

## EFFECTS OF ANTIMONY ON THE ELECTROCHEMICAL BEHAVIOUR OF LEAD DIOXIDE IN SULPHURIC ACID

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### Summary

The effect of antimony on the reduction of the two allotropic forms of lead dioxide in sulphuric acid electrolyte has been studied. The effects of antimony doping of the lead dioxide lattice and the effects of antimony contamination of the electrolyte have been considered separately. In the first case antimony increases the quantity of charge related to the reduction, and in the second it exerts a strong passivating influence on the lead dioxide electrodes.

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### Introduction

It is well known that antimony, present as an alloying element in the grids of various commercial lead-acid batteries, has an extensive influence on the electrochemical processes occurring in the cell plates. Antimony (Sb), liberated from the positive grids, by unavoidable lead alloy corrosion, contaminates the electrolyte and, during cycling, the active material [1].

It is present in the positive plates as a dopant of the oxides growing on the grids and of lead dioxide ( $\text{PbO}_2$ ). In the negative plates antimony is mostly found deposited as a metal on spongy lead. The antimony can also exist as adsorbed ions on the positive and negative active material. Its effects are various [2 - 5]: some of them are detrimental and some beneficial to battery operation.

On the negative plates antimony induces detrimental effects; self-discharge is increased and charge acceptance is decreased. On the positive plates antimony seems to increase the active mass utilization coefficient and capacity retention during deep cycling. These beneficial effects are probably related to the electrochemical characteristics of doped oxides.

One of the present authors [6] has already studied the behaviour of Sb-doped lead dioxide in alkaline solutions. These researches led us to consider the effects of antimony on the reduction of  $\text{PbO}_2$  to  $\text{PbSO}_4$  in a sulphuric acid electrolyte. In the present paper the effects of antimony doping on two

allotropic forms of the  $\text{PbO}_2$  lattice, and those of antimony added to the electrolyte as impurity, are considered separately.

## Experimental

The two allotropic forms of lead dioxide were prepared by anodic electrodeposition according to the procedure reported elsewhere [6]. The metal substrate was a platinum (Pt) foil having a surface area of  $2 \text{ cm}^2$ . The electrodes were painted, giving a working surface of about  $0.2 \text{ cm}^2$ . The quantity of charge employed during the  $\text{PbO}_2$  electrodepositions was  $5000 \text{ mC cm}^{-2}$  corresponding to a deposit thickness of approximately  $7 \mu\text{m}$ .

Antimony-doped lead dioxide was obtained by adding 100 ppm of trivalent Sb ions as  $\text{Sb}_2\text{O}_3$  dissolved in KOH to the solution used for the anodic depositions.  $\alpha\text{-PbO}_2$  and  $\beta\text{-PbO}_2$ , deposited under these conditions, contained 0.5% and 0.2% of Sb, respectively [6]. The electrodeposited samples were periodically monitored by means of X-ray analysis.

The lead dioxide electrodes were cycled, at a temperature of  $25 \text{ }^\circ\text{C}$ , in 8N and in 0.1N  $\text{H}_2\text{SO}_4$  under potentiodynamic conditions with a sweep rate of  $2 \text{ mV s}^{-1}$ . Platinum foil as a counter-electrode and an Hg/HgSO<sub>4</sub> half-cell as reference electrode were used. Cyclic voltammetric curves (LSV) have also been obtained at higher ( $5 \text{ mV s}^{-1}$ ) and at lower ( $0.2 \text{ mV s}^{-1}$ ) sweep rates and no relevant differences in the results were found.

In 8N  $\text{H}_2\text{SO}_4$  the voltammetric curves were traced between 1800 mV with reference to the normal hydrogen electrode (NHE) and 1100 mV (NHE). At the end of the reduction the electrodes were subjected to electrochemical oxidation: their potential was made more positive until oxygen was freely evolved (2050 - 2250 mV (NHE)). The potential was then reduced, at the same sweep rate, to the starting value of 1800 mV (NHE). After 3 min rest in this polarisation state a new cycle was completed.

