

# The diffusion of hydrogen and deuterium through self-stressed Pd<sub>77</sub>Ag<sub>23</sub> membrane

D. Dudek\*

*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*

Received 5 July 2004; received in revised form 19 November 2004; accepted 25 November 2004

Available online 7 July 2005

## Abstract

Hydrogen was introduced into palladium–silver Pd<sub>77</sub>Ag<sub>23</sub> membrane from a gas phase and self-stresses were created. The diffusion coefficients of hydrogen were determined for Pd<sub>77</sub>Ag<sub>23</sub> membrane with different initial contents of hydrogen at  $T = 303.2$  K. The non-local fluxes of interstitial component in the opposite direction than Fick's fluxes were observed at stress conditions. The diffusion of hydrogen through the Pd<sub>77</sub>Ag<sub>23</sub> membrane has been compared with deuterium diffusion. For Pd<sub>77</sub>Ag<sub>23</sub> membrane without initial content of hydrogen, the diffusion coefficients of hydrogen were determined at temperatures: 298.2, 303.2, 308.2, 318.2, 328.2 K.

© 2005 Elsevier B.V. All rights reserved.

PACS: 66.30.-h

Keywords: Diffusion; Hydrogen; Deuterium; Stresses

## 1. Introduction

Palladium–silver alloys are commercially used membranes for purification and separation of hydrogen, therefore diffusion and solubility of hydrogen in palladium–silver alloys were investigated in many papers [1–9]. The diffusivity of hydrogen in palladium–silver membranes depends on silver content. At temperature 296 K, the diffusion coefficient of hydrogen remains nearly constant up to about 25 at.% Ag, and next, it decreases by about three orders of magnitude with increasing of silver content [10]. Two types of octahedral interstitial sites in models of diffusion of hydrogen in palladium–silver alloys were assumed, differing each other by their environment with dominant amount of palladium or silver atoms [10,11].

The diffusion and solubility of deuterium in palladium–silver alloys were investigated in [12–14]. In [15,16], it was evidenced that isotope effect in some phenomena, evident in Pd–H(D), gradually disappears with increasing percentage of Ag in the Pd–Ag–H(D) system.

Input of interstitial component (hydrogen or deuterium) into palladium–silver membrane with some initial content of this component changes the volume of membrane, creates self-stresses and causes the creation of hydrogen or deuterium flux in the opposite direction than Fick's flux – uphill diffusion effect. So far, uphill diffusion effects were investigated experimentally in some palladium based membranes during diffusion of hydrogen [17–27] and deuterium [28,29] and by theoretical methods [30–32]. The measurements of diffusion of hydrogen in palladium–silver alloys Pd<sub>1-x</sub>Ag<sub>x</sub>:  $x = 9.9, 19.9, 23, 30, 39.9$  at.% [19,20,23] were done at chosen conditions, mainly by electrochemical method. In [29], the investigations of uphill effects during diffusion of deuterium in Pd<sub>77</sub>Ag<sub>23</sub> membrane were carried out by gas method at  $T = 303.2$  K.

In this paper, the permeation of hydrogen through the wall of Pd<sub>77</sub>Ag<sub>23</sub> membrane without initial content of hydrogen was measured by gas method at temperatures: 298.2, 303.2, 308.2, 318.2, 328.2 K and through membrane with chosen initial contents of hydrogen at  $T = 303.2$  K, at stress conditions. The measurements for hydrogen were compared with results for deuterium determined for the same Pd<sub>77</sub>Ag<sub>23</sub> membrane in [29].

\* Tel.: +48 343 32 21; fax: +48 632 52 76.

E-mail address: dand@ichf.edu.pl (D. Dudek).

