

Effects of electrochemical reaction and self-stress on hydrogen diffusion in tubular membranes during galvanostatic charging

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Abstract

Based on theories of hydrogen electrode reactions at the palladium surface and self-stresses of hydrogen in thin tubular shells established earlier, we numerically calculate transport properties of hydrogen across a tubular membrane under galvanostatic charging conditions. It is found that the exited hydrogen flux is much less than the charging current since the hydrogen combination reaction takes place at the outer surface. On the other hand, the overall system is in an unstable state after a long time charging; this makes the determination of hydrogen diffusivity difficult in experiments. The theoretical results are in good agreement with experimental data obtained before.

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1. Introduction

In earlier works, we presented models describing self-stresses and related effects produced by hydrogen interstitials in thin shells and circular-plates [1,2]. The up-hill diffusion (UHD) and related phenomena were demonstrated and interpreted by these theories. However, these results are qualitatively consistent with experimental data [3–9]; quantitatively comparisons need consider the surface kinetics and other processes that have been omitted previously. For example, the galvanostatic charging is always treated as the first or second boundary condition in diffusion problems [3–5,7,9]; nevertheless, experimental and theoretical studies have verified that the steady flux is less than the charging current, and the exited flux transient may differ from the result of concentration-step or flux-step assumption [10–12]. In Fig. 5 of Ref. [9], the maximum pressure change corresponds to an exited hydrogen flux of 0.07 mA cm^{-2} , which is only 0.54% of the actual charging current 13 mA cm^{-2} . Therefore, it is naturally concluded that the electrochemical process affects transport properties in self-stress experiments. In this paper, we will discuss the whole steps of hydrogen

diffusion across tubular membranes of Pd or Pd based alloys under electrochemical conditions using numerical methods based on models established earlier [1,2,13–15].

2. Model

Consider a metallic tube with one end sealed and another opened to a gauge for pressure measurement, the tube is immersed in an electrolyte. Similarly to the previous work [1], we use a one-dimensional model to simulate the actual processes; the coordinate z is along the thickness direction. There are three different processes taking place in this system, i.e. the electrochemical reaction at the interface of electrolyte|electrode ($z=0$), hydrogen diffusion in the tube wall ($0 < z < L$, L is the thickness of tube wall) and hydrogen adsorption–desorption at the interface of solid|gas ($z=L$).

Because the tube surface is plated with Pd-black in experiments [3–9], we only need concern the Pd|H₂ and Pd|H₂O interfaces, which has been studied extensively. At the electrolyte|electrode interface, the hydrogen electrode reaction is along the Volmer–Tafel route for Pd [13,14,16], the applied current density j is the same as the rate of the Volmer step with the capacity current omitted. The adsorbed hydrogen is removed by the recombination of H

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atom into H₂ molecule (Tafel step) and the penetration of H atom from the adsorbed state at outer surface into the absorbed state in bulk; these processes are expressed as:

$$j/F = J_T + J_p, \quad (1)$$

where J_T and J_p are rates of the Tafel and penetration steps, respectively. These two reactions are related to surface parameters by below Eqs. (13) and (14)

$$J_T = r^2 J_{0T} \left[\frac{g^2(\theta, u_s)}{g^2(\theta_0, u_s)} - \frac{g^2(1 - \theta, u_s)}{g^2(1 - \theta_0, u_s)} \right], \quad (2)$$

and

$$J_p = r J_{0p} \frac{g(\theta, u_s)}{g(\theta_0, u_s)} \frac{g(1 - n_H, u_b)}{g(1 - n_{H,0}, u_b)} \exp \left[\frac{u_\sigma (\bar{n}_H - n_H)}{2} \right] - r J_{0p} \frac{g(1 - \theta, u_s)}{g(1 - \theta_0, u_s)} \frac{g(n_H, u_b)}{g(n_{H,0}, u_b)} \exp \left[- \frac{u_\sigma (\bar{n}_H - n_H)}{2} \right], \quad (3)$$

