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# ELEMENTARY STEPS OF HYDROGEN EVOLUTION REACTION AT A GOLD ELECTRODE IN AQUEOUS SULFURIC ACID

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The rate and overvoltage of the constituent elementary steps of the hydrogen evolution reaction at a gold electrode in aqueous sulfuric acid were determined by means of a galvanostatic transient method together with a conventional steady state polarization method. It was concluded that the reaction proceeded through the discharge of hydrated proton which was followed by the recombination of adsorbed hydrogen atoms and the overvoltage of the former step was caused by the free charge on the electrode surface and that of the latter was attributed to the decrease in the electronic work function caused by the adsorbed hydrogen atoms.

Several authors have discussed the mechanism of the hydrogen evolution reaction ( h.e.r.) on gold in concentrated sulfuric acid solution based mainly on the b-value of the Tafel slope.[1−5] As pointed out by Horiuti et al.,[6,7] the predicted b-value of the Tafel slope, however, may vary from 28 to 120 mV depending upon the mutual interaction of the intermediate species including the activated complex of the reaction, even if the h.e.r. proceeds through a single mechanism. Therefore the b-value of the Tafel slope does not necessarily serve as a criterion for the mechanism of the h.e.r. The purpose of the present work is to elucidate the mechanism of the h.e.r. on gold in sulfuric acid based on the comparison of the rates of the constituent elementary steps of the h.e.r. which can be determined by a galvanostatic transient method.

In order to avoid the effect of impurities, the sulfuric acid solution was prepared from $SO_3$ gas distilled under vacuum and water distilled in quartz glass vessel. Gold foils degassed or gold films prepared under vacuum were used as the test, counter and reference electrode respectively. The electrolytic cell was made of quartz glass. The polarization curves and the galvanostatic transient curves were observed at 25 °C under strong stirring by forced hydrogen bubbles through sintered quartz glass.

The activity of the gold hydrogen electrode was increased by an anodic activation depending upon the condition of the anodic pre-treatment of the electrode. Fig. 1 shows the steady state polarization curves obtained with an electrode of different pre-treatments, where $I_s$ and $\eta_s$ denote respectively the polarizing current and the overvoltage which takes negative sign in the cathodic direction, and the suffix s means a steady state. The increase of the activity by an anodic treatment is not necessarily attributed to the increase of the surface area of the electrode, contrary to the arguments of Kuhn and Byrne,[4] since the activity was increased by about an order

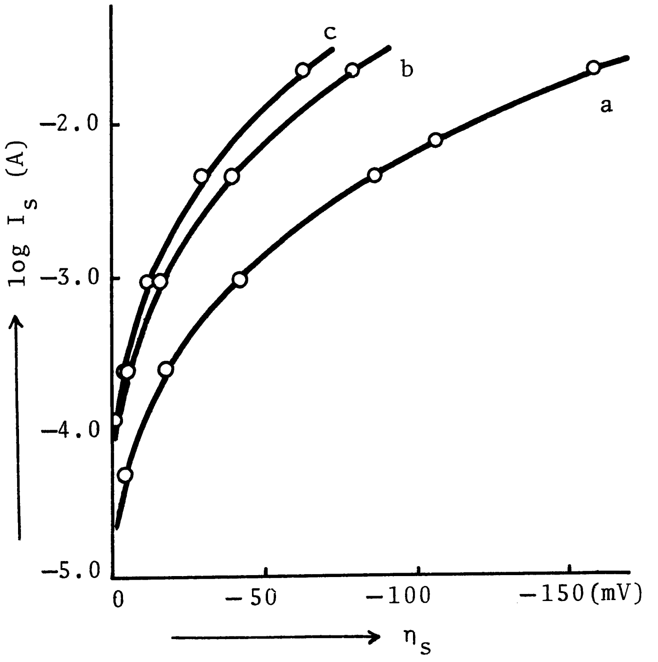

Fig. 1 The steady state polarization curves on gold, geometrical area 0.6 cm$^2$, in 0.30 N $H_2SO_4$aq. under the conditions; curve (a): immediately after the immersion of the electrode into solution, curve (b): after an anodic pre-treatment of the electrode for 0.1 sec. at 1.2 V referred to the r.h.e. in the same environment, curve (c): after a pre-treatment for 10 sec. at 1.7 V or at higher potentials.

