ANTIMONY IN LEAD–ACID CELLS
IV. REVIEW AND DESIGN CONSIDERATIONS

A A JENKINS

Gestetner Manufacturing Ltd , P O Box 466, London, N17 9LT (U K)

W C MASKELL*

Imperial College, Dept of Metallurgy & Materials Science, Prince Consort Road, London, SW7 2BP (U.K)

F L TYE

Middlesex Polytechnic, Bounds Green Road, London, N11 2NQ (U K)

Summary

The literature regarding the dissolution, transport, and sorption of Sb, and its effects in lead–acid batteries is briefly reviewed. Antimony is evolved in the V valency state principally from positive antimonial-lead grids. It is adsorbed by PbO_2 present in charged positive active material and is also taken up by the negative active material In the latter case this reduces the hydrogen overvoltage of the Pb electrode resulting in self-discharge and coulombic inefficiency on charging. On the other hand, the presence of Sb is beneficial to the performance of positive electrodes. Transfer of dissolved Sb between positive and negative electrodes is impeded by a separator with small pores. Design principles are proposed including antimonial and non-antimonial positive and negative grids, respectively, and a separator with small pores, which should improve the cycle life of batteries.

Introduction

The purpose of this communication is to review the dissolution and immobilisation of antimony in lead–acid cells and to consider the role of the separator in slowing the rate of poisoning of the negative active material. The possible incorporation of immobilising agents is suggested and implications for cell design are discussed.

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*Author to whom correspondence should be addressed

Previous work

Mechanical requirements of grids

Pure lead grids are soft and easily deformed. The incorporation of Sb results in stiffened grids which facilitate handling and pasting with the active materials Other alloys have been prepared and tested with the objective of replacing antimony while retaining suitable mechanical properties The most commonly discussed substitute for Sb is Ca [1 - 3]

Effect of Sb on the negative electrode

Thermodynamically, pure lead is unstable in H_2SO_4 solutions as the Pb/PbSO$_4$ couple has an electrochemical potential negative to that of hydrogen The kinetics of H_2 evolution on Pb, however, are very slow, *i e*, the H_2 overvoltage is high [4] Increasing contamination of Pb with Sb progressively lowers the H_2 overvoltage [5, 6] and gas evolution results in self-discharge of the electrode·

$$2H^+ + 2e \rightleftharpoons H_2 \tag{1}$$

$$Pb + SO_4^{2-} \rightleftharpoons PbSO_4 + 2e \tag{2}$$

so that the overall process is

$$Pb + 2H^+ + SO_4^{2-} \rightleftharpoons PbSO_4 + H_2 \tag{3}$$

Eventually a level of antimonial poisoning is reached where self-discharge is rapid and attempted recharge results principally in H_2 evolution rather than conversion of $PbSO_4$ to Pb (reaction (2))

Effect of Sb on the positive electrode

Measurements of the cycle life and capacity of positive electrodes with antimonial and non-antimonial lead grids show quite clearly the superior performance of the former [1, 2, 7 - 11] The presence of Sb appears to improve the adhesion and electrical contact between the grid and the positive active material

Dissolution of Sb from grids

Antimony tends to dissolve from both positive and negative grids due to corrosion processes Ruetschi and Angstadt [6] proposed the following reaction for dissolution from the positive electrode·

$$5PbO_2 + 2Sb + 5H_2SO_4 + 2H^+ \longrightarrow 2SbO_2^+ + 5PbSO_4 + 6H_2O \tag{4}$$
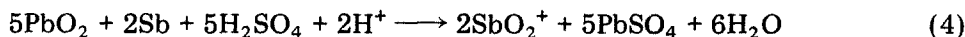
This reaction is in accordance with the finding [12, 13] that antimony is detected in the V valency state when released from the grid of a positive electrode Dawson *et al* [12] reported the formation of Sb(III) from corrosion of negative grids and suggested the reaction

$$Sb + O_2 + 4H^+ + 3e^- \longrightarrow SbO^+ + H_2\uparrow + H_2O \tag{5}$$
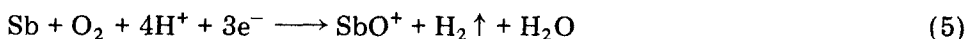
Jenkins *et al* [13], however, using sensitive techniques able to separate Sb(III) and Sb(V) quantitatively [14] could detect only Sb(V) dissolution from antimonial negatives, irrespective of the presence or absence of O_2. A possible scheme is·

