

Hydrogen/Deuterium Concentration in Pd under Cathodic Polarization

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ABSTRACT

Effective hydrogen pressure at hydrogen evolving cathode is discussed in connection with the mechanism of the hydrogen electrode reaction. A Nernst type expression involving hydrogen overpotential is not generally applicable. Experimental results on Pd and Pd-Ag alloy cathodes with and without addition of catalytic poison are presented. The highest pressure observed was ca. 10^6 atm at 0.25 A cm^{-2} , 30°C .

1. INTRODUCTION

The high reducing power of hydrogen evolving cathode in aqueous solution has been often quoted by the term *Nascent hydrogen*. An increasing attention is now paid on this phenomenon as the high activity of hydrogen produced by the hydrogen electrode reaction (HER) on Pd, or the hydrogen/deuterium concentration derived thereof in Pd, is believed to be one of the most vital factors involved in the alleged cold fusion.

The concentration of hydrogen in metal/alloy specimen should in general be determined by the pressure of hydrogen to which it is exposed, through the hydrogen absorption isotherm of Pd-H system. Alternatively, at the electrode at which HER is taking place, one may think of a hypothetical hydrogen pressure (which may be identified with the cavity pressure¹⁾) and the latter should in some way be related to the hydrogen overpotential. It is believed that hydrogen entry into metal takes place *via* hydrogen adatom H(a) which is the intermediate of the HER.^{1,2)} In other words, evaluation of the hypothetical hydrogen pressure may be reduced to the evaluation of chemical potential of H(a) during actual

progress of HER: Twice of the latter can be equated with that of the hypothetical hydrogen gas.

As demonstrated earlier³⁻⁶⁾, a Nernst-type expression to correlate the equivalent hydrogen pressure, \bar{P}_{H_2} , to the overpotential, η , as in Eqn.(1),

$$-\eta = (RT/2F) \ln \bar{P}_{H_2} / P_{H_2,eq} \quad (1)$$

is not generally justifiable. Thus, DeLuccia, Yamakawa and Nanis⁷⁾ carried out combined experimental observations of hydrogen permeation rates through a mild steel membrane electrode when its one face is exposed to gaseous hydrogen or alternatively to an electrochemical system where HER takes place. Experimentally observed relationship between such hydrogen pressures and overpotential values so as to yield the same rates of hydrogen permeation, reproduced in Fig.1(A), indicated that the corresponding hydrogen pressure was far lower than expected from a Nernst-type relation applied to the overpotential (dotted line). This is a clear indication that a revision of the model is necessary. A quantitative description will be discussed below.

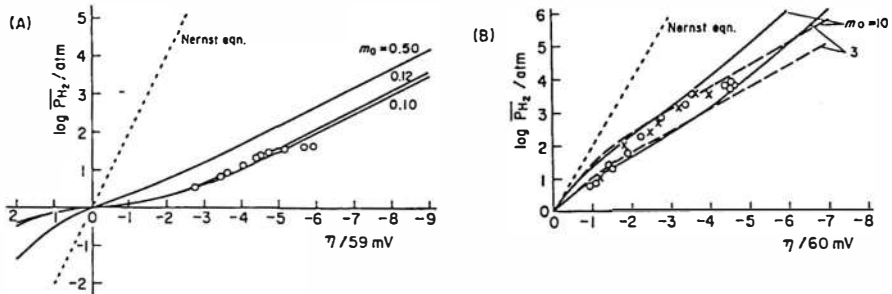


Fig.1. Equivalent hydrogen pressure vs. hydrogen overpotential relation. In both figures, the dotted lines represent Eqn.(1), namely, a Nernst equation applied to η .

(A) On mild steel electrode observed by DeLuccia *et al.*⁷⁾ at 25 °C. Solid lines are calculated for the Volmer-Tafel reaction route on the basis of the Langmuir isotherm with $m_0 = 0.50, 0.12$ (the best fit case) and 0.10.

(B) On Pd foil electrode⁵⁾ at 30 °C. Solid lines (Langmuir isotherm) and broken lines (Temkin isotherm) are calculated with $m_0 = 10$ or 3.

2. SHORT SUMMARY OF ELECTRODE KINETICS

(1) Basic Kinetic Equations

Only an outline of the analysis⁶⁾ will be presented below. Basic equations involved are;

(i) the relationship which connects the Gibbs free energy decrease $-\Delta G$ (the reaction affinity) of the overall reaction, with $-\Delta g_s$, that shared by the consecutive elementary step s ,

$$-\Delta G = nF\eta = \sum_s \nu_s (-\Delta g_s) \quad (2)$$

where ν_s is the stoichiometric number of step s .

