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A KINETIC STUDY OF ELECTRON TRANSFER STEP OF HYDROGEN EVOLUTION REACTION ON SILVER IN SODIUM HYDROXIDE BY A GALVANOSTATIC TRANSIENT METHOD

By

K. KUNIMATSU*) and A. MATSUDA*)

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Abstract

The hydrogen overvoltage on silver in aqueous sodium hydroxide has been split into two components by a galvanostatic transient method, the one (η_1) is caused by charging up of the double layer and the other ($\eta - \eta_1$) results from the change of the surface potential of the electrode caused by the adsorbed intermediate species.

It has been found that the rate of the electron transfer step can be expressed by the usual Tafel equation with $\alpha \approx 0.5$ as a function of η_1 and the discharging species is Na^+ ion and the intermediate species is adsorbed sodium atom Na(a) . The activity of Na(a) or ($\eta - \eta_1$) approaches a saturation value with increasing overvoltage, which strongly depends on the concentration of the solution. In the high overvoltage region where the saturation of Na(a) appears the electron transfer step becomes rate-determining.

1. Introduction

Study of the mechanism of hydrogen evolution reaction (h. e. r.) on silver in alkaline solutions has attracted much less attention than that in acid solutions. Ammar and Awad¹⁾ interpreted the pH-dependence of overvoltage on the basis of the water discharge mechanism, while Yamazaki and Kita²⁾ concluded the catalytic mechanism by observing a cathodic saturation current.

Some attempts^{3~5)} also have been made to determine the surface coverage of adsorbed hydrogen atoms on silver during cathodic polarization in alkaline solutions in connection with the study of the mechanism, indicating a low value for the coverage throughout the polarization.

Kabanov *et al.*^{6~8)} reported incorporation of alkali metal atoms into a series of electrode metals, including silver, and its influence on hydrogen overvoltage under cathodic polarization in concentrated alkaline solutions.

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However, the mechanism of h. e. r. on silver in alkaline solutions seems still to be in a black box.

In the previous paper⁹⁾ we reported the results of a kinetic study of the electron transfer step of h. e. r. on silver in sulfuric acid solutions together with the study of the double layer structure by a galvanostatic transient method. The present work is concerned with a similar kinetic study of the electron transfer step of h. e. r. on silver in aqueous sodium hydroxide by the galvanostatic transient method.

2. Experimental

The principle of the galvanostatic transient method and experimental details have been described in the previous papers.^{9,10)} The same silver bead electrode as reported in the previous work⁹⁾ is used in the present study in the same electrolytic cell. The sodium hydroxide and sodium sulfate used are all Merck Suprapur grade without further purification.

3. Results and Discussion

3.1 The pH-effect of the polarization curves of the overall reaction

The polarization characteristics of the overall reaction on silver in steady states were determined in sodium hydroxide solutions in the concentration range from 2.45×10^{-4} N to 0.817 N. Fig. 1 a and Fig. 2 show i vs η curves around the reversible potential and $\log i$ vs η curves in a wide range of η , respectively. There appears a small concentration dependence in the polarization curves around the reversible potential. Fig. 1 b shows the i vs η curves in the solutions of the same pH, but of different concentration of Na^+ ions. As seen from this figure, the concentration of Na^+ ion does not affect the i vs η curves. Therefore the small concentration effect on i vs η curves in Fig. 1 a may be regarded as the pH-effect.

Using the polarization resistance r_0 at the reversible potential, the exchange current density of the overall reaction i_0 can be determined by the equation

$$i_0 = \nu(R) RT/2Fr_0, \quad (1)$$

assuming that the stoichiometric number $\nu(R)$ equals unity. The values of i_0 calculated in this way are listed in Table 1.

On the other hand, a considerable concentration dependence can be seen in the $\log i$ vs η curves at high current densities, as seen from Fig. 2. It may therefore be suggested from the pH-dependence of the polarization

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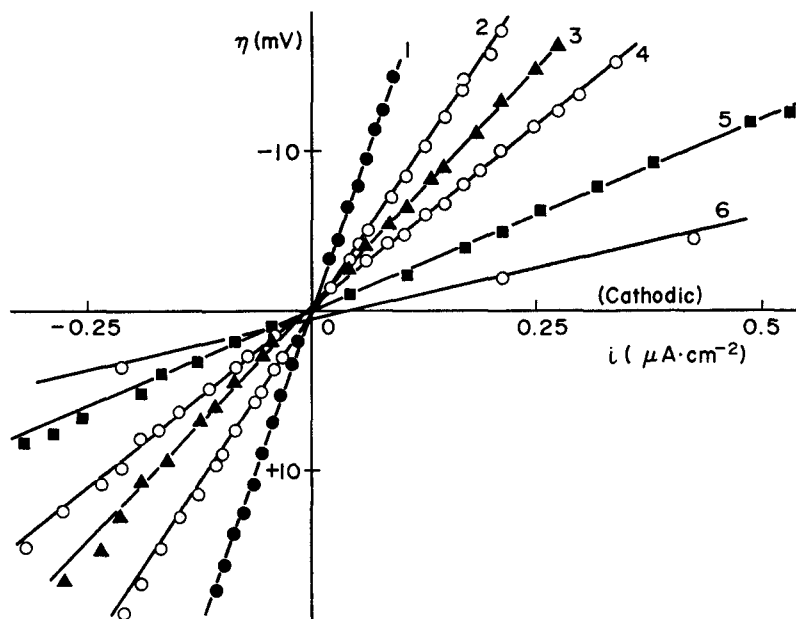


Fig. 1 a. $i \sim \eta$ relationships around the equilibrium potential of h. e. r. on silver in aqueous sodium hydroxide.

