INFLUENCE OF ACTIVATORS AND INHIBITORS ON THE POSITIVE ACTIVE MATERIAL OF LEAD/ACID BATTERIES

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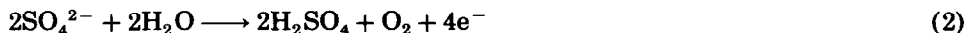
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Introduction

Two basic reactions proceed at the positive electrode of a lead/acid cell, *i.e.*, the anodic oxidation and reduction of divalent lead to tetravalent lead

$$PbO_2 + 3H^+ + HSO_4^- + 2e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} PbSO_4 + 2H_2O \tag{1}$$

and the evolution of oxygen on charging:

$$2SO_4^{2-} + 2H_2O \longrightarrow 2H_2SO_4 + O_2 + 4e^- \tag{2}$$

Modification of the reaction conditions greatly affects the contribution of each of these reactions to the overall charging process.

The purpose of the present work is to modify the operating conditions of the positive electrode so that the contribution of reaction (1) to the total energy balance is much greater than that of reaction (2). The reason for the modification is because oxygen evolution decreases the overall charging efficiency of the cell, a factor that is particularly disadvantageous in mainte-nance-free batteries.

Experimental

Modification of the operating conditions of a positive electrode was achieved through the introduction of additives to either the electrolyte or the electrode active material. Aqueous sulphuric acid solution (always 1.28 g cm^{-3}) was used as the electrolyte. The two-stage reaction of the oxidation of divalent lead to the tetravalent form (lead dioxide) was investi-gated using a potentiodynamic method.

Figure 1 shows a typical voltammetric curve. The anodic curve exhibits peaks that correspond to the oxidation reaction of divalent lead to lead dioxide. In particular, E_1 indicates the potential of α-PbO_2 formation, while E_2 indicates the potential of β-PbO_2 formation. Intense evolution of oxygen

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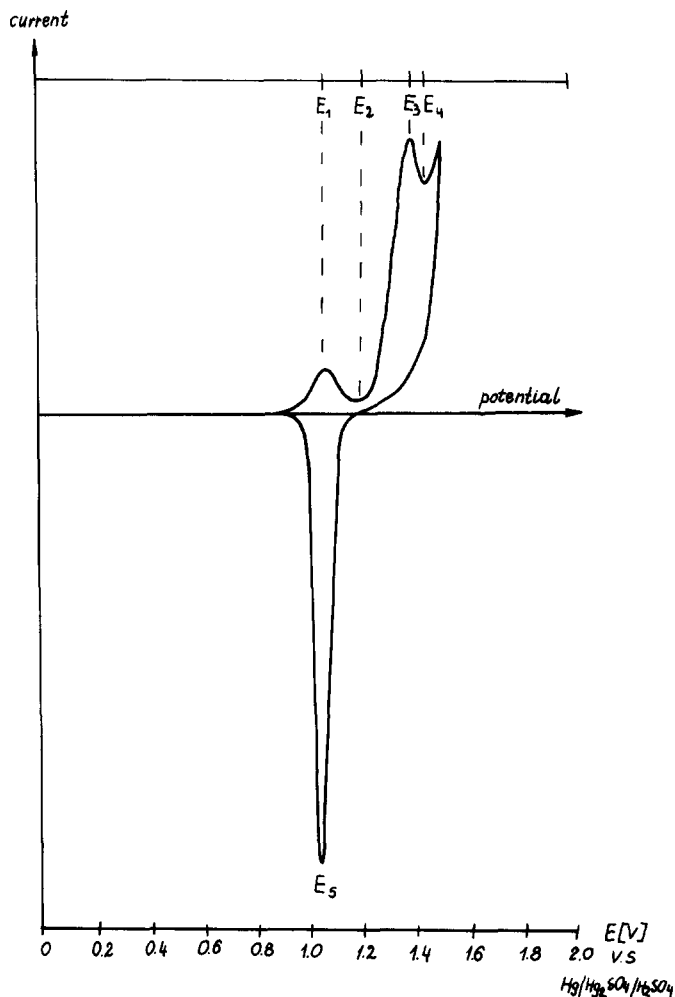*Author to whom correspondence should be addressed.

current

Fig. 1. Potentiodynamic curve for lead.

takes place beyond the E_4 potential. The E_5 potential on the cathodic curve represents the maximum rate of the reduction of lead dioxide to divalent lead (lead sulphate).

