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KINETIC STUDIES OF ELECTRON TRANSFER STEP OF HYDROGEN EVOLUTION REACTION ON PLATINUM IN AQUEOUS CESIUM HYDROXIDE

By

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Abstract

In the study of the hydrogen evolution reaction on platinum in cesium hydroxide and sulfate, the composition of the overvoltage due to free charges and the intermediate species on the electrode surface was determined separately by the galvanostatic transient method. It was found that the rate of the electron transfer step of the reaction in the steady state was expressed by simplified Frumkin Equation as a function of the overvoltge due to free charges on the electroed surface and that the overvoltage due to the intermediate species was responcible for the rate of the recombination of absorbed hydrogen atoms. The mechanism of the hydrogen evolution reaction was clarified on the basis of the composition of the hydrogen overvoltage.

Introduction

In the previous works[1,2] the electron transfer step of the hydrogen evolution reaction on platinum was studied by the galvanostatic transient method in aqueous sodium hydroxide and sulfate. It was concluded that: (i) the electron transfer step was composed of the discharge of a sodium ion, but not of a water molecule, (ii) in the course of the build up of overvoltage after switching on a polarizing current, the hydrogen overvoltage was first set up by free charges on the electrode surface and later by the intermediate sodium atoms, and the former was responsible for the rate of the electron transfer step and the latter for the rate of the recombination of adsorbed hydrogen atoms, (iii) the kinetic equation of the electron transfer step was expressed by simplified Frumkin Equation[3] in which the Ψ_1-potential term was neglected.

Is it really possible to determine separately these two components of the overvoltage in the steady state of the hydrogen evolution reaction? The present work is concerned with the study to answer this question.

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As reported previously,[4] it is possible by the galvanostatic transient method to determine the time constant τ_1 of the electron transfer step and the differential capacity C_D at the metal-solution interface at any electrode potential in the steady state of the reaction. Namely, when a constant current is superposed on the electrode which is in the steady state with a current density i_s and an overvoltage η_s, the value of τ_1 and C_D at i_s and η_s are given from the analysis of the resulting overvoltage-time curve by the following equation, insofar as the overvoltage is caused by charging up of the double layer ;

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

where Δi denotes an increment of the polarizing current i_s, $\dot{\eta}$ the time derivative of the overvoltage η and t the time measured from the moment of the superposition of the current. The sign of overvoltage is taken negative in the cathodic region. The τ_1 is given by the following equation[4] :

$$\tau_1 = C_D r_1 , \tag{2}$$

where r_1 is a kinetic parameter of the electron transfer step which is defined as :

$$r_1 = -(d\eta_1/di_1) . \tag{3}$$

In Eq. (3), i_1 denotes the rate of the electron transfer step and η_1 the overvoltage due to free charges on the electrode surface. When r_1 is known as a function of i_1, the integral of Eq. (3) gives the value of η_1, $i.e.$,

$$\eta_1 = \int_0^{\eta_1} d\eta_1 = -\int_0^{i_1} r_1 di_1 . \tag{4}$$

On the other hand, the value of r_1 at η_s can be estimated on the basis of Eqs. (1) and (2) from the initial stage of the overvoltage-time curves started from η_s. In the steady state i_1 equals i_s. Putting i_s instead of i_1 in Eq. (4), we have the overvoltage η_{1s} which is caused by free charges on the electrode surface at the current density i_s, $i.e.$,

$$\eta_{1s} = -\int_0^{i_s} r_1 di_s . \tag{5}$$

Observing the η, t-curves started from various values of η_s, r_1 is given as a function of i_s. The value of η_{1s} can be estimated from the graphical integration of the r_1, i_s-curve on the basis of Eq. (5).

