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Fundamentals of lead-acid cells. IX. The effect of alloying with antimony on the electrochemical properties of solid lead

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The electrochemistry of the Pb–Sb(5 wt %)/H_2SO_4 system has been followed using linear sweep voltammetry and the data compared with that from the Pb/H_2SO_4 system. Pre-cast lead rods aged for more than a month were used throughout in an effort to follow established industrial practice. The two areas covered are: (a) The rate of attainment of constant response of the cycled electrodes, and (b) the behaviour of stabilized electrodes. The results show that antimonial lead is corroded to a much greater extent than pure lead. Active material retention is also discussed in view of the differences between antimonial and pure lead.

1. Introduction

Lead–antimony alloys have been used as support grids for lead–acid positive and negative battery plates for a considerable number of years. The alloying antimony is added in order to improve castability and subsequent handleability. It is widely known that Sb in automotive positive grids extends the service life by improving the capability to resist deep cycling and extensive overcharge. This effect is believed to be due to the Pb/Sb alloy providing a corrosion layer which has good adhesion to the active material and a corrosion product which does not penetrate in between the crystallites of the grid alloy producing an intergranular attack. A pronounced disadvantage, however, is that the presence of antimony in the cell lowers the potential of hydrogen evolution due to the deposition of antimony on the negative plate with a consequent lowering of the hydrogen overvoltage at that electrode.

Attempts to substitute other materials for antimony have been fairly successful and alloys with calcium, tin and aluminium are in use in various parts of the world. There is no doubt that improvements in the suppression of the hydrogen evolution reaction have resulted from these substitutions but unfortunately the reduction in Sb from positive grids has resulted in rather inferior cycle lives.

It was thought of interest to investigate the electrochemistry of the simple alloy/sulphuric acid system in order to compare the data with that from the lead/sulphuric acid system. This paper records the linear sweep voltammetry part of the investigation.

2. Experimental

The working electrodes consisted of pure and alloy lead rods (C-metals, 3 mm diameter) shrouded in Teflon and placed in the centre compartment of a three-limb cell containing de-oxygenated sulphuric acid (5 M) prepared from AnalaR grade H_2SO_4 and tri-distilled water. The Hg/Hg_2SO_4 reference electrode was connected to the working electrode via a Luggin capillary system. All potentials are quoted on this scale at 23° C.

The experiments were performed using a Kemitron PS-40 potentiostat and function gener-

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ator and the output monitored on an X–Y recorder (Bryans, Series 26000). The electrode was pre-treated by cleaning on roughened glass (to give a smooth surface), chemical etching in 10% HNO_3, rinsing in tri-distilled water followed by potentiostating at – 1·150 V (H_2 region, 10 min) to reduce any surface oxides prior to sulphate formation. Chemical analysis of the lead used was: 0·0025 wt% Ag, 0·0026 wt% Cu, 0·0025 wt% Ti, 0·01 wt% Bi. The alloy contained 5·15 wt% Sb.

The experiments consisted of cycling to a constant response by sweeping between 400 mV and 1520 mV. The time required for constancy was approximately 1·5 h. It was found necessary to 'initiate' the reaction by sweeping up to 2000 mV in the first cycle otherwise no product lead dioxide was formed under the cycling conditions (7 mV s^{-1} to 100 mV s^{-1}) with the positive limit at 1520 mV. Once the reaction had been initiated it proceeded normally. The need for this procedure was expected in view of the early observations of Fleischmann *et al.* [1] who emphasized the need for a considerable initial overpotential.

3. Results and discussion

3.1. *Early cycle history*

A feature of the early cycle pattern is the small anodic current which flows during the negative-going sweep in the region of 1000–1200 mV. This was obtained with both antimonial and pure lead electrodes provided that the positive limit of the sweep was ~ 2000 mV; the shape was, however, much less well defined with the alloy (Fig. 1). This suggests that the response is not only connected with the metal itself but because of the limit required, is also connected with oxygen or related species. The charge of ~ 270 μC cm^{-2} contained in the integrated anodic area of the peaks suggests the formation of a monolayer of species equivalent to Pb^{2+}.

