

INFLUENCE OF THE LEAD DIOXIDE ACTIVE MASS ON THE CORROSION RATE OF THE SPINES OF POSITIVE LEAD-ACID BATTERY PLATES

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Summary

Weight measurements were used to determine the corrosion rate of the spines in tubular lead dioxide electrodes with active mass. It was established that the active mass decreases the corrosion rate on both lead- and lead-antimony spines. The spine corrosion rate was determined under continuous and discontinuous polarization and under charge-discharge cycling. It was found that under continuous polarization the corrosion rate is lower on lead spines than on lead-antimony ones. The opposite correlation was observed under cycling. A determination of the corrosion layer phase composition under various polarization conditions showed that the corrosion layer is very sensitive to polarization conditions despite the presence of active mass.

Introduction

The anodic corrosion of lead or lead alloy electrodes in the PbO_2 potential region (above +960 mV vs the $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{H}_2\text{SO}_4$ electrode) proceeds through a dense layer of PbO_2 . The metal is oxidized on the metal/oxide surface and oxygen is evolved at the oxide/solution interface. Kabanov *et al* [1, 2] suggested that part of the oxygen diffuses through the PbO_2 layer and oxidizes the metal. Pavlov [3] further developed this idea, suggesting a possible mechanism of the corrosion processes.

The lead-acid battery positive plate has the following structure
grid/corrosion layer/active mass/solution.

The oxygen evolution takes place at the active mass/solution interface. This implies that the corrosion rate of the grid has to depend on the thickness of the active mass layer. The influence of the active mass on the grid corrosion rate has been the subject of many investigations [4 - 10]

Cannone, Feder and Biagetti [4] determined that the active mass does not influence the corrosion rate of lead and lead alloy grids. Simon and Caulder [5] showed that the phase composition of the paste from which the active mass is formed, or the paste density, has an effect on the corrosion during the first few charge-discharge cycles. A recent paper of Felu, Otero and Gonzalez [8] determined that the grid corrosion rate is decreased by the active mass. Obviously, this problem needs further investigation. Such a study is the first purpose of the present paper. To obtain unambiguous results, the active mass thickness should be constant all over the corroding metal surface. Tubular electrodes meet this requirement, so the present corrosion study was carried out on tubular plate spines.

Lead-acid batteries are exploited under various operating conditions. We may suppose that oxygen evolution occurs only during the charging periods of cycle life and its rate varies during one cycle. Hence, the spine corrosion rate depends on the operating conditions. The second purpose of the paper is to determine this dependence.

The majority of lead-acid batteries are produced with lead-antimony grids. The third purpose of the paper is to determine the influence of antimony on the spine corrosion rate under three different sets of conditions.

Experimental methods

(i) Method of tubular electrode preparation

Spines with a diameter of 4 mm and a length of 150 mm were introduced into polyester tubes. The latter were filled with (66%) oxidized lead powder (15.0 g). The electrodes were immersed in 1.40 sp.gr. H_2SO_4 solution for two minutes. Curing followed for 5 days. Formation was performed at 10 mA/cm^2 spine area, with 0.70 A h/g of lead powder, in a 1.05 sp.gr. H_2SO_4 solution. In such an electrode the metal is covered by a 2.2 mm thick layer of active mass. The construction of this electrode is presented in Fig. 1. Obviously, the oxidation of the spine can only take place through the active mass layer. The spines were prepared from pure Pb as well as from the following alloys: Pb-4.9% Sb, Pb-7.35% Sb, Pb-10.60% Sb. Cells were made by combining negative plates with these electrodes. The cells were filled with 1.28 sp.gr. H_2SO_4 and placed in a thermostat at 50°C . This temperature was selected in order to accelerate the test.

