

Effect of dopants (Group Va) on the performance of the positive lead/acid battery plate

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Abstract

A tubular electrode is devised and filled with PbO_2 powder produced by grinding the active material obtained on a lead-grid plate. The spine of the tubular electrode is isolated in such a way that its contact with the H_2SO_4 solution is realized only through the pores of the active material. The effect of additions of antimony, arsenic and bismuth (introduced in the spine alloy or into the solution) on the rebuilding processes of the active-material structure is investigated. A critical density of the PbO_2 powder is determined below which restoration of the active-material structure is not possible. The investigations show that dopants decrease the value of the critical density; their impact is in the order antimony > bismuth > arsenic. This effect constitutes one of the basic features of the 'antimony-free effect'.

Introduction

Grids for lead/acid battery plates are made of lead alloys containing various alloying additives. More than a century ago, alloying additives were introduced with the aim of improving both the mechanical and alloying properties, and the corrosion resistance of battery grids. The first alloying additive used was antimony. Later on, in an attempt to reduce the rate of water decomposition during discharge, antimony was excluded from the grid alloy. Grids made from antimony-free alloys, however, undergo rapid passivation when subjected to deep discharges. Obviously, antimony exerts an influence on the transfer of electric charges in both the corrosion layer and the active material, and also on both the electrochemical and the crystallization processes taking place. This impact of antimony is called the 'antimony-free effect'.

Lead oxide and lead dioxide are degenerate semi-conductors. As such, their properties will depend upon the ions of the alloying additives. Because of this behaviour, the latter are known as dopants. Only a few reports in the literature deal with the effect of dopants on the properties of the active

Editorial note. Although the experimental data discussed here has been reported by the author in a previous issue of this Journal (*Journal of Power Sources*, 30 (1990) 117-129), he now presents an extended interpretation of the findings, including the new concept of dopants acting as 'electric bridges'. The work aroused considerable interest at the Conference.

material [1–6]. The objective of this paper is to determine the impact of the ions of group V elements (arsenic, antimony and bismuth) on the properties of both the corrosion layer and the active material of positive battery plates.

Experimental

The effect of dopants on the active material should be distinguished from their influence on the corrosion layer. Such discrimination can be achieved by the employment of a tubular PbO_2 electrode [6, 7]. The electrode is filled with PbO_2 active material that is ground to powder. The formation of the structure of the active mass is deduced from measurements of the electrode capacity, and the influence of dopants on this process is examined.

At the commencement of cycling, the skeleton of the active material does not exist, i.e., the latter is in the form of a powder [8]. During the first and the second discharges of the tubular powder electrode, the capacity is determined by both the corrosion layer and those particles of the active material that are in electronic contact with this layer. After 15 to 20 cycles, the skeleton of the active material is rebuilt and the capacity is determined mainly by the active material. The effect of the dopants can be determined by the dependence of the electrode capacity on the number of cycles.

The structure of positive plates can be presented by the following scheme:

grid/corrosion layer/active material/solution (1)

At the surfaces where the active material does not cover the grid, a second circuit operates:

grid/corrosion layer/solution (2)

Thus, there are two parallel circuits acting on the electrode. The presence of a second circuit may give rise to an error in determining the effect of dopants on the corrosion layer (1st and 2nd cycle). Therefore, those parts of the tubular-electrode spine that are in direct contact with the solution are isolated from the latter by means of a PVC tube and epoxy resin.

Figure 1 provides a schematic of the tubular electrode. Contact of the spine with the solution is realized only via the pores of the active material. This design ensures identical conditions at all locations of both the corrosion layer and the active material that are at an equal distance from the metal surface, i.e., the processes are distributed in terms of the radius of the electrode.

During discharge, the structure of the active material partially disintegrates; it should then be restored during charge. For a battery to have a long cycle-life, the processes of disintegration and reconstruction of the active-material structure should be reversible. The following investigation has been made of the effect of dopants on the restoration of completely disintegrated active material.

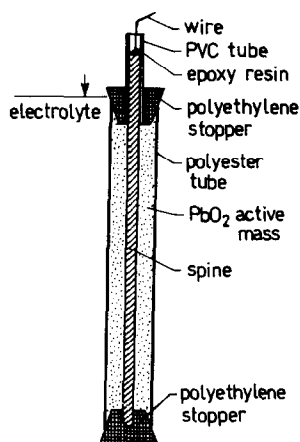


Fig. 1. Schematic of tubular electrode.

First, PbO_2 plates with pure lead grids were produced. The active material was then removed, ground to powder, and placed in tubular electrodes at a constant density. The electrodes were assembled into cells and subjected to 20 min charge, 10 min rest, discharge at 15 mA cm^{-2} to 0 V versus $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode. A sequence of 20 cycles was performed in order to allow restoration of the active-material structure. Dopants were introduced (arsenic, antimony, bismuth), either in the alloy or in the solution, and their effect on the battery capacity during cycling was followed [6, 7].

