

Numerical simulation of hydrogen (deuterium) absorption into β -phase hydride (deuteride) palladium electrodes under galvanostatic conditions

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Abstract

The kinetics of H(D) absorption into a β -phase PdH_x (PdD_x) electrode are discussed numerically, based on the Volmer–Tafel route of the hydrogen (deuterium) evolution reaction and thermodynamic and kinetic data of H(D) in the β -phase PdH_x (PdD_x). It is found that the asymptotic loading ratio of H(D) is determined only by the Tafel step under galvanostatic conditions. The kinetics of H(D) absorption can be characterised by a parameter $\lambda \propto d\Delta j/(\bar{D}\Delta x)$ where d is the dimension of the electrode (thickness for plate, radii for cylinder or sphere); Δj is the current density step; \bar{D} is the average diffusion coefficient; Δx is the loading ratio step of H(D) caused by the current step. If $\lambda \gg 1$ (large scale of dimension, high current density and/or low temperature), the absorption rate is controlled by diffusion; in contrast, if $\lambda \ll 1$, the rate-determining step is the interface process and the charging efficiency approaches 100%; otherwise, the kinetics are under mixed control if $\lambda \sim 1$. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Pd | H electrode; Pd | D electrode; Kinetics

1. Introduction

In earlier papers [1–3], we established a model describing the kinetics of a Pd | H(D) electrode in the cases of the pure α -phase or the $\alpha + \beta$ mixed phases. It is now time to discuss the situation of a pure β -phase. Unlike the above cases, the surface and bulk properties of the β -phase have four characteristics: (1) instead of strong adsorption, weak adsorption becomes the precursor of H absorption; (2) the Tafel step is accompanied by H absorption in the hydrogen evolution reaction (her) and the charging efficiency decreases correspondingly. This is in contrast with the previous cases [2,3] where the Tafel process is limited by H₂ diffusion in electrolyte; (3) the behaviour of H in Pd is affected strongly by H–H interaction and the non-ideal factor must be concerned in the kinetic equations; and

(4) the diffusion coefficient, hence the relaxation time of H absorption, depends strongly on the H concentration.

In the past few years, extensive work has focused on the kinetics, especially the charging–discharging of metal (Pd) hydride (deuteride) electrodes [4–18]. Among the theories of the metal (Pd) hydride electrode, Conway and Wojtowicz [10] proposed a model in which the kinetic process is limited by diffusion for H absorption into, and desorption from, electrodes with various geometries. Furthermore, Yang et al. [11] considered the Volmer step on an electrode surface for the galvanostatic discharge of the hydride electrode. Shortly afterwards, Lasia and Grégoire [12] considered the Volmer–Heyrovsky route in the her on a hydride electrode for the potentiostatic and galvanostatic steps for H absorption and desorption. At the same time, H absorption in the more general Volmer–Tafel–Heyrovsky route studied using the EIS method was discussed by Durand et al. [13] and Yang and Pyun [14,15].

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As concerns the Pd|D electrode, Szpak et al. [16,17] established a model describing the Volmer–Tafel–Heyrovsky route in the her, and the coupling of the interfacial processes with the transport of interstitial D in the Pd electrode interior. On the other hand, De Ninno and Violante [18] numerically simulated the D charging of a Pd electrode with one side participating in electrolysis while the other was exposed to an environment containing D₂ gas, and the concentration step condition was assumed to be on the electrolysis side in their work.

In this paper, we will discuss the kinetics of H(D) absorption into a β -phase PdH_x(PdD_x) electrode based on our earlier results [1–3]. Unlike the above-mentioned theories, our kinetic model is based on a more realistic physical picture and the thermodynamic properties of the Pd|H system are special cases of the kinetic properties. For simplicity, we consider only the Volmer–Tafel route in the her, which is appropriate at low cathodic overpotentials [1,19]. Although the effects of the Volmer–Tafel route on the kinetics of a permeable electrode have been discussed by Iyer et al. [20], we pay attention to the processes of absorption and desorption.

Although our treatment is confined to the Pd|H system, these results can be applied to the Pd alloy|H(D, T) or other metal|H systems with some bulk or surface parameters of the electrode adapted.

