Morphology of one-time coated palladium-alumina composite membrane prepared by sol-gel process and electroless plating technique

R Sari\textsuperscript{1,3}, R Dewi\textsuperscript{1}, Pardi\textsuperscript{1}, L Hakim\textsuperscript{2} and S Diana\textsuperscript{1}

\textsuperscript{1}Lhokseumawe State Polytechnic, 24301 Lhokseumawe, North Aceh, Indonesia
\textsuperscript{2}Malikussaleh University, 141 Reuleut, North Aceh, Indonesia

E-mail: ratnasari@pnl.ac.id

Abstract. Palladium coated porous alumina ceramic membrane tube was obtained using a combination of sol-gel process and electroless plating technique. The thickness, structure and composition of palladium-alumina composite membrane were analyzed by transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), and atomic force microscopy (AFM). Palladium particle size was 6.18 to 7.64 nm. Palladium membrane with thickness of approximately 301.5 to 815.1 nm was formed at the outer surface of the alumina layer. EDX data confirmed the formation of palladium-alumina membrane containing 45% of palladium. From this research it shows the combination of sol-gel process and electroless plating technique with one-time coating can produce a homogeneous and smoother palladium nano layer film on alumina substrate.

1. Introduction
Demand for hydrogen based fuels has increased due to the depletion of fossil fuel reserves and the large emission of greenhouse gas. The usage of hydrogen as a commodity feedstock for chemical, petrochemical and metallurgical process is well known. Hydrogen has gained interest as a clean alternative energy due to the recent and rapid advancement of fuel cells and internal combustion engines. Membrane technology has started to be applied for hydrogen separation in the recent years [1].

The membrane-based separation technique has received a considerable attention in petrochemical, pharmaceutical, food and biotechnology areas [2]. Energy saving and reduction in initial capital investment are the two main reasons for the preference for membrane separation rather than conventional separation processes, e.g. adsorption, absorption, distillation, etc.

Metal composite membranes are expected to play a key role in hydrogen separation. Palladium (Pd) based composite membranes have gained in importance in recent years due to their increased hydrogen permeation rates. Pd-based composite porous membranes consist of a thin dense layer of Pd or a Pd alloy on a porous support in the form of tubes or discs of porous glass, ceramics or stainless steel [3].\textsuperscript{3}

One of the deposition techniques frequently applied on ceramic materials is dip coating. Because of its simple procedure, sol-gel process to produce thin film has grown rapidly [4]. It consists of a

\textsuperscript{3} To whom any correspondence should be addressed.
substrate removal, where solid film from condensation reaction is deposited from the fluid sol by drainage and evaporation. Dip coating process produced a good and flexible powder form dispersion (sol) which can improve the characteristic of the support [5].

Electroless plating is a method for metallic films plating on a support involving redox reaction. Grain growth in Pd forms a film, in which the microstructure has an important effect on the membrane morphology. The desired morphological aspects are compactness and equal growth of the deposits in perpendicular and lateral direction to the surface of substrate [6]. Deposition of Pd and Pd alloy membranes on porous substrates by electroless plating technique has been popularly used with its good coating ability and the simplicity of experimental. Sari [7] reported that a Pd membrane synthesized with plating time of 7 hours formed a smooth and thick layer of Pd 7.146 µm.

2. Methodology/ Experimental

2.1. Materials
α-Alumina membrane tube with an outer diameter, length, thickness and pore size of 1 cm, 8 cm, 0.2 cm and 100 nm respectively is used. The chemical substances used in the sol solutions were aluminum nitrate nonahydrate (98%, Fluka), nitric acid (65% Merck), butanol and hydrochloric acid (37%, Merck). The sensitization solution was tin (II) chloride (Sigma-Aldrich) and hydrochloric acid (37%, Merck). The activation solution was Pd chloride (59.9%, Merck) and hydrochloric acid (37%, Merck). The electroless plating solution consisted of Pd chloride (59.9%, Merck), sodium phosphinate monohydrate (Merck), ethylene dinitrilo tetraacetic acid (Merck), and ammonium hydroxide (28%, Sigma-Aldrich).

2.2. Preparation of Pd Coated Alumina Ceramic Composite Membrane
Prior to sol-gel process, the α-Alumina membrane tube was cleaned by sequential washing with natrium hydroxide, deionized water, isopropanol and followed with drying at 120°C for 1 day to remove any traces of hydrocarbon existing in the membrane pores that might cause non-uniform coating. The preparation of Pd coated alumina ceramic composite membrane involves two steps. First, aluminium nitrate nonahydrate, nitric acid, and polyvinyl alcohol were added into deionized water and temperature was maintained at 80-90°C. Then, they were refluxed with stirring at 80-90°C for 24 hours to get a homogenous mixture for immersion process to the α-Alumina membrane for 2 hours for plating. After that it was dried at room temperature for 24 hours. Finally, it was calcined at 600°C for 3 hours. In a separate beaker, Pd chloride was dissolved in hot deionized water and hydrochloric acid. The addition of hydrochloric acid is expected to increase Pd chloride solubility. The membrane from the step above was immersed into the sensitization solution, SnCl₂ (1 g/L) and HCl (1 mL/L) for 2 minutes, and washed with deionized water for 30 s; it was then immersed into the activation solution, PdCl₂ (0.09 g/L) and HCl (1 mL/L) for another 2 minutes. Then, it was washed with deionized water for 30 s. This cycle was repeated for five times. Second, the electroless plating solution consisted of PdCl₂, NH₄OH, EDTA, and NaPO₃H₂ was used for plating process, carried out at room temperature for 1 hour without repetition. The ceramic membrane with a layer of Pd coating was then heated overnight at 373 K and stored in the desiccator to protect it from ambient humidity.

