Hydrogen Permeation of Pd-Cu/Alumina Composite Membranes Fabricated by Combined Sol-gel and Less-electric Plating Technique

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Abstract. The demand for purified hydrogen (CO < 10 ppm) has led to the development of the use of a dense Pd or Pd alloy membrane which selectively permeates the only hydrogen to produce ultra-pure hydrogen. In this work, a combined sol-gel process and a less-electric plating technique were used to prepare Pd-Cu coated ceramic alumina membranes tube. Scanning electron microscopy (SEM) and energy-dispersive X-ray(EDX) were used to characterize the membranes. Permeation tests hydrogen and nitrogen single gas were performed in a temperature range 300-500°C and with pressure range 1.08-1.38 atm. It is found that the highest hydrogen flux of 1.3 mol m⁻² s⁻¹ was obtained at temperature 500°C and pressure difference 0.38 atm. The highest H₂/N₂ selectivity of 105 was obtained at temperature 500°C and pressure difference 0.08 atm.

1. Introduction

As green energy, hydrogen plays an important role in recent years. The use of this fuel will reduce CO₂ emissions and problems related to global warming. During this time commercial hydrogen production is produced from natural gas or methane (CH₄) from fossils. As it is known that these energy sources are energy that cannot be renewed so that their availability is increasingly limited [1].

The membrane reactor is a combination of devices that combine the process of separation and chemical reactions in the same unit. Membrane reactors represent reactor configurations that incorporate membranes as part of the system for separation or purification. This technology combines the selectivity properties of membranes with chemical reactions. The unity of the two operating units provides advantages not only to the easier and cheaper systems, but also the improved product quality [2].

Currently, hydrogen separation using metal membranes is generally focused on the use of pure Pd and Pd alloy membranes. Both membranes could separate large amounts of hydrogen at a wide temperature range, not easily broken, resistant to oxidation processes, and have stability to heat. Hydrogen separation results using a pure Pd membrane that has a higher purity, but the permeability is lower compared to hydrogen resulting from separation using a Pd alloy membrane [3,4]. This is due to carbon compounds that 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 [5].

Fabricate Pd-Cu composite membrane has been studied through many deposition techniques. Sol-gel process and less-electric plating are wet deposition techniques. The simplicity of experimental, good coating ability, compactness and equal growth of the deposits in perpendicular and lateral direction to the surface of a substrate are advantages of these techniques. The publication by Li et al. [6] explained the permeation test of 7μm thick Pd0.7Cu7 membrane at a temperature of 673 and 773 K. Hydrogen flux reached 2.8 x 10^4 mol m^-2 s^-1. Peters et al. [7] varied the composition of Cu 5.8-52.6% in synthesizing 2μm 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 membranes prepared by the sol-gel process and the less-electric plating technique by varying the plating time and demonstrated that the composition of Cu below 5% can effectively increase the permeability of Pd-Cu membranes.

2. Methodology/Experimental

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). Pro-analytical chemicals were used for the preparation of sol solutions, namely aluminum nitrate nonahydrate (98% Fluka), nitric acid (Merck 65%), and polyvinyl alcohol (Merck 98%). 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 the less-electric plating process contained palladium chloride (Aldrich 99.9%), cuprum nitrate (Sigma-Aldrich), anhydrous sodium hypophosphate (Sigma-Aldrich), tetraacetic ethylene diamine acid (Sigma) 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 also to permeate through membranes.

2.2. Preparation of Pd Coated Alumina Ceramic Composite Membrane

Synthesis of Pd-Cu/alumina composite membranes was carried out through several stages, namely cleaning the membranes, sol-gel process, sensitizing and activating the membrane and coating by a less-electric 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. The sol-gel solution consisted of aluminum nitrate nonahydrate, nitric acid and polyvinyl alcohol mixed with a magnetic stirrer and heated under reflux conditions. The alumina membrane is dipped in the sol solution. Membranes are dried and calcined at 600°C for 3 hours. After the sol-gel process, 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 less-electric plating process is carried out. This process is carried out also for the activation of CuNO3. Less-electric plating Pd solution 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 NaPO4H with deionized water, then the mixture is stabilized for several hours. The membrane is dipped into the mixture without heating. The less-electric 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 less-electric plating process was repeated for the CuNO3 plating...
solution. For gas permeation tests using a single gas of hydrogen and nitrogen. The membrane placed in a module of the permeator and its temperature was controlled by a furnace.

2.3. Characterization

The cross-sectional image, thickness, and morphology of the 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.

![Image](a) ![Image](b)

**Figure 1.** Surface micrograph of the Pd-Cu/alumina membranes by plating time (a) 1 hand (b) 2 h

Figure 2 shows the cross-sectional micrograph of the Pd-Cu/alumina membranes. Both membranes displayed a clean interface between layers which is expected because of the very short plating time of sol and less-electric plating solution. The Pd and Cu metal contents in alumina pore decrease across the depth. The small gamma-alumina membrane precursor particles penetrated into the pores of the alpha-alumina support but not enough time to make the separating layer.

3. Results and Discussion

Figure 1 describes the morphology of the surface of the Pd-Cu/alumina composite membranes. Pd and Cu are spherically shaped and coated on the surface of alumina to form a Pd-Cu film layer. Small particles are coated between large particles to minimize the formation of defects. After Pd-Cu is coated on the surface of alumina, a pinhole is still visible in Pd-Cu film, especially film that has a short coating time. Fewer pinhole if the palladium film gets thicker due to the Pd-Cu particles sticking over the holes in the home's door.

The EDX spectrum of the Pd-Cu/alumina membrane surface detected Pd and Cu along with Al and O (Fig. 3). The result obtained by EDX data confirmed the formation of the Pd-Cu/alumina membrane containing 31% of Pd and 1% of Cu (Fig. 3.a) and 52% of Pd and 3% of Cu (Fig. 3.b). 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.
Figure 2. Cross Section of the Pd-Cu/alumina membranes by plating time (a) 1 h and (b) 2 h

Figure 3. EDX measurement on Pd-Cu/alumina membrane by plating time (a) 1 h and (b) 2 h
Figure 4. Hydrogen flux of Pd-Cu/alumina membrane by plating time (a) 1 h and (b) 2 h

Hydrogen flux profiles at different temperatures and pressures between the two Pd-Cu membranes illustrated in Fig. 4 (a and b). The increase of reaction pressure will lead to the improvement of the 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 Sievert's law, hydrogen permeation increased with increasing reaction pressure. This observation is supported by similar findings from Islam et al. [8] for Pd-Cu/alumina with a significant increase in hydrogen flux.

Fig. 5 plots selectivity H$_2$/N$_2$ versus transmembrane pressure at different temperatures. Four data were taken for each membrane and it indicated that the H$_2$/N$_2$ selectivity decreases with increasing pressure difference. The N$_2$ flux increases at a faster rate than that H$_2$ flux because of N$_2$ flux proportional to ΔP whereas the H$_2$ flux proportional to ΔP$^{0.5}$. It occurred due to these membranes is not gas-tight to nitrogen, indicating the presence of the pinholes in the Pd–Cu layer.
4. Conclusion
The thin Pd-Cu film layer on alumina has been fabricated by a combined sol-gel process and a less-electric plating technique. The EDX profile of the Pd-Cu/alumina membrane indicates that other elements (Al and O) except Pd and Cu were present in this membrane. The permeability of 31% of Pd and 1% of Cu higher than 52% of Pd and 3% of Cu film on the alumina support membrane.

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