EFFECT OF THE SUSPENSION'S AGGREGATIONAL STABILITY ON THE CHARGE TRANSFER RATE FROM THE CURRENT COLLECTOR OF A SUSPENSION ELECTRODE TO THE SUSPENSION PARTICLES

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It had been found in [1] when examining hydrogen ionization on a suspension of Pt black in 1 N H_2SO_4 that with increasing exchange current (I_0) of the H_{ads} there is an increase in the rate of charge transfer from the current collector of the suspension electrode (SE) to the suspension particles (step I)*. According to theoretical work [2, 3], particle size can also have an effect on the rate of step I. It is difficult in the case of platinum black to study the influence of this parameter on the performance of the SE, owing to the aggregational instability of the suspension [4]. A decrease in particle size can be attained by stabilizing the suspension with surface active materials, among them thiourea [5]. The aggregational stability of Pt [4] and Pd [6] black suspensions is also raised upon oxygen chemisorption. In the present work we studied the effect of thiourea on the H_2 ionization rate on Pt black suspension and on the O_2 ionization rate of Pt and Pd black suspensions.

The experimental conditions were such that the rates of the processes studied were determined by the rates of step I. The blacks were obtained by reducing H_2PtCl_6 or $PdCl_2$ with formaldehyde in alkaline medium. The curves reported in Figs. 1 and 2 were measured under conditions of potentiostatic polarization of the current collector. The design of the cell holding 20 cm^3 of electrolyte and having a current collector of 0.2 cm^2 surface area is described in [1]. All values of potential are reported relative to a reversible hydrogen electrode in the same solution. Base electrolyte was 1 N H_2SO_4. The experiments were done at 20 ± 2°C.

Figure 1 shows the $I-\varphi_c$ relations (I is the current at the current collector, φ_c is the potential of the current collector) for H_2 ionization on Pt black suspension at a potential $\varphi_s = 0$ V of the suspension particles in solutions of different composition. One can see by comparing curves 1 and 2 that in the presence of thiourea the rate of step I is reduced by about two orders of magnitude.

According to the equations reported in [1], the rate of step I should decrease with decreasing I_0 and decreasing electric double-layer capacity (C) of the suspension particles. It was found in [1] that the rate of step I decreases by only a factor of 2.5 to 3 when I_0 is reduced from the value typical for Pt black at $\varphi_s = 0$ V in 1 N H_2SO_4 to a value of zero. It is also difficult to visualize that thiourea adsorption should lead to a more than 30-fold decrease in C. Hence the decrease in the rate of step I which is seen here is chiefly due to the increase in the aggregational stability of the Pt black suspension.

This last statement is supported by the results obtained when studying H_2 ionization on Pt black suspension in the presence of methanol and I^- ions (Fig. 1, curves 3 and 4, respectively). Methanol adsorption on the smooth Pt electrode substantially reduces the value of I_0 and has little effect on the value of C near the reversible hydrogen potential [7], while I^- ion adsorption causes a decrease in both I_0 and C [8]. Likewise, the adsorption of methanol and of I^- ions causes no marked change in the aggregational stability of Pt black suspension [5]. It can be seen by comparing curves 3 and 4 with curve 1 that after the adsorption of methanol or I^- ions, the rate of step I decreases by no more than a factor of 1.5 to 2.

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*An approximate estimate of the resistance (R_c) between the current collector and the suspension particles in contact with it was reported in [1]. A printing error has occurred there, and instead of $R_e/R_c \approx 2$ (where $R_e = RT/nFI_0$) one should read: $R_c/R_e \approx 2$. This error does not reflect on the correctness of the conclusions drawn in [1].

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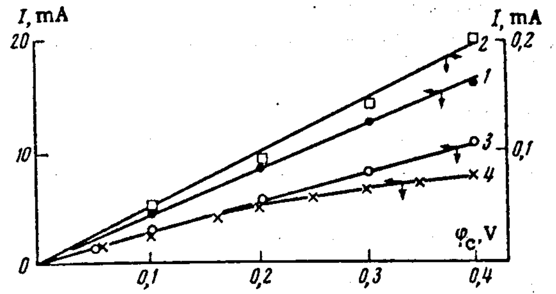

Fig. 1

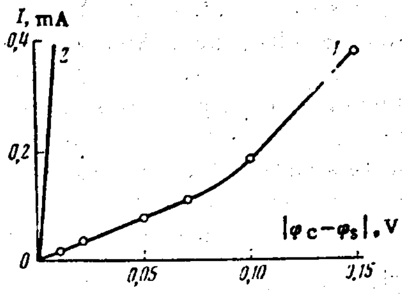

Fig. 2

Fig. 1. Polarization curves of H_2 ionization on Pt black suspension in the solutions: 1) 1 N H_2SO_4; 2) 0.02 M $(NH_2)_2CS + 1$ N H_2SO_4; 3) 1 M $CH_3OH + 1$ N H_2SO_4; and 4) 0.01 N $KI + 1$ N H_2SO_4. 1, 3, and 4) 0.3 g black, 2) 0.4 g black.

Fig. 2. Polarization curves of O_2 (1) and H_2 (2) ionization on a suspension of 0.4 g Pt black in 1 N H_2SO_4.

