Design and synthesis of thin palladium membranes on porous metal substrate for hydrogen extraction

Z Shi1, J A Szpunar1 and S Wu2

1Department of Materials Engineering, McGill University, M. H. Wong Building, 3610 University Street, Montreal, QC, Canada H3A 2B2
Email: jerzy.szpunar@mcgill.ca, zhongliang.shi@mail.mcgill.ca
2AH2T Inc., 225 President Kennedy Ave., PK6230, Montreal, QC, Canada H2X 3Y8

Abstract. Membrane separation is regarded nowadays as a preferred method for production of purified hydrogen. Palladium (Pd) is an attractive membrane material due to its ability to dissociate molecular hydrogen into atoms. It is usually deposited on the porous substrate that can provide good mechanical support and reduce the thickness of the membrane for maximizing hydrogen permeability. Pd membrane used for hydrogen separation must be thin enough to increase hydrogen flux and reduce cost while remaining thick enough to retain adhesion, attrition resistance and mechanical integrity during high temperature cycles. In this paper, the progress of electroless deposition of Pd around the pore area at surface of porous stainless steel was recorded and a bridge structure that was formed during the membrane deposition around the pore area of the substrate was illustrated. After that, the porous substrate was modified using micro-or nano-size metal or metal oxide particles in order to reduce pore size in the substrate surface. The experimental results obtained from hydrogen permeation through the Pd membranes having the thickness from 400 nm to 18 µm built on both modified and original porous stainless steel substrates demonstrate that these thin membranes are solid and they can be used at the temperature of 550°C and hydrogen pressure difference of 3.447x105 Pa. The proposed processing will allow optimizing the design and fabrication of thin Pd membranes on different porous substrates for hydrogen separation.

1. Introduction
Growing environmental concerns and global interest in the development of “hydrogen economy” are leading to an increased demand for hydrogen and a revival of interest in methods for separation and purification of hydrogen from gas mixtures [1]. The interaction between Pd and hydrogen has been studied extensively and applied widely in hydrogenation catalysts and chemical engineering because Pd absorbs hydrogen easily and Pd membranes have hydrogen permeability, chemical compatibility and excellent hydrogen selectivity. [2-6] So far, Pd membranes were always fabricated in the processes of electroless, electrochemical and sputtering depositions. Most efforts have been focused on how to reduce the membrane thickness for maximizing hydrogen flux and how to improve the membrane service time through alloying. [7-10] No matter what kind of process is employed, the fabricated Pd membrane should be dense enough for hydrogen extraction from a mixture of gases. For this reason, the preparation of an ultra-thin and pin-hole free Pd membrane may attract novel engineering applications. As we know, the mechanism of hydrogen permeation through a Pd membrane involves dissociative adsorption and recombinative desorption at the surface, as well as diffusion through the membrane. The flux of hydrogen permeating through the membrane is mainly dependent on the membrane thickness. So far, there was no report showing how a membrane was built on porous area of a substrate and how the membrane could be controlled through the deposition process. These questions will be answered in this paper. The purposes of this paper will demonstrate how a Pd membrane forms on a porous stainless steel substrate, and answer the question why the membrane is

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1 To whom any correspondence should be addressed: zhongliang.shi@mail.mcgill.ca
dense and how an ultra-thin Pd membrane can be designed and fabricated using an electroless deposition process.

