Discussions on the lead/acid battery

A guide to the influence of bismuth on lead/acid battery performance

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Abstract

A review is given of the literature that deals with the influence of bismuth on the microstructure, oxygen/hydrogen evolution kinetics and anodic corrosion of lead and lead alloys with regard to their performance in lead/acid batteries. Analysis shows that there is considerable disagreement as to the effect of bismuth on lead microstructure. For example, the various investigators report an increase, a decrease, or negligible change in grain size. In general, it is concluded that the oxygen overpotential on PbO_2 is lowered in the presence of bismuth. The effect is enhanced as the bismuth content is increased. It is postulated that the behaviour results from the formation of a mixed oxide, $PbO_2 \cdot BiO_x$. By contrast, cathodic hydrogen evolution is reported widely to be largely unaffected by bismuth. Nevertheless, there is evidence that the reaction is particularly sensitive to the surface characteristics of electrodes and that these features can induce either a suppression or an enhancement of the hydrogen-gassing rate. Many studies have shown that bismuth accelerates the anodic corrosion of lead alloys, especially at high concentrations of bismuth. At 0.1 wt.% bismuth and below, the effect on the corrosion rate is negligible. The authors of this discussion are of the opinion that much of the conflicting evidence in the areas reported is caused by spurious differences in grain structure that are introduced by variations in sample preparation, rather than by the action of bismuth itself. In battery-related tests, bismuth has usually been found to exert little influence on performance, but there is some suggestion that cycle life is increased. The present body of knowledge is insufficient to confirm the correctness of any currently specified maximum level for bismuth with respect to a given battery design.

Introduction

Despite limited, and often, conflicting experimental evidence, the presence of bismuth in the lead/acid battery system has long been considered undesirable by battery manufacturers. As a consequence, lead producers are required to restrict the amount

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of bismuth. This complicates metal processing and, therefore, adds to the production costs. In recent times, a bismuth level in lead of 0.03 to 0.05 wt.% has been quoted as the limit for battery applications [1, 2]. It appears that the present upper value is based on evidence gathered in the 1940s by Hoehne [3, 4]. Since then, a considerable amount of research has attempted to evaluate the possible influence of bismuth on the lead/acid battery system. The principal objective of this work has been the demonstration of a higher 'safe' level for bismuth because, obviously, this would reduce the costs of lead production and would improve battery reliability.

Despite the many experimental approaches adopted and the wide range of bismuth concentrations investigated, there is still extensive debate over whether bismuth is either beneficial or detrimental to the performance of lead/acid batteries. In order to focus this debate, a survey is given here of the literature dealing with the influence of bismuth in lead on alloy microstructure, hydrogen and oxygen evolution, alloy corrosion, and resulting battery behaviour.

Influence of bismuth on the metallurgical properties of lead–bismuth alloys

The physical properties of both lead itself and lead alloys have been reviewed comprehensively [5, 6]. Hofmann [5] reported that bismuth has little effect on the hardness of lead, and that lead–bismuth alloys recrystallize more readily than pure lead. The lead–bismuth binary phase diagram [5] indicates that bismuth forms a solid solution with lead up to 18 wt.% Bi at room temperature. At 184 °C, the bismuth solubility rises to 23.5 wt.%. This solubility prevents bismuth from reducing the grain size of cast or recrystallized lead. The grain-refining effect of soluble impurities is not well understood. For example, Greenwood [6] emphasized this paucity of knowledge on the influence of solutes on primary grain size, and noted the complex nature of solute effects. The same author further suggested that spontaneous recrystallization of lead alloys during deformation and/or polishing, at either ambient or slightly elevated temperatures, may have a dramatic effect on the grain size. This is important because grain structure is a key variable in lead electrochemistry. For example, the grain structure has been shown to influence both the gassing [7, 8] and the corrosion behaviour [9] of lead–bismuth alloys.

Myers et al. [10] examined the effect of bismuth additions of up to 0.1 wt.% on the hardening rate and strength of lead–calcium and lead–calcium–tin alloys. It was found that bismuth increased the rate of alloy age-hardening, but did not change the tensile strength of the alloys. In contrast to the above-mentioned assertion of Hofmann [5], Myers et al. [10] claimed that grain refinement did occur and this was shown to be the mechanism by which bismuth and calcium both accelerated the rate of age hardening.