- 1) $2.45 \times 10^{-4} \text{N}$ 2) $8.40 \times 10^{-4} \text{N}$ 3) $4.97 \times 10^{-3} \text{N}$
 4) $1.70 \times 10^{-2} \text{N}$ 5) 0.127N 6) 0.817N

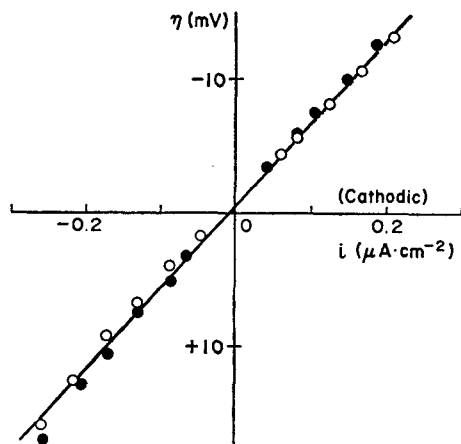


Fig. 1 b. Effect of Na^+ ion concentration on $i \sim \eta$ relation under a constant pH.

1. (●) $8.40 \times 10^{-3} \text{N-NaOH}$
 2. (○) After addition of $7.56 \times 10^{-2} \text{N-Na}_2\text{SO}_4$ to 1.

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TABLE 1. Exchange current densities of h. e. r. on silver in NaOH_{aq} . i_0 : overall, i_{10} : electron transfer step.

C_{NaOH} (N)	i_{10} ($\text{A}\cdot\text{cm}^{-2}$)	i_0 ($\text{A}\cdot\text{cm}^{-2}$)	i_{10}/i_0
2.45×10^{-4}	7.18×10^{-7}	1.59×10^{-7}	4.52
8.40×10^{-4}	1.49×10^{-6}	2.97×10^{-7}	5.02
4.97×10^{-3}	8.36×10^{-6}	4.29×10^{-7}	19.5
1.70×10^{-2}	4.21×10^{-5}	5.57×10^{-7}	75.6
1.27×10^{-1}	2.35×10^{-4}	1.05×10^{-6}	224
8.17×10^{-1}	8.18×10^{-4}	1.97×10^{-6}	415

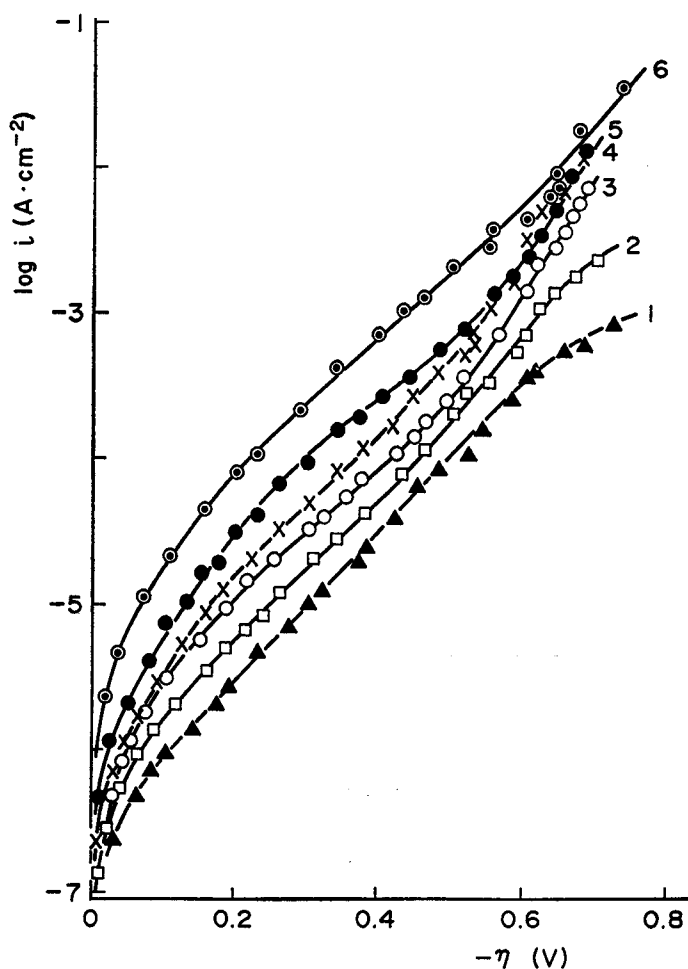


Fig. 2. Tafel lines of overall h.e.r. on silver in aqueous sodium hydroxide. The concentration for each curve is the same as in Fig. 1.

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curves in steady states that the mechanism of h.e.r. on silver in sodium hydroxide solutions is not a simple one. In fact the Tafel slope changes from a higher value (>120 mV) to 120 mV with increasing current density, as seen from the polarization curves 3~6 in Fig. 2. The bending in the polarization curves at high current densities, in dilute solutions (curves 1, 2 in Fig. 2) may be attributed to the concentration polarization.

