ANODE CORROSION OF LEAD IN SULFURIC ACID

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Many studies have recently appeared [1-10] on the investigation of the anode oxidation of lead in solutions of sulfuric acid. They give evidence of considerable successes in the study of the composition and structure of anode films; however, we still have very little information on the mechanism of their formation. In this work an attempt is made to elucidate the picture of the growth of anode oxide films on lead by a combination of electrochemical and structural methods of investigation.

We investigated films formed on smooth lead electrodes (visible surface 6 cm^2) during anode polarization by a current of 2 mA/cm^2. The polarizations lasted for 3, 24, and 48 h. The investigations were conducted in 2, 8, and 10.4 N solutions of H_2SO_4 at 25 and 65°. In addition, we investigated films formed in 44 h at a temperature of 30° in 2 N and 10.4 N solutions of H_2SO_4 with an addition of $CoSO_4$. The amount of corrosion products was determined by cathode reduction in a 1 N acidified solution of Na_2SO_4 [1]. Accuracy of the determination 3-5%. The composition of the anode films was determined by the x-ray method; the structure of the films was studied with an electron microscope, using carbon replicas.

In all the investigated cases, dense anode films are formed during the first few hours. X-ray difraction studies showed that these films consisted mainly of tetragonal lead oxide PbO_t. On the x-ray pictures of films obtained in 2 N H_2SO_4, in addition, a small admixture of β-PbO_2 is noticeable.

As the duration of the anode polarization is increased, the growth of the film in thickness is accompanied by changes in its structure. The nature of these changes is the same at the temperatures 25 and 65°. The changes are expressed macroscopically in the appearance of a porous outer layer. It is easily removed mechanically using a moist wad, and thus the porous and dense layers can be investigated individually. The method of electrochemical reduction showed that the thickness both of the porous and of the dense layers increases during the process of further polarization.

After 48 h of polarization, the amount of lead dioxide becomes approximately the same in the porous and dense layers in all the solutions we investigated. In all cases the dense layer consists of the oxide PbO_t, sometimes with a small admixture of α-PbO_2. The porous layer, obtained in 2 N H_2SO_4 at 25°, consists of fine, irregularly shaped crystals (Fig. 1a)* while that obtained at 65° consists of coarser, well formed crystals (Fig. 1b). X-ray diffraction studies showed that in both cases this ia a mixture of the α- and β-modifications of lead dioxide (in accord with the data of [5]). At 65° the relative amount of the β-modification in this layer is approximately twice as great as at 25°.

In 8 N and 10.4 N H_2SO_4, both at 25° and at 65°, the porous layer consists of fine crystals (Figs. 1c and 1d). X-ray diffraction studies showed that this is α-PbO_2, with only a small admixture of β-PbO_2, the β-PbO_2 content decreasing still more when the H_2SO_4 concentration is increased from 8 N to 10.4 N. No important dependence of the structure and composition of the porous layer on the temperature was detected in the corrosion of lead in 8 N and 10.4 N H_2SO_4. Qualitatively analogous results were obtained on the films obtained at 30° in 2 N and 10.4 N solutions of H_2SO_4 with an addition of $CoSO_4$: with increasing acid concentration, the amount of β-PbO_2 in the porous layer decreases. The thickness both of the porous and of the dense layers is considerably less in this case for films obtained under analogous conditions without an addition of cobalt sulfate. This is a confirmation of the

