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Abstract

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ON THE FORMATION AND ELECTROCHEMICAL PROPERTIES OF CRYSTALLINE MODIFICATIONS OF LEAD DIOXIDE

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The phenomenon of polymorphism in the case of lead dioxide has been described in a number of works ([1–5]). It has been established that PbO_2 exists in two modifications: tetragonal (β-form) and rhombic (α-form). The occurrence of one or the other modification of lead dioxide depends on the conditions under which it is obtained. Thus, the α-form is obtained by anodic deposition from neutral or alkaline solutions of lead salts, by oxidation of $PbSO_4$ in dilute H_2SO_4 solutions, and by transformation from the β-form under pressure; the β-form—by oxidation of $PbSO_4$ in concentrated H_2SO_4 solutions.

Analysis of the available data shows that the conditions for obtaining the α- or β-form at normal pressure differ, in essence, in whether the formation of PbO_2 proceeds in the presence or in the absence of H_2SO_4. It could therefore be assumed that the production of different crystalline forms is connected with the adsorption of sulfuric acid, which, as was shown earlier, is retained on PbO_2 very strongly and in large amounts ([6]).

To confirm this assumption, we carried out comparative measurements of the adsorption capacity and an investigation of the structure of electrodes made of PbO_2 obtained under various conditions. The results are given in Table 1. The adsorption measurements were performed by a radiochemical method, by measuring the activity of the electrodes; the structure was investigated by the X-ray diffraction method*. The initial PbO_2 electrodes were obtained in the form of a smooth deposit on gold from a 15% solution of $Pb(NO_3)_2$ at a current density of $2 \cdot 10^{-4}$ A/cm^2.

In accordance with the literature data, the deposits obtained by us from a neutral solution or by oxidation of $PbSO_4$ in $0.01\,N$ H_2SO_4 consisted mainly of α-PbO_2. As a result of electrochemical recrystallization of the electrode in $8\,N$ H_2SO_4—namely, cathodic reduction to $PbSO_4$ followed by anodic oxidation to PbO_2—irreversible adsorption of H_2SO_4 on PbO_2 and transformation of α-PbO_2 into β-PbO_2 occur**. The magnitude of adsorption in $8\,N$ H_2SO_4 is from $6 \cdot 10^{-8}$ to $40 \cdot 10^{-8}$ M/cm^2, depending on the thickness of the PbO_2 layer. Adsorbed H_2SO_4 can be removed from the PbO_2 deposit by displacing

it from the electrode with adsorbing cobalt ([6]). An X-ray structural analysis was carried out on lead dioxide which, after its deposition from 8 N H_2SO_4, was anodically polarized for 10-15 hours in a solution of 8 N H_2SO_4 + 5% $CoSO_4$. It turned out that desorption of H_2SO_4 is accompanied by the transformation of β-PbO_2 into α-PbO_2.

With regard to the nature of the adsorption of H_2SO_4 on PbO_2, one may make the assump–

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* We express our deep gratitude to Z. V. Semenova for carrying out the X-ray structural analysis of the lead dioxide samples.

** It should be noted that, in pure form, neither of the modifications is obtained under these conditions. In all cases we had a mixture of both crystalline forms, but from a neutral solution a deposit was formed consisting mainly of the α-form, and from an acid solution–of the β-form. These deposits we conventionally call, respectively, α-PbO_2 and β-PbO_2.

position, that the absorption of H_2SO_4 occurs in the bulk of the electrode at the intercrystalline surface. This is evidenced by the large magnitude of adsorption and by its dependence on the thickness of the PbO_2 layer (Table 1). In addition,

