Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1964

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1964. Volume 154, No. 2

PHYSICAL CHEMISTRY

L. MÜLLER, L. N. NEKRASOV

STUDY OF THE PROCESS OF ELECTROREDUCTION OF OXYGEN ON SMOOTH PLATINUM IN ACID SOLUTIONS BY THE METHOD OF A ROTATING RING-DISK ELECTRODE

(Presented by Academician A. N. Frumkin on 23 VII 1963)

Our previous work (^{1}) was devoted to the study of the process of cathodic reduction of oxygen on a smooth platinum electrode in alkaline solutions. In the present article we give the results of an investigation of this reaction in acid solutions, where the kinetic regularities are of a more complex character.

A substantially new feature, in comparison with the reduction of O_2 in alkaline solutions, is the rapid decrease with time in the activity of the smooth platinum electrode, as a result of which the form of the polarization curves measured on the disk electrode changes depending on the rate at which the potential is applied (Fig. 1). The decay of the current with time at constant potential obeys a logarithmic law and may be connected either with the deactivating action of anion adsorption, or with chemical dissolution in acid of surface oxides of platinum, as has been assumed in some works ($^{2-4}$).

Fig. 1. Polarization curves for the reduction of O_2 in $1\,N$ H_2SO_4, obtained at different rates of application of the potential: 1 —each measurement was made 10 sec after 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

In order to clarify the role of anion adsorption in the process under study, we carried out polarization measurements in $1\,N$ solutions of $HClO_4$, H_2SO_4, HCl, and HBr. The corresponding polarization curves obtained on the active electrode (each point of the curve was measured 10 sec after anodic-cathodic activation of the electrode) are shown in Fig. 2. As is seen from the figure,

Fig. 2 and Fig. 3 plots

Figure 2: Fig. 2 and Fig. 3 plots

the half-wave potential of oxygen reduction is shifted strongly in the negative direction in the series

$HClO_4 < H_2SO_4 < HCl < HBr$,

i.e., as the adsorbability of the anion increases, which had also been noted earlier (^{5}). At the same time, on active platinum in solutions of $HClO_4$ and H_2SO_4 it is possible to obtain limiting diffusion currents at electrode rotation rates reaching 6000 rpm, whereas in solutions of HCl and HBr, at the same values of the electrode rotation speed m, the polarization curves have a kinetic character, and the form of the dependence of the maximum current on $\sqrt{m}$ indicates the first order of the O_2 reduction reaction.

The inhibiting action of adsorbed anions is also indicated by the fact of partial activation of an electrode previously held at a given potential until a constant value of the current (I_0) was established, by means of—

by its cathodic polarization for five minutes at $\varphi_D = 0$ V, where SO_4^{2-} ions are desorbed. Upon returning to the initial value of φ_D, the current at the disk electrode proves to be higher than the initial one (Fig. 3); the maximum activation effect caused by desorption of anions is observed at a disk potential $\varphi_D = 0.43$—0.45 V*, corresponding to the current minimum on the polarization curves measured at a low rate of potential application (curves 6, 7 in Fig. 1).

These data indicate that adsorption of anions on the platinum electrode is a factor exerting a strong influence on the kinetics of the electroreduction of oxygen and leading, in particular, to a decrease in the reaction rate with time. Such ideas do not exclude the possibility of additional deactivation of the electrode under the influence of dissolution of platinum oxides, although on the basis of our experiments it is not possible to draw any reliable conclusions on this point.

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

Fig. 3. Dependence of the relative increase in current at the disk, caused by cathodic activation of the electrode at $\varphi = 0$, on the potential in a 1 N H_2SO_4 solution

A more detailed investigation of the mechanism of the process under study was carried out by us using the example of oxygen reduction in a 1 N sulfuric acid solution, by employing the previously described (^{6}) rotating disk electrode with a ring. A major advantage of this method is that it makes it possible to separate the non-diffusion stages of the reaction and to study quantitatively the influence of each of them on the overall rate of the process. The experiments were carried out at a potential-sweep rate of 25 mV/min, at which the polarization curves for O_2 reduction have a kinetic character (curve 1 in Fig. 4).

The fact that, throughout the entire range of oxygen-reduction potentials at the disk (smooth platinum), an anodic current of H_2O_2 oxidation was recorded at the ring electrode (platinized platinum) (curve 3 in Fig. 4) convincingly indicates that the process proceeds in two stages and that the second of them is slow:

$$O_2 + 2e^- + 2H^+ \xrightarrow{k_1} H_2O_2, \tag{1}$$

$$H_2O_2 + 2e^- + 2H^+ \xrightarrow{k_2} 2H_2O. \tag{2}$$

Owing to the specific features of the method, it proved possible to resolve a problem that is difficult to carry out by other means—to calculate the real polarization curve for the reduction of oxygen on Pt to hydrogen peroxide. Knowing the value of the limiting current for the oxidation of H_2O_2 at the ring, I_k, at a given disk potential φ_D (curve 3 in Fig. 4), and taking into account that, according to an approximate calculation by the formula of V. G. Levich and Yu. B. Ivanov (^{7}), for the ring-disk electrode with the geometrical parameters used, 41% of the hydrogen peroxide that had not had time to react at the disk was recorded at the ring, it is easy to calculate the cathodic curve for the reduction of O_2 at the disk, corresponding to the reversible course of reaction (2) and to the complete reduction to water of all oxygen participating in the process. Reducing the current by a factor of two, we obtain the polarization curve corresponding to reaction (1) (curve 2 in Fig. 4). Both the shape of the curve and the current values, lower than the diffusion limiting current for this reaction (I_1^d), indicate inhibition of the first stage of oxygen reduction.

