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STUDY OF THE PROCESS OF CATHODIC REDUCTION OF OXYGEN ON PLATINUM IN ALKALINE SOLUTIONS USING A ROTATING DISK ELECTRODE WITH A RING

(Presented by Academician A. N. Frumkin, 3 I 1963)

Although the process of the electroreduction of oxygen on platinum attracts the attention of researchers, its mechanism remains largely unclear. Up to now there has been no consensus in the literature even on the question of the possibility that hydrogen peroxide arises in the process of electroreduction of O_2 as an intermediate reaction product. Such a possibility, for example, is denied by Lingane (^{1}). On the other hand, hydrogen peroxide was detected during experiments in acidic solutions in the work of Sawyer and Interrante (^{2}). Most authors consider the formation of H_2O_2 during the cathodic reduction of oxygen on platinum in alkaline solutions to be unlikely. In this connection it seemed of interest to try to elucidate the mechanism of the process of reduction of O_2 on platinum by applying the method of the rotating disk electrode with a ring.

The present article gives the results of an investigation of the process of electroreduction of oxygen in alkaline solutions ($0.125\,N$ KOH) on a rotating disk electrode of smooth platinum. The experiments were carried out at room temperature and at an oxygen pressure in the system equal to 1 atm. The alkaline solution was subjected to careful preliminary purification by prolonged cathodic polarization on a platinum wire in a hydrogen atmosphere, with simultaneous adsorption purification on a platinized platinum gauze; it was then anodically depolarized in another vessel in an oxygen atmosphere. Before measurement of each curve, the working electrode was activated by alternating anodic and cathodic polarization. The polarization curves for oxygen reduction, measured at various rotation rates of the disk electrode, are presented in Figs. 1A and 2*. As is seen from the figures, the curves obtained at low rotation rates ($m < 700$ rpm) differ substantially in their form from the curves recorded at a larger number of revolutions of the electrode. In the first case (Fig. 1A), the polarization

Fig. 1 and Fig. 2: polarization curves

Figure 1: Fig. 1 and Fig. 2: polarization curves

curve has a horizontal plateau of the limiting diffusion current, the magnitude of which, in accordance with Levich’s formula (3) for a diffusion process at a disk, increases proportionally to $m^{1/2}$ (Fig. 3). The agreement of the experimental values of the limiting current with those calculated from Levich’ s formula on the assumption of the participation of four electrons in the reaction, and the fact that the height of the wave shown in Fig. 1A proved equal to the total height of the two waves of O_2 reduction observed under the same conditions when measured on a gold amalgamated disk electrode, unambiguously indicate the 4-electron character of the process. Thus, in agreement with literature data (1,2), the overall reaction of O_2 reduction on platinum in alkaline solutions may be written in the following form

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-. \tag{1}$$

On the polarization curves measured at higher rates of electrode rotation (Fig. 2), instead of a limiting diffusion current, a clearly expressed maximum is observed at the potential $\varphi_D = 0.5$ V. A further increase in cathodic polarization leads to a decrease in current to a certain minimum value at $\varphi_D \approx 0.05$–0.1 V, after which the current again increases. The new rise in current begins at potentials more positive than that of the reversible hydrogen electrode and, consequently, is associated with acceleration of the oxygen reduction reaction. At $\varphi_D < 0$, the hydrogen evolution process also affects the magnitude of the cathodic current. The drop in current on the polarization curve appears the more distinctly, the higher the disk rotation rate. The dependence of the maximum current on $m^{1/2}$ deviates from that required by the Levich formula (Fig. 3), which indicates the slowness of some non-diffusion stage.

Fig. 1. Polarization curve for the reduction of oxygen on a rotating disk electrode of smooth platinum in 0.125 N KOH at $m = 300$ rpm (A) and the corresponding dependence of the limiting current of H_2O_2 oxidation at the ring on the disk potential (B)

Fig. 2. Polarization curves for the reduction of O_2 on a platinum disk in 0.125 N KOH at values of m: 1 –1040 rpm; 2 –2950 rpm; 3 –4560 rpm. $1'$, $2'$, $3'$ – currents corrected for the amount of H_2O_2 evolved

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

We assumed that the reaction of cathodic reduction of O_2 on smooth platinum in alkaline solutions may proceed in two stages, similarly to how it occurs on mercury and a number of other electrodes:

$$O_2 + 2e^- + 2H_2O = H_2O_2 + 2OH^-, \tag{2}$$

$$H_2O_2 + 2e^- = 2OH^-. \tag{3}$$

(Practically, in alkaline solutions hydrogen peroxide exists in the form of the HO_2^- anion.) In this case the kinetic limitation observed experimentally must be associated with one of the two indicated stages.

Our investigation of the reaction of hydrogen peroxide reduction on a rotating platinum disk electrode in 0.125 N KOH solution containing no oxygen made it possible to establish a great similarity of the measured polarization curve to the oxygen-reduction curves both in form and in the values of the potentials corresponding to the minimum current values. The relative depth of the minimum on the peroxide curve proved to be somewhat greater than in the case of oxygen. The results obtained gave grounds to suppose that the slowest stage of the O_2 reduction reaction is the stage of hydrogen peroxide reduction. Direct proof of this supposition was carried out

by us through the use of the rotating disk electrode with a ring described earlier (^{4}), which represents a single mechanical system of two electrodes—the disk and the ring—insulated from one another by a thin Teflon gasket. The material of the ring was platinized platinum.

