Understanding the mechanism by which bismuth improves lead-acid battery capacity

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Abstract

To elucidate the mechanism by which bismuth enhances the capacity of valve-regulated lead-acid (VRLA) batteries, model experiments are performed on pulverized positive electrodes produced either from leady oxide, which contains virtually no bismuth (termed 'Bi-free oxide'), or from Pasminco VRLA Refined™ oxide, which is of high purity and contains a specified amount (0.05 wt.%) of bismuth. The electrodes are compressed under a range of pressures (1.4 to 60 kPa). Below 40 kPa, the presence of bismuth increases the initial capacity. At all pressures, bismuth enhances the rate at which the capacity develops during cycling. Reconnection of the separated agglomerates of lead dioxide is the key factor in restoring the capacity of the pulverized electrode. Electron micrographs reveal that there are two essential types of contact in the positive material: (i) 'micro-contact' between individual irregular-shaped or individual needle-like crystals, to form the agglomerates; (ii) 'macro-contact' between individual agglomerates, to form the skeleton of the positive mass. Bismuth encourages the growth of fine needle-like crystals on the surface of the agglomerates. These crystals spread out and inter-weld to form 'bridges' between the agglomerates and, thereby, consolidate the porous mass of the electrode. This influence of bismuth on morphology is considered to be responsible for the demonstrated improvements in capacity performance. © 2000 Elsevier Science S.A. All rights reserved.

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1. Background

An extensive collaborative research programme between CSIRO and Pasminco Metals has resulted in the development of VRLA Refined™ lead — a bismuth-bearing (0.05 wt.%), high-quality soft lead for the production of leady oxide (termed VRLA Refined™ oxide) for use in valve-regulated lead-acid (VRLA) batteries. Since the introduction of this new product, a number of Pasminco customers and CSIRO have demonstrated conclusively that VRLA Refined™ lead improves battery performance in terms of: (i) low oxygen- and hydrogen-gassing rates [1]; (ii) less risk of selective discharge of negative or positive plates during float duty [2]; (iii) high initial capac-ity [3]; (iv) low self-discharge rate [3]; (iv) long cycle-life [4]. The objective of this investigation is to elucidate the mechanism by which bismuth in the oxide improves the capacity of VRLA batteries.

The parameters which determine the capacity of a battery plate can be broadly classified into two groups. The 'external' parameters include charge–discharge current, voltage, temperature, and acid concentration. The 'internal' parameters include impurities in the leady oxide, grid design, pasting technique, curing route, and the physico-chemical characteristics (e.g., specific surface area, porosity, phase composition) of the formed-plate material. In the studies reported here, any possible influence from the pasting, curing, and formation processes is eliminated by conducting capacity tests on pulverized positive material produced from high-purity leady oxide without bismuth (termed 'Bi-free oxide') or from VRLA Refined™ oxide which contains 0.05 wt.% Bi. Under such experimental conditions, only the 'true' effects of bismuth are manifested for a given set of external parameters.

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2. Experimental

2.1. Compression study

2.1.1. Preparation of positive material

Positive and negative pastes were prepared according to the procedure reported previously [5]. One set of positive and negative pastes was made from VRLA Refined™ oxide, the other from Bi-free oxide. The latter oxide was supplied by a manufacturer in the USA. The pastes were applied to grids of the same dimensions and made from the same alloy. 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 r.h. (<10%) for 8 to 12 h. The cured plates from each oxide source were assembled into cells (one positive, two negatives). The cells were connected in series and sulfuric acid solution (1.07 rel.dens.) was introduced. After standing 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 material was removed from each grid and ground into powder.

