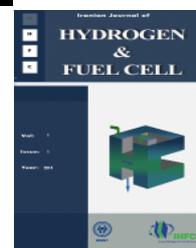Iranian Journal of Hydrogen & Fuel Cell

IJHFC

Journal homepage://ijhfc.irost.ir

Determination of thermodynamic parameters of hydrogen permeation of palladium membrane for considering the effect of stainless steel support

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Abstract

A palladium composite membrane was prepared by electroless plating on oxidized porous stainless steel support (ox-PSS). Hydrogen permeation flux through this composite membrane was measured in the temperature range of 574-674 K and the pressure difference of two sides of membrane up to 90 kPa. A simplified resistance model was employed to analyze the permeation behavior of hydrogen through Pd/ox-PSS membrane for calculating the contribution of each layer in resistance against the hydrogen transport. The amount of enthalpy of hydrogen dissolution of palladium membrane is -9.4 kJ/mol.

Considering a complete detailed model, this value was used for discussing the effect of interaction of metal- support on hydrogen exiting from the palladium layer at the downstream side. Several composite membranes which differ in support material has been compared with each other. It was confirmed that the metal-support interaction, plays an effective role in exiting activation energy. In Pd/ox-PSS composite membrane, the metal-support interaction decreases hydrogen exiting rate from Pd membrane's downstream side.

1.   Introduction

Need to clean and healthful environment forces the world to the pure hydrogen production and fuel cell application. However, almost all of the energy carriers are fossil fuels and hydrocarbon compounds. Production of clean and green hydrogen fuel from these energy carriers is performed in relatively high temperature through steam reforming reaction. For hydrogen separation purposes, palladium based membranes have been studied in many investigations owing to their suitable properties at high temperature, high permeability, selectivity and durability.

In order to construct the membrane, various supports such as PNS [1], PSS [2], α-alumina [3], anodic alumina [4], porous Hastelloy [5], and different diffusion barriers (e.g. Cr_2O_3 [6], α-Fe_2O_3 [7], ZrO_2 [8], TiO_2 [9], SiO_2 [10], CeO_2 [11]) have been used. Also, various palladium-based alloys

have been used. Also, various palladium-based alloys have been used as membrane such as Pd-Cu [12], Pd-Ag [13], Pd-Au and Pd-Au-Pt [14], Pd-Cu-Ni [15], Pd-Cu-Au [16], Pd-Cu-Ag [17], and other binary and ternary alloys [18]. In addition, membranes with different micro-structures [19,20], and geometries [21,22] have been used to evaluate the performance of them. However, the contribution of support in the permeation process has not been concern, particularly in experimental procedure.

Although there are few reports. Huang et. al., by investigating Pd/αAl$_2$O$_3$ composite membranes, reported hydrogen permeation activation energy, molar enthalpy and entropy of hydrogen dissolution in palladium layer [23].Zhang et. al., compare their data with a model and they investigate the effects of different diffusion barriers on the activation energy of hydrogen permeation [24].

In this study, we prepared a Pd/ox-PSS membrane and studied its permeation behavior. In the next section, the background theory of permeation through composite palladium membrane is explained. Then, the experimental procedure is stated. Finally, the contributions of Pd layer and support for hydrogen permeance are calculated. Furthermore, palladium layer's permeability, hydrogen permeation activation energy, molar enthalpy and entropy of hydrogen dissolution in Pd layer are investigated.

2.   Theory

A composite palladium membrane consists of a porous support and a thin layer of palladium. Although in many researches, the support effect is disregarded but it affects on the characteristics of permeation through the composite palladium membrane. To differentiate the contributions of porous support and palladium layer in the permeation resistance, we used the resistance model. This model was developed by Henis and Tripodi for gas permeation in a composite membrane [25]. The permeation resistance of a layer is defined as the reverse of its permeance. According to this model, the permeation behaviour of gas through a composite membrane is analogous to the flow of electricity through a series array of resistors.

In fact, the amounts of fluxes that permeated Figure 1 shows the schematic of composite membrane resistance model for a dense palladium composite membrane. The transport resistances

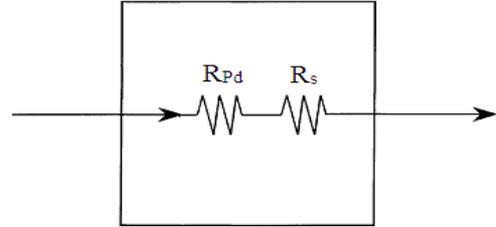in the support and palladium layer have been symbolized by R$_s$ and R$_{Pd}$, respectively.

