Reports of the Academy of Sciences of the USSR

I. I. Astakhov, E. S. Vaisberg, B. N. Kabanov

1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1964. Volume 154, No. 6

PHYSICAL CHEMISTRY

I. I. Astakhov, E. S. Vaisberg, B. N. Kabanov

ANODIC CORROSION OF LEAD IN SULFURIC ACID

(Presented by Academician A. N. Frumkin on October 5, 1963)

In recent years many works have appeared ($^{1-10}$) on the study of the anodic oxidation of lead in sulfuric acid solutions. They attest to considerable progress in studying the composition and structure of anodic films; however, we still have very little information on the mechanism of their formation. In the present work an attempt is made to clarify the picture of the growth of anodic oxide films on lead by combining electrochemical and structural methods of investigation.

Films forming on smooth lead electrodes (visible surface 6 cm^2) during anodic polarization with a current of 2 ma/cm^2 were studied. The duration of polarization was 3, 24, and 48 hours. The investigations were carried out in 2, 8, and 10.4 N solutions of H_2SO_4 at 25 and 65°. In addition, films forming over 44 hours at a temperature of 30° in 2 N and 10.4 N H_2SO_4 solutions with addition of $CoSO_4$ were studied. The amount of corrosion products was determined by cathodic reduction in a 1 N acidified solution of Na_2SO_4 (^{1}). The accuracy of the determination was 3-5%. The composition of the anodic films was determined by X-ray diffraction; the structure of the films was studied with the aid of an electron microscope using carbon replicas.

In all the cases investigated, dense anodic films form during the first several hours. X-ray examination showed that these films consist mainly of tetragonal lead oxide PbO_t. In the X-ray patterns of films obtained in 2 N H_2SO_4, a small admixture of β-PbO_2 is also noticeable.

With increasing duration of anodic polarization, the growth of the film in thickness is accompanied by changes in its structure. The character of these changes is the same at temperatures of 25 and 65°. Macroscopically the changes are expressed in the appearance of an outer loose layer. It can easily be removed mechanically with moist cotton wool and thus the loose and dense layers can be studied separately. The method of electrochemical reduction showed that, in the course of further polarization, the thickness of both the loose and the dense layer increases.

After 48 hours of polarization, in all the solutions we studied the amount of lead dioxide in the loose and dense layers becomes approximately the same. The dense layer in all cases consists of oxide PbO_t, sometimes with a small admixture of α-PbO_2. The loose layer obtained in 2 N H_2SO_4 at 25° consists of small crystals of irregular shape (Fig. 1a)*, while that obtained at 65° consists of larger, well-formed crystals (Fig. 1b). X-ray examination showed that in both cases this is a mixture of the α- and β-modifications of lead dioxide (in agreement 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 loose layer consists of small crystals (Figs. 1c and 1d). X-ray examination showed that this is α-PbO_2 with only a small admixture of β-PbO_2, and with an increase in the concentration of H_2SO_4 from 8 N to 10.4 N the content of β-PbO_2 decreases still somewhat. No substantial dependence of the structure and co-

---

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

To the article by I. I. Astakhov and E. S. Vaisberg, B. N. Kabanov

Fig. 1. Carbon replicas from the surfaces of electrodes polarized for 24 hours 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*)

No dependence of the composition of the loose layer on temperature was found in the corrosion of lead in 8 N and 10.4 N H_2SO_4. On films obtained at 30° in 2 N and 10.4 N H_2SO_4 solutions with the addition of $CoSO_4$, qualitatively analogous results were obtained: with increasing acid concentration, the amount of β-PbO_2 in the loose layer decreases. The thickness of both the loose and the dense layers in this case is considerably smaller than for films obtained under analogous conditions without the addition of cobalt sulfate. This confirms the conclusion ([1]) that the presence of $CoSO_4$ decreases the corrosion of lead because of an increase in its passivability.

