INVESTIGATION OF THE REDUCTION OF OXYGEN ON IRON AND OF THE IONIZATION OF IRON IN THE PRESENCE OF DISSOLVED OXYGEN

Z. A. Iofa and M. A. Makhbuba

UDC 620.193.01

The reduction of oxygen has been the subject of many articles [1-7], since this reaction is of interest for elucidating the corrosion of metals by oxygen depolarization. However, the research on this process in the case of iron is still inadequate.

In the work described herein, we studied the kinetics of the reduction of oxygen on iron and the ionization of iron in acidic and alkaline solutions in the presence of oxygen at different agitation rates.

METHOD

Disc electrodes were fabricated from pure iron obtained by zone melting and from Armco iron* and mounted in a Teflon ring. The iron was preliminarily hardened in a hydrogen atmosphere at 600° for 6 h and slowly cooled. The disc diameter was 0.6 cm and S = 0.283 cm^2. The rotation rate of the electrode, which was separated from the auxiliary by a closed cock, ranged from 0 to 7300 rpm and was determined with a strobotachometer. The solution was prepared from purified reagents and additionally purified in a separate portion of a glass cell by cathodic polarization at a platinum-plated electrode, with simultaneous passage of electrolytic hydrogen. Before each experiment, the electrode was polished with finely powdered glass and rinsed with alcohol and water. The potentials are given with respect to a normal calomel electrode. The experimental temperature was 20 ± 1°. We first compiled the polarization curves in a hydrogen or argon atmosphere and then in an air or oxygen atmosphere. No gas was passed through the solution during the measurements. We first determined the forward and reverse trend of the cathodic polarization curves and then that of the anodic curves. The electrolytes were solutions with a constant ionic strength $pH_2SO_4+qNa_2SO_4$ and $pNaOH + qNa_2SO_4$ at p + q = 1 N, with p = 1.0, 0.3, 0.1 and 0.03 N.

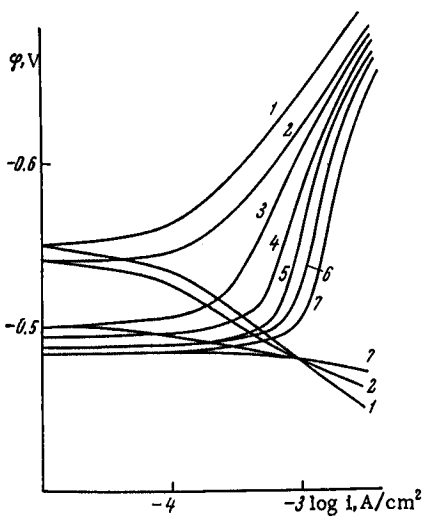

Fig. 1. Cathodic and anodic polarization curves for disc electrode of Armco iron in 0.3 N H_2SO_4 + 0.7 N Na_2SO_4 in atmosphere of hydrogen (1) and air (2-7). Rotation speed: 2) 0 rpm; 3) 305 rpm; 4) 1150 rpm; 5) 2350 rpm; 6) 3430 rpm; 7) 7300 rpm.

EXPERIMENTAL RESULTS

In conformity with the data in [1-7], the cathode potential (φ_c) in the absence of dissolved oxygen was independent of the agitation rate and the hydrogen-ion discharge proceeded with a kinetic limitation. The coefficient $\partial\varphi_k/\partial \log i = 0.116$ V.

The extent to which the steady-state potential was displaced toward positive values in the solutions containing oxygen increased with the speed at which the electrode was rotated and with the oxygen and acid concentrations; in the agitated solutions, the potential of the zone-melted iron was more negative than that of the Armco iron (Figs. 1-3 and 5, Table 1).

* The impurity contents in the zone-melted iron were C — less than 10^{-3}%, Mn — less than 10^{-5}%, P — less than 10^{-3}%, S — less than 10^{-4}%, Si — about 10^{-3}%, and Ni — 10^{-4}%, while those in the Armco iron were C — 0.04%, Mn — 0.02%, S — 0.03%, and P — 0.03%.

M. V. Lomonosov Moscow State University. Translated from Zashchita Metallov, Vol. 3, No. 4, pp. 387-393, July-August, 1967. Original article submitted September 26, 1966.