$$2Sb + 2H^+ + 4H_2O \longrightarrow 2SbO_2^+ + 5H_2 \uparrow \qquad (6)$$
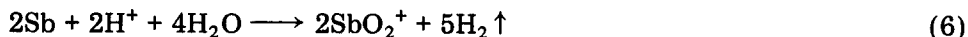
Although Sb is released from both positive and negative electrodes, by far the most originates from the former [12, 13, 15]

Uptake of Sb by cell constituents

Soluble Sb is strongly adsorbed by PbO_2 but only weakly by $PbSO_4$ [12, 13]. Consequently, when the positive electrode is cycled it adsorbs and desorbs Sb during charge and discharge, respectively [12, 16]. Clearly, the Sb concentration in solution may be substantial when the electrode is maintained in a discharged condition. It has been shown [13] that Sb released during discharge from a positive electrode is always in the V valency state, independent of whether Sb(III) or Sb(V) was originally adsorbed.

When a charged negative electrode is in contact with an H_2SO_4 solution containing Sb then elemental Sb is deposited onto the Pb surface. Dawson *et al* [12] found that this occurred rapidly from solutions containing Sb(III) and proposed the reaction:

$$2SbO^+ + 3Pb + 3H_2SO_4 \longrightarrow 2Sb + 3PbSO_4 + 2H^+ + 2H_2O \qquad (7)$$

These authors also sought to measure the uptake of Sb(V) but did not observe it: Jenkins and Maskell [13] showed that this was because insufficient time had been allowed for reaction to take place. Substantial amounts of Sb(V) are taken up by Pb when the solution and solid are in contact for times in excess of 10 h. It is probable that the lead electrode reduces Sb(V) slowly to Sb(III) prior to the more rapid reduction to Sb, *e.g*, reaction (8) followed by reaction (7)

$$SbO_3^- + Pb + H_2SO_4 + 2H^+ \longrightarrow SbO^+ + PbSO_4 + 2H_2O \qquad (8)$$
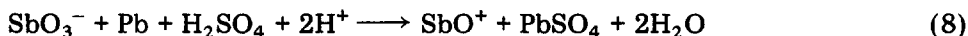
These results are particularly relevant to the practical lead–acid battery for the following reasons. Antimony always enters the solution in the 'V' valency state [13], whether dissolution is occurring by grid corrosion (positive or negative) or by desorption from the positive during discharge. Provided recharge takes place relatively soon after discharge, then the majority of the Sb released as Sb(V) will be readsorbed from solution by PbO_2 rather than being deposited onto Pb.

Role of the separator

During active operation of the lead–acid cell with antimonial grids the positive grids release approximately ten times as much Sb into solution as do the negatives [15]. During normal charge–discharge operation (as opposed to extended overcharge) Herrmann and Propstl [15], using a radiotracer technique, found that 95% of the Sb released from the positive grid was retained

TABLE 1

Redistribution of radioactive antimony 124, initially contained in the grid (s), resulting from 100 charge–discharge cycles [15]

	Initial location of [124]Sb		
	Positive	Negative	Positive and negative
A			
Positive active material (600 g)	4 5	0 12	5 5
Negative active material (700 g)	0 2	0 25	0 3
Separators (45 g)	0 1	0 1	0 2
B			
Positive active material	95	28	94
Negative active material	5	69	6
Separators	0 1	2	0 2
Electrolyte	0 1	2	0 1

A Final [124]Sb content of battery components (%)
B Final distribution of released [124]Sb in the battery components (%)

by the positive active material. Under the same operational conditions 70% of the Sb released from the negative grid was retained by the negative These results, which are summarised in Table 1, provide some important indicators to good cell design and are discussed later

