Pd Membranes Formed by Electroless Plating with Osmosis: H_2 Permeation Studies

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The synthesis of fully dense Pd-Vycor glass composite membranes by electroless plating with or without osmosis is reported. Use of osmotic flux allows one to rapidly form thin (a few microns), fully dense palladium films, which have submicron size microstructure. These features significantly enhance hydrogen permeability as compared to the conventional method. By accounting for resistance of the porous support, it is confirmed that for membranes prepared by the same technique, with gradually changing microstructural characteristics, those with smaller palladium crystallites exhibit larger hydrogen flux. Pd-stainless steel composite membranes were also prepared using electroless plating, either with or without osmosis. Membranes synthesized using osmosis exhibit superior thermal stability.

Introduction

Inorganic membranes are important for technological processes such as separation and purification of gases and chemical reactions in membrane reactors (Hsieh, 1996; Saracco et al., 1999). The most important membrane properties are high permeability and selectivity, along with mechanical, thermal and chemical stability. Owing to infinite hydrogen/nitrogen selectivity, dense Pd-based membranes are suitable for hydrogen separation from gas mixtures and use in reactions such as hydrogenation, dehydrogenation, and steam reforming (Shu et al., 1991; Uemiya, 1999). However, the main drawback of these membranes is relatively low hydrogen permeability, which may be enhanced by decreasing film thickness. Unfortunately, decrease of membrane thickness adversely affects its mechanical stability. Another approach to improve permeability is to synthesize Pd films with optimum microstructure. It has been hypothesized that due to larger volume fraction of grain boundaries, hydrogen permeation may be higher through Pd films with finer grains (Mutschele and Kirchhiem, 1987; Bryden and Ying, 1995). Recently, the importance of Pd film microstructure on the H_2 permeation rates has also been stressed by Ward and Dao (1999).

In order to synthesize stable thin membranes with good mechanical stability and high permeability, composite membranes were developed where metal films are deposited on porous supports (Uemiya et al., 1988; Gryaznov et al., 1993; Collins and Way, 1993; Yeung and Varma, 1995; Xomeritakis and Lin, 1996). In this case, when characterizing permeation properties of the metal film, transport resistance of gas through the porous support needs to be considered. In this context, a model was developed by Henis and Tripodi (1981), whereby the transport properties of each membrane layer can be isolated. This approach is required to establish a relationship between microstructure of deposited film and its permeation properties.

In the present work, we use the technique of electroless plating with osmosis, developed in our laboratory, to synthesize thin, dense palladium composite membranes [for details, see Yeung and Varma (1995); Souleimanova et al. (1999)]. As shown previously (Souleimanova et al., 2000), this method allows one to precisely regulate the film microstructural characteristics, including metal grain size, film thickness, and local Pd penetration into the porous support. The goal of this article is to identify the influence of these characteristics on membrane permeation properties, with special attention paid to the relationship between hydrogen permeation performance and Pd grain size.

Experimental Studies

Two different porous supports were used for synthesis of composite membranes. Porous Vycor glass disks (Corning,

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Table 1. Thickness and Grain Size of Pd Films on Vycor Glass Support

Sucrose Concentration	0 M	2 M	6 M	9 M
Plating time, h	8	5	4	2.5
Thickness of dense Pd film, μm	8	6	4	3
Avg. Pd grain size, μm	7	4	1.1	0.5

Inc.) were 1 in. in dia., with wall thickness 1.5 mm and average pore dia. 4 nm, while porous stainless steel disks (Mott Metallurgical Corp.) had 1 mm wall thickness and 0.2 μm pores. The glass substrates were characterized by nitrogen adsorption for pore volume and pore-size distribution using AUTOSORB-1 (Quantachrome Corp.). The disks were cleaned, activated, and plated using procedures described elsewhere (Souleimanova et al., 2000). During plating, different concentrations of sucrose osmotic solutions (0, 2, 6, 9 M) were used for Vycor glass, while 3×10^{-7} M solution of polyethylene glycol (molecular weight = 7.2×10^{6} g/mol) was used for porous stainless steel. All membranes were plated until they became fully dense, that is, H_2/N_2 permselectivity greater than 10^7 was reached.