In order to determine the mechanism of h.e.r. on silver in aqueous sodium hydroxide, the rate of the electron transfer step of h.e.r. will be determined separately by the galvanostatic transient method.

3.2 The galvanostatic transient studies

3.2.1. The time constant of the electron transfer step and the double layer capacity

The time constant of the electron transfer step τ_1 and the double layer capacity C_D can be determined from the transient curves of overvoltage caused by a current pulse Δi on the basis of eq. (2)

$$\ln(-\Delta i/\eta) = \ln C_D + \frac{t}{\tau_1}, \quad (2)$$

where τ_1 is given by the product of C_D and the reaction resistance r_1 of the electron transfer step which can be defined by the differential of the overvoltage of the electron transfer step η_1 with respect to the current density i as

$$r_1 = -\frac{d\eta_1}{di}. \quad (3)$$

Fig. 3 shows typical examples of the $\log\left(-\frac{\Delta i}{\eta}\right)$ vs t curves obtained from the transient curves which started from various steady overvoltages in 0.817 N sodium hydroxide solution. It may be possible to calculate τ_1 and C_D from Fig. 3 on the basis of eq. (2) as a function of the steady overvoltage η . Figs. 4 and 5 show the $\log \tau_1$ vs η and C_D vs η , respectively, in the solutions of various concentration.

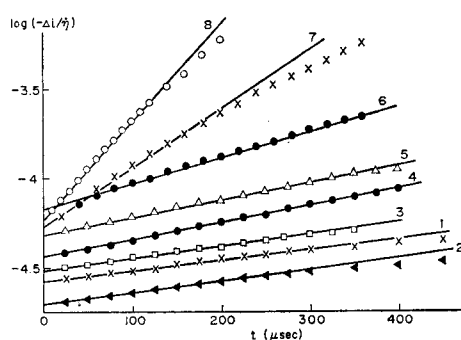


Fig. 3. Analysis of $\eta \sim t$ curves at various steady states in 0.817 N NaOH. The starting overvoltage of the transient curves:

- 1) 0 2) -0.3 V 3) -0.55 V 4) -0.6 V
- 5) -0.66 V 6) -0.7 V 7) -0.76 V
- 8) -0.8 V

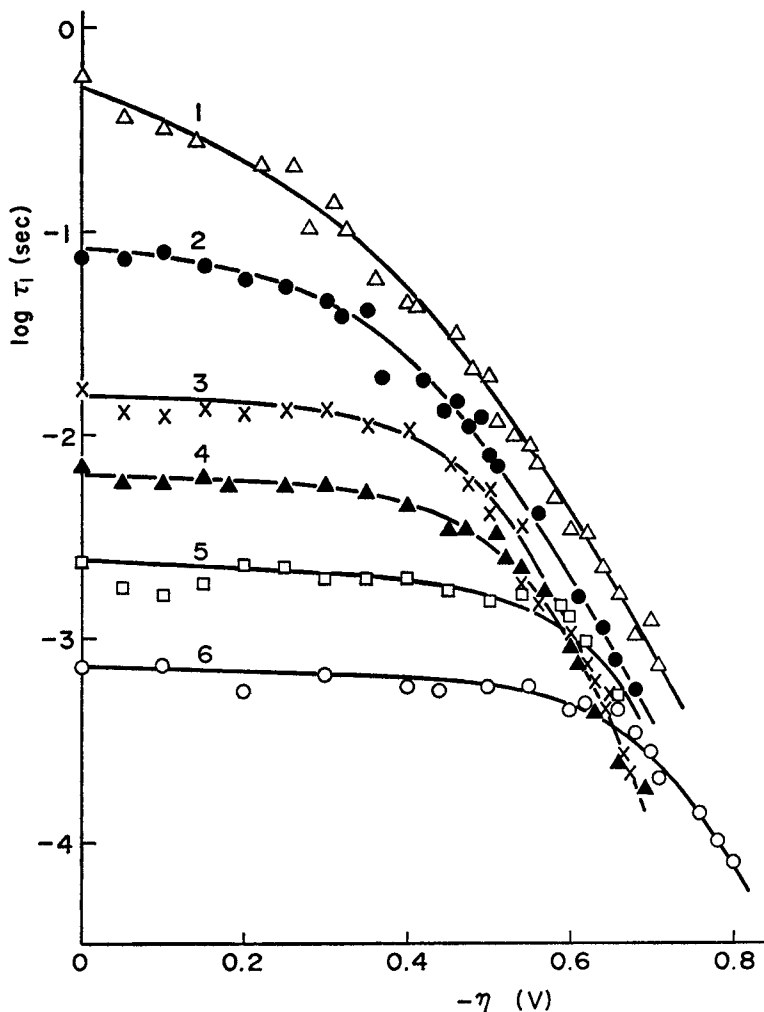


Fig. 4. Dependence on overvoltage of the time constant of the electron transfer step of h.e.r. on Ag in NaOH_{aq} .

