

Mechanism of PbO₂ formation in lead/acid battery positive plates

L. Zerroual* and F. Tedjar

Unité de Recherche Electrochimie, Université de Sétif, 19000 Sétif (Algeria)

J. Guitton

Laboratoire d'Ionique et d'Electrochimie des Solides de Grenoble (LIESG), Domaine Universitaire, BP 75, 38402 Saint-Martin d'Hères (France)

A. Mousser

Département Matériaux Inorganiques, Université de Constantine, 25000 Constantine (Algeria)

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Abstract

The processes which take place in the paste during preparation and formation of lead/acid battery positive plates in H₂SO₄ (sp.gr. 1.05) were studied using wet chemical analysis and X-ray diffraction. It was found that basic lead sulfate was obtained in two stages. During the first stage, free lead reacts in a basic character paste with H₂SO₄ added to the lead powder and gives lead sulfate with an overall stoichiometry equivalent to PbSO₄·H₂O. During the second period, PbO undergoes an acid/base reaction to 3PbO·PbSO₄·H₂O. When soaking and forming in free H₂SO₄, lead oxide (free PbO plus PbO in the basic sulfate) reacts with H₂SO₄ and gives lead sulfate PbSO₄. The X-ray diffraction data showed that PbSO₄·H₂O is converted to α-PbO₂, while PbSO₄ leads to the β-PbO₂ form.

Introduction

Two forms of PbO₂ are present in positive plates material: α-PbO₂ and β-PbO₂ [1, 2]. The former is the orthorhombic and the latter is the tetragonal modification. It has been shown previously that the amounts of α- and β-PbO₂ that are formed in the positive plate material vary with: (i) the density of the paste, i.e. the H₂SO₄/PbO ratio; (ii) the specific gravity of the forming acid; (iii) the rate, and (iv) the temperature of the formation [3–14].

On the other hand, the capacity and the life of the positive plate are determined by the ratio of the two polymorphs. The mechanism of the processes of α-PbO₂ formation in lead/acid battery positive plate has been subject of continuing interest these last years. Two schools of thought are found in the literature. According to the first one, solid state reactions within the basic lead sulfate crystals take place and yield α-PbO₂ [4, 6]. According to the second one, the solution in the pores of the paste, which is locally alkalized, leads to α-PbO₂ crystals [3, 7]. Other mechanisms have been proposed such as anodic oxidation of grid lead [1], of PbO in the paste [14], and tetrabasic lead sulfate (4PbO·PbSO₄) [15].

*Author to whom correspondence should be addressed.

In the present work the changes in phase and chemical composition occurring during paste preparation and formation of lead/acid battery positive plate in H_2SO_4 (sp.gr. 1.05), were studied by X-ray diffraction, and wet chemical analysis. The mechanisms of the electrochemical and chemical processes of formation suggested in this work are based on these results.

Experimental

Paste characterization

The paste was prepared by mixing lead powder with water and sulfuric acid (5 wt.% (w/o) with respect to lead powder). Samples were taken after 5, 15, 25, 35, and 45 min of mixing. The material was first homogenized in a mortar, then transferred to the sample holder of a Philips X-ray diffractometer (filtered copper radiation). Lead, lead oxide (free PbO plus PbO in the basic sulfates), and lead sulfate (free PbSO_4 plus PbSO_4 bonded in the basic sulfates) contents were chemically determined. The physicochemical characteristics of lead powder used in this work are summarized in Table 1.

Active-material characterization

Plates of dimensions 124 mm \times 134 mm \times 1.8 mm were soaked in H_2SO_4 (sp.gr. 1.05) for 15 min, then formed according to the following schedule: 4 h 1.25 A/plate, 10 h 1.6 A/plate, 3 h 1 A/plate, 2 h 0.75 A/plate. The temperature was maintained at 27 °C. For both negative and positive grids, lead-antimony alloy was used. Plates were removed every 5 h. After washing in running water for several hours to remove excess H_2SO_4 , they were dried at 140 °C for 5 h. Samples were taken close to the four corners and from the middle portion of the plate. The material was homogenized in a mortar and analysed by X-ray diffraction. The relative intensity of the X-ray characteristic diffraction lines was adopted as a measure of the phase changes in the plate during paste preparation and formation [16]. It is defined as the ratio of the 'i' phase characteristic reflection intensity and the sum of the intensities of the characteristic diffraction lines of all phases. PbO_2 and PbSO_4 contents were chemically determined.

