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HYDROGEN OVERVOLTAGE ON PLATINUM IN AQUEOUS SODIUM HYDROXIDE

Part III. Intermediates

By

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(Received September 12, 1966)

Abstract

The major intermediate of the hydrogen evolution reaction on Pt in aqueous NaOH and Na₂SO₄ was determined from the analyses of the overvoltage-time curves after switching on the polarizing current. It was found that the major intermediate is sodium atom which is produced by the discharge of Na⁺, but not H(a), and that the intermediate sodium atom penetrates into the lattice of Pt several atomic layers in depth under the cathodic polarizations and intermetallic compound or solid solution is formed at *ca.* -0.8 v (*vs.* NHE). This intermediate sodium atom is responsible for the hydrogen overvoltage, which causes the change in the electronic work function of the electrode and controls the chemical potential of adsorbed hydrogen atom through the second elementary step.

Introduction

In the previous papers^{1),2)} it has been concluded on the basis of the studies of the hydrogen overvoltage by means of the galvanostatic transient methods and its pH-dependence in steady state that the hydrogen electrode reaction is composed of the following elementary steps in alkaline solutions containing sodium ions:



where H(a) and Na(I) are respectively the adsorbed hydrogen atom and the intermediate sodium atom, and the last step is rate-determining. Further it has been verified that the overvoltage of the discharge step in course of build up is attributed to the change of the electrostatic potential of the electrode caused by charge up of the electric double layer at the metal-solution interface and

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the overvoltage in steady state can be attributed at least partly to the change of the work function of the electrode caused by the intermediate species Na(I) and/or H(a).

In the present paper the intermediate species will be discussed on the basis of the analysis of the decay curves observed in alkaline and acid solutions of various concentrations of sodium ions.

1. Theoretical analysis of the decay curves

As stressed in Part I, the discharge step can be regarded in equilibrium in the course of decay of the overvoltage after the lapse of time τ_1 , the time constant of the discharge step. The latter step being kept in equilibrium in this stage of the decay process, the intermediate species is consumed through the elementary steps which follow the discharge step. The change in the overvoltage in this stage is caused by the decrease of the quantity of the intermediate species accumulated on the electrode, so that

$$\frac{d\eta}{dt} = \frac{d\eta}{dC} \frac{d\tilde{C}}{dt}, \quad (1)$$

where C is the concentration of the intermediate species expressed in number of atoms per true unit area and $-dC/d\eta$ represents the so-called pseudocapacity of the electrode^{3),4)}. It is reasonable to assume that dC/dt in the decay process is given by the steady current density i at the same overvoltage as that at the moment, as

$$-\frac{dC}{dt} = \frac{N_A i}{F}, \quad (2)$$

where F is the Faraday and N_A the AVOGADRO number, since the overvoltage of the discharge step in steady states is quite small as compared with the total one as already shown in Part I. It follows from Eqs. (1) and (2) that

$$-\frac{dC}{d\eta} = \frac{N_A i}{F\dot{\eta}} \quad (3)$$

which enables $-dC/d\eta$ to be determined at any overvoltage in the decay process.

If H(a) is abundant as compared with Na(I), $-dC/d\eta$ at a given overvoltage in the decay process should be constant independent of pH and the concentration of sodium ion C^{Na^+} in solution, since the activity of H(a) at a given overvoltage in the decay process is defined by the equilibrium relation $\text{H}_2\text{O} + e \rightleftharpoons \text{H(a)} + \text{OH}^-$ at the overvoltage as

$$a^{\text{H(a)}} = k(a^{\text{H}_2})^{1/2} \exp(-F\eta/RT), \quad (4)$$

viz. the activity of H(a) depends only on η , but not on pH and $C^{\text{H}a^+}$, where $a^{\text{H}(a)}$ and a^{H_2} are respectively the activities of H(a) and hydrogen gas, and k a constant.

On the other hand, the activity of Na(I) is given by the equilibrium relation $\text{Na}^+ + e \rightleftharpoons \text{Na(I)}$ as a function of C^{Na^+} and the electrode potential referred to the normal hydrogen electrode E_{nhe} as

$$a^{\text{Na(I)}} = k' a^{\text{Na}^+} \exp(-FE_{\text{nhe}}/RT), \quad (5)$$

where $a^{\text{Na(I)}}$ and a^{Na^+} are respectively the activities of Na(I) and Na^+ , and k' a constant. When Na(I) is abundant as compared with H(a), $-dC/d\eta$ in a solution of constant C^{Na^+} should depend only on $a^{\text{Na(I)}}$, hence on E_{nhe} alone, but not on η . Comparing $-dC/d\eta$ at a given value of η or E_{nhe} in solutions of various pH's and concentrations of Na^+ , it is possible to determine the major intermediate, if any, of the hydrogen electrode reaction.

