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# *Morphological examination of the effect of antimony on the electrochemistry of lead*

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An SEM study of the oxidation of $PbSO_4$ on Pb and Pb–Sb alloys is presented. The formation of a duplex layer of $PbO_2$ on the antimonial alloy is established and the primary layer of $PbO_2$ on Pb–Sb is shown to be analogous to the single layer on pure lead.

## 1. Introduction

In our previous work [1, 2] we have studied the electrochemical responses of lead electrodes containing antimony as the main alloying ingredient and compared the data obtained with that from our work on pure lead electrodes. Firstly experimental procedures for obtaining a constant electrode response were investigated, followed by linear sweep voltammetry and potentiostatic pulse measurements. Several differences between pure-Pb and Pb–Sb alloys were observed, the most interesting of these being the appearance of a second rise and fall in the current transient during potentiostatic step experiments on antimonial lead. We explained the presence of this second peak, which was absent with a pure lead electrode, in terms of the formation of a duplex layer of $PbO_2$. Furthermore, by calculating the charge contained in the first peak and by noting the time taken to reach an $i_{max}$ value we concluded that the primary layer formed on antimonial lead is analogous to the single layer formed on a pure lead electrode, the latter being completely passivating. In this paper we present the morphological evidence in support of our electrochemical data and discuss mechanisms for the beneficial role of antimony in $PbO_2$ formation.

## 2. Experimental

The electrolytic cell, electrode preparation and electrical circuitry have all been described in previous publications [1, 2]. Electrodes were cycled to constant response between the limits 400 mV* and 1520 mV then held in the $PbSO_4$ region for a reductive period prior to potentiostatic pulse measurements. Experiments were performed in 5 M $H_2SO_4$ on a flat surface shrouded in teflon in the form of specially constructed stubs which screwed into the end of the rotating disc electrode. After completion of the electrochemical experiments, samples were washed with tri-distilled water, rinsed with acetone and stored in a vacuum dessicator. For microscopic study samples were coated with a thin layer of gold (10–20 nm) by diode sputtering and examination was carried out using a Jeol JSM 35 scanning electron microscope (tube voltage of 20 kV). Imaging was by secondary electron emission.

## 3. Results and discussion

Fig. 1 shows the surface morphology of a pure

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* All potentials refer to the $Hg/Hg_2SO_4$ electrode in 5 M $H_2SO_4$.

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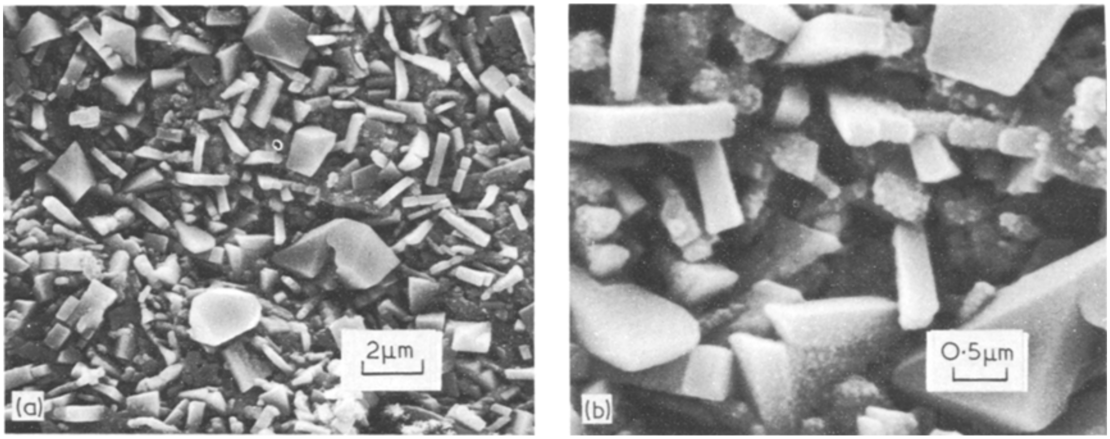