(ii) that between the step affinity and the forward and backward rates, v_{+s} and v_{-s} , of that step,

$$-\Delta g_s = -RT \ln v_{+s} / v_{-s} \quad (3)$$

(iii) that connecting the forward-to-backward rate ratio of the overall reaction V_+/V_- , and such ratios of elementary steps,

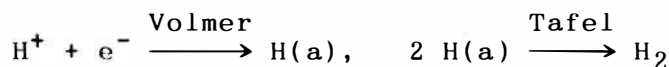
$$V_+/V_- = \prod_s v_{+s} / v_{-s} \quad (4)$$

(iv) a steady-state relationship connecting the overall net rate and step net rates,

$$V_+ - V_- = (v_{+s} - v_{-s}) / \nu_s \quad (5)$$

(2) The case of Hydrogen Electrode Reaction

As substantiated⁶⁾ well, HER on many electrocatalytically active metals obey the Volmer-Tafel reaction route,



In this case, Eqn.(2) is reduced to,

$$-\Delta G = 2F\eta = - (2\Delta g_v + \Delta g_T) \quad (6)$$

It is convenient, as will be seen later, to define the affinity distribution parameter m as,

$$m \equiv \Delta g_T / \Delta g_v \quad (7)$$

The function for m can be derived as below: From Eqn.(5) for these two steps,

$$\nu_{-v} (v_{+v} / v_{-v} - 1) / 2 = \nu_{-T} (v_{+T} / v_{-T} - 1)$$

Hence, giving appropriate rate expressions⁶⁾ for v_{-v} and v_{-T} and using Eqn.(3) for v_{+v}/v_{-v} , etc. which involves $-\Delta g_v$, etc., an equation which involves m and η may be derived, although in a transcendental form. Thence, m at any values of η can be computed, provided that appropriate rate expressions for v_{-v} , etc, together with other kinetic parameters are given.

It can be shown that m near equilibrium, denoted by

m_0 , is related to the exchange current densities of the two elementary steps as,

$$m_0 = i_{0v} / i_{0T} \quad (8)$$

This can be evaluated experimentally e.g. from transient measurements, isotope tracer experiments⁸⁾, etc.

3. QUANTITATIVE TREATMENT OF THE EQUIVALENT HYDROGEN PRESSURE

The equivalent hydrogen pressure can be formulated as follows: If no unique rate-determining step (RDS) exists, or the reaction is kinetically under mixed-control, then the chemical potential, $\mu(H)$, of H(a) in steady-state should be determined by a balance between Volmer and Tafel steps, and the pressure would be lower than that given by Eqn.(1). As $-\Delta g_T$ is given on the one hand by the following relation which is readily derived from Eqns.(6) and (7),

$$-\Delta g_T = 2mF\eta / (m + 2) \quad (9)$$

and related, on the other hand, to $\mu(H_2)$ as,

$$-\Delta g_T = 2\mu(H) - \mu(H_2) = \mu(H_2) - \mu(H_2) \quad (10)$$

it is straight-forward to calculate \bar{P}_{H_2} from m and η .

The above-quoted data on Fe can be quantitatively accounted for by choosing a suitable value for m_0 ; the value found in this particular case was ca. 0.12. No independent datum is available for m_0 for Fe, but the value appears to be reasonable if one refers to the datum, ca. 1 for Ni, which has been obtained from the isotope tracer work⁸⁾, and accepts a similarity between HER kinetics on these metals.

4. ANALYSIS OF OVERPOTENTIAL TRANSIENTS

(1) Basic Transient Equations

Direct experimental evaluation of $\mu(H)$ is not necessarily easy but it can be made conveniently on Pd, or perhaps on other hydrogen absorbing metals/alloys, through the observation of overpotential transients, due to the existence of a large pool for H(a) in the form of absorbed hydrogen, namely, H(Pd). A general equation to describe overpotential transient with time for the Volmer-Tafel route may be written, based on the mass-balance condition with respect to electric charge, as,⁶⁾

$$C \frac{d\eta}{dt} = i - i_{0v} \{ \gamma_{\uparrow} e^{\beta f\eta} - \gamma_{\downarrow} e^{-(1-\beta)f\eta} \} \quad (11)$$

with, if one accepts the Frumkin-Temkin isotherm for

hydrogen adsorption,

$$\gamma_{\uparrow} = \frac{\theta}{\theta_0} \exp\{ \delta u (\theta - \theta_0) \} \quad (12)$$

$$\text{and } \gamma_{\downarrow} = \frac{1-\theta}{1-\theta_0} \exp\{ -(1-\delta)u(\theta - \theta_0) \} \quad (13)$$

where C is the double layer capacitance of the electrode, i_{0v} is the exchange current density of Volmer step, θ is the surface coverage with H(a), $u \equiv U/RT$ in which U is the interaction energy parameter in the adsorption isotherm, δ ($0 < \delta < 1$) is a constant, β is the symmetry factor, $f \equiv F/RT$, and those with subscript 0 indicate quantities at equilibrium of HER.

