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An investigation of the surface structure of some lead dioxide and related electrodes

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S.E.M. observations have been carried out on PbO_2 and related electrodes after electrochemical reaction in 5 M H_2SO_4. The morphology of the surfaces examined is strongly effected by their history, particularly their charge/discharge cycles. $PbSO_4$ formed by the self-corrosion process is much more porous than that formed by the electrochemical reduction of PbO_2.

1. Introduction

Some time ago we investigated [1] the electrometric responses of massive and porous PbO_2 films on both Pt and Pb bases. We were able to show that a condensed surface of β-PbO_2, formed by electrodepositing on Pt, could be reduced to $PbSO_4$ by a simple mechanism in which the surface became progressively covered by a very thick film of $PbSO_4$. This film appeared to be thousands of Å thick and the electrode became passive when it was completely blocked. No nucleation step appeared to be needed in this process which led us to the conclusion that sulphate was adsorbed by PbO_2 in sulphuric acid. This conclusion reinforced earlier work in this laboratory [2] using the differential capacitance method; when a large pseudocapacitance and adsorption minimum was interpretable only as a consequence of bisulphate ion adsorption.

Early work by Fleischmann *et al.* [3] which has been confirmed in our work and by innumerable battery experiments, indicated that for a grown film of $PbSO_4$, overlaying massive lead, a nucleation step was necessary to intiate its conversion to PbO_2. Further work in these laboratories has suggested that there is a difference in quality of the PbO_2 formed in the first oxidation and that produced in subsequent cycles. Thus we found [3] that the first oxidation conformed to a progressive nucleation and growth process whilst PbO_2 formed after the reduction of the first PbO_2 layer conformed to an instantaneous nucleation and growth process. These results have important implications for the study of the PbO_2 positive and consequently it is desirable to check that results obtained electrometrically have morphological consequences.

This paper records a study of electrode surfaces which provides photographic results complementary to the earlier electrometric ones.

2. Experimental

Experiments were made on stubs especially made to fit into the examination chamber of the Scanning Electron Microscope (JEOL JSM 35R). These consisted of a Teflon shrounded electrode (Pt or Pb) which screwed into the end of a rotating disc electrode assembly with liquid tight sealing. Electrochemistry was carried out on the exposed metal ends after these were polished, (diamond abrasives) followed by suitable etching. PbO_2 electrodes were prepared by deposition (0·7 mA cm^{-2}) on to Pt from acid lead perchlorate (2·5 M ClO_4^-, 0·1 M H^+); Pb electrodes were prepared by electrodepositing Pb (5 mA cm^{-2}) on to polished Pb from acid lead perchlorate solution. Potentiostatic experiments (Chemical Electronics TR70/2A) were made at room temperature in 5 M H_2SO_4. The sweep rates (cathodic) were 10 mV s^{-1} for PbO_2/Pt reductions and 3 mV s^{-1} for PbO_2/Pb reductions.

After the electrochemical experiments, the specimens were taken from the electrolyte under potential control, washed in bi-distilled water and dried in a vacuum oven at 40° C. The dried specimens were gold shadowed and examined in the SEM.

3. Results and discussion

3.1. *Massive β-lead dioxide on platinum*

3.1.1. The reduction of β-PbO_2 to $PbSO_4$ in 5 M H_2SO_4. Fig. 1 shows a β-PbO_2 surface at two magnifications after prolonged contact with 5 M sulphuric acid at 1200 mV*. The surface consists of small condensed particles of even size (~ 5 × 10^2 nm); no evidence of $PbSO_4$ crystallites is visible. The true surface area is considerably greater than the apparent value in agreement with differential capacitance measurements [2]. Fig. 2 shows the effect on the surface of a potential sweep to 700 mV at 10 mV s^{-1} followed by a 10 min period in the electrolyte at 700 mV; the surface is shown tilted in Fig. 2c. Clusters of $PbSO_4$ crystals are observed to have grown orthogonally from the surface. It is evident that the surface is not completely

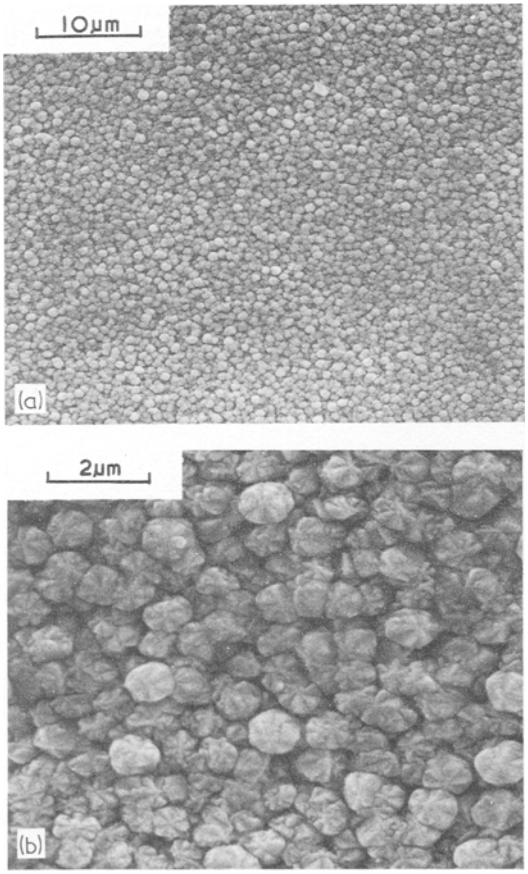

Fig. 1. Electrodeposited β-PbO_2 on a Pt base after immersion in 5 M H_2SO_4 at 1200 mV.

