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THE ROLE OF COMPONENTS OF OVERVOLTAGE IN THE KINETIC PROCESSES OF HYDROGEN EVOLUTION REACTION*)

By

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The hydrogen overvoltage is defined as the potential difference between the reversible and the irreversible states of a hydrogen electrode and thermodynamically is expressed by the difference of the electrochemical potential of the free electron in the electrode $\bar{\mu}_e$ between the two states, which may be proved to be a measure of the chemical affinity of the hydrogen electrode reaction.

As $\bar{\mu}_e$ can be divided into the electrostatic potential φ and the work function W of the electrode, the hydrogen overvoltage may be expressed in terms of the two quantities,

$$\eta = (\varphi - \varphi_0) + (W - W_0), \qquad (1)$$

where suffix 0 means a reversible state. The first and second terms of the right hand side of Eq. 1 will be denoted respectively by η_1 and η_2.

The component η_1 may be developed at the electrode-solution interface by the charging up of the electric double layer, while the component η_2 may be caused by the change of the surface states of the electrode.

It can be expected from the difference in the physical nature of the two components of overvoltage that the role of each component in the kinetic processes of the hydrogen evolution reaction may be different. Most of electrochemists, however, have not paid a special attention to the significance of dividing the hydrogen overvoltage into its components in discussing the reaction mechanism, although it was pointed out by LANGMUIR in 1916[1].

In the present work the role of η_1 and η_2 in the kinetic processes of the hydrogen evolution reaction on Au, Ga, Pt, Ni, Ag in alkaline or acid solutions will be discussed.

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From the experimental point of view, however, it may be difficult in general to separate these components of overvoltage, but at least it may be possible to know the component η_1 from the overvoltage-time curves in a galvanostatic transient method which may reveal the component separately in the course of the setting up of the overvoltage.

Let us consider a hydrogen electrode which remains stationary with a current density j and an overvoltage η. When j is changed instantaneously by a constant amount Δj, the corresponding transition of overvoltage may be caused by the charging up of the double layer at least in its initial stage. From the material balance of electrons in this stage of the transition of overvoltage, the following equation may be obtained in the potential region

$$\ln(-\Delta j/\dot{\eta}_1) = \frac{t}{\tau_1} + \ln C_D, \qquad (2)$$

where C_D denotes the differential capacity of the double layer, $\dot{\eta}_1$ is the time derivative of overvoltage, and τ_1 is the time constant of the electron transfer step which is given by the product C_D and the polarization resistance of the step γ_1. The values of C_D, τ_1 and γ_1 may be determined by the analysis of the $\eta-t$ curve on the basis of Eq. 2[2,3].

When γ_1 is given as a function of j, it may be possible to estimate η_1 by the graphical integration of the γ_1-j curve,

$$\eta_1 = -\int_0^j \gamma_1 dj, \qquad (3)$$

since γ_1 is defined as the differential of η_1 with respect to j. It should be noted here that Eq. 3 gives not only the value of η_1 which is included in η, but also gives the polarization curve of the electron transfer step.

The experimental validity of Eq. 2 will be exemplified in Fig. 1 in the case of liquid Ga in aqueous NaOH[4]. As seen from this Figure, a linear relation between $\log(-\Delta j/\dot{\eta}_1)$ and time can be obtained as expected from Eq. 2.

The amount of η_1 can be estimated from the integration of γ_1-j curve which is obtained from Fig. 1. In Fig. 2 the current density j is plotted against η_1 or η.

As seen from Fig. 2, both the $\log j$ vs. η_1 and $\log j$ vs. η curves on Ga in aqueous NaOH can be expressed by a single straight line with gradient 120 mV. It follows from this fact that the overall overvoltage η on Ga is substantially caused by the charging up of the electric double layer.