It is known ([11], [8], [3], [5]) that α-PbO_2 is formed during the anodic oxidation of divalent lead in neutral and alkaline solutions, in 0.01 N H_2SO_4 solution, and in 8 N H_2SO_4 solution in the presence of $CoSO_4$*. The formation of α-PbO_2 in weakly acidic solutions, observed during the formation of porous storage-battery plates, is explained in the literature by the creation of a weakly alkaline medium owing to the presence of PbO in the bulk of 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, during the anodic oxidation of lead sulfate at the equilibrium potentials of the $PbSO_4/PbO_2$ system, β-PbO_2 was always obtained. Consequently, the formation we observed of α-PbO_2 in the dense and loose layers on smooth lead anodes in pure 2, 8, and 10.4 N H_2SO_4 solutions cannot be explained on the assumption that the dioxide is formed by electrochemical oxidation of lead sulfate. In papers (^{1}, ^{2}) another possible mechanism for the formation of lead dioxide was proposed—by reaction in the solid phase between lead and oxygen**. In work (^{7}) it was shown that the crystal lattice of tetragonal PbO and α-PbO_2 can be obtained from the lead lattice by the successive incorporation into it of oxygen atoms. It is therefore quite natural that, when the reaction between oxygen and lead proceeds in the solid phase, precisely α-PbO_2 is formed.

From the results of our experiments there emerges the following picture of the changes occurring during the growth of anodic films under prolonged anodic polarization of lead in H_2SO_4 solutions. The films grow as a result of the interaction of lead with oxygen diffusing through the layer of lead oxides from the oxide–solution interface. At the boundary with the solution a thin layer of β-PbO_2 is formed from sulfate. Upon further polarization of lead at potentials exceeding the equilibrium potential for this system, oxygen penetrates through the β-PbO_2 layer into the lead, and near the surface the oxide α-PbO_2 is formed; with increasing distance from this boundary the oxygen content decreases, and we pass to tetragonal PbO and to lead. It is quite probable that between α-PbO_2 and PbO there is a layer of oxide of intermediate composition of the type PbO , where x may vary from 1.4 to 1.6. Such oxides, obtained by thermal decomposition of PbO_2, were investigated in papers (^{15}, ^{16}). The strongest lines on the X-ray patterns of these oxides coincide with the lines of PbO and α-PbO_2; therefore, in our studies it was difficult to detect oxides of intermediate composition against the background of comparatively large amounts of PbO or α-PbO_2.

With increasing duration of polarization, the anodic film reaches such a “critical” thickness at which it begins to undergo mechanical destruction from the surface because of the stresses present in it. Formation of the loose layer may occur both through migration of atoms in the film and by recrystallization through the solution according to the scheme

$$PbO_2\,(\text{film}) \rightarrow PbO_2\,(\text{solution}) \rightarrow PbO_2\,(\text{loose}), \tag{1}$$

since β-PbO_2 under normal conditions is more stable than α-PbO_2 (^{16}).

At a potential close to the equilibrium potential, and in a solution saturated with $PbSO_4$, electrochemical recrystallization can proceed sufficiently rapidly according to the scheme

* It should be noted that the authors (^{3}) did not obtain any one modification of PbO_2 in pure form. From the neutral solution a mixture was deposited, consisting mainly of the α-form, and from the strongly acidic solution—of the β-form.

** (^{7}) also came to this mechanism of lead corrosion, but subsequently abandoned this point of view (^{18}).

$$\alpha\text{-PbO}_2 \rightarrow \text{PbSO}_4 \rightarrow \beta\text{-PbO}_2. \qquad \text{(II)}$$

In addition, one might suppose that a comparatively unstable intermediate compound, for example $\text{PbO}_{1\cdot5}$, can decompose by disproportionation according to reaction (^{17})

$$2\text{PbO}_{1.5} \rightarrow \text{PbO}_2 + \text{PbO}, \qquad \text{(III)}$$

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, is oxidized by diffusing oxygen to PbO and to α-PbO_2.