2. Experimental results and discussions

Experimental apparatus and procedures are the same as described in Part I. Examples of the oscillograms of the potential-time curves are shown in

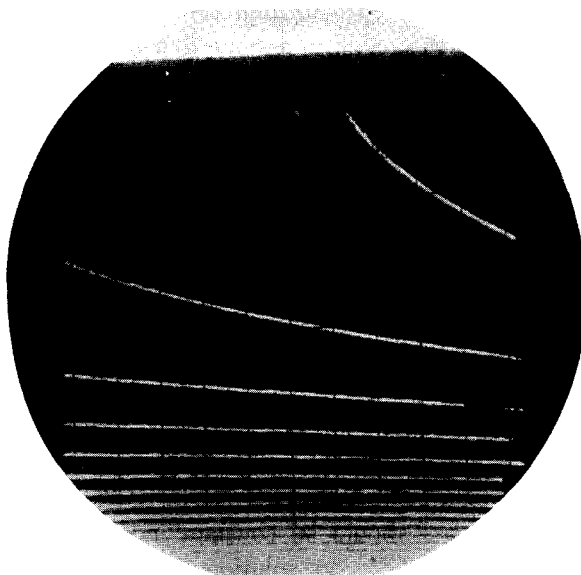


Plate 1. The potential-time variation after switching off a polarizing current on an evaporated platinum film in NaOH_{aq} , pH 13.3; $i = 2.0 \cdot 10^{-3}$ amp · cm⁻², the ordinate 20 mv/Div, the abscissa 100 μ sec/Div.

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Plate 2. The potential-time variation after switching on a polarizing current on an evaporated platinum film electrode in aqueous Na_2SO_4 , pH 2.83; the ordinate 100 mv/Div, the abscissa 5 m sec/Div, $i = 8.7 \cdot 10^{-2}$ amp $\cdot\text{cm}^{-2}$.

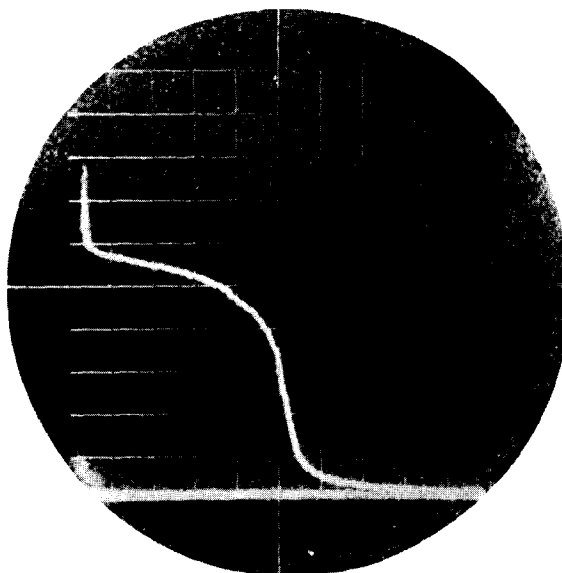


Plate 3. The potential-time variation after switching off a polarizing current on an evaporated platinum film electrode in aqueous Na_2SO_4 , pH 2.83; $i = 1.35 \cdot 10^{-1}$ amp $\cdot\text{cm}^{-1}$, the ordinate 100 mv/Div, the abscissa 100 msec/Div.

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Plates 1~3, observed on evaporated platinum film electrodes in NaOH_{aq} and $\text{Na}_2\text{SO}_{4,\text{aq}}$ acidified with sulfuric acid. The decay curves are analyzed as described in the foregoing section and the intermediate species in the cathodically polarized states are discussed on the results.

The $\log \dot{\eta}$ calculated from the decay curves in NaOH_{aq} of pH 13.3 is plotted against η in Fig. 1, together with $\log i$ in steady state plotted against η .

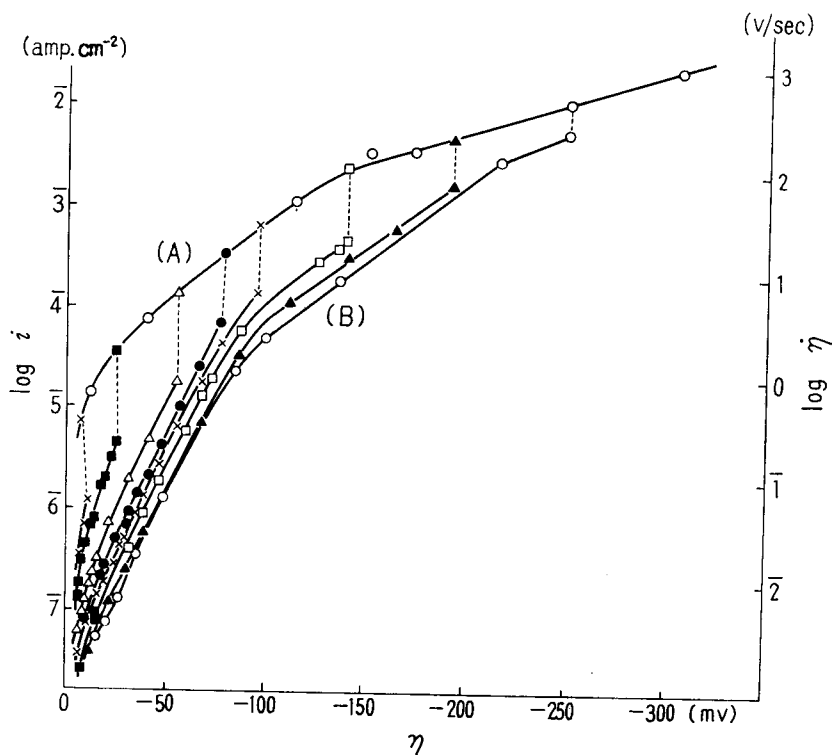


Fig. 1. The $\log i$ vs. η in steady states (A), and $\log \dot{\eta}$ vs. η in the decay processes starting from various steady states (B), on an evaporated platinum film in NaOH_{aq} , pH 13.3. The sign in curves (B) corresponds to the same sign in curve (A) from which the respective decay curve starts.

