



Toward effective membranes for hydrogen separation: Multichannel composite palladium membranes

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ABSTRACT

Composite palladium membranes can be used as a hydrogen separator because of their excellent permeability and permselectivity. The total membrane area in a hydrogen separator must be reasonably large for industrial use, and it is important that each membrane provides a large enough area. Such a demand can be well met by introducing multichannel composite membranes. In this work, a commercially available microporous ceramic filter with 19 channels was used as a membrane substrate, and the diameter of each channel was 4 mm. A uniform thin palladium layer was fabricated inside the narrow channels by using an electroless plating method, and the resulting membranes were highly permeable and selective. This membrane concept provides a high surface-to-volume ratio without causing significant pressure loss, making the hydrogen separator compact and capable. However, special attention should be paid to cleaning the membrane after electroless plating.

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1. Introduction

Owing to their perfect permeability and permselectivity for hydrogen, palladium membranes have attracted considerable interest in hydrogen separation and purification [1–3]. A great improvement in membrane permeance has been achieved in recent years by the use of composite membranes, i.e., thin membranes supported on porous materials such as ceramics and stainless steel [4–7]. Aiming at industrial uses, the total working area of the membranes in a hydrogen separator must be reasonably high to get enough output. Because the number of membranes in a separator should be limited owing to difficulties in membrane assembling and monitoring, it is important that the working area of each membrane is large enough. Moreover, the high surface-to-volume ratio of the membranes is also an advantage for making the separator more compact for portable, on-site hydrogen production. Palladium membranes based on a bundle of hollow-fiber ceramics seem to be an ideal choice [8–10], but their high cost, poor physical strength, and further difficulties in membrane preparation and handling are serious problems.

In the membrane filtration industry, the demand for a large filtering area has been perfectly met by applying multichannel filters. Similarly, we report a type of multichannel palladium membrane that is suitable for hydrogen separation. As shown in Fig. 1, the

substrate is a multichannel microporous ceramic filter, and the palladium layer is supported on the wall of each channel. Such a concept perfectly solves the above problems encountered by hollow-fiber membranes. Also, the geometry of multichannel palladium membranes also favors the protection of the thin membranes from damage and contamination during storage, shipment, assembly, and operation.

2. Experimental methods

2.1. Preparation

A 19-channel microporous ceramic filter (diameter, 30 mm; each channel diameter, 4 mm; fabricated by Jiushi High-Tech. Co., China) was used as a membrane substrate, which has an asymmetric structure, with macroporous Al_2O_3 as the base material and a microporous (average pore size, $0.2\ \mu\text{m}$) thin layer of ZrO_2 on the wall of each channel. The faces of the two ends were glazed to be non-porous. The palladium membranes were prepared by electroless plating. The composition of the plating bath was as follows: PdCl_2 ($5\ \text{g L}^{-1}$), $\text{Na}_2\text{-EDTA}$ ($70\ \text{g L}^{-1}$), and $\text{NH}_3\cdot\text{H}_2\text{O}$ (28% , $250\ \text{mL L}^{-1}$), and the reducing agent was 0.2 M hydrazine solution. Before plating, the shell-side of the substrate was wrapped with Teflon tape, and the channels were activated with a $\text{SnCl}_2/\text{PdCl}_2$ method [11,12].

The electroless plating was performed at room temperature. As illustrated in Fig. 2, we again wrapped the shell-side of the substrate with Teflon tape, connected its upper end to a glass vessel,

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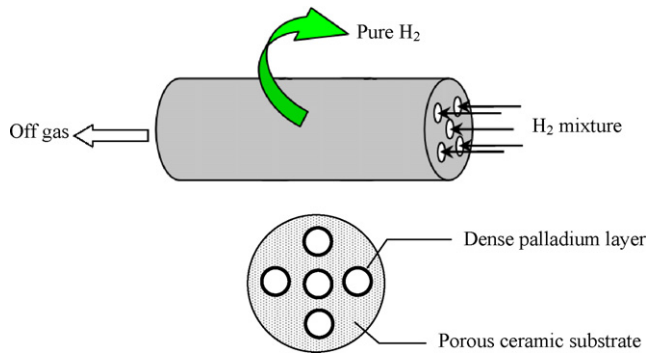