2.1.2. Compression cell

The compression cell used in this study is shown schematically in Fig. 1. The cell consisted of a cylindrical positive-electrode assembly and a pasted negative plate. A disc of pure lead was attached to the head of a piston, which could move freely inside the cylindrical electrode assembly. The outer face of the cylinder was fitted with a perforated retaining cap that allowed 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. The positive electrode was made from powdered formed-material (see Section 2.1.1) which was compressed by the piston via a cantilevered weight. With this design, a selected and constant force could be applied to the positive material during charge–discharge cycling experiments.
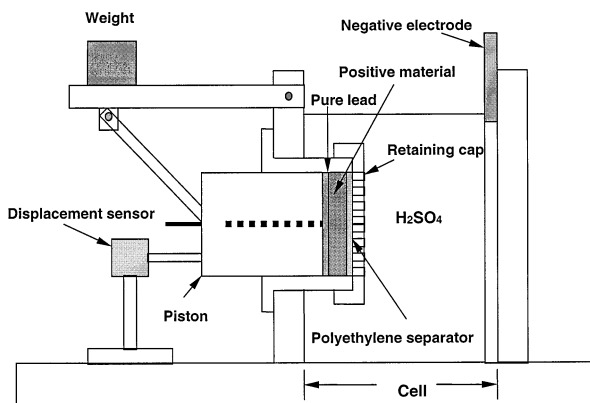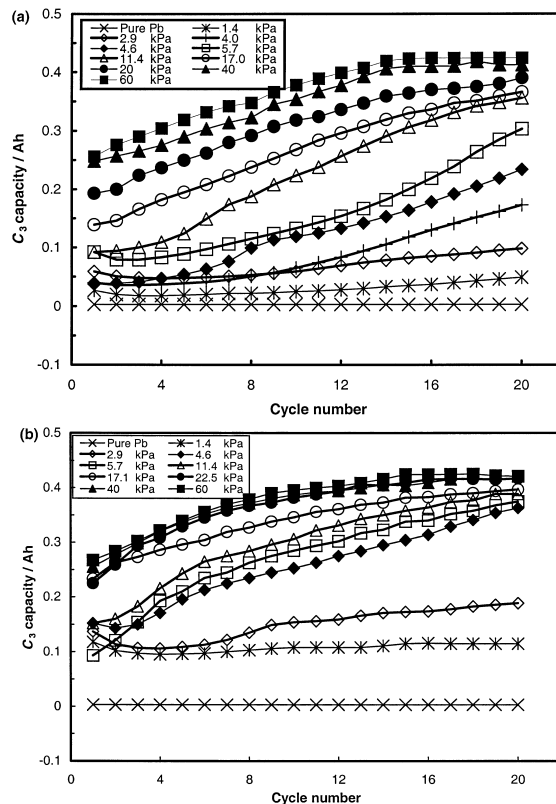

Fig. 2. Effect of pressure on capacity of (a) Bi-free (b) Bi-bearing electrode.

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. The positive material was then constrained at a pressure of 2.9 kPa and a current of 0.05 A was applied for 16 h (i.e., 0.8 A h). This procedure was considered to provide a 'full-charge' and was conducted before each capacity test in which the electrode was compressed under a given constant force and subjected to 20 cycles. Each cycle involved discharging the cell at a constant current 0.125 A to 1.75

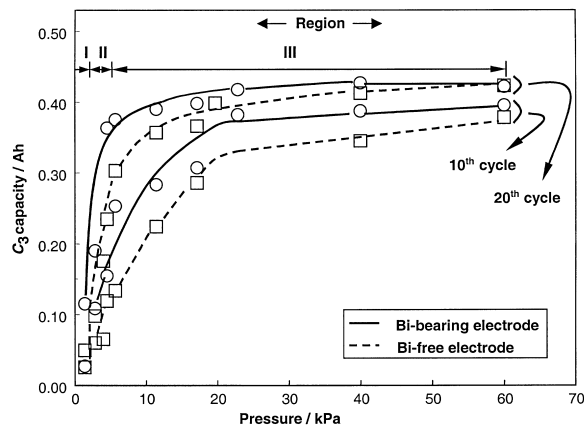Fig. 1. Schematic diagram of compression cell.

Fig. 3. Change in capacity with pressure of electrodes prepared from Bi-free and VRLA Refined™ oxide.
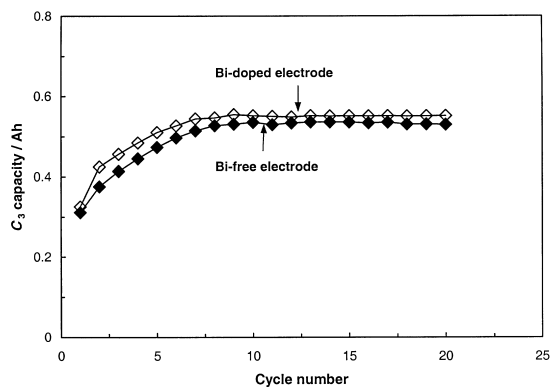
Fig. 4. Capacity of Bi-free and Bi-doped electrodes at 40 kPa.

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 further conducted at a low pressure of 1.4

kPa, which was also used to constrain the electrode during the full-charge stage.

2.2. Morphology examination

The morphology of samples of both formed and cycled powder was examined by means of a Hitachi S5000 in-lens field-emission scanning electron microscope (IFESEM) at an accelerating voltage of 2 kV. To provide satisfactory imaging, an iridium film (∼ 3.5 nm) was sputtered over the entire surface of each sample.

