

## EFFECT OF ANTIMONY ON THE ANODIC CORROSION OF LEAD AND OXYGEN EVOLUTION AT THE Pb/PbO<sub>2</sub>/H<sub>2</sub>O/O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub> ELECTRODE SYSTEM

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### Summary

When a Pb electrode immersed in H<sub>2</sub>SO<sub>4</sub> solution is polarized in the PbO<sub>2</sub> potential range the following electrode system is formed: Pb/PbO<sub>2</sub>/H<sub>2</sub>O/O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>. At the oxide/solution interface oxygen evolution takes place. The semiproducts of this reaction, O atoms and O<sup>-</sup> radicals, diffuse into the anodic layer and oxidize the metal. As a result of a solid-phase reaction the metal is oxidized first to tet-PbO and then further oxidized to PbO<sub>2</sub>. By examining the changes in the Tafel slopes of the above reactions and by analyzing the chemical composition of the anodic layer, the effect of Sb on the above processes is assessed.

Antimony was introduced into the electrode system either by alloying it with the metal or by adding it to the H<sub>2</sub>SO<sub>4</sub> solution. It was established that Sb lowers the oxygen overvoltage and increases the rate of anodic corrosion of lead irrespective of the way in which it was introduced into the system. Antimony increases the stoichiometric coefficient of the oxide layer, hence, it enhances the oxidation of PbO to PbO<sub>2</sub>. The results of these investigations confirm the mechanism of the processes proceeding during anodic oxidation of lead.

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### Introduction

When lead and lead alloy electrodes immersed in H<sub>2</sub>SO<sub>4</sub> solution are anodically polarized in the PbO<sub>2</sub> potential range (potentials more positive than 0.95 V *versus* an Hg/Hg<sub>2</sub>SO<sub>4</sub> reference) an anodical oxidation reaction of the metal proceeds at the metal/PbO<sub>2</sub> layer interface, while at the PbO<sub>2</sub> layer/H<sub>2</sub>SO<sub>4</sub> solution interface oxygen is evolved. As a result of these processes the Pb/PbO<sub>2</sub>/H<sub>2</sub>O/O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub> electrode system is formed [1]. Studying the effect which antimony has on these two types of reaction is not only of theoretical but also of practical interest. It is used as a main alloying additive for the grids of lead-acid batteries and its influence on the corrosion rate has been investigated by many authors [2 - 10].

The aim of the present study is to elucidate the effect which antimony has on the electrochemical processes in the Pb/PbO<sub>2</sub>/H<sub>2</sub>O/O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub> electrode system.

## Experimental

The effect which antimony has on the electrochemical behaviour of the Pb/PbO<sub>2</sub>/H<sub>2</sub>O/O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub> electrode system was investigated by studying its influence on the steady-state polarization curves of the two reactions. The polarization curves were obtained for 6.5 cm<sup>2</sup> plane electrodes, which were galvanostatically polarized. The electrode potential was measured *versus* an Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode in a 7 N H<sub>2</sub>SO<sub>4</sub> solution. The partial steady-state current of metal oxidation (anodic corrosion) was determined by the weight-loss method, described in some of our earlier papers [8, 11]. The partial steady-state current of oxygen evolution was calculated as the difference between the total polarization current and the anodic corrosion current. Since the PbO<sub>2</sub> layer has a very high conductivity, it was assumed that there is no potential drop in the anodic oxidation layer. Consequently, the electrode potential recorded refers to both partial currents. This allowed us to make Tafel plots for both processes. After oxidation, the electrodes were washed, dried and the phase composition of the anodic layer at the oxide/solution interface determined by X-ray diffraction. The main part of the oxide layer was brushed away and the remaining thin oxide film, firmly attached to the metal, was X-rayed again. This diffractogram is characteristic of the phase composition of the anodic layer at the metal/anodic layer interface. The potential dependence of the phase composition at the two interfaces was obtained.

