

Beneficial effects of red lead on non-cured plates for lead-acid batteries

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Abstract

In order to find a more convenient processing method and more suitable paste formula for making VRLA batteries, hydrogen peroxide solution and red lead (Pb_3O_4) have been used together during the paste preparation. The use of hydrogen peroxide solution to replace the conventional sulphuric acid solution can accelerate the oxidation of free lead in the paste and therefore reduce the time for the plate curing, while the addition of red lead can enhance the cell formation and improve the cell performance. Based on these two beneficial functions, a new process for making VRLA cells was proposed and investigated. Cells were assembled directly from freshly pasted plates without undergoing the conventional plate curing and drying process, and the battery formation that followed was successful. The new processing resulted in an increase in the production efficiency and a substantial reduction in production time and cost. The battery performance, in terms of both the initial discharge capacity and the cycle life, is also improved by the use of red lead.

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Keywords: Lead-acid battery; Additives; Red lead; Formation process; Hydrogen peroxide

1. Introduction

Tracing back the history of lead-acid batteries, it can be found that red lead (Pb_3O_4) was commonly used by early battery manufacturers, but was later replaced by “leady” oxide (Barton–pot or ball-mill oxide), mainly due to its high production cost [1]. However, it is still common to use a mixture of red lead and leady oxide in tubular positive plates to improve the formation efficiency and deep-cycle performance. Recently, the use of red lead has once again drawn the attention of the lead-acid battery manufacturers after many years of disinterest because of its beneficial effects on battery performance, especially for VRLA batteries [2,3].

The formation process in conventional lead-acid battery manufacturing is a time consuming and low efficiency process because of the poor conductivity of the lead sulphate, lead oxide and basic lead sulphates in the battery plate. In red lead, the lead is in a higher oxidation state than in lead monoxide and has a higher conductivity than that of PbO ($\sim 10^{-12} (\Omega \text{ cm})^{-1}$ versus $\sim 10^{-14} (\Omega \text{ cm})^{-1}$) [4]. Red lead is generally prepared in mechanical furnaces by the oxidation of PbO batches (usually Barton oxide) within the temperature range 450–500 °C and can be prepared in a finely-divided form.

When treated with sulphuric acid, it reacts as though its stoichiometric composition is $\text{PbO}_2 \cdot 2\text{PbO}$, with the lead monoxide forming lead sulphate and leaving the PbO_2 unaffected. When red lead is used in a positive plate paste mix, about one-third of the oxide is converted directly to PbO_2 before the charging process is started, and this assists in the formation process [5].

Hydrogen peroxide solution has been reported as a replacement for the sulphuric acid used in the paste mixing [6]. When mixed with lead dust, hydrogen peroxide performs the function of converting the free lead in the lead dust to oxides. Plates prepared with this paste can be directly assembled into batteries without going through the conventional curing process. This technique can greatly simplify the manufacturing process and reduce the processing time and cost.

The aim of the work presented here is to investigate the effects of red lead on a non-cured paste, which is prepared by using hydrogen peroxide solution mixed with lead dust.

2. Experimental

2.1. Plate preparation

Three types of positive pastes were prepared. Sample 1 was taken as the control sample and made from battery grade

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Table 1
Paste formulae

Component	Positive electrode		
	Pb ₃ O ₄ (0%)	Pb ₃ O ₄ (12.5%)	Pb ₃ O ₄ (25%)
PbO battery grade (g)	50	43.75	37.5
Pb ₃ O ₄ (g)	0	6.25	12.5
Cellulose (g)	0.125	0.125	0.125
TEFLO (g)	1.6	1.6	1.6
H ₂ O ₂ (5 vol.%) (cm ³)	5.5	5.5	5.5
H ₂ O (cm ³)	4	4	4
Paste density (g/cm ³)	3.8–4.0	3.8–4.0	3.8–4.0

