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OVERVOLTAGE OF ELECTRON TRANSFER STEP OF HYDROGEN EVOLUTION REACTION ON NICKEL IN AQUEOUS SODIUM HYDROXIDE

By

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Abstract

The steady state overvoltages of the individual elementary steps of the hydrogen evolution reaction on nickel in aqueous sodium hydroxide were determined through the analysis of the galvanostatic overvoltage-time curve. It is concluded that (1) the rate of the electron transfer step is expressed by the simplified FRUMKIN equation in which the Ψ_1-potential is neglected as a function of the overvoltage component that is caused by the charging up of the electric double layer at the metal-solution interface, whether or not the step is in the steady state or in the transient state, and (2) the overvoltage of the overall reaction at low current densities is practically attributable to the overvoltage of the recombination step of the hydrogen adatoms, whereas at high current densities that of the electron transfer step becomes responsible for the increase of the overvoltage of the overall reaction.

Introduction

In the previous reports[1-4] the hydrogen evolution reaction on nickel in aqueous sodium hydroxide was studied by a galvanostatic transient method in order particularly to clarify the kinetic law of the electron transfer step in the reaction. The rate of the electron tpansfer step was determined from the analysis of the initial stage of the overvoltage-time (η-t) curves based on the fact that the change of the overvoltage after switching on a polarizing current was initially caused by the charging up of the electric double layer at the metal-solution interface. It was concluded that the electron transfer step was composed of the discharge of sodium ion and its rate i_1 was expressed by the simplified FRUMKIN equation[5] as the function of the overvoltage η_1 due to the double layer charging,

$$i_1 = k(C_{Na^+})^{\frac{1}{2}}\left\{\exp(-\alpha F\eta_1/RT) - \exp(\beta F\eta_1/RT)\right\}, \qquad (1)$$

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where C_{Na^+} denotes the concentration of sodium ion, k is a constant, F, R and T are in their usual meaning, and α and β are the transfer coefficients in the forward and reverse directions, both equal to 0.5.

On the other hand it was also concluded previously[1] from the current-overvoltage relations under the steady state polarization that the rate of the hydrogen evolution reaction on nickel in alkaline solutions was controlled by the recombination of hydrogen adatoms. It followed that the hydrogen evolution reaction in aqueous sodium hydroxide was composed of the following three elementary steps[3],

$$Na^+ + e \longrightarrow Na(I), \qquad (I)$$

$$Na(I) + H_2O \longrightarrow H(a) + Na^+ + OH^-, \qquad (II)$$

$$2H(a) \longrightarrow H_2 \qquad (III)$$

where Na(I) and H(a) denoted respectively the intermediate sodium atom and the hydrogen adatom on the electrode surface.

However, it is not certain if Eq. (1) is applicable to the rate of the electron transfer step in the steady state, and how much extent the overvoltage η_1 of step (I) is included in the total overvoltage in the steady state polarization.

The purpose of the present work is on the one hand to establish the kinetic law of the electron transfer step under the steady state polarization, and on the other hand to clarify the distribution of the overvoltage among the constituent elementary steps mentioned above.

The overvoltage of step (I) in steady state can be determined from the analysis of the $\eta - t$ curve associated with the change of the polarizing current, on the basis of the equation deduced by NOTOYA[6], as reviewed briefly below. Let us denote the overvoltage and the current density of the overall reaction in the steady state as η_s and i_s, and the overvoltage component of j-th elementary step which is included in η_s as η_{js}. Then the reaction resistance r_{js} of j-th step is expressed as

$$r_{js} = -d\eta_{js}/di_{js} \qquad (2)$$

where the suffix s stands for a steady state, and i_{js} is the rate of j-th step expressed in terms of electric unit which equals i_s. The η_s is equal to the summation of η_{js}'s, *i.e.*

$$\eta_s = \sum_j \eta_{js}^{*)}. \qquad (3)$$

*) The chemical affinity of the electrode reaction ΔG is expressed by the summation of the affinities ΔG_j's of the constituent elementary steps of the reaction with the stoichometric

