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Preparation of Palladium-Alumina Membrane Tube by Combine Sol-gel Process with Electroless Plating for Hydrogen Permeation

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Abstract: In this study, the potential of utilizing the porous alumina ceramic membrane coated with palladium as a hydrogen permselective membrane has been studied. The ceramic membrane is characterized by high permeability but at low hydrogen selectivity. In order to increase the pure hydrogen selectivity and to obtain high hydrogen yield on the ceramic membrane, palladium was coated on the alumina membrane surface. Such an arrangement would also enable the ceramic membrane to be operated at higher temperature. The preparation of the palladium coated ceramic membrane was carried out using combine sol-gel process and the electroless plating technique. The effect of combine sol-gel process with electroless plating towards hydrogen permeation and hydrogen permselectivity were analysed. The thickness of the α -Alumina and Palladium composite membranes were analysed using a Scanning Electron Microscopy (SEM). The resulting membrane showed significantly higher hydrogen permeation but the same time decrease hydrogen permeability and permselectivity.

Key words: Palladium-alumina membrane tube, sol-gel, electroless plating, hydrogen permeation

INTRODUCTION

Metal composite membrane is becoming a promising choice for hydrogen separation, where recent efforts to increase the hydrogen permeation rates have led to the development of palladium-based composite membranes. Composite membranes with porous supports allow the considerable reduction of palladium (palladium alloy) layer thickness and membrane cost and at the same time ensure the enhanced permeability and good operating ability (Alexeeva *et al.*, 2007).

Palladium membranes were developed because of their high hydrogen permselectivity. This property results from the strong surface interaction between hydrogen and palladium. It firstly leads to the formation of a solid solution of hydrogen in palladium (α phase) and then, at higher hydrogen concentrations, to a hydride (β phase). However, the cost and the possible embrittlement of the palladium layer, mainly due to the phase transition (α phase to hybrid β phase) at low temperature in the presence of hydrogen, are important drawbacks (Ernst *et al.*, 2007).

Porous α -Alumina ceramic membrane tube was selected as the substrate due to its high α -alumina purity that gave rise to high chemical stability in acid, base and other reactive environments and possess high thermal and hydrothermal stability (Ernst *et al.*, 2007; Bissett *et al.*, 2008).

Electroless plating to date is the most successful technique for palladium-alumina composite membrane preparation. It involves cathode/anode reaction (autocatalytic reaction) where the metal cathode reduction and reductant anode oxidation occurs simultaneously. This technique is normally utilized because it provides distinct advantages such as low cost, as well as use of simple equipment and uniformity of deposition on complex shapes (Okazaki *et al.*, 2009).

To form a thin continuous membrane without defects, the support surface should be smooth. The problem in the α -alumina membrane support was surface roughness. To reduce the surface roughness, intermediate layer is necessary. Therefore it is necessary to use sol-gel derivated γ -alumina support. Palladium film with good adhesion could be coated on sol-gel γ -alumina support but not on α -alumina support (Huang and Dittmeyer, 2007). In this research, palladium composite membrane is prepared by sol-gel technique under reflux condition and followed by electroless plating. The best plating process for hydrazine-based hypophosphite bath was chosen based on the amount of palladium deposited. The objective of this study is to improve the performance of alumina membrane for application in hydrogen separation process. The discussion includes the thickness of palladium film and quality of the membrane which was evaluated with respect to permeation, permselectivity and permeability of hydrogen.

MATERIAL AND METHODS

Membrane preparation: Alpha- Alumina membrane tube with an outer diameter, length, thickness and pore size of 1 cm, 17.5 cm, 0.2 cm and 100 nm, respectively, was supplied by Jiangsu Jiuwu Hitech Co. Ltd. The chemicals used in the sol solutions were analytical grade materials, i.e., aluminium nitrate nonahydrate (98%, Fluka), nitrate acid (65% Merck), poly vinyl alcohol (98%, Merck). The sensitization solution was tin (II) chloride (Sigma-Aldrich) and hydrochloric acid (37%, Merck). The activation solution was palladium chloride (99.9%, Aldrich) and hydrochloric acid (37%, Merck). The electroless plating solution consists of palladium chloride (99.9%, Aldrich), sodium hypophosphite anhydrous (Sigma-Aldrich), ethylene diamine tetraacetic acid (Sigma) and ammonium hydroxide (28%, Sigma-Aldrich).

