Chemical Engineering Journal 112 (2005) 81–86

www.elsevier.com/locate/cej

The effect of diffusion direction on the permeation rate of hydrogen in palladium composite membranes

Weiqiang Liang [a], Ronald Hughes [b,*]

[a] Kunming University of Science and Technology, Kunming 650093, PR China
[b] Institute of Materials Research, University of Salford, Salford M5 4WT, UK

Received 10 January 2005; received in revised form 16 June 2005; accepted 29 June 2005

Abstract

The experimentally measured hydrogen permeability of a composite Pd/porous stainless steel membrane was found to be influenced by the direction of permeation. For pure hydrogen, the direction from the stainless steel support to the metal film gave the higher hydrogen permeance. However, for a hydrogen/nitrogen mixture the opposite effect was obtained. Simulation results showed that while permeation from the support to the metal gave the expected Sieverts' law value of the pressure exponent of 0.5, that from the metal to the support gave a higher value for this exponent of approximately 0.66.

Keywords: Palladium membranes; Hydrogen; Permeation direction

---

1. Introduction

The increased demand for hydrogen in recent years in both the petroleum refining and petrochemical industries [1], together with semi-conductor processing and fuel cell applications has led to a revival of interest in methods for separation and purification of hydrogen from gas mixtures. Due to their unique permselectivity to hydrogen palladium and palladium membranes have received increasing attention for this purpose. Originally used in the form of relatively thick dense metal membranes [2], current developments tend to the employment of composite membranes in which the palladium or palladium alloy is deposited as a thin film onto a porous ceramic or metal substrate [3–7]. A further area of application of increasing importance is the use of composite membranes in catalytic membrane reactors, where palladium membranes have been shown to have considerable benefits when employed for hydrogenation/dehydrogenation reactions [2] and steam reforming processes [4,5]. Such composite membranes have reduced material costs, but their main attribute is in providing a structure possessing both higher hydrogen fluxes and better mechanical properties than the thicker dense metal membranes. The influence of the various resistances in composite membranes has been analysed recently [8].

For these composite membranes, there are two possible permeation directions for hydrogen permeation, i.e. from the support to the metal film or from the metal film to the support. The direction of diffusion may affect the permeation rate. In previous publications [9,10], it has been shown that the performance of porous asymmetric membranes is affected by the direction of permeation. However, little work appears to have been done for composite dense membranes. Goto et al. [11] investigated the direction effect on hydrogen permeation through a palladium composite membrane. In their study, there were three layers of different pore size, i.e. 5.0, 1.0 and 0.5 μm, from the inner side to the outer side of the alumina support tube. The palladium film, 0.02 mm in thickness, was plated on the top of the layer with the smallest pore size. They found from experiment and modelling that the direction from large pores to fine pores would have a higher hydrogen permeation rate, provided that Knudsen diffusion and viscous bulk flow controlled the permeation rate. They concluded that when the resistance through the palladium film was much greater than that through the support, the effect of hydrogen

---

[*] Corresponding author. Tel.: +44 161 295 5081; fax: +44 161 295 5111.
E-mail address: r.hughes@salford.ac.uk (R. Hughes).

1385-8947/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2005.06.010

Nomenclature

F	permeability
J	flux
K	permeability constant
L	membrane thickness
M	molecular weight
P	pressure
r	pore radius
R	universal gas constant
T	temperature
Greek letters	
ε	porosity
η	viscosity
μ	shape factor
ν	defined by Eq. (3)
Subscripts	
av	average
f	feed
k	Knudsen flow
ms	metal to support direction
p	permeate
sm	support to metal direction
v	viscous flow

transfer direction would become unimportant. It is unusual, however (but it appeared to be the case in their research) that the hydrogen permeation resistance through the support was larger than that through the palladium film.

In general, the use of the support in palladium composite membranes is to provide a strong, yet open structure underlying the Pd layer. Therefore, the permeation resistance of supports should be much smaller than that through the effective metal film and it is of interest to study the effect of hydrogen transfer direction on this type of composite membrane.

