

Further demonstration of improved performance from lead-acid batteries manufactured with bismuth-bearing high-purity lead

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Abstract

This investigation examines the cycle-life of valve-regulated lead-acid (VRLA) batteries which have been fabricated either with the manufacturer's own leady oxide (termed 'factory oxide') or with leady oxide prepared from Pasmenco VRLA Refined™ lead (termed 'VRLA Refined™ oxide'). VRLA Refined™ lead is a soft lead of high purity with a specified amount (0.05 wt.%) of bismuth. To provide a comparison of performance, benchmark tests are performed on batteries of equivalent design that have been supplied by two different manufacturers. Batteries made from factory oxide exhibit cycle-lives which exceed the minimum life specified by the Japanese Industrial Standard (JIS) test and by the International Electrotechnical Commission (IEC) test. Under the JIS procedure, the failure of both types of battery is due to expansion of the positive-plate material and subsequent extensive loss in connectivity between the constituent agglomerates of lead dioxide. By contrast, battery failure under the IEC procedure is caused by undercharging of the negative plates. The use of VRLA Refined™ oxide produces a marked improvement in battery cycle-life. Gains in performance from 675 to 800 cycles and from 510 to 675 cycles are obtained under JIS and IEC tests, respectively. It appears that the presence of bismuth at the specified level extends battery life by strengthening and increasing the connectivity in the positive-plate material (JIS test) or by raising the chargeability of negative plates (IEC test). © 2000 Elsevier Science S.A. All rights reserved.

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1. Background

To improve the performance, reliability, and life of valve-regulated lead-acid (VRLA) batteries, increasing attention is being directed towards elucidation of the beneficial/detrimental influence of elements present in small or trace amounts in the raw lead materials employed in battery manufacture [1–3]. The ultimate aim is to define the critical levels for these so-called 'minor elements' and, thereby, formulate a more stringent specification for the starting lead (termed 'soft lead') used to produce the various battery components.

Following an extensive programme of collaborative research with CSIRO, Pasmenco Metals has introduced VRLA Refined™ lead — a bismuth-bearing (0.05 wt.%),

high-purity brand of soft lead. Application of this new product (termed 'VRLA Refined™ oxide') in the manufacture of leady oxide for VRLA batteries increases the initial capacity [4], reduces the rates of oxygen and hydrogen evolution during charging [5], minimizes the problem of selective discharge of negative or positive plates during float duty [6], and lowers the rate of self-discharge [4]. The investigation reported here now examines the influence of VRLA Refined™ oxide on the cycle-life of VRLA batteries.

2. Experimental

2.1. Japanese industrial standard (JIS) test

Cycle-life tests according to the JIS at 25°C [7] were conducted on VRLA batteries (6 V, nominal $C_{20} = 4$ A h) which were received from a manufacturer in Taiwan via

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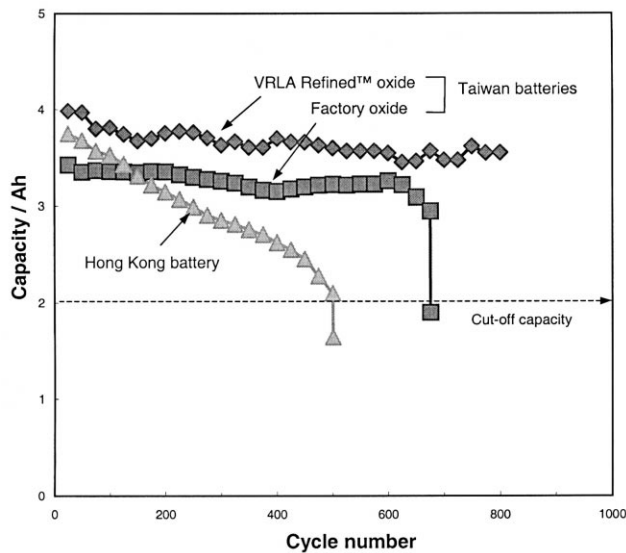


Fig. 1. Cycle-life of VRLA batteries under JIS test conditions.

Pasminco Metals. Half of the batteries were produced with the company's lead oxide (termed 'factory oxide') and the other half with VRLA Refined™ oxide. For comparison, JIS tests were also performed on batteries of similar design and capacity, but supplied from Hong Kong. These batteries were produced with the manufacturer's own factory oxide. In the JIS test, the battery is discharged at $0.25C_{20}$ A for 2 h and then recharged at a constant voltage equivalent to 2.45 V/cell (maximum current = $0.1C_{20}$ A) for 6 h. The discharge–charge sequence is regarded as 'one cycle' and the procedure is applied 24 times. On the next cycle, the battery is discharged at the same current ($0.25C_{20}$ A) until the voltage reaches 1.7 V/cell. The

25-cycle test is repeated until one of the following two conditions is met:

- (i) the discharge capacity on the 25th cycle is lower than 50% of the nominal C_{20} value;
- (ii) the battery voltage reaches 1.7 V/cell during the 2 h discharge of the JIS cycle.

