6 Engineering substrate surface for the synthesis of ultra-thin composite Pd membranes

6.1 Introduction

It is well known that the deposition of Pd on Porous Metal (PM) supports requires a thicker layer of Pd to achieve a gas tight membrane than Pd deposition on Al_2O_3 and vycor glass supports. This difference in the thickness of the Pd layer is due to the average pore size, pore size distribution, roughness and the size of the largest pore at the porous metal support surface. PSS supports are characterized by a rather broad pore size distribution (0.1-8 μm) and the size of pores on the surface ranges between 0.1 to 20 μm in diameter. The size of the largest pore at the support surface is the crucial parameter to achieve a thin dense layer (Ma et al., 2001). Ma et al. (2001) deposited thin Pd layers on three PSS supports characterized by different grades: 0.1, 0.2 and 0.5 μm. Mercury intrusion analysis showed that the 0.1μm grade support included the smallest pores on the surface while the 0.5 μm grade included the largest pores on the surface. The Pd thickness needed to obtain a gas tight membrane was shown to be approximately three times the diameter of the largest pore on the surface for the three membranes. The typical Pd layer deposited by the electroless deposition method on PSS supports had a thickness of 15-50 μm with support grades in the 0.1 to 0.5 μm range. When special techniques are coupled with the electroless deposition method, the thickness of the membrane can considerably be reduced. 8-10 μm Pd composite membranes were prepared on PSS (0.1μm grade) by the electroless plating method coupled with osmosis (Li et al., 1998; Souleimanova et al., 2000; Souleimanova et al., 2002; Souleimanova et al., 2001). Vacuum can also be applied across the porous support during Pd plating (Nam et al., 1999). The main disadvantage of osmosis and vacuum plating techniques is that Pd deposits very deep into the pore system of the porous support, thereby decreasing the permeance of the composite Pd membrane. Therefore, instead of "rushing" the deposition of Pd into the pores of the support, studies were undertaken to modify the pore size distribution at the surface of the porous support.

In order to smoothen the surface of the PSS supports, She (2000) performed a mechanical treatment by abrasion of the support (0.5 μm grade) with a metallic brush followed by treatment in 10 M HCl to reopen the pore structure. She (2000) prepared membranes as thin as 20 μm on polished supports by the electroless deposition method, which were quite thin taking into account the large grade of the support and the fact that no special technique (osmosis, vacuum plating) was used in addition to electroless deposition. Nam and Lee (2001) modified a PSS support (0.5 μm grade) by nickel powder deposition followed by the deposition of a silica layer by the sol-gel technique and obtained on such smoothed PSS support a 2 μm Pd-Cu membrane. Nam and Lee (2001) and Nam et al. (1999) obtained a 0.8 μm Pd-Ni membrane on a modified Ni powder-PSS support by using vacuum during electroless deposition. Poly-(dimethylsiloxane) sealing layer was also used to form a smooth surface on top of the α-Al_2O_3 (Athayde et al., 1994). They further prepared Pd/Ag membranes as thin as 0.25-1μm.

A new technique was described to smoothen the surface of any porous support characterized by a broad pore size distribution and large pores at the surface (Ma and Guazzone, 2004). This new technique consisted of depositing Pd seeded (pre-activated) Al_2O_3 powders of different sizes from a water-slurry, starting with coarse Al_2O_3 particles (3-5μm) and finishing with very fine Al_2O_3 particles (0.1-0.3μm). Each Al_2O_3 layer was consolidated by a short (10-15 min) deposition of Pd, which served as Al_2O_3 particle binder. The group of three Al_2O_3 layers was denoted as the grade layer.

The primary objective of the work described in this chapter was to understand the fundamental concepts behind the support surface modification leading to a regular and smooth surface. Hence, the surfaces of porous metal supports were modified by the deposition of Pd seeded Al_2O_3 powder (pre-activated powder), and the H_2 permeation properties of membranes formed on such supports were evaluated. Also, the ability of the grade layer to inhibit intermetallic diffusion was studied.

6.2 Experimental

6.2.1 Membranes considered in this chapter

Membranes C01-F03, C01-F04, C01-F05 and C01-F07 were prepared on oxidized PSS supports with no grade layer. Membranes C01-F08, C01-F09 and C01-F11b were prepared on graded oxidized PSS supports. Membranes Ma-32, Ma-32b, Ma-34, Ma-34b, Ma-41 and Ma-42 were prepared on graded oxidized PH supports. The grading of porous metal supports was performed according to the experimental protocol described in Section 3.1.2. However, different set of powders and different conditions were used for each support. Table 6-1 summarizes all composite Pd membranes prepared on graded supports and the Al_2O_3 powder or the mixture of Al_2O_3 powders used for each layer.

C01-F08 was the first composite Pd membrane prepared on a graded support and only had one coarse Al_2O_3 layer as grade layer. The binding of Al_2O_3 was performed under vacuum. All other supports were graded using three groups of powders. Also, for all other membranes, the Al_2O_3 binding step was performed in the absence of vacuum. The binding step was performed by immersing the support with the deposited alumina layer into the Pd plating solution with the composition listed in Table 3-1.

Table 6-2 summarizes the characteristics of all membranes studied in this chapter. When no grade layer was applied to the supports (0.1 μm grade), 20-30 μm of Pd were needed to form a gas tight membrane. All membranes prepared on graded supports were significantly thinner (8-15 μm) than membranes obtained on the bare rough support. The He leak of all membranes before H_2 characterization was too low to be detected by the 0.01 sccm (0.1 sccm for large membranes) sensitivity digital mass flow meter except for membrane C01-F09 which had an initial He leak equal to 0.039 $m^3/(m^2\ h\ bar)$. The initial He leak of C01-F09 was due to a large and deep pore on the bare support that could not be completely closed with Pd. The He leak did not pose problems during the membrane characterization since the selectivity (H_2/He) of the membrane equaled 170 at 250ºC and a pressure difference of 1 bar (see Section 5.4.2).

Table 6-1 Al_2O_3 powders and binding conditions for the grading of C01-F08/9/11 and Ma-32/34/41/42

	1st Al_2O_3 layer	Binding step	2nd Al_2O_3 layer	Binding step	3rd Al_2O_3 layer	Binding step
C01-F08	-59 wt% of α Al_2O_3 5μm -29 wt% of α Al_2O_3 3μm -12 wt% of γ Al_2O_3 0.01-0.02μm ACTIVATED	20-30 min Under vacuum	-	-	-	-
C01-F09	-30 wt% of α Al_2O_3 5μm -5 wt% of α Al_2O_3 3μm -65 wt% of α Al_2O_3 1μm NOT ACTIVATED	-	-30 wt% of α Al_2O_3 3μm -10 wt% of α Al_2O_3 1μm -60 wt% of α Al_2O_3 0.3μm ACTIVATED	5 min. No vacuum	-30 wt% of α Al_2O_3 1μm -10 wt% of α Al_2O_3 0.3μm -60 wt% of γ Al_2O_3 0.01-0.02μm ACTIVATED	5 min. No vacuum
C01-F11	Same as C01-F09					
Ma-32	Same as C01-F09					
Ma-34	γ Al_2O_3 3μm ACTIVATED	15 min No vacuum	α Al_2O_3 0.3μm ACTIVATED	10 min No vacuum	γ Al_2O_3 0.01-0.02μm ACTIVATED	10 min No vacuum
Ma-41	γ Al_2O_3 3μm NOT ACTIVATED	-	α Al_2O_3 0.3μm ACTIVATED	20 min No vacuum	γ Al_2O_3 0.01-0.02μm ACTIVATED	20-25 min No vacuum
Ma-42	Same as Ma-41					

Table 6-2 Characteristics of all composite Pd membranes studied in this work.

membrane	Support	Surface (cm^2)	Thickness (From weight gain) (μm)	Permeance at 250ºC (m^3/m^2-h-$bar^{0.5}$)	Permeance at 500ºC (m^3/m^2-h-$bar^{0.5}$)	Permeance at 500ºC (m^3/m^2-h-$bar^{0.5}$) (Equation 4-11)	Selectivity at 500ºC (H_2/He)
C01-F03	0.1μm PSS	8.4	32	5.6	4.3	14.2	120
C01-F04	0.1μm PSS	8.4	28	7.8	4.7	18.7	1000
C01-F05	0.1μm PSS	8.4	33	5.9	10.3	15.9	587
C01-F07	0.1μm PSS	23	23	5.7	8	21.8	43
C01-F08	0.1μm PSS graded	23	15	8	22.5	23.8	300
C01-F09	0.1μm PSS graded	23	14	16	n.m.[(a)]	17 (at 250ºC)	170 (250ºC)
C01-F11	0.1μm PSS graded	23	15	8.9 (at 300ºC)	20.6	34.9	683
C01-F11b	0.1μm PSS graded	23	17	8.32	23.5	30.8	478
Ma-32	0.1 μm PH graded	120	7.7	21	50	68.1	42
Ma-32b	0.1 μm PH graded	120	10	15	42	52.5	27000→280[(b)]
Ma-34	0.1 μm PH graded	120	4	26 (at 300ºC)	49.6	131	300
Ma-34b*	0.1 μm PH graded	120	8	9.7	20	58	820→86
Ma-42	0.1 μm PH graded	120	5.6	20	39	93	980→818

(a) n.m = not measured

(b) The "→" indicates the change in selectivity at 500ºC from the selectivity value measured at time zero and the selectivity value measured at the end of the characterization procedure.

