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PREPARING AND TESTING Pd FILMS OF THICKNESS 1–2 MICROMETER WITH HIGH SELECTIVITY AND HIGH HYDROGEN PERMEANCE

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ABSTRACT

Thin Pd films with high selectivity are advantageous both from a cost point of view as well as for achieving higher hydrogen fluxes through the film. Pd films of thickness down to 1 μm were deposited on the inside of asymmetric α-alumina membranes from the Societé des Céramiques Techniques (SCT) (200 nm pore size) by a modified electroless plating process. Pre-treatment, the plating rate during electroless plating and membrane post-plating treatment must be optimized individually to obtain very high quality films. Membrane defects develop when the substrate is not catalyzed properly before plating, when the plating rate is too fast and/or when the membrane is not cleaned thoroughly after plating. Hydrogen permeances varied between 6 and 15 μmol/m^2 Pa sec for temperatures from 330 to

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450°C and Pd films from 1.0 to 1.5 μm thickness. Hydrogen to nitrogen selectivity was above 100 for all membranes tested and above 400 for all but two membranes (thickness 1.0–1.5 μm).

Key Words: Electroless plating; Hydrogen and nitrogen permeance; Palladium membranes

INTRODUCTION

In the past decade, a lot of attention has been given to producing thin palladium and palladium alloy films for hydrogen separation (1,2) and for use in catalytic membrane reactors (3–8). The first work in this area employed metal foils of thickness greater than 20 μm (9). In recent years, many other studies also used Pd and Pd alloy foils of thickness 15–150 μm (10–14), but the hydrogen permeance was generally low due to the large thickness.

Improvements in inorganic membrane fabrication created new opportunities for preparing supported metal films of thickness 4–15 μm with electroless plating (15–20). Thinner films have been prepared by electroless plating, chemical vapor deposition or wet impregnation, but mainly on disks or the outside surface of membrane tubes (21–25). Shu (26,27) prepared Pd films down to 2 μm on the inside of asymmetric α/γ-alumina membranes from SCT. A thorough literature survey has not revealed the production of highly selective Pd films of less than 2 μm on the inside of a support membrane.

A high hydrogen permeance, combined with a high hydrogen to nitrogen selectivity, are important parameters for good membrane performance. Typically, hydrogen permeance will improve when films get thinner, but at a cost of poorer selectivity.

In this study, the different Pd film preparation steps were investigated. Hydrogen permeance was determined as a function of the Pd film thickness. Permeance and selectivity tests were performed using both a sweep gas and a positive pressure difference. Model values predicted the experimental data accurately.

EXPERIMENTAL SECTION

The membranes employed in this study were SCT membranes (Societé des Céramiques Techniques, Montpellier, France) consisting of three α-alumina layers with decreasing particle size. The structure is shown in Figs. 1 and 2.

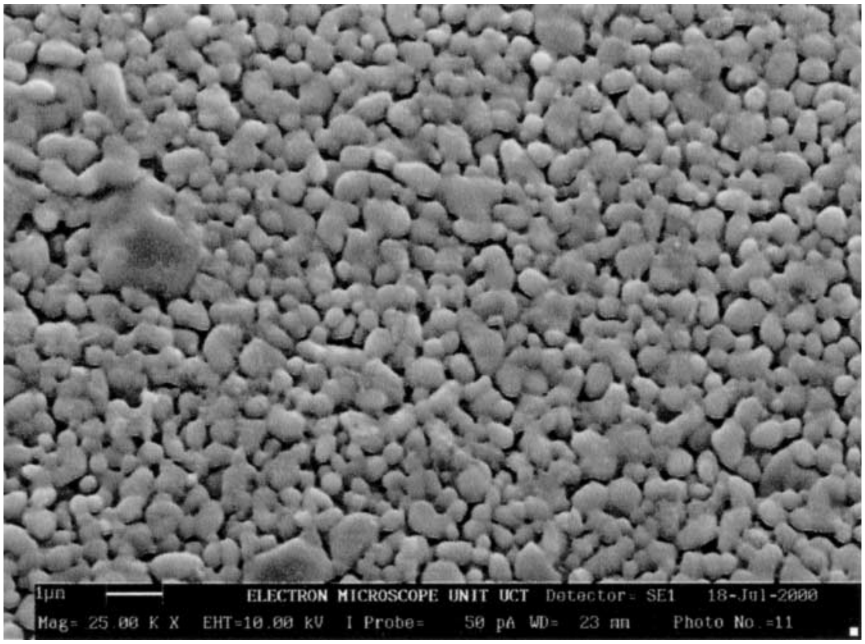

Figure 1. Top view of SCT membrane.

The membranes had a length of 250 mm, an outside diameter of 10 mm and an inside diameter of 7 mm. The final layer had a pore size of 200 nm. The membrane endings were enameled to obtain a proper seal.

Membrane Pre-treatment

The SCT membranes were stirred in distilled water for 30 min using an RW 11 basic stirrer from IKA Labortechnik, Germany. The samples were then placed overnight (14–16 hr) in an oven at 200°C. Their masses were recorded the following morning, after cooling of the membranes in the oven down to 60°C.

Prior to electroless plating, the membrane surface needs to be activated to provide catalytic centers for the plating process. A two-step process using a palladium salt and a tin chloride salt was used. Previously, it was found that the conventional composition of the pre-treatment solutions deposits small amounts of tin. Keuler (28) found about 0.2–0.4% Sn (with particle induced x-ray emission) in a 5 µm Pd film prepared with the conventional solutions. For thin Pd films of less than 2 µm this amount will become more significant and might cause

