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Preparation and characterization of palladium-based composite membranes by electroless plating and magnetron sputtering

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Abstract

Pd and Pd–Ag (24 wt.%) alloy composite membrane were prepared by electroless plating and magnetron sputtering, respectively. The membranes were characterized by scanning electron microscopy (SEM) and H_2 permeation measurement. Commercial microfiltration ceramic membrane were coated with γ-Al_2O_3-based layer by the sol–gel method and used as substrate of Pd and Pd–Ag alloy film. Both the as-prepared membranes were shown to be He gas-tight at room temperature with a thickness of $<1\,\mu$m. Permeation results showed that H_2 permeation through these composite membranes is mainly dominated by the surface chemistry of H_2 on or/and in the membranes. The membranes exhibited a high permeation rate of H_2 and a H_2/N_2 permselectivity of higher than 60 in the optimized operation conditions. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Electroless plating; Magnetron sputtering; Pd-based membrane; H_2 separation

1. Introduction

Pd-based membranes continue to be of great interest for potential applications involving H_2 separation from H_2-producing reactions and hot H_2-containing process streams [1,2]. Recently, many efforts in the above area have been devoted to development of Pd-based composite membranes, i.e. a thin Pd-based film supported on a mechanically stable porous substrate. Such Pd-based membranes are believed to offer high H_2 permeation rates and reduced material costs as compared with traditional symmetric Pd-based membranes.

Electroless plating [3–7], sputtering [8–10] and chemical vapor deposition [11–15] have been explored to produce Pd-based composite membranes. The pioneering work on electroless plating technique to prepare a Pd composite membrane was performed in the group of Kikuchi, et al. [3–6]. The composite membrane exhibited an H_2 permeation rate at least 10 times larger than that of a commercial Pd-based membrane with a thickness of 150 μm and had a high permselectivity of H_2. The same authors reported that Pd–Ag alloy composite membrane was synthesized by a sequence deposition of Pd and Ag using the electroless plating technique followed by high-temperature thermal treatment (900°C) in an inert atmosphere. Shu, et al. [7] made a further effort to produce Pd–Ag alloy composite membrane on porous stainless steel by electroless plating. In their work, the co-deposition of Pd and Ag was achieved by employing a composite electroless plating bath of a Pd and Ag salt. The alloy composite membrane was produced by thermal treatment at 400°C in an H_2 atmosphere. However,

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no permeation measurement was given. It has been demonstrated that electroless plating technique can produce a uniform metallic coating on a large surface area and complex-shaped substrates with very simple equipment. The main problems arise from the difficulty to prepare a Pd-based alloy composite membrane. Gryaznov, et al. [8] used a sputtering technique to prepare Pd–Ru–In alloy composite membrane with a thickness of 2 μm. It was shown that the membrane resisted to 450 temperature cycles of room temperature to 400°C in an H_2 atmosphere during one-month operation. It should be mentioned that the interfacial adhesion of sputtering-derived Pd-based membrane could be a problem. Chemical vapor deposition may offer an approach to this kind of problem. Morooka, et al. [11] demonstrated the feasibility of preparing a dense 2–5 μm thick Pd membrane inside macropores of α-Al_2O_3 tubes by chemical vapor deposition. Their membrane exhibited high H_2 permeation rate and H_2/N_2 permselectivity and good stability against temperature cycling in an H_2 atmosphere. Further work on chemical vapor deposition for confining Pd-based alloy material inside porous substrate may be interesting, resulting in an improved stability of Pd-based composite membranes.

In this paper, thin Pd and Pd–Ag alloy composite membranes were prepared by electroless plating and magnetron sputtering, respectively. The permeation properties of H_2 through the composite membranes were investigated. Furthermore, the thermal stability of the composite membranes was examined by H_2/N_2 separation.

2. Experimental

2.1. Electroless plating procedure

Electroless plating procedure consisted of the activation of substrate and the deposition of metal on the pre-activated substrate. A commercial plate microfiltration ceramic membrane was used as a substrate of Pd film. The substrate had an average pore size of 1.6 μm and a symmetric structure. The activation of the substrate was performed by the sol–gel process of Pd(II)-modified boehmite sol [16]. The casting sol contained 0.5–1.0 mol/l boehmite sol, Pd salt, polyvinylalcohol (PVA) and polyethylenglycol (PEG). Coating was carried out by slip-casting. After drying at 5°C and calcination at 600°C, the sol–gel-derived substrate was treated with H_2 at 500°C to reduce a Pd precursor.