Fig. 1. Multichannel palladium membrane for hydrogen separation.

and connected its lower end to a pipe to feed hydrazine solution and nitrogen. To start the plating, we controlled the nitrogen flow rate at about 60 mL min^{-1} , fed N_2H_4 solution (0.2 M) with a peristaltic pump, and then added the plating bath from the glass vessel. Typically, the amount of plating bath and the feed rate of the N_2H_4 solution were about 6.7 mL and $0.15 \text{ mL h}^{-1} \text{ cm}^{-1}$ length of the substrate, respectively, producing an approximately $0.7 \mu\text{m}$ palladium layer if the palladium in the plating bath was completely converted. After about 3 h of plating, the feed rate of the N_2H_4 solution was increased up to two times the original, and the plating was then continued for about 2 h to recover the precious palladium. Before renewal of the plating bath, the substrate was reversed to ensure uniform plating. This plating process was repeated until the desired thickness of palladium membrane was reached. The resulting membranes were thoroughly cleaned with de-ionized water at 358 K, soaked in anhydrous ethanol for 2 h, and finally dried at 393 K overnight. From the weight gain after electroless plating, one can estimate the thickness of a palladium membrane.

2.2. Characterization

The membrane surface was studied by SEM (QUANTA-2000). A metallographic microscope (LEICA, DM-4000M) was also used to analyze the membrane cross-section. Before analysis, a short piece of specimen was cut from a membrane, and it was encapsulated with epoxy resin curing at room temperature. The grinding

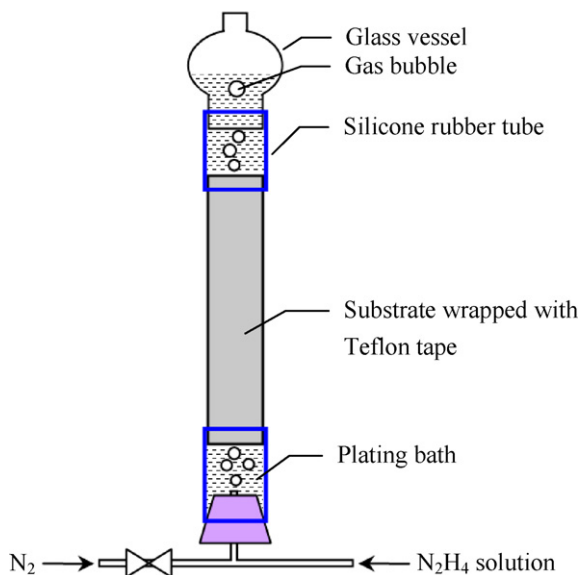


Fig. 2. Electroless plating of palladium membrane on a 19-channel substrate.

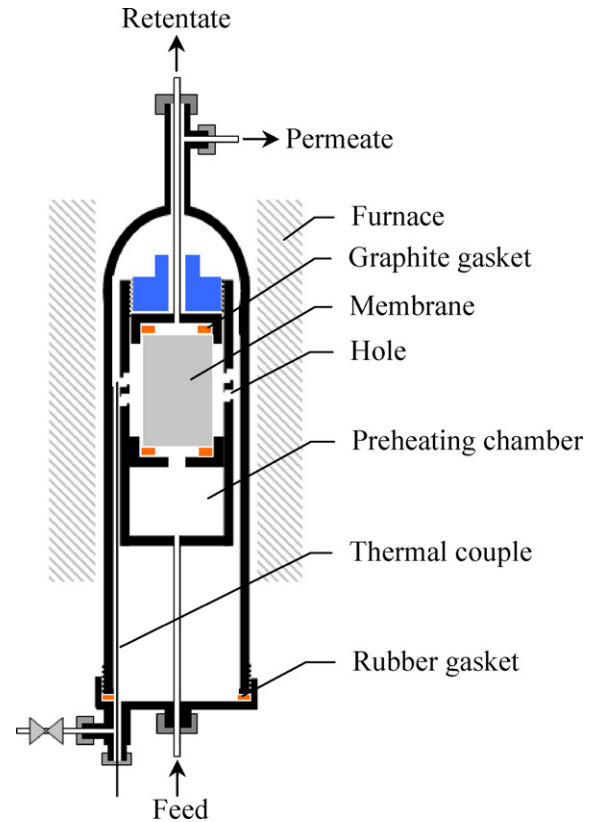


Fig. 3. Membrane module for hydrogen permeation tests.

