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The rôle of antimony in the lead-acid battery: Part 1. The effect of antimony on the anodic behaviour of lead

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Linear sweep voltammetric (LSV) and impedance studies of lead/antimony binary alloys (0–12% Sb) are described. The formation of a solid antimony-containing species in close contact with a passivating layer of lead sulphate at sufficiently positive potentials (before lead dioxide formation) is indicated. In the presence of antimony, changes in the characteristics of the passivating layer occur, in accordance with a reduction in thickness and an increase in porosity.

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1. Introduction

Antimony in the range 5–12% is added to the material of the support grids of lead-acid batteries in order to impart many well-known desirable properties. The only technical disadvantage of the addition has hitherto been thought to be the low hydrogen overvoltage of antimony which resulted in excessive self discharge of the negative active material; however, it has emerged that at low antimony contents grids often exhibit poor positive paste retention characteristics. The purpose of the present study has been to examine the electrochemical effects of antimony on the lead/lead sulphate/sulphuric acid system.

The mechanism of passivation of lead electrodes in H_2SO_4 solutions has been shown to involve two processes, namely dissolution-precipitation and solid-state reaction [1]. The relative importance of the two processes is dependent upon the surface preparation of the lead. Carr *et al.* [2,3] measured the impedance of a range of lead/antimony alloys in KNO_3 and HNO_3 solutions and concluded that the surface roughness increased with the antimony content up to the eutectic (12%) composition. Dawson, Gillibrand and Wilkinson [4] concluded from the results of spectroscopic, polarographic and radiochemical studies that several inter-related equilibria, involving antimony in various valency states occurred in the lead-acid battery. The main process by which antimony is removed from the positive grid is as Sb(V) followed by a two-stage reduction involving Sb(III) and deposition onto the negative plate. This mechanism is in accord with previously well-established technological conclusions [5].

2. Experimental

The LSV studies were made with a potentiostat (Chemical Electronics, TR70/2A) in conjunction with a Waveform Generator (O. R. Brown, Newcastle-upon-Tyne), the response being recorded graphically (Bryans type 26 000). The electrical impedance was measured as described by Carr *et al.* [3].

The electrolytes were prepared from AnalaR grade reagents and triply distilled de-ionized water followed by cleaning with charcoal [3].

Electrodes were prepared by drawing molten metal into glass capillary tubing and rapidly cooling. The composition of the resultant 'antimony in lead' phase was ~2%. The electrodes were mounted in polyethylene and cut at right angles to the principal axis.

Large area counter electrodes of lead (99·999%

Koch Light) were used in order to ensure that their impedance was negligible. The reference electrodes were Pd/H_2 for impedance measurements and Hg_2SO_4/Hg for LSV.

3. Results and discussion

3.1. *LSV Measurements*

With pure lead electrodes, anodic and cathodic sweeping experiments between −1020 mV and 1980 mV (versus Hg_2SO_4/Hg) in 1M H_2SO_4 verified earlier work by Panesar [6] and Carr *et al.* [2]. These authors found that at high sweep speeds, the anodic curve shows only the current peak due to the $Pb \rightarrow PbSO_4$ process, further oxidation to PbO_2 occurring with the wave corresponding to oxygen evolution. (At slow sweep speeds the second PbO_2 peak can be readily resolved on anodic sweeping [7].)

Cathodic sweeping gave three peaks: (a) (at ~+950 mV) corresponding to the reduction of lead dioxide to lead sulphate; (b) (at ~−950 mV) the reduction of lead sulphate to metallic lead; and (c) (at ~−800 mV). This last, small peak, was similar to that reported previously by Carr *et al.* [2] and Panesar [6] and is probably due to the reduction of a basic compound formed beneath the outer surface of the lead sulphate. A fourth peak reported by Panesar [6] as corresponding to the reduction of α-PbO_2 was not observed in the present studies, indicating the absence of this polymorph.

Experiments with lead/antimony alloys (Fig. 1) showed the presence of one additional peak in the anodic sweep (at −384 mV) and one in the cathodic sweep (at −648 mV). These additional peaks are ascribed to the formation and reduction of Sb(III) species. The height of both peaks increased with increasing antimony content. That such a well-defined reduction peak was present suggests that the majority of the antimony species do not leave the electrode but remain there within the passivating lead sulphate layer.

