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1992 J. Phys.: Condens. Matter 4 L439

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LETTER TO THE EDITOR

Strain gradient influences on apparent dependences of hydrogen diffusion coefficients on hydrogen content in the $\text{Pd}_{81}\text{Pt}_{19}\text{H}_n$ system

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Received 18 June 1992

Abstract. Consolidating studies are reported of 'uphill hydrogen diffusion' effects produced by lattice strain gradients during hydrogen permeation through tubular membranes of a $\text{Pt}_{81}\text{Pt}_{19}$ alloy at 25 °C. Hydrogen permeation has been initiated by outer surface introductions and removals of hydrogen both from and into the gas phase and also by means of electrolysis. Results demonstrate further effects of strain gradients in producing misleading trends of dependence of hydrogen diffusion coefficients on hydrogen content.

In addition to permeation experiments under conditions of hydrogen introduction into and removal from membranes through surface/gas phase interfaces (e.g. Hickman 1969), determinations of hydrogen diffusion coefficients from permeation studies, have employed electrochemical means of surface hydrogen charge and discharge combined with electrode potential measurement techniques (Devanathan and Stachurski 1962, Küssner 1966, Boes and Züchner 1976, Early 1978, Archer and Grant 1984, Kircheim 1988, Bucur and Klimecki 1990, Bucur *et al* 1991).

Amongst various other factors, differences between results have been attributed to variations of specimen geometry, deviations of surface catalytic activity and to influences of structural defects particularly dislocations (Wicke *et al* 1978, Bucur 1985, Kircheim 1988, Bucur *et al* 1991). A further complicating factor that has to be taken into consideration in analyses of studies of hydrogen diffusion, is that incorporations of hydrogen interstitials produce lattice expansions capable of creating more extended non-local stress (strain) fields (Gorsky 1935, Alefeld *et al* 1970, Wagner and Horner 1974, Lewis 1990, Mällo and Krozer 1991) that can induce a preferential attraction of the hydrogen interstitials towards such regions of lattice dilation.

Hydrogen self-induced strain (stress) fields may have to be rather more particularly taken into account in cases of high densities of absorbed hydrogen where the possibility of interlocking influences of diffusion-elastic and Gorsky effects (Čermák *et al* 1985) have been pointed out. Involvements of such a combination of diffusion elastic and Gorsky effect influences has been proposed to account for observations of temporary initial rates of hydrogen permeation in opposite 'uphill' flux directions to overall reimposed hydrogen concentration gradients across membranes of $\text{Pd}_{81}\text{Pt}_{19}$

and Pd₇₇Ag₂₃ alloys (Lewis *et al* 1983, 1987, 1988, 1989, Kandasamy *et al* 1991) and also recently across membranes of palladium itself (Tong *et al* 1990 and Sakamoto *et al* 1991).

Theoretical diffusion equations that may take account of such effects by including terms representing involvement of stress and strain gradients in addition to Fickian terms have latterly been the subject of increasing development (Li 1978, Larché and Cahn 1982, 1992, Kandasamy 1988, 1989, Baranowski 1989, 1992, Simon and Grzywna 1991). For comparison of such analyses with experimental information it is useful and important for the phase relationships of the particular chemical (metal/hydrogen) systems to be available to be taken into account (Kandasamy *et al* 1991, Simon and Grzywna 1991). Choices of the particular alloy compositions Pd₈₁Pt₁₉ and Pd₇₇Ag₂₃ (Tong and Lewis 1990, 1991) so far studied have been governed by their suitability with regard to available knowledge of their isothermal p - $c(n)$ relationships at temperatures near 25 °C (Lewis *et al* 1983, Baranowski *et al* 1983, Kandasamy *et al* 1991) with reference to the possibility of introductions of reasonably significant contents of hydrogen ($n = H/M$ (atomic ratio)), at conveniently measureable hydrogen pressures (p). In this letter further permeation measurements are reported with the Pd₈₁Pt₁₉ alloy composition for conditions of both hydrogen absorption and desorption by both electrolytic and gas phase methods to and from surfaces of comparable catalytic activity, of a tubular membrane containing comparable ranges of hydrogen contents over the course of each sequence of measurements.

