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# SIGNIFICANCE OF THE SURFACE POTENTIAL IN CHARGE TRANSFER ELECTRODE KINETICS

By

M. ENYO*)

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**Abstract**

Significance of the surface potential change, which may be caused by the accumulation of reaction intermediates on the electrode, in rate equations for charge transfer electrode processes was discussed. It was shown that exclusion of the term, proposed by Matsuda, introduces difficulties in interpreting experimental evidences.

## Introduction

The electrode potential $\phi$ consists of two components,[1] the electrostatic part (the Volta potential) $\psi$, and the surface potential $\chi$. In electrode kinetics for charge-transfer processes, exponential terms in $\phi$ directly appear in the rate expression. On the other hand, Matsuda[2~4] proposed that $\psi$ should be only the quantity to be used in those terms. It is intended in this paper to discuss those uses on the basis of experimental observations.

### § 1. *Basic Relations*

The forward and backward uni-directional rates, $v_{+s}$ and $v_{-s}$, of elementary step $s$ are respectively given by

$$v_{+s} = k_{+s} \exp\{-\Delta g^*_{+s}/RT\} \quad (1)$$

$$v_{-s} = k_{-s} \exp\{-\Delta g^*_{-s}/RT\} \quad (2)$$

where $k$'s are constants and $\Delta g^*$'s are free energies of activation. Accordingly,

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

where

$$-\Delta g_s = -(\Delta g^*_{+s} - \Delta g^*_{-s}) \quad (4)$$

is the free energy decrease (the chemical affinity) of the elementary step;

*) The Research Institute for Catalysis, Hokkaido University, Sapporo 060, Japan

$k_{+s}/k_{-s}$ is unity since $v_{+s}/v_{-s}=1$ when $\Delta g_s=0$. Evidently, $-\Delta g_s$ is uniquely determined by the nature of step $s$ and expressions of the activation free energy terms in rate expressions must conform to eqn. (4).

It is hoped in the present paper to investigate significance of the surface potential term in kinetic equations when step concerned is a charge-transfer reaction, *e.g.* the Volmer reaction involving hydrogen adatom H(a),

$$H_2O+H(a)\longleftrightarrow H_3O^+ +e \tag{5}$$

or sodium adatom Na(a),[2]

$$Na(a)\longleftrightarrow Na^+ +e \tag{6}$$

The free energy decrease of reaction (5) is given as*)

$$-\Delta g_V=\mu_{H_2O}+\mu_{H(a)}-\mu_{H_3O^+}-\mu_e \tag{7}$$

where $\mu$'s are chemical potentials (or electrochemical potentials if the species is electrically charged). At equilibrium, denoted by subscript o,

$$0=\mu_{H_2O}+\mu_{H(a),o}-\mu_{H_3O^+}-\mu_{e,o}$$

where $\mu_{H_2O}$ and $\mu_{H_3O^+}$ are assumed to be constant irrespective of irreversible occurrence of the reaction. Hence, combining this with eqn. (7), we have

$$-\Delta g_V=RT\ln\gamma_H+F\eta \tag{8}$$

where

$$\eta=-(\mu_e-\mu_{e,o})/F \tag{9}$$

is the overpotential, *i.e.* shift of the electrode potential from its value at equilibrium, and $\gamma_H$ represents variation of $a_H$, the activity of H(a),

$$\gamma_H\equiv a_H/a_{H,o} \tag{10}$$

Application of eqn. (4) to (8) indicates

$$-\Delta g^*_{+V}=RT\ln\gamma_\uparrow+\beta F\eta \tag{11}$$

$$-\Delta g^*_{-V}=RT\ln\gamma_\downarrow-(1-\beta)F\eta \tag{12}$$

where

$$\gamma_H=\gamma_\uparrow/\gamma_\downarrow \tag{13}$$

and $\beta$ is the symmetry factor. The following discussion will be concentrated on further developments of the terms which involve the overpotential in

*) The following discussion is performed only for reaction (5). Analogous argument can be developed for reaction (6).

