THE EFFECT OF CURRENT DENSITY AND THICKNESS OF THE ACTIVE MASS UPON THE CORROSION RATE OF THE SPINES OF LEAD–ACID BATTERY PLATES

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Summary

The effect of current density and the thickness of the active mass upon the corrosion of the spines of tubular lead–acid batteries has been determined by measuring the corrosion rate by the weight loss method. The presence of antimony in the alloy decreases the overvoltage of the corrosion reaction. Study of electrodes of different active mass layer thickness shows that with increase in thickness the corrosion rate decreases. If the thickness is above 3 mm, the corrosion rate remains constant, and is affected only by the nature of the alloy. The density of the active mass does not affect the corrosion behaviour of the electrodes. The experimental results confirm the validity of the oxygen corrosion model.

1. Introduction

The positive plate of the lead–acid battery in the discharged state can be represented as an electrode system by the following expression:

$$Pb/PbO_n \mid PbSO_4 \mid H_2SO_4 \cdot$$
$$\mid PbO_2 \mid PbSO_4 \mid H_2SO_4$$
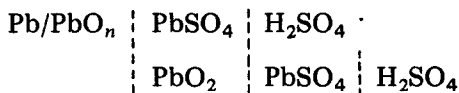
Here Pb represents the grid or spines of the plate, PbO_n — the corrosion layer, PbO_2 — the active mass, and $PbSO_4$ — the lead sulphate crystals formed on the surface of the PbO_2 and PbO_n components of the plate. The solution is in contact with $PbSO_4$, PbO_2 and PbO_n crystals.

During the anodic polarization of a completely charged positive plate, oxygen is evolved on the PbO_n and PbO_2–electrolyte interfaces. Part of the oxygen is dissolved in the active mass and in the corrosion layer, forming an oxygen electrode. Let us express it as O_2/H_2O. In this case the plate as an electrode system can be represented by the expression:

$$Pb/PbO_n \quad \bigg| \quad \begin{array}{l} H_2SO_4\,(O_2/H_2O) \\[6pt] PbO_2/H_2SO_4\,(O_2/H_2O) \end{array}$$
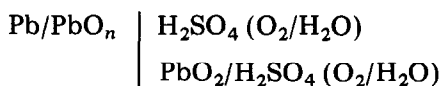
The grid is composed of lead and lead alloys. The active mass is highly porous and is composed of the α and β modifications of PbO_2. They have a non-stoichiometric composition and represent degenerate semiconductors with n-type conductivity. The specific conductivity of α-PbO_2 is 7×10^{-6} - 7×10^{-5} ohm^{-1} cm^{-1}, and that of β-PbO_2 1.2 - 4.0×10^{-5} ohm^{-1} cm^{-1} [1].

The corrosion layer is formed during the anodic polarization as a result of the oxidation of the grid. The thickness of the corrosion layer increases with the amount of electricity passed, and two sublayers are formed: one dense and the other porous. The dense sublayer covers the metal and insulates it completely from the solution. The porous layer is formed as a result of the cracking of the dense sublayer, which is subjected to the effect of internal stresses initiated in it, due to the different molar volumes of the lead and the oxide.

In two previous papers [2, 3] we have determined the effect of the active mass and the polarization conditions upon the anodic corrosion rate of the spines of tubular positive plates of traction batteries. The present work is aimed at the determination of the effect of the current density and the thickness of the active mass upon the corrosion rate of the spines.

2. Experimental

2.1. Conditions

Completely charged tubular positive electrodes containing the active mass were subjected to anodic polarization. Two types of reactions proceeded in this electrode system. At the PbO_2/H_2SO_4 and PbO_n/H_2SO_4 interface oxygen is evolved, while at the Pb/PbO_n interface lead is oxidized. Our concern during these experiments was to define the relationship between the rate of these two reactions. Experimental data indicate that both the reactions proceed concurrently, and the rate of the oxygen evolution is by two orders of magnitude faster than that of the corrosion process [3, 4]. As a result, the potential of the electrode system is defined by the oxygen evolution reaction.

