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COMPENSATION EFFECT OF ADSORBED INTERMEDIATE ON THE RATE OF ELECTRON TRANSFER STEP OF HYDROGEN EVOLUTION REACTION*)

By

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Abstract

A compensation effect of the intermediate species for the potential energy curves of the initial and final states of the electron transfer step of the hydrogen evolution reaction on low overvoltage metals in alkaline solution has been proposed in order to explain the experimental results that the overvoltage component caused by the change of the surface potential due to adsorption of the intermediate has no influence on the rate of the electron transfer step.

It has been developed through galvanostatic transient studies of the hydrogen evolution reaction on low overvoltage metals in alkaline solutions that:[1,2,3]

(i) the electron transfer step of the reaction consists of the discharge of alkali metal ions,

$$M^+ + e_m^- \longrightarrow M(a),$$

(ii) the rate of the step is expressed by the Tafel equation as a function of the overvoltage component η_1 which is caused by charging up of the electric double layer at the metal-solution interface,

(iii) the time constant τ_1 of the step remains constant with the increase of the overvoltage η in a considerably wide range of η, as exemplified in Fig. 1 for the case of nickel in aqueous sodium hydroxide solutions, where η is practically attributable to the change of the surface potential η_2 of the electrode caused by the adsorption of the intermediate M(a). It will be shown in the present work that no influence of η_2 on the time constant or the rate of the electron transfer step may be explained based on such

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a compensation effect of the intermediate species M(a) which changes equally the energy levels of the initial and final states of the electron transfer step.

Let us first consider the rate of the electron transfer step in the frame of the transition state method developed by Horiuti (H-theory)[4], and then by a quantum mehanical rate theory developed by Dogonadze, Kuznetsov and Levich (DKL-theory)[5].

According to the H-theory the rate $\vec{\epsilon}$ of the step may be written by the equation, the ϕ_1-term being neglected,

$$\vec{\epsilon} = AC_{M^+} \cdot \exp(-\Delta\mathscr{G}^{\ddagger}/RT), \quad (1)$$

where A is a constant, C_{M^+} is the concentration of M^+ ion in the solution, and $\Delta\mathscr{G}^{\ddagger}$ means the activation free energy of the step. The last quantity may be expressed by the Horiuti-Polanyi's rule[6] in terms of the electrode potential and the free energies of M(a) and M^+ ion, neglecting the entropy terms due to the surface coverage,

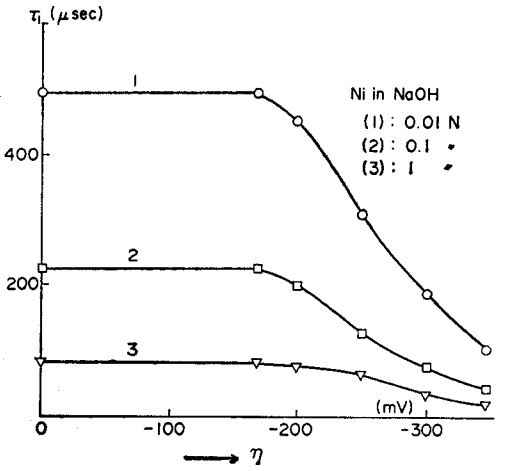

Fig. 1. Time constant of the electron transfer step of Ni-hydrogen electrode in aqueous NaOH, 0.01 n (○), 0.1 n (□), 1 n (▽).

$$\Delta\mathscr{G}^{\ddagger} = \Delta\mathscr{G}^{\ddagger}_0 + \alpha(\mathscr{G}_M - \mathscr{G}_{M^+} - \bar{\mu}_e), \quad (2)$$

where $\Delta\mathscr{G}^{\ddagger}_0$ is a constant, α is the transfer coefficient, and R, T and F have their usual meaning.

On the other hand, according to the DKL-theory $\vec{\epsilon}_1$ may be expressed by the following equation[7], assuming that the rate theory developed by them for the proton discharge may be applicable to the discharge of the alkali metal ion,

$$\vec{\epsilon}_1 = KC_{M^+} f(\varepsilon^*) \exp(-\Delta E/kT), \quad (3)$$

where K includes the transmission coefficient, $f(\varepsilon^*)$ is the Fermi distribution function at the energy level ε^* at which the transition probability of electron is the highest; ε^* can be identified with the Fermi level ε_F when the transfer coefficient equals 0.5. The activation energy ΔE can be expressed in terms of the reorganization energy E_s of the solvent molecule and the heat of reaction ΔJ_0 as

$$\Delta E = (E_s + \Delta J_0)^2/4E_s. \quad (4)$$

Further, ΔJ_0 is given by the difference between the minimal potential energies of the final and intial states,

$$\Delta J_0 = \varepsilon_M - (\varepsilon_f + \varepsilon_{M^+}), \quad (5)$$

where ε_M and ε_{M^+} are respectively the minimal potential energy of M(a) and M^+ ion.