2. Model

Zhang et al. [1] and Zhang and Zhang [2] established a model describing several types of H reaction (the Volmer, Tafel, Heyrovsky and penetration step) on a Pd surface and H diffusion in the α -phase. But for H movement in the β -phase in the her, the situation is somewhat complex because the Fick diffusion coefficient changes with x due to the thermodynamic factor and the blocking factor. Fick's second law can be written as:

$$\frac{\partial x}{\partial t} = F\Gamma_b \nabla \cdot (D \nabla x) \quad (1)$$

where $\Gamma_b = 0.1 \text{ mol cm}^{-3}$, the maximum molar number of available sites for H per unit volume of PdH_x (the expansion effect due to H insertion is concerned [21]). From the results of Majorowski and Baranowski [22,23], we obtain the expression of the Fick diffusion coefficient under the electrolysis conditions (no high pressure applied to PdH_x):

$$D = D_0 e^{-\Delta E/RT} (1 + u_b x (1 - x)) \quad (2)$$

where D_0 , the pre-exponential factor, is 0.0113 and 0.0105 cm² s⁻¹ for H and D, respectively; ΔE , the activation energy, is 27.1 and 25.9 kJ mol⁻¹ for H and D, respectively; u_b is the non-ideal factor for H in the

β -phase PdH_x [1,24]. Under the ambient conditions (298.15 K, 1 atm) we have:

$$D = D_*(1 + 18.144x(1 - x)) \quad (3)$$

with $D_* = 2.01 \times 10^{-7}$ and $3.03 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for H and D, respectively.

Because the Heyrovsky step is prominent at high cathodic overpotential, we will neglect it in the discussion below. As in the earlier works [1,2], we first discuss the plate shape of the Pd electrode with a hydrogen-impermeable inner surface. The plate thickness is $2d$ if both sides are exposed to the electrolyte or d if one side is exposed to the electrolyte.

The outer surface boundary condition ($y = 0$) is the equality of the penetration reaction and diffusion step; the inner one ($y = d$) is the zero flux of the diffusion current [2].

Eqs. (3)–(6) in Zhang et al. [1] and Eqs. (1)–(3) here with the boundary conditions of Eqs. (4) and (5) in Zhang and Zhang [2] form the basis of our discussion. The partial differential equations can be solved numerically using, e.g. the method described by Crank and Nicolson [25].

3. Results

Consider a constant cathodic current applied to a PdH_x electrode that has absorbed H to the equilibrium concentration $x_0 = 0.71$ (0.67 for D) under ambient conditions; the hydrogen produced on the Pd surface in the her is removed by bulk absorption and chemical recombination (the Tafel step). However, after a long enough time, the system will approach a steady state in which the electrode does not absorb H any more and x reaches a steady value, x_∞ . The x_∞ value is determined by the applied current and the H adsorption characteristics, but does not depend on the kinetics in the bulk of the Pd or the shape of the electrode. Fig. 1 shows x_∞ at different relative current densities (cd) $-j/j_{0T}$ ($j < 0$ corresponds to cathodic current, j_{0T} is the exchange current density of the Tafel step), and equilibrium values of fractional coverage θ_0 of H(D) on Pd; it is found that high $-j/j_{0T}$ and θ_0 benefit a high loading ratio. With the weak adsorption playing a key role in the her [1,26], the value of θ_0 adopted in Fig. 1 is less than 0.1.

The electrolyte pH also affects x_∞ , because θ_0 decreases with increase of pH and j_{0T} is proportional to the square of θ_0 from Eq. (3) in Zhang et al. [1], hence j_{0T} decreases ($-j/j_{0T}$ increases) more rapidly than θ_0 with the increase of pH. This means that high electrolyte pH results in high x_∞ at the same cd, as was observed in experiments [4,6].