and polishing were performed on a Phoenix Beta grinder–polisher (BUEHLER). The membrane permeation tests were carried out with a H_2/N_2 single gas method [11,12]; the membrane module is shown in Fig. 3. The length of the tested membranes was 5 cm, and the pressure of the permeate side was always ambient. Before testing, we first heated the membrane under a nitrogen atmosphere at 5 K min^{-1} up to 723 K and then maintained this temperature for 6 h under synthetic air ($\text{N}_2:\text{O}_2 = 4:1$) to burn any organic remnants. The fluxes of pure nitrogen and pure hydrogen were measured as a function of the retentate pressure. The membrane selectivity was defined as the ratio of hydrogen flux versus the nitrogen flux under the same temperature and pressure.

3. Results and discussion

Multichannel membranes have the advantages of both conventional tubular and hollow-fiber membranes, but a great challenge is to deposit a thin, uniform, and defect-free palladium layer inside the narrow channels. The multichannel substrate that we used in this work was a conventional microporous ceramic filter that has been commercially applied in the filtration industry. We used such an ordinary commercial filter with cheaper price to lower the final membrane cost. Although the cost of the precious palladium seems to be the main concern, one must also consider the cost of membrane substrate, which might be even more expensive. Researchers often tended to choose high-grade but extremely expensive substrates, such as nano-sized materials, to ease the difficulties of obtaining thin, homogeneous, and defect-free membranes.

As can be seen in Fig. 4, the surface of the substrate channels is rough and contains some defects (cf. Fig. 4(b)). Although such surface roughness would cause difficulties in membrane preparation, it favors the membrane adhesion and the consequent membrane stability [4,13,14]. Of the various techniques that have been reported

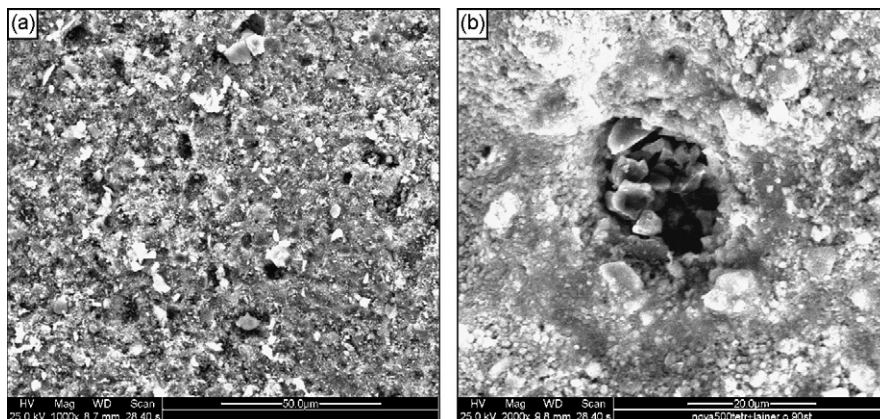
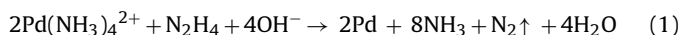


Fig. 4. SEM of the surface of substrate channel: (a) Surface overview and (b) view of a surface defect.

in preparation of palladium membranes [12,15–17], electroless plating is among the best so far, and was therefore used in this work. The key of quality control during electroless plating was to control the reaction rate along the narrow channels and avoid the formation of any palladium precipitates.

During electroless plating, the palladium layer gradually grows because of the following reaction:



Once the reaction was out of control in some regions, the dark-grey palladium precipitates would be deposited, and they were loosely agglomerated and eventually led to membrane defects. To avoid this problem and to ensure membrane uniformity, we carried out the plating as follows: (i) performing the plating at a lower temperature, e.g., room temperature; (ii) feeding the reducing agent slowly; and (iii) stirring the plating bath effectively by using a convection driven by N_2 bubbling through the membrane channels. Although the gas bubbling through the plating bath promoted the evaporation of ammonia in the plating bath, this will not be a problem at such a lower plating temperature. As shown in Fig. 2, the N_2H_4 solution was introduced by using nitrogen as a carrier because its feed rate was slow.