In the present work the relation between the rate of the electron transfer step and the overvoltage caused by free charges on the electrode surface will be established on the basis of Eq. (5) in the steady state of the hydrogen

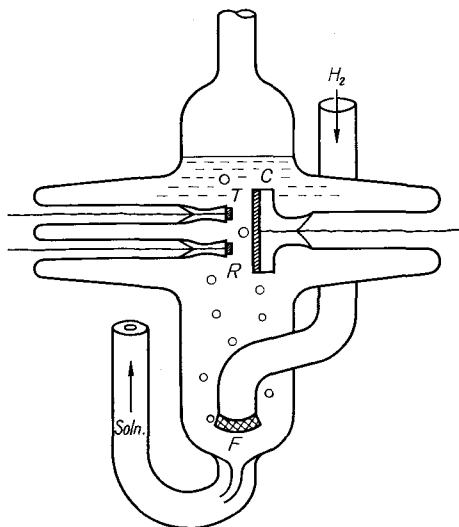evolution reaction on platinum in aqueous cesium hydroxide and sulfate by the galvanostatic transient method.

Experimental

The experimental procedure is the same as described previously.[1,2] In the present work the vessels for preparation and preelectrolysis of solution and the electrolytic cell are made of qualtz glass to avoid the influence of impurities from glass vessel on the activity of the electrode. The electrolytic cell is shown in Fig. 1, in which T, R and C are respectively the test, reference and counter electrodes. These electrodes are made of platinum film evaporated on the ground glass surface in vacuum, through the center of which Pt-foil is sealed for the electric contact.[*]

The activity of the platinum electrode in alkaline solutions decreases with time in a pyrex glass vessel, *e.g.*, after one week the current density at a constant overvoltage decreases to about one-tenth of its initial value, while in a quartz vessel the change of the activity of the electrode is not practically detectable for one week.

In cesium hydroxide the platinum electrode changes its colour with the electrode potential in the anodic polarization region, *i.e.*, yellowish at 1.0 V, brown at 1.5 V and black at higher potentials.[**] In aqueous sodium hydroxide the change of colour of the platinum electrode

Fig. 1. Electrolytic cell made of quartz glass. T, R and C are the test, reference and counter electrodes respectively, and F is a glass filter.

is not observed. This fact suggests that the platinum electrode is oxidized in the anodic polarization region more easily in aqueous cesium hydroxide than in aqueous sodium hydroxide.

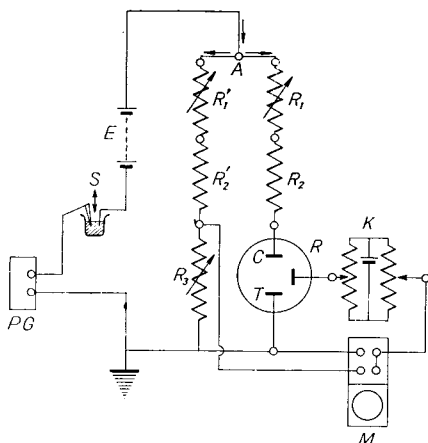Figure 2 shows the electric circuit for the observation of an overvoltage-

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*) The sealing of Pt-foil into quartz glass was suggested by Prof. R. E. Mardaleishvili in Moscow State University.

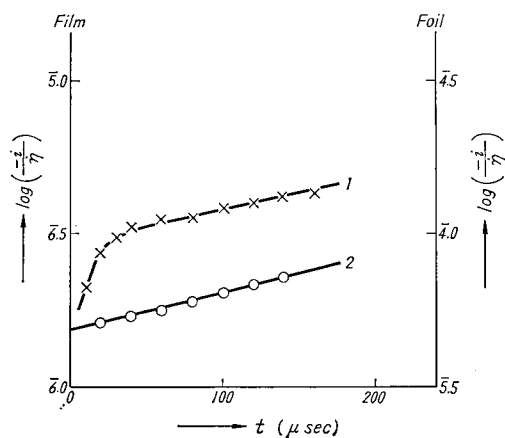**) The electrode potential is referred to the reversible hydrogen electrode potential in the same solution.

