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Author(s)	OHMORI, T.; MATSUDA, A.
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HYDROGEN ELECTRODE REACTION ON NICKEL IN ALKALINE SOLUTIONS

Part 2. Current-Overvoltage Relation of the Discharge Step

By

T. Ohmori[*] and A. Matsuda[*]

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Abstract

The kinetic law of the discharge step of the hydrogen evolution reaction on nickel in aqueous sodium hydroxide was determined from the overvoltage-time curves after switching-on of the polarizing current. It was found that the relation between the rate and overvoltage of the discharge step is expressed by the equation developed by Frumkin and Aladjalova with respect to the discharge step of the hydrogen evolution reaction on palladium.

Introduction

The rate of the hydrogen evolution reaction on nickel in alkaline solutions is limited by the elementary step of the recombination of adsorbed hydrogen atoms.[1-7] However the affinity of the discharge step is not completely negligible even in the steady state of the overall reaction[8-10] and may possibly be developed to its full extent in the transient state. The latter situation enables us to establish the kinetic law of the discharge step of the reaction by the galvanostatic transient method. In Part 1, the exchange rate of the discharge step of the reaction was found by this method to be proportional to the square root of sodium ion concentration independent of pH, indicating that the discharge step of the reaction consists in the discharge of sodium ion as in the case of platinum.[11-13] The present work is purposed to establish the current-overvoltage relation of the discharge step of the hydrogen evolution reaction on nickel in aqueous sodium hydroxide by means of galvanostatic transient method.[10-13]

The rate of the discharge step can be determined from the displacement of overvoltage after switching on a polarizing current by the following equation, provided that the displacement of overvoltage is caused by charging up of the double layer at the metal-solution interface and the differential capacity of the double layer is known:

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*) Research Institute for Catalysis, Hokkaido Univ., Sapporo, Japan.

$$i_1 = i + C_D \dot{\eta}, \tag{1}$$

where i_1—the rate of the discharge step expressed in the electric unit, i—the applied current density, C_D—the differential capacity of the electric double layer, η—the overvoltage, $\dot{\eta}$—the rate of the displacement of overvoltage. The sign of the current is taken positive and that of η negative in the cathodic direction. The value of C_D at the definite value of η is given by the following expression using the initial tangent of the $\eta - t$ curve which starts from that value of η:

$$C_D = -\left(\frac{\Delta i}{\dot{\eta}}\right)_{t=0}, \tag{2}$$

where Δi denotes the increment of the polarizing current density.

The displacement of overvoltage after switching on a constant polarizing current is however in general affected not only by charging up of the double layer, but also by accumlation of the intermediate species of the reaction or specifically adsorbed ions. Thus it is necessary to observe very fast change of overvoltage which is caused solely by charging up of the double layer in order
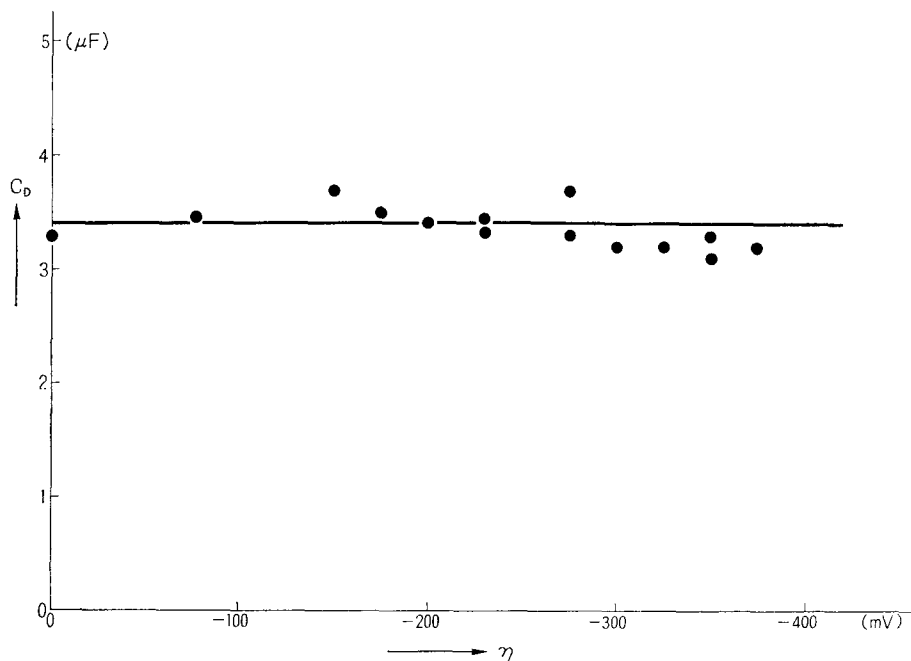