The ratio between the anodic and the cathodic charge was, for every cycle, greater than 3. Similar tests were undertaken to investigate the morphology of the electrode surface during the cycles. In these, the electrochemical process was stopped and the electrode surface examined using a scanning electron microscope (SEM). All the tests were repeated three times and substantial agreement between the results was obtained.

## Results and discussion

The cathodic LSV curves corresponding to four reductions of  $\alpha$ - and  $\beta$ -lead dioxide electrodes in 8N  $\text{H}_2\text{SO}_4$  are shown in Fig. 1. In both cases the first curve shows a single peak at 1560 mV (NHE). In subsequent reductions a second peak is present at 1645 mV (NHE) for  $\alpha\text{-PbO}_2$  and at 1655 mV (NHE) for  $\beta\text{-PbO}_2$ . Moreover, after the second reduction, the lower potential  $\beta$ -lead dioxide peak shifts approximately 30 mV towards more positive values.

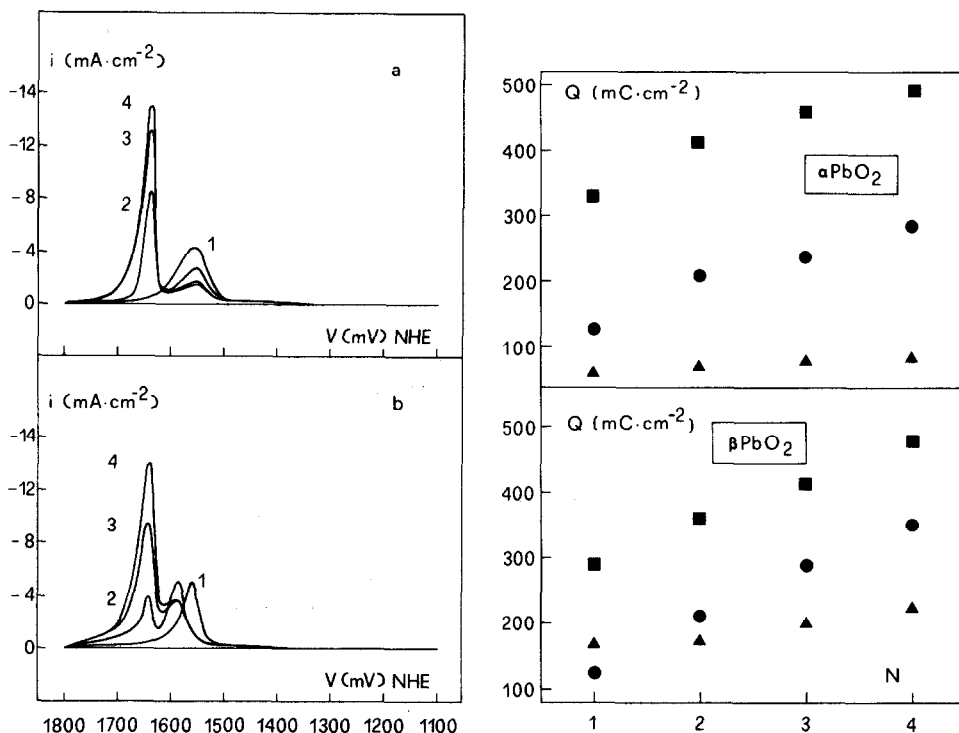


Fig. 1. Voltammograms of four reductions of (a)  $\alpha$ - $\text{PbO}_2$  and (b)  $\beta$ - $\text{PbO}_2$  (using 8N  $\text{H}_2\text{SO}_4$  at 25 °C and a sweep rate of 2 mV s<sup>-1</sup>).