Lead sulfate characterization

To prepare and characterize the different phases involved in the mechanism proposed in this work we have used:

(i) a commercial basic lead sulfate compound (sample A) identified by X-ray diffraction as $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$;

TABLE 1

Physicochemical characteristics of lead powder^a

Free Pb (%)	BET specific area ($\text{m}^2 \text{g}^{-1}$)	Acid absorption ($\text{mg H}_2\text{SO}_4 \text{g}^{-1}$)	Water absorption ($\text{cm}^3 \text{H}_2\text{O kg}^{-1}$)
28	2.1	245	125

^aThe BET specific area was measured using nitrogen as adsorbant.

(ii) a lead sulfate (sample B) prepared by addition of sample A or a manufactured lead/acid battery paste, identified as a mixture of 65.13% $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$, 27.27% tet-PbO, and 7.6% metallic lead, to a solution of acetic acid (12 wt.%). The mixture was allowed to boil for 1 h. After filtration, the precipitate was washed in distilled water and dried at 140 °C for 2 h;

(iii) a lead sulfate (sample C) prepared by heating sample B at 400 °C for 4 h;

(iv) a lead sulfate (sample D) prepared by soaking a manufactured lead/acid battery paste in H_2SO_4 (sp.gr. 1.05) for 10 days at room temperature.

The four samples A, B, C and D were characterized by X-ray diffraction, thermal analyses, infrared spectra, wet chemical analysis, and microscopic observations. Gravimetric and differential thermal analyses were obtained for the various samples after oven drying them overnight at 130 °C to remove surface water, then the samples were heated under nitrogen at 10 °C/min. The thermal gravitic (TG), the differential thermal gravitic (DTG), and the differential thermal analysis (DTA) curves were recorded.

Results and discussion

Unformed active material

Figure 1(a) shows the changes in intensities of the characteristic diffraction lines of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ $d=3.26$ Å, tet-PbO $d=3.12$ Å, and Pb $d=2.86$ Å measured on X-ray diffraction patterns during paste preparation. Figure 1(b) illustrates the chemical analysis results for PbO, PbSO_4 , and Pb.

From Fig. 1(a) it is seen that tet-PbO and metallic lead decrease from the beginning of the paste preparation; in contrast $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ increases. At the end of the preparation (after 45 min mixing) the X-ray diffraction data show that the paste contains 65.13% $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$, 7.6% Pb, and 27.27% tet-PbO. Figure 1(b) shows that, while the metallic lead paste content decreases, the amount of lead sulfate increases, but the global PbO content in the paste remains constant.

According to these results we can assume that no reaction between tet-PbO and H_2SO_4 is involved, and we arrive at the conclusion that lead sulfate originates as a result of a reaction between metallic lead and H_2SO_4 in the presence of air. The decrease in tet-PbO amount shown by X-ray diffraction analysis (Fig. 1(a)) may be related to an acid/base reaction between lead sulfate and tet-PbO to give basic lead sulfate $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$.

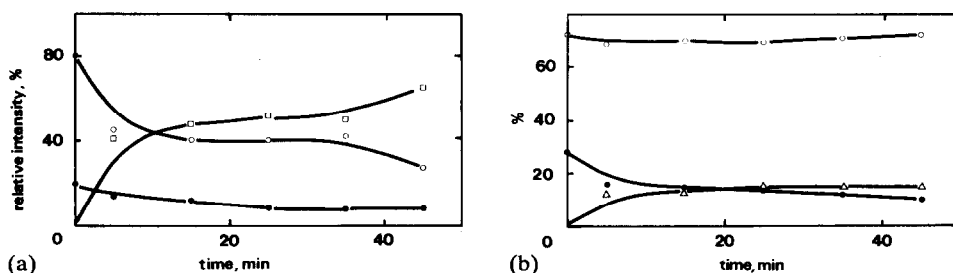


Fig. 1. (a) Intensity changes of the characteristic diffraction lines of (\square) $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$, (\circ) tet-PbO, and (\bullet) Pb during paste preparation; (b) changes in the percentages of (\circ) PbO, (\triangle) PbSO_4 , and (\bullet) Pb during paste preparation.