## 2. Experimental

The diffusion of hydrogen through the wall of Pd<sub>77</sub>Ag<sub>23</sub> membrane, at stress conditions, was investigated by determined earlier method [22,29]. The membrane was a tube, closed at one side and placed in a glass system. The thickness of the wall of tube was 0.5 mm, the length of tube was 70 mm and the internal diameter was 8 mm. Stresses were created in tube by introduction of hydrogen into membrane from a gas phase and by accompanied volume changes.

Before measurements, the Pd<sub>77</sub>Ag<sub>23</sub> membrane was annealed for 2 h at about 600 °C in vacuum. The surface of tube was covered by palladium black. The measurements were carried out at chosen constant temperatures from the range: 298.2–328.2 K. In our measurements, the pressure of hydrogen at outer side of membrane at time  $t = 0$  was changed from  $p_0$  to  $p_z$  and then decreased with time because of large solubility of hydrogen in membrane. The error of determined diffusion coefficients, caused by changing of  $p_z$  with time, was estimated to about 20%.

## 3. Results and conclusions

In Figs. 1–3, the influence of stresses on the diffusion of hydrogen through the Pd<sub>77</sub>Ag<sub>23</sub> membrane with chosen initial contents of hydrogen has been evidenced.

Before each measurement, the equilibrium pressure in the whole system was attained. After hydrogen pressure change at outer side of membrane from  $p_0$  to  $p_z$  (at  $t = 0$ ) the pressure of hydrogen in inside volume of the system as a function of time,  $p(t)$  was measured. In Figs. 1–3, the dependences  $\Delta p(t) = p(t) - p_0$  are presented, determined at different initial and boundary conditions: in Fig. 1, at almost the same value of  $p_0$  and at different values of  $p_z$ , in Fig. 2, at different

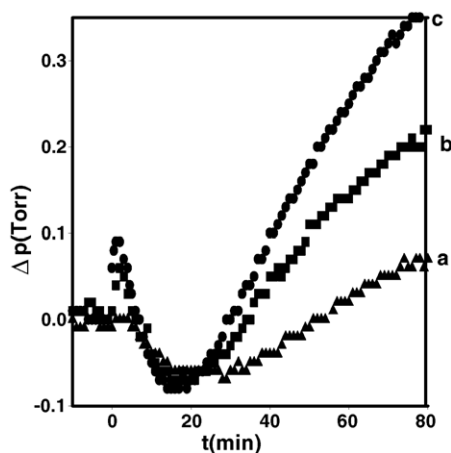


Fig. 1. The dependences  $\Delta p(t)$ , measured during diffusion of hydrogen in Pd<sub>77</sub>Ag<sub>23</sub> membrane at  $T = 303.2$  K and at following conditions: (a)  $p_0 = 1.36$  hPa,  $p_z = 30.0$  hPa, (b)  $p_0 = 1.33$  hPa,  $p_z = 55.5$  hPa, (c)  $p_0 = 1.63$  hPa,  $p_z = 79.3$  hPa.

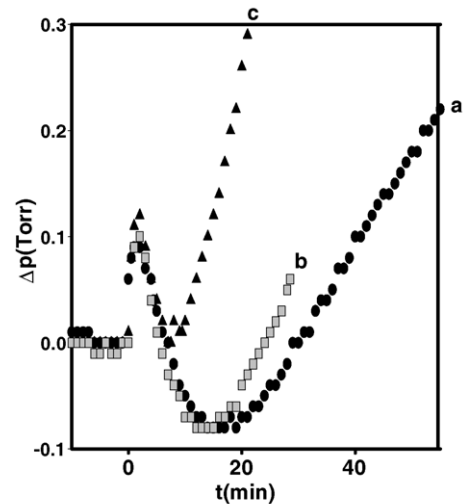


Fig. 2. The dependences  $\Delta p(t)$ , measured during diffusion of hydrogen in Pd<sub>77</sub>Ag<sub>23</sub> membrane at  $T = 303.2$  K and at following conditions: (a)  $p_0 = 1.63$  hPa,  $p_z = 79.3$  hPa, (b)  $p_0 = 1.68$  hPa,  $p_z = 75.8$  hPa, (c)  $p_0 = 2.28$  hPa,  $p_z = 78.7$  hPa.

values of  $p_0$  and at similar value of  $p_z \approx 80$  hPa, in Fig. 3, at different values of  $p_0$  and at similar value of  $p_z \approx 30$  hPa.