Fig. 2.  $\text{PbO}_2$  reduction quantity of charge,  $Q$ , vs. cycle number,  $N$ , in 8N  $\text{H}_2\text{SO}_4$  at 25 °C. ●, pure  $\text{PbO}_2$ ; ■, Sb doped  $\text{PbO}_2$ ; ▲, pure  $\text{PbO}_2$  cycled in 8N  $\text{H}_2\text{SO}_4$  containing 100 ppm of  $\text{Sb}^{3+}$ .

A feature common to both allotropic forms is the change in peak intensity with the number of cycles; the peak at higher potential always increases while the one at lower potential decreases. Correspondingly, the cathodic quantity of charge increases with the number of cycles for both allotropes, as shown in Fig. 2.

Comparison of the results indicates the existence of two main differences between the  $\alpha$ - and  $\beta$ -allotropic forms: (i) the cathodic quantity of charge is, in all cycles, higher for the  $\beta$  form than for the  $\alpha$  form, in agreement with previously published data [7, 8]; (ii) the oxygen overvoltage values are higher for the  $\alpha$  than for the  $\beta$  form, Fig. 3.

Additional information has been drawn from SEM observation of the electrodes surfaces. Figures 4 and 5 show micrographs of  $\alpha$ - and  $\beta$ -lead dioxide electrodes reduced, for the first time, to a potential of 1600 mV (NHE) and to a potential of 1100 mV (NHE), *i.e.*, to the end of the reduction. It can be seen that the lead sulphate crystals, progressively forming during the process, in no case cover the surface entirely. The lead dioxide areas still in contact with the electrolyte at the end of the reduction are

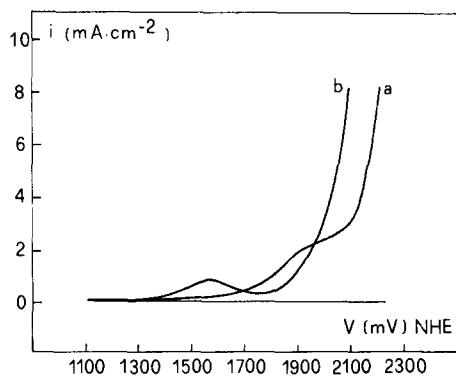


Fig. 3. Voltammograms of  $\text{PbSO}_4$  oxidation in  $8\text{N H}_2\text{SO}_4$  of (a)  $\alpha\text{-PbO}_2$  and (b)  $\beta\text{-PbO}_2$  (at  $25^\circ\text{C}$  and with a sweep rate of  $2\text{ mV s}^{-1}$ ).

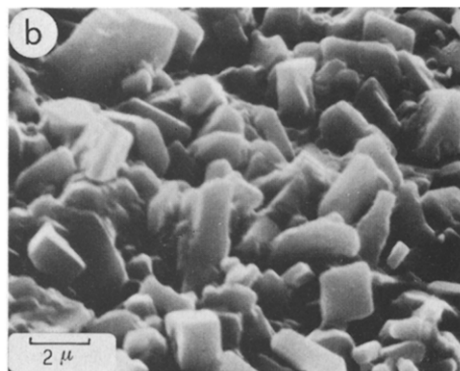
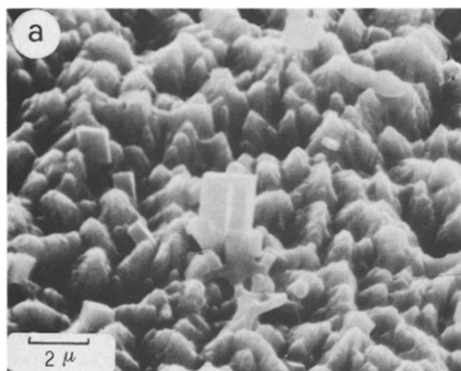


Fig. 4. SEM micrographs of  $\alpha\text{-PbO}_2$  electrodes reduced for the first time (a) from  $1800\text{ mV}$  to  $1600\text{ mV}$  (NHE); (b) from  $1800\text{ mV}$  to  $1100\text{ mV}$  (NHE).