Fig. 2. Electric circuit for galvanostatic transient method.

R_1, R_2 and R_3 are resistances for current control, current measurement and compensation of ohmic potential drop. E, S, PG and M are storage batteries, mercury switch, pulse generator and Memoscope Oscilloscope. K is a circuit for compensation of steady state potential.

time curve which starts from a given steady state. The current supplied by storage batteries is divided at A into nearly equal parts, one of which is used for the polarization of the electrode T and the other for the compensation of the ohmic potential drop. The polarizing current i_s is estimated from the potential drop through a fixed resistor R_2. The potential difference between T and R is measured by a memoscope oscilloscope, which is composed of the true hydrogen overvoltage and the ohmic one. The ohmic overvoltage is eliminated from a transient displayed on the oscilloscope screen by subtracting the potential drop through R_3 from the potential difference between T and R by means of a differential preamplifier in the oscilloscope. R_3 is fixed at a value nearly equal to that of the electric resistance of the solution between T and R. The position of the light spot on the oscilloscope screen in the steady state is adjusted to the base line

Fig. 3. The $\log(-i/\dot{\eta})$, t-curves on the evaporated, platinum film (1) and platinum foil (2) in 0.2 N $CsOH_{aq}$.

of the screen, controlling the contact point in the circuit K.

A current impulse of a constant value Δi is superposed by a pulse generator PG on the electrode which is in the steady state with the current density i_s and the overvoltage η_s. The change of the potential difference between T and R is recorded on the oscilloscope screen. The η, t-curves thus obtained enable us to estimate the value of τ_1 and C_D at η_s on the basis of Eq. (1).

First the η, t-curves started from the reversible hydrogen electrode potential were observed on platinum foil and film electrodes of different geometrical area in the same solution. The $\log(-i/\dot{\eta})$, t-curves obtained from the respective η, t-curves are shown in Fig. 3. As seen from Fig. (3), the $\log(-i/\dot{\eta})$, t-curves in 0.2N $CsOH_{aq}$ are expressed by Eq. (1) with the same value of τ_1 both in the cases of foil and film electrodes except that there appears a deviation from Eq. (1) in the initial stage of the $\log(-i/\dot{\eta})$, t-curve on a film electrode. This deviation has a tendency to decrease with the increase of the concentration of solution. On the other hand, LEIKIS, SEVASTIJANOV and KNOTZ[5] have worked out the frequency effect on the differential capacity of the double layer of the mercury electrode. They have shown that the differential capacity of the mercury electrode decreases with the increase of the frequency. This frequency effect was explained by the presence of the thin layer of solution between the glass wall and mercury in a capillary. The deviation appeared in the initial stage of the $\log(-i/\dot{\eta})$, t-curve on a platinum film electrode may be attributed to the solution penetrated into micropores on the electrode surface as expected from the work of LEIKIS *et al.* KUNIMATSU[10] has recently pointed out that the shape of the $\log(-i/\dot{\eta})$, t-curve is affected by the presence of micropores on the electrode surface. In the present work the evaporated platinum film electrodes are used because of their high activity. When the deviation from Eq. (1) appears in the initial stage of the $\log(-i/\dot{\eta})$, t-curves, the value of C_D is determined by the extraporation of the later linear part of the curve to time $t=0$.

Experimental results and discussion

The τ_1 and C_D at $\eta_s=0$ were obtained on evaporated platinum films from the η, t-curves as a function of the geometrical area of the electrode and the concentration of cesium hydroxide and sulfate. The τ_1 at $\eta_s=0$ thus obtained strongly depends on the concentration of the solution, but does not depend on the surface area of the electrode. On the other hand, C_D is proportional to the geometrical area of the electrode, but independent of the concentration of the solution. In Fig. 4, the value of $\log \tau_1$ is plotted against the logarithm

