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HYDROGEN ELECTRODE REACTION ON NICKEL IN ALKALINE SOLUTIONS

Part 1—Exchange Current of The Discharge Step

By

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Abstract

The exchange current density, i_{10} , of the discharge step of the hydrogen electrode reaction on nickel was determined by the galvanostatic transient method in sodium hydroxide and sodium sulfate solutions. The i_{10} was found to vary linearly with the square root of sodium ion concentration independent of pH. It was concluded from the result that the discharge step of the hydrogen electrode reaction on nickel consists in the discharge of sodium ion as in the case of platinum.

Introduction

Previously it was concluded that the hydrogen evolution reaction on nickel electrode in sodium hydroxide solutions follows the catalytic mechanism, in which the recombination of the adsorbed hydrogen atoms is rate-determining.¹⁾ The rate-determining step cannot, however, be ideally established to keep other steps practically in partial equilibrium, since the pH dependence of overvoltage was now found, if small, definitely observable in dilute solutions at higher current densities.¹⁾ The overvoltage imposed upon the discharge step is thus not negligible as compared with that laid upon the rate-determining recombination step in dilute solutions.

The present work is devoted to determination of the time constant and the exchange current of the discharge step of the hydrogen evolution reaction on nickel by the galvanostatic transient method.

Experimental Results and Discussion

In the galvanostatic transient method we observe the overvoltage-time curve after switching on a constant polarizing current. From the initial stage of the overvoltage-time curve the time constant of the discharge step, τ_1 , and

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the differential capacity of the electric double layer, C_D , are determined on the basis of the theoretical equations²⁾:

$$\ln(-i/\dot{\eta}) = t/\tau_1 + \ln C_D, \quad (1)$$

$$\tau_1 = C_D \cdot r_1, \quad (2)$$

where i is the polarizing current, $\dot{\eta}$ the differential coefficient of overvoltage with respect to time, r_1 the reaction resistance of the discharge step, and t the time elapsed after switching on the current. The exchange current of the discharge step, i_{10} , is derived from r_1 by the equation³⁾

$$i_{10} = \frac{RT}{F} \cdot \frac{1}{r_1}. \quad (3)$$

The overvoltage-time curves were observed on evaporated nickel film electrodes in solution of sodium hydroxide and sodium sulfate with varying concentrations. The structure of the electrolytic cell and the procedures of purification of solution and hydrogen have already been described in the previous papers.^{1),2)} The concentration of sodium ion was determined by a glass electrode. The value of $\dot{\eta}$ was determined from the η - t curves observed on a memoscope oscilloscope screen. The $\log(-i/\dot{\eta})$ - t relations thus obtained

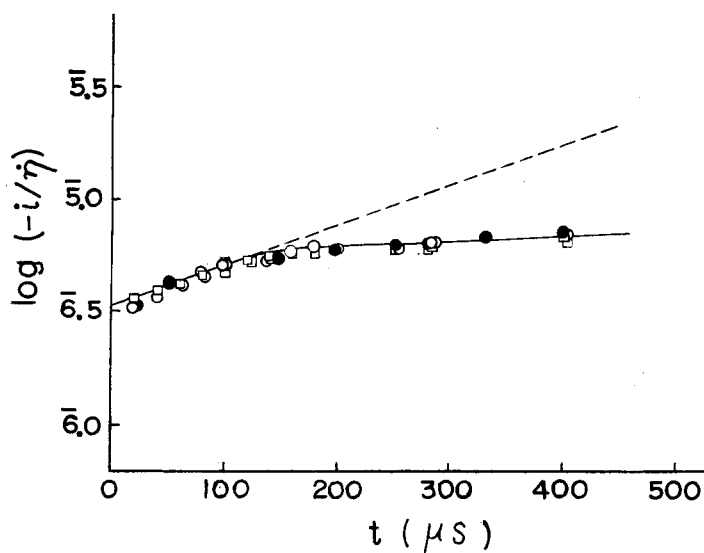


Fig. 1. The $\log(-i/\dot{\eta})$ versus time. Electrolyte: NaOH aq. of pH 13.0. Current i : (●) $2.50 \cdot 10^{-5}$ A., (○) $8.60 \cdot 10^{-5}$ A., (□) $4.45 \cdot 10^{-4}$ A., $C_D = 3.3 \mu F$, $\tau_1 = 230 \mu sec$.

