Preparation and characterization of Pd$_{93}$Cu$_{7}$/Al$_2$O$_3$ composite membrane for hydrogen permeation

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Abstract. In this work, an electroless plating technique was used to prepare Pd-Cu coated ceramic alumina membranes tube. The composition, surface morphology and cross-section of the Pd$_{93}$Cu$_{7}$/Al$_2$O$_3$ membrane is investigated by energy-dispersive spectrometry (EDS), and scanning electron microscopy (SEM). Hydrogen permeation and selectivity across a membrane is measured using pressure difference (1.05-1.5) at a temperature range (573-773 K). The reported membrane obtained a high flux of 3.4 mol H$_2$/ms at a temperature of 723 K, while the selectivity is above 75 for H$_2$/N$_2$.

1. Introduction

Industrial fossil fuels have developed since crude oil was discovered in the 19th century and is growing rapidly until now. The use of crude oil in the industry and daily use for more than 100 years has had a negative effect on human health and the environment. However, the need for fossil fuels is expected to continue to increase in the future along with the addition of energy use and the need for human living standards. The use of sustainable fossil fuels will cause the quantity of CO2 gas to continue to increase in the atmosphere, causing the temperature to warm up and the occurrence of global warming. At present, the problem of diminishing world fossil fuel sources is mounting, and this lack of fuel sources will cause prices to rise suddenly. The price of fuel is related to the level of economic growth, which if the price of fuel increases, the price of most goods will also increase. This causes inflation and the economic level will not develop [1].

Even though now hydrogen production can only contribute 3% of the basic needs of energy, hydrogen is believed to be emerging as an alternative energy source in the future. There is no effect of pollution resulting from the combustion process causing hydrogen to be the best choice. The final scenario for using hydrogen is that this hydrogen material will be produced from renewable energy sources [2].

Generally, the results of the hydrogen formation reaction contain by-products such as CO$_2$, CO and CH$_4$ gases. Separation using membranes that have high flux and selectivity in membrane reactors is needed to get hydrogen free of CO. There are three types of dense membranes that may be used at high temperatures, such as ceramic membranes, ceramic-metal membranes (cermets) and metal membranes. Ceramics membranes and cermet membranes have low hydrogen permeability and are still under investigation. Metal membranes for hydrogen separation are like palladium (Pd) and non-Pd membranes. Non-Pd (Nb, V, Ta, and its mixture) metal membranes have higher permeability compared to Pd membrane at temperatures around 0-700°C. But the surface obstacles of these metals to hydrogen permeation are greater than palladium. The tendency of these metals to fragility caused by hydrogen is also high. Indeed, the amount of Nb must operate at temperatures exceeding 420°C and Ta at temperatures exceeding 350°C. In addition, the permeation efficiency has also decreased with time.
Therefore, Nb and Ta can only be used as an alternative support for Pd. On the other hand, Pd or Pd alloy membranes are found to be not easily broken, have oxidation resistance, thermal stability and catalytic activities for hydrogen dissociation and association. Therefore, Pd or Pd alloy membranes are widely used for the production and separation of hydrogen in membrane reactors [3]. Hydrogen separation results using pure Pd membrane have a higher purity, but the permeability is lower compared to hydrogen resulting from separation using a Pd alloy membrane [4,5]. This is due to carbon compounds can be absorbed strongly on the surface of the Pd membrane competing with hydrogen while sulfur compounds can cover the location of hydrogen to dissociate and cause the formation of Pd-sulfide so that hydrogen permeability is lower [6].

Fabricate Pd-Cu composite membrane have been studied through many deposition techniques. Electroless plating is a wet deposition technique. The simplicity of experimental, good coating ability, compactness and equal growth of the deposits in perpendicular and lateral direction to the surface of substrate are advantages of this technique. The publication by Ryi et al. [7] explained the permeation test of 7 μm thick Pd₉₃Cu₇ membrane at a temperature of 673 and 773 K. Hydrogen flux reached 2.8 x 10⁻¹ mol m⁻² s⁻¹. Peters et al. [8] varied the composition of Cu 5.8-52.6% in synthesizing 2 μm thick Pd-Cu binary membranes and tested it at a temperature of 573-673 K. The Pd mixture with Cu caused the permeability value of hydrogen to decrease at an increased Cu concentration. This is due to the formation of the BCC structure (body center cubic). To address this problem, we investigate Pd-Cu composite membrane prepared by electroless plating technique and demonstrated that the composition of Cu below 10% can effectively increase the hydrogen permeability.