those equations. Division of $\gamma_H$ into $\gamma_\uparrow$ and $\gamma_\downarrow$ was discussed elsewhere.[5] Precise expressions of these quantities are not essential in the present discussion; they may be expressed as[5,6]

$$\gamma_H = \frac{\theta}{\theta_0}\frac{1-\theta_0}{1-\theta}\exp\left\{2u(\theta-\theta_0)\right\} \tag{14}$$

$$\gamma_\uparrow = \frac{\theta}{\theta_0}\exp\left\{u(\theta-\theta_0)\right\}, \qquad \gamma_\downarrow = \frac{1-\theta}{1-\theta_0}\exp\left\{-u(\theta-\theta_0)\right\} \tag{15}$$

where $\theta$ denotes surface coverage with H(a), and $u$ is the interaction/heterogeneity parameter.

## § 2. *Volta potential and Surface Potential*

Variation in electrode potential is caused by changes in $\phi$ and $\chi$. Accordingly, we may write,

$$\eta = \Delta\phi + \Delta\chi \tag{16}$$

where the reference value of each quantity was taken at equilibrium of the overall reaction. Hence, eqn. (8) becomes

$$-\Delta g_V = RT\ln\gamma_H + F(\Delta\phi + \Delta\chi) \tag{17}$$

In order to explain constancy of the time constant of the electron transfer step of the hydrogen electrode reaction with increase of overpotential,[2] Matsuda[2~4] considered on the basis of the thermodynamical electrode potential theory developed by Frumkin and his school[7] that the following relation holds when $\gamma_H$ varies under irreversible electrolysis

$$RT\ln\gamma_H = -F\Delta\chi \tag{18}$$

and accordingly porposed that $\Delta\phi$ is only the term which gives rise to the affinity for the charge transfer processes. Thus, for the Volmer reaction he writes,

$$-\Delta g_V = F\Delta\phi \tag{19}$$

Equation (18), however, does not appear to be reasonable since it implies that the surface metal-H(a) dipole has its positive end on H(a) as $\gamma_H > 1$ is required under cathodic polarization. Such a general and direct implication of the reaction kinetics to the sign of the dipole is physically not very likely, and indeed it is reported that the dipole may take both positive and negative signs depending on the electrode potential.[8]

Experimental test of importance of $\Delta\chi$ in electrode reaction kinetics is not frequently feasible and in fact, in many cases, $\chi$ is presumed to remain

constant independent of the application of polarization current because of assumed rapid step which removes the reaction intermediate, *e. g.*, $2H(a) \rightarrow H_2$. In other cases in which it may change, no simple technique seems to be available to detect the change. The following example of the Pd hydrogen electrode appeared to be an excellent system in this respect as it provides information concerning the influence of change of $\theta$ upon kinetics of the constituent elementary steps.

§ 3. *Transient Behaviors of the Pd Hydrogen Electrode*

The hydrogen electrode reaction on Pd takes place through the Tafel-Volmer reaction route,[5,9]

$$H_2 \underset{\text{Tafel}}{\overset{}{\rightleftharpoons}} 2H(a), \qquad H(a)+H_2O \underset{\text{Volmer}}{\overset{}{\rightleftharpoons}} H_3O^+ + e$$

Accordingly, we have eqn. (8) for $-\Delta g_V$ and the following equation for $-\Delta g_T$,

$$-\Delta g_T = -2RT \ln \gamma_H \tag{20}$$

The overall free energy decrease $-\Delta G$ is naturally given as,

$$-\Delta G = -(\Delta g_T + 2\Delta g_V) = 2F\eta \tag{21}$$

Overpotential decay transient on Pd hydrogen electrode exhibits two distinct components, one with high decay rate ($\eta_1'$) and the other with very