All membranes were characterized in H_2 atmosphere according to the characterization procedure described in Section 3.2.2 except for membrane C01-F09, which was only tested at 250°C to avoid the growth of the initial leak. Table 6-2 also lists the H_2 permeances all membranes should have had at 500ºC according to their thickness and equation (4-11). For ultra-thin membranes, Ma-32/34/34b/42, mass transfer limitations drastically decreased the performance of the membranes.

Figure 6-1 shows the surface of the thinnest (5.6 μm) composite Pd membrane, Ma-42, and the surface of membrane Ma-42, a Pd-Cu membrane. The surface of both membranes looked particularly shiny.

6.3 Results and discussion

6.3.1 The structure of composite Pd-graded support membranes

6.3.1.1 Thickness and structure of the grade layer

The thickness of the grade layer was difficult to measure since the weight gain after grading was close to the sensitivity of the scale, 0.01g, which corresponded to an average thickness of less than 1 μm. Table 6-3 lists the decrease in He permeance in percentage of the initial He permeance for C01-F08/9, Ma-32 and Ma-42 membranes. The grading of the supports led to a 20-60 % decrease of the initial He permeance. Such a broad variability in the He permeance loss was due to the support morphology, differences in Al_2O_3 powders used and differences in the short Pd deposition times used to bind Al_2O_3 particles.

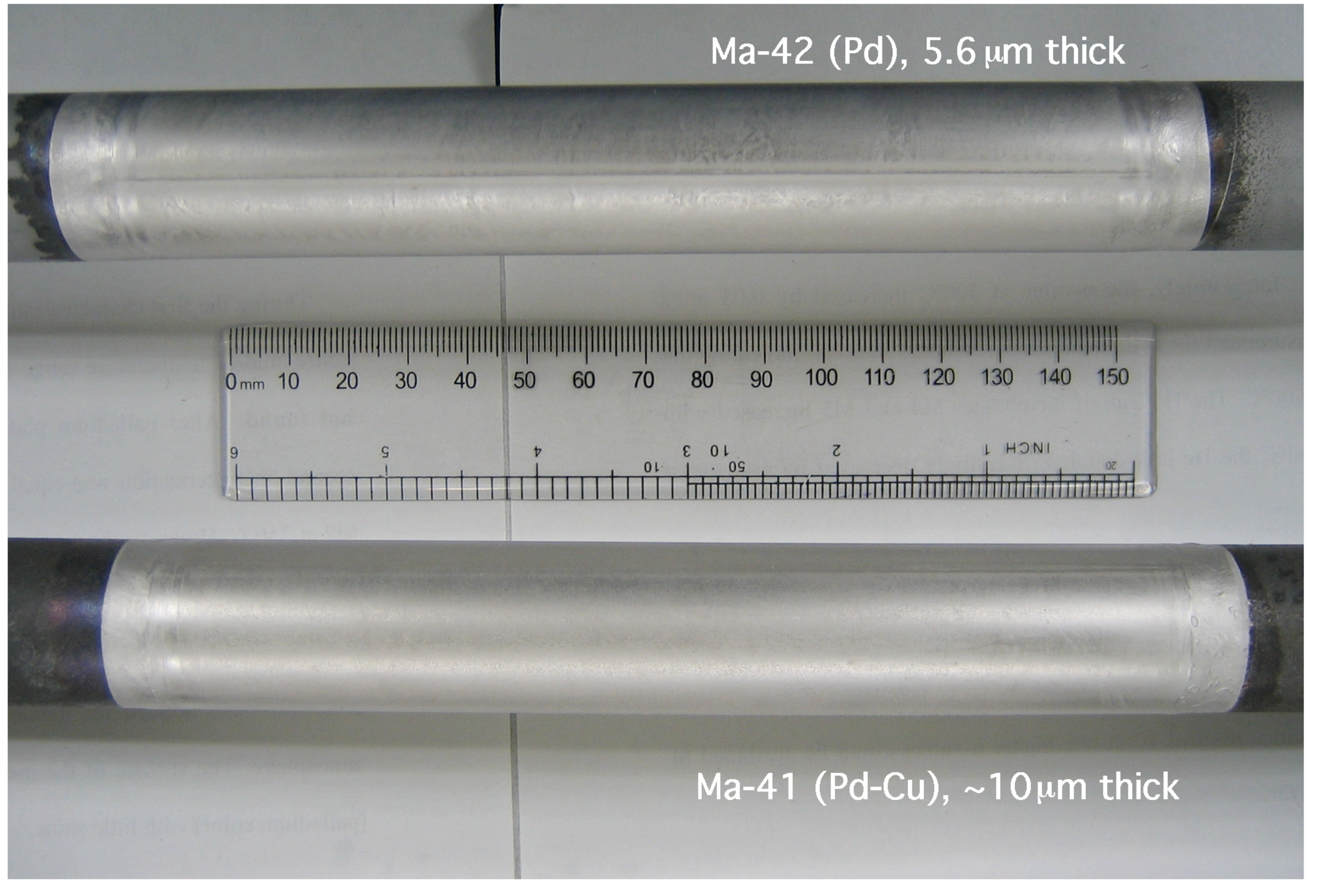

Figure 6-1 Surface of Ma-41 and Ma-42 composite Pd-based membranes.

Table 6-3 Percentage loss of the initial He permeance of the bare porous metal support after grading step.

membrane	He permeance after Ox. ($m^3/(m^2$ h bar))	He permeance loss. (% of initial flux)
C01-F08	274	16
C01-F09	286	25
Ma-32	155	60
Ma-42	114	20

Figure 6-2 is a high magnification SEM micrograph of a pore in membrane C01-F09. The figure clearly shows the structure of the grade Al_2O_3 layer within the mouth of the pore. The grade layer was exclusively located at the pores mouths of the support providing anchoring sites for the Pd layer to attach during the electroless plating deposition. The anchoring sites for the Pd layer are the tips[1] of PSS (or PH depending on the support) particles (see Section 3.1.2).

A 5 μm Al_2O_3 particle with no Pd on its surface (the first Al_2O_3 layer deposited on C01-F09's support was not activated) physically plugged the mouth of the pore allowing enough space for molecular H_2 to flow. The layer just on top of the 5 μm Al_2O_3 particle included fine Al_2O_3 particles (0.3-1 μm) coated with Pd. The third layer, including very small particles (0.01-0.3μm), was located on top of the second layer. Finally, the dense and uniform Pd layer was on top of the very fine Pd coated Al_2O_3 particles.

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[1] The anchoring sites or tips of PSS (or PH) particles are shown in Figure 6-3, page 144

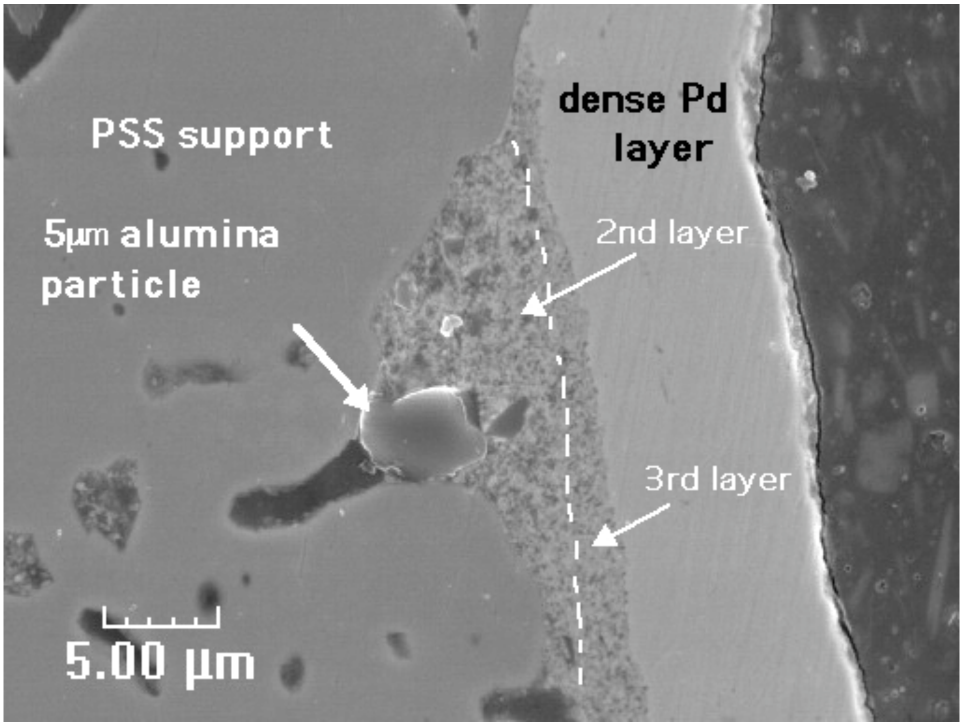

Figure 6-2 Structure within a pore achieved by sequential deposition of coarse, fine and very fine pre-activated powders.