When a constant cathodic current is applied to a plate electrode, there will be four types of process

taking place in different time scales. They are charging of the double-layer capacitance, charging of the adsorption layer, charging of the bulk electrode with the surface process (or the bulk diffusion) being the rate-determining step (rds). The shortest one is the charging of the double-layer capacitance, the timescale being $-rC/j$ where r is the roughness factor and C , the real area capacitance, is $16 \mu\text{F cm}^{-2}$. Choosing $-j=1$ to 10^3 mA cm^{-2} and $r=10$, we obtain a timescale in the range 10^{-4} to 10^{-1} s. The second shortest time process is the charging of the adsorption layer through the Volmer step [26]; the corresponding time scale is –

$rF\Gamma_s/j$ where Γ_s , the maximum for H molar number of available sites per real unit area, is $2.197 \times 10^{-9} \text{ mol cm}^{-2}$. We obtain the timescale in the range of 10^{-3} to 1 s with the same roughness factor and cd range as above.

The other two processes are attributed to the bulk absorption of H. To describe the absorption quantitatively, we introduce the absorption ratio:

$$M(t) = \frac{\bar{x}(t) - x_0}{x_\infty - x_0} \quad (4)$$

where $\bar{x}(t)$ is the average value of x in Pd at time t and can be measured in situ by monitoring the resistance change of the electrode [5,7,9,27] or the volume change of the oxygen and hydrogen gas produced during electrolysis [4]. To characterize the kinetics of absorption, we define the half absorption time τ as that at which $M=1/2$. First, we suppose the interface process is the rds and the Tafel step is negligible when $t < \tau$; the corresponding half absorption time is:

$$\tau_s = -\frac{F\Gamma_b d(x_\infty - x_0)}{2j} \quad (5)$$

Choosing the same cd range as above, $d=10^{-3}$ to 10^{-1} cm and $x_\infty=1$, we obtain $\tau_s=10$ to 10^6 s. Another process is H diffusion in Pd. Using the classical result of diffusion in a plate with concentration step condition at the outer surface, we obtain the corresponding half absorption time:

$$\tau_b = 0.1968 d^2/\bar{D} \quad (6)$$

from Eq. (4.23) in Crank [28]. Although this relation is derived with the assumptions, (1) constant H concentration on the outer surface, (2) no H_2 recombination and (3) constant diffusion coefficient, we can use it to estimate τ in some error range. For the above thickness range, $\tau=1$ to 10^4 s.

On the basis of the above discussion, we find the first two surface processes go much more rapidly than the bulk ones, so we will neglect the former in the numerical computation below. That is to say, the surface coverage approaches a new quasi-steady state simultaneously as the cathodic current is applied, and currents associated with the penetration and Tafel reactions appear instantly. Because τ_s and τ_b are in the same range, we expect the practical situation to depend on the specific electrode and experimental parameters.

Fig. 2 shows an example of charging of a Pd plate galvanostatically; a constant cd, j , is applied to an electrode that has absorbed H to the equilibrium concentration. Within a short time after beginning ($t < 80$ s in Fig. 2), $j_P/j \approx 1$ and $j_T/j \approx 0$. Most of the adsorbed H produced by the Volmer step moves to the Pd interior and the charging efficiency approaches 100%. Accompanied by the occupation of the bulk H sites, the diffusion current decreases with time. Consequently,

