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STUDY OF THE SURFACE OF AN IRON ELECTRODE BY MEASURING THE POTENTIAL DECAY AFTER CURRENT INTERRUPTION

(Presented by Academician A. N. Frumkin on 2 February 1961)

From the rate of potential decay after interruption of the polarizing current, the capacitance of the electrode can be calculated. The capacitance is calculated from the formula

$$\Delta\eta_t = b \lg\left(1 + \frac{2.3 i_0 t}{Cb}\right), \tag{1}$$

where $\Delta\eta_t$ is the decay of overvoltage by time t, i_0 is the density of the polarizing current, C is the capacitance of the electrode, and b is the coefficient in the Tafel equation. Equation (1) is strictly applicable only on the condition that the self-discharge current of the electrode depends on the potential according to the Tafel equation, and that the capacitance of the electrode is assumed to be constant over the overvoltage interval under consideration. Delays or plateaus on the curve of potential versus time after current interruption indicate a disturbance of the normal process of electrode self-discharge.

In our measurements, in the case of large capacitances or not very large values of i_0, when the initial portion of the decay curve proceeds over a time of not less than 10^{-3} sec, an MPO-2 loop oscillograph with a direct-current electronic amplifier on the loop, with a natural frequency of oscillation of 2000 Hz, was used. In calculating small capacitances, it was necessary to discard several points in the initial part of the decay curve, where distortion of the course of the curve was observed. For recording decay curves proceeding at a high rate, an electronic oscillograph was used, by means of which it was possible to measure the change in potential over time intervals down to $5.4 \cdot 10^{-6}$ sec. The error in

Figure 1-3

Figure 1: Figure 1-3

determining capacitance under different gain and sweep-rate conditions was 5-7% for the loop oscillograph and 3-4% for the electronic oscillograph.

During prolonged cathodic polarization in alkalis of iron, and also nickel, electrodes, an increase in the overvoltage η_0 with time is observed at high current densities; this, in ([1,2]), was associated with an increase in the adsorption of hydrogen on the electrode and the formation of surface hydrides. In ([3]), the increase in overvoltage on an iron electrode is explained by changes in the surface and by the penetration of hydrogen into the metal. In ([4]), the authors consider that the increase in overvoltage on iron and nickel is connected to a considerable extent with impurities leached from the glass of the cell, since in a polystyrene cell the increase in overvoltage was markedly reduced. Substances that poison metallic electrodes and increase the overvoltage may also increase the penetration and diffusion of hydrogen into the metal ([5,6]).

We carried out experiments recording the potential-decay curves of an iron electrode in 1 N KOH and 1 N LiOH, and also of an iron electrode poisoned with mercury in the same solutions and in 1 N H_2SO_4. The experiments were conducted in an atmosphere of hydrogen in a polystyrene cell.

The iron from Hilger used in our experiments (plates with a visible surface area of 0.2-0.5 cm^2) was reduced in a stream of hydrogen.

at 800-900°. Figure 1 shows the dependence of the capacitance of an iron electrode, calculated from equation (1), on the overvoltage in 1 N KOH. As the initial overvoltage η_0 is decreased, the capacitance calculated from the initial portions of the decay curves increases; however, after $\eta_0 = 0.4$ V is reached it decreases again; in this case a maximum is observed in the potential on the curve.

The capacitance values calculated from individual portions of the decay curve, as a rule, increase with the time elapsed after interruption of the current and pass through a maximum, but at a somewhat lower overvoltage (Fig. 1b). The large magnitude of the capacitance compared with the double-layer capacitance, as well as the increase in capacitance with the time elapsed after interruption of the current,

Fig. 1. Dependence of the capacitance of an iron electrode in 1 N KOH on overvoltage η:
a—capacitance calculated from the initial part of the decay curves (different symbols refer to different experiments);
b—capacitance calculated from individual portions of the decay curve after polarization at a current density of 10^{-2} A/cm^2.

Fig. 2. Stationary polarization curves of an iron electrode poisoned with mer-

cury in 1 N KOH over the course of:
a—30 sec, —3 min, —10 min, —poisoning for 10 min, the curve recorded immediately after switching on the current.

Fig. 3. Dependence of the potential decay $\Delta\eta_t$ on time at a current density $i_0 = 10^{-2}$ A/cm^2 for an iron electrode:
a—poisoned with mercury for 10 min, —for an unpoisoned electrode in 1 N KOH.

indicates a considerable filling of the surface with adsorbed hydrogen; the degree of coverage reaches 15-20% (^{4}). The decrease in capacitance at $\eta_0 = 0.4$-0.35 V is probably associated with the fact that at these potentials the amount of adsorbed hydrogen on the surface decreases, and consequently so does the rate of its ionization.

