The maximum hydrogen (deuterium) loading ratio in the Pd|H₂O (D₂O) electrochemical system

The maximum hydrogen (deuterium) loading ratio in the $Pd|H_2O$ (D_2O) electrochemical system

Wu-Shou Zhang [a,b,c] and Xin-Wei Zhang [a], Hai-Qin Li [d]

[a] *Institute of Applied Physics and Computational Mathematics, PO Box 8009, Beijing 100088, People's Republic of China*

[b] *Graduate School, China Academy of Engineering Physics, PO Box 2101, Beijing 100088, People's Republic of China*

[c] *Institute of Physics,Chinese Academy of Sciences, Beijing 100080, People's Republic of China*

[d] *Department of Physics, Qinhai Normal Training Scholl, Xining 81007, People's Republic of China*

Abstract

Based on the Volmer-Heyrovsky-Tafel mechanism, Frumkin adsorption and thermodynamic data of hydrogen (deuterium) absorption in Pd, effects of surface parameters on the hydrogen (deuterium) loading ratio into Pd in the hydrogen (deuterium) evolution reaction are discussed. There is a change of mechanism from the Volmer-Tafel route to the Volmer-Heyrovsky route when the current density rises, and there exists the maximum loading ratio at a certain current density when the symmetry factor of the Heyrovsky step is less than that of the Volmer reaction. The theoretical results fit the experimental data presented before very well; other factors that affect the loading ratio are discussed as well.

Keywords: Cold fusion; Hydrogen evolution reaction; Loading ratio; Pd|D system; Pd|H system

1. Introduction

Owing to its unique nature, the palladium-hydrogen system has attracted wide and continual interest among the metal-hydrogen systems [1-3]. Since Fleischmann et al. reported the cold fusion reactions in the electrolytically formed deuteride of palladium [4], much effort has been concentrated on the $Pd|H_2O$ (D_2O) electrochemical system, especially the $Pd|D_2O$ electrochemical system. It has been shown that there exists a threshold of loading ratio $x = 0.84$ D/Pd (atom ratio) for the generation of excess heat in cold fusion and the excess heat is proportional to x [5,6], so many researchers have focused on raising x and making it reproducible [7-9].

The supply of hydrogen (taken to include D and T, the same below) to palladium by the electrolytic loading technique is a simple and effective method. For example, loading H (D) into Pd to $x = 0.85$ H (D)/Pd at 298 K, needs pressure of 570 atm for H_2 and 2000 atm for D_2 [10], but for the electrochemical method, it is necessary only to raise the current density. Nevertheless, determining the loading ratio is complex, the value of x depends on not only the temperature and pressure as in the gas loading, but also on the overpotential, current density, electrolyte, presence of surfactants and pH value, etc. In other words, x is determined by the kinetic factors besides the thermodynamic quantities.

In the following sections, we will discuss the H absorption into Pd in connection with the hydrogen evolution reaction (her) which has been widely studied.

2. Model

Generally, the her takes place on a metal (Pd in this work) electrode surface through the Volmer-Heyrovsky-Tafel (V-H-T) route [11-13]. As palladium absorbs hydrogen, there exists another reaction, the adsorbed hydrogen atom penetrates the Pd surface layer and moves into an internal bulk site [13], we call it the Penetration reaction

$$Pd_s\, H_s + Pd_b \leftrightarrow Pd_s + Pd_b\, H_b$$
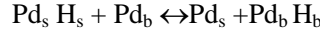
where subscripts s and b represent the surface and bulk states respectively.

The reaction velocity can be expressed in terms of the current density (cd). Defining the sign of net anodic cd and overpotential as positive, we obtain

$$j_V = r\ _sFk_{+V}a_R\theta e^{(1-\delta_V)u\theta}e^{\beta_V fE} - r\ _sFk_{-V}a_O(1-\theta)e^{-\delta_V u\theta}e^{-(1-\beta_V)fE}$$

$$= rj_{0V}\frac{\theta}{\theta_0}e^{(1-\delta_V)u(\theta-\theta_0)}e^{\beta_V f\eta} - rj_{0V}\frac{1-\theta}{1-\theta_0}e^{-\delta_V u(\theta-\theta_0)}e^{-(1-\beta_V)f\eta} \tag{1}$$