As stated above, in a 2 N H_2SO_4 solution the loose layer contains relatively much β-PbO_2, and there is a significant dependence of the structure and composition of the loose layer on temperature, with an increase in which the content of the β-phase increases still further. It is natural to assume that in this case the process of formation of the loose layer proceeds, especially at 65°, predominantly through solution by recrystallization according to scheme (I) and, possibly, by disproportionation. In 8 N and 10.4 N H_2SO_4, where there is no analogous temperature dependence and the loose 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}), one might have expected a higher rate of the recrystallization process through solution and, consequently, a higher content of β-PbO_2 in 8 N and 10.4 N H_2SO_4. The presence of the inverse dependence indicates that the disproportionation reaction proceeds in strong H_2SO_4 solutions much more readily than reaction (I). This is probably connected with kinetic hindrance to the dissolution of α-PbO_2. The formation, in our experiments, of the loose layer by electrochemical recrystallization (II) is unlikely, because the corrosion potential was considerably more positive than the equilibrium potential.

From the results obtained by us it follows, in agreement with (^{1}, ^{2}), that anodic oxidation of lead in strong sulfuric acid solutions proceeds mainly not through solution at the bases of pores and microcracks in the dioxide film, but by interaction of lead with oxygen diffusing through the film, with the formation of PbO , PbO , and α-PbO_2. The formation of β-PbO_2 during prolonged anodic oxidation of lead is a secondary process. CoSO_4 apparently reduces the rate of the primary process of incorporation of oxygen into the crystal lattice of lead and increases its passivability.

Institute of Electrochemistry, Academy of Sciences of the USSR
Podolsk Branch of the Scientific-Research Institute
of the Storage-Battery Industry

Received
5 X 1963

CITED LITERATURE

1. E. V. Krivolapova, B. N. Kabanov, ZhPKh, **14**, 335 (1941).
2. E. V. Krivolapova, E. S. Vaisberg, B. N. Kabanov, Proc. IV Conf. on Electrochemistry, Academy of Sciences of the USSR Press, 1956, p. 757.
3. I. G. Kiselëva, B. N. Kabanov, DAN, **122**, 1042 (1958).
4. J. J. Lander, J. Electrochem. Soc., **103** (1956), 105, 289 (1958).
5. J. Burbank, J. Electrochem. Soc., **103**, 87 (1956); **104**, 693 (1957); **106**, 369 (1959).
6. W. Feitknecht, Zs. Elektrochem., **61**, 795 (1958).
7. H. Bode, E. Voss, Zs. Elektrochem., **60**, 1053 (1956).
8. P. Rüetschi, B. D. Cahan, J. Electrochem. Soc., **104**, 406 (1957).
9. N. F. Razina, M. T. Kozlovskii, V. V. Stender, DAN, **111**, 104 (1956).
10. M. A. Dasonyan, DAN, **107**, 863 (1956).
11. A. I. Zalavskii, Yu. D. Kondrashov, S. S. Tolkachev, DAN, **75**, 559 (1950).
12. V. H. Dodson, J. Electrochem. Soc., **108**, 395 (1961).
13. P. Rüetschi, B. D. Cahan, J. Electrochem. Soc., **105**, 369 (1958).
14. L. V. Vanyukova, M. I. Isaeva, B. N. Kabanov, DAN, **143**, 377 (1962).
15. Shin-ichi Ikari, Shiro Yoshizawa, Shinzo Okado, J. Electrochem. Soc. Japan, **27**, 487 (1959).
16. R. T. Angstadt, C. J. Venuto, P. Rüetschi, J. Electrochim. Soc., **109**, 177 (1962).
17. P. Rüetschi, J. Sklarchuk, R. T. Angstadt, Electrochim. acta, **8**, 333 (1963).
18. Rüetschi, R. T. Angstadt, B. D. Cahan, J. Electrochem. Soc., **106**, 547 (1959).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the *original.*