A STUDY OF THE MECHANISM OF OPERATION OF A SUSPENSION ELECTRODE WITH THE REACTION OF IONIZATION OF HYDROGEN ON PLATINUM BLACK AS AN EXAMPLE

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The electrochemical process, occurring at a suspension electrode, consists of at least three stages: I) transfer of particles into the space occupied by the suspension electrode; II) charging of the particles at the current carrier; III) shift of potential of the particles in the direction of its equilibrium (or stationary) value at the time between two successive contacts of the particles with the current carrier [1]. In the case of dilute suspensions, the particles of which are completely entrained in the flow of electrolyte, we can assume that stage I is not limiting. With high enough rates for the electrochemical reactions we can also realize conditions when stage III is not limiting. Thus, the greatest interest arises from the study of the conditions governing stage II.

Linear polarization curves were observed [2] for the ionization of hydrogen on suspensions of Pt, Pd, and Ni; this could be explained by the determining influence of the ohmic resistance (R_k) between the current carrier and the contacting particles. It was shown experimentally that, at the moment of contact, less than 2% of the total charge on a particle was transferred, determined mainly by the quantity of adsorbed hydrogen, and that, during the time of contact, the particles were unable to acquire the potential of the current carrier. However, in a study [3] of the evolution of hydrogen at suspensions of Ni, Pt, and Pd, the authors concluded that, during the time of contact, a particle did acquire the potential of the current carrier. An equation was derived [4], on the basis of these conclusions, according to which the current, recorded with a suspension electrode, was proportional to the capacity of the double layer of the particle and did not depend on R_k. Thus, it was assumed that the electrochemical reaction, with participation of adsorbed hydrogen, could be neglected during the contact time. However, for Pt and Pd electrodes, on which the volume of adsorbed hydrogen was large, this assumption did not correspond to reality. The object of our work was to study the effect of H_{ads} on the process of charging of particles by contact with the current carrier.

As the topic for investigation we chose the reaction of ionization of H_2 on Pt black in 1 N H_2SO_4, since for this system there were sufficient data on the adsorption of hydrogen, the kinetics of charge (the ionization of hydrogen), and the structure of the electrical double layer.

The working compartment of the measuring cell consisted of a glass cylinder, ~22 mm in diameter, in which there were two electrodes, located at the same distance from the bottom of the cell. One of these was a platinum wire, 0.7 mm in diameter and ~10 mm long, which served as a current carrier. The other was a platinum plate, 0.5 cm × 0.5 cm, which was used to measure the potential of the suspension particles (φ_c) in the space occupied by the suspension electrode. The suspension was mixed up by a magnetic stirrer. It was found, in agreement with [2], that the current reached a limiting value with increasing intensity of stirring. All the data below were obtained under conditions such that the current was independent of the stirring intensity. The volume of electrolyte in the cell was 20 ml and the concentration of platinum black was 15.5 to 20 g/liter. The Pt black was produced by reduction of $PtCl_6^{2-}$ with formaldehyde in an alkaline medium, by the method of Zelinskii [5]. Using the system as described, we measured charging curves for Pt black, which were found to agree completely with those given in the literature. Polarization

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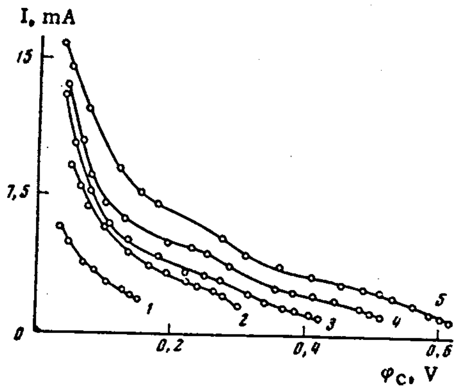

Fig. 1

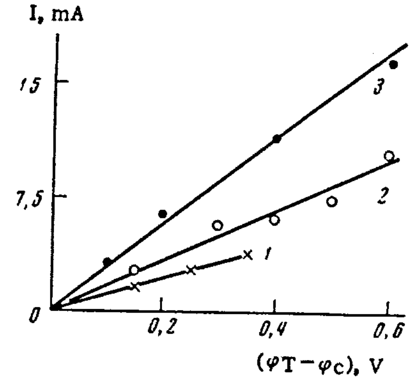

Fig. 2

Fig. 1. Relationships between the current at a Pt-black suspension and the potential of the suspension, for the following potentials of the current carrier: 1) 0.25; 2) 0.4; 3) 0.5; 4) 0.6; 5) 0.7 V. The Pt-black sample was 0.31 g.