2.2. International electrotechnical commission (IEC) test

Taiwan batteries were also subjected to the IEC test at $\sim 22^\circ\text{C}$ [7]. In this procedure, the battery is discharged at $0.17C_{20}$ A for 3 h and recharged at a constant voltage equivalent to 2.35 V/cell (maximum current = $0.3C_{20}$ A) for 9 h. The discharge–charge sequence is denoted as 'one cycle' and the procedure is applied 50 times. The battery is then discharged at the $C_{20}/20$ rate until the voltage reaches 1.75 V/cell. As with the JIS procedure, the 50-cycle test is repeated until one of the following two conditions is met:

- (i) the capacity measured at the $C_{20}/20$ rate is lower than 60% of the nominal C_{20} value;
- (ii) the battery voltage reaches 1.75 V/cell during the 3 h discharge of the IEC cycle.

2.3. Examination of plate morphology

After cycling, material was removed from positive and negative plates in the central cell of each battery, and was then washed and dried. Samples of the material were examined with a JEOL JSM-25S III scanning electron

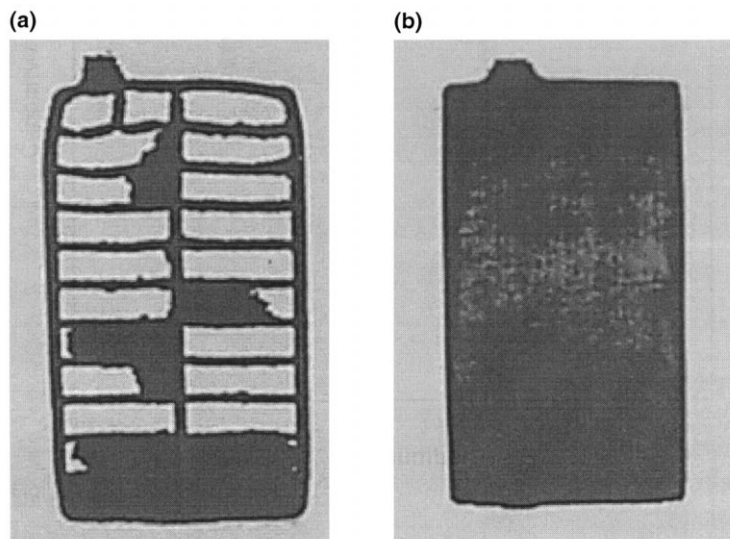


Fig. 2. Positive plates removed from (a) Hong Kong and (b) Taiwan batteries after failure under JIS test conditions.

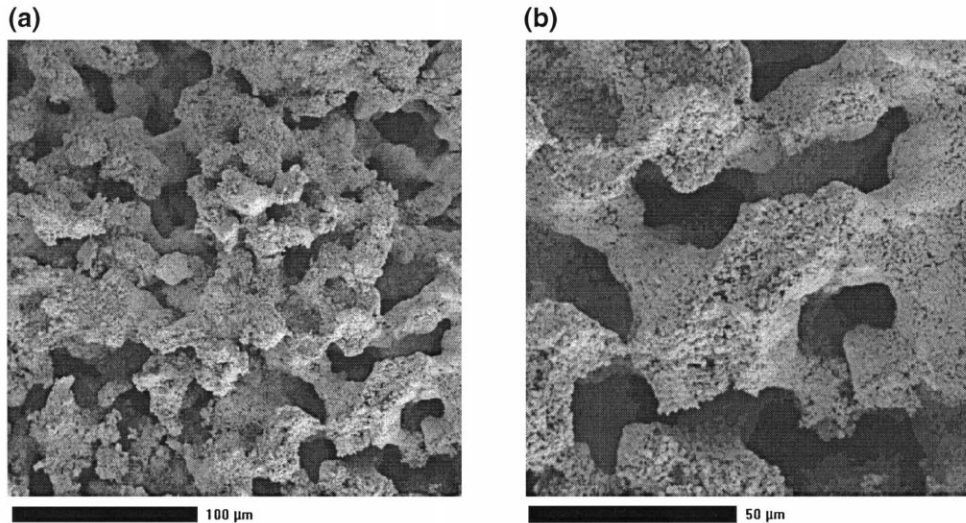


Fig. 3. Morphology (SEM) of positive-plates from Hong Kong batteries (made with factory oxide) after failure under JIS test conditions.

microscope (SEM) at an accelerating voltage of 5 kV, and with a Hitachi S5000 in-lens field emission scanning electron microscope (IFESEM) at 2 kV. To provide satisfactory imaging, a conductive film was sputtered over the entire surface of each sample; gold–palladium alloy and iridium films were used for SEM and IFESEM studies, respectively.

3. Results and discussion

3.1. JIS cycle-life

Typical results obtained from JIS tests are presented in Fig. 1. For Taiwan batteries using either factory oxide or VRLA Refined™ oxide, there is little change in capacity up to 600 cycles. With further service, however, the

capacity of the battery using factory oxide starts to decrease, while that of its counterpart using VRLA Refined™ oxide remains virtually constant. The former battery eventually failed after 675 cycles (the terminal voltage reached 1.7 V/cell during the 2 h discharge of the test regime), but the latter battery is still healthy after 800 cycles (tests are continuing). Both cycling performances are well in excess of the minimum life specified in the JIS test, viz., 200 cycles for batteries with C_{20} capacity < 24 A h [7]. Clearly, however, VRLA Refined™ oxide promotes high capacity and long life.