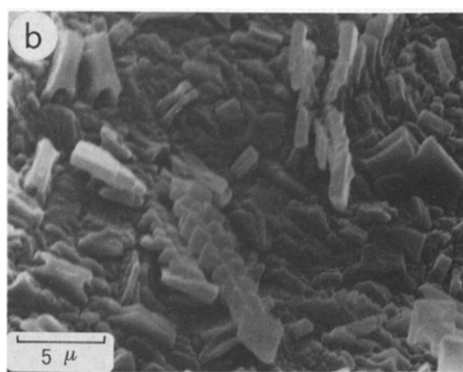
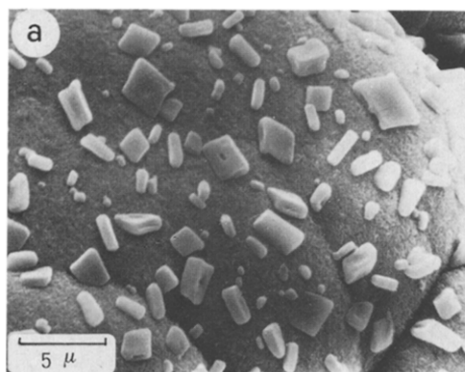


Fig. 5. SEM micrographs of  $\beta\text{-PbO}_2$  electrodes reduced for the first time from (a)  $1800\text{ mV}$  to  $1600\text{ mV}$  (NHE); (b) from  $1800\text{ mV}$  to  $1100\text{ mV}$  (NHE).

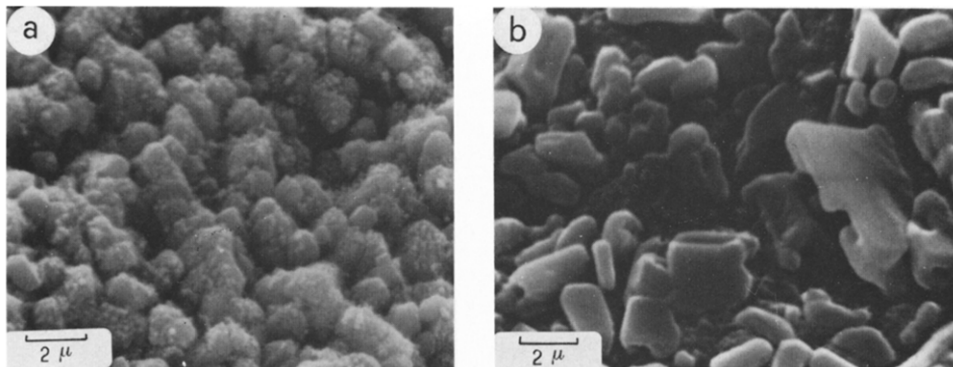


Fig. 6. SEM micrographs of (a)  $\alpha$ - $\text{PbO}_2$  and (b)  $\beta$ - $\text{PbO}_2$  at the end of the first oxidation.

therefore in a passive state owing to the potential attained. We believe that lead sulphate forms either as large crystals precipitating on the electrode surface or as a thin passivating layer growing on lead dioxide crystals. Such a thin layer can be formed on lead dioxide by electrochemical processes, such as oxygen discharge, which take place when the electrode is dipped into the electrolyte.

SEM micrographs also show lead sulphate crystal forms that can be described as flat tabular and box-like tabular with concave faces in the cases of crystals resulting from  $\alpha$ - and  $\beta$ -lead dioxide reduction, respectively.

Micrographs taken after the oxidations, Fig. 6, clearly show that, in spite of the fact that oxygen evolution has occurred, lead sulphate oxidation was incomplete. In the case of  $\alpha$ - $\text{PbO}_2$  the corresponding micrograph revealed that the  $\text{PbO}_2$  crystals were covered with  $\beta$ -lead dioxide.

Pure lead dioxide reductions in 0.1N  $\text{H}_2\text{SO}_4$  showed a behaviour very similar to that just described. In this case the peaks are found at approximately 1330 mV and 1380 mV (NHE) and have a less defined shape.