Papageorgiou et al. [7, 9, 11] measured the average grain size of rolled, binary lead alloy specimens containing 0 to 0.23 wt.% Bi. The latter were subjected to thermal treatment in order to re-establish the grain structure that was destroyed by the deformation. Although the grain size was observed to vary widely with bismuth content, no clear relationship could be detected between these two factors.

Johnson [12] compared the microstructures of mechanically polished and etched lead and lead–bismuth alloy specimens (0.061 to 1.061 wt.% Bi). Additions of bismuth between 0.061 and 0.5 wt.% produced a microstructure with a dramatically changed grain size — from small, regularly-shaped grains for pure lead to larger rectilinear grains for all of the alloys. Specimens with bismuth concentrations >0.5 wt.% clearly

showed recrystallization of the worked surface. A nitric acid etch was used for bismuth concentrations <0.5 wt.% and an acetic acid/hydrogen peroxide/nitric acid etch for bismuth concentrations >0.5 wt.%. This difference in treatment may have influenced the grain structure that was revealed. The small grain size observed for pure lead is surprising and this also may have been a consequence of the sample preparation method.

The effect of bismuth (0.012 wt.%) on the grain structure of pure lead, lead–calcium and lead–calcium–tin alloys was examined recently by Prengaman [2]. For lead–calcium alloys, it was found that bismuth promoted the segregation of calcium-rich and bismuth-rich regions and that this effect, in turn, accelerated the rate of grain-boundary movement. An enhanced segregation of tin and bismuth was observed in lead–calcium–tin alloys with high Sn:Ca ratios. It was suggested that the resulting development of high levels of bismuth and tin in localized areas may be advantageous from the point of view of improved battery recovery from deep discharge.

Koop *et al.* [13] examined the microstructure of electropolished lead and binary alloy specimens (0.71 to 5.65 wt.% Bi) that had been pressed at 25 °C. The mean number of grain boundaries was taken as a measure of grain size. The resulting data demonstrated a non-linear decrease in grain size with increasing bismuth content. Optical micrographs and grain boundary information revealed that, when a pressed alloy containing 5.56 wt.% Bi was subjected to thermal treatment at 160 °C, the grain size increased markedly to resemble that of pure lead. Such an observation supports the general conclusion that the metallurgical structure of lead–bismuth alloys is extremely sensitive to the methods that are employed for the fabrication and surface preparation of such alloys.

Influence of bismuth on oxygen- and hydrogen-evolution reactions

Until recently, the influence of bismuth on either oxygen or hydrogen evolution has received little attention. Pierson *et al.* [14] performed gas-generation experiments on cells that were constructed from lead–calcium plates and employed electrolyte that had been inoculated with bismuth or other contaminant elements up to concentrations of 0.5 wt.%. Compared with a standard (undoped) cell, the presence of bismuth caused a four-fold increase in the volume of gas generated at 2.35 V. Based on these results, it was suggested that 0.05 wt.% is the maximum bismuth concentration that can be tolerated in the electrolyte. No mention was made of the influence of bismuth on the relative volumes of the gases generated at the positive and the negative plates.

Oxygen-evolution reaction

From linear-sweep voltammetric experiments on binary lead–bismuth alloys (0 to 4.9 wt.% Bi), Rice [15] and Johnson [12] found that up to 0.6 wt.% Bi, oxygen evolution at 1.35 V (versus Hg/Hg_2SO_4) was unaffected. Between 0.6 and 2 wt.% Bi, the oxygen-evolution current doubled in magnitude. Cycling of the electrodes decreased the oxygen current at all bismuth concentrations and this was postulated to be due to both leaching of the bismuth from the corrosion layer into the electrolyte (with subsequent deposition on the negative) and to sulfation of the active mass. (Note, the oxygen current decreased with cycling on pure-lead electrodes as well as on lead–bismuth alloys.)