Figure 1. Schematic representation of H$_2$ permeation through Pd composite membrane.

The total resistance of the composite membrane R_{tot}, is the sum of resistances in the palladium layer and the support layer:

$$R_{tot} = \frac{1}{F_{tot}} = R_s + R_{Pd} \tag{1}$$

Where

$$R_s = \frac{P_i - P_l}{J}, \qquad R_{Pd} = \frac{P_h - P_i}{J}$$

F_{tot} is the composite membrane permeance, and P_h, P_i and P_l are feed side pressure (high pressure side), pressure (high pressure side), pressure in the palladium-support interface and permeate side pressure (low pressure side), respectively.

The permeance through porous support

In pressure-driven gas permeation process through a bare porous support, the transport mechanism mainly follows Knudsen diffusion and viscous (poiseuille) flow. The permeance through a bare porous disk vs. trans-membrane average pressure is correlated by a straight line:

$$J' = F'(P_h - P_l) \tag{2}$$

$$F' = F'_{k,s} + F'_{v,s}.P_{av} \tag{3}$$

The slope and intercept of the latter equation represents the contributions of viscous flow and Knudsen diffusion, respectively. $F'_{k,s}$ and $F'_{v,s}$ are defined as:

$$F'_{k,s} = \left(\frac{4\sqrt{2}\varepsilon\mu_k r}{3L\sqrt{\pi R}} \right) \frac{1}{\sqrt{MT}} \tag{4}$$

$$F'_{v,s} = \left(\frac{\varepsilon\mu_k r^2}{8RL} \right) \frac{1}{\eta T} \tag{5}$$

The symbols are defined in the nomenclature. The first items of $F'_{k,s}$ and $F'_{v,s}$ are fixed values for a given porous media, and the second items are functions of gas molecular mass and temperature.

The permeation through Palladium layer

The hydrogen permeation flux in the Pd layer by the solution-diffusion mechanism can be expressed as follows:

$$J = F\left(P_h^n - P_l^n\right) \quad (6)$$

If adsorption and desorption of hydrogen molecules (surface process) are done quickly, then the diffusion of hydrogen in the bulk palladium layer is the rate determining step and the hydrogen flux is described by:

$$J = F_{pl}\frac{P_h^{0.5} - P_l^{0.5}}{L} \quad (7)$$

Where

$$F_{pl} = DS = D\frac{N_b}{K_s}$$

The temperature dependence of permeability F_{pl} and diffusion coefficient D, can be expressed by an exponential form as the below equations:

$$F_{pl} = F_{pl,0}\exp\left(\frac{-E_a}{RT}\right) \quad (8)$$

$$D = D_0\exp\left(\frac{-E_d}{RT}\right) \quad (9)$$

The molar values for the enthalpy of hydrogen dissolution, $\Delta\overline{H}_H$ and the entropy of hydrogen dissolution in palladium layer $\Delta\overline{S}_H$, could be calculated by:

$$K_s = \exp\left(\frac{\Delta\overline{H}_H}{RT} - \frac{\Delta\overline{S}_H}{R}\right) \quad (10)$$

The contribution of palladium layer in permeation resistance

In a composite membrane, to obtain hydrogen permeance through Pd layer only and the contribution of this layer in the transport resistance, hydrogen pressure at palladium-support interface P_i, should be calculated by the resistances in series model as below:

$$P_i = \left[\left(\frac{F_{k,s}}{F_{v,s}}\right)^2 + 2P_l\left(\frac{F_{k,s}}{F_{v,s}}\right) + P_l^2 + \frac{2J}{F_{v,s}}\right]^{1/2} - \frac{F_{k,s}}{F_{v,s}} \quad (11)$$

This equation easily can be derived by considering the resistance model and solving Eq. (3) for calculating pressure at the interface.

3.   Experimental procedure

3.1.   Membrane preparation

PSS 316L disk with nominal particle retention size of $0.2\mu m$ and diameter of 29mm was purchased from Mott metallurgical corporation. According to the manufacturer, the disk has a porosity of roughly 20–23%. Such a plate made by metal powders has been widely used as the substrate to provide mechanical strength for palladium membrane. The PSS support was cleaned in an ultrasonic bath with a mixture of an alkaline sodium solution and an organic detergent at 333K for 30 min. The cleaning procedure was followed by rinsing in deionised water and isopropanol, respectively.
This step was finished after drying the PSS support at 393K for 3h.
Then it was oxidized in the stagnant air at 1173K for 12h to form an oxide intermetallic diffusion barrier at the intermediate of the support and the hydrogen selective Pd layer. Before electroless plating, the disk was sensitized and activated according to a conventional $SnCl_2/PdCl_2$ method [26]. Pd membrane was prepared using electroless plating over the ox-PSS disk support. The chemicals and conditions required for electroless plating bath of palladium are specified in Table 1. The volume/area ratio between the plating solution and the plated area was kept about $3cm^3/cm^2$.