6.3.1.2 Composite Pd membrane structure on "graded" supports

Figure 6-3(a) and (b) show the cross-section of membrane C01-F09 and Ma-34b respectively after exposure to H_2. Very uniform Pd layers were achieved on the rough surfaces of PM substrates after grading. Pd did not penetrate into the pore system due to the presence of the Pd coated Al_2O_3 grade layer. The grade layer is not visible in Figure 6-3(a) since Al_2O_3 particles initially present were removed during the polishing step[1] and left cavities between the PSS support and the Pd dense layer. Al_2O_3 particles remained on the support when the membrane was sintered at high temperatures increasing the cohesiveness of the grade layer. Since, membrane C01-F09 was only tested at 250ºC, the loosely packed powder was washed away except in small pores such as the one seen in Figure 6-2. The Al_2O_3 particles can be seen in Figure 6-3(b). Ma-34b was heated up to 600ºC in H_2 providing enough heat to the powder to bind and become more cohesive.

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[1] The polishing step was part of the preparation technique for scanning electron microscope samples.

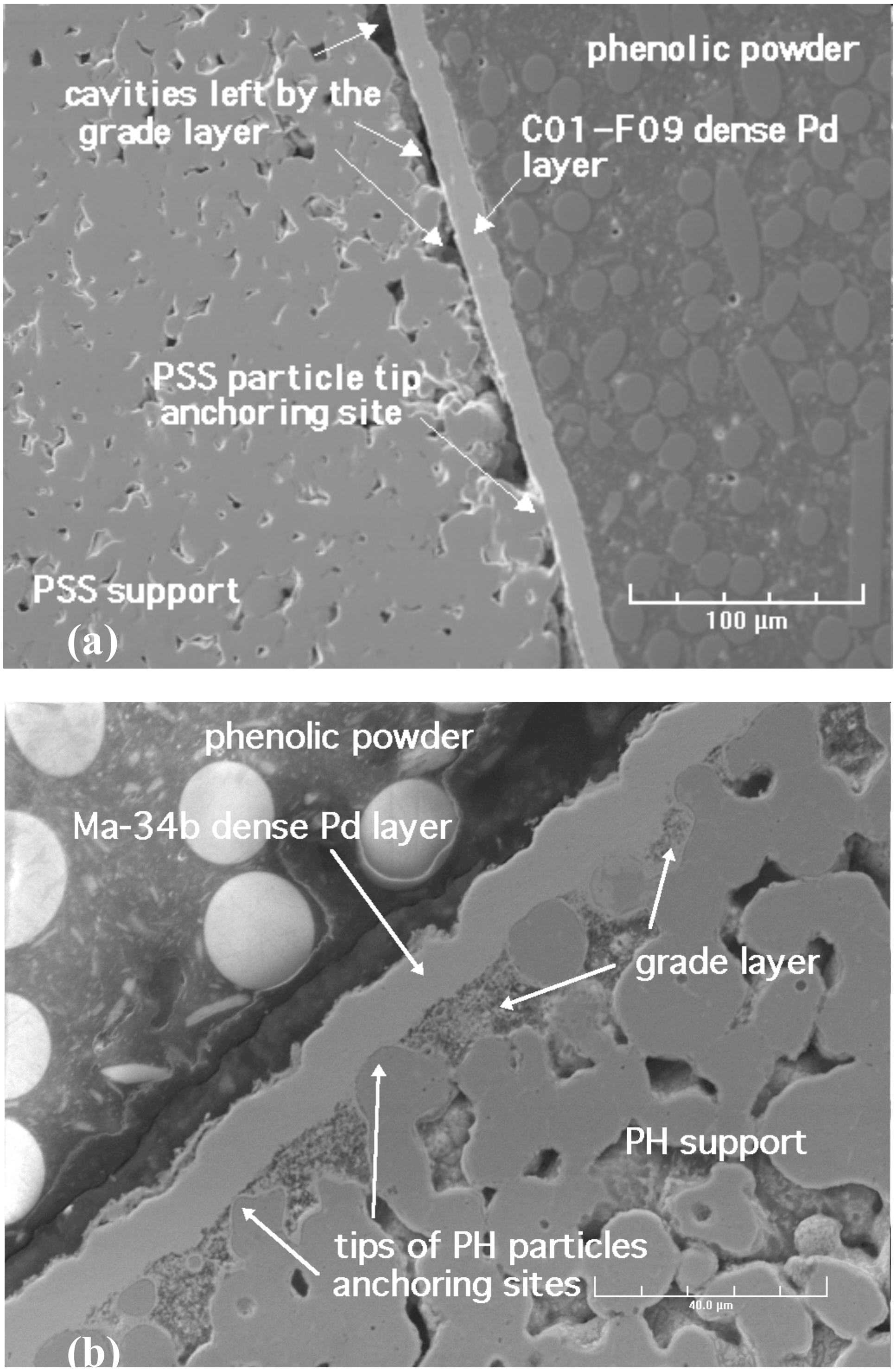

Figure 6-3 (a) Thin Pd layer (14µm) of C01-F09 membranes. (b) Thin Pd layer of (6-8µm) of Ma-34b membrane.

Figure 6-4(a) and (b) show the cross-section of membranes C01-F09 and C01-F03 respectively. C01-F03 was synthesized on a non-graded 0.1μm grade PSS support. When no pre-activated Al_2O_3 particles were deposited on the support, Pd penetrated quite deep into the pore system and the resulting Pd layer exhibited thicknesses that were at some points (inside the pores) twice as large as the ones determined by the gravimetric technique. Also, Figure 6-4(b) shows that the Pd layer followed the morphology of the support, therefore, grading the support provided a very smooth surface and the Pd layers of membranes C01-F09, Figure 6-4(a), and Ma-34b were very thin and uniform. C01-F04, C01-F05 and C01-F07 had a similar structure as C01-F03 since they were prepared following the same procedure as C01-F03

6.3.1.3 Effect of support quality on membrane thickness

Sequential deposition of coarse, fine and very fine pre-activated Al_2O_3 powders with intermediate short time of Pd deposition led to a smoother surface than the bare surface of the porous metal support. Theoretically, Pd layers having similar thickness would be obtained on graded supports independently of the original grade of the support. Indeed, it should be possible to form a thin Pd layer on a 0.5μm grade support after refining the pore size distribution at the surface with coarse, fine and very fine pre-activated powder.

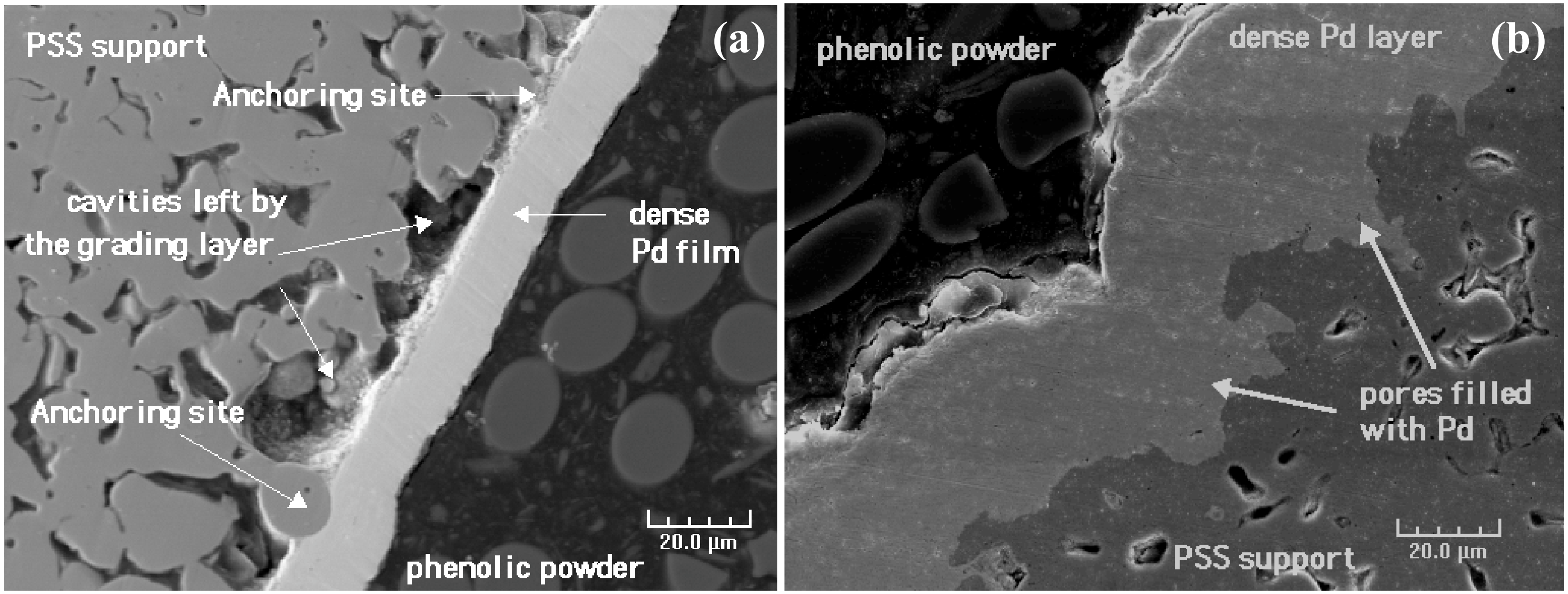

Figure 6-4 (a) SEM micrograph of membrane C01-F09. (b) SEM micrograph of membrane C01-F03. Mag: 1000X