1) $8.40 \times 10^{-4} \text{N}$ 2) $4.97 \times 10^{-3} \text{N}$ 3) $1.70 \times 10^{-2} \text{N}$ 4) $8.4 \times 10^{-3} \text{N}$ -
 $\text{NaOH} + 7.56 \times 10^{-2} \text{N Na}_2\text{SO}_4$ 5) 0.12 N 6) 0.817 N

It is seen from Fig. 4 that τ_1 increases with decreasing concentration of the solution and there appears a plateau at the initial stage of the $\log \tau_1$ vs η curve for a given solution and its length increases with increasing concentration of the solution. The existence of a plateau in the $\log \tau_1$ vs η curves suggests that η_1 remains practically zero until a considerable amount of η is established.

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As seen from Fig. 5, there appears a broad minimum in the C_D vs η curves in all solutions used. It should be noted, however, that the minimum in the C_D vs η curve does not correspond to that of the diffuse double layer

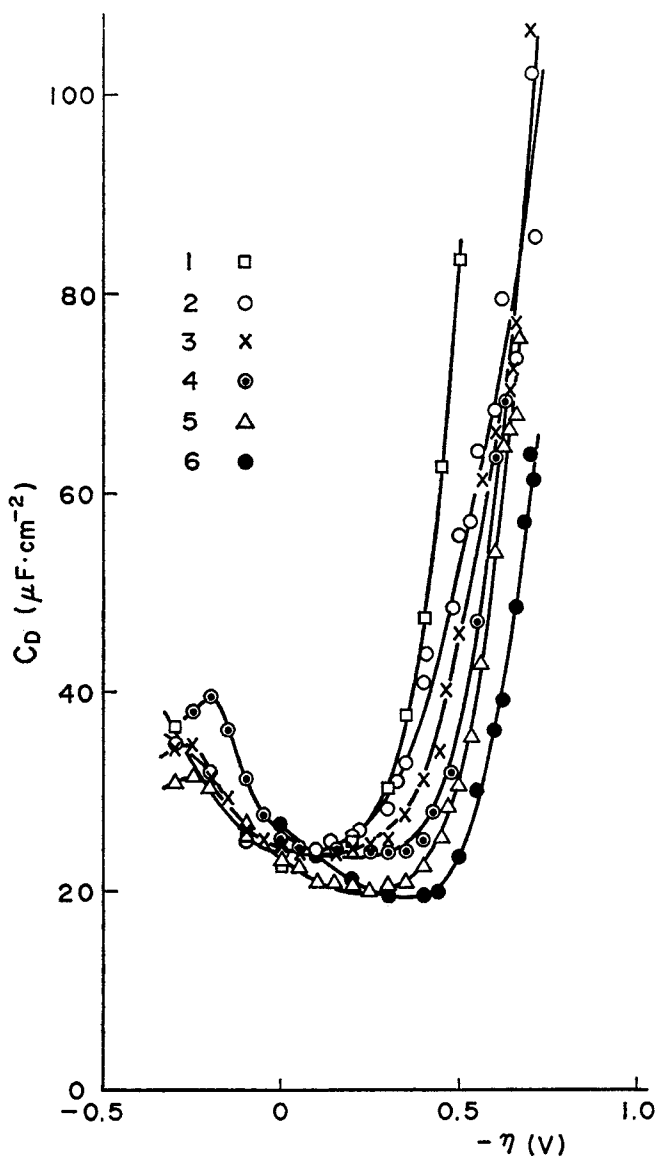


Fig. 5. Dependence of the double layer capacity of silver hydrogen electrode on overvoltage in NaOH_{aq} .

- 1) $2.45 \times 10^{-4} \text{N}$ 2) $8.40 \times 10^{-4} \text{N}$ 3) $4.97 \times 10^{-3} \text{N}$ 4) $1.70 \times 10^{-2} \text{N}$
 5) 0.12N 6) 0.817N

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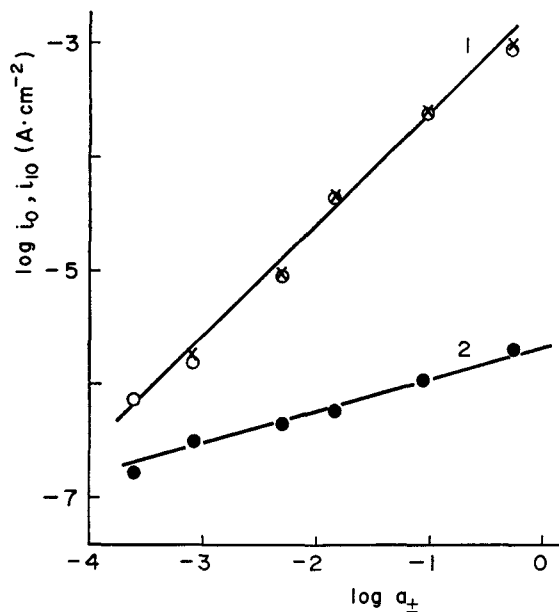


Fig. 6. Concentration dependence of exchange current densities. 1) Dependence of $\log i_{i0}$ on $\log a_{\pm}$ determined from r_{i0} (\circ) and from extrapolation of $\eta_1 \sim \log i$ relationships in Fig. 9 to the equilibrium potentials (\times), 2) Dependence of $\log i_0$ on $\log a_{\pm}$ determined from r_0 by assuming $\nu(R)=1$. a_{\pm} is the mean activity of sodium hydroxide in the solution.