3.2.   Membrane permeation testing

A conventional homemade disk type setup was used to measure the permeation of gas through the prepared membrane. The composite membrane was assembled in the compact testing cell, and the perimeter of that, was sealed fully with a high temperature resistant silver paste. The valid membrane diameter for the permeation test was 23mm. Permeation flux of pure gas of hydrogen was measured by introducing into the palladium membrane disk. Measurement of hydrogen permeation

Table 1. Palladium plating bath composition and conditions

Components (conditions)	Pd bath
$PdCl_2$ (g/lit)	5
$Na_2EDTA \cdot 2H_2O$ (g/lit)	70
NH_4OH (28%) (g/lit)	287
N_2H_5OH (80% g/lit)	2.5
pH	~11
Temperature (K)	298

flux was made at different temperatures and pressures. Before testing, the membrane was heated in nitrogen atmosphere up to 674K at 1K/min. Then the nitrogen introducing gas substituted with hydrogen. After taking hydrogen flux measurements at 674K and different pressures up to 90kPa, the temperature was lowered, and the experiment was repeated at the next point. At each pressure-temperature set point, the flux measurement continues some time to ensure of reaching to stability and equilibrium conditions. The equilibrated value of permeation flux is used for subsequent calculations. The pressure at the permeate side was always ambient (87.7kPa) without purging gas in any of the experiments. The flux of pure hydrogen was measured as function of its pressure at the membrane feed side by soap bubble flow-meter.

3.3. Characterization

Microstructural images of PSS and the membrane were taken by scanning electron microscope (SEM TESCAN/VEGA xmu). Pd layer thickness was measured by SEM, too.

4. Results and discussion

In the composite palladium membrane, the plating substrate should be neither too coarse to prevent forming a thin film nor too smooth to weaken adherence of the film onto the surface. Figures 2a and 2b show SEM micrographs of the cleaned PSS surface before and after oxidation, respectively. Although the surface of PSS is smooth, the morphology of the ox-PSS, presented in Figure 2b, shows homogenous nanoscale coarsen surface, which increases the metal-support interaction surface area. Figure 3 shows the morphology of the prepared membrane. As can be seen, the membrane has a compacted coating which seems to be dense. To confirm density of plated film, nitrogen permeation test was performed. According to the permeation test, the composite palladium membrane showed zero nitrogen per-

meation lux at room temperature and the pressure difference of 1 bar.
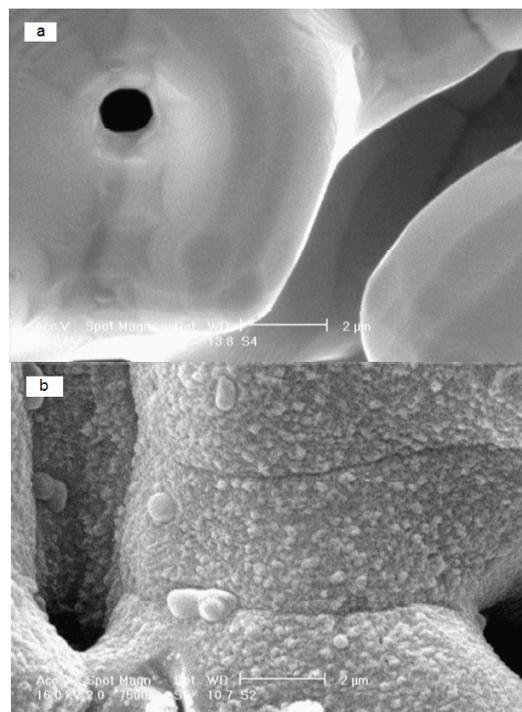
Figure 2. SEM micrographs of: a) the PSS disk surface before and b) after surface oxidation.

