Capacity and cycle-life of batteries using bismuth-bearing oxide

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Abstract

An examination is made of the capacity performance of lead–acid positive electrodes which are prepared from bismuth (Bi)-bearing oxide. This oxide is produced from Pasminco VRLA Refined™ lead which contains 0.05 wt.% Bi. For comparison, benchmark tests are performed on electrodes made from oxide with virtually no bismuth (< 0.005 wt.%). The change in capacity is investigated by means of a purpose-built 'compression cell'. With this design, the positive active-material is constrained under the action of a desirable, constant force during charge–discharge cycling. In general, the capacity increases with the compressive force. Importantly, the use of Bi-bearing oxide yields higher initial capacity and then a significantly faster rise in capacity to the full value with subsequent cycling. Commercial VRLA batteries made with Bi-bearing oxide exhibit a lower rate of self-discharge than those fabricated with conventional factory oxide. In addition, Bi-bearing batteries provide good cycle-life under the International Electrotechnical Commission (IEC) test. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Bismuth; Capacity; Compression; Lead–acid battery; Self-discharge; Valve-regulated

1. Background

Most of the present specifications for the purity of soft lead (Table 1) have evolved around battery technologies which are based on antimonial grid alloys. In these designs, antimony in the positive and negative grids dominates the performance of the battery and, by comparison, minor impurities in the starting leady oxide are of little significance. Thus, in several national standards for soft lead, the tolerance levels of many elements (e.g., antimony, arsenic, cobalt, chromium, nickel and tellurium) are not specified at all, or are specified at relatively high values even though the elements are known to be harmful to lead–acid batteries [1–3]. Batteries which use lead–antimony grid alloys (i.e., 3 to 6 wt.% Sb) give good cycling performance but, as expected, produce high rates of gassing and self-discharge. Consequently, these batteries require frequent maintenance in the form of water addition. Thus, for many present applications, the market demand has moved towards 'maintenance-free' flooded or valve-regu-

lated (VRLA) technology which does not require water make-up. Since such technology requires the replacement of lead–antimony alloys with lead–calcium–tin counterparts, the levels of impurities in the leady oxide become a matter of concern. In other words, a more stringent specification for soft lead has to be formulated and adopted.

CSIRO and Pasminco Metals have collaborated in a long-term project to examine the effects of minor elements in lead materials on the performance of both flooded and valve-regulated lead–acid batteries. The research programme has also included an examination of the role of bismuth. To gain maximum battery performance, particularly from VRLA designs, it has been shown [4] that a small amount of bismuth should be added to, rather than removed from, the starting lead material. As a result, Pasminco has recently proposed [5] a new specification for soft lead to meet the increasing performance requirements of VRLA batteries. In this specification (see Table 1), the levels of impurities such as antimony, arsenic, cobalt, chromium, nickel and tellurium, that are known to be harmful to VRLA batteries, are all stated and restricted to very low values. By contrast, bismuth—which has been demonstrated as being beneficial [4,6,7]—is increased to a level (0.05 wt.%) at which significant improvements in

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Table 1
Standard and proposed specifications for soft lead used in the production of VRLA batteries

Element	Present specified levels (ppm)				Pasminco VRLA Refined™ lead (ppm)
	AS 1812-1975 Pb 99.99	ASTM B29-92 Refined pure	BS 334-1982 Type A	DIN 1719-1986 Pb 99.99	
Ag	10	25	25	10	10
As	10	5	5	10	1
Ba	ns	ns	ns	ns	10
Bi	5	25	5	5	500
Co	see footnote	ns	ns	ns	1
Cr	ns	ns	ns	ns	5
Cu	10	10	30	10	10
Fe	10	10	30	10	5
Mn	ns	ns	ns	ns	3
Mo	ns	ns	ns	ns	3
Ni	see footnote	2	10	ns	2
S	10	ns	5	ns	10
Sb	10	5	20	10	1
Se	ns	ns	ns	ns	1
Te	ns	ns	ns	ns	0.3
V	ns	ns	ns	ns	4

ns = not specified.
Co + Ni < 10 ppm.

battery performance are achieved. Soft lead with the new specification is marketed by Pasminco as VRLA Refined™ lead and has been supplied to various Australian and overseas battery companies for conversion to leady oxide (either Barton-pot or ball-mill variety) and subsequent use in VRLA batteries. The oxides and batteries have then been sent to CSIRO for evaluation as part of a research programme to determine: (i) the physicochemical characteristics of the oxides; (ii) the effects of oxide properties on the rates of hydrogen and oxygen evolution [8]; (iii) the float-service [9] and deep-discharge performance of VRLA batteries made with these oxides.