The electroless plating bath contained Pd salt, EDTA, hydrazine and ammonia. A plastic filter device was employed to perform the electroless plating of Pd. The activated layer of the substrate faced up to electroless plating solution. During the deposition of Pd, the infiltration of the solution to the substrate was enhanced by vacuum-filtration. After a desired plating time, the membrane was washed with deionized water and acetone in sequence, then dried at ambient temperature.

2.2. Magnetron sputtering procedure

Magnetron sputtering procedure included substrate preparation and metal-sputtering deposition. The above microfiltration ceramic membrane was also used as substrate of Pd–Ag alloy film. Mesoporous γ-Al_2O_3layer was coated on the surface of the macroporous α-Al_2O_3 disk by the sol–gel process [17]. The coating–drying–calcination steps were repeated to produce a high-quality substrate with a smooth surface.

A single-target magnetron sputtering system equipped with turbomolecular pump was used to perform the deposition of the Pd–Ag alloy material. The target material was a Pd–Ag alloy (24 wt.%) with a purity of 99.95%. During sputtering the target was cooled by cycling water. The sample holder can be programmably heated. High purity Ar (99.998%) was used as working gas and its flux was controlled by a needle valve. In a typical sputtering experiment, the target–substrate distance was set to be 5 cm, and the sputtering chamber was filled with Ar to 20 mtorr and the cathodic discharge voltages were in a range of 700–1000 V. The thickness of the Pd–Ag alloy film was controlled by sputtering time.

2.3. Membrane characterization

The morphologies of the substrates and the membranes were examined by scanning electron microscopy (SEM) and the film thickness was also measured by SEM.

Pure gas permeation measurements were performed by a variable-volume method in a homemade set-up. The composite membrane was positioned in a stainless steel permeator and sealed by graphite gaskets. The side edge of the membrane was sealed by a commercial ceramic glass, which can resist to high temperatures up to 800°C. A NiCr–Ni thermocouple near the membrane on the feed side monitored temperature during the permeation experiment. The pressure of the permeate side was maintained at atmospheric pressure. The gas flow rate was measured with a soap-bubble flowmeter. Before measuring H_2 permeation, the composite membranes were activated in an H_2 atmosphere.

3. Results and discussion

3.1. Thin palladium composite membrane from electroless plating

Fig. 1 shows the SEM photographs of the activated substrates prepared by the sol–gel process. As seen in Fig. 1, the surface roughness of the activated substrate decreased as the sol–gel process was repeated and the activated substrate produced by the three-time sol–gel process displayed a smooth surface. Hence, this type of activated substrate was applied for the deposition of Pd film. In this case, the Pd film could be prepared as thin as possible and remain dense. By SEM-EDX (scanning electron microscopy, energy dispersion X-ray), it was demonstrated that Pd was uniformly distributed in the activated layer in the direction of thickness as well as along the surface of the activated substrate. Thus, a uniform Pd film on the activated substrate could be obtained with the electroless plating procedure. Furthermore, the TEM (transmission electron microscopy) micrograph of the Pd/γ-Al_2O_3 (4 wt.%) material showed the particle size of Pd was 10–20 nm, which is smaller than those produced by sequence impregnation of Sn(II) and Pd(II) solution (i.e. conventional substrate activation method [7]). Therefore, the sol–gel-derived Pd can catalyze the post-deposition of Pd more efficiently.

The composition of electroless plating bath (mainly the content of the reducing agent) was optimized both, as a function of the compactness of Pd film and the stability of the electroless plating bath. The compactness was characterized by He permeation measurement. Three concentrations of hydrazine (0.51, 1.03 and 2.06 g/l) were examined. The permeation result showed the Pd composite membranes produced with the electroless plating baths of 1.03 and 2.06 g/l hydrazine and a deposition time of 1–2 h at ambient temperature were gas-tight. The bath with a hydrazine concentration of 1.03 g/l remained stable, i.e. without spontaneous deposition of Pd in the bath solution. Therefore, the electroless plating bath with the hydrazine content of 1.03 g/l was employed in this work and its composition was shown in Table 1. Fig. 2 gives the SEM photograph of a resulting Pd composite membrane and shows that a uniform Pd film with a thickness of <1 μm was produced using the above conditions.

