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Hydrogen permeance and the effect of H_2O and CO on the permeability of $Pd_{0.75}Ag_{0.25}$ membranes under gas-driven permeation and plasma-driven permeation

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ABSTRACT

The hydrogen permeance of $Pd_{0.75}Ag_{0.25}$ membranes was measured in the presence of pure H_2 or mixtures of H_2 with CO and H_2O at temperatures in the range of 300–773 K and at atmospheric pressure under gas-driven permeation (GDP) and plasma-driven permeation (PDP). The Arrhenius plots of the permeability through these membranes versus the inverse temperature showed a small peak in the intermediate temperature range and different activation energies in the low and high temperature ranges. The experimental data also indicated a more pronounced effect of CO on the permeability than H_2O, and a similar effect of GDP and PDP. The stronger inhibition by CO was due to the strong interaction between CO and Pd, and this effect was eliminated at temperatures higher than 623 K.

1. Introduction

Pd and Pd-based membranes provide a convenient method of purifying hydrogen or of removing H_2 from gas mixtures because of their high H_2 permeability and selectivity. Therefore, they are expected to be used as hydrogen separation membranes in reforming reactors [1–3]. However, some investigators have recently reported that the main components of reforming reactions, H_2O and CO, negatively affect the performance of Pd-based membranes (i.e., poisoning effect) [2,4–10]. The addition of CO or H_2O to the H_2 stream during permeation through the membrane caused a reduction in the permeation rate of H_2. Typically, this reduction has been attributed to the blocking of the available H_2 dissociation sites by adsorption of these gases on the membrane surface, resulting in the reduction of the active available area for H_2 permeation [9,10]. Another mechanism of inhibition by CO is the adsorption of CO on the membrane surface, which affects the transition state energy of H_2 dissociation; in other words, CO increases the activation barrier for H_2 dissociation [11]. There is controversy regarding the effects of CO and H_2O. Some studies have concluded that steam has a much more pronounced effect than CO on H_2 permeance with both Pd and Pd–Ag membranes [9,10], while others have obtained the opposite result [2,12]. According to Li et al. [9] and Hou and Hughes [10], the reason why H_2O exhibits a stronger poisoning effect may be due to the stronger binding of the H_2O molecule on the membrane surface compared with that of CO. However, a theoretical study has shown that the binding energy of the H_2O molecule on the membrane surface is significantly weaker than that of CO [12]. In addition, Alfonso [12] has proved that the adsorbed CO molecules have a more inhibitive effect on the H binding energy in their surroundings than H_2O molecules. The poisoning effect of these gases therefore cannot be explained completely in terms of the site-blocking capability of the molecularly adsorbed CO and H_2O [12].

Hydrogen permeation has been studied by various methods, and it is known that the permeation is enhanced by (1) the gas pressure difference between the two surfaces (gas-driven permeation, GDP), (2) the atomization of hydrogen molecules (atomic-driven permeation), (3) exposure to hydrogen plasma (plasma-driven permeation, PDP) and (4) hydrogen ion beam injection (ion-driven permeation) [13]. Hydrogen permeation under GDP through palladium-based membranes consists of the following steps [14]: (i) adsorption of H_2 on the feed-side surface, (ii) dissociation of H_2 molecules to atoms on the same surface, (iii) dissolution of H atoms into the bulk, (iv) hydrogen bulk diffusion to the opposite membrane surface (permeate site), (v) formation of H_2 molecules from the H atoms on the permeate side, and (vi) desorption of H_2 molecules on the permeate side. The mechanism of H_2 permeation under PDP may be shortened by at least one step compared with that under GDP, since H_2 molecules can be dissociated into H atoms without adsorption on the membrane surface, due to the plasma. Nagasaki et al. [15] have claimed that the prominent difference between PDP and GDP is the way in which the hydrogen enters

