

# Effects of self-stress on the hydrogen absorption into palladium hydride electrodes of plate form under galvanostatic conditions

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Received 12 April 1999; received in revised form 2 July 1999; accepted 6 July 1999

## Abstract

Effects of diffusion induced stress on the hydrogen absorption into plate form electrodes of  $\beta$ -phase  $\text{PdH}_x$  are discussed numerically based on the Volmer–Tafel route of the hydrogen evolution reaction, and thermodynamic considerations involving stress fields and non-ideal interactions of hydrogen in the electrode. It is found that the self-induced stresses enhance the absorption rate and may exceed the yield stress, especially when the thickness of the plate and/or charging current (or negative potential) increase. On the other hand, a plate with both sides exposed to electrolyte absorbs hydrogen more rapidly than that with only one side exposed to electrolyte under the same equivalent thickness and other conditions. Of course, the stresses developed in the former plate are always greater than those of the latter. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Pd | H electrode; Stress; Diffusion; Kinetics

## 1. Introduction

The electrolytic loading method has been used extensively to prepare palladium hydrides [1–6]. Nevertheless, the hydrogen concentration and properties of  $\text{PdH}_x$  obtained in experiments are dependent on various parameters, such as current density (cd) or overpotential, temperature, electrolyte pH and additives, metallurgical–physical properties of the Pd bulk and surface etc.; the self-stress is one of the factors [6]. Experimental data analysis showed that the self-stress arising from very steep hydrogen concentration gradients is responsible for the well-known difficulty in obtaining reproducible high loading of samples [7,8]. Furthermore, possible damage induced by the loading process itself can modify the material during experiments in an unpredictable way, resulting in poor reproducibility. These results lead one to believe that the removal of the self-stress allows one to obtain, in a reproducible way, a high loading of hydrogen in palladium (close to stoichiometry) with an electrolytic procedure.

Because phase transitions and hydrogenation processes are accompanied by changes of palladium (and other metals) volume, so this change can induce internal stresses being maintained in solids. This self-stress can affect the chemical potential, hence the diffusion of hydrogen in palladium as described by the Gorsky effect, which was first formulated to describe the migration of interstitials in metal when an external bending is applied to a sample [9]. Additionally, Lewis and co-workers showed that self-stresses are generated during the insertion and diffusion of hydrogen interstitials and that the consequent strain developed results in a force opposing the flux generated by diffusion (see Ref. [10–20] for palladium and palladium alloys). Contemporary theoretical treatments of these effects, based on thermodynamics of stressed solids, have been presented in a review paper by Li [21], in a series of works by Larché and Cahn [22–24], and other papers by Kandasamy [25,26], Baranowski [27], Simon and Grzywna [28] and Zoltowski [29].

In this paper, we will discuss self-stresses generated in  $\beta$ -phase  $\text{PdH}_x$  electrodes based on the stress induced diffusion theory developed by Larché and Cahn [22–24] and presented more extensively in a review paper by Baranowski [27], and Pd | H electrode kinetics discussed

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in Zhang et al. [30–32]. Although there has been much work concerning the self-stress in solid solutions of hydrogen in metal, no theory has been applied to the metal hydride situation up to now.

## 2. Model

Consider hydrogen absorption into a  $\text{PdH}_x$  plate electrode in the hydrogen evolution reaction. The sample consists of dislocation-free crystals with no applied tractions or body forces, all stresses in the crystal arising from compositional inhomogeneity, provided that the stresses created are not relaxed at grain boundaries or by plastic flow. The plate thickness is small compared with the length and width ( $x-y$  plane) which allows our analysis to be reduced to a one-dimensional problem as illustrated in Fig. 1. There are two different situations, the unsymmetrical absorption (ua) and symmetrical absorption (sa), which have different stress effects. The ua is for a plate of thickness  $L$  with a hydrogen-impermeable substrate whereas the sa is for a plate of thickness  $2L$  submitted symmetrically to hydrogen absorption on both sides. The importance of these differences will become clear below.

