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A novel cureless pure lead oxide plate for valve-regulated lead-acid batteries

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Abstract

Pure lead oxide has been tested as a starting material for VRLA lead-acid batteries. The influence of the acid-to-oxide ratio and the paste density on the plate formation and battery performance has been investigated. The results show that the plates can be directly formed without undergoing the conventional plate curing process if pure lead oxide is used. The new process shows significant advantages in simplifying the conventional plate making processes for lead acid batteries and reducing the production cost and time.

1. Introduction

Currently, the plates used for lead acid battery manufacturing are made of leady oxide that is produced either via the Barton pot or by ball mill techniques [1]. These types of lead oxides have dominated the lead acid battery industry for more than 100 years. Despite the long acceptance of leady oxide as a plate making material, conventional lead acid batteries and their manufacturing processes have suffered some serious drawbacks because of the use of such material. In conventional plate making processes using leady oxide, the amount of free lead oxidised at each step (e.g. paste mixing, pasting, and curing) is very difficult to control accurately. This results in composition variations in the finished plates, which, in turn, affects the physical, chemical and electrochemical properties of the plates [2]. These causes reproducibility problems in terms of cell voltage and charge/discharge characteristics for cells made of these plates. Such reproducibility problems can be very serious for valve-regulated lead-acid batteries where the repeatability of cell-to-cell voltage and charge/discharge characteristics are very important as indicators of battery performance, such as the cycle life and capacity.

On the other hand, the plates produced from 'leady oxide' need to be cured to reduce free lead to 5% or less. Leady oxide currently employed in battery manufacture is typically a mixture of 70–80 wt % lead monoxide and 20–30 wt % lead particles (free-lead) [3, 4]. The paste is formed by mixing water and sulfuric acid with leady powder and small quantities of various additive materials. The metallic lead content has to be reduced to 5% or less after the curing process. A high free lead content (>5%) in the paste after curing may result in swelling, warping and/or extensive sludge formation during the formation of the positive plates [5]. Although the paste material used is generally satisfactory for the current manufacturing processes, there are still many aspects that can be improved. Recently, we have reported on using hydrogen peroxide to replace the currently used sulfuric acid [6, 7]. The use of hydrogen peroxide solution to replace the conventional sulphuric acid solution can convert free lead to lead oxide during paste mixing, so that the curing process can be eliminated. This technique can greatly simplify the manufacturing process, reducing production time and cost. The technique also provides the plate with sufficient flexibility for fabrication of non-flat plate construction batteries, such as the spirally wound cell configuration.

This work is aimed at exploring the feasibility of developing a non-curing plate making process using pure lead oxide for VRLA type batteries. The effects of the acid-to-oxide ratio of the paste and the paste density on the electrochemical performance of cells prepared with the non-cured plates were systematically investigated.

2. Experimental

2.1. *Plate preparation*

Positive pastes prepared from six formulae are specified in Table 1. These formulae yield three different paste densities: (1) 3.6 g cm^{-3} for samples 1 and 4; (2) 4.0 g cm^{-3} for samples 2 and 5; (3) 4.3 g cm^{-3} for samples 3 and 6. Two acid-to-oxide ratios were employed for each paste density, 3.9% for sample pastes 1, 2 and 3, and 6.6% for samples 4, 5 and 6. The positive pastes were

Table 1. Paste formulae

Component	Sample					
	1	2	3	4	5	6
PbO (Aldrich) (g)	50	50	50	50	50	50
TEFLON (g) (polytetrafluoro ethylene)	1.6	1.6	1.6	1.6	1.6	1.6
H_2SO_4 (1.40 sp.gr.) (cm^3)	2.8	2.8	2.8	4.4	4.4	4.4
H_2O (cm^3)	6.8	6.2	5.4	5.4	5.0	4.4
Acid-to-oxide ratio (%)	3.9	3.9	3.9	6.6	6.6	6.6
Paste density (g cm^{-3})	3.6	4.0	4.3	3.6	4.0	4.3

prepared by mixing 100 g pure PbO powder (99.9% Aldrich) with three-quarters of the required water. The acid (1.40 sp.gr.) was added to the powder at a slow rate under stirring. The pastes were then applied manually onto a lead-coated glass fibre grid with dimensions of 25 × 20 × 1.2 (height × width × thickness, in mm). The weight of the paste was controlled to ~5 g per plate.