For experiments with an iron electrode poisoned with mercury, galvanic coating of the electrode with mercury was carried out in a separate cell by cathodic polarization in a saturated solution of HgO in 1 N KOH with a current of 10^{-3} A/cm^2. The degree of poisoning was determined by the duration of cathodic polarization. Figure 2 presents polarization curves obtained at different degrees of poisoning of the iron electrode with mercury. At considerable poisoning the polarization curves consist of two parts. At high current densities $2 \cdot 10^{-2}$-$5 \cdot 10^{-3}$ A/cm^2, the coefficient $b = 0.12$-0.13; at lower current densities $5 \cdot 10^{-3}$-$6.3 \cdot 10^{-4}$ A/cm^2, the coefficient b varies within the limits 0.23-0.26. Similar polarization curves were obtained in (^{7}). On the potential-decay curves, at high degrees of poisoning and $i_0 = 2 \cdot 10^{-2}$-$1 \cdot 10^{-2}$ A/cm^2, plateaus are observed. After interruption of the current, the electrode potential at first decreases by only 50-70 mV and for a certain time (of the order of 0.1-1.0 sec) changes almost not at all, and then again decreases slowly (Fig. 3). When η_0 is decreased, this plateau disappears, and the capacitance values are 100-150 μF/cm^2.

With a further decrease of i_0 to values of $2.5 \cdot 10^{-3}$—$6.3 \cdot 10^{-4}$ A/cm^2, the capacitance of the electrode decreases to 25-35 μF/cm^2, i.e., to values close to the capacitance of the double layer. With weak(8) amalgamation for 30 sec, the capacitance at all current densities does not exceed 35 μF/cm^2.

In experiments on the study of the diffusion of atomic hydrogen through an iron plate it was found that the overvoltage of an electrode amalgamated with mercury decreases when hydrogen diffuses through it (8). As was shown in the work of A. N. Frumkin (9), this is possible at low surface coverage by atomic hydrogen as a result of an increase in the rate of electrochemical desorption. The value of the capacitance found by us also indicates an insignificant coverage of the surface of the iron electrode, amalgamated with mercury, by adsorbed hydrogen.

The plateaus on the decay curves indicate the presence of an anodic process occurring when the current is interrupted, which slows the fall of the potential. The amount of substance ionized at the plateau potential can be approximately calculated from the equation

$$n = \frac{i\Delta t}{q}, \tag{2}$$

where n is the number of ionizing atoms, i is the current corresponding to the plateau potential on the polarization curve, Δt is the duration of the delay, and q is the charge of the electron.

The value of n, obtained from the decay curves with a plateau, was $3–6 \cdot 10^{16}$. It is easy to see that plateaus and elevated capacitance values are observed only after the region of the polarization curve has been reached with coefficient $b = 0.12–0.13$ and values $\eta_0 = 1.0–1.1$ V. It may be assumed that at high overvoltages potassium amalgam is formed on the electrode surface in 1 N KOH. When the current is interrupted it decomposes and the electrode retains a potential close to the potential of the decomposing amalgam. Ionization of potassium dissolved in mercury is an anodic process, as a result of which a plateau is formed on the decay curve.

The value $\eta_0 = 1.1–1.2$ V is apparently sufficient for formation of the amalgam, since it corresponds to -2.19 V on the normal hydrogen scale, while the half-wave potential of the potassium ion is -2.17 V on the normal hydrogen scale.

The polarization curves presented in Fig. 2 *a*–*v* were obtained after prolonged polarization. Immediately after switching on the current, the polarization curve, even in the case of the greatest amalgamation, passes considerably below the stationary values (Fig. 2 *g*). During 1.5-2 h, η_0 rises and the polarization curve assumes the form shown in Fig. 2 *v*. Since, when the decay curves are recorded, plateaus are obtained only upon reaching $\eta_0 = 1.1$ V, in the case of electrode states corresponding to Fig. 2 *g*, in which this value of η_0 is not reached, the capacitance after current interruption for all initial current densities is the same as with weak amalgamation, i.e., 25-35 μF/cm^2.

Measurements of the capacitance of an iron electrode in 1 N LiOH, carried out from the initial portions of the decay curves, gave values close to those obtained for 1 N KOH, namely, they were 150-200 μF/cm^2, with the capacitance increasing with the time elapsed after interruption of the current. However, in 1 N LiOH, even in the case of an electrode amalgamated with mercury to the greatest extent, no plateaus or increased capacitance values compared with the double-layer capacitance were found on the decay curve. The capacitance of the electrode varied within the limits 15-25 μF/cm^2. The absence of a plateau on the decay curve in lithium alkali can be explained by the fact that at the overvoltages attained in the experiment no lithium amalgam is formed, since the half-wave potential of the lithium ion is -2.34 V on the normal hydrogen scale.

We also carried out measurements of the capacitance of an iron electrode amalgamated with mercury in 1 N H_2SO_4 using an electronic oscillograph—

It turned out that, for any degree of etching and for values of i_0 from $8 \cdot 10^{-2}$

to $6.3 \cdot 10^{-4}$ A/cm^2, the capacitance of the electrode was 17-20 μF/cm^2. Thus, plateaus on the potential-decay curves are obtained only in the presence of alkali-metal ions, which under the given conditions can form an amalgam; in all other cases the capacitance of the iron electrode etched with mercury is close to the capacitance of the double layer.

In conclusion, we express our sincere gratitude to Academician A. N. Frumkin for the attention and advice given during the execution and discussion of this work.

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Note: Figure translations are in progress. See original paper for figures.