Results and discussion

Critical density of active material

The influence of the density of active material on the capacity during cycling of a lead-spine powder electrode is shown in Fig. 2. The calculated capacity at 50% active-material utilization, denoted by η_{at} , is also given. The results indicate that there is a critical lower limit for the density of the PbO_2 active material below which restoration of the structure is no longer possible. For pure lead spines, this critical value is slightly less than 3.80 g cm^{-3} . For example, after cycling, analysis of electrodes with a powder density of 3.40 g cm^{-3} revealed that the active material had remained as a powder. An electrode with a powder density of 3.8 g cm^{-3} retained its cylindrical shape, but its structure could be easily destroyed. By contrast, the active material of electrodes with higher powder densities could withstand significant impacts. Hence, restoration of the active-material structure is only possible when the individual PbO_2 particles are inter-connected in such a way that a critical contact between them is achieved. From a macro-level point of view, this means that the density of the active material should be higher than the critical value.

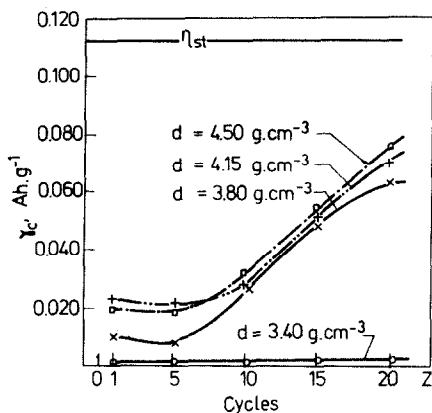


Fig. 2. Specific capacity of tubular electrodes as function of cycle-life; effect of PbO_2 powder density.

Influence of electrolyte dopants

The effect of arsenic, bismuth and antimony ions, introduced into the electrolyte, on the rebuilding of the active-material structure is shown in Fig. 3. For comparison, data for an electrode immersed in pure H_2SO_4 solution are also given. Spines of both lead and Pb-6wt.%Sb alloy were used.

The results show that 0.01 M arsenic prevents the rebuilding of the active-material structure. Antimony ions slow down, but do not stop, the formation of the structure. Maja and co-workers [1] have observed a similar passivating effect of antimony ions during discharge. The most interesting observation is that bismuth ions (0.005 M) accelerate the formation of the active-material structure. Hence, bismuth exerts a catalytic effect on the process of structure restoration.

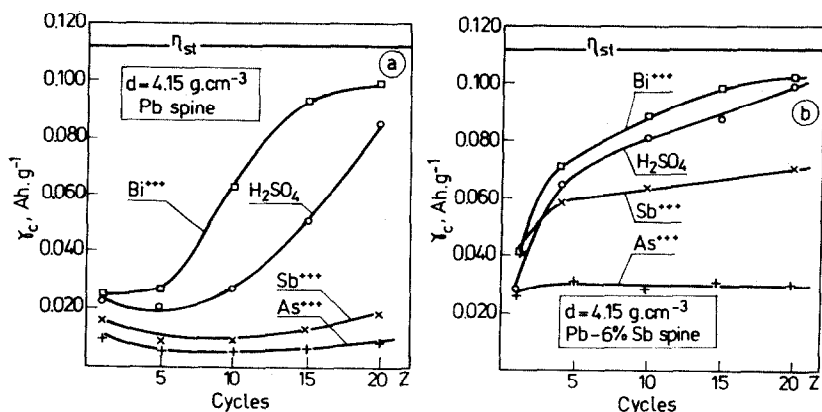


Fig. 3. Influence of arsenic, antimony and bismuth ions in the electrolyte on specific capacity/cycle-life. Tubular electrodes with: (a) lead; (b) Pb-6wt.%Sb spines.

Influence of arsenic doping of the spine alloy

The dependence of the specific capacity, at different numbers of cycles, on the arsenic content of the alloy, is given in Fig. 4. At an active-material density of 4.15 g cm^{-3} , an important effect of arsenic is observed: only 0.3 wt.% As in the alloy is required for the PbO_2 powder to be transformed into a well-organized structure that yields almost 50% utilization. Indeed, an arsenic content of only 0.05 wt.% increases the initial capacity of the powder electrode to an amount corresponding to 26% active-material utilization. By contrast, utilization in the lead spine electrode is only 5%. Finally, a comparison between the two sets of data shows that the density of the active material has a strong impact on the capacity of plates using lead-arsenic spines. For a density of 3.80 g cm^{-3} , even 0.8 wt.% of arsenic is insufficient for the plate to achieve 50% of performance capability after 20 cycles. Hence, arsenic increases the critical density to a value above 3.80 g cm^{-3} . It follows, therefore, that batteries using Pb-0.3 wt.%As grids will exhibit an efficient performance and long life only if the density of the positive active material is above 4.15 g cm^{-3} .