TABLE 1. Steady-State Potential of Iron (mV) in Air-Saturated Solutions Containing $pH_2SO_4 + qNa_2SO_4$

Rotation speed, rpm	p = 1 N Armco	p = 0.3 N Armco	p = 0.1 N Armco	p = 0.03 N Armco	p = 0.3 N Zone-melted
0	—500	—543	—564	—581	—543
305	—463	—502	—527	—564	—522
1150	—458	—496	—518	—562	—516
2350	—454	—488	—515	—562	—512
3430	—452	—487	—514	—559	—508
7300	—445	—485	—513	—557	—505

TABLE 2. Maximum Diffusion Density of Reduction Current of Oxygen on Iron

Rotation speed, rpm	$p = 1.0\,N$ Armco air	$p = 0.3\,N$ Armco air	$p = 0.3\,N$ zone-melted	$p = 0.3\,N$ Armco oxygen	$p = 0.1\,N$ Armco air	$p = 0.03\,N$ Armco air	0.1 N NaOH + $+ Na_2SO_4$ Armco air
305	0.42	0.42	0.42	1.5	0.41	0.42	0.43
1150	0.74	0.71	0.71	2.8	0.67	0.70	0.65
2350	1.05	0.95	1.02	3.8	0.85	0.95	0.95
3450	1.20	1.10	1.10	4.6	1.06	1.06	1.03
7300	1.66	1.50	1.52	—	1.55	1.48	1.52

The maximum oxygen-reduction current (Fig. 1) became more pronounced after introduction of a correction for the hydrogen-ion discharge current and the ionization of the iron (the dash lines in Fig. 2).* It can be seen from Table 2 that the maximum current (I_d) depended only on the oxygen concentration and the rate at which the oxygen reached the electrode by convective diffusion and was virtually independent of the acid concentration and the purity of the electrode material.

The values of the maximum current density (i_d) at different values of $\sqrt{m}$ (m is the electrode rotation speed) in air- or oxygen-saturated solutions laying near a straight line that tended toward the origin when extrapolated (Fig. 3), i.e., the reduction of the oxygen was limited by diffusion.

The number of electrons (n) participating in the reduction of the oxygen, as calculated from the experimental data by Levich's formula for a rotating disc electrode [8, 9], † was 3.8 in the air-saturated solutions and 3.2 in the oxygen-saturated solutions. These results are similar to the data of other authors [7, 10].

The curves for the reduction of oxygen in alkaline solutions had the same form as in the acidic solutions, the only difference being that φ_{st} and the half-wave potentials were displaced in the negative direction (Fig. 4). The maximum reduction current at this value of m coincided with i_d for the acidic solutions (Table 2), since the solubility and diffusion coefficient of the oxygen in these solutions were similar.

Intermediate formation of hydrogen peroxide is possible during the reduction of oxygen. In order to investigate the reduction of H_2O_2 on the iron electrode, solutions with the aforementioned composition were first freed of oxygen, hydrogen peroxide was added, and its concentration was determined before and after the experiment. Figure 5 presents the results of these measurements. Analysis showed that the values of φ_{st} were approximately the same at roughly equal O_2 and H_2O_2 concentrations when the hydrodynamic conditions and solution acidities were the same:

* The correction for the decrease in acidity during the reduction of the oxygen was small in comparison with the concentrations of the solutions used and was therefore not taken into account.

† We assumed the following values for the calculation with Levich's formula: $D = 1.75 \cdot 10^{-5}$ cm^2/sec, $\nu = 10^{-2}$ cm^2/sec, and the oxygen concentration $c = 0.95 \cdot 10^{-6}$ moles/cm^3.

