

Influence of bismuth on the charging ability of negative plates in lead–acid batteries

L.T. Lam^{a,*}, H. Ceylan^a, N.P. Haigh^a, J.E. Manders^b

^aCSIRO Energy Technology, Bayview Avenue, Clayton South, Vic. 3169, Australia

^bPasminco Metals, P.O. Box 129K, Melbourne, Vic. 3001, Australia

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Abstract

To examine the influence of bismuth on the charging ability of negative plates in lead–acid batteries, plates are made from three types of oxides: (i) leady oxide of high quality which contains virtually no bismuth (termed ‘control oxide’); (ii) control oxide in which bismuth oxide is blended at bismuth levels from 0.01 to 0.12 wt.%; (iii) leady oxide produced from Pasminco VRLA RefinedTM lead (0.05–0.06 wt.%Bi). An experimental tool—the ‘conversion indicator’—is developed to assess the charging ability of the test negative plates when cycling under either zero percent state-of-charge (SoC)/full-charge or partial state-of-charge (PSoC) duty. Although the conversion indicator is not the true charging efficiency, the two parameters have a close relationship, namely, the higher the conversion indicator, the greater the charging efficiency. Little difference is found in the charging ability, irrespective of bismuth content and discharge rate, when the plates are subjected to zero percent SoC/full-charge duty; the conversion indicator lies in the range 81–84%. By contrast, there is a marked difference when the negative plates are subjected to PSoC duty, i.e. consecutive cycling through 90–60, 70–40, 80–40 and 90–40% SoC windows. Up to 0.06 wt.%Bi improves the charging ability, especially with a low and narrow PSoC window (40–70% SoC) of the type that will be experienced in 42 V powernet automobile and hybrid electric duties. To maximize this beneficial effect, bismuth must be distributed uniformly in the plates. This is best achieved by using VRLA RefinedTM lead for oxide production. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bismuth; Charging ability; Conversion indicator; Lead–acid battery; Negative plate; Partial state-of-charge

1. Background

1.1. Charging process of negative plates

It is well known that two competing reactions take place during the charging of a discharged negative plate in a flooded-electrolyte battery (Fig. 1). These are the conversion of lead sulfate to lead and the evolution of hydrogen. Fortunately, the latter reaction is difficult on the surface of lead because of electrokinetic limitations. Thus, the conversion of lead sulfate to lead proceeds predominantly during the early stages of the charging process, and hydrogen gassing during the final stages. Given this behaviour, the preferential occurrence of these two reactions can be affected by the structure and deployment of the lead sulfate. If the discharged negative plate contains large crystals of lead sulfate with an uneven distribution, then conversion of this material to lead in the early stages of charging will become difficult and, consequently, hydrogen gassing can

take place. Expanders—mixtures of barium sulfate, ligno-sulfonates and carbon black—are used in negative plates to reduce the size and to improve the distribution of lead sulfate, as well as to increase the electrical conductivity of the discharged plate. Thus, expanders enhance the charging ability of negative plates.

Recently, carbon black with a finer particle size has been added at higher levels to increase the charging efficiency of negative plates in batteries intended for use in 42 V powernet automobiles and hybrid electric vehicles (HEVs) [1,2]. In such operations, the batteries are cycled under partial state-of-charge (PSoC) duty and this has been found to cause irreversible sulfation of the negative plates. This study explores an additional strategy—the addition of bismuth—to improve the charging efficiency of negative plates through modification of the structure of lead sulfate and/or through suppression of hydrogen gassing. The investigation focuses on oxide produced from Pasminco VRLA RefinedTM lead (called ‘VRLA RefinedTM oxide’) because this material contains 0.05–0.06 wt.%Bi and has been shown [3–5] to enhance battery cycle-life via increasing the connectivity of the active material of positive plates.

* Corresponding author. Tel.: +613-9545-8401; fax: +613-9545-8403.
E-mail address: lan.lam@det.csiro.au (L.T. Lam).