Lead alloys with varying Sb contents were prepared from pure metals: Pb, 99.999%; Sb, 99.95%, and then anodically polarized.

## Experimental results

### *The effect antimony has on the electrochemical reactions at the lead electrode*

The effect that Sb has on the anodic corrosion and oxygen evolution was investigated in two ways. In the first, Pb-Sb alloys were studied in H<sub>2</sub>SO<sub>4</sub> solution, and in the second, Sb was added to the H<sub>2</sub>SO<sub>4</sub> solution, thus forming Sb<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and pure lead electrodes were polarized. During polarization the Sb<sup>3+</sup> ion concentration is lowered. Antimony sulphate was added to the solution daily in order to maintain the Sb<sup>3+</sup> ion concentration, which was checked periodically by chemical analysis, within the 0.03 - 0.06 g l<sup>-1</sup> limits.

Figure 1 presents the current-voltage characteristics of the oxygen evolution and corrosion processes for pure Pb electrodes immersed in an

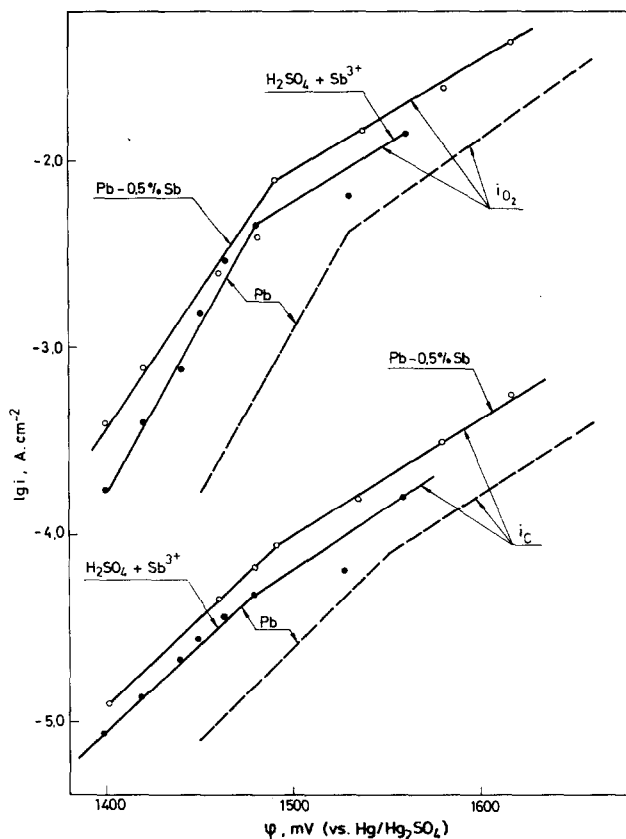


Fig. 1. Polarization curves of the oxygen evolution reaction and the corrosion reaction for both Pb-Sb alloy and when Sb is introduced into the solution. The polarization relationships of both reactions for a Pb electrode in  $H_2SO_4$  solution were taken from ref. 12 and are indicated by dashed lines.

$H_2SO_4 + Sb_2(SO_4)_3$  solution, as well as for Pb-0.5%Sb electrodes in an  $H_2SO_4$  solution. The data for the Pb/ $H_2SO_4$  electrode are taken from ref. 12 using the same methods and equipment and carrying out the experiments under the same conditions.

Antimony reduces the oxygen overvoltage by 50 - 80 mV, irrespective of the way in which it is added. If the above curves are considered at a constant potential then the introduction of Sb augments the oxygen evolution by one order of magnitude. As a result the polarization curve is shifted in the negative direction. Since the oxygen evolution determines the electrode potential, by shifting the potential curve of the former the corrosion curve is also shifted. Antimony increases the corrosion rate, irrespective of the way that it is added.

Figure 2 presents the polarization curves for the partial currents of corrosion and oxygen evolution of Pb-Sb alloys with different Sb contents. For comparison, the respective dependencies for pure lead are also presented.