Fig. 1. Front of flat lead electrode following potential step to 1275 mV for 10 s (2 magnifications).

lead electrode following a short oxidative period in the $PbO_2$ region (1275 mV). The lead dioxide matrix consists of crystallites which conglomerate into small spherical groups interspersed with well-defined prismatic crystals which are readily identifiable as residual lead sulphate still available for oxidation. The sulphate crystals are several orders of magnitude larger than the groups of $PbO_2$. Figs. 2–4 show that as the length of time the electrode is held in the $PbO_2$ region is increased the oxidation of residual $PbSO_4$ to $PbO_2$ is accomplished and complete surface coverage with $PbO_2$ is attained.

Similar experiments were performed on an electrode containing 5.15% Sb and the corresponding surface morphologies are shown in Figs. 5–8. Several differences between the pure lead and the antimonial alloy are immediately apparent; the first of these is the absence of unoxidized lead sulphate crystals on the surface which is completely covered with the finer grained $PbO_2$ structure (compare Figs. 1 and 5). This observation is significant since it suggests that the presence of antimony serves to somehow activate the surface of the electrode thus enabling the product $PbO_2$ to form more quickly than on an unactivated pure Pb surface. We have previously reported that one of the beneficial effects of antimony addition to lead is that it assists the efficiency of oxidation of the $PbSO_4$ deposit [2]; this conclusion was based on a series of potential step experiments from the $PbSO_4$ region into the $PbO_2$ region and is confirmed by the morphological evidence presented here.

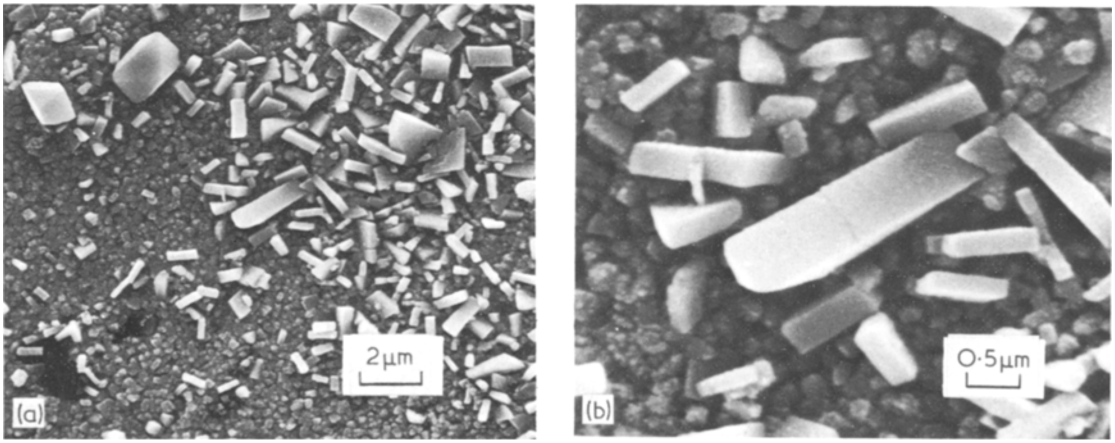

Fig. 2. As Fig. 1. but for 20 s.

