

Voltammograms of thin layer Pd | H(D) electrodes in the coexistence of α and β phases

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Abstract

The kinetics of a thin layer Pd | H(D) electrode at the coexistence of α and β phases in cyclic voltammetry are studied and the effects of various parameters are discussed. It is found that the voltammogram of the $\alpha \leftrightarrow \beta$ phase transition is trigonal in shape which differs significantly from those for diffusion and adsorption. The kinetic characteristics of the $\alpha + \beta$ mixed region are controlled by the deviation of parameters from the thermodynamic values. These results indicate that cyclic voltammetry can be used for studying the kinetics of phase transition occurring in a layer electrode. The present treatment is verified by comparison with the previous experimental results. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Phase transition; Cyclic voltammetry; Pd | H electrode; Pd | H system; Kinetics

1. Introduction

In earlier papers [1,2], we presented a model describing the amount of H(D) absorbed into a Pd cathode under steady state conditions in the hydrogen evolution reaction, and the dynamic behaviour of a thick plate Pd | H electrode within the pure α phase in cyclic voltammetry (CV). But for a practical Pd | H₂O electrochemical system, the dynamic behaviour of a hydrogen rich Pd | H electrode, especially the behaviour of the $\alpha \leftrightarrow \beta$ phase transition (pt) is a technologically important issue. For example, when a Pd sample absorbs hydrogen under ambient conditions (25°C and 1 atm), there is ca. 85% of absorbed H to be associated with the pt.

In the past few years, a considerable amount of experimental observations have accumulated concerning the kinetics of the pt in a Pd | H electrode [3–10]. At the same time, some theories were proposed: one is

favoured by Sakamoto et al. who described the $\alpha + \beta$ mixed phases as a single phase which has a diffusion coefficient different from those of either the α or β phase [9]; Yang et al. considered interstitial sites in the β phase as reversible trap sites, the $\alpha \leftrightarrow \beta$ pt as a trapping/de-trapping reaction [10]. Although these theories are effective in explaining some experimental phenomena, the physical picture is alienated from reality.

On the other hand, more than thirty years ago, H permeation through PdH_x membranes and Pd | H diffusion electrodes associated with $\beta \rightarrow \alpha$ pt have been carried out experimentally and explained theoretically [11–14]. The main point of the theory is that there exists a concentration discontinuity between the α and β phase regions and the pt is accompanied by the phase boundary moving. Based on these results and the latest experimental observations described below, we will study the kinetics of the pt in a thin Pd | H(D) electrode at the coexistence of α and β phases. As before, we will use the technique of CV. 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

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systems with some bulk or surface parameters of the electrode adapted.

2. Model

It has been verified that the $\alpha \leftrightarrow \beta$ pt is a first order transition, the equilibrium potential of a Pd | H electrode in the pt is constant which corresponds to the plateau pressure in the Pd | H₂ system as shown in Fig. 1 [14]. Another remarkable feature is that the pt is accompanied by hysteresis [15–17], i.e. the potential during $\alpha \rightarrow \beta$ pt, E_{ab} is lower than that of $\beta \rightarrow \alpha$ pt, E_{de} . It is the transition strain (during both the β phase formation and decomposition) that is responsible for hysteresis because it cannot be relaxed during hydride formation and decomposition in the solid-state transition. Based on the previous results of the Pd | H₂ system and the Pd | H electrode [14,15], we obtain $E_{ab} = 48$ mV and $E_{de} = 60$ mV versus RHE under ambient conditions, where the subscripts ab and de represent the absorption ($\alpha \rightarrow \beta$ pt) and desorption ($\beta \rightarrow \alpha$ pt) processes respectively. Accordingly, the maximum x ($=$ H/Pd) in the α phase is $x_{\alpha,ab} = 0.0128$ and $x_{\alpha,de} = 0.008$; the minimum x in the β phase is $x_{\beta,ab} = 0.628$ and $x_{\beta,de} = 0.607$. Similarly, we obtain the parameters for a Pd | D electrode [18–20]: $E_{ab} = 30$ mV and $E_{de} = 39$ mV; $x_{\alpha,ab} = 0.0125$ and $x_{\alpha,de} = 0.0087$; $x_{\beta,ab} = 0.618$ and $x_{\beta,de} = 0.603$.