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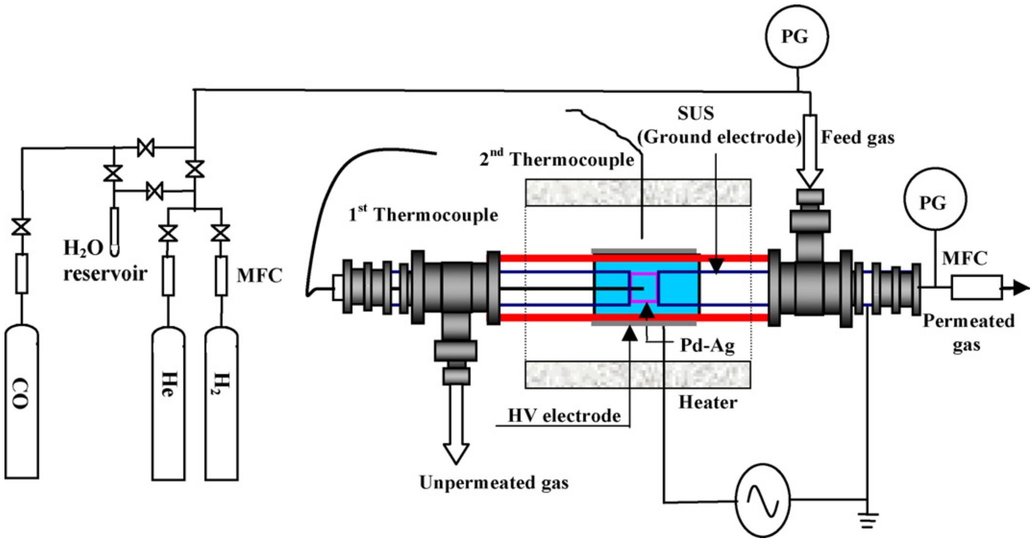

Fig. 1. Schematic diagram of the permeation apparatus.

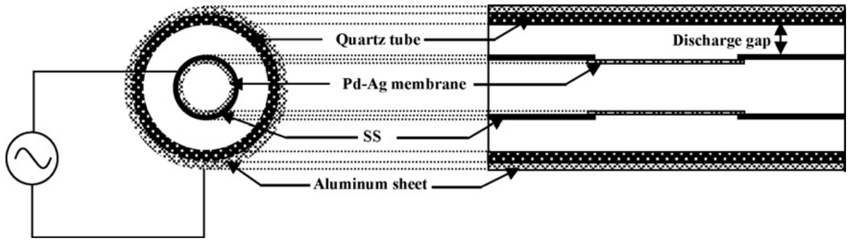

Fig. 2. Scheme of the cross-sectional DBD set-up.

the materials. Hydrogen is dissolved thermally into the materials in GDP, whereas it enters the materials with excess energy in PDP. Most data gathered to date evaluate H_2 permeance reduction under GDP, and useful data under PDP are rarely obtained, especially at atmospheric pressure. Takizawa et al. [16] have reported that adsorbed molecules such as H_2O and D_2O on the upstream surface reduced the GDP rate but enhanced the PDP rate at low pressure. The adsorbed H_2O obstructs H_2 dissociation and dissolution into the membrane in the case of GDP, but prevents the recombination and re-emission of H atoms under PDP.

The present work was part of a research program on the application of Pd–Ag membranes to the production of high-purity hydrogen via the reforming reaction using a plasma reformer. The combination of a plasma reactor with a membrane has not been reported yet. Plasma was generated by dielectric barrier discharge (DBD) at atmospheric pressure, in which the gas temperature can stay at or near room temperature while the electrons can reach temperatures of 10^4–10^5 K. This discharge demonstrates great flexibility with respect to its geometrical shape, working gas mixture composition and operation parameters (e.g., power input, frequency of feeding voltage, pressure and gas flow). In many cases, when these parameters have been previously optimized in small laboratory devices, there are no problems in scaling up the conditions to industrial dimensions [17]. The application of non-thermal plasma for fuel conversion and hydrogen production is especially effective, since plasma is used not as a source of energy but as a non-equilibrium generator of highly active species such as electrons, ions and radicals [18]. After the reaction, there are varying levels of hydrocarbons, H_2O, CO, CO_2, H_2, O_2 and traces of oxygenate compounds in the products [19,20]. These components may have an effect on hydrogen permeance. The objective of this study was to determine the hydrogen permeance as well as the effects of CO, H_2O, and CO and H_2O together on the permeance through $Pd_{0.75}Ag_{0.25}$ membranes under PDP and GDP across the temperature range from 300 K to 773 K and at atmospheric retentate total pressure.