Nickel Hydrogen Electrode in Alkaline Solutions. (I)

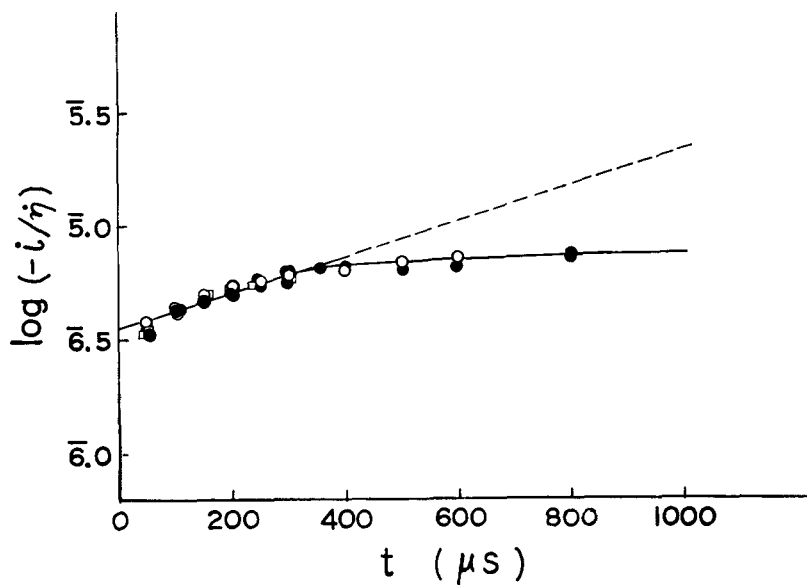


Fig. 2. The $\log(-i/i_0)$ versus time. Electrolyte: NaOH aq. of pH 12.3. Current i : (●) $1.96 \cdot 10^{-5} \text{ A.}$, (○) $5.84 \cdot 10^{-5} \text{ A.}$, (□) $2.65 \cdot 10^{-4} \text{ A.}$, $C_D = 3.6 \mu\text{F}$, $\tau_1 = 590 \mu\text{sec.}$

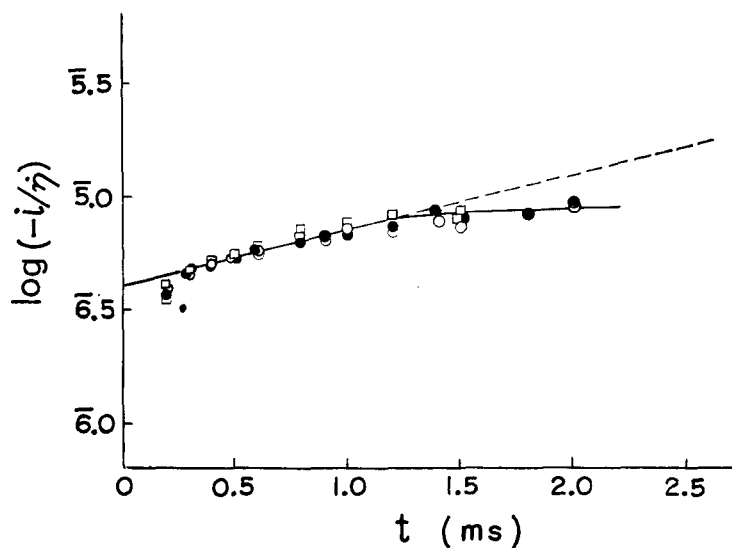


Fig. 3. The $\log(-i/i_0)$ versus time. Electrolyte: NaOH aq. of pH 11.8. Current i : (●) $9.65 \cdot 10^{-6} \text{ A.}$, (○) $1.77 \cdot 10^{-5} \text{ A.}$, (□) $4.75 \cdot 10^{-5} \text{ A.}$, $C_D = 4.0 \mu\text{F}$, $\tau_1 = 1.80 \text{ msec.}$