A series of studies [16–20] on bismuth-doped PbO_2 films that were electrodeposited on to gold or platinum rotating disc electrodes, from solutions of Pb^{2+} and Bi^{3+} in

HClO$_4$ or HNO$_3$, has given some insight into the electrocatalytic effect of bismuth on oxygen evolution. Yeo and Johnson [16] reported that mixed oxides with an average stoichiometry of PbO$_2 \cdot$BiO$_x$ ($x \sim 2.2$) exhibited significant increases in oxygen-transfer activity compared with pure PbO$_2$. Furthermore, electrodes of pure PbO$_2$ that were exposed briefly to a solution of Bi^{3+} also showed enhanced activity. It was concluded that the latter behaviour was due to Bi^{5+} ions that were either adsorbed on the PbO$_2$ or substituted into Pb sites. Larew et al. [17] later found that such Bi^{5+} ions in Bi–PbO$_2$ did not dissolve in acidic solutions, and therefore concluded that the ions were stabilized by the PbO$_2$ matrix. From Tafel plots for oxygen evolution, Yeo et al. [18] observed a decrease in the oxygen overpotential as the Bi:Pb ratio was increased in the deposited mixed oxides. Thus, it appears that Bi-oxide sites have a lower oxygen overpotential than their PbO$_2$ counterparts. In subsequent work, Feng and Johnson [19] found a substantial increase in the exchange current density for oxygen evolution on Bi–PbO$_2$/Ti electrodes in 1.0 M HClO$_4$. Chang and Johnson [20] offered an explanation for these effects. They suggested that adsorbed bismuth sites in the oxide increase the rate of anodic discharge of H$_2$O to hydroxyl radicals, and that the latter are subsequently adsorbed on bismuth sites. Hydroxyl radicals are the active intermediates in oxygen evolution and other oxygen-transfer reactions. Damjanovic and Jovanovic [21] have suggested that oxygen evolution may take place via such radicals; the latter abstract an O atom from metal oxides.

In summary, there is a general consensus of opinion that bismuth serves to catalyze oxygen evolution at lead-positive electrodes.

Hydrogen-evolution reaction

The hydrogen-evolution reaction on bismuth in 1 M H$_2$SO$_4$ has been examined by Kilimnik and Romiyan [22]. It was reported that the kinetic constants in the Tafel equation are dependent upon the sign of the surface charge on the electrode, and that the constants indicate a slow rate of hydrogen evolution on bismuth. From studies of hydrogen evolution on lead–calcium and lead–calcium–tin alloys, Caldwell et al. [23] demonstrated that low levels of bismuth (0.018 wt.%) had little influence on the gassing rate; a greater effect was promoted by the calcium and tin constituents. Mashovets and Fateeva [24], on the other hand, reported that the addition of bismuth increases the hydrogen overpotential on lead.

Maja and Penazzi [25] examined, *ex situ*, the effect of bismuth on hydrogen evolution and oxygen reduction at charged negative plates at open-circuit in a sealed, pressure-sensing, glass vessel. The plates were subjected to a pretreatment of 30 cycles at the C/10 rate in 1.28 sp. gr. H$_2$SO$_4$ that contained Bi^{3+} (0.002 and 0.02 wt.%). After cycling in a solution of 0.01 wt.% Bi^{3+}, analysis of the plates revealed that bismuth had been incorporated into the active material to a level of 0.006 wt.%. The amount of bismuth that was transferred was found to increase linearly with the initial bismuth concentration in the electrolyte. Results further showed that bismuth suppressed hydrogen evolution and enhanced oxygen reduction. This behaviour appeared to be independent of bismuth concentration. It was concluded that bismuth might improve the performance of gas recombination in valve-regulated batteries. The study provided no indication, however, of the *in situ* gassing behaviour of such plates during cycling.

An investigation by Johnson et al. [26] of the hydrogen-evolution reaction of lead–bismuth alloys (0.27 to 4.9 wt.% Bi) in 0.05 M H$_2$SO$_4$ indicated that the rate of the hydrogen-evolution reaction was not increased by the presence of bismuth. For example, the Tafel constants b and i_0 for hydrogen evolution were, respectively, -0.13 V and 1.58×10^{-10} A cm^{-2} for pure lead, and -0.14 V and 1.10×10^{-11}

A cm^{-2} for a Pb–0.275wt.%Bi alloy. Greater additions of bismuth had little, or no, effect on these constants. Following examination of the grain structure of the alloys, it was suggested that the slight variations in the Tafel constants were due to differences in surface heterogeneity rather than in grain structure. The authors concluded that the mechanism of hydrogen evolution on lead is dependent upon the presence of bismuth, but is independent of the alloy composition, i.e., the quantity of bismuth.

