INVESTIGATION OF THE LEAD DIOXIDE ELECTRODE WITH RESPECT TO POTENTIAL DROP AND OXYGEN EVOLUTION

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The present work was undertaken for the purpose of studying the processes taking place at a lead dioxide electrode subjected to high positive potentials. Being a higher oxide of lead, this electrode does not give rise to a series of difficulties which are associated with the study of oxygen evolution when the electrode material is a metal. Moreover, the lead dioxide electrode is an electronic conductor with a double layer whose properties are similar to those of the double layers of metallic electrodes [1].

A study of the release of oxygen at anode-polarized lead dioxide has revealed [1] that the rate of oxygen release depends on the structure of the double layer (as evident from its abrupt change with alternation of the sign of the surface charge and of the φ_1 value of the potential), and consequently that the rate-determining step in oxygen release at lead dioxide is the discharge.

We studied the process of oxygen evolution and of potential drop after cessation of anodic polarization on coated electrodes possessing a large true surface which permitted volumetric determination of oxygen simultaneously with measurements of the potential. The well-charged coated electrode was placed in a glass vessel containing sulfuric acid solution which was covered with a bell glass. Fitted through the latter by a ground-glass connection was a microburet for determination of the quantity of oxygen released; an electrolytic switch connected to a mercurous sulfate half-cell, was placed in close contact with the electrode under the bell glass. The cell was immersed in a water thermostat. Measurements of the potential and of the volume of evolved oxygen were carried out at intervals after anodic polarization of this electrode.

Typical plots of oxygen release and electrode potential versus time after cessation of anodic polarization are shown in Fig. 1. The potential falls steeply, but the rate of increase of volume of oxygen falls off gradually with time. At a certain instant the potential becomes steady, but the speed of oxygen release continues to fall and finally becomes constant.

A linear relation was found to exist (Fig. 2) during the first ten hours between the quantity of oxygen released after cutting out the current v_k and the magnitude of the potential drop $\Delta\varphi$. The experimental values were substituted in A. N. Frumkin's formula for potential drop:

$$\Delta\varphi = \varphi_0 - \varphi_t = b\lg\left(\frac{tI_0}{Cb}\cdot 2{,}3 + 1\right),$$

where φ_0 = electrode potential before cutting-out of current, φ_t = electrode potential after a period of time t after cutting out of current, b = a constant, C = total capacitance calculated from the ratio $C = v_k/\Delta\varphi$, I_0 = = strength of the anodic current.

The plot of $\Delta\varphi$ versus $\log\left(\frac{tI_0}{Cb}\cdot 2.3 + 1\right)$ is a curve with two rectilinear stretches whose slope coefficients are 0.1 and 0.14 (Fig. 3). In substantial agreement with published data [1, 2] the transition from one straight-line portion to the other occurs at a potential of 1.9 V, which is in the region close to the zero-charge potential of lead dioxide determined for the given concentration by the method of P. A. Rebinder on the basis of the hardness of the electrode [3].

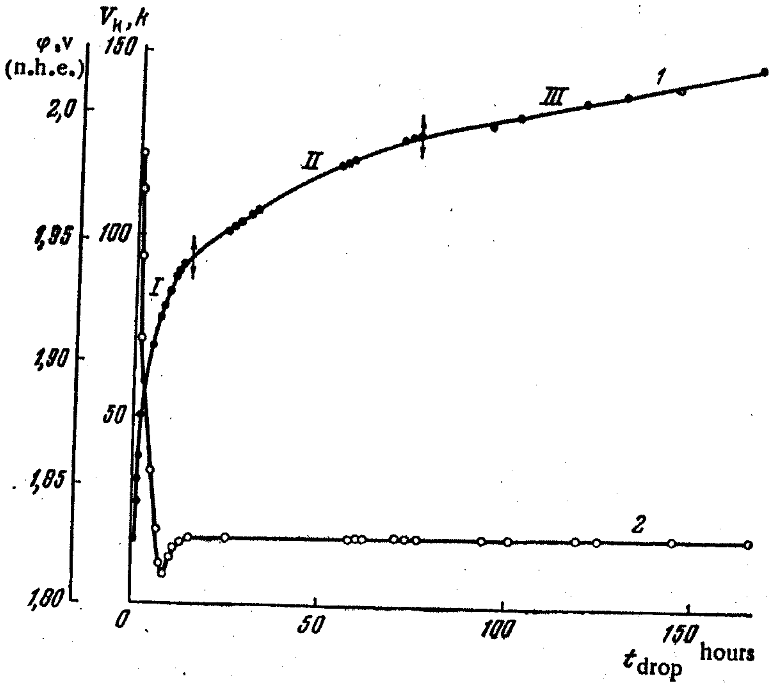

Fig. 1. Volume of oxygen (1) and potential of the plate electrode (2) after anodic polarization for t hr. Current strength $1.3 \cdot 10^{-3}$ a/cm^2 of visible surface. Temp. 20°. n.h.e. = normal hydrogen electrode.