3. Results

3.1. Effects of pressure and bismuth on electrode capacity

The effect of pressure on the development of the capacity of positive electrodes prepared from Bi-free and Bi-
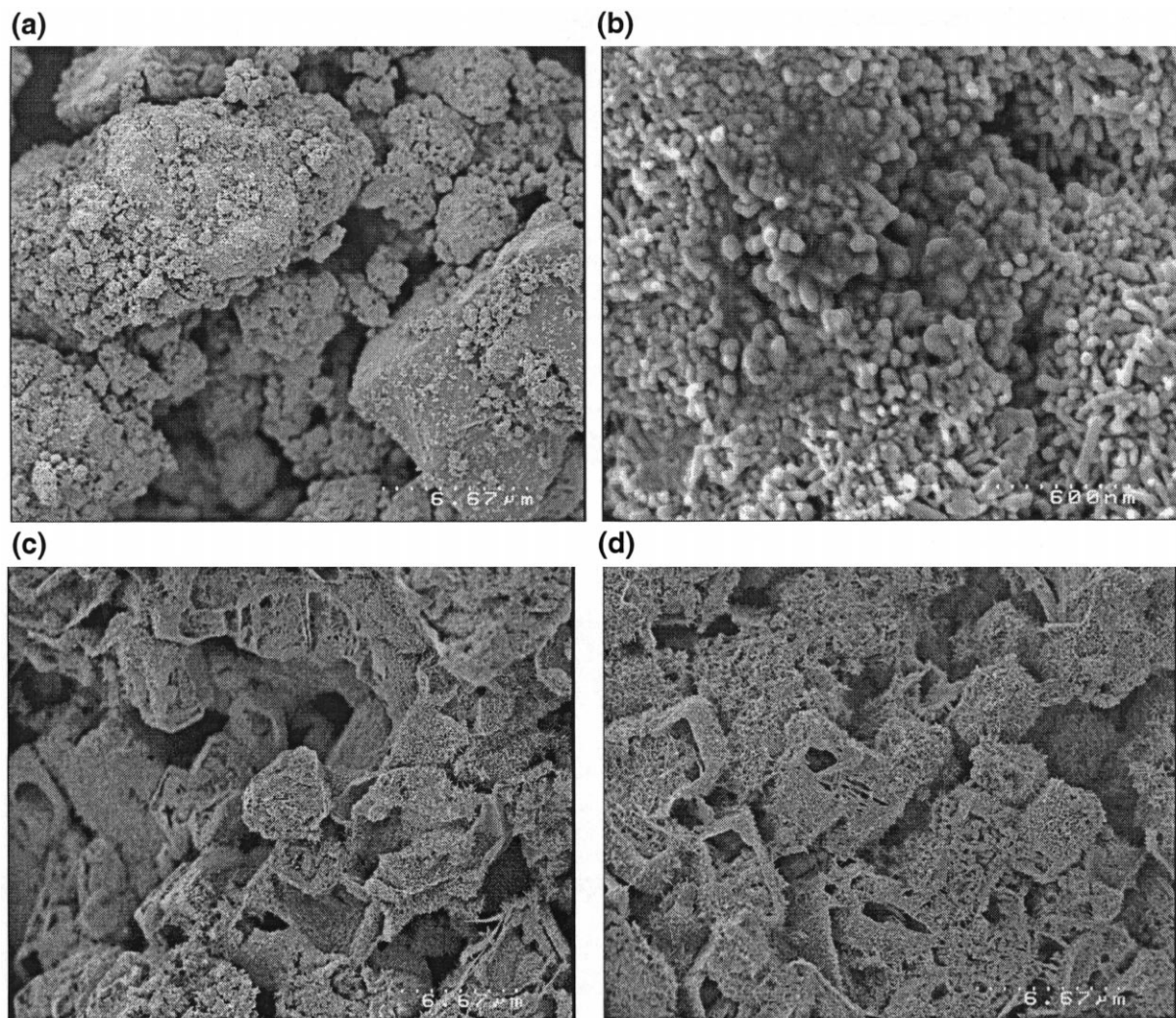

Fig. 5. Electron micrographs (IFESEM) of: (a,b) formed material, made with Bi-free oxide, after pulverization; (c) cycled material made with Bi-free oxide; (d) cycled material made with Bi-free oxide and doped with Bi metal particles after formation.

bearing oxides is shown in Fig. 2(a) and (b), respectively. The initial capacities of electrodes made from pulverized material are low but, as expected, higher than that of bare lead. This suggests that some degree of contact has been established between the powdered material and the pure-lead substrate during the full-charge stage. For pulverized electrodes, the initial capacity, the rate of capacity development, and the capacity at the 20th cycle all increase with increase in pressure up to ∼ 40 kPa, and are further enhanced by the presence of bismuth. At higher pressures, there is little difference in the initial and final capacities of the two types of electrode. The final capacity is now at a limiting (full) value. Importantly, though, this capacity is reached faster by the Bi-bearing electrode.