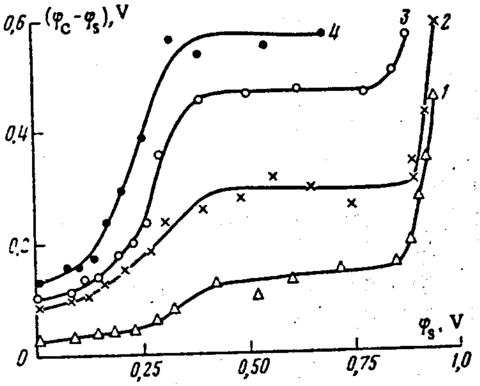

Fig. 3. Curves of $(\varphi_c - \varphi_s)$ vs φ_s on a suspension of 0.4 g Pt black in 1 N H_2SO_4 at currents of 2 (1), 4 (2), 5 (3), and 6.5 (4) mA.

The cathodic polarization curve of Pt black in O_2 atmosphere ($\varphi_s = 1.04$-1.06 V) is reported in Fig. 2 (curve 1). Over the range $\varphi_c = 1.02$ to 0.9 V, the current proved to be significantly smaller than that of H_2 ionization (curve 2). At $\varphi_c < 0.9$ V the current becomes nonstationary, and goes through a maximum a few minutes after the start of polarization, which is due to the intense adhesion of the black to the current collector. Such SE behavior is readily explained on the assumption that the increase in aggregational stability of Pt black suspension after oxygen chemisorption (i.e., at $\varphi_s > 0.8$ V) is due to formation of a stable electrolyte film at the Pt surface [4]. In this case the adhesion of the particles at $\varphi_c < 0.9$ V and $\varphi_s > 0.9$ V is due to the small size of the agglomerations in the suspension and to a decrease in the stability of the electrolyte film at the Pt surface of the current collector. Adhesion does not occur at φ_c and φ_s less than 0.8 V, because of the relatively coarse agglomerations of the Pt black suspension, while at $\varphi_c > 0.9$ V the adhesion is hindered by the stable electrolyte film at the Pt surface of the current collector.

The low values of current in the range $\varphi_c = 1.02$ to 0.9 V indicate that the charge transfer rate from the current collector to particles of the Pt black suspension which are covered by chemisorbed oxygen is relatively low. The palladium SE behaves similarly in the O_2 ionization reaction.

The effect exerted on the rate of step I by oxygen chemisorbed on Pt black can be demonstrated more clearly with the following results. In inert-gas atmosphere the current collector was polarized galvanostatically while the time dependence of φ_s and φ_c was recorded. The $(\varphi_c - \varphi_s)$–φ_s curves thus obtained for different values of I (but constant in each case) are reported in Fig. 3. To a first approximation the quantity $I/(\varphi_c - \varphi_s)$ is analogous to the slope of polarization curves measured with potentiostatic polarization, i.e., larger values of the rate of step I correspond to large $I/(\varphi_c - \varphi_s)$ values. In accordance with [1], the $(\varphi_c - \varphi_s)$ values increase with φ_s between 0 and 0.35 V, remain constant at $0.35\ V < \varphi_s < 0.8$ V, and rise sharply at $\varphi_s > 0.8$ V. It is clear from the shape of the curves of Fig. 3 that the decrease in the rate of step I at $\varphi_s > 0.8$ V is due to increasing aggregational stability of the Pt black suspension, since the value of C does not decrease as one goes from the "double-layer" ($\varphi_s = 0.3$ to 0.8 V) to the "oxygen" ($\varphi_s > 0.8$ V) region of potentials [9].

The decrease in the rate of step I which occurs with increasing aggregational stability of the Pt and Pd black suspensions can be caused both by increasing thickness of the electrolyte film between the particles and the current collector (increasing R_c, change in the time τ of contact of the particles with the current collector) and by decreasing particle size (increasing R_c, change in τ and in the collision frequency of the particles with the current collector). For a separate examination of the effect of these two factors it probably would be useful to study the SE performance with powder obtained by mechanical comminution of metallic Pt. It could be expected that because of the considerable weight the powder particles will not form larger agglomerations, and the suspension will consist of particles of constant, known size.

The powder was divided into fractions with particle sizes from 1 to 0.05 mm. A layer of Pt black was deposited onto the surface of the particles in order to increase the electric capacitance. However, even at a powder concentration of 120 g/liter (the usual Pt black concentration in our experiments was 10-20 g/liter), the H_2 ionization current in the presence of powder was only insignificantly higher than that in the absence of powder. The low efficiency of such an SE which made reliable experiments impossible probably is due to the low electrical capacitance of the particles and the small value of τ during collision of the heavy particles with the current collector.

An analysis of the relationships reported in [2, 3] showed that from these papers it is also impossible to obtain separate estimates for the effects of particle size and electrolyte film thickness on the rate of step I. But it can be asserted that there is no purpose in using an SE with Pt or Pd black in the presence of substances leading to higher aggregational stability of suspensions of these blacks, since the current which is transferred by the particles under these conditions is very low.

It was of interest to examine the performance of an SE using supported catalysts. It was found that in the presence of suspensions of 5% $Pt-SiO_2$, 5% $Pt-SiO_2-Al_2O_3$, and 10% $Pd-BaSO_4$, the H_2 ionization currents were significantly lower than those in the absence of suspensions. It seems that such a result can be explained by the catalysts (Pt, Pd) occupying only an insignificant part of the carrier surface, i.e., the segments occupied by Pt or Pd are separated from each other by nonconducting segments of carrier surface. Therefore, only a small part of the supported catalyst is operative during collisions with the current collector. In addition the light particles of the suspensions strongly adhere to the current collector, forming a poorly conducting layer. It follows from the above that such catalysts supported by a nonconducting base cannot be used in suspension electrodes.

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