The ratio between the rates of these reactions can be determined by changing the rate of one reaction, and checking the corresponding alteration of the rate of the other processes. The oxygen evolution reaction is inherently easy to control and check; therefore, in this work, its rate was altered, simultaneously monitoring the changes in the rate of the corrosion process. The rate of the oxygen evolution reaction was changed by two methods: (a) by altering the current density, keeping the thickness of the active mass constant; (b) by changing the area (thickness) of the active mass, while keeping the current constant.

2.2. Methods for the preparation of the electrodes

The net effect exerted by the active mass upon the corrosion rate can be determined only by using tubular electrodes. If standard pasted plates were used in the experiments, the grid bars would be covered with active mass of thickness from 0 up to 50% of the total thickness of the plate, and this would give ambiguous results.

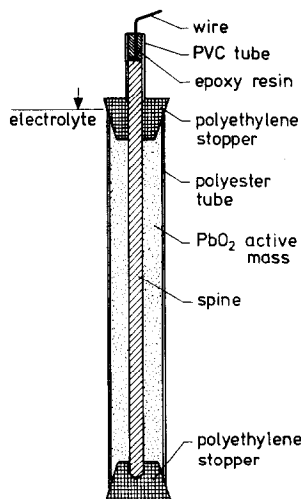The design of the tubular electrodes is shown in Fig. 1.

Fig. 1. Design of the electrode.

The preparation techniques are described in refs. 2 and 3. The 4 mm dia. and 95 mm long spines were mounted in 8.4 mm woven polyester tubes and the latter were filled with identical quantities of 66% leady oxide (oxidized lead powder). The electrodes were immersed for 2 min in H_2SO_4 solution (s.g. 1.10). After 5 days curing, the PbO_2 active mass was formed by a charge of 0.70 A h/g of oxidized Pb powder. The formation was carried out in 1.05 s.g. H_2SO_4 solution at 30 °C.

2.3. Method for the determination of the corrosion rate of the spines

The corrosion rate was determined by checking the loss of metal per unit area and unit polarization time.

The spines subjected to testing were cast from the following alloys: Pb–4.9%Sb; Pb–7.3%Sb; Pb–10.6%Sb; reference — pure Pb. The corrosion tests were carried out in a 1.28 s.g. H_2SO_4 solution at 50 °C. The steady-state corrosion rate was determined by a method described in [2, 5]. Eighteen accurately weighed spines of each alloy were subjected to polarization with an identical current. After intervals of 300 h 3 electrodes were removed. The active mass was removed mechanically, and the corrosion layer dissolved in a hot alkaline glucose solution. The spines were weighed again, and the quantity of corroded metal evaluated by the difference in the weights prior

to and after the oxidation test. The corrosion rate was determined by the slope of the linear part of the relationship: weight of corroded metal–polarization time. The corrosion current was evaluated on the basis of these data. The difference between the set galvanostatic current and the corrosion current value determines the oxygen evolution rate.

3. Results

3.1. Effect of the oxygen evolution reaction upon the corrosion layer

The tubular electrodes used in the tests had a 2.2 mm thick active mass layer. The current densities evaluated with respect to the area of the spines were 0.2, 0.5, 1.0, 6.0, 12.0, and 20.0 mA/cm^2. The electrodes were subjected to continuous polarization.

As has been already noted, lead dioxide has a high conductivity. Because of this the potential drop in the corrosion layer and the active mass will be very small and can be neglected. Hence the potential at the Pb/PbO$_n$ interface will be equal to that at the PbO$_2$/solution interface. This makes it possible to trace the polarization relationships of the two electrochemical reactions: oxygen evolution, and corrosion of the metal. Figure 2 shows this approach.
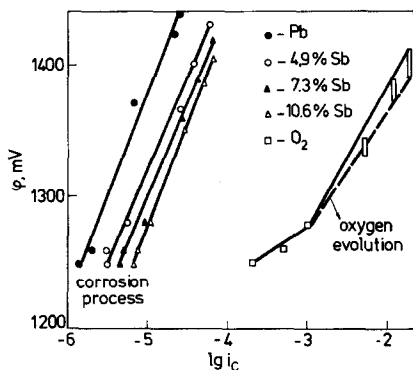

Fig. 2. Polarization curves of the corrosion and oxygen reactions.