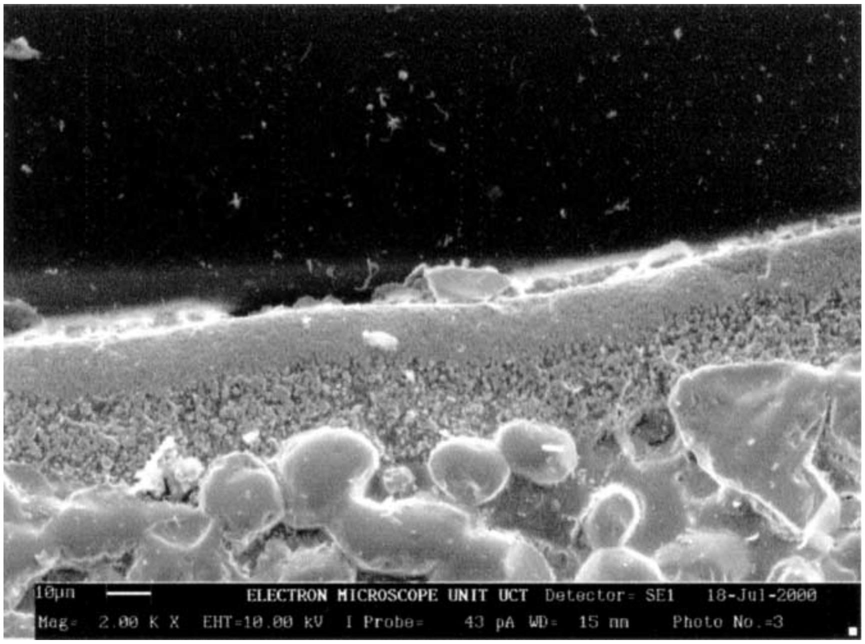

Figure 2. Side view of SCT membrane.

Table 1. Composition of Pre-treatment Solution

	Conventional Composition	This Study
Sensitizing solution (per liter)		
35 wt% HCl (mL)	1	—
$SnCl_2 \cdot 2H_2O$ (g)	1	0.45
Activation solution (per liter)		
35 wt% HCl (mL)	1	—
10 wt% $(NH_3)_4Pd(NO_3)_2$ (g)	1.5	—
23 wt% $PdCl_2$	—	1.4
Sn to Pd molar ratio	8.8	1.1

Table 2. Stirring Sequence and Times

	Pd Solution (min)	Distilled Water	Sn Solution (min)	Distilled Water
1. Repeat 3 times	10	Dip into 10 times	10	Dip into 10 times
2. Repeat 3 times	5	—	5	Dip into 10 times

a decrease in the hydrogen permeance through the film. A higher Pd concentration and a lower Sn concentration were chosen for pre-treatment and are indicated in Table 1. The conventional composition is similar to that used by Shu and co-workers (29).

The outside surface of the membrane tubes were wrapped with PTFE tape to catalyze the inside of the tubes only. The membrane was connected to a stirrer (an RW 11 basic stirrer from IKA Labortechnik) and placed into the pre-treatment solution. The stirring speed was set at about 1200 rpm. The sequence and procedure for the pre-treatment are shown in Table 2. Approximately 270 mL of each solution was used. Fresh tin solution was prepared for every membrane, while the Pd solution was changed after every three membranes catalyzed.

After pre-treatment, the teflon tape was removed and the membrane stirred in clean distilled water for an additional half an hour to remove any solution in the membrane pores. The membrane was placed in an oven at 200°C overnight and the mass recorded the next morning after cooling: the mass increase varied between 13 and 16 mg for different membranes prepared using a 0.45 g/L $SnCl_2$ sensitizing solution. Some membranes were pre-treated with a 0.25 g/L $SnCl_2$ sensitizing solution, in which case the mass increase was about 8–10 mg.

Electroless Pd Plating

A 2.00 g/L (2000 ppm) Pd solution was used for electroless plating. The composition of the solution is given in Table 3. The Pd solution was allowed to

Table 3. Pd Plating Solution Per Liter (for 2.00 g/L Pd in Solution)

$(NH_3)_4PdCl_2 \cdot H_2O$ (g)	4.94
28 wt% ammonia (mL)	400
EDTA (g)	80
35 wt% hydrazine (mL)	0.65 (hydrazine: Pd = 0.35:1) increased with time
Temperature (°C)	71–73

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Table 4. Plating Procedure for Producing Pd Films

Plating Session	Reaction Time for 11.5 mL Plating Solution (min)	1.75 wt% Hydrazine Added for 11.5 mL Solution (mL)
1	20	0.15
2	20	3 drops
3	20	0.5

stabilize for at least 12–16 hr prior to plating, without hydrazine in it. Hydrazine was added just before plating and only to the solution that was used for plating. For some membranes, higher hydrazine concentrations were used. The values in Table 3 represent the composition of the optimized plating solution. The hydrazine concentration in Table 3 is the initial amount that must be added to the palladium solution on a per liter basis. Table 4 lists how hydrazine was added to the palladium solution. The Pd-salt was purchased from Aldrich (Johannesburg, South Africa) (99.99% purity), the Sn-salt from Fluka (Johannesburg, South Africa) (>98%), hydrazine from Aldrich (35 wt% solution), EDTA from Saarchem (Cape Town, South Africa) (>99%) and ammonia solution from Saarchem.

The membrane was sealed in a teflon reactor with O-rings. The reactor had a single shell side outlet allowing vacuum to be pulled on the shell side (2). A defect-plugging technique was developed to produce thin films (<2 μm). An initial 1 μm Pd base was deposited on the inside of the membrane tube using 35 mL plating solution without any applied vacuum. The membrane was closed off at the bottom with a 10 mm silicon tube which was closed at one side. A silicon tube of about 15 cm was placed over the membrane at the top. A plating solution of 11–12 mL was introduced at a time into the membrane tube fixed in the reactor.

Three to four plating sessions with the same plating solution were performed. Repeated plating sessions ensured that all the Pd in solution was deposited on the membrane. The hydrazine concentration was increased after each plating session to compensate for thermal decomposition of hydrazine. The plating procedure is outlined in Table 4 and is essentially a batch process repeated several times. When preparing a 1 μm film, each session in Table 4 was repeated three times (11.5 mL × 3 = 34.5 mL solution). The first 0.15 mL of 1.75 wt% hydrazine that was added to the 11.5 mL plating solution (see Table 4) is equivalent to 0.65 mL of 35 wt% hydrazine per liter of plating solution as mentioned in Table 3.

The membranes were then cleaned and dried overnight before the next layers were applied. After the initial Pd layer was deposited, an additional one, two, or three layers were deposited to obtain the final product. For the second and third Pd layers, a vacuum was applied on the shell side of the teflon reactor. Pd solution would concentrate in the more permeable or defected areas in the membrane. More plating would occur in weakly plated (defected) areas, film defects would be covered with palladium and a film with less defects would result.