The current density was assigned to the true unit area calculated from the differential capacity of the electric double layer at the metal-solution interface¹⁾. The values of $-dC/d\eta$ calculated from Fig. 1 on the basis of Eq. (3) are plotted against η in Fig. 2.

It is found from Figs. 1 and 2 that $\log \dot{\eta}$ decreases while $-dC/d\eta$

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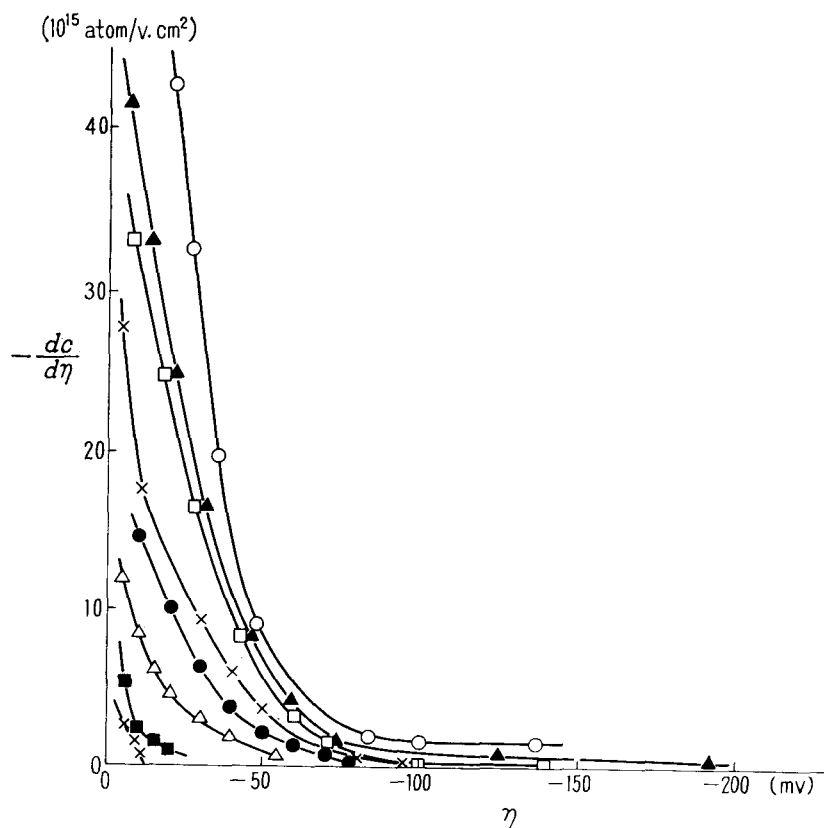


Fig. 2. The $-\frac{dc}{d\eta}$ vs. η calculated from Fig. 1. The signs correspond respectively to those in Fig. 1.

increases respectively with the displacement of starting overvoltage to more negative side. Integrating the curves $-\frac{dC}{d\eta}$ vs. η , the concentration of the intermediate species on the electrode can be determined from Fig. 2. The increase of the concentration ΔC referred to that at $\eta=0$ are plotted against η in Fig. 3. The ΔC obtained from a decay curve increases with increase of $-\eta$ toward a saturation value. It is, however, found from comparison of ΔC 's obtained from the decay curves starting from different overvoltage that ΔC at a given overvoltage is the larger, the higher the starting overvoltage as in the case of nickel hydrogen electrode in NaOH_{aq} ^{4),5)}, and that the value ΔC_s of ΔC in a steady state from which the decay curve starts, increases approximately proportionally to the starting overvoltage until it exceeds the quantity of the monolayer adsorption, as seen from Fig. 3. These results

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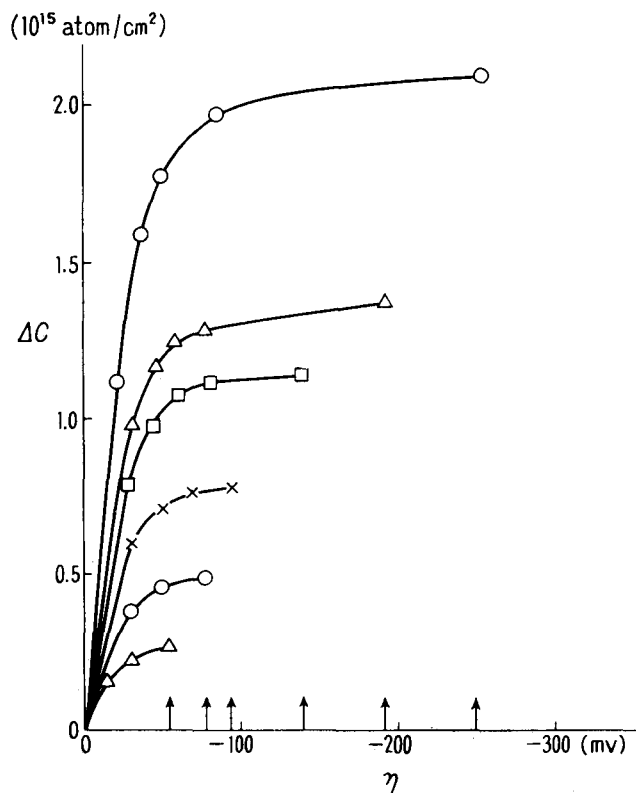


Fig. 3. The relation between the concentration of the intermediate species and overvoltage calculated from Fig. 2.

suggest that the intermediate species not only is adsorbed on the electrode surface but also penetrates into the lattice of platinum.