2.3. Characterization
Transmission electron microscope (TEM) (Philips CM12) was used to observe the shape and size of the palladium particles while the atomic force microscope (AFM) image for membrane morphology was analysed with AFM Ntegra Prima NT-MDT. The cross-sectional image, thickness and morphology of Pd composite membrane were analysed using a scanning electron microscope (SEM, LEO 1450VP Zeiss) coupled with the energy-dispersive X-ray (EDX) spectrometer. Pd-alumina membrane was broken into pieces for its characterization.
3. Results and Discussion
The substrate material employed in this research is macroporous asymmetric alumina. Figure 1 (a) shows the SEM image of the porous α-alumina surface. It can be seen that the surface is rough and heterogeneous. The macro particles were irregular with large pores size. Figure 1 (b) shows a micrograph from AFM for alumina surface. The alumina has an average pore of size 0.023 to 0.513 μm, consists of small grains with mean diameter of 40.54 to 717.6 nm. It can be observed from Figure 1 (c) that the average roughness of the alumina support was 84.129 nm.

![Figure 1. Surface micrograph of the α-alumina by (a) SEM and (b,c) AFM](image-url)
Figure 2. Transmission electron microscopy (TEM) image of Pd particles
Fine and homogeneous Pd particles from electroless plating is obtained as shown in Figure 2. From contacts between Pd particles with alumina depict structure of Pd-alumina composite membrane where Pd particles were observed as black small dots on the brighter alumina support. Pd particles were observed as black small dots on the brighter alumina support. These images reveal Pd particles to be well dispersed on the surface of alumina supports. The Pd particles are spherical in shape with diameters ranging from 6.18 to 7.64 nm. After plating process, the top surface of membrane shows a uniform film (Figure 3a). The substrate dipped into the plating bath had large activated surface area. When the surface area was occupied by samples, a big number of Pd particles was observed in the plating process and they continuously attached to each other on the surface and pores of alumina. α-alumina has been completely covered by a compact layer of Pd. The Pd-alumina is black. Pd adheres well onto the alumina substrate. Range of Pd film thickness were between 301.5 and 815.1 nm. The deposited Pd displays irregular surface as a result of rough alumina support. The thicker part of Pd film indicates the areas where they penetrated α-alumina pores. The adhesion strength between Pd layer and porous ceramic alumina surface is dependant on mechanical bonding strength [9]. This was consistent with the results reported by Zheng [8] and Li [3]. Pd-alumina has an average pore size of 0.017 to 0.119 μm, consists of small grains with mean diameter of 12.61 to 539.1 nm (Figure 3b). The average roughness of the Pd-alumina support was 43.686 nm (Figure 3c).

The EDX spectrum of the Pd-alumina membrane surface detected Pd along with Al and O (Figure 4). The result obtained by EDX data confirmed the formation of Pd-alumina membrane containing 45% of Pd. The oxygen peak observed on the film membrane validated the formation of an oxide layer. A monolayer of oxygen is adsorbed rapidly at room temperature by dissociative adsorption of oxygen on Pd. Guo [10] also reported similar trend for Pd plating on α-alumina support.

### 4. Conclusion

A uniform thin Pd film on α-alumina substrate was fabricated by a combination of sol-gel process and electroless plating technique. The morphology of palladium film was a microstructure, smoother, finer and more uniform. The EDX profile of palladium-alumina membrane indicates that other elements (Al and O) except Pd were present in this membrane. The composite Pd-alumina membrane exhibit excellent adherence between Pd layer and the alumina support.
Acknowledgement
The authors gratefully acknowledge the support for this work by Ministry of Research Technology and Higher Education, Indonesia in Hibah Fundamental grant.

References

[1] H. Lu, L. Zhu, W. Wang, W. Yang and J. Tong 2015 Int. J. Hydrogen Energy 40, 3548-3556
[2] D. Alique, M. Imperatore, R. Sanz, J. A. Calles and M. Giacinti Baschetti 2016 Int. J. Hydrogen Energy 41, 18901-19498
[3] Y. Li, W. Ding, X. Jin, J. Yu, X. Hu and Y. Huang, Int. J. Hydrogen Energy 40, 3528-3557 (2015).
[4] A. L. Ahmad and N. N. N. Mustafa 2007 Int. J. Hydrogen Energy 32, 2010-2021
[5] A. Bottino, M. Broglia, G. Capannelli, A. Comite, P. Pinacci, M. Scrignary and F. Azzurri 2014 Int. J. Hydrogen Energy 39, 4717-4724
[6] S. K. Ryi, N. Xu, A. Li, C. J. Lim and J. R. Grace 2010 Int. J. Hydrogen Energy 35, 2328-2335
[7] R. Sari, Z. Yaakob, M. Ismail, W. R. W. Daud and L. Hakim 2013 Ceram. Int. 39, 3211-3219
[8] L. Zheng, H. Li and H. Xu 2016 Int. J. Hydrogen Energy 41, 1002-1009
[9] S. Yun and S. T. Oyama 2011 J. Membr. Sci. 375, 28-45
[10] Y. Guo, Y. Jin, H. Wu, L. Zhou, Q. Chen, X. Zhang, X. Li 2014 Int. J. Hydrogen Energy 39, 21044-21052