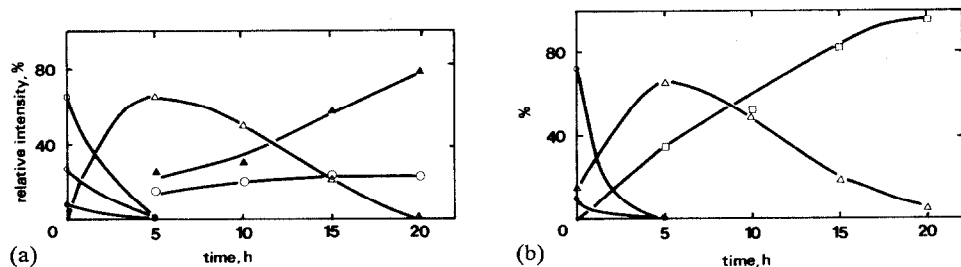


Fig. 2. (a) Intensity changes of the characteristic diffraction lines of (\square) $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$, (\circ) tet-PbO, (\bullet) Pb, (Δ) PbSO_4 , (\circ) $\alpha\text{-PbO}_2$, and (\blacktriangle) $\beta\text{-PbO}_2$ during formation; (b) changes in the percentages of (\circ) PbO, (Δ) PbSO_4 , (\bullet) Pb, and (\square) PbO_2 during formation.

Formed active material

Figure 2(a) shows the changes in the intensities of the characteristic diffraction lines of PbSO_4 $d=3.00$ Å, Pb $d=2.86$ Å, $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ $d=3.26$ Å, tet-PbO and $\alpha\text{-PbO}_2$ $d=3.12$ Å, and $\beta\text{-PbO}_2$ $d=3.50$ Å measured on X-ray diffraction patterns during formation. Figure 2(b) illustrates the chemical analysis results of Pb, PbO, PbSO_4 , and PbO_2 . From Fig. 2(a) it is seen that tet-PbO, $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$, and metallic lead disappear within the first 5 h of formation. This is also confirmed by chemical analysis: Fig. 2(b) shows that PbO reacts completely on the 5th h. Chemical reactions between H_2SO_4 , tet-PbO and basic lead sulfate produce lead sulfate crystals. This compound constitutes 65% of all lead compounds in the plate during the first 5 h of formation. After the 5th h, PbSO_4 begins to decrease and after 20 h forming only 4.9% of it remains. In addition, X-ray diffraction investigations (Fig. 2(a)) show that after 5 h forming 15% $\alpha\text{-PbO}_2$ is present; the amount of this compound reaches 23% at the end of the formation. It is obvious to remark that the 15% of $\alpha\text{-PbO}_2$ already formed coincides with the amount of lead sulfate bonded in the basic sulfate present in the paste before forming (see Fig. 2(b)). This let us conclude that $\alpha\text{-PbO}_2$ crystals are produced as a result of an electrochemical oxidation of this form of lead sulfate. This confirms the decrease in $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ during the first 5 h as shown in Fig. 2(a). In contrast, $\beta\text{-PbO}_2$ forms intensively from the start of the formation as a result of an electrochemical oxidation of a second lead sulfate variety, resulting from the chemical reaction between the global PbO and free H_2SO_4 . At the end of the formation, X-ray diffraction data show that the plate contains $\beta\text{-PbO}_2$ (77%) in an amount much larger than that of $\alpha\text{-PbO}_2$ (23%). These values correspond nearly to the PbO and Pb quantities initially present in the lead powder.

Identification of the lead sulfate compounds

Chemical analysis

The chemical analysis data are summarized in Table 2. It is easily deduced that the composition of the four samples correspond nearly to $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$, $\text{PbSO}_4 \cdot \text{H}_2\text{O}$, and PbSO_4 , respectively.

Thermal analyses

The TG and DTG curves for samples A and B are illustrated in Fig. 3(a) and 3(b), respectively. The TG weight losses for samples A and B were 2.5% and 5.6%

TABLE 2

Chemical analysis of the different samples

Sample	Pb (II) (%)	SO ₄ (%)	H ₂ O (%)
A	83	9.6	2.5
B	64	28	5.6
C and D	67.8	31	<0.1

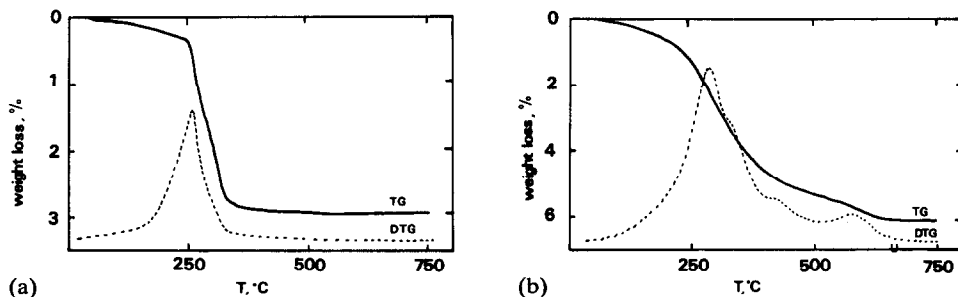


Fig. 3. (a) TG and DTG analyses of sample A; (b) TG and DTG analyses of sample B.