In every system studied, for example, Pt[2], Ni[5], Au and Ag in alkaline solutions and Au[6] in sulfuric acid, the value of C_D remained constant with

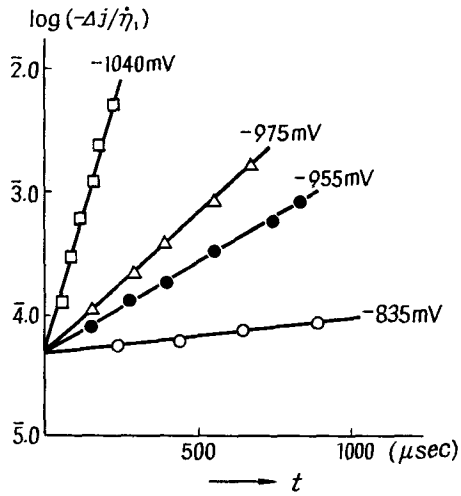

Fig. 1. $\log(-\Delta j/\dot{\eta}_1)$ vs. time curves on liquid Ga in 0.1 N NaOH at 31°C, obtained from the transient curves which started from different values of steady state overvoltage.

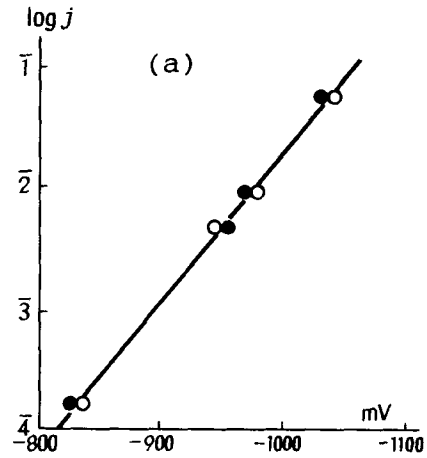

Fig. 2. $\log j$ plotted against η (●) or η_1 (○) on liquid Ga in aqueous 0.1 N NaOH at 31°C.

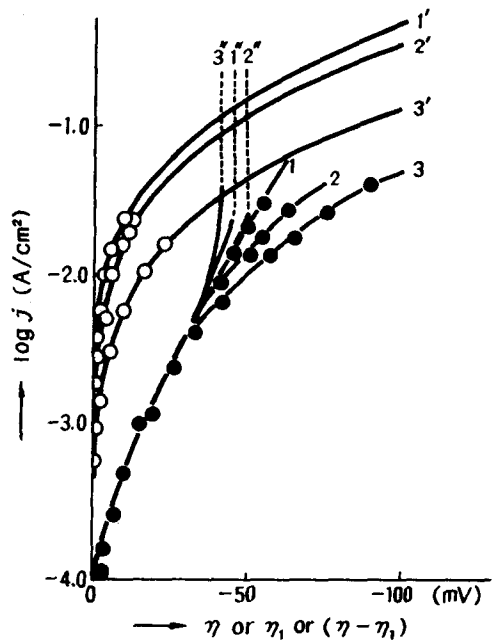

Fig. 3. $\log j$ plotted against $\eta(1, 2, 3)$, or $\eta_1(1', 2', 3')$ or $\eta - \eta_1(1'', 2'', 3'')$ on Au plate at 23°C in sulfuric acid: 1.3 N(1, 1', 1''), 0.67 N(2, 2', 2''), 0.3 N(3, 3', 3'').

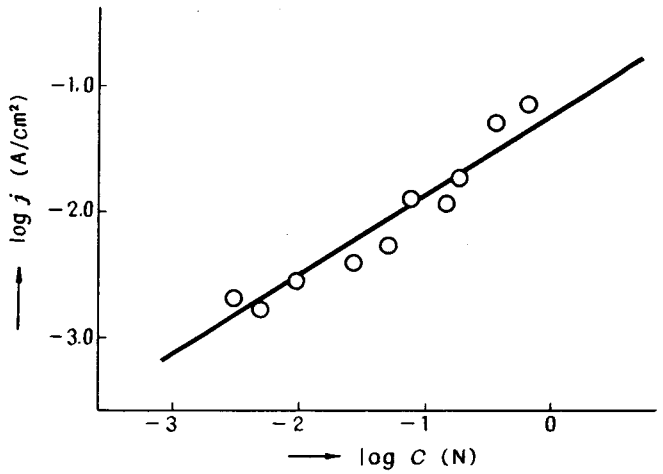

Fig. 4. The concentration dependence of the exchange rate of the electron transfer step on Au in sulfuric acid.

the change of η in the hydrogen overvoltage region independent of the solution concentration, while τ_1 varied depending on η, the solution concentration and the electrode material.