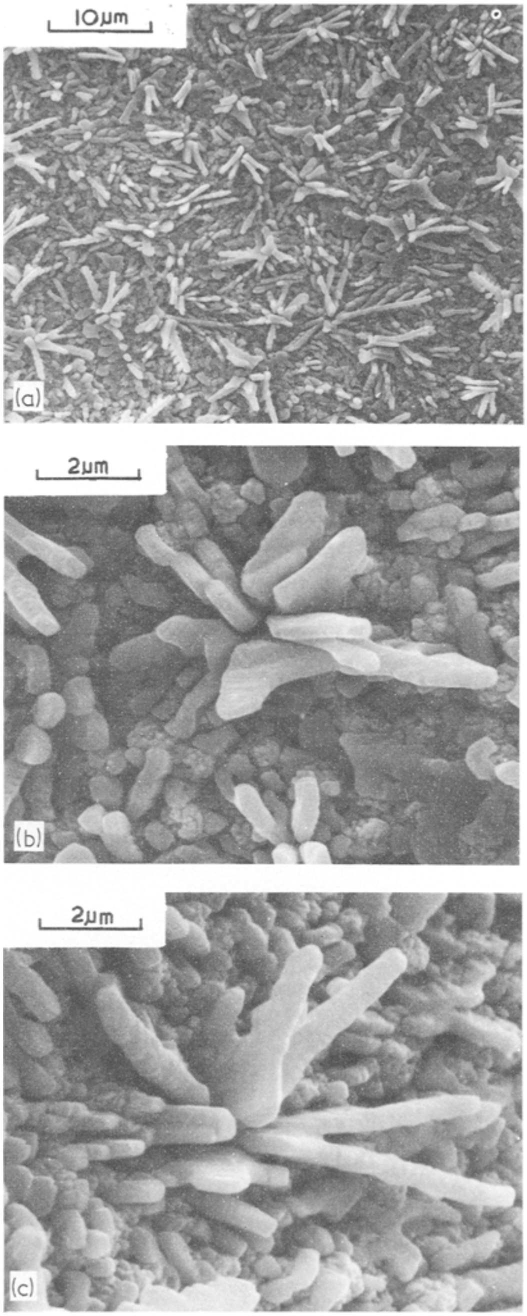

Fig. 2. $PbSO_4$ crystal clusters grown from the PbO_2 by a potential sweep at 10 mV s^{-1} from 1200 to 700 mV.

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* All potentials are referred to the $Hg/Hg_2SO_4/H_2SO_4$. 5 M electrode at the temperature of the experiment.

blocked by $PbSO_4$; some access of the sulphuric acid to underlying PbO_2 is possible. This again confirms earlier observations [1] that after 1 sweep to 700 mV the surface is not completely passive. A repeat sweep on the electrode results in a small amount of charging.

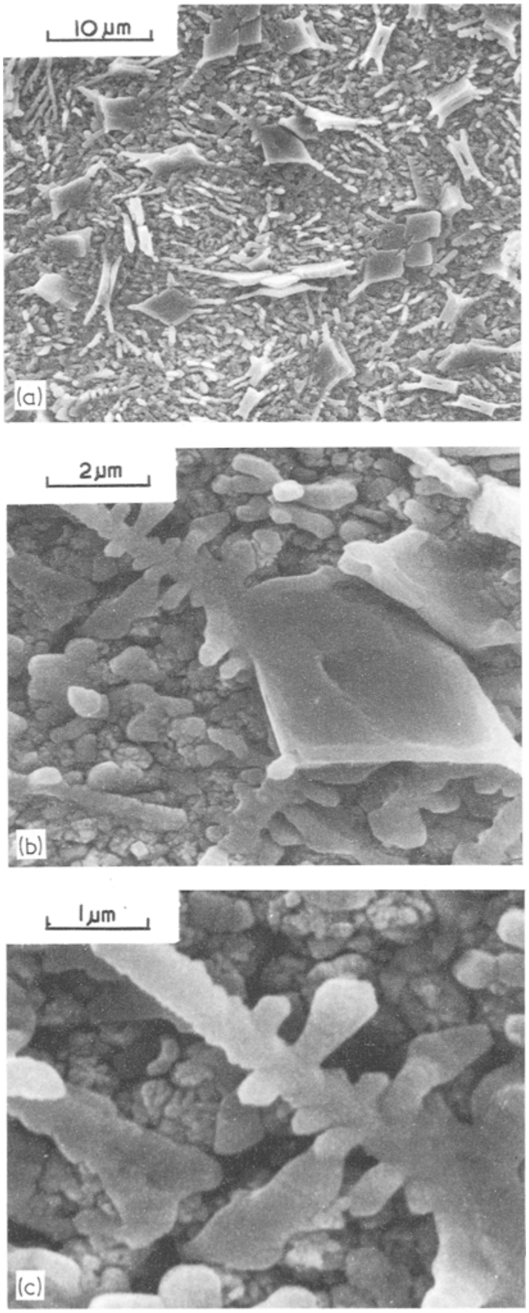

Fig. 3. Growth of PbO_2 from the grown $PbSO_4$ layer after 30 s at 1300 mV.