It means that at this condition, nitrogen permeation flux is lower than 10^{-5} mol/m^2.s, based on the permeation test equipment limit. SEM micrograph of the membrane's cross-section shows that the thickness of the membrane is 23μm.
In order to calculate the amounts of viscose
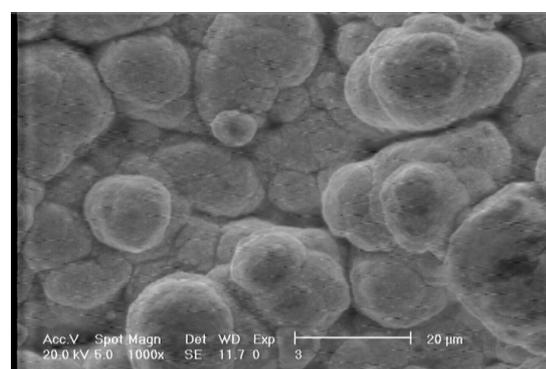
Figure 3. SEM micrograph of electrolessly plated palladium membrane.

and Knudsen constants for the ox-PSS support, we placed it in the permeation test cell and fed with hydrogen. Figure 4 shows the hydrogen

permeances at various trans-membrane average pressures at room-temperature for ox-PSS support. The regressed values for the constants of $F'_{k,s}$ (mol/ m^2.s.Pa) and $F'_{v,s}$ (mol/ m^2.s.Pa^2) at room temperature are $1.35{\times}10^{-5}$ and $1.62{\times}10^{-10}$, respectively. By measuring $F'_{k,s}$ and $F'_{v,s}$ in one temperature, their values can be calculated for other temperatures using their definition [Eqs. (4) & (5)].
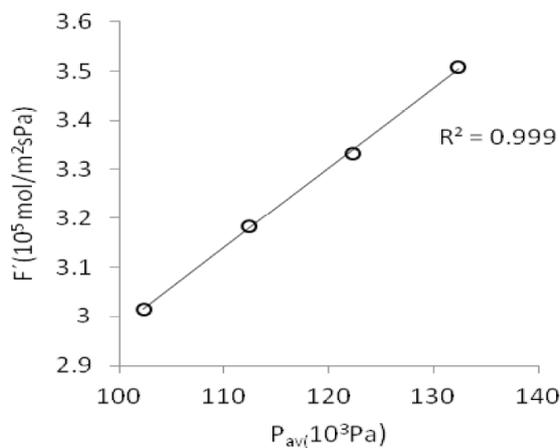

Figure 4. Hydrogen permeance of the support as a function of average pressure.

By using Eq. (11) the pressure at the interface was obtained. Then the permeance and resistance of each layer was calculated. Figure 5 shows the percentage of the palladium layer permeation resistance to composite membrane permeation resistance at different temperatures, where the feed side pressure of the membrane is adopted as the abscissa. It is shown that the support has averagely a contribution of 5% in hydrogen permeation resistance that is large enough to consider it in calculating thermodynamic properties of hydrogen permeation through palladium layer.
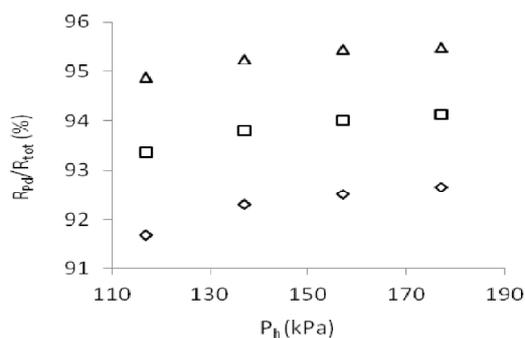

Figure 5. The ratio of R_{Pd}/R_{tot} (%) vs. feed side pressure at different temperatures: △ 674K, □ 624K, ◇ 574K.

It can be seen that by rising of temperature, the palladium layer's resistance decreased. It is due to the enhancement of palladium bulk permeance induced by temperature rise. In addition, more pressure in the feed side, leads to more palladium layer contribution in composite membrane permeation resistance.

Considering the Pd layer separately, the dependence of hydrogen fluxes on the pressure difference, is shown in Figure 6.
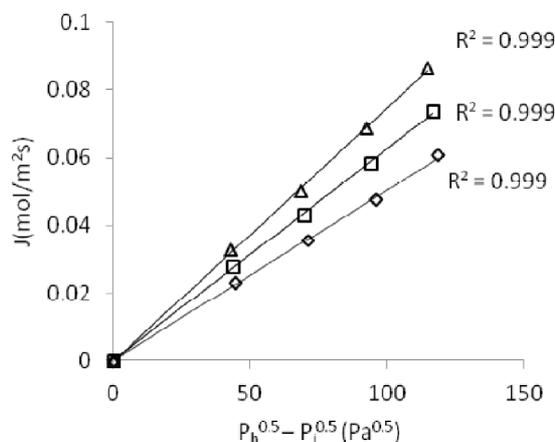

Figure 6. The pressure dependence of H2 flux through the palladium layer at different temperatures: △ 674K, □ 624K, ◇574K.