As in previous studies (Lewis *et al* 1983, 1988 and Kandasamy *et al* 1991) the tubular specimen of Pd₈₁Pt₁₉ alloy was 75 mm long with internal diameter 8.0 mm and wall thickness of 0.25 mm. It was rounded and closed at one end and the open end was sealed to glass tubing and connected to capacitance manometers (Baratron model 222A) for pressure measurements within the range 0–1000 Torr, a vacuum line and a hydrogen gas supply. Hydrogen was supplied to or removed from the outer surface of the tube wall by either of two alternative techniques. In one technique, the tube acted as one electrode of an electrolytic cell containing 1N H₂SO₄ (e.g. Lewis *et al* 1983). In the other technique, the tube was enclosed in a large volume vessel so that the outer surface could also be connected to a vacuum line, gas cylinders and pressure gauges (Lewis *et al* 1987, 1989, Kandasamy *et al* 1990 and Tong and Lewis 1991). In either technique both inner and outer surfaces of the tube wall had been preactivated by electrolytic deposition of palladium black, to produce a necessary high catalytic activity for clear observation of the effects illustrated in figures 1 and 2 below (Lewis *et al* 1983, Kandasamy *et al* 1991). Temperature was controlled to ± 0.2 °C.

Following the introduction of hydrogen through the outer surface by either form of experimental technique, subsequent changes of pressure (p) inside the initially hydrogen-free tube exhibited usual 'breakthrough' forms of pressure-time (p - t) dependence (Lewis *et al* 1983, 1987, Kandasamy *et al* 1991). In accordance with an assumption of a linear variation of concentration being finally adopted across the thickness δ of the membrane in the intermediately developed quasi steady state ($J_{\delta} = -D_H dn/d\delta$), values for the diffusion coefficient D_H were estimated by using the relation $D_H = \delta^2/6t_L$ (e.g. Crank 1975, Boes and Züchner 1976) where t_L was determined from extrapolations of post breakthrough regions of p - t plots back to the time axis.

For a series of experiments with initial values of $n_0 = 0$ for the hydrogen content of the tube wall but with various values of suddenly imposed hydrogen pressure p_0 within the range 0–900 Torr (corresponding to complementary values of n_0 in the

outer surface within the range $0 < n_0 < 0.05$ (Kandasamy *et al* 1991) obtainable from p - n relationships at 25 °C, experimentally determined values of t_L were found to have a consistently reproducible value of 12.5 ± 0.5 min which yielded a value of $D_H = 1.4 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ in good agreement with the previous results of Yoshihara and McLellan (1986), Čermák (1980) and Lewis *et al* (1987). A rather fortuitously identical value of 12.5 min also was estimated for t_L in the case of cathodically introduced hydrogen at the outer surface at a current density of $\approx 15 \text{ mA cm}^{-2}$ (as compared to $t_L = 15$ min cited earlier in the case of a similar series of experiments (Kandasamy *et al* 1991). From purely Fickian considerations it could also have been expected that values of subsequent quasi steady state permeation rates, dp/dt , also would be directly proportional to the values of n_0 at the outer surface. Steady state values of dp/dt were, however, found to be increasingly reduced with increase of n_0 from rates anticipated for a direct dependence of dp/dt on n_0 . This was a finding more in keeping with developments of curved steady state concentration profiles as suggested by Kandasamy (Kandasamy 1988, 1989 cf Simon and Gryzwina 1991) and supported by experimental findings of initial accelerations of permeation rates on interruptions of cathodization (Kandasamy *et al* 1991).

Examples of incremental changes (adjusted to allow for initial background drifts of pressure (Kandasamy *et al* 1991)) of hydrogen pressure Δp within the tube following abrupt further increases of outer surface hydrogen pressure are illustrated in figure 1(a). Figure 1(b) shows examples, for a series of comparable initial quasi-static hydrogen pressures p_0 within the tube, of effects produced by electrolytic cathodization of the outer surface. Examples of converse series of measurements of internal pressure changes during experiments in which hydrogen was being removed from outer surfaces by evacuative pumping and by electrolytic anodization, respectively, from tube walls again containing comparable initial hydrogen contents, n_0 , again estimated (table 1) through p_0 from the p - n relationships (Kandasamy *et al* 1991) within the range $0 < n_0 < 0.05$, are shown in figures 2(a) and 2(b).