In solutions of NaOH of pH 13.1 and 11.53, $\log \dot{\eta}$ and $-dC/d\eta$ at a given overvoltage also depend on the starting overvoltage as in the case of pH 13.3, as shown in Figs. 4 and 6, and Figs. 5 and 7. The ΔC_s in these solutions are plotted against the starting overvoltage η_s in Fig. 8. As seen from the Figure, ΔC_s at a given η depends considerably on the concentration of NaOH. It may be concluded from this result that the major intermediate is not H(a), but Na(I). The range of pH might not, however, be extensive enough to draw a definite conclusion on the intermediate species from the $-dC/d\eta$ vs. E_{nhe} curves.

In the previous paper¹⁾ it has been pointed out that the electron transfer step is the discharge of sodium ion in alkaline $\text{Na}_2\text{SO}_{4,\text{aq}}$ as in the case of

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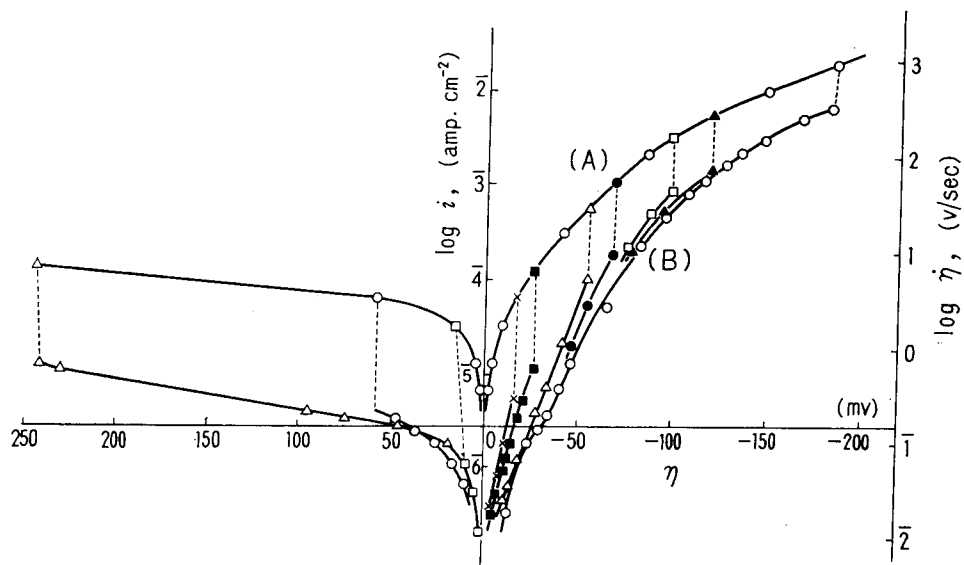


Fig. 4. The $\log i$ vs. η in steady states, and $\log \bar{\zeta}$ vs. η in the decay processes on a platinum film in NaOH_{aq} , pH 13.10.

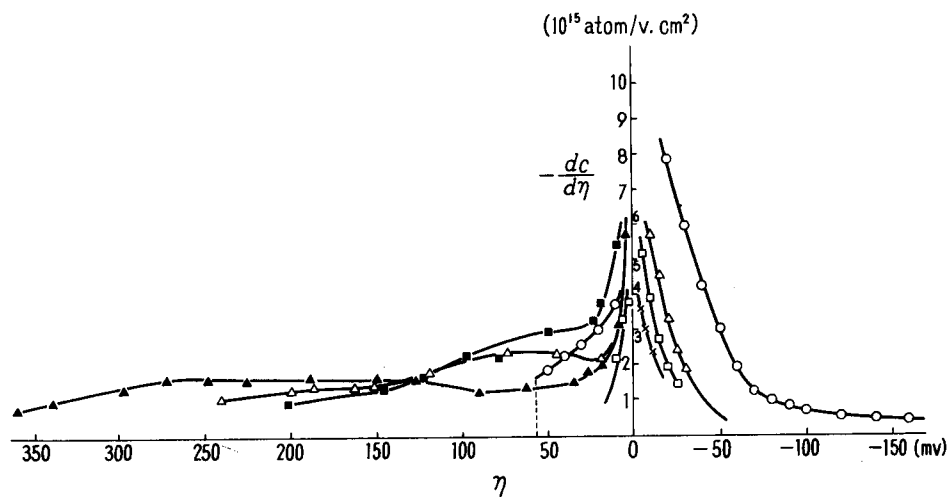


Fig. 5. The $-dc/d\eta$ vs. η on a platinum film in NaOH_{aq} , pH 13.10.

