ELSEVIER

Catalysis Today 56 (2000) 45–51

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Fabrication of dense palladium composite membranes for hydrogen separation

Anwu Li, Weiqiang Liang, Ronald Hughes *

University of Salford, Chemical Engineering Unit, Salford M5 4WT, UK

Abstract

Pd based membranes have the potential to separate hydrogen from gas streams due to the unique permeation properties of Pd metal to hydrogen. However, thin films of the metal are required in order to obtain the necessary flux; this is usually achieved by deposition onto a porous substrate.

Because of its simplicity and low cost, electroless plating has been used in the present work to deposit Pd as a thin film onto a porous alumina substrate. Due to non-uniform activation of the substrate surface and/or impurities present in the plating solution, defects occur in the Pd film. These defects can be repaired by the technique of electroless plating combined with osmosis. By this method a membrane with an initial H_2/N_2 permeation ratio of 10 could be repaired to give an increase of this ratio to approximately 1000. The hydrogen permeation performance of the resultant membrane was investigated using pure hydrogen at temperatures from 320 to 577°C. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Electroless plating; Osmosis; Defects; Palladium membranes; Hydrogen separation

---

1. Introduction

The increased demand for hydrogen in recent years in both the petroleum refining and petrochemical industries [1] and in semi-conductor processing and fuel cell applications has led to a revival of interest in methods for separation of hydrogen from gas mixtures and in purification of any separation hydrogen streams. Palladium and palladium membranes have consequently received growing attention for separation and purification of hydrogen, due largely to the unique permselectivity of palladium to hydrogen and good mechanical stability [2–6]. Originally used in the form of relatively thick dense metal membranes, current developments tend to the employment of composite membranes in which the palladium or palladium alloy is deposited as a thin film onto a porous ceramic or metal substrate [7–12]. The introduction of alloying elements into the palladium membranes has been used to improve their resistance to hydrogen embrittlement [13]. Such composite membranes based on a thin palladium film on a porous substrate have good stability and reduced material costs, but their main attribute is in providing a structure possessing both higher hydrogen fluxes and better mechanical properties than the thicker metal membranes.

Several methods have been proposed and developed to prepare Pd-based membranes including magnetron sputtering [14,15], spray pyrolysis [13], and chemical vapour deposition [12]. However, a generally simpler and often more effective method of preparation is the so-called electroless plating technique [7,8,15], which has a number of advantages over other preparation methods. These include, uniformity of deposits on complex shapes, hardness of the deposits, low cost

---

* Corresponding author. Fax: +44-161-295-5999.
E-mail address: a.li@chemistry.salford.ac.uk (R. Hughes).

PII: S0920-5861(99)00261-8

and very simple equipment. For palladium membrane preparation using the electroless plating technique, palladium particles are produced by reduction from the plating solution containing amine-complexes of palladium in the presence of reducing agents. These particles then grow on palladium nuclei which have been pre-seeded on the substrate surface through a successive activation and sensitisation procedure and which also act as a catalyst for the reduction of the palladium complexes. This creates the autocatalysed process of electroless plating.

Despite its inherent simplicity, defects in the palladium layer are frequently observed following deposition, when the membranes are tested for hydrogen permeation and separation. These defects occur due to the free growth process of the palladium particles and the co-deposition phenomena of impurities present in the plating solution. Furthermore, even if defects are not present originally in the deposited layer, any rapid temperature change may lead to the formation of defects caused by the potentially different thermal expansion coefficients of palladium and the substrate. Another problem which could occur is the deposition of carbonaceous impurities when an initially defect free palladium composite membrane is used for high temperature catalytic reaction and separation applications. The further diffusion of these deposited carbonaceous impurities into the bulk phase of the membrane can lead to defects in the membrane [16]. Therefore, it is necessary to be able to repair a membrane containing these defects. Provided that the repair does not change the hydrogen permeation characteristics of the membrane to any marked degree, such a repair technique would possess considerable practical and economic advantages.