The investigation reported here has sought further improvements in both the capacity and the cycle-life of VRLA batteries through the use of Bi-bearing oxide prepared from Pasminco VRLA Refined™ lead.

2. Experimental

2.1. Compression study

2.1.1. Preparation of positive active-material

Positive and negative pastes were prepared according to conventional formulae [4]. One set of positive and negative pastes was made from Bi-bearing oxide, the other from Bi-free oxide. The pastes were applied to grids of the same dimensions (height = 133 mm, width = 106 mm, thickness = 1.2 mm) and made from alloy of the same composition (Pb–0.09 wt.% Ca–0.3 wt.% Sn). Plate curing (for both positive and negative plates) was conducted at 50°C/100% relative humidity (r.h.) for 24 h, followed by 50°C/~60%

r.h. for a further 24 h. The plates were then dried at 60°C/ambient (< 10%) r.h. for 8 to 12 h. The cured plates were assembled into 2-V cells which were produced either from Bi-bearing oxide or from a Bi-free equivalent. Each cell comprised one positive plate (enclosed in a Daramic separator envelope) and two negative plates. The cells were connected in series and sulfuric acid solution (1.070 rel. dens.) was introduced. After standing (soaking) for 30 min at 25°C, a formation current of 1.25 A was applied for 20 h. The formed plates were then washed and dried. The positive active-material (with or without bismuth) was removed from each grid and ground into powder. The powders were stored separately in plastic containers which were placed in a refrigerator for later use (see Section 2.1.2).

2.1.2. Compression cell

The compression cell used in this study is shown schematically in Fig. 1. The main apparatus was constructed from polypropylene. The cell consisted of a cylindrical positive-electrode assembly and a conventional, pasted, negative plate. A piston was arranged to move freely inside the cylindrical electrode assembly. A disc of pure lead was sealed with epoxy resin to the head of the piston. Electrical contact to the pure lead was achieved via a copper wire which passed through the centre of the piston. The outer face of the cylinder was fitted with a retaining cap in which small holes were drilled to allow free access of acid to the positive electrode. A disc of polyethylene separator was placed between the positive electrode and the inner surface of the cap. Powdered active-material was then introduced into the cylinder. The
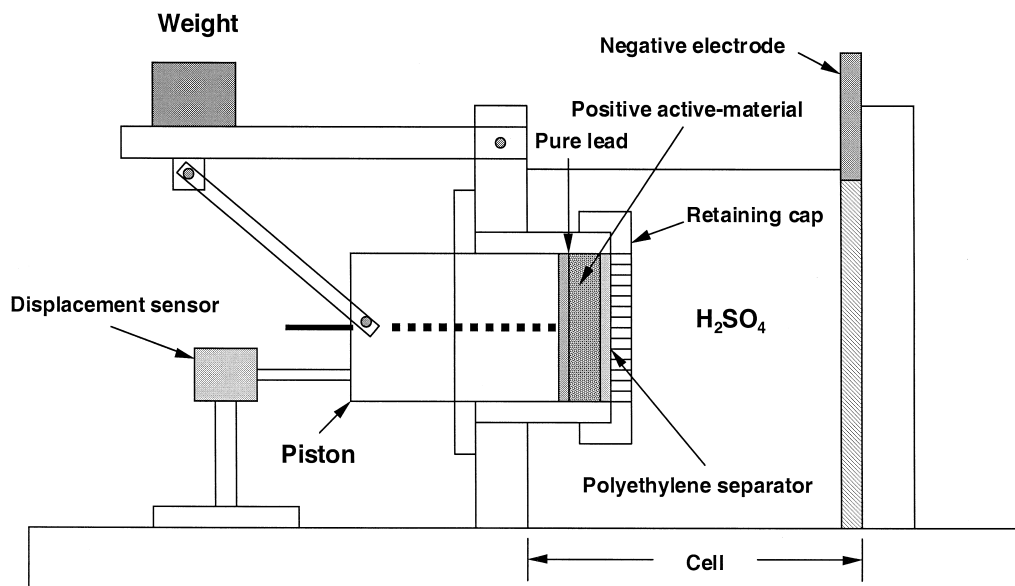
Fig. 1. Schematic diagram of compression cell.

powder was compressed by the piston via a cantilevered weight. With this design, a selected and constant force could be applied to the positive active-material during charge–discharge cycling experiments.