One important function required of the separator is that it should act as a barrier to dissolved Sb, to restrict transport to the negative of the substantial quantities released from the positive. Zehender *et al* [16] defined a product W^+D^+ which they showed to be related to the transport of Sb. W^+ is the ionic electrical resistance of the flooded separator in a given acid concentration while D^+ is the effective diffusion coefficient of soluble Sb divided by the separator thickness ($\bar{D}/\Delta x$) They showed that W^+D^+ was independent of thickness, Δx, and proposed that small values of the product indicated good Sb stopping power Wood separators (pore size $<1~\mu m$ [17]) had W^+D^+ values between 1 and 2 orders of magnitude lower than paper separators (pore size $>30~\mu m$ [17]) Thus, small pore size appears to be beneficial in retarding Sb movement, in line with the findings of other workers [6, 17]. Jenkins *et al* [18] confirmed the influence of pore size by measuring the ratio $(D/\bar{D})/(\kappa/\bar{\kappa})$ for a wide range of commercial materials (Fig. 1). D and $\bar{D}$ are the diffusion coefficients of Sb(V) in free solution and in the separator, respectively κ and $\bar{\kappa}$ represent the electrical ionic conductivities of bulk 3.4 M H_2SO_4 and the separator flooded with the same solution, respectively As D and κ are constants the ratio being studied is $\bar{\kappa}/\bar{D}$ which is, in fact, the reciprocal of W^+D^+ (when W^+ refers to unit area of material). It was found that when pore size was below 2 μm then transport was diffusion
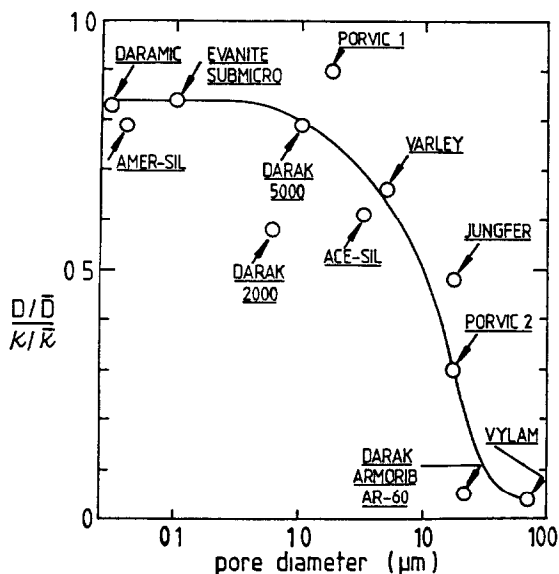
Fig 1 Plot of $[(D/\bar{D})/(\kappa/\bar{\kappa})]$ vs pore size for a range of commercial separators allowing determination of the transport mechanism [18]

controlled: above 20 μm convective flow was the principal mode of transport. Thus, for low rates of transport small pore size is preferable.

Other adsorbents for Sb

Other oxides besides PbO_2 also adsorb soluble Sb strongly [13]. Of particular interest are SnO_2 — cassiterite and TiO_2 — rutile as both adsorb more strongly than PbO_2 on a weight for weight basis and are only sparingly soluble in battery electrolyte.

Design considerations

On the basis of the work described above it is possible to make some suggestions which should increase the cycle life of lead–acid batteries by reducing the poisoning rate of negatives without introducing detrimental side effects.

A good design should allow the positive to operate in the presence of Sb, while reducing the Sb level in the electrolyte adjacent to the negative to a minimum. A separator with small pores will restrict transfer of Sb from the positive to the negative but will also tend to retain Sb released from the negative grid in the vicinity of the negative. The design suggested is the following

(1) The positive grid should be an antimonial alloy (preferably with low Sb content, *e g*, 3 - 5 wt.%)

(ii) The separator should have small pores (<2 μm).

(iii) The separator should ideally be formed as an envelope around one of the electrodes (either positive or negative) to prevent diffusion around the separator [12, 16, 19].

(iv) The negative grid should be Sb-free, possibly a Pb–Ca alloy The results of Herrmann and Propstl [15] suggest that with such a configuration the rate of poisoning of the negative might be only one third that of a conventional cell with antimonial grids throughout It would be anticipated that the above design might be particularly effective in traction service where depth of discharge is generally high and, hence, the release of Sb from positives during discharge is particularly great The possible incorporation of SnO_2 or TiO_2 might also be investigated

Acknowledgements

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