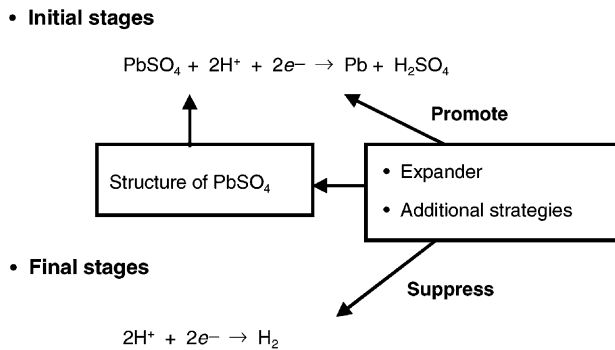


Fig. 1. Reactions during charging of negative plates in lead–acid batteries.

1.2. Conversion indicator

In order to assess the effect(s) of bismuth on the charging ability of negative plates, a rapid and useful procedure has been developed. In general, there is little change in the initial potential of the negative plate when charging with a constant current (Fig. 2). After a given time, the potential starts to increase, passes through a ‘turning point’, and eventually, reaches a maximum value. The reaction before the turning point is mainly the conversion of lead sulfate to lead. After the turning point, the evolution of hydrogen also takes place and, finally, becomes the main reaction when the potential is at its maximum value.

The time taken for the potential to reach the turning point depends upon the structure of the lead sulfate developed in the previous discharge stages and/or impurities in the negative plate. If the lead sulfate has a large crystal size and an uneven distribution, and/or the negative plates have been contaminated by impurities that reduce the evolution potential of hydrogen, the time taken for the potential to reach the turning point, t_{tp} , will become shorter. Thus, the ratio between the charge input ($I_c t_{tp}$) up to the turning point and the previous discharge capacity ($I_d t_d$) can be used to assess the charging ability of the negative plate. This parameter is called the ‘conversion indicator’, and is expressed in

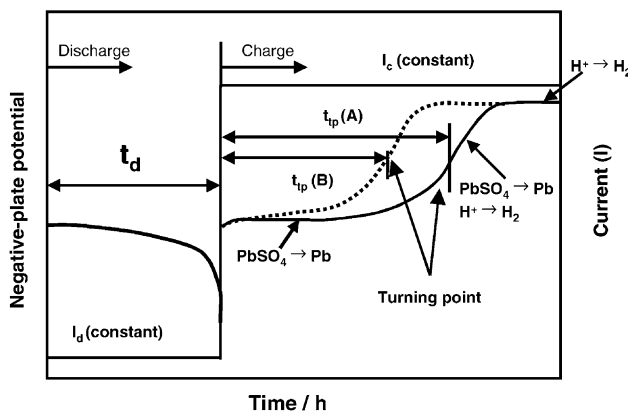


Fig. 2. Change in negative-plate potential during charging.

terms of a percentage, i.e. $I_c t_{tp} / I_d t_d \times 100\%$. In Fig. 2, the conversion indicator for condition A will obviously be greater than that for condition B. It should be noted that the conversion indicator is neither the charging efficiency nor the charge-acceptance. Nevertheless, the parameters are related, namely, the higher the conversion indicator, the greater the charging efficiency.

In this study, two cycling regimes are used. One is zero percent SoC/full-charge cycling, the other is PSoC cycling. More attention is focused on the latter regime because this duty will be experienced in imminent 42 V powernet automobile and HEV applications.

2. Experimental

2.1. Construction of battery plates

Pasted positive plates were made from leady oxide of high quality. On the other hand, the negative plates were produced from three types of oxide. The first was the same as that used for the positive plates and served as the ‘control oxide’. The second was the control oxide blended with bismuth oxide (Bi_2O_3) to give bismuth levels of 0.01–0.12 wt.%. The third was VRLA RefinedTM oxide. The paste formulae for the positive and the negative electrodes are presented in Table 1. For pastes prepared from control oxide blended with bismuth oxide, good dry-mixing was conducted prior to the addition of water and sulphuric acid solution. To exclude any contamination from the sulphuric acid required for paste mixing and battery electrolyte, analytical grade reagent was used throughout. After mixing, the corresponding paste was applied to positive or negative grids with the dimensions and composition given in Table 2. The pasted plates were cured at 50 °C/100% relative humidity for 24 h, and dried at 60 °C/ambient humidity for 8 h.