A new electroless plating technique in which conventional plating is combined with osmosis has been recently developed by Varma and co-workers [17–19]. By using this technique the initial loose structure of the deposited palladium can be densified by mass transfer of palladium in the plating solution to the vicinity of the defects. In the present work, Pd/α-Al_2O_3 composite membranes which contained an appreciable number of defects were repaired using this technique of electroless plating combined with osmosis. The effect of these repairs on the hydrogen/nitrogen permeation and separation and on the resultant thickness of the palladium layer have been investigated, in addition to measurements of the effect of temperature on the permeation of the final repaired membrane.

2. Experimental

2.1. Hydrogen permeation and separation

The fabricated composite membrane was checked for leaks with nitrogen at room temperature using a glass permeator.

Hydrogen permeation and separation experiments were carried out in an apparatus which consisted of a gas delivery system, a double-tube stainless steel permeator and a heating system. The fabricated palladium composite membrane was positioned in the stainless steel permeator by sealing both ends of the composite membrane in the permeator using moulded graphite rings. Feed gas flowed through the shell side of the permeator and the permeated gases were collected in the tube side, which was open to atmosphere. A pre-heater served to heat the gases prior to admission to the permeator. Temperatures for the permeation experiments using pure hydrogen ranged from 320 to 577°C. The separation experiments were carried out at 467°C using a hydrogen/nitrogen (50:50) mixture at various feed flow rates. Before the first hydrogen permeation measurement, the membrane was thermally treated and activated in a hydrogen atmosphere for 3 h at 450°C.

2.2. Membrane preparation

Several different types of mesoporous substrates are commercially available. Substrate materials for the palladium composite membrane are selected according to the pore structure and size, porosity, mechanical and thermal stability, and surface smoothness of the substrate. Among these, the pore size and smoothness of the surface of the substrate are the two key factors which determine the quality of the composite membrane. The surface pore size should be neither too large to support a thin film nor too small to allow the free flow of gas. Similarly, the surface should be neither too coarse to form a thin film successfully nor too smooth to prevent adherence of the film with the substrate. Asymmetric porous α-Al_2O_3 tubes provided by ECN in the Netherlands were selected as the

Table 1
Composition of sensitisation and activation solution

Sensitisation solution	
$SnCl_2 \cdot 2H_2O$	$5\,g\,l^{-1}$
HCl (37%)	$1\,ml\,l^{-1}$
Temperature	20°C
Activation solution	
$Pd(NH_3)_4Cl_2$	$5\times10^{-4}\,mol\,l^{-1}$
HCl (37%)	$1\,ml\,l^{-1}$
Temperature	20°C

substrates for this work. The tubes were 200 mm in length with an outside diameter of 14 mm and a wall thickness of 3 mm. The top layer, of an average pore size of 0.16 μm, was on the outside of the tube.

A membrane was prepared initially by the conventional electroless plating technique [20]. Details of the sensitisation and activation solutions are given in Table 1, while the composition of the plating bath is shown in Table 2. The membrane so prepared appeared to possess a good adherent film of palladium on the surface of the tube but on testing with hydrogen and nitrogen gave poor separation indicating the presence of defects.

On removal from the test rig the membrane was repaired by the process of electroless plating with simultaneous circulation of a 3 M NaCl solution for 11 h through the tube side of the membrane. This repaired membrane was then tested again for permeation of hydrogen and nitrogen. A further similar repair and permeation measurement was carried out finally on the membrane.

For all preparations, the plating solution temperature was maintained at 60°C. The membrane was kept overnight in an oven at 140°C for all drying steps and was weighed before and after palladium deposition. The palladium film thickness was estimated from the weight gain.