The beneficial effects of bismuth become more obvious when the electrode capacities obtained at 10th and 20th cycle are plotted as a function of pressure (Fig. 3). For both electrodes, the change in capacity 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 [6]. In region I, the capacities of both electrodes increase very slowly with cycling, or not at all when the electrodes are compressed at pressures smaller than 2.9 kPa. By contrast, in region II, there is a rapid increase in capacity within a narrow range of pressure. This indicates that 'bridges' are formed between the agglomerates and the pure-lead substrate and, progressively, between the individual agglomerates themselves. When sufficient bridges are formed, the increase in capacity slows down (region III). At this stage, the capacity performance of the electrode is also influenced by the rate of diffusion of acid into the porous mass. At the 10th cycle, the data demonstrate that, in all three regions, the Bi-bearing electrode always delivers a higher capacity than its Bi-free counterpart. This also holds for capacities obtained at the 20th cycle, except in region III when both electrodes are compressed at pressures above 40 kPa. Under such conditions, there is little difference in the capacities of the two electrodes. This is because the capacities have developed to their full values and are no longer
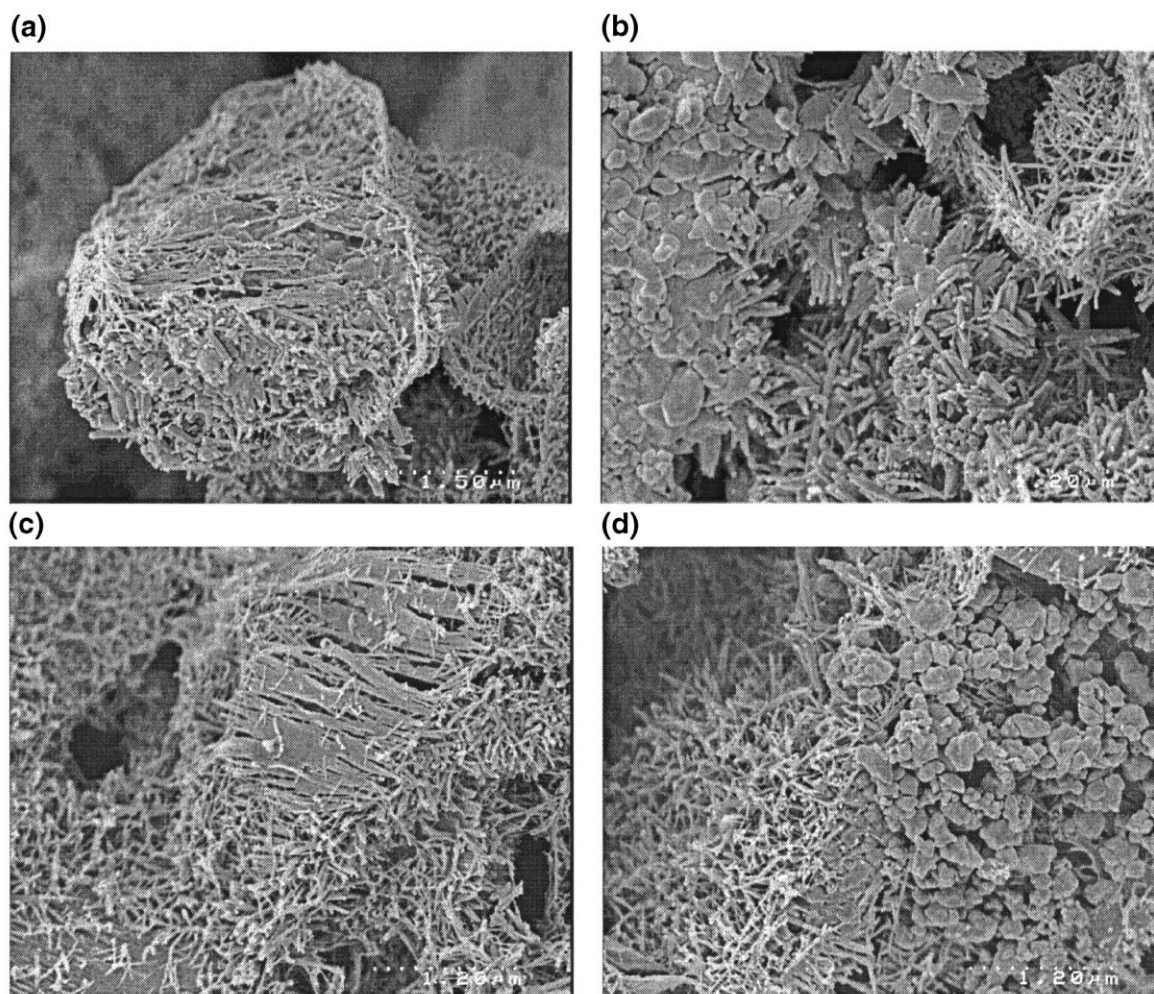

