CATHODIC REDUCTION OF PLATINUM DIOXIDE

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In the literature there are several investigations devoted to the study of the electroreduction of oxygen adsorbed on the surfaces of the platinum metals. However, we could find no work on the cathodic reduction of the oxides of platinum metals obtained by a chemical method. Only in [1] was there some information on the reduction of platinum dioxide by gaseous hydrogen in aqueous solutions. Meanwhile, at the present time, some data are being given [2] which indicate the higher activity of catalysts prepared by the reduction of platinum dioxide in electrochemical reactions in comparison with platinized electrodes and electrodes of platinum black.

We attempted to study the cathodic reduction of platinum dioxide and the properties of the platinum catalyst formed during this. The platinum catalyst prepared from platinum dioxide is called in the literature platinum Adams (Pt-Adams). The platinum dioxide was prepared by the method [3] of oxidation of H_2PtCl_6 by sodium nitrate at a temperature of about 550°C and it was placed in a cell enveloped in a pure platinum grid. The potentials φ_r are given relative to the reversible hydrogen electrode in the same solution at the experimental temperature. During immersion of the platinum dioxide washed with concentrated H_2SO_4 and bidistillate in air, into a solution of 1 N H_2SO_4 at 20°C, there was observed the establishment of a potential of about 900 mV, and at 95°C of about 850 mV. In 1 N NaOH, the initial φ_r at 20° is about 900 mV and at 95°C about 650 mV. The cathodic reduction of PtO_2 was carried out by the galvanostatic method. The current density was calculated for the same gravimetric quantity of PtO_2.

The reduction of PtO_2 is characterized by a high overpotential, particularly in alkaline solution (Fig. 1). At high current densities there are observed minima on the galvanostatic curves, as also in the case of the formation on the surface of the electrode of phase oxide layers [4]. From the shape of the galvanostatic curve, measured at a lower current density at 95°C, it may be concluded that the reduction of PtO_2 takes place at two stages which, on the reduction curve, correspond to two plateaus of approximately equal magnitude (curve 6 of Fig. 1). The latter result obviously indicates that the intermediate reduction product is platinum oxide. During measurements with low current densities, on the surface of the platinum dioxide it is possible to detect a small quantity of adsorbed oxygen as can be seen from curve 1 of Fig. 1 (initial part of the reduction curve of PtO_2).

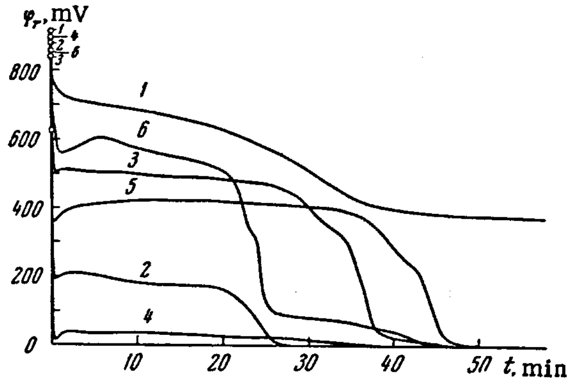

Fig. 1. Cathodic galvanostatic reduction of PtO_2. 1,2,4) 20°C; 3, 5, 6) 95°C; in 1 N H_2SO_4: 1) 27; 2) 380; 3) 295; 6) 65 mA/g; and in 1 N NaOH: 4) 350; 5) 350 mA/g.

As calculation shows, of the platinum reduced at 95°C, only about 10% forms the surface of the metallic phase and is accessible for adsorption of hydrogen. At room temperature, on the reduction curve for PtO_2, only the first plateau can be observed corresponding obviously to the reduction of PtO_2 to PtO. However, at potentials close to the hydrogen zero, it is probable that the reduction of PtO to Pt takes place on the surface of the catalyst by adsorbed hydrogen. This is indicated by the considerable displacement of potential in an anodic direction after switching off the cathodic polarization.* The shape of the adsorption isotherms for hydrogen on the catalyst samples reduced at room temperature is characteristic for platinum but on it there are no sharply expressed transitions between the regions of strongly and weakly bonded hydrogen as in the case of the reduction

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*From the obtained data it follows that the complete reduction of the oxides of platinum with φ_r in the hydrogen region requires considerable intervals of time.

