

PREPARATION OF PALLADIUM-SILVER ALLOY MEMBRANES FOR HYDROGEN PERMEATION

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Abstract— Pd-Ag alloy membranes (with different silver contents) have been prepared by electroless plating technique for hydrogen separation. The surface morphology and phase structures of the composite membranes were investigated using a scanning electron microscope and a X-ray diffractometer, respectively. Hydrogen permeation experiments through the membranes synthesized at different hydrogen pressures (50 – 250 kPa) and temperatures (623 – 823 K) are reported. The experimental results reveal that the membranes showed a considerable enhancement in the hydrogen permeation and that the contribution of surface process for permeation was significant at high temperatures.

Key words – Membrane preparation, palladium-silver, hydrogen permeation.

I. INTRODUCTION

Hydrogen selective membranes are important for technological process such as separation and recovery of hydrogen from process steam reforming, purification of hydrogen for fuel cell application and chemical reactions in membrane reactors (Chai *et al.*, 1995; Kikuchi, 1995; A.-Petersen *et al.*, 1998; Wieland *et al.*, 2002; Kusakabe *et al.*, 2005). Palladium membranes have been used in hydrogen separation because present high selectivity (Tosti *et al.*, 2003; Checchetto *et al.*, 2004). However, they present problem of hydrogen embrittlement, a phenomenon in which dissolved hydrogen tend to cause different elongation of metallic film on glass support, leading it to fracture after repeated pressure and thermal cycling (Tosti *et al.*, 2001). In order to avoid the embrittlement, alloying of Pd with group IB metals such a silver is generally made. (Fort *et al.*, 1975). Another advantage of alloying is that the mechanical strength can be higher than for pure palladium. In general, a Pd-membrane becomes brittle after certain cycles of α - β hydride transformations due to the accompanied lattice expansion. In, for example, palladium-silver alloys, the lattice has already been expanded by the silver atoms, and the PdAg lattice is less influenced by hydrogen and thus less brittle than the pure Pd lattice (Amandusson *et al.*, 2001). A optimal value of the hydrogen permeation rate is reached for a silver content around 25 wt. % Ag (Knapton, 1977; Uemiya *et al.*, 1991). Zhang *et al.* (2003) had observed that at 473 K or less, the hydrogen permeability of Pd-Ag alloy membranes increased with the Ag content until 30 wt. %. Other alloys like cerium-palladium, palladium-tantalum, palladium-niobium,

yttrium-palladium and copper-palladium showed high permeability and mechanical strength (Fort *et al.*, 1975; Buxbaum and Kinney, 1996; Roa *et al.*, 2003; Siriwardane *et al.*, 2003; Howard *et al.*, 2004; Tong *et al.*, 2006). There are various methods reported in the literature for fabrication of composite Pd-based membrane for hydrogen permeation such as chemical vapor deposition (Xomeritakis and Lin, 1998; Jun and Lee, 2000; Itoh *et al.*, 2005), sputter deposition (Jayaraman *et al.*, 1995; Jayaraman and Lin, 1995; McCool, *et al.*, 1999), electroless plating with osmosis (Souleimanova *et al.*, 2001; Souleimanova *et al.*, 2002) and electroless plating (Tong *et al.*, 2005; Lin and Chang, 2005; Tanaka *et al.*, 2005; Rahimi and Iraj, 2005), being this last more used for having as advantages low cost and the use of very simple equipment (Altinisik *et al.*, 2005).

The goal of this work was to prepare palladium-based membranes with different silver contents, in order to investigate the influence of Ag concentration on hydrogen permeation. Characterization studies of Pd-Ag alloy membranes were performed using SEM and XRD.

II. METHODS

Porous Vycor glass tube (Corning Glass, Inc.) was employed as support for the manufacturing of Pd-Ag alloy membranes. The specifications of the support are: length of 10 cm, outer diameter of 10 mm, inner diameter of 7 mm and average pore size of 50 Å. The porous tubes were first cleaned with hydrogen peroxide, trichloroethylene and deionized water as procedure described by Cheng and Yeung (1999). Following the cleaning, a procedure with palladium predeposition was performed before co-deposition of Pd-Ag by method electroless plating. Initially, the support was seeded with Pd crystallites that formed nucleation sites for subsequent plating of a Pd-Ag film on the substrate. This process involved immersion of the substrate in SnCl₂.2H₂O 5mM solution for 5 min followed by another 5 min in PdCl₂ 5mM solution. This sequence was repeated 9 times. Afterwards the palladium and silver deposition was carried out at 323 K, for 60 min in a plating bath containing a 70 mL solution with composition listed in Table1. After the plating the membrane was washed with deionized water and allowed to air dry. The total amount of metals in plating solution was kept constant at 0,911 mM, however the content of palladium and silver was altered in order to form a metallic film on the membranes with different silver contents. After the plating, the samples were sintered at 823 K in a pure hydrogen atmosphere for 3 h to promote alloying.