Comparison of figures 1 and 2 shows that in the cases of outer surface pressure change technique experiments (figures 1(a) and 2(a)), the initial stages exhibit an additional feature to those observed in the analogous 'electrolytic' experiments (figures 1(b) and 2(b)). Similarly to a preliminary report (Lewis *et al* 1987), the initial impingements of hydrogen gas (figure 1(a)) produced relatively sudden peak-like increases of p , while figure 2(a) illustrates that rapid reduction of pressure at the outer surface produced the counterpart feature of abrupt initial reductions of internal pressure. Although such effects had originally been attributed solely to equivalent decreases of internal volume (Lewis *et al* 1987) recent analogous studies with a $\text{Pd}_{77}\text{Ag}_{23}$ membrane (Tong and Lewis 1991, Lewis and Tong 1992) have demonstrated that they can primarily arise as consequences of mechanically produced strain gradients and subsequent Gorsky effect hydrogen transfer processes.

Following the rapid initial increases of internal hydrogen pressure, figure 1(a) illustrates further examples of the more clearly obvious 'uphill' second feature (Lewis *et al* 1987) of more gradual decreases of pressure to minimum values. Maximal increments of these decreases have been designated as Δp_{\min} and are listed in table 1 together with the complementary time increments, Δt_{\min} , required for attainments of Δp_{\min} . Values of similarly defined Δp_{\min} and Δt_{\min} corresponding to the *initial* 'uphill' features of decreases of pressure in the cases (in figure 1(b)) of electrolytically reintroduced hydrogen (Lewis *et al* 1983, 1988, 1989, Kandasamy *et al* 1991) are also recorded in table 1, together with the analogous converse 'downhill' parameters of