2.2. Electrochemical cells

The cell used in this study is shown in Fig. 3. The main apparatus was constructed from polypropylene. The cell comprised of two cured/dried positive plates and one cured/dried negative plate, together with polyethylene

Table 1
Paste formulae for positive and negative plates

Component	Positive electrode	Negative electrode
Leady oxide (kg)	1	1
Fibre (g)	0.3	0.6
BaSO ₄ (g)	–	4.93
Carbon back (g)	–	2.1
H ₂ SO ₄ , 1.400 relative density (cm ³)	57	57
Water (cm ³)	130	110
Acid-to-oxide ratio (%)	4	4
Paste density (g cm ⁻³)	4.5	4.7

Table 2
Dimensions and composition of positive and negative grids

	Positive grid	Negative grid
Height (mm)	68	68
Width (mm)	40	40
Thickness (mm)	3.3	3.3
Composition	Pb–0.09 wt.%Ca–0.8 wt.%Sn	Pb–0.09 wt.%Ca–0.3 wt.%Sn

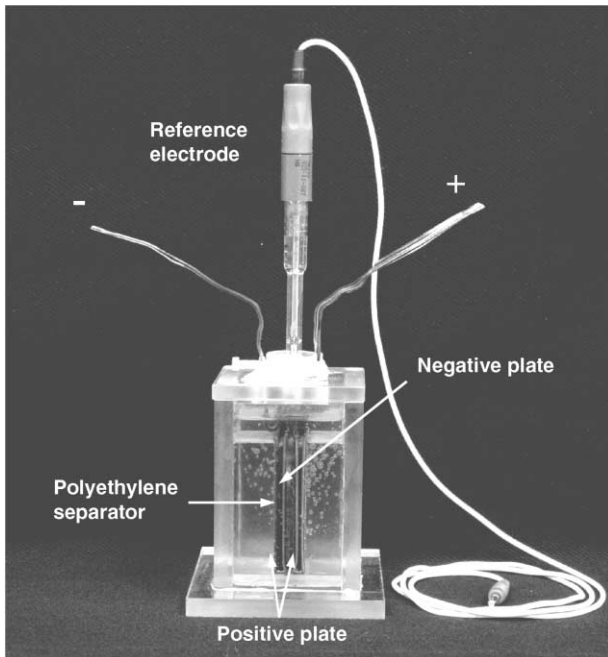


Fig. 3. Electrochemical cell used in this study.

separator sheets. Sulphuric acid of 1.25 relative density was introduced and the cell was allowed to stand for 30 min. A constant current of 0.98 A was applied for 20 h. After

formation, the acid density was adjusted to ~ 1.285 . The cell was then charged fully with a constant current of 0.5 A for 16 h. A mercury/mercury sulfate reference electrode was inserted into the cell for measuring the potential of the negative plate during cycling. All potentials are reported with respect to this electrode.

2.3. Cycling regimes

2.3.1. Zero percent SoC/full-charge cycling

The negative plates were cycled under two different discharge rates, namely, the 1 and 3 h rates. For the 1 h rate, the negative plate was discharged at 2.2 A until the potential fell to 0.6 V. The recharge was then conducted with a constant current of 1.1 A (without a top-of-charge potential limit) until a charge-to-discharge ratio of 1.2 was reached. For the 3 h rate, the negative plate was discharged to 0.6 V at 0.85 A and was recharged at 1.1 A again until a charge-to-discharge ratio of 1.2 was reached. Three cycles were conducted at each discharge rate, and the conversion indicator was determined for each cycle.

2.3.2. PSoC cycling

The cell was operated successively for 14 cycles through four different PSoC windows, namely, 90–60, 70–40, 80–40 and 90–40%, respectively (Fig. 4). In each PSoC window,