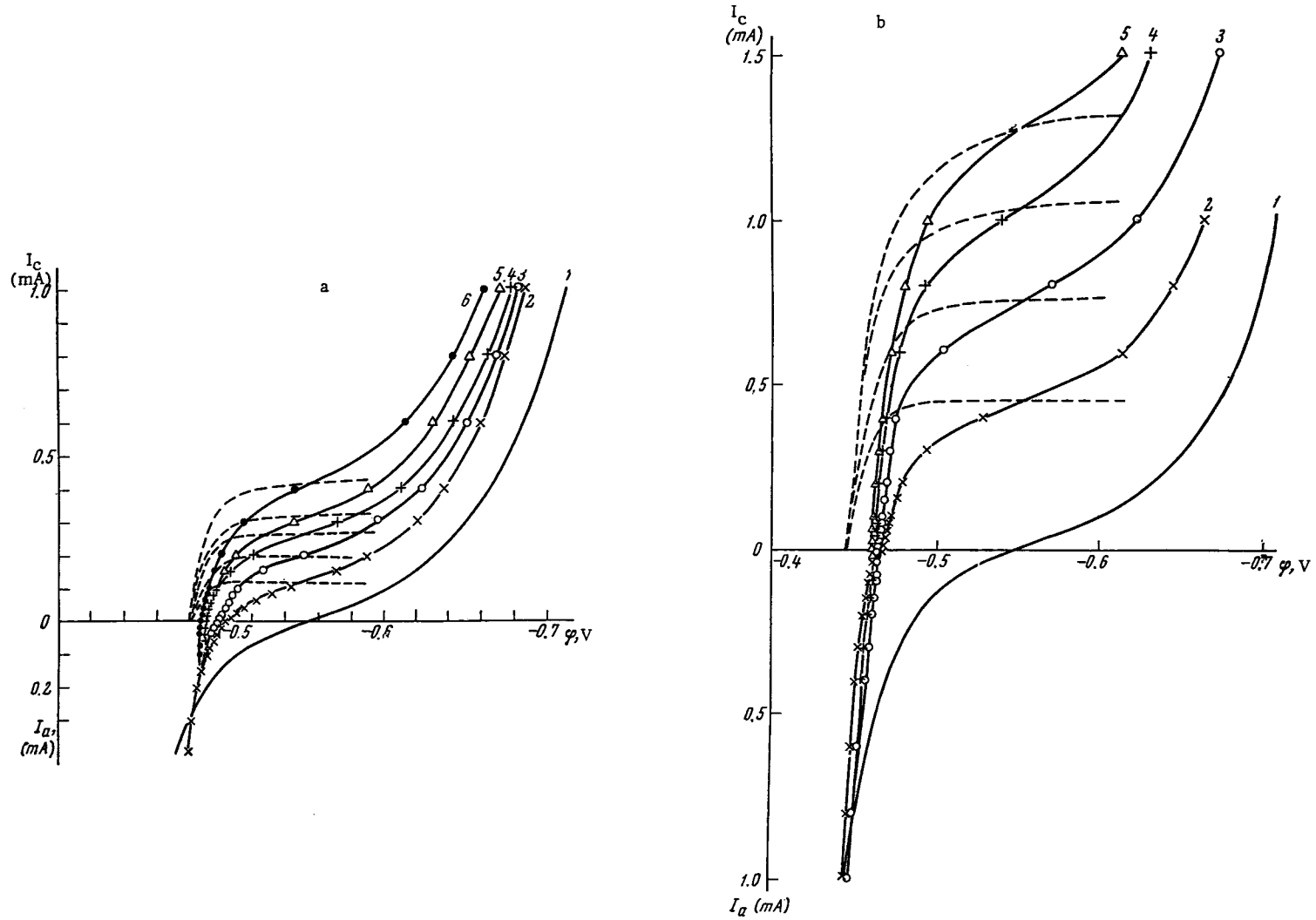

Fig. 2. Experimental (solid lines) and corrected (dash lines) cathodic polarization curves for Armco iron in solution containing 0.3 N H_2SO_4+0.7 N Na_2SO_4 saturated with air (a) and oxygen (b). Rotation speed: 2) 305 rpm; 3) 1150 rpm; 4) 2350 rpm; 5) 3430 rpm; 6) 7300 rpm.

m =		305	1150	2350	3430	7300 rpm
φ_{st} at	$[O_2] = 2.2 \cdot 10^{-4}$	−543	−502	−496	−487	−485
φ_{st} at	$[H_2O_2] = 5.5 \cdot 10^{-4}$	−550	−512	−496	−490	−484

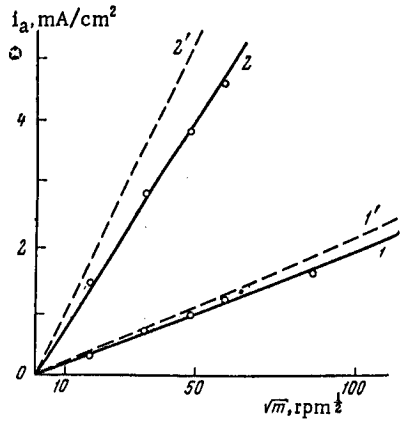

Fig. 3. Function i_d m in solution of 0.3 N H_2SO_4 + 0.7 N Na_2SO_4 saturated with air (1) and oxygen (2). 1' and 2') Calculated from Levich's formula at n = 4.

The dependence of i_d on $[H_2O_2]$ was linear and i_d was also found to be a linear function of $\sqrt{m}$ for different H_2O_2 concentrations. Reduction of the H_2O_2 on the oxidized iron thus obeyed the rules of diffusion kinetics, the O_2 and H_2O_2 reduction potentials at the same surface concentrations being similar. It is perhaps for precisely these reasons that we detected no separation of the overall reaction into individual stages in the oxygen-reduction curves.