lead oxide (with 22.5% free lead, provided by Equal Shine Industry, Hong Kong). Samples 2 and 3 were made from mixtures of the battery grade lead oxide and 12.5 and 25 wt.% Pb₃O₄ (99.9%, Aldrich), respectively. A 5% v/v (Aldrich) hydrogen peroxide solution was used during the paste preparation. The densities of these three pastes were adjusted to 4.0 g/cm³. The formulae for these pastes are listed in Table 1. The free lead content in each paste was analysed by means of a gravimetric method, and the results show that the free lead content in the three samples was always below 5%. These pastes were used to make positive plates by hand-pasting onto lead grids with dimensions of 40 mm × 35 mm × 1.2 mm (height × width × thickness). The pasted plates were dried with hot flowing air and then directly assembled into the battery case.

2.2. Cell assembly and formation

The test cells were composed of one positive plate and two commercial negative plates, separated by a microglass fiber separator. The sandwiched electrodes were inserted into a commercial battery case, and two separate polycarbonate fixing sheets were inserted into each cell within the battery case to provide the plate compression. Each test cell was filled with an electrolyte of H₂SO₄ (1.25 sp. gr.), and the cell volume was held constant. The test cells were sealed, and a rubber valve was fixed to each cell. After soaking with electrolyte for 2 h, the cell formation was applied at a constant current density of 25 mA/g of a active material. Plates were formed for different periods of 9, 14, 18, 21 and 24 h with input capacities of 225, 350, 460, 520 and 600 mAh/g of a active material, respectively.

2.3. PbO₂ content analysis

After the cell formation reached the predetermined time, the positive plates were removed from the cells, and the PbO₂ contents in the plates from different test cells was analysed using titrimetric analysis. The samples that had 24 h formation were subjected to X-ray diffraction (XRD) phase-analysis (Philips PW1010) and their compositions were determined by “Traces” software.

2.4. First discharge capacity and cycle life test

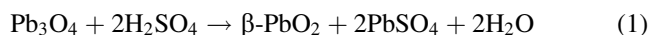
After formation, the first discharge capacity of each test cell was recorded at a discharge current density of 35 mA/g of a active material to a cut-off voltage of 1.75 V per cell. Then a charging/discharging cycle was initiated with the same current density. During charging, this constant current was maintained until the cell voltage reached 2.45 V, and then the charging was held at this voltage until 110% of the previous discharge capacity was reached. This charge/discharge sequence was repeated until the reserve capacity had fallen to 60% of the initial capacity value. The formation and the cycle life tests were carried out with an ARBIN cyler (BT4⁺).

3. Results and discussion

3.1. Effect of red lead addition on the formation efficiency

Fig. 1 presents the PbO₂ content versus formation time. After an early formation period of 9 h, the PbO₂ contents in the three samples were 49, 45 and 39 wt.%, corresponding to the addition of 25, 12.5 and 0 wt.% Pb₃O₄, respectively. The sample with 25 wt.% Pb₃O₄ required 14 h for the PbO₂ content to reach 60%, while the sample with 12.5% Pb₃O₄ required 17 h, and the sample without Pb₃O₄ required 18 h. At the end of formation, the PbO₂ contents of the three samples were 76.8, 71.9 and 67.8 wt.%, respectively. It can be seen from Fig. 1 that for a given time, the higher the red lead addition, the higher the PbO₂ formation. These results proved that the formation efficiency could be enhanced by increasing the addition of red lead and that an acceptable non-cured paste could be formed without undergoing the conventional curing process.

This enhanced effect on the plate formation can be also explained by the transformation of Pb₃O₄ to β-PbO₂ in the plate soaking and formation processes according to the following reaction [7]:



Small β-PbO₂ seed crystals that can be produced from the above reaction will promote a more efficient transformation of the entire pasted plate. However, at the end of the formation, although the input formation capacity had been increased to 250% of the theoretical input formation capacity, the precursor still remained about 23% of the plate mass for the sample with the highest Pb₃O₄ addition. This is because the lines of current density go directly to the patches of PbO₂, not to the remainder of the precursor, which has not undergone transformation [8]. At this stage, the formation efficiency becomes very low, and most of the input power generates gas as a side reaction.