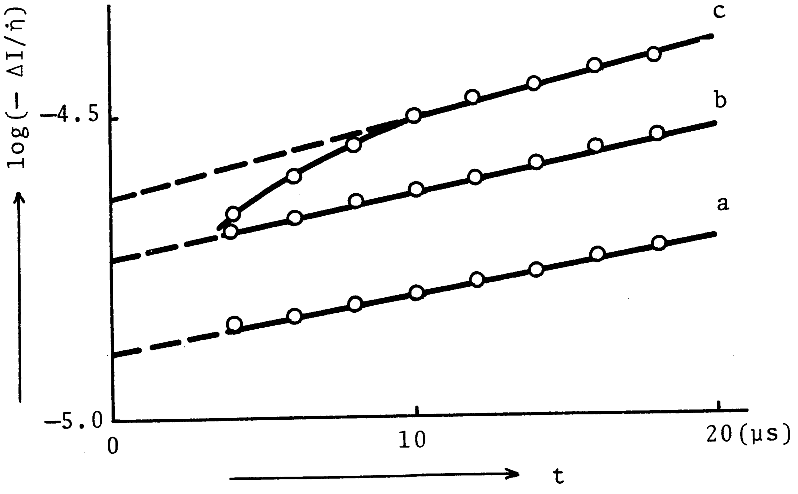

Fig. 2 The relation between log(− ΔI/$\dot{\eta}$) and time on gold under the same conditions as in Fig. 1.

of magnitude by the anodic treatment at 1.7 V, as seen from Fig. 1, whereas the surface area estimated from the differential capacity measurement was increased only by 1.8 times, as seen from Fig. 2. Fig. 2 was obtained from the galvanostatic transient $\eta - t$ curves.[8)] In Fig. 2, $\Delta I$ and $\dot{\eta}$ are the increment of the polarizing current and the time derivative of overvoltage respectively. The differential capacity of the double layer $C_D$ is given by the extrapolation of the linear part of the curves (a), (b) and (c) in Fig. 2 on the basis of the equation[8,9)]

$$C_D = - ( \Delta I/\dot{\eta} )_{t=0} . \qquad (1)$$

The value of $C_D$ of the gold electrode of geometrical area 0.6 $cm^2$ obtained from the curve (c) was 23 μF and that obtained from the curve (a), 13 μF. It follows from the comparison of these two values that the surface area is increased by 1.8 times by the anodic treatment of the electrode at 1.7 V. As seen from Fig. 2, a deviation from the linearlity is observed in the initial stage of the curve (c). According to Kunimatsu,[10)] this deviation may be explained by the effect of the micropores produced in the electrode surface by the anodic treatment. These micropores cause to increase the surface area of the electrode, but not to that extent to explain the increase in activity of the electrode.

On the other hand, the gradient of the $\log(- \Delta I/\dot{\eta}) - t$ curve in Fig. 2 gives the time constant of the electron transfer step of the h.e.r.[8,9)] As seen from Fig. 2, the time constant of the electron transfer step is not practically affected by the anodic treatment. It may be concluded from these facts that the increase in activity of the electrode by the anodic treatment is attributed partly to the increase of the surface area of the electrode and partly to the increase in the activity of the elementary step which follows after the electron transfer step.

Fig. 3 shows the polarization curves in 1.3, 0.67 and 0.30 N $H_2SO_4$ solutions obtained with an electrode of the highest activity which was achieved immediately after the anodic treatment at 1.7 V. The $\log j_s - \eta_s$ curve in the 1.3 N solution gives the b-value of 28 mV and in more dilute solutions the polarization curve shows a slight deviation from that in the 1.3 N solution at higher current densities. The b-value of 28 mV may be explained on the basis of either the diffusion of the molecular hydrogen[11)] or the recombination of atomic hydrogen at zero coverage[6,7)] as the rate-determining step. The former is not reasonable since the $\log j_s - \eta_s$ curve controlled by the diffusion of molecular hydrogen shows much higher activity than curve (1) in Fig. 3, as reported by Schuldiner and Hoare[1)] in the case of Pd-hydrogen electrode in the 2 N $H_2SO_4$ solution. The exchange current density $j_0$ evaluated from the $j_s - \eta_s$ curve in the neighbourhood of the reversible potential in solutions studied remains at a constant value of ( 4.3 ± 0.8 ) x $10^{-4}$ A/$cm^2$ independent of pH of the solution. It may be concluded from the results of the steady state polarization curves that the h.e.r. on gold in the $H_2SO_4$ solution is controlled by the recombination of adsorbed hydrogen atoms at low current densities.