with

$$g(x, u) = x \exp \left(\frac{ux}{2} \right), \quad (4)$$

$$u_\sigma = \frac{2V_H^2 EC_0}{3(1 - \nu)RT}, \quad (5)$$

and

$$\bar{n}_H = \frac{1}{L} \int_0^L n_H dz. \quad (6)$$

Where r is the roughness factor of Pd surface; θ and $u_s = U_s/RT$ are the surface coverage and nonhomogeneous factor of Frumkin adsorption, respectively; n_H is the atomic ratio of hydrogen to metal (M) and it takes the subsurface value in Eq. (3); \bar{n}_H is the average value of n_H in the overall thickness; $u_b = U_b/RT$ is the non-ideal interaction factor of H in metallic materials, $u_b = -21.8$ for the α -phase Pd–H at room temperature [17]; u_σ is the self-stress factor and is a dimensionless material constant, $u_\sigma = 16.3$ for the α -phase Pd–H at room temperature; $V_H = 1.7 \text{ cm}^3 \text{ mol}^{-1}$ is the partial molar volume of H in Pd and Pd-based alloys [18,19]; E is Young's modulus, $E = 112 \text{ GPa}$ for Pd; ν is Poisson's ratio, $\nu = 0.38$ for Pd; C_0 is the concentration of H in M corresponding to $n_H = 1$, $C_0 = 0.113 \text{ mol H cm}^{-3}$ for Pd. The subscript 0 indicates the equilibrium value of the corresponding quantity. The other symbols have their usual meanings.

Taking account of the mass balance on the outer surface, we obtain the time dependence of the adsorbed hydrogen coverage:

$$r\Gamma_s \frac{d\theta}{dt} = j/F - J_T - J_p, \quad (7)$$

where $\Gamma_s = 2.2 \times 10^{-9} \text{ mol H cm}^{-2}$ is the saturation coverage of H on Pd(100) surface [20].

At the subsurface, there is:

$$J_p = J_{\text{diff}}(0, t), \quad (8)$$

The hydrogen diffusion flux J_{diff} has the form [15]

$$J_{\text{diff}}(z, t) = -D_0 C_0 [1 + (u_b + u_\sigma)n_H(1 - n_H)] \frac{\partial n_H}{\partial z}, \quad (9)$$

where D_0 is the stress-free diffusion coefficient of H in M while $n_H \rightarrow 0$. Applying the mass balance condition to the flux expression, one gives

$$C_0 \frac{\partial n_H}{\partial t} = - \frac{\partial J_{\text{diff}}(z, t)}{\partial z}. \quad (10)$$

At the solid|gas interface ($z=L$), there is only the Tafel step taking place. Because the reaction is near equilibrium and there is Pd-black plated on this surface, we assume that the chemical potential of adsorbed hydrogen is the same as that of gas inside the tube

$$sp^{1/2} = \frac{n_H}{1 - n_H} \exp(u_b n_H), \quad (11)$$

where s is Sieverts constant, $s = 2.84 \times 10^{-3} \text{ torr}^{-1/2}$ for the α -phase Pd–H at room temperature.

The amount of hydrogen diffused across the tube wall and collected inside the tube can be measured by the pressure change

$$\Delta p = p - p_0 = \frac{RTA}{2V} \int J_{\text{ex}} dt, \quad (12)$$

where the exited flux $J_{\text{ex}} = J_{\text{diff}}(L, t)$, p_0 is the initial hydrogen pressure, A is the area of the tube wall involved in the diffusion process, V is the volume into which the exited hydrogen is collected and the other quantities have their usual meanings.

The initial condition is the equilibrium of hydrogen chemical potential being approached between the liquid, solid and gas phases, the homogenous distribution of hydrogen content in the tube wall, and the zero current of j , J_T and J_p .

The boundary condition at outer surface depends on techniques applied; for the galvanostatic charging as used experimentally [3–5,7,9], it is

$$j = \text{constant}, \quad t \geq 0. \quad (13)$$

In this work, we give numerical results based on Eqs. (1)–(13) and using the frame reported earlier [14].

