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Synergistic effects of novel battery manufacturing processes for lead–acid batteries. Part I: Charge/discharge cycling of batteries

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Abstract

The present research aimed to ascertain if the merging of novel battery manufacturing processes could achieve an enhancement in the improvement of battery cycle-life. We found that the melding of novel battery manufacturing processes leads to synergistic effects with regard to the cycling performance of lead–acid batteries. The novel battery manufacturing processes employed in this study include: (i) grid cleaning; (ii) positive active material compression; and (iii) conductive additives in the positive paste. It was found that a combination of positive active material compression and grid cleaning approximately doubles the durability of batteries and is consistent with the additive effects of the individual treatments, while a combination of positive active material compression and conductive additives yields an approximate 30% boost in performance compared to the additive effects of the isolated treatments. Synergistic effects were not noted for other combinations of the aforementioned battery manufacturing practices.

1. Introduction

Due to the wide use of lead–acid batteries (LABs), it is important to develop high performance and maintenance-free lead–acid batteries. Maintenance-free LABs can be produced by using nonantimonial grids in the fabrication of battery plates. The major drawback of these batteries is their inferior deep-discharge cycling performance compared to antimonial grid based systems.

A significant amount of research has been undertaken to improve the performance of LABs by using the following modifications: (i) varying the grid composition; (ii) altering the active material; (iii) improving the separators and containers; (iv) enhancing the pasting process; and (v) improving the charging regime.

In the area of grid modification, new alloys that give stronger casting, greater corrosion resistance, reduced gassing and/or a modified grid structure have been used [1–10]. The incorporation of tin in the positive grid (either in the alloy itself or as a surface layer) reduces the level of α-PbO, alleviating passivation problems relating to charge acceptance. Furthermore, recent work has shown that removing the basic lead carbonate phase, hydrocerrusite, from the surface of nonantimonial lead grids by etching in concentrated NaOH reduces the resistance of the grid–corrosion layer. This method ameliorates the problem caused by passivation of the grid corrosion layer through the formation of an uninterrupted underlayer of PbO, thereby improving battery cycling performance [7, 11, 12].

Improvements in the positive active material have endeavoured to increase its utilization. Factors that control the utilization of the active material are current density, plate thickness, active material structure, conductivity of active material, conductivity of grid, electrolyte volume and electrolyte density [13]. Many researchers have developed methods to increase the utilization of the active material, especially the positive active material. This is usually achieved by using an additive that alters the chemical and/or physical properties to improve the utilization of the positive active material. Additives such as tin oxide, bismuth oxide, boric acid, and tin dioxide-coated glass flakes represent some of the additives that have been used to enhance the performance of batteries [13–25].

Adding conductive tin oxide to the positive active material increases the electrical connectivity of particles within the positive active material, improving the conductivity of the active material and the cycle-life of batteries. It has been proposed that tin oxide forms bridges between the isolated lead dioxide particles during charge/discharge cycling, along with alleviating the grid corrosion problem that causes passivation of the grid/active material interface of lead–acid battery grids [20].

Other research has employed the compression of positive active material to improve the cycle-life of LABs [26–30]. The compression of plates increases the integrity of the active material, improving the connectivity between particles in the active mass. It was also found that a compression pressure of approximately 4 N cm^{-2} is necessary for achieving the optimum in battery cycle-life [29].

The purpose of the present research has been to conduct a systematic study of individual and combined effects of the aforementioned battery manufacturing processes (i.e., grid etching, active material spiking and active material compression). Our main goal has been to ascertain if there are synergistic effects arising from a melding of the aforesaid battery manufacturing processes, as this may lead to the development of high performance batteries.

2. Experimental details

2.1. *Preparation of positive pasted plates*

Eight types of positive plate were prepared; namely, control (13 cells), additive-spiked (11 cells), etched (10 cells), compressed (6 cells), additive-spiked + etched (8 cells), additive-spiked + compressed (6 cells), etched + compressed (6 cells) and additive-spiked + etched + compressed (10 cells), noting that the number of replicate tests have been included in parentheses. The positive paste was prepared using the paste formula given in Table 1 [16]. The etched plates were prepared by etching the grid in 10% (w/v) NaOH prior to pasting to rid the grid surface of detrimental hydrocerussite [12], while additive-spiked paste was prepared by spiking with 5 wt % SnO_2.

Barton-pot leady oxide obtained from the New South Wales plant of Exide Technologies Pty Ltd. and analytical reagent grade sulfuric acid (DBH, AnalaR) were used in the preparation of the paste.