2. Experimental

2.1. Pd–Ag membranes

Our present permeation studies were performed in a membrane module, schematically shown in Fig. 1. All the Pd–25%Ag membranes used in this study were commercial ones purchased from Nilaco, and the details on these membranes are reported in Table 1. This alloy composition was selected because of its high permeability and availability. In this study, appropriately thick membranes (0.075 mm, 0.1 mm, and 0.3 mm) were used. A Pd–Ag tube was cut to the desired length and jointed, by brazing, with two stainless steel tubes. One end of the membrane tube was capped by a thermocouple used to measure the permeation temperature. This membrane was inserted into a quartz tube in a shell-tube configuration. The permeator was placed in the center of the furnace.

Before each permeation test, the membrane was annealed at 773 K for 1 h in air, and then the furnace was cooled to room temper-

Table 1
Geometrical characteristics of the Pd–Ag membranes used in this study.

	Thickness (μm)	OD (mm)	*S* (cm^2)
Pd–Ag-1	75	1.4	2.64
Pd–Ag-2	100	5	4.71
Pd–Ag-3	300	2.5	3.93

ature. With this procedure, it was possible to obtain a clean surface, and reproducible permeability data could thus be obtained.

2.2. *Plasma source*

Dielectric barrier discharge is an easy way to generate non-thermal plasma conditions at low gas temperatures and elevated (typically atmospheric) pressures. DBD provides high-energy electrons which can generate atoms, radicals and excited particles. Fig. 2 shows a schematic of the experimental DBD set-up. Electrical discharge was generated in a 0.5-mm wide annular discharge gap formed by an outer quartz tube serving as the dielectric barrier and an inner membrane tube. An aluminum sheet, 8 cm in length, covering the outer of quartz tube was used as the high-voltage electrode, and the membrane tube was used as the ground inner electrode. A high-voltage generator supplied sinusoidal waveforms at about 6 kVpp in the frequency range of 1.3–3 kHz to the high-voltage electrode. At a discharge voltage of 6 kVpp and a frequency of 3 kHz, the average inside temperature could be raised up to 473 K. To compare PDP and GDP at high temperatures, i.e., higher than 473 K, additional heating by means of an electrical heater was necessary. The temperature obtained under PDP was measured by a thermocouple inserted inside the membrane at the center, and another thermocouple was used to control the heat supplied to the heater.

2.3. *Permeation test*

The permeation test for the Pd–Ag membranes was carried out across a wide range of temperatures (300–773 K), where the high pressure side was atmospheric pressure and the low pressure side was controlled by a rotary pump. The pressure difference was approximately 1 atm. The operating temperature in the case of GDP was controlled by an electric furnace, whereas, in the case of PDP, it was controlled by both an electric furnace and plasma ignition.

The permeation experiments were carried out with pure H_2 gas as well as with various gas mixtures: H_2 with CO or H_2O, or with CO and H_2O together. Pure hydrogen of seven–nine purity (7 N H_2) and CO (99.95%) were introduced into the membrane module by a mass flow controller (Kofloc, 3660). The H_2O reservoir was kept at room temperature to supply a constant water vapor pressure of about 2.4 kPa. The feed gases were flowed along the outer side of the membrane, and the permeated H_2 gas was extracted at the inner side of the membrane and measured by another mass flow controller (Kofloc, 3660).

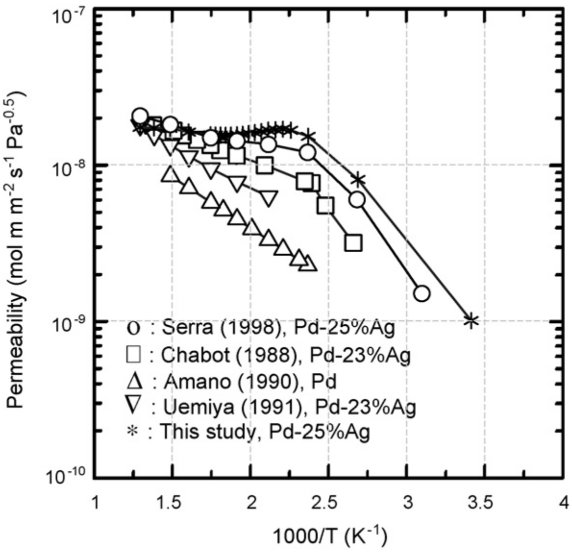

Fig. 3. Comparison of the H_2 permeation measurements for Pd-based membranes in GDP.