3.1.2. The reoxidation of $PbSO_4$ on β-PbO_2 to PbO_2. Fig. 3 shows the results of a potentiostatic experiment on a grown $PbSO_4$ layer (Fig. 2) in which the potential is stepped from 800 to 1300 mV and has been maintained at the higher potential for 30 s. It is evident that the formation of PbO_2 from the $PbSO_4$ crystals has commenced at selected spots and this is seen to be further developed in Fig. 4 which corresponds to a potentiostatic polarization time of 2 min. Here the quantity of large block-type crystals has decreased significantly, and the structure has become much finer-grained. Figs. 5 and 6, for reaction times of 5 and 15 min, show little difference in the quantity of fine-grained PbO_2 crystallites present. This is in agreement with electrometric measurements in which the Pb(II) → Pb(IV) oxidation current in a potentiostatic experiment (800 → 1300 mV) is negligible after 8 min.

The results of the incomplete cleaning of an electrode during the preparation of the PbO_2 surface was evident from Fig. 7. The effect appeared during the re-oxidation of the $PbSO_4$ surface rather than in the first reduction of the PbO_2. This is shown in Fig. 7 where the results of a potential step on a reduced 'contaminated' electrode was to leave unconverted a significant area (20%) of the sulphate. The nature of the contamination was a layer (possibly oxide or intruding organic) on the platinum upon which the PbO_2 was originally electrodeposited caused by an insufficient cleaning period in sulphuric acid prior to the electrodeposition. This observation is of considerable interest and indicates that the effect of contaminants on the positive plate in a lead acid battery is on the nucleation step in the recharging process. Confirmation of this exploration was provided by making experiments on insufficiently etched platinum electrodes, reduced to give coherent complete layers of sulphate. The worst cases of contamination were observed to have almost intact layers of $PbSO_4$ after several minutes potentiostatic polarization at 1400 mV. With the conventional sulphuric acid treatment (1 h), satisfactory oxidation was always observed.

3.1.3. The reduction of PbO_2 grown from $PbSO_4$ (2nd reduction cycle). Following the reduction of the electrodeposited β-PbO_2 surface the electrode was pulsed back to 1300 mV (from 700 mV) and held at that potential until the electrode was

