

# Preparation of palladium membrane by electroplating on AISI 316L porous stainless steel supports and its use for methanol steam reformer

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## Abstract

A novel electroplating method of preparing Pd-membrane on an AISI 316L porous stainless steel support is successfully developed by proper control of rotation speed of the support. The use of low-current density with high-rotation speed enables us to avoid hydrogen absorption during electroplating and to prepare smooth thin surfaced membrane with defect free. The electroplated-Pd-membrane shows well property in the hydrogen permeation, flux and excellent permselectivity ( $H_2/He > 100,000$ ), and is used in a membrane-assisted steam reformer of methanol for the production of high-purity hydrogen. It was also found that the membrane spontaneously exhibited to resist hydrogen embrittlement under the phase-transition temperature of 280 °C, when operated in the temperature range of 250–350 °C under the hydrogen pressure of 9 kgf/cm<sup>2</sup>.

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## 1. Introduction

With petroleum price surges upward rapidly, the desire for a sustainable alternative energy source becomes more urgent. Of several substitute energy sources, hydrogen is the most imminent choice of sustainable energy by several industrial countries owing to its clean and environmentally harmless during conversion and utilization, diversity and abundance in its supply source and versatility in the mutual conversion among different energy forms. Supply of high-purity hydrogen by a compact device is critical to the preservation of its high efficiency and the simplicity in the operation of fuel cell. Incorporation of Pd-membrane in a catalytic reformer to produce high-purity hydrogen in situ and onsite to the user offers important advantages in low cost, high-energy efficiency and space saving in the hydrogen production. As a result, hydrogen membrane reactors are classified as one of key activities of the hydrogen purification technology in the current development of advanced hydrogen technology [1].

Production of Pd-membrane on porous support by sputtering or electroless plating has been practiced for long time on a micropored ceramic, Vycor glass and metal support [2–7]. Successful preparation of defect-free Pd-membrane on the porous stainless steel (PSS) support became available only after 1998 by the electroless plating technique [7–9]. To achieve defect free in membrane fabrication and to yield high-purity hydrogen, a membrane thickness of 10 μm is generally required by repeating deposition of Pd-membrane to achieve such thickness. During electroless plating of Pd on the PSS support, one of the difficulties is the blocking of the surface by hydrogen causing pinholes formations. This surface blocking of hydrogen onto the membrane surface is mainly brought about by the drifting of hydrogen from the solution to the membrane surface. It is also reported that the hydrogen permeation properties of the Pd-membrane are associated with the pore size of substrate and thickness of membrane. Therefore, these properties can be modified and optimized using alternative preparation routes, such as mechanical polishing and filling of submicron powder [10]. Rei et al. employed submicron niobium powder to fill in the presence of water-based adhesive such as S-Bonder [9]. As a result it is slow in process and is prone to the development of membrane strain by repeating depositions.

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Electroplating of Pd thin film on a solid support is well documented and is widely used in jewellery and electronic part for surface protection from oxidation [11,12]. Unlike the electroless plating in which hydrogen blocking takes place from solution to substrate, hydrogen evolution during electroplating initiates right on the substrate surface by the electron attraction of proton onto the electrode/substrate. Thus, the hydrogen blocking during electroplating is much severe, and this has made electroplating of palladium membrane unsuccessful so far because of the hydrogen embrittlement from dissolution of this surface hydrogen. Although adding alloy element in the Pd-electroplating bath may prevent hydrogen severe embrittlement during plating, however, it may yield to phase separation at higher temperature or long hour of operation [13]. But it may not be helpful to the permeability of the hydrogen. Some researchers [11] employed a concentrated lithium chloride baths to electroplating PdAg alloy. Nam et al. [10,17] employed submicron nickel powder or/and silica particulates followed by using vacuum electroplating method of PdNi alloy on the porous stainless steel. However the method cited in this reference still appears to have some degree of hydrogen embrittlement of the Pd alloy membrane as shown in the low permselectivity,  $H_2/He$  in the range of only 120 to 1000. This result indicates the presence of some pinholes in the membrane brought about from the hydrogen embrittlement during the electroplating process. Till now, there is no report of successful and electroplating of defect-free palladium membrane on a PSS support for hydrogen purification. In this study, we report here our successful electroplating of Pd-membrane on a commercial PSS for direct production of high-purity hydrogen from the steam reforming of methanol and upgrading of industrial hydrogen to ultra pure hydrogen at 99.9999+%. The results of all these tests showed well hydrogen flux and excellent purity by electroplated-Pd-membrane on the PSS support.

## 2. Experimental

### 2.1. Pretreated of porous stainless steel supports

The commercial porous 316L stainless steel filter tube (Mott Corp. of USA, <http://www.mottcorp.com/>) was used as the support for deposition of Pd-membrane. The PSS filter tube has a diameter of 9.5 mm OD and 0.2  $\mu\text{m}$  filtration grade with an approximately 0.2  $\mu\text{m}$  pore openings although there always present some large craters in size of 50–100  $\mu\text{m}$  on the surface. The porous stainless steel was previously treated according to a procedure taken from the literature. Thereafter, the tube was further smoothed with electropolishing at 0.5  $\text{A}/\text{cm}^2$  in 2:1 (v/v) phosphoric and sulfuric mixed acids [15], and after degreasing and washing, it is used as a support for deposition of Pd-membrane by electroless plating or by electroplating. After electropolishing, the cathode PSS support was washed in de-ionized water to clean the residual solution and dipped in acetone solution for fast drying.

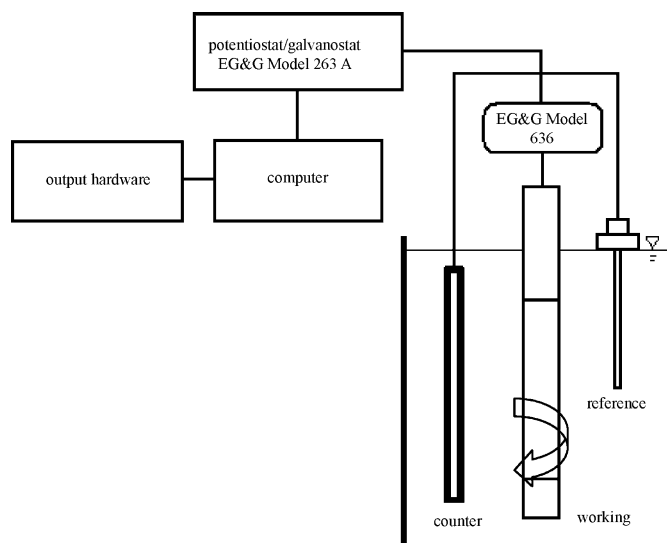


Fig. 1. Block diagram of electroplating setup.