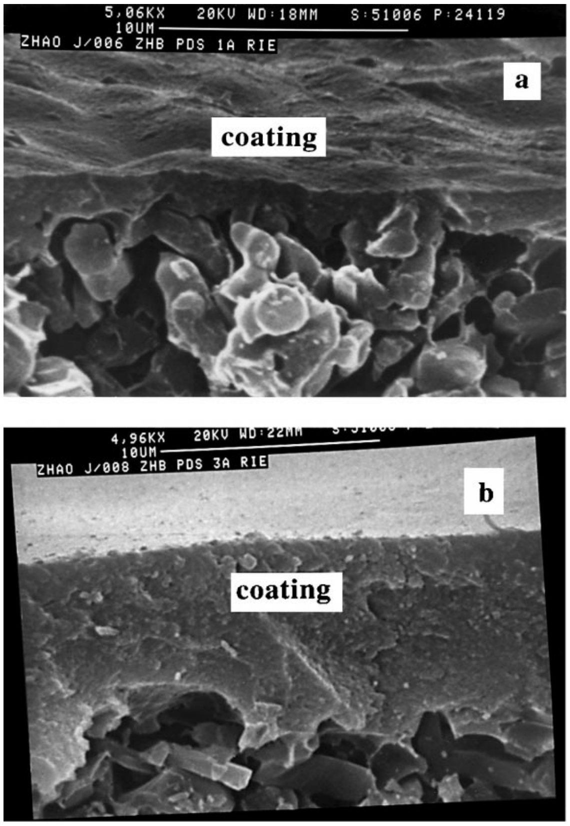

Fig. 1. SEM photographs of the cross section of activated substrates by the sol–gel process (a) one-time coating, (b) three-times coating.

Table 1
Typical electroless plating bath and deposition conditions

Component	Content
$PdAc_2$	3.37 g/l
$(NH_4)_2EDTA$	35.2 g/l
$NH_3{\cdot}H_2O$ (25 wt.%)	182 g/l
$N_2H_4{\cdot}H_2O$	1.03 g/l
pH	10.5
Deposition temperature	20–25°C

3.2. Thin palladium–silver alloy composite membrane from magnetron sputtering

Fig. 3 shows the SEM photographs of the γ-Al_2O_3-coated substrates prepared by the sol–gel process. As seen in Fig. 3, the γ-Al_2O_3-coated substrate produced by the two-time sol–gel process displayed a smoother surface. Therefore, the doubly coated γ-Al_2O_3 substrate was used as a support of Pd–Ag alloy film.

In the magnetron sputtering procedure, substrate temperature was optimized to produce dense Pd–Ag alloy composite membrane. The four substrate temperatures of 300, 350, 400 and 450°C were examined. Fig. 4 shows the He flow rate of the Pd–Ag alloy composite membranes as a function of substrate temperature. From Fig. 4, it was found that the Pd–Ag alloy composite membranes produced over the temperature range of 350–400°C had higher compactness. The Pd–Ag alloy composite membrane with a thickness of 1 μm was gas-tight using a substrate temperature of 400°C. Furthermore, the SEM photographs

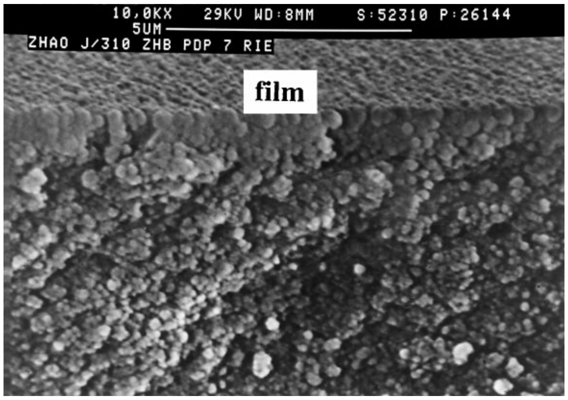

Fig. 2. SEM photograph of the cross section of Pd composite membrane.

