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KINETIC STUDIES OF ELECTRON TRANSFER STEP ON NICKEL HYDROGEN ELECTRODE IN AQUEOUS BARIUM HYDROXIDE

By

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Abstract

The polarization curves of the electron transfer step of the hydrogen evolution reaction on nickel in aqueous Ba(OH)₂ and Ba(ClO₄)₂ were obtained separately by a galvanostatic transient method.

It was concluded that the electron transfer step was composed of the discharge of Ba²⁺ ion and its rate was expressed by the Tafel equation with the transfer coefficient in the cathodic or anodic direction $\alpha=0.68$ or $\beta=1.37$ in terms of the overvoltage component caused by charging up of the electric double layer. The exchange rate of the electron transfer step was about 750 times larger than that of the overall reaction.

It has been developed in a series of works^{1~5)} that the overvoltage component η_1 which is imposed upon the electron transfer step of the hydrogen evolution reaction under the stationary polarization may be determined from the polarization resistance of the electron transfer step r_1 by the equation :

$$\eta_1 = - \int_0^i r_1 di. \quad (1)$$

The polarization resistance r_1 can be obtained experimentally by a galvanostatic transient method on the basis of the following equations :

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

$$\tau_1 = C_D r_1, \quad (3)$$

where Δi is the instantaneous change of the polarization current i , $\dot{\eta}$ the rate of corresponding change of the overvoltage (taken negative in the cathodic direction), τ_1 the time constant of the electron transfer step, and C_D the differential capacity of the electric double layer at the metal solution

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interface. η_1 thus determined is attributed to the charging up of the electric double layer.

It was previously concluded on the basis of the galvanostatic transient studies that in neutral and alkaline solutions with monovalent cations, for instance, Na^+ , Cs^+ and Li^+ , the electron transfer step was the discharge of these alkali metal ions, and its rate was expressed by the Tafel equation with the transfer coefficient 0.5 in terms of the overvoltage caused by charging up of the electric double layer, independent of the change of the surface potential caused by the intermediate species on the electrode surface.^{2-4,6,7)}

The present work is concerned with the polarization curves of the electron transfer step on a nickel hydrogen electrode in aqueous $\text{Ba}(\text{OH})_2$ and $\text{Ba}(\text{ClO}_4)_2$ with special attention to the kinetic behavior of the divalent cation.

The preparation of the reagents and the experimental procedure are the same as described previously.⁸⁾

The $\log(-\Delta i/\eta)$ vs. t curves obtained from the η vs. t curves starting from various steady states in 0.1N and 0.01N $\text{Ba}(\text{OH})_2$ at room temperature are shown respectively in Figs. 1 and 2.

From the initial linear part of these curves, C_D and τ_1 are determined on the basis of Eq. 2, and r_1 is calculated by Eq. 3. The values of C_D and τ_1 are plotted against η respectively in Figs. 3 and 4.

As seen from Fig. 3, C_D vs. η curves have a minimum at $\eta \approx -250$ mV,

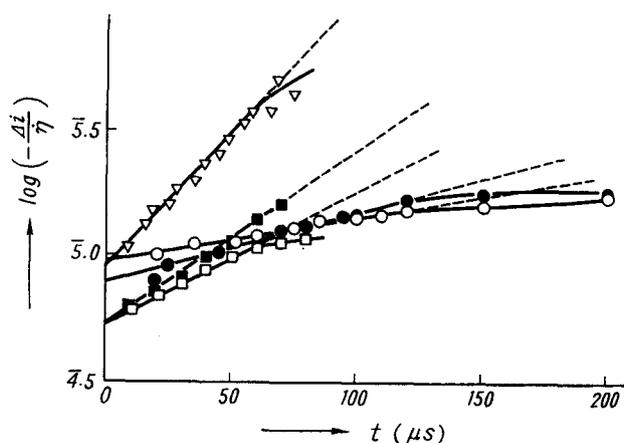


Fig. 1. $\log(-\Delta i/\eta)$ vs. t relation obtained from the η vs. t curves in 0.1N $\text{Ba}(\text{OH})_2$, pH 12.6 on an evaporated Ni film. The starting overvoltage in mV, (○) 0, (●) 130, (□) 225, (■) 264, (▽) 306.

in contrast to the case of aqueous NaOH where C_D remains constant throughout the electrode potential observed.²⁾ The presence of a minimum in C_D vs. η curves may probably be ascribed to the change of the surface state of the electrode.

