EFFECTS OF BISMUTH ON THE ELECTROCHEMICAL PERFORMANCE OF LEAD/ACID BATTERIES

D. M. RICE

Pasminco Metals, 114 William Street, Melbourne, Vic. 3000 (Australia)

Introduction

The lead/acid battery has been the world's most important secondary power source for over 100 years. Furthermore, despite the continued funding of research aimed at investigating and developing alternative secondary systems, the dominance of the lead/acid system persists. The factors to which the continued success of the system can be attributed include:
(i) comparatively low cost;
(ii) good storage life, particularly in the dry-charged state;
(iii) versatility in providing either short-duration, high current or long-duration, low current over a range of potentials.
A major end-use of lead and lead alloys is in the manufacture of grids for the lead/acid storage battery. The role of the grid is two-fold. First, it acts as a support for the active material involved in the electrochemical reactions that give rise to electrical current. Second, it acts as a collector and conductor of the electrical current thus generated. In the past, development of suitable alloys for positive and negative grids has resulted in a trade-off between three major considerations:
(i) electrochemical properties, such as cycle life and gassing characteristics;
(ii) mechanical properties, such as tensile strength and creep resistance;
(iii) processing properties, such as castability and susceptibility to hot tearing.
The most common alloying addition made to lead for the production of battery grids is antimony. The advantages gained by the addition of antimony include: improved strength and castability; refinement of grain size, which leads to a reduction in hot tearing; improved cycle life, particularly on deep discharge. Despite all of these advantages, however, there is one major disadvantage associated with the use of lead–antimony alloys, namely, the reduction of the hydrogen evolution overpotential. Recharging of a battery containing lead–antimony grids often gives rise to hydrogen evolution at the negative plate resulting in the loss of water from the electrolyte. This introduces the inconvenience of having to maintain a sufficient level of electrolyte to ensure effective operation of the battery. With the trend towards maintenance-free and sealed lead/acid batteries, there has been a tendency for the industry to move towards both low-antimony and

antimony-free alloys. In the low-antimony range of alloys, additions of grain-refining elements such as selenium, copper and sulphur are made to overcome casting difficulties arising from directionality of solidification [1]. The most common examples of antimony-free alloys are found in the calcium–tin range. The advent of these two new alloy systems has refocused attention on the effects that the various impurity elements common in lead have on the performance of the battery.

Lead, as a raw material, contains many impurities, most of which are removed by refining without too much difficulty. This is not the case with bismuth, however, which because of its chemical similarity to lead is both difficult and expensive to remove to levels below 250 ppm. Consequently, much work has been carried out in the past on the investigation of the various effects on battery performance caused by the presence of bismuth in lead–alloy battery grids. Many of the early results, however, have been contradicted by later work. Not surprisingly, there exists a good deal of confusion concerning just what effect bismuth does have. In an attempt to sort out this confusion, Pasminco Metals (formerly BHAS and AM&S Metals) have sponsored several projects aimed at determining the effect of bismuth additions on the electrochemistry of lead. Since the scope of the work could not include studies of all current alloy systems, experimental work has been restricted to investigating the various effects of bismuth in pure lead only. This paper gives a brief account of the results of this work to date.

The lead–bismuth system

According to early views, the lead–bismuth alloy system consisted of a single eutectic. Recent investigations, however, indicate the presence of an intermediate phase (β) having a hexagonal close-packed structure [2]. Figure 1 shows the phase diagram of the system. Under equilibrium conditions, the solid solubility of bismuth in lead extends from 18 wt.% at room temperature up to 23 wt.% at the peritectic temperature of 184 °C. Due to the nature of non-equilibrium solidification, in any given sample of the alloy
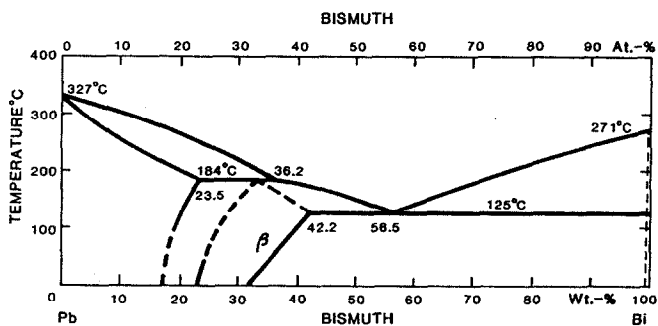

Fig. 1. Lead–bismuth phase diagram [2].

in this region of the diagram there is likely to be a non-uniform distribution of bismuth throughout the metal with concentration occurring in, or near, the grain boundaries. This micro-segregation is difficult to detect using conventional analysis techniques such as microprobe analysis owing to the atomic similarity of bismuth and lead.