Table 1. Composition of the electroless plating solution.

Component	70 mL solution
PdCl ₂	0.729-0.911 mmoles
AgNO ₃	0.046-0.182 mmoles
NH ₄ OH (28%)	12.9 mL
Na ₂ EDTA	1.13 g
N ₂ H ₄ (1M)	0.91 mL

The morphology of metallic film on membrane was analyzed by the scanning electron microscope (SEM) (Joel 2000FX) and the phase structures of the film were examined by a X-ray diffractometer (XRD) (Shimatzu, with a CuK α radiation). The thickness of the films was measured from the SEM micrographs. The surface compositions were analysed with an energy dispersive spectrometer (EDS, Joel).

Permeation experiments were carried out using pure hydrogen in a conventional gas permeation apparatus. The membranes were loaded into a stainless steel shell and centered in a tube furnace. For membrane sealing, graphite rings were used. The measurements were made in a temperature range between 623 and 823 K and pressure differences up to 250 kPa. The total area of the composite sample exposed to the gas was 20 cm². The volumetric flow rate of permeated gas was measured at ambient temperature and atmospheric pressure with a soap-bubble flow meter after steady state (approximately 1 h) had been achieved at the desired temperature.

The hydrogen permeation through palladium-based membranes was described by Eq. (1) as follows (Dittmeyer *et al.*, 2001; Huang *et al.*, 2003):

$$J = \beta (P_h^n - P_l^n) \quad (1)$$

where J is the gas flux, β is temperature dependent constant, n is a constant power of the pressure, $P_h - P_l$ are pressure on feed and permeate sides, respectively.

The measured hydrogen fluxes through palladium-based membranes at different temperatures served to estimate the activation energy as described by a Arrhenius law as follows:

$$\beta = \beta_0 \exp(-E_A/RT) \quad (2)$$

where E_A is the activation apparent energy, β_0 is the Arrhenius constant, R is the gas constant and T is the temperature.

III. RESULTS

Membranes prepared under different conditions exhibited differences in composition and thickness (see Table 2).

Table 2 depict the microstructures of membranes with silver content of 5, 24 and 35 wt.% Ag prepared from plating solutions with 5, 20 and 30 wt.% Ag, respectively.

Figure 1 and Fig. 2 shows the XRD patterns of M3 and M4 samples (before and after thermal treatment), respectively. It is observed that deposited Pd and Ag are in separate crystalline phases, before thermal treatment. After treatment in a hydrogen atmosphere at 823 K, the samples become Pd-Ag alloy crystallized. The

intensity of silver diffraction peak decreased with the thermal treatment to promote Pd-Ag alloying.

The surface morphology of M1, M2, M3 and M4 membranes is shown in Fig. 3, Fig. 4, Fig. 5 and Fig. 6, respectively. Figure 3 reveals that the grain growth of M1 sample was not uniform with some of the grains growing more rapidly than others, resulting in a metallic film with nonuniform grain size. The membranes containing silver had smaller grains than the pure Pd membrane, due to the preferential silver deposition

Table 2. Composition and thickness of membranes.

Membrane	Compositon (wt.%)		Thickness (μ m)
	Pd	Ag	
M1	100	0	31
M2	95	5	29
M3	86	24	22
M4	65	35	18

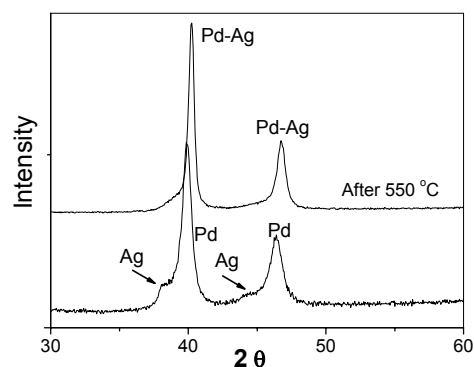


Fig. 1. XRD pattern of M3 membrane.

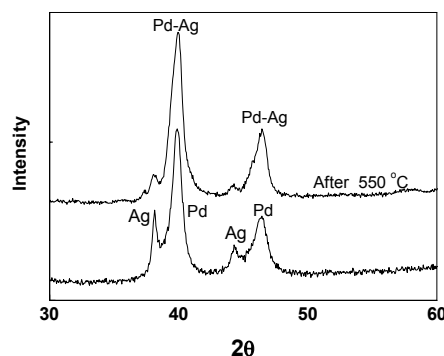


Fig. 2. XRD pattern of M4 membrane.

