OXYGEN OVERVOLTAGE: DISCUSSION

Mechanism of Oxygen Liberation on Electrodes by B. N. Kabanov

A. M. Ginzberg. B. N. Kabanov reported on oxidation on a lead anode covered with lead dioxide. It seems to me that the conclusions would have been more convincing if the following experimental facts had been considered: When we have a system consisting of a metal on which there is a layer of oxides and also a double layer, then naturally the fall in potential in this system is realized not only due to the double layer, but also, to some extent, to the envelope of oxides. The structure of the oxides may be different and the prognosis will differ, depending on the system. This was demonstrated conclusively by the work of V. I. Veselovskii and his school on a whole series of subjects. In particular, work on lead was published in 1952 and quite a large amount of experimental material showed conclusively that the potential in the system $Pb-PbO_2$ or Pb–sulfuric acid is realized due to some transition boundary, including the double layer. Therefore, when an attempt is made to establish the discharge mechanism in this system, naturally this circumstance should be considered in some form or other.

The picture of oxygen liberation on lead is much more complex than on other metals, for example, on platinum (classical work of A. I. Shlygin, A. N. Frumkin et al.). In the case of lead, the oxides have some form of semiconductor character, as has been demonstrated by a series of works. The lead plus the oxide envelope participate in some way in an act occurring on the electrode. Thus, the process does not consist of a simple electron transfer or a simple discharge act, considered by the normal equations. To determine the phenomenon, it is necessary to consider the fall in potential which V. I. Veselovskii illustrated on other subjects in a simplified form. The work of V. I. Veselovskii should be continued more thoroughly to obtain new electrochemical data on semiconductors.

P. D. Lukovtsev. I would like to make a few comments on the mechanism of oxygen liberation in connection with the reports of V. I. Veselovskii, B. N. Kabanov, and T. Erdey-Gruz.

In a series of works it has been shown quite conclusively that at least at high anode polarizations, when the electrode surface is practically covered with a phase film of oxides, the limiting stage in the liberation of oxygen is the discharge of hydroxyl ions. However, there is some disagreement on the mechanism of this stage. Some authors consider that there is discharge of a hydroxyl ion with the formation of an OH radical while others consider that surface oxides participate in the first stage and the discharge proceeds in accordance with the following equation, for example:

$$MeO_2 + OH^- \rightarrow MeO(OH) + O_{ads} + e.$$

In the two cases, the kinetic equations for the relation of overvoltage to current strength and solution composition are the same, and this offers no possibility of clearly distinguishing between these two mechanisms.

It seems to me that a wide investigation of the relation of oxygen overvoltage to the nature of the cation would be of some value in solving this problem. In the report of T. Erdey-Gruz it was shown quite clearly that the cation has an effect on the oxygen overvoltage on platinum in an acid medium. The author explained this relation by the effect of different cations on the structure of the double layer due to differences in the radii of the cations. At the same time, in the liberation of oxygen in alkaline solutions, cations are found to affect the overvoltage in a reverse order. For example, in the work of T. Erdey-Gruz it was found that cations may be arranged in the following series in respect to their effect on the overvoltage: $K^+ > Na^+ > Li^+$. In the liberation of oxygen on nickel in alkali, these cations are arranged in the reverse order: $Li^+ > Na^+ > K^+$.

The effect of cations on oxygen overvoltage in alkaline solutions cannot be explained on the basis of ideas of the effect of cations on the structure of the electrical double layer. This effect is more likely to be connected with the effect of the cation on the strength of the bond of the oxygen in the oxide on which the liberation of oxygen occurs. Therefore, it seems to me that a wide investigation of the effect of the nature of the cation on the oxygen overvoltage would be profitable for determining which of the two given mechanisms represents the first stage of oxygen liberation.

I would like to consider the problem raised by A. M. Ginzberg. I agree completely that it is necessary to consider the semiconductor properties of oxides in explaining the mechanism of reactions occurring on these oxides. It is precisely a consideration of the semiconductor properties which makes it possible to explain a series of phenomena occurring on oxide electrodes of chemical current sources. However, A. M. Ginzberg's comment on the mechanism of oxygen liberation on lead dioxide, whose conductivity is higher than that of mercury, has no value as here the considerations of some other distribution of electrons in the layer adjacent to the electrode would hardly contribute anything. It would be another matter if we considered the semiconductor properties of lead dioxide not from the point of view of its conductivity and the distribution of electrons in the surface layer, but, for example, from the point of view of the effect of various cations on the rate of oxygen diffusion in the oxides. Consideration of the semiconductor properties would be profitable in this case. In particular, the effect of cobalt on oxygen overvoltage on lead dioxide may be explained on the basis of these ideas.