Fig. 1. The η-dependence of C_D obtained from the build up curves started from various steady values of η with nickel film electrode of apparent area 0.03 cm^2 in NaOH$_{aq}$ of pH 12.3.

to deduce the rate of the discharge step from the overvoltage-time curve on the basis of Eq. (1).

Experimental Results and Discussion

In the present work the overvoltage-time curves were observed on evaporated nickel film electrodes within a few miliseconds after switching on a constant polarizing current, following the same procedures as described in the previous work.[8,11] Fig. 1 shows the overvoltage dependence of C_D calculated by Eq. (2) from the $\eta-t$ curves observed with a nickel film electrode of apparent area 0.03 cm² in NaOH$_{aq}$ of pH 12.2.

As seen from this Figure, the value of C_D practically remains constant at 3.4 μF independent of η. It may be assumed from the constancy of C_D that there is no necessity for taking into consideration the effect of the specific
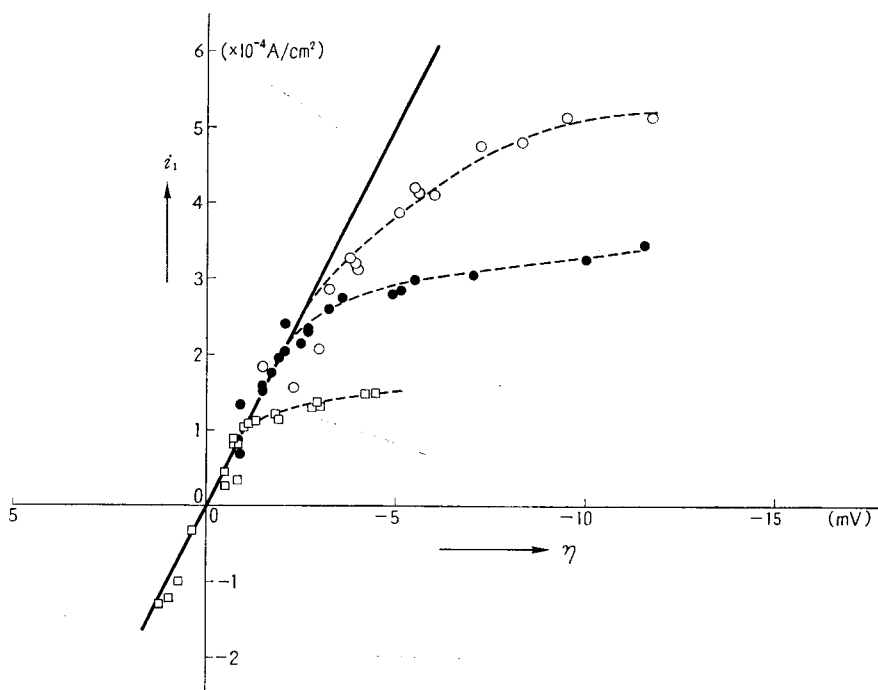

Fig. 2. The relation between i_1 and η obtained from the build up curve observed in NaOH$_{aq}$ of pH 12.8 at current densities: (□): $i=2$. 35·10⁻⁴ A/cm² (●): $i=5.58\cdot10^{-4}$ A/cm² (○): $i=1.03\cdot10^{-3}$ A/cm².

adsorption of ions or intermediate species on the displacement of overvoltage in such very fast change of overvoltage as observed.