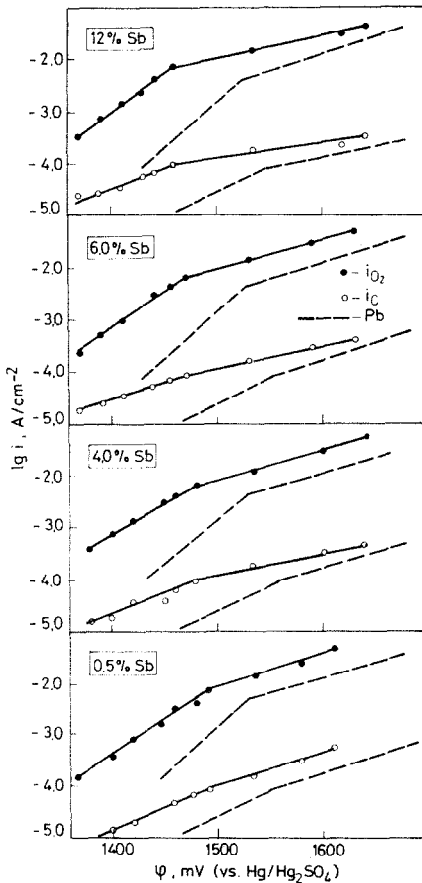


Fig. 2. Current-voltage relations of the oxygen evolution reaction and the corrosion reaction for lead electrodes alloyed with different amounts of Sb. The polarization relationships of both reactions for a Pb electrode in  $\text{H}_2\text{SO}_4$  solution were taken from ref. 12 and are represented by dashed lines.

The partial currents of Pb-Sb alloys follow a Tafel dependence with two slopes, as established with Pb oxidation [11]. With increased Sb content the polarization curves, as well as the potential,  $\varphi_k$ , at which their slope is changed, shift in the negative direction. Increased Sb content also increases the  $b_{\text{O}_2}$  value (from the Tafel equation) for  $\varphi > \varphi_k$ . For  $\varphi < \varphi_k$  it remains almost constant for different alloys.

The relationship between the rates of oxygen evolution current ( $i_{\text{O}_2}$ ) and of anodic corrosion current ( $i_{\text{C}}$ ) of Pb and Pb-Sb alloys is plotted in log-log coordinates in Fig. 3.

At the same current density of oxygen evolution increasing the Sb content in the alloys from 4 to 12% only brings about an insignificant rise in the corrosion rate.

Figure 4 presents the change in the steady-state corrosion rate of Pb-Sb alloys in relation to the Sb content and the total current density. It can be

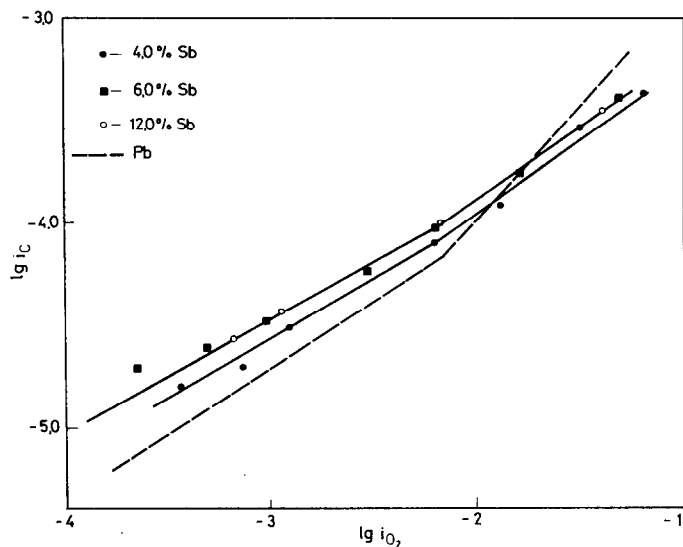


Fig. 3. Relationship between the corrosion and the oxygen currents for lead electrodes alloyed with different amounts of Sb. The dashed-line curve represents the ratio between the rates of both reactions for pure Pb in  $H_2SO_4$  solution (taken from ref. 12).