It will be noted that corrosion is enhanced by increase of polarization. The polarization curves are of the Tafel type.

$$\eta_c = a_c + b_c \lg i_c \tag{1}$$

$$\eta_{O_2} = a_{O_2} + b_{O_2} \lg i_{O_2} \tag{2}$$

The coefficient b_c for the corrosion reaction attains values between 140 and 160 mV. The corresponding b_{O_2} values for the oxygen evolution reaction are 45 mV at low potentials, and approximately 110 mV at high potentials.

If the curves are considered at a constant potential (*i.e.*, along a horizontal line) it will be noticed that the corrosion rate of the Pb–Sb alloys is higher than that of pure Pb. The increase of Sb content from 5 to 11% slightly enhances the corrosion of Pb–Sb alloys.

If the corrosion curves are compared at an identical corrosion current value (*i.e.*, along a vertical line) it will be noticed that Sb decreases the overvoltage of the corrosion reaction.

Because oxygen evolution is located upon the active mass, the effect of Sb is slight at low current densities, since small amounts of Sb are oxidized and adsorbed in the active mass. At high polarization current densities (when substantial amounts of Sb from the alloy enter the active mass) with increase of oxidation, the oxygen overvoltage slowly decreases. The dotted second curve reflects this process.

Since both electrochemical processes (corrosion and oxygen evolution) proceed simultaneously, by dividing the two Tafel equations at an identical potential, the ratio between the respective rates is derived.

$$i_c = A i_{O_2}^P \tag{3}$$

where P and A are constants. The value of P is between 0.55 and 0.62. A similar relationship was derived for the Pb electrode with no active mass [4].

3.2. The relationship: phase composition of the corrosion layer–electrode potential

It is well known that the corrosion layer comprises the α and β-modifications of PbO_2. The ratio between these two components depends on the amount of electricity passed [3]. The determination of the relationship between the phase composition of the corrosion layer and the potential at which the electrode system is polarized is of major importance. The phase composition was determined in the following manner: at the end of polarization, the active mass was mechanically separated from the layer. The corrosion layer was brushed off the spine and subjected to X-ray and chemical analyses. The β/α-PbO_2 ratio was evaluated by juxtaposing the intensity of the diffraction line $d = 3.49$ Å of the β-PbO_2 with that of the line $d = 3.12$ Å of α-PbO_2. Figure 3 presents the β/α ratio *vs.* the potential of the electrodes after 900 h polarization.

In the initial polarization stage the β/α-PbO_2 ratio has high values. As the amount of electricity passed increases, the quantity of α-PbO_2 also increases, and the β/α-PbO_2 ratio decreases and shows a tendency to reach a limiting value β/α-$PbO_2 = 0.10 - 0.20$. The higher the Sb content of the alloy, the faster the limit value is attained.

When the electrode potential is more positive than 1300 mV, regardless of the Sb content in the spines, under continuous polarization conditions the phase composition of the corrosion layer is always identical, with a predominant content of α-PbO_2, while at lower potentials β-PbO_2 prevails in all electrodes.
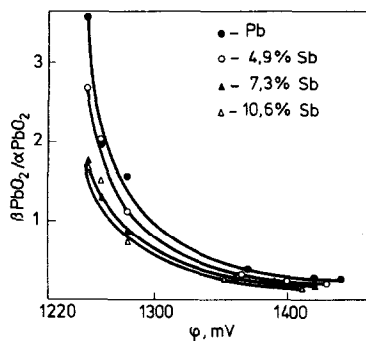
Fig. 3. The relationship between the β/α-PbO_2 ratio and the potential of the electrode after 900 h polarization.

3.3. Stoichiometry of the oxide in the corrosion layer

As established by Pavlov and Rogatchev [4], the composition of the corrosion layer is non-stoichiometric lead oxide, PbO_n, where n is the stoichiometric coefficient. Its value varies between $1.4 < n < 1.95$, which shows that the crystal lattice of the oxide contains Pb^{2+} and Pb^{4+} ions. The stoichiometric coefficient of the corrosion layer n was determined in a batch of electrodes. The Pb^{2+} content in the oxide was determined by complexometric analyses, and that of Pb^{4+} ions with $Na_2S_2O_4$ solutions [4]. The following values for n were obtained: pure Pb spines — 1.4 - 1.7; Pb–Sb alloys — 1.70 - 1.95. The n values of the corrosion layer of the pure Pb electrodes are similar to those obtained with pure lead electrodes without active mass [4]. The introduction of Sb into the alloy enchances the oxidation process and, hence, increases the stoichiometric coefficient of the alloy.