In this thick membrane (23μm) sievert permeation is obeyed and the best linear fitting of flux vs. pressure difference obtains with pressure exponent of 0.5. This means that the determining step of permeation rate is bulk diffusion process. Figure 7 shows the effect of temperature on the hydrogen permeance through the Pd layer. From the Arrhenius plot, the activation energy of hydrogen permeation through Pd layer in this membrane was evaluated to be 12.83kJ/mol.

Generally, hydrogen permeation through dense palladium layer involves several steps in series. These are in order from the feed side to the permeate side as:(1) molecular hydrogen transport from the bulk gas to the gas layer near the surface (2) dissociative adsorption (chemisorption) (3) atomic hydrogen absorption into the bulk metal (surface to bulk transition) (4) diffusion of the atomic hydrogen through the membrane via the lattice structure (5) transition of atomic (bulk to surface transition) (6) re-associative desorption of the hydrogen atoms into molecular hydrogen (7) movement of the resulting hydrogen molecules away from the downstream surface of the membrane [22]. At equilibrium, the adsorption and desorption rates (steps 2 and 6), are equal, as

are the transition rates between the surface and the bulk metal, i.e. surface-to-bulk metal transition (step 3) and bulk metal-to-surface transition (step 5). Each of these steps is characterized by a rate equation. Equating and combining these expressions as formulated by Ward and Dao, and using the ideal gas law, leads to the following relationship [27]:

$$\frac{\beta_0 k_0^{0.5} N_s \left(2\pi MRT\right)^{0.25}}{v_0 S_0^{0.5}} \left(\frac{F(\theta)(1-\theta)^2}{G(\theta)\theta}\right)^{0.5} \exp\left(\frac{E_A - E_B - E_d}{RT}\right)$$

$$= \exp\left(\frac{-\Delta\overline{S}_H}{R}\right)\exp\left(\frac{\Delta\overline{H}_H}{RT}\right) \qquad (12)$$

All parameters are defined in the nomenclature. E_A, E_B and E_d are activation energies for H atom's surface-to-bulk metal transition, activation energy for H atom's bulk metal-to-surface transition, and activation energy for hydrogen desorption, respectively. This equation shows that molar enthalpy of dissolution is proportional to $E_A-(E_B+E_d)$. It means that less activated H atoms transiting from upstream surface to bulk of the palladium layer (less E_A) and/or more activated hydrogen exiting from the downstream surface of the palladium layer (more E_B and E_d) make the molar enthalpy of dissolution to be more negative and vice versa.

Enthalpy of hydrogen dissolution in palladium layer can be calculated considering Eqs. (7)-(10). Data for hydrogen diffusion in palladium layer have been reported by a number of researchers [28-30]. There is some variation, but most values are reasonably consistent. We have chosen to use parameters based on thosereported by Holleck [28]. They have been determined in the temperature range of 533-913K for a thick palladium foil that hydrogen diffuses through palladium bulk. In this electroless plated palladium layer, as can be seen in Figure 3, the grain sizes appear to be on the order of the film thickness and therefore diffusion through the grain boundaries is not expected to have a significant impact on the bulk diffusion of H through the Pd film [31].With the data of D_0=2.94×10⁻⁷m²/s and E_d=22.2kJ/mol according to Holleck, the diffusion coefficients of hydrogen at different temperatures were calculated. Then, the solubility constants were evaluated by Eq.(7). By calculating the Sievert's constants at different temperatures (K_s), thermodynamic parameters have been obtained [Eq. (10)]. Based on this calculation, the enthalpy and entropy of hydrogen dissolution in the palladium layer ob-

tained as -9.4kJ/mol and -55.3J/mol.K, respectively. Few researchers report the molar enthalpy of hydrogen dissolution in palladium membrane [23, 28]. We used enthalpy of hydrogen dissolution in palladium layer of different membranes in order to compare their behaviour in hydrogen permeation steps. These values have been compared with each other in Table 2.

Table 2. A comparison of interdiffusion parameters of hydrogen through the Pd layer.

Membranes	Support	E$_a$ (kJ/mol)	(kJ/mol)	Temp. (K)
Holleck	Self-supported	13.8	-8.4	533-913
Zhang[a]	YSZ-PSS	13.7[b]	-8.5[b]	633-713
Huang[a]	αAl₂O₃	12.7	-9.5	523-669
This work[a]	Ox-PSS	12.8	-9.4	574-674

[a] prepared by electroless plating method

[b] These amounts extracted from reference data.