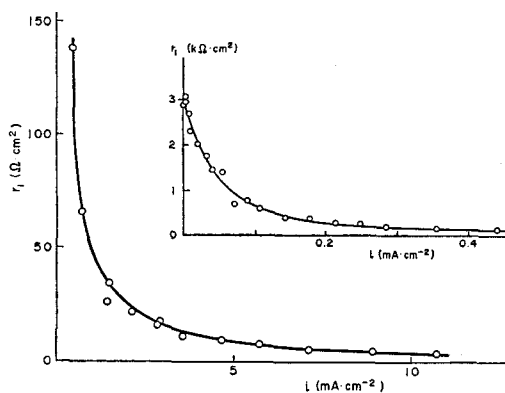


Fig. 7. Dependence of the polarization resistance of the discharge step of h.e.r. on silver on the polarizing current density in $4.97 \times 10^{-3} \text{N NaOH(aq)}$.

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at the zero charge potential, since the C_D at the minimum in Fig. 5 has a tendency to decrease with increasing concentration of the solution.

3.2.2. Kinetic law of the electron transfer step

The exchange current density of the electron transfer step i_{10} can be determined from its polarization resistance r_{10} at the reversible potential by eq. (4)

$$i_{10} = RT/Fr_{10} \quad (4)$$

The values of i_{10} calculated in this way are given in Table 1 for the solutions of various concentration. It is found that i_{10} strongly depends on the concentration of the solution, with a gradient

$$\frac{d \ln i_{10}}{d \ln a_{\pm}} = 1.0 \quad (5)$$

as shown in Fig. 6, where a_{\pm} is the mean activity of aqueous sodium hydroxide. It may be concluded from the comparison of i_{10} with i_0 that the electron transfer step cannot be rate-determining, since i_{10} is much larger than i_0 as seen in concentrated solutions or at least comparable with i_0 in the order of magnitude as seen in very dilute solutions.

The relation between the current density and overvoltage for the electron transfer step can be obtained by eq. (6)

$$\eta_1 = - \int_0^i r_1 di \quad (6)$$

The r_1 can be obtained as a function of η or i from the $\log r_1$ vs η curves in Fig. 4. An example of i -dependence of r_1 is illustrated in Fig. 7. As was done in the previous paper,⁹⁾ it is useful to express r_1 vs i curves in log-log scale. The $\log r_1$ vs $\log i$ curves are shown in Fig. 8 for various solutions. It can be seen that all the curves tend to a single straight line with increasing $\log i$, which can be expressed by eq. (7)

$$\log r_1 = -1.26 - \log i, \quad (7)$$

where i can be identified with the unidirectional rate of the electron transfer step \vec{i}_1 , and r_1 with $\vec{r}_1 = -d\eta_1/d\vec{i}_1$.

It follows from eqs. (6) and (7) using $i = \vec{i}_1$

$$\vec{i}_1 \vec{r}_1 = - \frac{d\eta_1}{d \ln \vec{i}_1} = 0.055 \text{ (V)}, \quad (8)$$

or

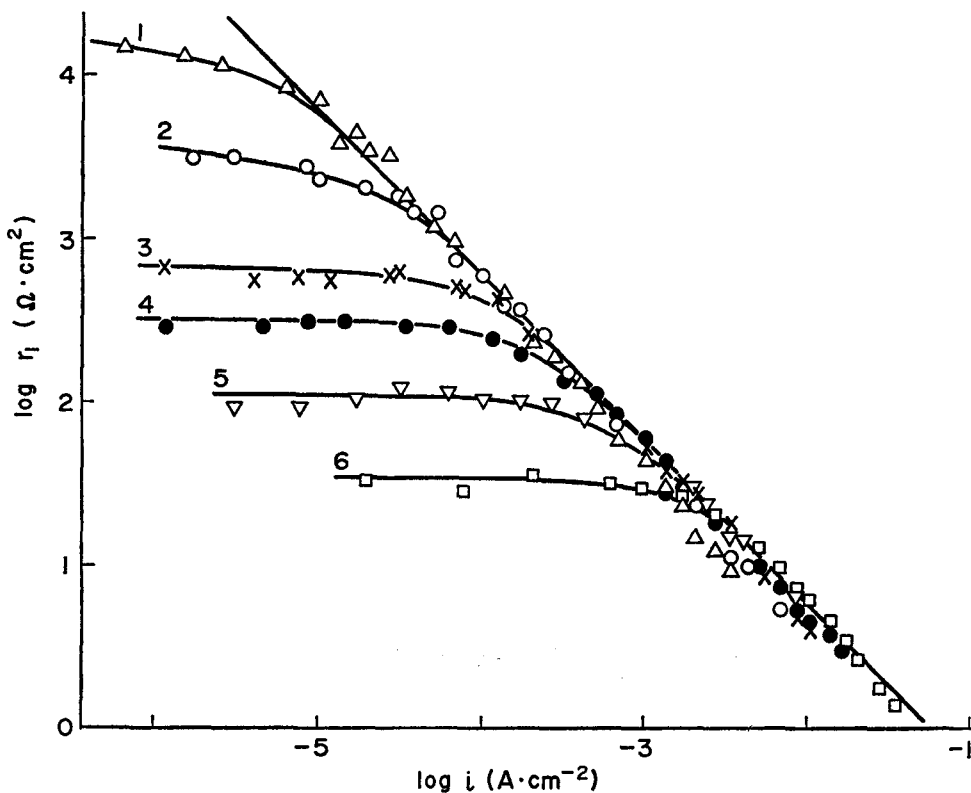


Fig. 8. Dependence of r_1 on i in a log-log scale on silver in NaOH_{aq} .