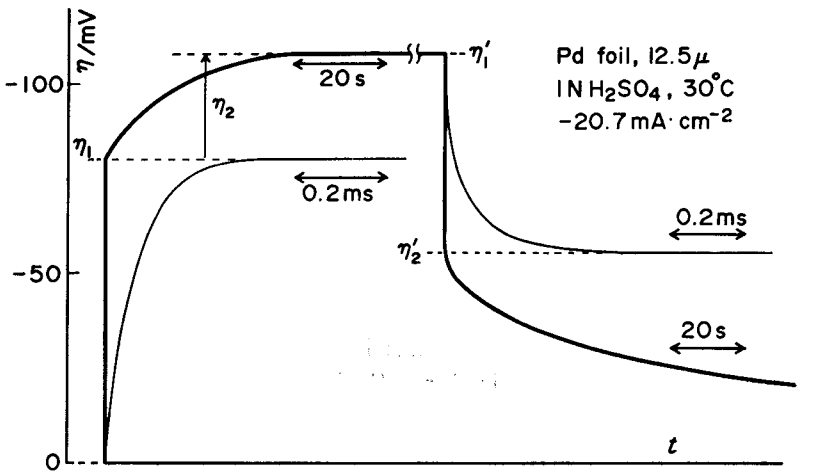


**Fig. 1.** Schematic presentation of galvanostatic overpotential rise and decay transients on Pd hydrogen electrode and the component overpotentials Thin solid curves show transients with expanded time scale.

slow rate ($\eta_2'$) (Fig. 1). It has been well established[5] that $\eta_1'$ represents the overpotential component for the Volmer reaction

$$F\eta_1' = -\Delta g_V = RT \ln \gamma_{H,\infty} + F\eta_\infty \tag{22}$$

and $\eta_2'$ that for the Tafel reaction,

$$2F\eta_2' = -\Delta g_T = -2\,RT \ln \gamma_{H,\infty} \tag{23}$$

where subscript $\infty$ is used to indicate that the quantity concerned is at the steady-state of polarization before the current interruption.

(A) The case of $\Delta g_V$ given by eqn. (22)

An ordinary way of analysis will be presented first. The overpotential transient may be given by the following simultaneous equations,[5]

$$C\frac{d\eta}{dt} = i - i_{0V}\{\gamma_\uparrow e^{\beta f\eta} - \gamma_\downarrow e^{-(1-\beta)f\eta}\} \tag{24}$$

$$Q\frac{d\theta}{dt} = i_{0T}\{\gamma_\downarrow^2 - \gamma_\uparrow^2\} - i_{0V}\{\gamma_\uparrow e^{\beta f\eta} - \gamma_\downarrow e^{-(1-\beta)f\eta}\} \tag{25}$$

where $f \equiv F/RT$, $i$ is the polarization c. d., $C$ is the double layer capacitance, and $Q$ is the amount of electricity needed to change $\theta$ from zero to unity; this quantity in the case of Pd electrode is far larger than that which corresponds to the monolayer coverage of H(a) because of simultaneous absorption of hydrogen by Pd metal. During the steady-state of polarization, obviously $d\eta/dt = 0$. Hence, the following relation determines the steady-state current *vs.* overpotential relation,

$$i = i_{0V}\{\gamma_{\uparrow,\infty} e^{\beta f\eta_\infty} - \gamma_{\downarrow,\infty} e^{-(1-\beta)f\eta_\infty}\} \tag{26}$$

The overpotential component $\eta_2'$ on the decay transient curve is given from eqn. (24) under the condition that $\gamma_\uparrow$ and $\gamma_\downarrow$ are practivally frozen respectively at their values at the steady-state of the polarization, since very small variation of $\theta$ is expected on Pd during initial short duration ($<10^{-2}$ sec). On the other hand, we may take with good approximation $d\eta/dt \simeq 0$ at the moment $\eta$ reached $\eta_2'$ (*cf.* Fig. 1). Thus, with $i=0$ for the decay,

$$0 = i_{0V}\{\gamma_{\uparrow,\infty} e^{\beta f\eta_2'} - \gamma_{\downarrow,\infty} e^{-(1-\beta)f\eta_2'}\} \tag{27}*$$

or referring to eqn. (13),

$$-f\eta_2' = \ln \gamma_{\uparrow,\infty}/\gamma_{\downarrow,\infty} = \ln \gamma_{H,\infty} \tag{28}$$

*) In reality, variation of $\gamma_\uparrow$ and $\gamma_\downarrow$ during the initial period was not perfectly negligible. This is due possibly to a finite rate of penetration of hydrogen through the metal surface region. In the present discussion, one may simply suppose the case that the penetration has an infinite rate at the surface of semi-infinite slab of Pd.