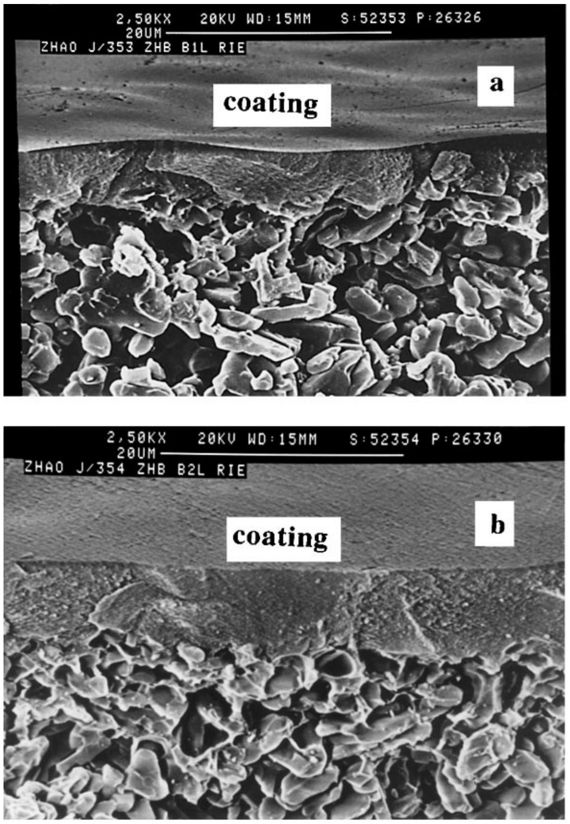

Fig. 3. SEM photographs of the cross-section of γ-Al_2O_3-coated substrates by the sol–gel process (a) one-time coating, (b) two-times coating.

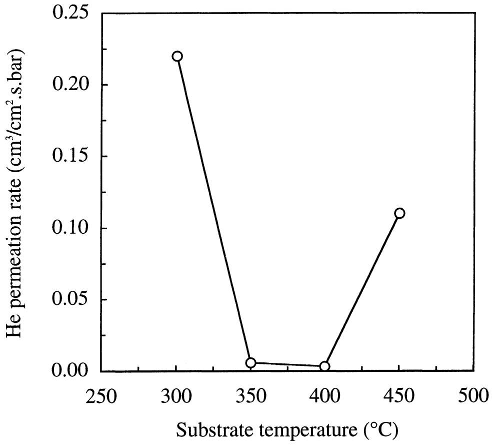

Fig. 4. The effect of substrate temperature on the tightness of the Pd–Ag alloy composite membrane.

of the Pd–Ag alloy composite membranes prepared at the above four temperatures are given in Fig. 5. As seen in Fig. 5, as a function of substrate temperature the columnar structures of the Pd–Ag alloy films were gradually modified and disappeared at temperatures >350°C.