2. Experimental

A 0.2 µm grade porous 316L stainless steel plate, purchased from Mott Metallurgical Corporation, was used as a substrate to support Pd membrane. The samples used have the sizes of 20 mm x 20 mm or φ 45 mm. These small size substrate samples were used to investigate the microstructure of Pd deposits in the initial stages of deposition and at different concentration of PdCl₂ in the plating baths. The bigger size substrate samples were used to deposit Pd membranes for hydrogen permeation tests. The substrates were cleaned in an ultrasonic bath with acetone for 15 min. One-side surfaces in some bigger porous substrate samples were soaked using micro- or nanosize metal or metal oxide powders (such as Ni, Al₂O₃ or V₂O₅ nano powders) and modified to be smooth in order to be built ultra-thin Pd membranes on them, as shown in Figure 1. Figure 1 (a) shows the original surface of the porous stainless steel substrate. The pore size measured on the substrate surface was in the range of 0.2~10 µm. Figures 1 (b-f) illustrate the microstructures of the substrate surface after soaking in nano size powder fluid and sintering at elevated temperature. The micrographs presented in Figures 1 (b-d) illustrate modified surface of the substrate with nanosize Ni powders (60 nm) before and after sintering at the temperature of 600°C for 2 hrs. The similar micrographs are shown in Figures 1(e, f), where substrates were treated using nanosize Ni powders (60 nm) and α-Al₂O₃ (50 nm) (the volume ratio 1:1) and sintered at the temperature of 600°C for 2 hrs. It can be seen that the pores at the substrate surfaces are fully filled and the surfaces become smooth. These surfaces were activated by an acid and rinsed with deionized water. After such treatments, the substrate samples were transferred immediately into the electroless plating baths for the deposition of Pd. The deposition time was from 30 s to 6 hrs at a constant temperature of 60°C and the baths contained different concentration of PdCl₂. The composition of the Pd plating baths using hydrazine (N₂H₄) as a reducing agent and Na₂EDTA.2H₂O as a chelating agent was described in Table 1. Microstructural characteristics of deposited Pd samples were observed and analyzed using a PHILIPS XL30 FE SEM (Field Emission Scanning Electron Microscopy) equipped with an EDS (Energy Dispersive Spectroscopy, GENESIS 2000 X-ray Microanalysis System). The gas-tightness of the membranes was examined and no leakage was detected with nitrogen gas at the pressure of 3.447x10⁵ Pa (50 psi) from room temperature to 550°C. The hydrogen permeation tests for the deposited membranes were carried out in a permeation cell at the temperature from 25°C to 550°C and hydrogen pressure difference from 1.379x10⁵ Pa to 3.447x10⁵ Pa. Hydrogen flux was measured at the temperature range from 300°C to 550°C using a
soap bubble meter. The experimental apparatus used for gas permeation tests was similar to the one described elsewhere.\textsuperscript{[11]}

Table 1. The composition of electroless plating solution and some experimental parameters

| Component or parameters | Concentration and temperature |
|-------------------------|-----------------------------|
| PdCl\(_2\)              | 1.8–2 g/l, 2.4 g/l, 3.0 g/l, 4.2 g/l |
| Na\(_2\)EDTA.2H\(_2\)O   | 40.1 g/l |
| NH\(_3\)H\(_2\)O (28%)   | 198 ml/l |
| N\(_2\)H\(_4\) (1M)      | 5.6 ml/l |
| PH                      | 10 ~ 10.4 |
| Temperature             | 60°C |

3. Results and discussion

![Figure 2. SEM micrographs showing the palladium deposits on the pore area of the substrate at different time (The deposition time: (a) 45 s, (b) 90 s, (c-e) 150 s and (f) 300 s)](image)

SEM images in Figure 2 show the Pd deposits on the pore areas at different deposition time from 45 s to 300 s. A great number of Pd nanoparticles (diameter about 100 nm) were deposited around the pore at time of 45 s as shown in Figure 2(a). With the extension of deposition time to 90 s, a Pd layer was built on the wall of the pore, as shown in Figure 2(b). Figures 2(c–e) show that network structures have already been created at some areas on the pores after the deposition time of 150 s. With increasing the deposition time to 300 s, Pd membrane almost covered completely the pore area, as illustrated in Figure 2(f). The surfaces and cross-sections of deposited membrane after the deposition time of 60 min are shown in Figure 3 (a–d). Micrographs in Figure 3(a, b) illustrate surface microstructure of the membrane after the deposition time of 60 min. The cross sections in Figure 3(c, d) clearly show how the membrane was built on the porous steel substrate. We can see that the Pd membrane is dense and relatively uniform and that the cross section is stretched across the pores of the substrate like a bridge. The thickness of the Pd membrane was about 3.5 µm.

As shown in Figures 1(b–d), the surface of porous stainless steel substrate was modified to become more flat using nanosize nickel powders (60 nm) before and after sintering at 600°C for 2 hrs. After this treatment, Pd was deposited in the plating bath with PdCl\(_2\) concentration of 1.8–2 g/l for about 20 min. The cross section images illustrate that the membrane deposited on the modified substrate was continuous and solid, as shown in Figure 3(e, f).

