

STUDY OF THE ELECTROREDUCTION OF OXYGEN ON SMOOTH PLATINUM IN ACID SOLUTIONS BY THE METHOD OF A REVOLVING DISC ELECTRODE WITH A RING

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Our previous investigation [1] concerned the process of cathodic reduction of oxygen on a smooth platinum electrode in alkaline solutions. Our present work concerns the same process in acid solutions, where the kinetics of the reaction is more complex.

In the case of reduction of O_2 in acid solutions the activity of the smooth platinum electrode drops rapidly. As the result, the shape of polarization curves measured with a disc electrode changes with the rate of application of the potential (Fig. 1). The decrease of the intensity of current with time at constant potential follows a logarithmic law and can be related either to the deactivating effect resulting from the adsorption of anions or to chemical dissolution of platinum oxides in acid, as was assumed by some investigators [2-4].

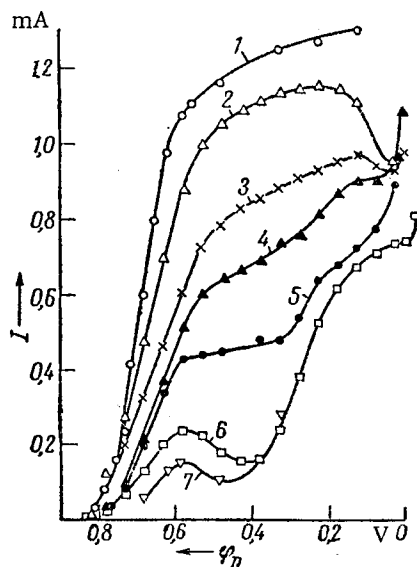


Fig. 1. Polarization curves of reduction of O_2 in 1 N H_2SO_4 obtained at different rates of application of the potential. 1) Measurements were made 10 sec after the activation of the electrode; 2) 335 mV/min; 3) 200 mV/min; 4) 50 mV/min; 5) 37 mV/min; 6) 25 mV/min; 7) potentiostatic curve.

To determine the role of adsorption of anions in the process investigated we measured the polarization curves in 1 N $HClO_4$, H_2SO_4 , HCl and HBr solutions. The polarization curves obtained with an active electrode (the different points of the curve were measured 10 sec after anodic-cathodic activation of the electrode) are shown in Fig. 2. It can be seen that the potential of half-wave reduction of oxygen is considerably displaced toward negative values. The amount of displacement varies in the following order: $HClO_4 < H_2SO_4 < HCl < HBr$, i.e., with increasing adsorbability of the anion, a result noted previously in [5]. On active platinum one obtains limit diffusion currents when the electrode rotates at the rate of 6000 rpm in $HClO_4$ and H_2SO_4 . In HCl and HBr the polarization curves obtained with the electrode rotating at the same speed $\bar{m}$ have a kinetic character and the type of variation of the maximum current with $\sqrt{m}$ indicates that the reduction of O_2 is a first-order reaction.

The fact that the electrode kept at a given potential until the intensity of current becomes constant (I_0) (as the result of cathodic polarization for 5 min at $\varphi_D = 0$ V when the SO_4^{2-} ions are desorbed) becomes partially activated indicates also that the adsorbed ions slow down the reaction. When φ_D returns to its initial value the current intensity on the disc electrode is higher than the initial value (Fig. 3); activation induced by desorption of anions is maximum when the potential of the disc φ_D is 0.43-0.45 V* and this maximum activation corresponds to the minimum current on the polarization curves obtained at a slow rate of application of potential (curves 6 and 7 in Fig. 1).

* All the potentials are measured with respect to the normal hydrogen electrode.

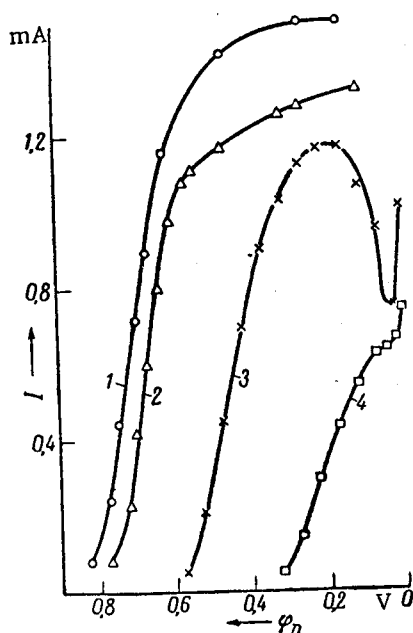


Fig. 2. Polarization curves of reduction of O_2 on an active Pt disc electrode in the following solutions: 1) 1 N $HClO_4$; 2) 1 N H_2SO_4 ; 3) 1 N HCl ; 4) 1 N HBr ($m = 2650$ rpm).