Pd membrane preparation focused on preparing a thin film of thickness less than 2 μm. Some films of between 2 and 5 μm were also prepared to study the effect of film thickness on hydrogen and nitrogen permeance through the film. Two methods were used to determine the amount of Pd deposited on the membrane supports. The membranes were weighed after pre-treatment and drying at 200°C overnight to get the initial mass. After the testing of the membranes was completed, the membranes were weighed again to get the final mass. The difference between the initial mass and final mass was taken as the amount of Pd deposited. ICP (with a Spectroflame Modula from Analytical Instruments) analysis of the plating solution was performed after plating to determine the amount of palladium deposited. Since the initial mass of the plating solution was known, the mass of the deposited Pd could be calculated. The average of this mass and the measured mass was used to calculate the Pd film thickness. The calculated film thickness is an average thickness value.

Membrane Cleaning

The same equipment used for pre-treatment was used for cleaning. The membrane was removed from the reactor and placed in a cylinder containing 270 mL of 15 wt% ammonia solution. The membrane was stirred at a rate of 1200 rpm for 1 hr. This process was repeated with fresh ammonia solution and finally the membrane was stirred in distilled water of similar volume for half an hour. The membrane was then placed overnight in an oven at 240°C. In the latter stages of the work, the membranes were dried at 100°C and again (two or three times) stirred in ammonia solution and water before drying them at 240°C. This was an attempt to try and extract more EDTA trapped in the membrane pores.

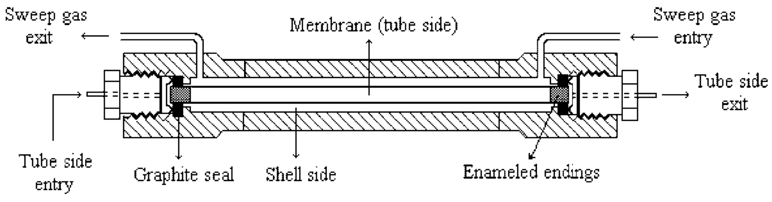

Figure 3. Membrane reactor.

Membrane Testing

Membrane permeation testing was performed in the reactor shown in Fig. 3.

The reactor was made from stainless steel, and graphite rings were used for obtaining an effective membrane to reactor seal. The rings had dimensions of 10.4 by 17.9 mm, a thickness of 5 mm and a density of 1.6 g/cm^3. They were purchased from Coltec Industries (Lyon, France). A detailed description of the testing equipment and the testing procedures are described in Ref. (2).

RESULTS AND DISCUSSION OF RESULTS

Effect of Plating Rate on Membrane Performance

The quality of the Pd coating was very dependent on the plating rate. If the plating rate was too fast, the coating showed poor selectivity characteristics. The plating rate would become too fast when the hydrazine concentration was too high, the temperature was too high and/or the EDTA concentration was too low.

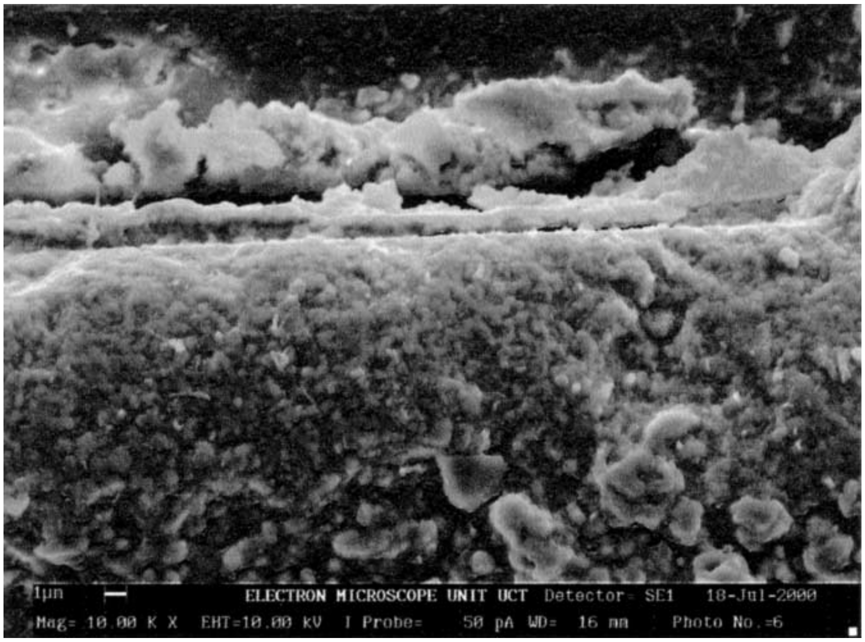

Figure 4. Cross-section of membrane (a) (10,000×).

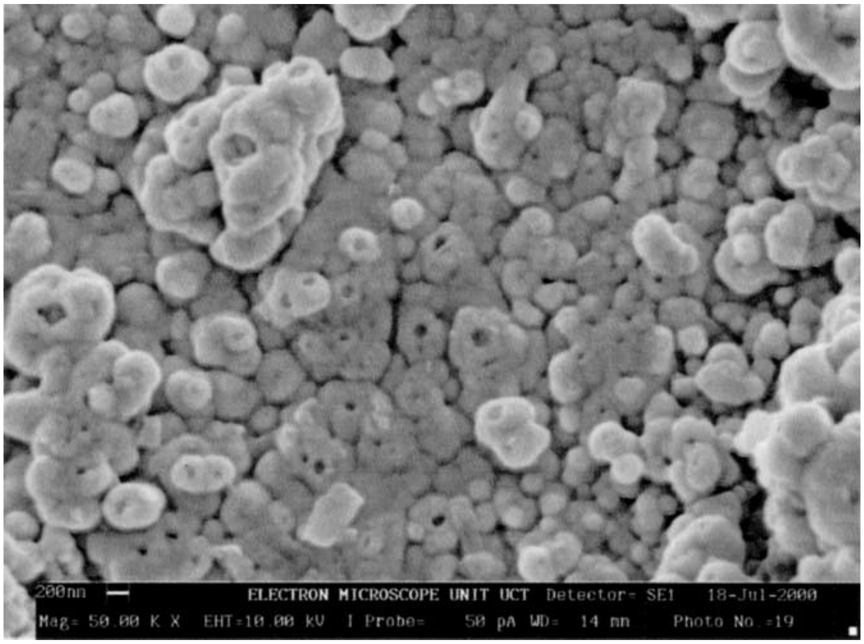

Figure 5. Top view of membrane (a) (50,000×).