Prior to sol-gel process, the membrane tube cleaned by sequential ultrasonic rinsing in sodium hydroxide 0.1% for 1 min, 100 mL deionized water for 2 min, rinsing in 100 mL isopropanol for 10 min and rinsing in 100 mL deionized water for 10 min. Finally it was dried at 120°C for at least 8 h. The second step is a preparation of palladium-alumina membrane by sol-gel technique (Othman and Sahadan, 2006). To do this, appropriate amounts of deionized water is heated at up to 80-90°C, then aluminium nitrate nonahydrate, nitric acid and poly vinyl alcohol were added into deionised water maintained a temperature of 80-90°C. The solution (Table 1) was thoroughly mixed at 80-90°C for 24 h under reflux condition before immersing the membrane for plating and then it was dried at 120°C for 2 h. In the third step, the sensitization and activation of membrane was carried out at room temperature and at pH 4-5. Prior to this process, the membrane tube was sealed at both ends with teflon to ensure the activation on the outer membrane surface only. The membrane was immersed into the sensitization solution of SnCl₂ and HCl for 2 min and then washed with deionized water for 30 sec. It was then immersed into the activation solution of PdCl₂ and HCl for another 2 min. After that, it was washed with deionized water again for 30 sec. This cycle was repeated for ten times. The electroless plating solution consist of PdCl₂, NH₄OH, EDTA, NaPO₂H₂ (Table 2). The Plating process is carried out at 45°C, pH 11 and speed of membrane 103 rpm by Heidolp RZR 2021 (Fig. 1) for 1.5 h. A rubber filler was put into alumina tube for sealing and the tube was immersed in a glass test cylinder containing the plating solution and connected to the drive of a stirrer. The ceramic membrane with palladium coated film was dried in furnace at 600°C for 3 h and stored in the desiccators to prevent from ambient humidity.

Table 1: Sol-gel solution

Component	Composition
Aluminium nitrate nonahydrate	18.76 g
Nitrate acid	3.1 mL
Poly vinyl alcohol	2.1 mL
Deionized water	90.3 mL

Table 2: Electroless plating solution

Component	Composition
PalladiumCl ₂	2.7 g L ⁻¹
NH ₄ OH (28%)	580.5 mL
NaPO ₂ H ₂ : PalladiumCl ₂	0.66 :1
EDTA	35 g

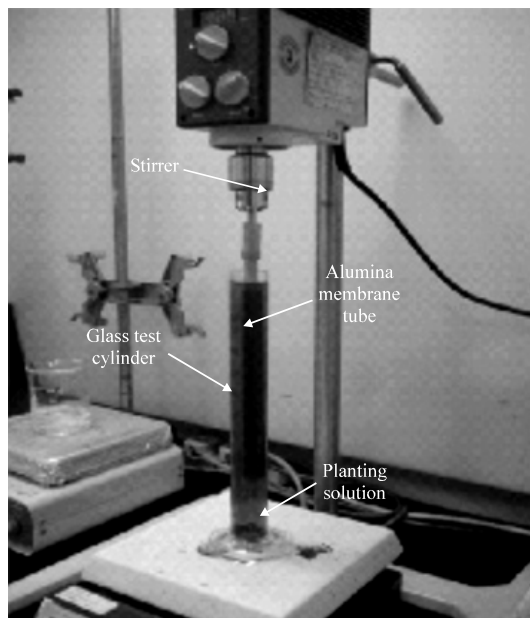


Fig. 1: Electroless plating process at 45°C and pH 11

Hydrogen permeation and selectivity test unit: Hydrogen permeation and selectivity setup used in this research was homemade apparatus (Fig. 2a).

The membrane module was composed of a stainless steel tube. Teflon made O-ring was used to seal end of the tubular palladium-alumina membrane (Fig. 2b). Membrane then is placed in a module and its temperature was controlled by furnace.

The gas permeation tests were carried out at temperature 300°C and pressure (2×10⁴-8×10⁴ Pa). Gas flow rate was 9,171 mL min⁻¹. The effective area of the membrane for permeation was 32.97 cm². The permeated gas flow rates were measured at a constant temperature with pressure difference across the membrane. Membranes were characterized by conducting permeability experiments with hydrogen and nitrogen.