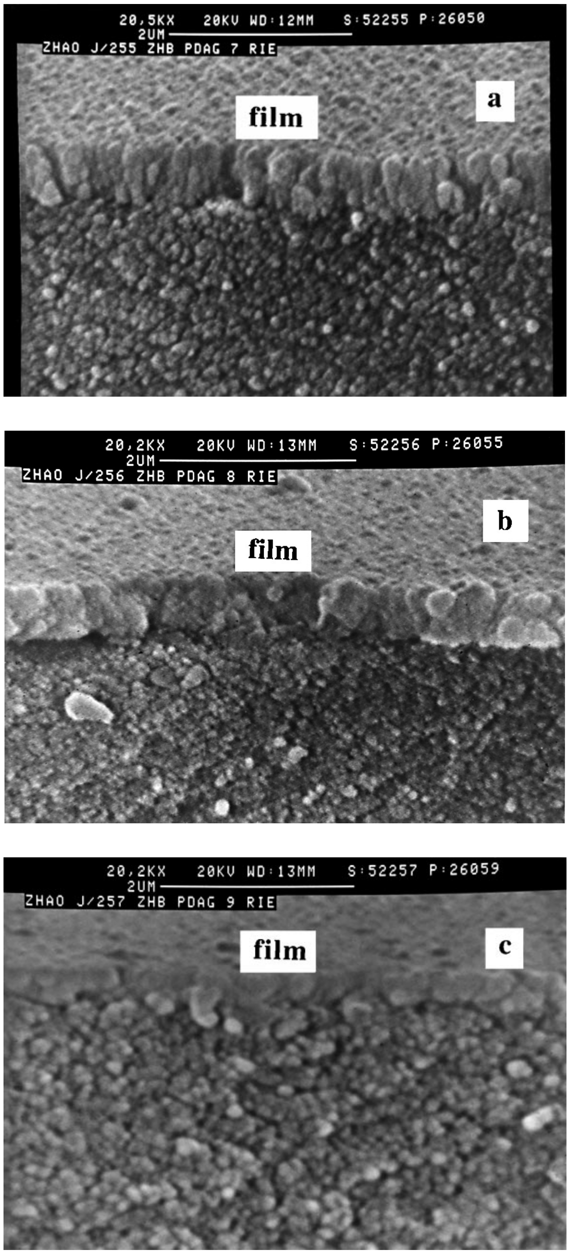

Fig. 5. SEM photographs of the cross section of Pd–Ag alloy composite membranes prepared as a function of substrate temperature of (a) 300, (b) 350, (c) 400 and (d) 450°C.

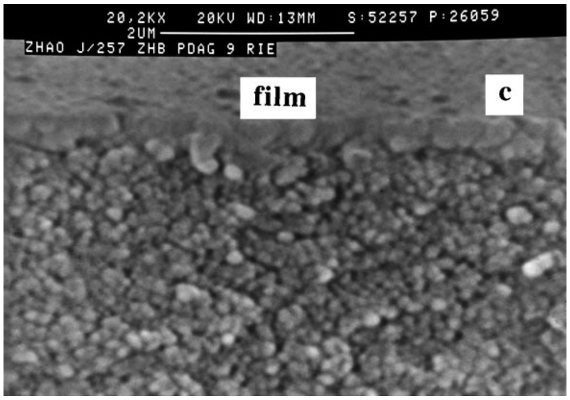

Fig. 5 (*Continued*).

The structure of vapor-deposited thin film has been widely investigated, and this has led to the development of the structure zone model (SZM), which relates the structure of a thin film to the normalized temperature (the ratio of substrate temperature to the melting point of a metal) [18–22]. According to SZM, structure development is controlled by both, the shadowing effect and metal atom diffusion during sputtering. At low substrate temperatures, higher points on a growing surface receive more vapor atoms than the valleys, resulting in a columnar structure, i.e. a shadowing effect. It is evident that the compactness of vapor-deposited thin film can be enhanced by using a substrate with smooth surface. With increasing substrate temperature thermo-induction metal atom diffusion becomes increasingly stronger. Thus, the columnar structure of vapor-deposited thin film can be modified and suppressed by substrate heating. Therefore, the more compact Pd–Ag alloy composite membranes were produced at substrate temperature s in the 350–400°C range. However, it should be noted that heating is coupled with thermal expansion, resulting in the development of thermal stress in composite materials [23]. The thermal stress may lead to the defects of the composite materials during its relaxation [24–27]. The reduced compactness of the Pd–Ag alloy composite membranes could be attributed to this kind of thermal stress. On the basis of the foregoing experiment, dense Pd–Ag alloy composites can be prepared by using a suitable substrate temperature and a smooth surface substrate.

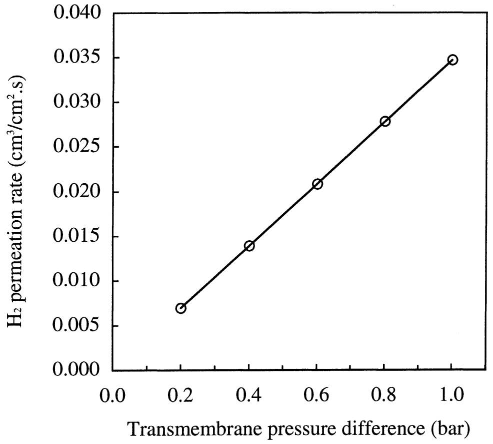

Fig. 6. Hydrogen permeation flux through Pd composite membrane as a function of transmembrane pressure difference at 314°C.