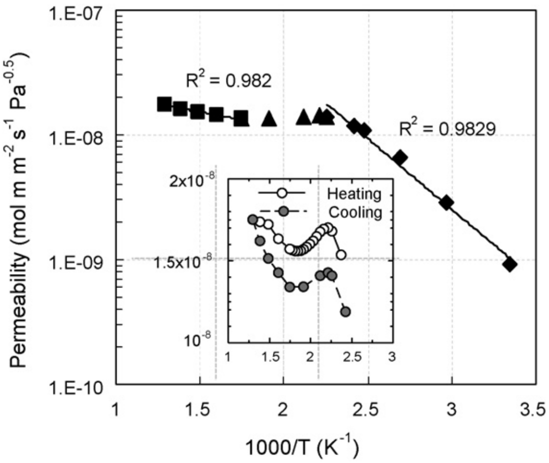

Fig. 4. Typical hysteresis in H_2 permeability under GDP during the heating and cooling cycle.

In this study, since appropriately thick membranes were used, the permeation of H_2 was governed by Fick's and Sieverts' laws, and the H_2 flux was calculated from the following expression: $J_{H_2} = Pe(P^{0.5}_{H_2,\mathrm{Ret}} - P^{0.5}_{H_2,\mathrm{Per}})/l$; the difference between the square root of the hydrogen's partial pressure on the feed and permeate sides of the membrane was used, which is consistent with diffusion-limited membranes. The flux, J (mol m^{-2} s^{-1}), was a function of the permeability, Pe (mol m^{-1} s^{-1} Pa$^{-0.5}$), l (m) was the membrane thickness, $P_{H_2,\mathrm{Ret}}$ (Pa) was the partial pressure of hydrogen on the upstream, or retentate, side of the membrane, and $P_{H_2,\mathrm{Per}}$ (Pa) was the partial pressure of hydrogen on the downstream, or permeate side of the membrane. The pressure-normalized flux, or permeance (mol m^{-2} s^{-1} Pa$^{-0.5}$) was defined as the ratio of the permeability to the membrane thickness. The temperature dependence of Pe was typically reflected in an Arrhenius-type relationship between Pe and the inverse absolute temperature (K^{-1}), yielding the activation energy (E_D, kJ mol^{-1}) and pre-exponential constant (Pe_o) for these membranes, $Pe = Pe_o \exp(-E_D/RT)$.

3. Results and discussion

3.1. *Determination of the H_2 permeability*

3.1.1. *GDP*

Fig. 3 shows the plot of the H_2 permeability of a 0.1-mm Pd–25%Ag membrane versus the temperature across the 300–773 K temperature range. These results were in reasonable agreement with the previous literature [4,5,26,27].

One of the most interesting results was the shape of the permeability versus temperature curves. The permeability of the Pd–Ag alloy did not show a continuous increase with temperature, as can be seen clearly in the inset of Fig. 4. Across a wide range of temperatures, the permeability remained constant or even decreased at higher temperatures before increasing again. In other words, there was a maximum permeability at around 453 K. This maximum point at a certain temperature depended on the pressure, and occurred only within a certain pressure range; at excessively low differential pressures or pressures above 6.8 atm, this maximum point was not pronounced [21]. The peak position shifted to the higher temperature side with increasing pressure. For instance, at the pressures of 0.68 atm and 2 atm, the maximum points occurred at 440 K and 470 K, respectively [21]. It is reported that permeability is a function of solubility and diffusivity [22]. For palladium, the solubility

Table 2
Activation energies of hydrogen permeation through Pd-based membranes.

	This study		Tosti et al. [1]		Yoshida et al. [24]		Serra et al. [26]
E_D (kJ mol^{-1})	23.4	5	15.5	4.3	30	5.9	5.2
Temperature range	<450 K	>550 K	<550 K	>550 K	<500 K	>500 K	>373 K

decreases and the diffusivity increases with temperature, resulting in an overall increase in permeation rate at higher temperatures. A possible explanation for the non-linear increase in permeability with increasing temperature is the sharp decrease in solubility for this Pd–25%Ag alloy, so that instead of a continued increase in diffusivity, the permeability remains constant or decreases [23].

The permeability was also measured during the course of a heating cycle. The data showed that hysteresis appeared during the heating and cooling cycle, as shown in Fig. 4. The same behavior has been reported for a Pd–Ag alloy membrane with the same composition [21]. Hughes and Harris [23] have given poisoning as the reason for this hysteresis, which was neutralized by the subsequent reactivation of the surface. However, in our study, this hysteresis still occurred after many rounds of treatment, and if the same data are obtained repeatedly, the hysteresis may be due to something other than surface contamination or defects. Further experiments are needed to clarify this phenomenon.

