

Short Communication

Effect of Curing on Positive Plate Behaviour in Lead-Acid Cells

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Summary

The physicochemical and electrochemical properties of lead-acid battery positive plates were studied with regard to the method of curing. It has been observed that curing conditions strongly influence electrode composition and electrical performance.

1. Introduction

The positive active material of lead-acid battery plates produced according to Faure's process generally consists of a mixture of the two PbO_2 modifications: orthorhombic $\alpha\text{-PbO}_2$ and tetragonal $\beta\text{-PbO}_2$ [1, 2]. The relative proportions of the two forms of PbO_2 have been found to influence the discharge capacity [3, 4]. Their relative amounts depend on the conditions of manufacture, *i.e.*, positive paste density, specific gravity and temperature of the formation acid, as well as formation rate [5]. Discharge capacities of both modifications have been measured, and it has been found that the capacity, in units of ampere hours per gramme PbO_2 , of $\alpha\text{-PbO}_2$ is lower than that of $\beta\text{-PbO}_2$ [6]. These measurements, although of practical value, do not consider several other variables that influence the capacity of porous electrodes. In addition to the earlier mentioned conditions, the morphology of the phases in the dry plate before formation would seem to be of considerable importance [7, 8]. The morphology in the cured state will depend on the conditions imposed during paste mixing and curing. In paste mixing the main parameters are properties of the battery oxide, and the temperatures and volumes of water and acid added. Curing is carried out either by drying the plates in air or under poly(ethylene) sheet, or by use of an oven. This paper describes recent work that has been carried out in order to investigate more fully the effect of three different methods of curing on

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the physicochemical behaviour of positive plates before, and after, formation in sulphuric acid solution.

2. Experimental

Positive paste was prepared by mixing lead oxide powder with water and sulphuric acid of 1.40 g cm^{-3} specific gravity. The apparent density of the paste was adjusted to $4.35 \pm 0.05 \text{ g cm}^{-3}$. This paste was applied to grids cast from a Pb/Sb alloy (5% Sb). The dimensions of the grids were $143 \times 124 \times 1.8 \text{ mm}$. The physicochemical characteristics of the lead oxide used in this investigation are listed in Table 1.

The positive plates made from this paste were cured according to three different methods:

(1) air dried for two days;

(2) subjected to saturated steam at $55 \text{ }^\circ\text{C}$ and 80% relative humidity for one day, then air dried for one day;

(3) covered at $55 \text{ }^\circ\text{C}$ with a poly(ethylene) sheet for one day, then air dried for a further day.

For all samples, the water content of the plates after "drying", did not exceed 0.2%.

Chemical analysis was carried out on the unformed plates to determine the free lead and lead sulphate contents. The porosity of the plates is determined according to the following equation:

porosity = $(1 - \text{apparent density/theoretical density})$.

Prior to electroformation, the unformed plates were soaked in 1.06 g cm^{-3} sp. gr. H_2SO_4 for 10 h and then formed at $40 \text{ }^\circ\text{C}$ according to the following schedule: 10 h, 3.8 A/plate; 4 h, 3.2 A/plate; 3 h, 2.6 A/plate; 2 h, 1.6 A/plate. The paste weight of each plate was 75 g. After formation was completed, the plates were washed in running water for several hours then dried in an oven at $120 \text{ }^\circ\text{C}$ for 24 h. The PbO_2 and PbSO_4 were determined by wet chemical analysis. X-ray procedures were used to identify the allotropic PbO_2 phases present in the formed plates. Specific area measurements were made according to the method of Brunauer, Emmett and Teller (BET), using nitrogen absorption.

Electrical performance tests were carried out on active material masses and on batteries. In the first case the experiments were carried out in a

TABLE 1
Physicochemical characteristics of lead oxide powder

Free Pb (%)	BET specific surface area ($\text{m}^2 \text{ g}^{-1}$)	Acid absorption ($\text{mg H}_2\text{SO}_4 \text{ g}^{-1}$)	Water absorption ($\text{ml H}_2\text{O kg}^{-1}$)
29.71	2.1	240	120

Pyrex-glass cell. The cell was divided into two compartments by means of a perforated wall. The test electrode (0.5 g) and the Hg/Hg₂SO₄ reference electrode were situated in one compartment and the counter electrode, a platinum foil, in the other. Discharges were undertaken with 25 mA cm⁻² current density. The potential/capacity curves were recorded. In the second case the batteries consisted of six 2 V cells connected in series, with each cell containing ten positive and eleven negative flat plates and having a nominal capacity of 110 A h. The active material content of each positive plate was 80 g. Positive plates were previously cured according to methods (1), (2), or (3).

Discharges were carried out with a current density of 31 mA cm⁻² to an end voltage of 10.5 V and with a current density of 2.76 A cm⁻² until the voltage fell to 6 V. The voltage/time curves were recorded. In all experiments the electrolyte was a sulphuric acid solution of specific gravity 1.28 g cm⁻³.

3. Results and discussion

3.1. Unformed plates

Chemical analysis data of the active material of the cured plates are given in Table 2. For all samples analysed, the average PbSO₄ content is equal to 19%. Plates cured under poly(ethylene) sheet give an active material which contains less free lead than those cured by methods (1) and (2). In addition, they are characterised by a higher porosity (63%) than the other plates.