According to Ref. [21–24,27], the chemical potential of H in Pd under a stress  $\sigma$  can be expressed as

$$\mu_{\text{H}} = \mu_{\text{H}}(0, n_{\text{H}}) - V_{\text{H}}\sigma \quad (1)$$

where  $\mu_{\text{H}}$  denotes the molar chemical potential of hydrogen interstitials in the Pd lattice and is, generally

speaking, a function of the  $z$  coordinate and time;  $\mu_{\text{H}}(0, n_{\text{H}})$  denotes the chemical potential of hydrogen in the stress-free state ( $\sigma = 0$ ) and it plays the role of the standard state with respect to the stress  $\sigma$ ;  $n_{\text{H}}$  symbolizes the relative concentration of H in Pd and is expressed as the atom ratio of H/Pd;  $V_{\text{H}}$  is the partial molar volume of H in Pd. Referring to Baranowski [33],  $V_{\text{H}} = 1.75 \text{ cm}^3 \text{ mol}^{-1}$  for  $n_{\text{H}} < 0.75$  and  $V_{\text{H}} = 0.46 \text{ cm}^3 \text{ mol}^{-1}$  for  $n_{\text{H}} > 0.75$  using high pressure cells. But the results of Schirber and Morosion [34] and Felici et al. [35] showed that  $V_{\text{H}} = 1.55 \text{ cm}^3 \text{ mol}^{-1}$  in all the  $\beta\text{-PdH}_x$ . Because the latter result was obtained under electrochemical conditions, we will use and maintain it as the only variable directly related to the stress in this treatment. Later on it will be assumed that  $V_{\text{H}}$  is neither concentration nor stress dependent, which is equivalent to its being effectively space independent.

The chemical potential of the  $\beta$ -phase  $\text{PdH}_x$  in the stress-free state in Eq. (1) may be replaced by the expression [30,36]

$$\mu_{\text{H}}(0, n_{\text{H}}) = \mu_{\text{H}}^0 + RTu_{\beta}n_{\text{H}} + RT \ln\left(\frac{n_{\text{H}}}{1 - n_{\text{H}}}\right) \quad (2)$$

where  $u_{\beta} = 18.1$  at the ambient temperature ( $25^\circ\text{C}$ ), is the non-ideal factor of H-H interaction in the  $\beta$ -phase  $\text{PdH}_x$ ,  $R$  is the molar gas constant,  $T$  is temperature in K.

Similarly to the discussion in Ref. [21,22,27], the stress in Eq. (1) is

$$\sigma = \sigma_{xx} + \sigma_{yy} + \sigma_{zz} \quad (3)$$

The components of stress in Eq. (3) are represented by

$$\sigma_{xx} = \sigma_{yy} = \begin{cases} -\frac{V_{\text{H}}Y\Gamma_{\text{b}}}{3} \left\{ \Delta n_{\text{H}} - \frac{1}{L} \int_0^L \Delta n_{\text{H}} dz - \frac{12(z-L/2)}{L^3} \int_0^L \Delta n_{\text{H}}(z-L/2) dz \right\}, \\ \text{for ua} \\ -\frac{V_{\text{H}}Y\Gamma_{\text{b}}}{3} \left\{ \Delta n_{\text{H}} - \frac{1}{2L} \int_0^{2L} \Delta n_{\text{H}} dz \right\}, \\ \text{for sa} \end{cases} \quad (4)$$

$$\sigma_{zz} = 0$$

where  $Y = E/(1 - \nu)$ ,  $E$  is Young's modulus,  $E = 1.16 \times 10^{11} \text{ Pa}$  [8];  $\nu = 0.39$ , Poisson's ratio;  $\Gamma_{\text{b}} = 0.1 \text{ mol cm}^{-3}$ , the maximum molar number of available sites for H per unit volume of  $\text{PdH}_x$  (expansion effect due to H insertion is concerned [33]);  $\Delta n_{\text{H}} = n_{\text{H}} - n_{\text{H},0}$ ,  $n_{\text{H},0}$  is the homogeneous initial value of  $n_{\text{H}}$  in the  $\beta$ -phase  $\text{PdH}_x$ . The first term in the braces for ua in Eq. (4) is the solution for a semi-infinite solid, the second and third ensure that the resultant forces and moments on the specimen are zero. Because the H distribution is symmetrical with respect to the central plane  $z = L$ , the third term for sa in Eq. (4) is absent.