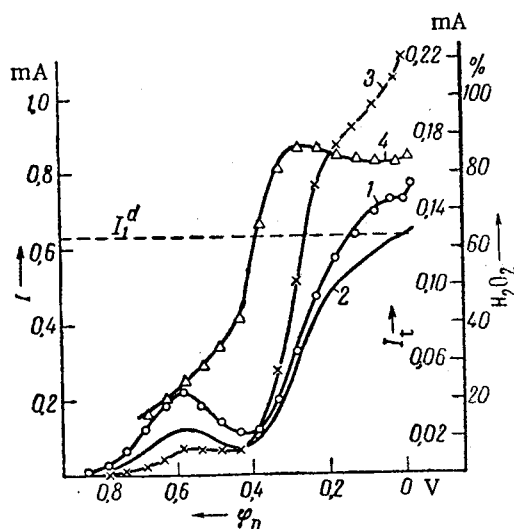


Fig. 4. 1) Experimental I, φ_D curve of the total process of reduction of oxygen on a platinum disc in a 1 N H_2SO_4 solution, the rate of application of the potential being 25 mV/min ($m = 2650$ rpm); 2) calculated I, φ curve of reduction O_2 to H_2O_2 ; 3) variation of the limit oxidation current of H_2O_2 on the ring (I_r) with the potential on the disc; 4) yield of H_2O_2 , %.

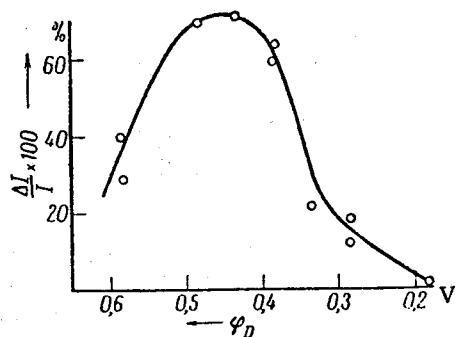
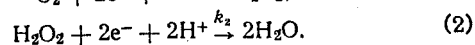
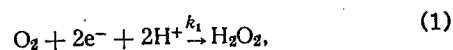


Fig. 3. Variation of the relative increment of current on the disc resulting from cathodic activation of the electrode at $\varphi = 0$ with the potential in a 1 N H_2SO_4 solution.

These results indicate that the adsorption of anions on the platinum electrode has a great effect on the kinetics of electroreduction of oxygen, particularly on the slowing down of the reaction. It is also possible that the electrode is additionally deactivated as the result of dissolution of platinum oxides, although our experiments do not allow us to make any definite conclusions.

We made a more detailed investigation of this mechanism by studying the reduction of oxygen in a 1 N H_2SO_4 solution, using the method of a rotating disc electrode with a ring (described in [6]). The advantage of this method is the possibility of separating the non-diffusional stages of the reaction and studying the quantitative effect of each of these stages on the total reaction rate. In these experiments the voltage was applied at the rate of 25 mV/min. At this rate the polarization curves of reduction of O_2 have a kinetic character (curve 1, Fig. 4).

The fact that within the whole range of oxygen reduction potentials on the disc (smooth platinum) the anodic oxidation current of H_2O_2 (curve 3, Fig. 4) on the ring electrode (platinum-plated platinum) remains constant indicates that the reaction is slowed down in two stages:



Because of the peculiarities of the method it was possible to calculate the real polarization curve of reduction of oxygen to H_2O_2 on the Pt electrode, which is very difficult with any other method. Knowing the value of the limit oxidation current of H_2O_2 on the ring I_r for a given potential of the disc φ_D (curve 3, Fig. 4) and taking into account the fact that (according to the equation derived in [7]) 41% of the hydrogen which did