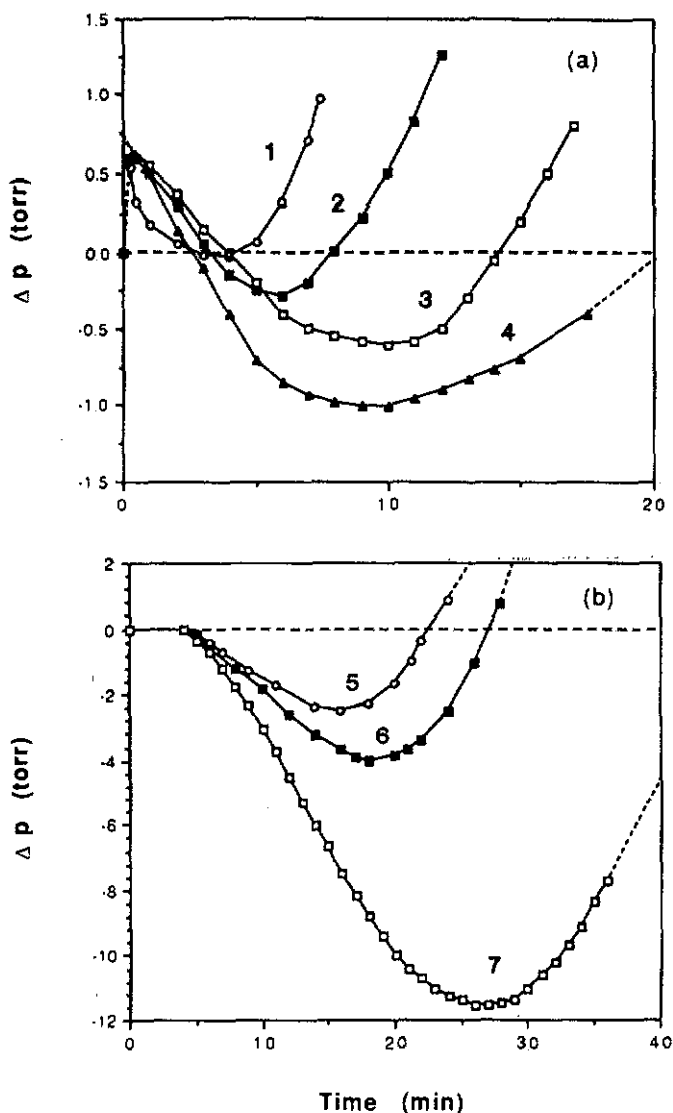


Figure 1. (a) Time dependences of incremental changes of hydrogen gas pressure Δp within a tubular $\text{Pd}_{81}\text{Pt}_{19}$ membrane, from initial pressures p_0 of 25 Torr (curve 1), 300 Torr (curve 2), 600 Torr (curve 3) and 740 Torr (curve 4) following increases of hydrogen pressures at the outer surface to 940 Torr (curves 1, 3 and 4) and 925 Torr (curve 2) 25 °C. (b) Time dependences of incremental changes of Δp from initial quasi-static pressures p_0 of 185 Torr (curve 5), 325 Torr (curve 6) and 650 Torr (curve 7) following recommencement of cathodization at outer surfaces at a current density of 15 mA cm⁻² (25 °C).

Δp_{\max} and Δt_{\max} determined from the results illustrated in figures 2(a) and 2(b).

A further pair of parameters recorded in table 1 are those of the approximate time lag constants t_L and t_L^* which again have been estimated from extrapolations of quasi-constant rates of permeation over time periods in $p-t$ plots subsequent to Δt_{\min} and Δt_{\max} . These values of t_L and t_L^* have also been utilized to obtain apparent values of D_H from the relationship $D_H = \delta^2/6t_L$. The values of Δp_{\min} ,

Table 1. Apparent dependences of D_H on n_0 (25 °C)

Curve symbol	p_0 (Torr)	n_0 (H/M)	$\Delta t_{\min} \Delta t_{\max}$ (min)	$\Delta p_{\min} \Delta p_{\max}$ (Torr)	$t_L t_L^*$ (min)	D_H (appar.) ($\text{m}^2\text{s}^{-1} \times 10^{11}$)
Outer surface hydrogen introduction by electrolytic cathodization						
	0	0	—	—	12.5	1.400
5	185	0.009	11.6	2.5	19	0.913
6	325	0.014	14.0	4.0	24	0.723
7	630	0.030	23.0	11.5	44	0.393
Outer surface hydrogen removal by electrolytic anodization						
13	240	0.011	7.0	0.4	17	1.021
12	510	0.023	11.5	2.1	24	0.723
11	720	0.040	17.0	6.9	32	0.543
Outer surface hydrogen introduction by gas phase pressure increases						
	0	0	—	—	12.5	1.400
1	25	0.001	3.5	0.52	5.5	3.157
2	300	0.013	5.0	0.89	9.5	1.827
3	600	0.029	9.5	1.21	14.0	1.239
4	740	0.042	9.5	1.60	20.0	0.868
Outer surface hydrogen removal by continued evacuative pumpin g						
10	445	0.020	7.7	1.25	15	1.157
9	640	0.031	8.0	2.50	14	1.239
8	825	0.046	9.5	3.80	17	1.021

Δp_{\max} and D_H are plotted as a function of n_0 in figures 3(a) and 3(b).

The plots in figure 3(b) show good quantitative agreement with other series of results under equivalent conditions (Kandasamy *et al* 1991) in demonstrating a close to direct dependence of $\Delta p_{(\max;\min)}$ on n_0 over the range $0 < n_0 < 0.05$. Comparisons in table 1 clearly confirm that these increasing magnitudes of $\Delta p_{(\max;\min)}$ have produced overall lengthening of the duration of the uphill process and complementary increases in the time lag constant t_L . This has caused the diffusion coefficients D_H to exhibit apparent decreases with increasing n_0 which are opposite trends to what could have been expected from essentially Fickian considerations based on lattice expansion effects (Wicke *et al* 1978, Larché and Cahn 1982, Kandasamy 1988, Baranowski 1989, 1992, Simon and Grzywna 1991) and further substantiate that uphill effects can introduce serious unreliability into derivations of hydrogen diffusion coefficients by breakthrough techniques (Lewis *et al* 1983, 1987, Kandasamy 1989, Baranowski and Lewis 1989, Baranowski 1989, 1992, Simon and Grzywna 1991).