From the comparison of the τ_1 vs. η curves in 0.1N and 0.01N solutions in Fig. 4, it can be seen that τ_1 in 0.1N solution remains constant in the potential region 0~−100 mV and then it begins to decrease with decrease of η , whereas in 0.01N solution it shows a gradual decrease with the decrease of η from the beginning of the polarization.

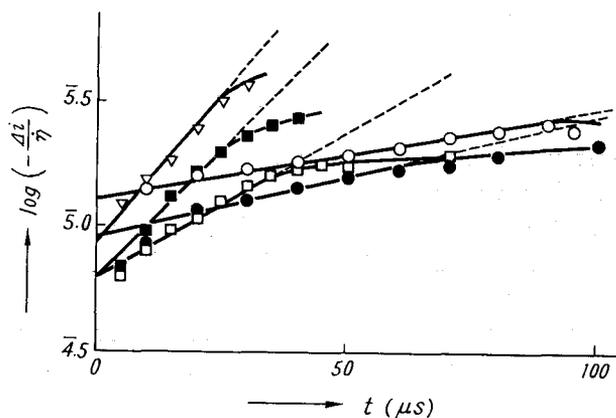


Fig. 2. $\log(-\Delta i/\eta)$ vs. t relation obtained from the η vs. t curves in 0.01N $\text{Ba}(\text{OH})_2$, pH 11.5 on an evaporated Ni film. The starting overvoltage in mV, (○) 0, (●) 116, (□) 246, (■) 272, (▽) 295.

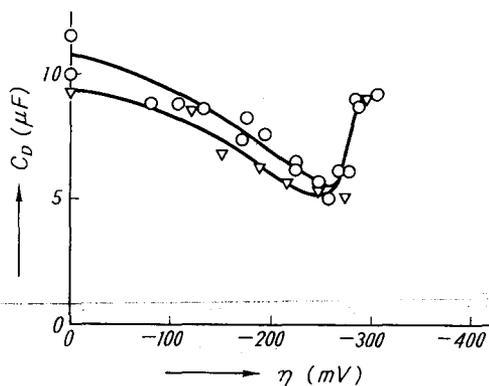


Fig. 3. Differential capacitance of the double layer, (○) 0.1N $\text{Ba}(\text{OH})_2$, pH 12.6; (▽) 0.01N $\text{Ba}(\text{OH})_2$, pH 11.5.

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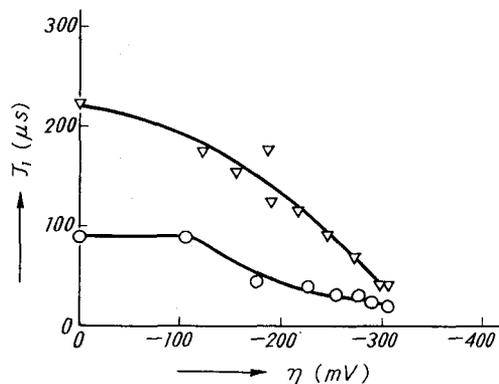


Fig. 4. Time constant of the electron transfer step, (○) 0.1N Ba(OH)₂, pH 12.6; (▽) 0.01N Ba(OH)₂, pH 11.5.

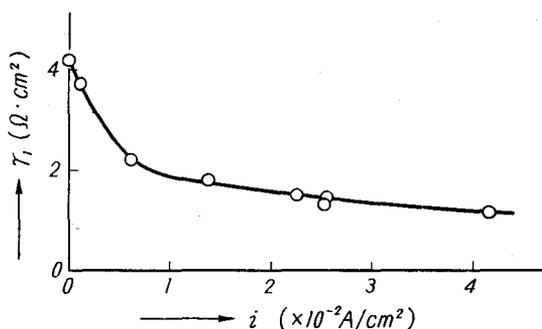


Fig. 5. Polarization resistance of the electron transfer step as a function of the polarizing current in 0.1N Ba(OH)₂.