The data mentioned above and used in Fig. 1 are deduced from the isotherm for the Pd | H₂(D₂) system through the Nernst equation with the assumption of the Volmer step under a pseudoequilibrium, Maoka and Enyo [21] have predicted that the practical potential is higher than here especially when the rate of the Volmer step decreases by adding surfactant (e.g. TBA) or raising the pH value of the solution [6–8].

As far as the microscopic mechanism of the pt is concerned, the $\alpha \rightarrow \beta$ pt occurring in the absorption process can be described as follows [22]: as the H concentration in PdH_x exceeds the saturation concentration of the α phase ($x_{\alpha,ab}$), the β phase is formed. The first β PdH_x nuclei appear usually at the locations of the highest H concentration and lowest activation energy for nucleation; evidently, the surface is such a favourable location. The next step of the pt is growing nuclei. The hydride (β phase) nuclei growing on the surface overlap eventually to form a continuous β phase layer, the hydride reaction kinetics are changed into a moving envelope and the bulk front velocity becomes the kinetic parameter. If the reaction rate of the pt is homogeneous, the growing direction of the β phase front in a bulk sample should be perpendicular to the outer surface.

Recently, Artemenko et al. have verified that the $\beta \rightarrow \alpha$ pt in PdH_x involves the nucleation and growth

processes of the α phase in a similar way to the above description [23]. At the same time, Asami et al. have observed the phase boundary between the α and β phases in a Pd | D electrode by scanning electron microscopy [24].

On the basis of the previous results [1,2,11–14] and the processes mentioned above, we discuss the kinetics of the $\alpha \leftrightarrow \beta$ pt in a Pd | H electrode. Consider a plate Pd | H electrode absorbing H and provided that the nucleation and growth processes are fast enough, when the H concentration x in the subsurface exceeds $x_{\alpha,ab}$, the β phase precipitates firstly beneath the surface. Then the β phase layer expands to the depth of the electrode. Suppose the reaction rate of the pt at the $\alpha | \beta$ interface is fast enough, the movement of the β phase front in the bulk Pd can be expressed as the Stefan equation [11,25] (Fig. 2).

$$D_{\beta} \left. \frac{\partial x}{\partial y} \right|_{y=l_{\beta}(t)-0} - D_{\alpha} \left. \frac{\partial x}{\partial y} \right|_{y=l_{\beta}(t)+0} = (x_{\beta,ab} - x_{\alpha,ab}) \frac{dl_{\beta}(t)}{dt} \quad (1)$$

with the boundary conditions at the $\alpha | \beta$ interface

$$\begin{aligned} x &= x_{\beta,ab}, & y &= l_{\beta}(t) - 0, & t &> 0 \\ x &= x_{\alpha,ab}, & y &= l_{\beta}(t) + 0, & t &> 0 \end{aligned} \quad (2)$$

and the initial conditions

$$l_{\beta}(t) = 0, \quad t = 0 \quad (3)$$

where y is the distance from the outer Pd surface; $l_{\beta}(t)$ the thickness of the β phase layer; t the time; $D_{\alpha(\beta)}$ the diffusion coefficient of H in the α (β) PdH_x. Eq. (1) implies that the pt obeys the mass conservation law.

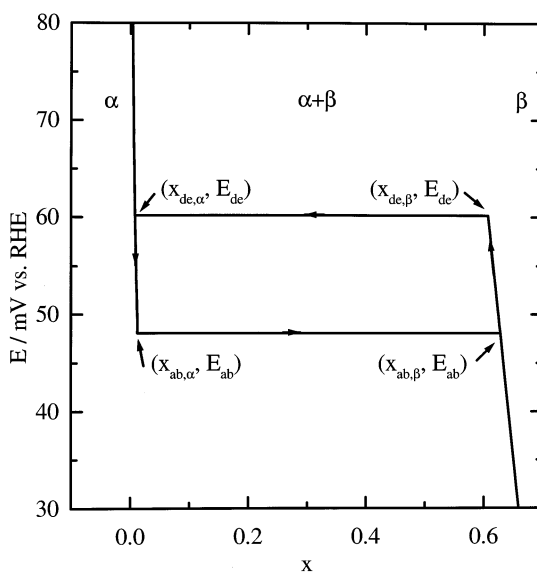


Fig. 1. Electrode potential (E)-H concentration ($x =$ H/Pd) isotherms for absorption and desorption under ambient conditions for Pd | H electrode. Subscripts ab and de represent absorption and desorption processes respectively.