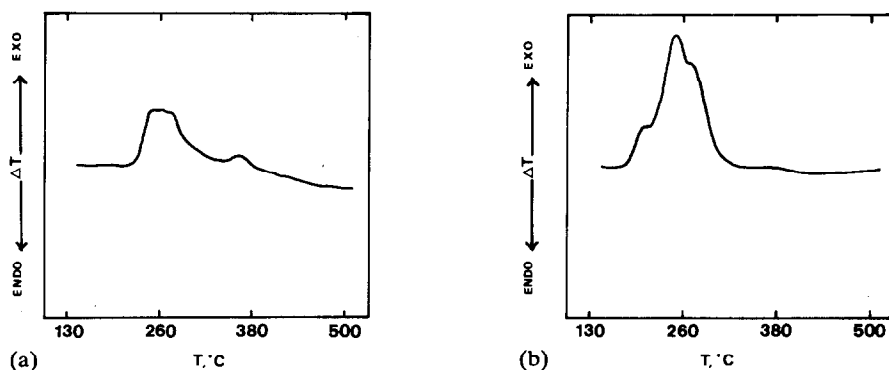


Fig. 4. (a) DTA analysis of sample A; (b) DTA analysis of sample B.

at nearly 250 °C. They correspond to one mole of H₂O per mole of PbSO₄ and 1.4 moles of H₂O per mole of 3PbO·PbSO₄·H₂O.

Figures 4(a) and 4(b) show the DTA curves obtained after heating the samples A and B under the same conditions previously described. For the two samples an exothermic peak due to the water loss at this temperature appears at nearly 250 °C. In the case of sample A this peak is less prominent. This may be related to the state and position of the H₂O molecules within the compound lattice. The TG analyses of the samples C and D showed no weight loss.

IR spectra analysis

Figures 5 and 6 show transmittance spectra of the samples A, B, C and D, respectively at room temperature. Figure 5 shows the IR spectra obtained for sample

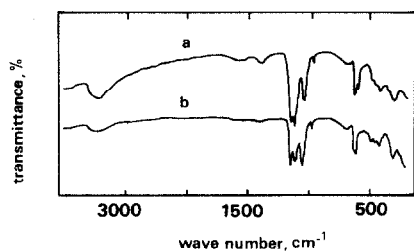


Fig. 5. Room temperature transmittance spectra of sample A: (a) before heating at 400 °C, and (b) after heating at 400 °C.

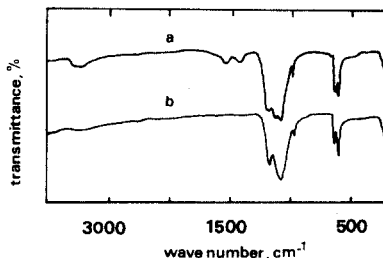


Fig. 6. Room temperature transmittance spectra of (a) sample B, and (b) samples C and D.

A before (Fig. 5(a)) and after heating at 400 °C (Fig. 5(b)). For the two spectra we remark the lead–oxygen bands in the region between 200 and 600 cm^{-1} , and the lead–sulfate bands which appear in the region between 600 and 1200 cm^{-1} . In addition, large bands were observed at 1600 and 3500 cm^{-1} (Fig. 5(a)) which correspond to the H_2O and/or OH groups. Similar bands were observed by Bonner [17], when he studied the IR spectrum of pure water. It is obvious to notice the absence of these bands after heating sample A at 400 °C (Fig. 5(b)).

Figure 6 shows the IR spectra of sample B (Fig. 6(a)), sample C and D (Fig. 6(b)). We observe the lead–sulfate bands in the region between 600 and 1200 cm^{-1} . In addition, the large bands corresponding to H_2O and/or OH groups are recorded at 1600 and 3500 cm^{-1} for sample B (Fig. 6(a)). From Fig. 6(b), it is seen that these bands disappear completely. For the three samples B, C and D no lead–oxygen bands were observed in the region between 200 and 600 cm^{-1} . This let us conclude that sample B is an hydrated lead sulfate, which is quite different from the $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ crystals; samples C and D are anhydrous lead sulfates.