$$j_H = r\ _sFk_{+H}a_R f_{H_2,0}(1-\theta)e^{-\delta_H u\theta}e^{\beta_H fE} - r\ _sFk_{-H}a_O\theta e^{(1-\delta_H)u\theta}e^{-(1-\beta_H)fE}$$

$$= rj_{0H}\frac{1-\theta}{1-\theta_0}e^{-\delta_H u(\theta-\theta_0)}e^{\beta_H f\eta} - rj_{0H}\frac{\theta}{\theta_0}e^{(1-\delta_H)u(\theta-\theta_0)}e^{-(1-\beta_H)f\eta} \tag{2}$$

$$j_T = 2r^2\ _s^2Fk_{+T}f_{H_2,0}(1-\theta)^2 e^{-2\delta_T u\theta} - 2r^2\ _s^2Fk_{-T}\theta^2 e^{2(1-\delta_T)u\theta}$$

$$= r^2 j_{0T}\left(\frac{1-\theta}{1-\theta_0}\right)^2 e^{-2\delta_T u(\theta-\theta_0)} - r^2 j_{0T}\left(\frac{\theta}{\theta_0}\right)^2 e^{2(1-\delta_T)u(\theta-\theta_0)} \tag{3}$$

$$j_P = r\ _sFk_{+P}(1-\theta)x(0)e^{-\delta_{Ps}u\theta}e^{(1-\delta_{Pb})u_b x(0)} - r\ _sFk_{-P}\theta[1-x(0)]e^{(1-\delta_{Ps})u\theta}e^{-\delta_{Pb}u_b x(0)}$$

$$= rj_{0P}\frac{1-\theta}{1-\theta_0}\frac{x(0)}{x_0}e^{-\delta_{Ps}u(\theta-\theta_0)}e^{(1-\delta_{Ps})u_b[x(0)-x_0]} - rj_{0P}\frac{\theta}{\theta_0}\frac{1-x(0)}{1-x_0}e^{(1-\delta_{Ps})u(\theta-\theta_0)}e^{-\delta_{Pb}u_b[x(0)-x_0]} \tag{4}$$

Where a_i is the activity of substance i; j_i is the current density of reaction i; j_{0i} is the exchange current density of reaction i (current per real unit area); β_i is the symmetric factor (or transfer coefficient) of electrochemical reaction i; δ_i is the symmetry factor of activation energy of reaction i, we choose all of $\delta_i = 1/2$ in this paper; $f = F/RT = 38.94$ V^{-1} at 298 K; f_{H_2} is the fugacity of H$_2$, $f_{H_2} = p$ when $p \leq$ 200 atm; r is the roughness factor; $u = U/RT$, is the heterogeneity factor of the Frumkin adsorption; $u_b = U_b/RT$, is the non-ideal interaction factor of H in Pd; $x(0)$ is the loading ratio of H in the subsurface of Pd (in the steady state, $x(0) = x$, the loading ratio of H in bulk Pd); Γ_b is the maximum H molar number of available sites per unit volume; Γ_s is the maximum H molar number of available sites per real unit area; η is the overpotential; θ is the fractional surface coverage of hydrogen on Pd; the subscripts V, H, T and P are the Volmer, Heyrovsky, Tafel and Penetration reactions respectively; O, R = H$_3^+$O, H$_2$O respectively in acidic solution and at low overpotential; O, R = H$_2$O, OH$^-$ respectively in basic solution or at high overpotential; +, - and 0 are the anodic, cathodic and equilibria respectively. The other symbols have their usual meanings or are defined obviously according to the relations in Eqs. (1) - (4).

Although there is no charge transfer in the Tafel and Penetration reactions, we still express the reaction velocity as a current density for comparison.

Taking account of the mass balance on the Pd surface, we obtain the time dependence of the

adsorbed hydrogen coverage

$$r_s F \frac{d\theta}{dt} = j_H + j_T + j_P - j_V \tag{5}$$

and the applied cd is given by

$$j = j_V + j_H + rC \frac{d\eta}{dt} \tag{6}$$

where C is the capacity per real unit area.