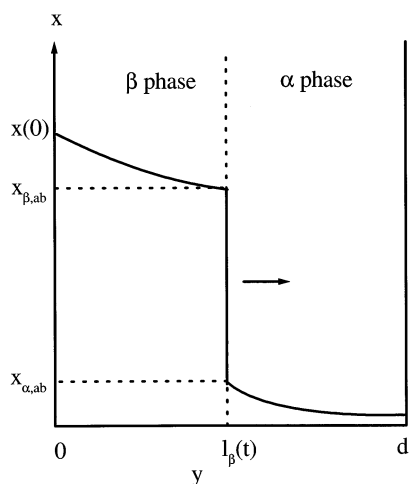


Fig. 2. Schematic plot of the moving boundary problem [11,13,25], an example of a Pd plate absorbs H accompanied with the $\alpha \rightarrow \beta$ phase transition, y is the depth from the outer surface, $l_\beta(t)$ the thickness of β phase layer, d the thickness of plate, $x(0)$ the H concentration in the subsurface.

Eq. (2) indicates there is a concentration discontinuity at the $\alpha | \beta$ interface, but the chemical potential of the two phases is a continuous variable at the same place. In the α phase region ($y \geq l_\beta(t)$), the diffusion process is the same as that discussed in the previous paper [2]; in the β phase region ($y \leq l_\beta(t)$), the diffusion coefficient decreases as x increases due to the blocking effect [26,27]. The outer surface boundary condition ($y = 0$) is the equality of the Volmer step, penetration reaction and diffusion step; the inner ($y = d$, the layer thickness with the inner side in contact with a H-impermeable substrate or a half of the thickness of layer with both sides exposed to the electrolyte) is the zero flux of diffusion current [2].

When H is desorbed from the Pd | H electrode, the above process is reversed and the kinetic equations are the same as Eqs. (1)–(3) with index α and β interchanged, and the subscript ab replaced with de.

Combining Eqs. 1–6 in Zhang et al. [1], Eqs. 1–5 in Zhang and Zhang [2] and Eqs. (1)–(3) in the present paper, we establish a model of Pd | H electrode kinetics that can describe the hydrogen evolution reaction, H absorption into Pd, H diffusion in the α phase and $\alpha \leftrightarrow \beta$ pt in a unified frame.

For simplicity, we discuss only the case of a thin layer electrode ($d^2 \ll \pi D_\alpha \tau$, τ is the period of the CV) in which the diffusion process is at pseudo-equilibrium and the voltammogram exhibits the pt characteristics prominently; Otherwise, there will be more factors involved in CV when the thickness of the Pd plate is in the range of or greater than the diffusion distance in one CV period, i.e. $d^2 \geq \pi D_\alpha \tau$.

The transport of H in Pd in the coexistence of two phases may be influenced by the lattice strain gradients

which can induce so-called ‘uphill’ hydrogen diffusion [28]; it has been shown for Pd both the magnitude and duration of the up-hill process have a tendency to increase proportionally with the sample thickness [29,30], so we will neglect this effect as the considered sample is rather thin.

3. Results

For a thin layer electrode, the diffusion process is fast and there is no measurable concentration gradient in the single phase, i.e. the chemical potential of H on the surface, in the α and β phases are equal to each other. From Eq. 1 in Zhang et al. [1] and Eq. 7 in Zhang and Zhang [2], we obtain the current density (cd) for $\alpha \rightarrow \beta$ pt