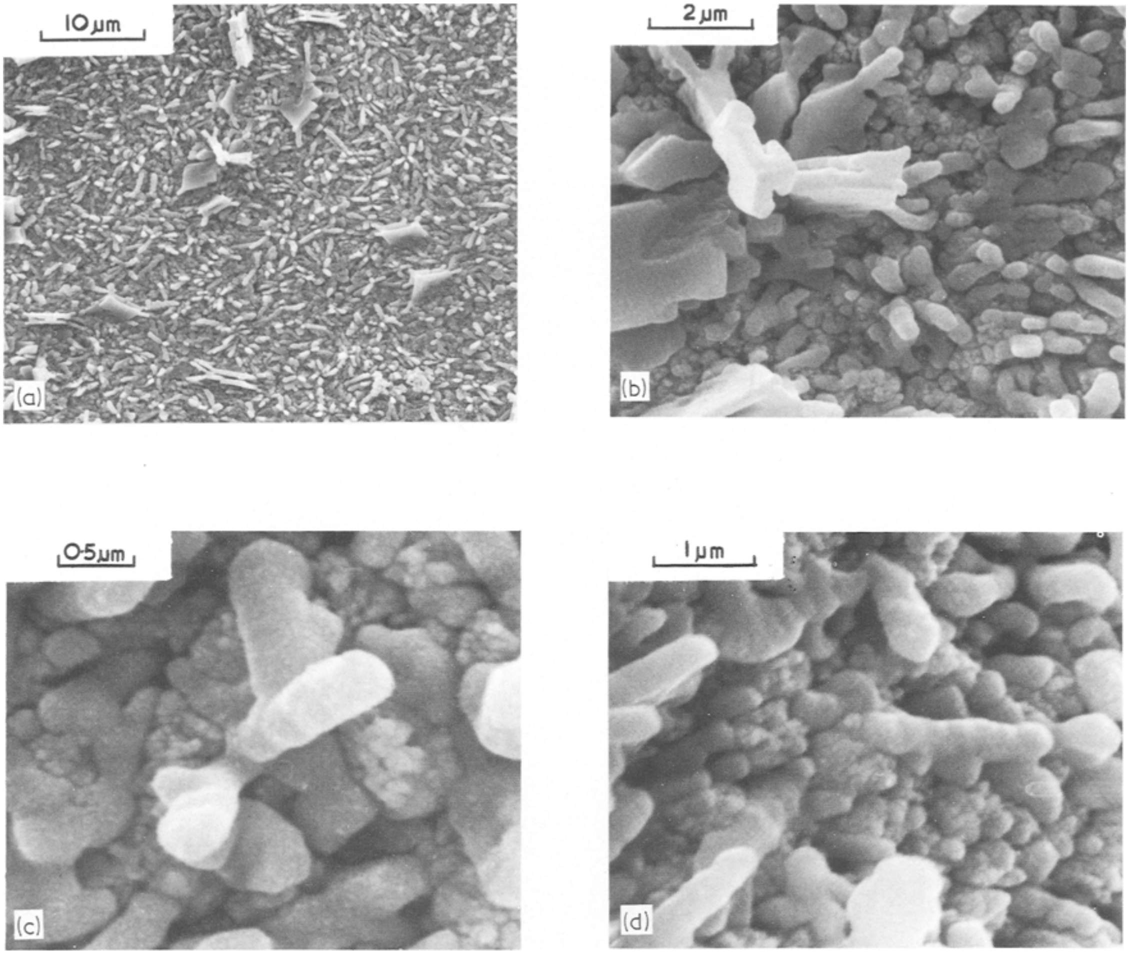

Fig. 4. Growth of PbO_2 from the grown $PbSO_4$ layer after 2 min at 1300 mV. Electrode tilted in (d) to show topography.

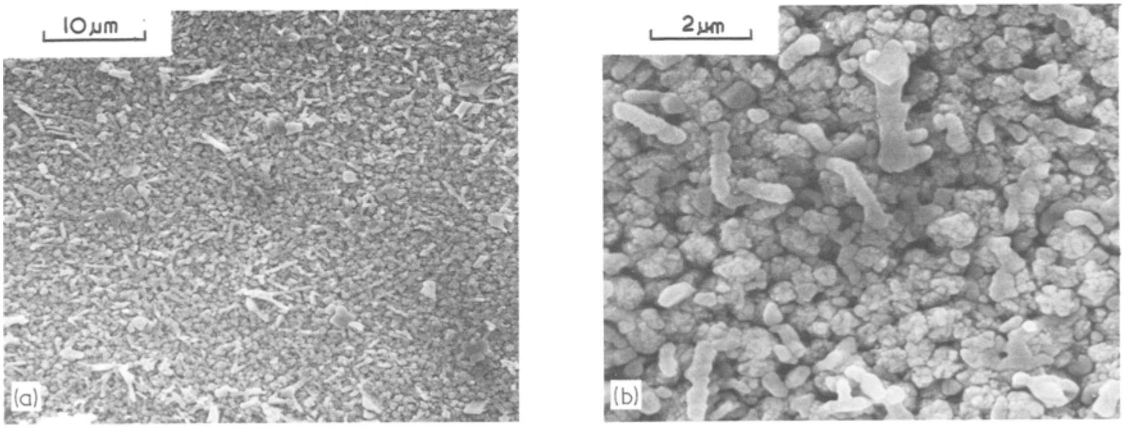

Fig. 5. Growth of PbO_2 from the grown $PbSO_4$ layer after 5 min at 1300 mV.

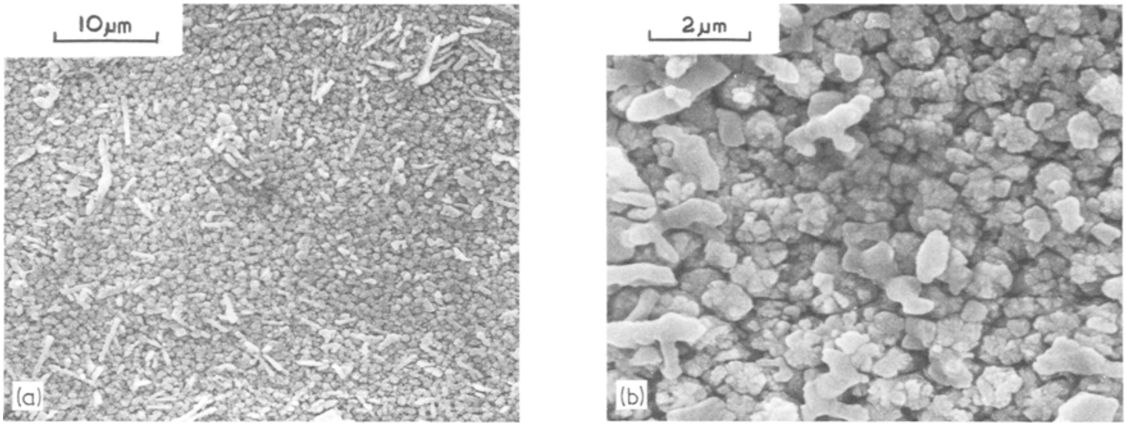

Fig. 6. Growth of PbO_2 from the grown $PbSO_4$ layer after 15 min at 1300 mV.

