Novel Method for Preparing Palladium Membranes by Photocatalytic Deposition

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An ultrathin palladium film on a porous TiO_2 ceramic membrane was successfully synthesized by a novel photocatalytic deposition (PCD) method. The mechanism was interpreted by the photocatalytic reaction between the surface of the TiO_2 semiconductor and the Pd(II) solution. Energy dispersive (EDS) analysis and argon permeability of the membrane were used to characterize the deposited Pd. During the PCD process, photoreaction took place with higher efficiency when the pH value of the solution was controlled at the 3—3.5 range. A short irradiation time of 18 min was enough for PCD at a normal reaction temperature. A methanol additive in the solution of about 40 vol. % was optimum for the deposition of Pd. XRD and SEM results on the Pd-based membrane prepared by PCD indicated that the metal existed in the form of a pure palladium element, with a layer thickness of about 0.1 μm. The gas permeation experiment was conducted in a high-temperature permeator from 623 to 723 K. The results indicated that there were contributions to the hydrogen flux attributable to both dense and microholes parts of the resulting Pd/TiO_2 membrane.

Introduction

In recent years there has been rapidly growing interest in the application of palladium-based membranes for hydrogen separation, hydrogenation/dehydrogenation membrane reactors, and catalytic reactions at high temperatures (Li et al., 1998; Zhao et al., 1998). Several methods have been used to prepare a Pd-based composite membrane, including chemical vapor deposition (CVD) (Collins and Way, 1993; Uemiya et al., 1994; Yan et al. 1994; Xomeritakis and Lin, 1996, 1998), sputter deposition (Jayaraman et al., 1995; Xomeritakis and Lin, 1997), electrodeposition (Nam et al., 1999), electroless plating (Uemiya et al., 1990; Paglieri and Way 1999; Huang et al., 1998; Zhao et al., 1998), and spray pyrolysis (Li et al., 1998). Major problems with the preparation of palladium-based membranes are thickness control, the need for strict processing conditions, interactions between the metallic layer and the support, and the high cost.

The thickness of the palladium film has a significant effect on the hydrogen flux through the membrane. In order to improve hydrogen flux by reducing the thickness of the palladium membrane, many efforts have been devoted to fabricating thinner membranes. Xomeritakis and Lin (1998) recently formed a palladium film of 0.5–5 μm thickness by the CVD method using palladium acetylacetonate and palladium chloride as Pd precursors. Also, the H_2:He permselectivity for membranes was about 200–300 at 300°C. The CVD process provided strong advantages such as uniformity of deposits on complex shapes, hardness and selectivity (Shu et al., 1991). However, the volatility of precursors commonly used, such as palladium chloride and palladium acetylacetonate, was not high enough to be adapted to large scale (Meng and Peng, 1996). Thus, in recent years, the main concern for the CVD process was to find a new precursor and source compound with a higher volatility and stability. A palladium membrane as thin as ≤ 1 μm on a porous ceramic support has been fabricated by a sputtering technique (Jayaraman et al., 1995), which could quickly deposit metallic films with good control of the thickness. However, this method, as well as the CVD process required strict processing conditions that affect the economics aspect.

The technique of electroless plating perhaps was one of the most popular methods to prepare Pd-based membranes.

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Using this method, Collins and Way (1993) reported the preparation of a composite palladium membrane with a thickness in the range of 11 to 20 μm. Uemiya et al. (1991) fabricated a 5 μm thick palladium alloy membrane and reported a 100% selectivity for hydrogen. A traditional electroless plating technique included a sensitization/activation process employing tin and palladium chloride, however, the membrane experienced a decline in selectivity at temperatures above 773 K due to the rapid deactivation by low melting point tin compounds or other co-deposition impurities at the palladium/ceramic interface (Paglieri and Way, 1999). In addition, it was difficult to control the film thickness and ensure adhesion between metal and the substrate. Thus, Zhao et al. (1998) modified the electroless plating procedure to deposit Pd on the activated porous alumina substrate with a thickness of about 1 μm and with a high compactness. However, this process was very cumbersome and time consuming.

In any case, it was desirable to develop a simple technique with a controllable metal layer thinness, without strict processing conditions, and with strong adhesion between the mental layer and the support. Also, the economic cost of the technique should be taken into account. In this study, a novel and simple technique called photocatalytic deposition (PCD) has been established for preparing an ultrathin supported Pd membrane. A photocatalytic reaction on the interface between the surface of a semiconductor and the solution containing Pd (II) will occur practically under the irradiation of UV light. Then, the reduced palladium will be deposited on the semiconductor surface in a thinner layer. Since TiO_2 ceramic membranes show many advantages, such as photochemical stability, commercial availability and relatively low cost, it was selected as the support of palladium membrane in this study. This formation mechanism of palladium film on the TiO_2 membrane was discussed in detail. The controlling factors, including pH value, irradiation time, reaction temperature, and the initial additive concentration in the solution, were investigated on the deposition of Pd. X-ray diffraction analysis (XRD), scanning electron micrographs (SEM), energy dispersive spectroscopy (EDS), and gas permeation experiments were used to characterize the membrane properties. The hydrogen permeation experiment was conducted in a high-temperature membrane permeator, using graphite gaskets as seals.

Mechanism of formation of Pd membrane by PCD

TiO_2 (anatase) is a good semiconductor, and is usually used as a photocatalyst to reduce noble metals. The corresponding couples of metal/TiO_2 are cited in Table 1. As shown, the reported TiO_2 used to deposit metals by photocatalytic reaction always existed as unsupported powders suspended in aqueous media. However, metal deposited on the surface of supported TiO_2 membrane has not been reported to-date. As stated, Pd deposited on a TiO_2 membrane by the PCD process was investigated in this study.