Two linear Arrhenius relations can be seen in the permeability versus reciprocal temperature plot in Fig. 4. The apparent activation energies at low temperature and high temperature were 23.4 kJ mol^{-1} and 5 kJ mol^{-1}, respectively. It has been mentioned in the literature that the Arrhenius plots of the permeability through palladium versus the inverse temperature can show total activation energies ranging from 1 kJ mol^{-1} to 33 kJ mol^{-1} (depending on the film's thickness, composition and deposition method), with values around 15 kJ mol^{-1} being the most common. The activation energy also decreases as the temperature increases [22]. For Pd alloyed with Ag, this activation energy decreases with increasing Ag content up to 30 wt.%, and increases at higher Ag contents [25]. Table 2 shows a comparison between the permeation parameters given by various sources. The parameters obtained in the present study are consistent with the experimental data found elsewhere in the literature.

3.1.2. PDP

This experiment was carried out using a membrane thickness of 0.1 mm across a temperature range of 373–773 K. The discharge voltage was maintained at 6 kVpp, whereas the discharge frequency was varied from 1.3 kHz to 3 kHz. The plot of the H_2 permeability versus the temperature is given in Fig. 8. The experimental results indicate that the permeability did not increase continuously with the temperature, a behavior similar to that observed in the case of GDP. A quick decrease in solubility and a slight increase in diffusion with temperature caused a non-linear increase in permeability versus the temperature for this Pd–25%Ag membrane [23]. The plasma experiments did not modify or destroy any properties of the membrane, whether they were related to the appearance or to the permeation behavior.

3.2. Effect of CO on H_2 permeance

According to the literature, the addition of CO to the gas stream over Pd-based membranes strongly reduces the H_2 permeation rate due to the blockage of the hydrogen dissociation and association sites. In this experiment, the effect of CO was investigated over a wide range of temperatures, from 400 K to 773 K, with various CO concentrations under both GDP and PDP.

CO gas was introduced into the H_2 stream at different ratios, where the lowest and highest concentrations of CO were 0.5% and 20%, respectively. Fig. 5 shows that the presence of CO had a negative effect on the hydrogen permeation under GDP. The effect of CO was strongly dependent on the temperature. At the lowest temperature of 400 K, a decrease of approximately 50% occurred with the lowest CO concentration, 0.5%. When the CO concentration was increased, the hydrogen permeation rate was brought to zero. The optimal operating temperature at which the effect of CO was negligible was dependent on the CO concentration as well as the temperature. Chabot et al. [4] reported that hydrogen permeation was totally extinguished at 423 K at arbitrary CO concentrations; meanwhile, Amadusson et al. [7] have demonstrated that it was totally quenched at 373 K with an equimolar mixture of H_2 and CO. For all CO concentrations, the negative effect of CO became less pronounced, i.e., the hydrogen permeation reduction was less than 10% at temperatures above 573 K. Gallucci et al. [8] have reported a negligible effect of CO at temperatures above 623 K. The hydrogen permeation reduction was due to the strong interaction between the CO and Pd atoms [8].

To clarify the competitive adsorption of CO on the membrane, the CO in the feed mixture was shut off. It was found that the permeation rate increased with time and then became stable after about 30 min; the hydrogen permeation rates before and after the membranes were exposed to CO gas attained the same value (Fig. 6). The restoration of the hydrogen permeation rate indicated that the CO gas did not change any properties of the Pd-based membranes and, therefore, it can be concluded that the effect of the addition of CO on the performance of the membrane was due to the adsorption of CO on the membrane surface; it can also be concluded that the adsorption of CO is reversible [8,9]. The transport of pure hydrogen across thick membranes was limited by bulk diffusion. It was mentioned above that the CO coverage of the Pd-based membranes when CO was added to the gas stream decreased the actual surface area for hydrogen permeation. This implies that the surface process may become the rate-limiting factor of hydrogen permeation.