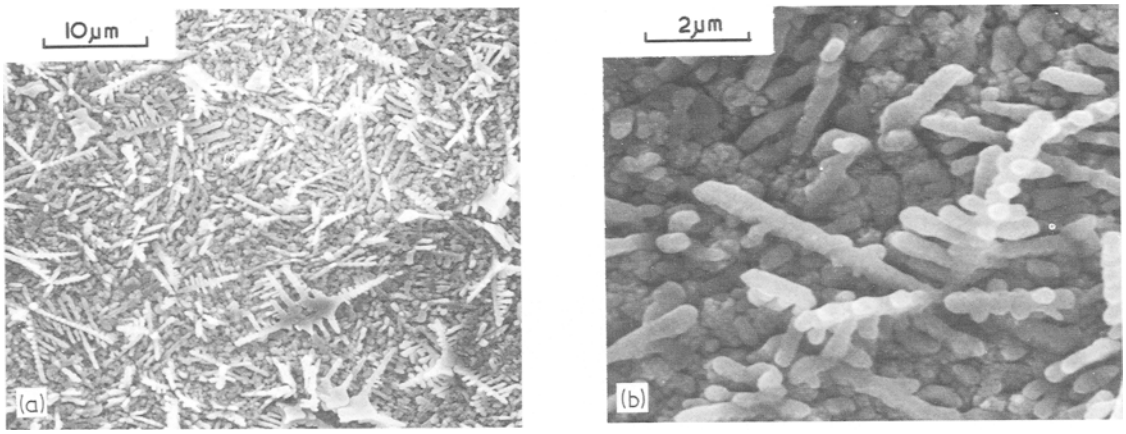

Fig. 7. Evidence of a contamination effect by the presence of $PbSO_4$ crystal structures on an electrode oxidized at 1300 mV for 15 min.

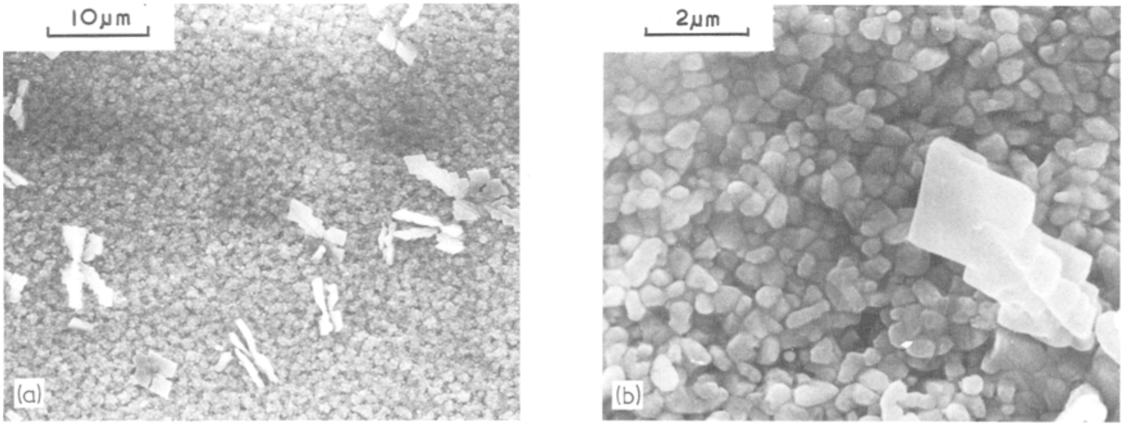

Fig. 8. Reduction of the grown PbO_2 to $PbSO_4$ by a potential sweep at 10 mV s^{-1} from 1300 to 700 mV.

effectively reconverted to PbO_2. Fig. 8 shows the effect on the surface of returning to 700 mV by a potential sweep. The most important feature is the surface closely packed with $PbSO_4$ which effectively blocks and thus passivates the surface of the underlying PbO_2. A comparison with the micrographs of Fig. 2 shows that there is an important difference between $PbSO_4$ surfaces produced from electrodeposited PbO_2 and that from PbO_2 formed via $PbSO_4$. This lies in the form of the $PbSO_4$ which is very fine-grained. Isolated large columnar crystals of $PbSO_4$ are however observed randomly; it appears that these remain from the first reduction.

We can conclude from our work with massive β-PbO_2 that there is a difference in morphology in the $PbSO_4$ formed in the initial and subsequent reductions. This agrees with earlier observations [2]. The effect of impurity in PbO_2 electrodes occurs in the nucleation step of the oxidation process ($PbSO_4 \rightarrow PbO_2$).