### 2.2. Cathodic polarization measurements

The electroplating of Pd is performed by a rotating cylinder electrode system (RCE, EG&G 636) and potentiostatic (EG&G 263A) as depicted in Fig. 1. The electroplating of Pd-membrane is performed in an alkaline bath with the composition and the plating conditions shown in Table 1. The rotating speed of the cathode PSS is kept at 0, 10, 50, 100 and 200 rpm, respectively. The Pt mesh and  $\text{Ag}/\text{AgCl}_{\text{sat.}}$  are used as the counter and the reference electrodes.

In order to obtain a suitable current density of the Pd in electroplating, the cathodic polarization test was employed to find suitable value. Cathodic polarization curves are measured from open-circuit potential to  $-1500 \text{ mV}$  (vs.  $\text{Ag}/\text{AgCl}_{\text{sat.}}$ ) at  $10 \text{ mV}/\text{s}$ . Before cathodic polarization measurement, the RCE is immersed in the bath for 5 min until a stable condition is established between the RCE and the plating bath. In all these cases, the deposition of Pd-membrane is performed at a constant cathodic current using different rotation speeds. After electroplating, the Pd deposit on the cathode surface was immersed in an acetone bath, and then dried in the air for scanning electron microscope (SEM, Hitachi S-4700) and further examination. The average thickness of the Pd-membrane is ca. 20  $\mu\text{m}$ . The leak test was performed to examine Pd-membranes under helium pressure of  $5 \text{ kgf}/\text{cm}^2$  from inside out.

Table 1  
Composition of electroplating-Pd and nickel bath

|                                    | Nickel | Pd    |
|------------------------------------|--------|-------|
| $\text{NiCl}_2$ (g/l)              | 220    | –     |
| HCl (ml/l)                         | 100    | –     |
| $\text{H}_3\text{BO}_3$ (g/l)      | 50     | –     |
| $\text{PdCl}_2$ (g/l)              | –      | 5     |
| $(\text{NH}_4)_2\text{SO}_4$ (g/l) | –      | 100   |
| $\text{NH}_4\text{OH}$ (ml/l)      | –      | 100   |
| pH                                 | 0.5    | 11    |
| Temperature ( $^\circ\text{C}$ )   | 50     | 45–50 |

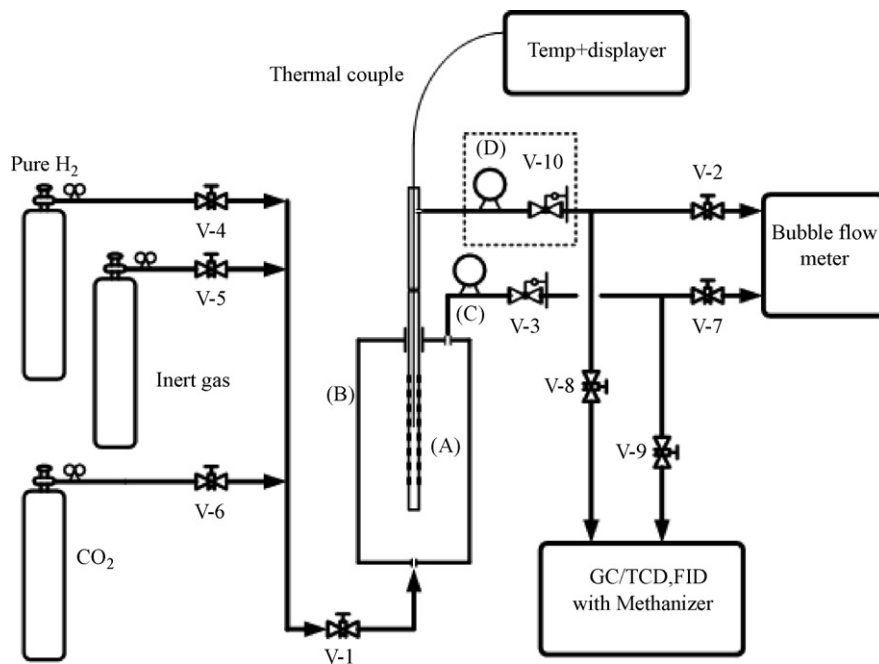


Fig. 2. Block diagram for hydrogen permeation.

### 2.3. Hydrogen permeation test

The Pd-membrane chamber for hydrogen permeation test is shown in Fig. 2. The chamber has a size of 32 mm OD  $\times$  426 mm L with one Pd-membrane tube in it. First, air in the chamber is flushed out by inert gas and is heated up to 350 °C with a program rate of 4 °C/min. Thereafter, hydrogen is introduced into the membrane chamber for 30 min to flush out the inert gas from the chamber by closing the valve V-5 and opening V-4 to make sure the chamber is filled up with hydrogen.

Hydrogen flux through Pd-membrane is measured by a mass flow meter from permeation side after V-2 is opened. In this study, retentate pressure,  $P_R$  varies from 2 to 9 kgf/cm<sup>2</sup> by adjusting V-4 and V-3 valves. The hydrogen flux and the pressure differential,  $\Delta P^{1/2} = (P_R^H)^{1/2} - (P_P^H)^{1/2}$  are plotted to obtain the corresponding hydrogen permeance of the membrane, here  $P_R^H$  and  $P_P^H$  are the hydrogen partial pressure of hydrogen on the retentate side (shell side) and permeate side (tube side). The concentration of the effluent from the permeate side was analyzed by gas chromatograph (GC/FID; GC/DID) to determine the hydrogen purity.

### 2.4. Hydrogen embrittlement test

We undertook three series of preliminary tests for hydrogen embrittlement in the jacketed permeators (250 mm ID with side arm at the top and bottom for retentate gas inlet and exit; the electroplated-Pd-membrane tube was connected to the top for exit of hydrogen permeate) under three series of different conditions. Except the permeation temperature difference, all three sets of tests have the same feed stream and operation pressure; the feed stream into retentate side contained 75% hydrogen H<sub>2</sub> with 25% CO<sub>2</sub> at an operation pressure of 9 kgf/cm<sup>2</sup> (Fig. 2). In

“A” and “B” tests the permeation temperatures were maintained at room temperature and 150 °C, respectively, for 19 days. In “C” test, the membrane was first brought up to 250 °C from room temperature under helium atmosphere, then the atmosphere was replaced with hydrogen at 250 °C. Thereafter, the membrane was subjected to temperature change between 250 and 350 °C with a heating rate of 1 °C/min; the holding time was 24 h for each temperature before switching to other temperature.