(ii) Method of spine corrosion rate determination

The steady-state spine corrosion rate was determined by a modification of the method proposed by Pavlov and co-workers [11, 12]. Eighteen spines of each alloy were weighed and electrodes were prepared from them. They were then subjected to anodic corrosion under the same conditions but polarized for six different periods of time. Three electrodes were taken out at each polarization time interval. The active mass was removed mechanically

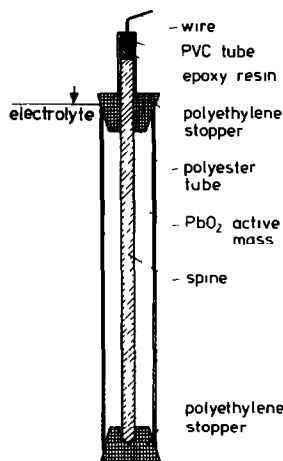


Fig 1 Construction of the electrode

The corrosion layer on the spine was dissolved in an alkaline solution of glucose and the spines again weighed. The weight loss gives the amount of corroded metal. For each polarization period and each alloy the weight loss was calculated as an arithmetical average of the three electrode measurements. The steady-state spine corrosion rate was determined from $\tan \alpha$ of the linear part of the amount of corroded metal/polarization time relationship

(iii) Conditions of polarization

The spine corrosion rate was determined under three different conditions

- continuous polarization of the electrodes. They were polarized at a constant current density of 6 mA/cm^2 of spine area,

- discontinuous polarization of the electrodes. The electrodes were polarized at a current density of 6 mA/cm^2 for 100 h and left for 68 h on open circuit. This constituted one cycle. After every 3 cycles, 3 electrodes were taken out and spine-weight-loss measurements were carried out. The corrosion rate was calculated from the weight loss of the spines during 18 cycles (the polarization plus rest time taken together);

- charge-discharge cycling. The electrodes were anodically polarized (charged) for 9 h at a current of 6 mA/cm^2 and cathodically polarized (discharged) for 3 h at 15 mA/cm^2 . This constituted one cycle. A charge/discharge cycle contains only 20% overcharge. After every 30 cycles, 3 electrodes were taken out and the amount of oxidized metal was measured. The corrosion rate was determined from the weight loss of the spines during 180 cycles (the charge plus discharge times taken together)

Experimental results

(i) Influence of the active mass on the spine corrosion rate

We first studied the dependence of the amount of corroded metal on time during continuous galvanostatic polarization. Figure 2 presents the weight of corroded metal as a function of the polarization time. It is seen that a linear relationship holds no matter whether the spine is covered with active mass or not

$$p = a + vt$$

p denotes the weight of corroded metal per cm^2 of spine surface and t marks the polarization time. The steady-state corrosion rate of the spine per cm^2 is given by the slope v .

The corrosion rate was determined over a period of 1500 h. The maximum weight loss per cm^2 was about 0.15 g in the presence of active mass and about 0.38 g for the spines without active mass. This corresponds to 0.1 mm and 0.3 mm (5 and 15%) decrease in the spine radius. We can suppose that the surface area does not change during the oxidation, i.e., the electrodes behave as if they were flat.

From Fig. 2 it is seen that the presence of active mass reduces the corrosion rate both for lead and for lead-antimony spines. The addition of antimony increases the corrosion rate of both types of spines. a is a constant

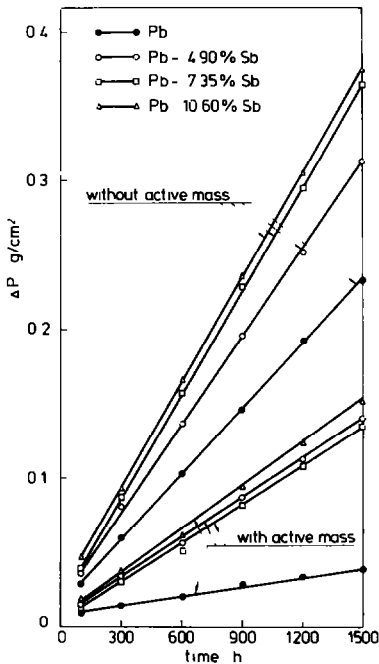


Fig. 2 Dependence of the amount of metal corroded from electrodes, with and without active mass, on polarization time