2. Experimental Procedure

2.1. Materials

The material used for membranes support is α-alumina with an outer diameter of 1 cm, 10 cm long, 0.2 cm thick and 100 nm pore size. The chemicals for membranes washing used were sodium hydroxide (Sigma-Aldrich) and isopropanol (Sigma-Aldrich). Stanum chloride (Sigma-Aldrich) and hydrochloric acid (Merck 37%) are chemicals used for the manufacture of sensitizing solutions. The activation solution used consisted of palladium chloride (Aldrich 99.9%) and hydrochloric acid (Merck 37%). The solution used for electroless plating process contained palladium chloride (Aldrich 99.9%), cuprum nitrate (Sigma-Aldrich), anhydrous sodium hypopospit (Sigma-Aldrich), tetraasetic ethylene diamine acid (Sigma), formaldehyde (Merck 37%) and ammonium hydroxide (Sigma-Aldrich 28%). Hydrogen is used to reduce membranes and to determine permeation through membranes while nitrogen is used as a purge gas and to permeate through membranes.

2.2. Membrane preparation

Synthesis of Pd-Cu/alumina composite membranes was carried out through several stages, namely cleaning the membranes, sensitizing and activating the membrane and coating by the electroless plating method. Membrane cleaning was carried out using sodium hydroxide solution, deionized water and isopropanol in an ultrasonic bath. Then the membrane is dried in an oven to remove all cleaning agents in the membrane pore. After that, the membrane is dipped in a sensitization solution consisting of SnCl₂ and HCl, then washed with deionized water. The membrane was then dipped into the activation solution of PdCl₂ and HCl. The membrane is washed again with deionized water. This process is repeated to produce sufficient Pd nucleus on the surface of the membrane support before the electroless plating process is carried out [9]. This process is carried out also for the activation of CuNO₃. Electroless plating Pd solution (Table 1) used was obtained from mixing PdCl₂ with HCl, then dissolved in deionized water. In a separate container, NH₄OH is mixed with EDTA and added with a mixture of NaPO₃H with deionized water, then the mixture is stabilized for several hours. The membrane is dipped into the mixture without heating. The electroless plating process is carried out at room temperature, alkaline pH with constant rotation speed. The membrane is washed with hot deionized water and heated in an oven.
The electroless plating process was repeated for Cu(NO$_3$)$_3$ plating solution (Table 2). Gas permeation tests were done using a single gas of hydrogen and nitrogen. Membrane placed in a module of the permeator and its temperature was controlled by G furnace.

Table 1. Pd electroless plating solution.

| Component       | Composition |
|-----------------|-------------|
| PdCl$_2$        | 0.27 wt %   |
| NH$_4$OH (28%)  | 58.5 mL     |
| NaPO$_3$H$_2$   | 0.02 wt %   |
| EDTA            | 5.25 g      |

Table 2. Cu electroless plating solution.

| Component       | Composition |
|-----------------|-------------|
| Cu(NO$_3$)$_3$  | 8.7 wt %    |
| NaOH            | 8.7 wt %    |
| Formaldehyde    | 2.6 mL      |
| EDTA            | 0.5%        |

2.3. Characterization

The cross-sectional image, thickness and morphology of Pd-Cu composite membrane were analyzed using a scanning electron microscope (SEM, HITACHI SU-3500) coupled with the energy-dispersive X-ray (EDX, HORIBA) spectrometer. Pd-Cu/alumina membrane was broken into pieces for its characterization.

2.4. Hydrogen permeation test unit

The gas permeation tests were carried out at a temperature of 573 K and a range of pressures (1.08–1.38 bar). The gas flow rate was 137 mL min$^{-1}$. The effective area of the membrane for permeation was 9.42 cm$^2$. The permeated gas flow rates were measured using a digital flow meter (Agilent technologies ADM2000) at a constant temperature with pressure difference across the membrane. Membranes were characterized by conducting permeation experiments with hydrogen and nitrogen.

3. Results and Discussion

3.1. Thickness and morphology membrane

Figure 1 illustrates the morphology Pd-Cu/alumina composite ceramic membrane. These images show the structure of Pd-Cu films. The distribution of grain size can be seen in all images. All film surfaces have morphology such as cabbage flowers where the smallest grains form aggregates into larger grain shapes.

Figure 2 shows the cross-sectional micrograph of the Pd-Cu/alumina membrane. Both membranes displayed unclean interface between layers which is expected because of the very short plating time of electroless plating solution. The Pd and Cu metal contents in alumina pore decrease across the depth.