2.1.3. Capacity test

After the introduction of sulfuric acid solution (1.275 rel. dens.), the cell was allowed to stand for 30 min with no compression. The positive active-material was then constrained under a force of 2.9 kPa and a current of 0.05 A was applied for 16 h (i.e., a charge of 0.8 Ah). This procedure was considered to provide a 'full-charge' and was conducted before each capacity test in which the cell was placed under a given and constant compressive force (i.e., 2.9, 4.0, 4.6,... or 22.5 kPa) and subjected to 20 cycles. Each cycle involved discharging the cell at constant current of 0.125 A to 1.75 V/cell (i.e., $C_3/3$ rate) and recharging at 0.05 A (no upper voltage limit) to 120% charge return. The repetitive C_3 capacity test was also conducted under a low compression of 1.4 kPa and, in this case, this force was also used to constrain the electrode during the preceding full-charge stage.

2.2. Self-discharge test

Three commercial VRLA batteries (6 V, nominal C_{20} = 4 Ah) were supplied by an overseas manufacturer. One was produced with existing factory oxide, the other two were made with Bi-bearing oxide. Three consecutive discharge tests at the $C_{20}/20$ rate were performed in order to check the stability of the battery capacity. The batteries were then fully charged (charge return = 110%) and allowed to stand on open-circuit at room temperature ($\sim 20°C$) for several months. The open-circuit voltage of each battery was monitored continuously and the C_{20} capacity was determined at the end of the stand period. Any decrease in voltage and/or capacity provided a measure of the self-discharge of the battery.

2.3. International Electrotechnical Commission (IEC) test

Two, commercial batteries (6 V, nominal C_{20} = 4 Ah) using Bi-bearing oxide were subjected to the IEC test. [1] The batteries were discharged at $0.17C_{20}$ A for 3 h and were recharged with a constant voltage of 2.35 V/cell using a maximum current of $0.3C_{20}$ A for 9 h. The discharge–charge sequence was regarded as 'one cycle' and the procedure was repeated 50 times. The batteries were then discharged at the $C_{20}/20$ rate until the battery voltage reached 1.75 V/cell. If the discharge capacity was lower than 60% of the nominal C_{20} value, the battery was considered to have failed. Otherwise, the 50-cycle test was repeated until the C_{20} capacity fell below the 60% limit.

3. Results

Data obtained both from Pasminco customers and from investigations in the CSIRO laboratories have shown conclusively that the presence of bismuth in leady oxide (i.e., 0.05 wt.% Bi) made from VRLA Refined™ lead produces a significant increase in the initial capacity of VRLA batteries. An example of this effect during the first 10 cycles is given in Fig. 2. Clearly, the VRLA battery with Bi-bearing oxide yields persistently a higher capacity than the battery with Bi-free oxide. The latter oxide was pro-

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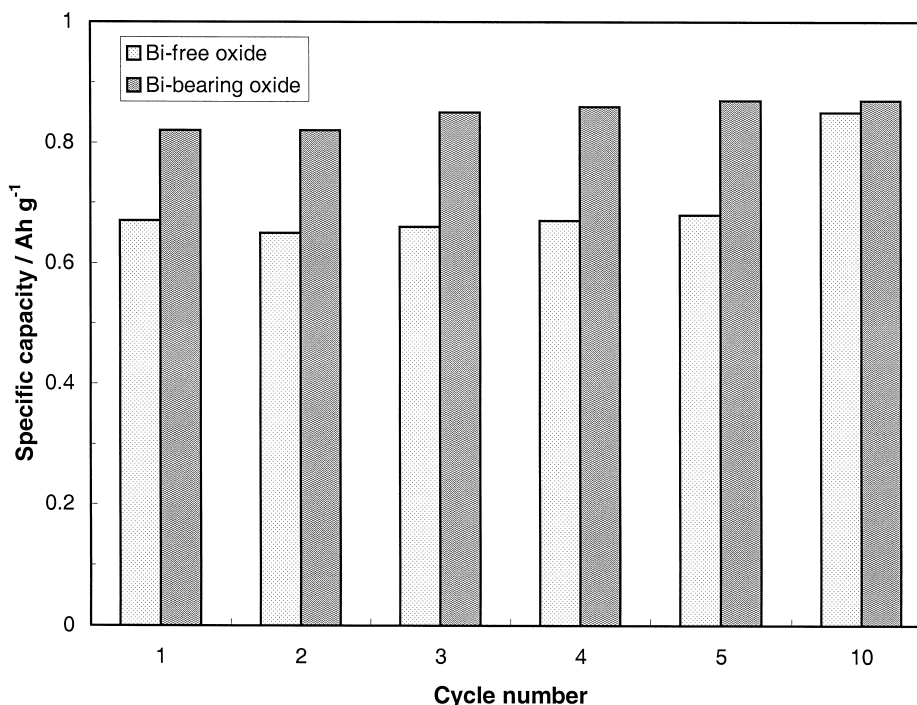[1] IEC test as stated in the Japan Industrial Standard, JIS C 8702, 1995.