In Fig. 3 the current density is plotted against η_1, or η, or $\eta-\eta_1$ in the case of Au in sulfuric acid of various concentrations[6]. It can be seen from this Figure that the electron transfer step is faster than the overall reaction and can be expressed by the Tafel equation with the transfer coefficient $\alpha=0.5$,

$$j=j_{10}\left\{\exp\left(-\alpha F\eta_1/RT\right)-\exp\left(\beta F\eta_1/RT\right)\right\}, \qquad (4)$$

where j_{10} is the exchange current density of the electron transfer step determined from the polarization resistance of the step at the reversible potential γ_{10} by the relation $j_{10}=RT/F\gamma_{10}$. j_{10} is found to be proportional to the square root of the concentration of the solution, as shown in Fig. 4. It can be concluded from these facts that the electron transfer step is composed of the discharge of the hydrated proton on Au in sulfuric acid.

As seen from Fig. 3, the polarization curves of the overall reaction the $\log j$ vs. η curves in solutions of different concentration coincide with each other at low current densities, but with the increase of the current density the dependence of η on the solution concentration appears. As to the $\log j$ vs. $\eta-\eta_1$ curves, these curves practically coincide with the $\log j$ vs. η curve at low current densities, since η_1 is negligiblly small as compared with η in this current region, but the $\log j$ vs. $\eta-\eta_1$ curves point to

a constant value of $\eta-\eta_1$ with the increase of the current density which little depends on the concentration of the solution.

These facts suggest that the $\log j$ vs. $\eta-\eta_1$ curve corresponds to the polarization curve of the recombination of the adsorbed hydrogen atoms generated by the electron transfer step and the existence of the limiting value of $\eta-\eta_1$ is due to the saturation of the surface coverage of the adsorbed hydrogen atoms although it is assumed to be very low judging from the transfer coefficient nearly equal to 2. In fact, the dipole nature of the adsorbed hydrogen atom with the positive end toward ouside the surface has already been reported in the electrochemical systems[7] and vacuum systems[8]. Thus $\eta-\eta_1$ may be attributed to the dipole moment of the metal-H bond.

The increase of η at high current densities where η exceeds the saturation value of $\eta-\eta_1$ may be explained by the increse of η_1, since the solution dependence of η appears in this region and the parallelism appears between the $\log j$ vs. η_1 and the $\log j$ vs. η curves.

In other systems, for example, Pt[9], Ni[10], Au and Ag in alkaline solutions, the electron transfer step was proved to be the discharge of the alkali metal ion and the succeeding steps were composed of the decomposition of a water molecule and the recombination of the adsorbed hydrogen atoms. The rate of the electron transfer step was also expressed by Eq. 4 in terms of the overvoltage component due to the charging up of the double layer.

The intermediate species, however, which affected the electrode potential in this case was proved by the capacitance measurements and the atomic absorption spectroscopy to be the alkali metal atom generated by the electron transfer step.

In this case the dipole moment due to the adsorption of the alkali metal atom or the contact potential difference between the surface layers and the bulk of the base metal due to the formation of some solid solution or surface compounds between the electrode metal and the alkali metal atom may act as the overvoltage of the hydrogen evolution reaction. It is found on the basis of the electrode potential theory developed by Prof. FRUMKIN and his school[11] that this component of overvoltage is proportional to the chemical potential of the intermediate alkali metal atom.

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