$$j = 2j_{ab} \sinh(f(E - E_{ab})/2) \quad (4)$$

with

$$j_{ab} = rj_{ov} \sqrt{g(\theta_{ab})} \quad (5)$$

$$g(\theta) = \frac{\theta(1 - \theta)}{\theta_0(1 - \theta_0)} \quad (6)$$

where $f = F/RT$; θ_{ab} is θ (the fractional coverage of H on Pd) at E_{ab} and $\theta_{ab} = 0.745$ in Fig. 3; r the roughness factor; j_{ov} the exchange current density of the Volmer reaction [1]; j_{ab} the exchange current density of $\alpha \rightarrow \beta$ pt through which surface parameters affect the overall rate of pt and $j_{ab} = 4.03 \text{ mA cm}^{-2}$ in Fig. 3. Because $g(\theta_{ab})$ depends essentially on E_{ab} but not θ_0 , so j_{ab} is determined mainly by j_{ov} ; this means the reversible adsorption of H on Pd and a rough surface of the electrode will be beneficial for the high overall rate of pt. Eq. (4) is exactly the Butler – Volmer equation and the cd is governed solely by the potential. When E is close to E_{ab} , the cd is a linear function of the potential and we obtain the area conductance of $\alpha \rightarrow \beta$ pt

$$G_{ab} = \left. \frac{\partial j}{\partial E} \right|_{E=E_{ab}} = fj_{ab} \quad (7)$$

which is equal to 0.157 S cm^{-2} in Fig. 3, G_{ab} is an easily measurable quantity from which j_{ab} can be obtained. Combining Eqs. (1)–(6), we obtain the thickness of the β phase layer

$$l_\beta(E) = 2l_{ab}(\cosh(f(E - E_{ab})/2) - 1) \quad (8)$$

with

$$l_{ab} = \frac{2j_{ab}}{\Gamma_b F(x_{\beta,ab} - x_{\alpha,ab})fv} \quad (9)$$

which is equal to $0.0309 \text{ }\mu\text{m}$, where $\Gamma_b = 0.113 \text{ mol cm}^{-3}$, the maximum molar number of available sites for H per unit volume of Pd; $v = |dE/dt|$, the potential sweep rate.

If d is so small that the β phase can occupy all parts of the electrode in one single direction scan, there will be two trigonal peaks in the voltammogram and the cathodic peak corresponds to the polarization relation given in Eq. (4) as shown in Fig. 3, the line B–C. It is easy to find the width of the peak potential

$$\Delta E_{mc} = \frac{2}{f} \cosh^{-1} \left(\frac{d}{2l_{ab}} + 1 \right) = \frac{2}{f} \times \begin{cases} (d/l_{ab})^{1/2}, & d < l_{ab} \\ \ln(d/l_{ab}), & d \gg l_{ab} \end{cases} \quad (10)$$