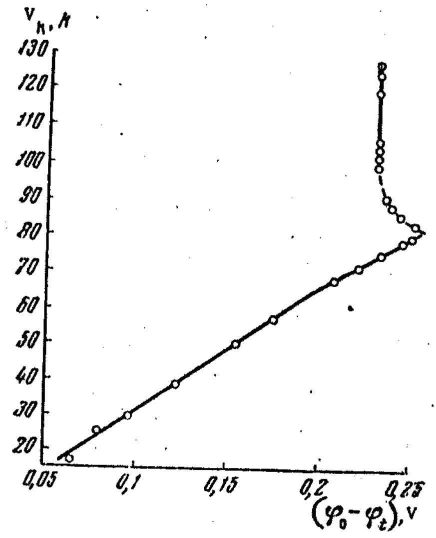

Fig. 2. Relation between potential drop and quantity of oxygen released.

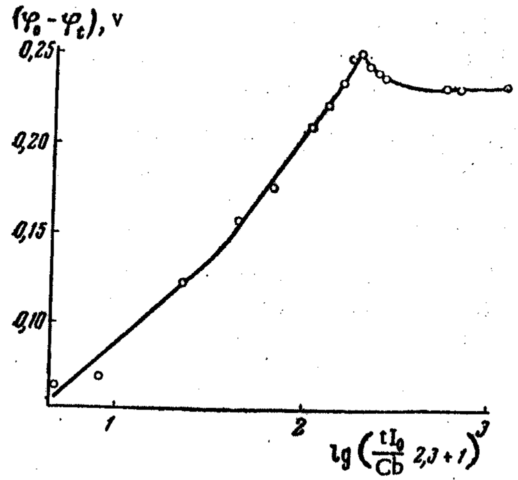

Fig. 3. Relation between potential drop and quantity of oxygen evolved log $\left(\frac{tI_0}{Cb} \cdot 2.3 + 1\right)$

The differential capacitance was determined with the help of data obtained by B. N. Kabanov for the ratio of the visible and true surfaces of a coated electrode by comparison of the overvoltage curves of hard and smooth electrodes. In this manner we obtained a capacitance of the order of 200 μ F/cm^2 on the assumption of a smooth surface.* At such potentials this means that there is no considerable adsorption and desorption of

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*I. G. Kiselev [2], using the variable-current method in less concentrated solutions, obtained similar capacitance values for a smooth electrode of PbO_2 deposited on gold.

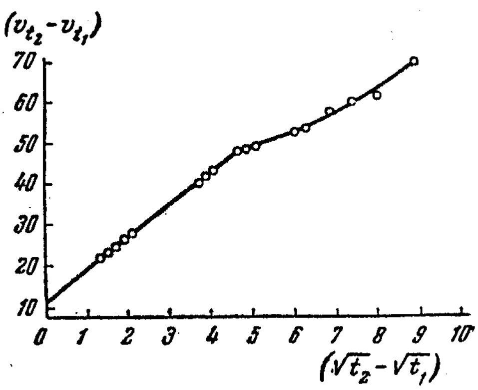

Fig. 4. Relation between ($v_{t_2} - v_{t_1}$) and ($\sqrt{t_2} - \sqrt{t_1}$).

oxygen on lead dioxide, since otherwise the capacitance of 1 cm^2 would have reached a value of thousands of microfarads. The slight increase in capacitance over the usual values for a double layer of smooth, hard electrode with negative charges of the double layer (40-60 $\mu F/cm^2$) may be due to deformation of the anions in presence of the positive charge on the double layer under our conditions.

Consequently, the oxygen released during the period of potential drop is mainly formed as the result of discharge of the ionic portion of the double layer. Due to the high oxygen overvoltage, the discharge of the double layer proceeds with sufficient slowness to enable measurements without the use of rapid methods. According to our results, the self-discharge of the double layer proceeds in the course of several days at low temperature (−20°).

As we see from portion II of the curve in Fig. 1, the attainment of constant potential was followed by a period of 50 hours during which oxygen was evolved at a gradually reducing rate. In order to explain the origin of this oxygen, it was assumed that during anodic polarization a part of the oxygen succeeds in diffusing into the lead dioxide grid. When the current is switched off, this oxygen diffuses in the opposite direction.

If this assumption is correct, then the evolution of oxygen (portion II, Fig. 1) should approximately obey the known equation for unsteady diffusion. In the present case the equation will have the following form:

$$v_{t_2} - v_{t_1} = \int_{t_1}^{t_2} \frac{\partial v_k \partial t}{\partial t} = \frac{\sqrt{D}C^\circ}{\sqrt{\pi}} \int_{t_1}^{t_2} \frac{dt}{\sqrt{t}} = \frac{\sqrt{D}\cdot C^\circ}{2\sqrt{\pi}} (\sqrt{t_2} - \sqrt{t_1}).$$