Fig. 2. Increase in capacity of VRLA batteries produced from Bi-free and Bi-bearing oxide.

duced from soft lead of 99.99% purity. Moreover, whereas the Bi-free battery requires over 10 cycles to develop full capacity, the Bi-bearing counterpart gives maximum performance after only 3 cycles. In order to examine this difference in behaviour in a more systematic and scientific way, the change in capacity has been investigated by conducting compression tests on ground positive active-material in a purpose-built cell. After grinding, the skeleton of the positive active-material, which developed during plate formation, had obviously been broken up into individual agglomerates. In order for such agglomerates to participate in subsequent discharge and charge reactions, they should be in overall electrical contact with each other and with the current-collector (i.e., the pure-lead substrate, see Fig. 1). The pulverizing procedure eliminates any possible influence from the pasting, curing and formation processes such that only the 'true' effects of bismuth are examined.

3.1. Effects of compression and bismuth on electrode capacity

The influence of compressive force on the development of the capacity of an electrode prepared from Bi-free oxide is shown in Fig. 3. As expected, the capacity of the pure-lead electrode (i.e., without pulverized positive material) is very low (~ 0.03 Ah) and does not increase with cycling irrespective of the degree of compression. The initial capacities of electrodes containing pulverized positive material are also low, but are higher than that of bare

lead. This latter observation indicates that some contact between the powdered positive material and the pure lead has been established during the full-charge stage. Under a given compressive force, the capacity of the Bi-free electrode increases with cycling, and the rate of capacity increase is faster as the applied force is raised. Similar behaviour is displayed by an electrode made from Bi-bearing oxide (Fig. 4). The Bi-bearing electrode does, however, exhibit a higher initial capacity and enjoys a significantly faster increase in capacity than the Bi-free equivalent, when both electrodes are cycled under the same compression. It can therefore be concluded that the
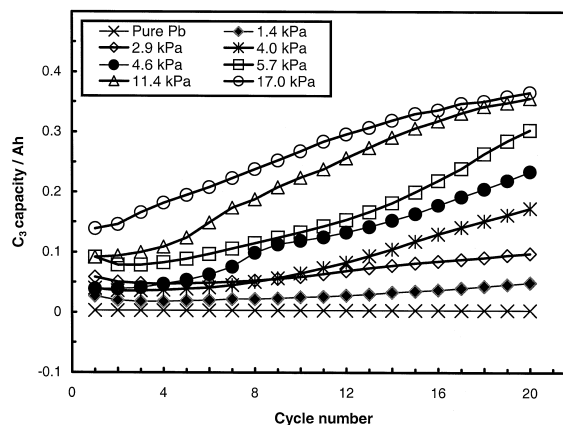

Fig. 3. Effect of compressive force on capacity of Bi-free positive electrode.
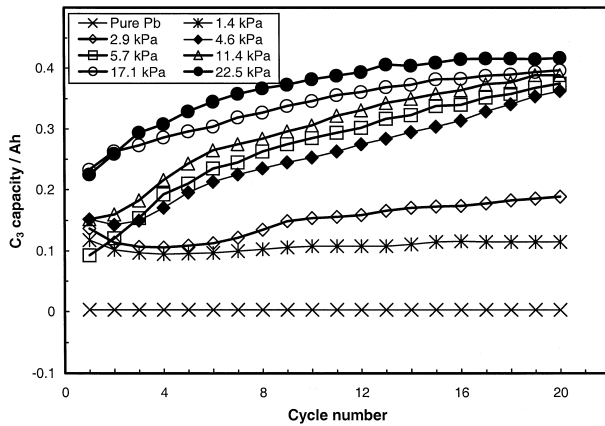
Fig. 4. Effect of compressive force on capacity of Bi-bearing positive electrode.