When the system is under the equilibrium state, from Eqs. (3) and (4), we have

$$f_{H_2,0}^{1/2} = K \frac{x_0}{1-x_0} e^{u_b x_0} \tag{7}$$

where $K = (k_{-T}/k_{+T})^{1/2} k_{+P}/k_{-P}$, this is the H absorption isotherm. When $x_0 \to 0$, this equation simplifies to the Sieverts law, and K is the Sieverts constant.

Under the ambient conditions (298K, 1 atm or higher pressures), the PdH_x is in the β phase, so fitting the β-PdH_x results of Wicke and Nernst [14], we obtain $K = \exp(6.44 - 6031.13/T)$ for H_2, $K = \exp(6.39 - 5741.78/T)$ for D_2, and $u_b = 5409.65/T$ both for H_2 and D_2. In the original paper of Ref. [11], Wicke and Nernst used pressure but not fugacity. Based on the analysis of Baranowski et al. [10], when the pressure rises, the behavior of H_2 will deviate from that of the ideal gas and the pressure p should be replaced by the fugacity f_{H_2}; Baranowski and coworkers verified that Eq. (7) is obeyed very well up to $x \approx 0.99$ [10,15].

From Eq. (7) and the parameters above, we obtain $x_0 = 0.71$ and 0.67 for H_2 and D_2 respectively at 298K, 1 atm.

In this paper we consider only the galvanostatic discharge, this means that after a long enough time electrolysis (the time scale depends on the electrode dimension and the parameters of Eqs. (1)-(6)), the system will approach a steady state (but not the equilibrium state). Under this condition, the Penetration reaction reaches a new equilibrium, i.e. $j_P = 0$, $d\theta/dt = 0$ and $d\eta/dt = 0$.

As usually done, we define the fugacity of H_2 all electrolysis conditions as

$$f_{H_2}^{1/2} = K \frac{x}{1-x} e^{u_b x} \tag{8}$$

Some researchers have predicted [16] that the rigorous expression of the loading ratio in terms of the fugacity (pressure) of H_2 obtained under the gas loading conditions will introduce errors. This is because in the process of high pressure H_2 absorption the chemical potential of PdH_x, includes the contribution of $V_H(p-p_0)$, where V_H is the partial molar volume of hydrogen in PdH_x, p and p_0 are the applied pressure and reference standard pressure respectively. When x approaches 1, the term $V_H(p-p_0)$ will increase and the absorption heat will decrease, the difference between the chemical potential of $Pd|H_2$ under a high pressure gas system and that under an electrolytic system at the same x value will increase. But making use of the measured isotherm results from the $Pd|H_2$ system in the region of interest ($x \leq 0.95$) does not introduce any marked error[1], so we can express the loading ratio in terms of the fugacity and utilize the results from the $Pd|H_2$ system.

Enyo and coworkers [17-19] have established a relationship between the fugacity and η_T, the overpotential of the Tafel step in the Volmer-Tafel (V-T) route

$$-f\eta_T = \frac{1}{2} \ln\left(\frac{f_{H_2}}{f_{H_2,0}}\right) \tag{9}$$

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[1] For example, when $x = 0.95$ D/Pd (in the cold fusion experiment, this value is large enough) the pressure p is about 0.92 GPa [10]; taking $V_D = 0.46$ cm^3 mol^{-1} [12], we obtain $V_D (p - p_0) = 423$ J mol^{-1}, and $V_D (p - p_0) / RT = 50.9$ K/T. Comparing this value of Eq. (7) at 298 K, we notice it is only 3.91% of $\ln K + u_b x$. For H, the required pressure at same x is less than that of D, so the deviation is even smaller.

η_T can be measured in an open-circuit transient experiment [17-19]. Combining Eqs. (7)-(9) and the β-PdH$_x$ parameters, we obtain

$$- f\eta_T = 6.44 - \frac{6031.13}{T/K} + \frac{5409.65x}{T/K} + \ln\frac{x}{1-x} - \tfrac{1}{2}\ln f_{H_2,0} \quad \text{for H} \tag{10}$$

$$- f\eta_T = 6.39 - \frac{5741.78}{T/K} + \frac{5409.65x}{T/K} + \ln\frac{x}{1-x} - \tfrac{1}{2}\ln f_{D_2,0} \quad \text{for D} \tag{11}$$

Based on the two equations, we show the x vs. η_T in Fig. 1.