Influence of bismuth doping of the spine alloy

Data obtained with lead-bismuth spines is presented in Fig. 5. It can be seen that only 0.2 wt.% of bismuth is needed to allow the PbO_2 powder to be transformed, after 15 cycles, into a well-organized active material with 50% utilization during discharge. This beneficial effect of bismuth is observed even at a powder density of 3.80 g cm^{-3} . Clearly, bismuth improves the contact between the PbO_2 particles and decreases the sensitivity of the plate capacity to the active-material density. On comparing Figs. 2 and 5, it can be seen that bismuth decreases the critical density of the active material. Thus, bismuth exerts a beneficial effect on battery cycle-life and enables the plate to reach its full capacity even at low active-material densities.

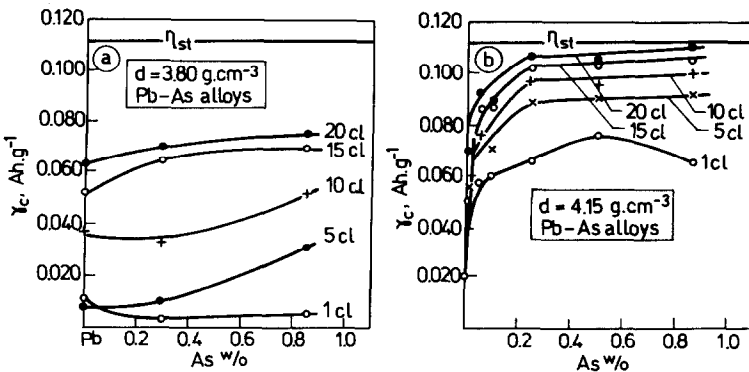


Fig. 4. Influence of arsenic (alloy) concentration on capacity. PbO_2 powder density: (a) 3.80 g cm^{-3} ; (b) 4.15 g cm^{-3} (cycle number denoted by cl).

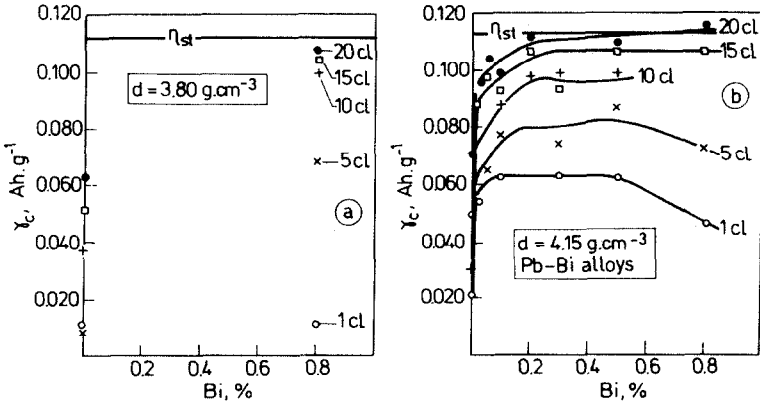


Fig. 5. Influence of bismuth (alloy) concentration on capacity. PbO_2 powder density: (a) 3.80 g cm^{-3} ; (b) 4.15 g cm^{-3} (cycle number denoted by cl).

Studies in the author's laboratories have shown that the corrosion rate at the interface spine/electrolyte/air is increased significantly when lead-bismuth alloys are used. This behaviour is dangerous to plate cycle-life. Yao and Johnson [2] have established that the transfer of oxygen through the PbO_2 layer is facilitated by the presence of bismuth. This effect causes a corresponding increase in the rate of spine corrosion. The mechanism of oxygen-involvement in the corrosion process has been discussed in refs. 8 and 9.

Influence of antimony doping of the spine alloy

Interesting behaviour emerges when lead-antimony spines are used (Fig. 6). With Pb-6wt.%Sb alloy, an electrode with an active-material density of 3.80 g cm^{-3} provides a greater capacity than that with 4.15 g cm^{-3} .

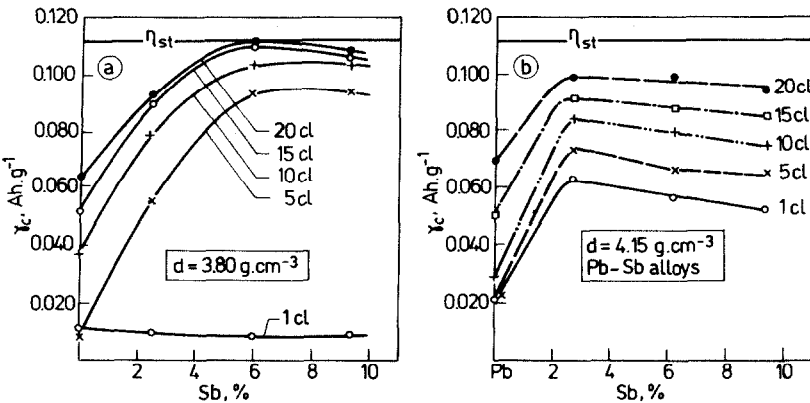


Fig. 6. Influence of antimony (alloy) concentration on capacity. PbO_2 density: (a) 3.80 g cm^{-3} ; (b) 4.15 g cm^{-3} (cycle number denoted by cl).