Fig. 6. Influence of compressive force on apparent density of powdered electrode material.

presence of bismuth enhances the electrical contacts, principally between the pulverized material and the pure-lead substrate during the full-charge stage and then mainly between individual agglomerates during subsequent cycling.

The beneficial effects of bismuth become more obvious when the electrode capacity is plotted as a function of the compressive force, see Fig. 5 (note, for clarity, only the capacity obtained on the 20th cycle is plotted for each value of the applied force). The data demonstrate that the Bi-bearing electrode always delivers a higher capacity than the Bi-free counterpart. Furthermore, the change in capacity with compressive force can be divided into three distinct regions—behaviour which is similar to the change in the specific conductivity of pressed metal oxide powders during compression [10]. In region I, the capacities of both electrodes increase very slowly with cycling, or not at all when the electrodes are compressed with forces below 2.9 kPa. By contrast, in region II, there is a rapid increase in both capacities within a narrow range of compression.
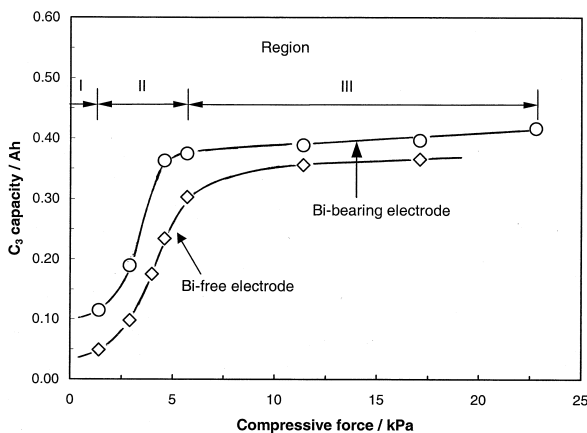
This indicates that 'bridges' are formed between the agglomerates and the pure-lead substrate and, progressively, between individual agglomerates in the electrode material itself. When sufficient bridges are formed, the increase in capacity slows down (region III). At this stage, the capacity performance of the electrode depends mainly on the rate of diffusion of acid into the porous mass.

The above findings suggest that, in order to promote bridging of the agglomerates, pulverized material electrodes should be compressed at a force above ~ 1.4 kPa. The data in Fig. 6 show that the apparent density of the material is 3.77 g cm^{-3} at this critical compressive force. Thus, in order to achieve effective discharge and charge, the pulverized material should be packed with an initial apparent density greater than 3.77 g cm^{-3}. This value is in excellent agreement with that found by Pavlov et al. [11], viz., 3.80 g cm^{-3}.

In summary, the capacity of electrodes made from pulverized active material is strongly dependent upon the 'connectivity' of the material. This connectivity is promoted and enhanced both by compression and by the presence of bismuth in the starting oxide. Consequently, Bi-bearing VRLA batteries display a more rapid development in capacity during early cycling.

3.2. Self-discharge of VRLA batteries

The change in voltage of three, commercial VRLA batteries during open-circuit stand at $\sim 20°C$ is given in Fig. 7. One battery was produced from existing factory oxide, the other two were made from Bi-bearing oxide prepared via Pasminco Refined™ lead. The initial capacity of each battery is the average value for three $C_{20}/20$ tests and the retained capacity is the discharge capacity delivered after open-circuit stand. Clearly, the two batteries using Bi-bearing oxide display the same self-discharge behaviour. After 216 days, the voltage has dropped from 6.52 to 6.39 V and the capacity from 4.82 to 3.67 Ah.
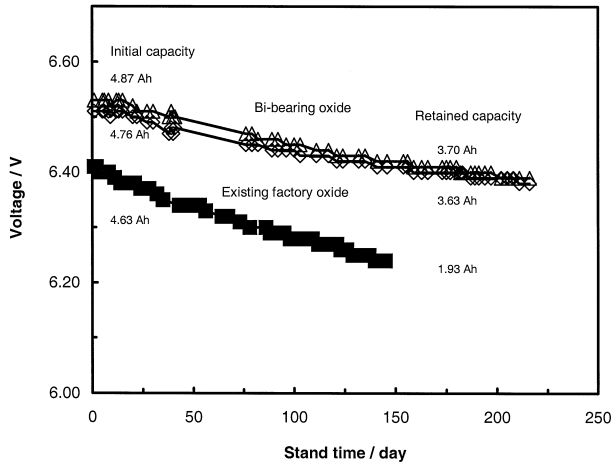