By contrast, the Hong Kong battery suffered an immediate, rapid and approximately linear decline in capacity (2.6 mA h per cycle). Failure occurred after 500 cycles. As observed with the Taiwan design, which used factory oxide, the terminal voltage of the battery reached 1.7 V/cell during the 2 h discharge of the test regime. Al-

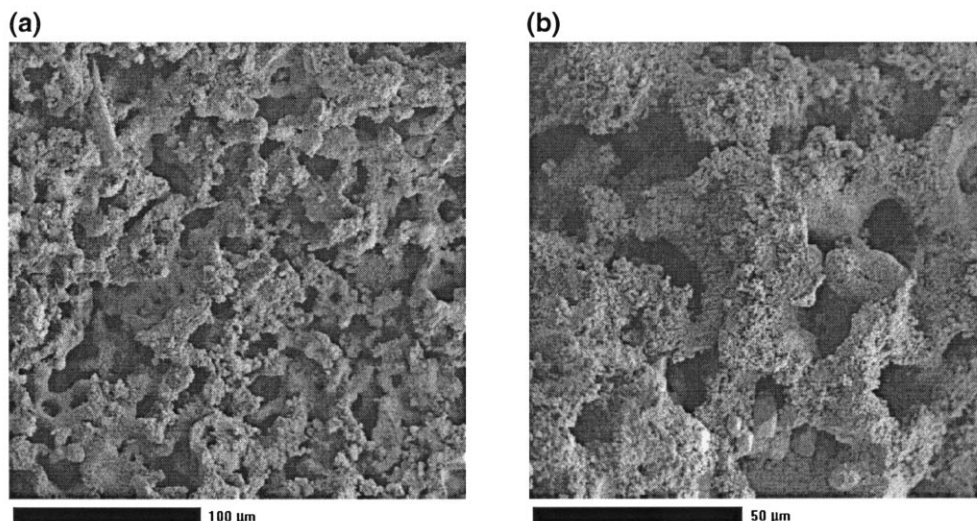


Fig. 4. Morphology (SEM) of positive-plates from Taiwan batteries (made with factory oxide) after failure under JIS test conditions.

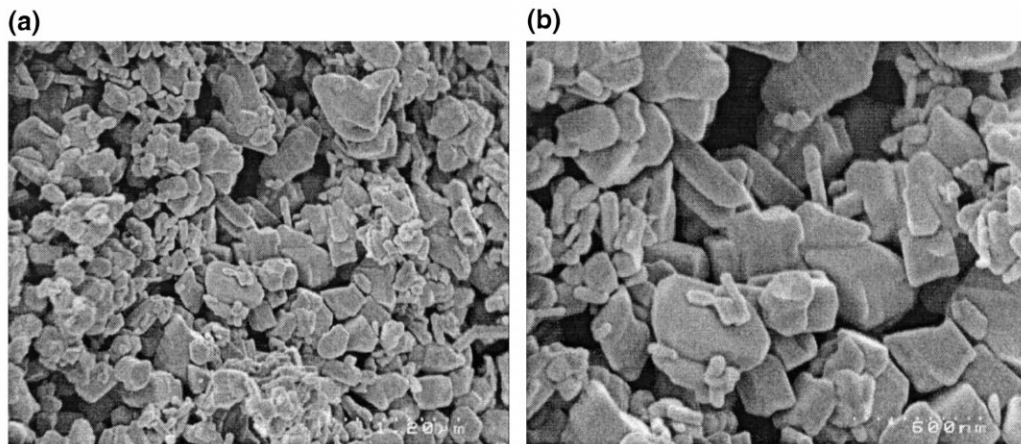


Fig. 5. Morphology (IFESEM) of positive plates from Hong Kong batteries (made with factory oxide) after failure under JIS test conditions — same sample as in Fig. 3.

though the cycling performance of the Hong Kong battery is greater than the minimum life specified in the JIS test, it is inferior to that of the Taiwan units.

After failure, the covers of the batteries were removed to allow the cell groups to be withdrawn and disassembled into individual plates. On inspection, the positive material of the Hong Kong battery was found to be very soft and, on parting of the plates, was extensively attached to the glass–microfibre separator. Accordingly, very little materials remained on the grids (Fig. 2a). Thus, although the degree of plate-group pressure (‘compression’) applied in the Hong Kong battery prohibited actual shedding, it did not prevent debilitating expansion of the positive-plate material. The positive material in the Taiwan battery also appeared to be very soft, but remained attached to the grid (Fig. 2b). All the negative plates in the Hong Kong and the Taiwan batteries exhibited good mechanical strength.

The morphology of positive-plate material in a failed Hong Kong battery is shown in Fig. 3. The structure is composed of small particles of PbO_2 that are gathered into agglomerates (Fig. 3a). The latter are interconnected to

form a three-dimensional network (Fig. 3b) with many channels (voids). These voids are considerably larger than those present in fresh (i.e., uncycled) plates and this indicates that significant expansion of the material has occurred during cycling. The positive-plate material of the Taiwan battery using factory oxide displays similar characteristics on failure (Fig. 4), but the voids are slightly smaller despite the fact that the battery had enjoyed a much longer life.