Table 1

PbO_2 from solution	Form of PbO_2	Thickness of PbO_2 layer, in μ	Adsorption of H_2SO_4 in moles, M/cm^2 on apparent surface	Adsorption of H_2SO_4 in moles, M/cm^3	Adsorption of H_2SO_4 in moles, M/cm^2 on intercrystalline surface
$Pb(NO_3)_2$	α	2–30	–	–	–
0.01 N H_2SO_4	α	20	$0.0_1 \cdot 10^{-8}$	–	–
8 N H_2SO_4	β	2	$6 \cdot 10^{-8}$	$3 \cdot 10^{-4}$	$3 \cdot 10^{-11}$
8 N H_2SO_4	β	20	$40 \cdot 10^{-8}$	$2 \cdot 10^{-4}$	$2 \cdot 10^{-11}$
8 N H_2SO_4 + $CoSO_4$	$\beta \rightarrow \alpha$	Pasted electrode	Desorption (6)	Desorption (6)	Desorption (6)

it has been established that appreciable irreversible adsorption occurs only in the process of formation of PbO_2 from $PbSO_4$, and is not observed during prolonged anodic polarization of PbO_2 in H_2SO_4*. This apparently means that

Figure 1

Figure 1: Figure 1

sulfuric acid is adsorbed not on the finished precipitate of lead dioxide, but in the course of its formation**. It is interesting to note that in 8 N H_2SO_4 the PbO_2 crystals obtained are 100 times smaller (in linear dimensions) than in $Pb(NO_3)_2$ solutions or 0.01 N H_2SO_4. This can be explained by the known phenomenon of hindered crystal growth due to chemisorption.

It is known that, with a change in crystalline modification, a number of properties of a substance change. In this connection it was of interest to compare the electrochemical behavior of α- and β-PbO_2. For this purpose, on smooth electrodes made of PbO_2 of the tetragonal and rhombic modifications, the rates of anodic formation of PbO_2 from $PbSO_4$ and of cathodic reduction of PbO_2 were measured. The rate of these reactions was measured by recording overvoltage curves in 8 N H_2SO_4. To measure the overvoltage, the electrode was partially discharged, i.e., part of the PbO_2 was converted into $PbSO_4$. The curves representing the dependence φ—lg i for two different modifications of PbO_2 are shown in Fig. 1***. The anodic curves, taken rapidly and at low current densities, as well as the cathodic curves, run parallel to one another with a displacement of 30—40 mV. The exchange current on both modifications is almost the same. The course of the curves is determined by deviations of the magnitude of the con—

Fig. 1. Overvoltage curves. 1 and 1a —α-PbO_2 from $Pb(NO_3)_2$ solution; 2 and 2a —β-PbO_2 from 8 N H_2SO_4; 3 —α-PbO_2 from 8 N H_2SO_4 + 5% $CoSO_4$

* In the presence of $CoSO_4$ in solution, a change in crystalline modification and adsorption of H_2SO_4 during continuous anodic polarization may be explained by recrystallization proceeding according to the scheme β-PbO_2 → $PbSO_4$ → α-PbO_2. This process is accelerated in the presence of $CoSO_4$ because of the lowering of the oxygen overvoltage and, consequently, the approach of the electrode potential to the equilibrium value. It is also possible that the principal role is played by the preferential reduction of β-PbO_2, occurring at the expense of oxygen evolution.

** The absorption of H_2SO_4 cannot be explained by the formation of a stoichiometric compound of H_2SO_4 with PbO_2 (7), since in that case the amount of H_2SO_4 absorbed should have been two orders of magnitude greater than in the experiment.

*** All curves were recorded on the same electrode in the order of their numbering.

concentration of $PbSO_4$ at the electrode surface on the value of the saturation concentration. However, on α-PbO_2, in the region of current densities 10^{-6} $-3 \cdot 10^{-6}$ A/cm^2, the overvoltage of the anodic process at one and the same

Fig. 2. Reduction of PbO_2 (discharge curves). 1 –25% β-PbO_2, 2 –50% β-PbO_2, 3 –75% β-PbO_2

Figure 2: Fig. 2. Reduction of PbO_2 (discharge curves). 1 –25% β-PbO_2, 2 –50% β-PbO_2, 3 –75% β-PbO_2

current density increases with time, rising by approximately 80 mV. Therefore the curve, taken comparatively slowly (over 3-4 hours), has an anomalous form (Fig. 1, 1), and when the measurements are carried out in the reverse order, from higher current densities to lower ones, hysteresis is observed (dotted line, curve 1b). After anodic polarization of PbO_2 for 10-15 hours in 8 N H_2SO_4 + $CoSO_4$, during which desorption of H_2SO_4 occurs and β-PbO_2 is transformed into α-PbO_2, the oxidation of $PbSO_4$ proves to be retarded, and the overvoltage curve (Fig. 1, 3) runs almost the same as on α-PbO_2 obtained from a neutral solution.