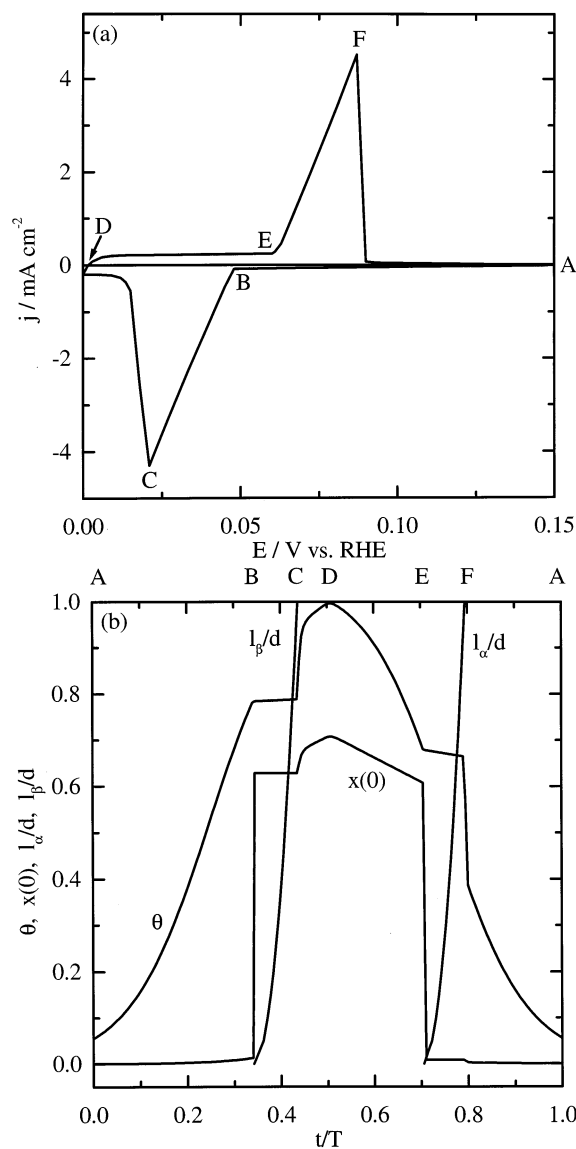


Fig. 3. An example of CV results of a thin layer Pd|H electrode. (a) the voltammogram; (b) the surface coverage of H, θ ; the subsurface H concentration, $x(0)$; the thickness of the β phase layer in the $\alpha \rightarrow \beta$ pt, l_β ; and the thickness of the α phase layer in the $\beta \rightarrow \alpha$ pt, l_α as functions of reduced time t/τ (τ is the period of CV). Parameters: $j_{0V} = 1 \text{ mA cm}^{-2}$, $\theta_0 = 0.95$, $u = 0$, $r = 2$; $d = 0.01 \text{ }\mu\text{m}$ and $v = 0.01 \text{ V s}^{-1}$ where u is the heterogeneity factor of the Frumkin adsorption isotherm. $t/\tau = 0 - 0.5$ is for the negative scan and $t/\tau = 0.5 - 1$ is for the positive scan. The bulk parameters of Pd–H interaction are the same as those in Fig. 1 and described in Section 1.

which is equal to 29.2 mV in Fig. 3. And the corresponding peak current density is

$$-j_{mc} = 2j_{ab} \sinh \left(\cosh^{-1} \left(\frac{d}{2l_{ab}} + 1 \right) \right) = \begin{cases} \Delta E_{mc} G_{ab}, & d < l_{ab} \\ j_{ab} d/l_{ab}, & d \gg l_{ab} \end{cases} \quad (11)$$

which is equal to 4.58 mA cm^{-2} in Fig. 3.

The $\beta \rightarrow \alpha$ pt can be described with expressions similar to Eqs. (4)–(11) with α and β interchanged and ab, mc replaced with de, ma respectively. We obtain similar characteristic parameters: $\theta_{de} = 0.646$, $j_{de} = 4.22 \text{ mA cm}^{-2}$, $G_{de} = 0.164 \text{ S cm}^{-2}$, $l_{de} = 0.0332 \text{ }\mu\text{m}$, $\Delta E_{ma} = 28.2 \text{ mV}$ and $j_{ma} = 4.63 \text{ mA cm}^{-2}$ with the parameters in Fig. 3.

Fig. 3 shows examples of the CV results. The potential covers both regions of α and β phases, so the voltammogram exhibits the characteristics of both of them, i.e. region A–B is for the α phase H absorption; region B–C the $\alpha \rightarrow \beta$ pt, region C–D the β phase absorption, region D–E the β phase desorption, region E–F the $\beta \rightarrow \alpha$ pt, region F–A the α phase desorption. By comparison with the voltammograms of adsorption [31–34] and diffusion [2,32,35,36], we find the main distinction is the trigonal shape of the pt peak. Besides the thermodynamic hysteresis, the voltammogram exhibits a similar effect, i.e. there is a difference, $(E_{ab} - E_{de}) + (\Delta E_{mc} + \Delta E_{ma})$ between the two peak potentials. The term $(\Delta E_{mc} + \Delta E_{ma})$ represents the kinetic hysteresis and it approaches zero when the scan rate is very low as indicated in Eqs. (9) and (10). Another character is that the voltammogram of the pt has a centre of symmetry about the point of $E = (E_{ab} + E_{de})/2$, $j = 0$ but no mirror symmetry about the line of $j = 0$ like a voltammogram of reversible adsorption. Of course, the hysteresis effect weakens the mirror symmetry to some extent. Fig. 3(b) shows the related parameters in CV. The H coverage θ does not change in pt; the subsurface H concentration $x(0)$ is $x_{\beta,ab}$ in the $\alpha \rightarrow \beta$ pt or $x_{\alpha,de}$ in the $\beta \rightarrow \alpha$ pt as the assumption; the thicknesses of the β and α phase layers are shown at the same time.

