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HYDROGEN ELECTRODE REACTION ON EVAPORATED NICKEL FILM IN AQUEOUS SODIUM HYDROXIDE

Part II. Galvanostatic Transients

By

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Abstract

The galvanostatic transients were observed with the hydrogen electrode of evaporated nickel film in aqueous sodium hydroxide of 13.10 and 13.75 pH. A method of the analysis of the build up and the decay curves was discussed. The analysis of the build up and the decay curves observed led to the conclusion that the overvoltage is imposed practically upon the recombination of adsorbed hydrogen atoms but scarcely upon the discharge step. The differential capacity of the hydrogen electrode was determined from the decay curve as a function of overvoltage.

Introduction

It was shown in Part I that the hydrogen overvoltage at a given current density is parctically independent of pH on evaporated nickel film electrode in concentrated sodium hydroxide solution in accord with the conclsion from the catalytic mechanism, that the overvoltage is caused by retarded recombination of hydrogen adatoms on the electrode surface. If then, hydrogen adatoms are accumulated on the electrode surface with increase of overvoltage, and in consequence the differential capacity of the hydrogen electrode is appreciably greater than that of the electric double layer. If, on the other hand, the slow discharge mechanism were operative, where the overvoltage is caused by retarded discharge, the differential capacity would equal that of the double layer. The differential capacity of a hydrogen electrode provides thus a distinguishing criterion for the reaction mechanisms.

FRUMKIN *et al.*[1] have advanced a method of determining the differential capacity of hydrogen electrode under cathodic polarization from the decay curve of hydrogen overvoltage after switch off of the polarizing current. PAST and JOFA[2] and LUKOWZEW and LEWINA[3] have determined by this method the differential capacity of mercury, iron and nickel hydrogen electrodes from the decay

curve. They determined the differential capacity, however, from the initial rate of decay of overvoltage, which may depend on the sweeping rate used for the observation of the decay by cathode ray oscillograph, since, as based on the catalytic mechanism, the rate-determining recombination is preceded by the discharge of hydrogen ion, which may be irreversible, if slightly, before switch off and after that approach equilibrium rapidly, contributing more or less to the observed differential capacity at the initial stage. Thus the results of these authors[2] may not be adequate to be attributed to the accumulation of adatom, unless the observed rate of decay is shown free from the above contribution of the discharge step.

The present paper is concerned with the determination of the differential capacity with due regards to the above points from the galvanostatic transients observed with evaporated nickel film electrode in aqueous sodium hydroxide, which has been found of remarkably reproducible and quick response.

§ 1 Analysis of Galvanostatic Transients

A method of analysis of the galvanostatic build up and decay of the hydrogen overvoltage is discussed here under the premises i) that the hydrogen electrode reaction alone occurs on the electrode, ii) that either the slow discharge or the catalytic mechanism is exclusively responsible for the hydrogen electrode reaction and, iii) that the transport processes of ions and dissolved hydrogen molecules in solution are practically in equilibrium.

The hydrogen electrode reaction in alkaline solution

$$2H_2O + 2\varepsilon = H_2 + 2OH^-$$

is composed of the two elementary steps in either case of the mechanism, *i.e.* the discharge step and that of the recombination of adsorbed hydrogen atoms,

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

$$2H\,(a) \longrightarrow H_2, \qquad (II)$$

where H (a) is an adsorbed hydrogen atom and ε a metal electron.

After the polarizing current is switched on, electrons supplied to the cathode partly charge up the electrode surface, rendering the electrode potential more negative, and partly pass into the solution through the discharge step (I), forming H(a) on the electrode surface and OH^- in the solution. Let δq be the total amount of electricity supplied to the cathode, $\delta q'$ the amount which charges up the electrode surface and $\delta q''$ that passes into the solution respectively in time δt; we have

$$\delta q = \delta q' + \delta q''. \tag{1}$$

The δq, $\delta q'$ and $\delta q''$ are expressed in terms respectively of the polarizing current density i, of the differential capacity C_D of the double layer and of current density i_1 appropriate to the net rate of step (I), as

$$\delta q = -i\delta t\,, \tag{2a}$$

$$\delta q' = -C_D\delta\eta\,, \tag{2b}$$

$$\delta q'' = -i_1\delta t\,, \tag{2c}$$

where η is the hydrogen overvoltage*). Substituting Eqs. (2) into Eq. (1), we have

$$C_D = \frac{i-i_1}{\frac{d\eta}{dt}} \tag{3a}$$

At the moment when the polarizing current is just switched on, but the double layer is not yet charged up, almost all electrons supplied to the cathode are used for charging up of the double layer, *i.e.* $i_1 \ll i$ at $t=0$. Thus we have from Eq. (3a)