The only variable that was changed was the hydrazine concentration. Initially, the hydrazine–Pd molar ratio at the start of plating was 1 to 1. Two Pd membranes prepared with the higher hydrazine concentration were defected, because Pd blisters formed on the membrane surface that caused leaks. After lowering the hydrazine concentration (to values in Table 3), this problem no longer occurred. Figures 4–7 show SEM images of the two poorly performing membranes. The calculated Pd thickness of membranes (a) and (b) were about 1.5 μm. Cross-section SEM images showed similar thicknesses.

For membranes (a) and (b) in Figs. 4–7, there were two different surface structures. In both cases, there were clear defects. Defects formed because the plating rate was too fast. Slower plating rates are necessary to form a dense layer. The cross-section view of membrane (a) (Fig. 4) indicates poor adhesion of the metal film to the alumina support. The Pd film is the thin layer on top of the alumina base. The surface was not smooth, but consisted of small metal clusters scattered over the surface area. Under high magnification (Fig. 5), there were tiny pores visible in the metal particles. The difference between a high selectivity membrane (membrane c in Fig. 11) and a low selectivity membrane (membrane a) were the defects visible in Fig. 5. Those pores or defects were suspected to cause poor selectivity.

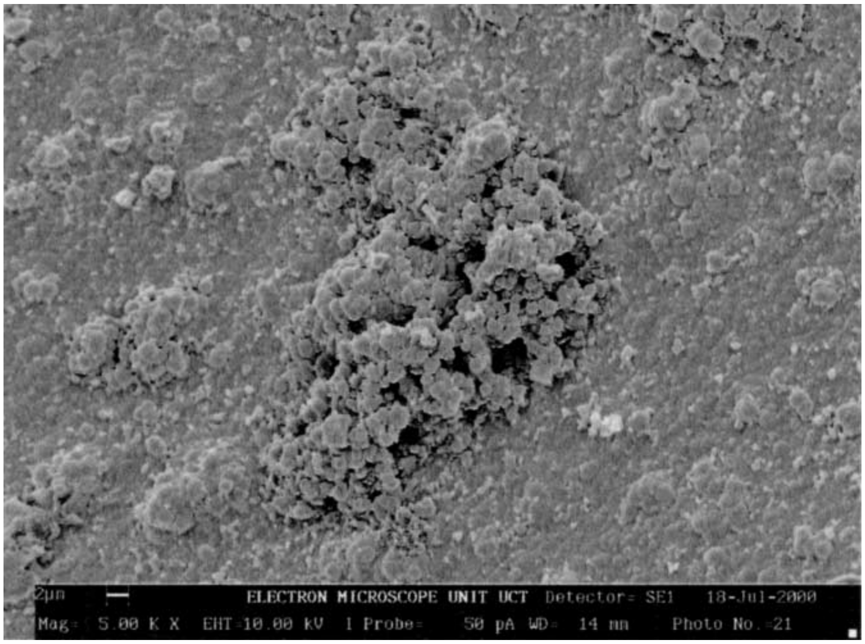

Figure 6. Top view of membrane (b) (5000×).

For membrane (b), the surface seemed dense both in the cross-section view and in the top view images. There were no continuous defects in the structure. Upon further investigation, some areas in the coating were identified where there were porous clusters on the top (Figs. 6 and 7). These clusters were spread out over the surface and suspected to be the cause for poor selectivity. The structures of membrane (a) and membrane (b) differed. For membrane (a) the pores were inside small metal clusters, while for membrane (b) the pores were between metal clusters.

Membrane Post Plating Treatment

After plating, the membranes were stirred in ammonia to dissolve EDTA in the membrane pores and then dried in an oven at 240°C. Stirring in ammonia and drying overnight at 240°C was not sufficient to remove all carbon from the membrane pores. In some areas on the outside membrane surface, brown spots were visible after drying at 240°C, indicating the presence of carbon. Two possibilities exist: either 240°C was too low for full oxidation, or the oxygen to carbon contact in the pores behind the dense palladium layer was very poor.

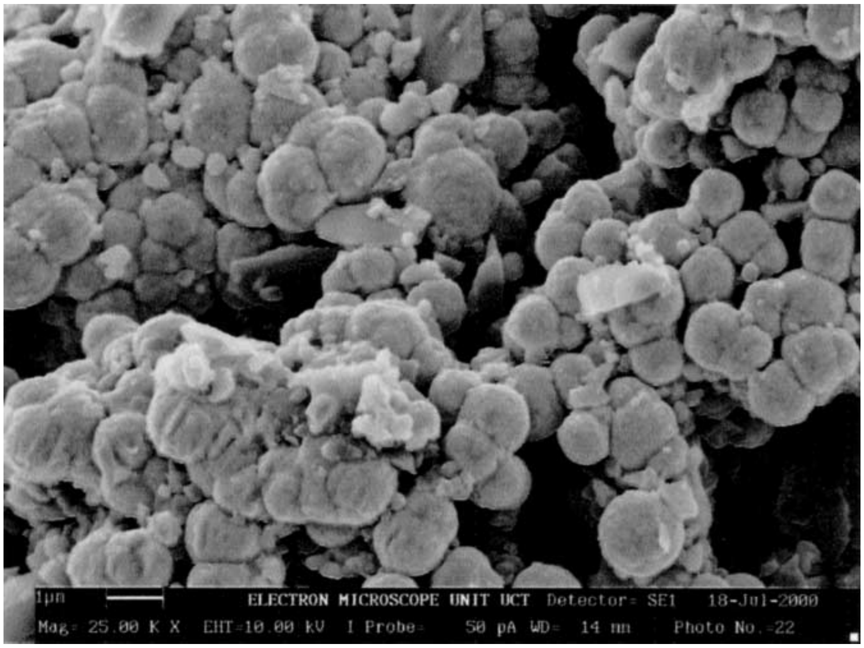

Figure 7. Top view of membrane (b) at higher magnification (25000×).

