- Note -

HYDROGEN OVERVOLTAGE ON TITANIUM IN SULFURIC ACID

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Titanium is a good absorber of hydrogen, but the mechanism of charging of titanium with hydrogen through the electrochemical processes has not yet been clarified1,2,3. In the present note the mechanism of setting up of the hydrogen overvoltage will be discussed on the basis of the time constant and the exchange rate of the proton discharge, the differential capacity of the electric double layer at the metal-solution interface and the pseudo-capacity of the electrode determined by galvanostatic transient methods.

The time constant $\tau_1$ of the proton discharge and the differential capacity $C_D$ of the double layer are determined on the basis of the following equation from the overvoltage transient caused by a current impulse4,6:

$$\ln \left( -\frac{i}{\dot{\theta}} \right) = \frac{t}{\tau_1} + \ln C_D$$  \hspace{1cm} (1)

where $i$ is the height of the current pulse, and $\dot{\theta}$ is the time derivative of the overvoltage.

The experimental procedures were the same as those described elsewhere,4,5 except that a digital transient recorder was used for the observation of the transient curve instead of a memoscope in order to determine the values of $\tau_1$ and $C_D$ by a computer analysis. A titanium plate of 2 cm$^2$ geometrical area, 0.5 mm thick and 99.5% purity was polished chemically with 4% HNO$_3$-2% HF mixture, washed with hot distilled water under hydrogen stream, and then evacuated at $\sim$750°C for 5 hours in an induction furnace. The concentration of sulfuric acid solution ranged from 0.0075 N to 0.713 N.

The polarization curves in steady states of hydrogen evolution on titanium show complicated pH- and $\eta$-dependence, as shown in Fig. 1. The exchange current density $i_0$ is obtained from the polarization resistance at the reversible potential to be $3.0 \cdot 10^{-7}$ A/cm$^2$ in 0.019 N sulfuric acid.

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The values of the time constant $\tau_1$ fall in the range $100 \sim 200 \mu\text{sec}$ in the overvoltage region $0 \sim -1100 \text{mV}$ in every solution used, but with a slight pH-dependence as seen from Fig. 2. The $\eta$-dependence of $C_D$ is also shown in this Figure. The exchange current density $i_{10}$ of the proton discharge is then found to be $3.0 \cdot 10^{-3} \text{A/cm}^2$ for 0.019 N sulfuric acid from the following equations, the value $C_D=18 \mu\text{F/cm}^2$ being used,

$$\tau_1 = C_D r_{10}, \quad i_{10} = \frac{RT}{F} \frac{1}{r_{10}},$$

(2 a), (2 b)

where $r_{10}$ is the polarization resistance of the proton discharge at $\eta=0$.

It can be seen from the comparison of the values $i_0$ and $i_{10}$ that the rate of the proton discharge is larger than that of the overall reaction by 4 orders of magnitude. The component of overvoltage $\gamma_1$ caused by charging up of the double layer which is given by the polarization resistance $r_1$ of the proton discharge as,

$$\gamma_1 = -\int_0^\eta r_1 di,$$

(3)

attains only $20 \sim 30 \text{mV}$ at the current density of $10^{-3} \text{A/cm}^2$ in 0.019 N sulfuric acid whereas $\gamma_1$ of the overall reaction extends to $-500 \text{mV}$ at this current density, i.e., the charging up of the double layer plays a trivial role in the establishment of the hydrogen overvoltage.

The pseudo-capacity $C_p$ vs. $\eta$ curves determined from the decay curves of overvoltage after switching off the polarizing current are shown in Figs. 3 (a) and 3 (b) as a function of overvoltage. As seen from

Fig. 1. Polarization curves of hydrogen evolution reaction on Ti in sulfuric acid at 23°C.
1: 0.0075 N, 2: 0.019 N, 3: 0.097 N, 4: 0.713 N.

Fig. 2. Time constant of proton discharge $\tau_1$ and differential capacity of the electric double layer $C_D$ plotted against $\eta$. 

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Fig. 3. Pseudo-capacity $C_p$ of titanium-hydrogen electrode obtained from the decay curve in sulfuric acid, (a) in 0.0075 N, (b) in 0.097 N.

The arrow shows the starting overvoltage value of the decay curve.

these Figures, the value of $C_p$ is much higher than that of $C_D$, and the higher the starting value of overvoltage of the decay curve, the larger is the value of $C_p$. These facts may be explained assuming that the hydrogen intermediate is not only adsorbed on the electrode surface but also penetrates into the bulk of the electrode. In fact, the surface concentration of the hydrogen intermediate calculated from the $C_p$ vs. $\eta$ curve in Fig. (3 a) exceeds that of the full coverage of the electrode surface at $\eta = -500$ mV.

It can be concluded from these facts that the hydrogen overvoltage on titanium is substantially attributed to the change of the surface potential due to the adsorbed hydrogen intermediate and to the decrease of the work function of the electrode due to the absorption of hydrogen in the metal bulk.

The double layer capacity of the titanium-hydrogen electrode shows a remarkable $\eta$-dependence with a maximum at about $\eta = -300$ mV in contrast with the cases of platinum and nickel. This fact suggests that the surface area of the titanium electrode changes with penetration of hydrogen into the bulk of metal. The X-ray and the electron diffraction analysis (not presented) of the titanium metal after the cathodic polarization showed patterns closely resembling to those obtained with TiH$_{1+a}$ ($a \approx 1$).

From the comparison of the polarization curves in steady states (Fig. 1) and $C_D$ vs. $\eta$ (Fig. 2) and $C_p$ vs. $\eta$ curves (Fig. 3), it is seen that the break of the polarization curve takes place at the potential which corresponds to the maximum
of the $C_D$ vs. $\eta$ or $C_p$ vs. $\eta$ curve. Taking into consideration the insignificant contribution of the charging up of the double layer in setting up of the hydrogen overvoltage, we may attribute the complicated $\eta$-dependence of the polarization curve to the change of the work function of the electrode caused by the interaction between hydrogen and titanium.

References