3.4. Effect of the thickness of the active mass upon the processes in the corrosion layer

3.4.1. Effect of the thickness of the active mass upon the potential of the electrode system during galvanostatic polarization

The investigations were carried out with electrodes prepared with spines cast from pure Pb and Pb alloys containing 4.9 or 10.6% Sb. The polyester tubes had the following dimensions: length, 60 mm; diameters, 6, 7, 8, 9, 10, 11 and 12 mm. The tubes, with symmetrically centered spines were filled with sufficient leady oxide to ensure identical density for all electrodes. After formation the electrodes were subjected to galvanostatic oxidation at a current density of 6 mA/cm² (spine surface).

The polarization measurements were carried out at 50 °C in a 1.28 s.g. H_2SO_4 solution.

Figure 4 shows the potential of the electrodes vs. the thickness of the active mass.

With increase in the thickness of the active mass layer, the potential of oxygen evolution decreases, since the surface of the active mass increases
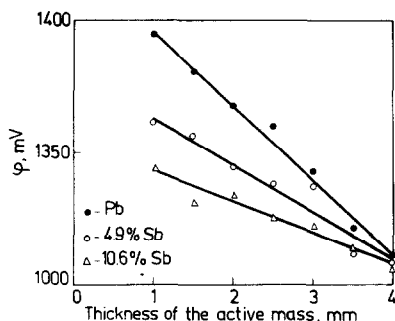
Fig. 4. The relationship between electrode potential and the thickness of the active mass.

and the real current density is reduced. When the area of the active mass is increased, the amount of antimony (formed as a result of the corrosion of the spines) adsorbed per unit surface of PbO_2 active mass decreases. The effect of Sb can be hardly detected in 4 mm thick active mass layers.

This Figure provides further information. When the thickness of the active mass layer is increased, its electric resistance should follow Ohm's law and also increase. As a result the polarization potential of the electrode system must increase to retain the galvanostatic polarization condition. However, Fig. 4 shows a completely different picture. As the thickness of the layer increases the potential decreases. This phenomenon proves that the effect of the ohmic drop in the active mass and the corrosion layer on the potential of the electrode system is negligible.

3.4.2. Effect of the thickness of the active mass upon the corrosion rate

The corrosion rate *vs.* thickness of the active mass layer is shown in Fig. 5.

It can be seen that the corrosion rate decreases with increase in layer thickness. One of the reasons for this phenomenon is the lower oxygen
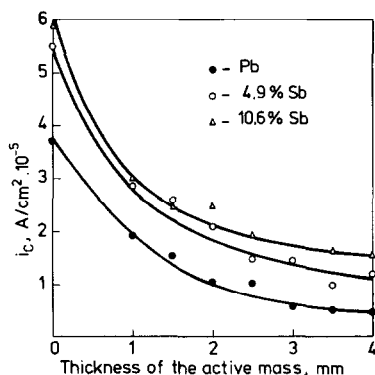

Fig. 5. The relationship between corrosion rate and the thickness of the active mass.

electrode potential, due to the reduced current density resulting from the increased area of the electrode (Fig. 4). Another reason is the increase in the resistance of the electrolyte in the pores, when the layer increases its thickness and the pores become longer. This also reduces the rate of the oxygen reaction in the internal regions of the active mass and at the corrosion layer/electrolyte interface.

3.4.3. Effect of the thickness of the active mass upon the phase composition of the corrosion layer

Figure 6 presents the relationship between the β/α-PbO_2 ratio and the thickness of the active mass layer after different polarization durations.