However, the quality of the support had a strong influence on the membrane thickness, even after deposition of the grade layer, thereby affecting the H_2 flux of the membrane. Membranes C01-F08, C01-F09 and C01-F11b were prepared on 0.1 μm grade PSS supports. Ma-32, Ma-34 and Ma-42 membranes were prepared on 0.1 μm grade PH supports, which had a smoother surface than 0.1 μm grade PSS supports according to the metal support manufacturer. That is the reason why thinner membranes (Ma-32, Ma-34 and Ma-42) were achieved on PH supports than membranes prepared on PSS supports (C01-F08, C01-F09 and C01-F11) even if all supports were graded.

Figure 6-5 shows the He permeance as a function of the Pd thickness in the 0-12 μm range for C01-F03, C01-F05, C01-F07, C01-F09, Ma-32, Ma-34 and Ma-42 membranes. When no grade layer was applied (C01-F03, C01-F05 and C01-F07 membranes), the He permeance decreased by a maximum factor of ten after deposition of 12-15 μm of Pd. Grading the same supports that were used for the synthesis of C01-F03/5/7 membranes led to C01-F08, C01-F09 and C01-F11/11b in which 10 μm of Pd were sufficient to decrease the He permeance of their supports by a factor of 1000 attesting the importance of obtaining a smooth layer for the formation of thin membranes. Grading supports with an even smoother initial surface (PH supports) led to very thin gas tight membranes with Pd thicknesses in the order of 5-7μm.

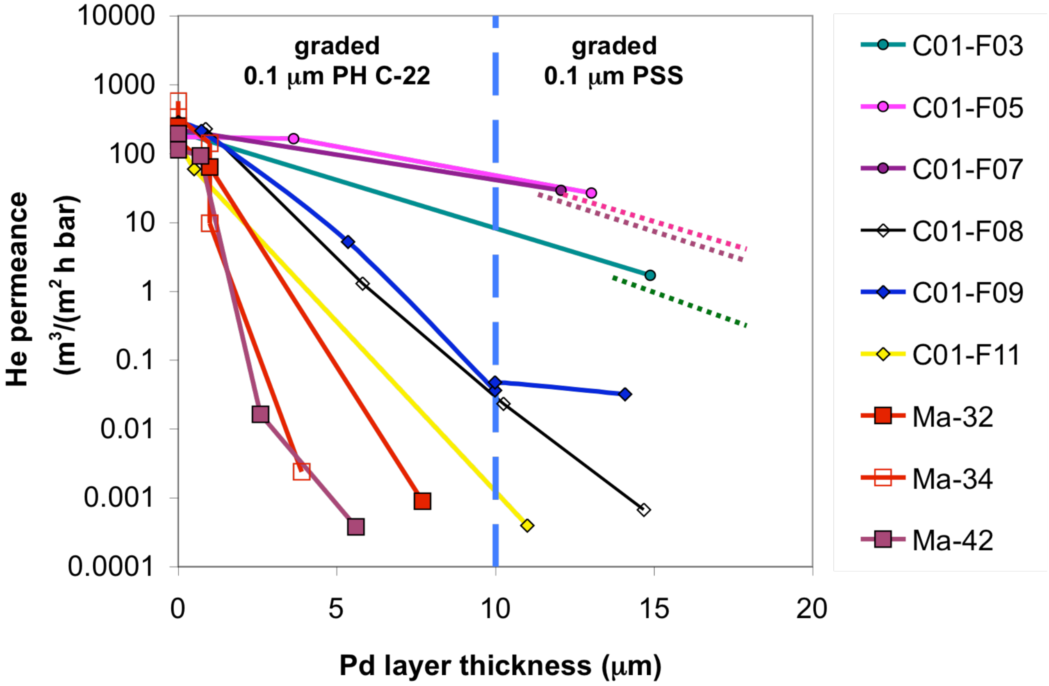

Figure 6-5 He permeance vs. Pd thickness for C01-F03/5/7 (PSS supports), C01-F08/9/11 (graded PSS supports) and Ma-32/34/42 (graded PH supports)

6.3.2 H_2 permeance, selectivity and long-term stability of composite Pd graded-support membranes

6.3.2.1 *The H_2 permeance of composite Pd-graded supports membranes*

Although membrane C01-F08 was only 15 µm thick, it showed a permeance of 15 $m^3/(m^2\ h\ bar^{0.5})$ at 500ºC, which was characteristic of a 21-25 µm membrane (see Table 6-2). This low permeance was attributed to a large quantity of Pd in the pores of the support. In deed, during synthesis, the pre-activated 3µm-5µm mixture Al_2O_3 powder was consolidated with Pd under vacuum (pulled from the tube side).

The driving force provided by the use of vacuum resulted in the Pd deposition very deep within the pores of the support. Pd plating after powder deposition resulted in a very thick membrane within the pores, i.e., around 5µm of pore path and 15µm of dense membrane led to a 20-25µm thick membrane. The first Al_2O_3 powder layer deposited on C01-F09 was not activated, thus preventing Pd deposition too deep into the pores, which allowed for a higher permeance than C01-F08.

Figure 6-6 shows the H_2 permeance, F_{H2}, at 250ºC of membrane C01-F09 as a function of time. The permeance was calculated from the H_2 flux at 1 bar pressure difference (2:1) assuming the pressure exponent equal to 0.5 (Sieverts' law). The H_2 permeance sharply increased up to 8.5 $m^3/(m^2\ h\ bar^{0.5})$, then showed a slower increase up to 16 $m^3/(m^2\ h\ bar^{0.5})$ in 40 hr. The mechanism leading to the H_2 flux increase with time in fresh composite Pd membranes was the opening of channels within the grade layer after either moisture desorption or slight rearrangements of Al_2O_3 particles. All composite Pd membranes prepared on graded supports showed a transition period where the permeance increased as a function of time for about 40 to 100 hr.

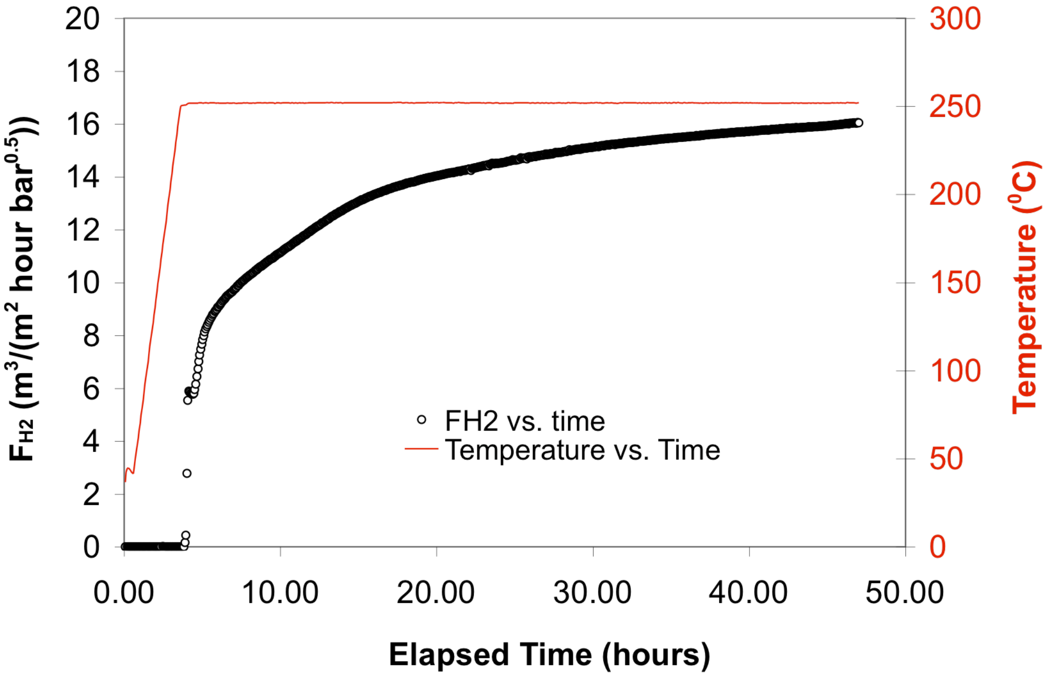

Figure 6-6 H_2 permeance vs. time at 250ºC for membrane C01-F09.