In order to find the distribution of the overvoltage of the overall reaction among the constituent elementary steps,[12)] the overvoltage of the electron transfer step was studied separately by a galvanostatic transient method.[8,9)] Let $\eta_{1s}$ be an overvoltage component which is caused by the charging up of the double layer at a

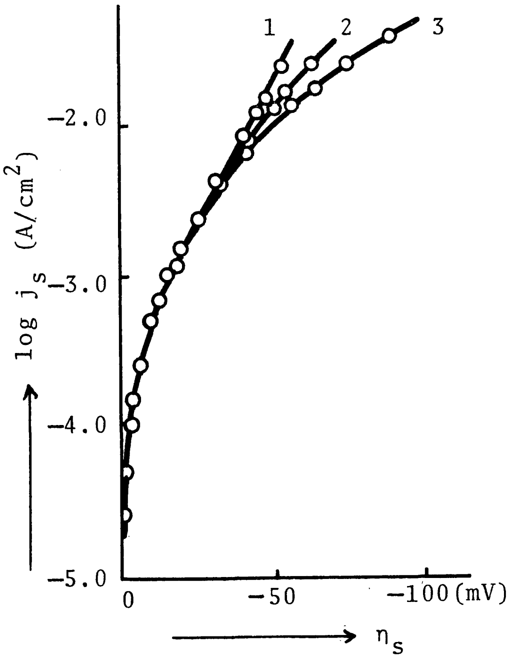

Fig. 3 The steady state polarization curves, concentration of $H_2SO_4$ : (1) 1.3 N, (2) 0.67 N, (3) 0.30 N.

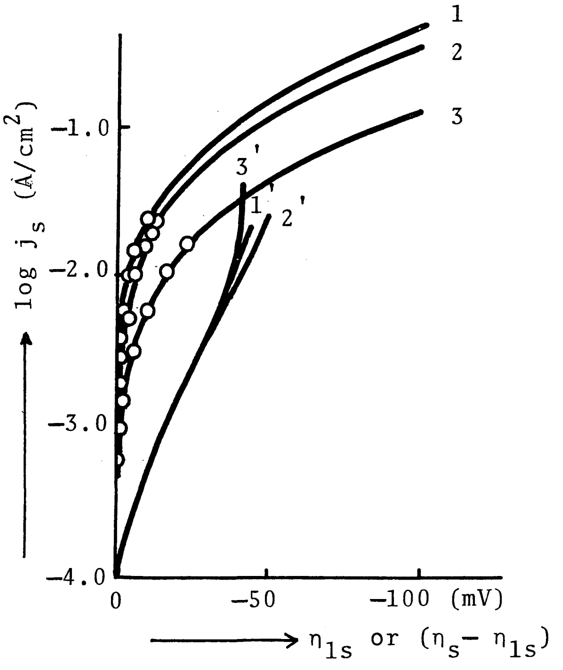

Fig. 4 The polarization curves of the elementary steps.

Curves (1), (2) and (3)—— the electron transfer step, and curves (1'), (2') and (3') —— the recombination of adsorbed hydrogen atoms. (1) and (1') —— 1.3 N, (2) and (2') —— 0.67 N, (3) and (3') —— 0.30 N, $H_2SO_4$.

