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ACTIVATION ENERGY OF CONSTITUENT ELEMENTARY STEPS OF HYDROGEN EVOLUTION REACTION ON NICKEL IN AQUEOUS SODIUM HYDROXIDE

By

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Abstract

The rate of the electron transfer step of the hydrogen evolution reaction on nickel in sodium hydroxide solution, where the step was concluded previously as the discharge of sodium ions, was determined by the galvanostatic transient method in the temperature range of 0~30°C. The real activation energy of this step was found to be 2.5 kcal/mole, and independent of the overvoltage of the overall reaction in the range from 0 to −200 mV in accordance with the compensation effect of the adsorbed intermediate sodium atom, as pointed out previously. The real activation energy of the overall reaction was also determined as a function of overvoltage from the temperature dependence of the polarization curves in steady states, which was 12 kcal/mole at the reversible potential.

Introduction

It has been reported previously on the mechanism of the hydrogen evolution reaction on platinum,[1~3] nickel[4] and gold[5] in alkaline solution that: (i) the overall reaction is composed of the following elementary steps;

$$M^+ + e^- \longrightarrow M(I), \qquad [I]$$

$$M(I) + H_2O \rightleftharpoons H(a) + M^+ + OH^-, \qquad [II]$$

$$2H(a) \longrightarrow H_2, \qquad [III]$$

in which step [III] is rate-determining in the range of overvoltage from zero to a few hundred millivolts and then the rate-determining step moves to step [I] with the increase of overvoltage, step [II] being kept in quasi-equilibrium; (ii) the overvoltage η of the overall reaction is composed of two independent components η_1 and η_2 which are caused respectively by charging up of the electric double layer at the metal-solution interface and by the

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surface potential due to the intermediate alkali-metal atom M(I); (iii) η_2 acts as the overvoltage of step [III], while η_1 acts as the overvoltage of step [I] and its rate can be expressed by the Tafel equation in terms of η_1 independent of η_2.

It might seem unreasonable that η_2 does not affect the rate of step [I], since η_2 should also reflect in the potential energy curve of the initial state of step [I] as well as η_1. However, the independence of the rate of step [I] from η_2 has been explained by the compensation effect of M(I) on the potential energy curves of the initial and final states of step [I] concluded from the Frumkin's electrode potential theory. According to this theory the adsorption bond energy of M(I) is decreased by the same amount as the decrease of the surface potential with the increase of the surface coverage of M(I).[6~8] As a result of this compensation effect the activation energy of step [I] is expected to be kept constant with increase of M(I).

The present work is concerned with the experimental verification of the compensation effect of M(I) by the activation energy measurements of the elementary step [I] as a function of overvoltage with the nickel hydrogen electrode in aqueous NaOH solutions, and the activation energy of step [III] will also be compared with that of step [I].

Experimental

A nickel foil of purity 99.99%, geometrical area 1.0 cm^2 was used as the test electrode after heating to dull red in a vacuum system by means of an induction furnace in the presence or absence of hydrogen gas. A few hundred atomic layers of nickel was evapolated from the foil surface during these heat treatments. The concentration of sodium hydroxide was fixed at 0.18 N. The temperature range was 0~30°C. The rate of step [I] was determined by means of the galvanostatic transient method as previously reported,[9] in which the overvoltage-time curve caused by double square current pulses was recorded by an oscilloscope (YHP type-180) or by a wave form recorder (Biometion type-6500).

The overvoltage-time curve was analyzed on the basis of the following equation;

$$\ln\left(-\frac{\Delta i}{\dot{\eta}}\right)=\frac{t}{\tau_1}+\ln C_D, \qquad (1)$$

in which Δi is the current pulse height, τ_1 is the time constant of step [I] and C_D is the differential capacity of the electric double layer. The polarization resistance of step [I] was deduced from τ_1 and C_D determined in this

way by the relation $\tau_1 = C_D r_1$ and the reaction rate i_1 of step [I] was deduced from the equation $i_1 = RT/F\ r_1$. The activation energy A_1 of step [I] at constant η_1 was determined from the temperature-dependence of i_1 by the equation,

$$A_1 = RT^2\left(\frac{\partial \ln i_1}{\partial T}\right)_{\tau_1} \tag{2 a}$$

and the activation energy of the overall reaction A was determined from the temperature dependence of the polarization curves of the overall reaction by the equation,

$$A = RT^2\left(\frac{\partial \ln i}{\partial T}\right)_{\eta} \tag{2 b}$$

which was attributable to the activation energy of step [III] in the overvoltage region where it is rate-determining.