On each  $p(t)$  line in Figs. 1–3, we see first a maximum, later large minimum. The maximum is caused by mechanically induced bending of membrane and by corresponding decreasing of internal volume – after increasing of hydrogen pressure at outer side of membrane, and by stresses caused in bending tube – Gorsky effect (see [19]).

The non-local fluxes of hydrogen – in the opposite direction than Fick's fluxes, seen as minima on  $p(t)$  dependences in Figs. 1–3, were caused by stresses, created after introduction of hydrogen into membrane (similar minima in different

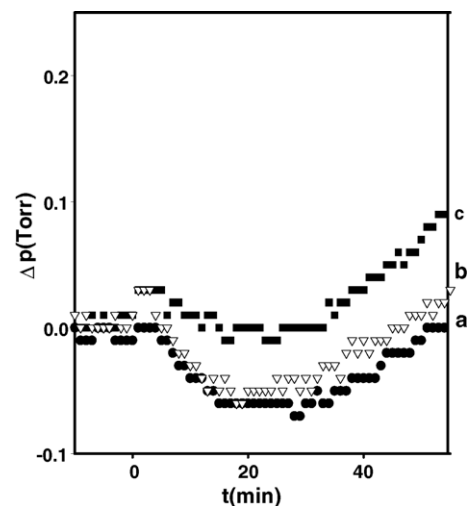


Fig. 3. The dependences  $\Delta p(t)$ , measured during diffusion of hydrogen in Pd<sub>77</sub>Ag<sub>23</sub> membrane at  $T = 303.2$  K and at following conditions: (a)  $p_0 = 1.36$  hPa,  $p_z = 30.0$  hPa, (b)  $p_0 = 1.56$  hPa,  $p_z = 31.5$  hPa, (c)  $p_0 = 0.99$  hPa,  $p_z = 31.4$  hPa.

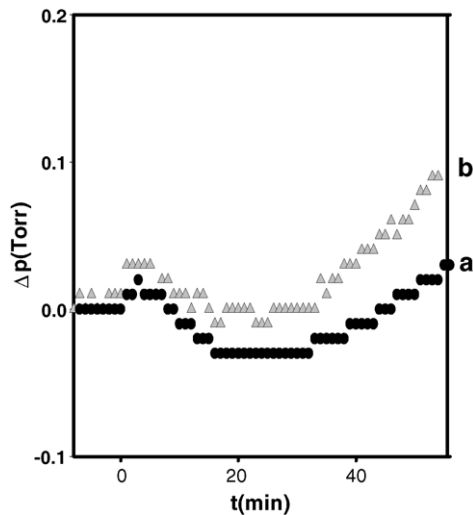


Fig. 4. The dependences  $\Delta p(t)$ , measured during diffusion of hydrogen in  $\text{Pd}_{77}\text{Ag}_{23}$  membrane at following conditions: (a)  $T = 298.2$  K,  $p_0 = 1.08$  hPa,  $p_z = 40.0$  hPa, (b)  $T = 303.2$  K,  $p_0 = 0.99$  hPa,  $p_z = 31.4$  hPa.

palladium-based membranes were observed and explained earlier in [17–29]). The introduction of hydrogen into membrane causes expansion of lattice and creation of stresses and the changes in the chemical potential of hydrogen in the whole membrane (see expressions in [30,31]).

In Figs. 1–3, we see that the magnitude of minimum on  $p(t)$  lines depends on initial content of hydrogen in membrane. In general, the total flux of hydrogen through the membrane depends on gradient of concentration of hydrogen, on gradient of stresses and on concentration of hydrogen (see expressions in [30,31]).