The results shown in Fig. 3 are the simplest; otherwise, if d is so thick that the maximum l_β

$$l_{\beta, \max} = 4l_{ab} (\cosh(f(E_c - E_{ab})/2) - 1) \quad (12)$$

(E_c is the lower potential limit) which can be attained in CV is less than d , the definition of peak potential and peak current given in Eqs. (10) and (11) is no longer suitable. In this case, when $E < E_{ab}$, the $\alpha \rightarrow \beta$ pt takes place at the two scan directions and the β phase does not occupy the Pd plate completely; when E increases and $E > E_{ab}$, H is desorbed from the β phase until x decreases to $x_{\beta,de}$, then the $\beta \rightarrow \alpha$ pt process commences and continues till the β phase layer is removed by the pt, finally, there is only the pure α phase existing in the Pd|H electrode. This situation is illustrated by the solid line in Fig. 4.

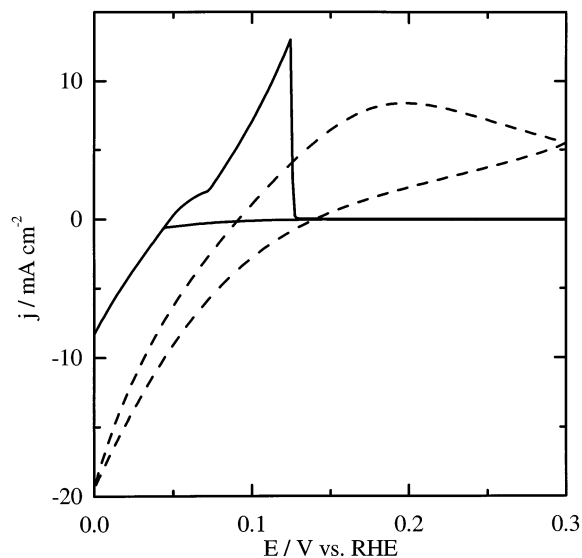


Fig. 4. Voltammograms of a Pd|H electrode with the Pd layer thicker than in Fig. 3 for $d = 0.12 \mu\text{m}$, $v = 0.01 \text{ V s}^{-1}$ (—) and $d = 10 \mu\text{m}$, $v = 0.1 \text{ V s}^{-1}$ (---), the other parameters not emphasized are the same as those in Fig. 3.

The case shown in Fig. 3 is for $d < l_{\beta, \text{max}}/2$, the middle case is for $l_{\beta, \text{max}}/2 < d < l_{\beta, \text{max}}$ in which the pt is completed in the positive scan at $E < E_{\text{de}}$ and there is a part coincidence between two scan directions in the voltammogram which is similar to the case of $d > l_{\beta, \text{max}}$ as shown in Fig. 4.

Similarly, we can obtain $l_{\alpha, \text{max}}$ from Eq. (12) with the subscripts changed as above. For a given electrode and CV parameters, the actual voltammogram of the pt is determined by $\min[l_{\beta, \text{max}}, l_{\alpha, \text{max}}]$.

If $d \gg l_{\beta, \text{max}}$, $l_{\alpha, \text{max}}$ and/or v , E_c increases, the system will become more irreversible. The voltammogram will be the same as the single phase situation and exhibit diffusion characters as shown by the dashed line in Fig. 4 and our previous results [2].

4. Comparison with experimental results and discussions

We compare the present treatment with the results of an experiment [5] as illustrated in Fig. 5. In the experiment a thin Pd layer absorbed D in 0.5 M D_2SO_4 at -0.3 V versus SCE for different times, then a linear sweep potential was applied to the Pd|D electrode and the voltammograms given by the dashed lines in Fig. 5 were obtained. The numerical simulation results are shown in the same figure and they are in agreement with those of the experiment. Because the absorption time is short, the β phase layer is less than the electrode thickness and we adopted $l_{\beta}/d = 0.08$ and 0.26 at the beginning of desorption for 5 and 20 s absorption time, respectively.