There was no hydrogen permeates at room temperature in A-series test; therefore, there was no purity analysis of hydrogen permeates in A-series test. In B- and C-series tests, the purity of hydrogen permeates were analyzed at 150 and 250 °C, respectively. Leak test with helium was conducted daily to ensure leak-proof of the membrane. Hydrogen purity was analyzed to check occurrence of severe deterioration of membrane, and was found to maintain at 99.9% so far.

## 3. Results and discussion

### 3.1. Pretreated of porous stainless steel supports

To prepare a thin defect-free Pd-membrane having a thickness of 15–20  $\mu$ m on a PSS support, two key process difficulties have to be overcome. First the rough and non-standardized porous support surface has to be smoothed out to a relatively even surface with an acceptable pore opening. Second the coverage of hydrogen on the support surface is to be avoided when plating is in process. The commercial PSS support is made for filtration rather than for surface deposition of membrane and is rated as 0.2  $\mu$ m filtration grade (Fig. 3(a)). However, these supports are always presented with 50–80- $\mu$ m sized deep craters. These large craters make the subsequent surface deposition difficult and unreliable and thus it is hard to prepare a defect-free mem-

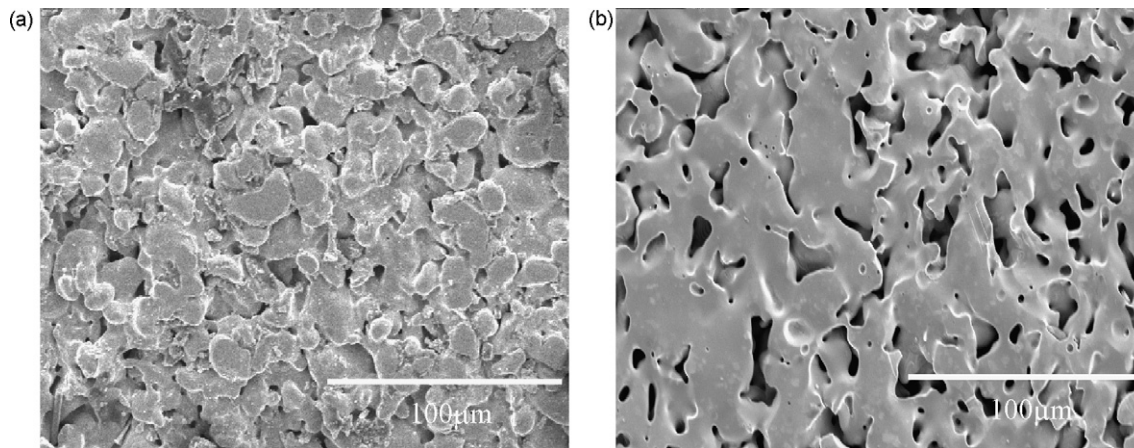


Fig. 3. Surface topology of PSS tube before (a) and after (b) electropolishing.

brane on such support. With the mechanical polishing followed by electropolishing of the PSS (Fig. 3(b)), the degree of the sharp edge of those craters are extensively smoothed out, and we are able to smooth out the rough surface of the irregular commercial support and control the pore opening to a desirable range of gas flow.

Due to the formation of dense oxide film on the support surface, the strength of adhesion between the deposited layer and the stainless steel is poor. Therefore, the electropolished support is pretreated by depositing a thin layer of nickel (@ 0.1 μm) as intermediate to enhance the interface bonding between Pd and support. There is no visible change in the flow rate after this thin nickel layer is plated as shown in Table 2. The electroplating of palladium was performed in an alkaline bath composed of PdCl<sub>2</sub> (5 g/l), (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (100 g/l), NH<sub>4</sub>OH (100 g/l) as displayed in Table 1. The effect of rotating speed on the success electroplating of palladium membrane on the PSS substrate is discussed in the latter section.

### 3.2. Cathodic polarization measurements

Fig. 4 shows the cathodic polarization curves of the RCE in the Pd plating bath with various rotation speed. The cathodic current density was raised keenly with the increasing rotation speed at the same potential in the corresponding polarization curves. Depending on the rotation speed of support, the rate of Pd deposition and the hydrogen evolution varies differently with respect to the current density. In this study, the apparent depolarizing effect of rotation speed on Pd electroplating was detected. The cathodic polarization curve of alkaline solution at 45 °C is shown in Fig. 5. This curve can be divided into three

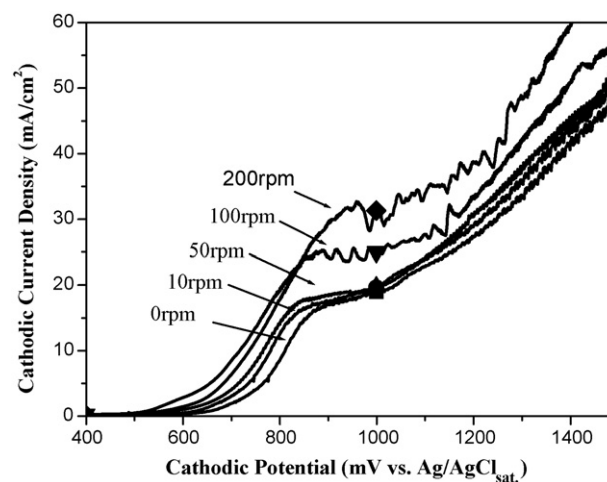


Fig. 4. The effects of rotation speed of support on the cathodic polarization.

stages: the first stage between 600 and 900 mV (region-I), the second stage of 900–1250 mV (region-II), and the third stage of 1250 mV and higher (region-III). Furthermore, based on the [11,16] studies, the hydrogen evolution reaction (HER) in of

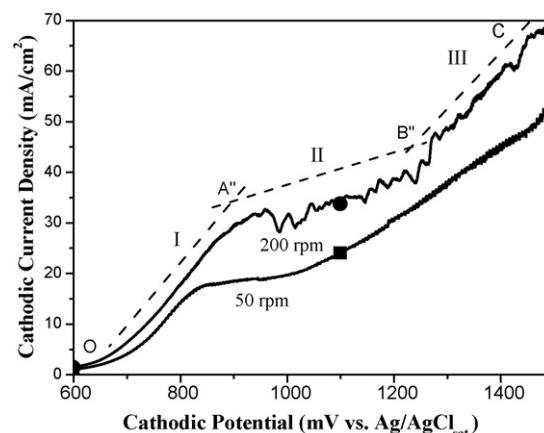


Fig. 5. The diagram of partition of three current profiles.