$$C_D = \frac{i}{\left(\frac{d\eta}{dt}\right)_{t=0}}, \tag{3b}$$

which enables us to determine the capacity C_D of the double layer. The double layer is now composed, according to the STERN's model[4], of the HELMHOLTZ layer and the diffuse layer in series, hence

$$\frac{1}{C_D} = \frac{1}{k} + \frac{1}{C_d} \tag{4}$$

where k is the capacity of the HELMHOLTZ layer and C_d that of the diffuse layer. The C_d is large enough, as calculated[5] for the electrolytes used for the present investigation, safely to ignore its reciprocal on the right-hand side of Eq. (4). It follows that C_D is practically constant independent of η or electrolyte concentration as later experimentally verified. The i_1 is determined as a function of η by (3a) at any point on the build up curve using appropriate value of $d\eta/dt$.

The differential capacity C of the hydrogen electrode is defined as the electricity required for unit increase of the electrode potential. The current used for charging up the electrode is now the overall current supplied less the

* Negative of the potential of the test electrode as referred to a reversible hydrogen electrode in the same environment.

current corresponding to the rate with which the acts of the hydrogen evolution reaction terminate. We have thus

$$C\delta\eta = (i-i_2)\,\delta t\,, \tag{5a}$$

or

$$C = \frac{i-i_2}{\dfrac{d\eta}{dt}}\,, \tag{5b}$$

where i_2 is the net rate of step (II), which terminates the hydrogen evolution reaction, in terms of current density. Eq. (5b) enables us to determine C at any overvoltage in course of the build up of overvoltage, if i_2 is known.

The above arguments apply also to the decay of the overvoltage after switching off the polarizing current, exceping that $i=0$ in the latter case. We have thus from Eqs. (3a) and (5b) for the decay curve

$$C_D = -\frac{i_1}{\dfrac{d\eta}{dt}}\,, \tag{6a}$$

$$C = -\frac{i_2}{\dfrac{d\eta}{dt}}\,, \tag{6b}$$

hence

$$C = \frac{i_2}{i_1}\,C_D\,. \tag{6c}$$

The i_1 at any point on the decay curve may be betermined by Eq. (6a) on the base of the constant C_D.

The $i_2(\eta)$ in Eq. (6c) is practically identified with $i_s(\eta_s)$ for $\eta_s=\eta$, where i_s or η_s denotes i or η at steady state, according to the following considerations. Let the catalytic mechanism be responsible for the hydrogen evolution reaction. The chemical potential of H(a) is then determined by η because of the equilibrium of step (I) practically attained, whereas the chemical potential of H_2 is fixed according to premise iii). The chemical potentials of the initial and the final states of the rate-determining step and in consequence its rate i_2 are determined respectively as sole functions of η and the function $i_2(\eta)$ is practically identical with $i_s(\eta_s)$ for $\eta_s=\eta$, excepting that the minute fraction of η or η_s to keep up the rate of the step (I) respectively at i_1 or i_s is different. Neglecting the difference, $i_2(\eta)$ is identified with $i_s(\eta_s)_{\eta_s=\eta}$.

If alternatively the slow discharge mechanism is operative, the chemical

potential of the initial state, *i.e.* $H_2O+\varepsilon$ of the rate-determining step (I) in this case is determined by η, whereas that of the final state $H(a)+OH^-$ is fixed constant by virtue of premise iii) and the equilibrium of step (II) practically attained. The rate of the rate-determining step (I) in this case and in consequence i_2 are respectively determined by η and hence the function $i_2(\eta)$ is identical with $i_s(\eta_s)$ for $\eta_s=\eta$ excepting that a minute fraction respectively of η or η_s imposed upon step (II) is different.

The $i_2(\eta)$ is thus identified with $i_s(\eta_s)_{\eta_s=\eta}$ in either case of the mechanism neglecting the difference between the minute fraction of overvltage imposed upon the step other than the rate-determining one, hence we have from Eq. (6c)

$$C=\frac{i_s(\eta_s)_{\eta_s=\eta}}{i_1}C_D\,. \tag{6c}$$

The particular forms of the above conclusions are now deduced below in the cases of the slow discharge and the catalytic mechanism respectively.

Slow discharge mechanism

The i_1 equals i_2 irrespective of η, since the accmulation of H(a) does not occur because of the equilibrium of step (II) practically attained and premise iii). Hence we have from Eqs. (5b) and (3a) in case ot build up of η,

$$C=C_D=\frac{i-i_1}{\dfrac{d\eta}{dt}}, \tag{7a}$$

or from Eqs. (6a) and (6b) in case of decay of η,

$$C=C_D=-\frac{i_1}{\dfrac{d\eta}{dt}}, \tag{7b}$$

which shows that C equals C_D at any overvoltage of build up or decay, as has already been shown by FRUMKIN *et al*[1]. The $i_1(\eta)$ is identical with $i_s(\eta_s)$ for $\eta_s=\eta$ in case of the build up or of the decay, since $i_1=i_2$ and $i_2(\eta)$ is identical with $i_s(\eta_s)$ for $\eta_s=\eta$ as shown above.