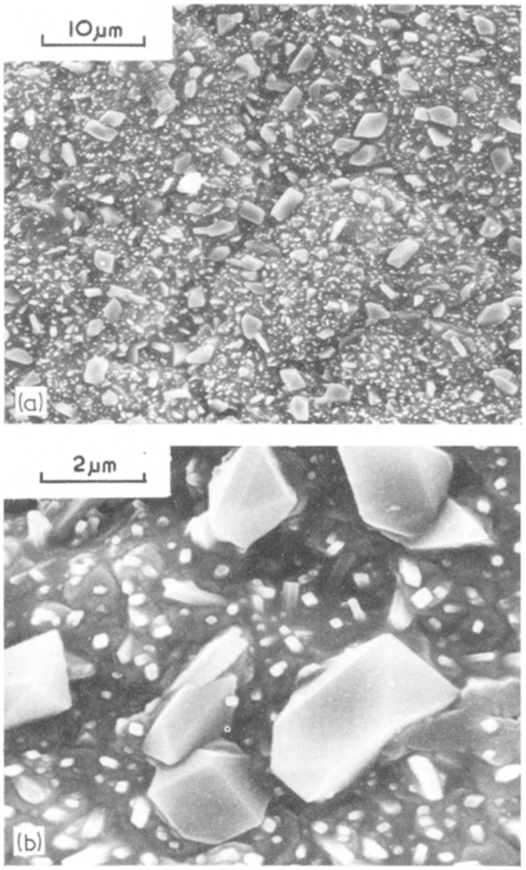

Fig. 9. $PbSO_4$ grown on electrodeposited Pb at 700 mV for 1 h.

3.2. *Massive lead electrodes*

3.2.1. The formation of $PbSO_4$ in 5 M H_2SO_4. Previous electrometric work [4] has shown that at a potential of 700 mV reaction times of the order of 1 h are required for the development of a completely blocking film of $PbSO_4$ on Pb. Fig. 9 shows such a film where it is apparent that we have large $PbSO_4$ crystals in the 'valleys' of the electrode surface and smaller crystals on the tops of the 'hills'. This is in agreement with a solution–precipitation process as envisaged by Harrison and Archdale [5], restricted diffusion in the hollows giving rise to larger crystals. This observation may account for differences in the response of lead electrodes to electro-oxidation in H_2SO_4 observed as a result of different surface treatments. Surfaces with large roughness factors would be expected to engender a large proportion of $PbSO_4$ crystals. When the reaction time at 700 mV is restricted to 15 min (Fig. 10), the gradual covering of the Pb base with $PbSO_4$ is observed. Here the surface topography of the lead appears to be followed by nucleation of the small crystallites occurring within the deep hollows of the surface. Such crystals once nucleated grow orthogonally to the surface, possibly in extreme cases developing to quite large sizes. This is actually seen in Fig. 10d which suggests that the point of crystallite development lies below the general surface level. It is clear that the explanation advanced here gives an adequate explanation of variability due to surface treatment factors. This possibly explains why electrodeposited Pb on Pb surfaces give the most reproducible electrodes, for with these types of electrode the number of gross surface defects would be expected to be constant for constant electrodeposition parameters.

3.2.2. The oxidation of $PbSO_4$ on Pb to PbO_2. Stepped from 700 up to 1350 mV, the $PbSO_4$ electrode is converted to PbO_2, exhibiting the well-known rising transients for phase growth [2–4]. As soon as potential control is removed, the reaction:

$$PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O \quad (1)$$

occurs between the underlying Pb, PbO_2 and any H_2SO_4 available at the boundary between these two solid phases. Fig. 11 shows an electrode on which this reaction was allowed to proceed, the