of the concentration of cesium ion $\log C$. As seen from this Figure, $\log \tau_1$ varies linearly with $\log C$ with gradient $-1/2$ independent of pH of the solution as in the case of alkaline solutions including Na^+ ion[1]. It follows that r_1 at $\eta_s = 0$ derived from τ_1 and C_D by Eq. (2) is inversely proportional to the square root of C, since C_D is a constant independent of the concentration of the solution. On the other hand, r_1 is inversely proportional to the exchange rate of the electron transfer step i_{10},

$$i_{10} = \frac{RT}{F} \frac{1}{r_1}, \tag{6}$$

where F is the Faraday, R the gas constant and T the absolute temperature respectively. It follows that i_{10} is proportional to $C^{1/2}$ independent of pH of the solution, *i.e.*,

$$i_{10} = k(C)^{1/2} \tag{7}$$

where k is a rate constant. It is concluded from these results that the electron transfer step of the hydrogen evolution reaction on platinum in aqueous cesium hydroxide and sulfate is composed of the discharge of Cs^+ ion. The exchange rate of Cs^+ ion is a little smaller than that of Na^+ ion.

The τ_1 and C_D at a given overvoltage η_s in a steady state were obtained from the η, t-curves started from η_s on an evaporated platinum film of geometrical area *ca.* 10^{-3} cm². Figure 5 shows a series of the $\log(-\Delta i/\dot{\eta})$, t-curves
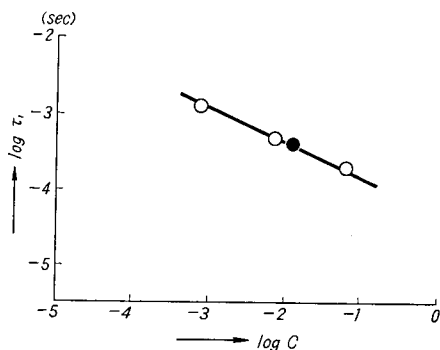
Fig. 4. The relation between the time constant of the electron transfer step τ_1 and the concentration of Cs^+ ion at the reversible hydrogen electrode potential.

Open circle in pure $CsOH_{aq}$, and solid circle in Cs_2SO_{4aq} of pH = 11.4.
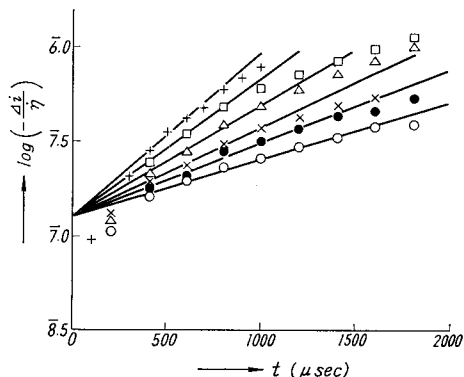
Fig. 5. The $\log(-\Delta i/\dot{\eta})$, t-curves obtained from η, t-curves started from various steady states in $CsOH_{aq}$, pH = 10.86.

Starting overvoltrge; (○) 0 mV, (●) −60 mV, (×) −100 mV, (△) −160 mV, (□) −190 mV, (+) −200 mV.
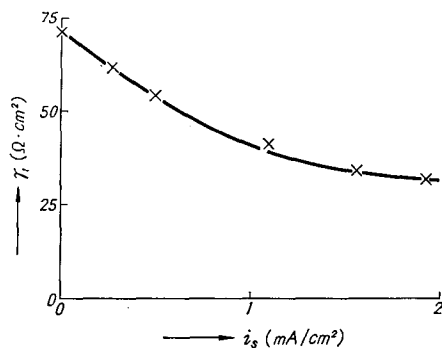
Fig. 6. The relation between r_1 and i_s in $CsOH_{aq}$, pH = 10.86.
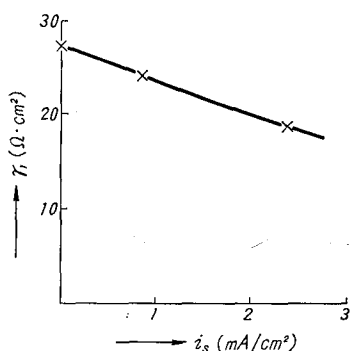
Fig. 7. The relation between r_1 and i_s in $CsOH_{aq}$, pH = 11.86.
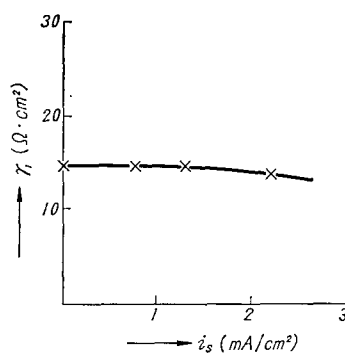
Fig. 8. The relation between r_1 and i_s in $CsOH_{aa}$, pH = 12.80.