Hydrogen and nitrogen permeation tests were performed on a membrane after it was dried at 240°C. When testing at temperatures from 450 to 330°C was completed, the membrane was cooled down to 320°C. Oxygen was forced under pressure (between 1.0 and 2.5 bar depending on the membrane selectivity) through the defects in the Pd film and the membrane support pores for one hour. The membrane was then heated in nitrogen to 450°C, reduced in hydrogen and retested at temperatures from 450 to 330°C. The results are shown in Figs. 8 and 9.

There was a significant increase in hydrogen permeance after oxidation at 320°C. These results confirmed the presence of either an EDTA or carbon layer in the pores behind the Pd film. Reduction at temperatures of up to 500°C in hydrogen did not decompose the layer thermally. Oxidation treatment at 320°C removed most of the remaining precursor in the membrane support. Oxidation resulted in higher hydrogen permeances through the Pd membrane and improved selectivity (see Figs. 8 and 9). The improvement in selectivity (Fig. 9) shows that the nitrogen permeance (and the oxygen permeance) was not significantly affected by the oxidation treatment. Hydrogen permeance increased, but not many additional defects were formed in the film.

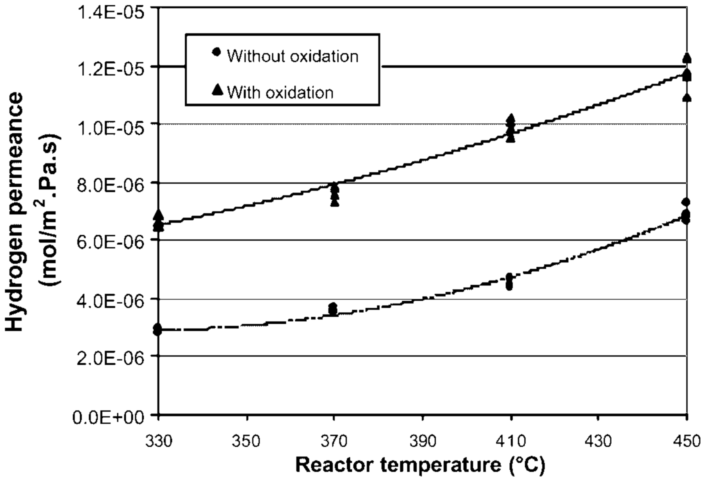

Figure 8. Effect of oxidation post-treatment at 320°C on H_2 permeance (1.43 μm Pd film).

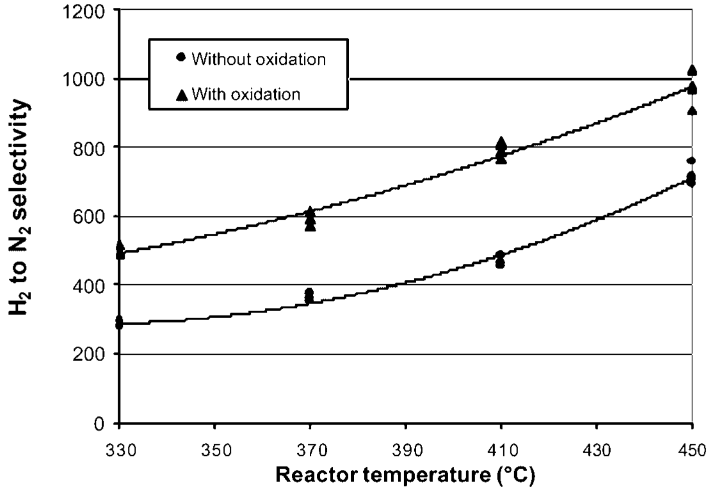

Figure 9. Effect of oxidation post-treatment at 320°C on selectivity (1.43 μm Pd film).

Structural Pd Membrane Characterization

The structure of a Pd membrane was investigated with a scanning electron microscope.

The calculated thickness of membrane (c) (1.45 μm) was in good agreement with the SEM thickness (ranged between 1.0 and 1.7 μm). Figure 10 shows a very dense layer on top of the 200 nm α-alumina support. A top view image (Fig. 11) confirmed this.

The Effect of ΔP and Temperature on H_2 and N_2 Permeance

Membranes were tested under positive feed pressure conditions and with a sweep gas. Under positive feed pressure conditions, the effects of temperature, pressure difference, and film thickness were studied. When a sweep gas was employed, the effects of temperature, space time, and sweep gas ratios were tested. The hydrogen flux is described by Eq. (1). Pressure data was required to calculate the value of the pressure exponent (n), which is an indication of the

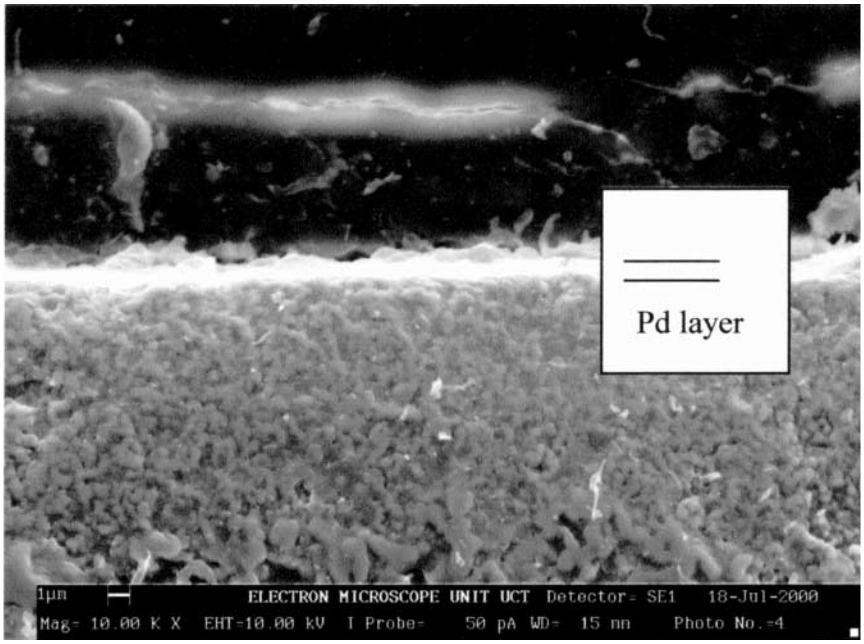

Figure 10. Cross-section of membrane (c) (10,000×).