The influence of bismuth on the surface grain structure of lead–bismuth alloys and its subsequent effect on hydrogen evolution has been investigated by Papageorgiou et al. [7, 11]. In this work, hydrogen evolution was determined on lead–bismuth alloys that were either etched to reveal the grains (0 to 0.2 wt.% Bi) or rendered 'featureless' by mechanical abrasion (0 to 5 wt.% Bi). For etched electrodes, measurements of the hydrogen overpotential were conducted with a current density of 1.6 mA cm^{-2} under steady-state conditions, and with 3.0 mA cm^{-2} during linear-sweep voltammetry. The hydrogen overpotential was found to decrease with increasing bismuth content in the alloys. It was argued that bismuth segregation at grain boundaries could lead to active sites for the hydrogen-evolution reaction and that a finer grain structure lowered the hydrogen overpotential. Subsequent microscopic examination and grain-size analysis of the etched surfaces revealed that the rate of hydrogen evolution was also influenced significantly by the surface structure of the alloy.

The same authors also measured the Tafel parameters b and i_0 on lead–bismuth alloy electrodes (0 to 5 wt.% Bi) that had no metallographic features. The electrolyte was 0.1 M H$_2$SO$_4$. The parameters were found to decrease with increasing bismuth content. This suggests that the hydrogen-evolution overpotential is lowered in the presence of bismuth. Based on the predicted values for the Tafel slope, it was asserted that a change occurs in the dominant mechanism for hydrogen evolution with increasing bismuth content, i.e., from a rate-determining cathodic discharge of H$^+$ and fast electrochemical desorption for low-bismuth alloys, to a fast cathodic discharge and rate-determining desorption for high-bismuth alloys.

The above experimental findings show that no definite relationship has emerged between bismuth content and hydrogen-evolution kinetics. Clearly, the morphological and structural features of the alloy surface — either induced by bismuth itself or by the alloy casting process — serve to complicate the situation.

Influence of bismuth on lead alloy corrosion

A summary of the conflicting evidence for the influence of bismuth on the corrosion of lead is presented in Fig. 1. It should be noted that the acid concentration, the alloy preparation method and the chosen experimental technique are not necessarily the same for the investigations listed.

The anodic corrosion of lead–bismuth alloys over the alloy range 0 to 40 wt.% Bi was evaluated in 1 M H$_2$SO$_4$ by Byrntseva et al. [27] through measurements of anode weight loss, sludge formation and cathode weight gain. An anodic corrosion current of 0.05 A cm^{-2} was applied over periods of 50 to 70 days. An increase in corrosive attack was observed for bismuth concentrations up to 3.6 wt.%. With further rise in bismuth content, the corrosion behaviour changed to display a gradual increase in alloy stability until a maximum resistance was displayed in the 25 to 40 wt.% Bi range.

Pelzel [28] performed weight-loss experiments on binary alloys (0.005 to 20 wt.% Bi) in boiling 55% H$_2$SO$_4$ and reported slight fluctuations in weight loss for alloys
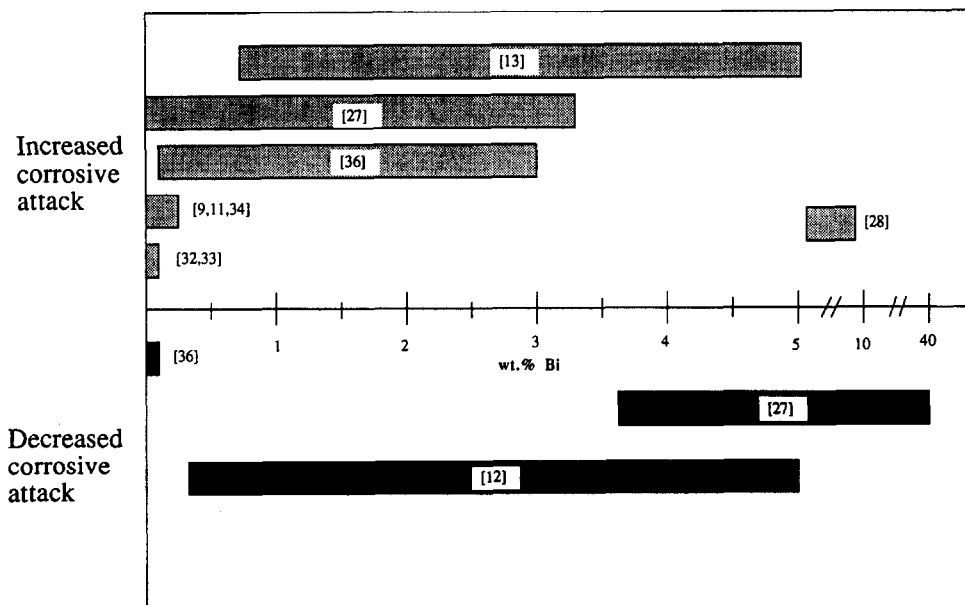
Fig. 1. Demonstration of the conflicting evidence for the influence of bismuth on lead/lead-alloy corrosion.

containing up to 3 wt.% Bi. By contrast, a threefold increase in weight loss was displayed by alloys containing 6 and 9 wt.% Bi.