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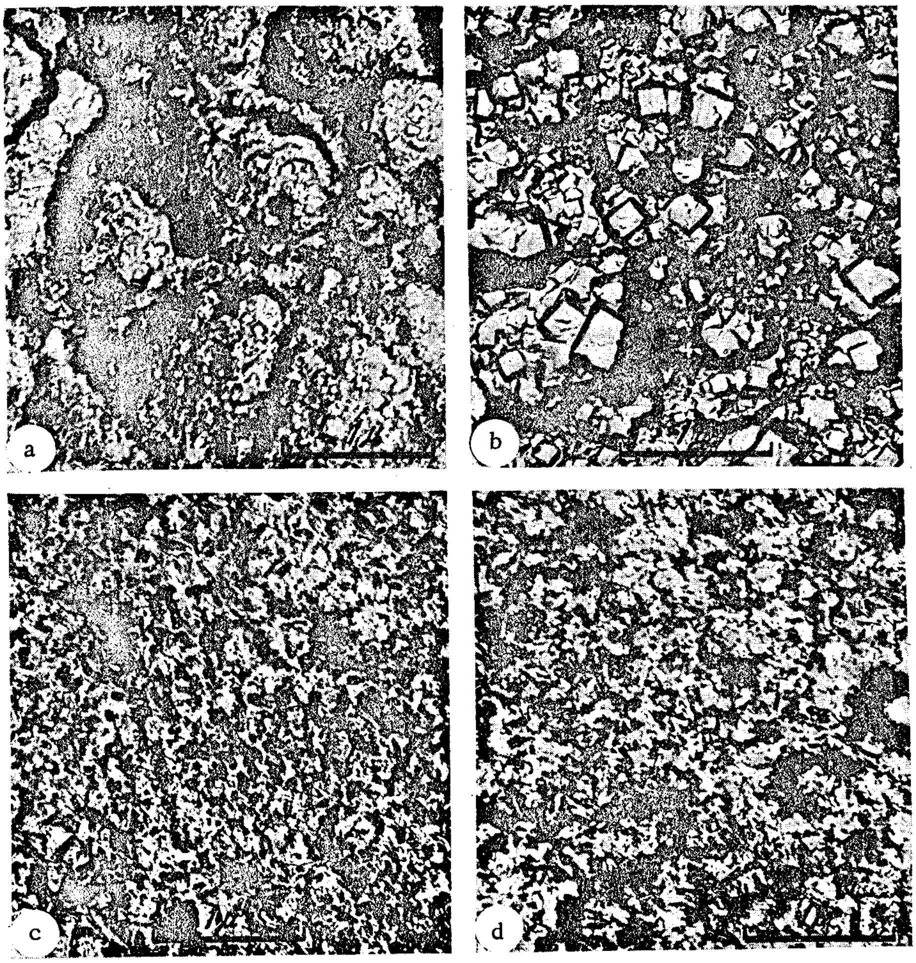
* The length of the line on the photograph corresponds to 1 μ.



Carbon replicas from the surfaces of electrodes polarized for 24 h in 2 N H_2SO_4 (a, b) and in 10.4 N H_2SO_4 (c, d) at 25° (a, c) and at 65° (b, d).

conclusion [1] that the presence of $CoSO_4$ reduces the corrosion of lead on account of an increase in its ability to become passivated.

It is known [11, 8, 3, 5] that α-PbO_2 is formed in the anode oxidation of divalent lead in neutral and alkaline solutions, in a 0.01 N solution of H_2SO_4, and in an 8 N solution of H_2SO_4 in the presence of $CoSO_4$.* The formation of α-PbO_2 in weakly acid solutions, detected in the formation of porous accumulator plates, is explained in the literature by the creation of a weakly alkaline medium on account of the presence of PbO within the electrode [12]. α-PbO_2 can also be obtained from β-PbO_2 by heating and under pressure [8]. In strong H_2SO_4 solutions, in the absence of additives, β-PbO_2 is always obtained in the anode oxidation of lead sulfate at equilibrium potentials of the system $PbSO_4/PbO_2$. Consequently, the formation of α-PbO_2 in the dense and porous layers, which we observed on smooth lead anodes in pure 2, 8, and 10.4 N solutions of H_2SO_4, cannot be explained on the basis of the assumption that the dioxide is formed by electrochemical oxidation of lead sulfate. In [1, 2], another possible mechanism of the formation of lead dioxide was proposed – on account of a solid phase reaction between lead and oxygen.† In [7], it was shown that the crystal lattice of tetragonal PbO_t and α-PbO_2 can be obtained from the lattice of lead by successive introduction of oxygen atoms into it. Hence it is quite natural that precisely α-PbO_2 is formed when a reaction occurs between oxygen and lead in the solid phase.

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* We should mention that the authors of [3] did not obtain 1 modification of PbO_2 in pure form. A mixture precipitated from the neutral solution, mainly consisting of the α-form, while a mixture consisting mainly of the β-form precipitated from highly acid solution.

† The same corrosion mechanism of lead was also arrived at in [8], but then this viewpoint was renounced [18].

