

THE INFLUENCE OF CURING PROCESS ON THE LEAD-ACID BATTERY PERFORMANCE

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Introduction

The evolution of lead acid battery technology has been driven by the introduction of new materials and new manufacturing processes. There are great efforts to make more efficient electrodes, to obtain better battery performance and also to improve the process of making these devices [1-5].

From the steps involved in the positive plate manufacturing process, curing is a key stage during in which the paste is converted into a cohesive, porous mass, with a good adherence to the grid. Poor control of the process will diminish the mechanical strength and the electrical performance of the plates during battery service life [6]. The transformations that take place during the curing are dependent on the composition of starting materials and the processes, which occurs, in the mixing and pasting steps [7-11]. The curing process is the longest step in the manufacture of lead-acid batteries. The relative amounts of 3BS and 4BS in the positive paste are influenced by: a) the proprieties of starting leady-oxide (composition, morphology, particles size, etc); b) the quantities of water and sulfuric acid added in the mixing stage; c) the temperature, duration and method of mixing; d) the temperature, humidity and duration of curing; e) the stand time of the paste before pasting on the grid.

The present work aims to find the conditions under which 3BS is formed and to detect the relationship between the phase composition of plates in the cured and formed states.

Experimental

Paste and plates preparation

Positive paste was prepared in a laboratory mixer system; by mixing leady-oxide powder namely Balox (Barton pot variety) with a definite quantity of water, and 8%(wt.) with respect to the leady-oxide, sulfuric acid (1.4 g/cm³). The phase composition (wt.%) of used precursor leady-oxide was: Pb 24%, α -PbO 71,40% and β -PbO 4.60%.

The prepared paste was applied to grid cast from Pb-Sb alloy (4% Sb). The resulting positive plates were cured according to the following three methods:

A. In an industrial curing micro pilot provided with temperature and humidity controls and an air recirculation system, in two steps a) at 36°C and 75% relative humidity (RH) for 16h and b) at 40°C and 40% RH for 48h.

B. Air-dried at 20⁰C in a closed curing chamber for 36h. The moisture content of the plates provided the humidity themselves.

C. Air-dried at 20⁰C, covered with a polyethylene sheet for 72h.

After curing all the plates were dried at 70⁰C until the moisture content not exceed 2.0 %(wt). Samples cured pastes were analyzed by X-ray diffraction (XRD) phase-analysis method, and wet chemical analysis.

Plate's formation

A series of test cells with 1 positive and 2 negative (produced under factory conditions) dried plates were assembled. After a soaking for 72h in H₂SO₄ (sp.g. 1.05 g/cm³) the plates were formed in 0.8M H₂SO₄ solutions according to the following schedule: 2h-1A/cell; 1h break; 10h-1.85A/cell; 1h break; 4h-1.50A/cell; 3h-0.85A/cell. Samples of these formed plates, after washing in running water and drying at 125⁰C for 10h were subjected to phase compositions, morphology and chemical composition analysis.

Battery performance

Electrical performance tests (nominal capacity, cold cranking ability, charge acceptance and reserve-capacity) were carried out on a series of 12V/45A batteries manufactured using the three cured types of plates.

Result and discussion

The results of phase composition analysis obtained by X-ray diffraction data on cured materials are given in Table 1.

Table 1 Phase-analysis for different cured positive plates (wt.%).

Method of curing	α -PbO	3BS	1BS	HC	Pb
Micropilot (A)	56.00	36.20	-	7.80	-
Closed chamber (B)	64.05	26.67	-	3.65	5.63
Polyethylene covered (C)	56.54	30.84	2.87	6.29	3.46

It can be seen that at the end of curing the lead content in paste decreased considerably in all three curing methods do to their conversion to α -PbO. No 4BS was formed. Very little amount of 1BS (variety which is harmful to battery performance,) was formed in the plates cured under polyethylene sheet. Basic lead carbonate (HC) is formed in all the curing methods. The formation of carbonate roughens the surface of 3BS crystals [8]. This improve the contact between the crystals and, consequently the toughness of the paste. The level of 3BS in plates materials cured under polyethylene sheet is higher than those cured by method B (in closed chamber) but the first contains 1BS and cracking and partial shedding of pastes were observed.