2. Experimental

The membrane used in the present research was a composite palladium/silver alloy of about 10 μm thickness deposited by sequential electroless plating of Pd and Ag [12] onto the outside of a symmetrical porous stainless steel support tube provided by Mott Metallurgical. These initial deposits were sintered at 500 °C in a hydrogen atmosphere for 10 h to promote alloying. The support tube had an outside diameter of 12.7 mm and a wall thickness of 2 mm. The average pore size of the support tube is about 1.2 μm, determined experimentally from the permeation behaviour of the gases N_2, H_2, He and CO_2 [13].

Permeation measurements for pure hydrogen and a hydrogen/nitrogen mixture were made for both shell to tube and tube to shell directions using a conventional stainless steel permeator in which the Pd/Ag composite membrane was sealed into the stainless steel shell using graphite rings. Permeation measurements were made with pure hydrogen and with a H_2/N_2 mixture containing 50% H_2. Hydrogen permeation measurements were conducted after steady state (approximately 3 h) had been achieved at the measurement temperature, when hydrogen was present on both sides of the membrane and permeation could be measured directly. However, a sweep gas was used for the mixed gas experiments.

3. Mass transfer relations

3.1. Pure hydrogen permeation through the support

When pure gases permeate through a porous media, if there exists no surface diffusion, capillary condensation or molecular sieving, the permeation rate is usually calculated by considering the combination of viscous flow (Poiseuille flow) and Knudsen diffusion. According to Keizer et al. [14] and Burggraaf [15], for homogeneous media and pure nonsorbable gases the total permeability F (mol/(m^2 sec Pa)) can be expressed as $F = F_k + F'_v P_{av}$, where F_k is the permeability due to Knudsen diffusion and $F'_v P_{av}$ is the contribution due to laminar flow, which is linearly dependent on the mean pressure and each can be defined as:

$$F_k = \frac{2\varepsilon\mu_k r\nu}{3RTL} \tag{1}$$

$$F'_v = \frac{\varepsilon\mu_v r^2}{8\eta RTL} \tag{2}$$

with the symbols as defined in the Notation and P_{av} the mean of the upstream and downstream pressures.

From molecular kinetics,

$$\nu = \left(\frac{8RT}{\pi M}\right)^{1/2} \tag{3}$$

where M is the molecular mass of the gas molecules.

Substituting Eq. (3) for ν in Eq. (1), this becomes

$$F_k = \frac{2\varepsilon\mu_k r\nu}{3RTL} = \left(\frac{4\sqrt{2}\varepsilon\mu_k r}{3L\sqrt{\pi RM}}\right)\frac{1}{\sqrt{T}} \tag{4}$$

and Eq. (2) can be written as

$$F'_v = \left(\frac{\varepsilon\mu_v r^2}{8RL}\right)\frac{1}{\eta T} \tag{5}$$

Both of the first factors of Eqs. (4) and (5) should not change for a given gas and support, and both second factors are only functions of temperature.

Fig. 1 is the experimentally determined relation between F and P_{av} for the stainless steel support when $T = 18\,°C$. The correlation expression is,

$$F = (304,157 + 2.93P_{av}) \times 10^{-10} \tag{6}$$

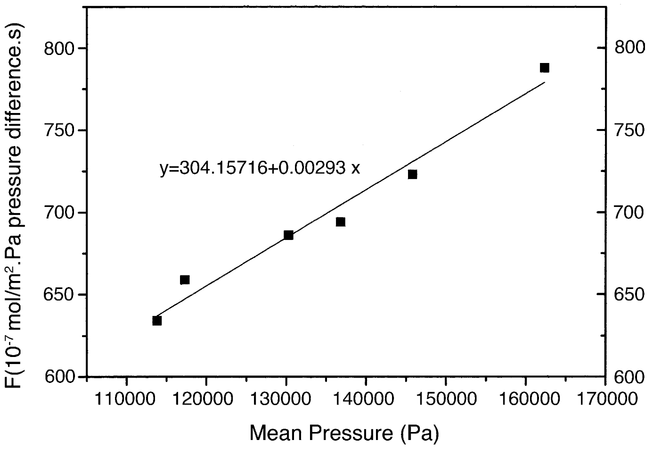

Fig. 1. Hydrogen diffusion flux vs. mean pressure for the stainless steel support at 18 °C.