To obtain more precise details of the PbO_2 crystals which make up the individual agglomerates, the same plate samples were subjected to IFESEM examination. The resulting electron micrographs reveal that in both Hong Kong (Fig. 5) and Taiwan (Fig. 6) batteries, the individual agglomerates are composed of irregular-shaped PbO_2 crystals of varying sizes. The crystals are interconnected in a very loose manner. Clearly, good ‘connectivity’ of material has been lost during charge–discharge cycling.

The morphology of the negative-plate material in a failed Hong Kong battery is shown in Fig. 7. The material is composed mainly of irregular-shaped crystals and plate-

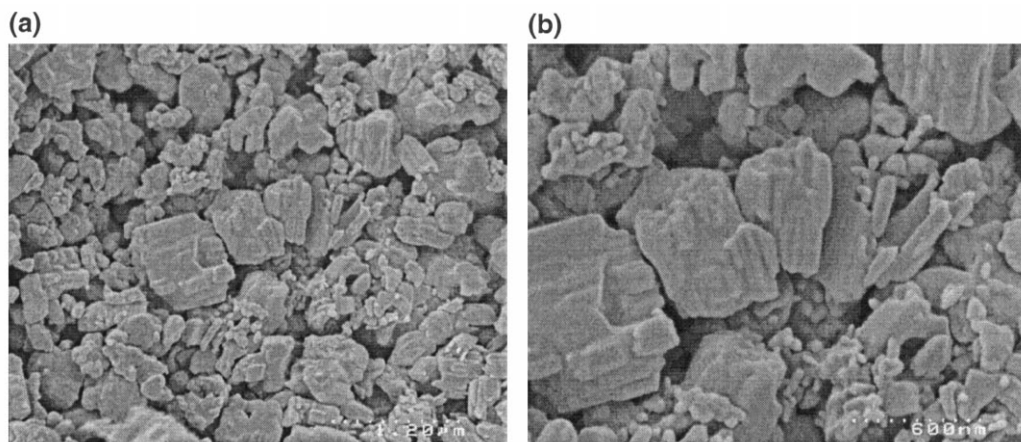


Fig. 6. Morphology (IFESEM) of positive plates from Taiwan batteries (made with factory oxide) after failure under JIS test conditions — same sample as in Fig. 4.

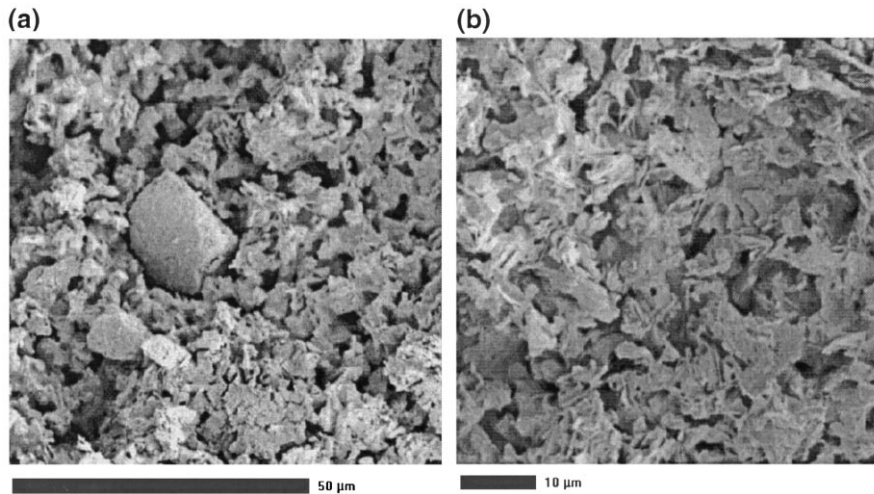


Fig. 7. Morphology (SEM) of negative-plate material from Hong Kong batteries (made with factory oxide) after failure under JIS test conditions.

like crystals. Furthermore, the negative plate still preserves an open structure. The negative plates of failed Taiwan batteries exhibit the same features.

X-ray diffraction (XRD) phase-analysis (Table 1) reveals that the positive plates of both types of battery (made with factory oxide) consist mainly of β -PbO₂, while the negative plates are comprised of either a mixture of Pb and β -PbO (Hong Kong battery) or a mixture of Pb, β -PbO, and PbSO₄ (Taiwan battery). This indicates that there is a difference in the charged state of the two plate polarities during JIS testing: the positive plate is fully charged, while the negative plate is insufficiently charged. Nevertheless, the failure of the Hong Kong batteries is due to the shedding of the positive material rather than undercharging of the negative plates. This is because the amount of material leaving the positives is greater than that remaining uncharged (as PbO) in the negatives. By contrast, the failure of the Taiwan batteries could be due to softening of positive material and/or undercharging of negative plates. To resolve this issue, one cell (under the positive terminal) from a failed battery was flooded with 1.3 rel.dens. H₂SO₄ and was then subjected to discharge at the C₂₀/20 rate. During discharge, a Hg/Hg₂SO₄ reference electrode was used to measure the positive- and negative-plate potentials.