Fig. 6. Electron micrographs (IFESEM) of: (a,b) cycled material made with Bi-free oxide; (c,d) cycled material made with Bi-free oxide and doped with Bi metal particles after formation.

affected by the degree of 'connectivity' of the positive material, but by the rate of diffusion of acid into the porous mass.

In summary, the capacity of an electrode made from pulverized material is strongly dependent upon the connectivity of the material. This property is enhanced by the application of a compressive force (as expected), and by the presence of bismuth in the starting oxide material. These effects provide an explanation for the more rapid development in the capacity, during early cycling, of VRLA batteries produced from VRLA Refined™ oxide.

3.2. How does bismuth improve battery capacity?

Studies in the CSIRO laboratories have revealed that bismuth, when added to the paste, is retained within the positive material during subsequent cycling. Research conducted by Pavlov et al. [7,8] has shown that the presence of bismuth, in either the grid alloy or the electrolyte, restores the capacity of tubular electrodes, which are filled with pulverized material obtained from charged automotive battery plates. It has also been documented [9–12] 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. Thus, it is reasonable to suggest that bismuth exerts its beneficial effect on capacity via crystal modification of the positive material. To test this hypothesis, a series of experiments was conducted in a second compression cell. The design of this cell was similar in all respects to that shown in Fig. 1, except that the holes drilled in the retaining cap were of a larger diameter. The modification allowed faster access of acid to the pulverized positive material and faster escape of oxygen bubbles from the electrode during charging.

Tests were conducted initially on a Bi-free electrode at 40 kPa for 20 cycles, and then on an electrode which contained the same formed-material powder but doped with small particles of bismuth metal. In the latter case, any improvement in capacity will be induced by bismuth itself. The capacity performance of both electrodes is given
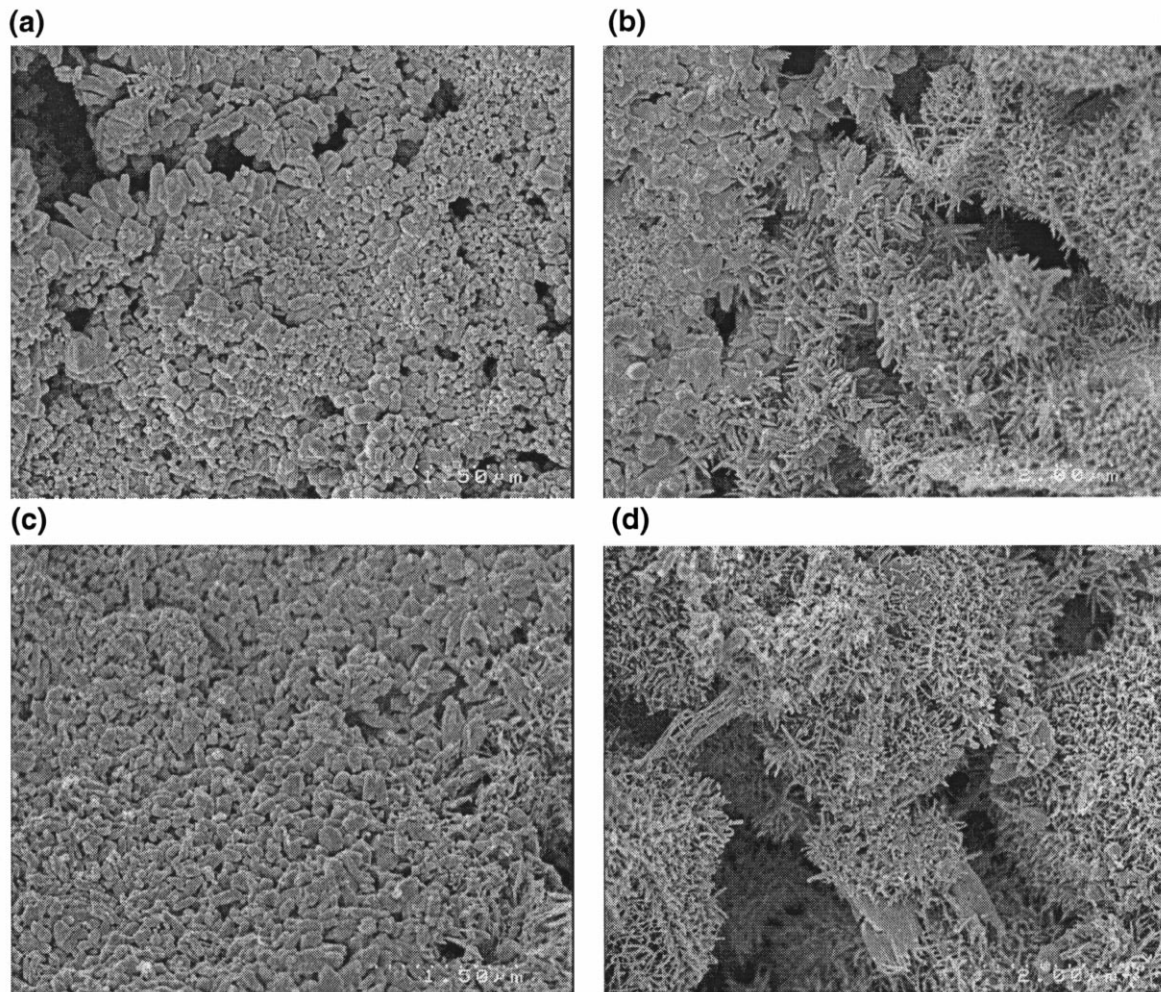
Fig. 7. Electron micrographs (IFESEM) of: (a,b) cycled material made with Bi-free oxide; (c,d) cycled material made with Bi-free oxide and doped with Bi metal particles after formation.