Note that all of them have been measured by considering only palladium layer contribution in permeance using the same diffusion parameters as Holleck. The value of $\Delta\overline{H}_H$ reported by Holleck [28] is -8.4kJ/mol. Comparison between our membrane and the Pd/Al₂O₃ composite membrane prepared by Huang, shows good accordance with each other in the value of $\Delta\overline{H}_H$ but is more negative than the value reported by Holleck. Since Holleck used self supported membrane, this difference should be attributed to metal-support interaction. This is the main difference.of Holleck's membrane with fabricated membrane in our lab and Huang's membrane [23]. In contrast to Pd/ox-PSS and Pd/Al₂O₃, the value of $\Delta\overline{H}_H$ in palladium layer of Pd/YSZ-Al₂O₃ composite membrane prepared by Zhang et. al. is similar to this value of Holleck's self supported palladium layer [24].

Given that all four membranes are made of pure palladium and considering the main difference between these palladium membranes i.e. support material and based on the direct proportion between $\Delta\overline{H}_H$ and $E_A-(E_B+E_d)$, more negative value of $\Delta\overline{H}_H$ implies to higher E_B+E_d. It means activated hydrogen exiting from downstream side of palladium layer, might be related to metal-support interaction in these membranes. It is known that the oxides are reduced to metallic state under H₂ atmosphere. After that, support's metal elements and palladium could migrate and diffuse to opposite layer. More chemical activity of support

causes to more diffusion and alloying with palladium layer. The investigation and comparison between Fe_2O_3, Al_2O_3 and YSZ, indicates high chemical activity of Fe_2O_3 and Al_2O_3 and inertness of YSZ [24,32,33]. Using cross sectional SEM and EDS of palladium supported membranes, Akis and Okazaki, showed that in composite palladium membranes Fe and Al are alloyed with palladium while no alloying occurs between Palladium and Yttrium or Zirconium of YSZ [32,33]. The formation of Pd-Fe and Pd-Al alloys lower the hydrogen solubility and diffusivity and increase the activation energy for hydrogen exiting [34,35]. In the case of Pd/YSZ-Al_2O_3 composite membrane, since Yttrium and Zirconium is more inert and stable as the support, no alloy layer might form in the palladium-support interface of Pd/YSZ-Al_2O_3 membrane [32]. In fact, in the Holeck's and Zhang's membranes, H exiting is less activated step and the value of obtains more positive.

This analysis shows that the support has an important role in permeation characteristics. In addition, it is reasonable to say that the molar enthalpy of hydrogen dissolution can be used to compare chemical activity of support surface in different composite membranes.

5. Conclusion

A palladium membrane was prepared on ox-PSS support by electroless plating method. It was shown that the support layer has averagely a contribution of 5% in hydrogen permeation resistance of the composited membrane. The permeation data of palladium layer was evaluated and the activation energy of hydrogen permeation and the molar enthalpy of hydrogen dissolution were calculated. The molar enthalpy of hydrogen dissolution in palladium layer deposited on ox-PSS obtained as -9.4kJ/mol which is similar to the value of $\Delta \overline{H}_H$ palladium layer deposited on Al_2O_3 and more negative than this value of self supported palladium layer and the palladium layer deposited on YSZ. Using a complete model, it was deduced that molar enthalpy of hydrogen dissolution is directly proportional with $E_A-(E_d+E_B)$. By comparing several composite membranes which differ in support material, it was confirmed that the metal-support interaction, plays an effective role in exiting activation energy. In Pd/ox-PSS composite membrane, the metal-support interaction decreases hydrogen exiting rate from Pd membrane's downstream side.

Nomenclature

D	Diffusion coefficient for H atoms in Pd (m^2/s)
D_0	Pre-exponential factor for D(m^2/s)
S	Solubility constant
F	Permeance ($mol/m^2.s.Pa$)
F_pl	Permeability ($mol.m/m^2.s.Pa^{-n}$)
F_{pl0}	Pre-exponential factor for F_{pl} ($mol.m/m^2.s.Pa^{-n}$)
E_A	Activation energy for H atom's surface-to-bulk metal transition (kJ/mol H)
E_B	Activation energy for H atom's bulk metal-to-surface transition (kJ/mol H)
E_d	Hydrogen desorption activation energy (kJ/mol H)
$F(\theta)$, $G(\theta)$	Functions of coverage factor
$\Delta \overline{H}_H$	Molar enthalpy of hydrogen dis solution at infinite dilution (kJ/mol H)
$\Delta \overline{S}_H$	Molar entropy of hydrogen dissolution at infinite dilution (kJ/mol K H)
J	Flux through composite membrane (mol/m^2s)
K_s	Sievert's law constant
N_b	Bulk metal Pd atom concentration (mol Pd/m^3)
S_0	Initial sticking coefficient (at zero coverage)
T	Absolute temperature (K)
r	Pore radius (m)
M	Molecular mass (kg/mol)