The membrane microstructures were analyzed by both scanning electron (SEM, JEOL-6400) and atomic force (AFM, Metris-2000, Burleigh Instruments, Inc.) microscopies. The obtained patterns of sample surfaces and cross sections were analyzed by using advanced image analysis software (Image Pro-Plus 4.0). Membranes prepared under different conditions of osmosis exhibited differences in grain size and thickness (see Table 1).

Single-gas permeability tests were conducted on the membranes at temperatures up to 873 K, and hydrogen and nitrogen pressures up to 827 kPa. For membrane sealing, Viton and graphite O-rings were used for Vycor glass and stainless steel, respectively. The volumetric flow rates of permeated gases were measured using a bubble flowmeter. For stainless steel based membranes, thermal stability was also investigated using thermal swing experiments.

Results and Discussion

Pd-Vycor glass composite membranes

Characterization of Vycor Glass Support. Nitrogen physisorption experiments were conducted to determine the pore size of Vycor glass support. The results were consistent with the vendor data (Corning Glass Works, 1997). Average pore diameter for Vycor glass was found to be 3.6 nm with narrow size distribution, as 90% of the pores were within 0.8 nm from the average. The porosity was determined experimentally to be 0.34. Owing to relatively small pore size and large thickness (1.5 mm), this support could have a significant effect on hydrogen transport through the composite membrane. Thus, it was necessary to account for its permeation properties.

Estimates show that Knudsen number values for the investigated experimental conditions are in the range of 7–20, thus Knudsen diffusion is expected to be the main mechanism for hydrogen transport through Vycor glass [see also Hwang and Kammermeyer (1966)]. To verify this conclusion, some experiments were conducted. It is known that for a porous medium of length L, consisting of parallel cylindrical capillaries, the permeability coefficient K for single gas permeation is given by (Carman, 1956)

$$K = \frac{JRTL}{\Delta P} = \frac{B_0}{\mu}\langle P\rangle + \frac{4}{3}K_0 \upsilon_m \qquad (1)$$

where J is the gas flux, R is the universal gas constant, T is the temperature, ΔP is the pressure difference between feed and permeate sides, $\langle P\rangle$ is the average pressure, μ is the gas viscosity, υ_m is the mean molecular velocity, and B_0, K_0 are constant structural parameters. Experiments showed that for the used Vycor glass membrane, K remains essentially constant (and equal to $1.606\cdot10^{-6}$ m^2/s), while the average hydrogen pressure, $\langle P\rangle$ changes from 150 to 450 kPa. Thus, the first term on the righthand side of Eq. 1 is negligible, and Knudsen diffusion predominates.

Permeation Through Composite Membrane. Composite membranes were synthesized using different osmotic conditions during electroless plating. The deposition procedure was carried out until palladium film became completely dense, that is, no nitrogen flow was detected for 3 h on the permeate side at 573 K, and pressure difference between feed and permeate sides were equal to 726 kPa. The experimental data on plating time needed to obtain fully dense Pd films and their thickness are presented in Table 1. It may be seen that Pd films become dense faster and are thinner when synthesized under higher osmotic pressures.

The hydrogen fluxes through dense Pd-Vycor glass membranes were measured at different ΔP and T values. For example, permeation of hydrogen (at $\Delta P = 526$ kPa and $T = 573$ K) through membranes obtained under different osmotic conditions is shown in Figure 1. It may be seen that hydrogen flux is higher for membrane synthesized with a higher su-

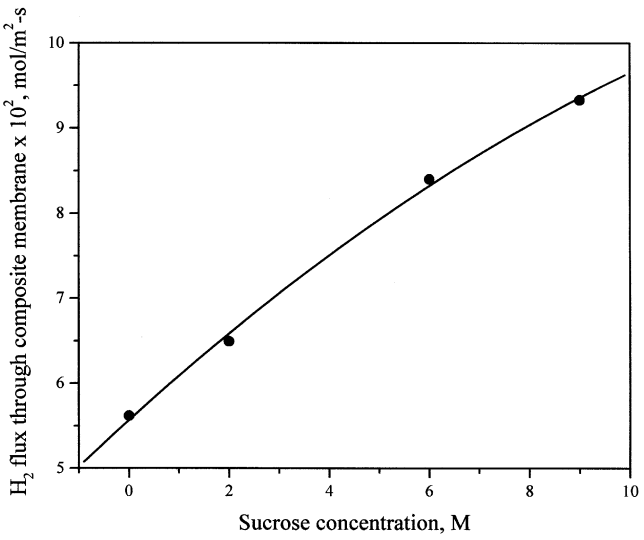

Figure 1. Hydrogen permeation flux for fully dense Pd-Vycor glass composite membranes as a function of osmotic solution concentration during synthesis; $T = 573$ K, $\Delta P = 526$ kPa.

crose concentration. This increase occurs due to changes in film thickness and microstructure. As noted previously, to isolate these effects, first the influence of porous substrate on gas permeation should be excluded.