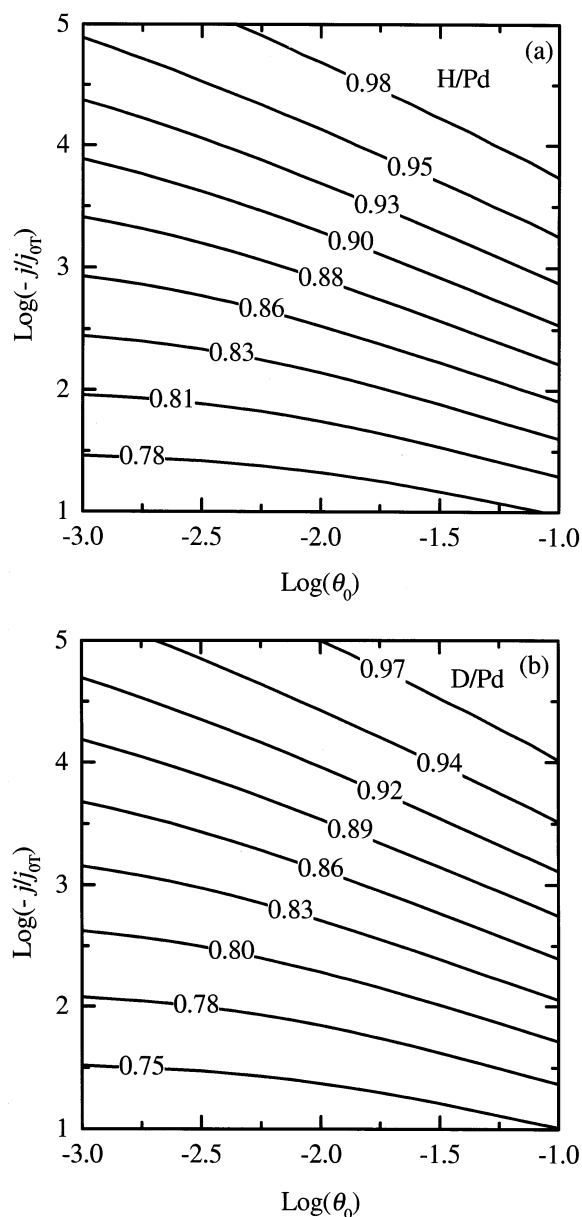


Fig. 1. Contour map of the steady-state H(D) concentration x_∞ for (a) Pd|H electrode and (b) Pd|D electrode at different relative current densities j/j_{0T} and equilibrium fractional coverage θ_0 . j_{0T} is the exchange current density of the Tafel step, the heterogeneity factor of the Frumkin adsorption is $u=10$.