These results suggest that the position of the peaks in the voltammetric curves are strictly related to the surface morphology (inhomogeneity, porosity, cracks, etc.) and do not depend on the thermodynamic characteristics of the two allotropes.

During the reduction, lead sulphate forms both a layer of tabular crystals and a thin layer passivating the  $\text{PbO}_2$  still uncovered by  $\text{PbSO}_4$  crystals. Such a barrier layer maintains its passivating properties until the electrode potential attains a critical value beyond which the electrochemical cathodic process can take place again. The peak at lower potential in the LSV curves corresponds either to the growth or to the formation of a more stable layer. In fact, this peak is most important during the first reduction because the passivating layer, due to the homogeneity of the freshly prepared surface, covers the  $\text{PbO}_2$  almost completely.

By considering the LSV curves traced for Sb-doped  $\alpha$ - and  $\beta$ - $\text{PbO}_2$ , Fig. 7, it can be seen that antimony influences  $\text{PbO}_2$  electrochemical behaviour in various ways:

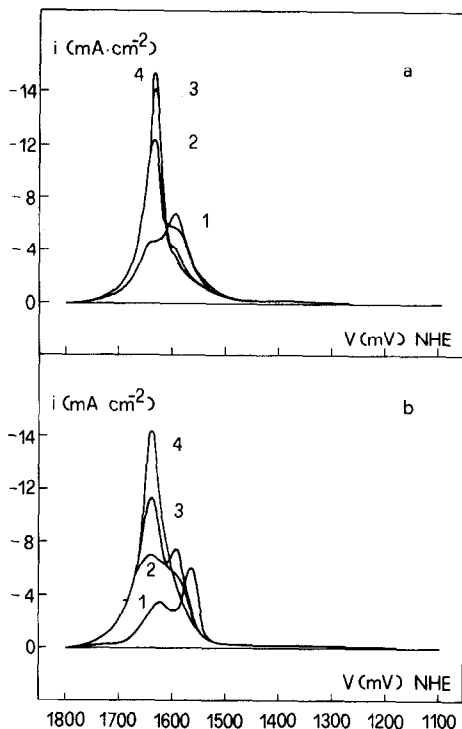


Fig. 7. Voltammograms of four reductions of (a) Sb doped  $\alpha$ - $\text{PbO}_2$  and (b) Sb doped  $\beta$ - $\text{PbO}_2$  (using 8N  $\text{H}_2\text{SO}_4$  at 25 °C and with a sweep rate of  $2 \text{ mV s}^{-1}$ ).

(i) A peak or a shoulder at higher potential (1645 mV for  $\alpha$ - $\text{PbO}_2$  and 1620 mV for  $\beta$ - $\text{PbO}_2$  in 8N  $\text{H}_2\text{SO}_4$ ) is already present from the first reduction.

(ii) In the case of  $\alpha$ - $\text{PbO}_2$  the lower potential peak is shifted about 40 mV towards positive values. Thus the peaks of  $\alpha$ - $\text{PbO}_2$  and  $\beta$ - $\text{PbO}_2$  appear at almost the same potential.

(iii) Oxygen overvoltage is decreased to a value which is nearly the same for both allotropes.

(iv) The cathodic quantity of charge is markedly increased. This is more evident for  $\alpha$ -doped lead dioxide, so that after three cycles the values for  $\alpha$ - and  $\beta$ -doped  $\text{PbO}_2$  are quite similar.

Micrographs of antimony doped  $\text{PbO}_2$  are shown in Figs. 8 - 10. Antimony, by influencing the lead dioxide crystalline structure [6], Fig. 8, modifies the active surface and, consequently, the cathodic quantity of charge. This effect can explain, on the basis of the previous discussion, the trend of the voltammetric curves. The increase in the active surface makes the formation of the passivating layer more difficult during the first cycle, allowing for the  $\text{PbO}_2$  reduction at a higher potential, Fig. 7.