In initial experiments, attempts were made to prepare electrodes of pure α-PbO$_2$ or β-PbO$_2$. On the basis of earlier studies [1], PbO$_2$ was anodically deposited on a platinum foil, from a solution of nitric acid saturated with lead nitrate, by electrolysis. The phase composition of the PbO$_2$ was investigated by X-ray diffraction (XRD) spectroscopy. The results are given in Tables 1 and 2. The data clearly show that an increase in both nitric acid concentration and current density results in a higher β-PbO$_2$ content.

TABLE 1

XRD analysis of electrodeposited PbO_2
Current density of 6 mA cm^{-2}.

Concentration of nitric acid for electrolysis (%)	α-PbO_2 content (%)	β-PbO_2 content (%)
5	45	55
12	25	75
20	trace	99

During the initial potentiodynamic cycles, electrodes with more than 90% β-PbO_2 failed due to shedding of lead dioxide from the platinum substrate. In addition, the overpotential of oxygen evolution on the platinum substrate was too low to obtain the full potentiodynamic curve — only the peak corresponding to α-PbO_2 formation was obtained. As a result, experiments were continued with a lead foil substrate because of this metal's higher oxygen overvoltage. The pure lead foil was subjected to potentiodynamic cycles. After the formation of the active lead dioxide layer, sulphates were introduced into the electrolyte solution together with the oxides of tin, mercury, cobalt, cadmium, silver, barium, and magnesium. Differences in the potentiodynamic curves resulting from the addition of tin sulphate and mercury sulphate are shown in Figs. 2 - 4.

The initial curves of Fig. 2 are for the lead electrode without additions. After the 5th cycle, the electrode was activated in sulphuric acid containing tin sulphate and then subjected to continuous potentiodynamic cycling. Little change was observed in the potentials corresponding to characteristic current peaks on the potentiodynamic curve. It was found, however, that even the presence of a slight amount of tin sulphate considerably improved the redox reaction of the lead electrode.

Figure 3 shows the influence of mercury sulphate; this was added after the 3rd cycle. In this case, even a small concentration of the additive

TABLE 2

XRD analysis of electrodeposited PbO_2 content
Nitric acid concentration 12%.