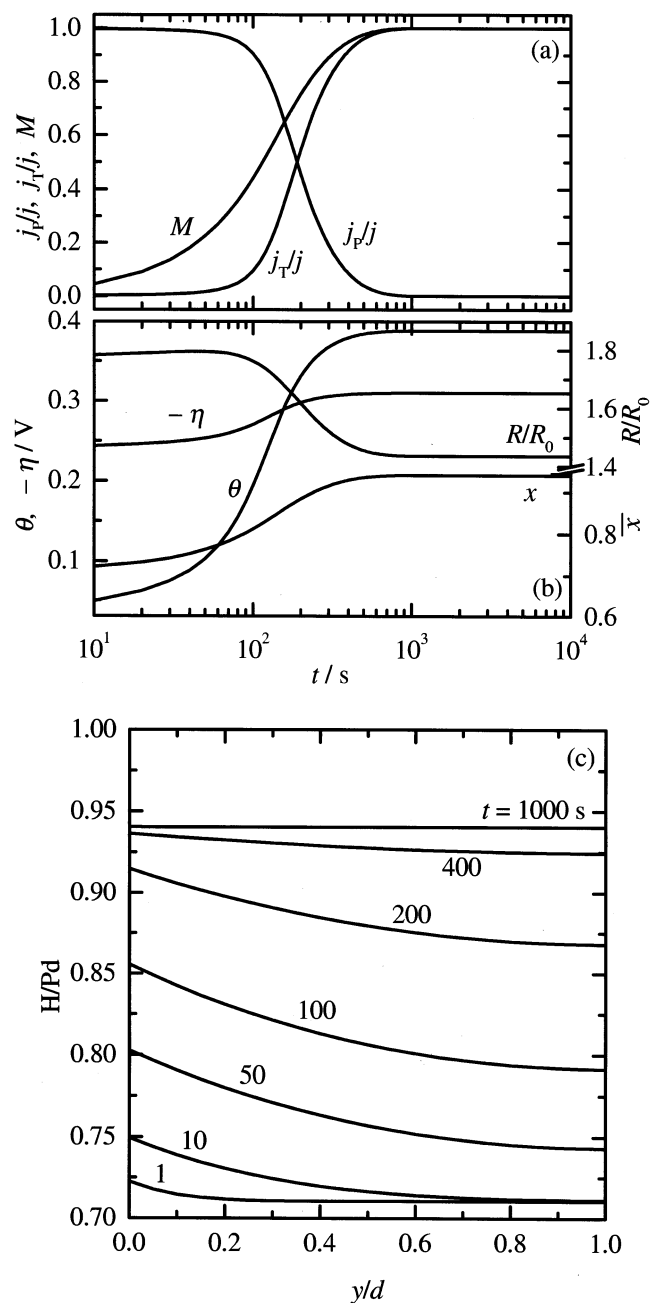


Fig. 2. An example of H absorption into a β -phase plate Pd|H electrode under galvanostatic conditions. (a) The relative absorption current j_P/j , Tafel current j_T/j and absorption ratio M as functions of time t ; (b) the fractional coverage θ , overpotential η , average H concentration \bar{x} and relative resistance R/R_0 vs. time; (c) H distribution at different times t , where y/d is the relative depth from the outer surface. The parameters: $\theta_0 = 0.01$, $u = 5$, $j_{OT} = 0.01 \text{ mA cm}^{-2}$, $j_{OV} = 1 \text{ mA cm}^{-2}$, $j_{OP} = 50 \text{ mA cm}^{-2}$, $j = -100 \text{ mA cm}^{-2}$ and $d = 0.01 \text{ cm}$, $r = 1$, where j_{OV} and j_{OP} are the exchange cd of the Volmer step and the penetration step, respectively.

more and more adsorbed H is removed by the Tafel step and the charging efficiency decreases correspondingly (80 to 500 s in Fig. 2). Finally, the loading ratio reaches the saturation value, $x = x_\infty$, and all the hydrogen produced leaves the Pd surface by the Tafel step

($j_T/j = 1$ and $j_P/j = 0$). M is shown in Fig. 2(a) as well. It is found that $\tau = 114 \text{ s}$.

In Fig. 2(b), we show the cathodic overpotential $-\eta$, which increases to a quasi-steady value (0.24 V) in a very short time corresponding to the charging of the adsorption layer [26]; then it increases and approaches a steady-state value like the behaviour of M and θ versus t . It must be pointed out that the exchange current density of the Volmer reaction j_{OV} does not affect the absorption kinetics except for the parameter η .

Resistance measurement has been used widely to estimate the H concentration in Pd [5,7,9,27]; the relative resistance R/R_0 (R_0 is the resistance R at $x = 0$) is illustrated in Fig. 2(b) based on the experimental data [29,30]. Because R/R_0 increases with x and passes a maximum value 1.8 at $x = 0.74$, then it decreases monotonically with x , so R/R_0 versus t exhibits a similar behaviour: R/R_0 reaches the maximum at time t ca. 50 s and then it decreases with t . R/R_0 shown in Fig. 2(b) is obtained by dissecting the electrode into small slabs and considering the parallel connection of each partial resistance. By comparison with $R(\bar{x})/R_0$, we found that there are only small differences ($< 1\%$) between them, except for the region around the maximum R/R_0 where the resistance changes slightly with x . In other words, the non-equilibrium distribution of H in Pd (Fig. 2(c)) does not affect the estimation of average H concentration.

To verify the effects of different parameters on the kinetics of H absorption, we calculate τ for various situations as shown in Fig. 3. Fig. 3(a) shows τ as a function of charging current while other parameters are fixed; it decreases with cd and approaches 410 s when the cd is large enough. At the same time, we illustrate the relative quantities τ/τ_s and τ/τ_b versus cd. It is found that τ/τ_s versus cd exhibits a constant value 1 at low cd, this means that the surface process determines the H absorption at low charging current. Otherwise, τ/τ_b approaches a constant value about 1.7 at high cd; this indicates the diffusion process becomes the rds of H absorption. Because the subsurface H concentration changes with time before the system approaches the steady state, τ is somewhat larger than that of the concentration step condition in our situation [28]. In the intermediate cd region, both the processes control the H absorption.

On the basis of the above discussion, we define a parameter:

$$\lambda = \frac{\tau_b}{\tau_s} = \frac{-Adj}{FT_b \bar{D}(x_\infty - x_0)} \quad (7)$$

where A is a constant and $= 0.3936$ for a plate electrode. When $\lambda \gg 1$, i.e. $\tau_b \gg \tau_s$, H diffusion is the rds; in contrast, when $\lambda \ll 1$, the surface process controls the H absorption; otherwise, the H absorption is under mixed control if $\lambda \sim 1$. λ versus j is shown in Fig. 3 as well.