1) $8.4 \times 10^{-4} \text{N}$ 2) $4.97 \times 10^{-3} \text{N}$ 3) $1.07 \times 10^{-2} \text{N}$ 4) $8.4 \times 10^{-3} \text{N NaOH} + 7.56 \times 10^{-2} \text{N Na}_2\text{SO}_4$ 5) 0.127N 6) 0.817N

$$-\eta_1 = 0.055 \ln \bar{i}_1/i_{10}, \quad (9)$$

as in the case of the proton discharge on silver in sulfuric acid solutions.⁹⁾ The unidirectional rate equation (9) leads to eq. (10) at room temperature

$$\bar{i}_1 = i_{10} \exp(-\alpha F \eta_1 / RT), \quad (10)$$

with $\alpha \approx 0.5$.

The net rate of the electron transfer step $i = \bar{i}_1 - \bar{i}_1$ can be obtained by eq. (6) as a function of η_1 . Fig. 9 shows the $\log i$ vs η_1 curves obtained from r_1 vs i curves on the basis of eq. (6). All the curves have a slope of $\sim 120 \text{ mV}$ at higher current densities and the value of i_{10} obtained from extrapolation of the linear part in Fig. 9 coincides with that obtained from r_{10} by eq. (4) as seen in Fig. 6. In this way the net rate of the electron

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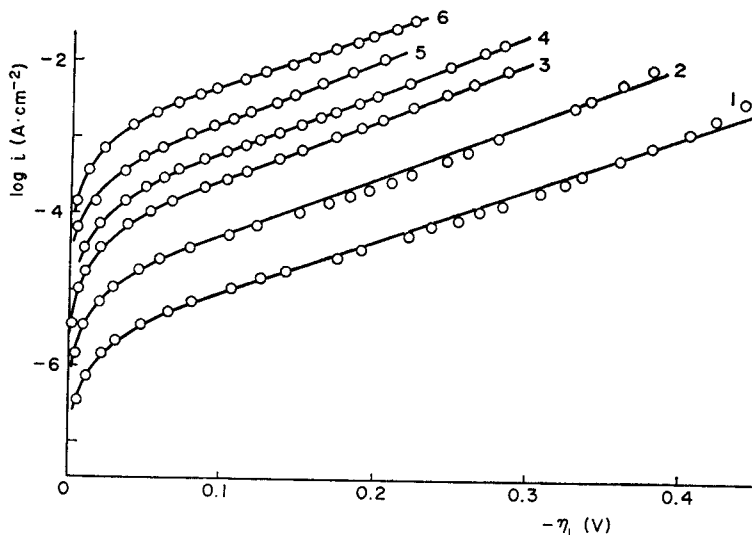


Fig. 9. Kinetics of the discharge step of h.e.r. on silver in NaOH_{aq} . The solutions are the same as in Fig. 8.

transfer step i_1 can be expressed as a function of η_1 by eq. (11)

$$i_1 = i_{10} \left\{ \left(\exp(-\alpha F \eta_1 / RT) - \exp(1 - \alpha) F \eta_1 / RT \right) \right\}, \quad (11)$$

with $\alpha \approx 0.5$.

Let us now discuss nature of the electron accepting species in the electron transfer step on the basis of the concentration dependence of i_{10} ; "which is the discharging species, sodium ion or water molecule?". As pointed out by eq. (5), the experimental value of $d \ln i_{10} / d \ln a_{\pm}$ equals unity. From the theoretical point of view i_{10} can be expressed for the discharge of a sodium ion by eq. (12)

$$i_{10} = k a_{\text{Na}^+} e^{-\frac{F\phi_1}{RT}} e^{-\frac{\alpha F}{RT}(\phi_{\text{eq}} - \phi_1)}, \quad (12)$$

and for the discharge of a water molecule by eq. (13)

$$i_{10} = k' e^{-\frac{\alpha F}{RT}(\phi_{\text{eq}} - \phi_1)}, \quad (13)$$

where ϕ_{eq} and ϕ_1 denote the potentials of the electrode and the outer Helmholtz plane at the reversible state, respectively, as referred to the bulk of the solution. On the other hand, ϕ_1 may be given by eq. (14) when the electrode surface is strongly negatively charged¹⁷⁾

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$$\phi_1 = \frac{RT}{T} \ln c + \text{const.} \quad (14)$$

where c is the normality of the solution.

As reported previously⁹⁾ we obtained the zero charge potential of the silver electrode at -0.6 V (vs NHE). It may therefore be assumed that the silver electrode at the reversible potential in aqueous sodium hydroxide is highly negatively charged.