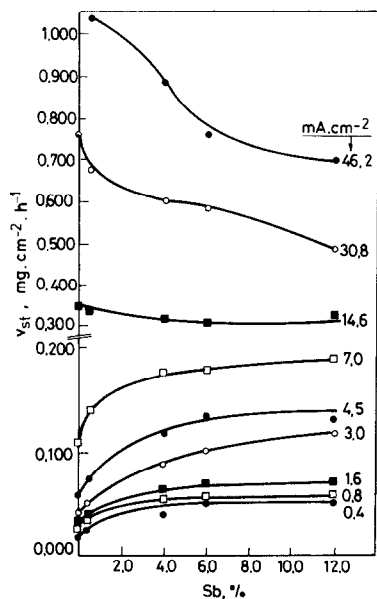


Fig. 4. Dependence of the corrosion rate of Pb-Sb alloys on the Sb content at different polarization current densities.

seen that Sb increases the corrosion rate of pure Pb. When the total current density grows to  $15 \text{ mA cm}^{-2}$  the corrosion rate of Pb-Sb alloys rises slightly. At an oxidation current density of  $14.6 \text{ mA cm}^{-2}$ , the corrosion rate, although

almost independent of the Sb content in the alloy, is lower than that of pure lead and is reduced even more with increasing Sb content.

The relationship between the steady-state potential and the Sb content in the alloy, at different total current densities is presented in Fig. 5. The potential of all Pb-Sb alloys is lower than that of pure lead and, for total current densities up to  $14.6 \text{ mA cm}^{-2}$ , increasing the Sb content reduces the potential between 70 and 100 mV. Above this current density the potential passes through a minimum and then rises by about 40 mV for higher Sb contents.