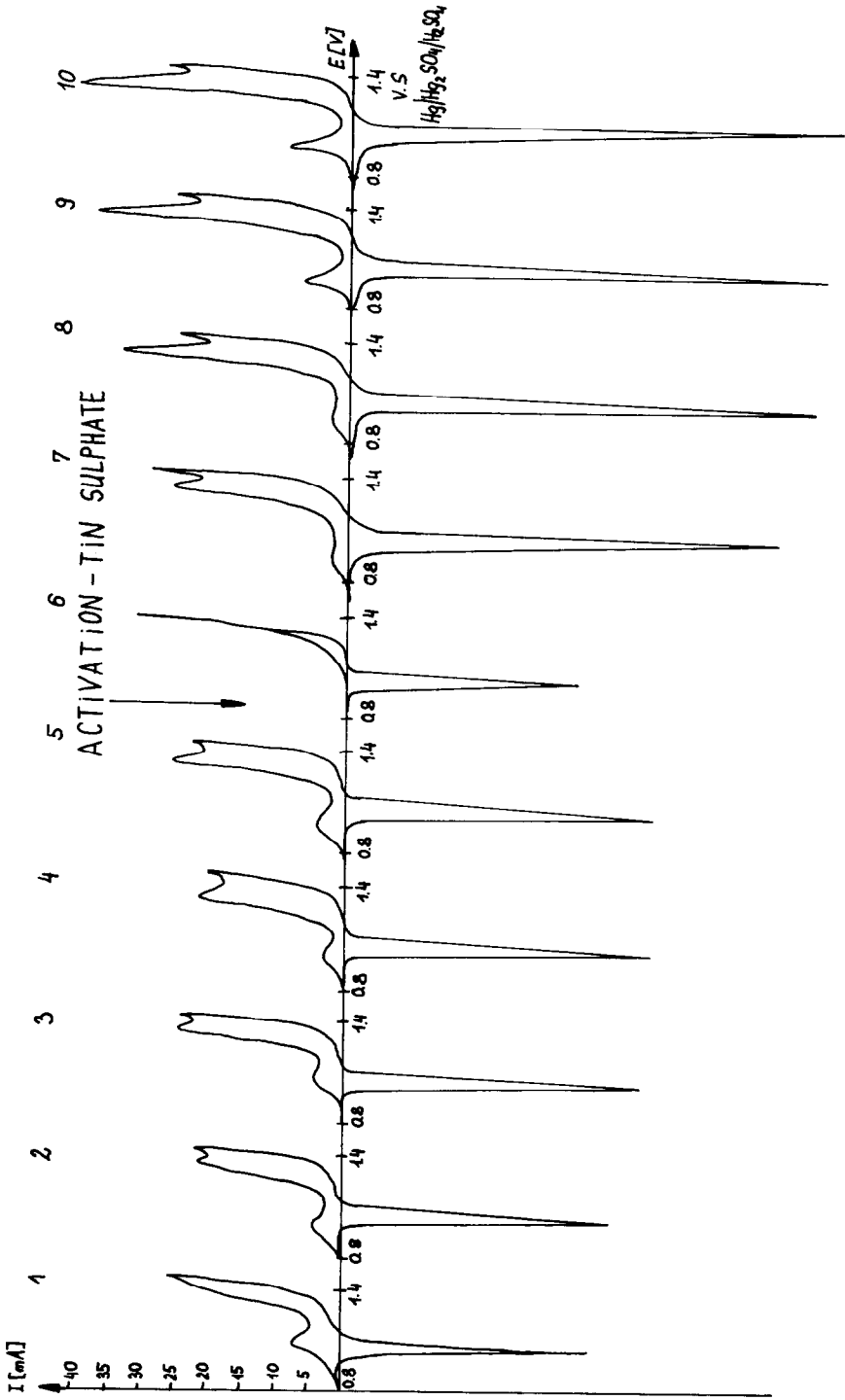| Current density (mA cm^{-2})	α-PbO_2 content (%)	β-PbO_2 content (%)
0.6	78	22
6	45	55
30	trace	~100