(2) Overpotential Decay Transients

Upon interruption of the polarization current after a state of steady polarization is reached, the overpotential initially decays rapidly at the expense of the electric charge accumulated on the electrode through the Volmer step. This decay ends within a very short time, with the time constant $\tau \approx 10^{-3}$ s for Pd in acidic solutions which is determined by values of C and effective polarization resistance R_v (which is overpotential-dependent) of the Volmer process, namely, $\tau = R_v C$.

The decay of η practically stops when the electrode potential reached the point which corresponds to the value practically fixed by the level of $\mu(H)$ that was realized during the steady-state polarization, namely, immediately before the moment of the current interruption. At that point, effectively, $C(d\eta/dt)$ becomes 0 in Eqn.(11). With $i = 0$ (current is off), the value of η at that moment, called⁹⁾ η_2' , is given as,

$$\eta_2' = (RT/F) \ln \gamma \quad (14)$$

where $\gamma \equiv \gamma_{\uparrow} / \gamma_{\downarrow}$. This Nernst-type relation may be accepted because, at this moment after the double layer discharge, Volmer reaction should practically be in quasi-equilibrium.

It can readily be seen from Eqns.(12) and (13) that γ is equal to the variation of activity $a(H)$ of H(a) as

$$\gamma = a(H) / a(H)_0 \quad (15)$$

It is clear, referring to Eqns.(10) and (14), that

$$-\eta_2' = (RT/2F) \ln P_{H_2} / \bar{P}_{H_2,eq} \quad (16)$$

This is of a similar form with, but definitely different from, Eqn.(1). Thus, Eqn.(1) should hold if $\eta_2' = \eta$ (rate-determining Tafel mechanism) but should be lower than that if $\eta_2' < \eta$ or no growth with η if $\eta_2' = 0$ (rate-determining Volmer mechanism).

The overpotential decay transients are very informative: First, the affinity value allotted to Tafel step is given by η_2' and second, the initial rapid portion which is allotted to Volmer step is then obtained ($\eta_1' + \eta_2' = \eta$). Accordingly, one can directly observe m on Pd HER at any value of η , because $-2\Delta g_v = F\eta_1'$ and $-\Delta g_T = F\eta_2'$, and hence the equivalent hydrogen pressure.

5. EXPERIMENTAL RESULTS ON PALLADIUM ELECTRODE

(1) Decay Transients on Pd

An extensive work on the overpotential transients has been carried out on Pd.³⁻⁵) Thanks to its high ability of absorption of hydrogen, galvanostatic overpotential rise and decay transients on Pd hydrogen electrode are clearly separated into two portions each, one with the time constant of $ca. 10^{-3}s$ (in acidic solutions) and the other $ca. 10^3s$ (or longer) for $\sim 10\mu m$ (or thicker) Pd foil.

Experimentally, η_2' was clearly defined on the decay transients as shown in Fig.2, (A) on Pd electrode in H_2SO_4 and (B) on $Pd_{60}Ag_{40}$ alloy electrode in $H_2SO_4 +$ thiourea; this also indicates that diffusion (and the ingress/egress rate of hydrogen) is sufficiently rapid in those cases.

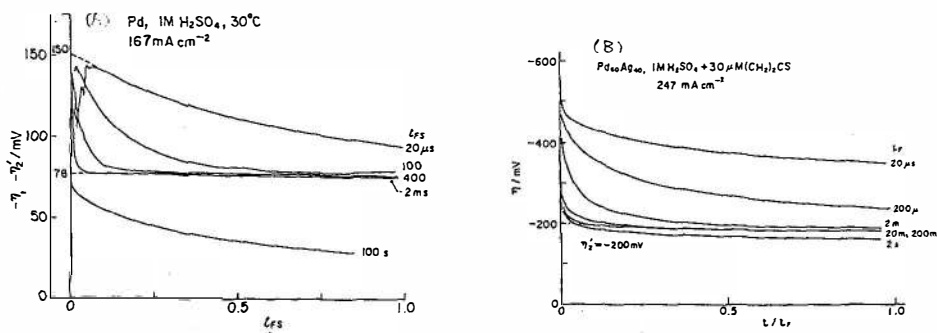
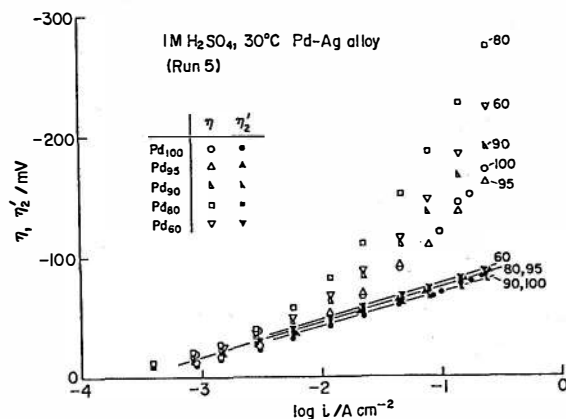