A considerable amount of work has been carried out to investigate the effect of impurity levels of bismuth on the mechanical properties of lead. As a general statement, the mechanical properties of pure lead show little deterioration with the addition of bismuth [3]. This includes properties relevant to battery production such as tensile strength, hardness, creep resistance, and fatigue resistance.

Effect of bismuth on positive-plate electrochemistry

In order to investigate the electrochemical characteristics of pure lead and lead–bismuth alloys, an experimental method known as linear sweep voltammetry has been employed. This technique involves the application of a potential that is scanned between two limits across an electrode that is immersed in an electrolyte. The current produced between the test electrode and a counter electrode is measured and recorded as a function of the applied potential. The resultant trace of current *versus* potential is referred to as a voltammogram. Figure 2 shows a typical voltammogram arising from the potential sweep represented in Fig. 3. Various features of the voltammogram such as current peaks, current peak potentials and switching currents reveal information about the nature of the reactions taking place on the surface of the test electrode. The rate of change of the potential sweep is critical. If it is too fast, then the electrochemical reactions occurring at the electrode surface will not be able to keep up. If, on the other hand, the sweep rate is too slow, noisy transients will be generated which may result in the masking of reaction currents.

In the case of the positive electrode in the lead/acid battery system, the reactions that take place in service can be simulated experimentally by
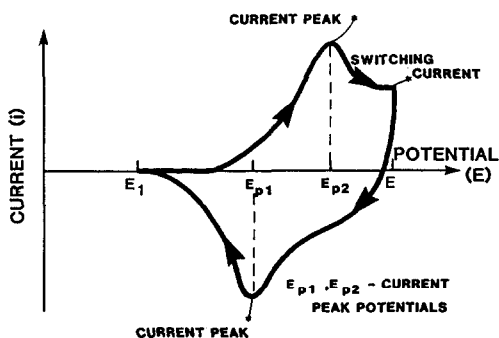

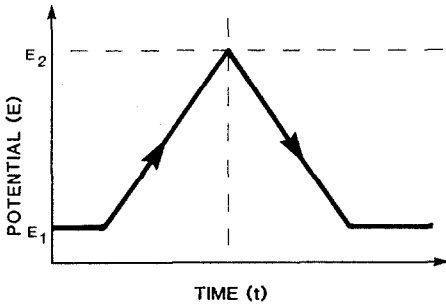Fig. 2. Typical current response to a LSV.

Fig. 3. Voltage–time trace for a LSV.

sweeping between potential limits of +600 and +1350 mV at a rate of 50 mV s^{-1} in an electrolyte of 5 M H_2SO_4. (Note, all electrode potentials are quoted with respect to a mercury/mercurous sulphate reference electrode.) An initial sweep to a maximum potential of 2000 mV is required, however, in order to initiate a layer of PbO_2 on the electrode surface. By continuous repetitive cycling between these limits, it is possible to build up a porous matrix on the electrode surface which, although not completely analogous to a pasted plate, does bear some similarities. For instance, the layer that is formed is both porous and in direct contact with the backing alloy. It is subjected to internal stresses that arise from the volume changes associated with transformation between lead sulphate and lead dioxide. As is the case with pasted positive plates, this will often lead to cracking and isolation of areas of the porous matrix from the backing alloy which, of course, results in a loss of capacity. Oxygen evolution will also occur on the electrode, bubbles of which can block pores and restrict reaction. Areas where the comparison breaks down, however, include:

(i) minimal variation in electrolyte molarity. In batteries, molarity can drop from 5 to as low as 1.5 when in a state of deep discharge;

(ii) lack of vibration during the test procedure that would simulate conditions experienced by batteries in applications such as SLI;

(iii) restrictions in both the range and the rate of change of the potential applied.

Despite these limitations, it is generally accepted that this experimental method yields both valid and useful data.