2.2. *Cell assembly and formation*

The test cells were composed of one positive plate and two commercial negative plates, separated by a micro-glass fibre separator. The sandwich test plates were inserted into the cell case and the cell was filled with H_2SO_4 electrolyte (1.25 sp.gr.). The cells were then sealed and a rubber valve was fixed to each cell.

After the plates were soaked for 2 h in the cell, the cell formation was applied with a constant current density of 25 mA g^{-1} for 24 h.

2.3. *Cell performance*

After formation, the reserve capacity of the cell was recorded at a constant current of 120 mA to a cut-off voltage of 1.70 V/cell. The product of current and time yields the 5 h discharge capacity. During charging, the constant current was maintained until the cell voltage reached 2.45 V, and then charging was held at this voltage until 110% of the previous discharge capacity was reached. This charge/discharge sequence was repeated until the measured capacity reached a maximum value.

2.4. *Accelerated cycle-life test*

The accelerated test conditions are listed in Table 2. The duty cycle (cycles/day) was 16, and the cell was discharged until the terminal voltage fell to 1.70 V. The test was repeated until the measured reserve-capacity had fallen to 80% of the initial capacity [8].

Table 2. Accelerated cycle-life test conditions

Duty cycle (cycle/day)	16
Discharge time (h)	0.5
Discharge current (mA)	1000
Charge time (h)	1
Charge current (mA)	550

2.5. *Characterisation of active materials*

The lead oxide, paste and formatted plate were all examined using X-ray diffraction (XRD, Philips PW1010) phase-analysis. The phase compositions were determined by an advanced XRD method developed in the CSIRO laboratories (Australia) [9]. The morphology of these materials was examined by scanning electron microscope (SEM, Leica, 440). The specific surface areas (BET) of oxides and pastes (before and after formation) were measured with a NOVA/1000 nitrogen adsorption analyzer.

3. Results and discussion

3.1. *Surface morphology*

The morphology of pure β-PbO particles is shown in Figure 1. It can be seen that the pure β-PbO phase consists of individual 'particles' of varying shapes and with a size distribution ranging from 1 to 10 μm.

Although further SEM studies showed no effects due to paste density, it was found that a change in the acid-to-oxide ratio in the paste resulted in a slight change in the size of the 3BS ($3PbO \cdot PbSO_4 \cdot H_2O$) crystals. Figure 2 shows the SEM images of pastes with the

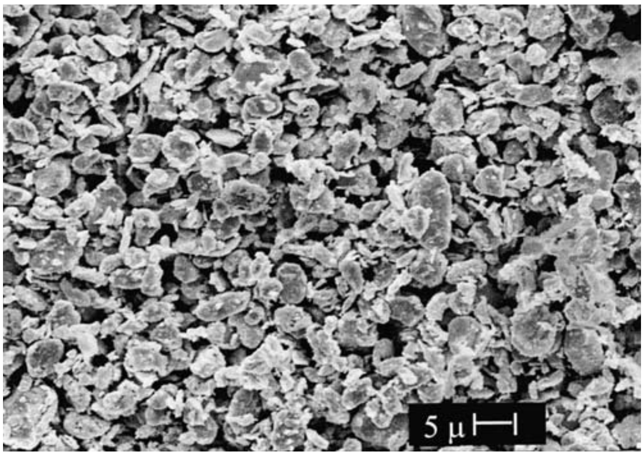

Fig. 1. Scanning electron micrographs of pure β-PbO.