Along with the process of electroless plating, the concentration of palladium in the plating bath steadily decreased, and the feed rate of hydrazine solution should be increased to shorten the plating time. Finally, the amount of hydrazine in the plating bath became excessive so that the precious palladium could be con-

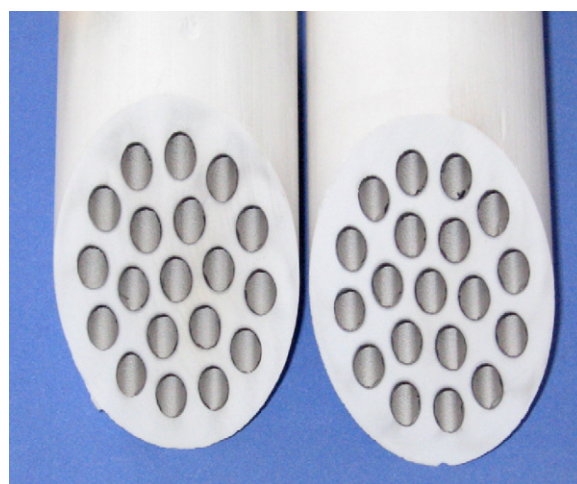


Fig. 5. Cutting fracture of a multichannel palladium membrane.

verted as completely as possible. Fig. 5 shows the cutting fracture of a typical palladium membrane, and the palladium layer is lustrous without any blistering or peeling. The color of the ceramic substrate changed little, indicating that there was no significant penetration of palladium into the porous ceramic material. On one hand, this outcome saves the precious palladium and on the other hand avoids pore fouling.

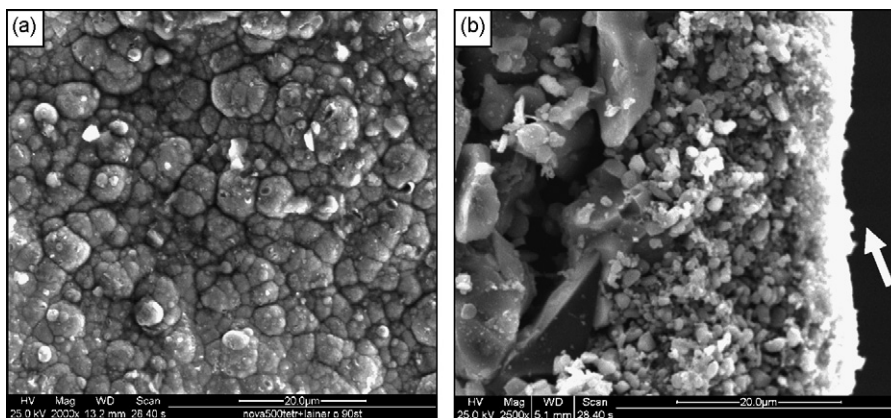


Fig. 6. SEM of the surface (a) and cross-section (b) of a palladium membrane.

The SEM micrographs of the surface and cross-section are shown in Fig. 6. The membrane surface is composed of palladium particles with a wide range of sizes, but the surface of these particles looks smooth, coinciding with the membrane lustrousness. Fig. 6(b) shows the cross-section of the membrane, but the boundary between the palladium layer and the substrate cannot be clearly seen. The specimen for SEM analysis was a fragment obtained by breaking the membrane with force. Palladium metal has perfect ductility, and consequently the fracture of the palladium layer is often irregular and may give misleading information; e.g., the observed membrane thickness may be lower than the actual value because of metal expansion. Because there is always a sharp optical contrast between the metal layer and the ceramic substrate after grinding and polishing, metallography is actually a more powerful technique on cross-section analysis [11,12]. As shown in Fig. 7, the palladium layer is compact, uniform, and well-anchored onto the contour of the substrate surface. As indicated by the circled region in Fig. 7(b), it was promising that the defects in the substrate (see Fig. 4(b)) may not lead to final membrane defects. Fig. 7(b) also shows that the average membrane thickness is about 5 μm , which is close to that estimated by weight gain (4.8 μm). Also, this membrane was prepared by seven platings, and each plating on average deposited a palladium layer of approximately 0.7 μm , indicating that the palladium in the plating bath had been almost completely deposited.