in Fig. 4. The initial capacity of the Bi-free electrode is very high (i.e., 0.31 A h) and develops to its full value after 8 cycles (i.e., 0.53 A h). The initial and full capacities are higher than those of any electrode examined previously (see Fig. 2). It is clear, therefore, that the change in cell design to facilitate the access of acid and the release of oxygen has exerted a marked effect on electrode capacity. The performance of the Bi-doped electrode is also improved and is slightly better than that of the Bi-free electrode. Thus, again, the presence of bismuth is found to enhance electrode capacity.

The morphology of each cycled material was examined, together with that of the formed-material powder. Electron micrographs reveal that powdered, Bi-free formed-material consists of agglomerates (Fig. 5(a)) that are composed of small, ill-defined crystals PbO_2 (centre, Fig. 5(b)). There are also many, tiny, needle-like crystals, which grow outwards from the surfaces of the agglomerates (bottom right, Fig. 5(b)). After cycling, the material is made up of PbO_2 agglomerates, which are of irregular shape and differing size, and have hollow centres (Fig. 5(c)). This change in morphology is independent of the presence of bismuth (cf. Fig. 5(c) with (d)). At higher resolution, it is found that the agglomerates of both types of material are composed of either well-defined, needle-like crystals or irregular-shaped crystals (Fig. 6). The needle-like crystals are woven into each other to form the walls of the hollow agglomerates, i.e., a 'bird's nest' type of structure is produced (Fig. 6(a) and (c)). It is also noted that these crystals have sizes which are much greater than those of crystals in the formed (i.e., uncycled) material (cf. Fig. 6 with Fig. 5(b)). The irregular-shaped crystals are packed into a crust (Fig. 6(b,d)). There is little difference in the size of the irregular-shaped crystals in Bi-free and Bi-doped material (cf. Fig. 7(a) with (c)). By contrast, the needle-like crystals in Bi-doped material are generally thinner or finer than those in the Bi-free equivalent (cf. Fig. 7(b) with (d)). Thus, the number of needle-like crystals per unit surface area of the agglomerates is greater in Bi-doped material.