Continued to next page

If r_{js} is known as a function of i_s, then we obtain η_{js} by the integration of Eq. (2),

$$\eta_{js} = -\int_0^{i_s} r_{js} di_s . \qquad (4)$$

The reaction resistance of the electron transfer step r_{1s} at η_s is determined through the analysis of the initial stage of the η-t curve which starts from η_s on the basis of the equation;

$$\ln(-\Delta i_s/\dot{\eta}) = t/\tau_{1s} + \ln C_D \qquad (5)$$

and

$$\tau_{1s} = C_D r_{1s} , \qquad (6)$$

where Δi_s is the increment of the polarizing current above i_s, $\dot{\eta}$ is the time derivative of η, and C_D and τ_{1s} are respectively the differential capacity of the double layer and the time constant of step (I) at η_s. As seen from Eq. (5), we obtain the value of τ_{1s} from the gradient of $\ln(-\Delta i_s/\dot{\eta})$-$t$ curve and C_D from $-\Delta i_s/\dot{\eta}$ at $t=0$. Consequently r_{1s} is obtained by Eq. (6). Once r_{1s} is known as a function of η_s or of i_s, the η_{1s} is obtained by a graphical integration of the r_{1s}-i_s curve on the basis of Eq. (4).

Results and Discussion

In order to determine r_{1s} the η-t curve caused by the change of i from i_s to $i_s+\Delta i_s$ was observed with an evaporated nickel film electrode of geometrical area 0.03 cm^2 in aqueous NaOH at 25°C.

Fig. 1 shows the $\log(-\Delta i_s/\dot{\eta})$-$t$ curve calculated from the η-t curves obtained at $\eta_s=0$, 248, 345, and 380 mV in 1N NaOH, and in Fig. 2 the

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number ν_j as[7],

$$\Delta G = \sum_j \nu_j \Delta G_j . \qquad (1)'$$

The overvoltage η_s is related with ΔG as

$$\eta_s = \frac{\Delta G}{nF} , \qquad (2)'$$

where n is the stoichometric coefficient of electron in the reaction. It follows from Eqs. (1)′ and (2)′ that

$$\eta_s = \sum_j \frac{\nu_j}{nF} \Delta G_j . \qquad (3)'$$

Accordingly, defining η_{js} as

$$\eta_{js} = \frac{\nu_j}{nF} \Delta G_j , \qquad (4)'$$

we readily obtain Eq. (3).

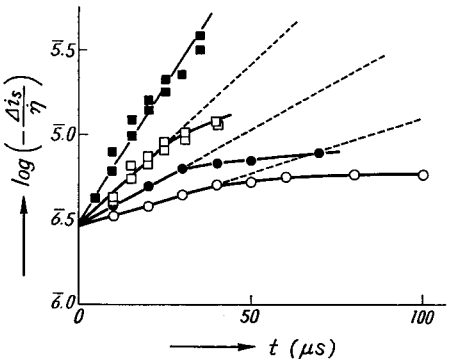

Fig. 1. Log $(-\Delta i/\dot{\eta})$-time curve in 1 N NaOH. Starting overvoltage η_s: (○) 0 mV, (●) 248 mV, (□) 345 mV, (■) 380 mV.

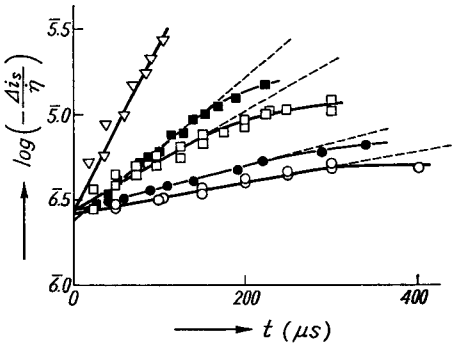

Fig. 2. Log $(-\Delta i/\dot{\eta})$-time curve in 0.01 N NaOH. Starting overvoltage η_s: (○) 0 mV, (●) 240 mV, (□) 300 mV, (■) 345 mV, (▽) 390 mV.

curves in 0.1 N NaOH at $\eta_s=0$, 240, 300, 345, and 390 mV. It is seen in these Figures that the initial stage of these curves satisfies Eq. (5) and hence the values of τ_{1s} and C_D are obtainable from the linear part of the curve. From Figs. 1 and 2, C_D is found to be constant independent of η_s and the concentration of NaOH.