Catalytic mechanism

The increment $\delta\theta$ of the surface coverage θ of H(a) is expressed as

$$\delta\theta=\frac{N_A}{GF}(i_1-i_2)\,\delta t, \tag{8a}$$

where N_A is the Avogadro number, F the Faraday and G the number of sites of adsorption per unit area. We have from Eqs. (3a), (5b) and (8a) or from (6a), (6b) and (8a) respectively in case of build up or decay of η,

$$C = C_D + \frac{GF}{N_A}\frac{d\theta}{d\eta}\,. \tag{8b}$$

The chemical potential $\mu^{H(a)}$ of H(a) varies with η in this case as

$$\delta\mu^{H(a)} = F\delta\eta\,. \tag{8c}$$

We have from Eqs. (8b) and (8c)

$$C = C_D + \frac{GF^2}{N_A}\frac{d\theta}{d\mu^{H(a)}}, \tag{8d}$$

which shows that C depends on the adsorption isotherm of H(a), but not on pH of solution.

Eqs. (7) and (8d) show that the catalytic mechanism is distinguishable from the slow discharge mechanism, as mentioned in the introduction, by comparing C with C_D respectively determined by the method so far developed.

§ 2. Experimental

The galvanostatic transients have been observed with the same apparatus

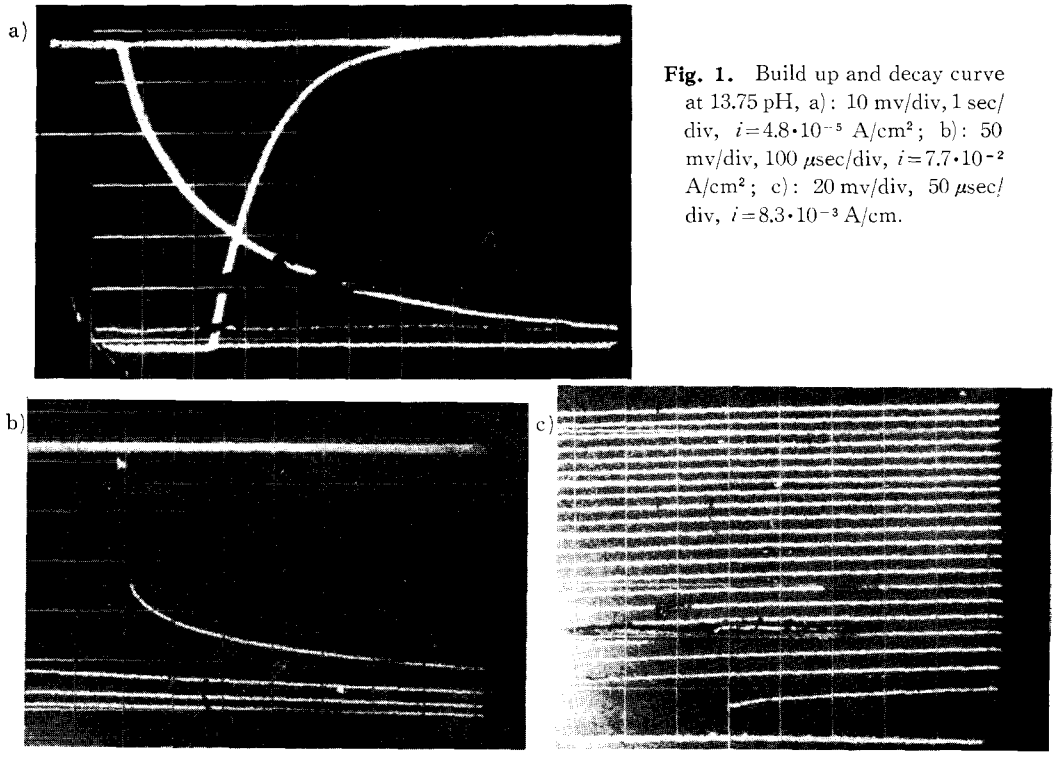


Fig. 1. Build up and decay curve at 13.75 pH, a): 10 mv/div, 1 sec/div, $i=4.8\cdot10^{-5}$ A/cm^2; b): 50 mv/div, 100 μsec/div, $i=7.7\cdot10^{-2}$ A/cm^2; c): 20 mv/div, 50 μsec/div, $i=8.3\cdot10^{-3}$ A/cm.

as those described in detail in part I. The polarizing current was switched on or off by means of a contact of mercury and nickel wire, which required less than 1 μ sec for switching on, but a few μ sec for switching off. The build up and the decay of overvoltage were traced by a memoscope over the range of sweeping time from 10^{-5} to 1 sec/div (the time required to cover one division on the screen of the memoscope), and that of current density from 10^{-6} to 10^{-1} A/cm; the electrolyte was aqueous sodium hydroxide of 13.75 or 13.10 pH. Fig. 1 shows the typical photograph of the build up and the decay curves of the potential difference E between the reference electrode and the test electrode. Instantaneous jump up or drop down of E is observed in the respective case, as seen in the Figure, which is respectively followed by its gradual increase or decrease. The former instantaneous change is the ohmic overvoltage and the latter gradual one that of the true hydrogen overvoltage as demonstrated in Part I.