where $\frac{\sqrt{DC^\circ}}{2\sqrt{\pi}}$ = a constant, t_1 = instant of commencement of the second period (constancy of φ), t_2 = time elapsed from instant of current switch-on, ($v_{t_2} - v_{t_1}$) = quantity of oxygen (expressed in coulombs) evolved in time $t_2 - t_1$. Since t_1 is a constant, while t_2 increases with the time of sampling, the quantity of oxygen released ($v_{t_2} - v_{t_1}$) must be directly proportional to ($\sqrt{t_2} - \sqrt{t_1}$). We see from Fig. 4 that up to a certain instant there is indeed a straight-line relation between ($v_{t_2} - v_{t_1}$) and ($\sqrt{t_2} - \sqrt{t_1}$). After this instant, $\underline{v}$ becomes a linear function of $\underline{t}$ (portion III of the curve in Fig. 1) due to spontaneous dissolution of lead dioxide in sulfuric acid. As had been expected, the slope of this portion increases with rising temperature and concentration of acid.

In order to show that oxygen diffuses from the PbO_2 grid and not from the solution filling the pores of the electrode, the conditions of the preliminary anodic polarization were altered. The following results were obtained. With increasing duration of the preliminary anodic polarization of the electrode in 9.6 N H_2SO_4 from 6 to 60 hr at a current density of $1.3 \cdot 10^{-3}$ a/cm^2 of visible surface, the quantity of oxygen diffusing from the electrode* increases 2.15 times. Calculation shows that even with the establishment of 100-fold oxygen supersaturation of the solution filling the pores of the electrode, less than 1 hr would be needed for the preliminary anodic polarization. Hence, the change in the period of preliminary polarization from 6 to 60 hr should not have influenced the volume of oxygen released at constant oxygen potential if this oxygen had been released from solution present in the pores of the electrode.

The oxygen-evolution overvoltage decreases when the temperature rises from 25 to 50°; at the same time the potential drop is accelerated and the diffused oxygen is easily detected after constancy of the potential has been established. Its quantity (other conditions being unchanged) rises with the temperature of preliminary polarization from 25 to 50° by a factor of 1.83. The increase in the quantity of oxygen with the temperature at which preliminary anodic polarization is effected may be explained on the assumption that it diffuses from the lead dioxide grid. Indeed, with rising temperature the rate of diffusion of oxygen into the interior of the

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*i.e., the oxygen release at constant potential follows the law of unsteady diffusion.

lead dioxide grid increases, so that its quantity diffusing from the lead dioxide grid when the duration of preliminary polarization is limited must likewise increase. Since with rising temperature the excess of oxygen in aqueous solution will decrease,due to the reduced solubility of the gas and the decreased supersaturation, its quantity discharged from the pores should also decrease. Calculation shows that when the temperature rises from 25 to 50°, the quantity of oxygen released ought to decrease, due only to the lowering of solubility, by a factor of 1.35. Hence the experiment contradicts the hypothesis that the released oxygen diffuses from the solution filling the pores of the electrode.

When experiments were carried out with different current densities during the preliminary polarization, the electrode was polarized in such periods of time as to give the same quantity of electricity in each case. The quantities of "diffused" oxygen, measured in experiments with different current densities during preliminary polarization, are similar in magnitude. Consequently,at a higher polarizing current density the oxygen diffuses with proportionately higher speed into the lead dioxide grid. This is only possible if the formation of oxygen molecules is not an instantaneous process but is slow, although it is many times faster than the discharge of oxygen from a molecule of water.

It should be noted that the results obtained are consistent with the theory previously enunciated by B. N. Kabanov about the mechanism of corrosion of the grid of the positive plate of a lead accumulator at high positive potentials. They are also in accord with the results of E. V. Krivolapova's investigation [4] of the corrosion of lead under these conditions.

According to B. N. Kabanov, corrosion under these conditions is caused by the oxygen diffusing across the layer of lead dioxide to the lead. Corrosion of the grid is indeed reduced by factors that hinder penetration of oxygen to the lead dioxide. Addition of cobalt sulfate to the solution has this effect. In our experiments we investigated the influence of addition of 0.05, 0.2 and 0.5% cobalt sulfate to 9.6 N H_2SO_4 at +25° and a current density of $1.3 \cdot 10^{-3}$ a/cm^2 of visible surface. During experiments with introduction of 0.2 and 0.5% cobalt sulfate, in order to exclude accumulation of oxygen formed at the expense of reduction of Co^{3+} Co^{2+} within the solution, the previously anodically polarized electrode was put into a container with sulfuric acid free of cobalt sulfate. The experiments showed that addition of cobalt sulfate sharply reduces the quantity of "diffused" oxygen. Factors that intensify the penetration of oxygen to the lead dioxide promote corrosion. Such factors are increased temperature,and increased duration and current density of the preliminary polarization. It is interesting to note that E. V. Krivolapova's data [4] indicate an increase in the corrosion of lead by a factor of 1.78 on rise of temperature from 25 to 50°, while our own data in the same temperature interval show that the quantity of oxygen succeeding in diffusing into the PbO_2 grid increases by a factor of 1.83.

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*Original Russian pagination. See C. B. Translation.