R	Universal gas constant $(8.314\ J/molK)$
L	Membrane thickness (m)
k_0	Desorption rate constant pre-exponential factor

Greek letters

ε	Porosity
η	Gas viscosity ($Pa\ s$)
θ	Surface coverage (atomic H/Pd ratio on surface)
μ	Reciprocal tortuosity
υ	Pre-exponential factor ($cm^3/mol\ H\ s$)
β	Pre-exponential factor ($cm^3/mol\ H\ s$)

Subscripts/Superscripts

av	average
s	support
p	pinhole
v	viscous flow
k	Knudsen flow
$'$	Parameters for bare porous media

6.   References

[1] Ryi S.K., Park J.S., Kim S.H., Cho S.H., Park J.S. and Kim D.W., "Development of a new porous metal support of metallic dense membrane for hydrogen separation" , J. Memb. Sci., 2006, 279: 439.

[2] Mardilovich I. P., Engwall E. and Ma Y. H., "Dependence of hydrogen flux on the pore size and plating surface topology of asymmetric Pd-porous stainless steel membranes", Desalination, 2002, 144: 85.

[3] Hu X., Yu J., Song J., Wang X. and Huang Y., "Toward low-cost Pd/ceramic composite membranes for hydrogen separation: A case study on reuse of the recycled porous Al₂O₃ substrates in membrane fabrication", Int. J. Hydrogen Energy, 2011, 36: 15794.

[4] Wu J. P., Brown I. W. M., Bowden M. E. and Kemmitt T., "Palladium coated porous anodic alumina membranes for gas reforming processes", Solid State Sci., 2010, 12: 1912.

[5] Ryi S.K., Xu N., Li A., Lim C. J. and Grace J. R., "Electroless Pd membrane deposition on alumina modified porous Hastelloy substrate with EDTA-free bath", Int. J. Hydrogen Energy, 2010, 35: 2328.

[6] Samingprai S., Tantayanon S. and Ma Y. H., "Chromium oxide intermetallic diffusion barrier for palladium membrane supported on porous stainless steel", J. Memb. Sci., 2010, 347: 8.

[7] Yepes D., Cornaglia L. M., Irusta S. and Lombardo E. A., "Different oxides used as diffusion barriers in composite hydrogen permeable membranes", J. Memb. Sci., 2006, 274: 92.

[8] Gao H., S. Lin J. Y., Li Y. and Zhang B., "Electroless plating synthesis, characterization and permeation properties of Pd–Cu membranes supported on ZrO₂ modified porous stainless steel", J. Memb. Sci., 2005, 265: 142.

[9] Huang Y. and Dittmeyer R., "Preparation and characterization of composite palladium membranes on sinter-metal supports with a ceramic barrier against intermetallic diffusion", J. Memb. Sci., 2006, 282: 296.

[10] Calles J. A., Sanz R. and Alique D., "Influence of the type of siliceous material used as intermediate layer in the preparation of hydrogen selective palladium composite membranes over a porous stainless steel support", Int. J. Hydrogen Energy, 2012, 37: 6030.

[11] Qiao A., Zhang K., Tian Y., Xie L., Luo H., Lin Y. S. and Li Y., "Hydrogen separation through palladium–copper membranes on porous stainless steel with sol–gel derived ceria as diffusion barrier", Fuel, 2010, 89: 1274.

[12] Morreale B. D., Ciocco M. V., Howard B. H., Killmeyer R. P., Cugini A. V. and Enick R. M., "Effect of hydrogen-sulfide on the hydrogen

permeance of palladium–copper alloys at elevated temperatures", J. Memb. Sci., 2004, 241: 219.

[13] Xie D., Yu J., Wang F., Zhang N., Wang W., Yu H., Peng F. and Park, A. H. A., "Hydrogen permeability of Pd–Ag membrane modules with porous stainless steel substrates", Int. J. Hydrogen Energy, 2011, 36: 1014.

[14] Coulter K. E., Way J. D., Gade S. K., Chaudhari S., Alptekin G. O., DeVoss S. J., Paglieri S. N. and Pledger, B., "Sulfur tolerant PdAu and PdAuPt alloy hydrogen separation membranes", J. Memb. Sci., 2012, 405–406: 11.