in $CsOH_{aq}$ of pH 10.86 obtained from the η, t-curves started from various values of η_s in the range from 0 to -200 mV. As seen from Fig. 5, the $\log(-\Delta i/\eta)$, t-curves satisfy Eq. (1) except the very initial part and τ_1 decreases with the increase of $-\eta_s$, while C_D remains constant. The value of r_1 at η_s is derived from τ_1 and C_D at η_s by Eq. (2). The r_1 thus obtained from Fig. 5 is plotted in Fig. 6 against the steady current i_s at η_s. The r_1, i_s-curves in $CsOH_{aq}$ of pH 11.86 and 12.80 are shown respectively in Figs. 7 and 8. The values of r_1 and i_s in Fgis. 6, 7 and 8 are those per true unit area which is estimated from the value of $C_D = 18$ $\mu F/cm^2$ in the case of a mercury electrode.[6]

The overvoltage η_{1s} due to free charges on the electrode surface in the steady state is determined by the graphical integration of the r_1, i_s-curves in Figs. 6, 7 and 8 on the basis of Eq. (5). For convenience the rate of the electron tansfer step in the steady state is denoted as i_{1s}, which is of course
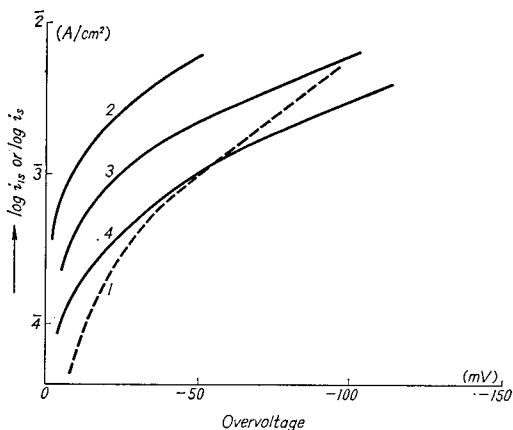
Fig. 9. 1; the relation between $\log i_s$ and η_{2s} in $CsOH_{aq}$ of
pH = 10.86, 11.86 and 12.80.
2, 3 and 4; $\log i_{1s}$, η_{1s}-curves in $CsOH_{aq}$ of pH = 12.80,
11.86 and 10.86.

equal to i_s. The relation between $\log i_{1s}$ and η_{1s} thus obtained from these Figures are shown respectively by the curves 2, 3 and 4 in Fig. 9. From these curves in Fig. 9, it is concluded that the kinetic equation of the electron transfer step in the steady state is expressed by simplified Frumkin equation with Tafel constant 1/2 in every solution used, *i.e.*,

$$i_{1s} = i_{10}\left\{\exp\left(-F\eta_{1s}/2RT\right) - \exp\left(F\eta_{1s}/2RT\right)\right\}. \tag{8}$$

Figure 9 also shows that $\log i_{1s}$ at a constant η_{1s} depends on the concentration of the solution as expected from the discharge of Cs^+ ion.