The following picture of the changes occurring during the growth of anode films during prolonged anode polarization of lead in H_2SO_4 solutions arises from the experimental results we obtained. The films grow on account of the interaction of lead with oxygen, which diffuses through the layer of lead oxides from the oxide-solution boundary of separation. On the boundary with the solution, a thin film of β-PbO_2 is formed from the sulfate. Upon further polarization of lead at potentials exceeding the equilibrium value for this system, oxygen is introduced into the lead through the layer of β-PbO_2, and the oxide α-PbO_2 is formed close to the surface; as the distance from this boundary increases, the oxygen content is reduced, and we come to tetragonal PbO and to lead. It is quite probable that there is a layer of oxide and an intermediate composition of the type PbO_x, where $\underline{x}$ can vary from 1.4 to 1.6, between the α-PbO_2 and PbO_t. Such oxides, obtained by the thermal decomposition of PbO_2, were investigated in [15, 16]. The strongest lines on the x-ray pictures of these oxides coincide with the lines of PbO_t and α-PbO_2; hence in our investigations it was difficult to observe oxides of intermediate composition against the background of comparatively large amounts of PbO_t or α-PbO_2.

With increasing duration of the polarization, the anode film reaches a "critical" thickness at which it begins to break down mechanically from the surface on account of the stresses present in it. The formation of the porous layer can occur both on account of migration of atoms in the film, and by recrystallization through the solution according to the scheme

$$PbO_{2\,(melt)} \rightarrow PbO_{2\,(sol.)} \rightarrow PbO_{2\,(porous)}, \qquad (I)$$

since β-PbO_2 is more stable under normal conditions than α-PbO_2 [16]. At a potential close to equilibrium, and in a solution saturated with $PbSO_4$, electrochemical recrystallization can proceed rather rapidly according to the scheme

$$\alpha\text{-}PbO_2 \rightarrow PbSO_4 \rightarrow \beta\text{-}PbO_2. \qquad (II)$$

In addition, it might seem that the relatively unstable intermediate compound, for example, $PbO_{1.5}$ can decompose by disproportionation according to the reaction [17]

$$2PbO_{1,5} \rightarrow PbO_2 + PbO, \qquad (III)$$

while the PbO formed either reacts with H_2SO_4 and is then oxidized to β-PbO_2, or, if it is not in contact with the solution, it is oxidized by the diffusing oxygen to PbO_x and to α-PbO_2.

As was stated above, in a 2 N H_2SO_4 solution, the porous layer contains a comparatively large amount of β-PbO_2, and there is a substantial dependence of the structure and composition of the porous layer on the temperature, with increases in which the content of the β-phase increases still more. It is natural to assume that in this the process of formation of the porous layer occurs, especially at 65°, primarily through the solution by recrystallization according to scheme (I), and perhaps disproportionation. In 8 N and 10.4 N H_2SO_4, where there is no analogous temperature dependence and the porous layer consists almost entirely of α-PbO_2, its formation probably proceeds by mechanical cracking of the dense film and disproportionation according to scheme (III). Since the solubility of lead dioxide increases somewhat with increasing sulfuric acid concentration [14], we might expect a greater rate of the recrystallization process through the solution, and, consequently, a larger content of β-PbO_2 in 8 N and 10.4 N H_2SO_4. The presence of the opposite dependence indicates that the disproportionation reaction proceeds in strong solutions of H_2SO_4 considerably more readily than does reaction (I). This is probably due to the presence of kinetic hindrance of the solution of α-PbO_2. The formation of the porous layer by electrochemical recrystallization (II) is relatively improbable in our experiments, as a result of the fact that the corrosion potential was considerably more positive than the equilibrium value.

It follows from the results we obtained, in agreement with [1, 2], that the anode oxidation of lead in strong solutions of sulfuric acid proceeds mainly not through the solution near the base of the pores and microcracks of the dioxide film, but by interaction of lead with the oxygen diffusing through the film, forming PbO_t, PbO_x, and α-PbO_2. The formation of β-PbO_2 upon further anode oxidation of lead is a secondary process. $CoSO_4$ apparently reduces the rate of the primary process of insertion of oxygen into the crystal lattice of lead and increases its ability to become passivated.

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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 this issue.