3. Results and discussion

An example of hydrogen charging process is shown in Fig. 1. The material bulk parameters are for the α -phase Pd–H at room temperature since its properties have been studied extensively, experimental parameters are taken from Ref. [4]. Fig. 1a shows pressure changes in the tube,

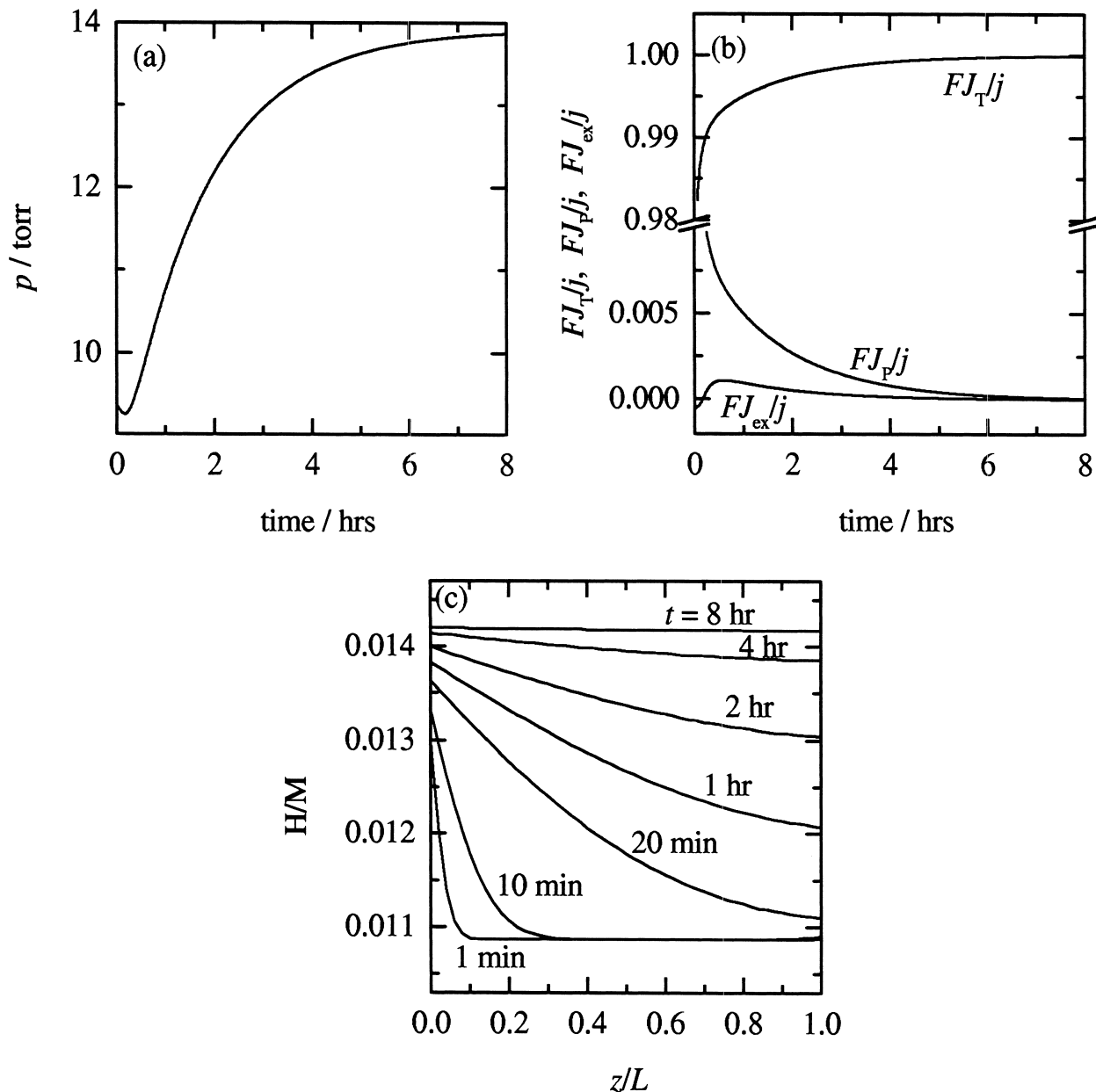


Fig. 1. An example of hydrogen absorption into a Pd tube under a galvanostatic charging. (a) Pressure changes inside the tube, (b) fluxes of the Tafel step, penetration reaction and released hydrogen in the desorption process, and (c) the hydrogen distribution at different times. The parameters are: $j = 13 \text{ mA cm}^{-2}$, $r = 10$, $u_s = 10$, $\theta_0 = 0.1$, $FJ_{0T} = 0.3 \text{ mA cm}^{-2}$, $FJ_{0p} = 10 \text{ mA cm}^{-2}$; $D_0 = 4.9 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$; $n_{\text{H},0} = 0.01087$, $u_\sigma = 16.4$, $u_b = -21.8$, $s = 2.84 \times 10^{-3} \text{ torr}^{-1/2}$; $p_0 = 9.36 \text{ torr}$, $L = 0.02 \text{ cm}$, $V = 23.2 \text{ cm}^3$, $A = \pi \times 0.82 \times 4 \text{ cm}^2$, $T = 298.15 \text{ K}$.

the UHD effect is demonstrated as expected. When the charging time is long enough, the inner pressure approaches an asymptotic value, which depends on j , j_{0T} , u_s and θ_0 as the behavior of n_{H} [13].

Fig. 1b shows the Tafel current, the penetration and exited fluxes, we find J_p and J_{ex} are much less than the charging current because the hydrogen combination step (J_T) takes place at the electrolyte/solid interface. The UHD effect also exhibits for J_{ex} as the behavior of p in the initial period. Another important point is that J_{ex} is much less than J_p in most of time, this means the system is in an