Permeation Through Palladium Film. The composite membrane consists of a Pd layer and porous substrate in series, where each layer presents resistance for hydrogen flow. The total resistance R_{tot} of the composite membrane is the sum of resistance in *pure* deposited metal (R_{Pd}) and the support (R_{sup}) layers

$$R_{\text{tot}} = R_{Pd} + R_{\text{sup}} \tag{2}$$

where

$$R_{Pd} = F(P_h, P_i, J), \tag{3a}$$

$$R_{\text{sup}} = (P_i - P_l)/J \tag{3b}$$

P_h and P_l (101 kPa) are pressures on feed and permeate sides, respectively; P_i is interface pressure and J is hydrogen flux. Note that in this case, in Eq. 1, $\Delta P = P_i - P_l$. Then, using the experimentally obtained value of K for Vycor glass substrate, data on flux through composite membrane for different P_h (such as shown in Figure 1 for $P_h = 627$ kPa) and taking into account Eqs. 1 and 3b, one may determine the P_i value for each composite membrane as follows

$$P_i = P_l + J \cdot (RTL/K) \tag{4}$$

It is worth noting that evaluation of P_i does not require the exact form of function F. However, this function is commonly expressed as

$$J = (P_h^n - P_i^n) \cdot DS/L_{Pd} \tag{5}$$

where D and S are the diffusion coefficient and solubility constant, respectively, at a given temperature, L_{Pd} is *Pd* film thickness and n is a constant. If the rate-limiting step is bulk atomic diffusion, then $n = 0.5$ (so-called, Sievert's law). For the experimental data, the value of n was calculated using nonlinear regression analysis, and found to be in the range 0.5008–0.5083 for all synthesized membranes. The hydrogen permeation flux as a function of $(P_h^{0.5} - P_i^{0.5})$ is presented in Figure 2, indicating that Sievert's law applies.

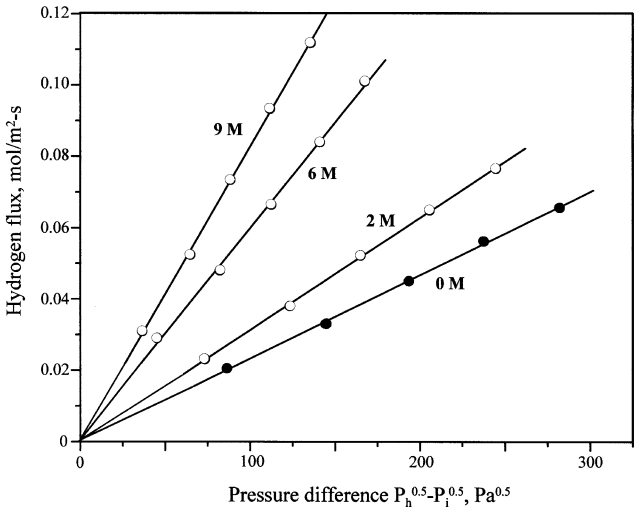

Figure 2. Hydrogen permeation flux through pure Pd film plated under different conditions in Sievert's law coordinates; $T = 573$ K.

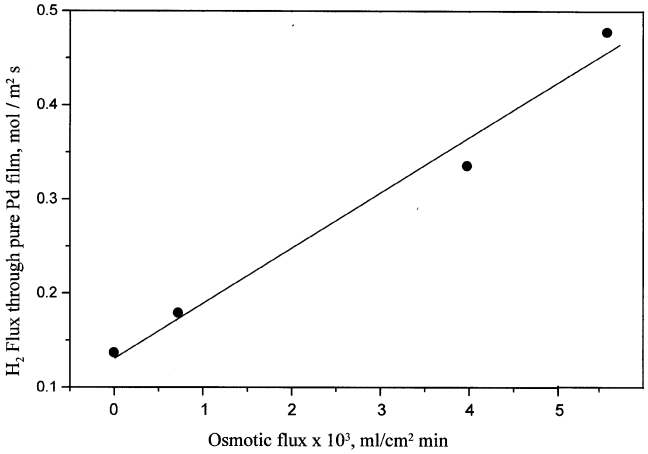

Figure 3. Hydrogen permeation flux through pure Pd film as a function of osmotic conditions; $T = 573$ K, $\Delta P = 690$ kPa.