Fig. 2. Relationship between current and potential difference between current carrier and suspension, for the following values of φ_c: 1) 0.35; 2) 0.1; 3) 0 V (in hydrogen atmosphere).

curves were recorded under potentiostatic conditions; the potential of the current carrier (φ_T) was maintained constant by means of a P-5827 potentiostat. Measurements were carried out in a hydrogen atmosphere, and after removal of dissolved hydrogen from the cell by inert gas. All the potentials are quoted as relative to a reversible hydrogen electrode in the same solution. The experiments were performed at 20 ± 2°C.

The curves shown in Fig. 1 relate the current at the current carrier (I) to the potential of the Pt black. They were obtained as follows: the suspension was saturated with hydrogen, then the dissolved H_2 was removed from the cell by a stream of nitrogen, a predetermined potential was applied to the current carrier, and finally the relationships of I and φ_c with time (t) were determined. From sections through the family of curves (Fig. 1) by normals to the potential axis, for various values of φ_c, we obtained relationships between I and $(\varphi_T-\varphi_c)$. Figure 2 shows two such relationships, for $\varphi_c = 0.35$ V and 0.1 V, and also the polarization curve for the ionization of hydrogen at a suspension electrode in an H_2 atmosphere, i.e., at $\varphi_c = 0$ V. It is evident from Fig. 2 that all these relationships were practically linear, and passed through the origin, but their slopes increased as φ_c shifted in the cathodic direction. Figure 3, curve 1, shows the relationship between the slopes of these lines and φ_c.

In order to elucidate the factors determining the course of curve 1 in Fig. 3, we may write the stationary current at the current carrier I in the form

$$I=\nu\Delta Q, \tag{1}$$

where $\nu = \nu_0 s$, ν_0 is the frequency of impingement of particles per unit area of current carrier, s is the area of the current carrier, and ΔQ is the charge transferred by a single particle which is related to the mean current $\bar{I}$, passing between the particles and the current carrier during the time of contact τ, by the equation

$$\Delta Q=\bar{I}\tau. \tag{2}$$

In turn,

$$\bar{I}=\frac{1}{\tau}\int_0^{\tau} I(t)\,dt, \tag{3}$$

where I(t) is the instantaneous current between the particles and the current carrier. The value of I(t) is related to φ_T, by the potential of the particle making contact with the current carrier φ_t, and by the resistance between the particles and the current carrier R_k, in accordance with Ohm's law:

$$I(t)=\frac{\varphi_{\text{т}}-\varphi(t)}{R_{\text{к}}}. \tag{4}$$

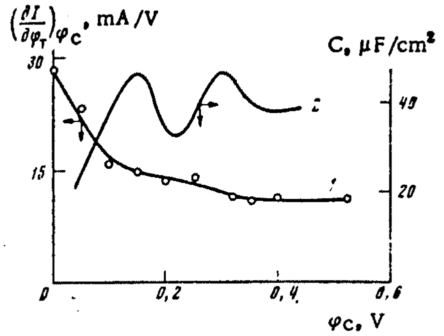

Fig. 3. 1) Dependence of the slope of the curves of Fig. 2 on φ_C. 2) Dependence of the capacity of the electric double layer of a smooth Pt electrode on potential, in a solution of 0.05 N H_2SO_4 + 1 N Na_2SO_4, according to data of [6].

The potential of a particle changes with the time of contact, in accordance with the equation

$$C\frac{d\varphi(t)}{dt}=I(t)-I_e, \tag{5}$$

where C is the double-layer capacity of the particle, I_e is the current of the electrochemical reaction at the particle surface resulting from the deviation of the particle potential from the equilibrium value. If this deviation is small, and the time τ is such ($\tau \simeq 10^{-4}$ sec according to the data of [2]) that the concentrations of the oxidized and reduced forms of the electrochemically-active substance on the (y) surface alter very slightly with the contact time, then:

$$I_e \approx \frac{nF[\varphi(t)-\varphi_c]I_0}{RT} = \frac{\varphi(t)-\varphi_c}{R_e}, \tag{6}$$

where $R_e = (RT)/nFI_0)$, and I_0 is the exchange current of the electrochemical reaction. From (1) to (6) we obtain

$$I=\tau\nu(\varphi_\tau-\varphi_c)\frac{R_e}{R_e+R_k}\left\{\frac{1}{R_e}+\frac{C}{\tau}\frac{R_e}{R_e+R_k}\left[1-\exp\left(-\frac{R_e+R_k}{R_eR_k}\frac{\tau}{C}\right)\right]\right\}. \tag{7}$$

In the case of real (polydisperse) suspensions we put in mean values of the parameters in equations (1) to (7). Let us consider some limiting cases following from Eq. (7).

If $R_k >> R_e$, we obtain from (7):

$$I \approx \frac{\tau\nu(\varphi_\tau-\varphi_c)}{R_k} \tag{8}$$

According to (8), the polarization curve for a suspension electrode should be linear. However, in order to explain the relation between its slope and φ_C, it is necessary to suppose that τ and/or R_k depends on φ_C. There are no direct data available on τ and R_k, but, on the basis of the results obtained in [6], we may assume that τ and R_k change little as φ_C ranges from 0 to 0.5 V.

