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Abstract

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The Influence of Surface Oxides on the Process of Electroreduction of Oxygen on Platinum in Alkaline Solution

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In works ($^{1-3}$) it was shown that surface oxides of platinum exert a substantial influence on the process of oxygen reduction on platinum. To explain this influence, various theories have been proposed in the literature. Anson and King (^{4}) explain the accelerating action of surface oxides of Pt on this process by the fact that reduction of the oxides leads to weak platinization of the electrode surface.

Söjer (^{3}), on the contrary, believes that the coincidence of the potential regions for the reduction of oxygen and of the surface oxides of platinum indicates that the reduction reaction on Pt is ultimately reduced to the electrochemical reduction of these oxides, which are regenerated by the chemical reaction of oxygen dissolved in the solution with platinum.

If Söjer' s mechanism is considered correct, one might expect that surface oxides accelerate precisely the process of reduction of O_2 to hydrogen peroxide (the first stage).

In this connection, using a rotating disk electrode with a ring, we investigated the reduction of O_2 in $0.125\,N$ KOH on smooth platinum as a function of the preliminary treatment of the disk electrode. Two methods of preliminary electrode treatment were used. In the first case the electrode was activated in the usual manner—polarized 6 times alternately anodically and cathodically at potentials of +1.8 and −0.2 V, respectively* (ordinary activation). After this, the electrode was held for one minute at a potential of +1.3 V. This gives weakly oxidized platinum (an oxidized electrode). By a reduced electrode we mean an electrode that had been activated in the manner described above, but was then held for 5 minutes at a potential of −0.25 V.

The polarization curves obtained on electrodes treated by these two methods are presented in Fig. 1. Simultaneous recording of the polarization curve for O_2 reduction on the disk and determination, from the current at the ring, of the amount of hydrogen peroxide not entering into reaction on the disk makes it possible to calculate the curve that would have been observed if the process of reduction of H_2O_2 to OH^- (the second stage) were reversible (Fig. 1), and accordingly to obtain the real curve for the reduction of O_2 to H_2O_2 (Fig. 1a, b).

As can be seen from Fig. 1, the half-wave potential of the first stage of O_2 reduction for the reduced electrode is more positive than for the oxidized one, which indicates that surface oxides do not accelerate but, on the contrary, slow the rate of the first stage. From this it follows that oxides do not participate in the reaction of reduction of O_2 to H_2O_2, as Söjer assumed in his works, and that the first stage of reduction is purely electrochemical.

The coincidence of the reduction potentials of O_2 and of the surface oxides is explained by the fact that, as shown above, surface oxides of platinum hinder the first stage of reduction, and oxygen can be reduced only when the surface is already partly free of surface oxides, as was noted in the work of Filippikh (^{5}).

In an earlier published paper (^{6}) we showed that surface oxides increase the rate of the second stage of the process, although the mechanism of their action was not clarified at that time. The data obtained by us cannot be explained by the theory of Anson and King, since it cannot explain the decrease in current on the polarization curve for the reduction of O_2 (Figs. 1, 2) (^{6}), caused by reduction of the platinum surface. It is evident that the reason for the influence of surface oxides must be sought in the features of the reduction mechanism itself.

As was shown in (^{7}-^{9}), H_2O_2 reacts very rapidly with platinum oxides, even at concentrations of 10^{-4} M, reducing them.

Since this reaction enters into the scheme of catalytic decomposition of H_2O_2 on Pt according to the Haber and Grinberg mechanism (^{10}),

$$\mathrm{Pt} + \mathrm{H_2O_2} \rightarrow \mathrm{PtO} + \mathrm{H_2O} \tag{1}$$

$$\mathrm{PtO} + \mathrm{H_2O_2} \rightarrow \mathrm{Pt} + \mathrm{H_2O} + \mathrm{O_2} \tag{2}$$

$$2\mathrm{H_2O} \rightarrow 2\mathrm{H_2O} + \mathrm{O_2} \tag{3}$$

one may assume that H_2O_2 diffusing to the electrode surface partly decomposes on it, and that the reduction of H_2O_2 is reduced to the reduction of O_2 formed as a result of its catalytic decomposition.

Fig. 1. Polarization curves for the reduction of O_2 on an oxidized (1) and reduced (2) electrode. Black points are polarization curves corrected for the

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* All potentials are given relative to the reversible hydrogen electrode in the same solution.

Fig. 1

Figure 1: Fig. 1

amount of H_2O_2 evolved. a, b are the calculated polarization curves for the reduction of O_2 to H_2O_2 for the oxidized and reduced electrode, respectively.

If this mechanism of action of the oxides takes place to some extent, then, according to equation (3), oxygen should be formed on the disk and can be registered on the ring electrode.

For this purpose we investigated, using a disk electrode with a ring, the process of H_2O_2 reduction on smooth active platinum in 0.125 N KOH in a nitrogen atmosphere (Fig. 2).

To calculate the amount of O_2 formed on the disk, it was necessary to determine the difference between the values of the anodic and cathodic diffusion limiting currents measured on the ring at a given disk potential. Indeed, in the anodic process only hydrogen peroxide is recorded on the ring, whereas in the cathodic process both H_2O_2 is reduced (in the same amount as in the anodic process) and a certain amount of oxygen formed as a result of decomposition is also reduced. Taking into account that, under our conditions, only 41% of the amount of O_2 evolved on the disk is captured on the ring, the degree of catalytic decomposition of hydrogen peroxide can be determined.