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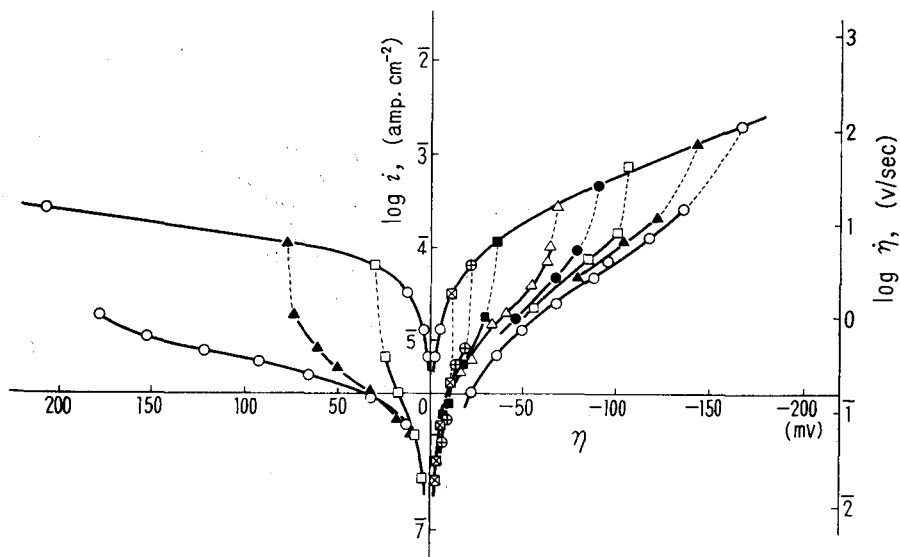


Fig. 6. The $\log i$ vs. η in steady states and $\log \dot{v}$ vs. η in the decay processes on a platinum film in NaOH_{aq} , pH 11.53.

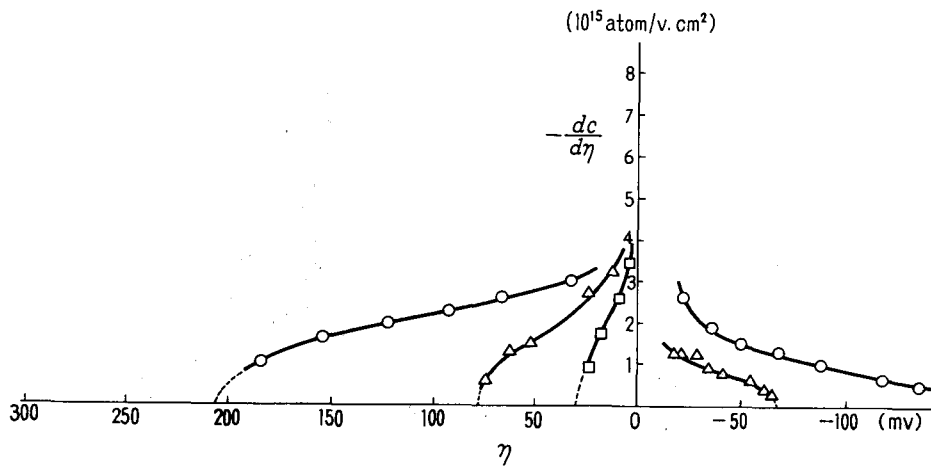


Fig. 7. The $-dc/d\eta$ vs. η on a platinum film in NaOH_{aq} , pH 11.53, calculated from Fig. 6.

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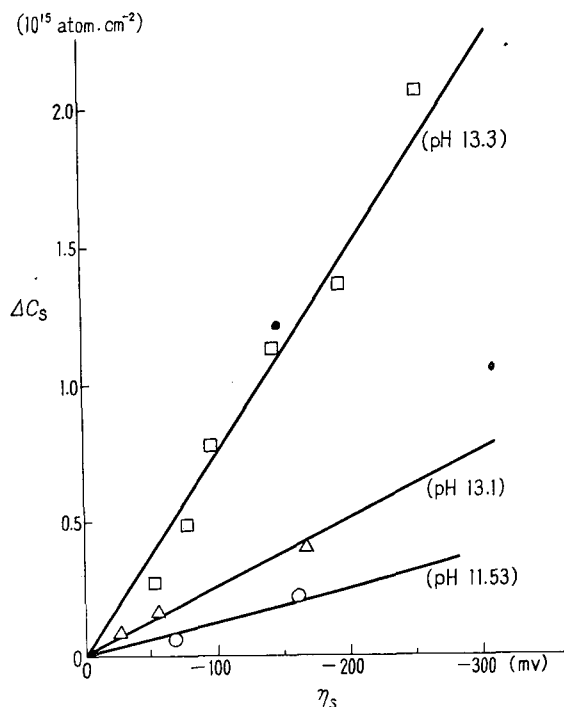


Fig. 8. The relation between the concentration of the intermediate species and overvoltage in steady states in NaOH_{aq} of various pH's.

NaOH_{aq} . The polarization curves in steady states and the decay curves were now observed in Na_2SO_4 acidified with H_2SO_4 or alkalized with NaOH in order to find the relations between $-dC/d\eta$ and E_{nhe} over a wide range of pH.