Comparing Eq. (6) with $F = F_k + F'_v P_{av}$, it can be seen that

$$\left(\frac{4\sqrt{2}\varepsilon\mu_k r}{3L\sqrt{\pi RM}}\right)\frac{1}{\sqrt{T}} = 3.042 \times 10^{-5} \tag{7}$$

$$\left(\frac{\varepsilon\mu_v r^2}{8RL}\right)\frac{1}{\eta T} = 2.930 \times 10^{-10} \tag{8}$$

When $T = 18\,°C$, the viscosity of H_2 is 8.61543×10^{-6} Pa s [16] and substituting ηT and T, respectively, into Eqs. (7) and (8), we have, for H_2 and this stainless steel support,

$$\frac{4\sqrt{2}\varepsilon\mu_k r}{3L\sqrt{\pi RM}} = 5.190 \times 10^{-4} \tag{9}$$

and

$$\frac{\varepsilon\mu_v r^2}{8RL} = 7.525 \times 10^{-13} \tag{10}$$

Therefore,

$$F = 5.190 \times 10^{-4}\frac{1}{\sqrt{T}} + 7.525 \times 10^{-13}\frac{1}{\eta T}P_{av} \tag{11a}$$

Here, the unit of F is mol/(m^2 s Pa), and the unit of P_{av} is Pa. The permeation area in this experiment is 71.7804×10^{-4} m^2. Therefore, the hydrogen permeation flux J (mol/(m^2 s)) can be expressed, for a pressure difference of ΔP as

$$J = 5.190 \times 10^{-4}\frac{1}{\sqrt{T}}\Delta P + 7.525 \times 10^{-13}\frac{P_{av}}{\eta T}\Delta P \tag{11b}$$

where $\Delta P = P_f - P_p$ and $P_{av} = \frac{1}{2}(P_f + P_p)$, and P_f and P_p are the hydrogen pressures at the high pressure and low pressure sides, respectively. Replacing these in Eq. (11b), the following equation is obtained:

$$J = 5.190 \times 10^{-4}\frac{1}{\sqrt{T}}(P_f - P_p) + 7.525 \times 10^{-13}\frac{P_f^2 - P_p^2}{2\eta T} \tag{11c}$$

3.2. Pure hydrogen permeation through the top metal film

According to Sieverts' law [17], when H_2 permeates through palladium or palladium and silver alloy, we have

$$J = \frac{Q}{\delta}(P_f^{0.5} - P_p^{0.5}) \tag{12a}$$

where J is the hydrogen permeation flux (mol/(m^2 s)), Q the permeability constant of hydrogen through the membrane (mol m/(m^2 s Pa$^{0.5}$)) and δ is the thickness of the metal film (m). Here, Q depends only on temperature for a given metal film. Therefore, for a given metal film, Eq. (12a) can be written as

$$J = K(P_f^{0.5} - P_p^{0.5}) \tag{12b}$$

where K depends on temperature only.

3.3. Pure hydrogen permeation through the combination of the two layers

For a composite membrane, H_2 permeates either through the porous stainless steel support first followed by the metal film (Support–Metal direction) or through the metal film first followed by the porous stainless steel support (Metal–Support direction). At steady state, the hydrogen permeation flux J should be the same for both layers, i.e.

$$J = J_{support} = J_{metal\ film} \tag{13}$$

Now let P_f, P_p and P_m represent, respectively, H_2 partial pressure at the high pressure (feed) side, low pressure (permeate) side and the interface between the support and metal film.