In the potential region where τ_1 is kept constant, the electron transfer step can be regarded as in equilibrium, since the polarization resistance r_1 is maintained at its equilibrium value in this region. This fact suggests that the charging up of the double layer makes a negligible contribution to the setting up of the overvoltage in this region.

The polarization resistance r_1 in 0.1N Ba(OH)₂ calculated from C_D and τ_1 in Figs. 3 and 4 is shown in Fig. 5 as a function of i which corresponds to the overvoltage η under the stationary polarization in Fig. 4. From the graphical integration of the r_1-i curve, the overvoltage of the electron transfer step η_1 can be obtained on the basis of Eq. 1. The relation between $\log i$ and η_1 thus obtained in 0.1N, 0.01N Ba(OH)₂ and 0.1N Ba(ClO₄)₂ is shown in Fig. 6.

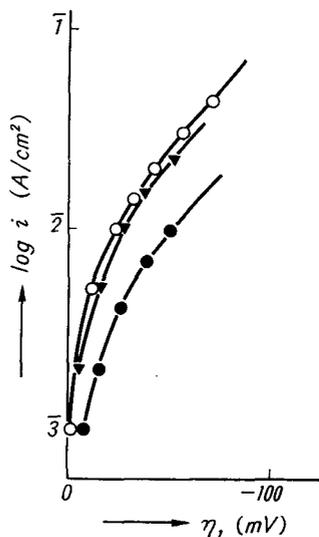


Fig. 6. Polarization curves of the electron transfer step, (○) 0.1N Ba(OH)₂, pH 12.6; (●) 0.01N Ba(OH)₂, pH 11.5; (▼) 0.1N Ba(ClO₄)₂, pH 10.0.

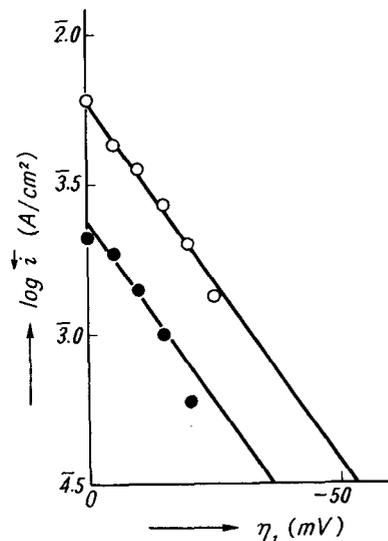


Fig. 7. $\log \bar{i}$ vs. η relations, (○) 0.1N Ba(OH)₂, pH 12.6; (●) 0.01N Ba(OH)₂, pH 11.5.

As seen from Fig. 6, the $\log i$ vs. η_1 curves in 0.1N Ba(OH)₂ and 0.1N Ba(ClO₄)₂ of different pH, respectively 12.6 and 10.0, practically coincide with each other within the experimental error, and the polarization curve in 0.01N Ba(OH)₂ lies below that in 0.1N Ba(OH)₂. It follows from these facts that the rate of the electron transfer step depends on the concentration of Ba⁺ ion, but not on the pH of the solution. It may hence be concluded that the electron transfer step is composed of the discharge of Ba⁺ ion, similar to the case of discharge of Na⁺ ion in aqueous NaOH.^{1,2)}

From the linear part of the $\log i$ vs. η_1 curves in Fig. 6, the transfer coefficient is found to be 0.68. The exchange rate i_{10} obtained by the extrapolation of the $\log i$ vs. η_1 curve coincides in each solution with that calculated by the equation $i_{10} = RT/F \cdot r_1$, with the value of r_1 at the reversible potential. Accordingly, the unidirectional current of the electron transfer step in the cathodic direction \bar{i}_1 may be expressed by the equation,

$$\bar{i}_1 = i_{10} \exp(-\alpha F \eta_1 / RT), \quad (4)$$

with $\alpha = 0.68$.