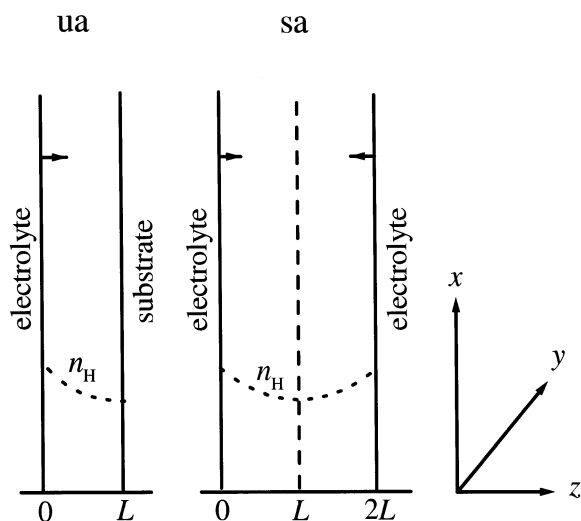


Fig. 1. Schematic picture of H absorption (H concentration profile) in Pd plate form, ua (unsymmetrical absorption): plate electrode of thickness  $L$  with a conductive hydrogen-impermeable substrate; sa (symmetrical absorption): plate electrode of thickness  $2L$  submitted to hydrogen absorption symmetrically on both sides. Arrows indicate the directions of hydrogen absorption.

The gradient of the stress may be expressed as

$$\frac{\partial \sigma}{\partial z} = 2 \frac{\partial \sigma_{xx}}{\partial z} = \begin{cases} -\frac{2}{3} V_H Y \left\{ \frac{\partial n_H}{\partial z} - \frac{12}{L^3} \int_0^L \Delta n_H(z-L/2) dz \right\}, & \text{for ua} \\ -\frac{2}{3} V_H Y \Gamma_b \frac{\partial n_H}{\partial z}, & \text{for sa} \end{cases} \quad (5)$$

Contrary to that of the  $\alpha$ -phase, hydrogen diffusion in the  $\beta$ -phase will be reduced by the blocking factor. According to the results of Majorowski and Baranowski [37,38], the hydrogen flux has the form

$$J_H = -\frac{D_0(1-n_H)\Gamma_b}{RT} \nabla \mu_H \quad (6)$$

where  $D_0 = 2.01 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  [37,38],  $(1-n_H)$  is the blocking factor. Introducing Eqs. (1–5) into Eq. (6) we obtain the equation for hydrogen flow in the most general form for present purposes

$$J_H = \begin{cases} -D_0\Gamma_b \left\{ \begin{array}{l} [1 + (u_\beta + u_\sigma)n_H(1-n_H)] \frac{\partial n_H}{\partial z} \\ -12u_\sigma n_H(1-n_H) \frac{1}{L^3} \int_0^L \Delta n_H(z-L/2) dz \end{array} \right\}, & \text{for ua} \\ -D_0\Gamma_b [1 + (u_\beta + u_\sigma)n_H(1-n_H)] \frac{\partial n_H}{\partial z}, & \text{for sa} \end{cases} \quad (7)$$

where

$$u_\sigma = \frac{2}{3} \frac{V_H^2 Y \Gamma_b}{RT} \quad (8)$$

may be regarded as the dimensionless material constant, which is 12.3 at the ambient temperature for the parameters aforementioned. Eq. (7) for ua can be regarded as composed of two parts, the local and non-local terms. The local term corresponds to the classical Fickian term, proportional to the gradient of concentration. In this term, the stress always enhances the diffusion since the additional term inside the square brackets is always positive; the presence of stress acts in a fashion like the non-ideal factor of palladium hydride. Because  $u_\sigma$  is comparable to  $u_\beta$ , the internal stress will accelerate hydrogen diffusion prominently for sa. Referring to Eq. (34) in Larché and Cahn [22], the form of diffusion coefficient for the stress contribution here is similar to that for substitution solid solutions. This is because the interstitial acts like a substitution impurity when its concentration approaches the saturation value. In the second part for ua in Eq. (7) a non-Fickian non-local term appears and is dependent on an integral taken over the total sample

considered and relies on the distribution of hydrogen. The existence of this term is due to the plate distortion (bending) that creates a flow of H induced by the Gorsky effect in each volume element of the specimen as soon as a non-negligible H/Pd exists. When  $u_\beta \rightarrow 0$  and  $n_H \rightarrow 0$ , Eq. (7) is simplified to the form for dilute solid solutions as was discussed extensively before [25–29]. When  $n_H \rightarrow 1$ , the term  $n_H(1-n_H) \rightarrow 0$ , thus, contributions of stress and non-ideality all vanish.