Our experiments showed that at the stationary potential of the disk ($\varphi_{\mathrm{st}} = 0.94$ V) such an amount of oxygen is recorded on the ring as corresponds to complete decomposition of all hydrogen peroxide diffusing to the surface of the disk electrode. At disk potentials more negative than φ_{st}, a cathodic current arises on it, and the amount of oxygen formed—

decreases. This decrease is observed to such an extent that correction of the cathodic current on the disk by the amount of O_2 recorded at this potential again gives the limiting diffusion current for hydrogen peroxide (Fig. 2, 2). The magnitude of the current at the maximum of the cathodic curve corresponds to the limiting diffusion current, and O_2 is no longer detected on the ring. A further increase in cathodic polarization again leads to a decrease of the cathodic current below the limiting value, but in this case as well O_2 is not recorded on the ring.

As is known, the very appearance of O_2 on the disk does not yet prove the correctness of the mechanism set forth above, since, as some authors believe (11,12), the catalytic decomposition of H_2O_2 on platinum may also proceed by a purely electrochemical route.

However, Winkelmann (12) observed catalytic decomposition of H_2O_2 at such negative electrode potentials that, according to his calculations, electrochemical oxidation can no longer proceed; this contradicts the idea of catalytic decomposition of H_2O_2 on Pt as an electrochemically coupled reaction and, on the

Fig. 2. Polarization curve for the reduction of H_2O_2 in 0.125 N KOH. Black points—correction of the polarization curve for the reduction of H_2O_2 by the amount of evolved O_2

Figure 2: Fig. 2. Polarization curve for the reduction of H_2O_2 in 0.125 N KOH. Black points—correction of the polarization curve for the reduction of H_2O_2 by the amount of evolved O_2

contrary, can readily be explained on the basis of the Haber and Grinberg mechanism.

In the work of Bianchi and co-workers (7) it was shown that the catalytic decomposition of H_2O_2 on platinum is a purely chemical process with cyclic chemical oxidation and reduction of the surface of the platinum electrode by peroxide. They established that surface oxides of platinum strongly accelerate the catalytic process, which in their absence proceeds at a low rate.

Fig. 2. Polarization curve for the reduction of H_2O_2 in 0.125 N KOH. Black points—correction of the polarization curve for the reduction of H_2O_2 by the amount of evolved O_2

On the basis of the foregoing, we assume that the catalytic decomposition of hydrogen peroxide on platinum is not a chemical process with the intermediate formation of surface oxides. It follows from this that the reduction of H_2O_2 on Pt in alkaline solutions in the initial part of the curve (up to the potential of the maximum, $\varphi_{\max}$) is mainly the reduction of oxygen formed by the catalytic decomposition of H_2O_2 through platinum oxides. The rate of direct electrochemical reduction of H_2O_2 in this part of the curve is very small and plays no significant role.

The decrease of the cathodic current on the disk at $\varphi_D < \varphi_{\max}$ is explained by reduction of the Pt surface as a result of increasing cathodic polarization. At the maximum of the cathodic curve, according to the charging curves, oxides are still present on the surface, and catalytic decomposition by the mechanism set forth above proceeds at a high rate, whereas at the minimum of this curve there are no oxides, and decomposition cannot proceed. The current observed at $\varphi_{\min}$ is apparently the current of direct reduction of hydrogen peroxide. Since it is lower than the limiting diffusion current, as the surface is reduced a decrease in current should be observed as a result of the decrease in the rate of catalytic decomposition of H_2O_2. The new rise at $\varphi_D \sim +0.1$ V corresponds to the dependence of the current of direct reduction of H_2O_2 on the potential. Determination of the constant b in the Tafel equation for the polarization curve in this region gives a value of ~ 0.4 V, which indicates a high degree of irreversibility of this reaction.

In this connection it becomes clear why the shape of the cathodic curve of "reduction" of $\mathrm{H_2O_2}$ depends so strongly on the preliminary treatment of the electrode. Preliminary anodic polarization for 15 sec at a potential of +1.8

Fig. 3

Figure 3: Fig. 3

V already has a noticeable effect (Fig. 3, 3). Such anodic polarization does not yet passivate the electrode with respect to electrochemical processes (direct oxidation and reduction of H_2O_2), as is shown, for example, by the anodic curve (Fig. 3, 4), but it very strongly lowers the rate of catalytic decomposition. The decomposition current measured at φ_{st} corresponds in this case to approximately 40% of the limiting diffusion current for H_2O_2. Since the cathodic process is mainly the reduction of O_2 formed as a result of catalytic decomposition, it is clear that a decrease in the surface concentration of O_2, due to the reduction in the rate of decomposition, leads to a lowering of the overall rate of the cathodic process. The anodic process, as would be expected, is in this case, on the contrary, accelerated.

Fig. 3. Cathodic (1, 3) and anodic (2, 4) polarization curve of H_2O_2. Holding the electrode after ordinary activation for 15 sec: **1, 2**—at a potential of +0.9 V, **3, 4**—at a potential of +1.8 V

The fact that O_2 on strongly reduced electrodes in acidic solutions is reduced only to hydrogen peroxide (^{2},^{3}), whereas on oxidized electrodes it is reduced to water, shows that the above-described mechanism of the action of surface oxides may also occur in acidic solutions.

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