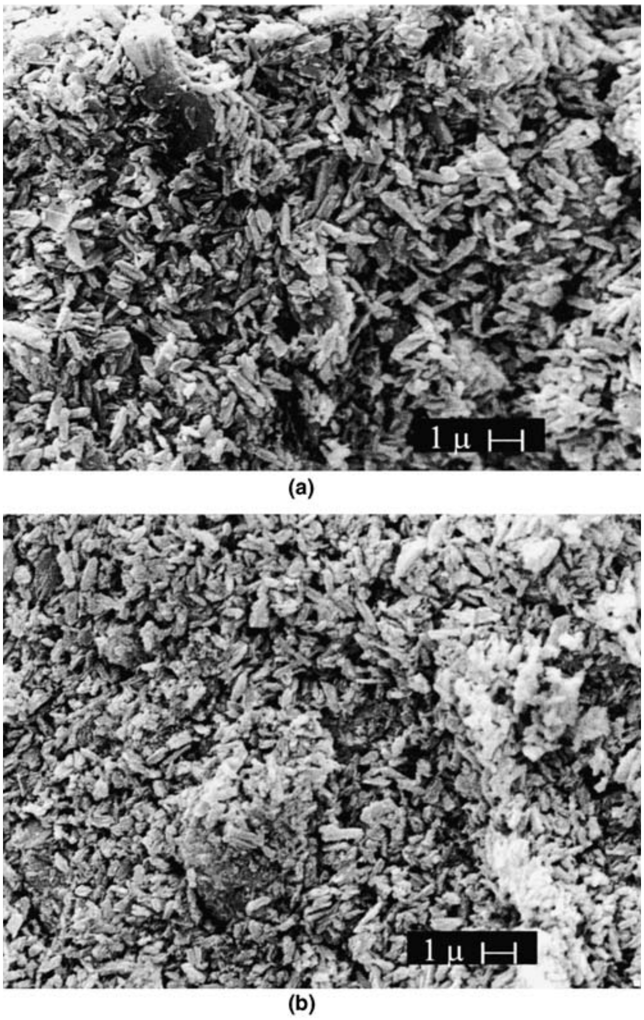

Fig. 2. Scanning electron micrographs of pastes before formation. (a) Acid-to-oxide ratio = 3.9%, paste density = 4.0 g cm^{-3}. (b) Acid-to-oxide ratio = 6.6%, paste density = 4.0 g cm^{-3}.

same paste density (4.0 g cm^{-3}) but different acid-to-oxide ratios (3.9 and 6.6%). Comparing Figure 1 with Figure 2, it can be seen that the morphology of the pastes changes from irregular shapes (β-PbO) to needle-liked shapes (3BS crystals in a matrix of lead oxide). The size of the 3BS crystal needles was decreased slightly when a higher acid-to-oxide ratio was used. This is similar to previous reports that the 3BS crystal size increased as the acid-to-oxide ratio decreased for conventional paste, which was made from leady oxide [10, 11].

Figure 3 shows the SEM images of non-cured plates with different acid-to-oxide ratios and paste densities after formation. It can be seen that all the plates exhibit similar morphology regardless of acid-to-oxide ratios and paste densities. It should be noted that the morphology of these non-cured plates was similar to what is seen for plates prepared from conventional leady oxide [10].

3.2. *X-ray diffraction analysis*

XRD patterns show that the paste before formation consists of the phases 3BS, β-PbO and 1BS (Figure 4a). The formed pastes contain the phases β-PbO, $PbSO_4$ and β-PbO_2 (Figure 4b). The percentages of the phase composition were calculated according the phase areas using an advanced XRD method developed in the CSIRO laboratories.

The phase composition data for the pastes prepared with various acid-to-oxide ratios and densities are shown in Figure 5. The results indicate that at a fixed acid-to-oxide ratio, the effect of the paste density on the paste composition was insignificant. In contrast, at a given paste density, a change in the acid-to-oxide ratio affected the paste composition dramatically. Figure 4 shows that the amount of 3BS phase in pastes prepared with a higher acid-to-oxide ratio is much greater than for pastes prepared with lower acid-to-oxide. The dependence of the phase composition of the paste on the ratio between H_2SO_4 and leady oxide was demonstrated previously by Pavlov and Papazov [12]. They reported that the amount of 3BS phase increases proportionally with increases in the H_2SO_4 content.

The phase composition results for the formed paste are shown in Figure 6. The β-PbO_2 contents were found