Formulation of the starting equation for calculation of the time–space dependence of  $n_H$  requires the introduction of the flow equation into the mass balance equation, Fick's second law [39]

$$\frac{\partial n_H}{\partial t} = -\frac{1}{\Gamma_b} \nabla J_H \quad (9)$$

The inner surface boundary condition is the zero flux of hydrogen, i.e.  $J_H = 0$ . In view of Eq. (7), we have

$$\frac{\partial n_H}{\partial z} = \begin{cases} \frac{12u_\sigma n_H(1-n_H)}{1 + (u_\beta + u_\sigma)n_H(1-n_H)} \frac{1}{L^3} \int_0^L \Delta n_H(z-L/2) dz, & z=L, \\ \text{for ua} \\ 0, & z=L, \text{ for sa} \end{cases} \quad (10)$$

At the outer surface, there are three steps, i.e. Volmer, Tafel and penetration reactions taking place in the hydrogen evolution reaction at the same time [30,40]. The rate of the Volmer step is the applied current density, the rates of the Tafel and penetration steps are

$$j_T = r^2 j_{0T} \left\{ \left( \frac{1-\theta}{1-\theta_0} \right)^2 e^{-u_S(\theta-\theta_0)} - \left( \frac{\theta}{\theta_0} \right)^2 e^{u_S(\theta-\theta_0)} \right\} \quad (11)$$

$$j_P = r j_{0P} \left\{ \begin{array}{l} \frac{1-\theta}{1-\theta_0} \frac{n_H}{n_H^0} e^{-\frac{1}{2} u_S(\theta-\theta_0)} e^{\frac{1}{2} u_\beta(n_H-n_H^0)} e^{-\frac{1}{2} \frac{V_H \sigma}{RT}} \\ -\frac{\theta}{\theta_0} \frac{1-n_H}{1-n_H^0} e^{\frac{1}{2} u_S(\theta-\theta_0)} e^{-\frac{1}{2} u_\beta(n_H-n_H^0)} e^{\frac{1}{2} \frac{V_H \sigma}{RT}} \end{array} \right\}, \quad z=0 \quad (12)$$

where  $j_T$  and  $j_P$  are cds of the Tafel and penetration steps respectively;  $j_{0T}$  and  $j_{0P}$  are the corresponding exchange current densities;  $r$  is the roughness factor,  $\theta$  is the fractional surface coverage of H on Pd;  $\theta_0$  is the equilibrium value of  $\theta$ ;  $u_S$  is the heterogeneity factor of the Frumkin adsorption of H on Pd surface;  $n_H^0 = 0.710$ , the equilibrium value of  $n_H$  at ambient conditions. For simplicity, we choose all of the symmetric factors to be 1/2 in Eqs. (11) and (12). Eq. (12) involves the effect of stress on the hydrogen absorption. Because  $\sigma < 0$  is for absorption and  $\sigma > 0$  is for desorption at the surface, the stress will suppress the interface process either for absorption or desorption. When  $j_P \rightarrow 0$ , Eq. (12) can be reduced to the hydrogen absorption isotherm under the stress  $\sigma$  [27]. The time dependent equation of the adsorbed hydrogen coverage is

$$\frac{d\theta}{dt} = \frac{1}{r\Gamma_S F} (j_T + j_P - j) \quad (13)$$

where  $\Gamma_S = 2.20 \times 10^{-9}$  mol H cm<sup>-2</sup>, the maximum H molar number of available sites on the real unit Pd area [41]. At the subsurface

$$FJ_H = -j_P, \quad z = 0 \quad (14)$$

where  $F$  is the Faraday constant; this equation couples the surface reactions with the bulk process.

Eqs. (7), (9), (11)–(13) with boundary conditions of Eqs. (10) and (14) form the basis for all consequent and exact treatments of hydrogen diffusion involving self-stresses. Combining Eqs. (7) and (9) results in a transport equation of hydrogen under the self-stress; this is a partial non-linear integro-differential equation of second order which can be solved numerically using, e.g. the method described by Crank and Nicolson [42] with some modification. The integrals involved in Eqs. (4), (7) and (10) are evaluated using the Simpson method. Eqs. (11)–(13) form a set of stiff differential equations that can be solved using, e.g. the Treanor method. In the numerical scheme the mesh size is  $\Delta z/L = 0.02$  and the time step  $\Delta t$  is chosen to ensure the solution being stable and a concentration calculation accuracy of  $10^{-5}$ . Of course, we compared the results at extreme conditions (e.g. stress-free condition when  $u_\sigma = 0$  or stable concentration distribution when  $t$  is sufficiently large) with the known solutions; they are completely consistent with each other.