The values of τ_{1s} thus determined in 0.01, 0.1, and 1 N NaOH are plotted against η_s in Fig. 3. The value of τ_{1s} is strongly dependent on the concentration of NaOH as seen in Fig. 3. In each solution, however, it remains constant at the overvoltage region $|\eta|<ca.$ 200 mV, whereas at the region $|\eta|>ca.$ 200 mV it decreases with the increase of $|\eta_s|$. In the low overvoltage region where τ_{1s} is constant the electron trasfer step can be regarded almost in equilibrium in spite of the increase of $|\eta_s|$ since the value of τ_{1s}

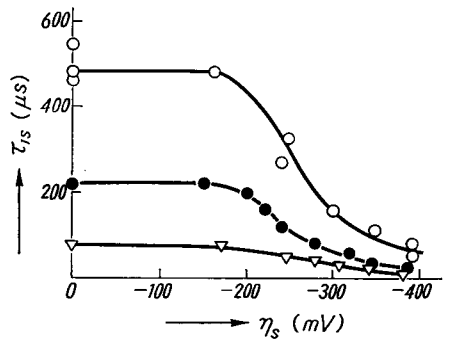

Fig. 3. Log τ_1-η_s relation in 0.01 N (○), 0.1 N (●), and 1 N (▽) NaOH.

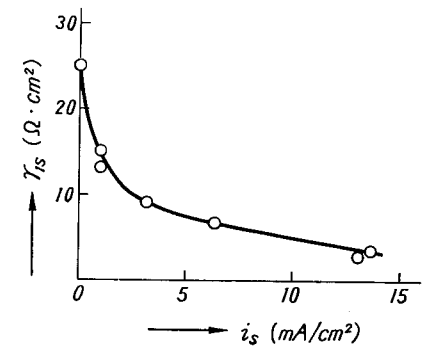

Fig. 4. r_{1s}-i_s relation in 0.01 N NaOH.

equals that at $\eta_s=0$, and hence the exchange current of the electron transfer step i_{10} can be calculated from this constant value of τ_{1s} by the equation, (*cf.* Eq. (6)),

$$i_{10}=\frac{RT}{F}\frac{1}{r_{1s}}=\frac{RT}{F}\frac{C_D}{\tau_{1s}}. \qquad (7)$$

In Fig. 4, r_{1s} in 0.01N NaOH calculated from Fig. 3 is plotted against i_s. From a graphical integration of Fig. 4 η_{1s} is obtained as a function of i_s on the basis of Eq. (4). Fig. 5 shows the relation between log i_s and η_{1s} thus obtained in 0.01N NaOH. For comparison the theoretical log i_s-η_{1s} relation as calculated by Eq. (1) using i_{10} evaluated from τ_{1s} at $\eta_s=0$ is also shown in this Figure. From the comparison of these two curves in Fig. 5, it is seen that the rate of the electron transfer step is well expressed by Eq. (1), namely, as a function of the overvoltage component caused by the charging up of the double layer whether or not the step is in the steady state or in the transient state[4]. It should be noted here that the surface state of the electrode is different for the steady and transient states, since the intermediate species are accumulated on the electrode surface in the steady state, whereas in the transient state the electrode surface is the same as that of the reversible hydrogen electrode except the change of the free charge density on the electrode surface, as discussed previously[4].

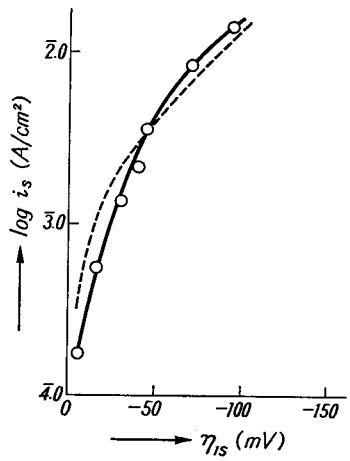

Fig. 5. Log i_s-η_{1s} relation in 0.01N NaOH.
(-○-) Experimental, (---) calculated by Eq. (5).

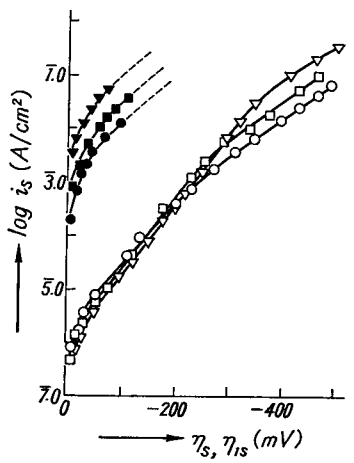

Fig. 6. Log i_s-η_s and log i_s-η_{1s} relations.
Electrolyte: (▽), (▼) 1N NaOH, (□), (■) 0.1N NaOH. (○), (●) 0.01N NaOH.
(▽), (□), (○) log i_s-η_s curve,
(▼), (■), (●) log i_s-η_{1s} curve.

Fig. 6 shows the relation between i_s and η_{1s} thus determined and that between i_s and η_s in 1, 0.1, and 0.01 N NaOH.