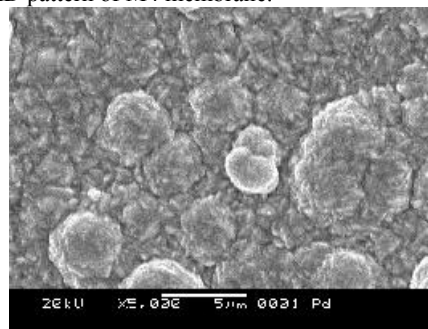


Fig. 3. Scanning electron micrograph of pure Pd membrane (M1 sample).

Comparing the microstructure of M2 (Fig. 4), M3 (Fig. 5) and M4 (Fig. 6) samples, it can be seen that the increase of silver content in the metallic film lead to finer grains and more uniform microstructures. Cheng and Yeung (1999) showed that Pd film microstructure can be significantly altered through addition of different silver contents in the electroless plating bath.

Tests of hydrogen permeation had only been carried with the M3 and M4 membranes. The M1 and M2 membranes presented problems during the tests, the metallic alloys peeled off the support. Some researchers had reported that at least 20 wt. % Ag is needed to prevent hydrogen embrittlement above ambient temperature (Fort *et al.*, 1975; Grashoff *et al.*, 1983; Paglieri and Way, 2002).

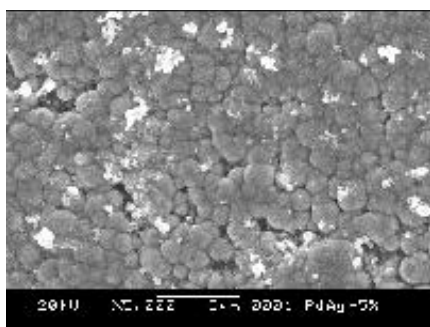


Fig. 4. Scanning electron micrograph of M2 membrane.

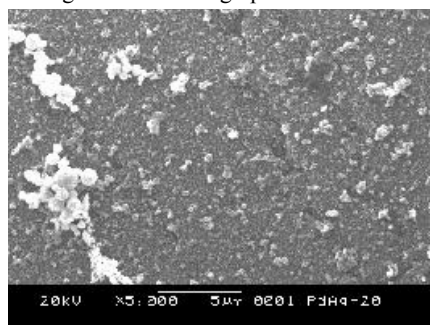


Fig. 5. Scanning electron micrograph of M3 membrane.

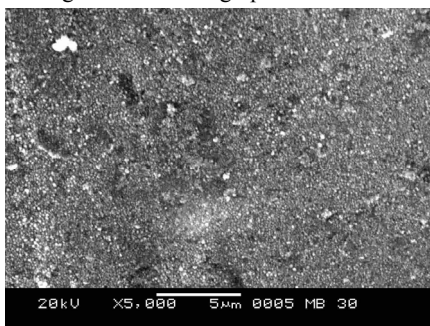


Fig. 6. Scanning electron micrograph of M4 membrane.

Figure 7 and Fig. 8 have shown the hydrogen permeation rate as a function of pressure difference at various temperatures, for M3 and M4 membranes, respectively. It can see that the values of n (determined by regression) of 0.57 and 0.67 shows that J is linear to $(P_h^n - P_l^n)$. It indicate that the hydrogen permeation through the membranes deviated from Sievert's law ($n =$

0.5). Value of 0.5 implicate that the diffusion through the membrane is rate limiting (Holleck, 1970). The values detected in these work indicate that the surface processes become rate limiting. Amandusson *et al.* (2001) and Jayaraman and Lin (1995) have found values of pressure power between 0.5 and 1, explaining that the surface process becoming rate determining step. Amandusson *et al.* (2001) conclude that for temperatures below 473 K, the bulk diffusion through the membranes is rate limiting, while at temperatures above 473 K, surface processes become rate limiting. Values of n between 0.5 and 1 have been reported for various types of palladium composite membranes (Dittmeyer *et al.*, 2001).

It is also observed through the Fig. 7 and Fig. 8 that the hydrogen flux increases with rising temperature and pressure difference for both membranes. The results had shown that the M4 membrane showed a slightly lower permeability than the M3 membrane. Zhang *et al.* (2006) had observed that the hydrogen permeability of the PdAg alloy membranes tended to decrease with reduction of membrane thickness. It indicated that the difference between the overall hydrogen permeation to the thick and thin composite membranes could not be simply ascribed to interface effects. The hydrogen permeation is a complex function of many parameters, such as, hydrogen pressure, temperature, surface composition, bulk composition and also the composition gradient between surface and bulk, and likely also the surface morphology, as reported by Amandusson *et al.* (2001). The authors explained that hydrogen permeation at temperature above 473 K can be influenced not only by surface concentration but as too for a sharp silver concentration gradient. To determine the role of each parameter on its own is unfortunately not possible in this study. Uemiya *et al.* (1991) and Knapton (1977) showed that the hydrogen permeation rate of 26 wt.% Ag membrane is lower than the 23 wt.% Ag alloys. The optimal composition for maximal hydrogen permeation rate has often been claimed around 23-25 wt. % (Knapton, 1977; Dittmeyer *et al.*, 2001; Amandusson *et al.*, 2001).