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Fig. 2. Potentiodynamic curves for lead activated by tin sulphate after 5th cycle. Potential scan = 50 mV min⁻¹.
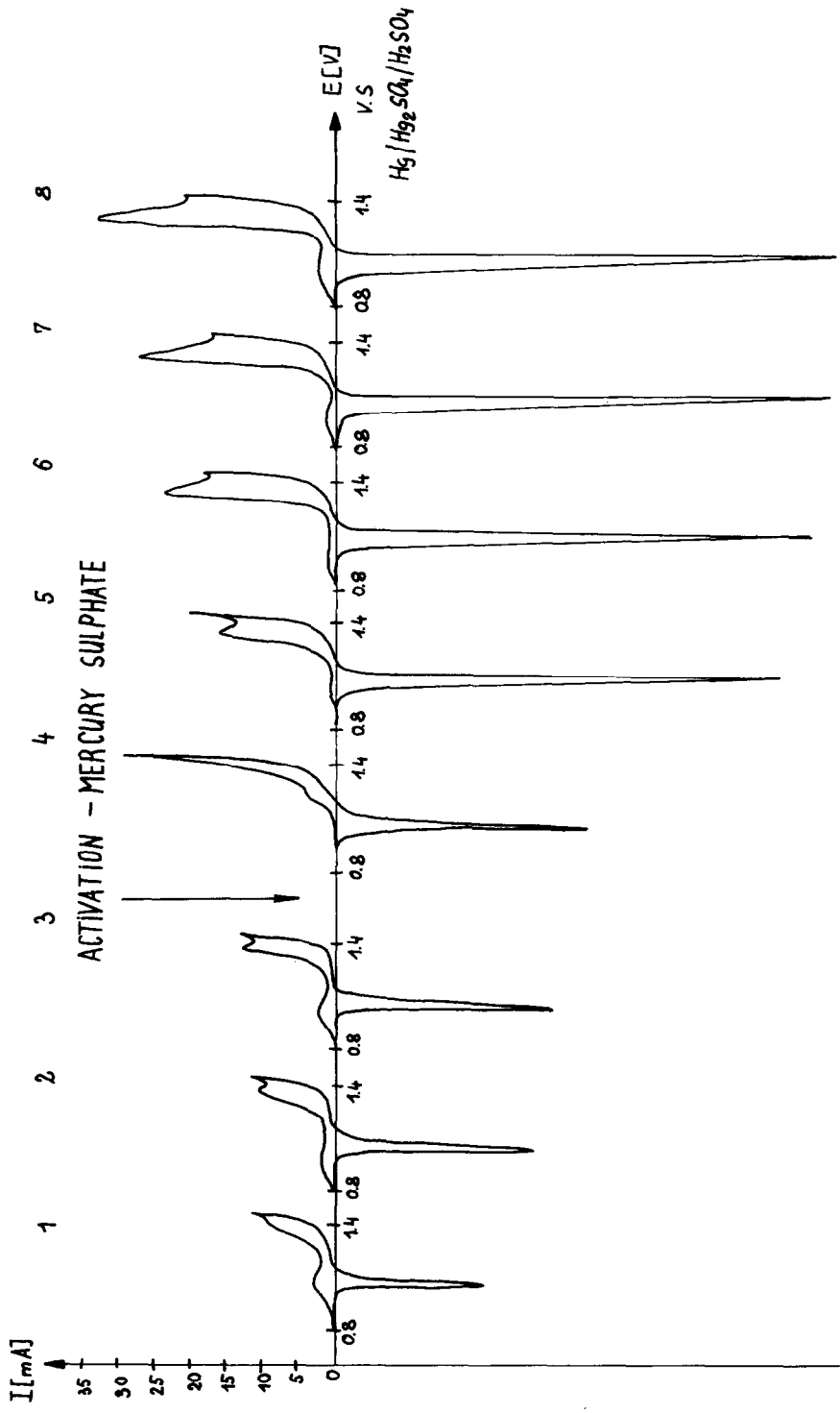
Fig. 3. Potentiodynamic curves for lead electrode activated by mercury sulphate after 3rd cycle. Potential scan = 50 mV min⁻¹.
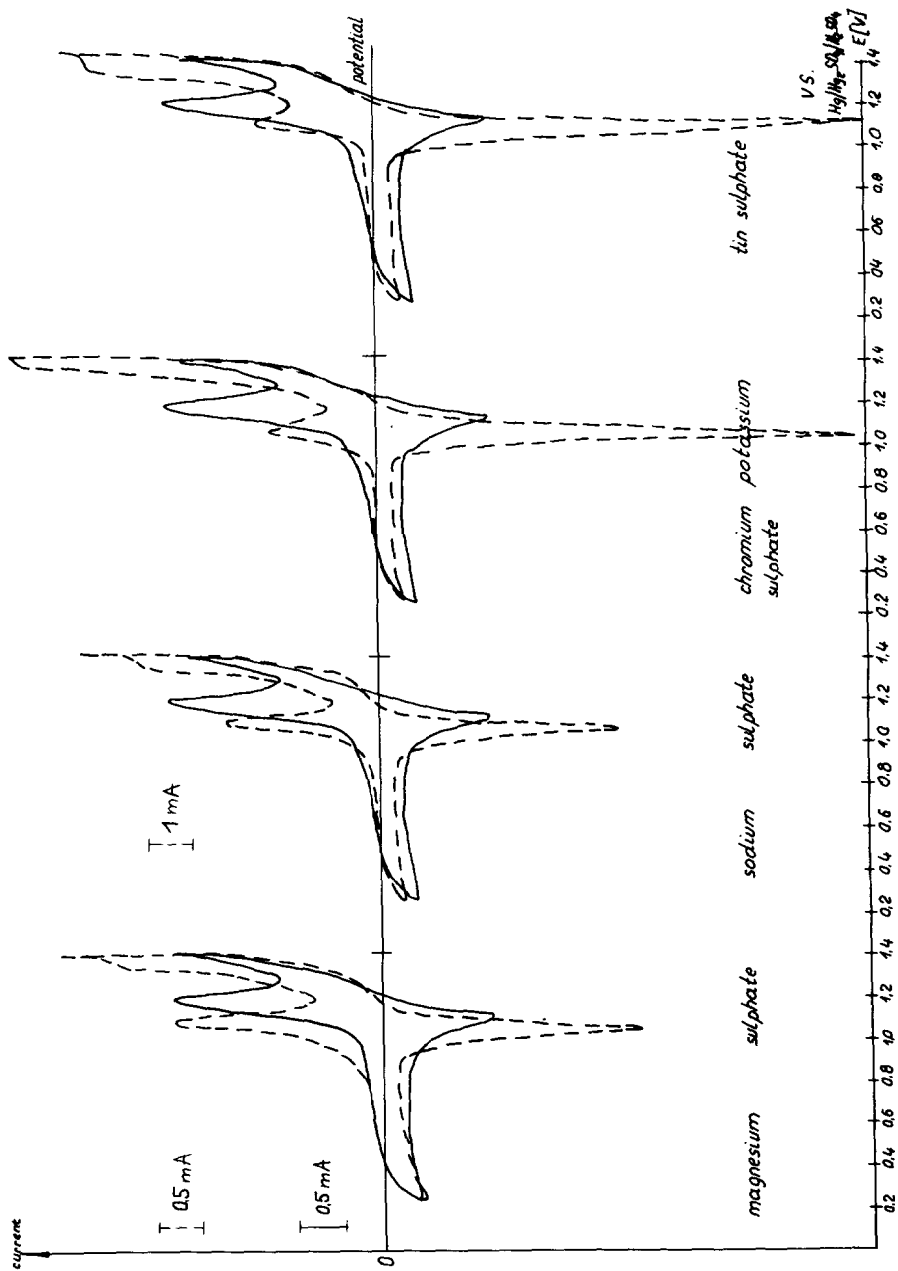