Similar peaks have previously been reported [2, 3]. The curve obtained by Panesar [2] with an almost identical system to ours shows a cathodic peak immediately preceding the anodic one. This cathodic signal can be explained if a certain amount of lead dioxide had been produced during the anodic excursion (somewhat greater than ours) into the oxygen region. The cathodic charge represents the extent of this PbO_2 formation. The absence of a cathodic region in Fig. 1, however, indicates that no highly oxidized species of Pb are present in our experiment and this throws doubt on the anodic peak being due to α-PbO_2 formation as suggested by Panesar [2].

Sunderland [3] also studied these small peaks using 0·5 M H_2SO_4 and observed a reversal in the peak order. He interpreted the anodic peak as an oxidation of water by an intermediate Pb^{3+}

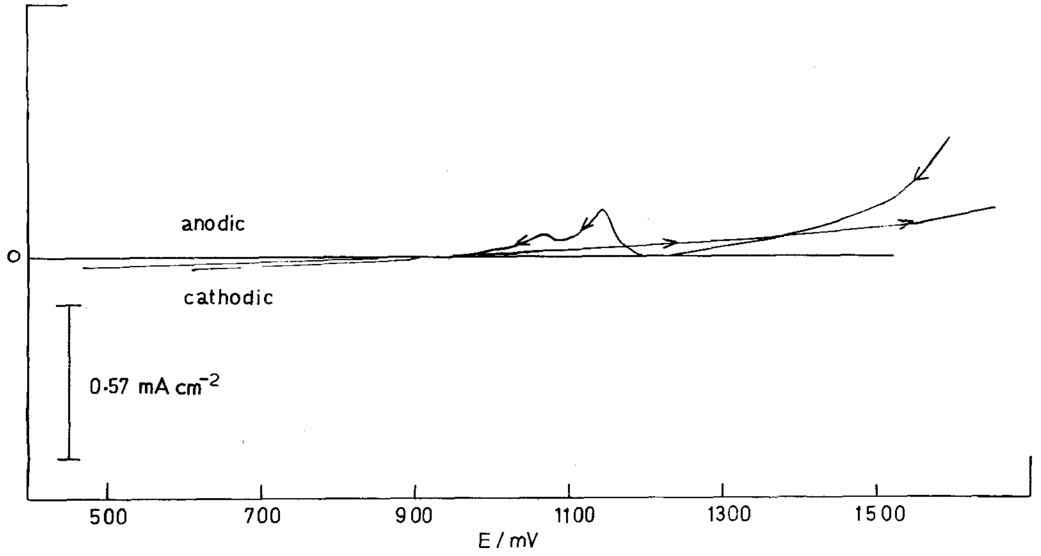

Fig. 1. Early cycle pattern (400–2000 mV) for pure Pb. Sweep rate 50 mV s^{-1}.

species. The displacement of the cathodic peak (PbO_2 reduction) from the potential noted by Panesar is readily explicable by the decade difference in acid concentration between Sunderland's experiments and the others, however, his explanation seems to be inadequate in the present case because of the non-appearance of a cathodic signal.

We suggest that a more reasonable explanation can be given in terms of the production of a layer of O_2 or related absorbed species during the potential excursion into the oxygen region which disrupts the $PbSO_4$ layer. On sweeping back, the desorption of O_2 exposes parts of the Pb surface which can undergo attack by the electrolyte requiring an anodic current flow to produce a passivating film.

The observed double peak can be interpreted if the surface is initially covered by O atoms (or OH radicals) produced by the high positive potential which remain at the electrode in the adsorbed state and which ultimately combine to form O_{2ads} and finally being evolved as gaseous O_2. These adsorption reactions will be dependent on the potential so that as the potential moves negatively from the positive limit the formation of O_{2ads} from O_{ads} renders a portion of the initially covered surface available for attack and conversion to a passivating film of $PbSO_4$. At somewhat lower potentials as O_2 is evolved the remainder can be oxidized giving a double peak. Thus the two peaks are produced as a result of depassivation of the electrode by the oxygen species [4–6] and should be equivalent to a monolayer of $PbSO_4$ as observed.