In the case of the  $\beta$ -doped  $\text{PbO}_2$  the increase in the cathodic charge is less marked and the voltammetric curves are also slightly affected by the Sb

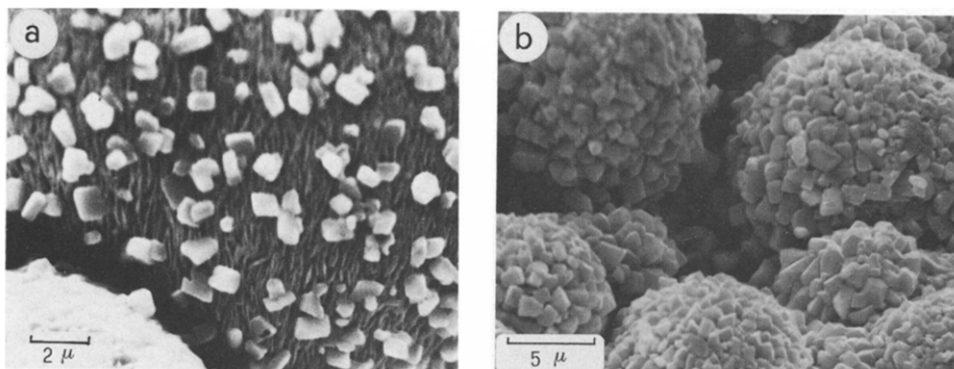


Fig. 8. SEM micrographs of Sb doped  $\alpha$ - $\text{PbO}_2$  electrodes after a first reduction from (a) 1800 mV to 1600 mV (NHE), and (b) from 1800 mV to 1100 mV (NHE).

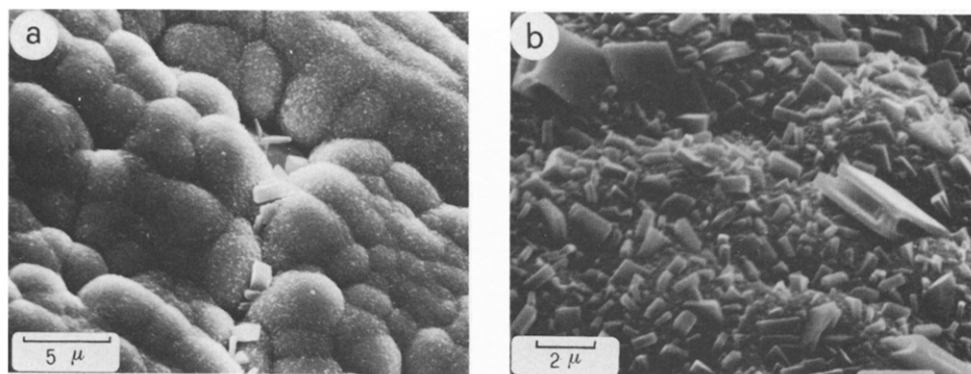


Fig. 9. SEM micrographs of Sb doped  $\beta$ - $\text{PbO}_2$  electrodes after a first reduction from (a) 1800 mV to 1600 mV (NHE), and (b) from 1800 mV to 1100 mV (NHE).

in the  $\text{PbO}_2$  lattice. No evidence, however, of changes of the surface morphology appears, Fig. 9, and this emphasises the great influence morphology has on the electrode behaviour. Antimony also lowers the oxygen overvoltage both for  $\alpha$ - and  $\beta$ - $\text{PbO}_2$ , which show the same value. Consequently, the oxidation processes are now very far from being completed, Fig. 10. The results obtained in 0.1N  $\text{H}_2\text{SO}_4$  are completely in agreement, from the electrochemical and morphological point of view, with those discussed above.