Table 2
Electroless plating bath

Component	Composition
$Pd(NH_3)_4Cl_2$	$4\,g\,l^{-1}$
EDTA 2Na	$67.2\,g\,l^{-1}$
$NH_3 \cdot H_2O$ (28%)	$350\,ml\,l^{-1}$
$N_2H_2 \cdot H_2O$ ($0.5\,mol\,l^{-1}$)	$10\,ml\,l^{-1}$
pH	11.2
Temperature	60°C

3. Results and discussion

3.1. Membrane preparation

Scanning electron micrographs (SEM) were obtained of the surface of the palladium membranes as initially prepared by the conventional electroless plating technique and after two repair steps using further electroless plating combined with osmosis. The results are shown in Fig. 1, where Fig. 1a shows the conventional plated membrane and Fig. 1b that after repair. It can be seen from Fig. 1a that the surface comprises loose packing of the palladium particles and the presence of ‘holes’ or defects is clearly visible. These defects are caused by the free growth of palladium particles during the conventional, initial, electroless plating technique used. However, following the repair of the membrane using the combined technique, the palladium particles were packed closely together and no defects are apparent in the SEM photograph of Fig. 1b. These figures confirm that the repair improved the structure of the deposited palladium layers by promoting a dense packing.

The thickness of the palladium film for successive depositions was estimated from the weight gain of the substrate by assuming that palladium formed a film of uniform thickness on the outside surface of the α-alumina tube and that the density of the deposit was identical with the palladium packing density. The results are shown in Table 3. As can be seen the main weight gain occurred during the original plating; subsequent repairs of the membrane gave only minor increases in weight gain and film thickness until the final thickness of 10.3 μm was obtained.

3.2. Hydrogen/nitrogen permeation measurements

When the initial membrane, prepared by the conventional electroless plating technique was checked for leaks with pure nitrogen at room temperature using a simple glass permeator, a significant leak was detected. This leakage was of the order of several $cm^3\,cm^{-2}\,min^{-1}$. The membrane was then repaired using the modified technique employing osmosis and the nitrogen leakage, measured at room temperature as before, was reduced to less than $0.1\,cm^3\,cm^{-2}\,min^{-1}$. Finally, following a further repair using the same

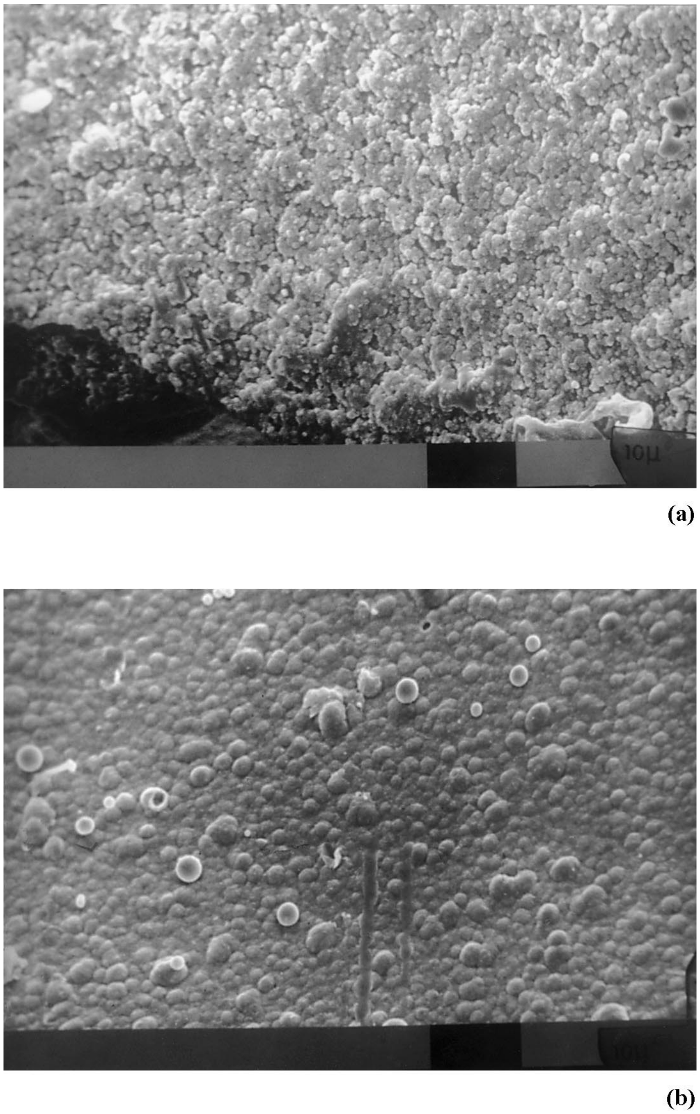

Fig. 1. The surface morphology SEM pictures of the palladium composite membrane (a) original preparation; (b) after repair.