unsteady state, so the steady-state assumption in determinations of hydrogen diffusivity by the time-lag method in experiments is doubtfully. The exited flux diminishes to zero and the system reaches the steady state after a long charging time ($>8 \text{ h}$), which is much greater than the experimental duration ($<23 \text{ min}$) [4].

Fig. 1c shows the hydrogen content in the tube wall at different times, it also verifies that the steady state need a long time to be approached.

There are many factors can influence the transport of hydrogen in this system. The first one is the exchange

current density of the Tafel step J_{0T} , a large J_{0T} induces a large Tafel rate J_T and small value of J_p for the fixed j , so the exited flux J_{ex} decreases correspondingly. Another parameter is the roughness factor r , a rough electrode surface induces J_T to increase more rapidly than J_p as shown by Eqs. (2) and (3), so J_{ex} also decreases. The equilibrium surface coverage θ_0 and the nonhomogeneous factor u_s affect J_T and J_p as well, when θ_0 and/or u_s increase, the positive part of J_T decreases [16] and J_{ex} increases.

Because available experimental evidences on Pd|H electrode indicate the penetration reaction is in pseudo-equilibrium, we take a large value of J_{0T} ; otherwise, the exited flux may be very small and the UHD may be difficult to be observed.

The interface parameters affect not only the exited flux, but also the amplitude and time interval of UHD and the apparent diffusion coefficient of H in M. However, we do not discuss them in detail due to the space limited.

Fig. 2 compares the theoretical results with experimental data in Ref. [4]; they are consistent with each other. Of course, the surface parameters utilized in this work are empirical because there are no related data on this system [4].