It follows from eqs. (12)~(14) for the discharge of a sodium ion and a water molecule, assuming $a_{\pm} = c$,

$$\frac{d \ln i_{10}}{d \ln a_{\pm}} = 2\alpha \approx 1 \quad (15)$$

In this way the concentration dependence of i_{10} obtained experimentally can

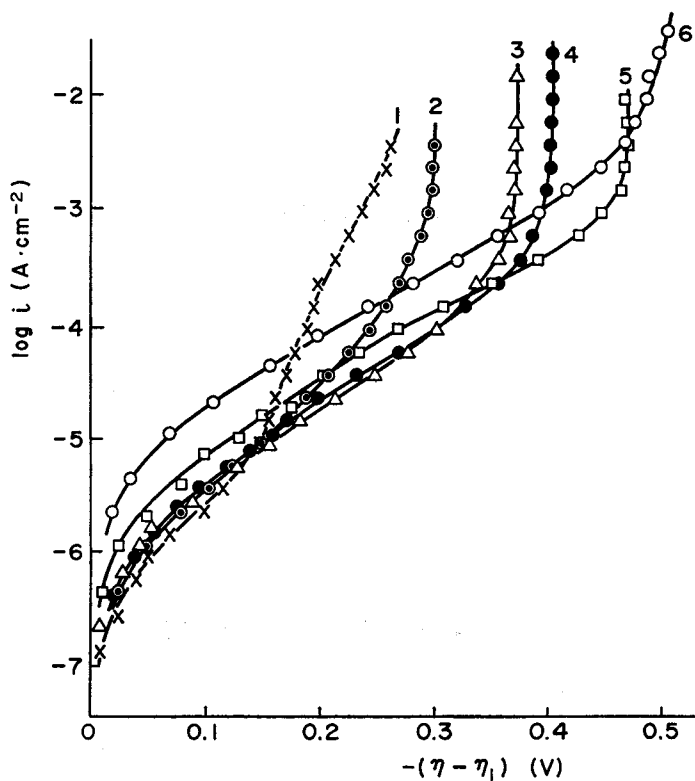


Fig. 10. Overall kinetics of the steps following the discharge step on silver in NaOH_{aq} . The solutions are the same as in Fig. 8.

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be explained equally well both in the cases of the discharge of a sodium ion and a water molecule.

The discharging species will now be discussed on the basis of the intermediate species produced by the electron transfer step. As seen from the comparison of Fig. 2 with Fig. 9, the overvoltage of the electron transfer step $-\eta_1$ which is caused by charging up of the double layer is much smaller than that of the overall reaction $-\eta$. The residual part of the overvoltage $-(\eta-\eta_1)$ may be attributed to the change of the surface potential of the silver electrode which may be caused by the adsorbed intermediate species formed by the electron transfer step and $-(\eta-\eta_1)$ for a given solution can be related to the activity a_I of the intermediate species I by the equation

$$-(\eta-\eta_1) = (RT/F) \ln a_I/a_{I,e} \quad (16)$$

where $a_{I,e}$ denotes the activity of I at the reversible potential of h. e. r.

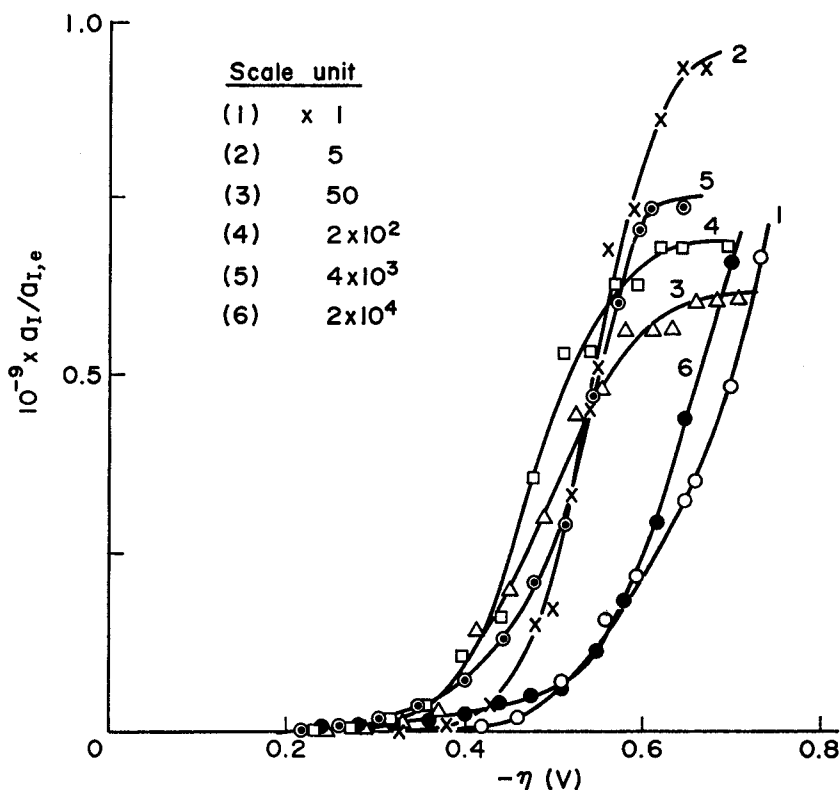


Fig. 11. Overvoltage dependence of activity of the intermediate of h. e. r. for the solutions in Fig. 8.