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Fig. 4. Potentiodynamic curves for lead: ——, without additives; – – –, with 2.5 wt.% of magnesium, sodium, chromium, potassium, or tin sulphates. Potential scan = 100 mV min^{-1}.
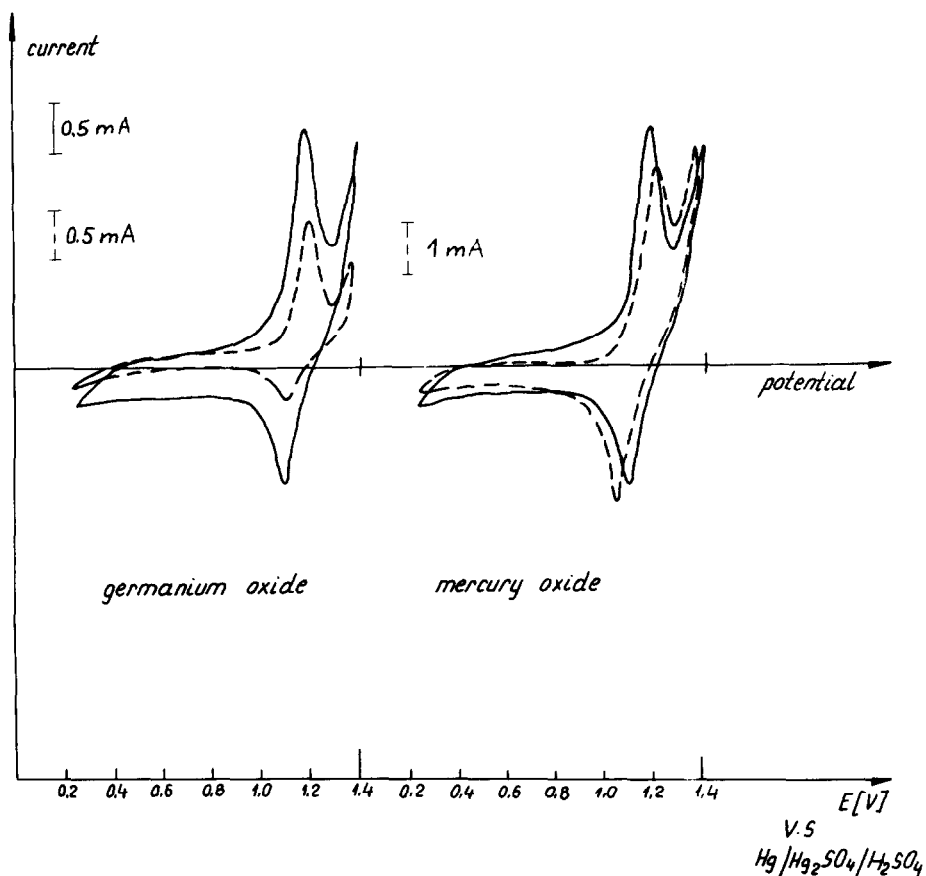
Fig. 5. Potentiodynamic curves for lead: —, without additives; – – –, with 2.5 wt.% germanium oxide or mercury oxide. Potential scan = 100 mV min^{-1}.