It is important to note that the permeance of C01-F09 at 250ºC was two times higher than the permeance of C01-F08 membrane (8 $m^3/(m^2\ h\ bar^{0.5})$) even though both membranes were prepared on graded supports. This result clearly demonstrated the fact that grading with pre-activated Al_2O_3 powders without the use of vacuum during powder binding avoided Pd deposition deep in the neck of the pores resulting in a very thin membrane. Hence, for all membranes prepared after C01-F08 (C01-F09, Ma-32 and Ma-42) powder consolidation with short time Pd deposition was performed in the absence of vacuum. The use of vacuum during powder binding and during Pd deposition was the cause for C01-F08 to have such a low permeance compared to C01-F09.

Figure 6-7 shows the Arrhenius plot of H_2 permeance for all membranes considered in this chapter. The H_2 permeance of membranes C01-F03 and C01-F04 decreased as the temperature was increased due to intermetallic diffusion. The causes and the mechanism of intermetallic diffusion are elucidated in Chapter 8 Sections 8.3.2 and 8.3.3. The H_2 permeance of membranes C01-F05 and C01-F07 were only slightly affected by intermetallic diffusion since the support of these membranes were oxidized at 500ºC as it will be explained in Chapter 8. Membranes C01-F08/9/11/11b did not show signs of intermetallic diffusion most probably due to the presence of the grade layer. Membranes C01-F08/9/11/11b also showed higher H_2 permeances than C01-F03/4/5/7 since they were prepared on graded PSS supports and had a thinner Pd layer. Membranes Ma-32 and Ma-42 showed very high H_2 permeance values due to the uniformity and the thinness of the Pd layers achieved on graded PH supports. The H_2 permeance of membranes Ma-32 and Ma-42 did not decline at high temperatures due to the good capability of the grade layer and oxidized PH supports to inhibit intermetallic diffusion (see Section 0). Figure 6-7 also shows the calculated H_2 permeance vs. 1/T (dashed line) of an hypothetical Pd foil with the same thickness as Ma-32. The H_2 permeance of this hypothetical Pd foil was calculated with equation (4-11) of Section 4.2.3. It appears then evident that Ma-32 had a low activation energy for H_2 permeance of 9 kJ mol^{-1} indicative of mass transfer resistance within the support.

Figure 6-8 shows the H_2 permeability of all membranes as a function of 1/T. The average H_2 permeability computed in Section 4.2.3 was also plotted in Figure 6-8 for comparison purposes.

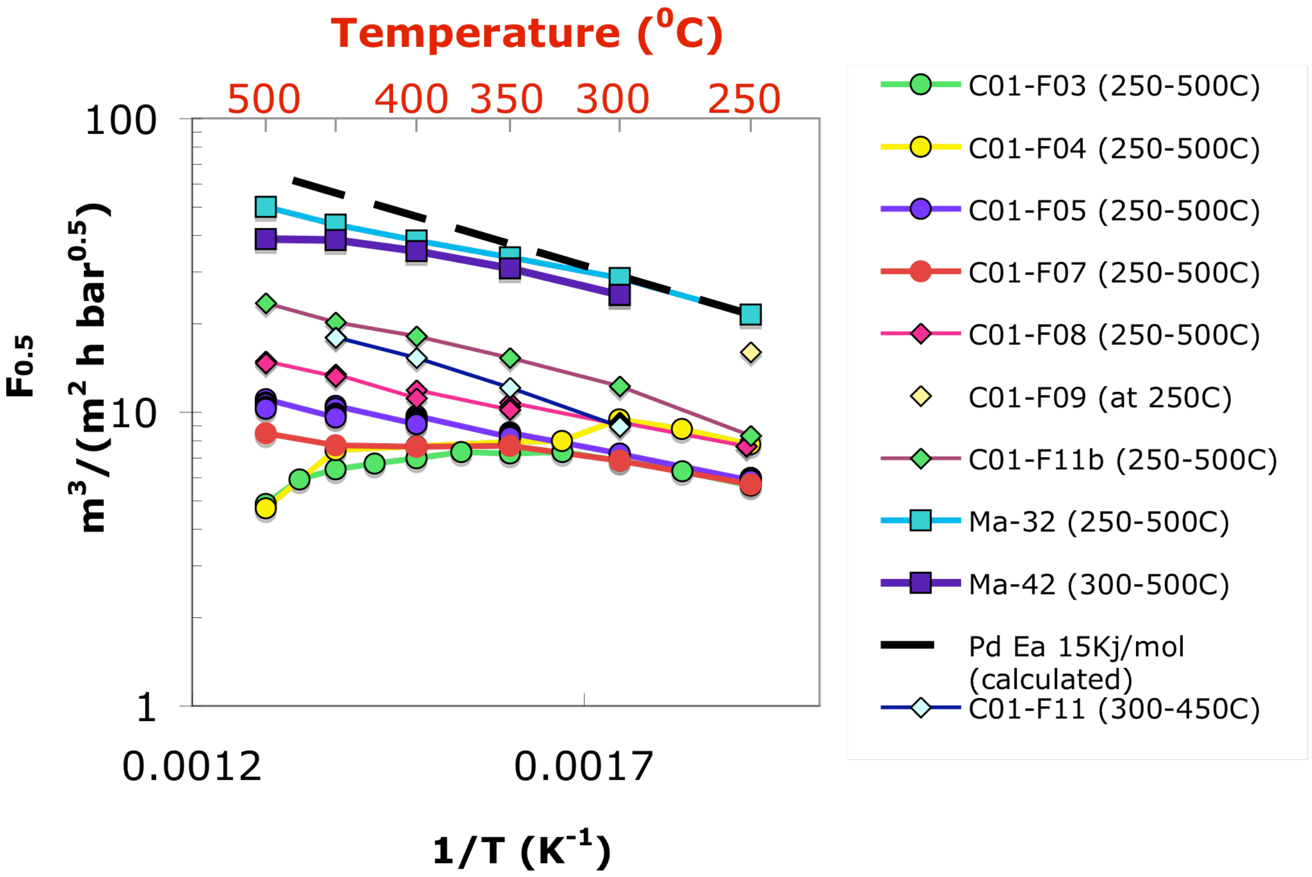

Figure 6-7 Arrhenius plot of H_2 permeance, $F_{0.5}$, for composite Pd membranes prepared on non graded supports (circles) and graded supports (squares)

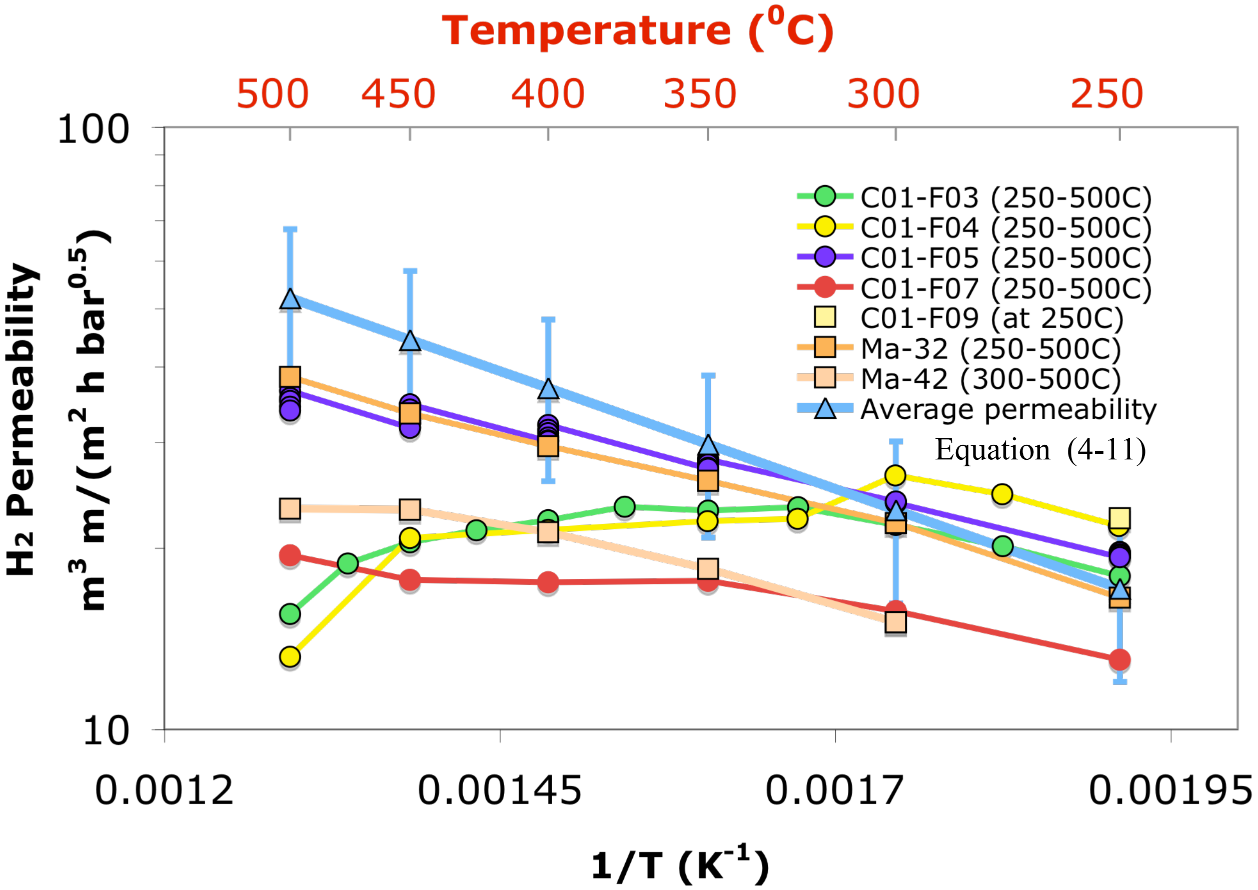

Figure 6-8 Arrhenius plot of H_2 permeability for composite Pd membranes prepared on non graded supports (circles) and graded supports (squares)