Table 2  
The flow rate of 2 kgf/cm<sup>2</sup> helium tested before electroplating

| Specimens    | PSS  | After pre-Ni coating |
|--------------|------|----------------------|
| Flux (l/min) |      |                      |
| 1            | 20.9 | 20.8                 |
| 2            | 20.5 | 20.5                 |
| 3            | 20.6 | 20.7                 |

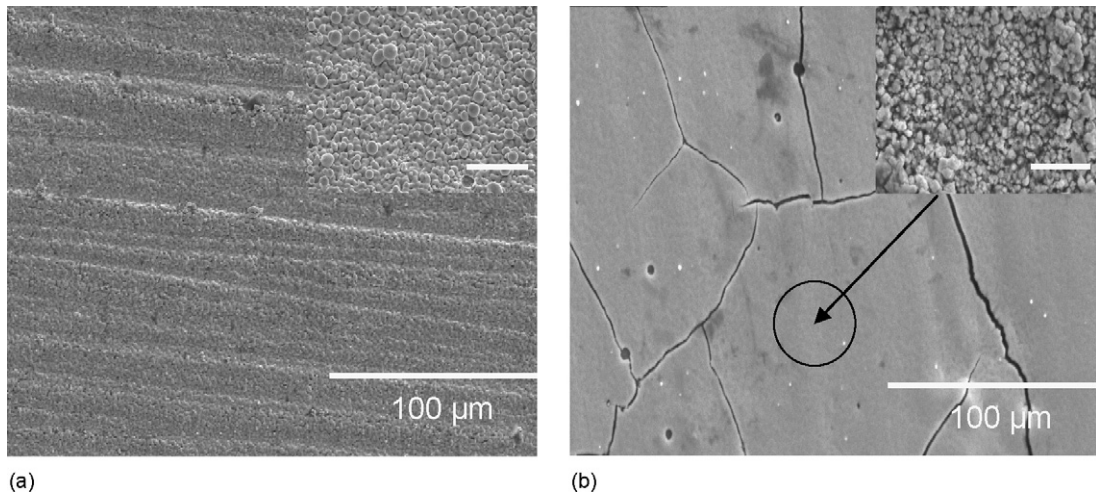
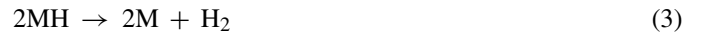
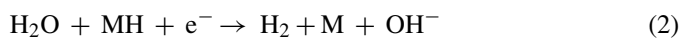
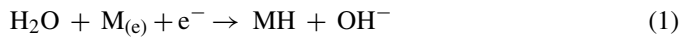


Fig. 6. The SEM of electroplated-Pd-membrane with varying current density at a rotating speed of 50 rpm: (a) 10 mA/cm<sup>2</sup>; (b) 18 mA/cm<sup>2</sup>.

metal deposition of in alkaline solution was proposed below:



where the (Volmer reaction (1)) is the electroreduction of the water molecules with the formation of hydrogen atom adsorbed on electrode surface, followed by (Heyrovsky reaction (2)) elec-

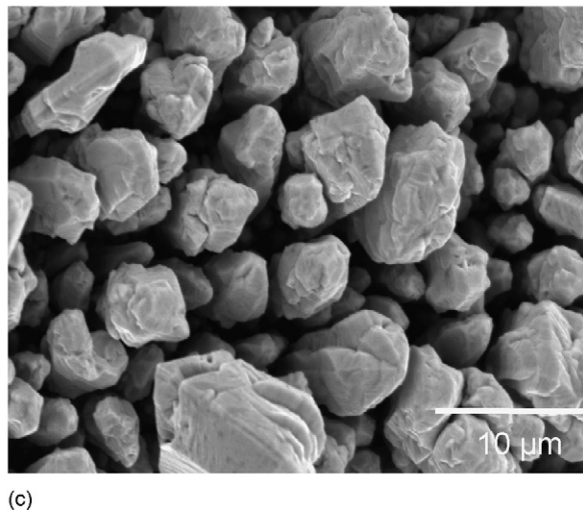
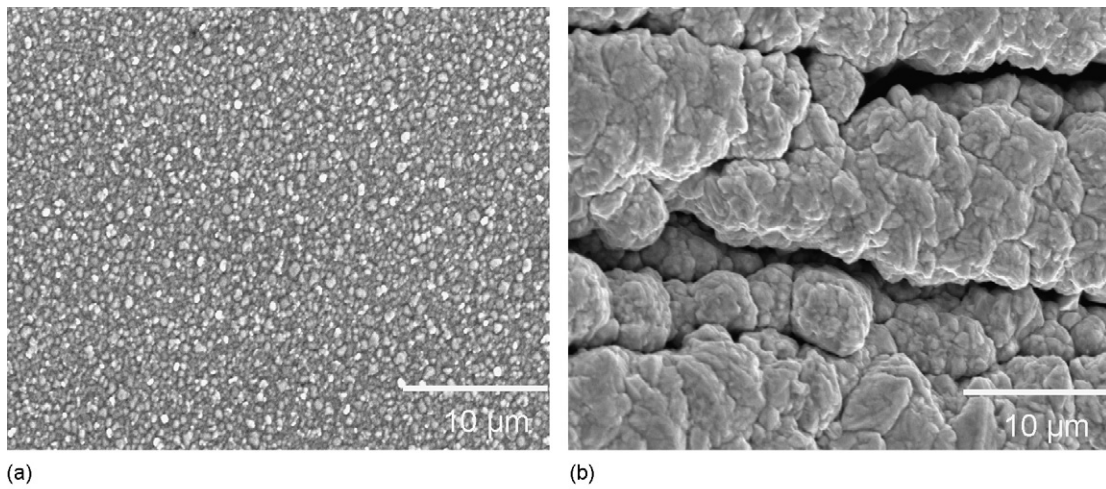


Fig. 7. The SEM of electroplated-Pd-membrane with varying current density at a rotating speed of 200 rpm: (a) 10 mA/cm<sup>2</sup>; (b) 15 mA/cm<sup>2</sup>; (c) 18 mA/cm<sup>2</sup>.