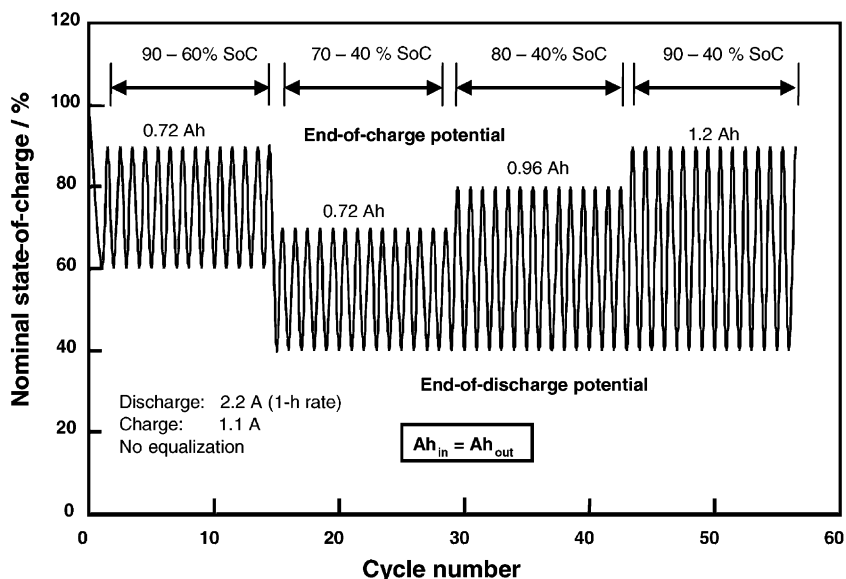


Fig. 4. PSoC cycling regime.

the cell was discharged at 2.2 A and recharged at 1.1 A with an equal amount of charge input and charge output. No equalization charge was applied between each PSoC window. During cycling, the end-of-discharge and end-of-charge potentials of the negative plate were recorded and the conversion indicator was determined for each cycle.

3. Results and discussion

3.1. Zero percent SoC/full-charge cycling

The conversion indicators of negative plates prepared from control oxide, oxide blended with bismuth, or VRLA Refined™ oxide are given in Fig. 5. Each value is the average for three cycles. Clearly, there are no major differences in the conversion indicators, irrespective of bismuth addition and discharge current. The conversion indicator is between 81 and 84%.

3.2. PSoC cycling

3.2.1. Performance of oxide blended with bismuth

The performance of negative plates prepared from control oxide, or oxide blended with different levels of bismuth, under PSoC cycling is shown in Fig. 6. The end-of-discharge potential (EoDP) of the plate made from control oxide decreases slowly over 42 cycles, and then experiences a rapid decline to 0 V. The cell completed 44 cycles. By contrast, the end-of-charge potential (EoCP) stayed mainly at -1.5 V, except when cycling between 70 and 40% SoC. In this window, the potential is about -1.1 V initially, but increases to -1.5 V in the latter stages.

The EoDP of the plate produced from oxide blended with 0.01 wt.%Bi also decreases with cycling, but at a much slower rate than that observed for the control oxide after 42 cycles. At the end of cycling, the negative-plate potential has fallen to -0.6 V. The EoCP displays behaviour similar to that of the control oxide, except that a potential of -1.1 V is maintained for a longer time when cycling between 70 and 40% SoC. Both the EoDP and the EoCP performance of a plate prepared from oxide blended with bismuth at 0.03 wt.% lies between that for the control oxide and the 0.01 wt.%Bi oxide.

It is well known that the charging efficiency of the negative plate is less than 100% because of the side reaction of hydrogen evolution. Thus, to maintain a full state-of-charge, the amount of charge put into the plate should be higher than that removed during the previous discharge. As mentioned in Section 2.3.2, all the plates cycled under the different SoC windows were partially discharged and charged with an equal output and input of charge. Therefore, in each PSoC cycle, the plates always receive insufficient charge. This can be deduced qualitatively by the decrease in the EoDP of plates using either control oxide or oxide blended with bismuth during cycling. This feature is indicative of the undercharging of plates, whilst an increase in the EoDP suggests overcharging. The charging is sufficient when the EoDP is constant. Although all the plates display a decrease in the EoDP, the overall decline is faster in the order: control oxide > 0.03 wt.%Bi oxide > 0.01 wt.%Bi oxide. This trend indicates that the charging efficiency is greater when the negative plate is made from oxide doped with bismuth.

In order to confirm the above observations, the conversion indicator of each type of negative plate when cycled under