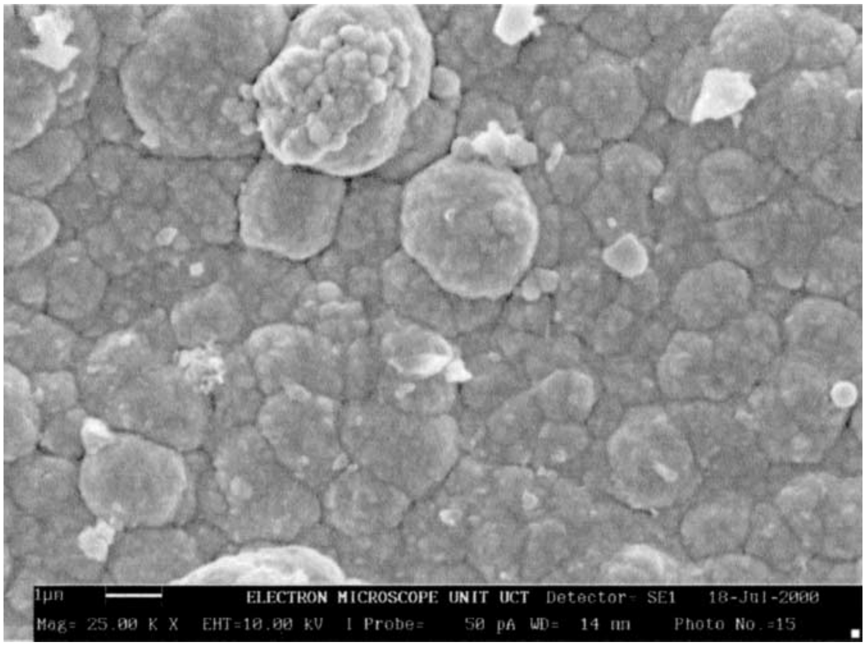

Figure 11. Top view of membrane (c) at higher magnification (25,000×).

flow process through the film. Temperature data was necessary to calculate the Arrhenius parameters (P_0 and E_D) in the Arrhenius equation (Eq. (2)).

$$J = \frac{S_c D_0 \, e^{-E_{D/R_0 T}}}{l}(P^n_{H_{2x}} - P^n_{H_{2y}}) = \frac{P_{er}}{l}(P^n_{H_{2x}} - P^n_{H_{2y}}) \tag{1}$$

$$P_{er} = S_c D_0 \, e^{-E_{D/R_0 T}} = P_0 \, e^{-E_{D/R_0 T}} \tag{2}$$

Membrane selectivity was determined using hydrogen and nitrogen as testing gases. Nitrogen permeance is an indication of membrane defects or leaking. There were three factors that contributed towards the measured nitrogen permeance. They were:

- leaking through defects in the electroless plated film;
- leaking at the membrane reactor, graphite ring, enamel interfaces; and
- leaking at the porous membrane, non-porous enamel, Pd film interfaces.

Figure 12 shows nitrogen permeances as a function of pressure and temperature. The average pressure between the tube and shell side was used.

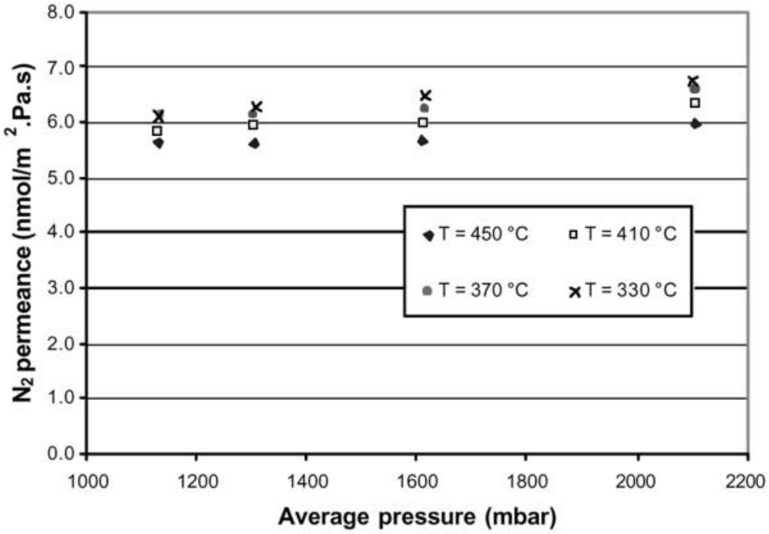

Figure 12. Effect of pressure on N_2 permeance for a 2.4 μm Pd film.

Theoretically, the average pressure should not have any effect on the nitrogen permeance (measured in mol/m^2 Pa sec) if it is Knudsen flow and the permeance will decrease with an increase in temperature if it is Knudsen flow. For viscous flow, the permeance will increase with an increase in average pressure and decrease with an increase in temperature. Data in Fig. 12 indicates that Knudsen flow was the main flow mechanism through defects in the film. The permeance did, however, increase slightly with an increase in the average pressure, which indicates that there was some viscous flow through the defects. The hydrogen permeance did not vary considerably with pressure. The hydrogen mass flow meter was limited to 1000 cm^3/min and the permeable membrane length varied between 20 and 23 cm.

Comments on the Pressure Exponent and Activation Energies for Pd Films

Different values for the pressure exponent, ranging from below 0.5 to just above 1.0, have been reported in literature (25–27,30,31). The *n*-value is influenced by a combination of transport effects and cannot necessarily be coupled to a single rate limiting step. While diffusion limitations tend to point towards a *n*-value of 0.5, higher values do not indicate the presence of a single rate limiting step. Other effects such as interphase mass transfer resistance, adsorption, desorption, dissociation, recombination and even experimental procedures play an important role. The contribution of each effect to the *n*-value is not clear at this stage. What has been observed is that the *n*-value increases with a decrease in film thickness (15,32) and that films of less than 2 μm thickness have a *n*-value approaching 1 (25,31). The *n*-value is also very dependent on the differential pressure across the film (experimental procedure) and tend to increase with a smaller pressure differential (26).