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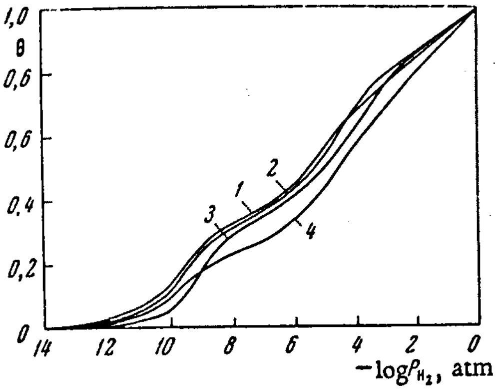

Fig. 2. Adsorption isotherms for hydrogen on Pt/Pt on Adams platinum in 1 N H_2SO_4. 1) Freshly prepared Pt/Pt electrode; 2) platinum–Adams, heated with φ_r 500 mV to 95°C; 3) platinum–Adams, heated with φ_r 500 mV to 200°C in 15 N H_3PO_4; 4) Pt/Pt electrode heated with φ_r 500 mV to 95°C.

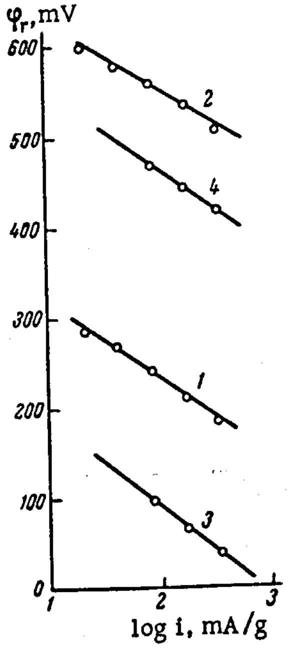

Fig. 3. Polarization curves for the reduction of PtO_2 in 1 N H_2SO_4 at 20 (1) and 95°C (2) and in 1 N NaOH at 20° (3) and 95°C (4).

of PtO_2 at 95°C. Evidently with increase in temperature there is a change in crystal structure of the catalyst. The adsorption isotherms for hydrogen on Pt-Adams, as can be judged from Fig. 2 (curves 1, 2), are similar to the adsorption isotherms for hydrogen on a Pt/Pt electrode.

From a comparison of the data for the cathodic reduction of the surface oxides of platinum [5] and platinum dioxide it follows that, in the second case, the overpotential for the process is considerably higher. Only Obrucheva [4], during strong anodic polarization of smooth platinum, was successful in obtaining on its surface formations which, to some degree, behave similarly to the phase oxides of platinum.*

Figure 3 gives polarization curves for the reduction of PtO_2 to PtO in 1 N H_2SO_4 and 1 N NaOH at 20 and 95°C. These curves were constructed from potentials of the plateaus of the reduction of PtO at various current densities. The gradient of the curves both in the acid and in the alkaline solution at room temperature is about 120 mV. From the dependence of the overpotential on current density and temperature the value for the activation energy for the reaction was approximately determined, and in a solution of 1 N H_2SO_4 with $\varphi_r = 400$ mV it is about 25 kcal/mole. During the reduction of the surface oxides of platinum [5], there is no strong dependence on temperature. Evidently, with increase in temperature, the bond of the oxygen with the platinum is strengthened and the oxide layer becomes in its properties more close to the phase formation which, as we saw above, is reduced with great difficulty.

The problem of the mechanism of the reduction of PtO_2 is a subject for further study. From the dependence of the rate of reaction on the potential and the occurrence of the process at high temperatures in the double layer region, it may be proposed that an electrochemical mechanism of reduction of PtO_2 is occurring. In this case, there is great interest in the observed dependence of the rate of reduction on the pH of the solution: with increase in pH, the rate of the process with φ_r = const considerably decreases, whereas by an electrochemical mechanism the reverse picture will be expected. It is possible that, for an interpretation of this result, it is necessary to take into account the formation on the surface of PtO_2 of compounds of the type $Pt(OH)_4$ in aqueous solutions.

One of the interesting characteristics of Pt-Adams is its stability toward sintering at high temperatures and to poisoning during the action of contaminants from electrolyte solutions. As was shown by experiments in 15 N H_3PO_4 during heating to 200°C, the surface of the Pt–Pt electrode is decreased by more than 10 times, after which the reversibility of the charge curves is considerably worsened and their shape is distorted. In the case of Pt-Adams, with a similar operation, the surface is decreased by only about 5 times and the reversibility of the charge curves and the

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*During the treatment of platinum used in [4], its surface acquires a brown tint, i.e., change in color also indicating the formation of a phase oxide.

shape of the hydrogen adsorption isotherms (Fig. 2, curve 3) changes very little. These results enable us to give preference to electrodes made from Pt-Adams for operation at high temperatures.

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