The anodic polarization curves for the iron were identical when the H_2O_2 and O_2 concentrations were the same, all other conditions being equal.

DISCUSSION OF RESULTS

The reduction of oxygen to water on an iron electrode in acidic solutions involves the consumption of four electrons to form H_2O_2 as an intermediate product, by the reaction:

$$O_2 + 2H^+ + 2e \rightarrow H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O \qquad (1)$$

It is possible that the reduction of oxygen goes directly to water or that both these reactions occur simultaneously. The reduction of oxygen on an iron electrode in acidic solutions proceeds

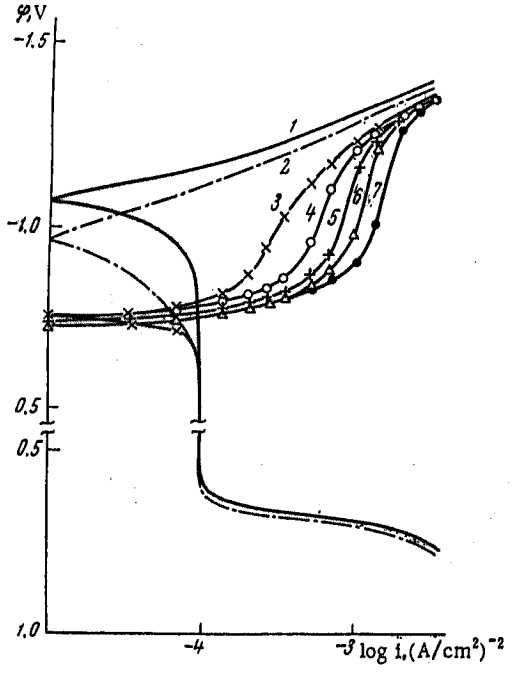

Fig. 4

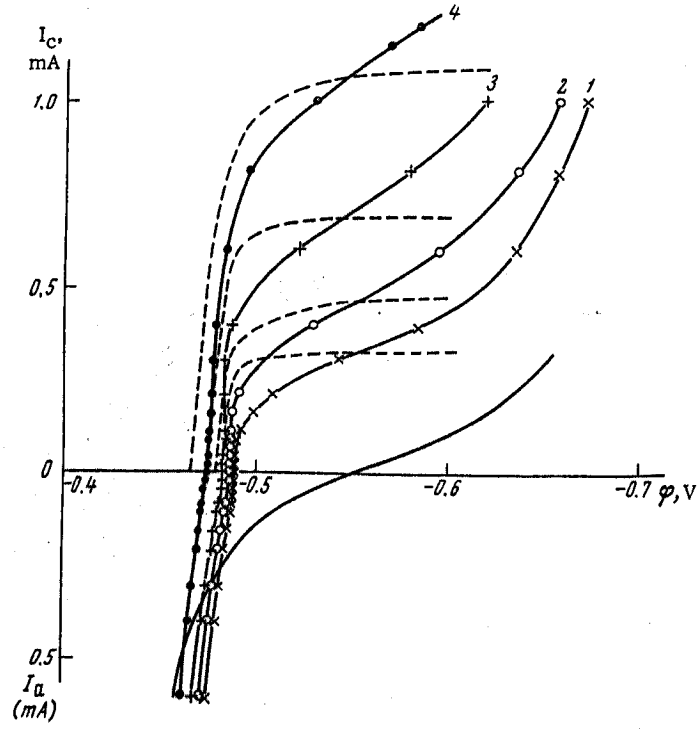

Fig. 5

Fig. 4. Cathodic and anodic polarization curves for zone-melted iron in solution of 0.1 N KOH + 0.9 N Na_2SO_4 saturated with hydrogen (1) and air (2–7). Rotation speed: 2) 0 rpm; 3) 305 rpm; 4) 1180 rpm; 5) 2400 rpm; 6) 3550 rpm; 7) 7600 rpm.

Fig. 5. Function, I, φ for Armco iron in solution containing 0.3 N H_2SO_4 + 0.7 N Na_2SO_4 + 0.003 M H_2O_2 at rotation speeds of: 1) 305 rpm; 2) 1150 rpm; 3) 2350 rpm; 4) 7300 rpm.

with a higher overvoltage than on mercury [9] or certain other metals [11]; the increase in the overvoltage of the reduction of H_2O_2 is smaller. It must be kept in mind that H_2O_2 is catalytically decomposed on an iron surface to liberate O_2, which is then again reduced in accordance with reaction (1). It is therefore probable that the H_2O_2 cannot be detected analytically in the solution.