Table 1. Couples of Metal/TiO_2 Obtained by Photocatalytic Reaction

Metal Reduced	TiO_2 in Suspension	Irradiation Source	Reference
Pd, Rh	Particles	1,500-W Xenon Lamp	Borgarello et al. (1986)
Pt	Powder	XBO-450-W Xenon Lamp	Kiwi and Gratzel (1984)
Ag	Particles	100-W Hg Spotlight	Huang et al. (1996)
Cr	Powder	125-W Mercury UV Lamp	Aguado et al. (1991)
Cu	Particulate	Sylvania Black Light 365 nm	Foster et al. (1993)

The mechanism of the PCD process is described as follows. Under irradiation on the TiO_2 surface by UV light, the semiconductor absorbs at or above the band-gap energy, exciting electrons from the valence band to the conduction band. Pairs of electron/holes appear which are able to promote redox reactions at the TiO_2-liquid interface. Thus, in the absence of any reducing agent, the fundamental process is given by the following reactions that proceed at different active sites of the TiO^2

$$\mathrm{TiO_2} + h\nu(<400\mathrm{nm}) \rightarrow \mathrm{TiO_2}(e^- + h^+) \tag{1}$$

$$4\mathrm{TiO_2}(e^- + h^+) + 2\mathrm{H_2O} \rightarrow 4\mathrm{TiO_2}(e^-) + 4\mathrm{H^+} + \mathrm{O_2} \quad \text{(hole reaction)} \tag{2}$$

$$\mathrm{TiO_2}(e^- + h^+) \rightarrow \mathrm{TiO_2} \quad \text{(recombination)} \tag{3}$$

$$2\mathrm{TiO_2}(e^-) + \mathrm{PdCl_2} \rightarrow \mathrm{Pd} + 2\mathrm{Cl^-} \quad \text{(electron trapping reaction)} \tag{4}$$

The overall photoredox reaction leading to Pd-metal deposition and O_2 formation is

$$\mathrm{PdCl_2} + 2\mathrm{H_2O} \xrightarrow{h\nu,\, TiO_2} \mathrm{Pd} + \mathrm{O_2} + 4\mathrm{H^+} + 2\mathrm{Cl^-} \tag{5}$$

It was verified that the reaction did not proceed without irradiation (lamp off). Once the irradiation begins, the photocatalytic reaction will occur on the surface of the TiO_2 and solution. Therefore, the pH value, the irradiation time, the reaction temperature, and the initial concentration of the additive in the solution are the main influence on the photocatalytic deposition. The resulting metal that gets deposited on the TiO_2 semiconductor substrates will form a palladium membrane.

However, note that the activity of the TiO_2 photocatalyst will be lost during the process of metal deposition. The reason is that the coverage of reduced palladium between UV light and the substrate prevents the radiation from arriving at the surface of anatase TiO_2. That means, once palladium is deposited on the TiO_2 top layer, photocatalytic reaction will not occur any longer, whether the irradiation is continued or not. Therefore, an ultrathin metallic layer may be theoretically formed on the surface of the TiO_2 membrane.

Furthermore, Mordkovich and coworkers (1992) pointed out that interaction between the various layers of the palladium membrane would probably prove to be the most important problem to overcome when they forecasted future developments and possible applications of the membranes. Since the palladium membrane prepared by a conventional electroless plating technique is built up by packing Pd particles deposited initially from the activation step and then from the plating solution through the autocatalytic decomposition of a palladium complex (Li et al., 1998), the adhesion between metallic film and the substrate is questionable. Because the interaction between palladium and the TiO_2 membrane by the PCD method is based on the photochemical reaction, the adhesion of the two layers should be much stronger.

Experimental Studies

Preparation of anatase TiO_2 membranes

The microfiltration α-Al_2O_3 membrane (ϕ30 mm, dia., developed by our research center) with pore sizes about 0.1 μm was used as the support for the TiO_2 layer. TiO_2 membranes were prepared using a colloidal route of a sol-gel technique from hydrolysis of tetrabutyl titanate (TBT). An aqueous-based sol with TiO_2 concentration of 0.05 M was employed in the fabrication of the TiO_2 membrane by dip-coating onto the α-Al_2O_3 supports at ambient temperature and humidity. The resulting sample was sintered at 450°C for 3 h in order to form the predominantly anatase TiO_2 membrane. The argon permeability of the supported TiO_2 membrane was about 2.5×10^{-6} $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$.

Photochemical deposition of palladium (II) chloride on TiO_2 membranes

Palladium (II) was deposited onto TiO_2 membranes by PCD. The experimental setup is shown in Figure 1. An aqueous palladium (II) chloride solution with initial concentration of 2.5×10^{-3} $mol \cdot L^{-1}$. was added to a thermostated Pyrex reactor with a mesh glass baffle on which samples were mounted. Palladium chloride, methanol additive, and hydrochloric acid of at least analytical grade were used for the photocatalytic reaction. Water was deionized and doubly distilled. The reactor was closed with a rubber septum and fitted with a quartz optical cover, which is used for filtering the UV light. Irradiation was performed at 35°C with a 150 W Gallium lamp. The solution was purged with N_2 prior to and during light exposure. A magnetic stirrer at high rotating speed was used to ensure uniform mixing of the solution.

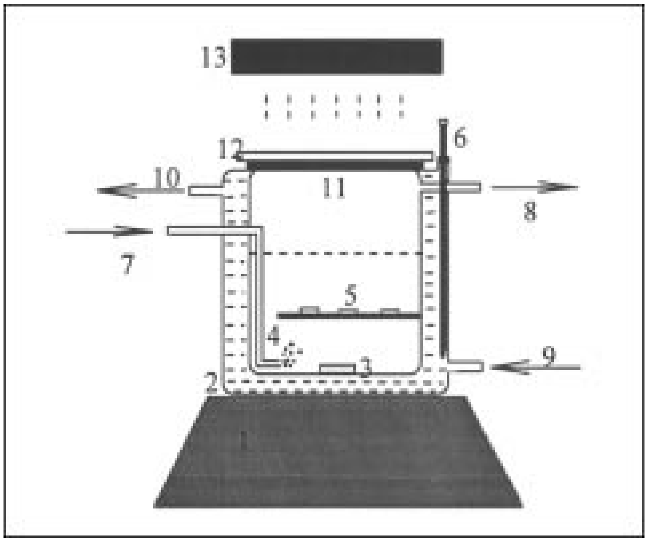

Figure 1. Experimental setup for a photocatalytic reaction

(1) Magnetic stirrer; (2) thermostatic Pyrex reactor; (3) stirring rod; (4) glass baffle sheet; (5) supported TiO_2 membranes; (6) thermometer; (7) purging gas; (8) gas outlet; (9) cooling water inlet; (10) cooling water outlet; (11) rubber sealing; (12) quartz cover; (13) 150-W gallium lamp.

The concentration of Pd (II) remaining in the reaction solution was analyzed by atomic absorption spectroscopy (GFU-202, Beijing Analysis Instrument Manufactory, China). After the PCD process, the irradiated membrane was rinsed with distilled water to remove the remainder of palladium (II) chloride on the surface of the membrane.