### 3. Results

Consider a constant cathodic current being applied to a  $\beta$ -PdH<sub>x</sub> electrode (for ua) which has absorbed H to a steady concentration  $n_{H,0}$  under ambient conditions, the hydrogen produced on the Pd surface in the hydrogen evolution reaction being desorbed by the bulk absorption and chemical recombination (the Tafel step) together. At the initial short times, the absorbed hydrogen atoms diffuse into the electrode and locate in the region near the outer surface (see Fig. 2(a)); this non-homogeneity induces self-stresses as illustrated in Fig. 2(b). The stresses near the outer surface increase with  $z$ ,  $\partial\sigma/\partial z > 0$ , and enhance the hydrogen diffusion. But the stresses near the substrate decrease with  $z$  and weaken the concentration diffusion up to the hydrogen flux in an opposite direction as is to be expected from Fickian behaviour. This induces  $n_H < n_{H,0}$  near the inner surface as predicted also by Kandasamy [25], and Simon and Grzywna [28]. Along with the hydrogen absorption, the Fickian diffusion flux near the inner surface increases, the inhomogeneity is weak and the amplitude of  $\partial\sigma/\partial z$  near  $z = L$  decreases correspondingly, so the inhibition effects of stress on the diffusion diminish but do not disappear.

Fig. 2(c) shows the stress profile for sa with parameters being the same as those of Fig. 2(a) and (b). This figure and Eq. (7) all indicate that the self-stress enhances the hydrogen absorption into the electrode for sa. Although the penetration step is suppressed by the self-stress as indicated by Eq. (12), it does not influence the absorption rate prominently due to the fact that this reaction is a fast step. We do not show the hydrogen distribution for sa owing to its trivial nature. As the self-stresses are symmetrical with respect to the central plane  $z = L$ , we show only their profile in a half-space.

Since the outer surface concentration is larger than the concentration anywhere inside the plate and therefore larger than the average concentration, the stress at the outer surface has the largest magnitude at any time. Such a surface stress is plotted in Fig. 2(d). It is seen that the maximum stress does not appear instantly when the current is applied; this is different from the results of the concentration step boundary conditions [21]. Furthermore, we calculated the stresses developed under potentiostatic conditions and reached the same conclusion. Of course, for either potentiostatic or galvanostatic conditions, the absorption of hydrogen into PdH<sub>x</sub> is a progressive process, so the creation and release of self-stress need corresponding times. The concentration step condition is an ideal situation but not the practical case. Fig. 2(d) shows also that increase of stress needs only a short time ( $< 10$  s) but its decrease takes quite a long time ( $\sim 10^3$  s). On the other hand, the maximum stresses for both situations in Fig. 2 all exceed the yield stress of PdH<sub>x</sub> (0.10 ~ 0.28 GPa) [8], this means the self-stresses may cause plastic flow or dislocation slipping to release the stresses [43]. Thus a large cd will destroy the perfection of the electrode and it must be avoided for hydride preparation in experiments. Between the two curves in Fig. 2(d), we conclude that the amplitude of the maximum stress developed for ua is less than that for sa under the same conditions.

The self-stresses affect the absorption rate as well as the mechanical properties. To describe this quantitatively, we introduce the absorption ratio

$$M(t) = \frac{\bar{n}_H(t) - n_{H,0}}{n_{H,\infty} - n_{H,0}} \quad (15)$$

with  $\bar{n}_H(t)$  and  $n_{H,\infty}$  being the average and saturation values of  $n_H$ , respectively. We define the half absorption time  $\tau$  at which  $M = 1/2$ .  $\tau_0$ ,  $\tau_{ua}$  and  $\tau_{sa}$  are  $\tau$  values for the stress-free condition ( $V_H = 0$  or  $u_\sigma = 0$ ), ua and sa respectively. For example,  $\tau_0$ ,  $\tau_{ua}$  and  $\tau_{sa}$  for the parameters in Fig. 2 are 42.3, 39.6 and 35.2 s, respectively. The self-stresses promote rather than inhibit the absorption as expected, and our numerical results indicate that the hydrogen flux is always greater than the stress-free situation except in the initial time intervals for ua.