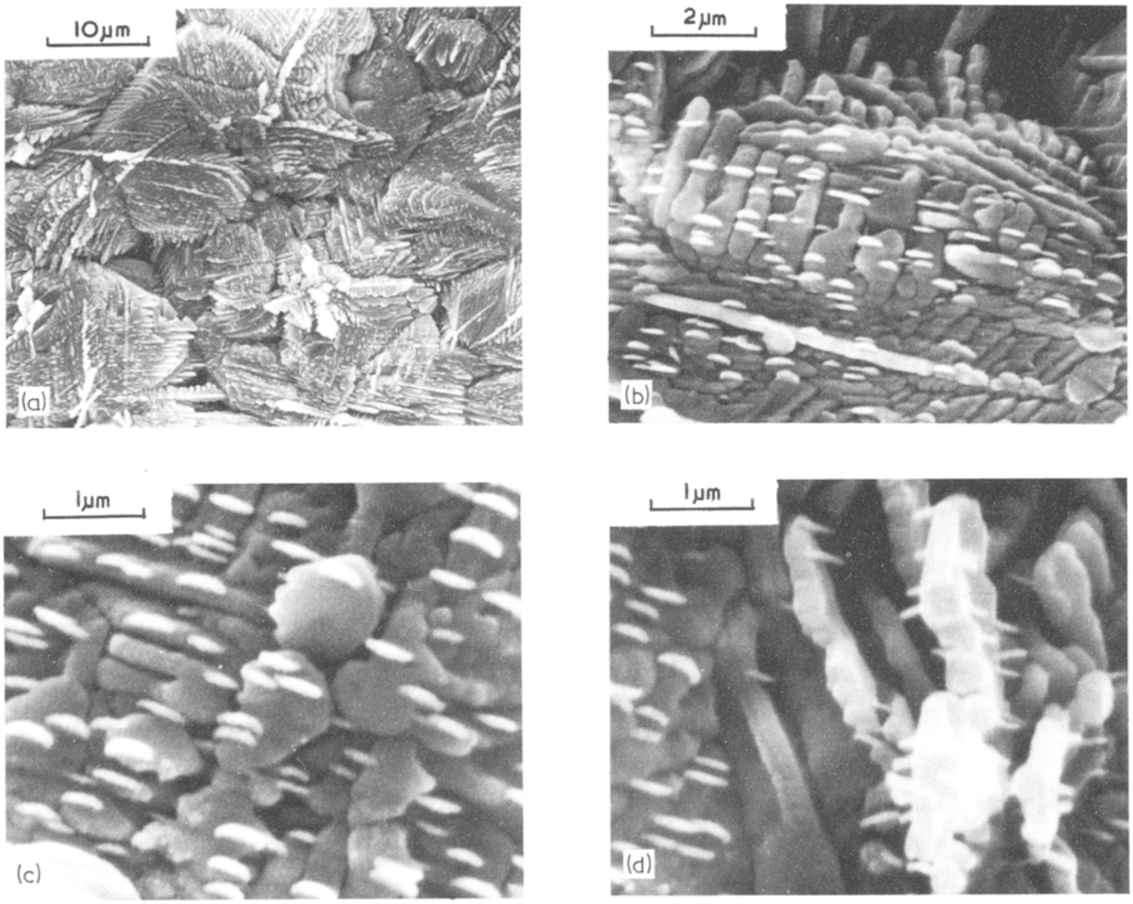

Fig. 10. $PbSO_4$ grown on electrodeposited Pb at 700 mV for 15 min.

potential falling to that characteristic of $PbSO_4$ rather than PbO_2. The large crystals of $PbSO_4$ observed have never been transformed to PbO_2 (if sufficient conversion to PbO_2 occurs the surface is 'passivated' inasmuch as H_2SO_4 cannot penetrate the PbO_2 layer and Reaction 1 cannot take place). The highly porous $PbSO_4$ structure observed between the isolated large crystals is the developed surface due to Reaction 1. This emphasizes the beneficial effects of rests in positive battery plate formation; an increase in porosity improves the ultimate discharge behaviour.

3.2.3. The reduction of PbO_2 on Pb to $PbSO_4$ in 5 M H_2SO_4. A coherent complete film of PbO_2 was prepared by completely converting the $PbSO_4$ layer to PbO_2 at 1350 mV and then sweeping down to 700 mV at 1 mV s^{-1}. Fig. 12 shows that the results differ markedly from those shown in Fig. 11. In the swept electrode, the product $PbSO_4$ is very ordered and composed of quite large crystals, the porous deposit of the self-discharged electrode being absent. It can be concluded that the self-discharge of the reaction in which Pb is consumed is much more effective in surface area development than the single electrochemical conversion of a $PbSO_4$ surface.

3.2.4. The second oxidation of $PbSO_4$ to PbO_2 (2nd cycle). Following the reduction corresponding to Fig. 12, a subsequent potentiostatic oxidation at 1350 mV produced the surfaces shown in Fig. 13. Here rod-like crystals of PbO_2 were observed to be growing across the deposit. It is clear that morphological changes between subsequent cycles occur and these are the reasons for differences in the responses of PbO_2 electrodes in charge/discharge cycling.