Membrane characterization

The morphology of the resulting palladium membranes was examined by high-resolution SEM (JEOL JSM-6300). Surface elemental analysis of palladium membranes prepared was performed by energy dispersive X-ray spectroscopy (EDS, U.S. Kevex-Sigma, electron source 15.0kV, beam current 100.0 pico Amps). The phase development of the palladium membranes was studied by X-ray diffraction (XRD) (Rigaku D/MAX-rB diffractometer, with CuKα radiation).

The effects of deposition conditions on membrane formation were also determined by argon permeability at room temperature. The thickness of Pd deposited on TiO_2 was evaluated by: (1) a cross-sectional SEM photograph of the resulting palladium membrane; (2) dividing the weight difference in the deposited and nondeposited membranes by the deposited surface area and palladium density. The weight of the membranes was measured by electronic scale (DF-200A, Changshu Weighing Apparatus Factory, China).

High-temperature gas permeation measurement

The gas permeation through palladium membranes at high temperatures was measured on the permeation apparatus shown in Figure 2. The membrane was connected with the body of a stainless steel permeator using graphite gaskets for sealing. The permeator was surrounded by a tubular furnace

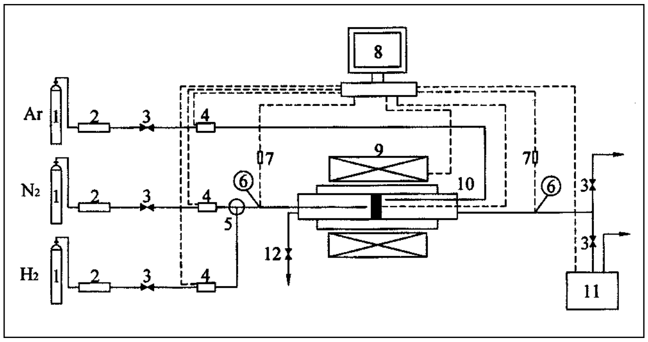

Figure 2. Apparatus for gas permeation through Pd-based/TiO_2 composite membrane at high temperature.

(1) Gas cylinders; (2) purifying traps; (3) flow control valves; (4) mass-flow controllers; (5) gas mixer; (6) pressure gauge; (7) pressure transfer; (8) computer; (9) furnace; (10) stainless steel permeator; (11) GC-TCD; (12) back pressure regulator.

and the temperature was measured by a type K thermocouple encased in an alumina tube. A microprocessor temperature controller (Model 708PA, Xiamen Yuguang Electronics Technology Research Institute, China) was used to control the temperature to within ±1°C of the set points. During the gas permeation measurement, the feed gases (H_2 and N_2) were supplied from gas cylinders and the flow rate of each gas was controlled by mass-flow controllers (Models D07-7A/ZM, Beijing Jianzhong Machine Factory, China), Hydrogen and nitrogen were joined together to be mixed and introduced to the Pd side of the disk-type membrane. Both the upstream and the downstream were maintained at atmospheric pressure. Argon, as the sweep gas for the permeating gases, was fed to the support side of membrane in order to adjust the partial pressure of hydrogen. The effluent streams were analyzed by a gas chromatograph (GC, Model Shimadzu GC-7A), which was equipped with a 2 m column of 5A molecular sieve operated at 40°C with helium as the carrier gas. The separation efficiency and the hydrogen, and nitrogen fluxes through the membrane were calculated from the data collected.

Results and Discussion

Properties of TiO_2 membrane

Figure 3a and 3b show top surface and cross-section SEM photographs of the TiO_2 membrane used for the palladium membrane preparation, respectively. As can be seen, the surface of the TiO_2 membrane was quite smooth and homogeneous, which was suitable for depositing palladium. The thickness of the TiO_2 layer coated on the surface of the α-Al_2O_3 disk was about 1.5 μm, which was equal to the optical absorption depth of TiO_2 (White and O'Sullivan, 1987). Anatase was the main crystal phase of the TiO_2 substrates indicated by XRD. Properties of the two-layer TiO_2 substrates used for palladium deposition are summarized in Table 2.

Table 2. Properties of Two-Layer TiO_2 Membrane for Deposition of Palladium

Layers	Pore Size (nm)	Porosity (%)	Thickness (μm)
α-Al_2O_3	80—100	30	35
TiO_2	2—3	47	1.5—2

Factors affecting on the deposition of palladium

pH Value. The pH value of the reaction solution had a significant effect on the photochemical reduction of palladium (II) on TiO_2 membranes. Borgarello et al. (1986) reported that, for the TiO_2 particles photoreducing Pd (II), the pH value of the solutions was always kept below 7, especially at the range of 3–5. For TiO_2 membranes in this study, pH values less than 7 were investigated. Three important factors, including the concentration of Pd (II) remaining in the solution, the Pd/Ti mol ratio on the surface of the Pd deposited membrane, and the argon permeability of the resulting membrane, were investigated at various pH values. The relationship between them is shown in Table 3. As can be seen, when the pH value was at 3 and 3.5, the concentration of Pd (II) remaining in the solution decreased significantly, demonstrating that the photoreaction proceeded with more efficiency after a 30 min irradiation. Moreover, the Pd/Ti mol ratio (EDS results) of the top layer (that is, the amount of Pd deposited on the TiO_2 membrane) was higher at the pH of 3 and 3.5, which further confirmed the reduction of Pd (II) concentration remaining in the solution. Finally, argon gas permeability at room temperature also indicated that in this specific pH range the argon permeability through the