Table 3
Estimated thickness of the palladium film

Plating experiment	Weight gain (g)	Estimated thickness (μm)	Plating time (h)
Original plating	0.815	7.6	8
First repair	0.983	9.2	11
Second repair	1.10	10.3	14

process no further nitrogen leaks were detected at room temperature.

These results indicate that defect-free dense composite membranes could be obtained by repairing the original membrane containing defects. This is because the loose structure of palladium film for the original plating was densified by the very high pressure resulting from the osmotic effect due to the concentrated NaCl solution. Simultaneously, the defects in the palladium film from the first plating may also be repaired by the combination of electroless plating with osmosis. Driven by the osmotic pressure, the water in the plating solution near the defects in the Pd film permeated from the plating solution to the NaCl solution. This increases the concentration of $Pd(NH_3)_4^{2+}$ in the area near the defects and simultaneously, the flow of water can improve the transfer of $Pd(NH_3)_4^{2+}$ from the bulk solution to the pinhole area. Both can lead to a faster palladium deposition rate in the pinhole, compared to other areas. Therefore, the dense or defect-free palladium membrane was obtained without causing a significant increase in the thickness of the palladium film after it was repaired, as shown in Table 3.

However, after thermal treatment of the composite membrane with hydrogen, a nitrogen leak still occurred, which means that some defects were still present. This was not a result of the repair process. The formation of defects due to the thermal treatment might be attributed to the decomposition of impurities which were co-deposited with palladium plating during plating process. These defects could be avoided if chemicals with high purity are employed for the preparation of activation, sensitisation and plating solutions.

Fig. 2 shows the hydrogen and nitrogen fluxes for the initially prepared membrane as a function of applied differential pressure at a temperature of 467°C. As noted above although a high hydrogen permeation flux was obtained (up to 140 $cm^3\,cm^{-2}\,min^{-1}$) the nitrogen flux was significant and increased with pressure difference.

This is characteristic of Knudsen diffusion. These results imply the presence of a large number of defects in the palladium deposited film for the original plated membrane even though the thickness of the palladium film was as high as 7.6 μm, as shown in Table 3. The membrane with the initial plating had a very high hydrogen permeation flux and the hydrogen/nitrogen permeation rate was about 10, which is higher than the ideal hydrogen/nitrogen Knudsen separation factor of 3.74. This indicates the presence of the solution–diffusion mechanism for hydrogen permeation. Obviously, this low hydrogen/nitrogen ratio is not high enough to meet the requirements of hydrogen separation.

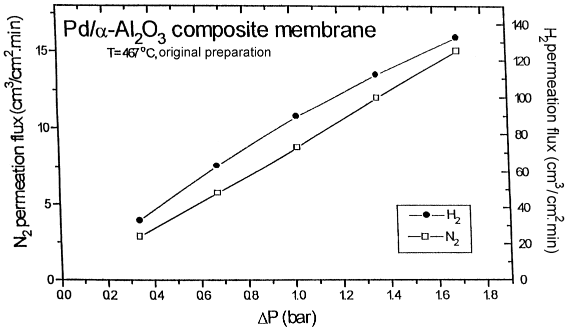

Fig. 2. Hydrogen and nitrogen permeation flux as a function of differential pressure for the originally prepared membranes at 467°C.

However, following the first repair achieved under osmotic conditions, the performance improved with the nitrogen flux decreasing to a value of about 5% of that obtained originally. In contrast the hydrogen flux was reduced by only one half. Although as shown in Table 3 the thickness of the membrane had increased from 7.6 to 9.2 μm for this first repair, this cannot be responsible for a decrease of hydrogen flux by 50% since the permeation flux of hydrogen is inversely proportional to the palladium thickness. Therefore, the decrease in hydrogen flux results mainly from the removal of defects in the palladium film by the repair process.

