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— Note —

HYDROGEN OVERVOLTAGE ON TITANIUM IN SULFURIC ACID

By

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Titanium is a good absorber of hydroden, but the mechanism of charging of titanium with hydrogen through the electrochemical processes has not yet been clarified[1,2,3]. 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 τ_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 impulse[4,6]:

$$\ln\left(-\frac{i}{\dot{\eta}}\right) = \frac{t}{\tau_1} + \ln C_D \qquad (1)$$

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

The experimental procedures were the same as those described elesewhere,[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 τ_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 ~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 η-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 τ_1 fall in the range 100~200 μsec in the overvoltage region 0~−1100 mV in every solution used, but with a slight pH-dependence as seen from Fig. 2. The η-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 $3.0 \cdot 10^{-3}$ A/cm^2 for 0.019 N sulfuric acid from the following equations,[4] the value $C_D = 18\ \mu$F/cm^2 being used,

$$\tau_1 = C_D r_{10}, \quad i_{10} = \frac{RT}{F}\frac{1}{r_{10}}, \qquad (2\,a),\ (2\,b)$$

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 η_1 caused by charging up of the double layer which is given by the polarization resistance r_1 of the proton discharge as,[6]

$$\eta_1 = -\int_0^i r_1 \mathrm{d}i, \qquad (3)$$

attains only 20~30 mV at the current density of 10^{-3} A/cm^2 in 0.019 N sulfuric acid, whereas η of the overall reaction extends to −500 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.* η 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

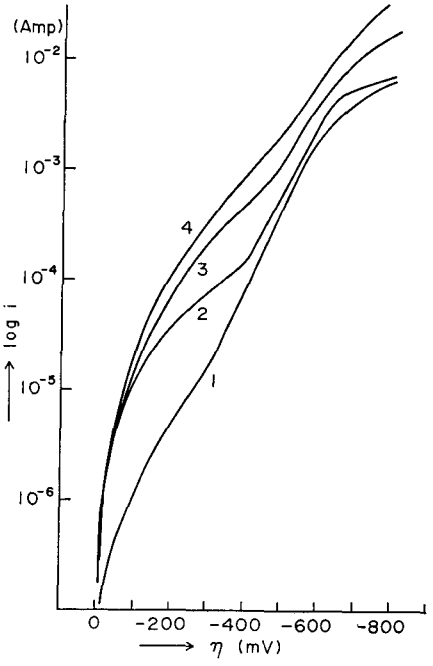

Fig. 1. Polarization curves of hydrogen evolution reaction on Ti in sulfuric acid at 23°C.
1: 0.0075 N, 2: 0.019 N, 3: 0.097 N, 4: 0.713 N.

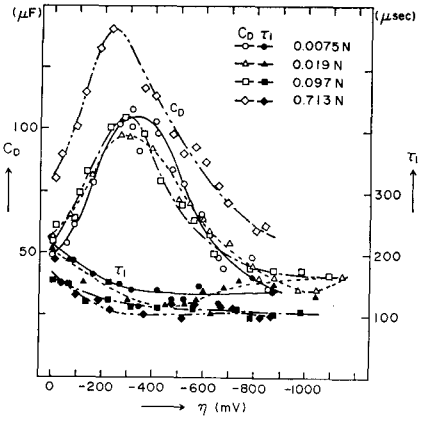

Fig. 2. Time constant of proton discharge τ_1 and differential capacity of the electric double layer C_D plotted against η.

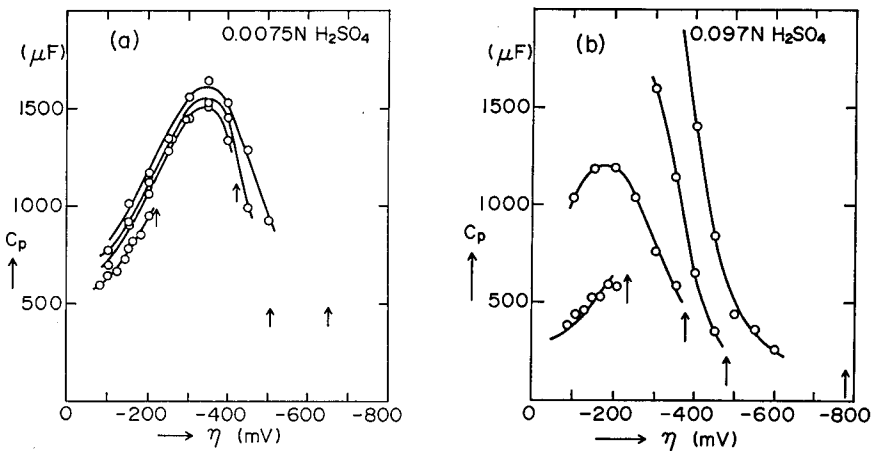

Fig. 3. Pseudo-capacity C_p of titanium-hydrogen electrode obtained from the decay curve in sulfuric acid, (a) in 0.0075 N, (b) in 0.097 N.
The arrow shows the starting overvoltage value of the decay curve.

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.* η 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 η-dependence with a maximum at about $\eta = -300$ mV in contrast with the cases of platinum[7] and nickel.[8] 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 $TiH_{1+\alpha}$ ($\alpha \approx 1$).

From the comparison of the polarization curves in steady states (Fig. 1) and C_D *vs.* η (Fig. 2) and C_p *vs.* η 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.* η or C_p *vs.* η 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 η-dependence of the polarization curve to the change of the work function of the electrode caused by the interaction between hydrogen and titanium.

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