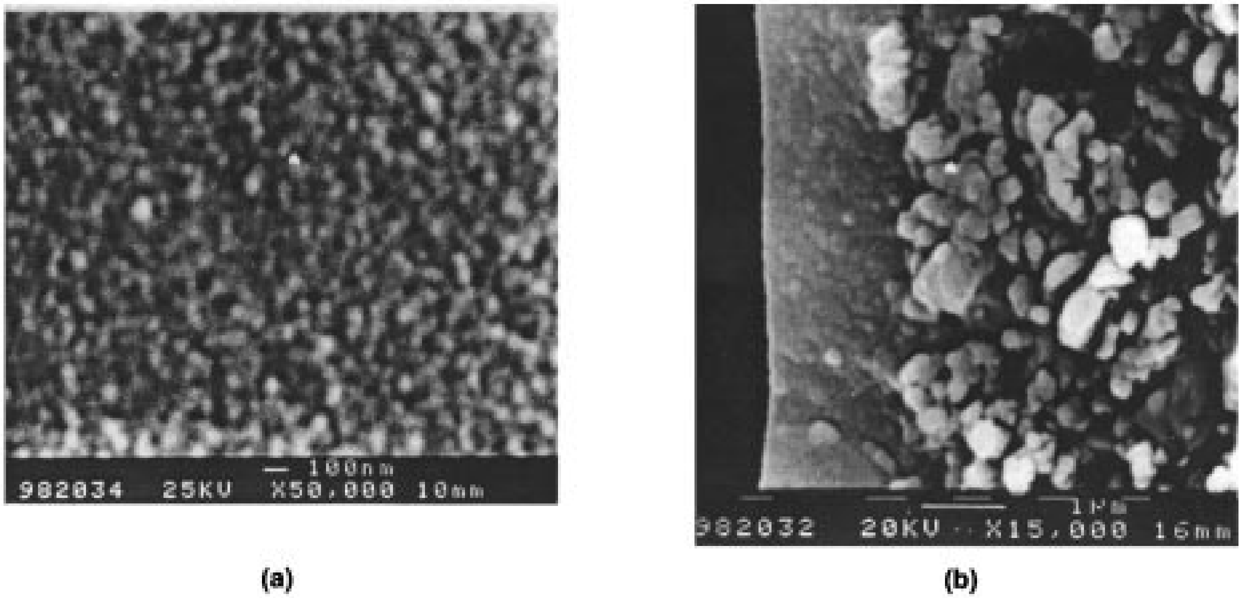

Figure 3. SEM photographs of a two-layer support for preparing palladium membrane: (a) top surface and (b) cross section.

Table 3. Effect of pH Value on Pd(II) Concentration, Surface Pd/Ti Mol Ratio and Argon Permeability of Deposited Membrane

pH Value	Pd(II) Conc. ($\times 10^{-3}$ M)	Pd/Ti Mol Ratio	Argon permeability ($\times 10^{-6}$mol$\cdot$m$^{-2}\cdot$s$^{-1}\cdot$Pa^{-1})
1.6	2.48	0.033	2.5
3.0	0.57	1.44	0.08
3.5	1.5	0.81	0.18
4.3	2.27	0.17	1.20
5.5	2.33	0.14	1.65
6.2	—	0.1	2.41
7.1	—	0.03	2.48

*Irradiation time: 30 min.

Pd/TiO$_2$ composite membrane was much less than that through only the TiO$_2$ membrane, because of the deposition of Pd. Therefore, the pH value at the range of 3–3.5 was suitable for the formation of palladium membranes.

Irradiation Time. Figure 4 shows the Pd (II) concentration remaining in the solution as a function of the irradiation time at specific pH values. Curves in Figure 4 showed the same decreasing trends of the Pd (II) concentration for pH values of 3.0 and 3.5 with increasing irradiation time. Although the rate of change of the Pd (II) concentration was much faster for a pH of 3.0 than that for a pH of 3.5, the Pd (II) concentration leveled off after 18 min of irradiation time in both cases. Therefore, 18 min of irradiation time was used in subsequent membrane preparations.

For pH = 3.0, the mass balance between the decreased amount of the Pd (II) in the solution, and the corresponding increased amount of the Pd deposited on the support was calculated for increasing irradiation time, as shown in Table 4. The molar amount of palladium in both cases essentially coincided, indicating that palladium film formed was indeed a result of PCD.

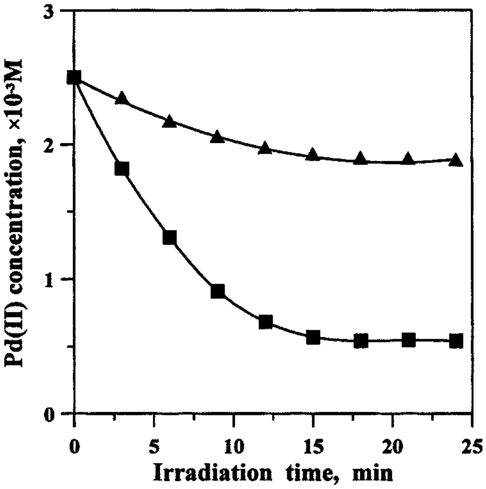

Figure 4. Pd (II) concentration remaining as a function of irradiation time at specific pH values in the photocatalytic reaction solution.

(▲) pH = 3.5; (■) pH = 3.0.

Table 4. Mass Balance Calculation of Pd(II) Concentration Remaining in the Solution and Corresponding Pd Deposition on TiO$_2$ Substrates*

Irradiation Time (min)	6	12	18	21
Pd(II) conc. remaining in solution ($\times 10^{-3}$ mol$\cdot$l^{-1})	1.310	0.680	0.540	0.545
Decrease in Pd (II) ($\times 10^{-3}$ mol)	0.613	0.937	1.009	1.007
Increased weight of substrates (g)	0.066	0.100	0.107	0.107
Increase in Pd on the substrates ($\times 10^{-3}$ mol)	0.620	0.940	1.006	1.006

*pH = 3.0.

Reaction Temperature. Figure 5 depicts the effect of reaction temperature on the thickness of the palladium layer and the argon permeability of the resulting palladium membrane. The thickness of the Pd layer was calculated according to the weight increase of the substrates. As seen in Figure 5, it was obvious that as the reaction temperature increased, the metal layer thickness was essentially unchanged after a 18 min irradiation and was about 0.13 μm. The phenomenon was consistent with the argon permeability of the resulting membrane, which is shown as another line in Figure 5. The argon permeability was almost at the same level for different palladium membranes prepared at different reaction temperatures, further confirming that the thickness of the palladium membranes prepared at different reaction temperatures was close. In addition, the value of the argon permeability through the deposited membrane was nearly 1×10^{-7} mol$\cdot$m$^{-2}\cdot$s$^{-1}\cdot$Pa^{-1}, which is much lower than that of the TiO$_2$ membrane at about 2.5×10^{-6} mol$\cdot$m$^{-2}\cdot$s$^{-1}\cdot$Pa^{-1}. This further proved that the deposition of Pd occurred on the surface of TiO$_2$ membrane.

