

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

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Despite the attention which has been given to the electroreduction of oxygen on platinum, the reaction mechanism is still undecided. There is no general agreement even on the appearance of hydrogen peroxide as an intermediate product in the reaction. The possibility of this occurring has been denied by Lingane [1]. On the other hand, Sawyer and Interrante [2] have detected hydrogen peroxide in experiments with acidic solutions. Most consider that there is little likelihood of the formation of H_2O_2 in the cathodic reduction of oxygen on platinum in alkaline solution. Thus interest attaches to an attempt at elucidating the mechanism of the reduction of O_2 on platinum by use of the rotating disk and ring electrode.

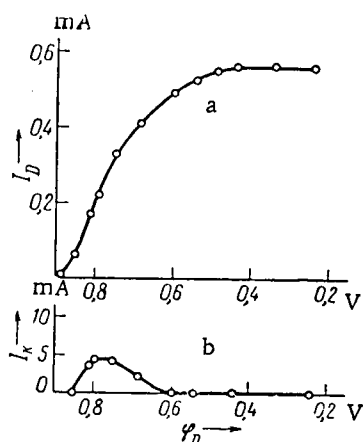


Fig. 1. Polarization curve for the reduction of oxygen on a smooth platinum rotating disk electrode in 0.125 N KOH with $m = 300$ rpm (a), and the corresponding relation between the limiting current for H_2O_2 oxidation on the ring and the disk potential (b).

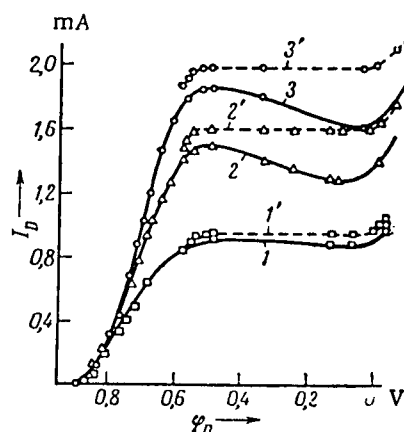


Fig. 2. Polarization curves for the reduction of O_2 on the platinized disk in 0.125 N KOH at the following values of m : 1) 1040 rpm; 2) 2950 rpm; 3) 4560 rpm. 1', 2', 3' are points which have been corrected for the amount of evolved H_2O_2 .

The present article will present the results of a study of the electroreduction of oxygen on a smooth platinum rotating disk electrode in alkaline solution (0.125 N KOH). Experiments were carried out at room temperature with a 1 atmosphere pressure of oxygen in the system. The alkaline solutions were first carefully purified by extended cathodic polarization on a platinum wire in an atmosphere of hydrogen, with simultaneous adsorption on a platinized platinum gauze, and were then subjected to anodic polarization in an atmosphere of oxygen in another vessel. The working electrode was activated by alternate anodic and cathodic polarization prior to the development of each curve. Polarization curves for the oxygen reduction at various rates of rotation of the disk electrode are presented in

Figs. 1a and 2.* It is clear from these figures that the curves obtained at low rotation rates ($m < 700$ rpm) are essentially different from those obtained at high rotation rates. Curves of the first type (Fig. 1a), show a horizontal segment corresponding to a diffusional current and the length of this segment is proportional to $m^{1/2}$ as required by the Levich Equation [3] for diffusional processes at the disk (Fig. 3). The fact that this is a four-electron process is indicated by the agreement of the experimental value of the limiting current with the value calculated from the Levich Equation by assuming participation of four electrons in the reaction, and by the observation that the height of the wave of Fig. 1a is the sum of the heights of the two waves for O_2 reduction on an amalgamated gold disk electrode under the same conditions. Thus one can follow the literature [1, 2] and represent the over-all reaction of O_2 reduction on platinum in alkaline solution by



Polarization curves obtained at higher rotation rates (Fig. 2) do not show a limiting diffusional current, but pass through a clear-cut maximum at a potential, φ_D , of 0.5 V. Increase of the cathodic polarization beyond this point causes the current to fall, reach a minimum value at $\varphi_D \approx 0.05-0.1$ V, and then begin to increase once more. This new increase in the current takes place at potentials more positive than the potential of the reversible hydrogen electrode and it is therefore related to an accelerated reduction of oxygen. The magnitude of the cathodic current at $\varphi_D < 0$ is also affected by the evolution of hydrogen. The fall-off of current on the polarization curve is the more pronounced the higher the rate of rotation of the disk. The fact that the relation between $m^{1/2}$ and the current maximum is different from that required by the Levich Equation (Fig. 3), is an indication of the presence of some slow, non-diffusional step.

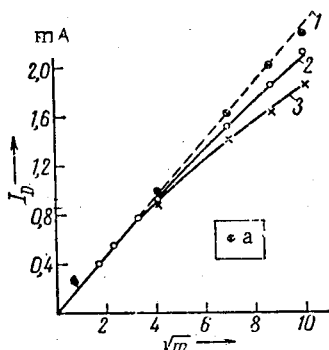


Fig. 3. Relation between the current on the disk electrode and $\sqrt{m}$: 1) For limiting diffusion currents; 2) for maximum currents at $\varphi_D = 0.5$ V; 3) for currents at the minimum on the polarization curve. $\underline{a}$ designates "corrected" current values.