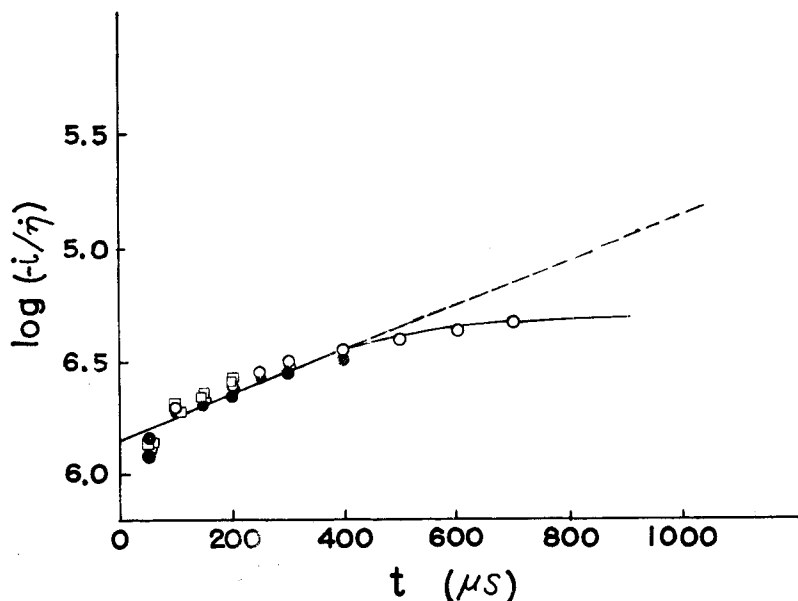


Fig. 4. The $\log(-i/i_0)$ versus time. Electrolyte: 0.01 N Na_2SO_4 aq. of pH 9.9. Current i : (●) $1.60 \cdot 10^{-5}$ A., (○) $4.58 \cdot 10^{-5}$ A., (□) $8.84 \cdot 10^{-5}$ A., $C_D = 1.8 \mu\text{F}$, $\tau_1 = 610 \mu\text{sec}$.

are shown in Figs. 1–4, which are linear in the initial stage for different values of the polarizing current densities.

It is induced from the result that the increase of overvoltage in the initial stage consists in the charging up of the electric double layer, hence τ_1 and C_D determined from the $\eta-t$ curves on the basis of Eq. (1) are respectively the time constant of the discharge step and the differential capacity at the metal-solution boundary. The values of τ_1 thus determined from the $\log(-i/i_0)-t$ relation are plotted against the logarithm of sodium ion concentration $\log C_{\text{Na}^+}$ and pH in Fig. 5, which shows that $\log \tau_1$ in aqueous sodium hydroxide varies linearly with pH, while $\log \tau_1$ in aqueous sodium sulfate is independent of pH as in the case of platinum.^{2),4)} The $\log \tau_1$ lies, however, in both the cases on one and the same line when plotted against $\log C_{\text{Na}^+}$, and this line has a gradient, $-1/2$, *i.e.*

$$\tau_1 = k(C_{\text{Na}^+})^{-1/2}. \quad (4)$$

It follows from Eqs. (2), (3), and (4) that

$$i_{10} = k'(C_{\text{Na}^+})^{1/2}, \quad (5)$$

where k and k' are constants. The exponent of C_{Na^+} in Eq (5) is identifiable

Nickel Hydrogen Electrode in Alkaline Solutions. (I)