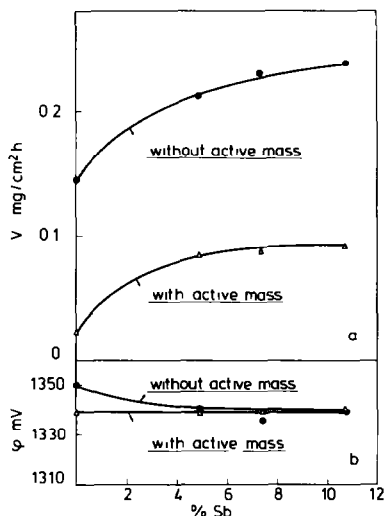


Fig 3 Dependence of corrosion rate and electrode potential on Sb content in the alloy

with a dimension of g/cm^2 . It takes into account the thickness of the corrosion layer which is formed before the corrosion rate reaches a constant value. The value of a is lower in the case of electrodes with active mass. Perhaps the reason for this is that a part of this layer is formed during the active mass formation.

Figure 3(a) presents the spine corrosion rate plotted against the amount of antimony in the alloys. It is seen that antimony increases the corrosion rate. The ratio of the corrosion rates for spines without and with active mass is 7 in the case of lead electrodes whereas it is 2.5 in the case of lead-antimony spines. Therefore antimony decreases the effect of the active mass by a factor of almost three.

The values of the stationary electrode potentials of the various electrodes are presented on Fig. 3(b).

(ii) Dependence of the corrosion rate on the polarization conditions

The time dependence of the amount of metal corroded during discontinuous polarization is presented on Fig. 4. It shows that the corrosion of lead is lower than that of Pb-Sb alloys. Within the time of this experiment no effect of the Sb content of the alloy on the corrosion rate was apparent.

The time dependence of the amount of metal corroded during cycling of the electrode is presented in Fig. 5. With cycling, the corrosion of lead is higher than that of the Pb-Sb alloys. The corrosion rate decreases with increase of the Sb content.

Figure 6 presents the corrosion rate of spines under the three conditions mentioned previously, plotted against the antimony content of the alloy. The corrosion rate of lead under charge-discharge cycling is three

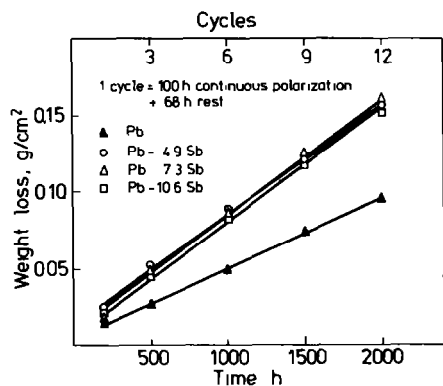


Fig 4 Time dependence of the amount of corroded metal during discontinuous polarization of the electrodes

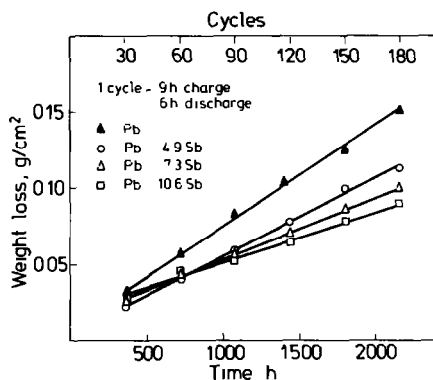


Fig 5 Dependence of the amount of metal corroded from electrodes during cycling

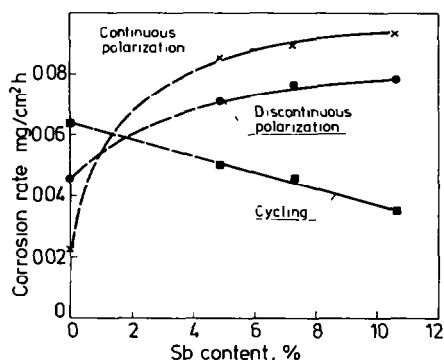


Fig 6 Dependence of corrosion rate on the Sb content of the spine polarized under three different operating conditions