SEM micrographs in Figure 4 showed the Pd nanoparticles deposited on the stainless steel substrate for the same time of 150 s but for different concentration of PdCl\(_2\) in the plating baths. One can see that the Pd nanoparticles were relatively well distributed on the solid surface area (without pore area), and the particle size was varying with the concentration of PdCl\(_2\) in the plating bath. The higher the concentration of PdCl\(_2\) in the plating bath was, the smaller the Pd nanoparticles were. However, the size of Pd nanoparticles did not change much with the extension of deposition time at the same concentration of PdCl\(_2\) in the plating bath. However, the size of deposited Pd nanoparticles
for different concentration of PdCl$_2$ at the same deposition time of 150 s, as shown in Figures 4(a) and (b), has changed significantly. One can see that the size of deposited Pd nanoparticles changed from 30–50 nm to 50–70 nm when the concentration of PdCl$_2$ in the plating bath was reduced from 4.2 g/l to 3 g/l. Similar observations for the PdCl$_2$ concentrations of 2.4 g/l and 1.8–2.0 g/l demonstrate that the size of deposited Pd nanoparticles respectively increased to 70–100 nm and 100–130 nm, as shown in Figures 4(c) and (d). This experimental result is different from presented in some other reports that claimed the size of deposited nanoparticles is increasing with the deposition time. [12-15]

Figure 3. SEM micrographs showing the surface and cross-section structures of the Pd membrane deposited on the porous stainless steel substrates ((a, b) Surface microstructures of Pd membrane after the deposition of 60 min, (c, d) Cross-section of the membrane, and (e, f) Cross-section of the membrane built on modified porous steel substrate after the deposition of 20 min)

Figure 4. SEM micrographs showing Pd nanoparticles on the surface of stainless steel substrate for different concentration of PdCl$_2$ in the plating bath under the same time of 150 s (Concentration of PdCl$_2$ in the plating bath: (a) 4.2 g/l, (b) 3.0 g/l, (c) 2.4 g/l, and (d) 1.8–2 g/l)

Figure 5. SEM micrographs showing nanoparticle-monolayer membranes deposited on the substrate surface at the deposition time of 150 s (a, b) and the relationship between radius of nanoparticles and number of nanoparticle layers (c) (PdCl$_2$ concentration: (a) 2 g/l, (b) 2.4 g/l)

As demonstrated in the literature [15], in order to obtain nanosize metallic particles, a high supersaturation concentration is often required, which are best achieved when starting with highly reactive metallic species and very strong reducing agents. If the fraction of atoms consumed in the nucleation step is high, the increase in particle size due to the diffusional growth that immediately follows the nucleation burst is drastically limited and only slightly larger particles than the nuclei can be obtained. When the concentration of PdCl$_2$ in the plating baths increases, this chemical reaction is
carried out from left to right and the reduction of Pd is fast. Pd deposition and nucleation on the substrate is also fast. In the case of instantaneous nucleation on the stainless steel substrate, all the nuclei form instantaneously and subsequent growth of Pd deposits is limited. The deposited particle size is obviously small with increasing the concentration of PdCl₂ in the plating baths. Therefore, the size of Pd nanoparticles deposited on the substrate in the initial stages can be controllable through the concentration of PdCl₂ in plating bath. The formation mechanism of Pd nanoparticles deposited on the porous steel substrate and their size control are being further investigated.

\[ 2\text{Pd}[\text{NH}_3]_4^{2+} + \text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow 2\text{Pd}^0 + \text{N}_2 + 4\text{H}_2\text{O} + 8\text{NH}_3 \]  

(1)

SEM micrographs in Figures 5(a, b) showed that nanoparticle-monolayer Pd membranes made of nanoparticles were deposited on the wall of a pore area and surface of the substrate. The thickness of Pd membrane in this case in Figure 5(a) was about 100 – 130 nm which was the same as the diameter of deposited Pd nanoparticles. When the concentration of PdCl₂ in the plating bath increased to 2.4 g/l, the thickness of Pd layer decreased to 70–100 nm, as shown in Figure 5(b). One can see that the Pd nanoparticles are packed and well-organized one by one. The nanoparticle-monolayer are dense except that some small areas were not fully filled. Such monolayer membranes made of nanoparticles cannot guarantee that they are dense enough and ready for hydrogen purification. However, the membrane assembled by a few layers should be dense enough for extracting hydrogen from a mixture of gases. As illustrated in Figure 4, the size of Pd nanoparticles can be effectively controlled by the concentrations of PdCl₂ in the plating bath. Therefore, the thickness of an ultra-thin membrane built on a relatively smooth substrate can be well controlled by the electroless deposition process.