For permeation directions from support to metal film, represented by subscript sm,

$$J_{sm} = K_{sm}(P_m^{0.5} - P_p^{0.5}) = 5.190 \times 10^{-5}\frac{1}{\sqrt{T}}(P_f - P_m) + 7.525 \times 10^{-13}\frac{P_f^2 - P_m^2}{2\eta T} \tag{14a}$$

For permeation directions from metal film to support, represented by subscript ms,

$$J_{ms} = K_{ms}(P_f^{0.5} - P_m^{0.5}) = 5.190 \times 10^{-5}\frac{1}{\sqrt{T}}(P_m - P_p) + 7.525 \times 10^{-13}\frac{P_m^2 - P_p^2}{2\eta T} \tag{14b}$$

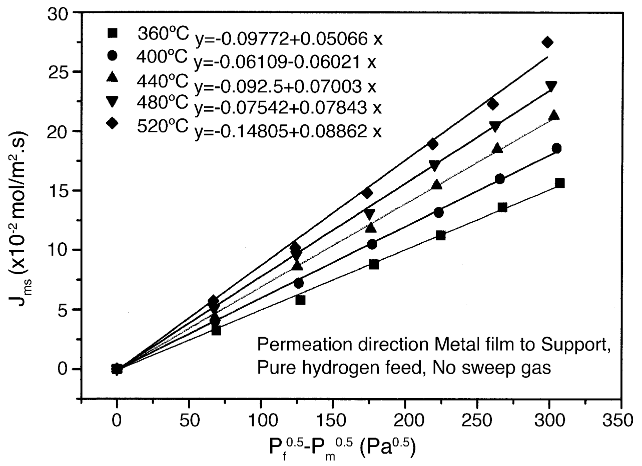

Fig. 2. Hydrogen permeation flux vs. pressure square root difference across top metal film.

The unknown P_m may be estimated from Eq. (14a) for a given temperature if experimental values of J_{sm} are available, since P_f and the viscosity are known.

In Fig. 2, experimental permeation data for J_{ms} at temperatures of 360, 400, 440, 480 and 520 °C are plotted against the difference of the square roots of P_f and P_m. The permeate side hydrogen pressure is 1.013×10^5 Pa, i.e. no sweep gas was used. From these data of J_{ms}, by using Eq. (14b), K_{ms} for any corresponding temperature may be easily calculated. From Eq. (14b), K_{ms} is the slope of the linear plot of J_{ms} and $(P_f^{0.5} - P_m^{0.5})$. Furthermore, because of the symmetric nature of the metal film, K_{sm} should be equal to K_{ms}; therefore, it is represented by K in the following section. K's for the temperatures, 360, 400, 440, 480 and 520 °C, are shown in Table 1.

4. Results and discussion

4.1. The pure hydrogen feed situation

Fig. 3 shows experimental results for both permeation directions at $T = 520$ °C and with pressure differences within the range from 50,000 up to 300,000 Pa. It can be observed that J_{sm} is always bigger than J_{ms} at the same operational conditions within this experimental region. This result is consistent with that of Thomas et al. [10], who noted that when hydrogen permeated a two-layer asymmetric porous membrane, it was found that the hydrogen permeation rate was higher in the direction from the support to the separation layer than that from the opposite direction. They claimed that the greater resistance difference of the two layers led to a greater influence of the permeation direction on the permeation rate.

Table 1
Values of K for Eq. (14b) at various temperatures

Temperature (°C)	K for Eq. (14b) (mol/(m^2 s Pa$^{0.5}$))
360	5.066E−04
400	6.021E−04
440	7.003E−04
480	7.843E−04
520	8.862E−04

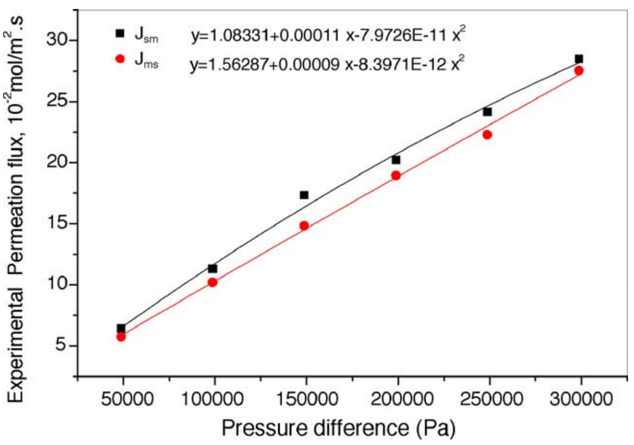

Fig. 3. Experimental permeation fluxes J_{sm} and J_{ms} vs. pressure difference at $T = 520$ °C.