Eqs. (10) and (11) indicate that gain of η_T will yield x. For different her mechanisms, there are different tendencies of the η_T and x vs. cd; we will discuss them specifically.
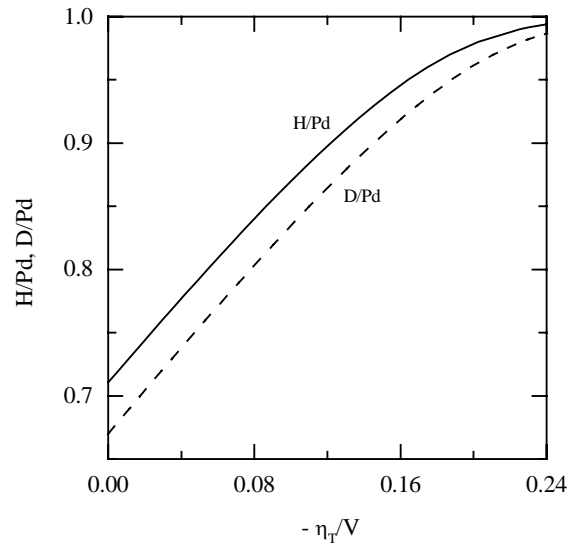

Fig. 1. Dependence of the loading ratio, x = H/Pd (D/Pd), on η_T, the overpotential of the Tafel step. $f_{H_2} = f_{D_2}$ = 1 atm, T = 298 K.

3. Results

For simplicity, we consider the V-T route and the Volmer-Heyrovsky (V-H) route first before taking into account the complete V-H-T route.

3.1. V-T route

As many researchers verified, when the cathodic overpotential is low, the her on the Pd electrode follows the V-T route, and η_T will increase with the cathodic cd. There are two situations for this route: when $j_{0T} < j_{0V}$ (in acidic solution), $\eta_T \approx \eta$ at low overpotential and this corresponds to the Tafel-Horiuti mechanism, the fugacity of H in Pd can be expressed by the Nernst relation, x increases with the cathodic cd; when $j_{0T} \ll j_{0V}$ (in basic solution and at high pressure), $\eta_T = 0$ and the her follows the V-T mechanism at low overpotential, the fugacity remains at the equilibrium value, as well as x. At high overpotential, the her follows the linked V-T mechanism for both situations and η_T/η approaches $2(1-\beta_V)/(3-\beta_V)$ as predicted by Enyo as early as 1973 [20].
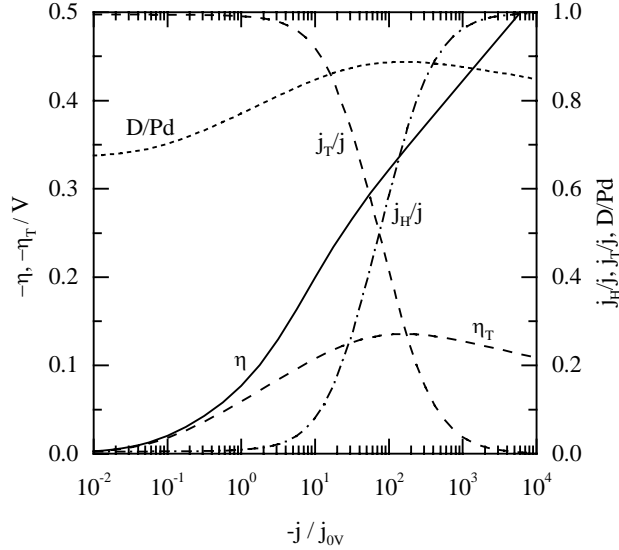
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Fig. 2. Different regions of the her mechanism in the V-H-T route, $j_{0T} < j_{0V} = 0.05$, $j_{0H} / j_{0V} = 2.5 \times 10^{-4}$, $\theta_0 = 0.1$, $u = 10$, $\beta_V = 0.5$, $\beta_H = 0.3$, $r = 1$.