Due to the high hydrogen permeances through the films, the pressure differences across the membranes typically varied only from 15 to 120 mbar. The pressure exponent in the flux equation (Eq. (1)) was assumed to be one and the square of the Pearson product moment correlation coefficient (R^2-value) was calculated. The R^2-value was greater than 0.995 for the majority of the calculations. However, since the pressure differences were so small, accurate values for *n* could not be calculated. Changes in the *n*-value resulted in similar R^2-values, because of the low pressure difference. A *n*-value of 1 indicates that hydrogen chemisorption on the palladium surface was the rate limiting step according to Refs. (25,30). Sievert's law, where $n = 1/2$ (in Eq. (1)), was not applicable for the thin films synthesized in this study. Diffusion was not the rate limiting step, but it seemed to be adsorption and desorption.

A literature study indicated that the preparation mechanism of the film and the resulting film microstructure have a larger effect on the *E*-value than the film thickness. For example:

- Shu (6) reported *E*-values of >20 kJ/mol for thick films;
- Ilias (15) reported *E*-values of 5–13 kJ/mol for films of 8–12 μm;
- Xomeritakis (23) measured *E*-values of >20 kJ/mol for films <2 μm;
- Jun (24) measured *E*-values of about 5 kJ/mol for films <2 μm;
- Jayaraman (31) measured *E*-values of about 23 kJ/mol for films <1 μm; and
- Shu (26) measured *E*-values of about 17 kJ/mol for films of 2 μm.

Sputtering tends to yield high activation energies (23,24,31). Furthermore, the rate limiting step cannot necessary be coupled with a specific activation energy.

Temperature data in this study (330–450°C) fitted the Arrhenius equation accurately. The electroless plating process produced films with low activation energies. There was a decrease in activation energy with a decrease in film thickness as shown below:

2.4–6.0 μm Pd films: E = 12.7–18.5 kJ/mol
1.0–1.5 μm Pd films: E = 7.1–13.2 kJ/mol

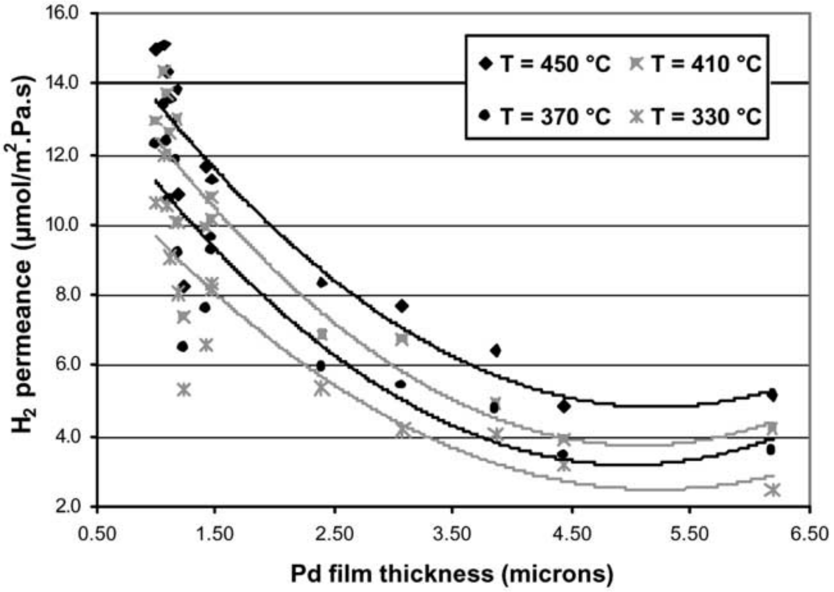

Figure 13. Hydrogen permeance for Pd films from 1 to 6.5 µm.

The Effect of Film Thickness on Permeance

The effects of film thickness on hydrogen permeance and membrane selectivity are depicted in Figs. 13–15. Data in Fig. 13 shows a decrease in hydrogen permeance with an increase in film thickness for films of a thickness up to 3.5 µm. Thereafter, the permeance started to level off. The permeance increased with temperature as mentioned previously. The decrease in permeance was linear, but not directly proportional to the inverse thickness for films from 1.5 to 3.5 µm.

Figure 14 depicts permeances for Pd films from 1.0 to 1.5 µm thickness. The values ranged between 6 and 15 $\mu mol/m^2$ Pa sec for temperatures from 330 to 450°C. For nitrogen, the general trend was a decrease in permeance with an increase in the Pd film thickness. For films of less than 1.5 µm thickness, the effect of thickness on hydrogen permeance became less important. The hydrogen permeance was more dependent on other factors such as adsorption and desorption kinetics and interphase mass transfer resistance than on diffusion kinetics. The presence of carbon contaminants also influenced the hydrogen permeance. In Fig. 14, the low permeances at 1.2 µm thickness was probably due to carbon contamination. For films from 1.18 to 1.0 µm, there was no significant improvement in hydrogen permeance, because adsorption and desorption limited

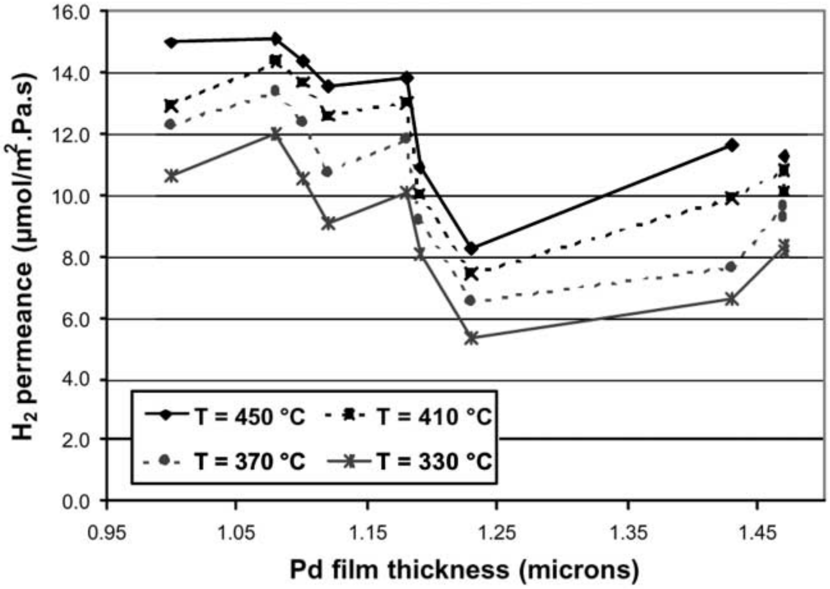

Figure 14. Hydrogen permeance for Pd films from 1 to 1.5 µm.