Results and Discussion

An example of the transient of overvoltage observed by the wave form recorder is shown in Fig. 1. The value of $\dot{\eta}$ is determined from this diagram as the ratio of the potential jump $\Delta\eta$ to the time length Δt of the step. Fig. 2 shows the temperature dependence of C_D at $\eta = 0$. The increase of C_D with temperature may be explained by the change of the surface area or also by the intrinsic change of the structure of the double layer. The latter explanation seems to be preferable because of good reproducibility in the case of rapid change of temperature. The current density i_1 of step [I] per true unit area was calculated from the roughness factor of the electrode surface 1.4 obtained by dividing the experimental C_D-value at 25°C by 18 $\mu F/cm^2$ of mercury electrode.[10]

The kinetic parameters τ_1, r_1 and i_1 obtained from the transient curves in the range of η from 0 to -310 mV and temperature from 0.5°C to 21°C are shown in Table 1, in which the values of the parameters are normalized to those in aqueous NaOH of mean activity 0.1 utilizing the concentration

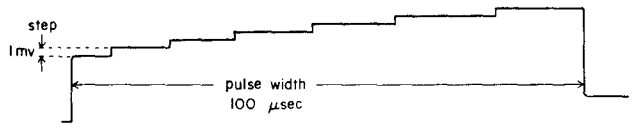

Fig. 1. A transient of overvoltage observed by a wave form recorder corresponding to a current pulse of height 1.9 mA and width 100 μsec., vertical potential step corresponds to 1 mV.

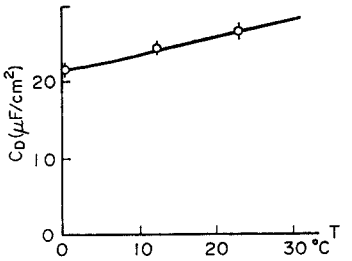

Fig. 2. Temperature dependence of C_D per apparent unit area.

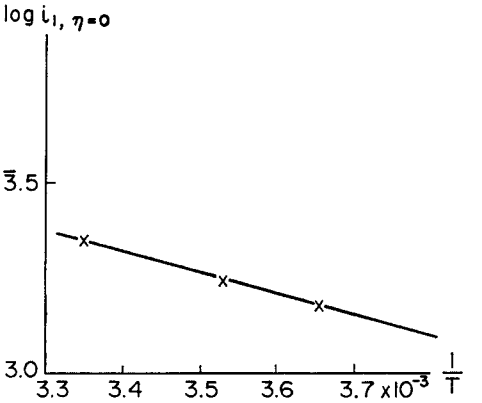

Fig. 3. Temperature dependence of the exchange rate of the discharge step in $NaOH_{aq}$. with mean activity of 0.1.

dependence of these parameters. It should be emphasized that i_1 remains constant in the range of $-\eta$ from 0 to about 200 mV at any temperature used. Therefore step [I] can be regarded as practically in equilibrium, although η has changed about 200 mV which corresponds to the change of the surface potential due to the increase of the intermediate species Na (I), as concluded previously.[1~9] The temperature dependence of i_1 at $\eta=0$ mV is shown in Fig. 3. The activation energy A_1 calculated from this relation is 2.5 kcal/mole. The A_1 value also remains constant independent of η, as expected from the compensation effect of Na (I) on the potential energies of the initial and final states of

TABLE 1. Time constant τ_1, polarization resistance r_1, and rate i_1 of step [I] at various overvoltages and temperatures in $NaOH_{aq}$ of mean activity 0.1

	$-\eta$ (mV)	T (°C)	τ_1 (μ sec)	r_1 ($\Omega\cdot$cm^2)	i_1 (mA$\cdot$cm^{-2})
Ni	0~180	21	225	13.1	1.9
		11	240	15.3	1.6
		0.5	250	16.9	1.4
	220	21	210	12.2	2.1
		0.5	240	16.6	1.4
	310	21	185	10.8	2.3
		0.5	200	13.8	1.7
Pt	0	20	90	5.0	5.0
Au	0	20	360	20.5	1.2

step [I]. When $-\eta$ is increased above 200 mV, A_1 has a tendency to decrease with $-\eta$.