Experimental evaluation of $\eta_2'$ (and hence $\gamma_{H,\infty}$), relevance of $\gamma_{H,\infty}$ to hydrogen sorption into Pd electrode, *etc.* have been satisfactorily conducted on the basis of eqn. (28), as reported elsewhere.[9]

(B) $\Delta g_V = F\Delta\phi$

If $\Delta\phi$ alone determines the affinity of the Volmer process, we may write instead of eqn. (24),

$$C\frac{d\phi}{dt} = i - i_{0V}\{e^{\beta f\Delta\phi} - e^{-(1-\beta)f\Delta\phi}\} \tag{29}$$

The difference between $d\eta/dt$ and $d\phi/dt$ respectively in the left hand side (lhs) of eqns. (24) and (29) is not of essential importance in the present discussion since $d\eta/dt \simeq d\phi/dt$ at the initial portion of both rise and decay transients and $d\eta/dt \simeq d\phi/dt \simeq 0$ near the steady-state. The difference may play a role in determining precise shape of the overpotential rise or decay transient.

It is readily seen that eqn. (29) should yield the same magnitude of $\eta_1$ and $\eta_1'$ on the rise and decay transient, respectively. Thus, for the rise transient, the lhs of eqn. (29) is approximately zero at the moment $\eta$ reached $\eta_1$, or

$$i = i_{0V}\{e^{\beta f\Delta\phi_1} - e^{-(1-\beta)f\Delta\phi_1}\} \tag{30}$$

where $\Delta\phi_1$ means the value of $\Delta\phi$ at this moment. In this model, further rise of $\eta$ is totally attributed to $\Delta\chi$ and hence we find $\Delta\chi = \eta_2$. On the other hand, $\Delta\chi$ should be equal to $\eta_2'$ in this model and hence for the decay $\eta_1' = \eta_\infty - \eta_2' = \eta_\infty - \Delta\chi$, but as seen above this is equal to $\eta_\infty - \eta_2 = \eta_1$. Experimentally, however, the transients are non-symmetrical ($\eta_1 \neq \eta_1'$) or do not support this relation.[9]

Employing eqn. (16), we rewrite eqn. (29) as

$$C\frac{d\phi}{dt} = i - i_{0V}\{e^{-\beta f\Delta\chi}e^{\beta f\eta} - e^{(1-\beta)f\Delta\chi}e^{-(1-\beta)f\eta}\}$$

or referring to eqn. (18) which must hold in the present case

$$C\frac{d\phi}{dt} = i - i_{0V}\{\gamma_H^{\beta}e^{\beta f\eta} - \gamma_H^{-(1-\beta)}e^{-(1-\beta)f\eta}\} \tag{31}$$

Comparison with eqn. (24) shows that eqn. (31) has $\gamma_H^{\beta}$ in place of $\gamma_\uparrow$ and $\gamma_H^{-(1-\beta)}$ in place of $\gamma_\downarrow$, and in addition a slight difference in the lhs. It appears in the framework of the rate theory[10] that $\gamma_\downarrow$ should be close to unity at low values of $\theta$ and $\theta_0$. Accordingly, the use in this place of $\gamma_H^{-(1-\beta)}$, which may be largely separated from unity under this condition according to eqn. (14), is not readily acceptable.

## § 4. *Affinity Distribution among the Constituent Steps*

The affinity of the overall reaction distributes among the constituent steps. The distribution is readily discussed on the basis of the steady-state mass-balance relations among the steps,[11,12] namely, the net rate $V$ expressed in terms of the forward and backward rates, $v_{+s}$ and $v_{-s}$ respectively, of any step $s$,

$$V=(v_{+s}-v_{-s})/\nu_s=v_{-s}(v_{+s}/v_{-s}-1)/\nu_s$$

where $\nu_s$ represents the stoichiometric number of the step and $V$ and $v_{+s}$ *etc.* are counted in terms of number of times of occurrence per unit time of the overall and the elementary reaction. If we count the rate in c. d. unit, we have, noting $i=nFV$ and $i_{+s}=nFv_{+s}/\nu_s$,

$$i=i_{-s}(i_{+s}/i_{-s}-1) \tag{32}$$

The ratio $i_{+s}/i_{-s}$ is related to the individual affinity of the step, $\Delta g_s$, as readily seen from eqn. (3).