In order to determine the effect bismuth has on the performance of the positive grid, it is first necessary to investigate the electrochemical behaviour of pure lead. Figure 4 shows the linear sweep voltammogram (LSV) of lead sulphate to lead dioxide on a pure lead (99.999%) electrode. The first feature to note is that a relatively sharp current peak is generated as the lead suphate is oxidised to lead dioxide on the surface of the electrode. The reverse process, however, exhibits a much shallower curve. This indicates that on reduction the layer formed by the sulphate on and around the crystals of lead dioxide acts as an insulating medium. This is due to the
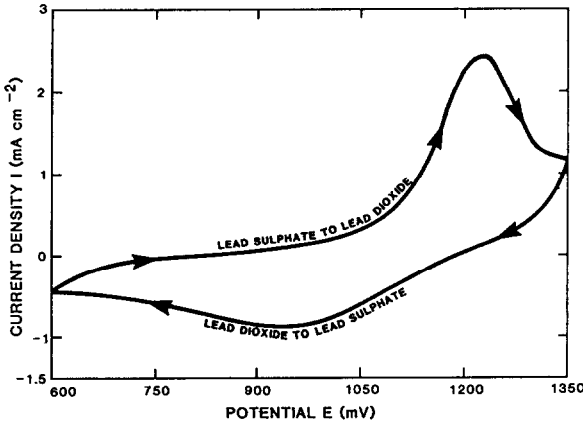
Fig. 4. LSV of lead sulphate to lead dioxide on pure lead (99.999%) (positive electrode).

relatively high electrical resistance of the sulphate. Thus, in order to reduce the shielded lead dioxide, higher overpotentials are required.

The LSVs generated by cycling the electrode, Fig. 5, reveal several important points.

(i) Increasing cycle number gives rise to a change in the shape of the oxidation curve. The broadening of the peak with increased cycle number represents the development of the porous matrix which spreads out the current response to the changing potential. Reduction in the peak reaction current after reaching a maximum at 1000 cycles indicates that sulphation of the active matrix is becoming dominant, resulting in a loss of capacity of the electrode.

(ii) The value of the lead suphate to lead dioxide peak current potential (E_p) varies little with cycle number; this suggests that there is little change in the electrochemical behaviour of pure lead as cycling proceeds.
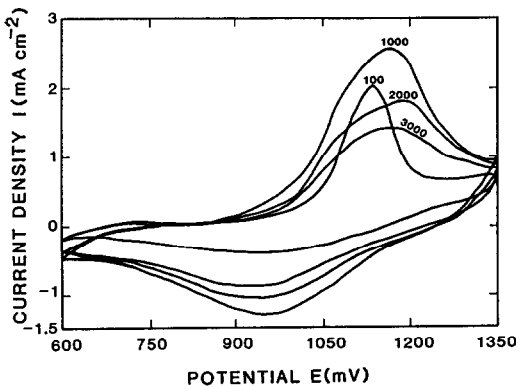

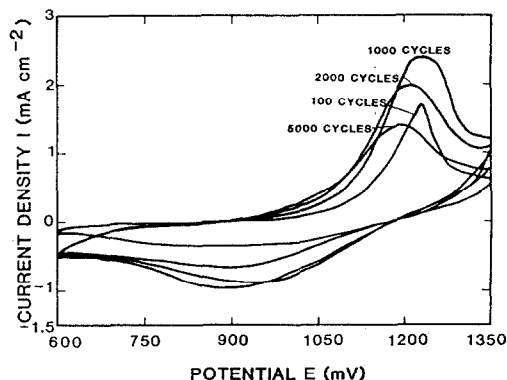Fig. 5. LSVs for pure lead (99.999%) after various cycle numbers (positive electrode).

Fig. 6. LSVs for 3.59 wt.% Bi–Pb after various cycle numbers (positive electrode).

Figure 6 shows the LSVs generated by cycling a 3.59 wt.% Bi alloy electrode. Comparison with the LSVs obtained for pure lead reveals several similarities:

(i) the oxidation peak becomes broader with cycling;

(ii) the peak reaction current reduces beyond 1000 cycles.

There are, however, two important differences. First, the value of E_p has been increased by the presence of bismuth. For example, the peak current potential measured after 100 cycles ($E_{p\,100}$) is 1260 mV in the case of the 3.59 wt.% Bi electrode compared to 1150 mV for the pure lead electrode. Plots of E_p versus bismuth content after 100, 1000 and 2000 cycles, Fig. 7, reveal a linear increase in E_p up to levels of around 0.5 to 1.0 wt.% Bi beyond which a plateau region is evident. These results indicate that the presence of bismuth in the positive lead electrode inhibits the
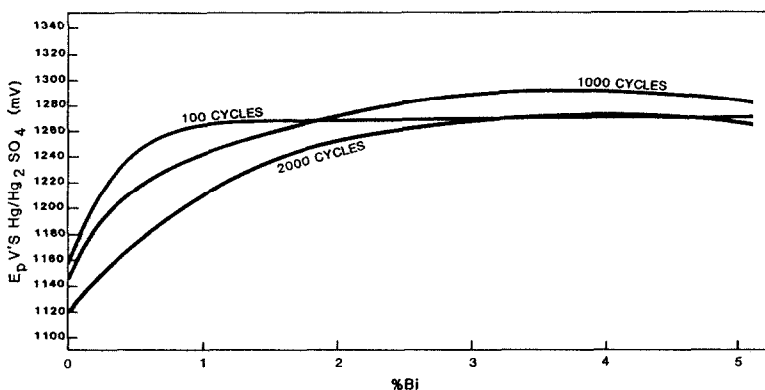