It is seen from Fig. 6 that the log i_s-η_{1s} curve are expressed by Eq. (1) in every solution used and the value of η_{1s} becomes detectable only in the region of i_s higher than i_{10}, although η_s of the overall reaction readily attains a few hundred mV in such a ragion.

The difference $\eta_s-\eta_{1s}$ in Fig. 6 gives, as seen from Eq. (3), the sum of the overvoltage component of the steps of the decomposition of water molecule η_{2s} and of the recombination of the hydrogen adatoms η_{3s}. The relation between log i_s and $\eta_s-\eta_{1s}$ obtained from Fig. 6 is shown in Fig. 7.

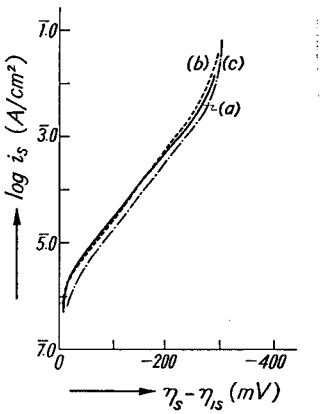

Fig. 7. Log i_s-($\eta_s-\eta_{1s}$) relation in (a) 0.01 N NaOH, (b) 0.1 N NaOH and (c) 1N NaOH.

As seen in this Figure, the log i_s-($\eta_s-\eta_{1s}$) curve is practically independent of the concentration of sodium ion or pH of solution. It may be concluded from this fact that $\eta_s-\eta_{1s}$ is attributable to η_{3s}, viz., to the excess of the activity of H(a) over that at the reversible hydrogen electrode potential. As seen from Fig. 7 $\eta_s-\eta_{1s}$ shows a tendency to approach a limiting value as i_s increases, in contradiction to the theory[8] that there should exist a saturation value in the *rate* of the recombination of H(a)'s because of saturation of the surface coverage of H(a) with the increase of the activity of H(a). The existence of the limiting value in $\eta_s-\eta_{1s}$ suggests that the surface concentration of the intermediate species will have a certain limiting value. This will be discussed in later work.

From the comparison of the polarization curve in Figs. 6 and 7, it can be seen that the increase of η_s with i_s is due to the increase of $\eta_s-\eta_{1s}$ at low current densities, whereas to the increase of η_{1s} at high current densities. In fact a break appears in the overall polarization curve in Fig. 6 at a point between these two regions.

The rate of the electron transfer step in the course of the decay of the overvoltage after switching off the polarizing current is analogously determinable from its initial stage on the basis of the following equation,

$$i_1 = C_D\dot{\eta}\,. \qquad (8)$$

This is because the decay of η in the initial region is caused by the double layer discharge as already discussed in the previous work[2]. According to

Eq. (8), i_1 is given at any value of η during the course of the decay, and consequently i_1 is obtained as a function of η. The log i_1-η curve thus obtained in 0.1N NaOH is shown in Fig. 8. As seen in the Figure, the initial stage of the log i_1-η curve coincides with the log i_s-η_s curve of the steady state and then deviates from the latter curve at the potential near the break of the log i_s-η_s curve. The agreement between log i_s-η_s and log i_1-η curves verifies the view that the decrease of $|\eta_s|$ with the decrease of i_s is caused by the discharge of the double layer[2]. The deviation of the log i_1-η curve from the log i_s-η_s curve shows that the decay of η in this region is no longer attributable to the discharge of the double layer, but to the decrease of the intermediate species on the electrode surface, and the differential capacity due to the intermediate species is deduced from the comparison of the log i_1-η and the log i_s-η_s curves as discussed previously[2]. The adsorption isotherm of the intermediate species obtained from the differential capacity will be discussed in the following work.

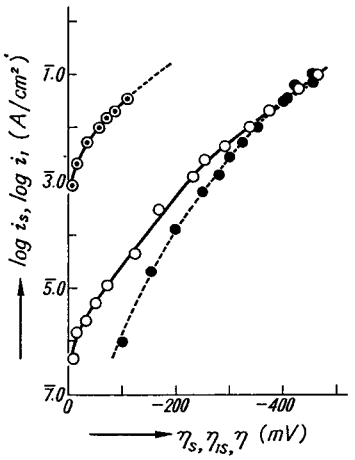

Fig. 8. Log i_s-η_s, log i_s-η_{1s} and log i_1-η relations in 0.1N NaOH. (○) log i_s-η_s curve, (◎) log i_s-η_{1s} curve, (●) log i_1-η curve obtained from decay curve.

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