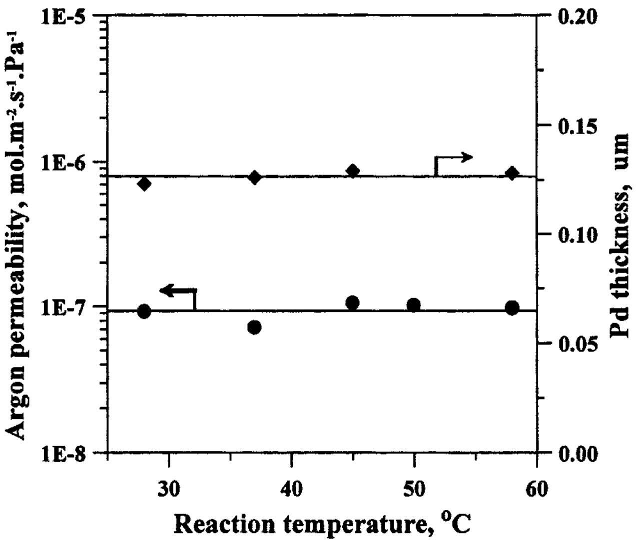

Figure 5. Effect of reaction temperature on the thickness of deposited palladium layer and on Ar permeability of the resulting membrane, respectively.

(pH: 3.0; irradiation time: 18 min); (◆) thickness of palladium film; (●) Ar permeability data of Pd-deposited membrane; (—) average lines.

More importantly, after an 18 min irradiation time that the deposition of the Pd was almost independent of the reaction temperature. This suggested that the PCD could be easily controlled in such a short time.

Additive. In this study, methanol was selected as an additive for the photoreaction for two reasons. First, because methanol was more sensitive to oxidation than water ($E_{0H_2O} = -1.229$ V and $E_{0CH_3OH} = -0.232$) (Angelidis et al., 1998), methanol acted as a hole scavenger” offering more electrons for the palladium reduction process and precluding the oxidation of water. The possible reaction is as follows

$$2TiO_2(e^- + h^+) + CH_3OH(aq) \rightarrow TiO_2(e^-) + 2H^+ + 2HCHO(aq) \tag{6}$$

Secondly, the presence of methanol suppressed the formation of oxygen, which could compete with the metal deposition reaction (White and O’Sullivan, 1987). The possible reaction may occur as follows (Miyake et al., 1979)

$$CH_3OH + O_2 \xrightarrow{h\nu} HCHO + H_2O_2 \tag{7}$$

and/or

$$2CH_3OH + O_2 \xrightarrow{h\nu} 2HCHO + 2H_2O \tag{8}$$

In acidic media reduction of O_2 is a thermodynamically more favorable process. According to these two aspects, for TiO_2 photoreducing Pd (II), more complete photochemical reaction might be obtained for higher methanol concentrations.

Figure 6 shows the EDS results of the mole ratio of deposited Pd to Ti as a function of the initial methanol concentration after the irradiation time of 18 min. The data indicated that the amount of the Pd deposited increased with the methanol concentration. However, the increase became insensitive to methanol when vol. % of methanol in the solution was higher than 40. Therefore, in this study about 40 vol. % of methanol in the reaction solution was judged sufficient for the deposition of Pd.

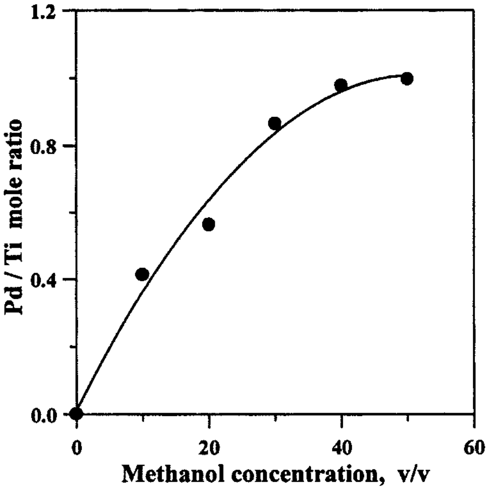

Figure 6. Effect of initial concentration of methanol in the reaction solution on the deposition of palladium.

pH value: 3.0; irradiation time: 18 min.

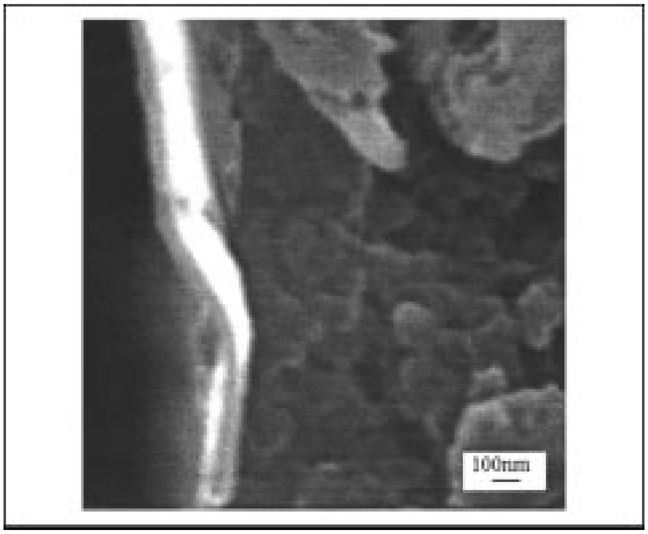

Figure 7. Cross-sectional SEM photograph of the resulting Pd/TiO_2 composite membrane.

Properties of palladium membrane

Figure 7 shows the cross-section photograph of the resulting membrane, indicating that a thin metal layer was on the surface of the TiO_2 support. As seen, the thickness of the metal layer was about 0.1 μm, which is slightly lower than the calculated value (0.13 μm) as mentioned above. In fact, during the PCD process, some of the Pd (II) solution might have filtrated into the pores of TiO_2 membrane, and would be included in the weight of the deposited Pd used in calculating thickness. Thus, the calculated thickness of the Pd membrane could be larger than the actual value. This argument was supported by further observation of Figure 7, which showed something lustrous in the support part of the cross-section photograph.

The elemental analysis of the ultrathin top layer was performed on the same sample when the SEM photograph was being taken. Figure 8 shows the EDS results of the top layer, indicating that palladium was the dominant component. Further results were provided by the XRD analysis. The XRD pattern of the Pd/TiO_2 composite membrane made by PCD is shown in Figure 9, demonstrating that the Pd was deposited as pure elemental palladium as the result of PCD.