Based on the fact that Sievert's law applies well for the *Pd film*, it is possible to calculate the H_2 flux through metal films prepared under different osmotic conditions. An example of such flux values for $T = 573$ K and $\Delta P = 690$ kPa ($P_h = 791$ kPa, $P_l = 101$ kPa) is shown in Figure 3. It may be seen that for identical permeation conditions, hydrogen flux is approximately four times larger for films deposited with 9 M sucrose solution as compared to conventional plating. Recognizing that the *Pd* film thickness varies with osmotic flux (see Table 1), it is necessary to compute normalized hydrogen permeability for different membranes to isolate the effect of membrane microstructure. The *Pd* grain sizes of different films are shown in Figure 4, where it is evident that higher osmotic conditions lead to finer grains and more uniform microstructure. Combining the results shown in Table 1, Figure 3 and Figure 4 lead to Figure 5, and the conclusion that under otherwise identical conditions, *hydrogen permeation flux is higher for films with finer Pd grains*, confirming the hypothesis presented earlier.

Using hydrogen flux from Figure 2 and value of solubility constant S from Peachey et al. (1996), from Eq. 5, the diffusion coefficients D for different membranes were calculated to be in the range $6.2 - 7.9 \times 10^{-9}$ m^2/s, which are in good agreement with literature data (Shu et al., 1991).

The activation energies E_a values for hydrogen permeation through both the composite membranes and the pure deposited *Pd* films were also determined. For the composite membranes, the Arrhenius plots shown in Figure 6a give apparent activation energy of 11.8 kJ/mol and 10.1 kJ/mol for membranes synthesized without or with osmosis (6 M sucrose solution), respectively. The former value is in good agreement with data reported in the literature for Pd/glass membranes (Uemiya et al., 1988). The corresponding activation

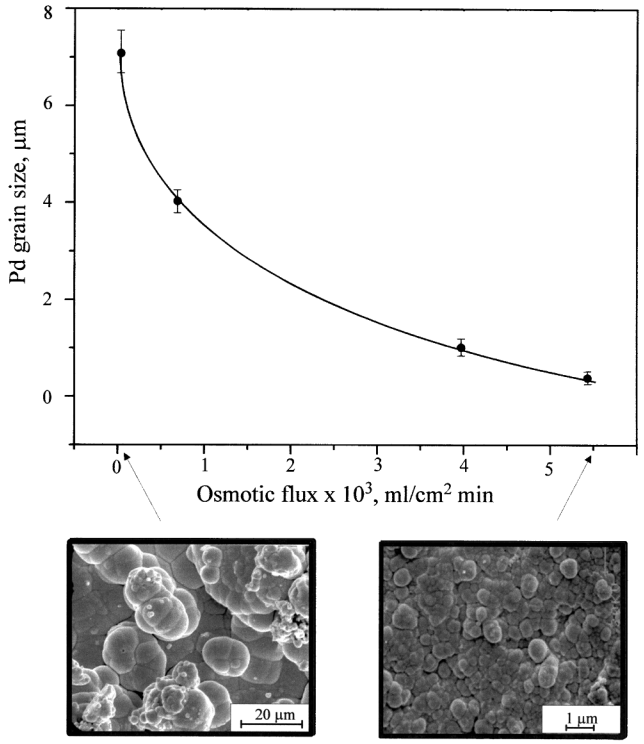

Figure 4. Average Pd grain size for fully dense Pd-Vycor glass composite membranes as a function of osmotic conditions.

energy values for the pure Pd films (Figure 6b) are 20.9 kJ/mol and 18.1 kJ/mol, respectively. The former value is again in good agreement with literature data, which indicates a range of 20–22 kJ/mol (Holleck, 1970; Shu et al., 1991). Note that