Fig. 5. Change in capacity of Bi-free and Bi-bearing electrodes with compressive force.

Fig. 7. Self-discharge performance of VRLA batteries.

Fig. 9. Cycle-life performance of VRLA batteries using Bi-bearing oxide. (Note, the nominal C_{20} capacity has been underrated by the manufacturer.)

Thus, the self-discharge rate is 0.6 mV or 5.3 mAh per day. By contrast, both the voltage and the capacity of the battery made from factory oxide decrease more rapidly, to give a higher self-discharge rate of 1.2 mV or 18.6 mAh per day.

The rates of hydrogen (negative plate) and oxygen (positive plate) evolution influence the degree of self-discharge of flooded lead–acid batteries during open-circuit stand. These rates can be accelerated by the presence of impurities [8,12]. With VRLA batteries, the self-discharge of the negative plate is enhanced by the additional reaction of oxygen recombination. The gassing rates of hydrogen and oxygen are both low for Bi-bearing oxide produced from Pasminco Refined™ lead [8], and thus the lower
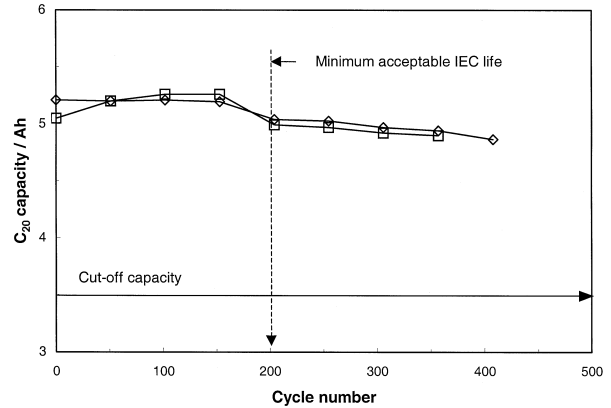
degree of self-discharge experienced by Bi-bearing VRLA batteries (Fig. 7) is understandable.

3.3. Cycle-life performance of VRLA batteries using Bi-bearing oxide

The cycle-lives of two commercial VRLA batteries (6 V, $C_{20} = 4$ Ah) using Bi-bearing oxide were evaluated under IEC test conditions. As mentioned above, the cycling involves discharging the batteries at 0.17 C_{20} A for 3 h and then charging with a constant voltage of 2.35 V per/cell using a maximum current of $0.3C_{20}$ A for 9 h. The charge return during this stage is between 102 and 106%. After 50 IEC cycles, the batteries are discharged at
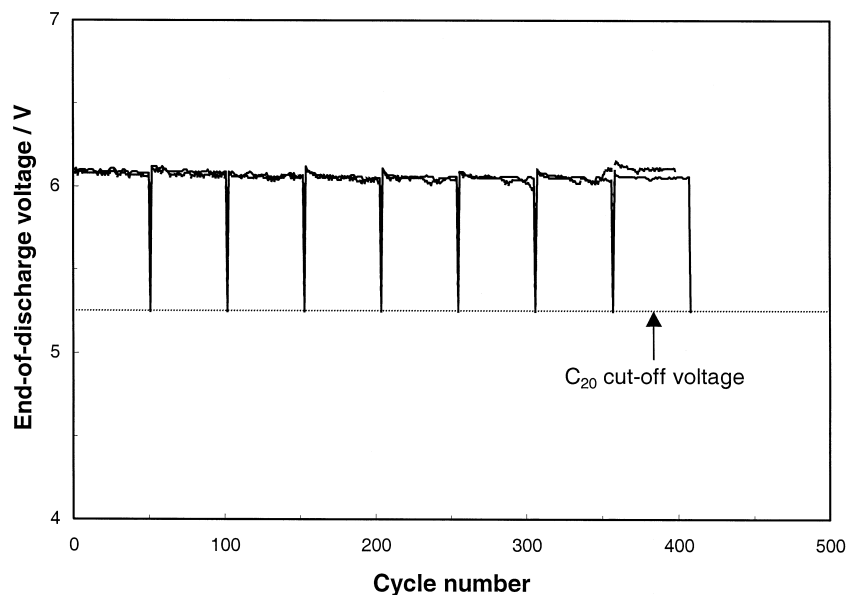