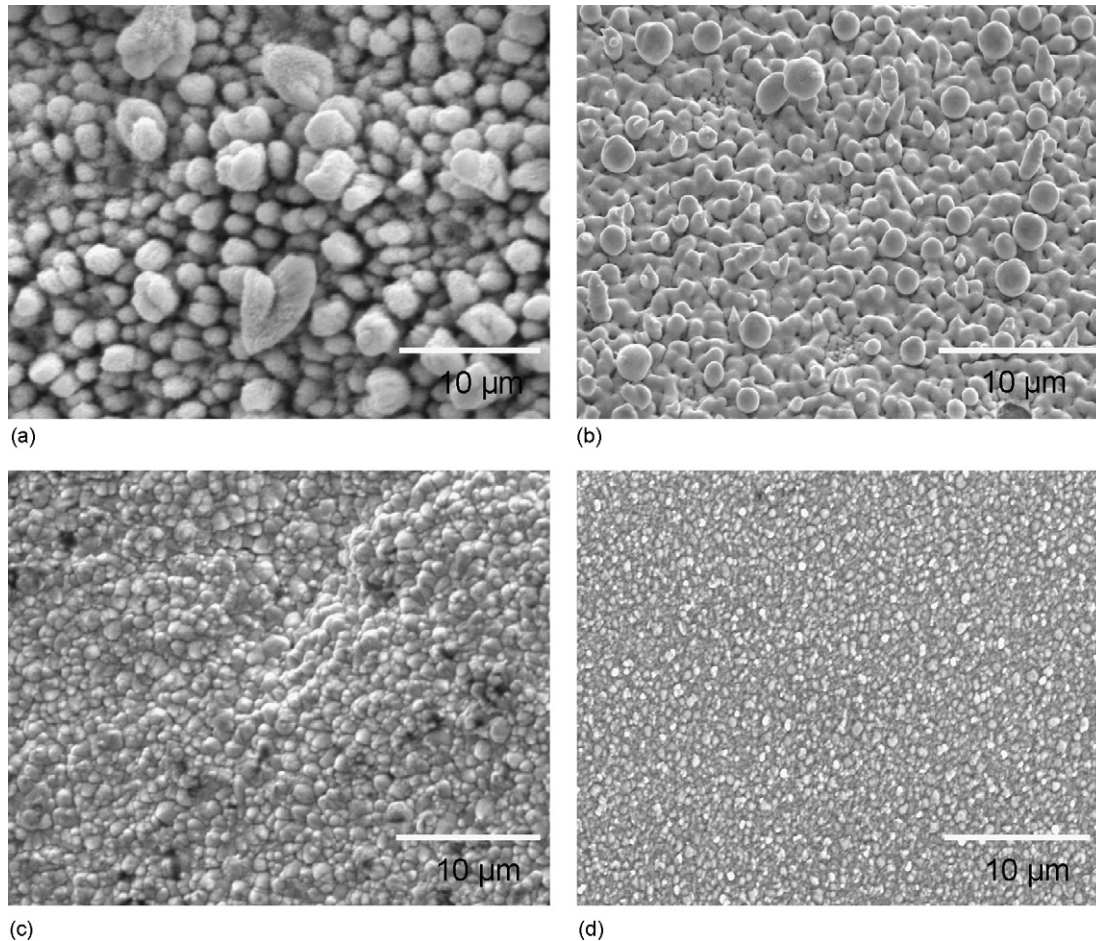


Fig. 8. The SEM of electroplated-Pd-membrane with varying rotation speed at a constant current density of  $10 \text{ mA/cm}^2$ : (a) 10 rpm; (b) 50 rpm; (c) 100 rpm; (d) 200 rpm.

trochemical and/or (Tafel reaction (3)) chemical desorption of hydrogen molecule. Moreover, as the current density increases, there is an interchange of mechanism from the Volmer–Tafel path to the Volmer–Heyrovsky path. Accordingly, in this study, in the low-current density stage, region-I, the dominant reaction is the reduction of metal cation to metal deposit. In the high-current density stage, region-III, HER and deposition of  $\text{PdH}_x$  become the major reaction during the processing. Between these two regions, region-II, the concentration and mobility of metal ions, and the degree of solution agitation dictates the limiting current. To rationalize the two facts, the characteristic of the Pd-membrane needs further studied with SEM and hydrogen embrittlement test.

### 3.3. SEM observation of electroplated-Pd-membranes

Fig. 6 shows the growth morphology of Pd-membrane for 50 rpm at different current density. The surface morphologies show that surface seems to become denser when current density is increased. It shows a round-shaped nodules and the size in the range of  $1\text{--}4 \mu\text{m}$ ,  $10 \text{ mA/cm}^2$  (Fig. 6(a)). The Pd-deposit reveals a grayish white appearance. When current density is increase to  $18 \text{ mA/cm}^2$  (Fig. 6(b)), the Pd-deposit yields coarse and large nodules. The Pd-deposited also shows a

grayish white appearance. But the crack line grows and leads into peeling-off as the strain builds up by the rapid deposition of the thick layer of Pd-membrane. Thus, the interference of the hydrogen makes the electroplated-Pd-membrane liable to hydrogen embrittlement during the electrodeposition in the region-II.

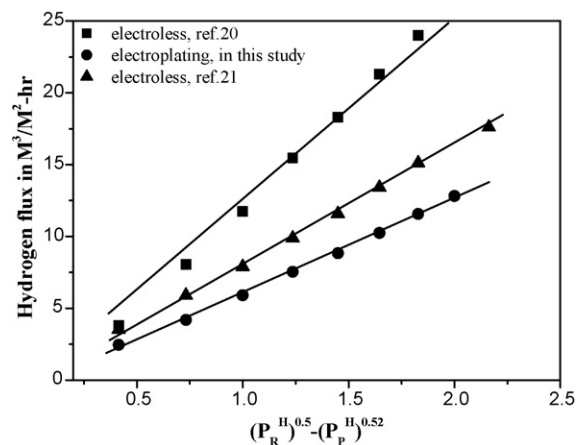


Fig. 9. Correlation of hydrogen flux with pressure differential with  $P_2 = 1 \text{ kgf/cm}^2$  and  $T = 350^\circ\text{C}$ .

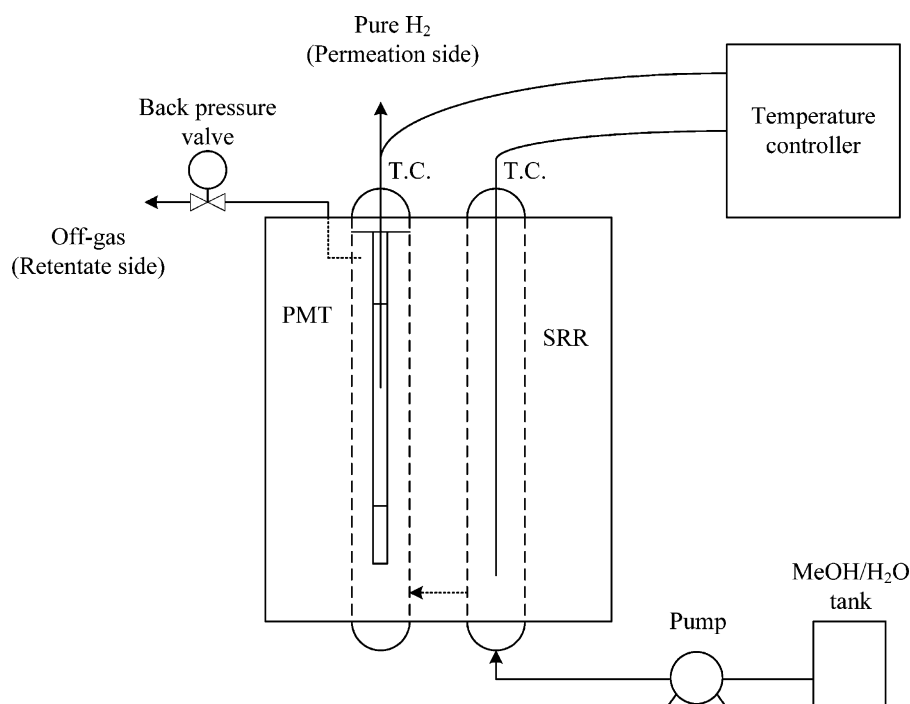


Fig. 10. The Pd-membrane-assisted methanol steam reformer.