During curing, the two reactions (oxidation of metallic lead and evaporation of moisture) occur simultaneously and complement each other since water is a necessary catalyst in the exothermic metallic lead oxidation and heat is required to evaporate the moisture from the plate. It appears that curing in moist conditions under poly(ethylene) sheet produces higher humidity conditions and encourages a higher temperature from the exothermic oxidation of lead. Thus plate porosity increases and metallic lead oxidation is accelerated.

3.2. Formed plates

The chemical analysis and X-ray diffraction data on formed plates are given in Table 3. The results show that the active material of plates previ-

TABLE 2

Physicochemical analysis of cured, unformed active material

Method of curing	Free Pb (%)	PbSO ₄ (%)	Porosity (%)
(1)	6.7	19.7	43
(2)	4.7	19.1	51
(3)	2.0	18.6	63

TABLE 3

Physicochemical and X-ray diffraction analysis of formed active material

Method of curing	PbSO ₄ (%)	PbO ₂ (%)	α-PbO ₂ (%)	β-PbO ₂ (%)	BET specific surface area (m ² g ⁻¹)
(1)	13.7	85.4	4.2	81.2	4.8
(2)	8.1	89.9	3.7	86.16	5.0
(3)	1.4	97.3	Traces	97.3	6.2

ously cured under poly(ethylene) sheet appears to convert completely to lead dioxide on formation, and shows a higher BET specific area in comparison with that of the other plates.

X-ray diffraction indicates the presence of about 4% α-PbO₂ in samples (1) and (2), while in sample (3) only traces of α-PbO₂ are observed. According to these results, the formation of plates cured under poly(ethylene) sheet seems to lead to a higher PbO₂ content than in those cured under conditions (1) and (2). As shown in Table 2, curing method (3) leads to a lower free lead content and to a higher porosity, and these two parameters make the diffusion of the electrolyte through the active mass easier and favour PbO₂ formation.

Anodic oxidation of plates cured under poly(ethylene) sheet gives an active material which contains more β-PbO₂, and has a higher BET specific area than that of plates cured under conditions (1) and (2).

3.3. Electrical capacity

3.3.1. *Electrode test.* The electrode test gives the discharge curves shown in Fig. 1. We observe that electrode (3), with active material cut from a positive plate (previously cured by method (3)), gives the highest electrical capacity (0.096 A h g⁻¹ PbO₂) compared with the other electrodes.

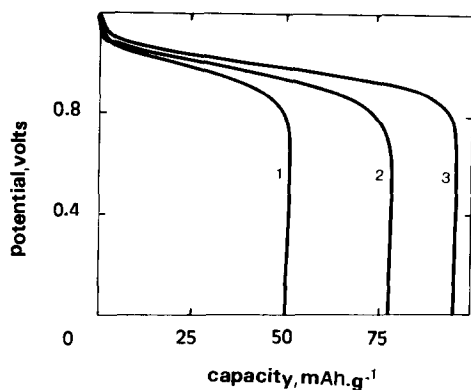


Fig. 1. Potential-capacity curves of the electrodes discharged under a current density of 25 mA cm⁻². 1, Paste formed (1); 2, paste formed (2); 3, paste formed (3).

3.3.2. *Battery test.* The discharge curves at low (31 mA cm^{-2}) and high (2.76 A cm^{-2}) current densities are shown in Figs. 2 and 3, respectively. Battery (3) gives the longest discharge times: 18 h and 240 s at low and high discharge current densities, respectively. In the light of these results, it can be seen that the positive plate active material (previously cured by method (3)) gives high electrical performance. This must be attributed to the large $\beta\text{-PbO}_2$ and total PbO_2 contents since the capacity and the surface area of $\beta\text{-PbO}_2$ are each larger than that of $\alpha\text{-PbO}_2$.

In conclusion, it has been clearly observed that curing conditions lead to important modifications of the physicochemical properties of positive plate active material and of the electrochemical performance. Kinetics and thermodynamic investigation on PbO_2 formation are in progress.

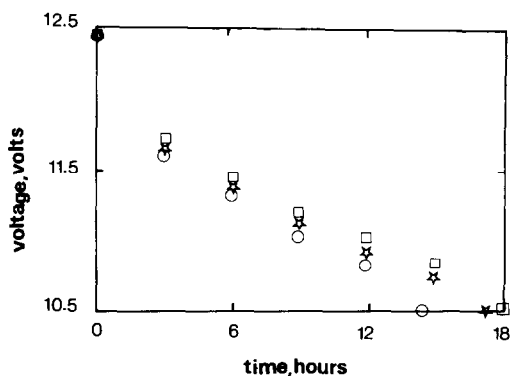


Fig. 2. Voltage-time curves of the batteries discharged under a current density of 31 mA cm^{-2} . \circ , Battery (1); \star , battery (2); \square , battery (3).

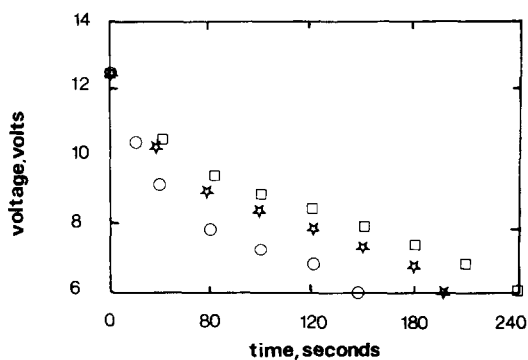


Fig. 3. Voltage-time curves of the batteries discharged under a current density of 2.76 mA cm^{-2} . \circ , Battery (1); \star , battery (2); \square , battery (3).

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