For the Tafel-Volmer route, we have

$$i_{-\mathrm{T}}(\mathrm{e}^{-\Delta g_{\mathrm{T}}/RT}-1)=i_{-\mathrm{V}}(\mathrm{e}^{-\Delta g_{\mathrm{V}}/RT}-1) \tag{33}$$

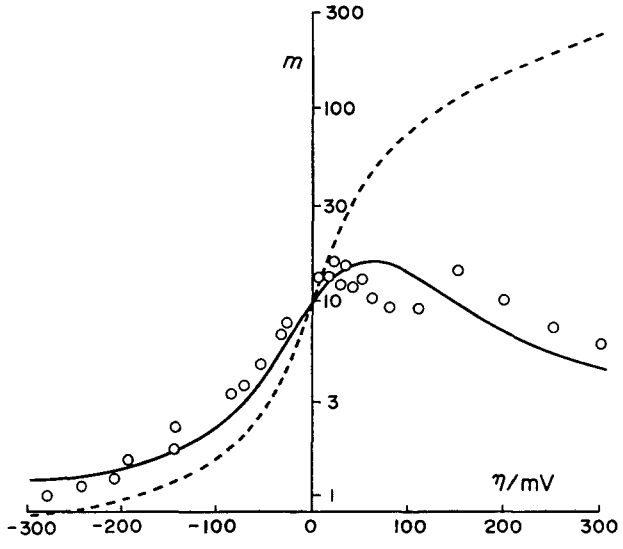


**Fig. 2.** Affinity distribution as a function of overpotential $m\equiv\Delta g_{\mathrm{T}}/\Delta g_{\mathrm{V}}$. Theoretical curves were calculated with $m_0=10$ and $\theta_0\ll 1$ from eqns. (33)–(35) for ordinary rate expressions (solid line) or from eqns. (33), (34) and (36) for rate expressions which excluded $\Delta\chi$ (dotted line). Experimental data (circles) were obtained with Pd foil hydrogen electrode (12.5 $\mu$ thick) in 1N $H_2SO_4$ at 30°C.

*cf.* eqns. (8) and (23) for $\Delta g_V$ and $\Delta g_T$, respectively. Use of proper expressions for $i_{-T}$ and $i_{-V}$ in terms of $\theta$ and $\eta$ together with eqn. (14) thus enables us to obtain $m \equiv \Delta g_T / \Delta g_V$ as a function of $\eta$ as reported elsewhere[11,12]. It is to be noted that $m$ is directly obtainable on Pd hydrogen electrode and hence appropriateness of the rate expressions employed could be investigated experimentally.

A typical example is given in Fig. 2 (solid line); the rate expression employed are[12]. *cf.* eqn. (25),

$$i_{-T} = i_{0T} \gamma_{\uparrow}^2 \tag{34}$$

$$i_{-V} = i_{0T} \gamma_{\downarrow} \exp\left\{-(1-\beta) f\eta\right\} \tag{35}$$

with the approximation $\gamma_{\downarrow}=1$ (which holds for $\theta_0 \ll 1$) and hence $\gamma_{\uparrow}=\gamma_H$, *cf.* eqn. (13). Also shown in this Figure are experimental data obtained on Pd. It is seen that general trends of the $m$ *vs.* $\eta$ relation observed are well represented by the theoretical curve obtained with $m_0=10$ and $\theta_0 \ll 1$.

Use of the relation devoid of $\Delta\chi$, namely, *cf.* eqn. (31),

$$i_{-V} = i_{0V} \gamma_H^{-(1-\beta)} e^{-(1-\beta) f\eta} \tag{36}$$

instead of eqn. (35) results in a different $m$ *vs.* $\eta$ relation as shown in Fig. 2 (dotted line). Comparison with the experimental data clearly indicates that the expression for $i_{-V}$ employed above is not supported experimentally.

## Conclusion

Exclusion of the surface potential term from rate expressions for charge transfer processes introduces physical unlikeliness and difficulties in interpreting experimental observations on Pd hydrogen electrode. The surface potential as well as the activity of the species involved in the charge transfer process plays a significant role in determining the reaction rate.

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