Results from a second repair of the membrane are given in Fig. 3. It can be seen that the nitrogen flux measured at 467°C is now much reduced having values lying in the range from about 0.01 to 0.07 $cm^3\,cm^{-2}\,min^{-1}$ as the differential pressure is increased from 0.3 to 1.7 bars.

A comparison of the results from the original and the two repaired membranes is shown in Table 4, which also includes the separation factors for H_2/N_2 for each membrane, for a temperature of 467°C and a pressure differential of 1.03 bar.

Thus, although the hydrogen permeability has been reduced following the repair processes, the selectivity

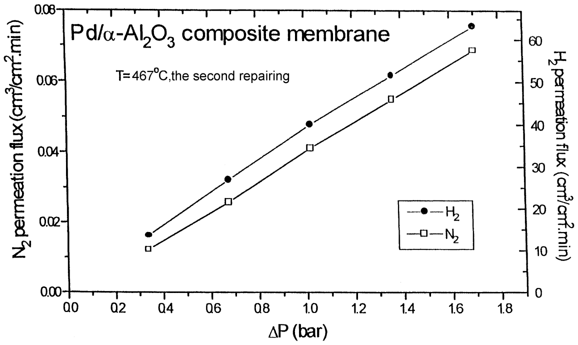

Fig. 3. Hydrogen and nitrogen permeation flux as a function of differential pressure after the second repair at 467°C.

has been boosted considerably increasing by about one order of magnitude after each repair.

Further experiments on the permeability of the final membrane as a function of temperature for the temperature range of 320–577°C with pressures on the high pressure side from 1.34 to 2.7 bar while the low pressure side was maintained at 1 bar are shown in Fig. 4.

The mechanism for hydrogen permeation through the palladium membrane has been studied extensively and is generally considered to include three steps.

Table 4
Hydrogen and nitrogen permeation results for the original and repaired membranes

Plating	Permeation flux ($cm^3\,cm^{-2}\,min^{-1}$)		
	N_2	H_2	H_2/N_2
Original	8.73	89.74	10.27
First repair	0.483	46.59	96.52
Second repair	0.0412	40.12	970

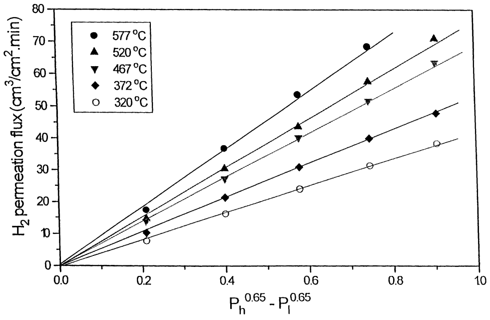

Fig. 4. Hydrogen permeation flux as a function of temperature and the driving force for permeation.

These are:

1. reversible dissociative chemisorption of hydrogen on the membrane surface,
2. reversible dissolution of surface atomic hydrogen into the bulk of the metal,
3. diffusion of atomic hydrogen in the membrane.

The hydrogen permeation may be expressed in terms of the general equation [15].

$$J = Q\frac{A}{t}(p_{\mathrm{h}}^{n} - p_{\mathrm{l}}^{n}) \tag{1}$$

where J is the hydrogen permeation flux, Q the permeability constant for hydrogen through the membrane, A the permeation area, p_{h} and p_{l} the hydrogen partial pressures on the high and low pressure sides of the membrane, respectively, and n is a constant.

If step 3 is rate determining, then according to Sievert's Law, n should have the value of 0.5. However, if steps 1 and 2 exhibit some influence on the rate determining process, n should be larger than 0.5.

From Eq. (1) the hydrogen permeation fluxes at different temperatures were plotted as shown in Fig. 4. The value of n was found to be 0.65, which suggests that the permeation rate of hydrogen through the α-Al_2O_3 composite membrane was dependent not only on bulk phase diffusion, for which the pressure exponents should be 0.5, but also on the surface processes of hydrogen chemisorption and dissolution. From the temperature dependence a value of the apparent activation energy for hydrogen permeation through the palladium composite membrane of 12.3 kJ mol^{-1} was obtained. This value compares very well with that of 10.7 kJ mol^{-1} by Uemiya et al. [15] and 13.0 kJ mol^{-1} by Ilias et al. [20] who also used electroless plating for preparation of their membranes.