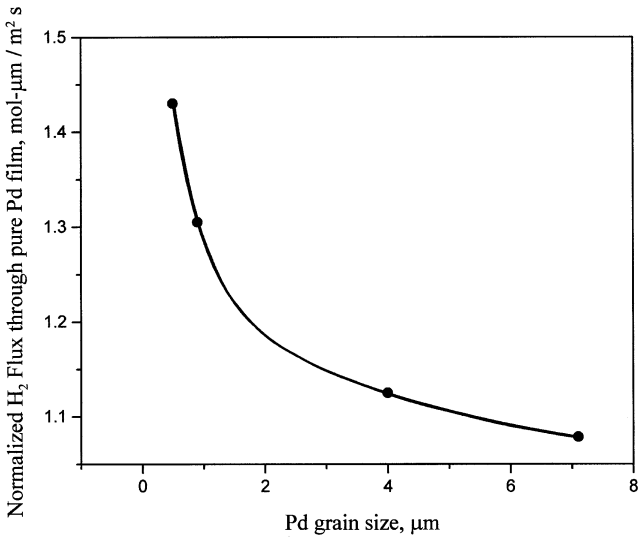

Figure 5. Normalized hydrogen flux through pure Pd film plated under different osmotic conditions, as a function of average Pd grain size; $T = 573$ K, $\Delta P = 690$ kPa.

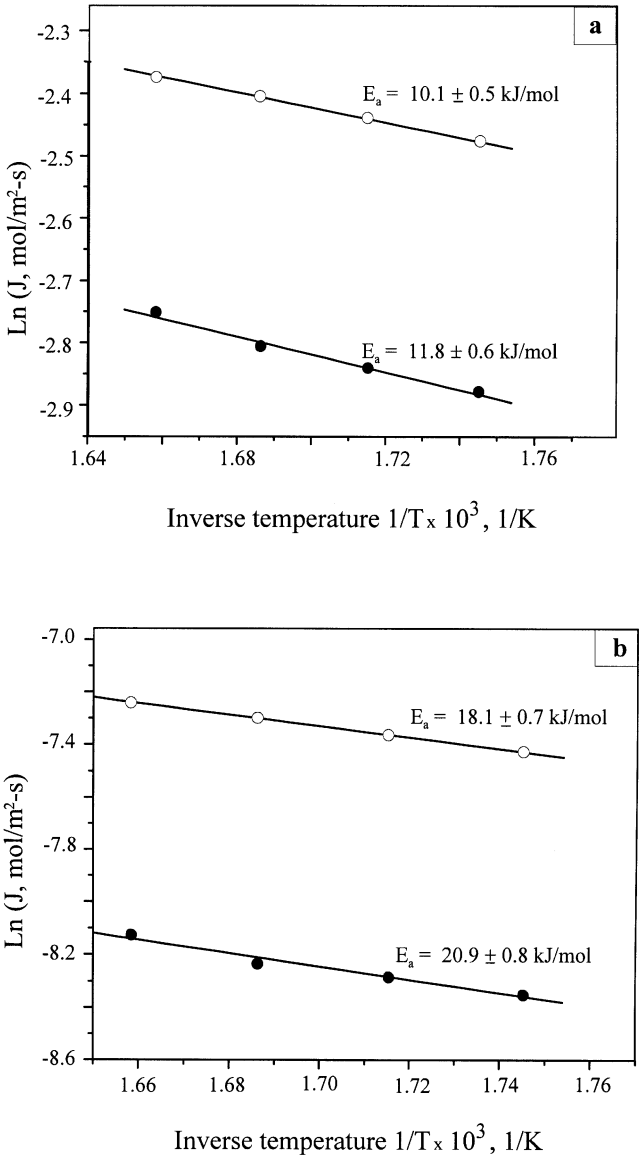

Figure 6. Arrhenius plot of hydrogen flux ($\Delta P = 690$ kPa) through: (a) dense Pd-Vycor glass composite membranes synthesized by (●) conventional electroless plating and (○) electroless plating with osmosis (6 M); (b) pure Pd films deposited by (●) conventional electroless plating and (○) electroless plating with osmosis (6 M).

each point used for the calculation of activation energy was an average of at least five measurements. The difference in E_a values between the pure Pd film and composite membranes arises because of the relatively high transport resistance of Vycor glass support. This feature is similar to the decrease of activation energy in catalytic diffusion-reaction systems where diffusional resistance is significant (Weisz and Prater, 1954). The lower value of activation energy for Pd films synthesized using electroless-plating with osmosis (Figure 6b) again suggests that diffusion is enhanced in finer

grains, as was demonstrated above for a constant temperature (see Figure 5).