The retardation of the oxidation process of $PbSO_4$ on α-PbO_2 in 8 N H_2SO_4 is probably connected with the hindrance of the electrocrystallization process ([9]), which

Fig. 2. Reduction of PbO_2 (discharge curves). **1** –25% β-PbO_2, **2** –50% β-PbO_2, **3** –75% β-PbO_2

can be explained by adsorption of H_2SO_4. It is known that anodic oxidation of Pb^{2+} ions in 8 N H_2SO_4 leads to the formation of β-PbO_2. If the electrode is PbO_2 of the same modification, the electrocrystallization process proceeds easily, since growth of the existing crystal lattice continues ([10]). In the case of an electrode of α-PbO_2, however, on which H_2SO_4 has not yet had time to be adsorbed, a deposit of α-PbO_2 is readily formed at the active sites. Gradually the number of active sites decreases, probably because of the specific adsorption of H_2SO_4 (which occurs slowly), as a result of which the deposition of α-PbO_2 gradually ceases. After this, already at an increased overvoltage, only β-PbO_2 can form. In this case the increase in overvoltage is due not only to the formation on the surface of a deposit that is foreign with respect to the PbO_2 being formed, but also to the adsorption of sulfuric acid on this surface. Therefore, after the first portions of the deposit have been obtained, the rate of the process does not increase, as would be expected. Apparently, the increase in potential attained promotes very strong specific adsorption of H_2SO_4, which hinders the growth of the forming PbO_2 nuclei, and the process continues to proceed at a retarded rate.

Judging from curves 1a and 2a (Fig. 1), at a given potential the reduction of α-PbO_2 proceeds at an incomparably lower rate than that of β-PbO_2. Accordingly, during discharge of an electrode consisting of a mixture of both modifications of PbO_2, two plateaus appear on the discharge potential–time curve, differing in potential by approximately 30 mV (Fig. 2). The starting material for obtaining such electrodes was α-PbO_2 deposited from a neutral solution of $Pb(NO_3)_2$,

or from 0.01 N H_2SO_4. By partial reduction of PbO_2 followed by oxidation of the $PbSO_4$ formed in 8 N H_2SO_4, the corresponding part of α-PbO_2 was transformed into β-PbO_2. The length of the first plateau is determined by the amount of β-PbO_2. In the case of curves 1, 2, and 3 in Fig. 2, the partial preliminary discharge of α-PbO_2 amounted, respectively, to 25, 50, and 75% of the capacity.

A similar phenomenon was observed in the experiments of Ruetschi and Cahan (*4*). However, the authors were inclined to explain it both by a difference in the discharge potentials of α-PbO_2 and β-PbO_2, and by passivation phenomena. Burbank (*5*) concluded that the discharge of α-PbO_2 is slowed on the basis of the experimental fact that, in the corrosion products of lead covered with a mixture of α-PbO_2 and β-PbO_2, α-PbO_2 is found along with $PbSO_4$.

Thus, the investigation carried out permits one to consider that the cause of the slowing of the process $PbO_2 \rightarrow PbSO_4$, as well as of the formation of the β-form, is the chemical adsorption of sulfuric acid on the surface of PbO_2. The influence of H_2SO_4 adsorption on the rate of another anodic process on PbO_2 (oxygen evolution) had already been established earlier (*8*).

In conclusion it should be noted that further study of the conditions for the appearance of various modifications of lead dioxide and of their properties is of practical interest. Thus, using deposits of lead dioxide on gold as an example, we observed a considerable difference in mechanical strength between deposits of α-PbO_2 and β-PbO_2. In addition, it is known that the hardness of PbO_2 from 8 N H_2SO_4 is less than that of PbO_2 from 0.1 N H_2SO_4 (*11*). Consequently, it is possible that the so-called "creep" of the active mass of the positive electrode in a lead storage battery is connected with a decrease in strength due to the transformation of α-PbO_2 into β-PbO_2 during cycling (*3*).

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