Fig.2. Typical galvanostatic overpotential decay transients at 30 °C on: (A) Pd electrode in 1M H_2SO_4 , (B) Pd-Ag alloy electrode in 1M $H_2SO_4 + 30 \mu M (CH_2)_2CS$, 30 °C. Abscissa is given in unit of full-scale time, t_{FS} , assigned to each curves.

Tafel plots of η and η_2' on Pd and Pd-Ag alloy electrodes in 1M H_2SO_4 are plotted in Fig.3. It may be seen that no systematic influence of alloy composition upon η was noted; the electrocatalytic activity was, as usual, strongly influenced by its surface condition, etc.. On the other hand, η_2' was much more stable and practically independent of the alloy composition.

Fig.3. Tafel Plots of η and the slowly decaying overpotential component η_2' on Pd and Pd-Ag alloy electrodes. $1M H_2SO_4$, $30^\circ C$.



Typical results of evaluation of \bar{P}_{H_2} from η_2' on Pd in $1M H_2SO_4$ are shown above in Fig.1(B). The data are not at all in agreement with Eqn.(1). On the other hand, it is noteworthy that they are satisfactorily interpreted by the theoretical curves calculated with m_0 of 3~10, which is observed from the overpotential decay transient, as seen by solid lines calculated on the basis of Langmuir adsorption isotherm, or dotted lines on the Temkin isotherm with U arbitrarily taken as 5 ($u = 5RT$ in $U \equiv u/RT$).

(2) Effects of Catalytic Poisons

A numerous investigations have been carried out on poisons in catalysis, but not much is known as to on which elementary steps they are exerting effects. Such effects of poisons on elementary steps are clearly observable on Pd. For example, tetrabutylammonium ion was effective to retard Volmer step. On the other hand, thiourea was effective in retarding Tafel step. It is evident from the discussion presented above that the latter may be an effective additive to Pd HER system if one is to increase hydrogen in Pd. Other additives, I^- , CN^- , SCN^- , As_2O_3 , etc. were found to have intermediate characters, exerting comparable degrees of poisoning effects on both Volmer and Tafel steps. It may be interesting to investigate other additives and accumulate information on their poisoning effects on various elementary steps.

Similar results in $1M H_2SO_4$ with the addition of 10 or 30 μM $(CH_2)_2CS$ are plotted in Figs.4 and 5 for Pd and Pd₈₀Ag₂₀ electrodes, respectively. It is evident that overpotential values, especially η_2' , are much larger in the presence of thiourea: The latter reaches the value

as high as ca. -200 mV at 0.25 A cm^{-2} and this value corresponds to the equivalent hydrogen pressure of some 10^6 atm according to Eqn.(16). This level of hydrogen pressure would correspond to the atomic ratio H/Pd of ca. 1.0 at 30°C according to an empirical relation,

$$\text{H/Pd} = 0.70 + 0.05 \log P_{\text{H}_2}/\text{atm} \quad (30^\circ\text{C}) \quad (17)$$

which may be derived on the basis of the absorption isotherm reported by Frieske and Wicke¹⁰⁾.

Attention was paid so far to the catalytic effects on the elementary steps of HER, but there may be similar effects on the mobility of H(a), in particular on the ingress/egress of hydrogen at the surface-to-bulk layer. In this connection, CN^- ¹¹⁾ and CO ¹²⁾ were reported to retard such steps: Systematic studies may lead us to have more detailed picture of the effects of poisons on various catalytic reactions.