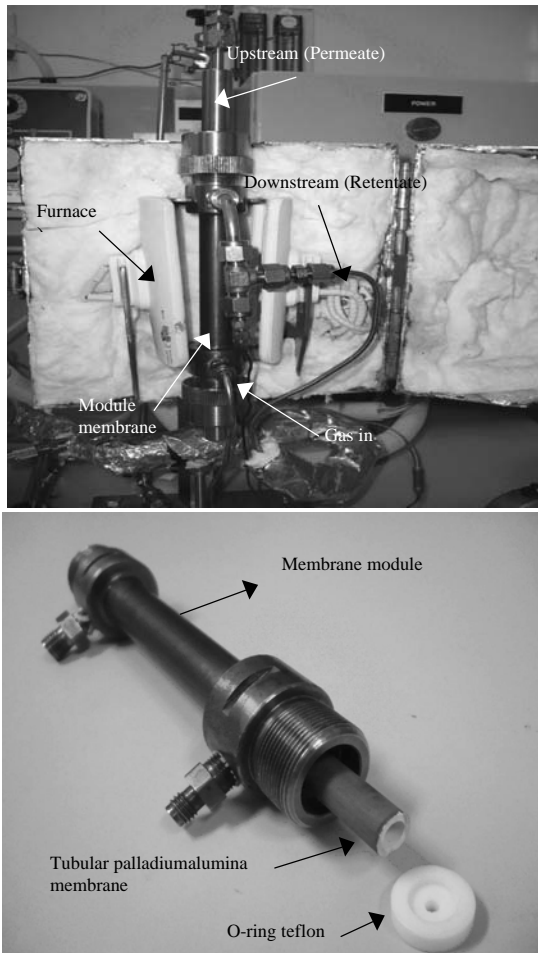


Fig. 2: (a) Hydrogen permeation and selectivity tests apparatus. (b) Membrane module, tubular palladium-alumina membrane and O-ring teflon

RESULTS AND DISCUSSION

The thickness and morphology of the α -Alumina and palladium composite membranes were analyzed using a scanning electron microscopy (SEM) TM-1000 Tabletop microscope, Hitachi. The SEM images (Fig. 3a) obtained after first layer of palladium coating confirms the measured thickness. The thickness of palladium as a function of number of layers is also shown in Fig. 3b. The maintained immersion time to get a layer of palladium coating was 24 h.

The measured thickness of palladium after first and fifth layer of coating was 27.9 and 90.4 μm , respectively. As it is seen in the Fig. 3b, the amount of palladium loaded was minimum at the first plating step for 45°C of bath temperatures whereas the maximum value of palladium loading was obtained at the fifth plating step.

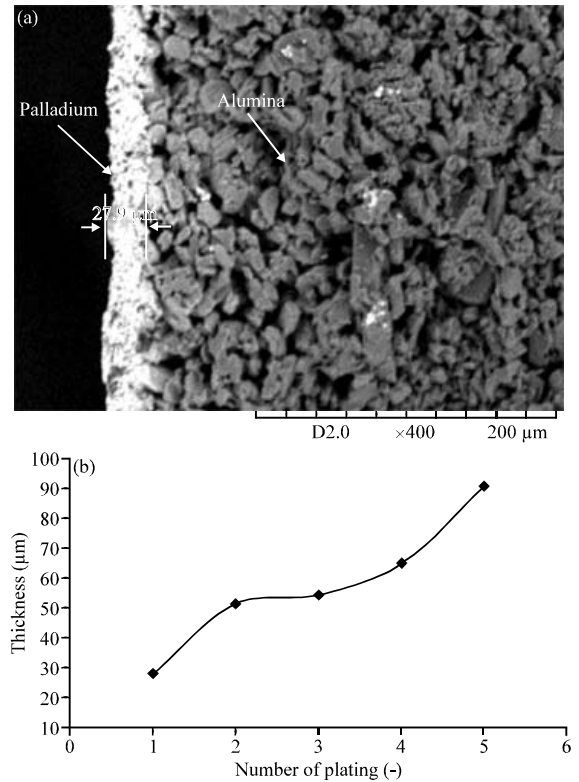


Fig. 3: (a) Thickness of palladium-alumina membrane. (b) Thickness of palladium coating film in variation number of plating

The substrate dipped into the first plating bath had a large activated surface area (Dogan and Kilicarslan, 2008). When the surface area was considerably filled in the samples in which high mass gains were observed in the first plating step, it was seen that palladium amount deposited in the second until fifth steps increased.

Figure 4 shows the SEM image morphology of the prepared membrane for one until five coatings. With extension of number of plating, since a layer of palladium already deposited on the alumina surface, the subsequent layers grow over the smoother surface thus result a more homogenous and denser palladium layer.

The increased of membrane thickness enhance the various surface morphology (Fig. 4a-e). A lot of holes were observed in the palladium film. It can be seen from Fig. 4e, the surface of the palladium-alumina is quite rough. In the electroless plating process, surfaces on the alumina membrane tube have gas bubbles, caused porous of the coating.