Eq. (7) indicates that the plate thickness d also affects the kinetics as shown in Fig. 3(b). We find that the H absorption tends to be controlled by diffusion with the increase of d .

The parameters θ_0 and j_{0T} that determine x_∞ do not affect λ markedly, as shown by Eq. (7).

In experiments [4–9], cylindrical and spherical electrodes are generally used. Referring to Eqs. (5.23) and (6.20) in Crank [28], we obtain a relation which is the same as Eq. (7) with the thickness d replaced by the radius r , and $A = 0.2514$ and 0.1833 for cylindrical and spherical electrodes, respectively.

At room temperature, Eq. (7) is simplified to $\lambda = -$

$A'dj$ with $A' = 0.1-1 \text{ cm mA}^{-1}$. This relation can be used as a brief criterion to judge the kinetics of a Pd | H electrode.

If a higher charging current is applied to an electrode which has already approached steady state with a lower current, as is done in many experiments [5,7], Eq. (7) is also suitable with j replaced by Δj , the cd step, and $x_\infty - x_0$ replaced by Δx , the H concentration step caused by the current step, i.e.:

$$\lambda = \frac{-Ad\Delta j}{F\Gamma_b D \Delta x} \quad (8)$$

In this case, λ depends on the initial cd besides the parameters described above. If the other parameters are the same, a larger initial cd will result in small values of the H concentration step and the diffusion coefficient, hence the H absorption process tends to be controlled by H diffusion.

4. Discussion

Practical experiments are carried out at different temperatures. Because D increases with T as shown by Eq. (2), so a higher T results in lower τ_b and λ , the H absorption tends to be determined by the interface process and the charging efficiency increases correspondingly as was observed by Riley et al. [4]. As far as electrolyte pH is concerned, this affects the values of θ_0 , j_{0T} and x_∞ ; a high electrolyte pH makes the absorption time increase as indicated in Eq. (5), but the effects on the kinetics are not significant as is shown by Eq. (7).

Although we discuss only the situation of the β -phase PdH_x , our method, combined with our earlier results [1–3], can be extended to the case of charging of a blank Pd electrode. In this case, the α -phase in Pd is formed first, and then the $\alpha \rightarrow \beta$ phase transition takes place until the electrode is occupied by the β -phase. Because the chemical potential of H in PdH_x with $x < x_0$ (taken to include α -, $\alpha + \beta$, and part of the β -phase) is lower than that of H on the outer surface, the H penetration current is much greater than that of the Tafel step and the initial charging time with a high charging efficiency is much longer than that described here, as was observed in most of the experiments [4–9].

We have been concerned only with the Volmer–Tafel route in the her, otherwise, x_∞ will decrease [1,19] if the Heyrovsky step (electrochemical recombination) is involved. It is because this reaction consumes current that the charging efficiency will decrease as its exchange current density increases. In practice, the specific mechanism of the her is affected by the pre-electrolysis treatment of the electrode and additives in the electrolyte.

Due to the inverse isotope effect, the diffusion coefficient of D is greater than that of H, hence $\lambda_D < \lambda_H$,