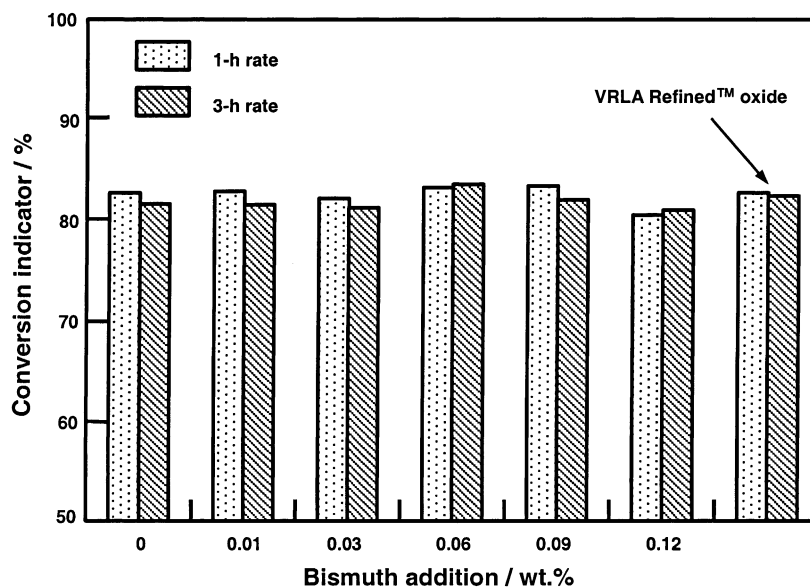


Fig. 5. Conversion indicator of negative plates made from control oxide (0 wt.%Bi), oxide blended with bismuth (0.01–0.12 wt.%Bi), or VRLA Refined™ oxide (0.05–0.06 wt.%Bi).

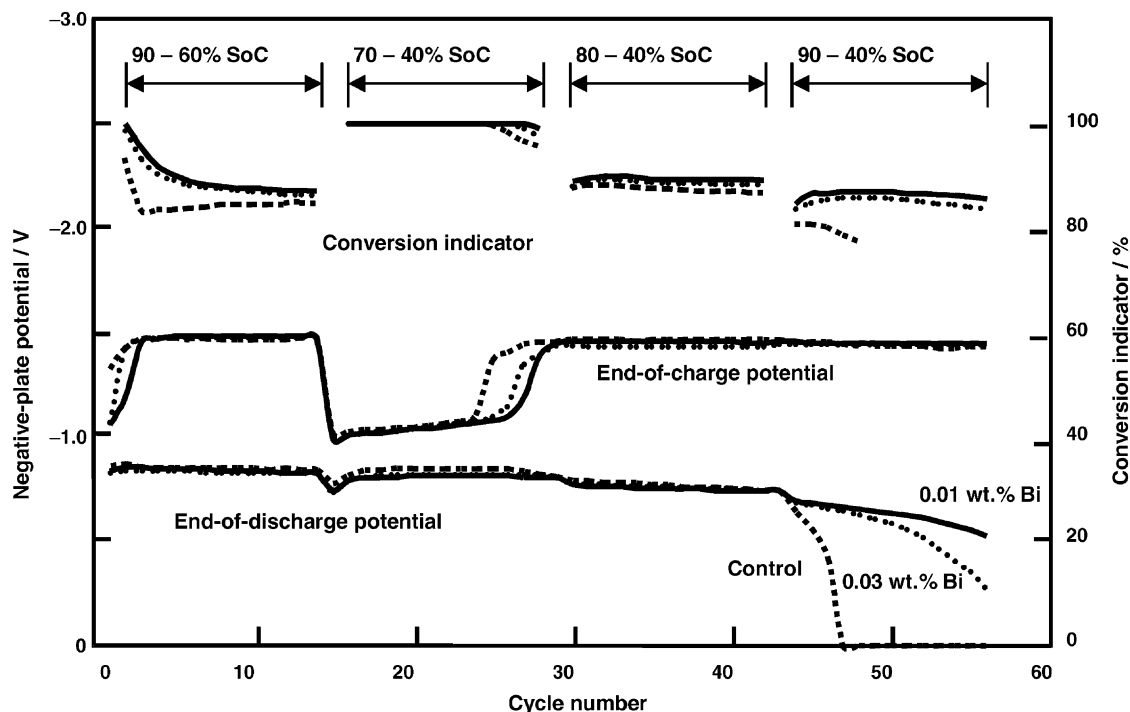


Fig. 6. Performance of negative plates prepared from control oxide or oxide blended with bismuth (i.e. 0.01 and 0.03 wt.%).