Fig. 7. Peak current potential (E_p) vs. bismuth content after 100, 1000 and 2000 cycles (positive electrode).

oxidation of lead sulphate to lead dioxide. (Since, however, this effect conforms to a linear relationship, it can be assumed that the low levels generally present in primary lead of less than 0.05% will have an insignificant effect.)

The second important difference between the behaviour of pure lead and lead–bismuth alloy is that as cycling proceeds, the E_p values for the alloys, particularly for those containing less than 1.0 wt.% Bi, become less positive. One possible explanation for this phenomenon is that bismuth is removed from the electrode surface. Hence, the electrochemical characteristics of the bismuth alloy approach those exhibited by pure lead.

Experiments show that pure bismuth in 5 M H_2SO_4 gives a reversible potential of −403 mV at 20 °C, with subsequent oxidation and dissolution at potentials more positive than this. Thus, with electrodes containing bismuth being cycled between +600 and +1350 mV, it is not surprising that bismuth is removed from the test piece. The leached bismuth can either reside in the porous layer, or it can dissolve in the electrolyte. Given a reversible potential of −403 mV, any bismuth that escapes into the electrolyte is almost certain to plate out on the counter electrode.

Referring back to Figs. 5 and 6, it can be seen that the current does not drop to zero at the most positive switching potential. This is attributed to the evolution of O_2 on the lead dioxide which is formed on the surface of the electrode. Plots of current response at +1350 mV *versus* bismuth content after 100 and 1000 cycles, Fig. 8, reveal two important features. First, the extent of O_2 evolution, reflected by the reaction current, is dependent upon the quantity of lead dioxide at the electrode surface. In the first stages of the experiment, *i.e.*, after 100 cycles, when lead dioxide layer development is at an early stage, the oxygen evolution current is low. After 1000 cycles,
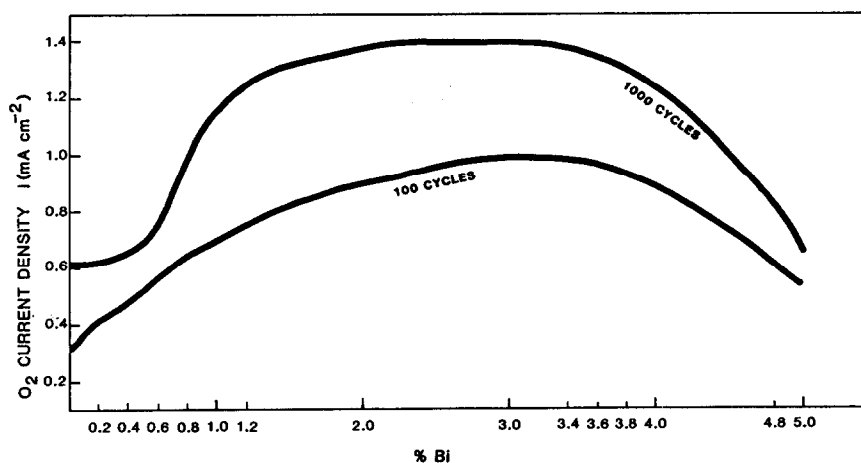

Fig. 8. Oxygen evolution current *vs.* bismuth concentration after 100 and 1000 cycles (positive electrode).
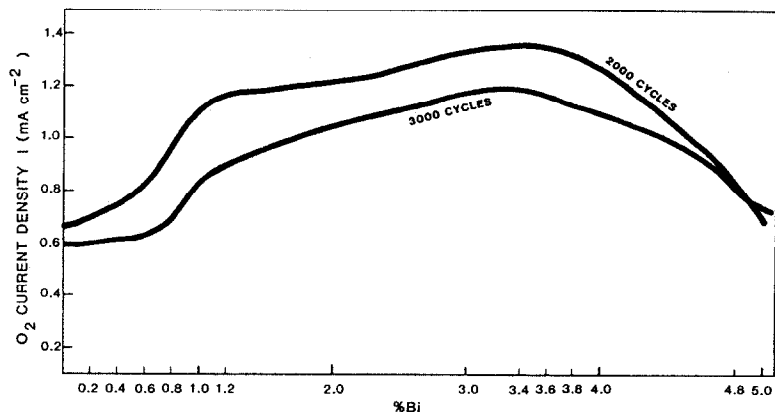
Fig. 9. Oxygen evolution current *vs.* bismuth concentration after 2000 and 3000 cycles (positive electrode).

however, when layer formation is more advanced, the oxygen evolution current is significantly higher. The second feature of note is the presence of what appears to be a critical level of bismuth of around 0.6%, below which there is little effect, but above which O_2 evolution is doubled.