As a result of the great affinity of iron for oxygen, reduction of the latter can also proceed through intermediate formation of chemosorbed oxygen by the reaction:

$$Fe + O_2 \rightarrow Fe(O_2)_{ads} \quad (2)$$

$$Fe(O_2)_{ads} + 4H^+ + 4e \rightarrow 2H_2O + Fe \quad (3)$$

Strengthening of the bond between the adsorbed oxygen molecules and the iron atoms weakens the bond between the atoms and the oxygen molecule, which facilitates reaction (3).

The fact that the process obeyed the rules of diffusion kinetics requires that the rate of the proposed reactions (2) and (3) exceed the rate at which oxygen reaches the electrode by diffusion. This condition is apparently satisfied at rather low rotation speeds. When m increases, the experimental data deviate from the straight line $i_d, \sqrt{m}$, which indicates the appearance of a kinetic limitation.

In alkaline solutions, the reduction of oxygen proceeds by the reaction:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \quad (1')$$

Reaction (3) is apparently somewhat inhibited by the stronger bonding between the oxygen and the iron in an alkaline solution.

The experimental data obtained in this work still do not enable us to make a quantitative evaluation of the extent to which each of the aforementioned stages participates in the reduction of oxygen on iron.

The anodic polarization curves obtained in the absence of dissolved oxygen have a linear segment with a slope of 60 mV, which is independent of the rotation speed. This indicates a kinetic limitation and shows that the Fe^{2+} ions produced during this reaction have a very small effect. When m increases in the presence of dissolved oxygen, the curves are displaced toward positive potentials and intersect one another (Fig. 1).

The slope of the anodic curves before the point of intersection is distorted by the oxygen reduction proceeding at commensurable rates.

The catalytic effect of the adsorbed OH^- ions becomes manifest at higher current densities [12-16].

In alkaline solutions, ionization of iron is possible only at low current densities and soon ceases, since the electrode is rapidly passivated in the presence of oxygen; as can be seen from Fig. 4, its potential shifts by about 1.5 V, to a value at which evolution of oxygen begins.

CONCLUSIONS

1. We have shown that the reduction rate of oxygen on a rotating iron disc electrode is governed by its diffusion rate to the surface. The number of electrons participating in this reaction is about four.

2. Reduction of hydrogen peroxide occurs at potentials close to those of the reduction of oxygen.

3. We have considered possible paths for the reduction of oxygen and the ionization of iron on a rotating disc electrode in oxygen-containing solutions.

LITERATURE CITED

1. A. I. Krasil'shchikov, Zh. Fiz. Khimii, 18, 537 (1944); 20, 1187 (1946).
2. N. D. Tomashov, Corrosion of Metals by Oxygen Depolarization [in Russian], Izd. AN SSSR, Moscow (1947).
3. L. A. Poluboyartseva, L. M. Anisimova, M. Sh. Blokh, and V. M. Novakovskii, Khim. Prom., 10, 782 (1963).
4. I. P. Anoshchenko, Transactions of the Novocherkassogo Polytechnical Institute [in Russian], 27/40 (1962).
5. A. Lee, Trans. Faraday Soc., 111, 13 (1964).
6. I. L. Rozenfel'd, Atmospheric Corrosion of Metals [in Russian], Izv. AN SSSR, Moscow (1950).

7. I. L. Rozenfel'd and O. I. Vashkov, Zashchita Metallov, 1, 70 (1965).
8. V. G. Levich, Zh. Fiz. Khimii, 18, 335 (1944); 22, 575 (1948).
9. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, and B. N. Kabanov, Kinetics of Electrode Processes [in Russian], Izd. MGU, Moscow (1952).
10. P. Delahay, J. Electrochem. Soc., 97, 205 (1950).
11. V. V. Sobol', E. I. Krushcheva, and V. A. Dogaeva, Elektrokhimiya, 1, 1002 (1965).
12. B. Kabanov, R. Burshtein, and A. Frumkin, Disc. Faraday Soc., 1, 259 (1947).
13. K. Heusler, Z. Elektrochem., 62, 582 (1958); 63, 492 (1958).
14. K. Heusler and G. Cartledge, J. Electrochem. Soc., 108, 732 (1961).
15. I. Om Bockris, D. Drazic, and A. Despic, Electrochem. Acta, 4, 325 (1961); 7, 293 (1962).
16. W. Lorenz and G. Eichkorn, Bericht Bunseng, 70, 99 (1966).