3.2. V-H route

In this situation, the Tafel step is very slow, i.e. $j_T \rightarrow 0$ and $j = 2j_V = 2j_H$. Supposing that $j_{0V} \gg j_{0H}$, we can omit the anodic component of the Heyrovsky reaction, and referring to Eqs. (1), (2) and (9), we have

$$e^{-f\eta_T} = \left(e^{f\eta} + \frac{j_{0H}}{j_{0V}} e^{-\Delta\beta f\eta} \right)^{-1} \tag{12}$$

where $\Delta\beta = \beta_V - \beta_H$. Although there is no Tafel reaction, we can consider the Tafel step to be very slow and the η_T can be applied as well.

At low cathodic overpotential, the first term in the parentheses of the rhs of Eq. (12) is greater than the second one, so $\eta_T = \eta$ and the fugacity of H in Pd can be expressed by the Nernst relation. When the cathodic overpotential increases, the first term in the parentheses of the rhs of Eq. (12) reduces to zero. Hence

$$\eta_T = -\frac{1}{f} \ln \frac{j_{0V}}{j_{0H}} - \Delta\beta\eta \tag{13}$$

As there are different values of $\Delta\beta$, there will be three cases.

When $\Delta\beta < 0$, η_T increases with η, as well as x; when $\Delta\beta = 0$, $\eta_T = -1/f \ln (j_{0V}/j_{0H})$ or $f_{H_2} = f_{H_2,0} (j_{0V} / j_{0H})^2$, and x approaches a limiting value [12, 21]; when $\Delta\beta > 0$, we notice that η_T (same as f_{H_2}, x) will decrease. This means η_T reaches the maximum value at a certain cd. Based on Eqs. (9) and (12), the maximum fugacity is given by

$$\left(\frac{f_{H_2}}{f_{H_2,0}} \right)_{\max} = \left(\frac{j_{0V}}{j_{0H}} \right)^{2/1+\Delta\beta} (\Delta\beta^{1/1+\Delta\beta} + \Delta\beta^{-\Delta\beta/1+\Delta\beta})^{-2} \tag{14}$$