The early cycle patterns also show that the alloy takes longer to give a constant response than the pure Pb electrode. PbO_2 formation is somewhat more developed on the pure Pb electrode after cycling for only a short while.

Another interesting feature of the early potentiodynamic curves is that the anodic current due to the formation of PbO_2 occurs at a more negative potential on antimonial lead than on pure lead suggesting that the kinetic barrier to the oxidation of Pb^{2+} to Pb^{4+} is lowered in the case of the alloy. This may be due to the effect of antimony on the grain structure of the lead producing a more attackable form or the production of a more conducting layer of $PbSO_4$ by the incorporation of antimonial species into the $PbSO_4$ layer.

3.2. *Constant response curves*

Fig. 2 shows stabilized potential curves for both lead and antimonial lead. These curves show

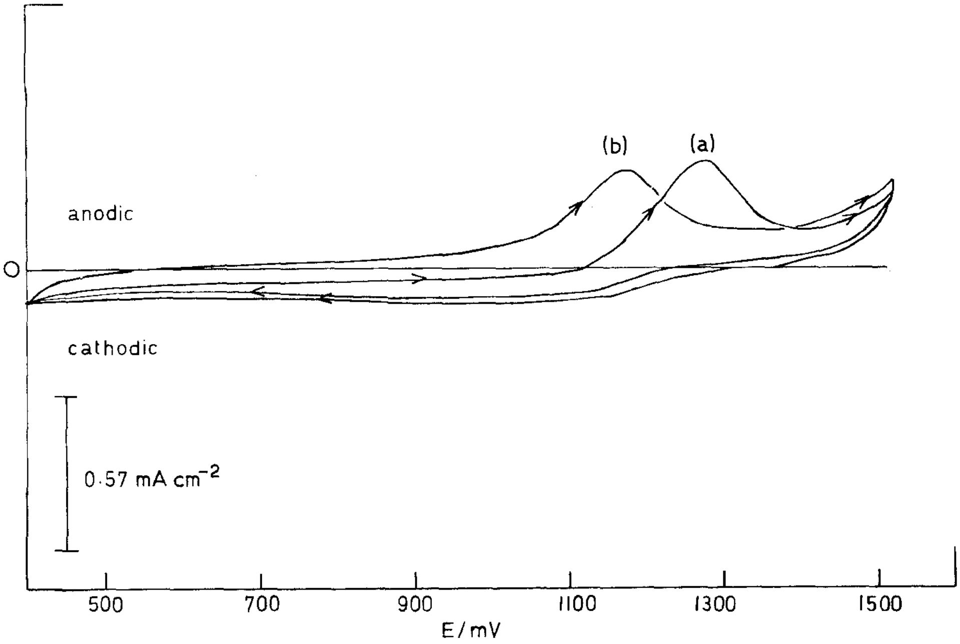

Fig. 2. Constant response curves for (a) Pb and (b) Pb/Sb. (400–1520 mV, 40 mV s^{-1}) after cycling for 1·5 hours.

much broader peaks than those obtained by Casson *et al.* [7]. This difference arises from the mode of electrode pre-treatment; Casson *et al.* following Fleischmann *et al.* [1] used lead freshly electroplated onto massive lead. It was our intention to follow established industrial practice and so pre-cast lead rods, aged for at least one month, were used. With the more reactive freshly plated electrode a thick deposit of compact PbO_2 is readily formed. With our present electrode the deposit is more porous with a consequent broadening of the peaks as the reaction is driven through the porous layer by the increasing overpotential.

A well-defined anodic current is observed during the positive-going sweep on the alloy whereas the current remains cathodic up to 1100 mV (40 mV s^{-1}) in the case of the pure Pb after which PbO_2 formation rapidly occurs confirming that corrosion begins at a lower potential with the alloy.