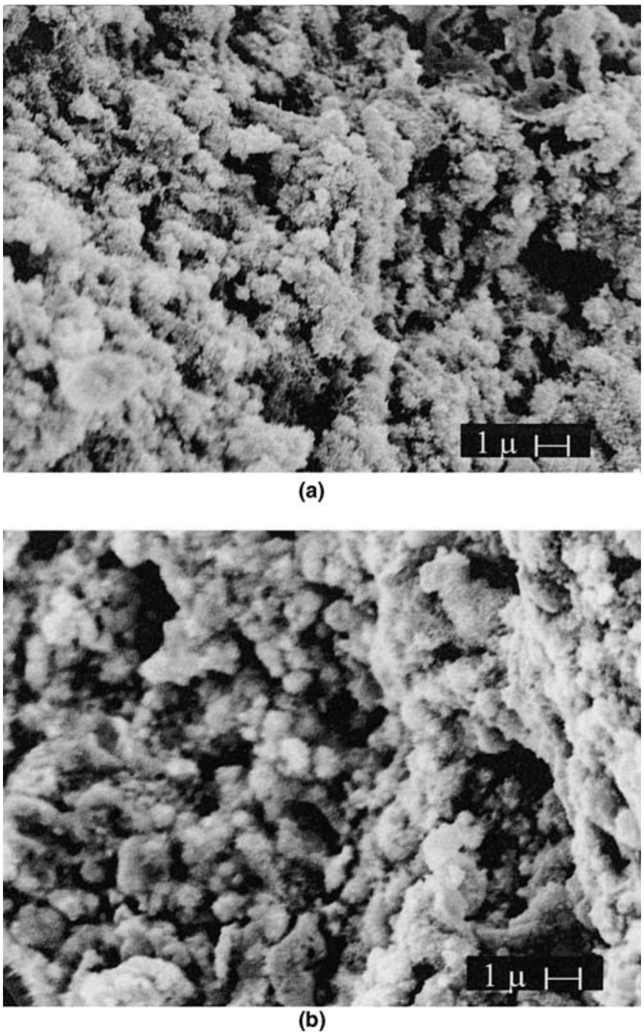

Fig. 3. Scanning electron micrographs of pastes after formation. (a) Acid-to-oxide ratio = 3.9%, paste density = 4.0 g cm^{-3}. (b) Acid-to-oxide ratio = 6.6%, paste density = 4.3 g cm^{-3}.

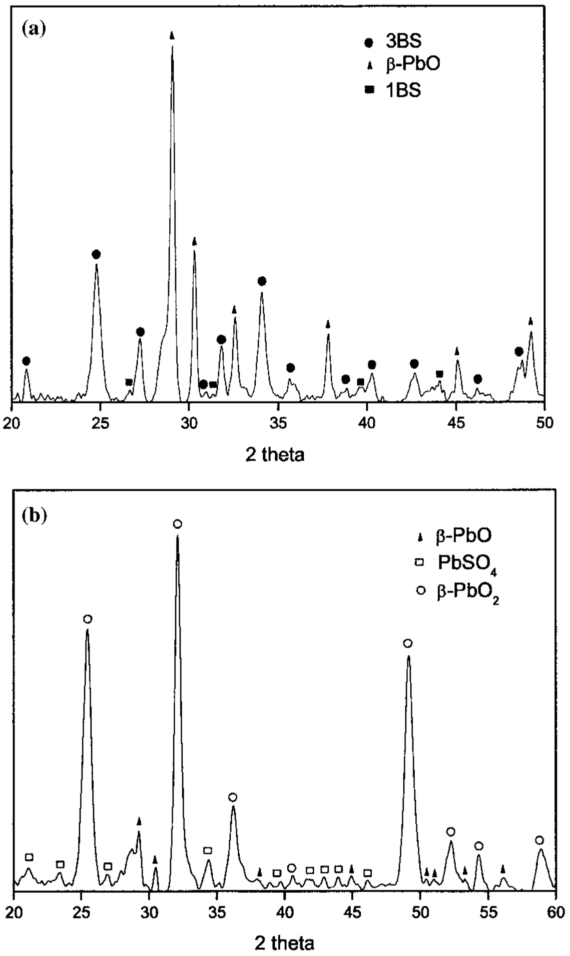

Fig. 4. XRD patterns of paste. (a) Before formation. (b) After formation.

to be over 70% for samples 1, 4, 5 and 6. The β-PbO$_2$ contents in samples 2 and 3 were 63 and 68%, respectively, slightly lower than for the other samples. The results indicate that plates prepared from pure lead oxide can be formed directly without having undergone a conventional curing process. Both the acid-to-oxide ratio and the paste density can affect the results of plate formation through changes in the β-PbO$_2$ content of the formed plates. When the acid-to-oxide ratio was fixed, the proportion of β-PbO$_2$ increased with decreasing paste density. At a fixed paste density, a relatively higher proportion of β-PbO$_2$ was observed in the formatted plate when a high acid-to-oxide ratio was used.