§ 3. Results and Discussions

3. 1) The differential capacity of the double layer

It has been shown in § 1 that C_D is determined from the initial part either

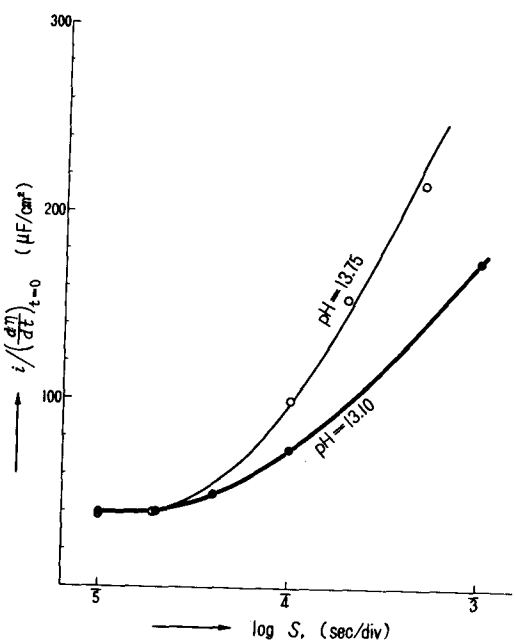


Fig. 2. $i/(d\eta/dt)_{t=0}$ *vs.* sweeping time S sec/div, determined from the initial stage of build up, $i=10^{-1}\sim10^{-4}$ A/cm².

of the build up curve by (3b) or of the decay curve by (6a). The C_D was actually determined from the build up curve on account of the smaller time required for switching on as mentioned in § 2. The C_D is determined according to Eq. (3b) as the limiting value of $i/(d\eta/dt)_{t=0}$. Fig. 2 shows the values of $i/(d\eta/dt)_{t=0}$ plotted against the logarithm of the sweeping time S in the solutions of 13.10 and 13.75 pH. We see in the Figure that $i/(d\eta/dt)_{t=0}$ for a solution of a definite pH is given as a definite function of S irrespective of the current density. The $i/(d\eta/dt)_{t=0}$ thus found is constant independent of pH in either solution for the sweeping time of from 10 to 20 μ sec/div ; $i/(d\eta/dt)_{t=0}$ increases with increase of sweeping time beyond 20 μ sec/div. This indicates that almost all electrons supplied to the cathode are used for the charging up of the double layer within the sweeping time of 20 μ sec/div, while $(d\eta/dt)_{t=0}$ for longer sweeping time includes the contribution from the formation of H(a) through the step (I). The constant values of $i/(d\eta/dt)_{t=0}$ observed for the sweeping time from 10 to 20 μ sec/div has been identified with the relevant value of C_D. The C_D

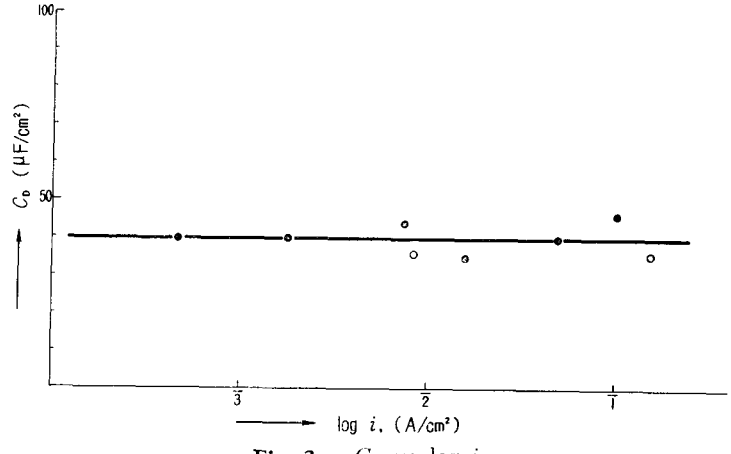


Fig. 3. C_D *vs.* log i.

thus determined is, as shown in Fig. 3, constant at 40 ± 5 μF per apparent area independent of current density as well as pH.