The maximum value decreases with increasing of $\Delta\beta$, and the limiting values of the fugacity are: $f_{H_2,\max} = f_{H_2,0} (j_{0V}/j_{0H})^2$ for $\beta_V = \beta_H = 1/2$ and $f_{H_2,\max} = f_{H_2,0} (j_{0V}/4j_{0H})$ for $\beta_V = 1$, $\beta_H = 0$.
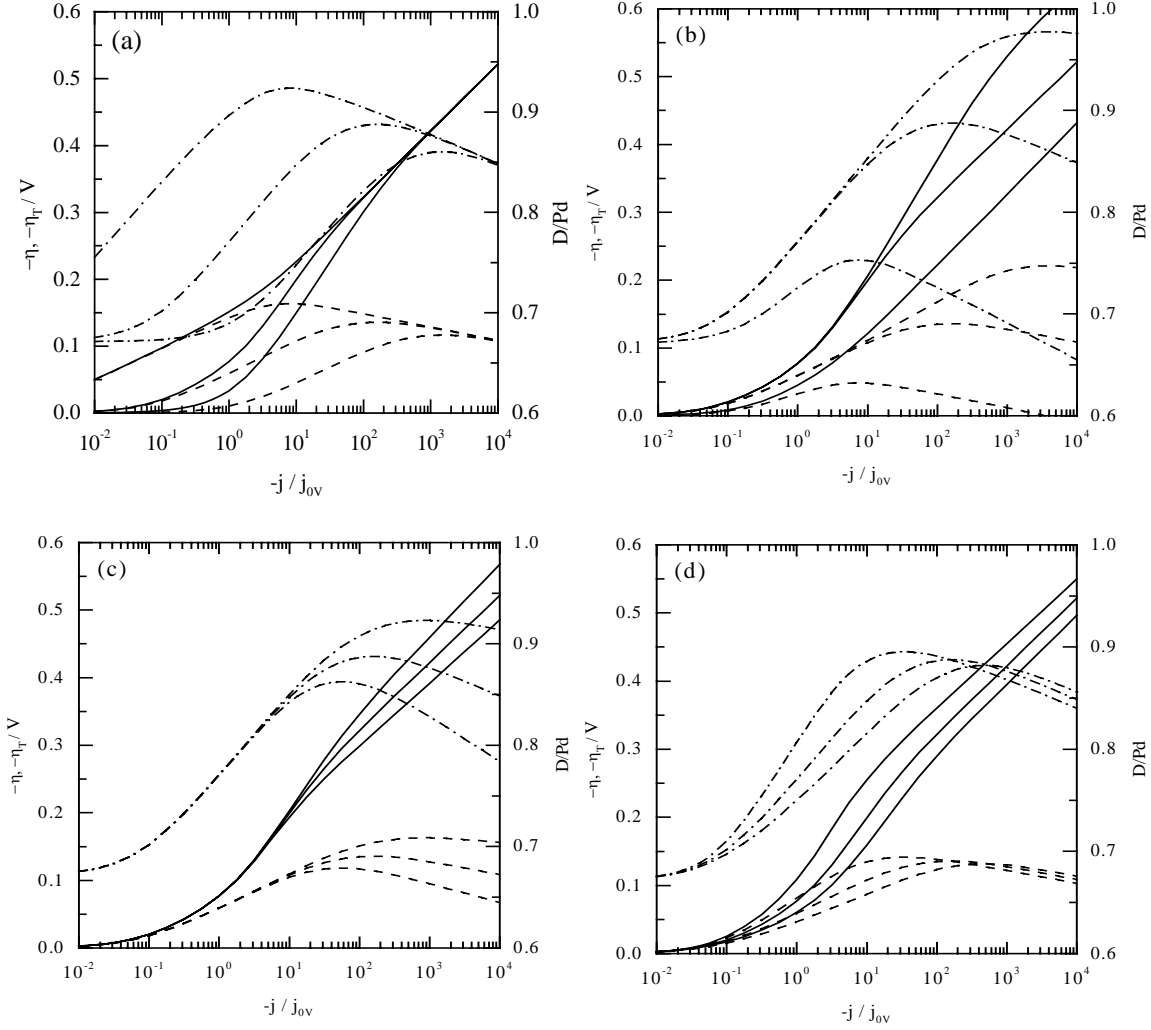
Fig. 3. Effects of different parameters on the loading ratio x = D/Pd (–.–), and related η (———), η_T (—–).
(a) effect of j_{0T}/j_{0V}, j_{0T}/j_{0V} = 2.5 × 10^{-4}, 0.05 and 1 for upper, middle and lower curves; (b) effects of j_{0H}/j_{0V}, j_{0H}/j_{0V} = 1.25 × 10^{-6}, 2.5 × 10^{-4} and 0.05 for upper, middle and lower curves; (c) effects of $\Delta\beta$, $\Delta\beta = \beta_V$ $-\beta_H$, β_H = 0.4, 0.3 and 0.2 for upper, middle and lower curves; (d) effects of θ_0, θ_0 = 0.5, 0.1 and 0.02 for upper, middle and lower curves. Other parameters not emphasized are the same as those of Fig. 2.

3.3. V-H-T route

We assume j_{0V}, $j_{0T} \gg j_{0H}$ and this is held at most times for the Pd electrode. The adsorbed hydrogen produced in the Volmer step is removed by the Tafel step and Heyrovsky step together [12]. At low cathodic overpotential, it is the Tafel step that plays a key role in the hydrogen desorption, the her follows the V-T route as discussed in Section 3.1. As the overpotential (or cd) rises, the share of the Heyrovsky step in the hydrogen removal increases, and the mechanism of the her follows the V-H-T route; at high overpotential, the produced hydrogen is almost removed by the Heyrovsky step, and the V-H route dominates the her as discussed in section 3.2.

Because the factor $\exp(u\theta)$ in the expression of j_T (see Eq. (3)) increases slowly and is limited by θ ($\theta \leq 1$), but the behavior of $\exp(-f\eta)$ in the expression of j_H (see Eq. (2)) is the contrary, the Heyrovsky step will control the hydrogen desorption sooner or later with increasing of overpotential. Bockris et al. supposed the change of mechanism from the V-H route to the V-T route on Pd with rise of cathodic

overpotential [22], but it is readily understood from our discussion that this cannot take place.