The effect of CO on the membranes was also studied with different membrane thicknesses. Three membranes with a thickness of 0.075 mm, 0.1 mm and 0.3 mm were used in this experiment. The experiment was carried out with a CO concentration of 1.5%

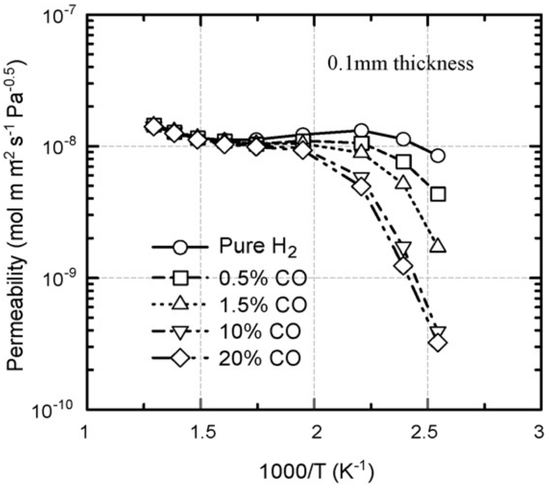

Fig. 5. Effect of the CO concentration on H_2 permeability.

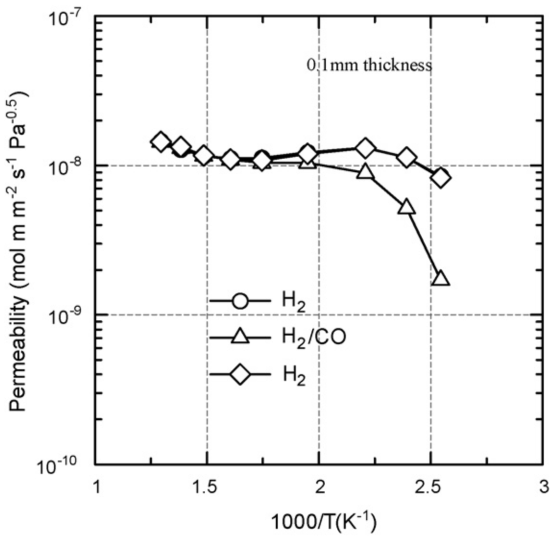

Fig. 6. Hydrogen permeability for pure H_2 and H_2/CO mixture gases.

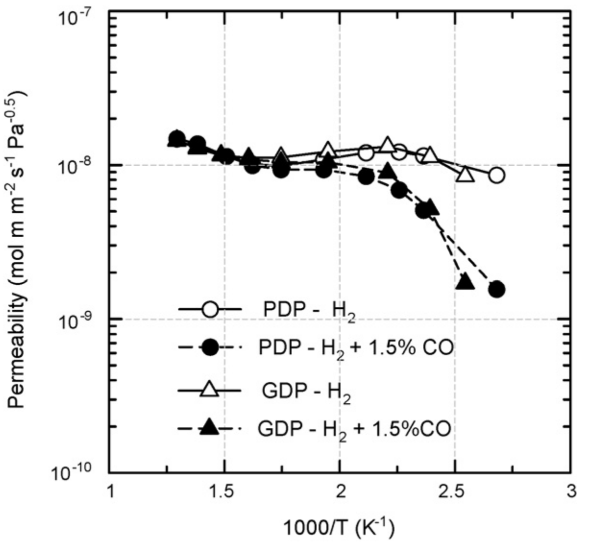

Fig. 8. Effect of GDP and PDP on H_2 permeability for H_2/CO mixture gases.

under GDP. There was a minor change in hydrogen permeability through the three membranes with or without CO (Fig. 7). However, it can be seen that the effect of CO was more pronounced for the thinner membranes. For example, at a temperature of 573 K, a decrease of 3% occurred with the 0.3-mm thick membrane, whereas a decrease of 7% and 20% occurred with the 0.1 mm and 0.075 mm thick membranes, respectively. Again, the permeability did not show a continuous increase with temperature for the three membrane thicknesses regardless of the presence of CO.

Finally, the effect of CO was investigated under GPD and PDP. The membrane used in this experiment had a thickness of 0.1 mm. The experimental results (Fig. 8) indicate a minor difference in hydrogen permeability with or without CO under GDP and PDP. For example, the permeability in the case of PDP was a little higher than that in the case of GDP at low temperature; however, at intermediate temperature, the permeability under PDP was lower than under GDP; finally, the permeability was similar in the two cases at high temperature. This difference was due to the non-uniform temperature distribution under PDP. An experiment was performed to check the temperature distribution along the membrane in the plasma region. It was found that the highest temperature occurred at the center of the plasma region or the membrane, and that the further away from the center of the membrane, the lower the temperature. In addition, during the experiment, the temperature observed under PDP fluctuated, while remaining constant under GDP. The permeability under PDP was expected to be higher than that under GDP, but this did not happen in this study. The reasons for this could be the high upstream pressure and the type of discharge used in the plasma chamber, which limited the dissociation rate of hydrogen.