It must be noted that trends of decreases of D_H with n_0 over analogous lower hydrogen content α phase regions in the cases of PdH_n and $\text{Pd}_{77}\text{Ag}_{23}\text{H}_n$ systems (Kandasamy *et al* 1990, Tong *et al* 1990, Sakamoto *et al* 1991) have been found to maximize over ranges of n_0 corresponding to regions of quasi ($\alpha + \beta$) phase coexistence that could only have been attained in the case of the $\text{Pd}_{81}\text{Pt}_{19}\text{H}_n$ system at higher pressures or lower temperatures than could be covered in the presently reported studies.

Comparisons of the dependences of $\Delta t_{\min;\max}$, t_L and t_L^* and D_H on initial hydrogen content n_0 in table 1 and figure 3(a) indicate that magnitudes and durations of uphill effects are clearly dependent on the type of technique employed. Thus for com-

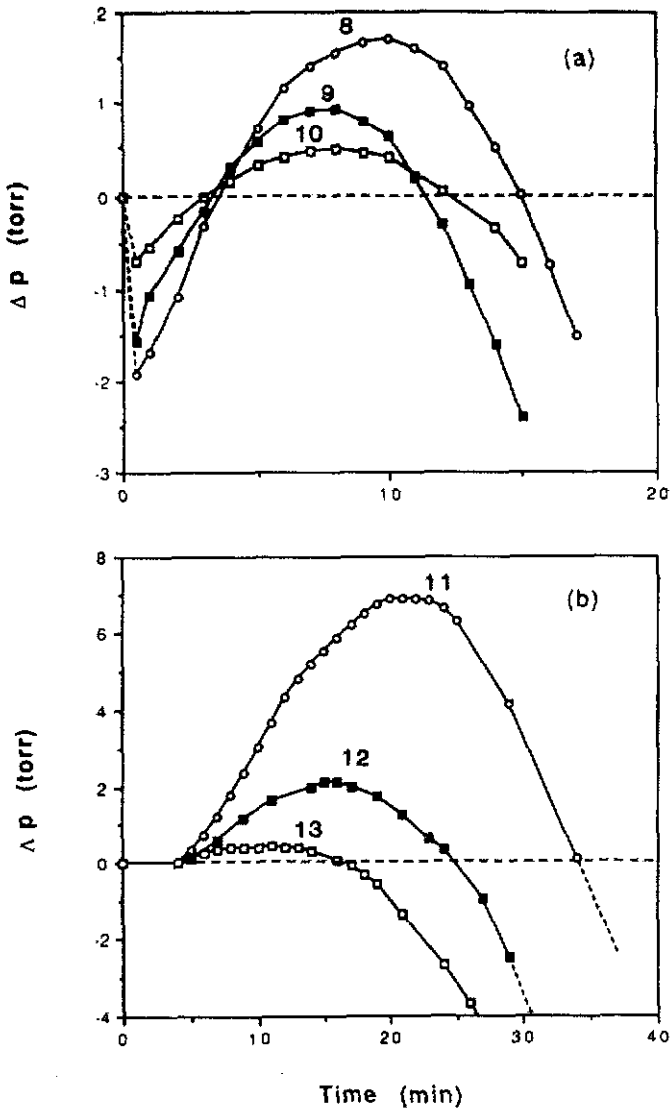


Figure 2. (a) Time dependences of incremental changes of hydrogen pressure Δp within a $\text{Pd}_{81}\text{Pt}_{19}$ membrane from initial pressures p_0 of 45 Torr (curve 10), 640 Torr (curve 9) and 825 Torr (curve 8) following sustained evacuative removal of hydrogen from the outer surface (25°C). (b) Time dependences Δp from initial quasi-static pressures p_0 of 240 Torr (curve 13), 510 Torr (curve 12) and 720 Torr (curve 11) following commencements of anodizations of outer surfaces at a current density of 15 mA cm⁻² (25°C).