Judging from Eqs. (14a) and (14b), it is known that changes in K will not change this trend. Therefore, this trend is maintained for other temperatures.

The most interesting finding is (see Fig. 4) that when J_{sm} for both experimental and calculated data is correlated with $(P_f^{0.5} - P_p^{0.5})$, a straight line through the origin is apparent. The appropriate linear equation for the J_{sm} fluxes is shown in Fig. 4 and the least square analysis quoted shows that excellent agreement between the experimental and calculated values of J_{sm} are obtained. However, for J_{ms} the calculated values do not agree with either the experimental or calculated values for J_{sm} and it is obvious that the exponent is not 0.5, but has some value higher than this. A corresponding plot for an exponent of 0.66 (Fig. 5) shows that J_{ms} is now linear and a good linear correlation is obtained as shown in the equation in this figure. In other words, J_{ms} is approximately linear to $(P_f^{0.66} - P_p^{0.66})$, and also goes through the origin. Attempts

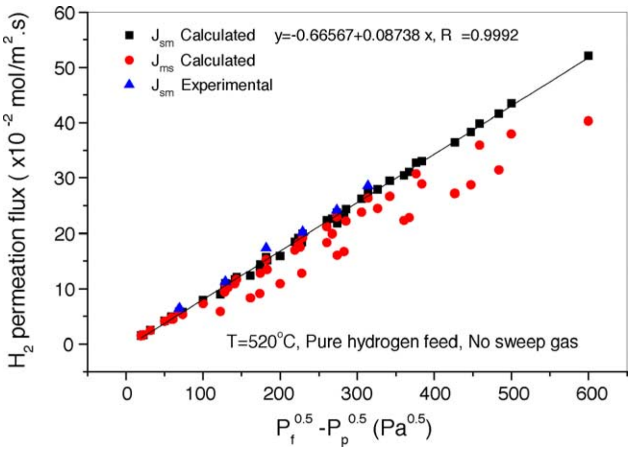

Fig. 4. Experimental and calculated hydrogen permeation fluxes J_{sm} and J_{ms} vs. square root pressure difference.

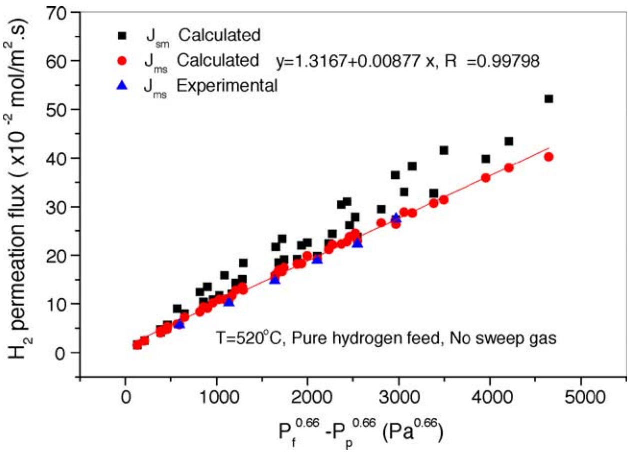

Fig. 5. Experimental and calculated hydrogen permeation fluxes J_{sm} and J_{ms} vs. pressure to the 0.66 power difference.

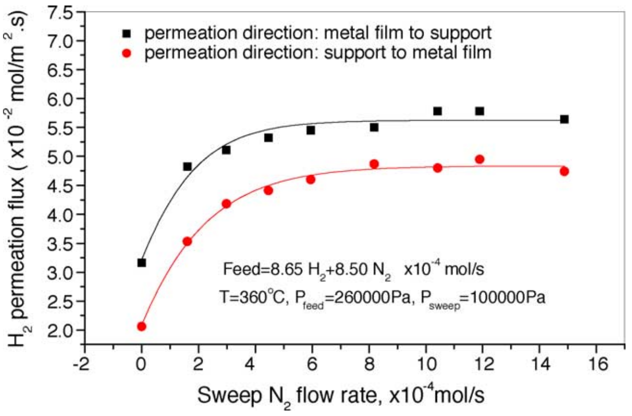

Fig. 6. Effect of transfer direction on hydrogen permeation rate for a hydrogen mixture feed at 360 °C.