The $\log i$ plotted against E_{nhe} in steady states are shown in Fig. 9, together with $\log \dot{\eta}$ in the decay process, which were obtained in sulfuric acid of pH 2.4, in 0.8 N Na_2SO_4 of pH 2.83 and in 0.5 N Na_2SO_4 of pH 11.4. The rate of the hydrogen electrode reaction at a given overvoltage was very high in sulfuric acid, but lowered reproducibly by addition of Na_2SO_4 , and a potential jump occurred on the $\log i$ vs. E_{nhe} curve in the acidic Na_2SO_4 at a certain current density, as in the case of platinum hydrogen electrode in $\text{K}_2\text{SO}_{4,\text{aq}}$ observed by SCHULDINER⁶). As the current density was increased beyond the potential jump, the $\log i$ vs. E_{nhe} curve in the acidic Na_2SO_4 practically coincide with that in the alkaline Na_2SO_4 . It is further found from comparison of the $\log i$ vs. E_{nhe} curves in acidic Na_2SO_4 in Fig. 9 with the $\log i$ vs. η curves in pure NaOH_{aq} in Fig. 3 in Part II both under the cathodic polarization that

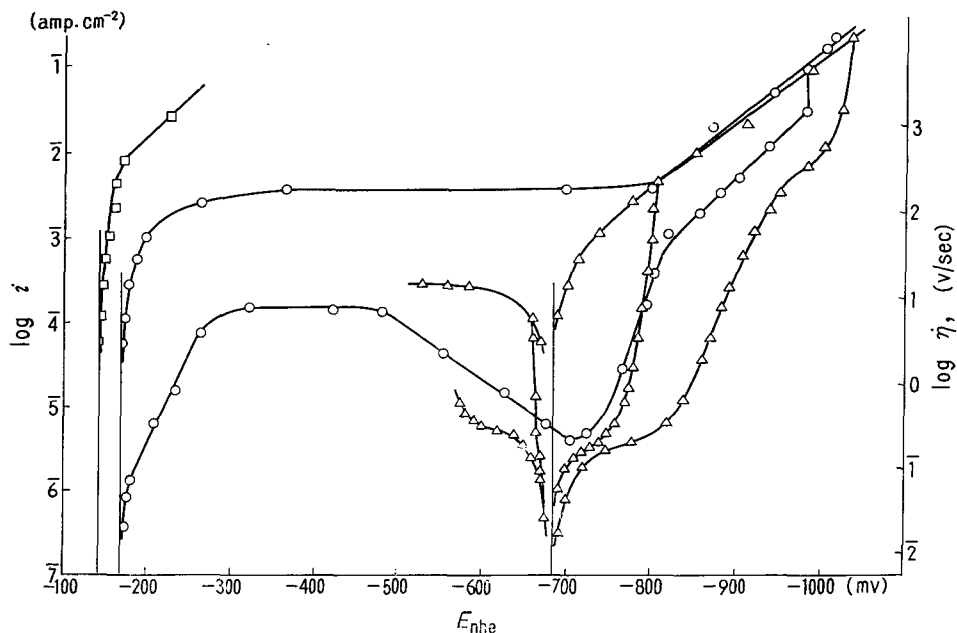


Fig. 9. The $\log i$ vs. E_{nhe} in steady states, and $\log \dot{\eta}$ vs. E_{nhe} in the decay processes on Pt; (□) in H_2SO_4 pH 2.4, (○) in 0.8 N $Na_2SO_4 + H_2SO_4$, pH 2.83, (△) in 0.5 N $Na_2SO_4 + NaOH$, pH 11.4.

the $\log i$ vs. E_{nhe} curves in the acidic $Na_2SO_{4,aq}$ practically coincide after the potential jump with the polarization curves in pure $NaOH_{aq}$ of *ca.* pH 11 plotted against E_{nhe} in place of η .

In order to examine the potential jump in detail the polarization curves in steady states were observed in $Na_2SO_{4,aq}$ of various pH's and C^{Na^+} 's as shown in Fig. 10. The potential jumps on to a more negative value, as seen from the Figure, on cathodic polarization in the acidic solutions from E_{nhe} more positive than the equilibrium potential, -420 mv, of the reversible hydrogen electrode at pH 7. In the alkaline $Na_2SO_{4,aq}$ the potential jumps down to a more positive value on anodic polarization from E_{nhe} more negative than the same equilibrium potential -420 mv. The current density, at which the potential jump occurs, is lowered as pH or C^{Na^+} increases in the acidic solutions, while in alkaline solutions reverse is the case. The extent of the potential jump and the current density at the jump were found to vary slightly with intensity of stirring the solution with hydrogen bubbles. These facts suggest that the potential jump is associated with the pH change of the

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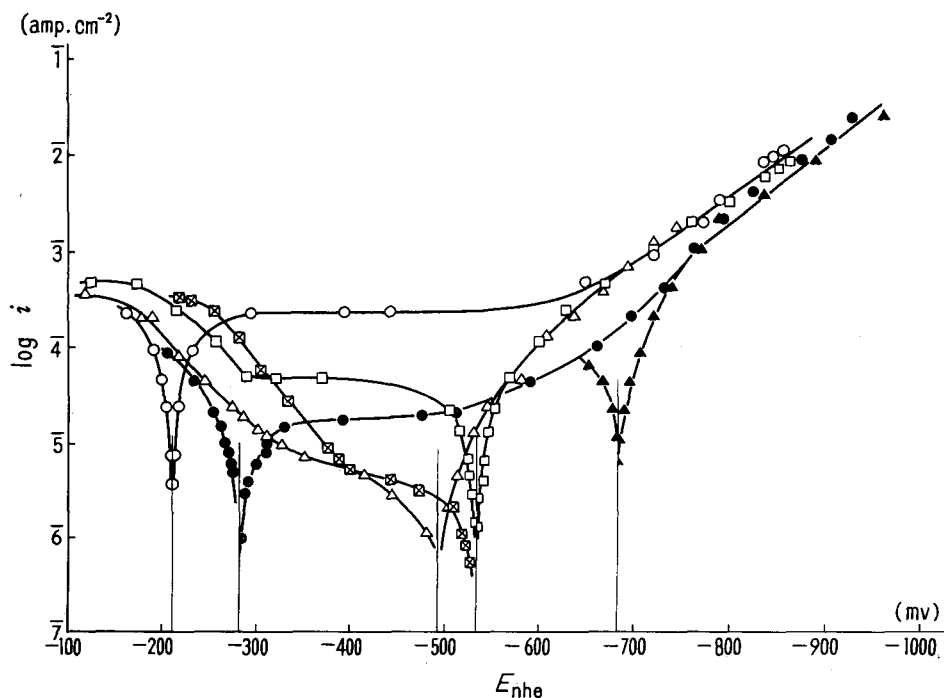