When the active mass layer is very thick, during the initial polarization stage the corrosion layer contains substantial quantities of β-PbO_2. With increase in the amount of electric charge, the α-PbO_2 content in the corrosion layer increases, and the β/α-PbO_2 ratio tends to reach the limiting value 0.10 - 0.20. Electrodes with Pb–Sb alloy spines attain this value faster than pure Pb electrodes.
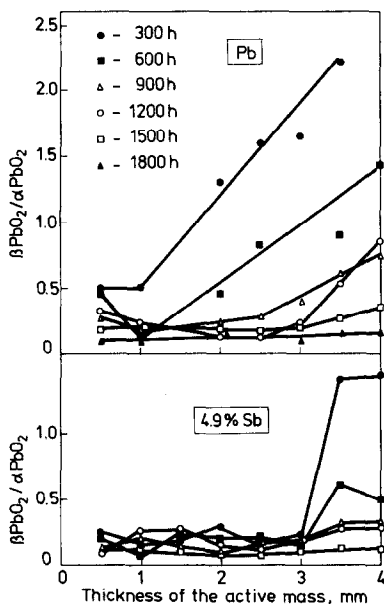

Fig. 6. The relationship between the β/α-PbO_2 ratio and the thickness of the active mass.

3.5. The effect of the density of the active mass upon the corrosion rate

Electrodes were prepared with spines cast from a Pb alloy containing 7.3% Sb. The diameter of the polyester tubes was 8.4 mm and the thickness of the active mass was 2.2 mm. The tubes were filled with different amounts of leady oxide, so that various densities of the active mass were obtained. The oxidation was carried out at a current density of 6 mA/cm^2. The results are presented in Fig. 7.
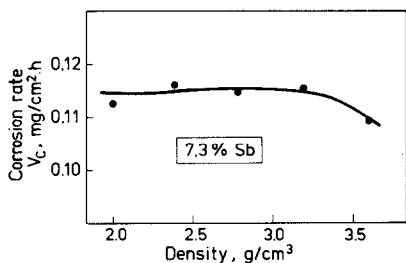
Fig. 7. Relationship between the corrosion rate and the density of the active mass.

Within the active mass range (2.0 - 3.6 g/cm^3) investigated the corrosion rate was slightly affected by density. This is probably due to the low density values of the active mass. The corrosion rate decreases as the density of the active mass reaches 3.6 g/cm^3.

4. Results and discussion

4.1. The mechanism of the processes during corrosion

Figure 8 shows a diagram of the basic reactions and the sites where they occur during the anodic polarization of the plate, as suggested in ref. 7.
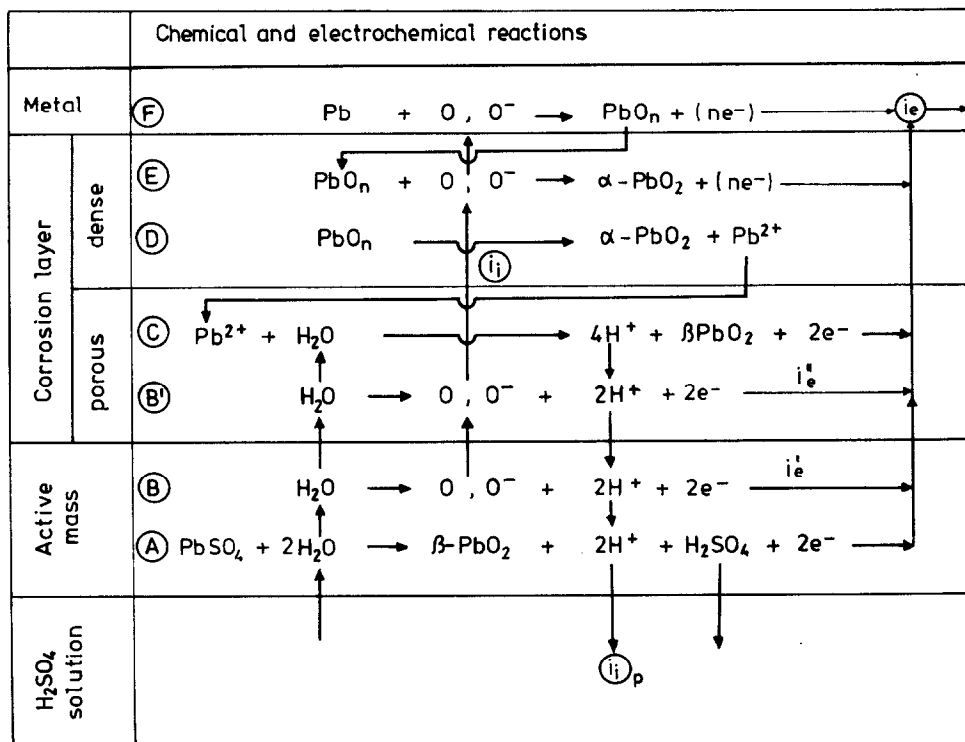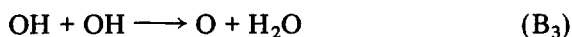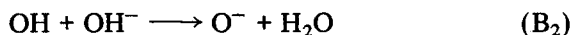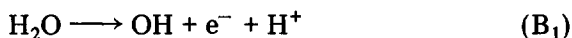

Fig. 8. A diagram of the structure of a PbO$_2$ plate and the basic reactions.

