

# THE EFFECT OF SURFACE OXIDES ON THE ELECTROREDUCTION OF OXYGEN IN ALKALINE SOLUTION

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It has been shown in [1-3] that surface oxides have a decisive influence on the reduction of oxygen on platinum. Various theories have been advanced in the literature to account for this fact. Anson and King [4] have explained this promotion by assuming the electrode to be weakly platinized as a result of reduction of the surface oxides of Pt.

Sawyer [3], on the other hand, considers the coincidence of reduction potentials of oxygen and the platinum surface oxides as indication that the oxides undergo electrochemical reaction and are then chemically regenerated by reaction between the platinum and dissolved oxygen.

Acceptance of the Sawyer mechanism suggests that it would be the reduction of  $O_2$  to hydrogen peroxide (first step) which would be promoted by the surface oxides.

We have used a rotating disc and ring electrode to study the reduction of  $O_2$  on smooth platinum in 0.125 N KOH, and its dependence on the preliminary treatment of the electrode. Two different types of preliminary treatment were used here. The first of these involved an ordinary activation in which the electrode was carried through six cycles of alternate anodic and cathodic polarization at +1.8 and -0.2, respectively, \* and was then held for one minute at +1.3 V. This produced a weakly oxidized platinum (oxidized electrode). This same activation with the electrode held for five minutes at -0.25 V was used to prepare the so-called reduced electrode.

Polarization curves for electrodes which had undergone these two types of treatment are shown in Fig. 1. The curve which would correspond to reversible reduction of  $H_2O_2$  to  $OH^-$  (second step) was built up by combining a polarization curve for  $O_2$  reduction on the disc with a simultaneous determination of the amount of hydrogen peroxide failing to enter the disc reaction, this determination being based on the ring current (Fig. 1); from this the true curve for the reduction of  $O_2$  to  $H_2O_2$  (Fig. 1a, b) was obtained.

It is seen from Fig. 1 that the half-wave potential for the first step in the  $O_2$  reduction was more positive for the reduced than for the oxidized electrode, the indication being that surface oxides do not promote this step, but actually retard it. From this it follows that these oxides do not participate in the reduction of  $O_2$  to  $H_2O_2$ , as Sawyer assumed, the first step in the reduction being purely electrochemical.

The fact that the oxides retard the first step in the reduction so that the oxygen reduction can only occur on a surface which is already at least partially oxide-free accounts for the identity of reduction potentials of  $O_2$  and the surface oxides. This point has been brought out by Vielstich [5].

Our earlier work showed [6] that surface oxides promote the second stages of reaction, but did not lead to an understanding of mechanism of this action. The theory of Anson and King is inadequate for interpreting our data since it offers no explanation for the fall-off of the polarization curve for  $O_2$  reduction (Fig. 1, 2) [6] following reduction of the platinum surface. An understanding of the effect of the surface oxides must clearly be sought in the details of the reduction mechanism itself.

It has been shown in [7-9] that  $H_2O_2$  will rapidly reduce platinum oxides, even in  $10^{-4}$  M solution.

\*All of the cited potentials were measured with respect to a reversible hydrogen electrode immersed in the same solution.

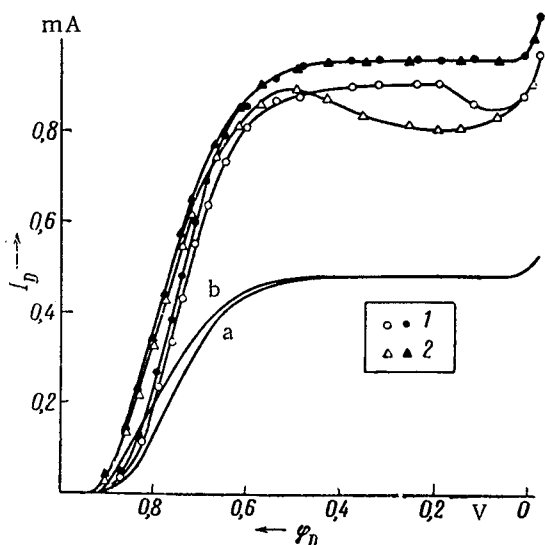


Fig. 1. Polarization curves for  $O_2$  reduction on an oxidized (1), and a reduced (2), electrode. The black points are polarization data corrected for the amount of evolved  $H_2O_2$ . a) and b) are calculated polarization curves for the reduction of  $O_2$  to  $H_2O_2$  on oxidized and reduced electrodes, respectively.

cess involves reduction of both  $H_2O_2$  (in the same amount as in the anodic process) and the oxygen resulting from peroxide decomposition. The degree of catalytic decomposition of the hydrogen peroxide could be determined from the fact that only 41% of the  $O_2$  evolved on the disc was captured by the ring under the working conditions employed here.