Pd-Stainless steel composite membranes

As shown in the last section, Pd-Vycor glass-composite membranes synthesized using electroless-plating with osmosis have high permeability and infinite hydrogen permselectivity. However, owing to its fragility and transport resistance, it is desirable to consider other supports. Stainless steel is good candidate material (Shu et al., 1993; Yeung et al., 1996; Mardilovich et al., 1998) because it has high mechanical strength. Stainless steel-based membranes are expected to have good thermal stability due to the relatively small difference in thermal expansion coefficients between palladium and stainless steel. Another important difference between Vycor glass and stainless steel supports is the pore size: 4 nm for Vycor glass and 200 nm for stainless steel. As a result, the transport resistance of stainless steel is negligible. However, as noted in the Experimental Studies section, the larger pore size requires an osmotic solute of larger molecular dimension. In this section, results for Pd-stainless steel composite membranes, prepared with or without osmosis are presented. It is shown that in this case, as well, osmosis influences the microstructure and thickness of fully dense Pd film, and, hence, the permeation properties.

The dependence of Pd grain size as a function of plating time is shown in Figure 7. It may be seen that the use of osmosis during synthesis resulted in smaller grain size and

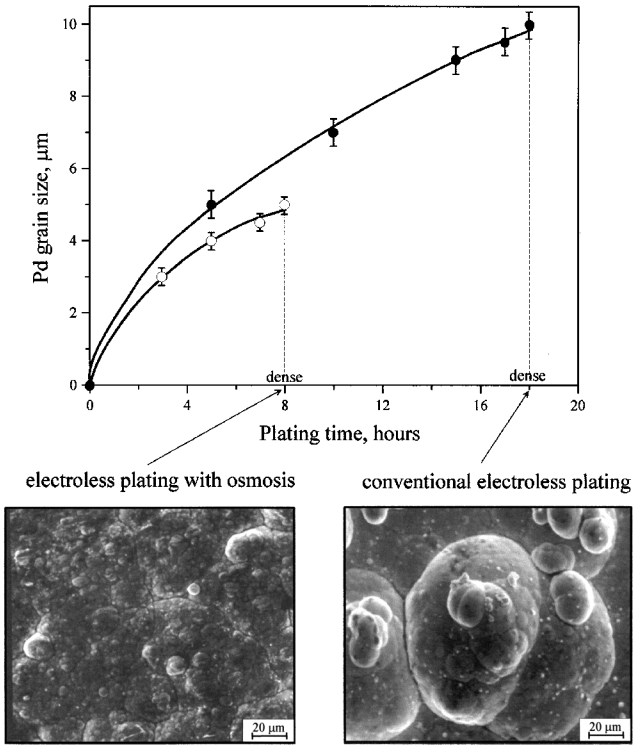

Figure 7. Pd grain size as a function of plating time for Pd-porous stainless steel composite membranes synthesized by (●) conventional electroless plating and (○) electroless plating with osmosis.

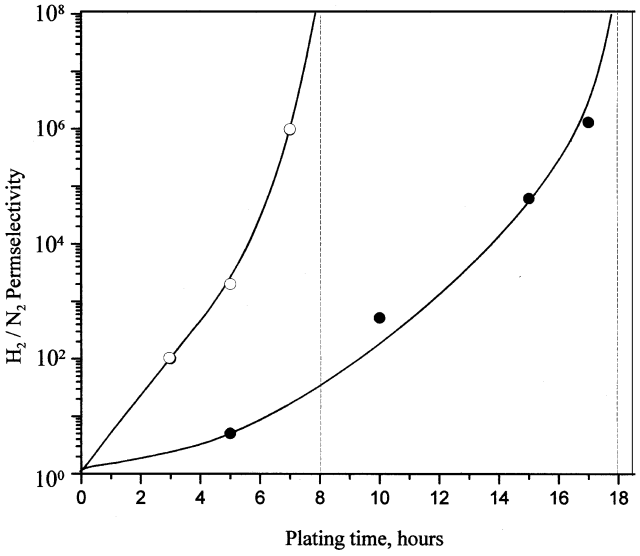

Figure 8. H_2/N_2 permselectivity as a function of plating time during synthesis of Pd-porous stainless steel composite membranes synthesized by (●) conventional electroless plating and (○) electroless plating with osmosis; $\Delta P = 526$ kPa, $T = 573$ K.