The charging reaction of the positive plate is marked A. Under galvanostatic conditions, when the $PbSO_4$ crystals are oxidized, the potential begins to increase, and the rate of oxygen evolution is enhanced. The mechanism of the elementary processes of the oxygen electrode is not quite clear, but the following reactions are frequently given in the literature for anodic water oxidation:

$$H_2O \longrightarrow OH + e^- + H^+ \qquad (B_1)$$

$$OH + OH^- \longrightarrow O^- + H_2O \qquad (B_2)$$

$$OH + OH \longrightarrow O + H_2O \qquad (B_3)$$

$$O^- \longrightarrow O + e^- \qquad (B_4)$$

$$2O \longrightarrow O_2 \qquad (G)$$

These reactions occur on the surface of the active mass and in the porous part of the corrosion layer. The electrons obtained during reaction B form the electronic current i_e', which flows through the active mass, the corrosion layer, and enters the metal. The same reactions proceed in the porous corrosion sublayer, the electrons form the current i_e'', which flows through the corrosion layer and enters the metal. The area of the active mass which is in contact with the solution, is greater by several orders of magnitude than that of the porous corrosion layer. Due to this difference the ratio between the currents $i_e'/i_e'' \gg 1$.

The resistance of the solution in the pores of the active mass (R_p) acts in a similar way. If the rate of reaction B_1 is determined by the transport of H^+ ions in the pores of the active mass toward the bulk electrolyte, this reaction should proceed at a maximum rate on the surface of the outer layers of the plate, and at a minimum rate on the surface of the corrosion layer. The corrosion process F (Fig. 8) proceeds on the Pb/PbO_n interface. The growth of the corrosion layer is related to the transport of particles through this layer.

Kabanov et al. [8, 9] have proposed that the oxygen evolved at the PbO_2/solution interface diffuses through the corrosion layer, reaches the metal, and oxidizes it, forming tet-PbO. Within the corrosion layer itself a gradient of non-stoichiometric oxides is present ranging between tet-PbO and α-PbO_2.

Pavlov and Rogatchev [4] have quantitatively investigated the phase and stoichiometric compositions of the corrosion layers formed at different potentials. On the basis of these experimental results, Pavlov [6] further developed the model for the oxygen mechanism of lead corrosion as follows:

The oxygen evolution process proceeds through the elementary reactions mentioned above, in which OH, O^- radicals and O atoms are formed as intermediate products. Since O atoms and O^- radicals have smaller radii than that of O^{2-} ions, they penetrate into the crystal lattice of the corrosion layer which contains a high concentration of oxygen vacancies, $O_\square^{2+}$. It is very probable that the O atoms and the O^- radicals move in the oxide through these vacancies.

When O atoms and O^- radicals reach the metal, they oxidize the lead into non-stoichiometric PbO_n, which has the crystal lattice of tet-PbO, but a stoichiometric coefficient higher than 1.4.

$$Pb + nO^- \longrightarrow PbO_n + ne^-$$

$$Pb + nO \longrightarrow PbO_n$$
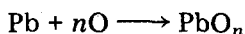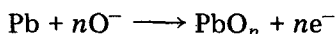
Tet-PbO displays a very high ohmic resistance. The non-stoichiometric oxide with a stoichiometric coefficient between 1.0 and 1.3 has a specific resistance between 10^8 and 10^{11} Ω cm, and when this coefficient is higher than 1.4 the resistance decreases sharply down to that of PbO_2 [10]. If tet-PbO was formed as a phase, at the Pb/corrosion layer interface, as required by the Kabanov model, the electrode should be highly polarized. But experimental data show the reverse phenomenon — a low polarization of the electrode. Therefore, as Pavlov claims, a non-stoichiometric tet-PbO_n oxide is formed, with a stoichiometric coefficient near to 1.5, and a tet-PbO-type crystal lattice.