increases both the reaction rate and the potentials corresponding to oxygen evolution and the oxidation of divalent lead to lead dioxide.

Although the above experiments with a lead foil detected an influence by the given additives, difficulties occurred in defining their real concentration due to the activation method used. In consequence it was decided to prepare new electrodes that contained the test compounds in a known concentration. Accordingly, electrodes were made by the traditional paste method used in battery manufacture. The additive content of the paste (in %) was determined in relation to the lead powder used for paste preparation. Figures 4 - 6 present potentiodynamic curves for these electrodes together with curves for electrodes without additives. In both cases, the curves were obtained on the same potentiodynamic cycle. Table 3 compares the characteristic features of the potentiodynamic curve (see Fig. 1) for electrodes with different additives.
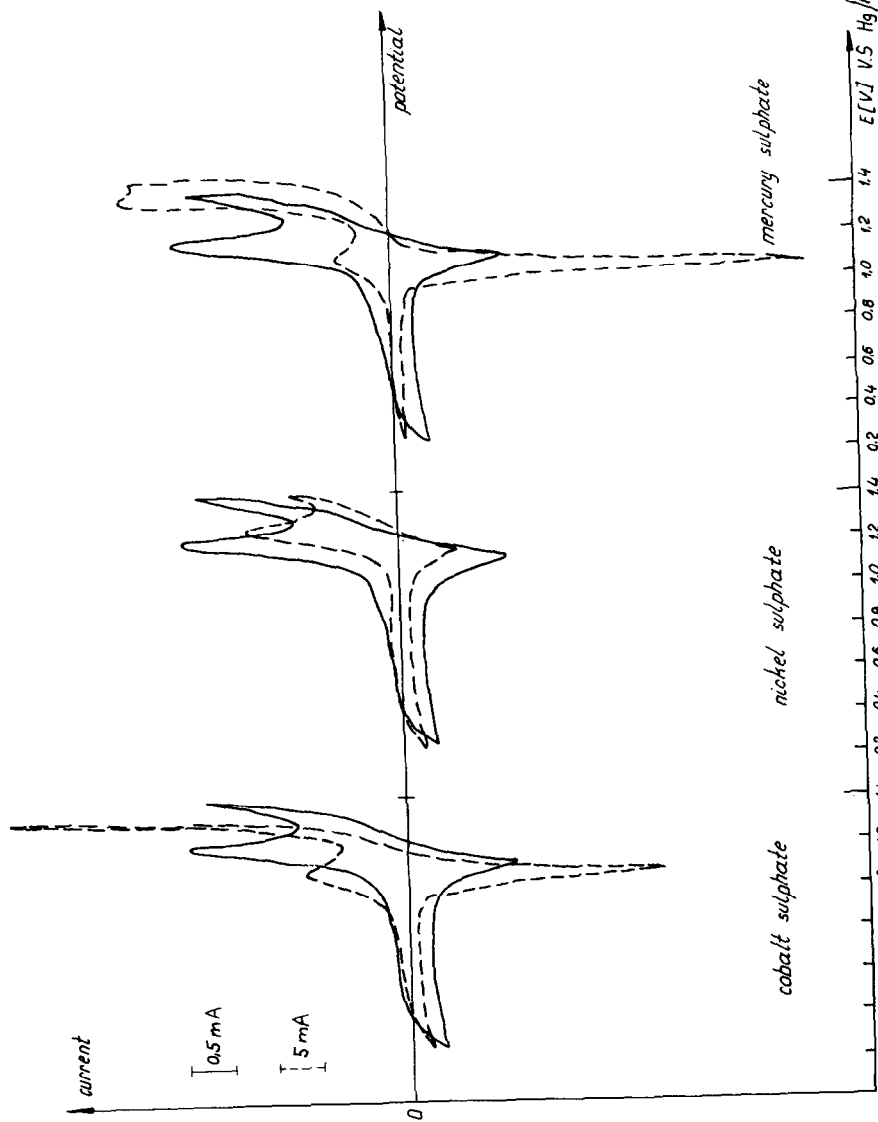
Fig. 6. Potentiodynamic curves for lead: ——, without additives; ———, with 2.5 wt.% cobalt, nickel, or mercury sulphates. Potential scan = 100 mV min^{-1}.