With further increase of rotating speed to 200 rpm, Pd grain deposits at 10 mA/cm<sup>2</sup> current density in the region-I. The membrane thus obtained is composed of nodules in size of @ 0.5 μm; the nodules grow uniformly in horizontal expansion and seal into a smooth pinhole-free surface free of cracking as shown in Fig. 7(a). The Pd-deposited has bright metallic vision. As the current density is now increased to 15 and 18 mA/cm<sup>2</sup>, the nodules grow rapidly to 5–13 μm in vertical direction without horizontal sealing and present cracks between large nodules as shown in Fig. 7(b) and (c). They reveal grayish white and charcoal gray on visual. Further increase of current density to 25 mA/cm<sup>2</sup> causes severe hydrogen evolution on the cathode surface and the membrane becomes sponge and falling. This result conforms with the overpotential characteristic of transforming compact to powdery deposit in electroplating. Some researchers [11] reports that Pd-deposited with hydrogen content below 10 ml H<sub>2</sub>/g Pd or atomic H/Pd ratio below 0.1 has a metallic brilliance. For higher H/Pd ratios, the Pd-deposited become gray and dark. For H/Pd over 0.8 ratios, it tends to become black and powdery. Therefore, when current density is increased, the H/Pd ratio of Pd-deposited also increases rapidly.

The above inference to the dominant Pd-deposition in the low-current density, region-I, is born out as shown in Fig. 8 when support speed is set from 10 to 200 rpm. The unwanted hydro-

Table 3  
Leak test of electroplated-Pd-membrane under helium pressure of 5 kgf/cm<sup>2</sup> at room temperature with helium from inside out

| Current density (mA/cm <sup>2</sup> ) | 0 rpm | 10 rpm | 50 rpm | 100 rpm | 200 rpm |
|---------------------------------------|-------|--------|--------|---------|---------|
| Flux (l/min)                          |       |        |        |         |         |
| 10                                    | 20.2  | 5.6    | 0.8    | 0.5     | 0       |
| 15                                    |       |        |        | 3.2     | 2.8     |
| 18                                    | 19.5  | 15.8   | 12.6   | 10.5    | 10.2    |

gen evolution is indeed suppressed and a smooth Pd deposition is obtained with the substrate rotating over 200 rpm. Apparently this is in agreement with the speculation that metal deposition is dominant in the low-current density at high-rotating speed. In the intermediate region-II, the nodules grow fast with the high-current density and lead to rough surface without sealing of the enlarged inter-cluster space leading to crack. As a result, one can conceivably avoid or reduce the interference of hydrogen if the electroplating is controlled in the region-I. Table 3 was shown that the Pd-membrane tubes prepared by varies current density and rotating speed of electroplating are subjected to leaking test with helium by first having test gas introduced from the tube side under a pressure of 5 kgf/cm<sup>2</sup> and immersed the whole tube in a water bath to see the bubbles if any. Apparently the Pd-deposited grows so fast at the same deposition site

Table 4  
the hydrogen purity before and after pass through electroplated-Pd-membrane under pressure of 9 kg/cm<sup>2</sup>

| H <sub>2</sub> purity of feed (%) | Impurity in feed (ppm) | Impurity in permeate (ppm) | Purity of H <sub>2</sub> permeate (%) |
|-----------------------------------|------------------------|----------------------------|---------------------------------------|
| 99.99                             | 100                    | 0.02                       | 99.999998 (7N8)                       |
| 99.95                             | 5,000                  | 0.5                        | 99.99995 (6N5)                        |
| 95                                | 50,000                 | 50                         | 99.995 (5N5)                          |
| 75                                | 250,000                | 200                        | 99.98 (3N8)                           |

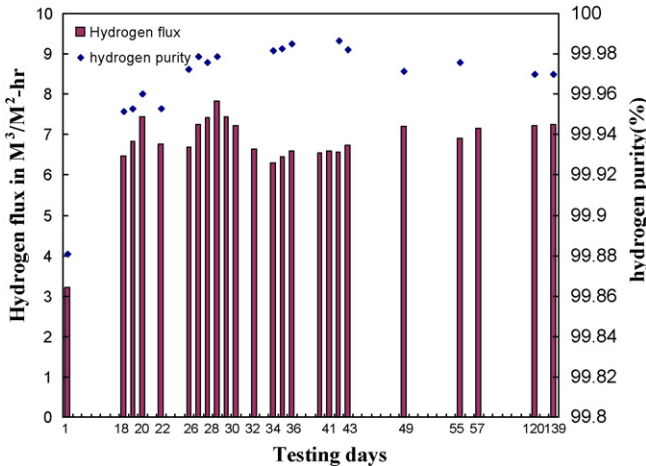


Fig. 11. The time test of hydrogen flux and purity from methanol steam reforming at 350 °C and  $P = 1 \text{ kgf/cm}^2$ .

and forms larger nodules making sealing of inter-grain space difficult.