given value of the total overvoltage $\eta_s$. The relation between the rate $j_s$ and $\eta_{1s}$ thus determined in the 1.3, 0.67 and 0.30 N solutions are shown by open circle in Fig. 4, and the curves (1), (2) and (3) are those obtained by the theoretical calculation on the basis of Frumkin Equation$^{13)}$ with the Tafel constant 1/2,

$$j_{1s} = j_{10} \{ \exp(- F\eta_{1s}/2RT) - \exp(F\eta_{1s}/2RT) \quad , \qquad (2)$$

where the numerical values of the exchange rate of the electron transfer step $j_{10}$, $6.6 \times 10^{-2}$, $4.6 \times 10^{-2}$ and $1.7 \times 10^{-2}$ A/cm$^2$ in the 1.3, 0.67 and 0.30 N $H_2SO_4$ solutions respectively were determined experimentally by the galvanostatic transient method. It can be seen from Fig. 4 that the rate of the electron transfer step may be expressed by Frumkin Equation as a function of the overvoltage which was caused by the charging up of the double layer. Comparing the exchange current densities of the electron transfer step with that of the overall reaction, it is found that the former is larger than the latter by about two orders of magnitude.

In order to clarify the remaining part of the overvoltage ( $\eta_s - \eta_{1s}$), which may be attributed to the change of the electronic work function of the electrode, log $j_s$ is plotted against ( $\eta_s - \eta_{1s}$) in Fig. 4 in the curves (1'), (2') and (3') which are obtained from the log $j_s - \eta_s$ and log $j_s - \eta_{1s}$ curves in the same solution. As seen from the Figure, these curves practically coincide with each other irrespective of pH of the solution, and indicate to approach a saturation value of overvoltage. From the comparison of the curves (1), (2) and (3) in Fig. 3 and (1'), (2') and (3') in Fig. 4 it can be seen that log $j_s - (\eta_s - \eta_{1s})$ curves practically coincide with log $j_s - \eta_s$ curves at low current densities. It may be concluded from this fact that ( $\eta_s - \eta_{1s}$) is attributed to the overvoltage of the recombination of adsorbed hydrogen atoms which may result in the decrease of the work function of the electrode surface.$^{14-16)}$ A saturation value of ( $\eta_s - \eta_{1s}$) suggests that the surface coverage of adsorbed hydrogen

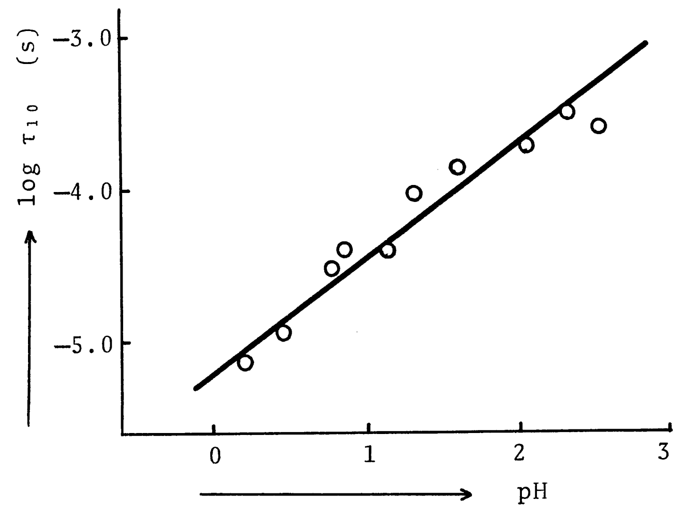

Fig. 5 The relation between the time constant of the electron transfer step and pH of solution.

atoms approaches a saturation value, although it may be quite small as estimated from the b-value of the polarization curve. As suggested from Fig. 4, the overvoltage of the electron transfer step may exceed that of the recombination of hydrogen atoms when the current density is increased.

The time constant $\tau_{10}$ of the electron transfer step in equilibrium determined by the galvanostatic transient method is plotted against pH of the solution in Fig. 5. The linear relation between log $\tau_{10}$ and pH in Fig. 5 suggests that the electron transfer step is composed of the discharge of a hydrated proton, but the value of the gradient 0.76 is a little higher than the theoretical one 0.5.[13)] The deviation of the pH dependence of log $\tau_{10}$ from the theoretical one will be discussed in a later work.

It can be concluded on the basis of the galvanostatic transient studies that the h.e.r. on gold in aqueous sulfuric acid proceeds through the discharge of a hydrated proton followed by the recombination of adsorbed hydrogen atoms, and the overvoltage of the former step is caused by the free charge on the electrode surface and that of the latter step is caused by the adsorbed hydrogen atom which tends to a saturation value with the increase of the current density.

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