Fig. 10. $\log i$ vs. E_{nhe} in steady states on Pt; (O) in 0.1 N Na_2SO_4 , pH 3.53; (Δ) in 0.01 N Na_2SO_4 , pH 8.2; (\square) and (\boxtimes) in 0.1 N Na_2SO_4 , pH 8.9, respectively in vigorous stirring by hydrogen bubbles and weak one; (\bullet) in 1 N Na_2SO_4 , pH 4.7; (\blacktriangle) in 1 N Na_2SO_4 , pH 11.38.

solution surrounding the test electrode, as in the case of titanium hydrogen electrode in acidic $\text{K}_2\text{SO}_{4,\text{aq}}$ reported by KOLOTYRKIN⁷.

In case where the potential jump occurs on a steady $\log i$ vs. η curve of cathodic polarization, a sharp rise of η appears on the build up curves, while nearly a stationary value of η is observed on the decay curves, as illustrated in Plates 2 and 3. Fig. 11 shows the relations between $-dC/d\eta$ and E_{nhe} on the decay curves in $\text{Na}_2\text{SO}_{4,\text{aq}}$ of various pH's and C^{Na^+} 's. As seen from this Figure $-dC/d\eta$ begins to increase at $E_{\text{nhe}} \approx -600$ mv, passes through a maximum at $E_{\text{nhe}} \approx -800$ mv and practically vanishes at $E_{\text{nhe}} \approx -900$ mv both in the cases of the acidic and the alkaline solutions. Comparing $-dC/d\eta$ vs. E_{nhe} curves in 1 N $\text{Na}_2\text{SO}_{4,\text{aq}}$ of pH 4.7 and 11.38, it is found that the relation between $-dC/d\eta$ and E_{nhe} is practically independent of pH within experimental errors. The maximum value of $-dC/d\eta$ has a tendency to increase with increase of C^{Na^+} . It is concluded from these results that the major intermediate

is the sodium atom Na(I) both in the cases of acidic and alkaline $\text{Na}_2\text{SO}_{4,\text{aq}}$.

The ΔC 's are plotted against E_{nhe} in typical cases of acidic and alkaline $\text{Na}_2\text{SO}_{4,\text{aq}}$ in Fig. 11, which shows that ΔC varies with E_{nhe} similarly both in the cases, and the saturation value of ΔC corresponds to several atomic layers of the electrode metal. This fact shows that Na(I) penetrates into the lattice of platinum and forms an intermetallic compound or a solid solution with platinum, which causes the change of the work function of the electrode or

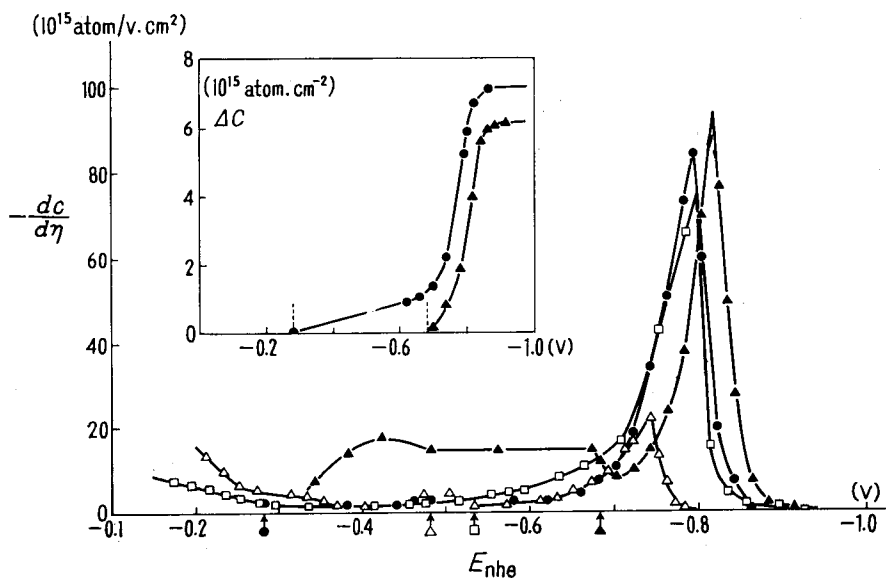


Fig. 11. The $-dc/d\eta$ vs. E_{nhe} in the decay processes, signs correspond respectively to those in Fig. 10.