For comparison, the values of i_1 on Pt and Au hydrogen electrodes at 20°C,[1,5] are also shown in this Table. It can be seen that there is no remarkable difference of the values of i_1 among Pt, Ni and Au hydrogen electrodes, although the exchange rates of overall reaction of these electrodes differ by 2 or 3 orders magnitude. A slight difference of i_1-values among these different electrode metals may suggest a slight difference of the adsorption bond of Na (I) among these metals, since the rate of the discharge reaction should be constant at a constant electrode potential independent of the electrode material when there is no specific adsorption of the products on the electrode surface as pointed out by Frumkin and his school.[11,12]

The polarization curves of the overall reaction in steady states at temperatures 0.5, 11 and 21°C are shown in Fig. 4, which can be expressed by

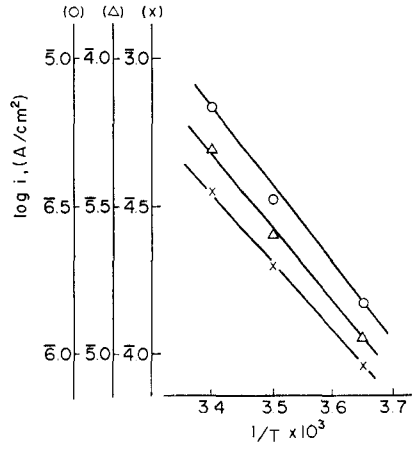

Fig. 5. Temperature dependence of the rate of the overall reaction in 0.18 N $NaOH_{aq.}$ at $\eta = 0$ (○), -100 (△) and -200 mV (×).

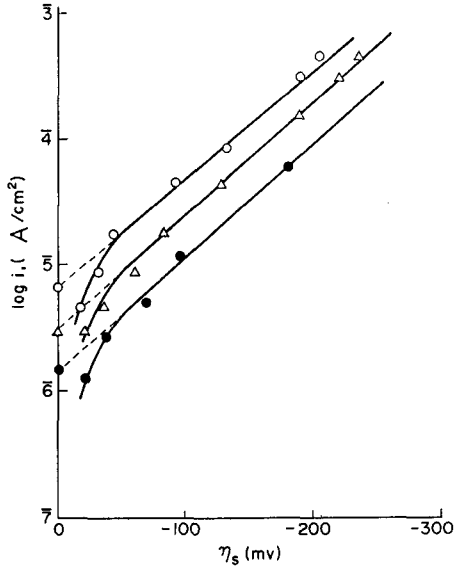

Fig. 4. Polarization curves of the overall reaction in 0.18 N $NaOH_{aq.}$ at temperature 21 (○), 11 (△) and 0.5°C (●).

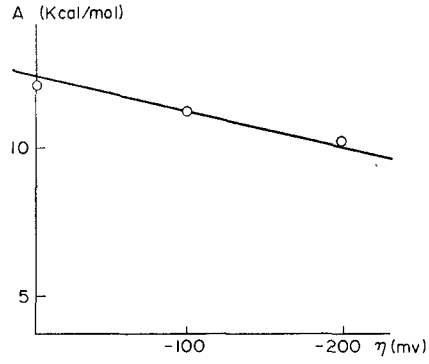

Fig. 6. Overvoltage dependence of the activation energy A of the overall reaction.

Tafel relation with the transfer coefficient α equal to 0.5. The temperature dependence of i-values at $-\eta=0$, 100 and 200 mV is shown in Fig. 5. The i_0-values in this figure are obtained from the extrapolation of the polarization curve or from the polarization resistance at the reversible potential. The values of the activation energy A of the overall reaction calculated from Fig. 5 are found to be 12, 11.2 and 10.2 kcal/mole at $-\eta=0$, 100 and 200 mV, respectively. The overvoltage dependence of A can be expressed by the relation $A=A_0+\alpha F\eta$ with the coefficient $\alpha=0.5$, as shown in Fig. 6., which is the same as that deduced by Temkin and Frumkin[13] for the case of the proton discharge. The A-value in this overvoltage region can be attributed to that of step [III], *i. e.*, the recombination step of adsorbed hydrogen atoms, since step [I] is in quasi-equilibrium and step [III] is rate-determining in this region as mentioned above.

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