Pure  $\alpha$ - and  $\beta$ - $\text{PbO}_2$  electrode reductions in 8N  $\text{H}_2\text{SO}_4$  with added trivalent Sb ions were finally considered. Some LSV curves are shown in Fig. 11. Both  $\alpha$ - and  $\beta$ - $\text{PbO}_2$  electrodes behave, during the first reduction, as passive electrodes until potential values lower than 1400 mV (NHE) are reached. This characteristic behaviour, more evident for  $\alpha$ -lead dioxide, can be ascribed to the presence of a passivating layer formed, at the beginning of the reduction, by the oxidation of trivalent Sb ions present in the electrolyte. Such a layer shows a much better insulating effect than the  $\text{PbSO}_4$  layer formed during the cathodic reduction in antimony-free acid solution.

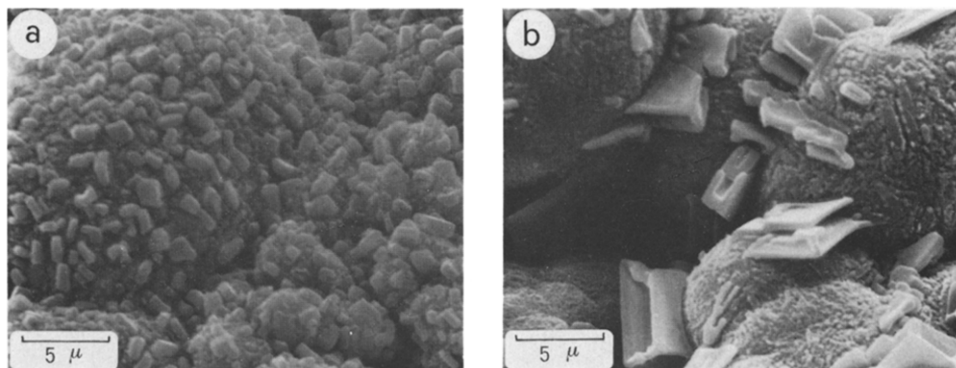


Fig. 10. SEM micrographs of (a) Sb doped  $\alpha$ -PbO<sub>2</sub> and (b) Sb doped  $\beta$ -PbO<sub>2</sub> at the end of the first oxidation.

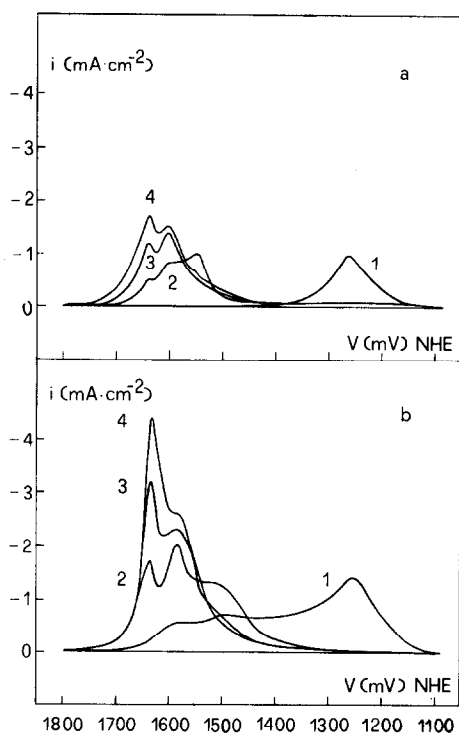


Fig. 11. Voltammograms of four reductions of (a)  $\alpha$ -PbO<sub>2</sub> and (b)  $\beta$ -PbO<sub>2</sub> (using 8N H<sub>2</sub>SO<sub>4</sub> containing 100 ppm of Sb<sup>3+</sup> at 25 °C and with a sweep rate of 2 mV s<sup>-1</sup>).