Fig. 8. End-of-discharge voltage of VRLA batteries using Bi-bearing oxide during IEC test.

the $C_{20}/20$ rate until the voltage reaches 1.75 V/cell. For both batteries, the voltage at the end of discharge of each IEC cycle remains virtually unchanged with prolonged cycling (Fig. 8). This indicates that the charge return during each cycle is sufficient to maintain the energy balance of the battery. Thus, the batteries remain healthy, even after about 400 cycles (Fig. 9). This cycling performance is much greater than the minimum life specified in the IEC test, viz., 200 cycles for batteries with C_{20} capacity < 24 Ah ([1]).

4. Discussion

Pavlov et al. [11] and Pavlov [13] have also investigated the effect of bismuth on the reconstruction of pulverized active material (obtained from charged automotive battery plates). The pulverized material was packed into tubular electrodes with spines which contained 0 to 0.8 wt.% Bi and then subjected to charge–discharge cycling. Electrodes using spines of pure-lead and Pb–6 wt.% Sb were also cycled, but in sulfuric acid solution doped with 0.005 M Bi^{3+}. When present in either the alloy or the electrolyte, bismuth was found to restore the capacity of the electrode.

Similar behaviour is also invoked by antimony [11,13,14]. On the other hand, other workers showed [15,16] that Pb^{4+} ions in the PbO_2 lattice can be substituted by antimony. The complex oxide contains Pb^{2+}, Sb^{5+} and O^{2-} ions and may have the formula $PbSb_2O_6$. It has been suggested [17] that there is an epitaxial relationship between this compound and α-PbO_2. In other studies, Dawson et al. [18] found that Sb^{3+} ions are adsorbed on PbO_2 and $PbSO_4$ much more rapidly than Sb^{5+} ions, and that adsorption of antimony (i.e., Sb^{3+} and Sb^{5+}) on PbO_2 is substantially greater than that on $PbSO_4$. These observations strongly indicate that antimony ions, after oxidative leaching from Pb–Sb grids, become incorporated in the lattice of PbO_2 and, thereby, modify both the size of the crystals and the macroscopic structure of the active material. Similar effects of antimony on the modification of PbO_2 crystallinity and on the morphology of the plate material have been observed by other authors [19–22]. Recently, Lam et al. [23] have found that the capacity loss in lead–acid batteries is governed by a progressive increase in the size of the PbO_2 particles/aggregates in the active material; this, in turn, causes a decrease in the specific surface area, in the connectivity, and in the electrochemical reactivity with acid [24]. The use of antimonial grids delays this change in morphology (smaller, more crystalline PbO_2 crystals are preserved) and, thereby, prolongs battery life.

Studies in the CSIRO laboratories reveal that bismuth, when added to the paste, is retained within the positive active-material during subsequent cycling. Furthermore, it has been well-established [25–28] that bismuth can replace Pb^{4+} ions in the PbO_2 lattice. The resulting complex oxide contains Pb^{4+}, Bi^{5+} and O^{2-} ions. Given that this oxide is similar to that formed by antimony, it is reasonable to conclude that bismuth also modifies both the size of the crystals and the macroscopic structure of the active material and, thereby, provides a similar beneficial impact on battery performance. Nevertheless, this possible influence of bismuth on crystal size and active-material structure has yet to be confirmed.

Since antimony has a low hydrogen overpotential, batteries containing this element will have high rates of hydrogen gassing and self-discharge. By contrast, Bi-bearing oxide has been shown [8] in our previous studies to produce low rates of hydrogen and oxygen evolution. Accordingly, VRLA batteries made from this oxide display low self-discharge rates and low float-currents and do not experience 'selective discharge' of either the negative or the positive plate during float service [9]. Given its low hydrogen overpotential, it is not acceptable to introduce antimony into maintenance-free, flooded or VRLA battery designs, either as a grid alloy component or as an impurity in the soft lead. The experimental results presented here demonstrate that bismuth is a suitable replacement, in terms of both preserving cycle-life and restricting self-discharge.