For the other limiting case, $R_e >> R_k$, we have:

$$I \approx \tau\nu(\varphi_\tau-\varphi_c)\left\{\frac{1}{R_e}+\frac{C}{\tau}\left[1-\exp\left(-\frac{\tau}{R_kC}\right)\right]\right\}. \tag{9}$$

If $\tau/R_kC << 1$, Eq. (9) transforms to Eq. (8), and, if

$$\frac{\tau}{R_kC} \gg 1$$

then:

$$I \approx \tau\nu(\varphi_\tau-\varphi_c)\left(\frac{1}{R_e}+\frac{C}{\tau}\right). \tag{10}$$

If now $1/R_e << C/\tau$, then Eq. (10) transforms into the previously given relationship [4]:

$$I \approx \nu C(\varphi_\tau-\varphi_c) \tag{11}$$

Curve 2 of Fig. 3 shows the relationship between the capacity of the double layer and the potential, measured on smooth Pt, at an alternating-current frequency of 100 kHz, in a solution of 0.05 N H_2SO_4 + 1 N Na_2SO_4 [7]. A similar course for the C, φ curve would be expected in 1 N H_2SO_4. It is clear, from a comparison of curves 1 and 2 of Fig. 3, that Eq. (3) cannot be used to represent the experimental data, if the true capacity [7] of the electrical double layer (i.e., the capacity at constant coverage of the surface Pt H_{ads}*) is used for C. On the other hand, Eq. (10) gives a qualitative explanation of the course of curve 1

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*Instead of the true capacity, it is evidently correct to use in Eq. (11) values of the capacity obtained by a successive scheme of replacement, at alternating-current frequencies which correspond with the time of contact of the particle with the current carrier τ.

of Fig. 3. But, with φ_C close to 0 V, the assumed relation $R_e >> R_k$ is not confirmed by estimation of the value of R_k on the basis of Eq. (7).

In fact, from Eq. (7) and assuming that $\tau/R_kC >> 1$, it follows that

$$\left(\frac{\partial I}{\partial \varphi_T}\right)_{\varphi_0} = \tau\nu \frac{R_e}{R_e+R_k} \quad \frac{1}{R_e} + \frac{C}{\tau}\frac{R_e}{R_e+R_k}\Big). \tag{12}$$

If $\varphi_C > 0.3$ V ($R_e \rightarrow \infty$), we obtain from Eq. (10):

$$\left(\frac{\partial I}{\partial \varphi_T}\right)_{\varphi_c > 0.V} = \nu C. \tag{13}$$

Using Eqs. (12) and (13), and also the experimentally determined ratios of the slopes of the polarization curves at $\varphi_C = 0$ and $\varphi_C > 0.3$ V, we have

$$\left(\frac{\partial I}{\partial \varphi_T}\right)_{\varphi_c = 0} \Big/ \left(\frac{\partial I}{\partial \varphi_T}\right)_{\varphi_c > 0.V} = \frac{\tau}{C}\frac{R_e}{R_e+R_k}\left(\frac{1}{R_e} + \frac{C}{\tau}\frac{R_e}{R_e+R_k}\right) = 2.6. \tag{14}$$

We assume that $I_0 = 10^{-1}$ A/cm$^2 \cdot s_0$ (s_0 is the surface area of a particle) at $\varphi_C = 0$ V ($R_e = 0.25$ ohm $\cdot$ cm$^2/s_0$), $C = 50$ μF/cm$^2 \cdot s_0$, and $\tau = 10^{-4}$ sec.

From Eq. (14) we obtain $R_e/R_k \approx 2$, i.e., R_k is comparable with R_e.*

Equation (7), as given above, may be considered as a first coarse approximation, since the assumptions as to the small deviation of the particle potential from φ_C, and as to constancy of coverage of the H_{ads} surface at the moment of contact, are strictly correct only for small values of $(\varphi_T - \varphi_C)$. However, as can be seen from Fig. 2, there is no basis for assuming an interruption of the linear coarse of the polarization curves as $(\varphi_T - \varphi_C) \rightarrow 0$. However, the use of Eqs. (12) to (14), to explain the course of curve 1 of Fig. 3, is fully satisfactory.

It follows from the above that, in the case of the reaction of ionization of H_2 on a suspension of Pt black in 1 N H_2SO_4, it is necessary to take account of part of the H_{ads} at the time of contact of the particles with the current carrier.

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*In principle, on the basis of the obtained approximate value of R_k and Eq. (8) of [8], it should be possible to estimate the thickness of the electrolyte film between the particles and the current carrier, but such an estimate requires a knowledge of the value of s_0.