TABLE 3

Comparison of potentials of characteristic potentiodynamic features for electrodes with different additives
Potentials measured vs. mercury/mercurous sulphate reference electrode.

Additive (%)	E_1 (V)	E_2 (V)	E_3 (V)	E_4 (V)	E_5 (V)
No additive	1.18	1.28		none	1.10
0.5 Magnesium sulphate	1.18	1.28		none	1.12
2.5 Magnesium sulphate	1.08	1.18	1.36	1.40	1.04
2.5 Sodium sulphate	1.08	1.18	1.36	1.40	1.04
2.5 Chromium potassium sulphate	1.04	1.14	1.36	1.40	1.04
0.5 Cobalt sulphate	1.20	1.30		none	1.12
2.5 Cobalt sulphate	1.08	1.18		none	1.12
0.5 Nickel sulphate	1.18	1.28		none	1.12
2.5 Nickel sulphate	1.24	1.34		none	1.14
2.5 Tin sulphate	1.08	1.16	1.36	1.42	1.04
2.5 Mercury sulphate	1.06	1.18	1.36	1.42	1.04
2.5 Mercury oxide	1.20	1.28		none	1.04
2.5 Germanium oxide	1.20	1.30		none	1.02

Discussion

Our investigations revealed that a 0.5% addition does not change the shape of the potentiodynamic curves when compared with the addition-free electrode. Distinct changes in the potentiodynamic curves occur after the addition of 2.5 wt.% of active material.

On the addition of the sulphates of mercury, tin, magnesium, potassium, chromium and sodium, β-PbO$_2$ is formed together with α-PbO$_2$ during rapid potentiodynamic cycling. According to earlier studies [2, 3], improved β-PbO$_2$ formation occurs through the adsorption of SO$_4^{2-}$ ions in the active sites. The ions mask oxygen evolution sites and, as a result, increase the oxygen overvoltage on lead dioxide.

The different effect of cobalt on the positive electrode of the lead/acid battery can be interpreted as follows. The equilibrium of Co^{2+} (or Co^{3+}) ions and solid cobalt dioxide occurs in the potential range of the anodic oxidation of divalent lead to lead dioxide in acid medium. Cobalt dioxide is absorbed on the surface of crystals of lead compounds. The absorbed cobalt dioxide forms preferential sites for oxygen evolution and this contributes to a decrease in the oxygen evolution overpotential.

The effect of nickel sulphate is similar to that of cobalt sulphate as no distinct β-PbO$_2$ is formed. In contrast to cobalt sulphate, however, nickel sulphate increases the potentials of lead oxide oxidation and lead dioxide reduction.

Germanium oxide and mercury oxide do not give rise to any significant effects on the potentials of the characteristic features of the potentiodynamic curve.

The effect of mercury sulphate is particularly interesting as it increases the oxygen evolution overpotential more than any of the other sulphates, promotes the formation of β-PbO$_2$, and makes the charging process more efficient. It appears that the effect of tin sulphate is similar, although not so distinct. These findings have been confirmed by tests conducted in a lead/acid battery.

References

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