Fig. 2 shows the relation between i_1 and η calculated by Eq. (1) from the

$\eta-t$ curves observed with lower current densities in $NaOH_{aq}$ of pH 12.8. The values of i_1 and i in Fig. 2 are expressed by the current density per true unit area, using the C_D-value 18 $\mu F/cm^2$ which is the differential capacity of the double layer of the mercury electrode reported by VORSINA and FRUMKIN.[14] As seen from Fig. 2, i_1 increases proportionally to η in the neighborhood of $\eta=0$ with a constant gradient independent of the applied current density and
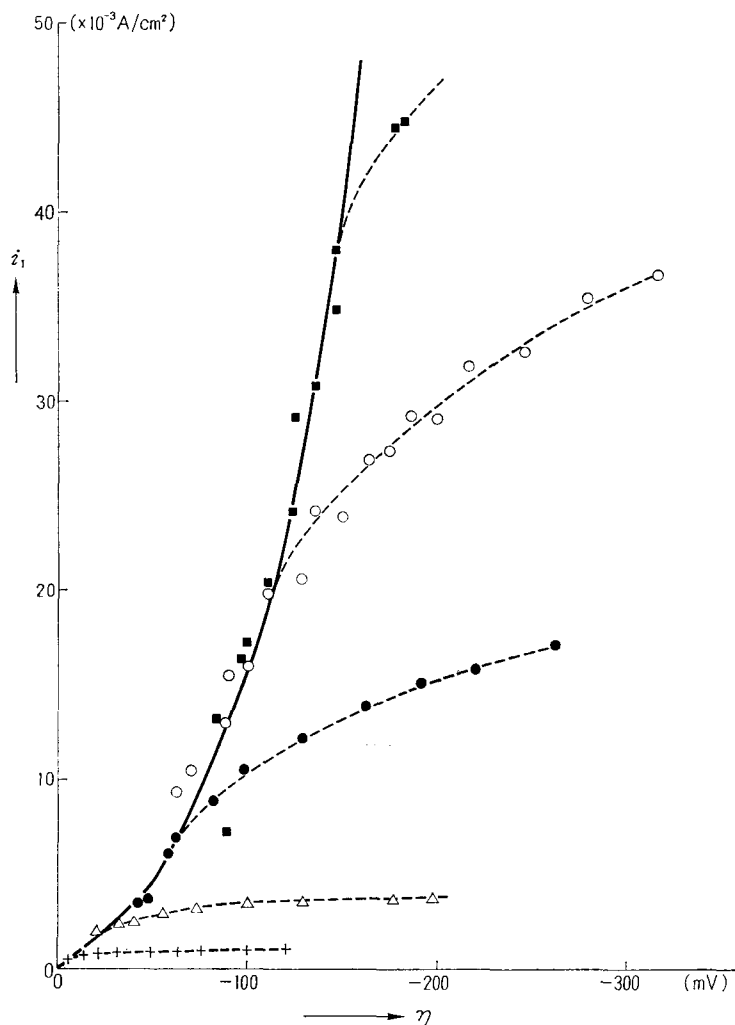

Fig. 3. The relation between i_1 and η obtained from the build up curve observed in $NaOH_{aq}$ of pH 13.0 at current densities: $(+)$: $i=$ $1.41 \cdot 10^{-3}$ A/cm^2 $(\triangle)$: $i=5.34 \cdot 10^{-3}$ A/cm^2 $(\bullet)$: $i=2.40 \cdot 10^{-2}$ A/cm^2 $(\bigcirc)$: $i=4.94 \cdot 10^{-2}$ A/cm^2 $(\blacksquare)$: $i=1.00 \cdot 10^{-1}$ A/cm^2.