different SoC windows was examined. For the 90–60% SoC window, the conversion indicator of the plate using control oxide is high initially, but levels down rapidly to about 82%. Similar behaviour is shown by plates doped with 0.01 or 0.03 wt.%Bi. Nevertheless, the overall indicators of these latter two plates are higher than that of the control and the 0.01 wt.%Bi plate displays the highest value. When the SoC window is changed from 90–60 to 70–40%, the conversion indicator of the control oxide is close to 100% initially, but decreases to 96% in the final stages. The conversion indicators of the two bismuth-doped plates display similar characteristics but remain at higher values at the end of cycling. On keeping the lower SoC at 40% but increasing the upper SoC to 80%, the conversion indicators of the plates made from the three oxides all decrease to 82–85%. The plates doped with bismuth, however, have conversion indicators which are slightly higher than that of the control. On increasing the upper SoC level further, to 90%, the conversion indicator of the control plate falls rapidly while that of each of the bismuth-doped plates remains at about 82%.

The above results show clearly that under all the PSoC windows employed here, the conversion indicator increases in the order: control oxide < 0.03 wt.%Bi oxide < 0.01 wt.%Bi oxide. This order is consistent with that observed for the EoDP (versus).

There is another important finding from this study. Negative plates, either made from control oxide or from control oxide blended with bismuth, receive the best charging when cycled over a low and narrow PSoC window, namely, 70–40% SoC. This feature is very important for batteries to be used in 42 V powernet automobiles or HEVs because the

driving duties in these vehicles require batteries to have sufficient power as well as good charge-acceptance under all circumstances. Sufficient power is demanded to assist the internal combustion engine in stop-start operation (i.e. in 42 V powernet vehicles) or in hill-climbing/overtaking situations (i.e. in HEVs). On the other hand, good charge-acceptance is necessary to store energy efficiently via regenerative braking. It is clear that the batteries will not provide sufficient power when the SoC is low and will not accept charge efficiently when the SoC is high. Therefore, to meet these two demands, the batteries should be cycled at least within 70 and 40% SoC.

The performance of the negative plates made with control oxide or oxide doped with bismuth at higher levels, e.g. from 0.06 to 0.12 wt.%, is shown in Fig. 7. The negative plate doped with 0.06 wt.%Bi still shows improvement over the control plate. It gives a higher conversion indicator at all PSoC windows and slightly longer cycling than the control plate. The performance deteriorates, however, when the bismuth content is increased to 0.09 or 0.12 wt.%. Both the conversion indicator and the cycling ability decrease significantly for the plate doped with 0.12 wt.%Bi.

3.2.2. Performance of VRLA Refined™ oxide

The charging ability of negative plates using VRLA Refined™ oxide is given in Fig. 8. For the purpose of comparison, the performance of control oxide and oxide doped with 0.01 or 0.03 wt.%Bi is also included. Clearly, the plate using VRLA Refined™ oxide gives the best conversion indicator at all PSoC windows and, correspondingly, this plate maintains the highest EoDP both during and at the