Eq. (4) indicates that the overall rate of the pt is determined by the deviation of parameters from the thermodynamic values. For a PdH battery, if the Pd surface is rough enough (has higher r), the potential of Pd|H will be close to a constant (E_{ab} or E_{de}) in the mixed phases which cover the region of 85% H concentration under ambient conditions [9]. In cold fusion experiments, if the cd is low enough in the pt process, the overall rate of the pt will be very slow, internal stress fields generated in the pt have enough time to be released and it is advantageous to avoid the occurrence of cracking in samples [37,38].

Using Eqs. (7), (10) and (11) and Fig. 3, we can obtain the thermodynamic and kinetic parameters of the Pd|H electrode. E_{ab} (E_{de}) is at the intersecting point of the line $j = 0$ and the extension of line B–C (E–F); G_{ab} (G_{de}) is the slope of line B–C (E–F) from which we obtain j_{ab} (j_{de}) that determines the rate of $\alpha \rightarrow \beta$ ($\beta \rightarrow \alpha$) pt; the integration of the $\alpha \rightarrow \beta$ ($\beta \rightarrow \alpha$) pt peak with respect to time yields $x_{\beta, \text{ab}} - x_{\alpha, \text{ab}}$ ($x_{\beta, \text{de}} - x_{\alpha, \text{de}}$). At the same time, other parameters can be deduced correspondingly.

On the other hand, CV can be applied to other metal|H electrodes, the physical quantities of the pt can be obtained from the voltammogram in a similar way. Because many metal|H (e.g. Ti|H, Nb|H) systems have more than two phases involved in the absorption/desorption process, so we expect that the corresponding voltammogram will exhibit multiple pt peaks and their properties can be described using the same method.

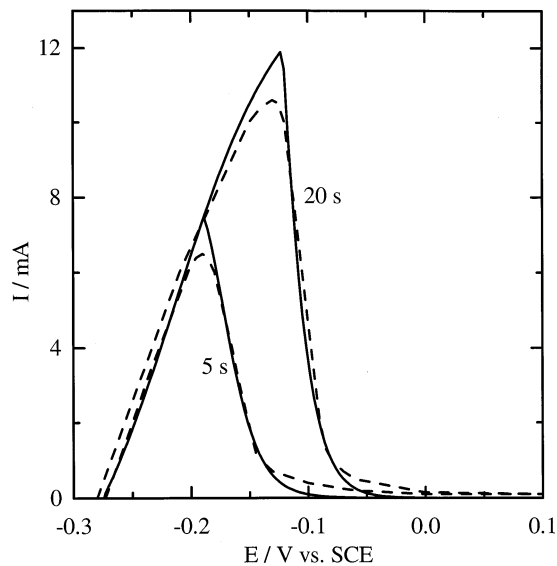


Fig. 5. Fitting the voltammograms of Pd|D in Fig. 3(a) of Ref. [5] (---) with numerical results (—). Parameters: $j_{0V} = 0.34 \text{ mA cm}^{-2}$, $\theta_0 = 0.95$, $u = 0$, $r = 10$, surface area is 0.6 cm^2 , $v = 0.01 \text{ V s}^{-1}$, $d = 1 \mu\text{m}$. The bulk parameters of Pd–D interaction are the same as those described in Section 1.

In reality, the pt peak in voltammogram is smoother than that described here [3–8] due to reasons such as: (1) at the beginning of the pt, the practical processes of nucleation and growth of new hydride phase are gradual, not abrupt as our model assumption; (2) a practical sample is not homogenous as a single crystal, defects such as crystal grains having different sizes, impurities and crystal boundaries, etc. make the phase boundary more rough than assumed here, and the voltammogram observed is an average effect in practical cases. In spite of these drawbacks, CV can give the primary information for a phase transition occurring in metal|H electrodes. We expect that our results will stimulate further experimental study of a phase transition in metal|H electrodes using CV or LSV.

5. Conclusions

Based on the relationship between surface reactions developed in Zhang et al. [1], the bulk diffusion equation in Zhang and Zhang [2] and the phase transition equation [11,25], we discuss the kinetics of a thin layer Pd|H(D) electrode in cyclic voltammetry in the coexistence of α and β phases. The voltammogram of pt has trigonal shape peaks which differ drastically from those of diffusion or adsorption. We find that CV can be used to study the properties of a phase transition occurring in Pd|H or other metal|H electrodes. The present model is verified by comparison with previous experimental results [5].

Acknowledgements

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