

Uphill Effects on Hydrogen Diffusion Coefficients in Pd₇₇Ag₂₃ Alloy Membranes

INFLUENCES DUE TO GORSKY EFFECT AND LATTICE STRAIN GRADIENT FACTORS

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The choice of palladium (Pd) and Pd alloys selected for use in hydrogen permeation membranes is determined by the values for hydrogen solubility and hydrogen diffusion coefficients, D_H , with high values being preferred (1–5). Using pure Pd membranes at temperatures $\leq 300^\circ\text{C}$ can be complicated by the possible involvement of the $\alpha \leftrightarrow \beta$ phase hydride transition regions, with the likely consequent formation of irreversible distortions (1–10). However, the problems of phase transition and related hysteresis effects can be much reduced by using membranes made of carefully chosen Pd alloys.

For example, Pd-Ag (palladium-silver) alloys in the composition range Pd₇₇Ag₂₃ to Pd₇₅Ag₂₅ have been successfully used as hydrogen purification membranes over a wide range of equilibration conditions with respect to hydrogen pressure, p , hydrogen content, n ($n = \text{H}/\text{M}$ atomic ratio, where M is metal) and temperature, T , (from p - $c(n)$ - T relations). Relationships between n and D_H , have been derived by using both electrochemical and gas-phase equilibration techniques (6–10).

Representations of D_H - n Relations

Figure 1 compares various forms of the D_H - n relationship, for catalytically preactivated surfaces, at 50°C (4–10). It shows satisfactory agreement between results obtained either by gas-phase or electrolytic techniques over the higher, β -phase, range, where D_H increases with increasing n . However, over the lower, α -phase ranges of n , studies using the electrochemical technique, have shown an initial opposing trend of decreasing values of D_H with increasing values of n (8–10).

Tubular Membrane Studies

Tubular membranes have been used in a more recent series of studies on electrochemical hydrogen permeation in 0.02 N H₂SO₄ at 25 or 50°C (15–23, 25, 26). Parameters measured were the inner-tube hydrogen-gas pressures and internal surface electrode potentials. In electrolytic experiments, essentially analogous to those of Küssner (8), further progressive increases in the hydrogen content (n) of membrane surfaces were introduced by a stepwise series of electrolytic cathodisations.

Uphill Hydrogen Transfer Effects

After interruptions made to each additional outer-surface hydrogen-charging process, open-circuit conditions were maintained for both

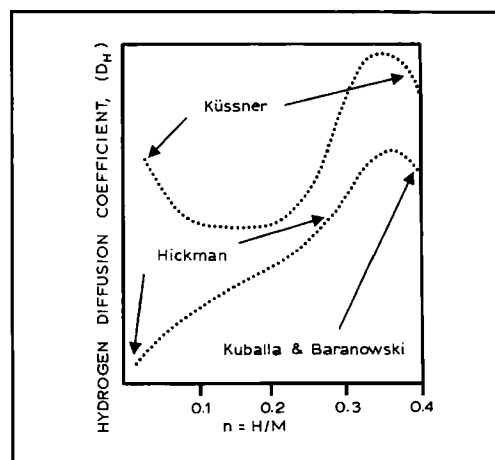


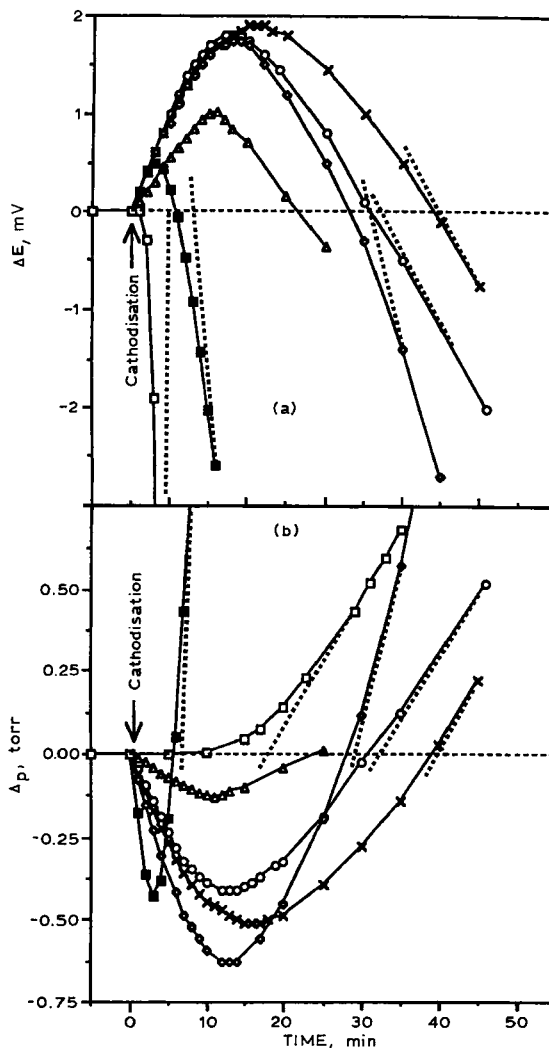
Fig. 1 Representation of the dependence of hydrogen diffusion coefficients in Pd₇₇Ag₂₃ alloys on initial hydrogen contents from work by: Küssner (8); Hickman (9); Kuballa and Baranowski referred to in (4)