It may be possible to deduce the unidirectional rate in the anodic direction \bar{i}_1 under the cathodic polarization from the polarization curves in

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Fig. 6 based on Eq. 4 and the relation,

$$i = \bar{i}_1 - \tilde{i}_1. \quad (5)$$

The polarization curves in the reverse direction $\log \tilde{i}$ vs. η_1 thus obtained are shown in Fig. 7.

The transfer coefficient β in the anodic direction is found to be 1.37. Thus the rate of the electron transfer step is now expressed by the equation

$$i_1 = i_{10} \{ \exp(-\alpha F \eta_1 / RT) - \exp(\beta F \eta_1 / RT) \}, \quad (6)$$

with $\alpha = 0.68$ and $\beta = 1.37$. It seems to be unnecessary to introduce the Frumkin correction to the change of ϕ_1 -potential due to dilution of solution as is discussed in the case of the electrodes of low activity, since in the present case most of the potential change may be caused by the surface potential, but not by the potential drop across the double layer.

The transfer coefficients in the right and reverse directions satisfy the relation

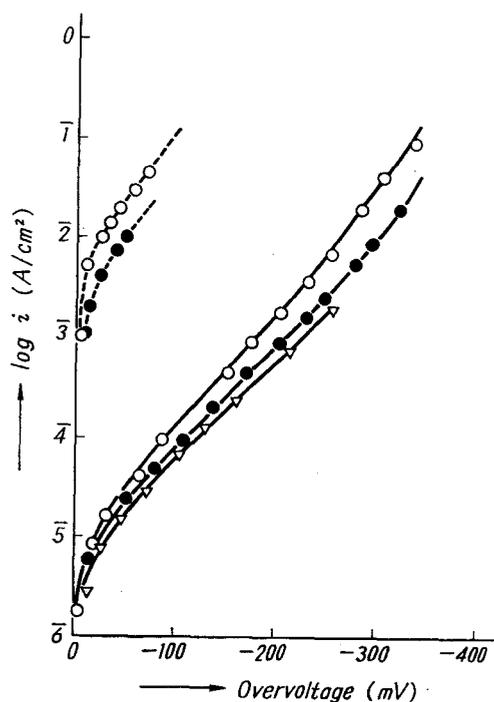


Fig. 8. Polarization curves of the electron transfer step (dotted lines) and those of the overall reaction (solid lines), (○) 0.1 N Ba(OH)₂, pH 12.6; (●) 0.01 N Ba(OH)₂, pH 11.5; (▽) 0.001 N Ba(OH)₂, pH 10.3.

$$\alpha + \beta = 2,$$

which suggests that the discharge step proceeds with the transfer of two metal electrons to Ba^+ ion at one step.

In Fig. 8 the polarization curves of the electron transfer step are shown together with those of the overall reaction for the comparison of η_1 with η at a constant polarizing current density.

As seen from Fig. 8, η_1 is much less than η and too small to be detected at current densities lower than i_{10} in spite of the appearance of the total overvoltage of about -200 mV at 10^{-3} amp/cm². The exchange current of the electron transfer step in 0.1N $\text{Ba}(\text{OH})_2$ $i_{10} = 6.7 \times 10^{-3}$ amp/cm² exceeds that of the overall reaction $i_0 = 9.0 \times 10^{-6}$ amp/cm² by about 750 times in 0.1N $\text{Ba}(\text{OH})_2$. The electron transfer step cannot be rate-determining in the hydrogen evolution reaction at the current densities lower than i_{10} . The polarization curves of the overall reaction show very little pH dependence at potentials near the reversible potential. This fact may be explained by assuming the rate-determining step in this region to be the recombination of atomic hydrogen which is produced by the decomposition of water molecule by the intermediate Ba atom. At current densities higher than i_{10} the overvoltage of the electron transfer step cannot be neglected and the discontinuity of the polarization curves of the overall reaction appears at the current density approximately equal to i_{10} , as seen from Fig. 8.

Experimental proof of the presence of the intermediate Ba atom on the electrode surface will be discussed later on the basis of spectroscopic data.

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