Experiments with both pure lead and 12% antimony/lead alloy in which the anodic limit of the sweep was progressively reduced showed that in both cases reduction of the anodic limit to 1560 mV resulted in the elimination of the PbO_2 reduction peak. Confirmation is thereby provided that PbO_2 is produced during the oxygen region for both pure and alloy electrodes and, more importantly, that the presence of antimony does not confer any increased reactivity on the electrode for the development of PbO_2. For the alloy electrode, reduction of the anodic limit to −120 mV still left unaffected the 'antimony' peaks indicating the relatively unpolarizable nature of the antimony reaction *vis-à-vis* the formation of PbO_2.

3.2. *Impedance Measurements*

The results of experiments in which the resistance and capacitance components of the electrode impedance are shown as a function of the bias

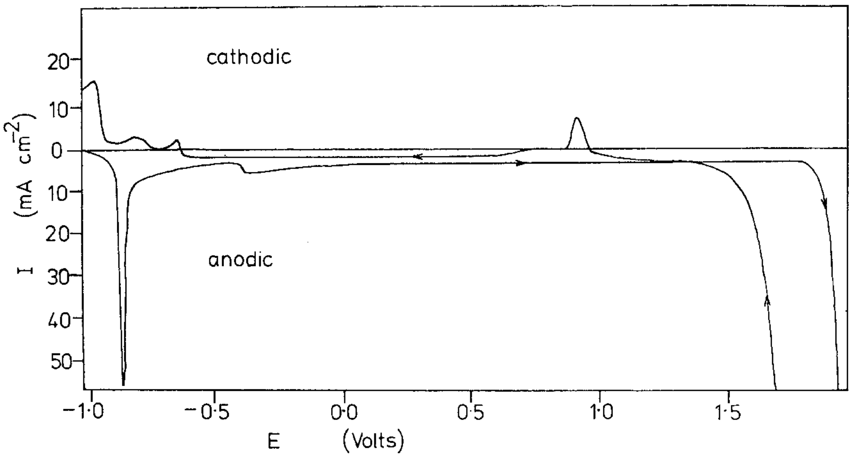

Fig. 1. LSV curves, cathodic and anodic, for lead/antimony alloy (12%) in 1M H_2SO_4 23°C, 600 mV min^{-1}.

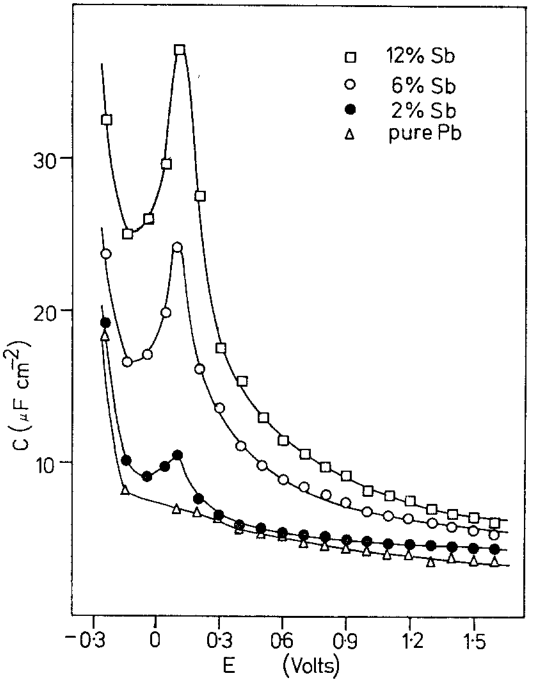

Fig. 2. Differential capacitance versus bias-potential curves for lead/antimony alloys. 1 kHz, 23°C, 1M H_2SO_4.

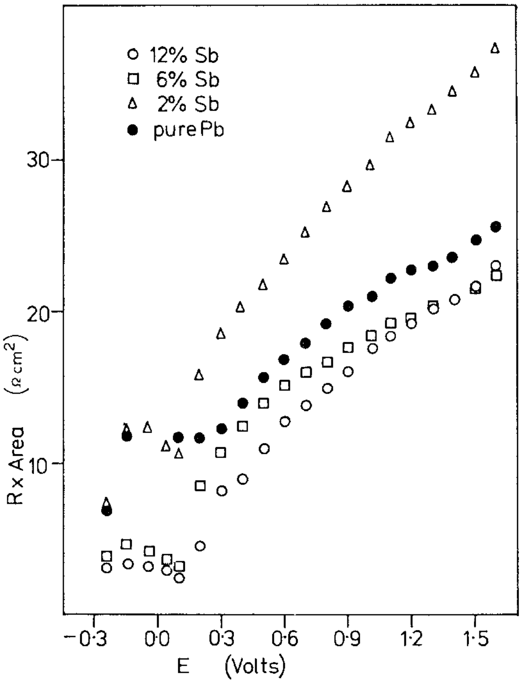

Fig. 3. Resistance versus bias-potential curves for lead/antimony alloys. 1 kHz, 23°C, 1M H_2SO_4.