times higher than that on continuous polarization. On a lead-antimony spine, the above dependence of corrosion rate on the polarization condition is inverse. The corrosion rate of Pb-Sb alloys is highest with continuous polarization and lowest under charge-discharge cycling.

The introduction of a rest period (during the discontinuous polarization) decreases the spine corrosion rate of the Pb-Sb alloys and increases the corrosion rate of Pb. The introduction of a discharge increases this tendency and the corrosion rate of Pb becomes higher than that of the Pb-Sb alloys.

Under charge-discharge cycling increase of the antimony content decreases the corrosion rate

(iii) *Dependence of the corrosion layer phase composition on the polarization conditions*

The phase composition of the spine corrosion layer was determined by means of X-ray diffraction analysis. After mechanical removal of the active material the corrosion layer was brushed off and X-rayed. The characteristic reflection for β -PbO₂ was $d = 3.49 \text{ \AA}$ and for α -PbO₂ $d = 3.12 \text{ \AA}$. The latter overlaps with the strongest diffraction line for tet-PbO. As was determined in ref 13, the corrosion layer has a nonstoichiometric composition.

Figure 7 presents the ratio of the reflection intensities $\gamma = I_{3.49}/I_{3.12}$ as a function of time with continuous polarization. At the beginning of polarization, the anodic layer contains a considerable amount of β -PbO₂. Then the phase composition changes and after 600 - 900 h of oxidation it reaches a constant value. From a comparison of Figs. 3 and 7 it follows that the corrosion resistance and the amount of β -PbO₂ in the corrosion layer are higher on lead spines than on those of lead-antimony alloys.

Figure 8 presents the dependence of γ on time with discontinuous polarization. Under this condition the β -PbO₂ content in the layer is also highest at the beginning of the polarization. It decreases rapidly until the 900th h, after which it changes rather slowly.

Under charge-discharge cycling the values of γ vary between 5 and 10 and show no clearly expressed dependence on the number of cycles. The value of γ tends to be higher on lead spines than on Pb-Sb spines.

A comparison of the γ values for the three conditions shows that the lowest content of β -PbO₂ is found in the corrosion layer which is formed under continuous polarization. It increases when periods of open circuit

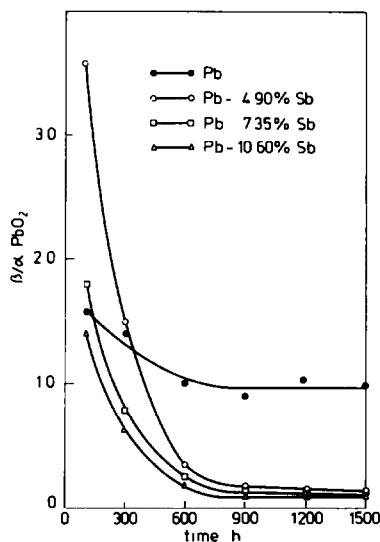


Fig 7 Change of β/α PbO₂ ratio in the corrosion layer during continuous polarization of electrodes with active mass

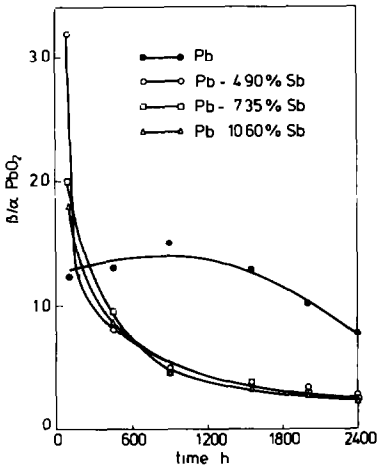


Fig 8 Change of β/α PbO_2 ratio in the corrosion layer during discontinuous polarization of electrodes with active mass

are introduced. With charge-discharge cycling this trend becomes more marked. These experimental results suggest that during the periods of open circuit or discharge the processes are not confined solely within the active mass, but take place in the corrosion layer too.