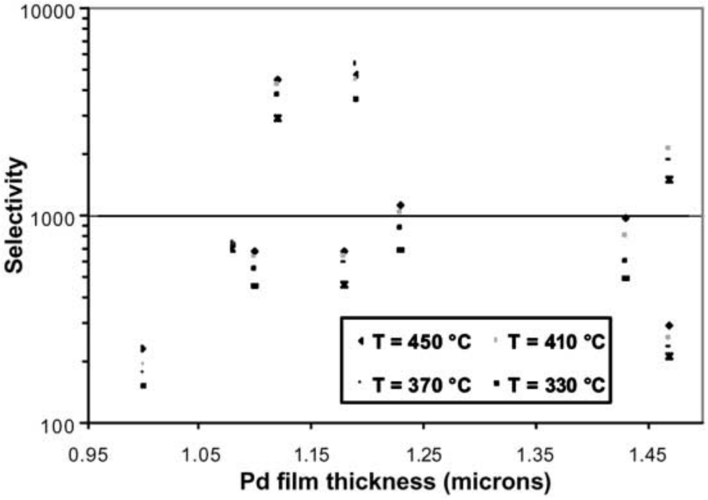

Figure 15. H_2 to N_2 selectivity for Pd films from 1 to 1.5 µm.

the permeance and not diffusion. Furthermore, the hydrogen to nitrogen selectivity declined sharply for films from 1.18 to 1.0 μm thickness (see Fig. 15). This suggests that there is little to gain by making films thinner than 1.2 μm, because hydrogen permeance will not improve significantly and the hydrogen to nitrogen selectivity will decline sharply.

The ideal selectivity data, which is the pure hydrogen permeance divided by the pure nitrogen permeance, is presented in Fig. 15. At all the tested temperatures, the selectivity remained above 100, which is an indication of high quality membranes. All films from 1.0 to 1.5 μm thickness had a selectivity of at least 400 except the 1.0 μm film and a 1.47 μm film (see Fig. 15). The selectivity was more dependent on changes in the nitrogen permeance than changes in hydrogen permeance. Since the nitrogen permanence was very low, a small increase resulted in a large decline in selectivity. There were a number of unpredictable effects that were not necessarily linked to the quality of the film, which influenced the nitrogen permeance (and selectivity). These are listed in the "Effect of ΔP and Temperature on H_2 and N_2 Permeance" section.

Comparison with Literature Data

Keuler (2) published an extensive list of hydrogen permeances for Pd based membranes. Some general remarks are:

- The surface structure of Pd films prepared by CVD appears to be unfavorable for high hydrogen permeance. Films typically had a hydrogen permeance of less than 1 $\mu mol/m^2$ Pa sec, except for work performed by Yan et al. (30) where values of up to 4 $\mu mol/m^2$ Pa sec were obtained.
- Some of the best values for hydrogen permeance have been obtained with alumina substrates. Most hydrogen permeances for films on porous glass were less than 1 $\mu mol/m^2$ Pa sec, for films on porous stainless steel it were less than 1 $\mu mol/m^2$ Pa sec and for films on refractory metals it were less than 2 $\mu mol/m^2$ Pa sec.
- The best values obtained with alumina supports and electroless plating were:
  - (a) 9.75 $\mu mol/m^2$ Pa sec at 450°C for plating on a disc by Zhao et al. (21), but the H_2 to N_2 selectivity of the film was only 23.
  - (b) 2.86 $\mu mol/m^2$ Pa sec at 400°C for plating on the outside of a tube by Kikuchi (16). The selectivity was not mentioned.
  - (c) 5.27 $\mu mol/m^2$ Pa sec at 500°C for plating on the inside of a tube by Shu et al. (27). The selectivity was not mentioned.

The best hydrogen permeances that have been published were for Pd films on modified porous stainless steel discs prepared by wet impregnation. Film thickness varied from 0.5 to 0.8 μm. The hydrogen permeance was 15.8 μmol/m^2 Pa sec at 450°C (24) and 17.8 μmol/m^2 Pa sec at 550°C (25). In both cases, the H_2 to N_2 selectivity was above 1000. Porous stainless steel membranes are, however, much more expensive than alumina membranes and disks are not very practical. Tubes are the preferred geometry for practical applications.

CONCLUSIONS

Each step in the electroless plating process must be optimized to produce thin, highly selective Pd films. For pre-treatment, a low Sn to Pd ratio was employed to limit the Sn deposition and increase thermal stability of the film. The quality of the Pd film depended highly on the plating rate. A high plating rate due to a high hydrazine concentration, a low EDTA concentration and/or a high plating temperature must be avoided to produce thin selective films. In some cases, the Pd films had defects due to high plating rates. The last critical step is post plating cleaning. After plating, membranes were stirred in ammonia solution for several hours, dried and then further oxidized at 320°C in pure oxygen before reduction.

Pd films of thickness down to 1 μm were deposited on the inside of asymmetric α-alumina membranes from SCT (200 nm pore size). Hydrogen permeances varied between about 6 and 15 μmol/m^2 Pa sec for temperatures from 330 to 450°C and Pd films from 1.0 to 1.5 μm thickness. Hydrogen to nitrogen selectivity was above 100 for all membranes tested and above 400 for all but two membranes (thickness 1.0–1.5 μm). These values are a significant improvement over other published results for membranes prepared on the inside of alumina support tubes.

For films in the order of 1.0–1.2 μm, adsorption and desorption are more likely to be the rate limiting steps rather than diffusion. There was little advantage to gain by reducing the film thickness below 1.2 μm. Below 1.2 μm, the hydrogen permeance improved only marginally, while the hydrogen to nitrogen selectivity declined sharply.

NOMENCLATURE

List of Symbols

D_0	pre-exponential factor of diffusion coefficient (m^2/sec)
E	activation energy (J/mol)

E_D	diffusion activation energy (J/mol)
J	flux (mol/m^2 sec)
l	film thickness (m)
n	pressure exponent
P	pressure (Pa)
P_0	pre-exponential factor of permeability coefficient (mol m/m^2 Pa sec)
P_{er}	permeability coefficient (mol m/m^2 Pa sec)
R_0	Universal constant (8.314 J/mol K)
S_c	Sievert's constant

Subscript

H_2	hydrogen
x	high pressure side
y	low pressure side

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