2.2. *Assembly of 2 V cells*

The plates were assembled into 2 V cells comprising one positive plate surrounded by two negative plates. The negative plates were produced by Exide Technologies using a paste recipe and curing conditions similar to those described by Manders [16]. The alloy of the negative plates was identical to the one used in the positive plates. The positive and negative plates were separated by using glass-fibre separators (~3 mm thick) manufactured by Exide Technologies Pty Ltd. These cells were assembled in Exide Technologies Powersafe battery containers.

Table 1. Paste formula for the preparation of positive plates

Component	Positive paste
Leady oxide/kg	2
Fibre/g	0.6
Carboxymethyl cellulose/g	5
1.4 r.d. (s.g.) H_2SO_4/mL	132
Water/mL	300
Acid-to-oxide ratio/wt.%	4.7
Paste density/g mL^{-1}	4.00–4.4

The compression treatment entailed the forceful introduction of several folded separators into cells, and this reduced the sulfuric acid electrolyte volume by approximately 4%.

2.3. *Cell formation*

All plates were formed in 1.180 L of 1.07 relative density (formerly s.g.) H_2SO_4 using a constant current of 5 A for 6 h, and rested at open circuit for 1 h to allow the sulfuric acid depleted diffusion layers of the pores to be replenished by the permeation of fresh electrolyte. The charge–rest period was repeated, followed by a final charge at 5 A for 6 h. After formation, the sulfuric acid and separators were discarded, and the cells were reassembled and filled with 1.270 r.d. H_2SO_4 (~1.3 L) [12].

2.4. *Cycle-life evaluation of cells*

The cycle-life performance of the 2 V cells was assessed by employing a Digatron BTS-500 computerized charge/discharge unit (Digatron GmbH, Germany) in repetitive charge/discharge cycling at the 3 h rate. After charging to 2.55 V at 5.6 A, the cells were held at the top-of-charge voltage until the current had tapered to 1 A. At this point, the cells were discharged at 5.6 A until the voltage had fallen to 1.75 V. The charge/discharge procedure was repeated until the discharge capacity had fallen below 50% of the initial value [12].

3. Result and discussion

Battery performance has been gauged by the number of cycles required to reduce the battery discharge capacity to 35 Ah kg^{-1}. The control cells were used in a comparative evaluation of battery performance.

The charge/discharge cycling results for all cells are presented in Figures 1 and 2, while Figure 3 presents a bar graph of the number of cycles required to reduce the discharge capacity to 35 Ah kg^{-1}. For the control cells, it was found that the number of cycles to failure was 20 cycles. As for additive-spiked, etched and compressed cells, it was found that the number cycles required to reach the discharge capacity cut-off were 22, 29 and 35 cycles, respectively. These values were used as a ‘second control’ to evaluate if a combination of treatments gave rise to synergistic effects.

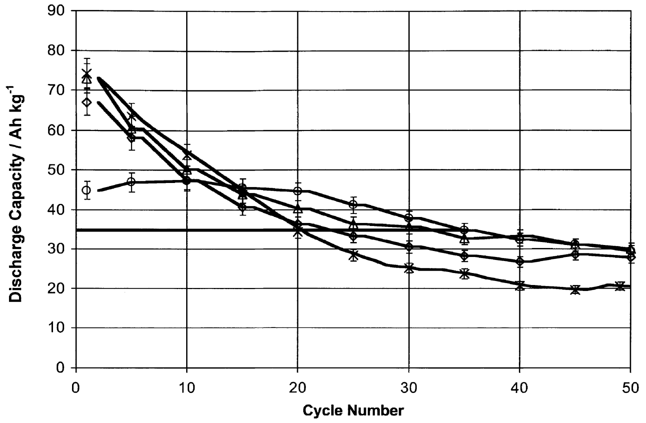

Fig. 1. Battery performance (discharge capacity against cycle number) for control, tin oxide doped, etched grid and compressed plates. Key: (×) standard; (◇) tin oxide doped; (△) etched grid; (○) compressed plate.

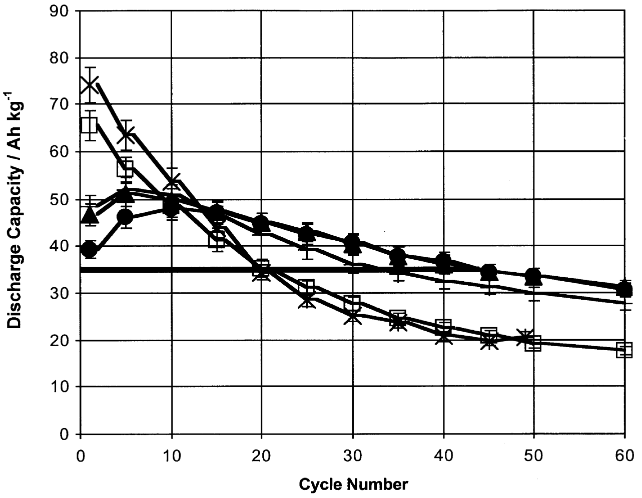

Fig. 2. Battery performance (discharge capacity against cycle number) for control, tin oxide doped + etched grid, tin oxide doped + compressed plate, etched grid + compressed plate and all treatments. Key: (×) standard; (□) tin oxide doped and etched grid; (●) tin oxide and compressed plate; (▲) etched grid and compressed plate; (–:–) tin oxide doped, etched grid and compressed plate.

