-glass composite membranes were prepared, one by the novel electroless plating technique described above (referred to as UEP-Pd) and the other from the conventional electroless plating technique (CEP-Pd) [4].

The pore size distributions of UEP-Pd, CEP-Pd and the original porous glass membrane were calculated by the BJH method [5]. The results are shown in Fig. 2. Of most importance is the observation that the pore size distribution of the UEP-Pd membrane did not change

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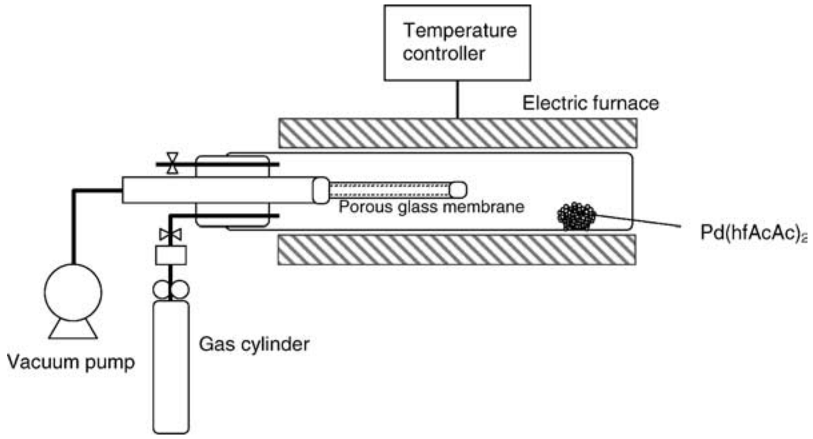

Figure 1 Schematic diagram of the apparatus used for the vapor deposition.

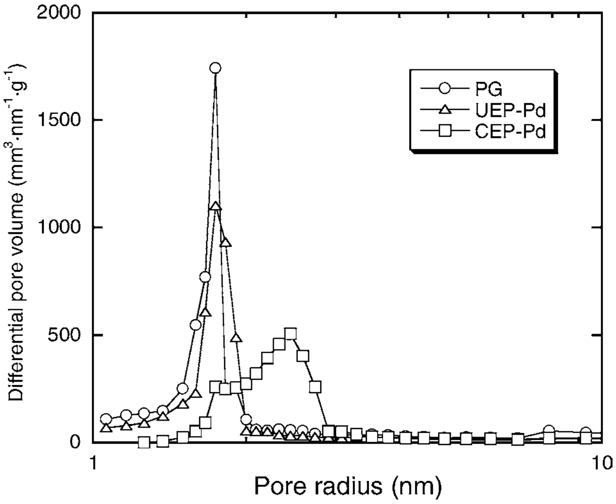

Figure 2 Pore size distributions of UEP-Pd membrane (UEP-Pd), CEP-Pd membrane (CEP-Pd) and original porous glass membrane (PG).

from that of the original porous glass membrane. However, the pore size distribution of CEP-Pd membrane was different and shifted toward large pores. These results indicate that the UEP-Pd membrane comprises of a thinner Pd layer than that of the CEP-Pd membrane.

Pd electroless plating is an autocatalytic deposition process during which Pd^{2+} ions diffuse to and are initially reduced on seeded Pd nuclei of the substrate and meantime N_2 gas from N_2H_4 oxidation are observed as bubbles and the overall reaction is given as follows:

$$2Pd^{2+} + N_2H_4 + 4OH^- \rightarrow 2Pd + N_2 + 4H_2O$$

In such heterogeneous chemical systems, Pd deposition is kinetically determined by Pd^{2+} or/and N_2H_4 mass transfer toward the activated substrate. As is well known, ultrasound in a liquid can induce cavitations involving the formation, growth and implosive collapse of bubbles. Collapse of cavitation bubbles near extended liquid/solid interfaces causes the formation of local fluid microjets that create vigorous local fluid motion and intense pressure fields. This vigorous local fluid motion gives rise to acoustic streaming on a solid surface, which substantially reduces the thickness of the diffusion layer at liquid/solid interfaces and hence strongly facilitates mass transfer between a liquid and a solid [6, 7]. We therefore conclude that by ultrasonic assisted vacuum filtration, the bath solution is able to better penetrate the substrate during the initial stages of plating. On this basis, it is predicted that ultrasonic radiation during plating accelerates Pd deposition due to generally enhancing the mass transport of the bath solution toward to Pd seeds. Therefore, under ultrasonic assisted vacuum filtration it is believed that Pd deposits more uniformly in the pores of the substrate. In the absence of ultrasonic irradiation, Pd deposition in pores of the glass substrate is governed by pore impregnation under capillary force, in which smaller pores are more significantly modified than the larger pores, and thus, the average pore size distribution of the CEP-Pd membrane is shifted toward large pore dimensions.

Single gas permeation through the membranes was measured 623, 673 and 723 K using H_2 and N_2, under the same experimental procedure as described by [8]. The pressure difference of the gases through the membranes was kept constant at 101.3 kPa. Table I shows the ratios of the permeance of H_2/N_2 through the original porous glass membrane, UEP-Pd membrane and CEP-Pd membrane at 623, 673 and 723 K. The UEP-Pd membrane showed a high hydrogen selectivity. For the UEP-Pd membrane, the ratio of the permeances, H_2/N_2 was 511 at 623 K, 520 at 673 and 723 K. The value at 723 K is more than 140 times the theoretical Knudsen value ($PH_2/PN_2 = 3.7$). Fig. 3 shows the relationship between temperature and permeance of H_2

TABLE I Ratios of the permeance of H_2/N_2 through UEP-Pd membrane (UEP-Pd), CEP-Pd membrane (CEP-Pd) and original porous glass membrane (PG) at 623, 673 and 723 K

Membrane	Temperature (K)	Ratio of permeances (H_2/N_2)
UEP-Pd membrane	623	511
	673	520
	723	520
CEP-Pd membrane	623	103
	673	145
	723	280
Porous glass membrane (Substrate)	623	3.4
	673	3.5
	723	3.5

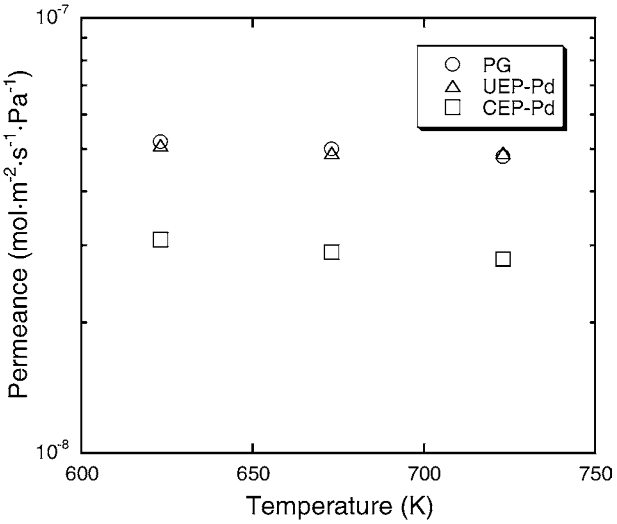

Figure 3 Relations between the permeances of H_2 and temperatures for UEP-Pd membrane (UEP-Pd), CEP-Pd membrane (CEP-Pd) and original porous glass membrane (PG).

through the membranes. The permeance of H_2 through UEP-Pd membrane was high and the value at 723 K was 4.9×10^{-8} $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$. This value was almost same as the original porous glass membrane (the substrate). However, the measured permeance of H_2 through the CEP-Pd membrane was half of the UEP-Pd membrane. These results also supported the belief that UEP-Pd membrane has a thinner and more dense Pd layer than that of the CEP-Pd membrane.

Pore-filled palladium-glass composite membranes were prepared by a novel electroless plating procedure that used vapor deposition for substrate activation, and a low Pd concentration electroless plating half-bath with ultrasonic irradiation and evacuation to aid the deposition of Pd into the pores of a porous glass (substrate). Results indicate that the proposed procedure allows the production of pore-filled palladium-glass composite membranes with high H_2/N_2 selectivity, high permeance of H_2, while decreasing the content of Pd.

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