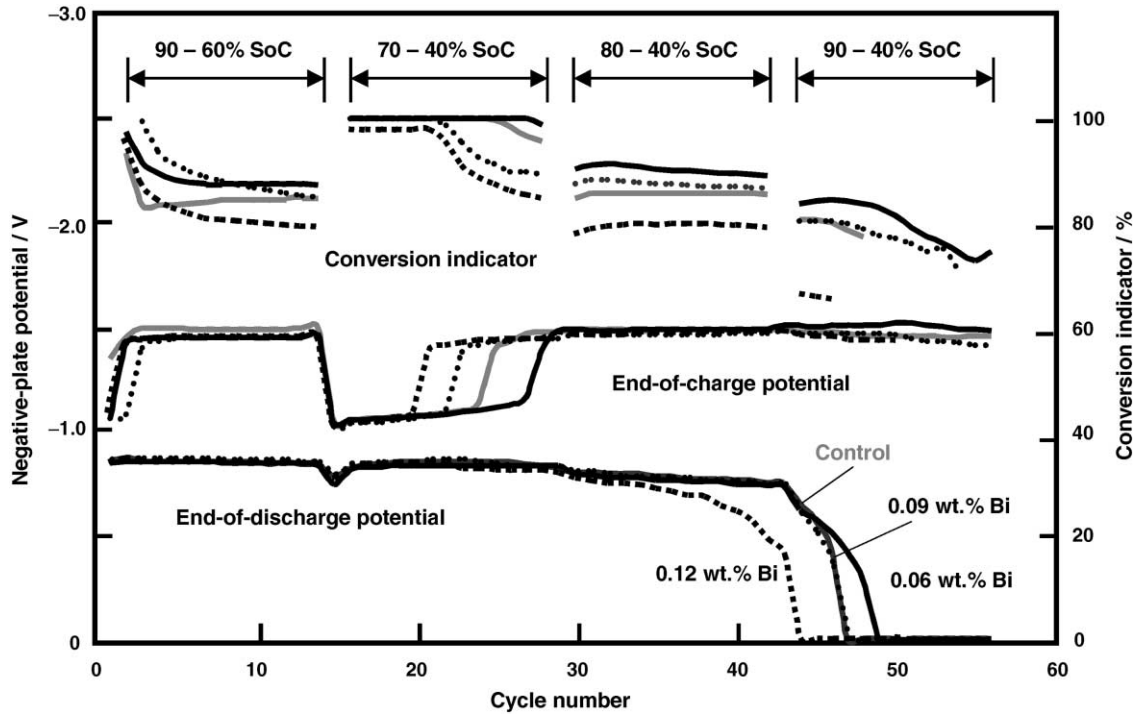


Fig. 7. Performance of negative plates prepared from control oxide or oxide blended with bismuth (i.e. 0.06, 0.09, 0.12 wt.%).

end of cycling. In other words, batteries made from VRLA Refined™ lead will enjoy longer PSoC cycling before application of an equalization charge.

To date, results show that there is inconsistency between the performance of negative plates using VRLA Refined™

oxide or control oxide blended with bismuth oxide. The plate made from oxide doped with 0.01 wt.% Bi shows better charging ability than the control, but the degree of improvement becomes less when the level of bismuth is increased upto 0.06 wt.%. On the other hand, although the VRLA

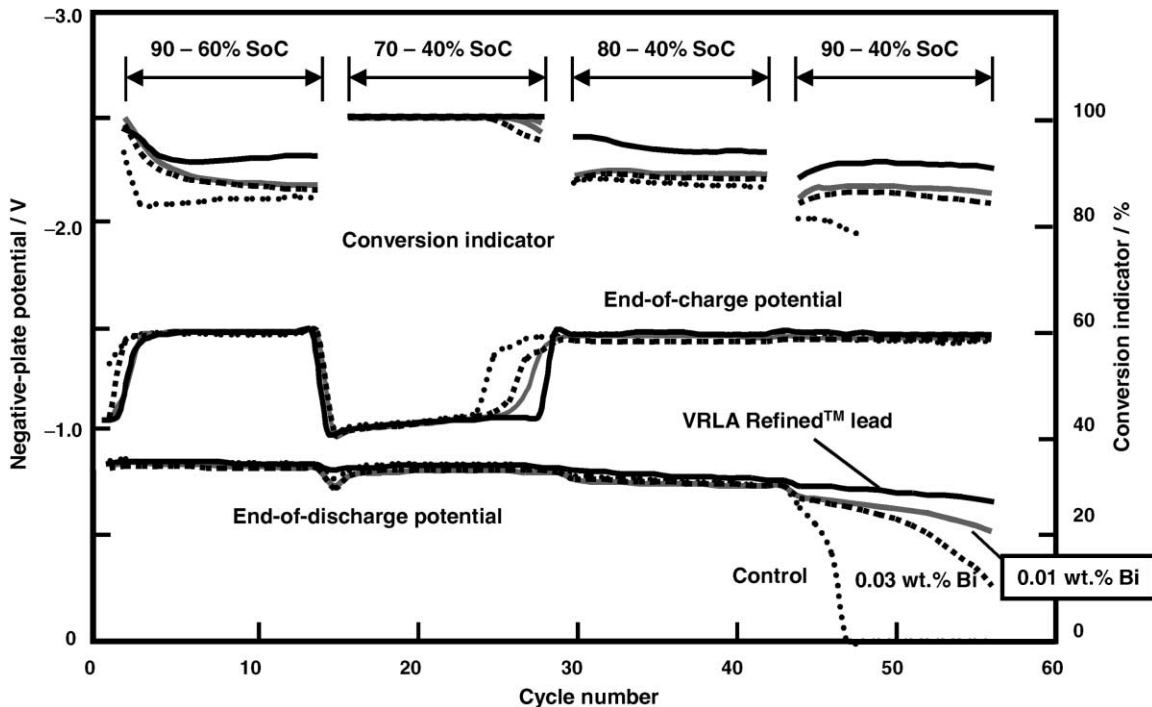


Fig. 8. Performance of negative plate using oxide prepared from VRLA Refined™ lead.