The different mechanisms of the her in the different cd regions and related other parameters are shown in Fig. 2 for $j_{0V} > j_{0T} > j_{0H}$ and $\beta_H = 0.3$. There is the Tafel-Horiuti mechanism in the low cd region ($-j/j_{0V} \leq 0.1$) the linked V-T mechanism in $0.1 \leq -j / j_{0V} \leq 10$, the V-H-T mechanism in $10 \leq -j / j_{0V} \leq 1000$ and the V-H route in the high cd region.

In the V-H route region, if $\Delta\beta > 0$, there is the maximum η_T (as well as f_{H2} and x) i.e. After some derivations, we obtain

$$\left(\frac{f_{H_2}}{f_{H_2,0}}\right)^{(3/4)+[1-\beta_V/(2\Delta\beta)]} g(\theta)^{1/2}$$

$$= \left[(1-\beta_V)^{1-\beta_V}(1-\beta_H)^{1-\beta_H}\Delta\beta^{\Delta\beta}\left(\frac{j_{0V}}{j_{0H}}\right)^{1-\beta_V}\left(\frac{j_{0V}}{rj_{0T}}\right)^{\Delta\beta}\right]^{1/\Delta\beta} \tag{15}$$

Where $g(\theta) = \theta(1-\theta)/\theta_0(1-\theta_0)$. Because the first three terms in the parentheses of the rhs of the equation are slowly varying quantities, so the equation simplifies to

$$f_{H_2,max} \approx f_{H_2,0}g(\theta)^{-2\Delta\beta/[3\Delta\beta+2(1-\beta_V)]}\left(\frac{j_{0V}}{j_{0H}}\right)^{4(1-\beta_V)/[3\Delta\beta+2(1-\beta_V)]}\left(\frac{j_{0V}}{rj_{0T}}\right)^{4\Delta\beta/[3\Delta\beta+2(1-\beta_V)]}$$

$$\tag{16}$$

Based on the Eq. (15), there are limiting situations: $f_{H_2,max} = f_{H_2,0}(j_{0V}/j_{0H})^2$ for $\beta_V = \beta_H = 1/2$ and $f_{H_2,max} = f_{H_2,0} g(\theta)^{-2/3}(j_{0V}/rj_{0V})^{4/3}$ for $\beta_V = 1, \beta_H = 0$.

Fig. 3 demonstrates the effects of different parameters in the V-H-T route on the loading ratio of D in Pd.

Fig. 3(a) shows that when j_{0T} increases, η_T and x at the same cd will decrease. It is easy to understand from the discussion of Section 3.1. Some additives such as thiourea (THU) are used to assist H absorption in experiments [8,17,19]; this is attributed to the additives suppressing the Tafel step, so that the j_{0T} decreases and j_{0V}/j_{0T} increases [17], as well as x_{max} from Eq. (15). At the same time, there are some additives (As$_2$O$_3$, etc.) that can suppress the Volmer reaction: the j_{0V}/j_{0T} will decrease and the loading ratio will decrease correspondingly.

Referring to Eq. (15), we find x_{max} is inversely proportional to r. This means that a rough electrode is not favorable for H absorption. Contrary to one's expectation, the plated Pd black can accelerate hydrogen absorption but reduce the amount of hydrogen absorbing; the latter case has been verified in Ref. [7]. Some researchers recommend using smooth electrodes (r is small) in cold fusion experiments which may be due to a similar mechanism [23]. After repeated cycles of absorbing and desorbing of hydrogen, the Pd surface becomes rough and r rises, the loading ratio will decrease at the same time.

The effect of parameter j_{0H} on the maximum loading ratio is illustrated in Fig. 3(b), the less is j_{0H} the larger is x_{max}. If there are additives that can suppress the Heyrovsky reaction, the maximum loading ratio will increase.

The effect of $\Delta\beta$ (Fig. 3(c)) is similar to the discussion of section 3.2, x_{max} decreases by increase of $\Delta\beta$.

The equilibrium surface coverage θ_0 affects the loading ratio too, as shown in Fig. 3(d). The loading ratio at the same cd will increase by increasing θ_0. This can be understood from Eq. (15): if θ_0 is too small, $g(\theta)$ will be large, so x_{max} will be small.