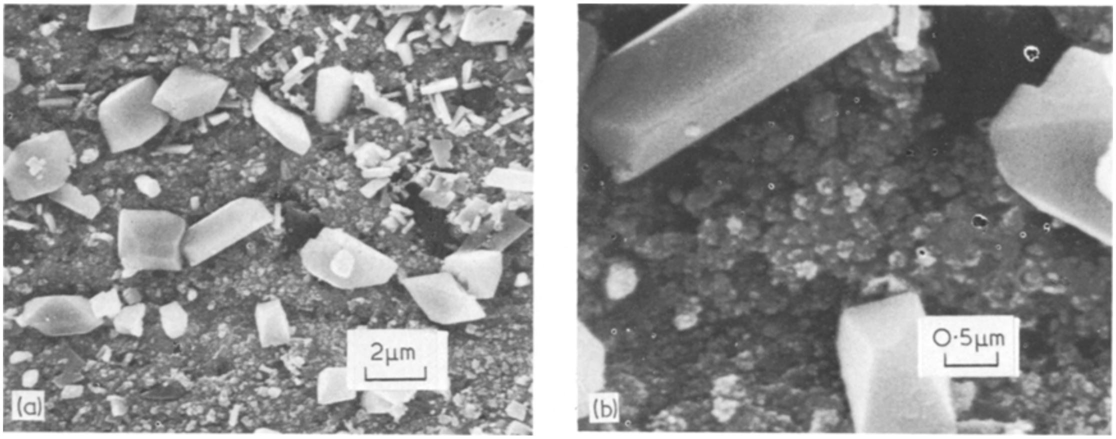

Fig. 3. As Fig. 1 but for 30 s.

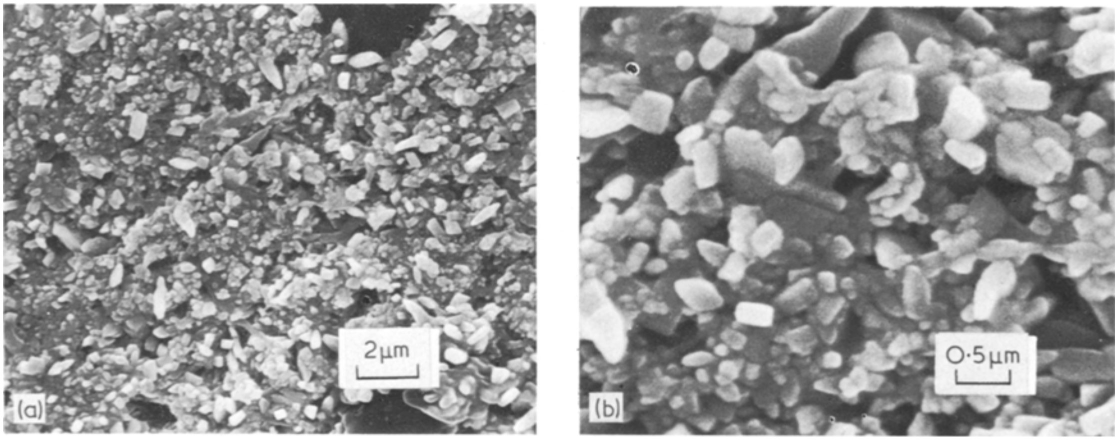

Fig. 4. As Fig. 1 but for 50 s.

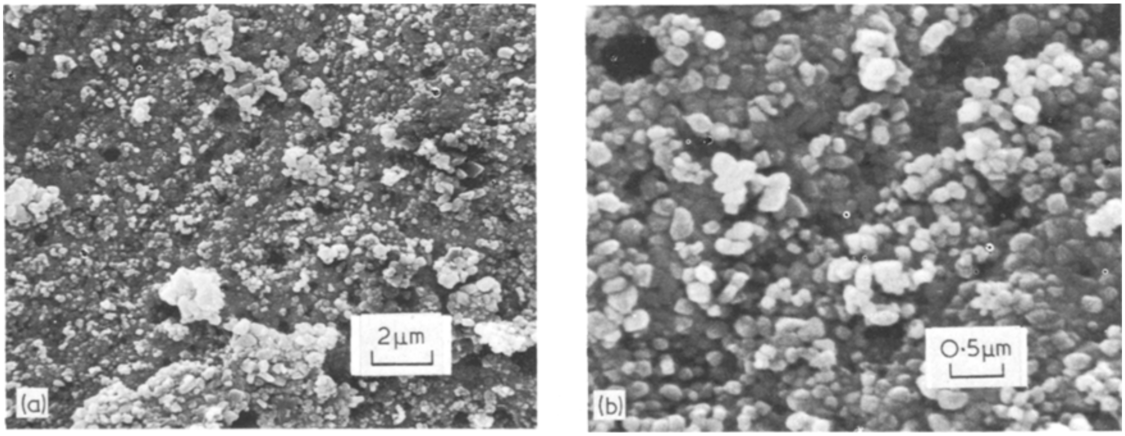

Fig. 5. As Fig. 1 but on Pb–Sb (5.15%).