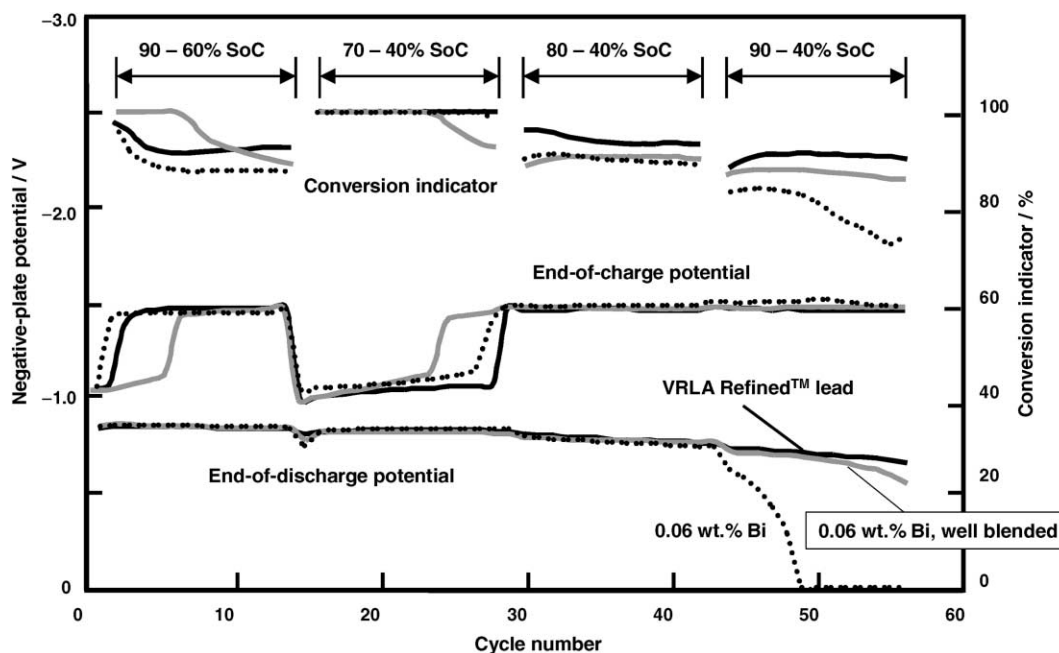


Fig. 9. Performance of negative plate prepared from well-blended, 0.06 wt.%Bi oxide.

Refined™ lead contains 0.05–0.06 wt.%Bi, the plate produced from this material gives the best performance. To resolve this discrepancy, the bismuth distribution in the cured plates has been examined with an electron probe microanalyzer (JEOL, Model 8900 Super Probe). The plate made from VRLA Refined™ lead is found to contain an even distribution of bismuth, while those prepared from oxide blended with bismuth oxide contain regions of bismuth segregation. Furthermore, the degree of segregation increases with increase in the bismuth level. Therefore, it is concluded that the beneficial effect of bismuth on charging ability is reduced because of the uneven distribution and segregation of this element in the plates.

Accordingly, the pasting was repeated. In the new experiment, the pasting was repeated. In the new experiment, the bismuth oxide was ground to a very fine powder and then introduced, with leady oxide, into a plastic container. The container was shaken for about 30 min before pasting mixing. The results are given in Fig. 9, together with those for negative plates using VRLA Refined™ oxide and oxide blended with 0.06 wt.%Bi under conventional practice. The plate containing 0.06 wt.%Bi prepared via the well-mixed procedure yields a performance close to that of a plate made from VRLA Refined™ oxide.

4. Conclusions

This study has demonstrated the benefits of bismuth addition to negative plates of lead–acid batteries. Bismuth levels upto 0.06 wt.% improve the charging ability under PSoC cycling, especially, for the low and narrow PSoC windows experienced in 42 V powernet automobile and HEV applications. In order to provide this beneficial effect, the bismuth must be distributed uniformly in the negative plates. This is best achieved by using VRLA Refined™ lead for oxide production.

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