Under discontinuous polarization the reduction of active material is negligible and the electrode potential remains almost unchanged. The processes in the corrosion layer, however, go on and they change its phase composition. The corrosion layer is therefore very sensitive to the polarization condition and should influence the corrosion rate.

Under both continuous and discontinuous polarization, after 600 h the value of γ of the corrosion layer on the lead spines is higher than that on the lead-antimony spines. An opposite correlation holds in respect of the corrosion rates. From these correlations it follows that the corrosion layer phase composition influences the corrosion rate but the dependence between them is not unambiguous.

Discussion

The above results may be of interest in two respects. First, they are useful as a guide to the choice of the right alloy for the positive plate spines of various types of batteries. Second, they pose problems whose solution is essential to the further development of the model of the lead anodic corrosion mechanism.

From Fig. 6 it follows that the corrosion rate under float and discontinuous polarization is lowest if the spines are made from lead or low-antimony-lead alloys. Stationary batteries are exploited under the above condition. Traction and load levelling batteries are operated under cycling.

To prolong their life, the spines of their tubular electrodes should be made of high-antimony alloys.

The electrode system has the following structure

metal/corrosion layer/active mass/solution.

The corrosion layer of nonstoichiometric PbO_n ($1.4 < n < 2$) is built up of two sublayers—dense (at the metal interface) and porous (at the active mass interface). This assumption is also valid for tubular electrodes. This is supported by the experimentally obtained linear relationship, shown on Figs. 2, 4 and 5. The oxidation of the metal is connected with the transport of O^{2-} ions, O^- radicals and O atoms through the dense sublayer, and the reaction at the Pb/PbO_n interface [3]

If we accept this model, it follows that the corrosion rate of the spine is controlled by oxygen transport through the corrosion layer. The maximum corrosion rate should be expected under continuous polarization where oxygen is evolved continuously. The corrosion rate under discontinuous polarization would be lower since oxygen is only evolved during current flow. Finally, under charge–discharge cycling the oxygen evolution only takes place for a short time during charging, i.e., after PbSO_4 has turned into PbO_2 . Hence, the lowest corrosion rate should be expected under charge–discharge cycling. The experimental evidence given in Fig. 6 shows that this is only true in the case of lead–antimony alloys. An opposite correlation is observed in the case of lead spines. The highest corrosion rate on lead corresponds to charge–discharge conditions and the lowest to continuous polarization.

The above conclusions on the influence of the polarization regime on corrosion rate are made on the assumption that the dense sublayer thickness and its electric and electrochemical properties (concentration and mobility of crystal lattice defects, which determine the concentration and mobility of O^{2-} , O^- and O) do not depend on the additives in the alloy and on the polarization regime.

However, the experimental data on Figs. 7 and 8 and the data for the corrosion layer phase composition under cycling indicate that the layer is highly sensitive both to the polarization regime and to the type and quantity of additives. This is proved by the different phase compositions of the corrosion layer under the three polarization regimes on both the lead and the lead–antimony alloys.

The influence of potential on the corrosion rate was experimentally determined in ref. 13. The experimental results of the present paper indirectly lead to the conclusion that the corrosion rate might also depend on the thickness, electrical and electrochemical properties of the dense sublayer. The present investigation does not use methods which could provide experimental data on the change of the dense sublayer thickness and its properties with different polarization regimes and alloys. Obviously, to clarify the mechanism of the corrosion processes it is necessary to determine the above relationships experimentally.

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