3.2. First discharge capacity after formation

Fig. 2 shows that the first discharge capacity increased with an increasing of the red lead content for any given

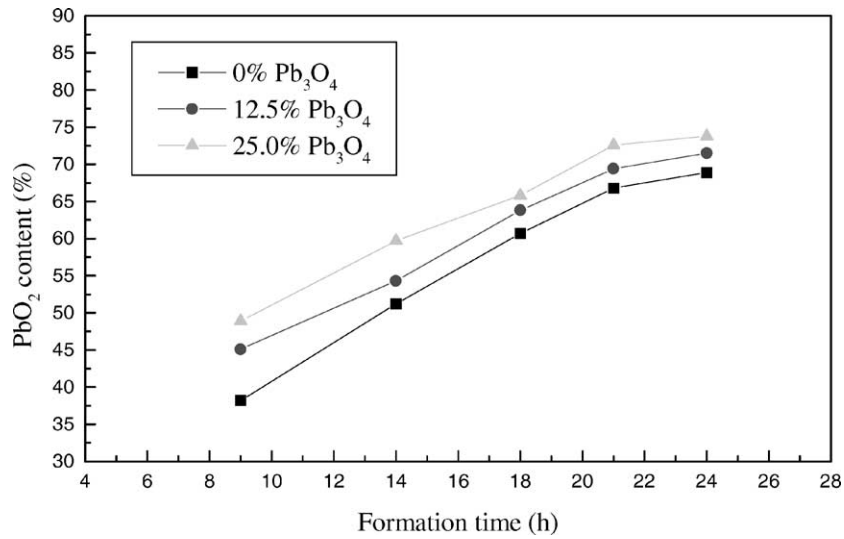


Fig. 1. PbO₂ content vs. formation time.

formation time. This indicates that the red lead can also improve the discharge capacity. After 24 h formation, all sample plates were analysed by X-ray diffraction. The results are listed in Table 2. These results confirmed that the β -PbO₂ content in the plates was increased with the addition of Pb₃O₄ and that the higher discharge capacity corresponding to a higher red lead content occurred because β -PbO₂ crystals always give a higher discharge capacity than α -PbO₂ [9,10].

3.3. Active materials utilisation

The active material utilisation is defined as the ratio of the measured capacity to the corresponding theoretical capacity. It represents the percentage of materials that participate in the discharge process. Fig. 3 shows that the active material utilisation was improved for the samples with red lead

Table 2
Composition of the plates after formation

Samples	Composition (wt.%)			
	α -PbO ₂	β -PbO ₂	α -PbO	PbSO ₄
1 (with 0% Pb ₃ O ₄)	30.1	42.9	15.0	12.0
2 (with 12.5% Pb ₃ O ₄)	21.9	52.6	13.2	12.3
3 (with 25% Pb ₃ O ₄)	9.5	67.8	10.6	12.1

additions. At the end of the formation, the material utilisation for cells with 12.5 and 25 wt.% Pb₃O₄ were about 43 and 52%, respectively, but for the cell without Pb₃O₄ was only about 35%. The active material utilisation is increased by the addition of red lead, but no significant difference in the material utilisation occurred during the early stages of formation. This can be attributed to the fact that the contribution of red lead was to provide small β -PbO₂ seed