to obtain linear equations for J_{ms} in Fig. 4 and J_{sm} in Fig. 5, proved to be unrealistic due to scatter of data and curvature of the plots, respectively. The experimental results of J_{sm} and J_{ms} which are inserted in their corresponding figures demonstrate that they are consistent with the calculated results and the above reasoning.

Many researchers have found that their membranes' behaviour does not follow Sieverts' law and usually they attribute this deviation to some kinds of surface process. However, from the calculation done here and the results shown in Figs. 4 and 5, it is clear that the deviation from Sieverts' law of J_{ms} may have nothing to do with any kind of surface process, because in the calculation it is assumed that hydrogen permeating through the top metal film strictly follows 0.5 exponent rule. It is the combined effect of the top metal film and the porous support that makes J_{ms} linearly dependent on $(P_f^{0.66} - P_p^{0.66})$. Therefore, if a membrane is a composite one and the permeation direction is from the metal film to the support, the deviation of the exponent from 0.5 may well be due to the combined effect of the metal film and the porous support, rather than to any surface process.

4.2. The hydrogen mixture feed situation

If the feed stream contains another component, the hydrogen permeation will be affected. To simplify, assume the added component does not have any surface mechanism with the film and the support.

For the permeation direction from the metal film to the support, i.e. ms, the added component only affects the hydrogen permeation in the way of dilution provided that the top metal film is completely dense. Therefore, for this ms case, hydrogen will permeate through the membrane in the same way as when pure hydrogen feed is used except that the hydrogen partial pressure is not equal to the feed pressure. However, for the permeation direction from the support to the metal film, i.e. in the sm case, at first both hydrogen and the added component will permeate into the pores of the support and then hydrogen alone permeates through the metal film. After reaching the steady state, only hydrogen transfers from the support side (tube side) to the metal film side (shell side), but hydrogen has to diffuse through the added gas by molecular diffusion as well as Knudsen diffusion. Compared with pure hydrogen feed, the resistance of hydrogen transfer through the support becomes larger and hence the hydrogen partial pressure at the high pressure side of the metal film becomes lower than that in the bulk feed stream. Therefore, the hydrogen permeation flow rate will become less at the same cross membrane pressure difference.

Figs. 6 and 7 are the experimental hydrogen permeation results for a hydrogen mixture feed at temperatures of 360 and 440 °C, respectively. It can be seen that at the same operational conditions, the permeation rate for the sm case is always significantly lower than that for the ms case. This result is completely opposite to that obtained from pure hydrogen feed. Further studies are necessary to ascertain how the molecular fraction of the added component affects the hydrogen permeation rate.

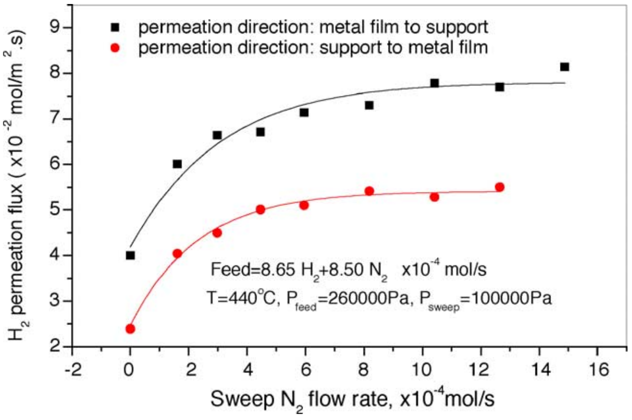

Fig. 7. Effect of transfer direction on the hydrogen permeation rate for a hydrogen mixture feed at 440 °C.