In order to clarify the setting up of overvoltage in the transient state, the η, t-curves were observed which were initiated from the reversible hydrogen electrode potential by a constant current density i. The rate of the electron transfer step i_1 at given overvoltage in the course of the build up of overvoltage is determined by the following equation from the η, t-curve:

$$i_1 = i + C_D\dot{\eta}. \tag{9}$$

Using the value of $\dot{\eta}$ at a given value of η, i_1 is estimated as a function of η in the course of the build up of overvoltage. The $\log i_1$ thus obtained in $CsOH_{aq}$ of pH 10.86 is plotted against the overvoltage η in Fig. 10, curves 2 and 3. These curves are those obtained from the different build up curves observed with different current densities. For comparison the $\log i_{1s}$, η_{1s}-curve is shown in Fig. 10, curve 1, together with the $\log i_s$, η_s-curve, curve 4.
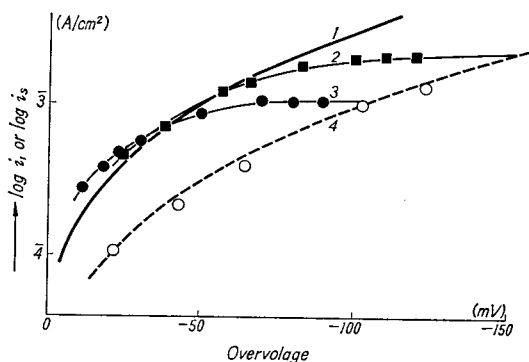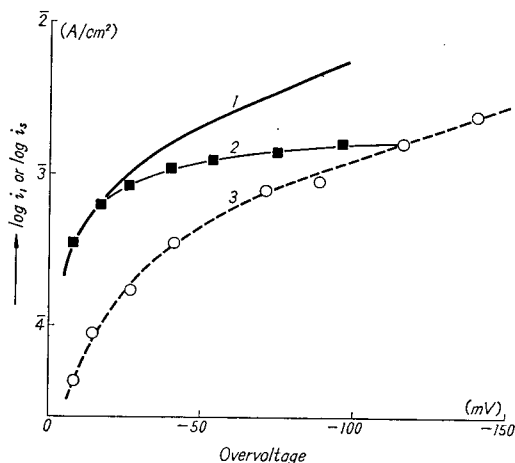
Fig. 10. The relation between the rate and overvoltage of the
electron transfer step in CsOH$_{aq}$of pH $=10.86$.

1; log i_{1s}, η_{1s}-curve,
2 and 3; log i_1, η-curves in the course of build up of η,
4; log i_s, η_s-curve of the overall relation.

The log i_1, η-curves in the course of the build up of overvoltage in CsOH$_{aq}$
of pH 11.86 and 12.80 are shown respectively in Figs. 11 and 12 together
with the log i_{1s}, η_{1s}-curves and log i_s, η_s-curves.

As seen from Figs. 10, 11 and 12, the initial stage of the log i_1, η-curve
in the course of the build up of overvoltage coincides with the log i_{1s}, η_{1s}-

Fig. 11. The relation between the rate and overvoltage of the
electron transfer step in CsOH$_{aq}$ of pH $=11.86$.

1; log i_{1s}, η_{1s}-curve,
2; log i_1, η-curve in the course of build up of η,
3; log i_s, η_s-curve of the overall reaction.
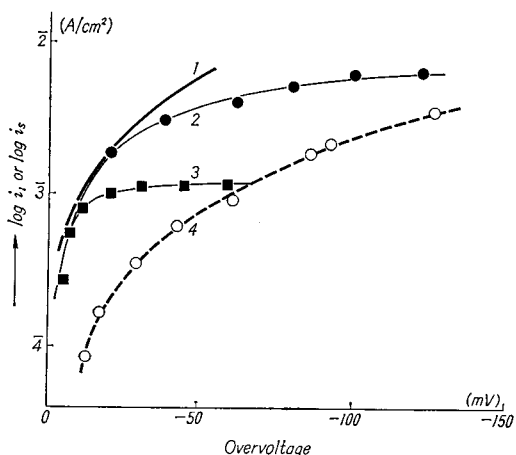
Fig. 12. The relation between the rate and overvoltage of the electron transfer step in $CsOH_{aq}$ of pH$=12.80$.