3.3. Hydrogen permeation properties

Fig. 6 shows the H_2 permeation rate through the Pd composite membrane as a function of transmembrane pressure difference. It should be mentioned that the H_2 flux was corrected with regard to the mass transfer resistance of the activated substrate. In addition, Fig. 7 shows the N_2 permeation rate as a function of average pressure for both, the Pd and Pd–Ag alloy composite membrane. As seen in Fig. 7, the N_2 permeation rates of the membranes remained nearly unchanged as a function of average pressure. The slight fluctuation of the experimental points may be attributed to a gas leak of the sealing materials and stabilization from one experimental point to another. However, basically Fig. 7 indicates that N_2 permeation through the membranes is via a Knudsen diffusion mechanism. This means that some defects (microcracks and pinholes) in the membranes were formed after the membranes were applied in H_2 atmosphere. Accordingly, the H_2 flow through the composite membranes consisted of two parts, one from the defects and the other from the dense part. Based on the Knudsen diffusion mechanism, the ratio of H_2 to N_2 permeation rate is 3.74. From the ratio, and the N_2 permeation rates shown in Fig. 7, the H_2 permeation rates through the defects were obtained. The H_2 flux through the dense part was obtained by subtracting the H_2 flux through the defects from the total H_2 flux through the composite membranes. As seen in Fig. 6, the H_2 flux through the Pd composite membrane is proportional to the transmembrane pressure difference of H_2, and not the square root of the partial pressure of H_2.

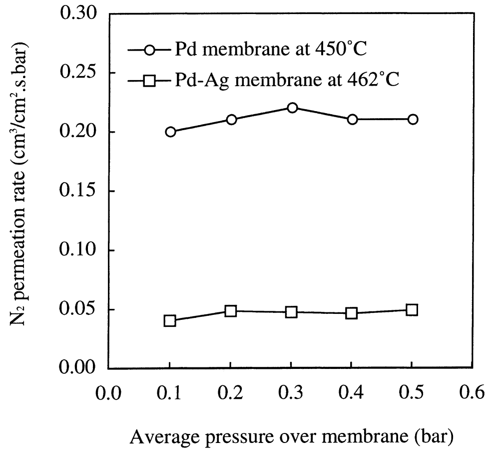

Fig. 7. Nitrogen permeation rate through the Pd and Pd–Ag composite membrane as a function of average pressure.

It is well known that H_2 permeation through Pd-based film involves the dissociative adsorption of molecular hydrogen and the solution and diffusion of atomic hydrogen in Pd lattice and associative desorption [28]. For thick Pd-based sheet, the bulk diffusion usually becomes the rate-determining step for H_2 permeation process. In this case, the power of H_2 pressure is 0.5 in the permeation equation of H_2 [29]. Recently, much effort has been made to produce Pd-based composite membranes with various thickness and configuration by electroless plating, sputtering and chemical vapor deposition technique. Collins, et al. [30] produced Pd/alumina composite membranes with a thickness of 11.4 μm by electroless plating. In their work, the power of H_2 pressure approached unity. It was suggested that the defects of the Pd composite membrane could have an effect on the value of the power of H_2 pressure. Li, et al. [9,10] reported the H_2 permeation property of the thin (<0.5 μm) Pd and Pd–Ag alloy composite membrane at the permeation temperatures of <300°C. Those membranes were prepared by the sputtering technique. In their work, high the power of H_2 pressure (>0.5) was attributed to the surface adsorption/desorption steps of H_2. In our work, the elevated-temperature permeation result showed that the power of H_2 pressure is unity for the Pd composite membrane. This suggests that the