### 3.4. Hydrogen permeation test

According to the results of cathodic polarization test and SEM observation, all electroplated-Pd-membranes with hydrogen permeation test were prepared under conditions of 10 mA/cm<sup>2</sup> and 200 rpm. The membrane tube is further tested for pinhole leakage with the helium gas on the shell side under 9 kgf/cm<sup>2</sup> pressures at 350 °C with an illustration as shown in Fig. 2. The electroplated-Pd-membrane tubes are leak-proof even with helium as the test gas at the shell pressure of 9 kgf/cm<sup>2</sup> and 350 °C. The electroplated-Pd-membrane is further characterized with permeation of single hydrogen and with a hydrogen mixture containing 25% of carbon dioxide; as shown in Fig. 9 [20,21], the results are revealed together with those of membrane tube prepared by electroless plating for comparison. The hydrogen fluxes for two types of membrane tubes are comparable. In General, the defected membranes on PSS supports are characterized by high-permeation flux with low permselectivity. The

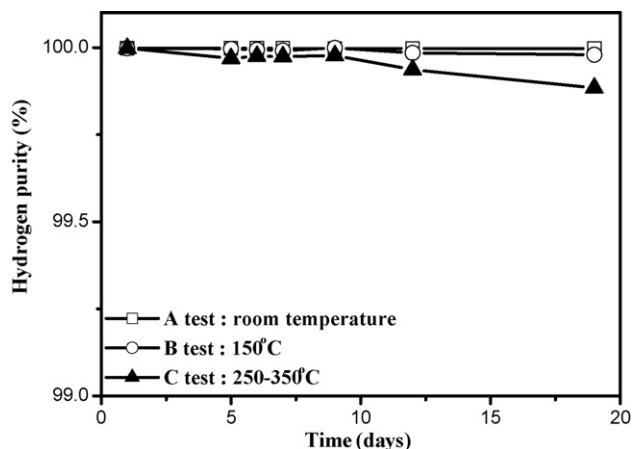


Fig. 12. The hydrogen purity and testing time during hydrogen embrittlement test.

defect-free membrane, on the other hand, has high permselectivity. In this study, all the electroplated-Pd-membranes have a permselectivity, H<sub>2</sub>/He, in the range >100,000. Table 4 presents the upgrading of hydrogen purity before and after passing through the Pd-membrane. It shows when 75% hydrogen feed permeates through electroplated-Pd-membrane, the hydrogen purity increases to 99.98%. Furthermore, a 99.99% hydrogen feed can be upgraded to ultra high purity of 99.999998% (Fig. 10).

When the electroplated-Pd-membrane is used to fabricate a methanol steam reformer [18], 70% of hydrogen permeate at 99.98% is obtained. The rest of hydrogen is forwarded to a jacket heater for catalytic combustion to sustain the endothermic conversion without external fuel for heat; this way a thermal efficiency of 72% is achieved. The reactor has been tested continuously for over 139 days during day time and overnight under helium stream until now (Fig. 11).

### 3.5. Hydrogen embrittlement test

When the newly made electroplated-Pd-membrane was accidentally exposed to hydrogen first at low pressure of 5–9 kgf/cm<sup>2</sup> at room temperature, we were surprised to find that there appeared to have no embrittlement of Pd-membrane. With this unexpected encouragement, we undertook a hydrogen embrittling test of the electroplated-Pd-membrane. The hydrogen embrittlement tests were performed to examine the extent of embrittling resistance of the electroplated-Pd-membrane. Based on the previous experience with the electroless-Pd-membrane, if there is hydrogen embrittlement, hydrogen will burst through the membrane tube and shows falling down of Pd-membrane flakes.

Three series of embrittling tests are undertaken as described in Section 2. There is no leakage or embrittlement when the membrane is exposed under hydrogen at room temperature.

Table 5

The leaking test of palladium membrane of electroplating under helium pressure of 9 kgf/cm<sup>2</sup> before, during and after hydrogen embrittlement test

|                                    |                  |
|------------------------------------|------------------|
| Before hydrogen embrittlement test |                  |
| Pressure (kg/cm <sup>2</sup> )     | 9                |
| Flow direction                     | Tube side        |
| (1)                                | N/D <sup>a</sup> |
| (2)                                | N/D <sup>a</sup> |
| (3)                                | N/D <sup>a</sup> |
| During hydrogen embrittlement test |                  |
| Pressure (kg/cm <sup>2</sup> )     | 9                |
| Flow direction                     | Shell side       |
| Room temperature (1)               | N/D <sup>a</sup> |
| 150 °C (2)                         | N/D <sup>a</sup> |
| 250–350 °C (3)                     | N/D <sup>a</sup> |
| After hydrogen embrittlement test  |                  |
| Pressure (kg/cm <sup>2</sup> )     | 9                |
| Flow direction                     | Tube side        |
| (1)                                | N/D <sup>a</sup> |
| (2)                                | N/D <sup>a</sup> |
| (3)                                | N/D <sup>a</sup> |

<sup>a</sup> There is no He bubble detected during 20-min immersion in a water bath.



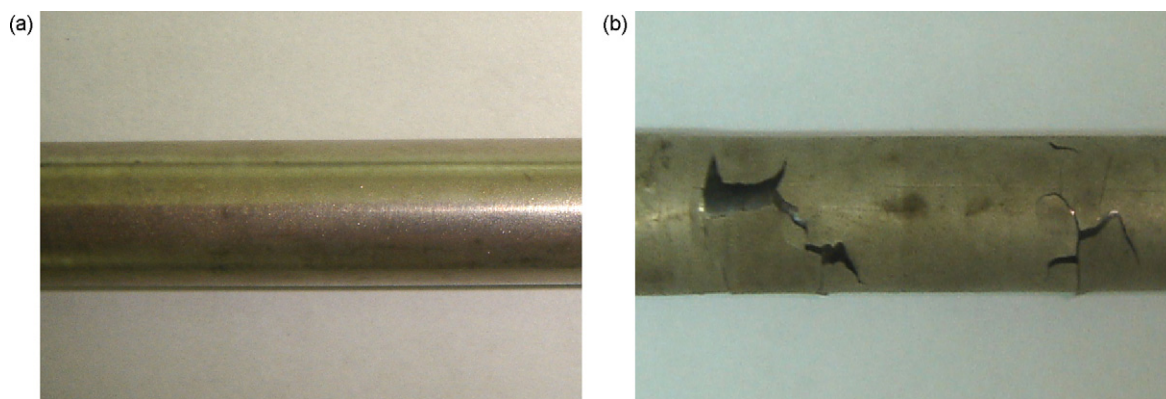


Fig. 13. The surface photo-images (a and b) of the electroless-Pd-membrane before and after embrittling test at  $250 \leftrightarrow 350^\circ\text{C}$  under  $9 \text{ kgf/cm}^2$  of hydrogen.