Fig. 3 shows the relationship between E_p the peak potential in the oxidation of $PbSO_4$ to PbO_2 and sweep rate in the form of E_p versus log (sweep rate). This follows the expected equation developed by Canagaratna *et al.* [8] for the development of a single layer on an electrode. It is clear from the lines in those figures that formation of PbO_2 occurs at a much less positive potential on the alloy than on the pure metal.

Fig. 4 shows the relationship between i_p the peak current and the potential sweep rate as plots of i_p versus $\surd$(sweep rate). Similar straight line plots are obtained with both the pure lead and the electrode in the range 7–100 mV s^{-1}. Here we are apparently dealing with a process in which the current is controlled by diffusion in the solid state. This is supported by the fact that the current flowing in the peak was not dependent on the rotation speed of the electrode, the diffusion of oxygen species through the electrode taking place

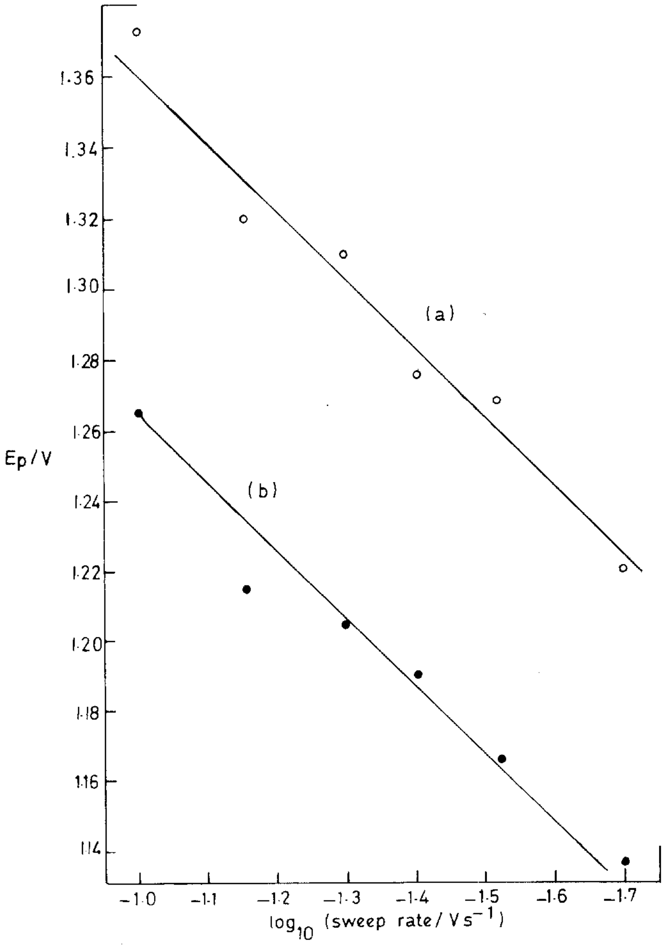

Fig. 3. Plot of E_p versus log ν for (a) Pb and (b) Pb/Sb in the range 7–100 mV s^{-1}.