Moreover, it has been verified by means of particular tests that the effectiveness of this layer depends on the dipping time of the electrode in the electrolyte before tracing the cathodic LSV curves. Antimony present in the solution also influences the electrode behaviour during the subsequent cycles; the cathodic charge values are considerably lower than in the previous



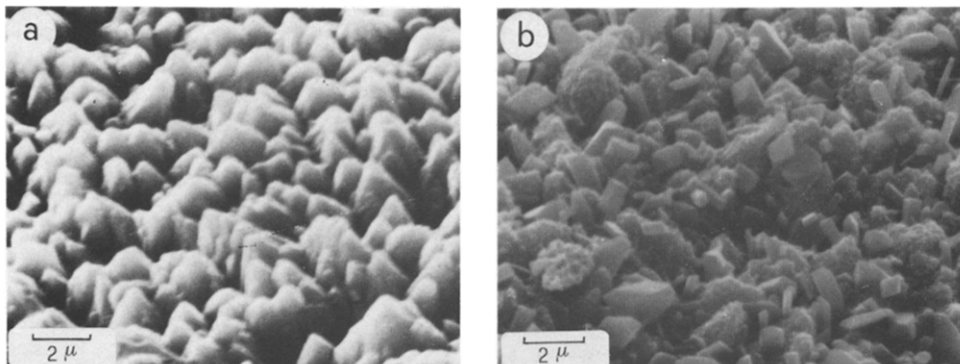


Fig. 12. SEM micrographs of  $\alpha$ - $\text{PbO}_2$  electrodes after a first reduction in 8N  $\text{H}_2\text{SO}_4$  containing 100 ppm of  $\text{Sb}^{3+}$  from (a) 1800 mV to 1600 mV (NHE), and (b) from 1800 mV to 1100 mV (NHE).

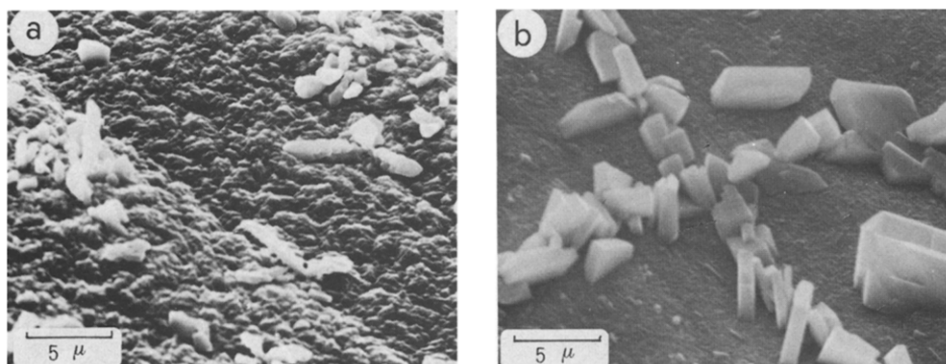


Fig. 13. SEM micrographs of  $\beta$ - $\text{PbO}_2$  electrodes after a first reduction in 8N  $\text{H}_2\text{SO}_4$  containing 100 ppm of  $\text{Sb}^{3+}$  from (a) 1800 mV to 1600 mV (NHE), and (b) from 1800 mV to 1100 mV (NHE).

cases, Fig. 2. The SEM observations further show that the lead dioxide is, at the end of the reduction, covered by  $\text{PbSO}_4$  crystals, Figs. 12 and 13, having a smaller size than those formed during the reduction in pure electrolyte.

## Conclusions

The experimental results obtained indicate that:

(i) The trend of the LSV curves is strictly related to the morphology of the lead dioxide surface. The thermodynamic characteristics of  $\text{PbO}_2$  have a slight influence on electrode behaviour.

(ii) Antimony doping of the  $\text{PbO}_2$  lattice increases the quantity of charge involved in the reduction to  $\text{PbSO}_4$ , decreases the oxygen overvoltage on  $\text{PbO}_2$ , and reduces the differences between the behaviour of the two allotropic forms of lead dioxide. All these effects can be principally ascribed to surface electrode change.

(iii) Antimony present in the electrolyte as an impurity exerts a passivating effect on  $\text{PbO}_2$  causing a marked decrease in the cathodic quantity of charge.

### Acknowledgment

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