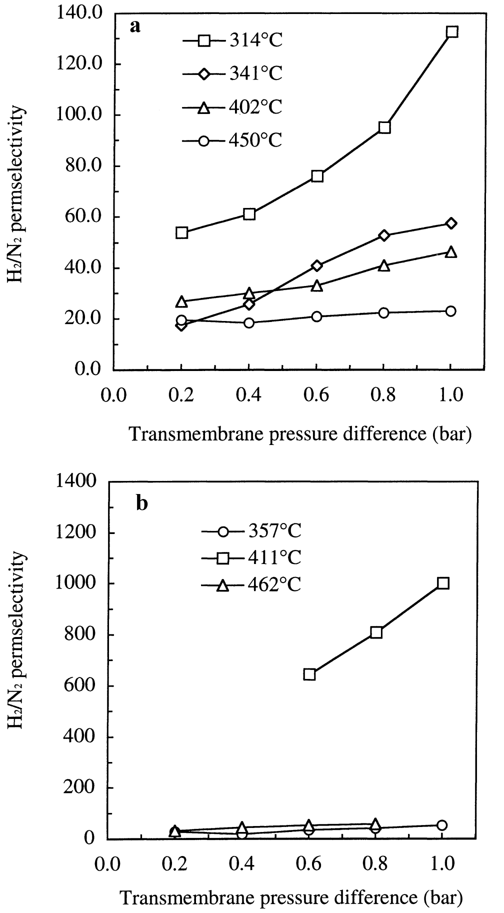

Fig. 8. (a) The hydrogen permselectivity of Pd composite membrane as a function of transmembrane pressure difference at four temperatures. (b) The hydrogen permselectivity of Pd–Ag alloy composite membrane as a function of transmembrane pressure difference at three temperatures.

surface chemistry of H_2 involving adsorption/desorption and surface diffusion on and/or in the membranes may contribute to the rate-determining step of H_2 permeation. However, at present the further detailed mechanism of H_2 permeation through our membranes is not clear.

3.4. Hydrogen permselectivity

In this work, H_2 permselectivity was defined as the ratio of H_2 to N_2 fluxes at the same conditions. Fig. 8 shows the H_2 permselectivity of the Pd and Pd–Ag alloy composite membrane as a function of transmembrane pressure difference at elevated temperatures. From Fig. 8, the Pd composite membrane exhibited a decrease in H_2 permselectivity as the temperature increased, and the Pd–Ag alloy composite membrane achieved a maximum of H_2 permselectivity at 411°C. These are related to their respective preparation methods. The structure of the Pd composite membrane was developed by the electroless plating at ambient temperature. However, that of the Pd–Ag alloy composite membrane was formed at 400°C by annealing during the deposition of the Pd–Ag alloy material. Higher operation temperatures than those of the preparation methods of the Pd and the Pd–Ag alloy composite membrane can lead to further sintering of the Pd and the Pd–Ag alloy film. This kind of the thermo-induction sintering may cause the failure of the Pd-based composite membranes, i.e. formation of some defects in the membranes. Therefore, in view of the high-temperature H_2 separation, high-temperature preparation methods need to be applied.

Fig. 8A, B show that the permselectivity of H_2/N_2 increased with transmembrane pressure difference. In this work, the mesoporous γ-Al_2O_3-based membrane was used as substrate of the Pd and Pd–Ag alloy film. The H_2/N_2 permeation rate ratio would remain constant on the basis of a Knudsen diffusion mechanism through this porous membrane. However, with the Pd or Pd–Ag alloy film, the surface diffusion of H_2 in the membranes may make a significant contribution to the total permeation of H_2, which is related to H_2 pressure. Hence, the membranes exhibited higher H_2/N_2 permselectivity at higher H_2 pressure. For the membranes which were less N_2 gas tight, the contribution of H_2 Knudsen diffusion is larger relative to the surface diffusion. Thus, the increase in H_2/N_2 permselectivity as a function of transmembrane pressure difference was lower for less N_2 gas-tight membranes.

4. Conclusion

Thin and dense Pd and Pd–Ag alloy composite membranes on mesoporous γ-Al_2O_3-based substrate can be produced by electroless plating and magnetron sputtering, respectively. The H_2 flux through the Pd-based composite membranes is proportional to the transmembrane pressure difference of H_2. This result indicates that the surface chemistry of H_2 on or/and in these membranes may become the rate-determining step of H_2 permeation process.

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