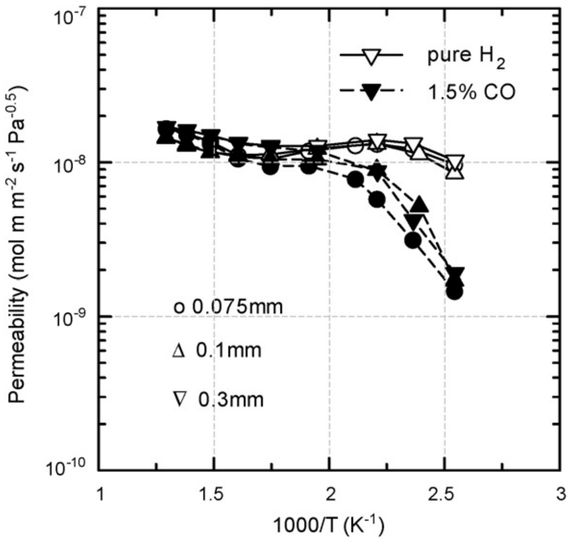

Fig. 7. Effect of the membrane thicknesses on H_2 permeability for H_2/CO mixture gases.

3.3. *Effect of H_2O on permeance*

In this experiment, the effect on permeability of passing H_2O through Pd-based membranes was carried out at a fixed vapor pressure at room temperature of about 2.4 kPa, corresponding to 2.4% H_2O, in the temperature range of 400 K to 773 K under GDP and PDP, using two membrane thicknesses, 0.075 mm and 0.1 mm. There is ambiguity about the influence of H_2O on the permeability of Pd-based membranes. Some researchers have reported a more pronounced effect of H_2O than that of CO [9,10], while others have proposed opposite results [2] under GDP. For instance, Hou and Hughes [10] have reported that the hydrogen permeation rate was reduced by 70% in the presence of 5% H_2O, while the addition of the same amount of CO to hydrogen only reduced the permeation by less than 40% at 548 K. Arstad et al. [2] have observed that a hydrogen stream with 20% CO caused a 88% reduction in the hydrogen permeation rate, while the same amount of H_2O only reduced the hydrogen permeation rate by 40% at 528 K. They reported only a minor effect of H_2O, and this effect was mainly dilution, since the same amount of N_2 caused a reduction of about 34%. In this study, the influence of H_2O on permeability can be considered negligible: a decrease of less than 5% occurred at any temperature and with any membrane thickness, as shown in Fig. 9, while, in the presence of 1.5% CO, the hydrogen permeation rates were reduced by 80% and 15% at 400 K and 513 K, respectively. The effect of water vapor on the performance of Pd-based membranes was mainly dilution. The weaker poisoning effect of H_2O compared with that of CO is due to the weaker binding energy of the H_2O molecule on the membrane surface compared with that of CO, and also to the stronger inhibitive effect of the adsorbed CO molecules on the H binding energy in their surroundings compared to that of H_2O [12]. The reduction of H_2 permeability also depends on the material. Perng and Altstetter [28] have reported the effect of H_2O on H_2 permeation in stainless

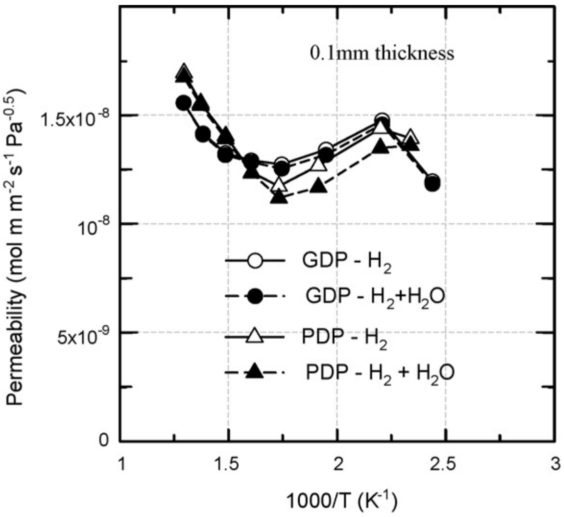

Fig. 9. Effect of GDP and PDP on H_2 permeability for H_2/H_2O mixture gases.

steel (SS) at low temperatures of 373–633 K. Water had no effect on the H_2 permeability through Pd-coated, deformed SS 304; however, the addition of H_2O reduced the H_2 permeability by a factor of two or three through uncoated SS 302. In this study [28], H_2O reacted with uncoated specimens to form oxides which acted as a barrier to hydrogen permeation, and the Pd coating prevented the SS from reacting with H_2O.