In Fig. 4, the  $\Delta p(t)$  dependences at similar initial and boundary conditions, at two different temperatures are compared: at 298.2 and 303.2 K.

On  $p(t)$  lines for  $\text{Pd}_{77}\text{Ag}_{23}$  membrane without initial content of hydrogen minima were not observed (see Fig. 5), because uphill flux of hydrogen is proportional to concentration of hydrogen in membrane. The measurements of  $p(t)$  dependences for membrane without initial content of hydrogen were carried out at following conditions: (a)  $T = 298.2$  K,  $p_z = 53.2$  hPa, (b)  $T = 303.2$  K,  $p_z = 56.3$  hPa, (c)  $T = 308.2$  K,  $p_z = 56.3$  hPa, (d)  $T = 318.2$  K,  $p_z = 57.7$  hPa, (e)  $T = 328.2$  K,  $p_z = 57.9$  hPa. Hydrogen permeated through the wall of  $\text{Pd}_{77}\text{Ag}_{23}$  membrane after breakthrough time. The values of breakthrough times ( $\tau$ ) and the values of diffusion coefficients ( $D$ ) were determined by method described earlier in [24,29,33,34] ( $D = L^2/6\tau$ , where  $L$  is the thickness of the wall of membrane). The results for  $\text{Pd}_{77}\text{Ag}_{23}$  membrane without initial content of hydrogen at different temperatures are presented in Table 1 and ones for membrane with chosen initial contents of hydrogen at  $T = 303.2$  K are placed in Table 2.

In Table 2, we see that at 303.2 K, the values of  $\tau$  increase with  $p_0$  increasing up to about 1.36 hPa (end of  $\alpha$  phase and

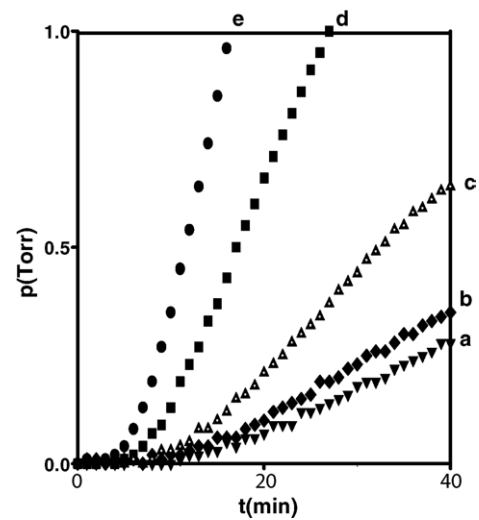


Fig. 5. The  $p(t)$  dependences for  $\text{Pd}_{77}\text{Ag}_{23}$  membrane without initial content of hydrogen at following conditions: (a)  $T = 298.2$  K,  $p_z = 53.2$  hPa, (b)  $T = 303.2$  K,  $p_z = 56.3$  hPa, (c)  $T = 308.2$  K,  $p_z = 56.3$  hPa, (d)  $T = 318.2$  K,  $p_z = 57.7$  hPa, (e)  $T = 328.2$  K,  $p_z = 57.9$  hPa.

Table 1

The values of breakthrough times and diffusion coefficients of hydrogen determined at different temperatures for  $\text{Pd}_{77}\text{Ag}_{23}$  membrane without initial content of hydrogen

$T$ (K)	$p_0$ (hPa)	$p_z$ (hPa)	$\tau$ (min)	$D$ ( $\text{m}^2/\text{s}$ )
298.2	0	53.2	16	$4.34 \times 10^{-11}$
303.2	0	56.3	13	$5.34 \times 10^{-11}$
308.2	0	56.3	11	$6.31 \times 10^{-11}$
318.2	0	57.7	8	$8.68 \times 10^{-11}$
328.2	0	57.9	6	$11.57 \times 10^{-11}$

beginning of ( $\alpha + \beta$ ) region). In ( $\alpha + \beta$ ) two-phase region, uphill effects and  $\tau$  values decrease with  $p_0$  increasing, and in the investigated region of concentrations are larger than  $\tau$  for the membrane without initial content of hydrogen at the same temperature.