Figure 6-8 shows that composite Pd membranes prepared in this entire study have the same H_2 permeability at low temperatures (250-350ºC) as the average H_2 permeability in Pd foils. At higher temperatures (350-500ºC) the H_2 permeance declined due to intermetallic diffusion (C01-F03/4/5) or deviated from the ideal H_2 permeability due to mass transfer resistance in the porous support (Ma-32 and Ma-42). Figure 6-7 and Figure 6-8 clearly show that the overall effect of mass transfer resistance was the lowering of the activation energy for H_2 permeance from 14.9 $kJmol^{-1}$ to 9-10 $kJ\ mol^{-1}$. This effect is modeled in Section 5.2.1 and experimentally confirmed in Section 5.4.3.

The higher permeance of composite Pd membranes prepared on graded supports was essentially due to the thinness and uniformity of the Pd layer that one can achieve on “graded” supports. Indeed, as listed in Table 6-2, membranes prepared on non-graded supports had a relatively thick Pd layer ranging from 20 to 30μm while composite Pd membranes prepared on graded supports had a thinner Pd layer ranging from 6 to 14 μm. Such thin Pd layers were only possible due to the support uniformity achieved after grading.

Figure 6-9 shows the H_2 permeance, $F_{0.5}$, of C01-F09, Ma-32/34/42 membranes as a function of 1/T as well as the H_2 permeance of recent composite Pd membranes reported in the literature and listed in Table 6-4. It is quite interesting to note that Tong et al. (2005c), who graded their PSS support with $Al(OH)_3$ colloids, achieved similar H_2 permeance as the H_2 permeance shown by Ma-32/34. Su et al. (2005) also reported quite high H_2 permeance values for composite Pd membranes prepared on PSS supports graded with a SiO_2 layer deposited by the sol-gel technique.

Table 6-4 Characteristics recent composite Pd membranes reported in the literature.

Reference	Support	Deposition method	Thickness (μm)	Temperature (ºC)	Permeance at Temp. (m^3/m^2-h-$bar^{0.5}$)	Selectivity
(Li et al., 1998)	PSS	Electroless+Osmosis	10	480	19[1]	1400 (H_2/N_2)
(Yan et al., 1994)	Al_2O_3		8	500	41	1000 (*which gas?)
(Uemiya et al., 1991d)	Al_2O_3	electroless	4.5	400	36.9	$\propto$
(Collins and Way, 1993)	Al_2O_3	electroless	11.4	550	31.8[2]	650 (H_2/N_2)
(Mardilovich et al., 1998)	PSS	electroless	21	500 (350)	16.4 (7.8)	5000 (H_2/N_2)
(Jun and Lee, 2000)	Al_2O_3	MOCVD	1-2	450	38[3]	780 (H_2/N_2)
(Jun and Lee, 2000)	Ni-PSS	MOCVD	0.5-3	450	324[4]	1600 (H_2/N_2)
(Wang et al., 2004)	ZrO_2-PSS	electroless	10	500	16.5	156 (H_2/Ar)
(Tong et al., 2005c)	Al(OH)-PSS	electroless	6.4	500	50[5]	Not reported
(Tong et al., 2005c)	Al(OH)-PSS	electroless	6.4	500	58.8[5]	Not reported
(Cheng et al., 2002)	γ-Al_2O_3/α-Al_2O_3	electroless	3	450	12.1	250 (H_2/N_2)
(Su et al., 2005)	SiO_2-PSS	electroless	5-6	500	49.5[6]	300 (H_2/N_2)

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[1] Determined from Figure 4 in the original publication

[2] Calculated assuming n=0.5 with the original data: J_{H2} = 0.71 mol/(m^2 s); feed pressure: 790610 Pa; permeate pressure: 101325 Pa.

[3] Calculated assuming n=0.5 with the original data: J_{H2} = 18.8 (cm^3/ cm^2 min); ΔP: 51.7 cm Hg; permeate pressure: 101325 Pa.

[4] Calculated assuming n=0.5 with the original data: J_{H2} = 160 (cm^3/ cm^2 min); ΔP: 51.7 cm Hg; permeate pressure: 101325 Pa. The H_2 flux value is obviously mistaken.

[5] Calculated assuming n=0.5 with the original data: J_{H2} = 0.260 mol/(m^2 s); feed pressure: 100 kPa; permeate pressure: 101325 Pa. (J_{H2} = 0.302 mol/(m^2 s) for the membrane having a permeance of 58.8 m^3/(m^2 h $bar^{0.5}$)).

[6] Reported H_2 permeance: 2.5-2.7 10^6 mol/m^2 s Pa. The permeance of 49.5 m^3/(m^2 h $bar^{0.5}$)) was determined by calculating the H_2 flux at ΔP=0.5 bar, n = 0.5 and the permeate pressure = 1 bar.

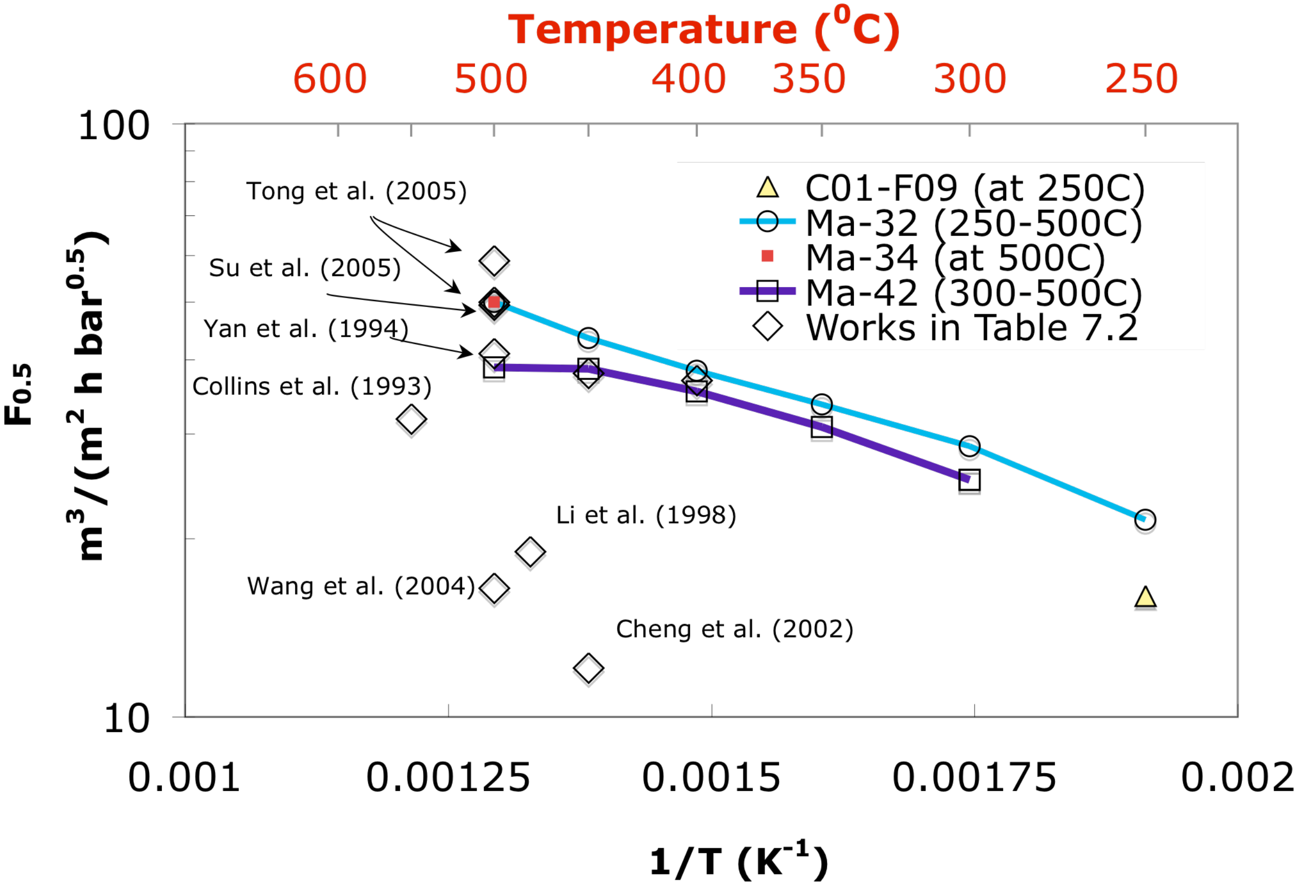

Figure 6-9 Comparison of H_2 permeance for membranes C01-F09 Ma-32/34 and Ma-42 with recent works listed in Table 6-2