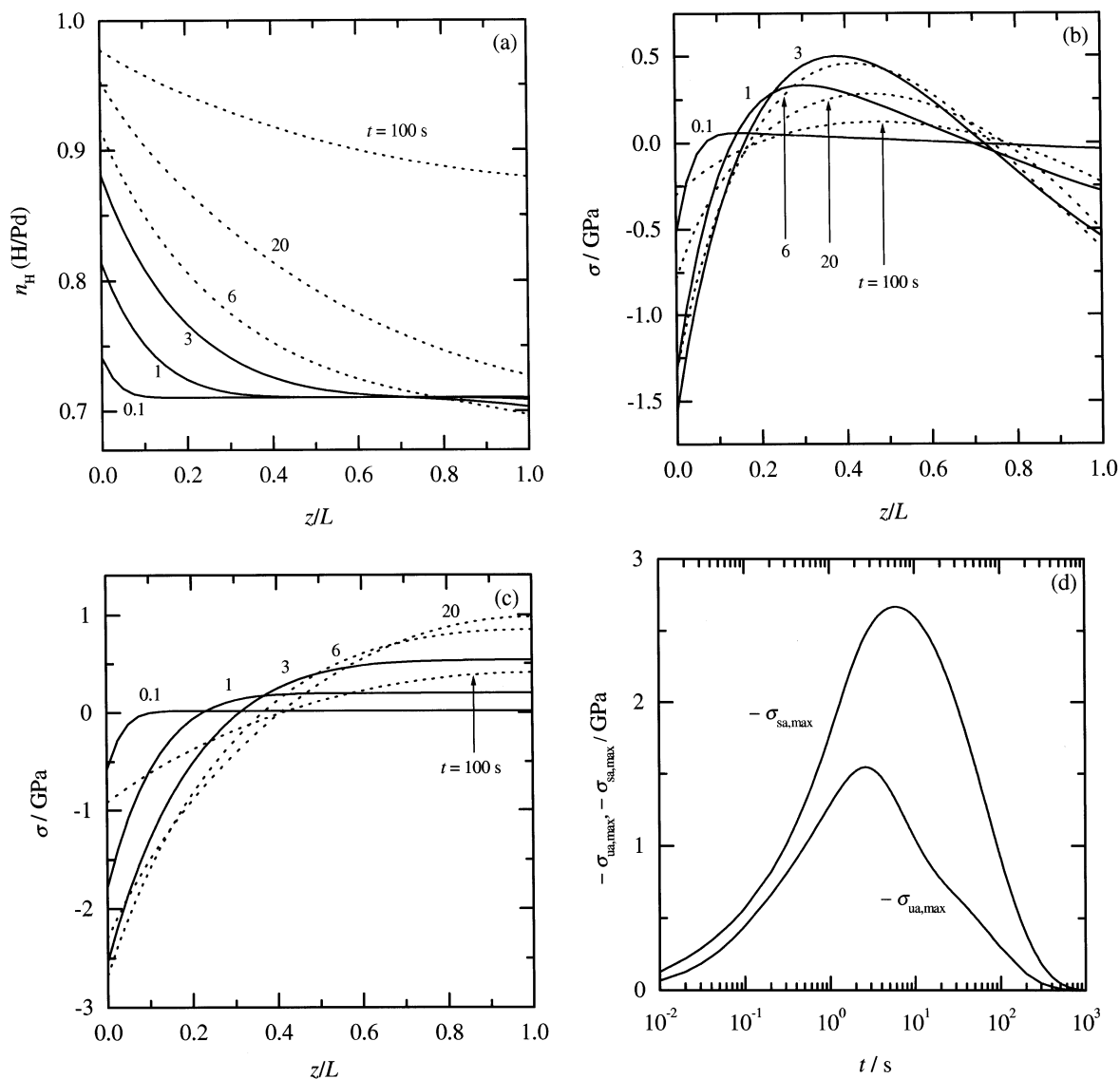


Fig. 2. An example of effects of self-stress on the H absorption into  $\beta$ -phase plate Pd|H electrodes under galvanostatic conditions. (a) H distribution at different times  $t$  for ua; (b) stress developed for ua; (c) stress developed for sa; (d) surface stress developed for ua and sa. The parameters:  $\theta_0 = 0.01$ ,  $u_s = 5$ ,  $j_{OT} = 2.5 \times 10^{-3} \text{ mA cm}^{-2}$ ,  $j_{OP} = 50 \text{ mA cm}^{-2}$ ,  $j = -10^3 \text{ mA cm}^{-2}$ ,  $r = 2$  and  $L = 0.01 \text{ cm}$ .

For demonstration of effects of different parameters on the hydrogen absorption, we calculate  $\tau$  and show their ratios  $\tau_{ua}/\tau_0$ ,  $\tau_{sa}/\tau_0$  and  $\tau_{sa}/\tau_{ua}$  and the maximum surface stresses,  $\sigma_{ua,max}$  and  $\sigma_{sa,max}$ , for various situations as shown in Fig. 3. Although  $\tau_{ua}/\tau_0$  and  $\tau_{sa}/\tau_0$  have only the theoretical sense, the value  $\tau_{sa}/\tau_{ua}$  can be measured experimentally. Fig. 3(a) illustrates ratios of  $\tau$  as functions of charging current while the other parameters are fixed. It is seen that ratios of  $\tau$  all decrease and the maximum stresses increase with cd as expected. When the cd is very low, instead of the bulk process the surface process becomes the rate determining step of the hydrogen absorption [32]. Consequently, the bulk process, which is modified slightly by the small

stresses, does not affect the absorption rate and ratios of  $\tau$  approach 1 as shown in Fig. 3(a).