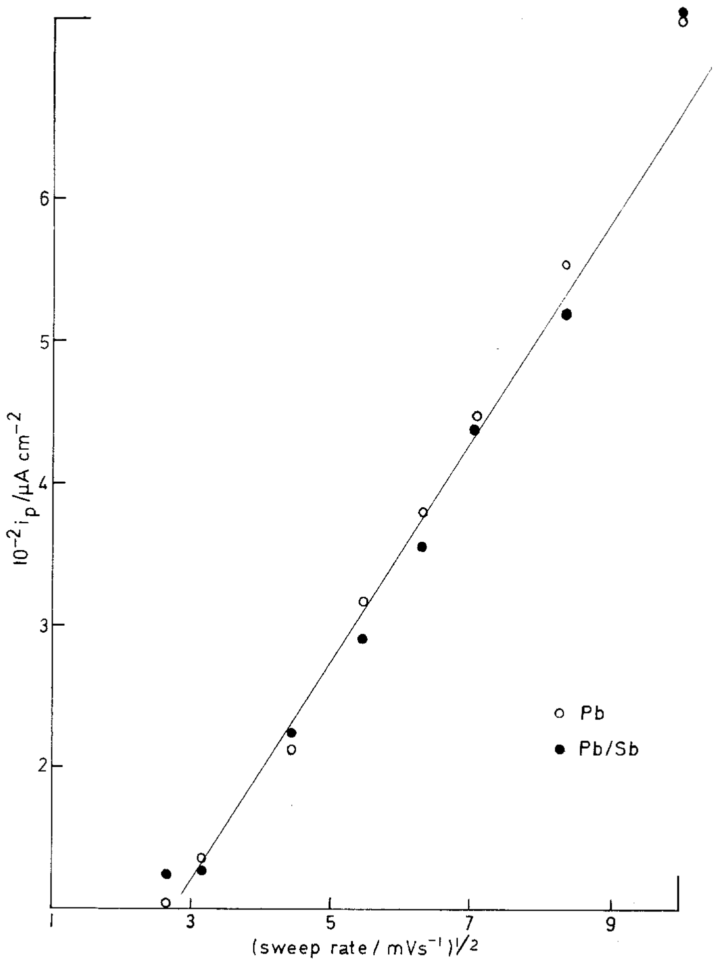

Fig. 4. Plot of i_p versus $\sqrt{\nu}$ for Pb and Pb/Sb in the range 7–100 mV s^{-1}.

via a solid state process. The correspondence of the data for the alloy and single metal systems indicate that the kinetics of the transport of mass and charge through the electrodes are the same.

Table 1. A comparison of the charge contained in the positive-going sweep and its dependency on the sweep rate ν

ν(mV s^{-1})	*Charge* (mC cm^{-2})	
	Pure Pb	*Pb/Sb*
7	−2·233*	7·332
10	−0·785	5·545
20	0·721	3·822
30	0·780	3·260
40	0·946	2·815
50	1·010	2·731
70	1·021	2·236
100	0·988	2·075

* The minus sign denotes a cathodic charge

The charge contained in the positive-going sweep was calculated by dividing the integrated area under the peaks by the sweep rate, following Canagaratna *et al.* [8]. This data is summarized in Table 1 which shows differences between pure lead and the alloy. First there is the much greater quantity of charge obtained with the alloy. This indicates that the extent of attack occurring in the electrochemical cycling is much greater for the alloy than the pure metal. This may be the reason for the superior active material retention of Sb-containing grids than pure Pb grids. The relatively large material development with the antimonial alloy gives rise to a more mechanically sound junction between grid and paste in the battery. This fact may also explain the known behaviour of antimonial lead in the oxygen region where certain stationary batteries have exhibited a high degree of top bar corrosion. The conclusion must be drawn that the passivating layer on lead forms more rapidly, is tighter and more mechanically sound than antimonial lead. Our observation is confirmed by calculation of the charge in the negative-going sweep which again is considerably greater in the case of the alloy. Secondly, the alloy exhibits a larger sweep-rate dependency of charge than pure Pb. This indicates that the oxidized layer on pure Pb is of fairly constant thickness and discharges to about the same extent throughout all our experimental conditions. The alloy on the other hand reacts in a way more typical of a porous layer in which the reaction is driven further into the porous mass at lower sweep rates, i.e. a more efficient electrochemical process when more time is available for this to occur.

4. Conclusions

The following conclusions were reached:

(a) The LSV curves for pure lead and antimonial lead show considerable differences.

(b) The antimonial lead was initially less reactive than the pure lead as indicated by the current response in the early cycles of the potentiodynamic curve.

(c) The ultimate net charges in the potentiodynamic curves were considerably greater in the case of the alloy.

(d) The peak current dependencies on the rate of potential sweeping for both pure Pb and the alloy were similar and in agreement with data obtained from similar systems.

(e) A small anodic current flowing in the early cycle history seems to have been previously misassigned, we consider it due to lead sulphate formation at a surface previously passivated by oxygen.

(f) Active material retention can be usefully discussed within the framework of the differences in the electrochemical behaviour of lead and antimonial lead.

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