The experiments carried out showed that, during the reduction of oxygen on the disk, an anodic current of oxidation of some intermediate product formed in the course of the cathodic reaction can be observed on the ring electrode. The fact that the polarogram of oxidation of the intermediate product on the ring electrode proved to be completely identical with the polarization curve for the oxidation of H_2O_2 on the same electrode makes it possible to identify with certainty the recorded intermediate product as hydrogen peroxide. Figure 1B presents the dependence of the limiting current of H_2O_2 oxidation on the ring on the potential of the disk electrode at $m = 300$ rpm. As the cathodic polarization increases, the current on the ring first rises, reaches a maximum value, and then falls, becoming equal to zero in the region of the limiting diffusion current on the disk, where the surface concentration of H_2O_2 is also equal to zero. Such a course of the curve on the ring is characteristic of the case in which the reaction of conversion of the intermediate product on the disk into the final product is irreversible.

Fig. 3. Dependence of the current on the disk electrode on $\sqrt{m}$: 1—for limiting diffusion currents; 2—for maximum currents at $\varphi_D = 0.5$ V; 3—for currents at the minimum of the polarization curve. a—values of the "corrected" currents

Figure 3

Figure 2: Figure 3

Figure 4

Figure 3: Figure 4

At $m > 700$ rpm, i.e., under conditions in which there is no limiting diffusion current on the disk, hydrogen peroxide can be detected throughout the entire range of oxygen-reduction potentials; however, in the present work we shall confine ourselves only to considering phenomena at potentials lying more negative than the maximum on the polarization curves (Fig. 2), and shall not touch upon the rising portion of the curve on the disk ($\varphi_D > 0.5$ V), where the observed processes apparently have a more complex character. Since the rate of formation of H_2O_2 at these potentials remains practically constant, while the rate of its disappearance should have increased with cathodic polarization, one might have expected a rapid decrease of the anodic current on the ring as the cathodic polarization of the disk increased. The actual picture proved to be quite different (Fig. 4). Instead of a decrease in the current on the ring, a considerable increase in it was observed, up to the potential corresponding to the minimum on the cathodic curve, and only in an even more negative region did the amount of hydrogen peroxide detected decrease.

Fig. 4. Curves of the dependence of the limiting current of H_2O_2 oxidation on the ring on the potential of the disk in 0.125 N KOH solution at m values: 1—1040 rpm; 2—2950 rpm; 3—4560 rpm

The unusual form of the dependence of the yield of H_2O_2 on the potential turns out to be a consequence of inhibition of reaction (3) and indicates a decrease in the catalytic activity of the electrode, thereby explaining the reason for the decline of the current on the polarization curves of cathodic reduction of O_2 on platinum. Im-

The data available in the literature concerning the acceleration of both the process under study (^{1,2,5}) and certain other (^{6}) processes on freshly oxidized electrodes, as compared with reduced ones, made it possible to associate the decrease in the catalytic activity of the electrode with a change in the physicochemical state of its surface as a result of the reduction of surface platinum oxides. This point of view is confirmed by data from charging curves (^{7,8}), according to which the potential of the maximum on the $i - \varphi$ curve lies in the region of oxygen retardation on the charging curve, while at the potential of the minimum oxygen is completely absent from the platinum surface. The decrease in the yield of H_2O_2 at potentials lying more negative than the minimum reflects the normal dependence of the rate of H_2O_2 reduction on potential at the reduced electrode.

According to the calculation by the formula for the ring disk electrode (^{9}), with the geometrical parameters used, approximately 41% of the H_2O_2 formed at the disk was recorded at the ring. Knowledge of this ratio made it possible to correct the cathodic curve at the disk by the value of the current corresponding to the unreacted part of H_2O_2, i.e., to construct a curve under the assumption of complete reduction to hydroxyl ions of all the oxygen participating in the process. The correction carried out in this way, as is seen from Fig. 2, leads to the appearance on the polarization curves of limiting diffusion currents that obey the Levich relation well (Fig. 3). From this result it follows that, in the reduction of oxygen on a platinum electrode in alkaline solution, reaction (2) under the experimental conditions is reversible, and the rate of the process is determined by reaction (3). One further argument in favor of this conclusion may be the closeness of the values of the rate constants for the reduction of H_2O_2 and oxygen. Thus, at $\varphi_D = 0.5$ V, $k_{H_2O_2} \approx 8.5 \cdot 10^{-1}$ cm/sec (found from measurements with the ring disk electrode) and $k_{O_2} = 8.7 \cdot 10^{-1}$ cm/sec (calculated from the polarization curve for the reduction of O_2, obtained by extrapolating the data to $m \to \infty$).

Regularities analogous to those described—the decrease in the catalytic activity of the electrode in the cathodic process, the formation of H_2O_2, and the presence of a limiting diffusion current on the "corrected" polarization curve—were also observed by us in the reduction of oxygen in the same solution on a rotating disk electrode made of gold, which indicates a similar character of the mechanism of the process on both metals investigated.

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