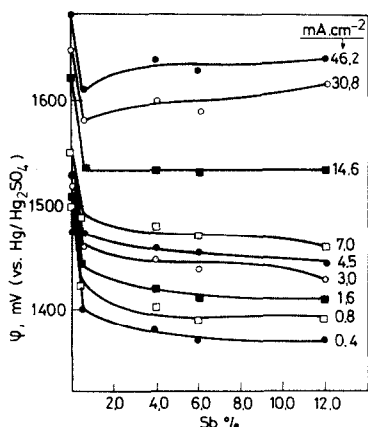
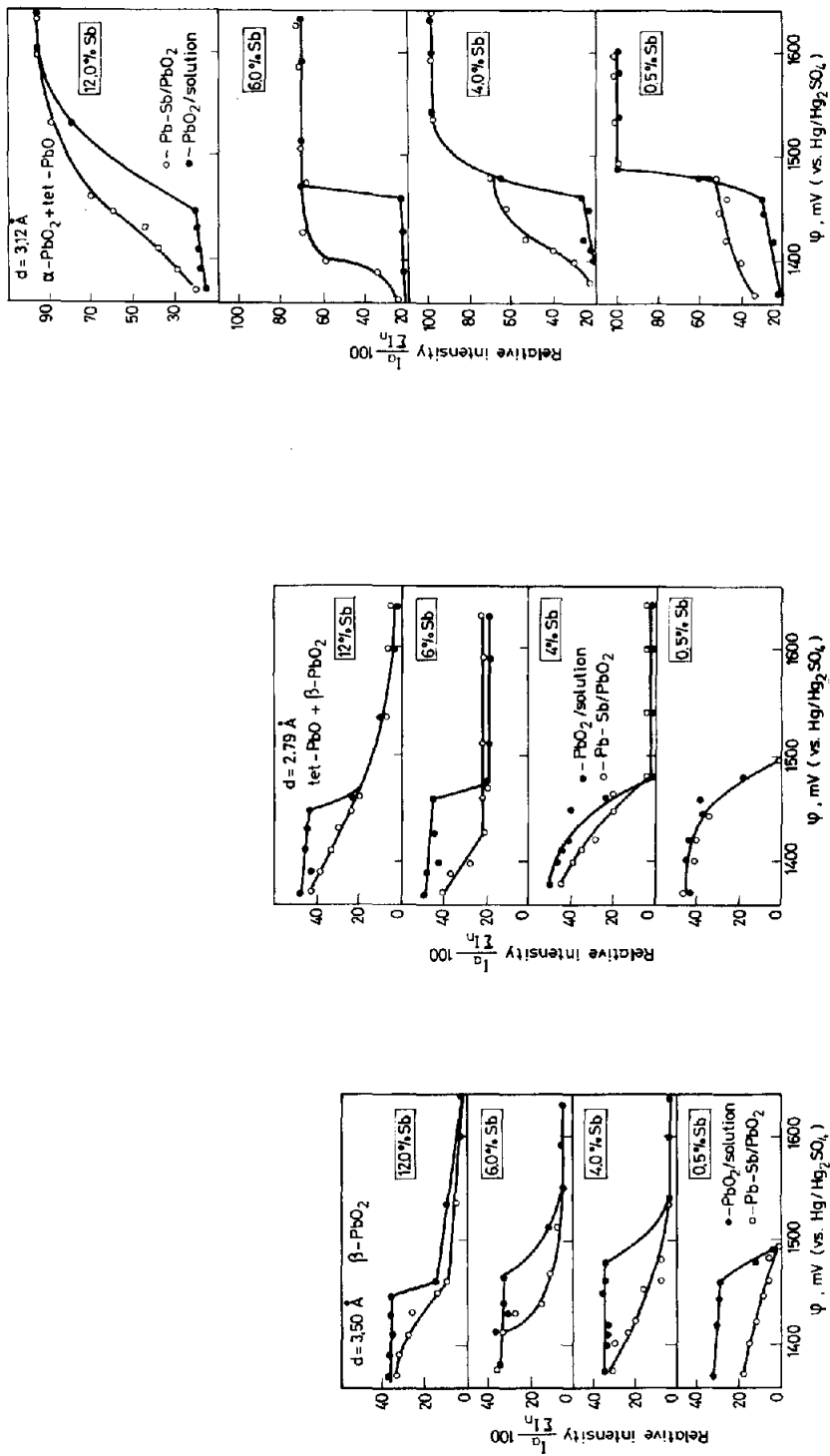


Fig. 5. Dependence of the steady-state potential of Pb-Sb alloys on the Sb content at different polarization current densities.

A relationship was sought between the change in the Tafel slopes and the phase composition of the anodic layer. For this purpose, the phase compositions of the anodic layer at the  $\text{PbO}_2/\text{solution}$  and at the alloy/ $\text{PbO}_2$  interfaces were established by X-ray diffraction. The content of a given phase (a) in the anodic layer was assessed by the relative intensity of the characteristic diffraction line  $(I_a/\Sigma I_n) \times 100$ , where  $\Sigma I_n$  is the sum of the intensities of all the diffraction lines, and  $I_a$  is the intensity of the characteristic diffraction line of phase (a).

Figure 6(a) illustrates the distribution of the  $\beta\text{-PbO}_2$  phase at the two phase interfaces, Fig. 6(b) the distribution of  $\beta\text{-PbO}_2$  and tet-PbO, and Fig. 6(c) that of tet-PbO and  $\alpha\text{-PbO}_2$ , after 300 hours of oxidation as a function of the steady-state potential.

By comparing Figs. 2 and 6 it can be seen that the change in the Tafel slopes is related to the alteration of the phase composition of the anodic layer. At  $\varphi < \varphi_k$  the slope is determined by the  $\beta\text{-PbO}_2$  phase and the oxygen evolution proceeds mainly on it, while at  $\varphi > \varphi_k$  it is determined by the  $\alpha\text{-PbO}_2$  phase. When the amount of Sb at the alloy/ $\text{PbO}_2$  interface is increased the  $\beta\text{-PbO}_2$  content in the anodic deposit grows. With pure Pb electrodes  $\beta\text{-PbO}_2$  is formed only at the  $\text{PbO}_2/\text{solution}$  interface [12], while with