Russian workers examined the corrosion behaviour of pure-alloy components [29] and binary lead alloys [30, 31] immersed in 1 M H_2SO_4. It was demonstrated that lead–bismuth alloys have a lower corrosion resistance than either lead–antimony or lead–tin counterparts. This finding was consistent with the corrosion resistance of the individual bismuth, antimony and tin components. For alloys below the eutectic composition, (i.e., <24 wt.% Bi), the corrosion rate was greater than for pure lead, but exhibited little change with bismuth content.

Galvanostatic corrosion tests on alloys (0.001 to 0.1 wt.% Bi) in 1.25 sp. gr. H_2SO_4 were conducted by Gonzales et al. [32, 33]. Over periods of 56 days, the weight loss increased with bismuth content at all the applied current densities.

Hampson et al. [34] applied linear-sweep voltammetry and potential-step techniques to examine the corrosion of lead–bismuth alloys (0.063 to 0.267 wt.% Bi) in 5 M H_2SO_4. The results showed that a bismuth concentration of as little as 0.06 wt.% rendered the alloy more susceptible to corrosive attack than either pure lead or Pb–5wt.%Sb. The extent of the corrosive attack appeared to be a non-linear function of the bismuth content; a minimum was observed between 0.1 and 0.2 wt.% Bi. Later work revealed [35] that lead–calcium–tin–bismuth alloys also exhibit this behaviour; an alloy containing 0.15 wt.% Bi was the least susceptible to anodic corrosion.

A further study by Webster et al. [36] on a series of alloys (0.04 to 3 wt.% Bi) confirmed that while small additions of bismuth exert an overall protective effect, with maximum stability at 0.1 wt.% Bi, an increase in the corrosion rate occurred thereafter. The authors proposed that incorporation of bismuth into the lead lattice, together with subsequent grain refinement, would deplete the amount of lead that is available for anodic attack at the surface and, thereby, increase the stability of the alloy.

In discussing corrosion phenomena in lead/acid batteries, Peters and Young [37] emphasized that attack of the lead alloys occurs preferentially at the grain boundaries. Thus, grain size and structure are important parameters when considering the mode and rate of the corrosion phenomena. It was further stressed that interpolation or extrapolation of weight-loss data could often be misleading when used as a guide to corrosion rates. In this respect, the authors suggested that metallographic examination of corroded alloys yields important information on the mode and/or extent of corrosion when associated with potentiostatic corrosion measurements.

The influence of bismuth content on the grain refinement and subsequent corrosion behaviour of alloys (0 to 0.23 wt.% Bi) in 2 M or 5 M H_2SO_4 was evaluated by Papageorgiou et al. [9, 11] in terms of cyclic voltammetric and weight-loss measurements. Experiments conducted over a potential range similar to that used by Hampson et al. [34] confirmed a non-linear relationship between the oxidation of lead sulfate to lead dioxide and the bismuth content; a maximum was observed for alloys containing between 0.03 and 0.07 wt.% Bi. Weight-loss experiments with short-term exposure of alloy electrodes (168 to 235 h) at constant potentials of 1.0 to 1.12 V, which yield the maximum corrosion rate of lead in H_2SO_4 [38, 39], revealed an inverse relationship between the extent of corrosion and the alloy grain size, i.e., large grains hindered weight loss. By contrast, the bismuth content did not appear to effect the corrosion rate. With longer exposure times, the grain size ceased to dominate the weight-loss behaviour. The corrosion rate increased steeply with bismuth content in a monotonic fashion, but a diminished grain-size effect was still evident. It was concluded that bismuth accelerates attack of the alloy by influencing the rate of penetration of the corrosion front, both along the grain boundaries (where micro-segregation occurs) and within the grains. The authors also recognized that both grain size and grain-boundary length determine the extent of corrosion by modifying the number of corrosion pathways.