narrower size distribution. For example, the Pd grain size of fully dense films changed from 10 μm (conventional method) to 5 μm (with osmosis). Also, much less time is required to deposit fully dense films in the latter case. The dynamics of H_2/N_2 permselectivity ratio is shown in Figure 8. Palladium deposited with osmosis fully covers all pores in stainless steel support in 8 h, while it takes 18 h for the conventional method. In turn, thicknesses of metal layers deposited by electroless plating with or without osmosis were about 8 and 18 μm, respectively. It is interesting that the same mean-plating rate was also observed for the Vycor glass support (1 μm/h).

Correspondingly, permeation experiments conducted at 573 K and $\Delta P = 526$ kPa, showed higher hydrogen flux through the fully dense Pd membrane synthesized with osmosis as compared to conventional plating. Note that while the thickness of dense Pd films differs by a factor of 2.2, hydrogen permeability is about three times higher for membrane synthesized in the presence of osmosis. As in the case of Vycor glass support, this effect is related to differences in Pd grain size.

The dependence of hydrogen flux as a function of transmembrane pressure difference at different temperatures for dense Pd composite membranes synthesized with or without osmosis is shown in Figures 9a and 9b, respectively. Since in both cases the flux is proportional to $(P_h^{0.5} - P_l^{0.5})$, one can conclude that diffusion through Pd lattice is the rate-determining step, following Sievert's law.

These experiments also allow one to determine activation energy for hydrogen permeation through Pd composite membranes. Since stainless steel substrate does not contribute any transport resistance, the activation energy should be the same as for pure dense palladium films. Figure 10 shows these values to be 18.8 and 21.6 kJ/mol, for electroless plating with

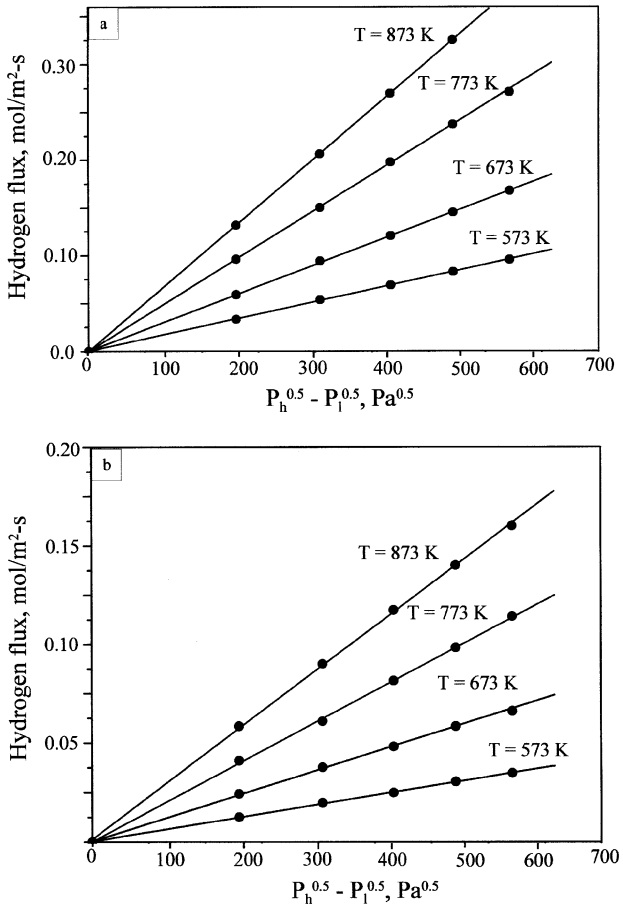

Figure 9. Hydrogen flux through dense Pd-porous stainless steel composite membranes synthesized by electroless plating (a) with osmosis, (b) without osmosis, in Sievert's law coordinates at different temperatures.