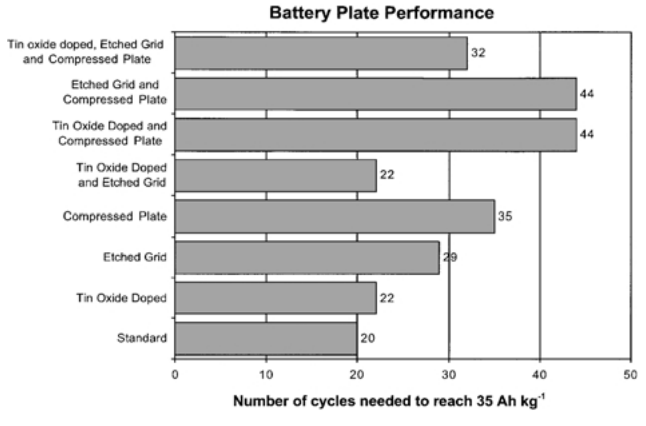

Fig. 3. Number of cycles needed to reach 35 Ah kg^{-1} for all types of batteries.

A combination of additive-spiking of active material and etching of grids (additive-spiked + etched cells) gave rise to a diminution in battery performance, as compared to the additive effects for enhanced performance of the individual factors, namely, 20 cycles + (22–20) cycles + (29–20) cycles $>$22 cycles. This result demonstrates a negative synergy for the combination of grid etching and additive-spiking of positive-plates.

There is a significant improvement by using a combination of grid etching and compression of the active material. Nevertheless, a comparison of untreated control cells against the enhancement in performance for individual treatments shows that this outcome is ascribable to the additive effects of the individual treatments, viz., 20 cycles + (29–20) cycles + (35–20) cycles = 44 cycles.

A significant improvement in performance was noted for a combination of additive-spiking and active material compression. This combination gave a 30% enhancement in performance compared to the additive effects of the isolated treatments, namely, 20 cycles + (22–20) cycles + (35–20) cycles $<$44 cycles. This represents a statistically significant improvement ascribable to a positive synergistic effect, as the variability in the aforesaid cycling data is approximately 5% relative.

Suprisingly, a combination of all three novel manufacturing processes (etching, additive-spiked, and active material compression) did not yield synergistic effects on the cycling performance. In fact, it gave an inferior performance compared to active material compression alone. It seems there is a negative effect on cycling performance through the merging of grid etching, conductive additive-spiking and active material compression of plates. Furthermore, it was alluded to earlier that a combination of grid etching and additive-spiking also gave rise to a diminution in performance compared to the additive effects of the individual treatments. These outcomes may be attributed to a cross-reaction between residual NaOH from grid etching, and the active material under the influence of external pressure, and in the presence of tin oxide. Whatever the reason, the high reproducibility of the cycling data demonstrate it is a real effect.

It can also be gleaned from Figures 1 and 2 that batteries employing active material compression started at a lower capacity compared to other cells. Moseley [18] stated that the acid supply is an important factor in the regulation of discharge capacity for LABs, as a consequence of its effect on the diffusion-controlled supply of acid to reaction sites in the positive active material. As we employed a lower volume of sulfuric acid ($\sim$1250 mL compared to $\sim$1300 mL in control cells) due to a diminished cell void volume as a result of the forceful insertion of additional plate separators, the starting capacity is significantly lower (compare 45 Ah kg^{-1} against 75 Ah kg^{-1} for control cells). Despite this offset in initial battery capacity, the number of cycles required to reduce the discharge capacity to $<$35 Ah kg^{-1}, as shown in Figure 3, shows that the durability of the cells employing active material compression is vastly improved, as compared to the control cells.

4. Conclusions

The results of this study demonstrate a combination of conductive additive-spiking and compression of active material yields a significant improvement in battery cycle-life. This combination was shown to exhibit a positive synergistic effect on the cycling performance of batteries. On the other hand, a combination of grid etching and active material compression yielded a negligible synergistic effect, while a combination of all plate preparation procedures yielded a diminution in battery durability, as compared to the results for isolated treatments using the aforesaid procedures.

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