Table 1
Phase composition of failed positive and negative plates under JIS test conditions
Taiwan battery with VRLA Refined™ oxide is still on JIS test.

| Battery ^a | Pb | β -PbO | PbSO ₄ | α -PbO ₂ | β -PbO ₂ |
|--------------------------|----|--------------|-------------------|----------------------------|---------------------------|
| <i>Hong Kong battery</i> | | | | | |
| Positive plate | – | – | – | – | 100 |
| Negative plate | 64 | 36 | – | – | – |
| <i>Taiwan battery</i> | | | | | |
| Positive plate | – | – | 2 | – | 98 |
| Negative plate | 60 | 25 | 15 | – | – |

^aBoth types of battery are manufactured with factory oxide.

A rapid fall in the potential of the positive plate was observed as the cell voltage approached 1.7 V; there was little change in the potential of the negative plate. This indicates that undercharging of the negative plates is not a major contributor to the decline in battery capacity during cycling.

In summary, significant expansion of the positive-plate material is the principal failure mode of both Hong Kong and Taiwan batteries under JIS test conditions. This expansion causes extensive loss in the connectivity of the plate material.

3.2. IEC cycle-life

The cycle-lives of Taiwan batteries under IEC test conditions are presented in Fig. 8. The capacity of both types of battery is virtually constant up to 350 cycles, but then declines. During the latter stages of service, the capacity of the battery using factory oxide decreases much faster than that of the battery using VRLA Refined™

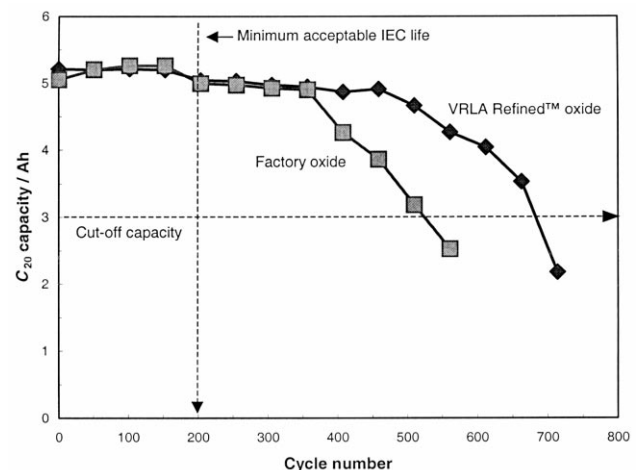


Fig. 8. Cycle-life of Taiwan batteries under IEC test conditions (note that the nominal C₂₀ capacity is underrated by the manufacturer).

oxide. Consequently, the former battery failed after 510 cycles and the latter after 675 cycles. These performances are much greater than the minimum life specified in the IEC test (200 cycles for batteries with C_{20} capacity < 24 A h [7]). Nevertheless, the battery using VRLA Refined™ oxide offers a superior cycle-life.

After failure, the positive plates of both types of battery were found to have suffered material softening. On battery disassembly, however, the material remained attached to the grid. By contrast, there was no significant loss in the mechanical integrity of the negative plates. Examples of plate condition are shown in Fig. 9.

XRD phase-analysis revealed that the positive plates in both batteries contain a high combined level of α - PbO_2 and β - PbO_2 (≥ 87 wt.%, remainder PbSO_4). This indicates that the positive plates have been charged sufficiently during the IEC test.

Cross-sectional views of the positive plates reveal (Fig. 10) that there is no difference in the extent of grid corrosion in batteries using either factory oxide or VRLA

Refined™ oxide, even though batteries with the latter oxide enjoy much longer cycle-lives. Moreover, there is still reasonable contact between the positive material and the corroded grid.

The morphology of positive plates produced from factory or VRLA Refined™ oxide is presented in Fig. 11. There is little difference in the structural features. The positive-plate material contains numerous channels similar to those observed in batteries that had failed under the JIS test (cf., Fig. 11 with Figs. 3 and 4). This indicates that expansion of material also occurs during IEC cycling. Under high magnification, IFSEM electron micrographs (Figs. 12 and 13) show that the individual agglomerates are composed of both needle-like and rectangular PbO_2 crystals. The rectangular crystals develop via the interwelding (growth) of needle-like crystals that are grouped parallel to each other (Figs. 12a and 13b). Overall, the individual PbO_2 crystals in each agglomerate have better connectivity than those in positive plates that have failed under JIS test conditions.