(a)

(b)

(c)

Fig. 6. Relationship of the relative intensity of the X-ray characteristic diffraction lines at both interfaces of Pb-Sb electrodes vs. oxidation potential. (a)  $\beta$ -PbO<sub>2</sub> diffraction line with  $d = 3.50 \text{ \AA}$ ; (b) tet-PbO and  $\beta$ -PbO<sub>2</sub> diffraction line with  $d = 2.79 \text{ \AA}$ ; (c) tet-PbO and  $\alpha$ -PbO<sub>2</sub> diffraction line,  $d = 3.12 \text{ \AA}$ .

Pb-Sb electrodes it is formed at both phase interfaces. At potential more negative than  $\varphi_k$  the anodic layer at the  $\text{PbO}_2/\text{solution}$  interface consists of a considerable amount of  $\beta\text{-PbO}_2$  and, with the addition of Sb in the alloys, this amount rises slightly. The intensity of the 2.79 Å line is weakened; probably due to the oxidation of tet-PbO to  $\beta\text{-PbO}_2$ . The characteristic lines of  $\alpha$  and  $\beta\text{-PbO}_2$  on the diffractograms are very broad, which implies that the anodic deposit has a fine crystalline structure, *e.g.*, antimony causes a decrease in the PbO crystal size.

It is impossible, however, to determine the exact amount of tet-PbO and  $\text{PbO}_2$  in the anodic layer using X-ray diffraction alone and we used chemical analysis [12] to assess the stoichiometric coefficient  $n$  of the oxide layer ( $\text{PbO}_n$ ). Table 1 presents values of  $n$  obtained after oxidation of Pb-Sb alloys for 300 h at various current densities.

TABLE 1

% Sb	0.5	4.9	7.3	10.6
$n$	1.40 - 1.70	1.60 - 1.75	1.65 - 1.75	1.75 - 1.85

These numbers are overall values since the chemical analysis was performed for the total amount of the anodic layer. Figure 6 shows that the PbO and  $\text{PbO}_2$  contents vary through the depth of the anodic layer. This change has not been accounted for in the data of Table 1.

The stoichiometric number increases with the amount of Sb and is lowest for oxides obtained on a pure Pb electrode [12]. This implies that antimony enhances the oxidation of tet-PbO to  $\text{PbO}_2$ .

## Discussion of results

Kabanov *et al.* [13] advanced the idea that the anodic corrosion of lead is caused by oxygen which penetrates the anodic layer. In a series of papers [11, 12, 14] this idea was developed and in ref. 11 a model was evolved of the processes proceeding during oxidation of the Pb/non-stoichiometric  $\text{PbO}_2/\text{O}_2/\text{H}_2\text{O}/\text{H}_2\text{SO}_4$  electrode system in the  $\text{PbO}_2$  potential range. The electrode potential is determined by the oxygen evolution reaction. Hence, it determines the concentration of O atoms and  $\text{O}^-$  radicals in the anodic layer. These concentrations in their turn affect the rate of the corrosion process. Consequently, in spite of the chemical character of the reaction between Pb and  $\text{O}_2$ , it depends on the potential. This is illustrated by the polarization relations,  $i_c/\varphi$ , in Figs. 1 and 2.

There are three main items upon which antimony may have an effect:

(a) On the oxygen overvoltage. The effect of Sb is expressed by a shift in the polarization potential curve. This influence is demonstrated in a clear-cut manner when the additive is introduced into the solution.



(b) On the rate of metal oxidation to tet-PbO. This effect is exerted when the additive is alloyed with the metal and the electrodes thus prepared are subjected to anodic oxidation.