The permeation of hydrogen through metals are expected to follow a multistep process which involves; (1) reversible dissociative chemisorption of molecular hydrogen on the membrane surface, (2) reversible

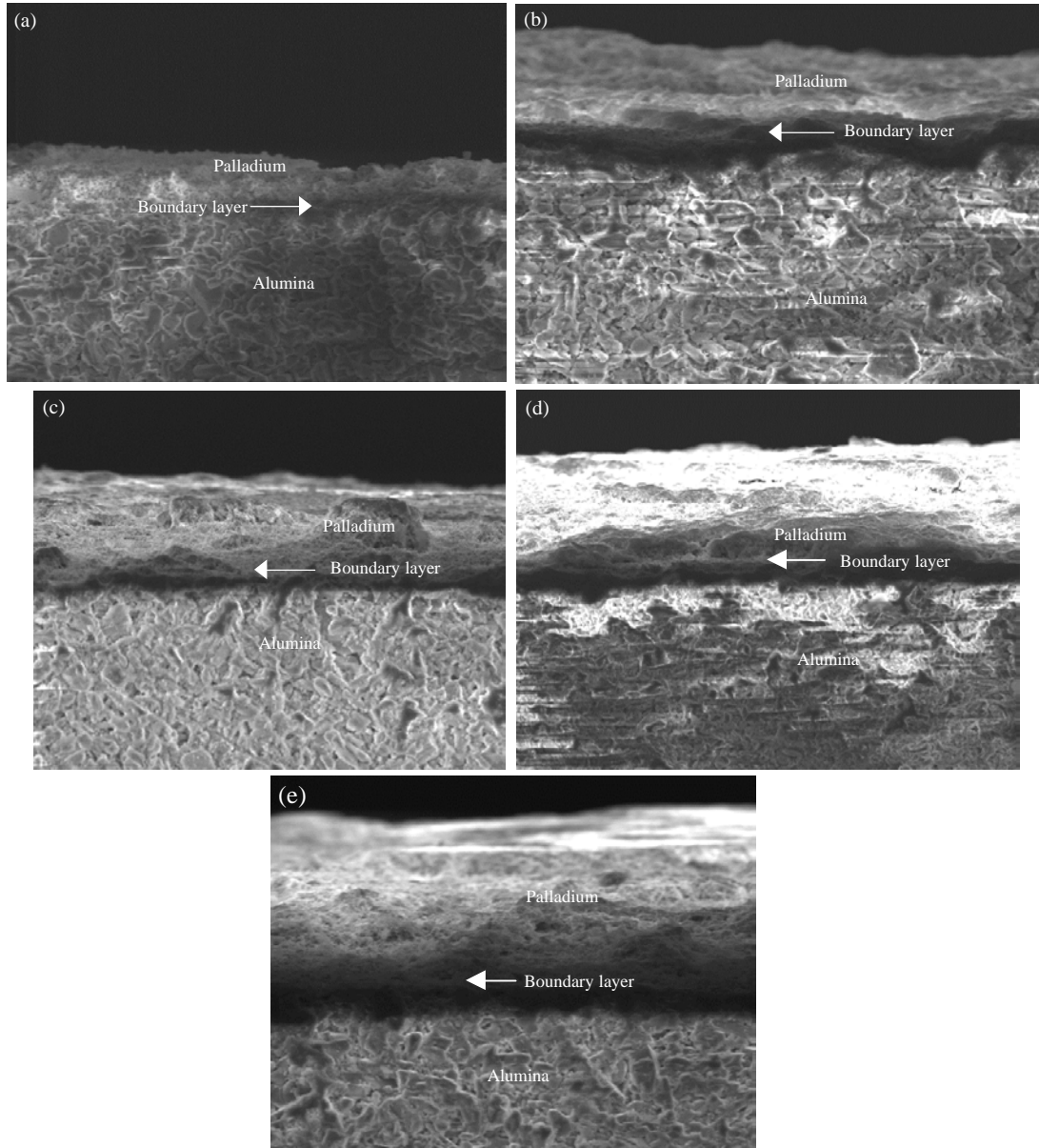


Fig. 4: SEM micrographs of the alumina ceramic membrane morphology with palladium coating after: (a) First, (b) second, (c) third, (d) fourth and (e) fifth plating

dissolution of surface atomic hydrogen in the bulk layers of the metal and (3) diffusion of atomic hydrogen through the bulk metal. Hydrogen permeates through dense palladium membrane via the atomic diffusion mechanism (Kikuchi, 1997). Therefore, the rate of hydrogen permeation can be expressed as a function of the difference in the square root of hydrogen partial pressures (Kikuchi, 1997). Thus the rate of hydrogen permeation J can be expressed as:

$$J_H = \frac{QA}{d} (P_{Re\ lentsile}^{0.5} - P_{Permeate}^{0.5}) \quad (1)$$

where, Q is the permeation coefficient, A is the cross sectional area d is the thickness of the membrane, p_1 and p_2 are the hydrogen partial pressure in upstream and downstream.