φ_D, V	$k_1, \text{cm/sec}$	$k_2, \text{cm/sec}$	φ_D, V	$k_1, \text{cm/sec}$	$k_2, \text{cm/sec}$
0,68	$3,3 \cdot 10^{-3}$	$9,4 \cdot 10^{-2}$	0,28	$1,6 \cdot 10^{-2}$	$4,3 \cdot 10^{-3}$
0,58	$7,2 \cdot 10^{-3}$	$6,1 \cdot 10^{-2}$	0,18	$6,0 \cdot 10^{-2}$	$4,0 \cdot 10^{-3}$
0,48	$8,2 \cdot 10^{-3}$	$4,4 \cdot 10^{-2}$	0,08	$1,5 \cdot 10^{-1}$	$3,8 \cdot 10^{-3}$
0,38	$6,2 \cdot 10^{-3}$	$1,9 \cdot 10^{-2}$	—	—	—

not have time to react on the disc is fixed on the ring (in the case of a disc electrode with the given geometric parameters), it is easy to calculate the cathodic reduction curve of O_2 (on the disc) corresponding to the reversible reaction (2) and to complete reduction to water of all the oxygen participating in the reaction. By decreasing the current 50% we obtain the polarization curve corresponding to reaction (1) (curve 2, Fig. 4). The shape of the curve as well as the value of the current (which is lower than the limit diffusion current i_1^d for this reaction) indicate that the first stage of reduction of oxygen is slowed down.

By using the ordinary kinetic equation:

$$i_1 = 2Fk_1 [O_2]_0 \left(1 - \frac{i_1}{i_1^d}\right) \quad (3)$$

we found from the polarization curve obtained in this manner the rate constant k_1 of reaction (1), the current density i_1 for a given potential, the limit diffusion current i_1^d and the concentration of oxygen in the solution $[O_2]_0$. Knowing the intensity of the current on the disc for the first stage of the reaction I_1 , and using the equation for the ring disc electrode

$$I_t = \frac{0,41 I_1}{1 + k_2 \frac{\delta_{H_2O_2}}{D_{H_2O_2}}} \quad (4)$$

we calculated the rate constant k_2 for the second stage of the reduction of oxygen (reaction 2). Here I_t is the intensity of the limit diffusion current for the oxidation of H_2O_2 on the ring electrode; $\delta_{H_2O_2}$ and $D_{H_2O_2}$ are the thicknesses of the diffusion layer and the diffusion coefficient of H_2O_2 . According to our measurements in 1 N H_2SO_4 on the rotating disc electrode, $D_{H_2O_2} = 1,6 \cdot 10^{-5} \text{ cm}^2/\text{sec}$ (21°C).

The values of k_1 and k_2 at different potentials of the disc electrode are shown in the table.

The table and Fig. 4 show that the rates of reactions (1) and (2) vary differently with the potential. The oxygen reduction rate during the first stage of the reaction first increases with cathodic polarization, then drops to a minimum at $\varphi_D = 0,43 \text{ V}$, and finally increases again. Consequently, the polarization curve relative to this reaction is the same as the curve relative to the total process, and is probably determined to a great extent by the decelerating effect of the SO_4^{2-} ions adsorbed on the electrode. The adsorption of anions decreases with increasing cathodic polarization ($\varphi_D < 0,43 \text{ V}$) and this results in the acceleration of reaction (1). If the potential of the disc electrode is zero ($\varphi_D = 0$) and most of the SO_4^{2-} ions are desorbed, the rate of the first stage of the reaction is equal to the diffusion rate.

The rate of the second stage of the reduction of O_2 decreases with decreasing positive values of φ_D within the whole range of potentials investigated and the amount of H_2O_2 formed increases correspondingly, reaching 70-90% (curve 4, Fig. 4). The deceleration of reaction (2), which we noted earlier [1] (although in a weaker form in the case of reduction of O_2 on Pt in alkaline solutions), can be explained by the change in the physicochemical state of the surface of the electrode resulting from the reduction of platinum oxides on the surface. These assumptions are verified by the data obtained in [8] (which indicate that oxygen is reduced only to H_2O_2 on Pt electrodes in acid solutions) and also by the results obtained in [2, 9].

Thus, we conclude that the rate of the total oxygen reduction process in H_2SO_4 solutions on oxidized platinum is determined essentially by reaction (1) when the potential φ_D is sufficiently positive. Under these conditions the value of k_2 is about one order higher than that of k_1 (see table). The roles of the two stages of the reaction are reversed on a reduced electrode surface, i.e., k_1 is greater than k_2 .

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