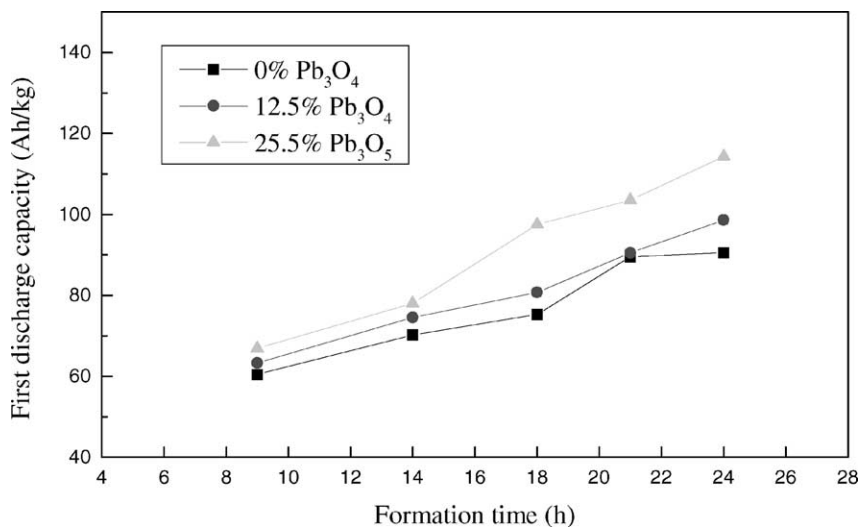


Fig. 2. Discharge capacity vs. formation time.

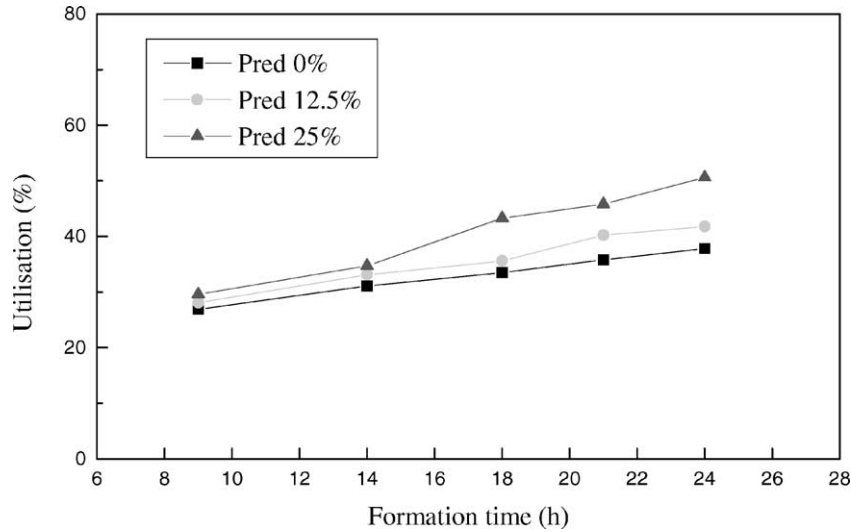


Fig. 3. Material utilisation vs. formation time.

crystals, according to the above Eq. (1). However, only a comparatively small ratio of β - PbO_2 (to the whole active mass) was present during the early formation. As the formation continued, those small β - PbO_2 seed crystals have promoted a more efficient transformation of the entire pasted plate from PbSO_4 to PbO_2 , allowing a significant difference to be observed only in the later formation stages.

3.4. Effect of red lead on cycle life

Fig. 4 shows cycle life test results for cells with different Pb_3O_4 additions. The reserve capacities of the cells with Pb_3O_4 were higher than for the cell without Pb_3O_4 and the cycle behaviour was also improved with the Pb_3O_4 addition.

A conventional H_2SO_4 -based cured plate contains tribasic lead sulfate ($3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O} = 3\text{BS}$) before formation,

and this is converted to PbO_2 during formation. Different phase transformation mechanisms could be involved in the new H_2O_2 -based plate during the plate formation. The non-cured H_2O_2 -based plate could be formed from its original state, mainly from $\text{PbO} \rightarrow \text{Pb}^{+2} \rightarrow \text{PbO}_2$, without going through the conventional process which follows the phase transformation of $\text{PbO} \rightarrow 3\text{BS} \rightarrow \text{PbO}_2$. The new process could produce less volume change in the positive plates during formation and be favourable for reducing the volume change during subsequent charge/discharge cycles. The extension of cycle life for cells containing Pb_3O_4 could be attributed to the combined contribution from the red lead and the H_2O_2 -based plate. The red lead could favour the proposed phase transformation of $\text{PbO} \rightarrow \text{Pb}^{+2} \rightarrow \text{PbO}_2$. However, the mechanisms behind the extension in the cycle life of cells with the red lead are still not clear, and further study is needed to explore it.