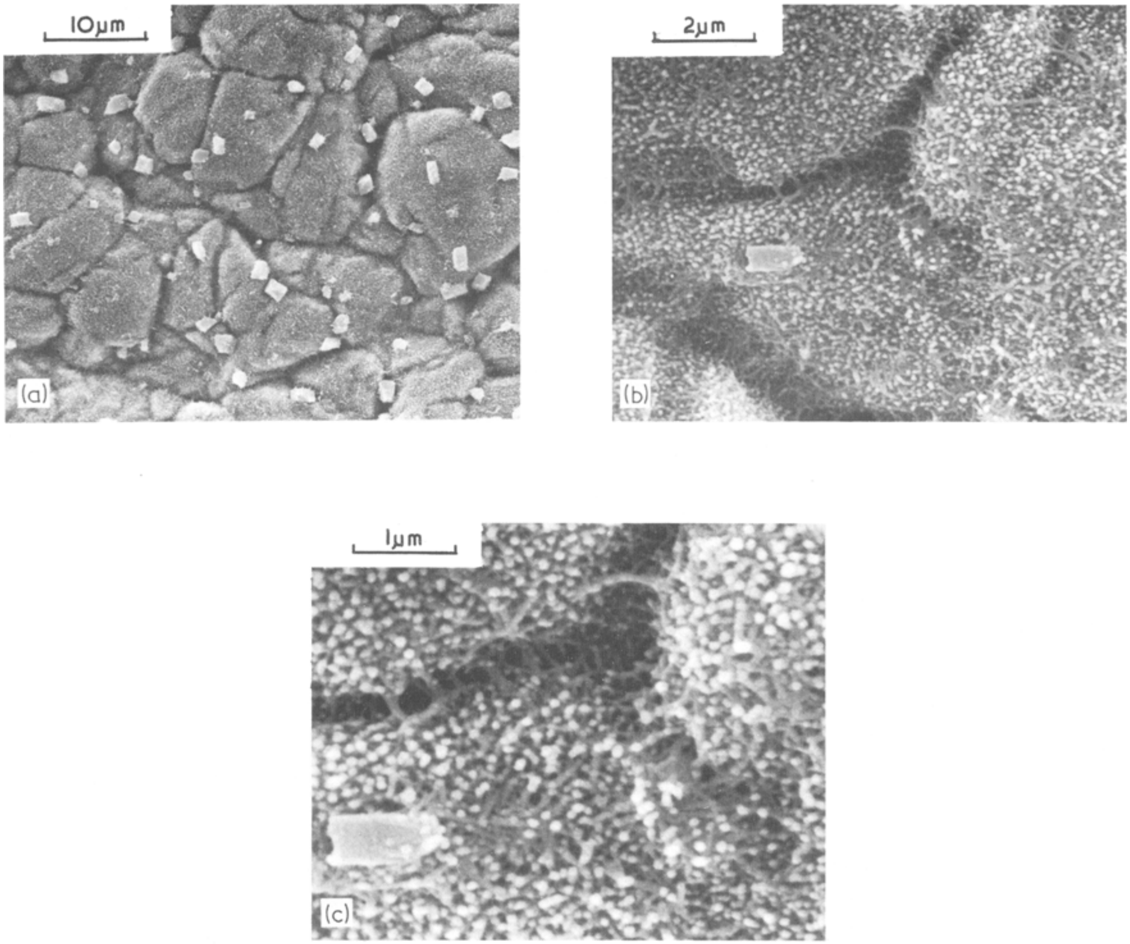

Fig. 11. Effect of oxidation of the $PbSO_4$ layer at 1350 mV.

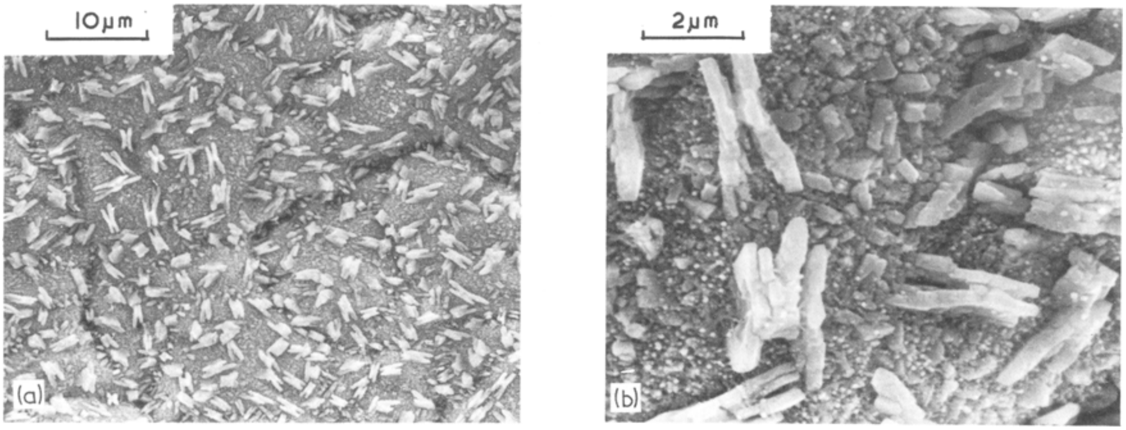

Fig. 12. Reduction of the grown PbO_2 to $PbSO_4$ by a potential sweep from 1350 to 700 mV at 1 mV s^{-1}.

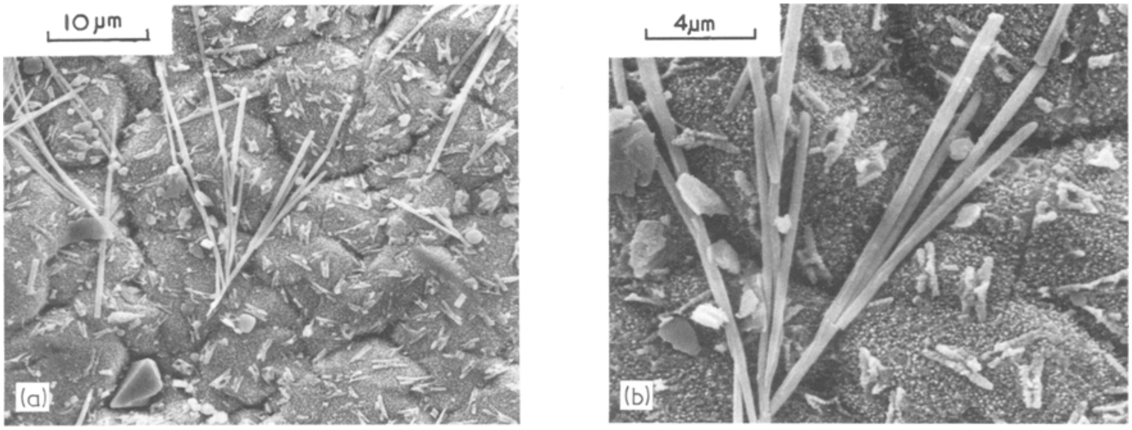

Fig. 13. Effect of oxidation of the $PbSO_4$ layer shown in Fig. 12 at 1350 mV.

4. Conclusions

The difference between the morphology of the surface after the initial and subsequent electrochemical cycles is again emphasized. The unique porous character of the surface obtained by a self-corrosion process is of considerable importance in the surface development process.

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