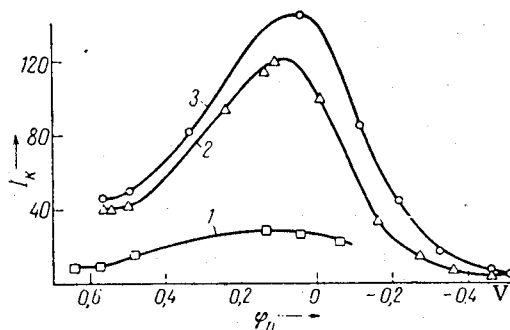


Fig. 4. Curves showing the relation between the limiting current for H_2O_2 oxidation on the ring and the potential of the disk in 0.125 N KOH at the following values of m : 1) 1040 rpm; 2) 2950 rpm; 3) 4560 rpm.

We assume that the cathodic reduction of O_2 in alkaline solution can occur in two steps on smooth platinum electrodes, just as on mercury and certain other electrodes:



The hydrogen peroxide of alkaline solutions is actually in the form of the anions HO_2^- . Thus the experimentally observed kinetic limitation must be related to one or the other of these two steps.

Our experiments on the reduction of hydrogen peroxide on the rotating disk electrode in a 0.125 N oxygen-free KOH solution made it possible to show that the measured polarization curves and the oxygen reduction curves are similar in form and in minimum current potentials. The minimum is more pronounced on the peroxide curve than on the oxygen curve. These results give reason to suppose that the reduction of hydrogen peroxide is the slow step in the O_2 reduction. Direct proof of this fact was obtained through the use of the rotating disk and ring electrode

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

which has been described earlier [4]. This is a single mechanical system of two electrodes, the disk and the ring, the one separated from the other by an insulating layer of teflon. The ring was constructed of platinized platinum.

Experiment showed that it was possible to measure an anodic current for oxidation of an intermediate in the cathodic reaction on the ring while oxygen reduction was taking place on the disk. The fact that the polarogram for oxidation of this intermediate on the ring was identical with the polarization curve for H_2O_2 oxidation on the same electrode permitted the intermediate to be identified unambiguously as hydrogen peroxide. Figure 1b shows the relation between the limiting current for H_2O_2 oxidation on the ring and the potential of the disk at $m=300$ rpm. With increasing cathodic polarization, the ring current rises, reaches a maximum, and then falls, to vanish in the region of the limiting diffusion current on the disk where the surface concentration of H_2O_2 is zero. Such ring curve is characteristic of cases in which disk conversion of an intermediate to a final product is irreversible.

Hydrogen peroxide can be detected over the entire range of oxygen reduction potentials when $m > 700$ rpm and there is no limiting diffusion current on the disk. However we have limited ourselves in the present work to effects occurring at potentials more negative than that of the maximum on the polarization curve (Fig. 2) and, therefore, do not touch on the rising segment of the disk curve ($\varphi_D > 0.5$ V) where the processes are clearly more complex. It was to be expected that the ring anodic current would fall off sharply as the disk cathodic polarization increased since the rate of formation of H_2O_2 is essentially constant at these potentials while the rate of peroxide consumption increases with the cathodic polarization. The actual situation proved to be quite different, however (Fig. 4). Instead of diminishing, the ring current rose sharply to a potential corresponding to the minimum on the cathodic curve and the quantity of fixed hydrogen peroxide diminished only in the more negative region.

The existence of this unusual type of relation between the potential and the H_2O_2 yield results from retardation for Reaction (3) and points to a reduction of the electrode activity which would account for the current fall-off on polarization curves for the cathodic reduction of O_2 on platinum. Data relative to the reactions under study here [1, 2, 5] (and other processes [6]) on freshly oxidized electrodes and their relative acceleration with respect to reduction opens the possibility of relating this decrease in catalytic activity with the alteration of the physical chemical state of the electrode resulting from reduction of surface oxides of platinum. This point of view is supported by work on charging curves [7, 8] which has shown that the potential of the maximum on the i, φ curves lies in the region of oxygen entrapment on the charging curve, the platinum surface being entirely free of oxygen at the potential of the minimum. The reduction in the H_2O_2 yield at potentials more negative than that of the minimum reflects a normal relation between the potential and the rate of H_2O_2 reduction on the reduced electrode.

Calculations based on the equation for the ring and disk electrode [9] show a ring having the geometrical parameters of the one used here to be capable of fixing $\sim 41\%$ of the H_2O_2 formed on the disk. A knowledge of this fact makes it possible to correct the cathodic disk curve for the unreacted portion of the H_2O_2 , thus permitting construction of a curve for complete reduction to hydroxyl ions of all of the oxygen involved in the reaction. Figure 2 shows that limiting diffusion currents which are well described by the Levich Equation (Fig. 3) will appear on the polarization curves obtained through such correction. From this it can be concluded that oxygen reduction in alkaline solution proceeds in such way that Reaction (2) is reversible and Reaction (3) is rate determining. Another argument in support of this conclusion is found in the fact that the rate constants for the reduction of H_2O_2 and oxygen are very nearly the same in value. Thus with $\varphi_D = 0.5$ V, $k_{\text{H}_2\text{O}_2} \approx 8.5 \cdot 10^{-1}$ cm/sec on the basis of the measurements with the ring and disk electrode while $k_{\text{O}_2} = 8.7 \cdot 10^{-1}$ cm/sec, on the basis of calculations made from a polarization curve for O_2 reduction obtained by extrapolating the experimental data to $m \rightarrow \infty$.

Relations similar to those described here, that is, reduction of the catalytic activity of the electrode during the cathodic process, formation of H_2O_2 , and the presence of a limiting diffusion current on the "corrected" polarization curve, were also observed in oxygen reduction on a gold rotating disk electrode in this same solution. This indicates similar reaction mechanisms for the processes occurring on the two metals.

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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.