3.2) The rate of the discharge step

The rate i_1 of the discharge step is determined by Eqs. (3a) and (6a) from $C_D=40$ $\mu F/cm^2$, i and the appropriate value of $d\eta/dt$ on the build up and the decay curve. The log i_1 thus obtained is plotted against η in Figs. 4 and 5 side by side with log i_s plotted against the overvoltage η_s at a steady state. We see in the Figures that the log $i_1\sim\eta$-curves do not coincide with the log $i_s\sim$ η_s-curve in either solution, which disproves the discharge step as rate-determining

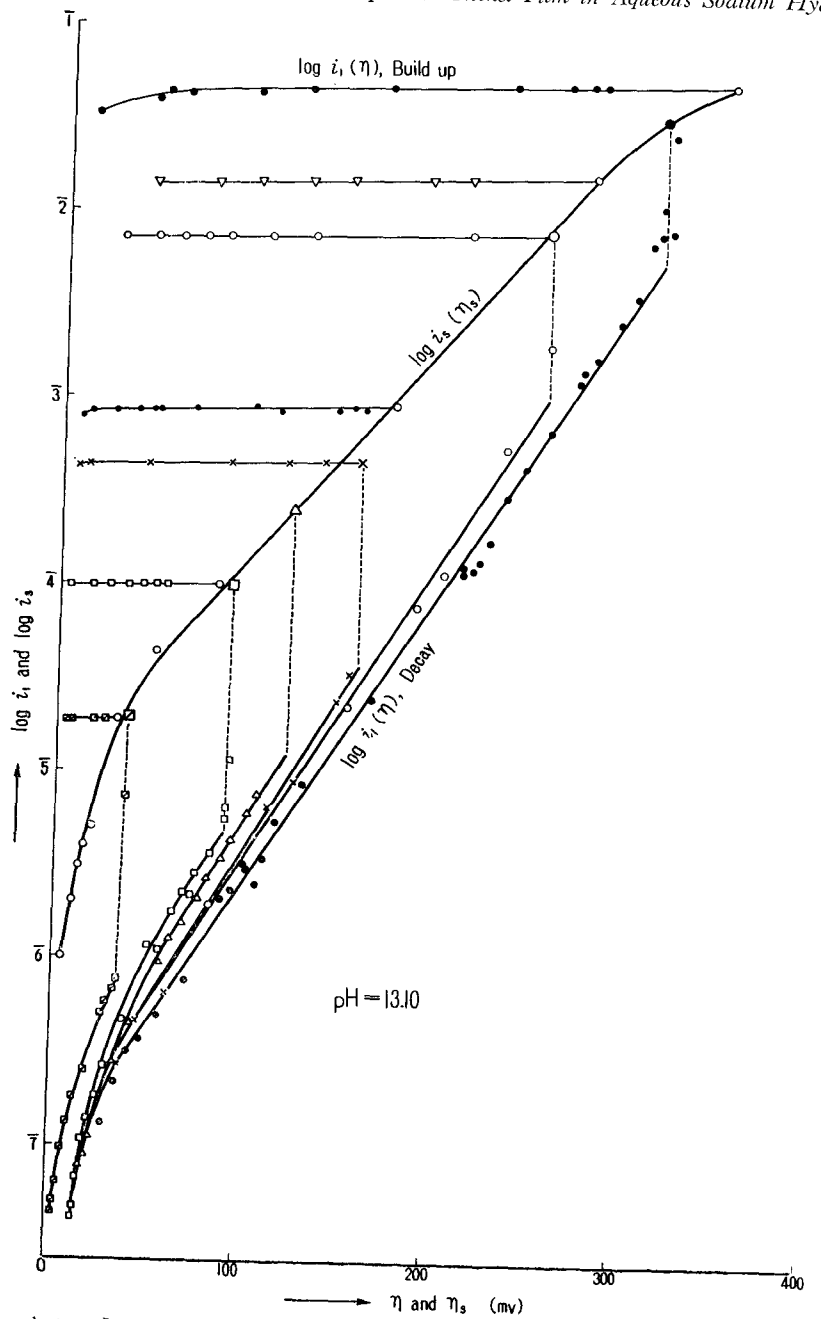
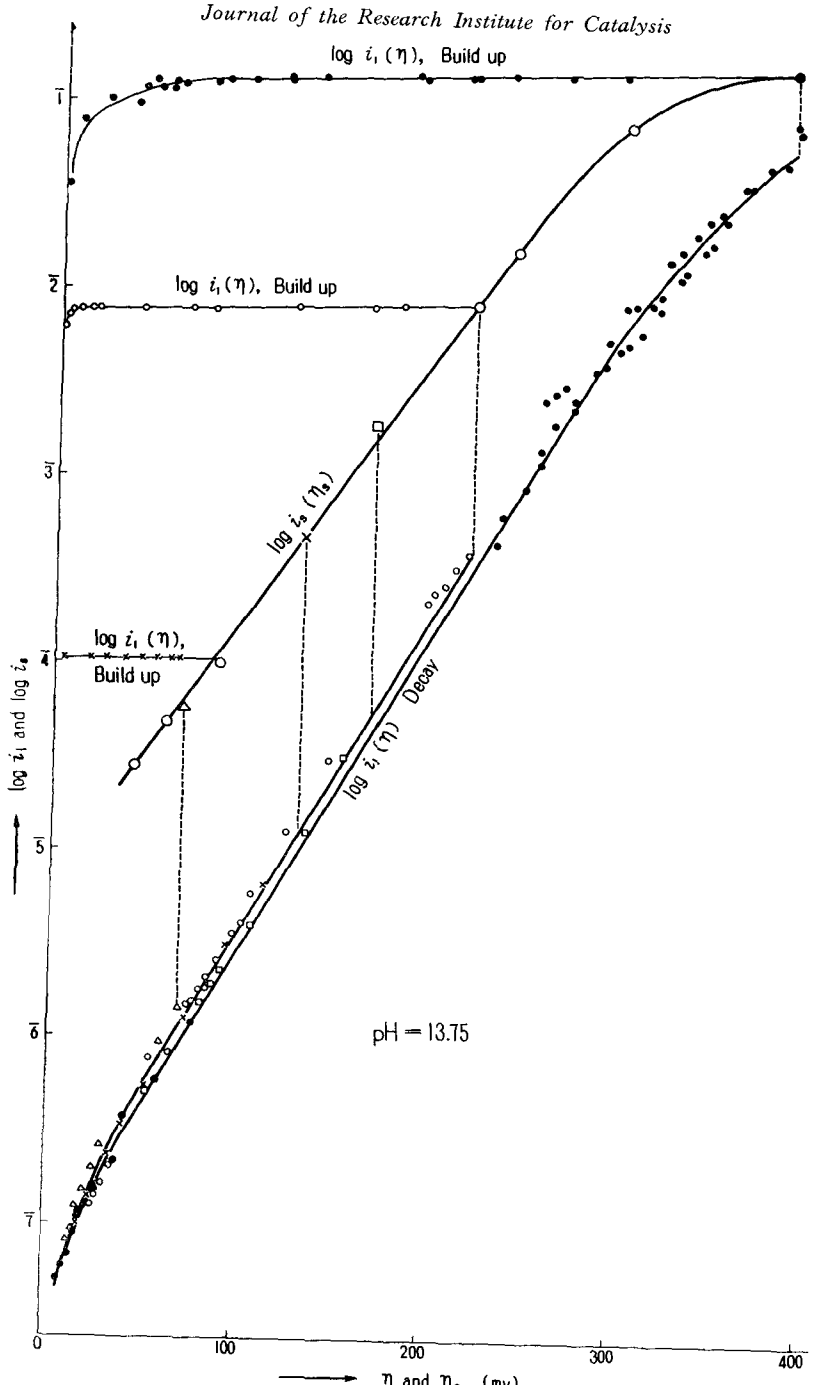