From the above IFESEM examination, it is deduced that two types of contact can exist in both Bi-free and Bi-doped positive material. One is the contact between
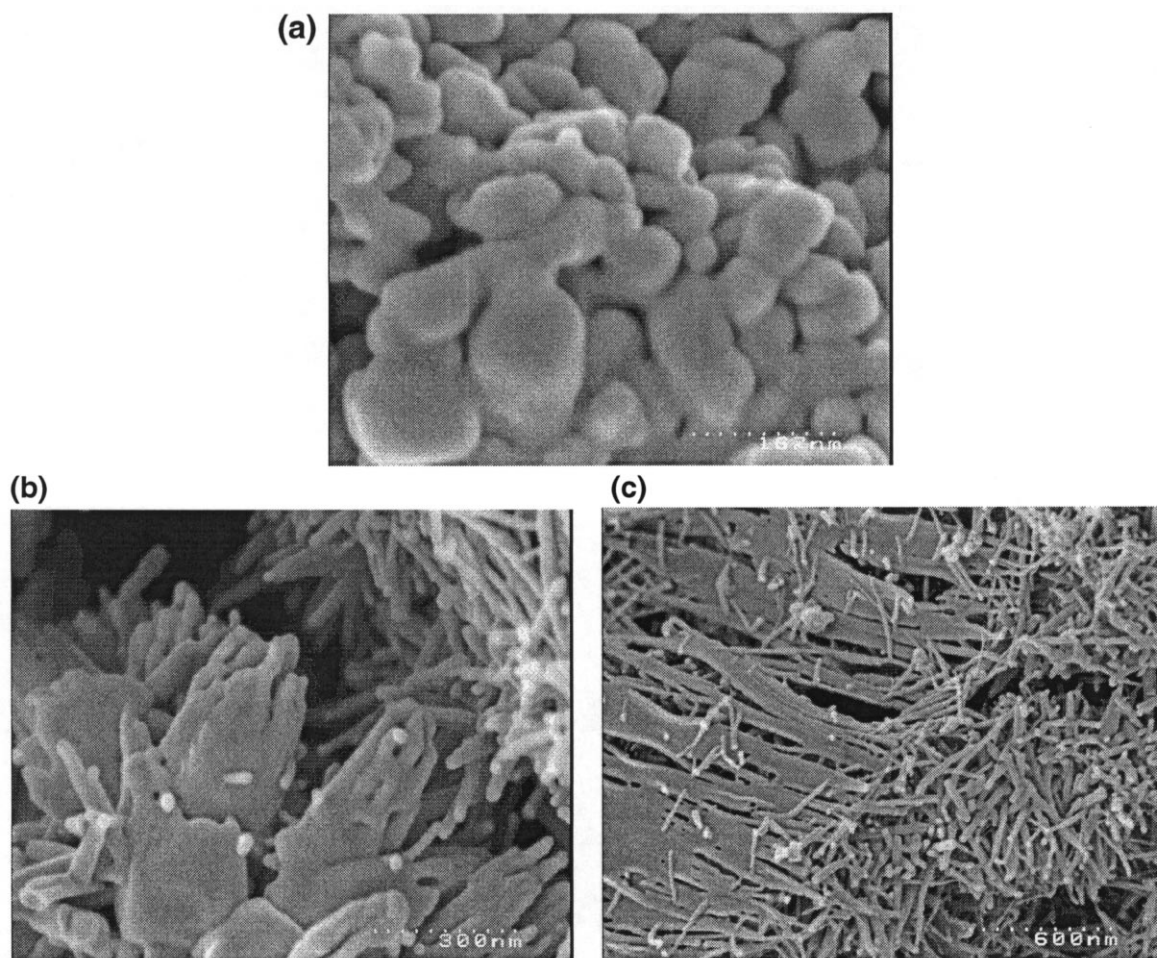

Fig. 8. Electron micrographs (IFESEM) showing micro-contact between: (a) irregular-shaped crystals in cycled material made from Bi-free oxide; (b) needle-like crystals in cycled material made from Bi-free oxide; (c) needle-like crystals in cycled material made from Bi-free oxide and doped with Bi metal particles after formation.
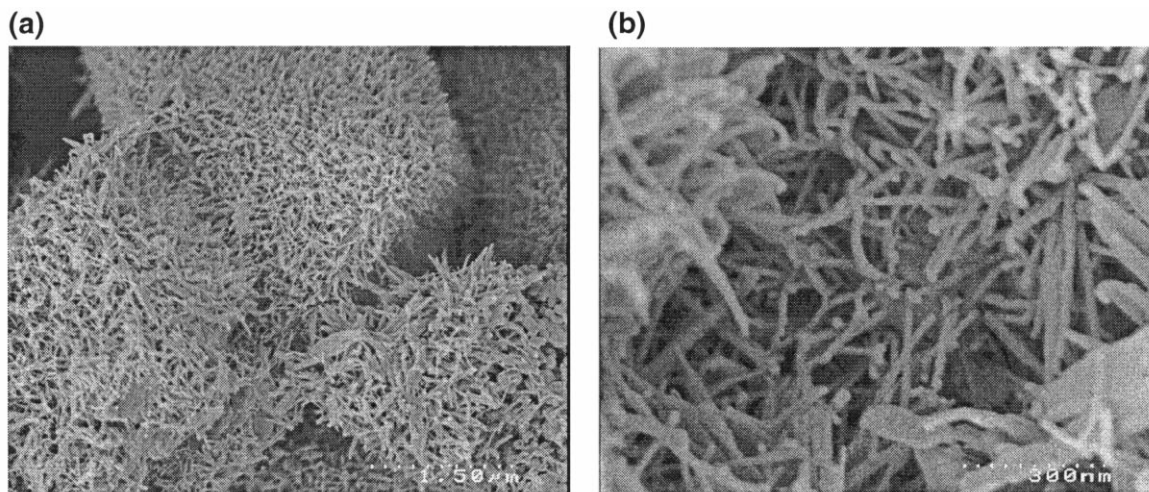
Fig. 9. Electron micrographs (IFESEM) of cycled material made from Bi-free oxide and doped with Bi metal particles after formation.