Gas permeability of palladium membrane

The gas permeation through the porous membranes was described mainly by Knudsen diffusion and Poiseuille flow. The gas flux in the porous membranes can be given (Huang et al., 1998) by

$$J = F(P_h - P_l)/L = F_0(P_h - P_l), \tag{9}$$

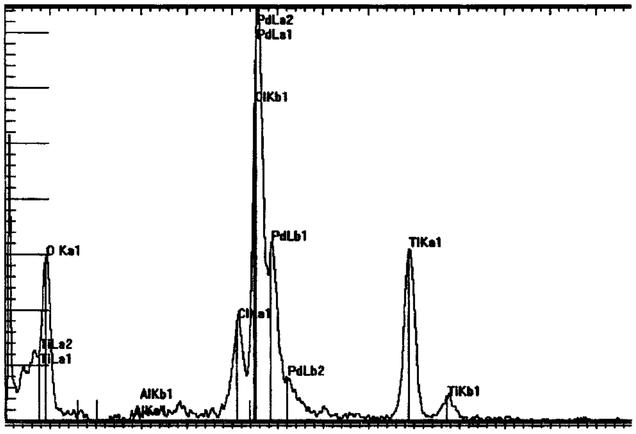

Figure 8. EDS results of Pd/TiO$_2$ composite membrane prepared.

where J is the rate of gas permeation per unit area (mol·m^{-2}·s^{-1}), F was the permeability of gas, F_0 was the gas permeation coefficient, and P_h and P_l were the partial pressures of gas in the feed side and permeate side, respectively. Thus, nitrogen permeation through porous membranes may be described by

$$J_{N_2} = F_{0_{N_2}}(P_h - P_l), \tag{10}$$

and for a porous membrane dominated by Knudsen diffusion the hydrogen flux may be

$$J''_{H_2} = F''_{0_{H_2}}(P_h - P_l) = K_n F_{0_{N_2}}(P_h - P_l), \tag{11}$$

Where K_n is the Knudsen ratio. For the TiO$_2$ membranes prepared in this work, the actual ratio was about 3.5 from our previous work (Wu et al., 2000).

Hydrogen flux through palladium film J_{H_2} via a solution-diffusion mechanism can be expressed in terms of Fick's first law

$$J'_{H_2} = F'_{0_{H_2}}(P_h^n - P_l^n) \tag{12}$$

where n is the order of the dependence of the permeation rate on pressure. In terms of the mechanism of hydrogen permeation through the palladium-based membrane, the thickness had a significant effect on the pressure exponent n. Hurlbert and Konecny (1961) reported that the bulk diffusion of hydrogen was the rate determining step for palladium membranes whose thickness was greater than 20 μm. In this case, hydrogen concentration was proportional to the square root of hydrogen pressure, in accordance with Sievert's law ($n = 0.5$). Nam and his co-workers (1999) concluded that the pressure exponent was close to 1 when the thickness of palladium alloy membrane was 0.8 μm, which suggests control by a surface process (H_2 chemisorption on the membrane surface). Thus, the values of n is expected to range from 0.5 to 1.0, depending on the relative mass-transfer resistance of those layers.

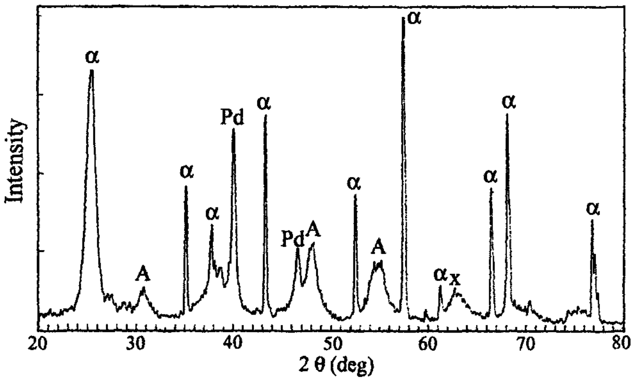

Figure 9. XRD pattern of Pd/TiO$_2$ composite membrane made by PCD.

(α) α-Al$_2$O$_3$; (A) anatase TiO$_2$; (Pd) pure palladium; (×): impurity peak.

The data for argon permeation at room temperature in Table 3 and Figure 5 indicated that the resulting membrane was less gas-tight under the reaction conditions in this study. Therefore, hydrogen permeation behavior is considered to consist of two parts, one from the microholes of the membrane and the other from the dense part through which nitrogen could not penetrate. So, the hydrogen permeation flux can be given as

$$J_{H_2} = J'_{H_2} + J''_{H_2} = F'_{0_{H_2}}(P_h^n - P_l^n) + K_n F_{0_{N_2}}(P_h - P_l). \tag{13}$$

Figure 10 shows experimental nitrogen permeation data at various temperatures as a function of partial pressure differences, and shows a good linear relationship between the nitrogen flux and the partial pressure difference. Nitrogen permeability through the composite membrane prepared at a different temperature was obtained by calculating the slope of the lines in Figure 10. Thus, hydrogen flux through the

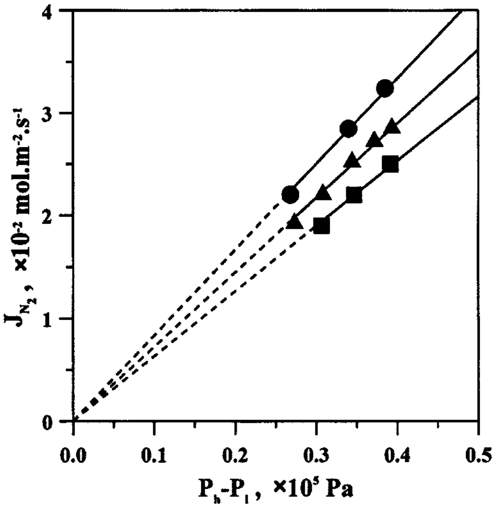

Figure 10. Dependence of nitrogen flux on partial pressure differences at various temperatures.

(■) T = 623 K; (▲) T = 673 K; (●) T = 723 K.

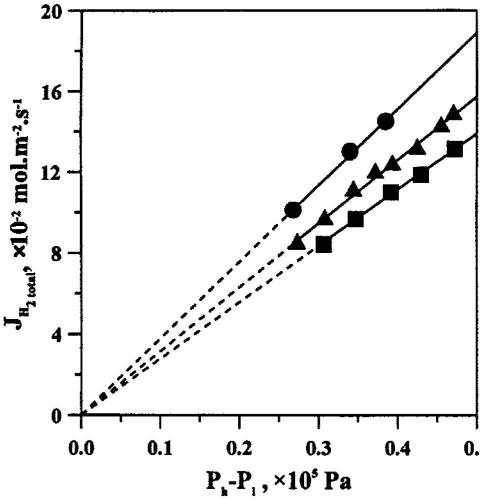

Figure 11. Dependence of total hydrogen flux on hydrogen partial pressure differences at various temperatures.