[15] Ryi S. K., Park J. S., Kim S.H., Kim D. W. and Cho K. I., "Formation of a defect-free Pd–Cu–Ni ternary alloy membrane on a polished porous nickel support (PNS)", J. Memb. Sci., 2008, 318: 346.

[16] Coulter K. E., Way J. D., Gade S. K., Chaudhari S., Sholl D. S. and Semidey-Flecha, L., "Predicting, Fabricating, and Permeability Testing of Free-Standing Ternary Palladium-Copper-Gold Membranes for Hydrogen Separation", J. Phys. Chem. C, 2010, 114: 17173.

[17] Tarditi A. M. and Cornaglia L. M., "Novel PdAgCu ternary alloy as promising materials for hydrogen separation membranes: Syn thesis and characterization", Surf. Sci., 2011, 605: 62.

[18] Peters T. A., Kaleta T., Stange M. and Bredesen R., "Development of thin binary and ternary Pd-based alloy membranes foruse in hydrogen production", J. Memb. Sci., 2011, 383: 124.

[19] McCool B. A. and Lin Y. S., "Nanostructured thin palladium-silver membranes: Effects of grain size on gas permeation properties", J. Mater. Sci., 2001, 36: 3221.

[20] Souleimanova R. S., Mukasyan A. S. and Varma A., "Effects of osmosis on microstructure of Pd-composite membranes synthesized by electroless plating technique", J. Memb. Sci., 2000, 166: 249.

[21] Kim D., Donohue D., Kuncharam B., Duval C. and Wilhite B. A., "Toward an Integrated Ceramic Micro-Membrane Network: Effect of Ethanol Reformate on Palladium Membranes", Ind. Eng. Chem. Res., 2010, 49: 10254.

[22] Boeltken T., Belimov M., Pfeifer P., Peters T. A., Bredesen R. and Dittmeyer R., "Fabrication and testing of a planar microstructured concept module with integrated palladium membranes", Chem. Eng. Process. Process. Intensif., 2013, 67: 136.

[23] Huang T. C., Wei M. C. and Chen H. I., "A Study of the Hydrogen Transport Properties of Palladium/Alumina Composite Membranes", Chem. Eng. Commun., 2002, 189: 1340.

[24] Zhang K., Wei X., Rui Z., Li Y., Lin Y. S., "Effect of metal-support interface on hydrogen permeation through palladium membranes", AIChE J., 2009, 55: 630.

[25] Henis J. M. S. and Tripodi M. K., "Composite hollow fiber membranes for gas separation: the resistance model approach", J. Memb. Sci., 1981, 8: 233.

[26] Yun S. and Ted Oyama S., "Correlations in palladium membranes for hydrogen separation: A review", J. Memb. Sci., 2011, 375: 28.

[27] Ward T. L. and Dao T., "Model of hydrogen permeation behavior in palladium membranes", J. Memb. Sci., 1999, 153: 211.

[28] Holleck G. L., "Diffusion and solubility of hydrogen in palladium and palladium--silver alloys", J. Phys. Chem., 1970, 74: 503.

[29] Hurlbert R. C. and Konecny J. O., "Diffusion of Hydrogen through Palladium", J Chem. Phys., 1961, 34: 655.

[30] Hara S., Caravella A., Ishitsuka M., Suda H., Mukaida M., Haraya K., Shimano E. and Tsuji T., "Hydrogen diffusion coefficient and mobility in palladium as a function of equilibrium pressure evaluated by permeation measurement", J. Memb. Sci., 2012, 421–422: 355.

[31] Bhargav, A., Jackson, G. S., Ciora Jr, R. J. and Liu, P. T. K., "Model development and validation of hydrogen transport through supported palladium membranes", J. Memb. Sci., 2010, 356: 123.

[32] Okazaki J., Ikeda T., Pacheco Tanaka D. A., Llosa Tanco M. A., Wakui Y., Sato K., MizukamiF. and Suzuki T. M., "Importance of the support material in thin palladium composite

membranes for steady hydrogen permeation at elevated tem peratures", Phys. Chem. Chem. Phys., 2009, 11: 8632.

[33] Akis B. C., "Preparation of Pd-Ag/PSS Composite Membranes for Hydrogen Separation". Ph.D. Thesis, Worcester Polytechnique institue, 2003.

[34] Bryden K. J. and Ying J. Y., "Nanostructured palladium–iron membranes for hydrogen separation and membrane hydrogenation reactions", J. Memb. Sci., 2002, 203: 29.

[35] Wang D., Flanagan T. B. and Shanahan K. L., "Hydrogen permeation measurements of partially internally oxidized Pd–Al alloys in the presence and absence of CO", J. Memb. Sci., 2005, 253: 165.