TABLE I. The time constant τ_1 of the discharge step of platinum hydrogen electrode reaction in aqueous H_2SO_4 , NaOH and Na_2SO_4 .

| Sign in Fig. 12 | Solution | pH | τ_1 (μ sec) |
|-----------------|---------------------------------|-------|-----------------------|
| (○) | H_2SO_4 | 0.70 | < 5 |
| (▲) | 2.1 N Na_2SO_4 | 0.95 | < 8 |
| (□) | 0.1 N " | 3.50 | 31 |
| (△) | 0.1 N " | 11.00 | 84 |
| (●) | NaOH | 13.00 | 90 |
| (■) | 0.01 N Na_2SO_4 | 8.20 | 250 |

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the contact potential difference between the compound and the base metal, as suggested in Part I. The similar formation of the intermetallic compounds of alkali metals with electrodes under polarization has been reported by KABANOV *et al*^{8;9)} in cases of Ag, Cd, Pb, and Zn hydrogen electrodes in aqueous hydroxide of alkali metals, and also suggested by Dubpernell¹⁰⁾.

The potential jump observed as mentioned above was now investigated with reference to the time constant τ_1 of the discharge step. The build up curves were observed in acidic and alkaline $\text{Na}_2\text{SO}_{4,\text{aq}}$. Fig. 12 shows the

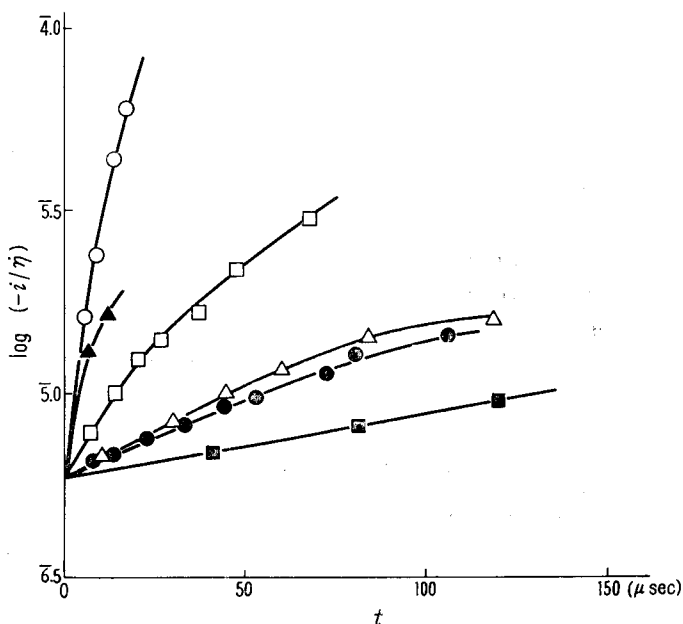


Fig. 12. $\log(-i/i_0)$ vs. t in the build up processes on Pt in acid and alkaline solutions; (○) in H_2SO_4 , pH 0.7; (▲) in 2.1 N Na_2SO_4 , pH 0.95; (□) in 0.1 N Na_2SO_4 , pH 3.5; (△) in 0.1 N Na_2SO_4 , pH 11.0; (●) in NaOH, pH 13.0; (■) in 0.01 N Na_2SO_4 , pH 8.2.

relation between $\log(-i/i_0)$ and t of these build up curves from which τ_1 's were determined as listed in Table 1. The Table shows that τ is extremely small in pure sulfuric acid, while it is increased by addition of Na_2SO_4 to the sulfuric acid amounting, for example, to 31 μsec in a solution of 0.1 N $\text{Na}_2\text{SO}_{4,\text{aq}}$ of pH 3.5, or to 84 μsec in an alkaline solution of 0.1 N $\text{Na}_2\text{SO}_{4,\text{aq}}$ of pH 11.0 which nearly equals that in pure NaOH of pH 13.0. As concluded in Part I, the electron transfer step is the discharge of sodium ion in alkaline $\text{Na}_2\text{SO}_{4,\text{aq}}$ and NaOH_{aq} . It may further be concluded from the present results

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that the discharge step in sulfuric acid involves the discharge of sodium ion when Na_2SO_4 is added to the sulfuric acid. On the other hand, it is found from comparison of the polarization curves and $-dC/d\eta \sim E_{\text{nhe}}$ curves in acidic and alkaline $\text{Na}_2\text{SO}_{4,\text{aq}}$ in Figs. 10 and 11 respectively that the concentration of Na(I) increases rapidly with E_{nhe} beyond the jump both in the cases of acidic and alkaline $\text{Na}_2\text{SO}_{4,\text{aq}}$. The potential jump in steady $\log i \sim E_{\text{nhe}}$ curves may thus be attributed, as mentioned above, to the change of pH caused by the formation or consumption of OH^- through the elementary step $\text{Na(I)} + \text{H}_2\text{O} \rightarrow \text{H(a)} + \text{Na}^+ + \text{OH}^-$.

Conclusive remarks

It has been found from analyses of the overvoltage-time curves after switching off the polarizing current that the major intermediate of the hydrogen electrode reaction on platinum is not the adsorbed hydrogen atom, but the sodium atom produced by the discharge of sodium ions in NaOH_{aq} and $\text{Na}_2\text{SO}_{4,\text{aq}}$, although the rate-determining step of the hydrogen electrode reaction is the recombination of adsorbed hydrogen atoms. It was concluded in Part I that the hydrogen overvoltage on platinum in these solutions includes the change of the electronic work function of the electrode. The latter change is now reasonably attributed to the major intermediate Na(I).

Acknowledgement

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