4. Conclusions

A new preparation procedure was employed to repair defects in Pd/α-Al_2O_3 composite membranes. The final composite membrane with a thin palladium film of 10 μm in thickness showed a large hydrogen permeation flux and a very high hydrogen selectivity. The repair has a considerable favourable effect on the morphology and microstructure of the deposited palladium film and on the permeation and separation performance of the composite membrane. The repair procedure can densify the palladium film and dramatically improve the hydrogen permselective performance without causing a large reduction of its hydrogen permeation flux and without a significant increase in the palladium thickness.

Measurements of the temperature coefficient for hydrogen permeation through the final repaired membrane gave a value of 12.3 kJ mol^{-1} in good agreement with previous reports. The pressure exponent value of 0.65 obtained suggests that surface processes have some effect on the permeation behaviour.

Acknowledgements

The authors gratefully acknowledge the support for this work by the European Commission under the Joule Programme (Contract JOE CT95 0018). We also thank Dr. Janet O'Brien for provision of the Scanning Electron Micrographs.

References

[1] V.M. Gryaznov, Plat. Met. Rev. 30 (1986) 68–72.
[2] V.M. Gryaznov, V.M. Ermilova, L.S. Morozova, N.V. Orekhova et al., J. Less-Common Met. 89 (1983) 529–535.
[3] N. Itoh, AIChE J. 33 (9) (1987) 1576–1578.
[4] R. Govind, D. Atnoor, Ind. Eng. Chem. Res. 30 (1991) 591–594.
[5] E. Gobina, R. Hughes, J. Membr. Sci. 90 (1994) 11–19.
[6] N.N. Mikhalenko, E.V. Khranova, V.M. Gryazanov, Russ. J. Phys. Chem. 59 (1985) 1533–1534.
[7] J. Shu, B.P.A. Grandjean, S. Kaliaguine, Appl. Catal. A 119 (1994) 305–325.
[8] J. Shu, B.P.A. Grandjean, S. Kaliaguine, Catal. Today 25 (1995) 327–332.
[9] Z.D. Ziaka, R.G. Minet, T.T. Tsotsis, J. Membr. Sci. 77 (1993) 221–232.
[10] R.E. Buxbaum, T.L. Marker, J. Membr. Sci. 85 (1993) 29–38.
[11] J. Shu, B.P.A. Grandjean, A. van Neste, S. Kaliaguine, Can. J. Chem. Eng. 69 (1991) 1036–1060.
[12] S. Yam, H. Maeda, K. Kusakabe, S. Morooka, Ind. Eng. Chem. Res. 33 (1994) 616–622.
[13] Z.Y. Li et al., J. Membr. Sci. 78 (1993) 247–254.
[14] V. Jayaraman, Y.S. Lin, M. Pakals, R.Y. Lin, J. Membr. Sci. 99 (1995) 89–100.
[15] S. Uemiya, N. Sato, H. Ando, Y. Kude, T. Matsuda, K. Kikuchi, J. Membr. Sci. 56 (1991) 303–313.
[16] A.F.Y. Al-Shammary, I.T. Caga, J.M. Winterbottom, A.Y. Tata, I.R. Harris, J. Chem. Technol. Biotechnol. 52 (1991) 571–585.
[17] K.L. Yeung, A. Varma, AIChE J. 41 (9) (1995) 2131–2139.
[18] K.L. Yeung, R. Aravind, J. Szegner, A. Varma, Stud. Surf. Sci. Catal. 101 (1996) 1349–1358.
[19] K.L.s Yeung, J. Sebastian, Catal. Today 25 (1995) 231–236.
[20] S. Ilias, N. Su, U.I. Ado-Aka, F.G. King, Sepn. Sci. Technol. 32 (1997) 487–504.