The effect of H_2O on permeability under PDP showed a trend similar to that under GDP (Fig. 9); this influence can be considered negligible. At low temperature, the effect of H_2O under PDP was slightly stronger than that under GDP. This can be interpreted in terms of H_2O dissociation, caused by the plasma. It has been reported that H_2O acts as a strong inhibitor when it dissociates, even stronger than CO. The O atoms dissociated from H_2O molecules have a stronger inhibitive effect on hydrogen adsorption than the adsorbed CO [12]. Takizawa et al. [16] have mentioned a positive effect of H_2O film, which reduced the hydrogen permeation rate in the case of GDP but enhanced it in the case of PDP with SS 304. Our results were in apparent contrast to Takizawa's findings. The differences may be attributed to the different experimental materials, experimental conditions and plasma source. As mentioned above, water had no effect on the H_2 permeability through Pd-coated SS, but reduced the H_2 permeability through uncoated SS [28]. Furthermore, Takizawa's experiments were carried out in severe conditions, at low pressure. Their findings should be particular to high-vacuum conditions, since plasma is effective at low pressure. Plasma generated at elevated pressure (atmospheric pressure) is suitable for industrial applications.

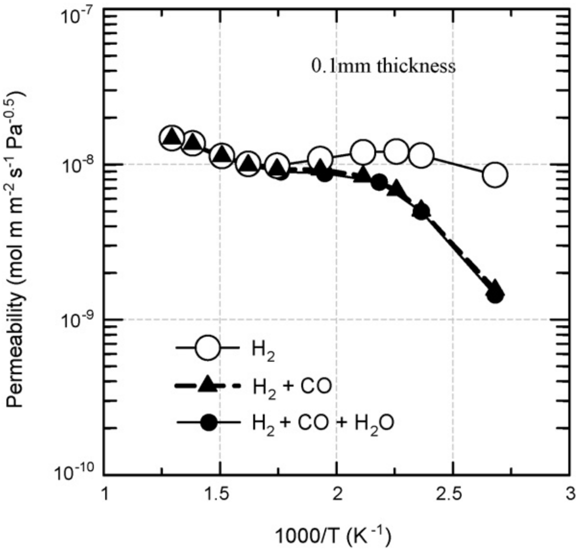

Fig. 10. Effect of CO and H_2O together on H_2 permeability.

3.4. *Effect of CO and H_2O together on permeance*

The experiment with CO and H_2O together was carried out at a fixed partial pressure of CO and H_2O of 1.4% and 2.4%, respectively, under PDP. Fig. 10 indicates that the results for CO + H_2O and for CO alone as a function of the inverse temperature through the 0.1 mm thick membrane were similar. This again proves the negligible influence of H_2O on hydrogen permeation through Pd-based membranes.

4. Conclusions

The permeability of $Pd_{0.75}Ag_{0.25}$ alloy membranes in the presence of pure H_2 and mixtures of H_2 with CO or H_2O or with CO and H_2O together were determined across a temperature range of 300–773 K at atmospheric pressure on the retentate side under GDP and PDP. Hydrogen permeation showed a small peak in the intermediate temperature range, and two activation energies in the low and high temperature ranges. The addition of CO resulted in the reduction of the permeability under both PDP and GDP. Poisoning became more significant with increasing CO at low temperature. It was noted that the thinner the membrane, the stronger the effect of CO on the permeability. The effect of CO was negligible at temperatures above 623 K. The influence of H_2O on permeability can be considered negligible; a decrease of less than 5% occurred at any temperature and with any membrane thickness under both PDP and GDP. At low temperature, the effect of H_2O under PDP was stronger than under GDP, but there was a minor difference in permeability between GDP and PDP. The effect of CO was much stronger than that of H_2O on permeability at any temperature. To minimize the effect of these gases in the plasma reformer, the reforming experiment should be carried out at temperatures higher than 623 K.

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