The plate thickness  $L$  has effects similar to that of the current density as discussed in an earlier paper [32] and illustrated in Fig. 3(b). This result indicates that shortening the electrode dimensions can reduce the self-stress effects as verified experimentally [19,20].

In experiments, step-wise increasing cd (step-up mode) is applied in order to obtain high  $n_H$ . For simulating this situation, we choose different initial values  $n_{H,0}$  which have been reached with different cds, then raise the cd to a fixed value ( $10^3 \text{ mA cm}^{-2}$  in this case). These results are presented in Fig. 3(c). As expected, when  $n_H^0 \rightarrow 0.986$  (which is  $n_{H,\infty}$  at  $j = 10^3 \text{ mA}$

$\text{cm}^{-2}$ ),  $\tau_{\text{ua}}$  and  $\tau_{\text{sa}} \rightarrow \tau_0$ . There are two arguments to explain this phenomenon, firstly, when  $n_{\text{H}}^0 \rightarrow n_{\text{H},\infty}$ , the amplitude of the self-stresses decreases, as well as the stress effect. Secondly, when  $n_{\text{H}}^0 \rightarrow 1$ , the contribution of stress to the diffusion vanishes as shown by Eq. (7). This result and Fig. 3(a) all indicate that for preservation of the perfection of the sample in obtaining high  $n_{\text{H}}$ , the safest way is loading the palladium by step-up mode but not using a large cd at once.

#### 4. Discussions

Besides the galvanostatic charging, our method has been applied to potentiostatic conditions. It is found

that the stresses developed are slightly greater than those under galvanostatic conditions with the same saturation H/Pd values and other parameters. Most of the above conclusions can be generalised to potentiostatic situations.

In addition to absorption, this method can be used to described hydrogen desorption from  $\beta\text{-PdH}_x$  electrodes under galvanostatic and/or potentiostatic conditions. Also, a converse effect has been observed, i.e. the self-stresses have signs opposite to those for absorption and enhance the bulk process as a whole.

The situation discussed above is for coherent crystals. The opposite case is that in which the internal stress can be removed either by plastic deformation or dislocation motion [43]; such a stress-free strained crystal is