Johnson [12] conducted weight-loss experiments on lead alloys (0 to 4.9 wt.% Bi) in 5 M H_2SO_4 at 0 V (versus Hg/Hg_2SO_4) for periods of 120 h. The presence of bismuth reduced the growth of corrosion product; the latter went through a minimum at 0.565 wt.% Bi. A difference in the structure of the corrosion layers formed on the electrodes was revealed by scanning electron microscopic (SEM) analysis. The layers on pure lead had a porous, crystalline appearance while those on lead–bismuth alloys possessed an amorphous structure that was penetrated by both cracks and large crystals of lead sulfate. After removal of the corrosion products, electron micrographs revealed that, with increase in bismuth content up to 1 wt.%, uniform corrosion was replaced by preferential attack along the grain boundaries. It was presumed that bismuth was concentrated at these boundaries. Corrosion of alloys containing >2.1 wt.% Bi tended to be uniform, although some grain-boundary attack was still evident. It was concluded that the presence of bismuth creates a more compact, and hence protective, lead sulfate layer and that leaching of bismuth from grain boundaries could be detrimental to the performance of positive plates.

An investigation by Koop et al. [13] employed cyclic voltammetry to examine the corrosion behaviour of pure lead and lead–bismuth alloys (0.71 to 5.65 wt.% Bi) in 5 M H_2SO_4. The specific capacities for anodic and cathodic features were measured from voltammograms over the potential range -1.8 to 1.25 V (versus Hg/Hg_2SO_4). The specific capacities of features associated with PbO and basic lead sulfates exhibited a positive linear dependence on the number of grain boundaries in the alloys. The quantities of PbO and basic lead sulfates also increased with increasing Bi^{3+} concentration in H_2SO_4 solutions up to 2×10^{-4} M. The latter data were obtained from similar experiments on pure-lead electrodes with bismuth-doped electrolyte. Electron micro-

graphs of the corrosion films revealed that bismuth (either alloyed or added to the electrolyte) affects the morphology of the $PbSO_4$ layer. It was suggested that resulting changes in the porosity modify the pH of the underlying region and thus facilitate the formation of lead oxides and basic lead sulfates in that region. It was concluded that bismuth influences the corrosion of lead by modifying the grain structure of lead–bismuth alloys and by changing the morphology of the passivating $PbSO_4$ layer so that increased attack takes place on the underlying alloy substrate.

A recent Japanese patent [40] claims that control of the bismuth content to ≤0.02 wt.% in lead or lead-alloy grids, joints and/or terminals prevents the corrosion of such parts.

In summary, the majority of evidence gathered to date suggests that bismuth will enhance the corrosion of grid alloys. The diversity of the data for the relationship between bismuth content and alloy corrosion rate makes it difficult, however, to define precisely the extent to which the presence of bismuth at a level typical of that found in commercial batteries (viz., <0.03 wt.%) is advantageous or disadvantageous. Furthermore, little of the gathered information is relevant to the action of bismuth in the common grid alloys of lead–antimony and lead–calcium–tin.

Influence of bismuth on battery performance

Early investigations of the effect of bismuth on the performance of lead/acid batteries were conducted by Hoehne [3]. In particular, a study was made of the behaviour of pasted positive plates with grids containing 5.5 wt.% Sb and 0.006 to 0.23 wt.% Bi, as well as grids made from pure lead (Planté design) containing 0.006 to 0.205 wt.% Bi. Cycle-life tests on the antimonial plates revealed that the presence of bismuth had little effect on the capacity, voltage or self-discharge of the batteries, as well as on grid growth or shedding of active material. By contrast, the antimony-free Planté plates exhibited enhanced grid growth and shedding. There was also an increase in the bismuth content of the sludge, and this could be related to the bismuth content in the plates. As a result of these studies, Hoehne [3] concluded that the bismuth content should be kept to a minimum for Planté cells. It is interesting to note the deleterious effects of bismuth were moderated when antimony was also present in the lead substrate.

Grosheim-Krisco et al. [41–43] performed similar experiments on Planté plates containing 0 to 0.55 wt.% Bi. While there was only a limited effect on sludge formation, plate growth was encouraged and reached values of up to 14% at the highest levels of bismuth. Pitting was also noted in some of the plates [43].