Figure 5 shows the influence of partial pressure difference on the hydrogen permeation flux at a

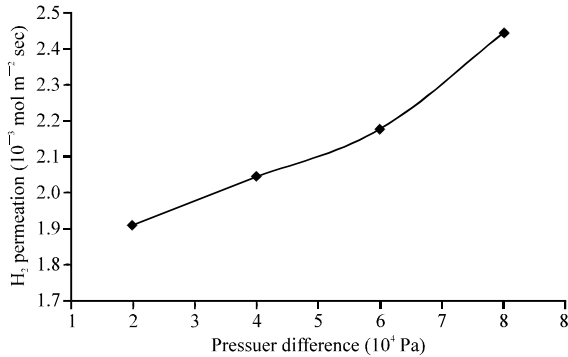


Fig. 5: Hydrogen flux of palladium-alumina membrane at 300°C with pressure difference 2×10^4 - 8×10^4 Pa

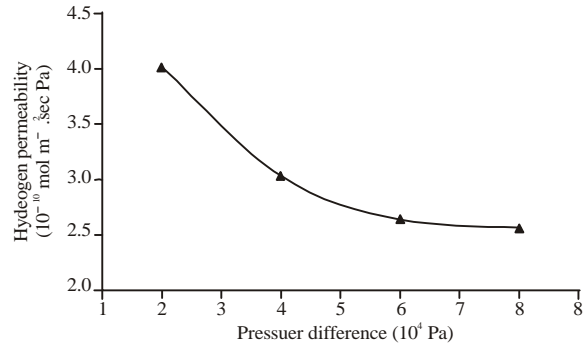


Fig. 7: Hydrogen Permeability at 300°C with pressure difference 2×10^4 - 8×10^4 Pa

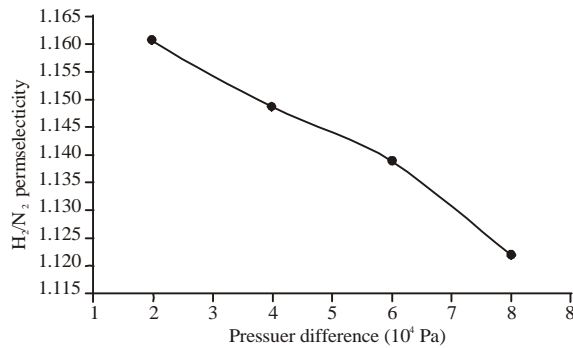


Fig. 6: H₂/N₂ permselectivity at 300°C with pressure difference 2×10^4 - 8×10^4 Pa

temperature of 300°C. It can be observed from the figure that, the hydrogen permeation flux of palladium-alumina membrane increased with increasing the pressure difference. Hydrogen flux for single gas is influenced by the atomic hydrogen diffusion because of support diffusion resistance limitation. The atomic hydrogen diffusion is pressure function. Therefore, an increased the square root of pressure lead to an increased of hydrogen flux, it follows Sieverts law (Eq. 1).

The hydrogen permselectivity profiles at pressure difference are illustrated in Fig. 6. The hydrogen permselectivity over the composite palladium membrane increases sharply with decreasing pressure difference. This result suggests a primarily solution diffusion mechanism for hydrogen gas on this membrane.

Permeability is defined as gas permeation flux over the average pressure difference across the membrane. In the case of macropores, the mechanism of gas transport through the membrane is viscous flow and/or Knudsen flow. If viscous flow is involved, permeability will be expected to increase with pressure (Chang *et al.*, 2002). Membranes with cracks exhibited such behavior. Gas permeation through mesopores, on the other hand, occurs

primarily by Knudsen diffusion and in this case, gas permeability has been shown to be independent of pressure drop (Chang *et al.*, 2002). For this study, the calculated results of permeability at various pressure differences across the membrane are given in Fig. 7. Hydrogen permeability at 300°C of operation condition is decreased with the increasing of pressure difference. The permeability was independent of pressure difference, indicating an absence of viscous flow contribution to gas transport.

CONCLUSIONS

By using α -Alumina membrane ceramic tube as the support, a composite membrane of a palladium-alumina membrane tube was synthesized by sol-gel and electroless plating techniques. Hydrogen permeation and hydrogen permselectivity of palladium-alumina membrane was measured by varying pressure difference. The hydrogen flux of the membrane increased significantly with the increasing of pressure difference. The hydrogen permselectivity and permeability of the membrane increased significantly with the decreasing of pressure difference.

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