If the intermediate species can be identified with the adsorbed hydrogen atom $H(a)$, $\alpha_{1,e}$ should be constant under the atmospheric hydrogen pressure independent of the solution composition, and $-(\eta-\eta_1)$ would be a measure of the chemical potential of $H(a)$, as seen from eq. (16), which promotes the rate of the step of the recombination of adsorbed hydrogen atoms. Then we can expect a single polarization curve $\log i$ vs $-(\eta-\eta_1)$ irrespective of the concentration of the solution. Fig. 10 shows the $\log i$ vs $-(\eta-\eta_1)$ curves obtained from Figs. 2 and 9. It is seen that there is practically no concentration dependence at low current densities in dilute solutions, but a strong concentration dependence can be seen in concentrated solutions and furthermore there appears a saturation value of $-(\eta-\eta_1)$ with increasing current density which strongly depends on the concentration of the solution. Therefore it may be concluded that $H(a)$ cannot be regarded as the intermediate species.

If the intermediate species can be identified with the adsorbed sodium atom $Na(a)$, then $\alpha_{1,e}$ depends on the concentration of Na^+ ion and $-(\eta-\eta_1)$ depends on the activities of Na^+ ion and $Na(a)$. The ratio $\alpha_1/\alpha_{1,e}$ calculated

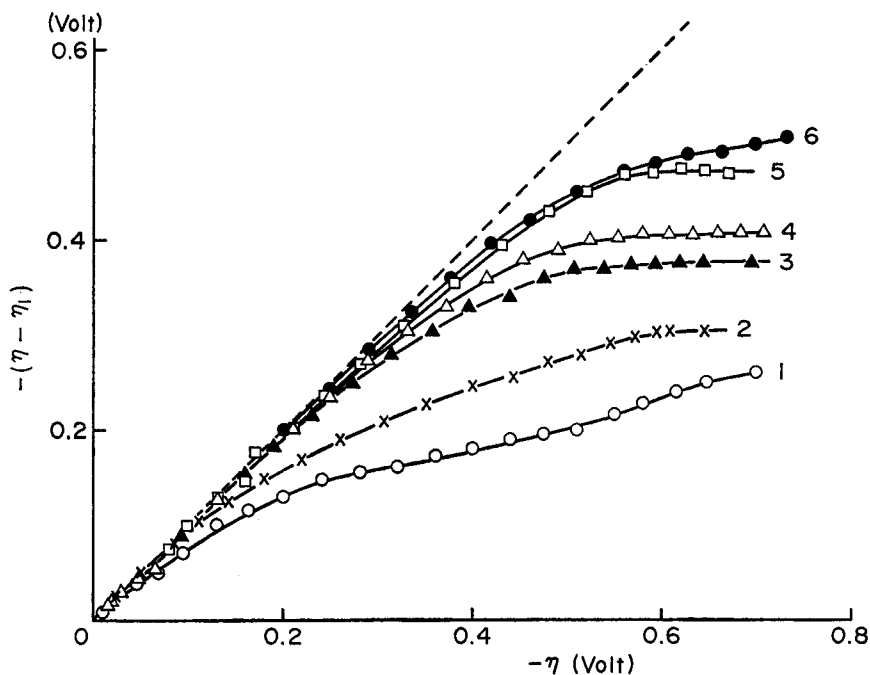


Fig. 12. The relation between $-(\eta-\eta_1)$ and $-\eta$ for the solutions in Fig. 8.

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by eq. (16) for various solutions is plotted against $-\eta$ in Fig. 11. It is seen that $a_1/a_{1,e}$ strongly depends on the concentration of the solution. It may therefore be reasonable to assume that the intermediate species can be identified with Na(a) and consequently the electron transfer step of h. e. r. on silver in aqueous sodium hydroxide can be regarded as the discharge of Na^+ ion as in the case of platinum,¹⁰⁻¹³⁾ nickel^{14,15)} and gold.¹⁶⁾

The relation between $-(\eta-\eta_1)$ and $-\eta$ is shown in Fig. 12 for the comparison of η_1 and η , in which the dotted line shows the relation when $\eta_1=0$. It can readily be seen from this figure that η_1 practically equals zero at low values of $-\eta$ irrespective of the concentration of the solution, but the region of η in which $\eta_1 \approx 0$ increases with increasing concentration of the solution and $-(\eta-\eta_1)$ has a tendency to approach a saturation value with increasing $-\eta$, which strongly depends on the concentration of the solution. It is seen from the comparison of Figs. 12 and 2 that the Tafel constant of the polarization curve of the overall reaction approaches 120 mV in the high overvoltage region in which the saturation of $-(\eta-\eta_1)$ appears, suggesting that the increase of $-\eta$ in this region is caused exclusively by charging up of the double layer and the electron transfer step becomes rate-determining.

Conclusion

(1) The electron transfer step of h. e. r. on silver in aqueous sodium hydroxide can be regarded as the discharge of Na^+ ion and its rate can be expressed by eq. (11) as a function of the overvoltage η_1 which is caused by charging up of the electric double layer.

(2) The surface potential caused by the adsorbed sodium atom contributes greatly to the establishment of the overvoltage of the overall reaction.

(3) The activity of the adsorbed sodium atom approaches a saturation value with increasing overvoltage, which strongly depends on the concentration of the solution.

(4) The electron transfer step is rate-controlling in the high overvoltage region in which the saturation of the adsorbed sodium atom appears.

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