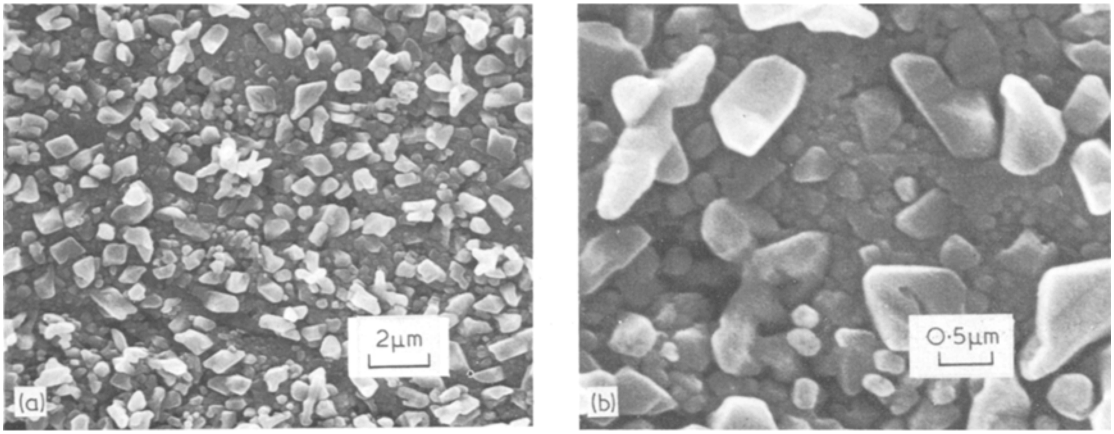

Fig. 6. As Fig. 2 but on Pb–Sb.

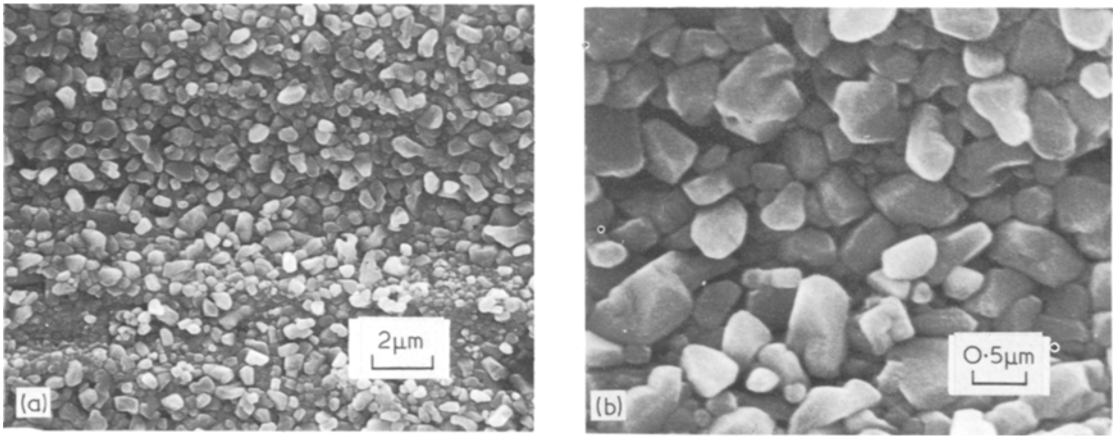

Fig. 7. As Fig. 3 but on Pb–Sb.