parable initial values of hydrogen content, n_0 , all three parameters are significantly lower in the cases corresponding to figures 1(a) and 2(a), where sudden incremental changes of surface hydrogen contents were effected by hydrogen pressure changes, rather than by electrolysis. These differences are consistent with evidence from analogous studies with $\text{Pd}_{77}\text{Ag}_{23}\text{H}_n$ membranes (Tong and Lewis 1991, Lewis and Tong 1992) that initial pressure alterations such as conditions of figure 1(a) have produced strain gradients of mechanical origination that have induced significant Gorsky effect

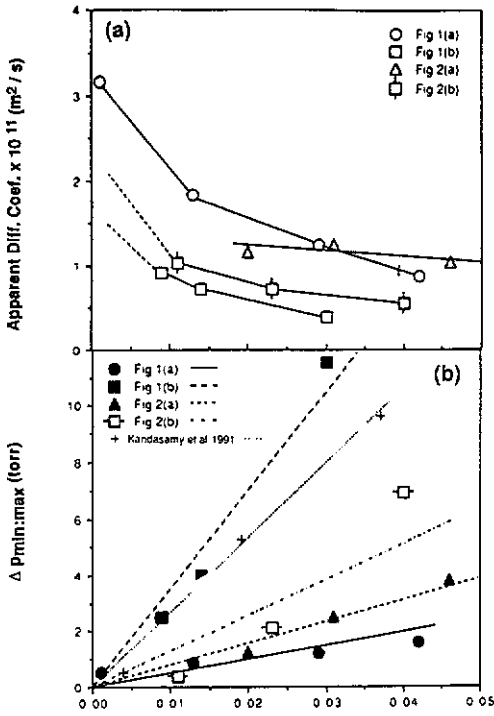


Figure 3. (a) Dependences on n_0 of apparent hydrogen diffusion coefficient, D_H calculated from values of the time lag constant, t_L , derived from data plotted in figures 1 and 2. (b) Dependences on n_0 of the magnitudes of uphill effects represented by maximum incremental decreases (or increases) $\Delta P_{(\min;max)}$ for experiments in figures 1 and 2.

transfers of hydrogen in the same direction as the Fickian concentration gradients subsequently created as absorption of hydrogen proceeds at the outer surface.

Despite the reduced detail in terms of measurement points on figures 1(a) and 2(a) compared to analogous measurements possible over a wider range of hydrogen content in the case of studies with a thicker walled $Pd_{77}Ag_{23}$ membrane (Kandasamy *et al* 1990, Tong and Lewis 1990, 1991, Lewis and Tong 1992), the trends indicated by the few data points effectively available for definition in figure 1(a) within the initially rapid increase of internal pressure do, however, show an essential similarity with the $Pd_{77}Ag_{23}H_n$ case, in indicating that magnitudes of this initial effect are also dependent on initial hydrogen contents n_0 that would be available for such additional exercises of Gorsky effect hydrogen transfer (Kandasamy *et al* 1990, Tong and Lewis 1992). The overall forms of results in the cases of hydrogen pressure change produced effects in figures 1(a) and 2(a) thus seem consistent with generalized forms of representation of permeation J_δ such as:

$$J_\delta = -f(D_H(n)\text{grad}n) + f(D_H(n), n_0, \text{grad}\epsilon(\text{diff} - \text{elas})) - f(D_H(n), n_0, \text{grad} \epsilon(\text{mech})) \tag{3}$$

in which 'uphill' effects are represented by the second term and downhill effects by the first and third terms. The influence of the third term can be expected to be dependent on the effective degree of deformation and it would seem the accountable factor for the apparent increase of D_H with initial increases of n_0 in table 1 under the particular conditions of comparison of the present study.

Grateful acknowledgement is due to Johnson Matthey Plc for fabrication and loan of the specimens of Pd₈₁Pt₁₉ alloy. Thanks also are due to J Čermák and S G McKee for very helpful discussion and experimental assistance and to Queen's University for Visiting Research awards to KK and XQT.

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