Beside stresses, concentration of hydrogen can influence on values of diffusion coefficients of hydrogen. In literature, one can find the dependences of diffusion coefficients on concentration for hydrogen in palladium–silver membranes, but the results are often completely different (see [3,27,35,36]).

Table 2

The values of breakthrough times and diffusion coefficients of hydrogen determined at  $T = 303.2$  K for  $\text{Pd}_{77}\text{Ag}_{23}$  membrane with different initial contents of hydrogen

$p_0$ (hPa)	$p_z$ (hPa)	$\tau$ (min)	$D$ ( $\text{m}^2/\text{s}$ )
0.99	31.4	33	$2.10 \times 10^{-11}$
1.33	55.5	34	$2.04 \times 10^{-11}$
1.36	30.0	52	$1.34 \times 10^{-11}$
1.56	31.5	46	$1.51 \times 10^{-11}$
1.63	79.3	30	$2.31 \times 10^{-11}$
1.68	75.8	24	$2.89 \times 10^{-11}$
2.07	57.8	30	$2.31 \times 10^{-11}$
2.28	78.7	21	$3.31 \times 10^{-11}$

In paper [29], where the influence of stresses on diffusion of deuterium in the same membrane was investigated, the magnitude of minimum on  $p(t)$  lines and values of breakthrough times increased with  $p_0$  increasing up to about  $p_0 = 5.5$  hPa (beginning of  $(\alpha + \beta)$  region).

Comparing the diffusion coefficients of hydrogen and deuterium for the same Pd<sub>77</sub>Ag<sub>23</sub> membrane without initial contents of interstitial component, we see that the diffusion coefficients of hydrogen are larger than diffusion coefficients of deuterium (from [29]) at all investigated temperatures, what means that at constant temperature hydrogen permeated faster than deuterium through membrane. The fitting of straight line to the dependence  $\ln D(1/T)$ , where experimental points from Table 1 were taken, allowed for evaluation of activation energy of diffusion of hydrogen and value of  $D_{0H}$ . The determined activation energy of diffusion of hydrogen in Pd<sub>77</sub>Ag<sub>23</sub> membrane equals  $E_H = 26.3$  kJ/mol and  $D_{0H} = 1.82 \times 10^{-6}$  m<sup>2</sup>/s, what means that  $E_D < E_H$  and  $D_{0D} < D_{0H}$  (for deuterium in Pd<sub>77</sub>Ag<sub>23</sub> membrane from [29])  $E_D = 16.7$  kJ/mol and  $D_{0D} = 2.6 \times 10^{-8}$  m<sup>2</sup>/s).

#### 4. Summary

The diffusion coefficients of hydrogen in Pd<sub>77</sub>Ag<sub>23</sub> membrane without and with some initial contents of hydrogen were determined. The minima on  $p(t)$  lines at  $T = 303.2$  K, caused by stresses, were observed. The diffusion of hydrogen was compared with diffusion of deuterium for the same Pd<sub>77</sub>Ag<sub>23</sub> membrane.