(c) On the rate of oxidation of tet-PbO to PbO<sub>2</sub>. A way of assessing the effect of a given additive on this reaction is by calculating the stoichiometric coefficient. When the additive is introduced into the alloy during electrode oxidation it is also oxidized and its ions are either built into the oxide in the form of a solid solution or they form a separate phase in the anodic layer. Introduced in this way they affect the phase composition of PbO<sub>2</sub> and the mobility of O atoms and O<sup>-</sup> radicals in the PbO<sub>2</sub> layer. They also influence the rate constant of the oxidation reaction of Pb<sup>2+</sup> ions to Pb<sup>4+</sup> ions in the oxide.

The experimental results of Figs. 1 and 2 demonstrate that antimony, irrespective of the way it is added, reduces the oxygen overvoltage, *i.e.*, it enhances oxygen evolution, whereby the polarization curve is shifted in the negative direction. Thus, the concentration of O atoms and O<sup>-</sup> radicals at the oxide/solution interface is increased as a result of which the rate of oxygen diffusion towards the lead surface grows. The experimental results confirm the model of the processes in the electrode system Pb/non-stoichiometric PbO<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub> described in ref. 11. The corrosion process (reactions (1) and (2)) is by itself a chemical reaction preceded by an electrochemical one (oxygen evolution).



The corrosion rate can be expressed by the following equation

$$i_c = V_c = K_c C_O^M$$

where  $K_c$  is the rate constant of the metal oxidation reaction,  $C_O^M$  is the concentration of O atoms in the oxide layer at the metal surface. It is determined by the concentration of O atoms and O<sup>-</sup> radicals at the oxide/solution interface and by the rate of diffusion through the corrosion layer. It also depends on the potential.

Part of the O atoms participate in reaction (2), hence, their flow through the anodic layer is decreased:



The data on Figs. 1, 2, and 3 imply that antimony increases the corrosion rate. This may be due either to a rise in the rate constant of reaction (2), or to changes in the diffusion coefficients of the O atoms and radicals during their movement through the anodic layer, or to the effect of both parameters simultaneously.

#### List of symbols

$\varphi$	Stationary potential
$\varphi_k$	Critical potential

$i$	Oxidation current density
$i_C$	Partial corrosion current
$i_{O_2}$	Partial oxygen evolution current
$V_{st}$	Stationary corrosion rate
$I_a$	Characteristic diffraction line of phase "a"
$I_n$	Characteristic diffraction line of phase "n"

## References

- 1 D. Pavlov, in B. D. McNicol and D. A. J. Rand (eds.), *Power Sources for Electric Vehicles*, Elsevier, Amsterdam, 1984.
- 2 J. Burbank and A. Simon, *J. Electrochem. Soc.*, **100** (1953) 11.
- 3 J. Burbank, *J. Electrochem. Soc.*, **104** (1957) 693; **118** (1971) 525.
- 4 W. Hofmann, *Blei und Bleilegierungen*, Springer, Berlin, 1962.
- 5 P. Ruetchi and B. Cahan, *J. Electrochem. Soc.*, **104** (1957) 406; **105** (1958) 396.
- 6 J. J. Lander, *J. Electrochem. Soc.*, **98** (1951) 213; **103** (1956) 1; **99** (1952) 467.
- 7 V. P. Mashovets and A. Z. Lyanders, *Zh. Prikl. Khim.*, **21** (1948) 441.
- 8 D. Pavlov, M. Boton and M. Stojanova, *Bull. Inst. Chim. Phys.*, **5** (1965) 55.
- 9 F. Arifuku, H. Jonogama and H. Tamura, *J. Appl. Electrochem.*, **9** (1970) 629.
- 10 A. Simon, *J. Electrochem. Soc.*, **114** (1967) 1.
- 11 D. Pavlov and T. Rogatchev, *Electrochim. Acta*, **31** (1986) 241.
- 12 D. Pavlov and T. Rogatchev, *Electrochim. Acta*, **23** (1978) 1237.
- 13 I. I. Astachov, E. S. Weisberg and B. N. Kabanov, *Dokl. Acad. Nauk, USSR*, **154** (1964) 1414.
- 14 D. Pavlov, *Electrochim. Acta*, **23** (1978) 845.