Our experiments showed the quantity of oxygen recorded on the ring at stationary disc potential ( $\varphi_{st} = 0.94$  V) to be that corresponding to complete breakdown of all of the hydrogen peroxide diffusing to the disc surface. A cathodic current arose at disc potentials more negative than  $\varphi_{st}$ , and the amount of oxygen produced diminished. This reduction was extensive enough so that correction of the cathodic disc current for the  $O_2$  recorded at this potential once more gave the limiting diffusional current for the hydrogen peroxide (Fig. 3, 2). The maximum on the cathodic curve corresponded to the limiting diffusional current, and  $O_2$  was no longer recorded on the ring. Further increase in the cathodic polarization again carried the cathodic current below the limiting value, but  $O_2$  was still not recorded on the ring.

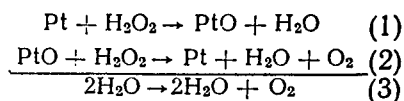
The appearance of  $O_2$  on the disc was, in itself, no proof of the validity of the proposed mechanism, since it has been pointed out by various authors [11, 12] that the decomposition of  $H_2O_2$  on platinum could be a purely electrochemical process.

Winkelmann [12] has, however, observed the catalytic decomposition of  $H_2O_2$  at high negative electrode potentials where calculation showed electrochemical oxidation to be impossible. This fact stands in contradiction to the assumption that the decomposition of  $H_2O_2$  on Pt is an electrochemical reaction, but can be readily understood in terms of the Haber-Grinberg mechanism.

Bianchi and co-workers [7] have shown the catalytic decomposition of  $H_2O_2$  on platinum to be a purely chemical process involving cyclic chemical oxidation and reduction of the electrode surface by the peroxide. These investigators proved that the catalytic reaction is strongly promoted by the platinum surface oxides, proceeding quite slowly unless these oxides are present.

We have assumed from this that the catalytic decomposition of hydrogen peroxide on platinum is a chemical process involving the formation of intermediate surface oxides. On this basis the entering segment of the curve (up to maximum potential,  $\varphi_{max}$ ) for the reduction of  $H_2O_2$  on Pt in alkaline solution is associated, essentially, with

Since these processes enter into the reaction scheme of Haber and Grinberg [10] for the catalytic decomposition of  $H_2O_2$  on Pt



the  $H_2O_2$  can be assumed to diffuse to the electrode and partially dissolve in the surface of the latter, with the result that  $H_2O_2$  reduction is actually reduction of the  $O_2$  resulting from catalytic peroxide decomposition.

Equation (3) suggests that oxygen would form on the disc and be registered as a current on the ring electrode if this mechanism is even partially correct.

To test this point, we have used the disc and ring electrode to study  $H_2O_2$  reduction on smooth active platinum in 0.125 N KOH under an atmosphere of nitrogen (Fig. 2).

Calculation of the amount of  $O_2$  formed on the disc requires a knowledge of the difference of the anodic and cathodic limiting diffusional ring currents measured at fixed disc potential. The ring actually records only hydrogen peroxide in the anodic process, but the cathodic proc-

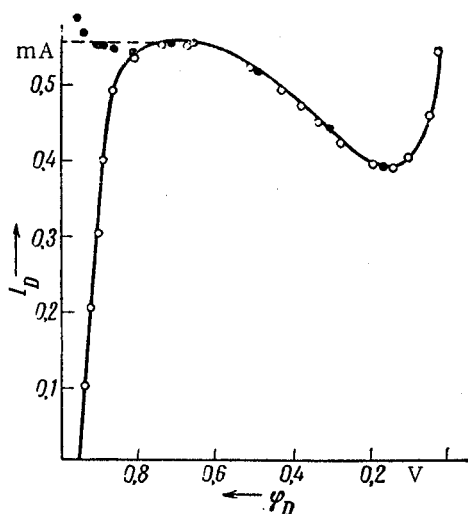


Fig. 2. Polarization curve for  $\text{H}_2\text{O}_2$  reduction in 0.125 N KOH. The black points represent values which were corrected for the evolved  $\text{O}_2$ .