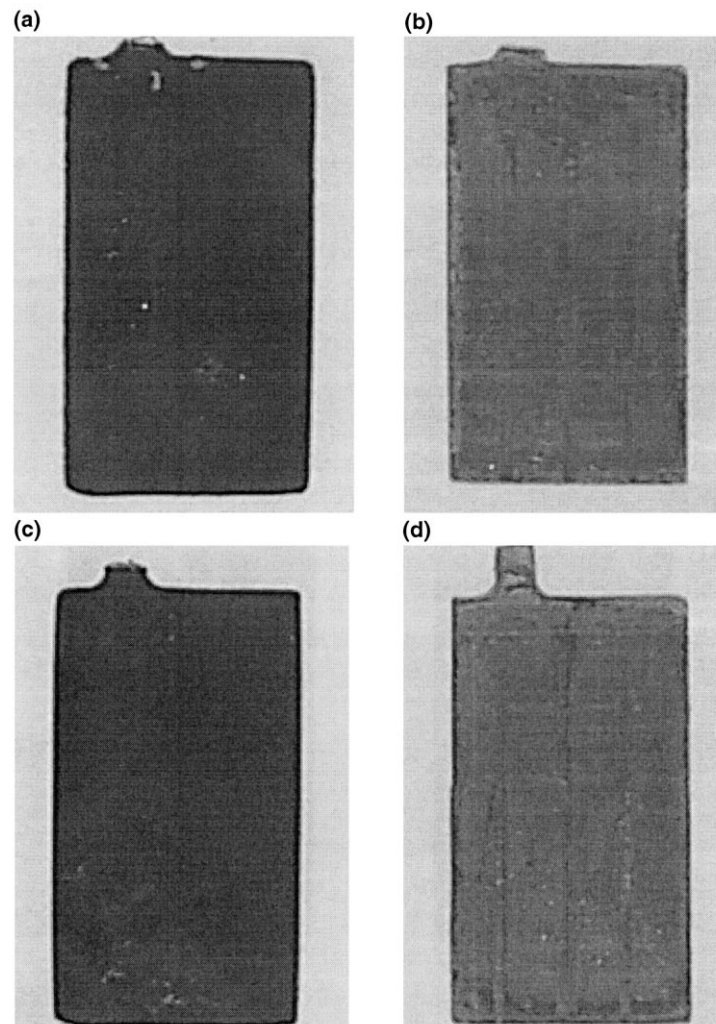


Fig. 9. Appearance of (a, c) positive and (b, d) negative plates from Taiwan batteries after failure under IEC test conditions: (a, b) factory oxide, (c, d) VRLA Refined™ oxide.

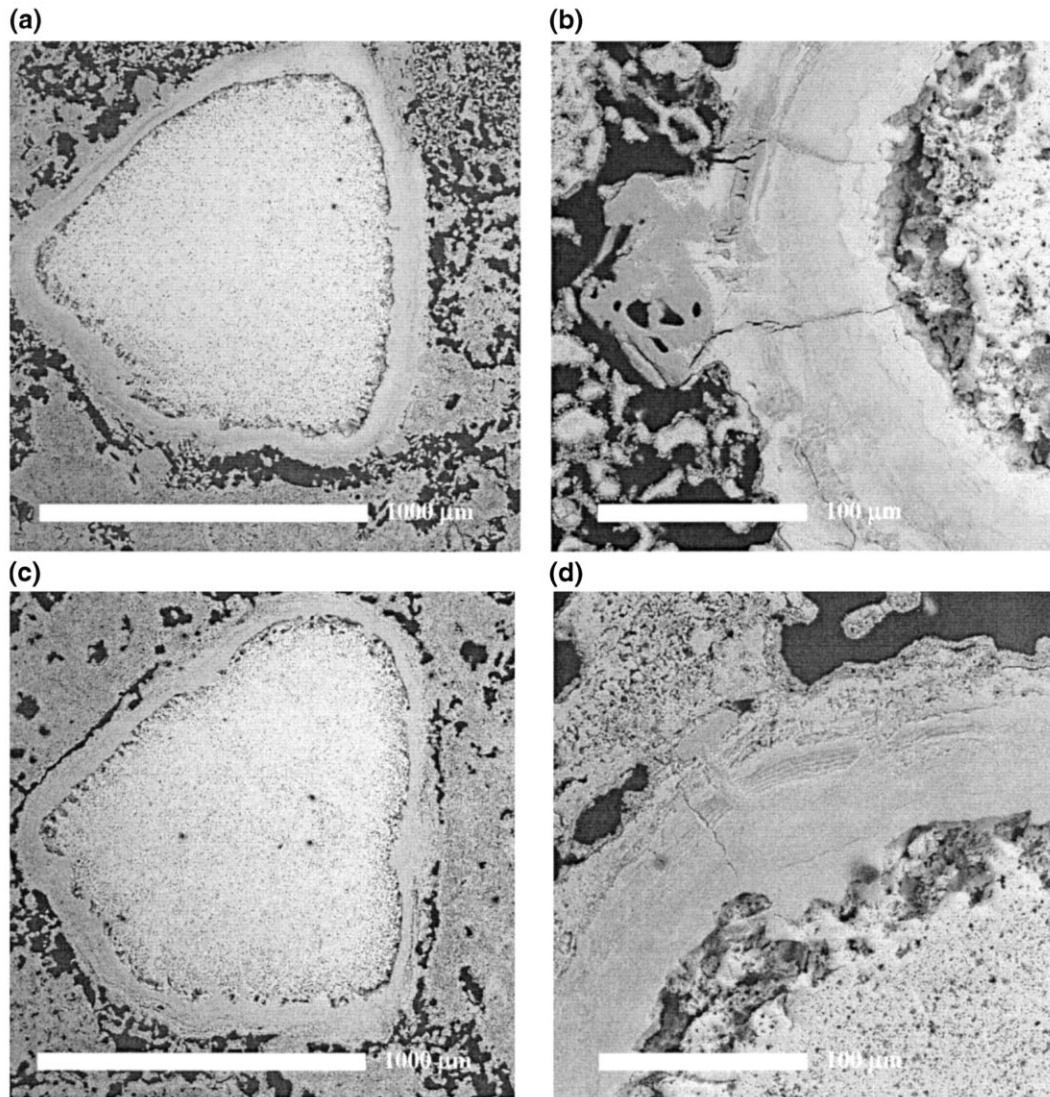


Fig. 10. Cross-sectional views (SEM) of positive plates from Taiwan batteries [made with: (a, b) factory oxide; (c, d) VRLA Refined™ oxide] after failure under IEC test conditions.