In summary, the electrochemical reaction affects the

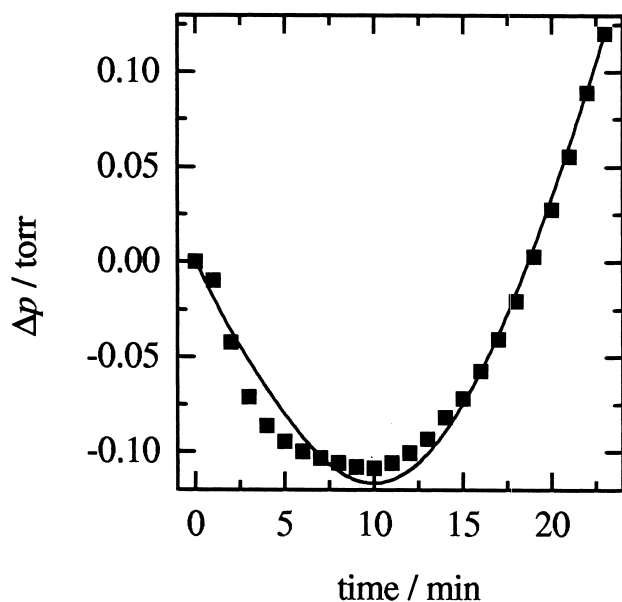


Fig. 2. Comparison of pressure changes in Ref. [4] and the present results. The parameters are the same as those in Fig. 1.

self-stress and other transport properties strongly, the determination of the diffusivity and verifications of UHD must consider these factors in experiments.

Acknowledgements

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References

- [1] W.S. Zhang, Z.L. Zhang, X.W. Zhang, *J. Alloys Comp.* 336 (2002) 170.
- [2] W.S. Zhang, Z.L. Zhang, *J. Alloys Comp.* 346 (2002) 176.
- [3] F.A. Lewis, J.P. Magennis, S.G. McKee, P.J.M. Seebuwufu, *Nature* 306 (1983) 673.
- [4] X.Q. Tong, K. Kandasamy, F.A. Lewis, *Scripta Metall.* 24 (1990) 1923.
- [5] Y. Sakamoto, X.Q. Tong, F.A. Lewis, *Scripta Metal. Mater.* 25 (1991) 1629.
- [6] F.A. Lewis, B. Baranowski, K. Kandasamy, *J. Less-Common Met.* 134 (1987) L27.
- [7] K. Kandasamy, X.Q. Tong, F.A. Lewis, *J. Phys.: Condens. Mater.* 4 (1992) L439.
- [8] D. Dudek, B. Baranowski, *Pol. J. Chem.* 69 (1995) 1196.
- [9] B. Baranowski, *J. Less-Common Met.* 154 (1989) 329.
- [10] V. Breger, E. Gileadi, *Electrochim. Acta* 16 (1971) 177.
- [11] R.N. Iyer, H.W. Pickering, M. Zamanzadeh, *J. Electrochem. Soc.* 136 (1989) 2463.
- [12] B.G. Pound, in: J.O'M. Bockris, B.E. Conway, R.E. White (Eds.), *Modern Aspects of Electrochemistry*, Vol. 25, Plenum, New York, 1993, p. 63.
- [13] W.S. Zhang, X.W. Zhang, H.Q. Li, *J. Electroanal. Chem.* 434 (1997) 31.
- [14] W.S. Zhang, Z.L. Zhang, X.W. Zhang, *J. Electroanal. Chem.* 474 (1999) 130.
- [15] W.S. Zhang, X.W. Zhang, Z.L. Zhang, *Phys. Rev. B* 62 (2000) 8884.
- [16] M. Enyo, in: B.E. Conway, J.O'M. Bockris, E. Yeager, S.U.M. Khan, R.E. White (Eds.), *Kinetics and Mechanism of Electrode Processes*, Vol. 7, Plenum, New York, 1983, p. 241.
- [17] T. Kuji, W.A. Oates, B.S. Bowerman, T.B. Flanagan, *J. Phys. F: Met. Phys.* 13 (1983) 1785.
- [18] B. Baranowski, S. Majchrzak, T.B. Flanagan, *J. Phys. F: Met. Phys.* 1 (1971) 258.
- [19] Y. Fukai, *The Metal-Hydrogen System, Basic Bulk Properties*, Springer, Berlin, 1993, p. 95.
- [20] R. Woods, in: A.J. Bards (Ed.), *Electroanalytical Chemistry: A Series of Advances*, Vol. 9, Marcel Dekker, New York, 1976, p. 1.