On the other hand, a second type of reaction proceeds on the Pb/PbO_n interface — a solid state oxidation of lead, during which oxygen vacancies $(O_{\square}^{2+})$ are formed [6].

$$Pb \longrightarrow PbO_{\square}^{2+} + 2e^-$$

The oxygen vacancies diffuse through the corrosion layer and reach the solution interface, where they react with water.

As a result of those two processes, an ionic current (i_i) flows through the corrosion layer, which is parallel to the electronic current (i_e) and determines the corrosion rate.

According to the above described mechanism, the corrosion layer contains a certain concentration of O^-, O, and $O_{\square}^{2+}$. The oxygen radicals and atoms are strong electron acceptors. They oxidize the PbO_n oxide into PbO_2, and during this process the crystal lattice of tet-PbO_n is rearranged into an α-PbO_2 lattice. The stoichiometric coefficient of α-PbO_2 is lower than 2. The oxidation of tet-PbO_n proceeds as a solid state reaction and the α modification of PbO_2 is formed. Since a great similarity exists between both crystal lattices, this transformation of tet-PbO_n into α-PbO_2 appears to be the most favourable in terms of energy.

If the internal stresses which are initiated in the corrosion layer cause a cracking of the dense layer, however, and the H_2SO_4 solution contacts the tet-PbO_n, a reaction starts, during which PbO_2 and Pb^{2+} ions are formed. In acidic media Pb^{2+} ions are oxidized, forming β-PbO_2 (reaction C, Fig. 8). This process proceeds at low polarizations and when the corrosion layer is thin.

4.2. Analysis of the experimental results in the light of the model

The flow of O^- and O will obviously depend on the rate of the oxygen reaction on the surface of the porous corrosion layer. This reaction, on the other hand, depends strongly on the thickness of the active mass.

When the thickness of the active mass is large, the rate of the oxygen reaction is affected in two ways: (a) the real current density of the oxygen reaction is decreased, and as a result the potential of the electrode is lowered (Fig. 4); (b) as the pores in the active mass become longer, the movement of the H^+ ions, formed during the oxygen reaction, is hindered (Fig. 8). The H^+ ions maintain the electroneutrality of the electrolyte in the pores. When their transport is hindered, the solution becomes positively charged. This lowers the rate of the oxygen reaction, as a result of which they are formed. The overall result of these two phenomena is that the rate of the oxygen reaction on the surface of the corrosion layer is lowered. This, in turn, decreases the concentration gradient of the O^- and O atoms in the corrosion layer. The experimental data for this effect are shown in Fig. 5.

The increase in the current density raises the concentration of the adsorbed O^- and O atoms on the surfaces of the corrosion layer and the PbO_2 active mass. As a result the corrosion rate is increased (Fig. 2).

The results of the present investigation also reveal the effect of antimony upon the corrosion processes. During the oxidation of the alloy, antimony is also oxidized to Sb ions. According to Dawson et al. [11], Sb is oxidized to Sb^{5+}. The antimony ions are embedded in the crystal lattice of the corrosion layer as defects. They alter both the mobility of the oxygen vacancies, O^- radicals, or O atoms, as well as the rates of the reaction $Pb \longrightarrow PbO_n$. Figures 2 and 5 show that Sb increases the corrosion rate of the Pb–Sb alloys. The higher the Sb content, the faster the corrosion rate of the alloy.

Experimental data also show that the stoichiometric coefficient of the corrosion layer attains higher values with Pb–Sb alloys ($PbO_{1.70-1.95}$) than with pure lead ($PbO_{1.45-1.70}$). Obviously, the antimony ions in the crystal lattice of the corrosion layer enhance the reaction tet-$PbO_n \longrightarrow \alpha$-$PbO_2$. The experimental curves for the phase composition of the corrosion layer vs. electrode potential are given in Fig. 3. They show that at potentials higher than 1350 mV the formation of α-PbO_2, i.e., the solid state oxidation of the PbO_n layer, is the predominant process.

It can be concluded that, on the one hand, the results are in good agreement with the oxygen model of the corrosion process, and on the other hand they show that increase in the thickness of the active mass lowers the corrosion rate, thus improving the service life of traction batteries with tubular plates.

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