Hydrogen permeation through a dense palladium membrane follows the solution–diffusion mechanism [18]: (i) hydrogen molecules are dissociatively chemisorbed on the palladium surface, and the hydrogen atoms are dissolved into the membrane bulk; (ii) hydrogen atoms diffuse from one side of the membrane to the other; and (iii) hydrogen atoms escape to the surface from the membrane, recombine as hydrogen molecules, and are finally desorbed. Steps (i) and (iii) can be called the surface step, and (ii) can be called the bulk diffusion step. The permeation kinetics may be universally described by the following:

$$J_{\text{H}_2} = F(P_{\text{Ret}}^n - P_{\text{Perm}}^n) \quad (2)$$

$$F = F_0 \exp(-E_A/RT) \quad (3)$$

where J_{H_2} is the hydrogen flux; F is the hydrogen permeance; P_{Ret} and P_{Perm} are the pressures at the retentate and permeate sides, respectively; n is the pressure exponent; F_0 is the pre-exponential factor; E_A is the apparent activation energy; R is the universal gas constant; and T is the absolute temperature. Bulk diffusion is usually the rate-determining step, and $n=0.5$. As long as the surface step starts to influence the hydrogen flux, then $0.5 < n < 1$ [19–22]. This outcome may occur particularly when the bulk diffusion is

extremely fast (e.g., for ultrathin membranes) or the surface step is too slow (e.g., the membrane surface is contaminated [23–27]). Once the surface reaction becomes the rate-determining step for the overall permeation process, then $n \approx 1$.

During our permeation tests, the membranes were sealed with graphite gaskets, which were imperfect and generated small leaks. The effect of such leaks on the huge hydrogen flux J_{H_2} was negligible, but it caused a significant error in measurement of the small nitrogen flux J_{N_2} through membrane pinholes, and consequently the membrane selectivity ($J_{\text{H}_2}/J_{\text{N}_2}$) would be remarkably and even exponentially underestimated. This problem can be solved by measuring J_{N_2} at room temperature, when the membranes were perfectly sealed by rubber gaskets, and J_{N_2} at high temperature can be approximately calculated according to the function of $J_{\text{N}_2} \propto T^{-0.5}$ [11].

Fig. 8 shows the permeation results of a palladium membrane with a thickness of 4.0 μm . The selectivity decreases with the increasing pressure but still above 1000 under pressures within 2 bars, indicating that the membrane is highly permselective. The hydrogen fluxes per meter length of membrane under 1 bar will be 2.5, 3.0, 3.4, and 3.7 $\text{m}^3 \text{h}^{-1}$ at 623, 673, 723, and 773 K, respectively, indicating that the membrane is highly permeable.

For Eq. (2), we plotted the hydrogen fluxes J_{H_2} versus $(P_{\text{Ret}}^n - P_{\text{Perm}}^n)$ and found that the best linear correlation can be established when $n \approx 0.8$. Because n has been larger than 0.5, there must be a factor, other than the bulk diffusion of hydrogen in palladium membrane, that influences the permeation kinetics, and it would most likely be the diffusion resistance by the substrate because the multichannel geometry tends to create larger diffusion resistance [28]. The permeation of a gas through microporous material follows mainly Knudson diffusion or Hagen–Poiseuille diffusion, both of which have a larger pressure exponent. On the other hand, the diffusion resistance in these two cases will increase with increasing temperature. On the contrary, Fig. 8(a) reveals that the increase in temperature steadily led to an increase in hydrogen flux, indicating that the diffusion resistance by the ceramic substrate has not yet been a deciding factor even though it played a role on permeation kinetics. Therefore, the advantages of the multichannel membrane become apparent. This membrane concept provides a high surface-to-volume ratio without causing significant pressure loss, making the hydrogen separator compact and capable.