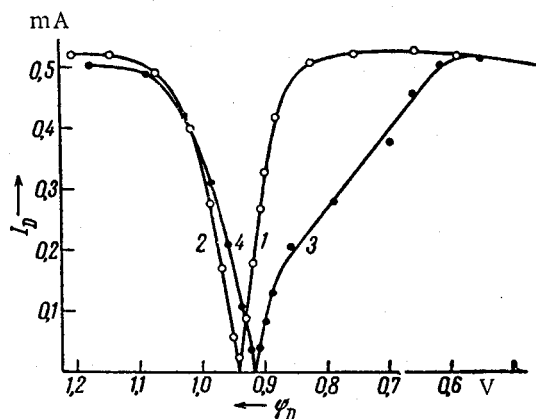


Fig. 3. Cathodic (1, 3) and anodic (2, 4) polarization curves for  $\text{H}_2\text{O}_2$ . Electrode given ordinary activation and then held for 15 sec at: 1,2) A potential of +0.9 V; 3,4) potential of +1.8 V.

the reduction of the oxygen resulting from catalytic  $\text{H}_2\text{O}_2$  breakdown by the platinum oxides. Direct electrochemical breakdown of  $\text{H}_2\text{O}_2$  proceeds very slowly over this portion of the curve, and is of minor significance.

The drop in the cathodic disc current at  $\varphi_D < \varphi_{\text{max}}$  is explained in terms of the reduction of the Pt surface resulting from increased cathodic polarization. The charging curves indicate the continued presence of surface oxides, even at the maximum on the cathodic curve, so that catalytic breakdown according to the proposed mechanism should proceed here at high velocity; these oxides are lacking at the minimum and decomposition cannot then take place. The current observed at  $\varphi_{\text{min}}$  is clearly associated with the direct hydrogen peroxide reduction. The fact that this current is lower than the limiting diffusional current is indication that surface reduction leads to a progressive reduction of the rate of catalytic decomposition of the  $\text{H}_2\text{O}_2$  with an accompanying diminution in the current. The new up-turn at  $\varphi_D \sim +0.1$  V is that corresponding to the potential - current relation for direct  $\text{H}_2\text{O}_2$  reduction. The Tafel constant  $\underline{b}$  for this portion of the polarization curve proves to be  $\sim 0.4$  V, and the reaction is therefore highly irreversible.

These facts make it understandable that the form of the cathodic curve for the  $\text{H}_2\text{O}_2$  "reduction" should depend markedly on the previous treatment of the electrode. Even a preliminary anodic polarization for 15 sec at +1.8 V (Fig. 3, 3) has a pronounced effect here. An anodic polarization of this kind does not passivate the electrode with respect to the electrochemical process (direct oxidation and reduction of  $\text{H}_2\text{O}_2$ ), as the anodic curve shows (Fig. 3, 4), but decreases the rate of catalytic breakdown markedly. In this case, the decomposition current at  $\varphi_{\text{st}}$  corresponds to about 40% of the limiting diffusional current in  $\text{H}_2\text{O}_2$ . Since the cathodic process is principally the reduction of  $\text{O}_2$  formed through catalytic decomposition, it is understandable that a drop in the surface concentration of  $\text{O}_2$  should lead to a reduction in the over-all rate of the cathodic reaction by diminishing the rate of breakdown. The anodic reaction is accelerated under these conditions, just as would be anticipated.

The fact that  $\text{O}_2$  is reduced to hydrogen peroxide on a strongly reduced electrode in acid solution [2, 3], and to water on an oxidized electrode, is indication that the proposed mechanism for the action of the surface oxides is also applicable to acid solutions.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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