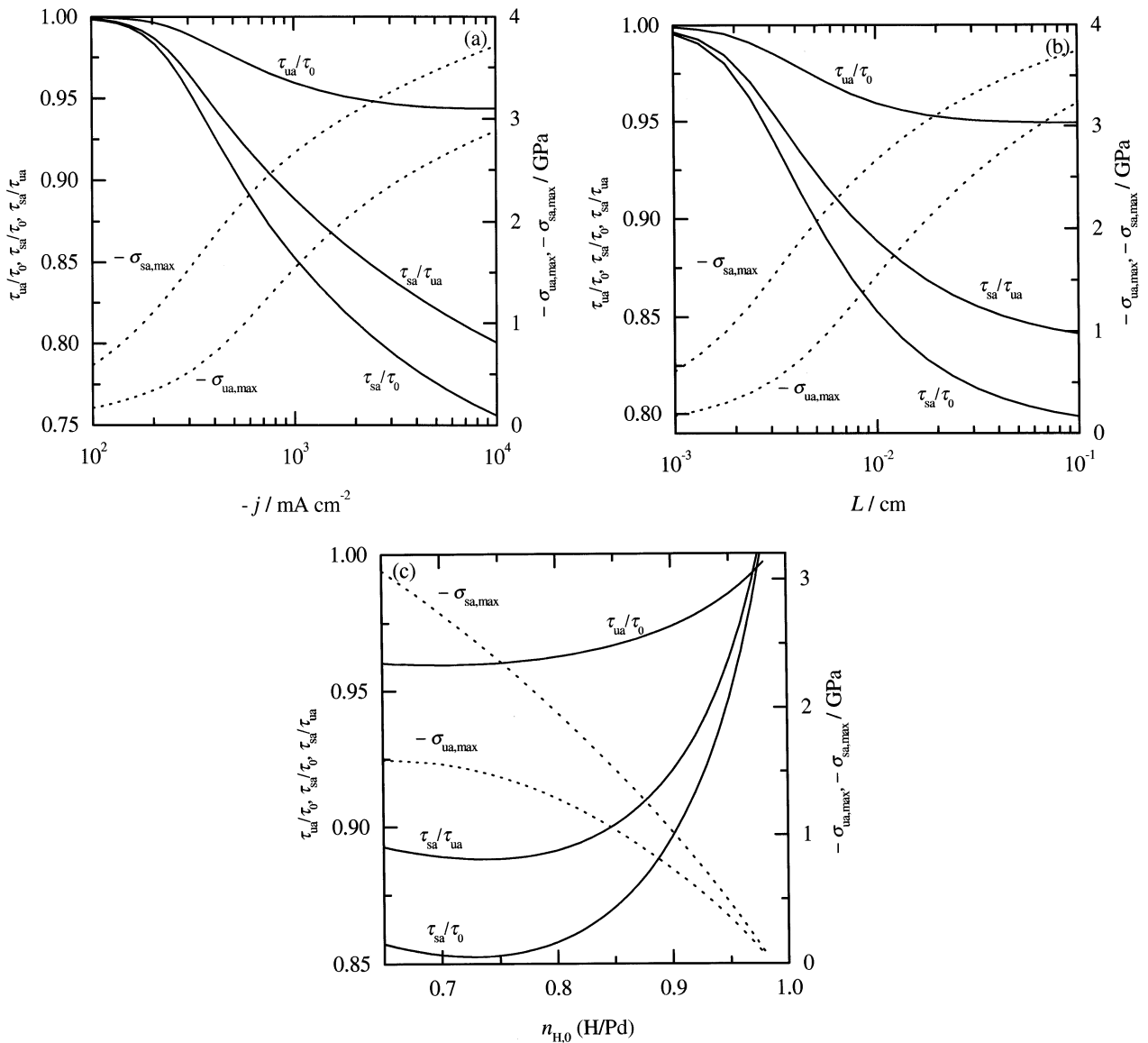


Fig. 3. Effects of different parameters on the ratios of half absorption time:  $\tau_{\text{ua}}/\tau_0$ ,  $\tau_{\text{sa}}/\tau_0$ ,  $\tau_{\text{sa}}/\tau_{\text{ua}}$  and the maximum surface stresses  $\sigma_{\text{ua,max}}$  and  $\sigma_{\text{sa,max}}$ . (a) Effects of  $j$ , (b) effects of  $L$ , (c) effects of  $n_{\text{H}}^0$ . Other parameters not emphasised are the same as those of Fig. 2.

always denoted 'incoherent'. The actual crystal is a mixture of the two cases depending on the initial metallurgical state and hydrogen charging and/or discharging processes. The stress produced may be released partly and the promotion of stress on the H absorption may be slighter than the coherent situation.

As observed experimentally and predicted theoretically, the plate will bend in the ua process. What will take place in the sa process? The above results indicate that the self-stresses are symmetrical with respect to the central plane of the plate, which will prevent the plate from distorting. There is also another mechanism that is in favor of the maintenance of the plate shape: the penetration step will be suppressed by the induced stress at the protruded surface. But the assumption of identical outer surfaces, and homogeneity and a dislocation free state of the parent crystals in our analysis is difficult to ensure experimentally. Therefore, it is not surprising to observe the distortion of the flat plate even when it is submitted to hydrogen absorption symmetrically on both sides when the induced hydrogen concentration step is high [44].

Despite our treatment which is confined to the Pd | H system, the above method and conclusion can be applied to the Pd alloy | H(D,T) or other metal | H system with some bulk or surface parameters of the electrode adapted.

## 5. Conclusions

Based on various reactions of hydrogen on a Pd surface, and the thermodynamics of stressed palladium hydride, we discussed the self-stresses arising from hydrogen inhomogeneity in a palladium hydride plate and their effects on various parameters of the hydrogen diffusion. Our results indicate that self-stresses accelerate hydrogen absorption into palladium, and the hydrogen absorption rate is higher for symmetrical absorption than for unsymmetrical absorption. At the same time, a high charging current or a large thickness of plate may destroy the samples.

## Acknowledgements

The work is supported by the Pan-Deng Project of Department of Science and Technology of China under Grant No. 95-yu-41, Natural Science Foundation of China and Foundation of China Academy of Engineering Physics. We are grateful to Professors Chen Neng-Kuan and Zhao Xian-Geng for encouragement and help, and to Professors F.A. Lewis and P. Zoltowski for supplying offprints.

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