1; $\log i_{1s}$, η_{1s}-curve,
2 and 3; $\log i_1$, η-curves in the course of build up η,
4; $\log i_s$, η_s-curve of the overall reaction.

curve in the steady state, and in the later stage the former deviates from the latter and the overvoltage increases sharply, i_1 being practically kept at a constant nearly equal to the polarizing current i. The coincidence of the initial stage of the $\log i_1$, η-curve with the $\log i_{1s}$, η_{1s}-curve shows that the overvoltage is set up by free charges on the electrode surface in the initial stage of the build up curve, and that the rate of the electron transfer step in this stage is related to the overvoltage caused by free charges on the electrode surface by simplified Frumkin equation. The increase of overvoltage in the later stage, on the other hand, is attributed to the intermediate species produced by the electron transfer step as discussed in the case of platinum and nickel electrodes in aqueous sodium hydroxide.[7~9] It should be stressed here that the overvoltage components due to free charges and intermediate species appear separately in the course of the build up of overvoltage.

The overvoltage component due to the intermediate species in the steady state is estimated as the difference $\eta_s - \eta_{1s}$ at a given current density i_s. The relation between $\log i_s$ and η_{2s} obtained from Figs. 10, 11 and 12 are shown by curve 1 in Fig. 9, where $\eta_{2s} = \eta_s - \eta_{1s}$. As seen from Figs. 9, the $\log i_s$, η_{2s}-curves coincide with each other irrespective of the difference in the concentration of cesium hydroxide among these solutions. This fact will be interpreted that the adsorbed hydrogen atoms is produced by the decomposi-

tion of a water molecule by the intermediate cesium atom and η_{2s} is imposed upon the step of the recombination of adsorbed hydrogen atoms. In this case η_{2s} is expressed by the excess of the chemical potential of the adsorbed hydrogen atom $\Delta\mu_{H(a)}$ over that at the reversible hydrogen electrode potential as ;

$$\eta_{2s} = -\Delta\mu_{H(a)}/F, \tag{10}$$

and $\Delta\mu_{H(a)}$ depends neither on pH nor on the Cs^+ ion concentration.

Taking into consideration the discharge of Cs^+ ion and the step of the recombination of adsorbed hydrogen atoms, the constituent elementary steps of the hydrogen evolution reaction is written as :

$$Cs^+ + e \longrightarrow Cs(I), \tag{I}$$

$$Cs(I) + H_2O \longrightarrow H(a) + OH^- + Cs^+, \tag{II}$$

$$2H(a) \longrightarrow H_2, \tag{III}$$
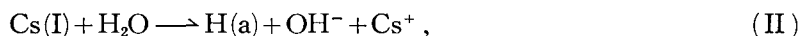
where $Cs(I)$ and $H(a)$ denote respectively the intermediate cesium atom and the adsorbed hydrogen atom. The overvoltage of the step (I) is caused by free charges on the electrode surface and its rate is expressed by simplified Frumkin Equation with Tafel constant 1/2, as mentioned above. Comparing the $\log i_{1s}$, η_{1s}- and $\log i_s$, η_s-curves at low current densities, in Figs. 10, 11 and 12, it can be seen that η_{1s} is quite small as compared with η_s, while at higher current densities η_{1s} becomes comparable to η_s, *i.e.*, at low current densities the step of the recombination of adsorbed hydrogen atoms is rate-determining, while at higher current densities the rate-determining step of the reaction is not detected. The above conclusions on the mechanism of the hydrogen evolution reaction and on the composition of the hydrogen overvoltage in the present system are in agreement with those in aqueous sodium hydroxide reported in the previous works.[1,2]

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