More evidence supporting the finding that bismuth is leached from the positive electrode is presented in Fig. 9 where additional plots of oxygen evolution current *versus* bismuth content after 2000 and 3000 cycles reveal a decrease in current with further increase in cycle number. This suggests that the catalytic effect of bismuth on oxygen evolution is being reduced by the leaching out of the bismuth, although a proportion of the observed decrease in current could also be attributed to sulphation.

Examination of cycled electrodes under a scanning electron microscope reveals that the sulphate formed on the pure lead sample, Fig. 10, consists of a coherent film with regularly shaped crystals. By contrast, the sulphate
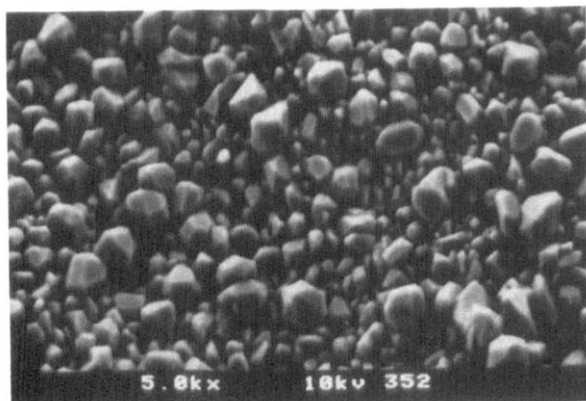

Fig. 10. Scanning electron micrograph of sulphate layer formed on pure lead sample after 5000 cycles (positive electrode).
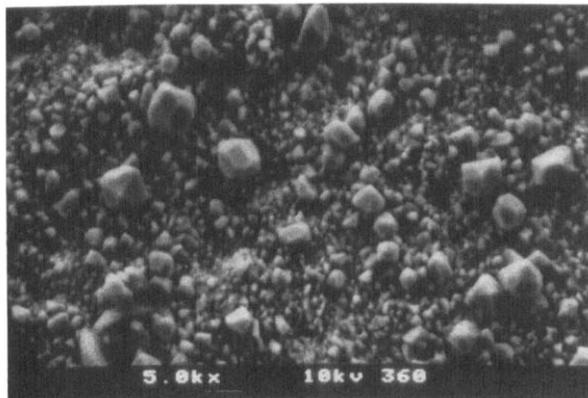
Fig. 11. Scanning electron micrograph of sulphate layer formed on 0.57 wt.% Bi–Pb after 5000 cycles (positive electrode).

film formed on a 0.57 wt.% Bi alloy electrode, Fig. 11, consists of a greater range of crystal sizes together with a fine, almost amorphous, layer. From these observations, it can be concluded that bismuth enhances the nucleation of lead sulphate.

Thus, bismuth has four main effects when added to the pure lead positive electrode:

(i) inhibits the oxidation of lead sulphate to lead dioxide;

(ii) increases the amount of oxygen evolved;

(iii) prevents the formation of a more open sulphate film on the surface of the electrode due to an enhancement of the nucleation of lead sulphate;

(iv) leaches from the electrode and is deposited on the negative plate.

Effect of bismuth on negative-plate electrochemistry

Hydrogen evolution reaction

In the past, a considerable amount of work has been carried out on the nature of hydrogen evolution on the negative lead electrode. Unfortunately, however, not until recently has it become well recognised that the purity of the reactants and the system alike is of paramount importance if any reliability is to be attached to the results. The need for purity arises from the fact that hydrogen has low activity on lead. Therefore, any effects due to the presence of impurities in the system will be greatly magnified. Because of this, a significant proportion of early experimental work should be regarded with some caution.