Fig. 4 and 5. Log i_1 *vs.* η and log $i_s \sim \eta_s$ respectively at 13.10 and 13.75 pH. "log i_s (η_s)" in the Figures shows log i_s at the steady state plotted against η_s. "log i_1 (η), build up" is the plot of log i_1 against η in course of the build up and "log i_1 (η), decay" is that in course of the decay; points derived from the same decay curve and i_s-value from which the curve starts,



are shown by the same symbol. The segment of vertical dotted line indicates the decrease of log i_1 at practically constant η_s.

according to the argument in § 1.

We now discuss the $\log i_1 \sim \eta$ relation with regard to the part played by the constituent step (I) of the hydrogen electrode reaction. Fig. 4 and 5 show that the $\log i_1 \sim \eta$-curve of the build up process is composed of two distinctly separable parts, *i.e.* that of a sharp rise of i_1 and the subsequent part of a steep increase of η. The i_1 attains to its final value i_s through its sharp rise, while η remains negligibly small as compared with its final value η_s. The η then increases steeply until η_s is attained, while i_1 practically remains constant throughout. This shows clearly that the double layer is charged up in the first stage to cause prompt increase of i_1 almost up to i_s, whereas H(a) is accumulated in the second stage just to increase overvoltage. It follows that the overvoltage is imposed practically exclusively upon the recombination of H(a).