(■) $T = 623$ K; (▲) $T = 673$ K; (●) $T = 723$ K.

microholes part J''_{H_2} can be calculated using Eq. 11. Figure 11 shows experimental total hydrogen permeation flux at various temperatures as a function of hydrogen partial pressure differences. Thus, hydrogen permeation flux through the dense part, J'_{H_2} was calculated by subtracting the hydrogen flux of the microholes from the total hydrogen flux by Eq. 13. Figure 12 provides the calculation results of hydrogen permeation flux through the dense part as a function of hydrogen pressure differences at various temperatures. Note that the data in Figures 11 and 12 all produced a linear fit between the hydrogen partial pressure differences and the hydrogen flux of both the total and the dense part. Compared with Eq. 12, the pressure exponent n approached 1 for the Pd-promoted diffusion, which indicated that hydrogen permeating through the dense part of the resulting membrane was determined mainly by the surface process. Table 5 provides the comparison of palladium film thickness and exponent n between this study and other researchers.

Table 5. Relationship between the Thickness and Exponent Value of Pd-Based Composite Membrane

Membrane	Thickness (μm)	n	Ref.
Pd/Al$_2$O$_3$	15	0.67—0.69	Huang et al. (1998)
Pd/Al$_2$O$_3$	11.4	0.6	Collins and Way (1993)
Pd/Al$_2$O$_3$	1	~ 1	Zhao et al. (1998)
Pd-Ni/stainless steel	0.8	1	Nam et al. (1999)
Pd/TiO$_2$	0.1	1	This work

Hydrogen selectivity was defined as the ratio of hydrogen flux to nitrogen flux at the same conditions. The separation factors of H_2/N_2 are shown in Figure 13. As can be seen, the hydrogen selectivity decreased with the increase of transmembrane pressure drop and the temperature, respectively. Generally, the contribution of hydrogen flux through the dense palladium increases (Collins and Way, 1993; Mardilovich et al., 1998), and that ($\propto 1/\sqrt{T}$) through defects by Knudsen diffusion decreases, with increasing temperature. The same result for Pd-promoted diffusion was obtained in this study, as shown in Figure 12. However, Figure 10 showed the opposite result for the Knudsen diffusion. This is because there are more defects in the membrane as the temperature is increased. The membrane thickness reported here (about 0.1 μm) is in a range covered by few reports in the literature. The hydrogen selectivity decrease at elevated temperature is mainly due to a greater contribution of Knudsen diffusion to the hydrogen transport. On the other hand, the hydrogen permeation fluxes via Pd-promoted diffusion and Knudsen diffusion increase exponentially with the pressure difference. For Pd-promoted diffusion governed by surface diffusion, the

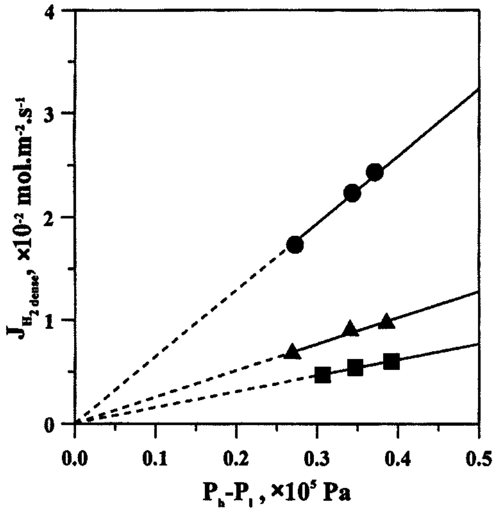

Figure 12. Calculation data of Pd-promoted hydrogen flux as a function of hydrogen partial pressure differences at various temperatures.

(■) $T = 623$ K; (▲) $T = 673$ K; (●) $T = 723$ K.

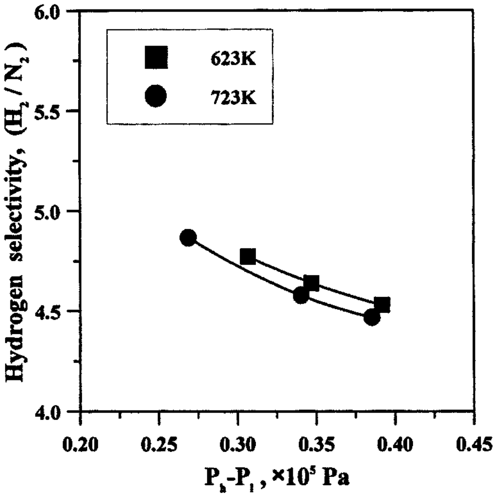

Figure 13. Separation factors of hydrogen to nitrogen as a function of hydrogen partial pressure differences at various temperatures.

(■) $T = 623$ K; (●) $T = 723$ K.

exponents of the pressure n approached 1, which is different from Knudsen diffusion. At elevated pressure, the hydrogen flux via both diffusion mechanisms increases, but in this case the increased amount of Pd-promoted diffusion would be lower in comparison to that of Knudsen diffusion. Therefore, the hydrogen selectivity decreased with the elevated transpressure.

Conclusions

A novel method for preparation of Pd-based membranes was developed using the existing technique of photocatalytic deposition (PCD). An anatase TiO_2 membrane was used as the support of a palladium membrane due to its outstanding semiconductive property. The deposition of palladium occurred on the surface of the TiO_2 membrane via a photocatalytic reaction between the Pd (II) solution and TiO_2. During the deposition of palladium, when the pH value was controlled at the range of 3–3.5 and about 40 vol. % of methanol additive was in the reaction solution, photoreaction took place with more efficiency. Within only 18 min, the deposition of palladium by the PCD process was accomplished. The palladium membrane prepared by PCD is about 0.1 μm thick, and was almost independent of the reaction temperature. The hydrogen permeation through the resulting palladium membrane contained contributions from diffusion through both a dense part and a microhole part. Both the total hydrogen flux and the dense part of the hydrogen flux were proportional to the hydrogen partial pressure difference. Also, the hydrogen selectivity of the membrane decreased with increasing temperature and hydrogen partial pressure differences.

The PCD technique developed in this study seems to be one of the most promising methods to prepare various metal/ceramic membranes for gas separation and/or prepare selective catalytic membranes for membrane reactors. On the other hand, dense palladium membranes can be obtained by further modifying the membrane prepared by the PCD process, which is being investigated in our research center.

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Literature Cited

Aguado, M. A., J. Gimenez, and S. Cervera-March, “Continuous Photocatalytic Treatment of Cr (VI) Effluents with Semiconductor Powders,” *Chem. Eng. Comm.*, **104**, 71 (1991).