3.3. *BET surface area*

The surface areas of plates before and after formation were analysed using BET surface measurements and the results are presented in Figures 7 and 8. Before formation, at a fixed acid-to-oxide ratio, the surface areas of plates decrease with increasing paste density. At a given paste density, the plates with a low acid-to-oxide ratio have a lower surface area than those with a high ratio of acid-to-oxide. This is because the size of the 3BS crystals is larger when the paste has a low acid-to-oxide ratio (see Figure 2).

After formation, the surface areas of the formed plates increase with an increase in the acid-to-oxide ratio. At each given acid-to-oxide ratio, the surface area of the formed plate increased slightly as the paste density was decreased.

3.4. *Formation efficiency*

A study of the effect of the acid-to-oxide ratio on the formation efficiency was carried out by determining the first discharge capacities since the first discharge capacity can be used to evaluate the formation efficiency [13]. The results are shown in Figure 9. It was found that at a given acid-to-oxide ratio, an increase in the paste density resulted in a decrease in the first discharge capacity. When a plate with the same density had a higher acid-to-oxide ratio, it showed a higher first discharge capacity.

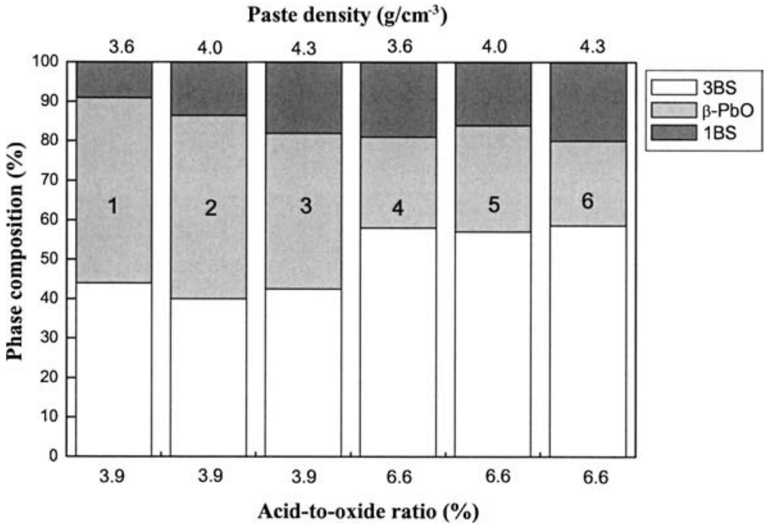

Fig. 5. Phase composition of the pastes before formation.

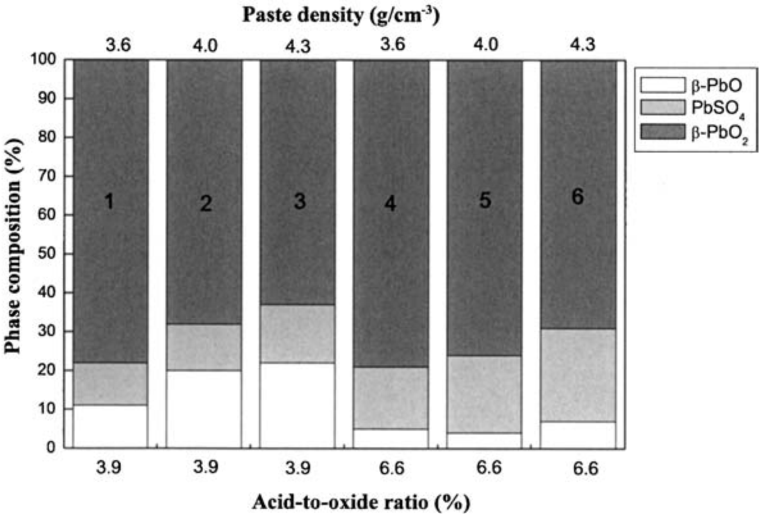

Fig. 6. Phase composition of the pastes after formation.