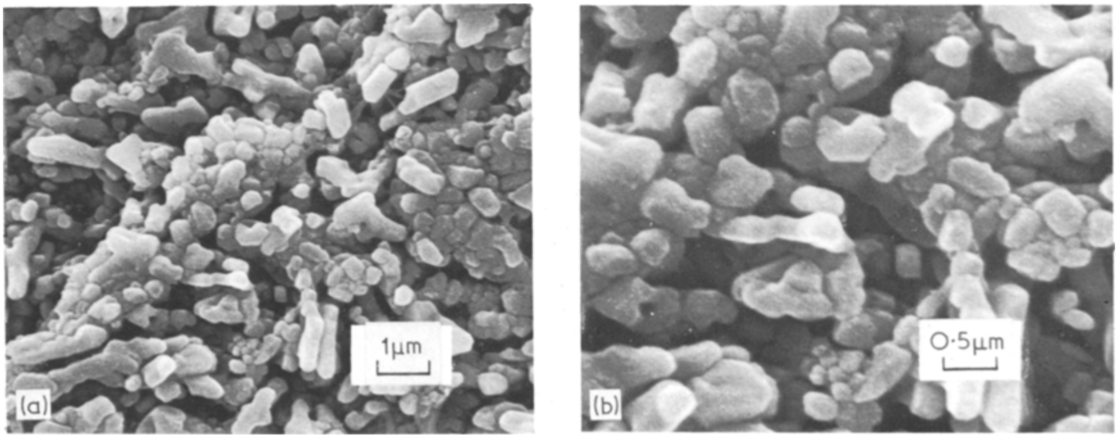

Fig. 8. Potential step to 1275 mV on Pb–Sb (5.15%) for 90 s.

A second interesting comparison between $PbO_2$ formation on pure and antimonial lead is the gradual development of a secondary layer of $PbO_2$ in the presence of antimony. This is in excellent agreement with our previous electrochemical data from which we had predicted the existence of this duplex layer [2]. Figs. 5–7 show the primary layer of spongy $PbO_2$ (diameter ~ 0.1 μm) being covered with a further layer of much larger, well-defined crystals (diameter ~ 0.5 μm) which do not appear to bond to each other. We have previously shown that both processes (i.e. formation of the primary and secondary layers on antimonial lead) start from zero time since no time correction was necessary when analyzing the second peak obtained in the potential step experiments. As the oxidation time is increased this secondary layer of $PbO_2$ is seen to form voids which multiply until eventually the layer breaks up (Figs. 8 and 9). Burbank [3] has observed a similar phenomenon during deep cycling experiments on antimonial alloys, the reason given being the extreme stress caused as the larger crystals grow in size resulting in the fracture of mechanical bonds between the larger and smaller crystals.

Further comparison of Figs. 1 and 5 shows that the structure of $PbO_2$ on the pure lead electrode is similar to the primary layer formed on antimonial lead; this is once again in good agreement with our previous electrochemical data when analysis of the charge in the transients and the shape led to the same conclusion.

Many works have attempted to explain the mechanism of the action of antimony on lead dioxide formation. Anodic dissolution of Sb from the electrode has been recognized for many years [4, 5] and subsequent behaviour of the dissolved antimony has been studied by tracer techniques [6, 7] and SIMS studies [8, 9]. It is also acknowledged that the presence of antimony in the electrolyte has an effect on the surface morphology of the oxidation product [10, 11] and Arifuku *et al.* [8] have shown that the distribution profile of Sb in oxide films on Pb–Sb is virtually independent of the final polarization potential. X-ray diffraction techniques have been used [3] to examine the structure of Pb and antimonial lead alloys during cycling experiments; the author has reported the major presence of $\beta$-$PbO_2$ in the outer layer of the cycled oxidation film on Pb–Sb while beneath a mixture of $\alpha$- and $\beta$-$PbO_2$ formed a microcrystalline coating firmly attached to the metal surface. The absence of a firmly-bound secondary layer of $\beta$-$PbO_2$ on the pure lead surface was explained in terms of the ability of Sb to nucleate the $\beta$-$PbO_2$ in the primary corrosion layer which bonds with $\beta$-$PbO_2$ produced on further cycling [3]. A probable explanation for our observations can be given along these lines; the formation of $\alpha$-$PbO_2$ in the corrosion film can be explained in terms of acid depletion within the pores of the film as the oxidation proceeds resulting in the formation of a medium which is effectively alkaline in nature (Fig. 10). The presence of Sb in