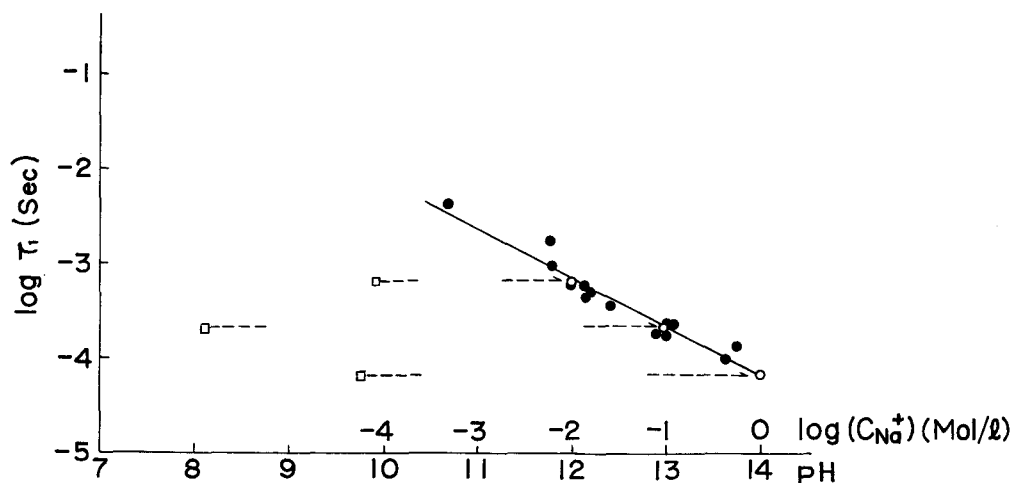
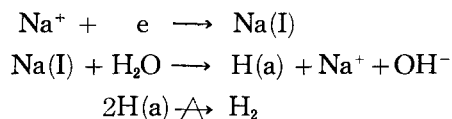


Fig. 5. $\log \tau_1$ versus pH or $\log C_{Na^+}$. Electrolyte: 0.001 N-1 N NaOH or 0.01 N-1 N Na_2SO_4 .

- : Plot against pH for NaOH aq.
- : Plot against pH for Na_2SO_4 aq.
- : Plot against $\log C_{Na^+}$ for Na_2SO_4 aq.

with the Tafel constant in accordance with FRUMKIN's discharge theory.⁵⁾ It is concluded from these facts that the discharge step of the hydrogen evolution reaction on nickel is not the discharge of water molecule but that of sodium ion in aqueous sodium hydroxide as well as in sodium sulfate.

It is concluded from this fact, taking the pH-dependence of overvoltage in steady state into account, that the hydrogen evolution reaction is composed of following elementary steps;



with the last step determining the rate, where Na(I) is sodium intermediate, and H(a) adsorbed hydrogen atom on the electrode surface.

Table I shows the exchange current densities of the discharge step, i_{10} , calculated by Eqs. (2) and (3) from the values of τ_1 and $C_D = 18 \mu F/cm^2$.^{2,6)} The i_{10} is far greater than, in every solution dealt with, the exchange current density of the overall reaction $i_0 = 7.4 \cdot 10^{-6} A/cm^2$ as reported previously.¹⁾ This result confirms the previous conclusion that the hydrogen evolution reaction on nickel follows the catalytic mechanism; however, i_{10} decreases with decrease of the concentration of sodium ion to increase the overvoltage imposed upon

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TABLE I. Kinetic parameters of the discharge step of nickel-hydrogen electrode reaction in alkaline solutions containing sodium ions

Sol.	C _{Na⁺}	pH	τ_1 μ sec	i_{10} A/cm ²
NaOH	0.60 mol/l	13.6	128	$3.52 \cdot 10^{-3}$
	0.47 "	13.5	97	$4.60 \cdot 10^{-3}$
	0.13 "	13.0	226	$2.00 \cdot 10^{-3}$
	0.10 "	12.9	168	$2.66 \cdot 10^{-3}$
	0.080 "	12.8	174	$2.59 \cdot 10^{-3}$
	0.025 "	12.3	589	$7.60 \cdot 10^{-4}$
	0.018 "	12.2	498	$9.05 \cdot 10^{-4}$
	0.009 "	11.9	580	$7.76 \cdot 10^{-4}$
	0.007 "	11.8	970	$4.64 \cdot 10^{-4}$
	0.007 "	11.8	1770	$2.55 \cdot 10^{-4}$
	0.0006 "	10.8	4660	$1.01 \cdot 10^{-4}$
Na ₂ SO ₄	1.0 N	9.7	66	$6.84 \cdot 10^{-3}$
	0.1 N	8.1	217	$2.07 \cdot 10^{-3}$
	0.01 N	9.9	609	$7.40 \cdot 10^{-4}$

$$i_0 = 7.4 \cdot 10^{-6} \text{ A/cm}^2 \text{ (1)}$$

the discharge step along with decrease of the concentration of solution, degrading the rate-determining recombination step to that extent from ideality. The kinetic behaviors of the discharge step will be dealt with in detail in a following paper.

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