A study by Agruss et al. [44] examined the effect of bismuth on the capacity, cycle life, shelf life and positive-plate voltage of batteries when present in the alloy at 0.017 wt.% and in the active material at up to 0.25 wt.%. No significant effects were observed on any of the parameters. By contrast, George and Ensslin [45] reported that trace amounts of bismuth (0.01 wt.%) in the component lead increased the self-discharge of lead/acid batteries.

The cycle life of batteries constructed with lead–calcium–tin grids containing 0.0007 to 0.042 wt.% Bi was examined by Devitt and Myers [46]. Two cycling regimes were applied. The first, based on the SAE J537 procedure, was designed to cause failure by grid corrosion. The second, based on the SAE J240 procedure, simulated automobile service. No influence of bismuth on cycle life was obtained with batteries subjected

to the SAE J537 regime. Overcharge currents at a given voltage were also insensitive to the bismuth content. It was asserted that bismuth at these levels had no effect on either the gassing or the corrosion rates. By contrast, the cycle life of batteries under the SAE J240 test was extended with increasing bismuth content. In similar work, Miyazaki and Sumida [47] performed deep-discharge cycling experiments (with a cutoff voltage of 1.70 V) on plates with lead–antimony grids and paste that was doped with 0.016 wt.% Bi and 0.016 wt.% Tl. Addition of these elements was found to increase the total discharge durations by up to 20%. Gibson *et al.* [48] found that lead–calcium–tin alloys with bismuth additions of up to 0.26 wt.% gave no improvement in performance when used in automotive batteries that were subjected to deep-discharge cycling. In more recent work [49], battery plates were prepared from leady oxide that was derived from pure lead doped with given amounts of bismuth. Battery tests showed that the presence of bismuth in the oxide at levels up to 0.02 wt.% did not influence the performance obtained under cycling conditions that corresponded closely to automotive service. There was also no significant effect on the self-discharge rate, even at a bismuth concentration of 0.043 wt.%.

Hampson *et al.* [50] examined the behaviour of porous positive electrodes under a cycling duty that comprised linear potential-sweep discharges followed by potential steps to 1.3 V and constant-current charging at 25 mA. Electrodes with Pb–Ca–Sn–0.229wt.%Bi grids exhibited cycle lives that were similar to bismuth-free electrodes, but were inferior to electrodes with lead–antimony grids. Kelly *et al.* [51] performed a series of potential-step discharges from the PbO_2 potential region to various potentials on a Pb–0.13wt.%Bi alloy electrode and noted that the ability to accept potentiostatic recharge varied with the applied discharge potential. The electrode accepted charge readily if the discharge potential was above 700 mV (versus Hg/Hg_2SO_4), but charge acceptance was poor if the electrode was discharged below this potential. Unfortunately, no comparison was made with other alloys and no explanation was offered for the effect of bismuth.

Bialacki *et al.* [52] measured the impedance of porous PbO_2 on lead-alloy supports. During discharge, porous electrodes with a Pb–Ca–Sn–0.15wt.%Bi grid exhibited higher charge transfer, adsorption and external resistances than electrodes with either lead–antimony or lead–calcium–tin supports. It was therefore concluded that addition of bismuth to the alloys would not enhance the behaviour of porous electrodes. Curiously, this conclusion appears to contradict earlier findings by workers from the same laboratories [53]. In the latter, impedance studies performed on PbO_2 electrodes that were formed by polarization of lead or lead alloys in 5 M H_2SO_4 showed that the addition of 0.15 wt.% Bi produced a sulfate film with improved conductivity. It was claimed that bismuth imparts semiconducting properties to the lead sulfate via a doping process.

Rice [15] summarized the extensive experiments of Johnson [12] that examined the effect of bismuth on reactions at both the positive and negative plates of lead/acid batteries. The studies employed linear-sweep voltammetric and potential-step techniques. At the positive plate, it was concluded that bismuth will: (i) inhibit the conversion of lead sulfate to lead dioxide; (ii) reduce the overpotential of oxygen evolution, and thereby possibly increase grid corrosion during charging; (iii) enhance the nucleation of lead sulfate, and thus yield a more compact layer that promotes the electrical isolation of the positive active-material. At the negative plate, it was concluded that bismuth (transferred following leaching from the positive plate) will increase the hydrogen-evolution overpotential, improve the distribution of current at the electrode surface, and enhance the nucleation of lead sulfate. It was also concluded

that a bismuth level of 0.05 wt.% could be tolerated at either plate of a lead/acid battery.