From the polarization curve constructed in this way, using the ordinary kinetic equation

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

the values of the rate constant for reaction (1), k_1, were found; i_1 and i_1^d are, respectively, the current density at the given potential and the diffusion limiting current; $[O_2]_0$ is the concentration of oxygen in the bulk of the solution. Knowing the current on the disk for the first stage of the reaction I_1 and using the equation for the ring-disk electrode

---

* All potentials are given relative to the normal hydrogen electrode.

$$I_k = \frac{0.41 I_1}{1 + k_2 \frac{\delta_{H_2O_2}}{D_{H_2O_2}}} \tag{4}$$

Fig. 4. 1—experimental I, φ_D-curve of the overall process of oxygen reduction on a platinum disk in 1 N H_2SO_4 solution at a potential sweep rate of 25 mV/min ($m = 2650$ rpm); 2—calculated I, φ-curve for O_2 reduction to H_2O_2; 3 —dependence of the limiting current for oxidation of H_2O_2 at the ring (I_k) on the disk potential; 4—yield of H_2O_2 in percent

Table 1

φ_D, V	k_1, cm/sec	k_2, cm/sec	φ_D, V	k_1, cm/sec	k_2, 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	$6.2 \cdot 10^{-3}$	$1.9 \cdot 10^{-2}$	–	–	–

also made it possible to calculate the values of the rate constant for the second stage of oxygen reduction (reaction 2), k_2. I_k is the diffusion limiting current for oxidation of H_2O_2 at the ring electrode; $\delta_{H_2O_2}$ and $D_{H_2O_2}$ are the thickness of the diffusion layer and the diffusion coefficient of H_2O_2. According to our measurements, carried out in 1 N H_2SO_4 on a rotating disk electrode,

$$D_{H_2O_2} = 1.6 \cdot 10^{-5}\ \text{cm}^2/\text{sec}\ (21^\circ\text{C}).$$

The values of the rate constants k_1 and k_2 at various potentials of the disk electrode are compared in Table 1.

As is seen from the data of Table 1 and Fig. 4, the rates of reactions (1) and (2) vary with potential according to different laws. The rate of the first stage of oxygen reduction, as the cathodic polarization increases, first rises, then falls to a certain minimum value at $\varphi_D = 0.43$ V and, finally, rises again. The course of the polarization curve of this reaction thus repeats the course of the curve for the overall process and is probably determined to a considerable extent by the inhibiting influence of SO_4^{2-} anions adsorbed on the electrode. With increasing cathodic polarization ($\varphi_D < 0.43$ V), adsorption of the anions decreases, which leads to acceleration of reaction (1). At a disk-electrode potential $\varphi_D = 0$, when the greater part of the SO_4^{2-} ions is desorbed, the rate of the first stage becomes equal to the rate of diffusion.

By contrast, the rate of the second stage of O_2 reduction over the entire investigated potential interval decreases as the positive value of φ_D decreases, while the yield of hydrogen peroxide correspondingly increases, reaching 70–90% (curve 4 in Fig. 4). The phenomenon of inhibition of reaction (2), which in a weaker form was also observed by us in the case of O_2 reduction on Pt in alkaline solutions ([1]), may be explained by a change in the physicochemical state of the electrode surface as a result of reduction of surface oxides of platinum. Such ideas are supported, for example, by the data of Sojer and Interrante ([8]), according to which, on a reduced platinum electrode in acid solutions, oxygen is reduced only as far as H_2O_2, as well as by data of other authors ([2,9]).

Summarizing all the foregoing, it should be concluded that on oxidized platinum, at sufficiently positive φ_D, the rate of the overall process of oxygen reduction in an H_2SO_4 solution is determined mainly by reaction (1). Under these conditions the value of the constant k_2 exceeds the value of k_1 by approximately an order of magnitude (Table 1). On the reduced electrode surface the roles of the two stages change, and k_1 becomes considerably greater than k_2.

The authors express their deep gratitude to Academician A. N. Frumkin for his help in discussing the results.

Moscow State University
named after M. V. Lomonosov

Received
15 VII 1963

REFERENCES

[1] L. N. Nekrasov, L. Müller, DAN, **149**, 1107 (1963).
[2] J. J. Lingane, J. Electroanalytical Chem., **2**, 296 (1961).
[3] T. R. Blackburn, J. J. Lingane, J. Electroanalytical Chem., **5**, 216 (1963).
[4] Zh. V. Strel' nikova, V. P. Lebedev, ZhFKh, **37**, 920 (1963).
[5] V. N. Modestova, ZhFKh, **25**, 1138 (1951).
[6] A. N. Frumkin, L. N. Nekrasov, DAN, **126**, 115 (1959); A. Frumkin, L. Nekrasov et al., J. Electroanalytical Chem., **1**, 84 (1959–1960).
[7] V. G. Levich, Physicochemical Hydrodynamics, Moscow, 1959, p. 337.
[8] D. T. Sawyer, L. V. Interrante, J. Electroanalytical Chem., **2**, 310 (1961).
[9] G. Bianchi, F. Mazza, T. Mussini, Electrochim. Acta, **7**, 457 (1962); M. Mochizuki, J. Electrochem. Soc. Japan, **28**, 583 (1960).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.