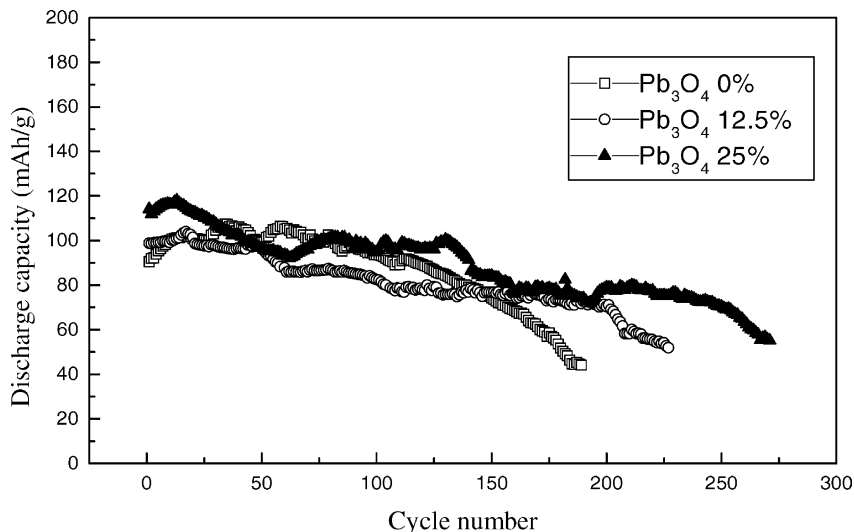


Fig. 4. Relative reserve capacity as a function of the number of 100% DOD cycles for cells.

4. Conclusions

Additions of red lead, together with the use of hydrogen peroxide solution allowed successful plate formation without the conventional curing/drying process. The influence of the addition of red lead to the positive plates on plate formation, active material utilisation and cycle life was investigated. The results confirmed that the use of red lead could bring significant benefits in terms of high formation efficiency and enhanced cycle life. Although the cost for using these two substitutes would be higher than for using conventional materials, the resulting advantages will outweigh the increased cost of battery manufacturing.

Acknowledgements

This was financially supported by the Australian Research Council under an ARC-SPIRT project (C89805127). The

authors also thank Dr. T. Silver and Dr. G. Walter for critical reading of the manuscript.

References

- [1] T.L. Blair, *J. Power Sources* 73 (1998) 47.
- [2] C.V. D'Alkaine, J. de Andrade, P.R. Impinnisi, *J. Power Sources* 85 (2000) 131.
- [3] J.P. McKinley, M.K. Dlaska, R. Batson, *J. Power Sources* 107 (2002) 180–186.
- [4] D.P. Boden, *J. Power Sources* 73 (1998) 58.
- [5] M. Barak, *Electrochemical Power Sources, Primary and Secondary Batteries*, The Institution of Electrical Engineers, London/New York, 1980, p. 184.
- [6] C. Morris, A. Datta, P. Howard, US Patent 4909955 (4 November 1988).
- [7] L.T. Lam, I.G. Mawston, D. Pavlov, D.A.J. Rand, *J. Power Sources* 48 (1994) 257.
- [8] C.V. D'Alkaine, J. de Andrade, P.R. Impinnisi, *J. Power Sources* 85 (2000) 131–136.
- [9] H. Bode, *Lead-Acid Batteries*, Wiley, New York, 1977.
- [10] M.G. Mayer, D.A.J. Rand, *J. Power Sources* 59 (1996) 17.