XRD phase-analysis data for the negative plates reveal that the material is comprised mainly of PbSO_4 (i.e., ~ 82 wt.%). This shows that the negative plates of both batteries are significantly undercharged. Moreover, the degree of undercharging is much greater than that observed in batteries that had failed under JIS test conditions. This may be due to the difference in the top-of-charge voltages, which are employed in these two test procedures (i.e., 2.45 V/cell in JIS vs. 2.35 V/cell in IEC). As expected, electron micrographs show that the negative plates are composed mainly of small crystals of PbSO_4 (Fig. 14). Thus, the failure of Taiwan batteries under the IEC test is due to undercharging of the negative plates.

3.3. How does VRLA Refined™ oxide improve cycle-life?

As shown above, battery failure under the JIS test is due to expansion and subsequent loss in the connectivity

of the positive-plate material. On the other hand, battery failure under the IEC test results from undercharging of the negative plates. In both tests, battery cycle-life is extended through the use of VRLA Refined™ oxide. It should be noted that this oxide contains an appreciable level of bismuth (0.05 wt.%). Other studies in the CSIRO Laboratories [4,8] have demonstrated that bismuth promotes and enhances the mechanical strength of the positive-plate material through the development of ‘bridges’ between the agglomerates. This increase in connectivity provides an explanation for the cycle-life benefits obtained with VRLA Refined™ oxide when operating batteries under JIS duty. The features by which VRLA Refined™ oxide imparts cycle-life advantages under IEC test conditions have still to be determined. It has been documented [9,10] that bismuth, either in the grid alloy or dissolved in acid, affects the morphology of PbSO_4 . The resulting

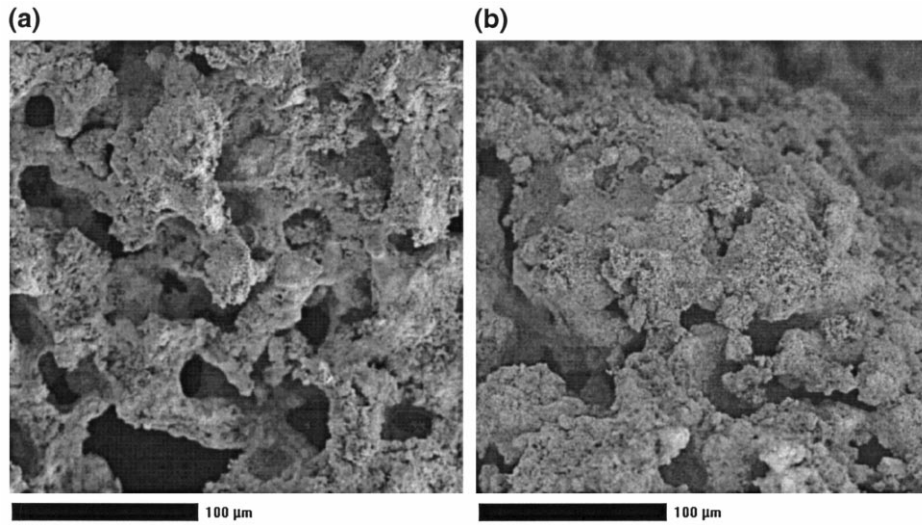


Fig. 11. Morphology (SEM) of positive plates from Taiwan batteries [made with: (a) factory oxide; (b) VRLA Refined™ oxide] after failure under IEC test conditions.

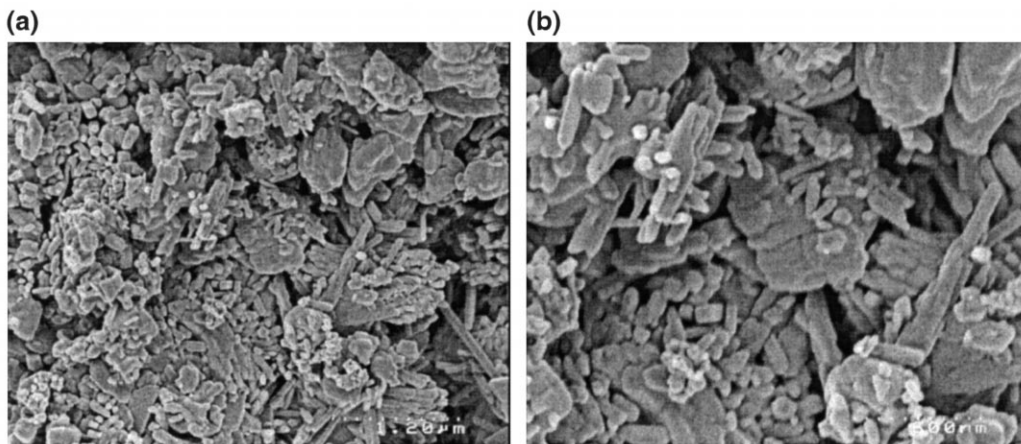


Fig. 12. Morphology (IFESEM) of positive plates from Taiwan batteries (made with factory oxide) after failure under IEC test conditions.