5. Conclusions

The transfer direction has an effect on the hydrogen transfer rate. For pure hydrogen feed, without exception, hydrogen transfer rates obtained from the direction of support to metal film are all higher than those obtained from the other transfer direction. For a composite palladium membrane, if the hydrogen transfer through the top metal film follows Sieverts' law and that through the support by Knudsen diffusion and viscous flow, then when the transfer direction is from the support to the metal film, the hydrogen transfer rate will have a linear relation with $(P_f^{0.5} - P_p^{0.5})$. However, when the transfer direction is from the metal film to the support, the hydrogen transfer rate will have a higher pressure exponent, approximately linear with $(P_f^{0.66} - P_p^{0.66})$. In this case, the pressure exponent deviation from 0.5 is not a result of any kind of surface process.

However, for a feed consisting of hydrogen and another component or components, the hydrogen transfer rates for the sm direction are significantly lower than the opposite transfer direction under the same operational conditions.

References

[1] R. Ramachandran, R.K. Menon, An overview of industrial uses of hydrogen, Int. J. Hydrogen Energy 23 (1998) 593.

[2] V.M. Gryaznov, V.M. Ermilova, L. Morozova, N.K. Orekova, Palladium alloys as hydrogen permeable catalysts in hydrogenation and dehydrogenation reactions, J. Less Common Met. 89 (1953) 529.

[3] R. Govind, D. Atnoor, Development of a composite palladium membrane for selective hydrogen separation at high temperature, Ind. Eng. Chem. Res. 30 (1991) 591.

[4] J. Shu, J.P.A. Grandjean, S. Kaliaguine, Methane steam reforming in asymmetric palladium and palladium/silver porous stainless steel membrane reactors, Appl. Catal. A 19 (1994) 327.

[5] J. Shu, J.P.A. Grandjean, S. Kaliaguine, Asymmetric Pd-Ag/stainless catalytic membranes for methane steam reforming, Catal. Today 25 (1995) 327.

[6] S.N. Paglieri, K.Y. Foo, J.D. Way, J.P. Collins, D.L. Harper-Nixon, A new preparation technique for Pd/alumina membranes with enhanced high temperature stability, Ind. Eng. Chem. Res. 38 (1999) 1925.

[7] K.L. Yeung, A. Varma, Novel preparation technique for thin metal–ceramic composite membranes, AIChE J. 41 (1995) 2131.

[8] K. Hou, R. Hughes, Preparation of thin and highly stable Pd/Ag composite membranes and simulative analysis of transfer resistance for hydrogen separation, J. Membr. Sci. 214 (2000) 43.

[9] O. Schramm, A. Seidel-Morgenstern, Comparing porous and dense membranes for the application in membrane reactors, Chem. Eng. Sci. 54 (1999) 1447.

[10] S. Thomas, R. Schaefer, J. Caro, A. Seidel-Morgenstern, Investigation of mass transfer through inorganic membranes with several layers, Catal. Today 68 (2001) 205.

[11] S. Goto, S. Assabumrungrat, T. Tagawa, P. Prasenthdam, The effect of direction of hydrogen permeation on the rate through a composite palladium membrane, J. Membr. Sci. 175 (2000) 19.

[12] A. Li, W. Liang, R. Hughes, Characterisation and permeation of palladium/stainless steel composite membranes, J. Membr. Sci. 149 (1998) 259.

[13] W. Liang, Ph.D. Thesis, University of Salford, 2003.

[14] K. Keizer, R.J.R. Uhlhorn, R.J. van Duren, A.J. Burggraaf, Gas separation mechanisms in microporous modified gamma alumina membranes, J. Membr. Sci. 39 (1988) 285.

[15] A.J. Burggraaf, Transport and separation properties of membranes with gases and vapours, in: A.J. Burggraaf, L. Cot (Eds.), Fundamentals of Inorganic Membrane Science and Technology, Elsevier Science BV, 1996 (Chapter 9).

[16] K. Raznjevic, Handbook of Thermodynamic Tables and Charts, Hemisphere Publ. Corp., 1976.

[17] A. Sieverts, W. Kumbhaar, Solubility of gases in metals and alloys, Ber. Dtsch. Chem. Ges. 43 (1910) 893.