individual irregular-shaped crystals or between individual needle-like crystals that binds the PbO_2 particles into agglomerates; this is termed 'micro-contact'. The other is the contact between individual agglomerates that forms the skeleton of the positive mass, termed 'macro-contact'.

The micro-contact of irregular-shaped and needle-like crystals is demonstrated in Fig. 8(a), (b), and (c), respectively. By virtue of their greater aspect ratio, needle-like crystals can produce two forms of aggregate structure. A column or layer structure develops when the crystals are in parallel (Fig. 8(b,c)), whereas a network structure is created between randomly oriented crystals (bottom right, Fig. 8(c)).

In this study, the formed material was ground into individual agglomerates and, therefore, the reconnection of these agglomerates via macro-contact is the key factor in restoring the electrode capacity during cycling. As mentioned above, Bi-doped material is comprised of agglomerates that are covered with larger populations of needle-like crystals than the Bi-free counterpart. Through widespread, three-dimensional interconnection (Fig. 9), these crystals serve to enhance the macro-contact between the agglomerates and, thereby, account for the beneficial effect of bismuth on capacity development.

The application of a compressive force will also influence the macro-contact between the agglomerates of the electrode material. When the compressive force is raised, the distance between the agglomerates is reduced. Consequently, the connectivity of the material increases via the greater number of contacts between the needle-like crystals. Clearly, such an increase in connectivity will occur not only in Bi-doped material but also in the Bi-free equivalent, and thus the effect of bismuth on capacity will become less prominent at higher pressures (see region III, Fig. 3). On the other hand, the pore volume of the material also reduces progressively with an increase in compressive force. This may restrict the access of acid to such an extent

that the capacity is determined mainly by the diffusion rate of acid, rather than by the improvement in material connectivity. In this situation, the beneficial effect of bismuth will fade.

The use of VRLA Refined™ oxide has also been found [4] to extend battery life under the Japanese Industrial Standard (JIS) test. Furthermore, battery failure under this test is due to expansion, and consequent loss in the connectivity, of the positive material. Given that the presence of bismuth strengthens the connectivity of the positive mass, the increase in battery life when using VRLA Refined™ oxide is understandable.

References

[1] L.T. Lam, N.P. Haigh, O.V. Lim, D.A.J. Rand, J.E. Manders, D.M. Rice, J. Power Sources 73 (1998) 36–46.
[2] 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 Fransico, USA, 1998, pp. 452–460.
[3] L.T. Lam, N.P. Haigh, O.V. Lim, D.A.J. Rand, J.E. Manders, J. Power Sources 78 (1999) 139–146.
[4] L.T. Lam, N.P. Haigh, D.A.J. Rand, J.E. Manders, J. Power Sources 88 (2000) 2–10.
[5] L.T. Lam, J.D. Douglas, R. Pillig, D.A.J. Rand, J. Power Sources 48 (1994) 219–232.
[6] A. Winsel, E. Voss, U. Hullmeine, J. Power Sources 30 (1990) 209–226.
[7] D. Pavlov, A. Dakhouche, T. Rogachev, J. Power Sources 30 (1990) 117–129.
[8] D. Pavlov, J. Power Sources 33 (1991) 221–229.
[9] I.H. Yeo, D.C. Johnson, J. Electrochem. Soc. 134 (1987) 1973–1977.
[10] I.H. Yeo, S. Kim, R. Jacoboson, D.C. Johnson, J. Electrochem. Soc. 136 (1989) 1395–1400.
[11] H. Change, D.C. Johnson, J. Electrochem. Soc. 137 (1990) 2452–2457.
[12] L.A. Larew, J.S. Gordon, Y.L. Hsiao, D.C. Johnson, D.A. Buttry, J. Electrochem. Soc. 137 (1990) 3071–3078.