Since the Pd membrane is essentially built from the nanoparticles, one can assume that the same size Pd nanoparticles are packed in the simple geometrical arrays. The thickness of a membrane is T (nm), where n is the number of nanoparticles layer, and R is the radius of palladium nanoparticles. The relationship between T, n and R can be expressed in the equations (2) and (3).

\[ T = 2R + (n-2) \times 0.414R \]  

(2)

\[ n = \left(\frac{T}{R - 1.172}\right)/0.414 \]  

(3)

If the thickness of an ultra-thin Pd membrane is 200 nm, the layer number n, and the radius of particle is R, the relation is shown in Figure 5(c). For example, the membrane having thickness of 200 nm is approximately assembled by 45 nanoparticle-layers if the radius of nanoparticle is 10 nm. As the particle size in Figures 3(e, f) and 4(d) was about 100–130 nm and the thickness of the membrane built on modified substrate ranged from 300 nm to 400 nm, according to the equation (3), this membrane should have 9 ~ 17 nanoparticle layers. This type of membrane having the diameter of φ = 45 mm was used for hydrogen permeation tests. The tested area for hydrogen permeation at this membrane was 42 mm in diameter. The membrane was solid and dense because no leakage was detected when the gas tightness of the membrane was examined using nitrogen gas at gas pressure difference of 3.447x10⁵ Pa. This test was carried from room temperature to 550°C. The membrane thickness was about 300–400 nm as shown in Figure 3(f). Hydrogen flux through this membrane is a function of hydrogen pressure and test temperature, as shown in Figures 6(a, b). One can see that hydrogen flux transported through the membrane linearly rises with increasing the temperature and hydrogen pressure. The experimental results demonstrate that these membranes can be used for hydrogen extraction up to the temperature of 550°C and hydrogen pressure difference of 3.447x10⁵ Pa.

The thickness of such continuous and dense membrane is controlled by the diameter of the particles. Assuming that the ultra-thin membrane is packed from 3 one-particle layers, the dense membrane thickness T can be calculated as equation (4).

\[ T = 2.414R \]  

(4)

So, if the diameter of Pd nanoparticles is controlled effectively, the thickness of a dense membrane deposited on a relatively smooth substrate surface will be controlled.

Based on the observation of Pd deposition progress on the porous steel substrate, the minimum thickness of a dense Pd membrane is around 1.5–2 µm. Over 100 Pd membrane samples having thickness from 1.5 to 18 µm were prepared for hydrogen permeation tests. All samples were dense and no leakage was detected as they were examined by nitrogen gas at the absolute pressure difference of...
3.447x10^5 Pa and the temperature from 300°C to 550°C. These experimental results show that the Pd membranes were dense. After the leakage tests, hydrogen fluxes through the membranes were measured under the absolute pressure difference of hydrogen gas at 3.447x10^5 Pa and for the temperatures from 300°C to 550°C. The average hydrogen fluxes are shown in Figure 7. The experimental results reveal that hydrogen flux is dependent on the membrane thickness. Thinner membrane has higher hydrogen flux. If the pores at the substrate surface are modified and the surface becomes smooth, an ultra-thin Pd membrane will be easily built.

Figure 6. Hydrogen flux vs. hydrogen pressure difference (a) and temperature (b)

4. Conclusions

Based on the observation of Pd membrane formation on porous steel substrate, the thickness of the membrane can be effectively controlled by the electroless process. The size of nanoparticles from which the membrane is built depends on the concentration of PdCl_2 in the plating bath. The smaller the size of Pd nanoparticles, the thinner the dense Pd membrane can be built. Hydrogen permeability test, supported by the observation of microstructure and theoretical analysis, will allow optimizing the design of ultra-thin Pd membranes by modifying the surface microstructure and porosity.

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