The development of maintenance-free technology has generated increased interest in the hydrogen evolution reaction, together with the concomitant effects of alloying and impurity elements. It is well recognised that additions of antimony aimed at improving grid strength cause a reduc-

tion of the hydrogen overpotential on the negative electrode. A low hydrogen overpotential gives rise to two major effects:

(i) current efficiency on recharge is reduced due to hydrogen evolution occurring preferentially to the reduction of lead sulphate to lead;

(ii) hydrogen evolution takes place at impurity centres on the surface of the plate, resulting in self discharge.

Because of the chemical similarity of bismuth and antimony (they are both in the same periodic group), it is important in the context of maintenance-free batteries to investigate the influence of bismuth on the hydrogen evolution reaction.

Once again, linear cyclic voltammetry was employed. An electrolyte of 0.05 M H_2SO_4, rather than 5 M H_2SO_4, was used. Standard battery strength acid was not chosen as it was found that the high concentration of H^+ ions leads to excessive hydrogen evolution, which limits the amount of extractable data. Electrodes under test were swept between potentials of -1200 mV and -2300 mV at a rate of 100 mV s^{-1}.

Figure 12 shows a typical LSV for the evolution of hydrogen on pure lead (99.999%). The major peak corresponds to the reduction of H^+ ions to hydrogen gas, while the pseudo-peak at the switching potential can be attributed to the reduction of water in the electrolyte.

The value of the hydrogen overpotential, where the overpotential (η) is defined by the Tafel equation

$$\eta = a + b \log i$$

can be determined by plotting potential *versus* log i. The slope of the resultant graph is b and the intercept at log $i = 0$ is a. Table 1 lists the values of a and b calculated using this method, together with values of i_0, the exchange current measured against the hydrogen reference electrode, for pure lead and a range of lead–bismuth alloys. Examination of these results reveals that the addition of bismuth to pure lead gives rise to an increase of approxi-
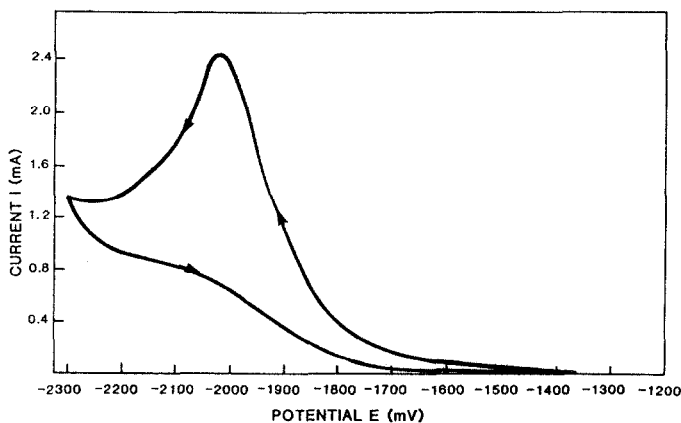

Fig. 12. Current response to a LSV in the hydrogen evolution reaction region.

TABLE 1

Kinetic constants for the hydrogen evolution reaction on various Pb–Bi alloys in 0.05 M H_2SO_4 and 1.0 M Na_2SO_4 at 22 °C

Bi (wt.%)	b (V)	a (V)	i_0 (10^{-11} A cm^{-2})
—	−0.13	−1.31 ± 0.04	15.80
0.275	−0.14	−1.58 ± 0.04	1.10
0.565	−0.15	−1.59 ± 0.03	4.27
1.063	−0.14	−1.53 ± 0.04	2.09
2.109	−0.15	−1.51 ± 0.01	3.89
3.587	−0.16	−1.54 ± 0.04	14.80
4.909	−0.14	−1.51 ± 0.01	1.23

mately 0.2 V in the value of a, indicating that the overpotential is increased. The corresponding effect on i_0, which reflects the rate at which the reaction takes place at equilibrium, is a marked reduction with bismuth content indicating that the volume of hydrogen produced at the electrode has been reduced also. Thus, it can be concluded that bismuth alleviates hydrogen evolution. Since, however, there is little change in any of the variables with increasing bismuth content it is assumed that a critical bismuth level exists, which lies somewhere between 0 and 0.27 wt.%, where this effect is triggered.