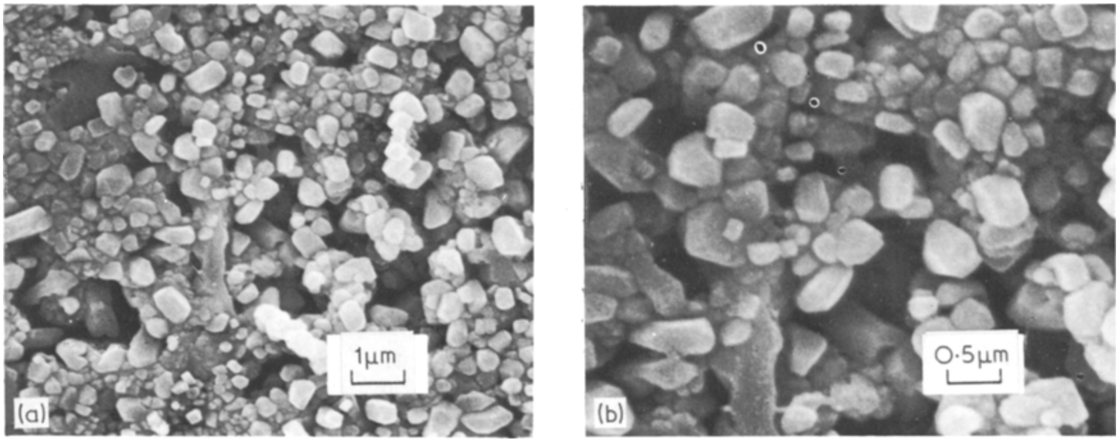

Fig. 9. As Fig. 8 but for 150 s.

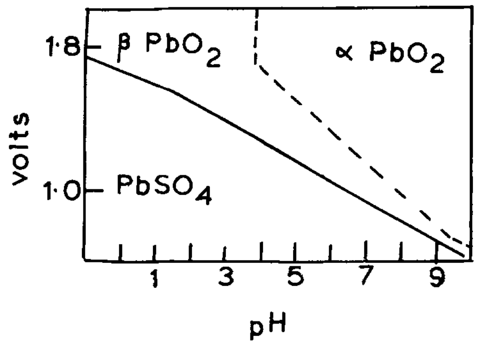

Fig. 10. Potential–pH diagram showing stability regions for α- and β-$PbO_2$ [12]. Potentials shown versus standard hydrogen electrode.

the oxidation layer effects the formation of nucleation centres for β-$PbO_2$ which is present in far greater quantities than on a pure Pb surface. The β-$PbO_2$ so formed bonds to β-$PbO_2$ already present in the corrosion layer to form a secondary corrosion film.

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## References

[1] N. A. Hampson, S. Kelly and K. Peters, *J. Appl. Electrochem.* 10 (1980) 91.
[2] *Idem, ibid* **10** (1980) 261.
[3] J. Burbank, NRL Report 7256, May (1971).
[4] J. Burbank, *J. Electrochem. Soc.* **104** (1957) 693.
[5] T. F. Sharpe, *J. Appl. Electrochem.* **124** (1977) 168.
[6] J. L. Dawson, M. I. Gillibrand and J. Wilkinson, *Power Sources* 3 (1970) 1.
[7] J. L. Dawson, J. Wilkinson and M. I. Gillibrand, *J. Inorg. Nucl. Chem.* **32** (1970) 501.
[8] F. Arifuku, M. Yonyama and H. Tamura, *J. Appl. Electrochem.* 9 (1979) 629.
[9] *Idem, ibid* 9 (1979) 635.
[10] J. Burbank, *J. Electrochem. Soc.* **111** (1964) 11 12.
[11] E. J. Ritchie and J. Burbank, *J. Electrochem. Soc.* **117** (1970) 229.
[12] J. Burbank, *J. Electrochem. Soc.* **104** (1957) 699.