Pavlov *et al.* [54–56] examined the effect of bismuth on the reconstruction of the PbO_2 active mass when PbO_2 powder was subjected to charge/discharge cycling in tubular electrodes; the grid spines contained 0 to 0.8 wt.% Bi. Electrodes with spines of pure lead and Pb–6wt.%Sb were also cycled, but with H_2SO_4 solutions containing 0.005 M Bi^{3+} ions. When present in either the alloy or the electrolyte, bismuth was found to facilitate the development of the active-mass structure for all types of spine alloy. For example, with electrodes using alloy spines containing >0.20 wt.% Bi, the active mass was restored sufficiently after 20 cycles to give capacities that were equivalent to 50% utilization of the active material. It was also noted that bismuth in the spine alloy reduced the sensitivity of the specific capacity of the electrode to the active-mass density, and that corrosion was enhanced at the spine-electrolyte-air boundary in the presence of bismuth.

Conclusions

Table 1 presents a summary of the influence of bismuth on alloy corrosion, oxygen evolution, hydrogen evolution and battery performance. As noted before, the acid concentration, alloy preparation and experimental techniques vary between the investigations cited.

TABLE 1

Reported effects of bismuth on lead/acid battery characteristics

Parameter	Increased effect		Decreased effect	
	wt.% Bi	Reference	wt.% Bi	Reference
Alloy corrosion	0.001 to 0.01	32, 33	0.0 to 0.1	36
	0 to 0.23	9, 11	0 to 4.9	12
	0.063 to 0.267	34	3.6 to 40	27
	0.1 to 3	36		
	0 to 3.6	27		
	0 to 5.65	13		
	6 to 9	28		
Oxygen evolution	0. to 4.9	12, 15		
		16–20		
Hydrogen evolution	0 to 0.2	7	0.018	23
	0 to 5	11	0.1 to 1	24
			0.002 to 0.02 in acid	25
			0.27 to 4.9	26
			100	22
Battery performance	0.013	51	0.006 to 0.023	3
	0.017	44	0.15	52
	0.0007 to 0.042	46	0 to 0.55	41–43
	0.229	50	0 to 4.9	12, 15
	0 to 0.8	54, 55		

It appears that while bismuth generally causes an increase in the corrosion rate, the attack on alloys containing <0.2 wt.% Bi passes through a minimum at 0.1 wt.% [12, 32–34, 36]. Both weight-loss and cyclic-voltammetric experiments suggest that alloy grain structure and lead sulfate morphology play an important role in the corrosion mechanisms of lead–bismuth alloys. Unfortunately, the ease with which lead and lead–bismuth alloys recrystallize at both room temperature and during deformation, coupled with the lack of information regarding the age, physical history, thermal history and specimen preparation, makes it difficult to determine whether the presence of bismuth alone is responsible for the grain structures observed in microstructural and corrosion investigations. In this respect, it should be emphasized that spurious changes in grain structure can be imposed by the procedure that is employed to prepare the alloy sample.

It is clear that bismuth, either alloyed with lead or added to the electrolyte, increases significantly the rate of anodic oxygen evolution on PbO_2 via adsorption or substitution for lead atoms. Bismuth sites may catalyze oxygen transfer, and hence oxygen evolution, by increasing the production of hydroxyl radicals from the anodic dissociation of water. Apart from one recent study [7], the majority of the evidence reviewed here also suggests that the presence of bismuth tends to unaffect, or possibly suppresses, the rate of hydrogen evolution on lead.

While early studies [3, 4, 41–43] indicated that bismuth is detrimental to Planté plates, several later investigations [44, 46–51, 54–56] have found that bismuth has no effect on, and even enhances, the performance of the positive active-material. Among the benefits, increases in cycle life, discharge duration and active-mass utilization have been observed. On the other hand, a few papers [14, 45, 52] have presented a conflicting view. This has been based on results from investigations of a.c. impedance, self-discharge, corrosion and gassing rates, as well as of lead sulfate morphology.

In summary, this review has revealed that the published experimental evidence for both the perceived and actual effects of bismuth on lead/acid battery performance is complex and often contradictory. The problem is compounded by the wide range of alloys and cell designs that are presently in use. Clearly, a definitive set of studies is required in order to set an optimum/maximum level for grid bismuth in the different types of lead/acid battery technology.

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