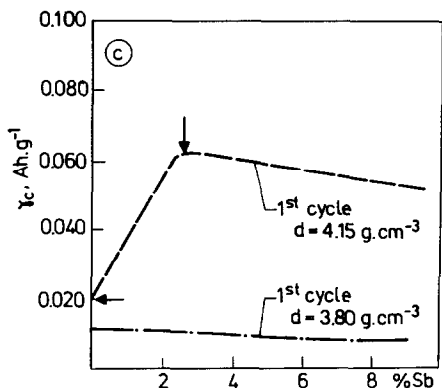


Fig. 7. Comparison of capacity vs. antimony content of spine alloy for the 1st cycle.

Hence, antimony causes the critical value of the density to fall below 3.80 g cm^{-3} . This allows the battery life to be prolonged, and may be an important factor contributing to the 'antimony-free effect'. Figure 7 shows that with an active-material density of 4.15 g cm^{-3} , lead electrodes give a specific capacity of 20 mA h g^{-1} , while those with Pb-2wt.%Sb spines have a capacity of 60 mA h g^{-1} . Obviously, the three-fold increase in capacity is due to the effect of antimony.

Prior to the first discharge, the electrodes were charged for 20 min to allow the formation of a corrosion layer on the spines. The antimony oxidized during this period is sufficient both to influence the properties of the corrosion layer and to improve the electrical contact between this sub-layer and the PbO_2 particles, as well as between the PbO_2 particles themselves. An active-material utilization of 25% is achieved during the first discharge

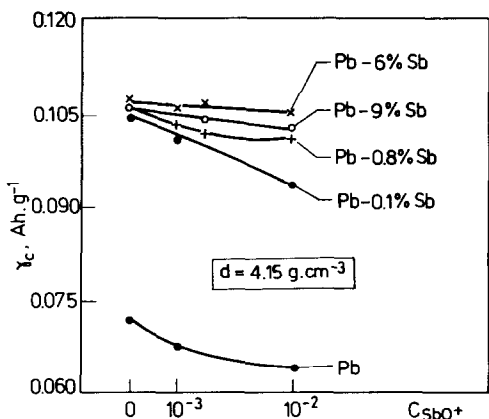


Fig. 8. Dependence of capacity on SbO^+ ion concentration in H_2SO_4 after 20 cycles.

despite the fact that the contact between the PbO_2 particles is only mechanical in nature. At a density of 3.80 g cm^{-3} , the effect of antimony is not manifested (Fig. 7). It would appear, therefore, that at this powder density, the antimony bridges between the PbO_2 particles are too short for most of these particles. As mentioned above, bismuth ions play a similar role as 'electric bridges'.

Influence of antimony doping of spine alloy and electrolyte

In a series of experiments with cells assembled from powder electrodes with lead-antimony spines, antimony was also added to the solution. The specific capacity on the 20th cycle is given in Fig. 8 as a function of antimony ion concentration. Comparison of the curves for pure lead and lead-antimony electrodes reveals that antimony, when present in the alloy, exerts a marked beneficial effect on the electrode capacity. On the other hand, antimony added to the solution exerts a passivating action in electrodes with Pb-0.1wt.\%Sb spines. The passivating effect disappears at antimony concentrations above 0.8 wt.% in the spine alloy. Thus, the effect is not observed in commercial batteries where much higher antimony contents are used.

Conclusions

The following conclusions can be drawn from the experimental findings discussed in this paper.

1. The structure of the active material in tubular powder PbO_2 electrodes can be restored completely provided the powder density is above a certain critical value. The specific capacity reaches values equal to those obtained from commercially produced electrodes.

2. Rebuilding of the active-material structure in powder electrodes is influenced by different alloying additives, and also by the presence of foreign ions in the electrolyte.

3. When introduced as alloying additives, arsenic, antimony and bismuth act as a 'bridge' for the transport of charges between the PbO_2 particles. In other words, these elements serve as 'binders' that facilitate the restoration of the active-material structure. Antimony has the strongest effect in both respects, followed by bismuth and arsenic.

4. The impact of dopants on decreasing the critical active mass density is in the order antimony > bismuth > arsenic. The lower the value of the critical density, the longer the plate-life.

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