Another influencing factor on permeation kinetics cannot be ruled out: the contamination of membrane, which may slow down the surface step during hydrogen permeation. This postulation can be also associated with the high diffusion resistance in multichannel substrate, because it may lead to a difficulty in membrane cleaning after electroless plating, and the residual plating bath

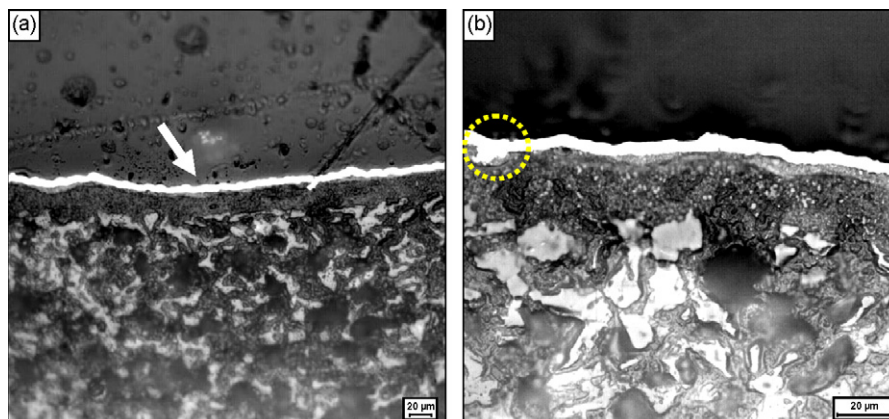


Fig. 7. Metallographic photomicrographs of the cross-section of a palladium membrane: (a) 100 \times and (b) 500 \times .

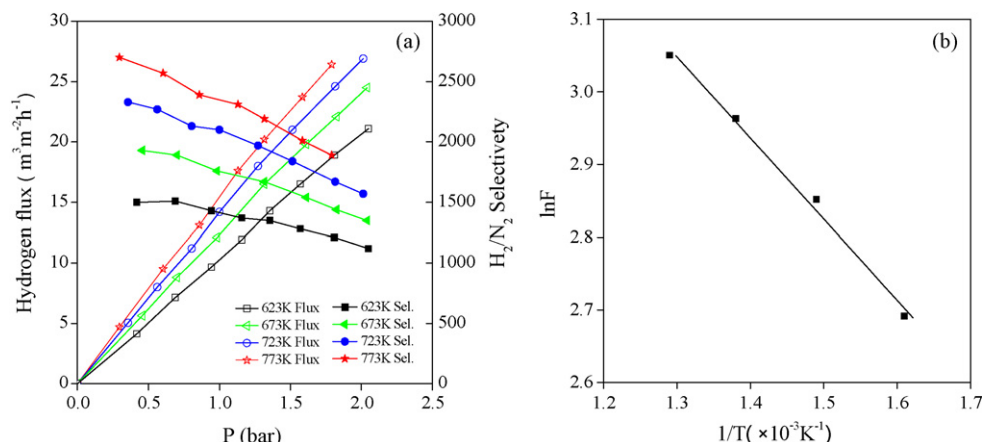


Fig. 8. Permeation results of a multichannel palladium membrane with a thickness of 4.0 μm . (a) Effect of pressure on membrane flux and selectivity and (b) Arrhenius plot to calculate the apparent activation energy E_A .

(particularly EDTA) in the porous substrate would contaminate the membrane when heated. Once the surface of the palladium membrane at the substrate side was contaminated, the escape of hydrogen atoms will be suppressed.

Fig. 8(b) shows the Arrhenius plotting, and the apparent activation energy E_A can be calculated as 9.6 kJ mol^{-1} . In the literature, many E_A data for various palladium and alloy membranes have been reported, and they were collected by some researchers [1,29–31]. From the statistics, we did not see a clear correlation between E_A and membrane thickness, preparation methods, or alloy composition, but most of the reported E_A values ranged between 10 and 20 kJ mol^{-1} . The E_A in this work seems to be at a lower level, which might also be related to the diffusion resistance in the substrate or the membrane contamination.

4. Conclusions

Thin palladium membranes were fabricated by electroless plating on an ordinary microporous multichannel ceramic filter with 19 channels, and a uniform lustrous palladium layer, which was highly permeable and selective, was obtained inside the narrow channels. The permeation kinetics may be slightly influenced by the diffusion resistance in the multichannel substrate, and we suggest paying attention to membrane cleaning after electroless plating.

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