REACTION OF ELECTROCHEMICAL REDUCTION OF OXYGEN AS A PARTICULAR CASE OF THE REACTIONS OF ELECTROCHEMICAL REDUCTION

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A review article by A.I. Krasil'shchikov, "Electrochemical Ionization of Oxygen" was printed in Zashchita Metallov, No.6, 1965 [1].

The introductory part indicated: "At first it was considered that the effect of oxygen amounts only to oxidation of hydrogen atoms formed as a result of a discharge and their removal from the surface of the metal. Subsequently opinions on the reduction of oxygen and the evolution of hydrogen as two completely independent cathode processes began to be developed. Below we will see to what extent each of these points of view is correct" (p. 611). Further, on the basis of analyzing experimental investigations, the author [1] arrived at his own main opinion that the process of electrochemical reduction of oxygen occurs differently depending upon the cathode material. On cathodes of silver and mercury the delayed stage of reduction is the addition of an electron to the adsorbed oxygen molecule with the production of the molecular ion O_2^-, the further fate of which depends upon the acidity of the medium. Here adsorbed hydrogen atoms are not involved in the reaction at a single one of the stages of overall reduction. On the other hand, on cathodes of platinum and palladium the adsorbed atomic nitrogen is the reducing agent and the rate of its addition to the oxygen molecule determines the kinetics of the entire reaction.

I would like to call to the attention of the readers of this journal that these results follow, as a particular case, from the theory of electrochemical reduction formulated as long ago as in 1946-1954.* Actually, one of the initial premises of this theory is that owing to the different adsorption capacity of metals with respect to hydrogen, two extreme electrochemical groups of metals with a specific mechanism of reduction should exist. To one of them, arbitrarily called group I, were relegated Pt, Pd, and certain other metals with a low hydrogen overvoltage [3-4]. Metals of group I are characterized by a high adsorption capacity with respect to hydrogen atoms and an appreciable role of the stage of hydrogen removal in the kinetics of its cathodic formation. For such metals it was natural to assume the direct participation of hydrogen atoms in the process of electrochemical reduction as one of the pathways facilitating their removal from the surface of the cathode. To the other group, arbitrarily called group II of metals, were relegated mercury and zinc and also certain other metals with a high hydrogen overvoltage [3, 4]. A low adsorptivity of hydrogen and a limitation of the rate of its cathodic evolution by the discharge stage are characteristic for them. The reactions of electroreduction on metals of group II should therefore occur without the participation of atomic hydrogen. Electrons and (or) ions of hydrogen activated during discharge act as hydrogenizing agents here; their addition is the probable limiting stage [2, 3, 4].

It is not difficult to see that all the differences between the conclusions made in review [1] and in article [4] reduce to the fact that the arbitrary enumeration of the groups of metals proposed in [4] is replaced in [1] by the opposite.† The assertion that the kinetics of the reaction of electroreduction of oxygen should be treated as a particular case of processes of electrochemical reduction also follows from the identity of equations (1) and (4) in review [1] with equations (7), (9), and (20) of articles [2] and [3].

* I already pointed this fact out earlier both in print [2] and at the conference on electrochemistry at Novocherkassk in 1965 in connection with the report of A. I. Krasil'shchikov.

† It is completely incomprehensible why A. I. Krasil'shchikov, citing an extensive literature in his review, did not consider it possible and necessary to mention works in which an opinion he himself advocates is presented. This is all the more surprising since in the well-known monograph of A. N. Frumkin et al [5], which A. I. Krasil'shchikov repeatedly cites, the works of L. I. Antropov devoted to this problem (pp. 199-200 [5]) are mentioned; their presentation is also given in the review article of N. A. Izgaryshev and N. Ya. Fioshin [6].

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LITERATURE CITED

1. A. I. Krasil'shchikov, Zashchita metallov, 1, 11 (1965).
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3. L. I. Antropov, Transactions of the 2nd All-Union Conference on Theoretical and Applied Electrochemistry [in Russian], Kiev, Izd. AN UkSSR, 138, (1949).
4. L. I. Antropov, Zh. fiz. khimii, 24, 1428 (1950).
5. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, and B. N. Kabanov, Kinetics of Electrode Processes [in Russian], Izd. MGU (1952).
6. A. N. Izgaryshev and M. Ya. Fioshin, Uspekhi khimii, 25, 4(1956).

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 the first issue of this year.