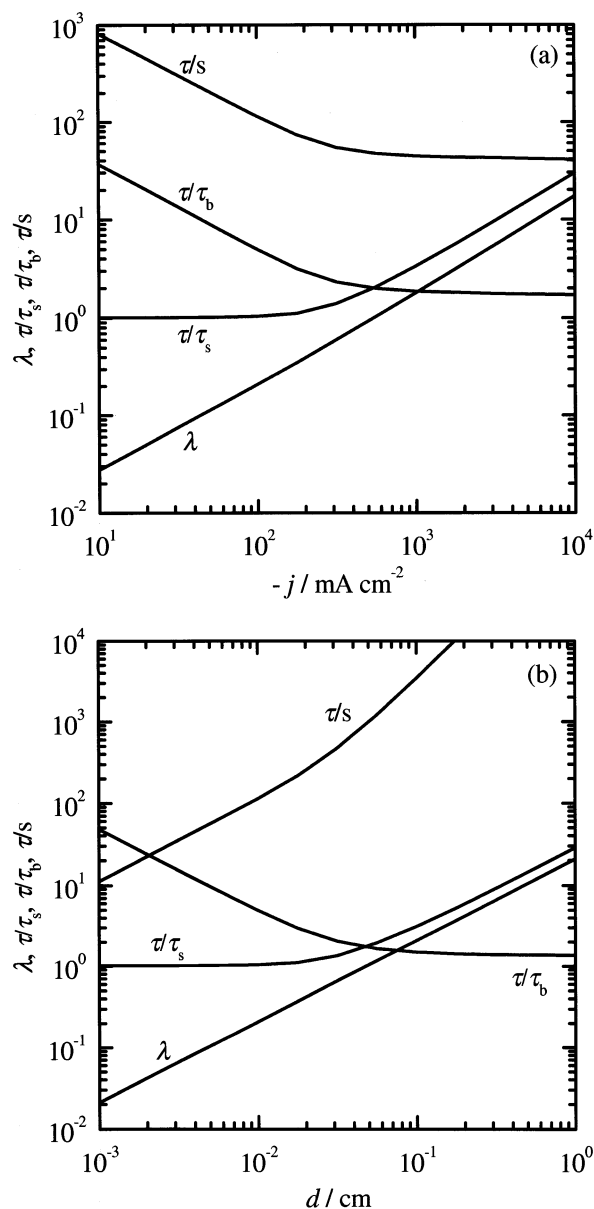


Fig. 3. Effects of different parameters on the half absorption time τ , the relative half absorption time τ/τ_s and τ/τ_b and the kinetic parameter λ . (a) effects of j , (b) effects of d . Other parameters not emphasised are the same as those in Fig. 2.

which means that D absorption tends to be controlled by the surface process.

For potentiostatic charging, because the cathodic component of the Volmer step is inversely proportional to θ , which increases with time, the current will increase to its maximum value in a short time for charging of the adsorption layer, then it decreases as the diffusion current decreases (x increases) with time and approaches its steady-state value [16].

On the other hand, our method can be used to describe the galvanostatic H desorption from PdH_x , but the process is not the simple inverse of absorption. It can be divided into four situations: (1) if j is so small that $\theta > \theta_0$ but the chemical potential of H on the surface is still less than that in the bulk, the H in bulk Pd is desorbed by the Volmer and Tafel step together until $\theta < \theta_0$; (2) if j is so large or the desorption time is so long that $\theta_{\alpha\beta,\text{de}} < \theta < \theta_0$, where $\theta_{\alpha\beta,\text{de}}$ is θ at the $\beta \rightarrow \alpha$ phase transition, because the Tafel step (H_2 dissociation) is limited by H_2 diffusion in the electrolyte, H is removed only by the Volmer step until $\theta \leq \theta_{\alpha\beta,\text{de}}$ and the process below takes place; (3) if j is in a range such that $\theta \leq \theta_{\alpha\beta,\text{de}}$, the H desorption process must be described by the $\beta \rightarrow \alpha$ phase transition as in Zhang et al. [3] until the end of the phase transition; and (4) H is desorbed from the single α -phase PdH_x and the process can be described using the method established in Zhang and Zhang [2]. Unlike the H absorption process, because the Tafel step is limited by H_2 diffusion in the electrolyte, the discharge current is limited to the limiting value of j_P , i.e. $j < j_{\text{OP}}x(0) \exp(u\theta_0/2 + u_0(x(0) - x_0)/2) / ((1 - \theta_0)x_0)$, where j_{OP} is the exchange current density of the the penetration reaction; $x(0)$ is x at the subsurface.

5. Conclusions

On the basis of the relations of surface reactions developed by Zhang et al. [1], the bulk diffusion equation described here and the boundary conditions in Zhang and Zhang [2], we have discussed the kinetics of H absorption into a β -phase PdH_x electrode in the her. The rds is determined by the dimension (thickness for plate, radii for cylinder or sphere) of the electrode and the charging current. For a small dimension and/or low current, it is the surface process that controls the H absorption; otherwise, H diffusion is the rds.

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