#### References

- [1] A. Kuesner, Z. Phys. Chem. 36 (1963) 383.
- [2] H. Brodowsky, E. Poeschel, Z. Phys. Chem. N. F. 44 (1965) 143.
- [3] A. Kuesner, Z. Naturforsch. 21a (1966) 515.
- [4] G. Bohmholdt, E. Wicke, Z. Phys. Chem. N. F. 56 (1967) 133.
- [5] G.L. Holleck, J. Phys. Chem. 74 (1970) 503.
- [6] H. Zuechner, Z. Naturforsch. 25a (1970) 1490.
- [7] H. Buchold, G. Sicking, E. Wicke, Ber. Bunsenges. 80 (1976) 446.
- [8] Y. Sakamoto, S. Hirata, H. Nishikawa, J. Less-Common Met. 88 (1982) 387.
- [9] E. Serra, M. Kemali, A. Perujo, D.K. Ross, Metall. Mater. Trans. 29A (1998) 1023.
- [10] L. Opara, B. Klein, H. Zuechner, J. Alloys Compd. 253–254 (1997) 378.
- [11] H. Berlag, L. Opara, H. Zuechner, J. Alloys Compd. 330–332 (2002) 434.
- [12] G. Holleck, E. Wicke, Z. Phys. Chem. N. F. 56 (1967) 155.
- [13] R.G. Hickman, J. Less-Common Met. 19 (1969) 369.
- [14] R. Laesser, G.L. Powell, J. Less-Common Met. 130 (1987) 387.
- [15] W. Buckel, B. Stricker, Phys. Lett. 43A (1973) 403.
- [16] R.J. Miller, C.B. Satterthwaite, Phys. Rev. Lett. 34 (1975) 144.
- [17] F.A. Lewis, J.P. Magennis, S.G. Mc Kee, P.J.M. Seebuufu, Nature 306 (1983) 613.
- [18] K. Kandasamy, F.A. Lewis, J.P. Magennis, S.G. Mc Kee, X.Q. Tong, Z. Phys. Chem. 171 (1991) 213.
- [19] X.Q. Tong, F.A. Lewis, J. Less-Common. Met. 169 (1991) 157.
- [20] F.A. Lewis, Y. Sakamoto, K. Kandasamy, X.Q. Tong, Defect. Diffus. Forum 115–116 (1994) 39.
- [21] F.A. Lewis, X.Q. Tong, K. Kandasamy, R.V. Bucur, Y. Sakamoto, Thermochim. Acta 218 (1993) 57.
- [22] D. Dudek, B. Baranowski, Pol. J. Chem. 69 (1995) 1196.
- [23] Y. Sakamoto, H. Tanaka, F. Sakamoto, F.A. Lewis, Int. J. Hydrogen Energy 20 (1995) 35.
- [24] D. Dudek, B. Baranowski, Z. Phys. Chem. 206 (1998) 21.
- [25] D. Dudek, J. Alloys Compd. 329 (2001) 1.
- [26] D. Dudek, Defect Diffus. Forum 203–205 (2002) 225.
- [27] F.A. Lewis, K. Kandasamy, X.Q. Tong, in: F.A. Lewis, A. Aladjem (Eds.), Hydrogen in Metal System, vol. II, Scitec Publications Ltd., Ueticon-Zuerich, 2000, p. 463.
- [28] D. Dudek, Collect. Czech. Chem. Commun. 68 (2003) 1046.
- [29] D. Dudek, Collect. Czech. Chem. Commun. 70 (2005) 1.
- [30] B. Baranowski, in: S. Sieniutycz, P. Salomon (Eds.), Advances in Thermodynamics, Flow Diffusion and Rate Processes, Taylor and Francis, NY, 1992, pp. 168–199.
- [31] B. Baranowski, J. Less-Common Met. 154 (1989) 329.
- [32] K. Kandasamy, Int. J. Hydrogen Energy 20 (1995) 455.
- [33] J. Crank, The Mathematics of Diffusion, Oxford University Press, 1956, p. 48.
- [34] R.M. Barrer, Diffusion in and through Solids, Cambridge University Press, 1951, p. 19.
- [35] S. Majorowski, B. Baranowski, J. Phys. Chem. Solids 43 (1982) 1119.
- [36] F.A. Lewis, X.Q. Tong, R.V. Bucur, K. Kandasamy, Defect Diffus. Forum 148–149 (1999) 161.