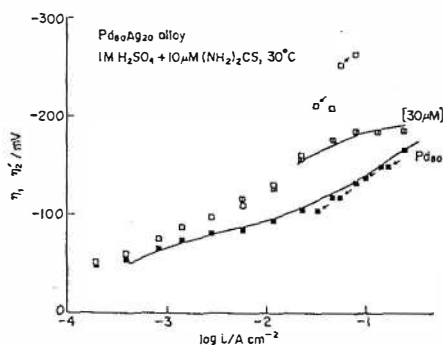
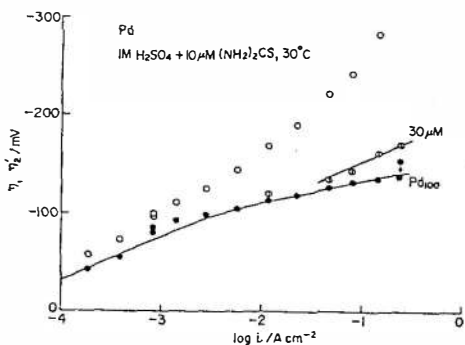


Fig.4(left). Tafel Plots of η (open symbols) and the slowly decaying overpotential component η_2' (full or half closed symbols) on Pd electrode. $1 \text{ M H}_2\text{SO}_4 + 10$ (and 30) $\mu\text{M (CH}_2)_2\text{CS}$, 30°C .

Fig.5(right). Tafel Plots of η (open symbols) and the slowly decaying overpotential component η_2' (full or half closed symbols) on Pd₈₀Ag₂₀ alloy electrode. $1 \text{ M H}_2\text{SO}_4 + 10$ (and 30) $\mu\text{M (CH}_2)_2\text{CS}$, 30°C .

(3) Characterization of η_2' by Anodic Stripping

It seems important to confirm if the electrode potential at and after the moment of observation of η_2' is indeed maintained because of high concentration of H(a), and hence of H(Pd). Characterization in this respect was conducted by application of an anodic stripping charge and observing the response of the electrode potential.

The amount of anodic charge to be applied should be much larger than that required to remove a monolayer of H(a). If the electrode potential is locked up *e.g.* by any unknown adsorbed substance, then the potential after the anodic stripping would be anywhere far apart from the potential at which the stripping was started. On the other hand, if H(a) is supplied by rapid ingress/egress of H/Pd, then the potential after the stripping should quickly recover the original value.

Such tests are shown in Fig.6. Successive anodic pulses with the charge up to 114 mC cm^{-2} (curves 1-4) were applied after observing η_2' (ca. -135 mV in this example), but in each time the original electrode potentials were restored. Only after application of 972 mC cm^{-2} (curve 5), ca. 15 mV of potential shift was noted. On the other hand, the amount of electricity needed to remove monolayer of H(a) should be roughly 0.5 mC cm^{-2} (roughness factor was usually ca. 2). Namely, the electrode restores its negative potential even after application of anodic stripping charges that correspond to almost 10^3 times of the charge which corresponds to a monolayer of H(a). This seems to be a sufficient evidence to prove that the electrode after cathodization as described above indeed contains hydrogen of the amount evaluated from η_2' .

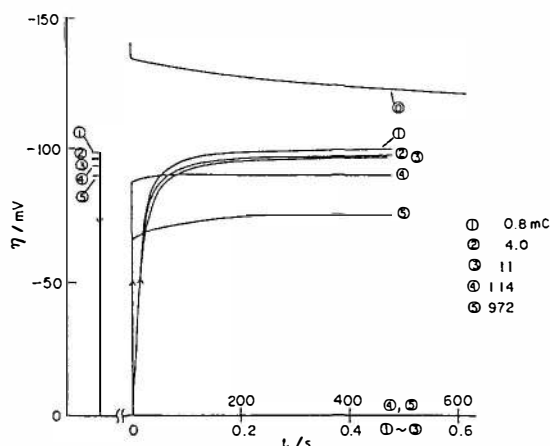


Fig.6. Electrode potential decay (curve 0) after observation of η_2' (ca. -135 mV) and change of electrode potential after application of various amounts of anodic stripping charge. 0.8 mC cm^{-2} (curve 1), 4.0 (2), 11 (3), 114 (4), and 972 (5). Pd₉₀Ag₁₀ electrode, $1 \text{ M H}_2\text{SO}_4$, $30 \text{ }^\circ\text{C}$.

The quick recovery ($<0.1s$) of potential after the application of anodic stripping charge in Fig.6 indicates that the rate of recovery of hydrogen by the outward diffusion from the bulk of Pd as well as by the egress process at the surface zone is sufficiently rapid as compared with that of escape of hydrogen by the Tafel step. This may be an evidence in support of the model that hydrogen is confined in Pd because of slowness of the Tafel step, and hence augmentation of the concentration is made possible by the use of catalytic poisons that retard that rate: Otherwise, the rate of escape of hydrogen should be too rapid during the electrolysis that no significant accumulation of hydrogen up to such a high level as reported above by cathodization may be possible.

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