then deviates downward from the proportionality along with increase of η. The reaction resistance r_{10} defined as $(\partial\eta/\partial i_1)_{\eta=0}$ is found 9.8 $\Omega\cdot$cm^2 from Fig. 2, which coincides with the value previously obtained from the time constant of the discharge step τ_1 at $\eta=0$.[10] The exchange current of the discharge step i_{10} calculated from r_{10} by Eq. (3) in Part 1 is $2.6\cdot10^{-3}$ A/cm^2, which is far larger than the exchange rate of the overall reaction $i_0=7.4\cdot10^{-6}$ A/cm^2 obtained from the extraporation of the Tafel line.[8] This fact verifies that the

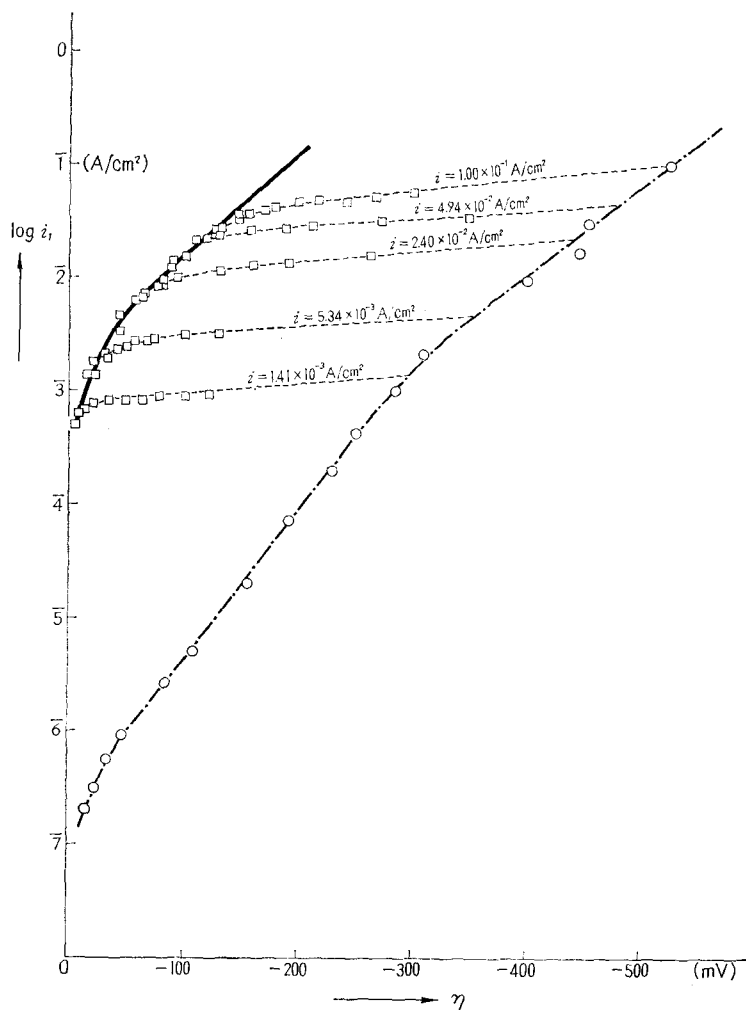**Fig. 4.** The relation between $\log i_1$ and η obtained from Fig. 3 (□), and the $\log i-\eta$ relation in steady states (○) in NaOH$_{aq}$ of pH 13.0; (—) theoretical $\log i_1-\eta$ curve calculated by Eq. (3).

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discharge step is not rate-determining in the hydrogen evolution reaction at the reversible hydrogen electrode potential.