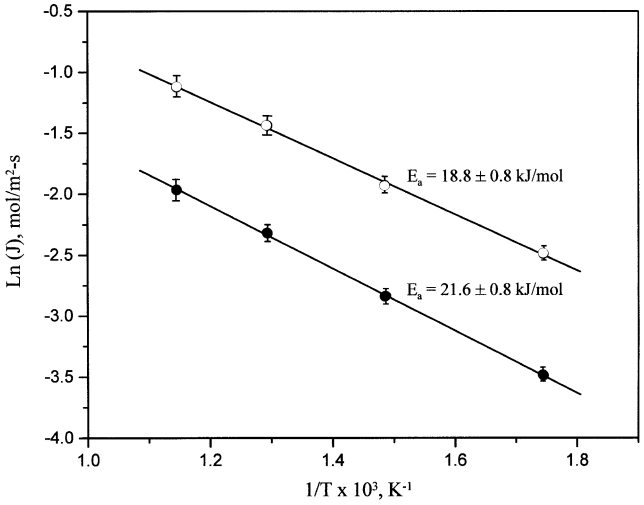

Figure 10. Arrhenius plot of hydrogen flux ($\Delta P = 690$ kPa) through dense Pd-porous stainless steel composite membranes synthesized by (●) conventional electroless plating and (○) electroless plating with osmosis.

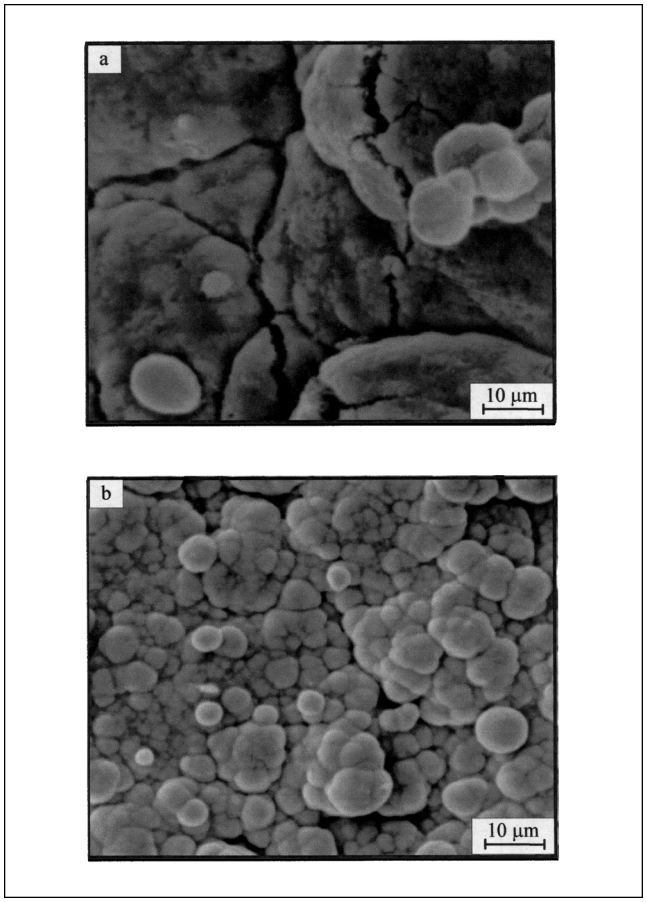

Figure 11. SEM micrographs of Pd films deposited by (a) conventional method, and (b) electroless plating with osmosis, after thermal swing experiments.

osmosis and conventional method, respectively. Again, the lower value of activation energy for membranes synthesized by electroless plating with osmosis may be related to finer grains, as in the case of Vycor glass support.

Finally, thermal stability of palladium membranes prepared by both techniques was tested in thermal swing experiments, where the membranes were heated to 973 K in air at 25 K/min, and rapidly quenched to room temperature in cold water. The membranes prepared by conventional electroless plating developed cracks after 4 cycles (Figure 11a), while those prepared using osmosis remained dense (Figure 11b) and impermeable to nitrogen even after 15 quenching cycles. This enhanced performance can be explained by the effect of osmosis on deeper penetration of Pd into porous support (Souleimanova et al., 2000).

Concluding Remarks

The use of osmosis allows one to synthesize membranes on different porous supports with thinner dense Pd film and finer grained microstructure, which leads to higher hydrogen permeability and superior thermal stability. In addition, the novel method described in this article can be used to produce different types of thin (with thickness approaching the rough-

ness of the substrate) dense metal films of desired composition (Pd, Ag, Cu, Pd-Ag, and so on) and uniform microstructure that can be used in a variety of applications.

Acknowledgments

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