However, when the membrane is brought up to  $150^\circ\text{C}$  from room temperature under hydrogen pressure, there is a burst of hydrogen flow rate and falling down of membrane flakes after dismantle from the test. Therefore, in the later test, the membrane is first exposed to helium and then raised the test temperature up to the desired temperature of  $150$  or  $250^\circ\text{C}$ . This modified procedure appears to prevent instant embrittling of the membrane under hydrogen pressure even at the temperature region of phase transition between  $\alpha$ -phase and  $\beta$ -phase. As shown in Table 5, all the membranes remain leak-proof

with helium test under a pressure difference of  $9 \text{ kgf/cm}^2$  in the three series of tests. This indicates a good resistance to hydrogen embrittlement of these electroplated-Pd-membranes under a hydrogen pressure of  $9 \text{ kgf/cm}^2$  at a temperature from room temperature to  $350^\circ\text{C}$ . Moreover, in order to monitor the possible micro-cracking of membrane during the test, a feed of 75% hydrogen with 25% carbon dioxide is used to allow careful analysis of ppm level of methane in the hydrogen permeate by GC-FID with online methanizer. The purity holds fairly steady over 99.9% in a testing duration over 19 days; the

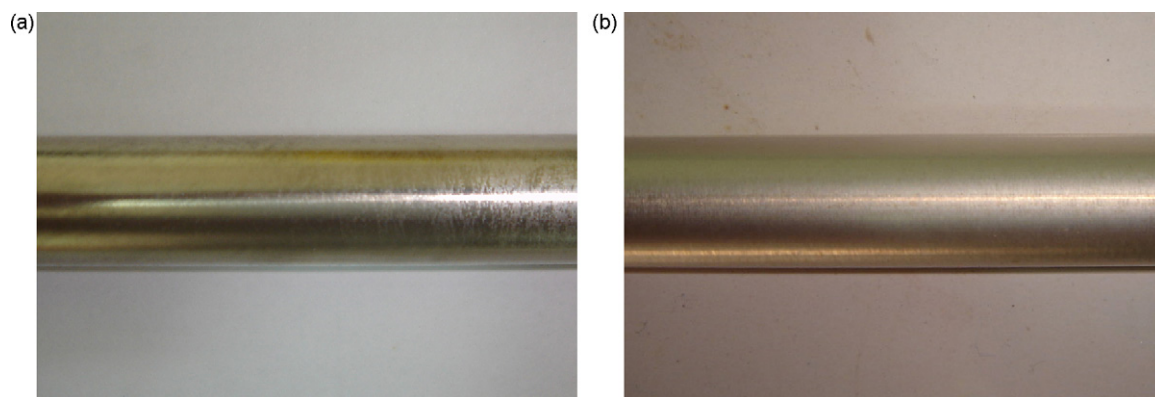


Fig. 14. The surface photo-images (a and b) of the electroplated-Pd-membrane before and after embrittling test at  $250 \leftrightarrow 350^\circ\text{C}$  under  $9 \text{ kgf/cm}^2$  of hydrogen.

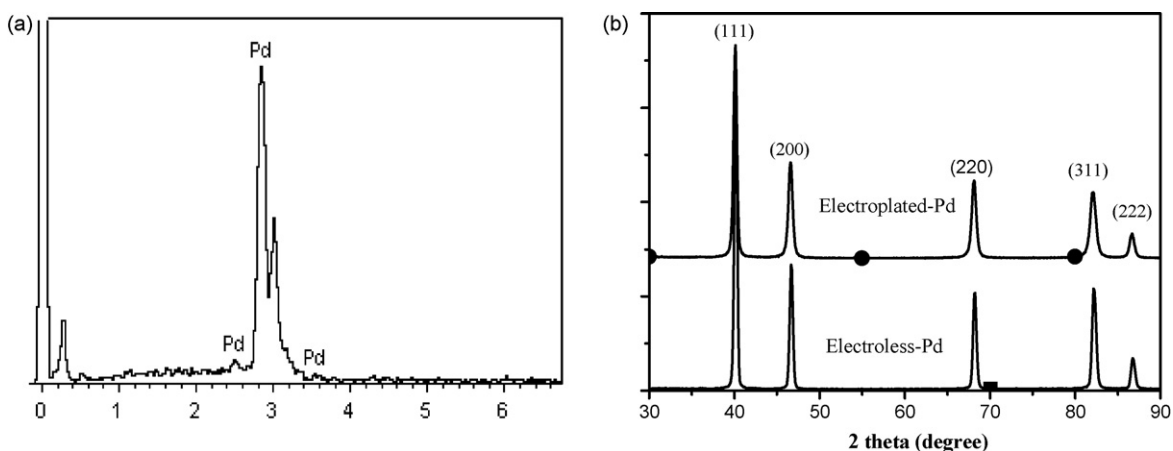


Fig. 15. The SEM-EDS and XRD analysis of palladium membranes.

minor drop of hydrogen purity at higher temperature test and longer testing time may be attributed to the structure change. We are still not quite understood of the observed new phenomena and are pursuing the role of membrane structure aspect on the observed resistance to the embrittlement and purity change (Fig. 12).

Fig. 13 shows a set of photo-image of the electroless-Pd-membranes before and after exposing to 9 kgf/cm<sup>2</sup> of hydrogen atmosphere at cycling temperatures. Under the same condition the electroplated-Pd-membrane shows clean membrane surface before and after hydrogen exposure for 19 days. We are not clear of this “abnormal” phenomenon observed in these embrittlement tests (Fig. 14). One possibility is the formation of thin layer of Pd–Ni alloy because we have a thin layer of Ni as an interface between PSS and Pd deposit during membrane deposition. We, therefore, examine the composition of the membrane with SEM-EDS and XRD analysis (Fig. 15), and found no evidence of alloy formation with only minor Ni deposit at the interface layer with PSS. However, we did find different crystal structure of the electroplated-Pd-membrane when compare with the electroless-Pd-membrane. We would report this structure phenomenon later after we have opportunity to conduct more fact-finding study.

#### 4. Conclusion

Hydrogen interference during electroplating can now be suppressed at region-I under high-rotation speed of support. This technique leads us to a successful preparation of defect-free electroplated-Pd-membrane on a PSS support. On studying cathodic polarization curve of electroplating of Pd, we find that there are three regions having different rates of Pd deposition and HER. Under region-I, hydrogen evolution is practically suppressed and Pd deposition is clear of hydrogen absorption. This clean region of Pd deposition is widened on the increase of support spinning rate. Therefore, by proper choice of current density under high-spinning rate, the Pd-membrane is safe from hydrogen evolution to form PdH<sub>x</sub> alloy which tends to exert stress on the membrane leading to embrittling and crack. The electroplated-Pd-membrane on a stainless steel support with 200 rpm under a current density of 10 mA/cm<sup>2</sup> has very homogeneous grain size, @ 0.5 μm, and has no helium leakage detected under a pressure of 9 kgf/cm<sup>2</sup>.

The resultant electroplated-Pd-membrane shows slightly higher hydrogen flux, excellent selectivity and purity. Furthermore, the electroplated-Pd-membrane shows well resistant to the hydrogen embrittlement between room and phase-transition

temperature while the electroless-Pd-membrane does have normal embrittling property as expected. We are effort continue to study of this important observation.

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