Fig. 3 shows the relation between i_1 and η calculated by Eq. (1) from the $\eta-t$ curves observed with higher current densities in $NaOH_{aq}$ of pH 13.0. As seen from this Figure, i_1 first increases proportionally to η in the neighborhood of $\eta=0$ as in the case of Fig. 2 and then increases exponentially with increase of η contrary to the case of Fig. 2 and latter deviates from the exponential relation. The deviation of the $i_1-\eta$ curve from the exponential relation begins at higher overvoltage when the polarizing current is increased. Now the logarithm of i_1 in Fig. 3 is plotted against η in Fig. 4. For comparison,
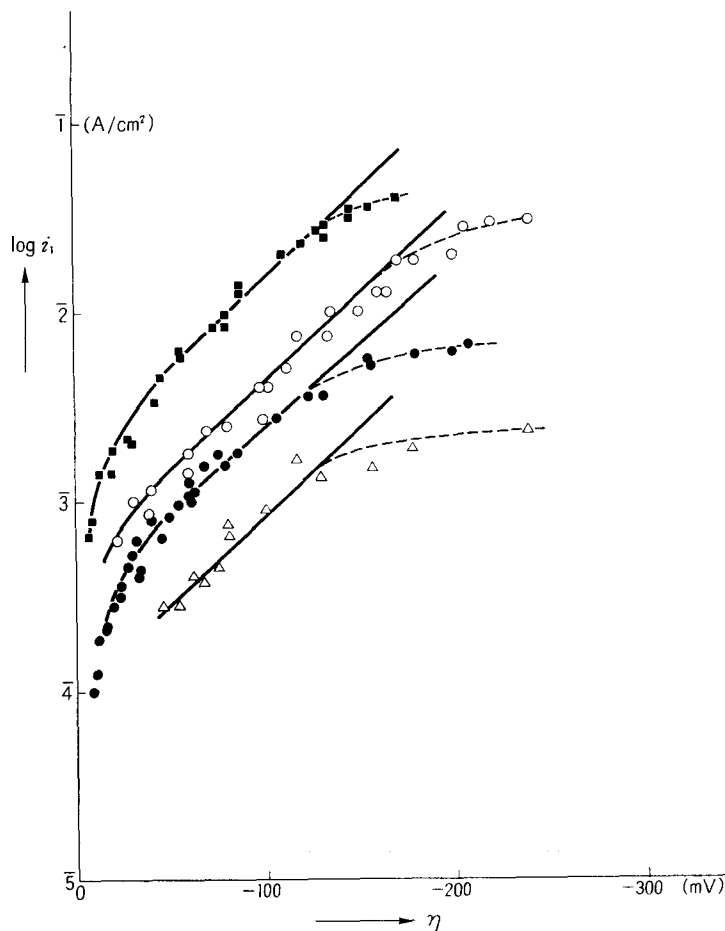

Fig. 5. The $\log i_1 - \eta$ curves in $NaOH_{aq}$ of various concentrations:
(■): pH 13.0; (○): pH 12.3; (●): pH 11.8; (△): pH 10.8.

the $\log i - \eta$ curve in steady states is also shown in this Figure. As seen from this Figure, the relation between $\log i_1$ and η can be separated in two stages. The first stage can be expressed by Tafel's formula with the coefficient 1/2, *i. e.*,

$$i_1 = i_{10} \left\{ \exp(F\eta/2RT) - \exp(-F\eta/2RT) \right\}, \tag{3}$$

where F, R and T denote Faraday, the gas constant and the absolute temperature respectively. As reported in Part 1, i_{10} is proportional to the square root of the sodium ion concentration,

$$i_{10} = k(C_{Na^+})^{1/2}. \tag{4}$$

The concentration dependence of the first stage of the $\log i_1 - \eta$ curve is shown in Fig. 5. It can be seen from this Figure that the overvoltage at a constant value of i_1 is shifted to the negative side by *ca.* 65 mV with decrease of the concentration of solution by one order. It is found from these results that the relation between i_1 and η deduced from the initial stage of the $\eta - t$ curve on the basis of Eq. (1) can be expressed by the equation developed by FRUMKIN and ALADJALOVA with respect to the discharge step of the palladium hydrogen electrode reaction.[15] In the second stage where the $\log i_1 - \eta$ relation deviates from TAFEL's formula, the change of overvoltage may be caused by the accumulation of the intermediate species produced by the discharge step rather than by charging up of the double layer. The distribution of overvoltage among constituent elementary steps will be discussed in later works.

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