Fig. 2a Time dependent incremental changes of internal surface electrode potentials at 50°C, for Pd₇₇Ag₂₃ tubular membranes (dia. 8.0 mm, wall 0.4 mm thick) with Pd black coats after cathodisation in 0.02N H₂SO₄ at 15 mA cm⁻², and after establishment of steady state values for E₀. Corresponding values for hydrogen content, n₀, were derived from p(E)-n-T (15, 25, 30) relationships. Breakthrough times, t_L, are indicated interpolations

	E ₀ , mV	t _L , min
□	867.9	4.8
△	50.40	22.0
○	40.40	32.0
×	38.10	39.5
◇	33.75	30.5
■	22.40	7.8

Fig. 2b Complementary incremental changes of thermodynamically equivalent values of hydrogen gas pressures within the tubular Pd₇₇Ag₂₃ membranes, calculated via the amended 2FE ≈ RT ln p relationships, F and R are the Faraday and gas law constants, respectively

	p ₀ , torr	n ₀ (H/M)	t _L , min
□	0.00	0.000	18.3
△	0.42	0.023	23.9
○	0.91	0.044	32.3
×	1.09	0.049	39.9
◇	1.53	0.062	29.0
■	3.70	0.195	6.8



surface and internal hydrogen equilibration processes, during periods of gradual decay to new steady state interim values of internal hydrogen pressure, p, and electrode potential, E. The p and E interim open-circuit values were then adopted as new initial values, p₀ and E₀, together with the next initial value of hydrogen content, n₀, determined from available p(E)-c(n)-T relationships (4–10).

Figure 2a shows an example of time-dependent measurements of inner-surface electrode potential plots for a membrane of 8.0 mm inner diameter, 0.4 mm wall thickness, with inner and outer Pd

black coats. This followed the resumption (at 50°C) of cathodisation at 15 mA cm⁻². Earlier established equilibration conditions are at the E₀ values (23).

In Figure 2b, the values of p have been calculated from the values of E given in Figure 2a, using the thermodynamically equivalent, when corrected, correlation:

$$2F \frac{E}{E_0} \approx RT \ln \frac{p}{p_0} \quad (1)$$

F is the Faraday constant and R is the gas constant. The time dependent paths of the ΔE-t and the

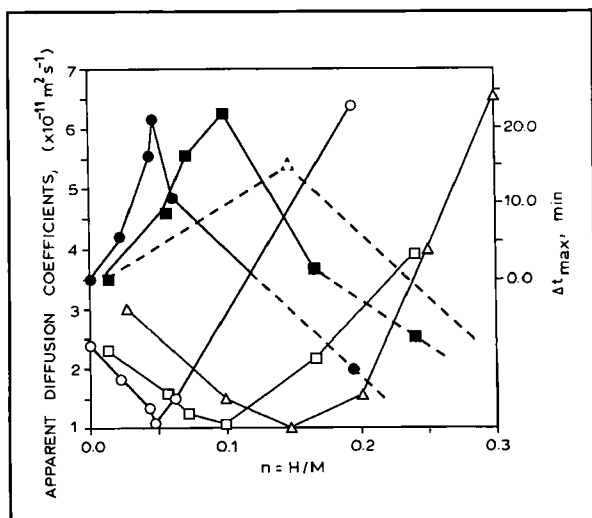


Fig. 5 Comparison of catalytic activity in NOx conversion of three catalysts impregnated onto an industrial α -Al₂O₃ support:
 V_r = velocity of gas mixture
 1 catalyst prepared from cluster (I) and phen. containing 0.1% Pd
 2 catalyst based on the platinum salt, H₂PtCl₆, containing 0.1% Pt
 3 industrial catalyst APK-2; this catalyst contains 2% Pd

derived Δp - t plots (Figures 2a and 2b, respectively) are typical of similar results that have been interpreted in forms of the uphill Gorsky Effect (15, 18, 21). These involve hydrogen interstitial transfer processes which operate in a direction opposite to the hydrogen permeation flux.

The values of the breakthrough times, t_b , in Figures 2a and 2b correspond to intersection points between the ΔE -(Δp)- t axes and the later, more linear, stages of the time plots. Values of D_H were then calculated (15, 20) using Relation (ii):

$$D_H = \frac{l^2}{6t_b} \quad (\text{ii})$$

l is the thickness of the membrane wall (0.4 mm).