Composite Pd membranes prepared on either α-Al_2O_3 or γ-Al_2O_3-α-Al_2O_3 supports were thinner (Cheng et al., 2002; Jun and Lee, 2000; Uemiya et al., 1991a) although their H_2 permeance was lower than the H_2 permeance of Ma-32/32b/34 and membranes prepared by Tong et al. (2005c) and Su et al. (2005), which were prepared on porous metal supports. Alumina supports have a lower porosity than porous metal supports, therefore, a possible reason for the low H_2 permeances reported by Jun and Lee (2000) and Uemyia et al. (1991a) was the presence of mass transfer resistance within the alumina support. Tong et al. (2005c) and Su et al. (2005) did not report the long-term H_2 permeance and selectivity stability for their membranes.

6.3.2.2 The selectivity of composite Pd graded-support membranes

Figure 6-10 shows the selectivity (H_2/He), or ideal separation factor, of membranes C01-F11/11b and Ma-34b/41/42 as a function of temperature. For some membranes, e.g. Ma-34b, several data points were plotted at a given temperature when the selectivity was determined several times at a given temperature. All membranes showed very high selectivities at temperatures equal to or lower than 400ºC. The selectivity at T<400ºC for all membranes was higher than 1000. C01-F11 and Ma-34b/42 membranes showed selectivities values higher than 3000 at temperatures lower than 400ºC. The selectivity of all membranes started to decrease at 450ºC and became low at 500ºC. The red line at 475ºC in Figure 6-10 represents the temperature above which the selectivity of all membranes was lower than 1000, which is still a very good selectivity. Membrane Ma-42 showed a high selectivity of 818 even after 185 hr at 500ºC in pure H_2.

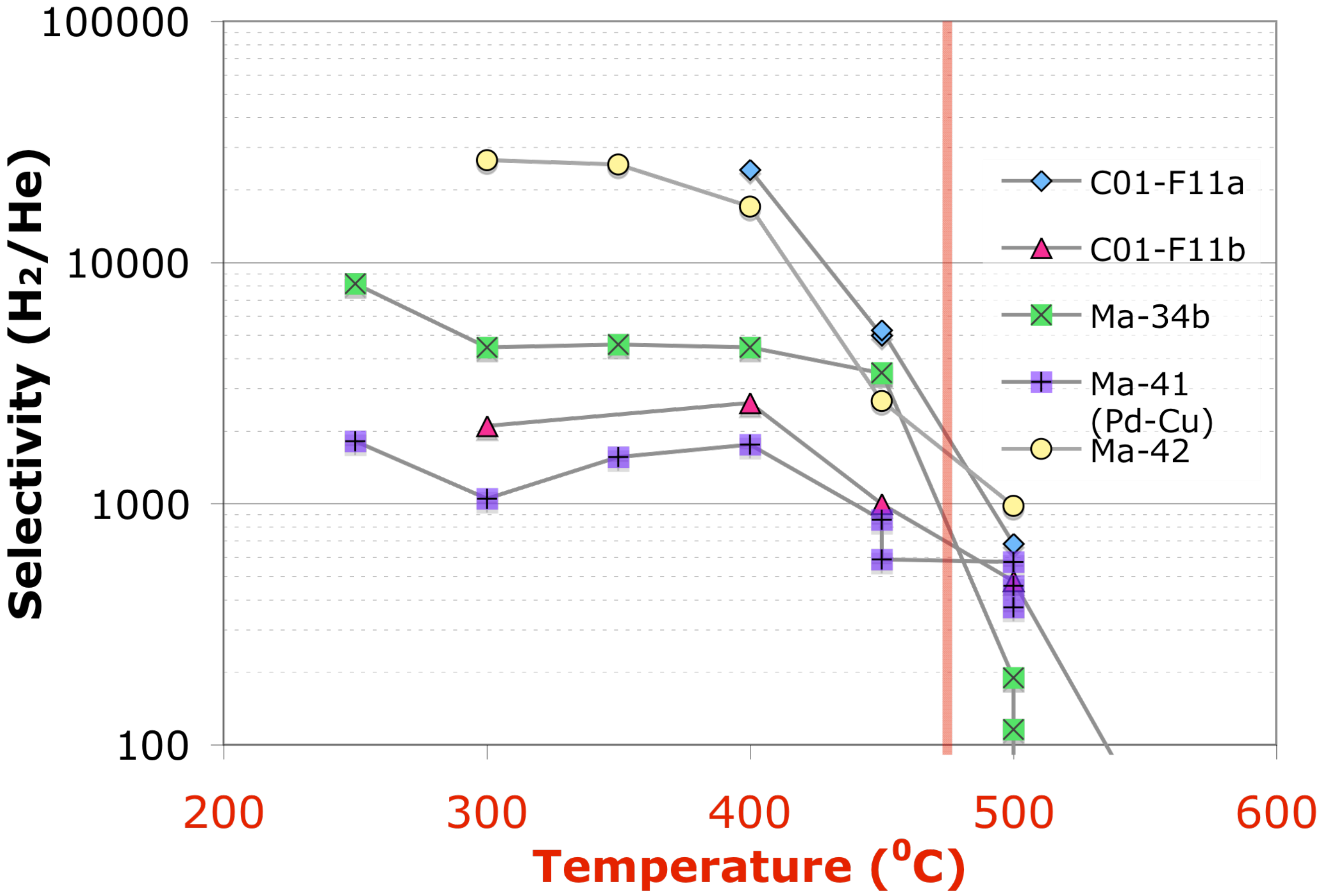

Figure 6-10 Ideal selectivity of some membranes prepared on graded supports as a function of temperature

Ma-41 also showed a good selectivity of 370 even after 215 hr at 500ºC in pure H_2.

The selectivity of C01-F03 membrane was not plotted since its He leak rate was only measured at room temperature after cooling the membrane from 500ºC. The He leak rate at room temperature was equal to 0.0148 $m^3/(m^2$ h bar), hence, its selectivity at 500ºC was above 120. The selectivity of C01-F04 was only determined at 500ºC and was close to 1000. The selectivity of C01-F05 was equal to 587 after 100 hr at 500ºC in H_2 and higher than 380 after excursions up to 700ºC for a few hours in H_2. The membrane suffered from severe intermetallic diffusion at 700ºC. The Pd layer and the PSS support fused and blocked all the porosity at the Pd-PSS interface.

6.3.2.3 Long term stability of composite Pd graded PH membranes

All composite Pd membranes prepared on graded oxidized PH supports showed a very good H_2 permeance long-term stability. Figure 6-11 shows the H_2 flux, J_{H2}, and the H_2 permeance, F_{H2}, as a function of time at 500ºC for membrane Ma-32b. The H_2 permeance was equal to 39 $m^3/(m^2$ h $bar^{0.5})$ and slowly increased up to 42.5 $m^3/(m^2$ h $bar^{0.5})$ after 1100 hr at 500ºC in H_2 atmosphere. As of today, no research group reported stable H_2 permeance over 1000 at the high temperatures of 500ºC for composite Pd membranes prepared on PM supports. Figure 6-12 shows the selectivity, the H_2 permeance and the He leak rate of Ma-32b as a function of time at 500ºC in H_2 atmosphere. The selectivity (H_2/He) of Ma-32b decreased from 27000 at the beginning of the experiment to 300 at the end of the experiment. Hence, even though the H_2 flux through defects slightly increased, it did not affect the H_2 permeance value (see Section 5.4.2) and the membrane was still considered as a composite Pd membranes with high separation properties.