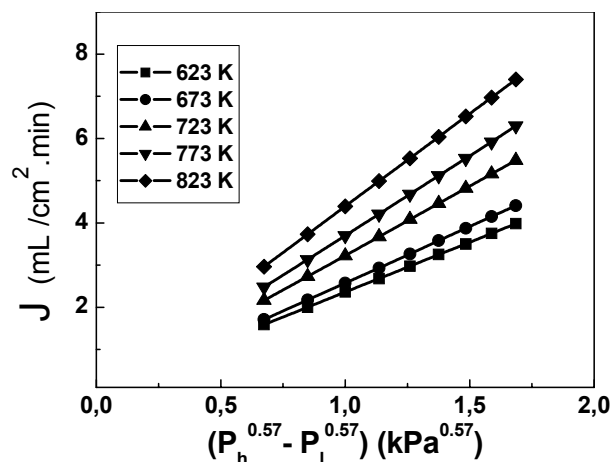


Fig. 7. Hydrogen permeation rate through the M3 membrane as a function of pressure difference to the 0.57 exponent power, at various temperatures.

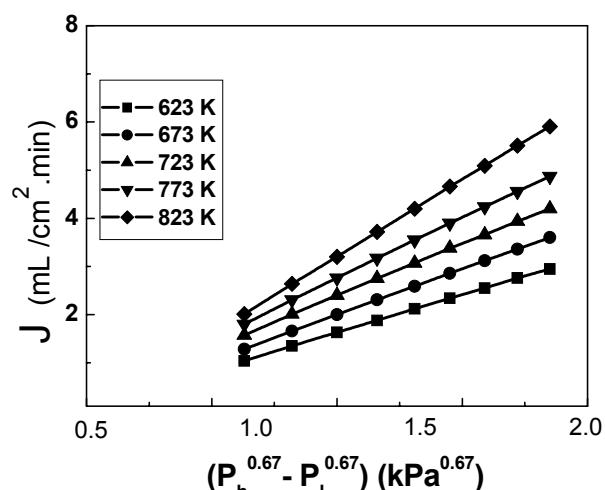


Fig. 8. Hydrogen permeation rate through the M4 membrane as a function of pressure difference to the 0.67 exponent power, at various temperatures.

Figure 9 shows the Arrhenius plots for determination of activation apparent energy for both the membranes. The values were found to be approximately 13.63 and 14.30 kJ/mol for the M3 and M4 membranes, respectively, and are in a good agreement with literature data, which indicates a range of 10–22 kJ/mol (Holleck, 1970; Shu *et al.*, 1991; Weyten *et al.*, 2000; Li *et al.*, 2000; Souleimanova *et al.*, 2002).

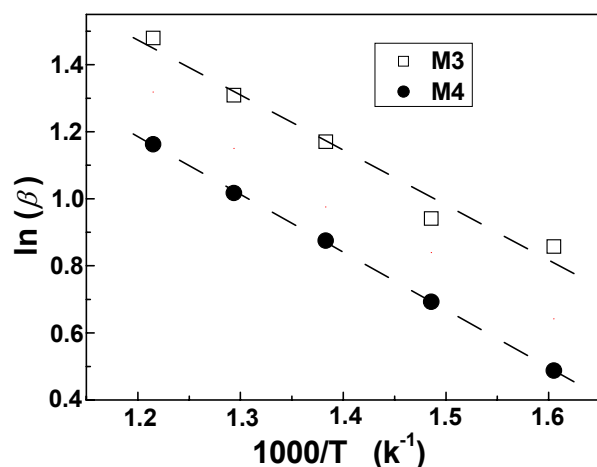


Fig. 9. Arrhenius plots of hydrogen permeation for M3 and M4 membranes.

IV. CONCLUSIONS

Pd-Ag alloy membranes were synthesized by electroless plating technique and tested for hydrogen permeation on different temperatures (623 – 823 K) and pressures (50 – 250 kPa). On temperatures above 623 K, silver content is an important parameter that influences hydrogen permeation through the membranes. Other important parameters are pressure, temperature and probably surface morphology. The membrane with higher silver content (M4) presented a lower hydrogen permeation rate than the membrane M3, and we suggest that this occurred probably because the first membrane is formed by a metallic alloy with lower grain size comparing to

the second, and it would cause a higher hydrogen diffusion resistance through membrane. Under the conditions tested in this work, the surface reactions become rate limiting.

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