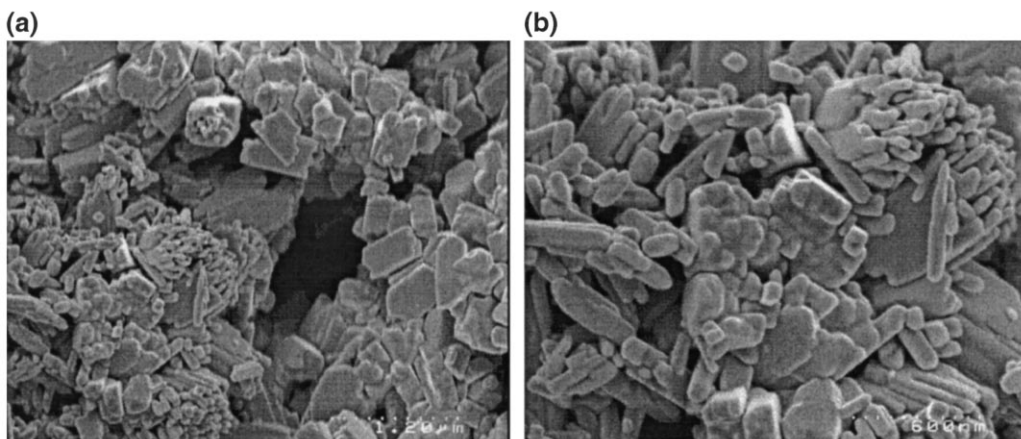


Fig. 13. Morphology (IFESEM) of positive plates from Taiwan batteries (made with VRLA Refined™ oxide) after failure under IEC test conditions.

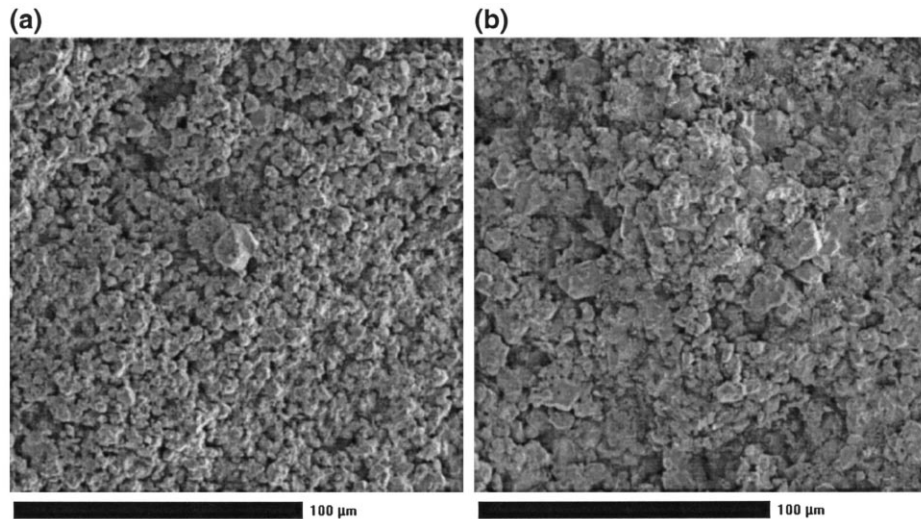


Fig. 14. Morphology (SEM) of negative plates from Taiwan batteries [made with: (a) factory oxide; (b) VRLA Refined™ oxide] after failure under IEC test conditions.

crystals display a wider range of sizes [9] and form aggregates which give rise to surfaces of greater roughness and, therefore, greater porosity [10]. Thus, it appears that bismuth can improve the chargeability of negative plates.

References

- [1] A. de Guibert, B. Chaumont, L. Albert, J.L. Caillerie, A. Ueberschaer, R. Hohn, W. Davis, M.J. Weighall, *J. Power Sources* 42 (1993) 11–24.
- [2] D.M. Rice, J.E. Manders, *J. Power Sources* 67 (1997) 251–255.
- [3] J.L. Caillerie, *J. Power Sources* 78 (1999) 182–187.
- [4] L.T. Lam, N.P. Haigh, O.V. Lim, D.A.J. Rand, J.E. Manders, *J. Power Sources* 78 (1999) 139–146.
- [5] L.T. Lam, O.V. Lim, N.P. Haigh, D.A.J. Rand, J.E. Manders, D.M. Rice, *J. Power Sources* 73 (1998) 36–46.
- [6] L.T. Lam, N.P. Haigh, C.G. Phyland, N.C. Wilson, D.G. Vella, L.H. Vu, D.A.J. Rand, J.E. Manders, C.S. Lakshmi, in: *Proceedings INTELEC '98*, San Francisco, USA, 1998, pp. 452–460.
- [7] IEC test as stated in Japan Industrial Standard, JIS C 8702, 1995.
- [8] L.T. Lam, N.P. Haigh, D.A.J. Rand, *J. Power Sources* 88 (2000) 11–17.
- [9] D.M. Rice, *J. Power Sources* 28 (1989) 69–83.
- [10] M.J. Koop, D.F.A. Koch, D.A.J. Rand, *J. Power Sources* 34 (1991) 369–380.