The EDX spectrum of the Pd-Cu/alumina membrane surface detected Pd and Cu along with Al and O (Figure 3). The result obtained by EDX data confirmed the formation of Pd-Cu/alumina membrane containing 93% of Pd and 7% of Cu. 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-Cu.
3.2. **Hydrogen Permeation**

The rate of hydrogen permeation ‘\( J \)’ can be expressed as:

\[
J = \frac{Q}{d} \left( P_1^n \text{retentate} - P_2^n \text{permeate} \right)
\]

where \( Q \) is the hydrogen permeability (mol m\(^{-1}\) s\(^{-1}\) bar\(^n\)), \( d \) is the thickness of the membrane (m), \( P_1 \) and \( P_2 \) are the hydrogen partial pressure in the retentive and permeate (bar), and \( n \) is the pressure dependence factor (0.5-1). Figure 4 shows the influence of pressure on the hydrogen permeation flux at a temperature range of 573-773 K. It can be observed from the Fig. 4 that the increase of pressure will lead to the improvement of surface rate on the feed side and then the surface resistance will become less significant compared to the bulk diffusion in the metal layer. Therefore, according to Sieverts’ law, hydrogen permeation increased with increasing reaction pressure. This observation is supported by similar findings from Ryi et al. [7] for Pd-Cu/alumina with thickness 7 μm, the hydrogen flux was 0.21 mol m\(^2\) s\(^{-1}\).

\( \text{N}_2 \) permeation tests were performed in order to check the presence of any defect in the Pd-Cu layer. The ideal \( \text{H}_2/\text{N}_2 \) selectivity, defined as the ratio of the hydrogen flux to nitrogen can be expressed as follows:

\[
\alpha_{\text{H}_2/\text{N}_2} = \frac{J_{\text{H}_2}}{J_{\text{N}_2}}
\]

Ten data were taken and the \( \text{H}_2/\text{N}_2 \) selectivity was plotted as a function of the difference between the pressure in the retentive and permeate sides at temperature range 573-773 K (Figure 5). Data obtained
for Pd-Cu/alumina membrane indicated that the ideal \( \frac{H_2}{N_2} \) selectivity (\( \alpha_{H_2/N_2} \)) decreases with increasing pressure difference. This can be explained by following equations that assume the existence of defects through which Knudsen diffusion happens. The total hydrogen flux is sum of fluxes through the Pd-Cu membrane and defects:

\[
F_{H_2}^T = J_{H_2} + F_{H_2}^K
\]

where \( J_{H_2} \) is the hydrogen flux through a defect-free Pd-Cu/alumina membrane given by Eq. (1) and \( F_{H_2}^K \) is the Knudsen diffusion flux of hydrogen, both hydrogen and nitrogen diffuse through defects are given by:

\[
F_i^K = \frac{D_i^K}{RTL} \Delta P
\]

where \( D_i^K \) is Knudsen diffusivity, \( T \) the temperature, and \( L \) is thickness of the membrane. Equation (2) can be written as:

\[
\alpha_{H_2/N_2} = \frac{F_{H_2}^T}{F_{N_2}^T} = \frac{F_{H_2}^K + J_{H_2}}{F_{N_2}^K}
\]

The ratio of the hydrogen and nitrogen Knudsen fluxes is given by:

\[
\frac{F_{H_2}^K}{F_{N_2}^K} = \sqrt{\frac{M_{N_2}}{M_{H_2}}} = 3.74
\]

where \( M \) is the molecular weight of gas. The expression for \( \alpha_{H_2/N_2} \) can then be re-expressed as:

\[
\alpha_{H_2/N_2} = 3.74 + \frac{QRTL \Delta P^{0.5}}{dD_{N_2}^K \Delta P}
\]

It is noted from Eq. (7) that the nitrogen flux is proportional to \( \Delta P \) whereas the hydrogen flux is proportional to \( \Delta P^{0.5} \). The nitrogen flux increases at a faster rate than that hydrogen flux, and as a result, the ideal \( \frac{H_2}{N_2} \) selectivity (\( \alpha_{H_2/N_2} \)) decreases with increasing pressure difference. According to Ke Zhang et al. [5], leak development in fresh Pd-Cu composite membranes that the Pd-Cu layer deposited by the electroless deposition method will always, and in an inherent manner, occur at temperatures higher than 673-723 K. Results of \( \frac{H_2}{N_2} \) selectivity done by Islam et al. at 523-823 K with thickness 16.73 μm were 15-89 [10].

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Figure 4. Hydrogen Permeation versus pressure

Figure 5. \( \frac{H_2}{N_2} \) selectivity for different pressure
4. Conclusion
The manufacturing, characterization, and hydrogen permeation properties of approximately 15 µm membrane are reported. Film surface of Pd$_{93}$Cu$_7$/Al$_2$O$_3$ membrane has morphology such as cabbage flowers. EDX data confirmed the formation of Pd-Cu/alumina membrane. Increasing pressure and temperature had a positive effect on the hydrogen permeation. The highest hydrogen flux of Pd$_{93}$Cu$_7$/Al$_2$O$_3$ in this work was 0,34 mol m$^{-2}$ s$^{-1}$ with H$_2$/N$_2$ selectivity of 260 at 773 K.

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