Reversible lead–lead sulphate reaction

The effect of bismuth additions on the reversible lead to lead sulphate reaction was investigated by cycling electrodes between potentials of −1300 and −500 mV at a rate of 50 mV s^{-1} in an electrolyte of 5 M H_2SO_4. Figure 13 shows a typical LSV for pure lead after 2000 cycles. There are several
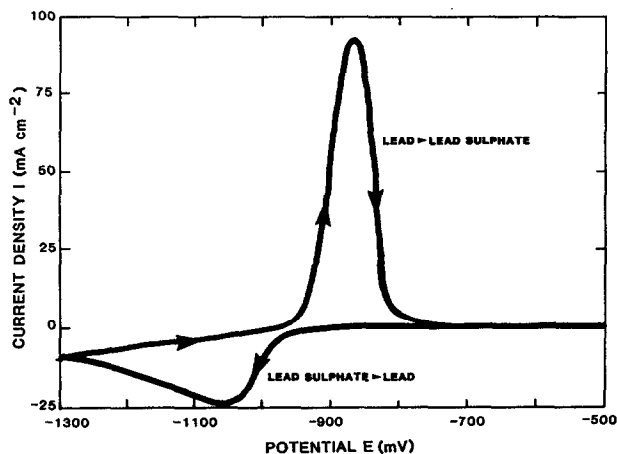

Fig. 13. Typical LSV of lead to lead sulphate reaction on the negative plate.

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features of note. First, as the potential is swept from −1300 mV, reduction of the final amount of lead sulphate occurs. This explains the negative current in this portion of the curve. On reaching approximately −950 mV, the current becomes positive reflecting the initiation of the oxidation of lead to lead sulphate. The reaction proceeds smoothly until around −800 mV at which point a high-resistance layer of lead sulphate completely covers the electrode resulting in passivation. The current returns to zero and remains there until the reduction of the film commences at around −970 mV where the current once again becomes negative. The reduction curve is much shallower than the oxidation curve reflecting the high resistivity of the sulphate film.

Figures 14 and 15 show a series of LSVs at various cycle numbers for pure lead and 0.265 wt.% Bi, respectively. Several similarities are evident:
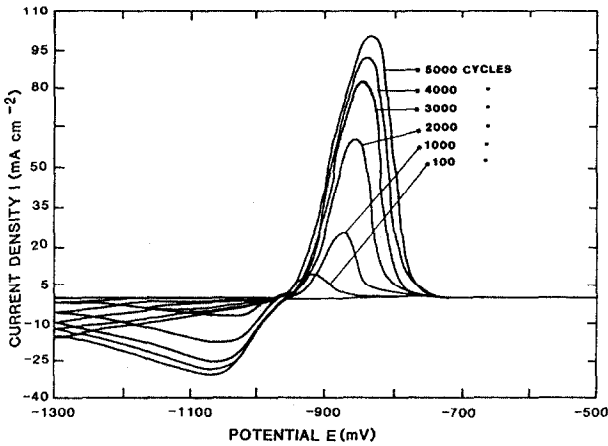

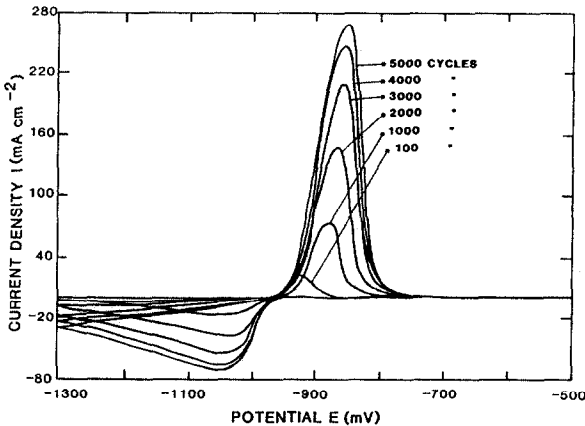Fig. 14. LSVs for pure lead (99.999%) after various cycle numbers (negative electrode).

Fig. 15. LSVs for 0.265 wt.% Bi–Pb after various cycle numbers (negative electrode).

(i) broadening of the oxidation peak with cycling occurs in both cases, reflecting the development of a porous matrix;

(ii) peak oxidation reaction current increases with increasing cycle number.

There are, however, several dissimilar features. Plotting the peak height against bismuth level, Fig. 16, illustrates that even with additions of up to 4.9 wt.% bismuth, the electrode capacity is increased. The latter can be attributed to the fact that bismuth in the electrode aids in the distribution of current as the passivating layer forms, thereby facilitating the development of a porous layer.