The values of $\mathscr{E}_M$, ε_M, ε_F, and $\bar{\mu}_e$ may change with the increase of surface coverage of M(a) because of the mutual interaction between M(a)'s and also because of the surface dipole of M(a). Therefore, the activation free energy expressed by the H-theory and the heat of reaction in the DKL-theory may be written, taking into consideration the change of the surface coverage of M(a),

$$\Delta\mathscr{E} = \Delta\mathscr{E}_0 + \alpha(\mathscr{E}_{M,0} - \mathscr{E}_{M^+} - \bar{\mu}_{e,0}) + \alpha(\Delta\mathscr{E}_M - \Delta\bar{\mu}_e), \tag{6 a}$$

$$\Delta J_0 = (\varepsilon_{M,0} - \varepsilon_{F,0} - \varepsilon_{M^+}) + (\Delta\varepsilon_M - \Delta\varepsilon_F), \tag{6 b}$$

where suffix 0 means the reversible state of the overall reaction, and Δ means the increment of the respective quantities referred to the reversible state.

The last terms on the right-hand side of these equations can be rewritten, respectively, as

$$\Delta\mathscr{E}_M - \Delta\bar{\mu}_e = \Delta\mathscr{E}_M + F(\eta_1 + \eta_2) \tag{7 a}$$

$$\Delta\varepsilon_M - \Delta\varepsilon_F = \Delta\varepsilon_M + F(\eta_1 + \eta_2) \tag{7 b}$$

since $\Delta\bar{\mu}_e = \Delta\varepsilon_F = -F\eta = -F(\eta_1 + \eta_2)$.

According to the Frumkin's electrode potential theory η_1 and η_2 can be expressed in terms of the chemical potential μ_M of M(a)[8,9],

$$F\eta_2 = -\Delta\mu_M \simeq -\Delta\mathscr{E}_M, \tag{8 a}$$

$$\simeq -\Delta\varepsilon_M, \tag{8 b}$$

the entropy terms due to the surface coverage of M(a) or the vibration of M(a) being neglected in (8 a) or (8 b).

It should be emphasized that Eq. (8 a) or (8 b) means a compensation effect of M(a) in the free energy curves or potential energy curves between the initial and final states, since $F\eta_2$ displaces the free energy or potential energy curve of the initial state upwards, whereas $-\Delta\mathscr{E}_M$ or $-\Delta\varepsilon_M$ moves the free energy or potential energy curve of the final state upwards by the same amount as $F\eta_2$, as shown in Fig. 2. Therefore, the activation energy of the step would not change with the increase of the surface coverage of M(a).

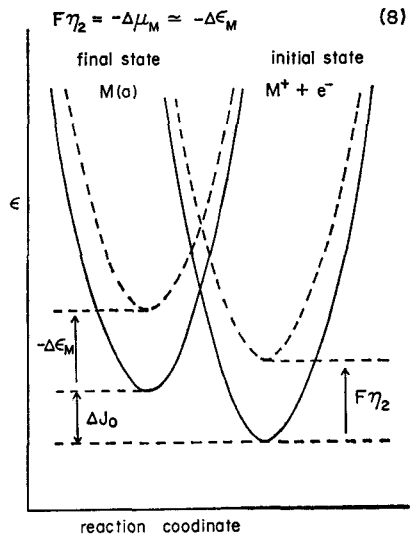

Fig. 2. Compensation effect in the potential energy diagram of the electron transfer step $M^+ + e^-_m \longrightarrow M(a)$.

Putting Eqs. (8 a) and (8 b) respectively into Eqs. (6 a) and (6 b), we have for the activation energy

$$\Delta\mathscr{E} = \Delta\mathscr{E}_0 + \alpha(\mathscr{E}_{M,0} - \mathscr{E}_{M^+} - \bar{\mu}_{e,0} + F\eta_1), \tag{9 a}$$

$$\Delta E = (E_s + \varepsilon_{M,0} - \varepsilon_{F,0} - \varepsilon_{M^+} + F\eta_1)^2/4E_s \,. \tag{9 b}$$

Eqs. (9 a) and (9 b) show that the activation free energy or the activation energy of the step can be expressed as a function of η_1 and not of η_2 as a result of the compensation effect of the adsorbed intermediate species. This is in conformity with the experimental results cited above[1,2,3,10].

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