The i_1 in case of the decay process falls off practically instantaneously after switching off the polarizing current, while the overvoltage remains practically constant at η_s, as seen in Figs. 4 and 5. The overvoltage imposed upon the dischage step is thus quite small at the steady state. After the rapid fall of i_1 at practically constant η_s, $\log i_1$ decreases linearly with decrease of η with a constant inclination of $d\eta/d \log i_1 \approx 60$ mv over a wide range of η except at extremely high or low η equal to η_s, where the $\log i_s \sim \eta_s$-curve or the TAFEL line bends, and the $\log i_1 \sim \eta$-curves are approximately coincident with each other irrespective of η_s, from which a decay curve starts, and of the concentration of the solution. This verifies a necessary conclusion from the catalytic mechanism as shown below. The equilibrium of step (I) practically attained defines the chemical potential of H(a) and in consequence θ as a sole function of η. It follows by Eq. (8b) that C is a sole function of η. The i_2 is, on the other hand, another sole function of η as discussed in § 1. The i_1 should in consequence depend solely on η according to Eq. (6c) irrespective of η_s, from which the decay curve is started, as verified by the above experimental result.

3. 3) The differential capacity of hydrogen electrode

The differential capacity C was determined as a function of η from the decay curve by Eq. (6b) identifying $i_2(\eta)$ with $i_s(\eta_s)$ for $\eta_s = \eta$ or by Eq. (6c) according to the arguement in § 1. Fig. 6 shows $C \sim \eta$-curve as started from the highest value of η, where C is referred to the true area by multiplying its apparent value by the ratio of $C_D = 18\ \mu F/\text{cm}^2$ as observed by FRUMKIN *et al.*[9] with mercury electrode to $C_D = 40\ \mu F/\text{cm}^2$ for the apparent area.

It was found that C thus determined was independent of the magnitude of sweeping time except at $t = 0$. The value of $(d\eta/dt)_{t=0}$ decreased with increase of sweeping time S and attained a constant value beyond a critical value S_c

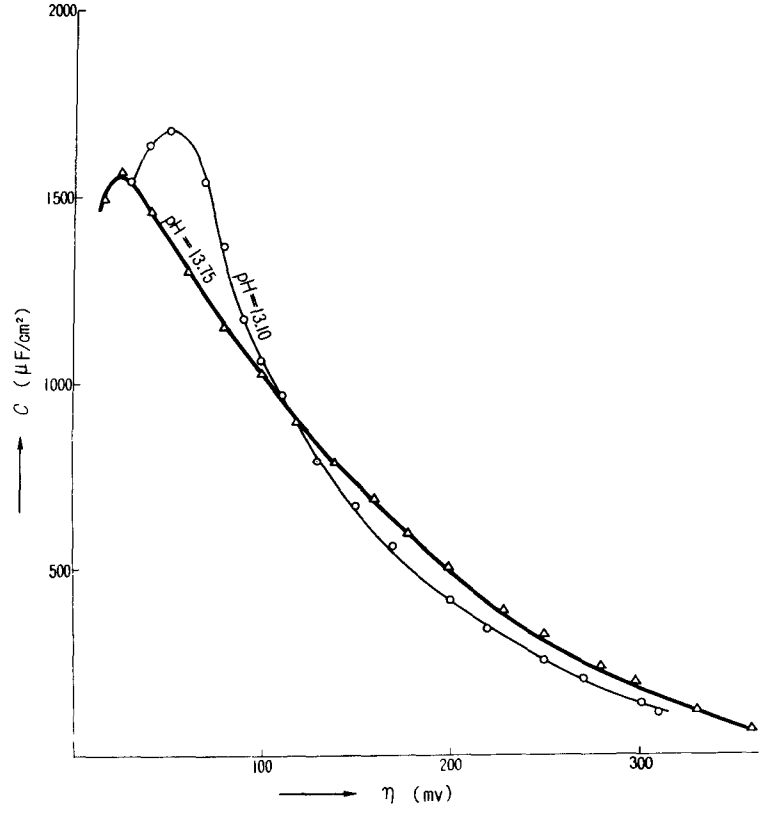


Fig. 6. Differential capacity C *vs.* η, derived from decay curve.

of S, which depends on i_s varying from $S_c \approx 100\ \mu$ sec/div for $i_s = 0.1$ A/cm² to $S_c \approx 0.1$ sec/div for 10^{-6} A/cm². The constant value of $(d\eta/dt)_{t=0}$ was observed from S_c up to 1 sec/div. The constant value of $(d\eta/dt)_{t=0}$ for $S > S_c$ was found coherent with $d\eta/dt$ for $t > 0$ as a function of t. This result realizes the point raised in the introduction with regard to the method of analysis of PAST and JOFA[2] that the differential capacity or $(d\eta/dt)_{t=0}$ may include a contribution from the equilibriation of the discharge step. Based on this result the differential capacity was determined from $(d\eta/dt)$ for $t > 0$ inclusive of $(d\eta/dt)_{t=0}$ for $S > S_c$ as relevant to the accumulation of H(a) with the discharge step practically in equilibrium.