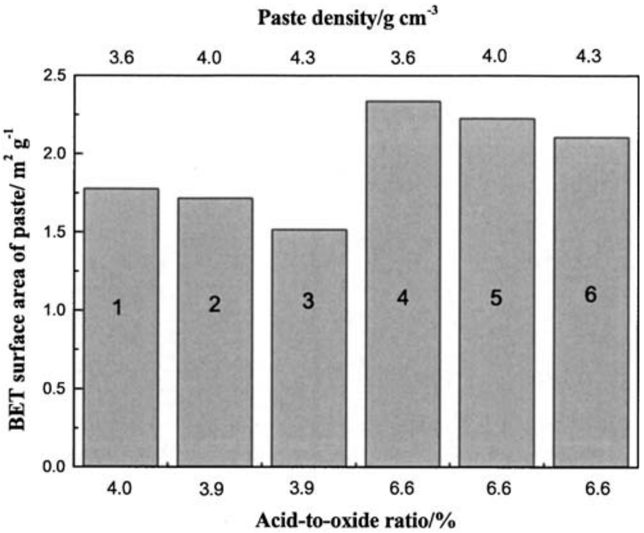

Fig. 7. BET surface area of the pastes before formation.

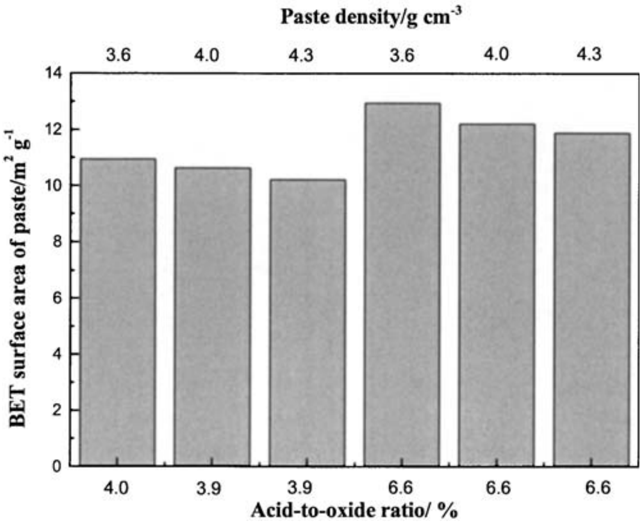

Fig. 8. BET surface area of the pastes after formation.

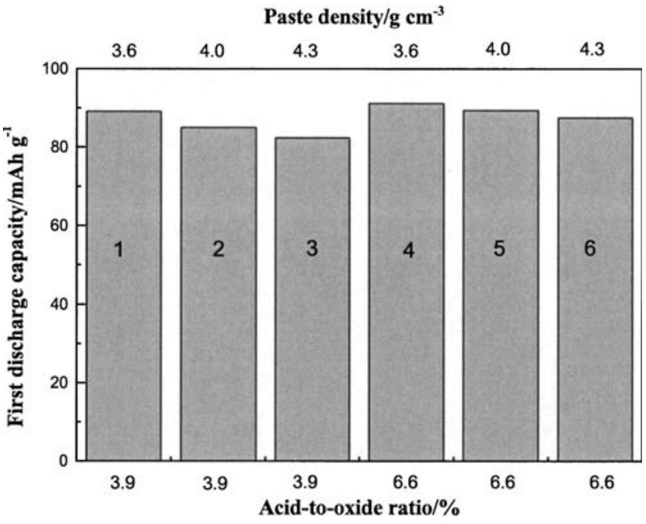

Fig. 9. First discharge capacity of the test sample.

The highest initial capacity of 91 mA h g^{-1} was achieved for the plate prepared with a 6.6% acid-to-oxide ratio and a 3.6 g cm^{-3} paste density. This initial capacity is acceptable by industry standard.

3.5. *Active-material utilization*

The active-material utilization represents the percentage of material that participates in the discharge process. It is defined as the ratio of the measured maximum capacity at a particular discharge current density to the theoretical capacity. The theoretical capacity is 229 mA h g^{-1} of active material (PbO).

As the energy density of a battery depends on the percentage utilization of the active materials, the effect of the acid-to-oxide ratio on the percentage of active material utilization was investigated (see Figure 10). It was found that for a given acid-to-oxide ratio, the active-material utilization increased slightly as the paste