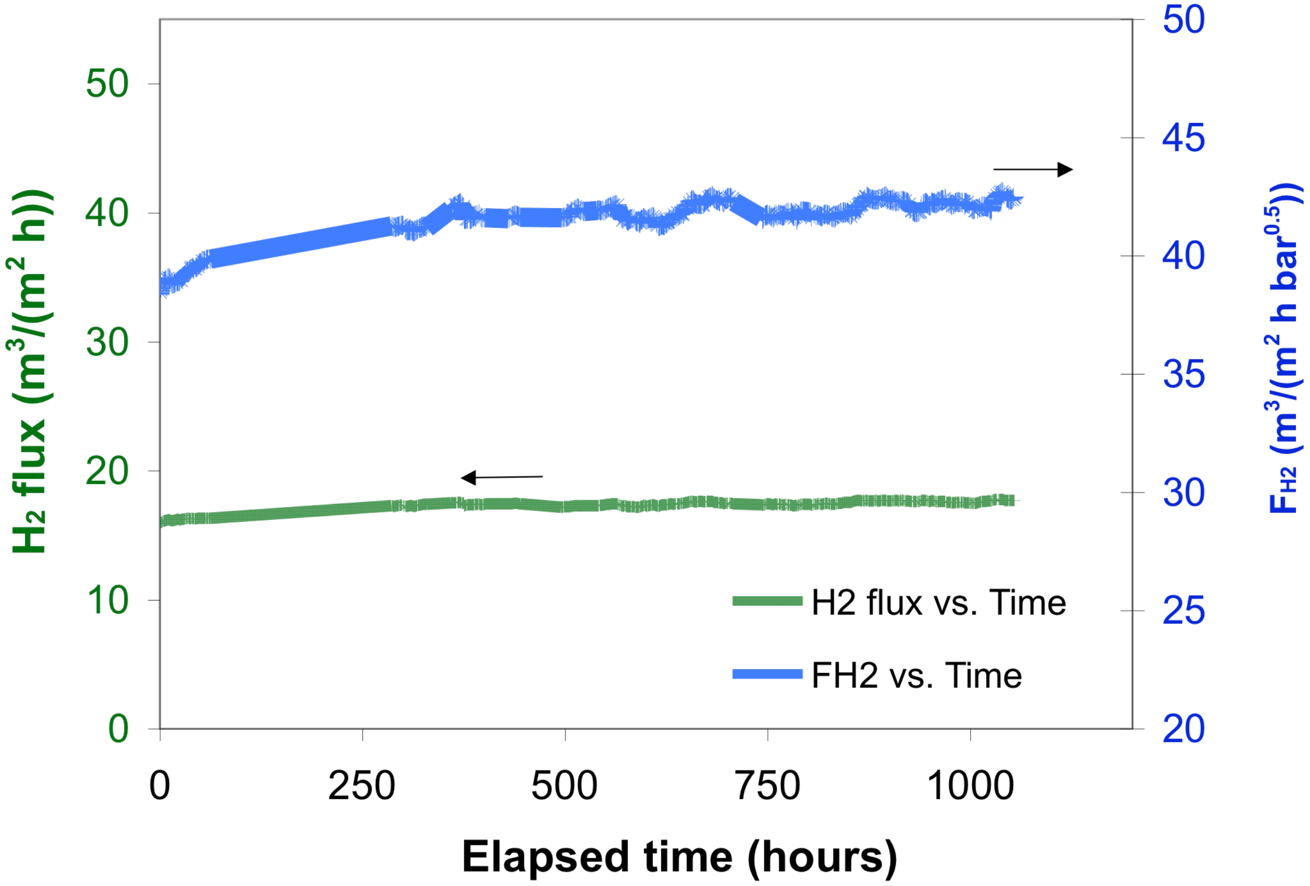

Figure 6-11 Long-term H_2 permeance stability at 500ºC for membrane Ma-32b

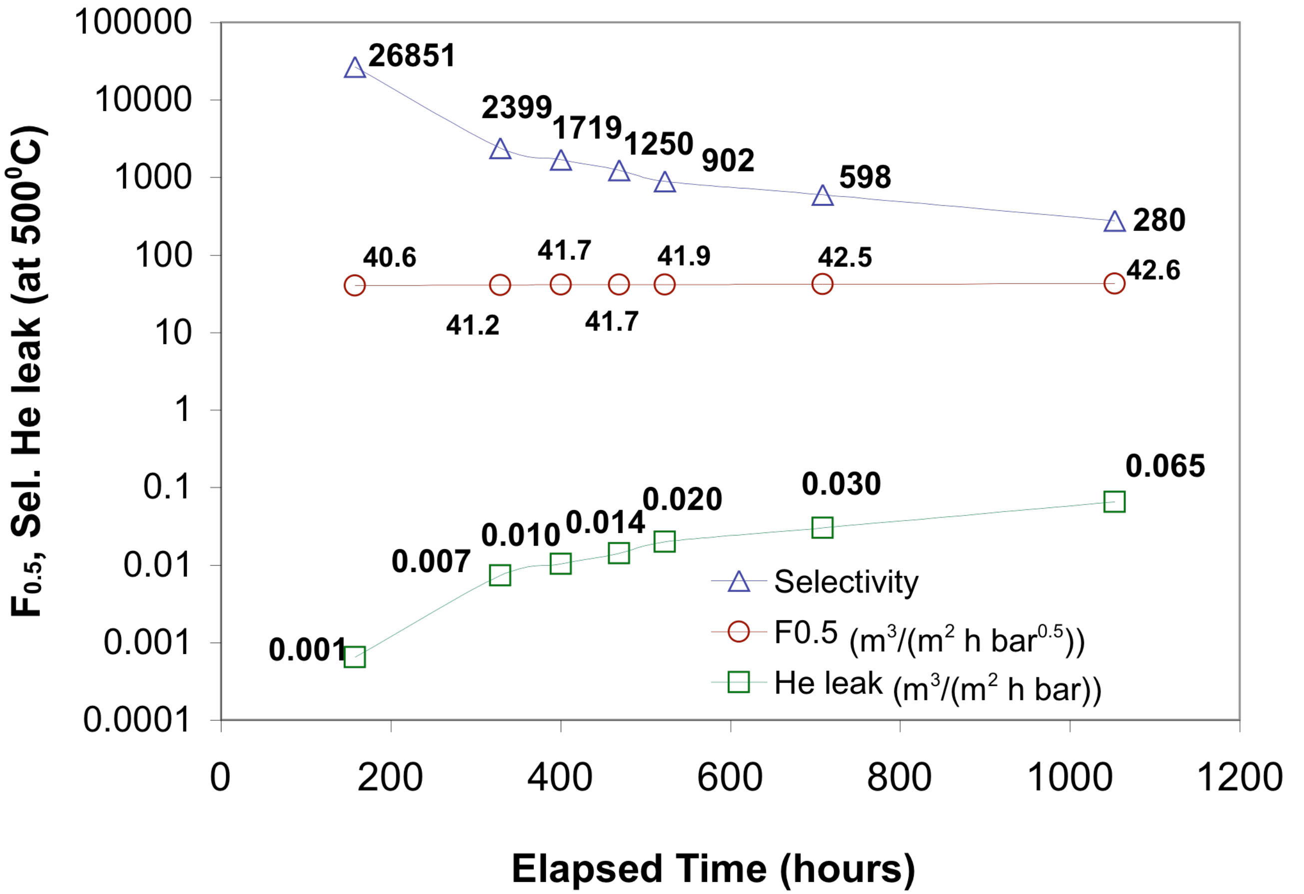

Figure 6-12 Selectivity, H_2 permeance and He leak rate as a function of time at 500ºC for Ma-32b

The increase from 39 to 42.5 $m^3/(m^2\ h\ bar^{0.5})$ was due to structural changes in the grade layer as explained in Section 6.3.2.1. The good long-term H_2 permeance stability of composite Pd membranes prepared on graded PH supports was due to: (1) the fact that only Cr_2O_3 oxide appeared on the surface of PH after oxidation, (2) the low driving force for Fe diffusion due to the low Fe concentration in PH and (3) the presence of the Pd-Al_2O_3 grade layer as it is explained in the following section. Points (1) and (2) are discussed in Chapter 8.

6.3.3 The grade layer as a barrier against intermetallic diffusion

6.3.3.1 The H_2 flux stability at high temperatures (>500ºC) of membrane C01-F08

The H_2 flux stability at high temperatures was tested on membrane C01-F08. The H_2 permeance and He leak of membrane C01-F08 were measured at 500, 550 and 600ºC. The membrane was held at a given temperature for 72 hr. Figure 6-13 shows H_2 permeation of membrane C01-F08 and the temperature as a function of time. At 500ºC the H_2 permeance of membrane C01-F08 equaled 22.5 $m^3/(m^2\ h\ bar^{0.5})$) and stayed relatively stable for 72 hr. When the temperature was increased to 550ºC a linear decrease in H_2 permeance was observed. Such a decrease in H_2 permeance was attributed to the diffusion of mostly Fe (see Section 8.3.1.2) from the support into the dense Pd layer, which became important at temperatures above the Tamman temperature of stainless steel (550ºC). At 600ºC a large H_2 flux loss was recorded during the first 17 hr followed by a large H_2 flux increase from 25.8 to 29.7 $m^3/(m^2\ h\ bar^{0.5})$) due mainly to defects formation in the dense film. Figure 6-14 shows the H_2 permeance, He leak and selectivity (H_2/He) for membrane C01-F08.