Plotting the peak current potential E_p versus cycle number for the various bismuth contents, Fig. 17, shows that bismuth causes a negative shift in the E_p. This indicates that bismuth enhances the nucleation of lead sulphate at the surface of the lead electrode thus leading to a tighter, more compact layer.
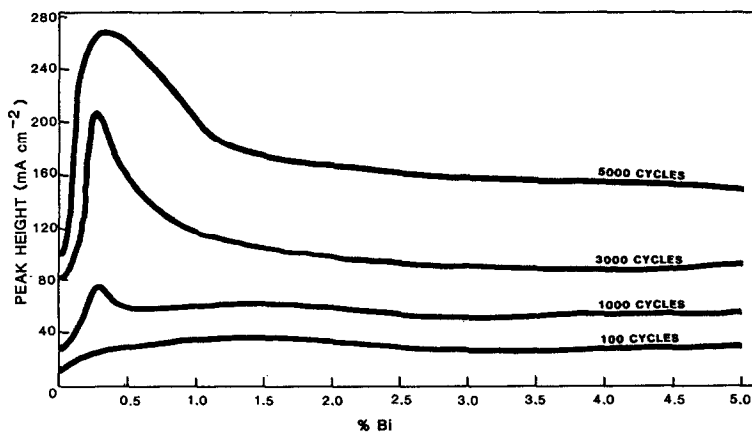
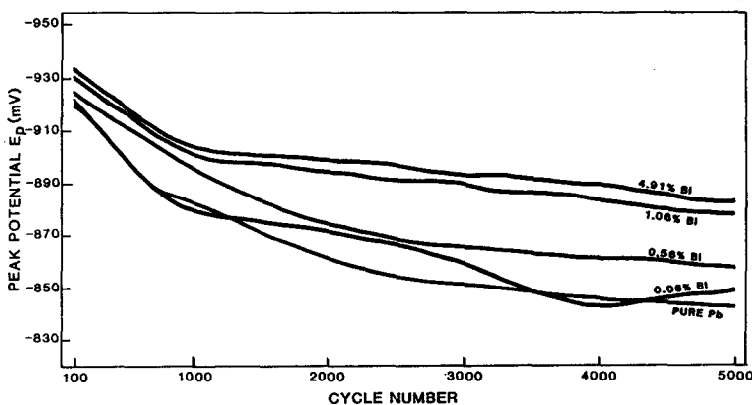Fig. 16. Peak current vs. bismuth content for various cycle numbers (negative electrode).

Fig. 17. Peak potential vs. cycle number for various bismuth contents (negative electrodes).

These two effects actually act in opposition to one another. The first, by promoting porous layer development, leads to an increase in capacity. The second, by improving the formation of a passivating layer, will eventually deny access to the electrolyte, thereby reducing capacity.

Thus, the addition of bismuth has three main effects when added to the pure lead negative electrode:

(i) increases the hydrogen evolution overpotential;

(ii) aids in the distribution of current at the electrode surface;

(iii) enhances the nucleation of lead sulphate.

Conclusions

By investigating the effect of bismuth on various constituent parts of the lead/acid cell, it is possible to gain some insight into any problems that may arise as a result of its inclusion. Unfortunately, however, difficulties present themselves when attempting to assess the relative importance of each of the separate effects in the context of the whole system. Nevertheless, it is possible to draw some valid and worthwhile conclusions.

In considering the pure lead positive electrode, the study has revealed that any bismuth present will be leached out and then deposited on the negative electrode. It has also been shown that additions of bismuth to the positive electrode will give rise to the following three effects.

(i) The lead sulphate to lead dioxide transformation reaction will be inhibited; this may lead to problems in recharging.

(ii) The oxygen evolution overpotential will be reduced which, apart from resulting in water loss, may also increase corrosion of the grid on charging.

(iii) Nucleation of the lead sulphate will be enhanced which will result in the isolation of positive active material on cycling.

Just which of these effects predominates is, at present, unknown. Nevertheless, by referring back to Figs. 7 and 8, it can be concluded that for the levels of bismuth commonly found in primary lead (usually in the order of 0.02 wt.%), the first two of the above three effects will be negligible. Similarly, at low levels of bismuth, enhancement of the nucleation of lead sulphate will be minimal and will largely be cancelled out by the leaching action on the bismuth which will result in the rupture of the lead sulphate layer.

Turning to the pure lead negative electrode, it has been demonstrated that the addition of bismuth also gives rise to three major effects, namely:

(i) increased hydrogen evolution overpotential;

(ii) improved distribution of current at the electrode surface;

(iii) enhanced nucleation of lead sulphate.

Thus, bismuth reduces gassing and also improves the kinetics of both the charge and discharge reactions. Referring back to Fig. 17, it is evident,

in the case of levels of less than 0.06 wt.%, that the presence of bismuth has little, or no, effect on the nucleation of lead sulphate on the negative plate.

In conclusion, the amount of bismuth that can be tolerated in either the positive or negative plate of a lead/acid battery appears to be 0.05 wt.%.

Acknowledgements

References

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