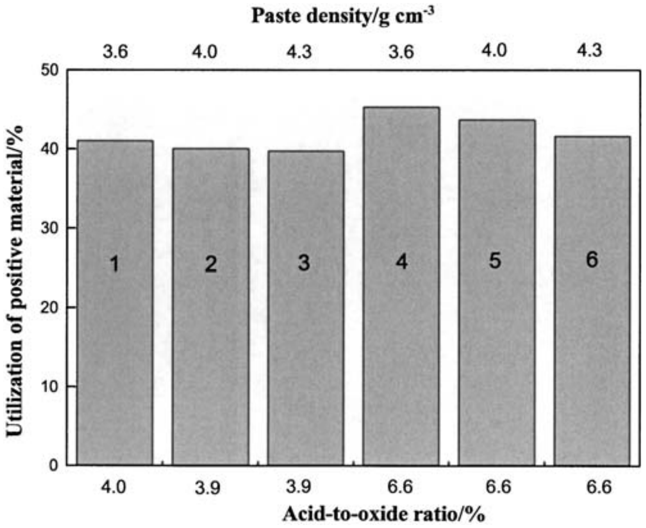

Fig. 10. Material utilization of the test samples.

density was decreased. At a fixed paste density, the active-material utilization increased when the acid-to-oxide ratio was increased. These imply that a plate prepared with a lower paste density and higher acid-to-oxide ratio may lead to a relatively higher active-material utilization.

3.6. *The results of accelerated cycle-life testing*

Accelerated cycle-life tests were performed to evaluate the cycle life of the cells. The results are given in Figure 11. It was found that an increase in the acid-to-oxide ratio resulted in an increase in the cycle life regardless of paste density. It was also found that when the acid-to-oxide ratio was fixed, the observed cycle life was increased with increasing paste density.

It should be noted that an increase in paste density had negative effects on the active material utilization, while the effect of the increased paste density on the cycle life was positive. This phenomenon occurs because the BET surface area decreases with an increase in the paste density of the active material. When the BET surface area increases, the reactivity of the active material with the sulphuric acid electrolyte increases, and thus the material utilization increases as the paste density decreases. On the other hand, the mechanical strength of the electrode increases when the paste density increases, so the softening of the plate will be reduced during cycling. This is why the cycle life increased. Therefore, in order to achieve maximum active material utilization, the cycle life has to be sacrificed, so that an optimum balance has to be considered when the paste density is selected.

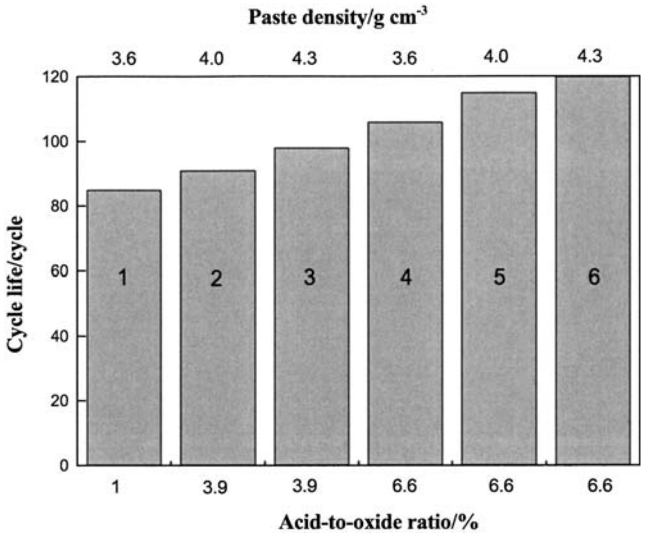

Fig. 11. Cycle life of the samples tested under accelerated cycle-life test conditions.

4. Conclusions

(1) Pure lead oxide was used as a starting material in the fabrication of lead acid cells to explore a non-cured plate making process. Non-cured plates with different acid-to-oxide ratios and paste densities can be formed acceptably without the conventional curing processing. This new process has demonstrated many advantages over the conventional process, including simplification of the manufacturing process, a short production time, and low cost.

(2) A change in paste density does not affect the morphology of the plate, but the various acid-to-oxide ratio used in the paste preparation slightly affects the size and shape of the 3BS crystals in the paste.

(3) At a given acid-to-oxide ratio (3.9 or 6.6%), a change in paste density does not have much influence on the phase composition of the paste. By contrast, at a fixed paste density, the acid-to-oxide ratio exerts a significant effect on the paste composition. Both the acid-to-oxide ratio and the paste density can affect the results of plate formation through changes in the β-PbO_2 content of the formed plates.

(4) The active material utilization increases with an increasing acid-to-oxide ratio. The cycle life increases with an increase in paste density at given acid-to-oxide ratios. At any given paste density, the cycle life increases with an increase in the acid-to-oxide ratio. A better active material utilization always needs to be traded off against the cycle life.

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