Comparison of D_H - n Relations

Figure 3 compares results obtained using alternative ways of deriving the relationship between D_H and n at 50°C. The sources used to determine the D_H values are:

- [a] a set of measurements obtained from direct hydrogen pressure records (26)
- [b] calculations using Relation (ii) with t_b values from Figure 2b
- [c] replotting the corresponding diffusion data of Küssner (Fig. 9 in (8))

From Figure 3 it can be seen that there are overall similarities between the results presented by Küssner (8) and more recent analogous data

(23, 26, 27). In particular, each D_H - n plot has regions of apparent decrease of D_H with increasing n over an initial range from $n = 0$ to ~ 0.1 – 0.2 .

For the two more recent determinations, [a] and [b], the results are again similar to earlier analogous Pd₇₇Ag₂₃H _{n} reports (25, 26, 29). In these cases the temporary sign reversal of the incremental changes of permeation rate, when hydriding is restarted, has been identified with periods of elastic strain gradient-induced uphill Gorsky Effect (opposing the permeation direction) (15–26, 28–34) on internal hydrogen transfer.

Küssner had not considered this explanation when he described the reversed sign (Fig. 7 in (8)) in terms of a transition to a type of plastic viscoelastic state (8, 10). He did not however cite or present physical evidence of any associated structural or defect changes.

Figures 2 and 3 also show that Küssner's results (8) over the lower range of hydrogen contents: $n \sim 0.0$ – 0.2 in Pd₇₇Ag₂₃, could have been interpreted differently in terms of concurrent uphill hydrogen interstitial diffusion effects (Δt_{\max} in Figure 3) without significantly altering the overall elasticity characteristics.

Summary

For each example in Figure 3, the apparent decrease in D_H with increase in the α -phase hydrogen content, n , can be equated with longer time inter-

vals and corresponding longer periods of uphill opposing-direction hydrogen permeation flux. This leads to longer times for attaining the breakthrough times, t_b , and so, through Relation (ii), causes misleading apparently decreasing values of D_H with increasing n . In a broader context, this survey also seems to support suggestions of a non-Fickian classification of Pd alloy-hydrogen

diffusion systems, with possibilities for easy control of concentration gradients and boundary conditions (4, 12–15, 29, 30).

Acknowledgements

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Platinum Group Metals Technology in Ekaterinburg

Research and development undertaken at the Ekaterinburg Non-ferrous Metals Processing Plant in Russia into metallurgical aspects of the platinum group metals (pgms) is described in a recent issue of the Russian journal *Tsvetnyye Metally* (1), translated into English.

With over 80 years' experience, the plant is a leader in platinum (Pt) jewellery production which forms, together with jewellery alloys, a large part of the Pt output at the plant. Casting and moldings are done in an inert atmosphere or under vacuum and jewellery soldering alloys for Pt alloys are being developed. A volatile oxide-forming component is added to a jewellery alloy to counter gas absorption.

Dispersion hardened alloys for glass production, particularly glass fibre production, have been developed. The protection of pgm equipment and reduction of metal loss during fabrication has been achieved by plasma technology, in a 'PM-plasmo-ceramic' system. This has been adopted by several industries. Sputtered coatings on the outer surface of equipment result in less metal use and metal loss.

The brittle fracture of Pt alloys caused by various molten metals and elements, such as iron, manganese, calcium and silicon, has been investigated. Iridium (Ir) research is a speciality at Ekaterinburg, so a short item from V. A. Dmitriev, N. I. Timofeyev and A. V. Ermakov on brittle fracture in Ir and Ir alloys and the effects of molten additions is of note. Ir only fails by brittle fracture under tensile stress (2). Ir crucibles used in reprocessing lead-zinc 'cakes' containing high concentrations of gold and silver at > 1300°C have operated for a few hundred hours without failure.

Other technologies with improved results are: knitted gauze catalysts and catchment gauzes for ammonia oxidation, Pd alloy powders for capacitors, and new materials for dental alloys. Au-Cu-Pd alloy phase diagrams have also been investigated.

The plant at Ekaterinburg recycles pgms waste. Their rhodium refining scheme is very flexible. There are new processes for osmium (Os) recovery and separation, and a method for the production of high purity Os powder uses gaseous phase extraction at up to 2000°C. A sample from a placer deposit from the Inagli field, Yakutia, contained 0.89% Os, 71.55% Pt, etc. Iron, nickel and copper were the major impurities. The recovery of up to 95% Os in a full processing cycle of placer Pt, and 100% recovery from the gaseous phase is claimed.

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Noble and Rare Metals Conference

The 4th international conference on noble and rare metals (NRM-2003) will be held in Donetsk, Ukraine, on 22nd to 26th September, 2003. Geology, extraction, recovery and secondary refining, alloys and alloy properties, and industrial uses will be covered.

Information can be obtained from Professor V. A. Goltsov of Donetsk National Technical University, Ukraine; E-mail: goltsov@physics.dgtu.donetsk.ua; and from the internet at: <http://dgtu.donetsk.ua/NRMworld/files/eng/>.