Another factor is the heterogeneity factor u, we have chosen $u = 5$, 10 and 15 ($U = 12.4$ to 37 kJ mol^{-1} correspondingly) and find that there are no notable differences (not shown here). Practically, the

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difference of u is embodied by the value of θ_0: the larger u will result in a small θ_0 and hence a small x_{max}.
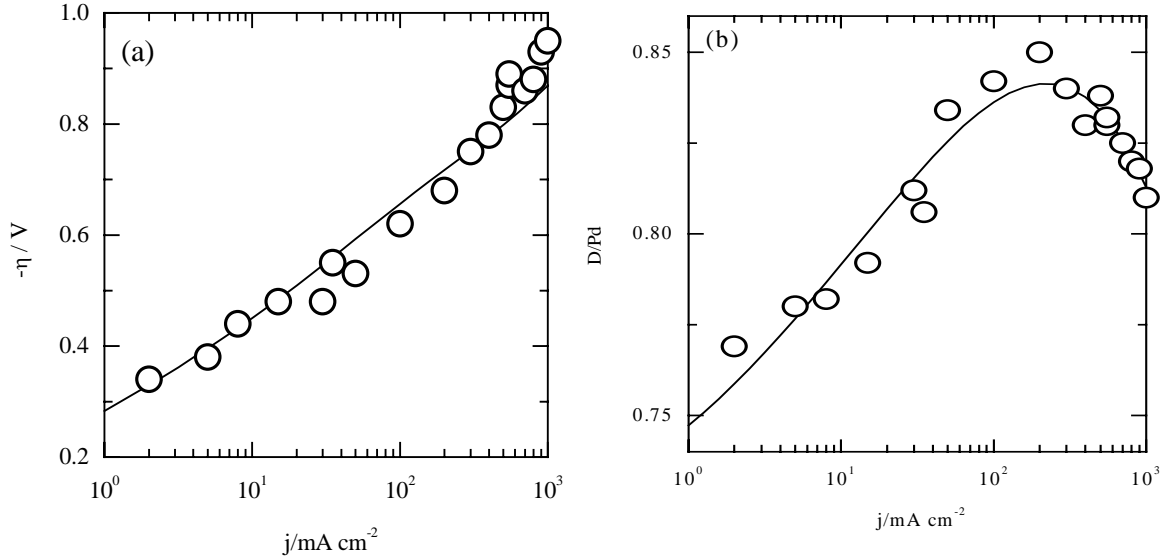

Fig. 4. Comparison of the theory with the experimental results of Akita et al. [8]. $j_{0V} = 6 \times 10^{-3}$ mA cm^{-2}, j_{0T} = 0.5mA cm^{-2}, $j_{0H} = 6 \times 10^{-6}$ mA cm^{-2}, $\theta_0 = 0.01$, $u = 10$, $\beta_V = 0.5 - 0.2\eta$, $\beta_H = 0.5 - 0.05\ \eta$, $f_{D_2,0} = 6$ atm, T = 283 K, $r = 1$.

4. Comparison with experimental results

In order to test the validity of the present treatment, we compared the numerical results with experimental data. There is much evidence indication the existence of maximum loading ratios [7,8]. We chose one that had enough data for our analysis [8]; this is shown in Fig. 4. We find that the shapes of the curves are similar to the previous ones, and the numerical results give good agreement with those of experiment.

5. Conclusions

The increasing of loading ratio of H in Pd and other metals interested (e.g. Ti, Ni, etc.) is very important in cold fusion experiments, so many methods are adopted for this purpose. One of them is raising the cathodic overpotential (or the current density), but according to our discussion there is a change of mechanism from the V-T route to the V-H route when the current density rises, and there exists a maximum loading ratio at a certain overpotential (or current density) when the symmetry factor of the Heyrovsky step is less than that of Volmer step. The numerical results are consistent with those of the experiment of Akita et al. [8].

On the other hand, for increasing the loading ratio, there are some other methods that can be used: for example, choosing a smooth electrode, raising the pressure, reducing the rate of the hydrogen desorbing step by adding surfactants, etc.

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