5. Conclusions

This study has highlighted the benefits of using bismuth-doped soft lead of high purity in the production of VRLA batteries. The presence of bismuth serves to enhance the electrical connectivity, both between the individual agglomerates of the positive material and between this material and the grid member. Consequently, the use of Bi-bearing oxide provides higher initial capacity and significantly faster attainment of full capacity. Importantly, VRLA batteries made from this oxide have low self-discharge rates and promise appreciably longer cycle-lives.

References

[1] B.K. Mahato, W.H. Tiedemann, J. Electrochem. Soc. 130 (1983) 2139–2144.
[2] H. Sanchez, Y. Meas, I. Gonzalez, M.A. Quiroz, J. Power Sources 32 (1993) 43–53.
[3] L.T. Lam, J.D. Douglas, R. Pillig, D.A.J. Rand, J. Power Sources 48 (1994) 219–232.
[4] L.T. Lam, R. De Marco, J.D. Douglas, R. Pillig, D.A.J. Rand, J. Manders, J. Power Sources 48 (1994) 113–128.
[5] D.M. Rice, J.E. Manders, J. Power Sources 67 (1997) 251–255.
[6] M. Maja, N. Penazzi, J. Power Sources 22 (1988) 1–9.
[7] K. Miyazaki, M. Sumida, in: K.R. Bullock, D. Pavlov, (Eds.), Proc Symp. Advances in Lead–Acid Batteries, Proc Vol. 84-14, The Electrochemical Society, Pennington, NJ, USA, 1984, pp. 78–85.

[8] 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.

[9] 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, Proceedings INTELEC '98, San Fransico, USA, 1998, pp. 452–460.

[10] A. Winsel, E. Voss, U. Hullmeine, J. Power Sources 30 (1990) 209–226.

[11] D. Pavlov, A. Dakhouche, T. Rogachev, J. Power Sources 30 (1990) 117–129.

[12] D. Berndt, Maintenance-Free Batteries, Research Studies Press, Taunton, Somerset, England, pp. 97–100.

[13] D. Pavlov, J. Power Sources 33 (1991) 221–229.

[14] D. Pavlov, A. Dakhouche, T. Rogachev, J. Power Sources 42 (1993) 71–88.

[15] D.E. Swets, J. Electrochem. Soc. 120 (1973) 925–926.

[16] A. Arifuku, H. Yoneyama, H. Tamura, J. Appl. Electrochem. 11 (1981) 357–360.

[17] R.J. Hill, J. Solid State Chem. 71 (1987) 12–18.

[18] J.L. Dawson, M.I. Gillibrand, J. Wilkinson, in: D.H. Collins (Ed.), Power Sources 3, Oriel, Newcastle-upon-Tyne, 1970, pp. 1–9.

[19] H.N. Cong, A. Ejjenne, J. Brenet, P. Faber, J. Appl. Electrochem. 11 (1981) 373–386.

[20] J. Burbank, J. Electrochem. Soc. 111 (1964) 765-768, 1112-1116.

[21] E.J. Richie, J. Burbank, J. Electrochem. Soc. 117 (1970) 299–305.

[22] T.F. Sharpe, J. Electrochem. Soc. 124 (1977) 168–173.

[23] L.T. Lam, H. Ozgun, O.V. Lim, J.A. Hamilton, L.H. Vu, D.G. Vella, D.A.J. Rand, J. Power Sources 53 (1995) 215–228.

[24] J. Yamashita, Y. Matsumaru, J. Appl. Electrochem. 18 (1988) 595–600.

[25] I.H. Yeo, D.C. Johnson, J. Electrochem. Soc. 134 (1987) 1973–1977.

[26] I.H. Yeo, S. Kim, R. Jacoboson, D.C. Johnson, J. Electrochem. Soc. 136 (1989) 1395–1400.

[27] H. Change, D.C. Johnson, J. Electrochem. Soc. 137 (1990) 2452–2457.

[28] L.A. Larew, J.S. Gordon, Y.L. Hsiao, D.C. Johnson, D.A. Buttry, J. Electrochem. Soc. 137 (1990) 3071–3078.