It is thus found that the value of C is very high as compared with C_D at any overvoltage and the $C \sim \eta$-curve has a maximum at an overvoltage around 50 mv and is independent of pH within experimental errors. These results confirm the conclusions from the catalytic mechanism rereferred to in § 1. It

has already been theoretically shown by one of the authors[5] that C has a maximum at an overvoltage, where θ equals 1/2 in case of the catalytic mechanism. The value of C is found also far greater than the differential capacity observed by PAST and JOFA[2] with nickel electrode in concentrated alkaline solutions, which is an average of C over a finite range of η along the decay curve*). This discrepancy is accounted for as due to the inclusion of contribution from the discharge step at the initial stage of the decay curve, which increases $(d\eta/dt)_{t=0}$ or decreases C according to Eq. (6b).

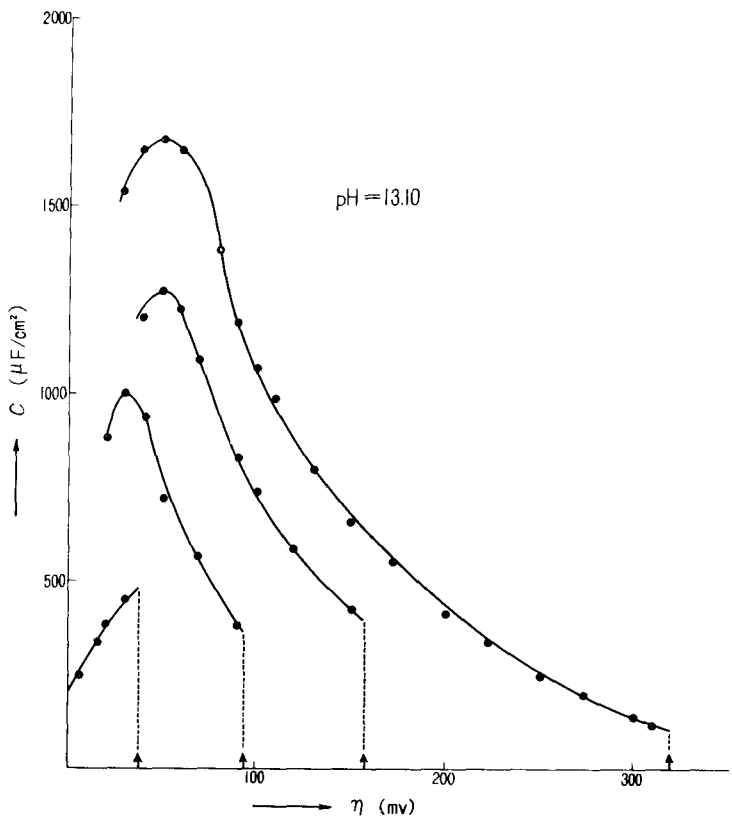


Fig. 7. Differential capacities derived from different η_s's indicated by the symbol ↑.

*) They used an integral formula of Eq. (6b) for determining the differential capacity as $C = \dfrac{2.3 I_0 (t_1 - t_2) \exp\left[\dfrac{2.3}{b}(\eta_1+\eta_2)\right]}{b\left[\exp\left(\dfrac{2.3}{b}\eta_1\right) - \exp\left(\dfrac{2.3}{b}\eta_2\right)\right]}$ for higher η's or $C = \dfrac{t_1 - t_2}{\omega \ln(\eta_2/\eta_1)}$ for lower η's assuming $i_2(\eta) = i_s(\eta_s)$ for $\eta_s = \eta$ and expressing i_s, in accord with experimental results, as $i_s = I_0 \exp\left(\dfrac{2.3}{b}\eta_s\right)$ for higher η's or $i_s = \eta_s/\omega$ for lower η's, where ω is the resistance.

It is found further that the $C\sim\eta$-curve lies the higher, the higher the η_s from which the decay curve starts, as seen in Fig. 7, qualitatively in accord with the results obtained previously by LUKOWZEW and LEWINA[3]. This is attributed as follows to the diffuse-out of hydrogen dissolved into the electrode metal. The higer the η_s, the higher the chemical potential $\mu^{H(a)}$ in accord with the catalytic mechanism, hence that of dissolved hydrogen provided that the latter is practically in equilibrium with H(a). As η lowers from η_s along the decay curve, the dissolved hydrogen should diffuse out more or less to reduce the decrease of $\mu^{H(a)}$ through the step (II). This defers the decay of η by Eq. (8c) or apparently increases C by Eq. (6b) in accord with the observation.

The analysis of the build up and the decay curves observed on the hydrogen electrode of evaporated nickel film in aqueous sodium hydroxide leads to the conclusion that the overvoltage is imposed upon the recombination of H(a) but scarcely upon the discharge step, *i.e.* the catalytic mechanism holds good.

Acknowledgement

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