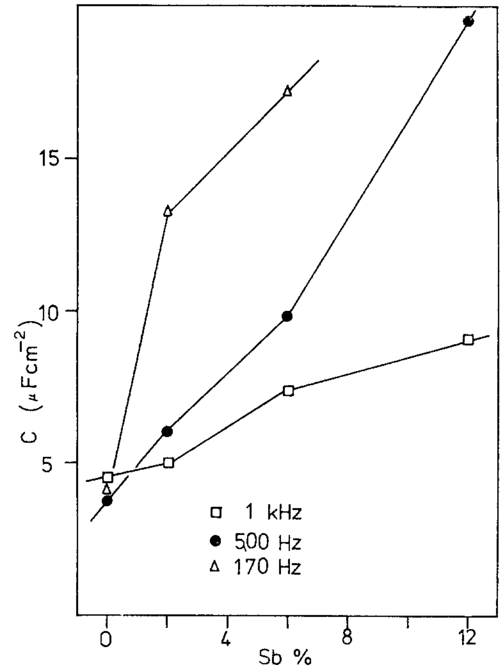

Fig. 4. Frequency dispersion of capacitance for lead/antimony alloys. 23°C, 1M H_2SO_4, E = +0·9 V.

potential are presented in Figs. 2–4. The presence of antimony in the alloy results in the development of a capacitance peak at $\sim$190 mV (Pd/H_2) which becomes more pronounced as the antimony content is increased. Corresponding resistance minima are also observed. The potentials at which these peaks occur correspond to observed peaks for pure antimony in very dilute acids [8] and also in nitrate solutions [3] and can be ascribed to the onset of dissolution of antimony from the alloy lattice. In general the behaviour of the electrode resistance was complementary to that of the capacitance – increased antimony content giving rise to a lowered resistance. The 2% alloy was anomalous in giving a significantly higher resistance; this effect was consistent throughout a series of experiments.

The magnitude of the electrode capacitance and the electrode potential ($>$300 mV) indicate that the electrode is covered with a film of lead sulphate. The increase in the conductance of this electrode (film) with increased antimony content of the alloy is of considerable importance. This effect may arise in one of two ways:

(a) By the incorporation of antimony species into the $PbSO_4$ lattice the electrical conductance of the bulk material may be increased due to the development of non-stoichiometry.

(b) The crystalline structure of the passivating deposit may be modified to make it more porous or to alter the thickness.

Fig. 4 shows that the frequency dispersion of capacitance was increased with increasing antimony content and hence it seems that of the two (b) is more likely than (a). These results agree with Carr *et al.* [2] that the roughness of the alloy itself increases as the antimony content is increased although the effect observed by these authors with lead/antimony alloys in different solutions are smaller than those observed here.

The slope of the resistance-potential curves indicates that the passivation of the electrode was not complete and a small number of Pb^{2+} ions was passing through the lead sulphate resulting in a continuous thickening of this layer. For the 6% and 12% antimony alloys the magnitude of the layer resistance was much less than in the case of the low antimony alloys, i.e. passivation was achieved more efficiently. This may be due to the plugging of unpassivated areas by antimony species.

The reasons for the anomalous behaviour of the 2% alloy are not immediately apparent. However, the behaviour observed confirms technological observations that the corrosion resistance and positive plate retention of Pb-Sb battery plates is greatly reduced at an antimony content of ~2%.

4. Conclusions

1. The corrosion behaviour of lead/antimony alloys is more complex than that of pure lead, in that antimony is removed from the lattice at ~ −384 mV (versus Hg_2SO_4/Hg) and remains incorporated in the layer of lead sulphate covering the electrode.

2. The presence of antimony in the alloy causes passivation of the electrode to occur more efficiently. The electrode dissolution reaction is reduced by a thinner, less resistive covering of $PbSO_4$ (nominally) when antimony is present. This may, therefore, be the mechanism by which corrosion and grid-paste resistance are reduced.

3. Alloys containing ~2% Sb are anomalous, this could be related to the fact that the solid solutions are unsaturated.

Acknowledgement

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