Angelidis, T. N., M. Koutlemani, and I. Poulios, “Kinetic Study of the Photocatalytic Recovery of Pt from Aqueous Solution by TiO_2, in a Closed-Loop Reactor,” *Appl. Catal. B: Environmental*, **16**, 347 (1998).

Borgarello, E., N. Serpone, G. Emo, R. Harris, E. Pelizzetti, and C. Minero, “Light-Induced Reduction of Rhodium (III) and Palladium (II) on Titania Dioxide Dispersions and the Selective Photochemical Separation and Recovery of Gold (III) Platinum (IV) and Rhodium (III) in Chloride Media,” *Inorg. Chem.* **25**, 4499 (1986).

Collins, J. P., and J. D. Way, “Preparation and Characterization of a Composite Palladium-Ceramic Membrane,” *Ind. Eng. Chem. Res.*, **32**, 3006 (1993).

Foster, N., R. Noble, and C. Koval, “Reversible Photoreductive Deposition and Oxidative Dissolution of Copper Ions in Titanium Dioxide Aqueous Suspension,” *Environ. Sci. Technol.*, **27**, 350 (1993).

Huang, T.-C., M.-C. Wei, and H.-I. Chen, “Study of Hydrogen Permeation through Palladium/Alumina Composite Membrane,” *Proc. 5th Int. Conf. Iorg. Membranes*, S.-I. Nakao, Nagoya, Japan, 580 (June 1998).

Huang, M., E. Tso, A. K. Datye, M. Prairie, and M. Stange, “Removal of Silver in Photographic Processing Waste by TiO_2-Based Photocatalysis,” *Env. Sci. Technol.* **30**, 3084 (1996).

Hurlbert, R. C., and J. O. Konecny, “Diffusion of Hydrogen through Palladium,” *J. Chem. Phys.*, **34**, 655 (1961).

Jayaraman, V., Y. S. Lin, M. Pakala, and R. Y. Lin, “Fabrication of Ultrathin Metallic Membranes on Ceramic Supports by Sputter Deposition,” *J. Memb. Sci.*, **99**, 89 (1995).

Kiwi, J., and M. Gratzel, “Optimization of Conditions for Photochemical Water Cleavage. Aqueous Pt/TiO_2 (Anatase) Dispersion under Ultraviolent Light,” *J. Phys. Chem.*, **88**, 1302 (1984).

Li, A., W. Liang, and R. Hughes, “Characterization and Permeation of Palladium/Stainless Steel Composite Membranes,” *J. Memb. Sci.*, **149**, 259 (1998).

Mardilovich, P. P., Y. She, Y. H. Ma, and M.-H. Rei, “Defect-Free Palladium Membranes on Porous Stainless-Steel Support,” *AIChE J.*, **44**(2), 310 (1998).

Meng, G. Y., and D. K. Peng, “Inorganic Membrane—A New Industrial Revolution,” *Nature* (China), **18**(3), 151 (1996).

Miyake, M., H. Yoneyama, and H. Tamura, “An Electrochemical Study of the Photocatalytic Oxidation of Methanol on Rutile, *J. Catal.*, **58**, 22 (1979).

Mordkovich, V. Z., Y. K. Baichtock, and M. H. Sosna, “The Large Scale Production of Hydrogen from Gas Mixtures,” *Platinum Metals Rev.*, **36** (2), 90 (1992).

Nam, S.-E., S.-H. Lee, and K.-H. Lee, ‘Preparation of a Palladium Alloy Composite Membrane Supported in a Porous Stainless Steel by Vacuum Electrodeposition,” *J. Memb. Sci.*, **153**, 163 (1999).

Paglieri, S. N., and J. D. Way, “A New Preparation Technique for Pd/Alumina Membranes with Enhanced High-Temperature Stability,” *Ind. Eng. Chem. Res.*, **38** 1925 (1999).

Shu, J., B. P. A. Grandjean, A. V. Neste, and S. Kaliaguine, “Catalytic Palladium-Based Membrane Reactors: a Review,” *Can. J. Chem. Eng.*, **69**, 1036 (1991).

Uemiya, S., H. Sasaki, T. Matsuda, and E. Kikuchi, “Preparation of Thin Palladium Films by Use of an Electroless Plating Technique,” *Nippon Kagaku Kaishi*, **6**, 669 (1990).

Uemiya, S. T., Matsuda and E. Kikuchi, “Hydrogen Permeable Palladium-Silver Alloy Membrane Supported on Porous Ceramics,” *J. Memb. Sci.*, **56**, 315 (1991).

Uemiya, S., M. Koseki, and T. Kojima, “Preparation of Highly Permeable Membranes for Hydrogen Separation Using a CVD Technique,” *Proc. 3rd. Int. Conf. Inorg. Membranes*, Y. H. Ma, Worcester, MA, 545 (July 1994).

White, J. R., and E. J. M. O’Sullivan, “The Kinetics of Palladium Reduction at Particulate TiO_2 Photocatalysts,” *J. Electrochem. Soc.*, **134**(5), 1133 (1987).

Wu, L. Q., P. Huang, N. Xu, and J. Shi, “Effects of Sol Properties and Calcination on the Performance of Titania/α-Alumuna Composite Membranes,” *J. Memb. Sci.*, in press (1999).

Xomeritakis, G., and Y. S. Lin, “Fabrication of a Thin Palladium Membrane Supported in a Porous Ceramic Substrate by Chemical Vapor Deposition,” *J. Memb. Sci.*, **120**, 261 (2000).

Xomeritakis, G., and Y. S. Lin, “Fabrication of a Thin Palladium Membrane by MOCVD and Sputtering,” *J. Memb. Sci.*, **133**, 217 (1997).

Xomeritakis, G., and Y. S. Lin, “CVD Synthesis and Gas Permeation Properties of Thin Palladium/Alumina Membranes,” *AIChE J.*, **44**(1), 174 (1998).

Yan, S., H. Maeda, K. Kusakabe, and S. Morooka, “Thin Palladium Membrane Formed in Support Pores by Metal-Organic Chemical Vapor Deposition Method and Application to Hydrogen,” *Ind. Eng. Chem. Res.*, **33**, 616 (1994).

Zhao, H.-B., K. Pflanz, J.-H. Gu, A.-W. Li, N. Stroh, H. Brunner, and G.-X. Xiong, “Preparation of Palladium Composite Membranes by Modified Electroless Plating Procedure,” *J. Memb. Sci.*, **142**, 147 (1998).

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