The higher free lead content of plates cured after method B and C provides evidence that the curing process was incomplete (has been stalled probably, by the less humidity conditions existent in the chamber).

The above observations confirm that the cured material phase-composition is largely dependent on the humidity level and its variation during the process.

Table 2 gives the XRD analysis of the formed active materials.

Table 2 X-ray diffraction analysis of formed active mass

Method of curing	PbO	PbSO ₄	Pb	PbO ₂	α -PbO ₂	β - PbO ₂
Micro pilot (A)	9.33	1.68	-	88.99	7.83	81.16
Closed chamber (B)	12.43	5.35	2.76	79.46	12.18	67.28
Polyethylene covered (C)	12.38	3.56	0.73	83.33	10.09	73.24

The results shows that the active mass of plates previously cured after method A lead to a higher PbO₂ content than those cured under conditions B and C. In addition, the formed active material cured in micro pilot contains after oxidation more β -PbO₂ but the formed plates derived from material cured after method B and C still contains appreciable levels of unoxidized residues, i.e., PbO, PbSO₄ and Pb. It can be concluded therefore that the conditions of curing have a notable effect on the level of PbO₂ active mass formation.

After formation, the fully charged state of the cell was achieved by applying a constant current (2.25 A) until both the terminal voltage and the acid density (1.28 g/cm³) were kept constant for two hours. For the determining of nominal capacity, C₂₀, the full charged batteries were discharged at a constant current of 2,25 A until the terminal voltage fell to 10.5 V. The product between the current intensity and the discharge time yields the nominal capacity.

For the determining of charge acceptance, the fully charged batteries were discharged with a constant current $I=0.1C_{20}$ A, at 25⁰C. The batteries were then kept at 0⁰C for 25 hours and fully charged at a 14.4 V constant voltage. The current intensity value after 10 min. charge was recorded.

In the reserve-capacity tests, the fully charged batteries were subjected to two complete C₂₀ charge-discharge cycles and deposited for 28 days at (20 $\pm$ 5) ⁰C. The batteries were then discharged at 0.05 C₂₀ A, until the terminal voltage was 10.5 V. The measured reserve capacity was reported to the initial capacity.

In the cold-cranking ability tests, after three complete C₂₀ charge-discharge cycles, the fully charged batteries were kept at -18⁰C for 24h. The batteries were then discharged at 3.5 C₂₀ A and the recorded time until the terminal voltage to fell to 6 V was taken as a measure of cold-cranking ability.

Table 3 summarizes the electrical testing results of batteries manufactured using the three different cured plates. The results were recorded after technical requirements for quality included in Romanian STAS 444/1 - 74.

In the light of these results, it can be seen that the positive plate active mass previously cured by method A gives the highest electrical performance.

This could be attributed to the large β -PbO₂ and total PbO₂ contents since the capacity of β -PbO₂ (0.164 Ah/g) is larger than that of α - PbO₂ (0.135 Ah/g) [12]. Because during lead-battery discharge, the potential of negative plate is the first to reach the cut-off value, the cold-cranking ability (deep discharge at - 18⁰C) of battery is "negative-potential limited". Thus this propriety is not so much affected by positive plate structure.

The obtained results give us ground to conclude that curing methods B and C are not a successful technology for positive plates production.

Table 3 Electrical batteries parameters

Electrical characteristics	Method of curing		
	(A)	(B)	(C)
Initial capacity, E_{xp}/C_{20} (%)	109.8	100	104
Charge acceptance (A)	6.85	6.15	7.55
Reserve capacity (%)	93	83	85
Cold-cranking ability (sec.)	185	182	184

Conclusions

The above investigation illustrates that curing conditions are determinant for the modifications of the chemical and phase composition of positive active mass and for the electrochemical performance. Thus, a better understanding of the curing mechanisms is required in order to optimize the positive plate's performance.

It has been observed that the key to successful curing is the maintenance of an exact balance between the moisture content, temperature and duration of process (method A). It is essential to conduct the curing in an enclosed chamber that allows precise regulation of the ambient conditions.

Further experimental work is required to determine in detail, the influence of these parameters on curing reactions.

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