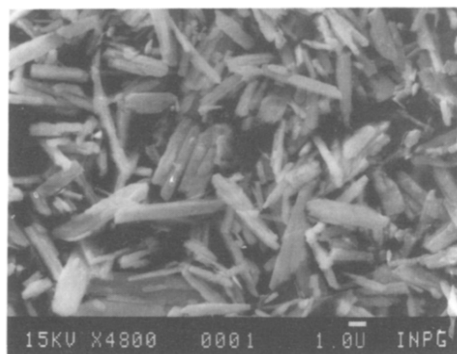
Microscopic observation

Microscopic examinations of the different phases are illustrated in Fig. 7. The micrographs show a great difference in form and size of the particles. We observe in Fig. 7(a) the common needle particles of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$. Similar micrographs were found by Burbank [9] in her study on basic lead sulfates synthesized from reagent grade PbO and H_2SO_4 . Figure 7(b) and 7(c) present the micrographs corresponding to $\text{PbSO}_4 \cdot \text{H}_2\text{O}$ prepared from $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ and $\text{PbSO}_4 \cdot \text{H}_2\text{O}$ prepared from an unformed lead/acid battery plate, respectively. The micrographs show for both samples a group of assembled small particles which are quite different in form and size in comparison with $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ ones. Figures 7(d) and 7(e) show the micrographs obtained from samples C and D, respectively. From these Figures, it is seen that both samples are composed of assembled particles different in form and size with comparison to those observed for sample B. This difference may be explained by the fact that, material B presents a high surface area which leads to a higher water content.

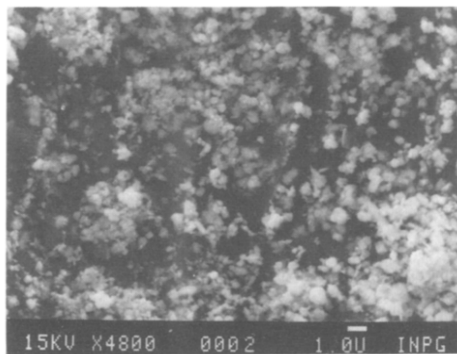
In the light of all these results we can suggest that the process giving basic lead sulfate during paste preparation takes place in two stages:

(i) during the first stage free lead is transformed to an hydrated lead sulfate according to the following reaction, which takes place in a basic character paste:

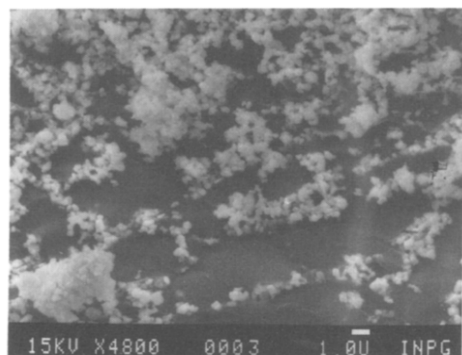




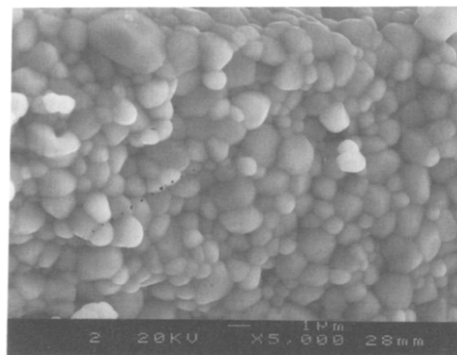
(a)



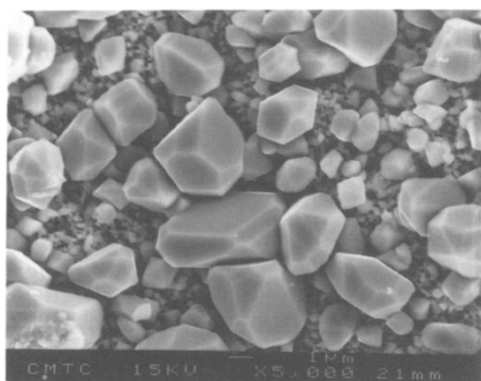
(b)



(c)



(d)



(e)

Fig. 7. Scanning electron micrographs of the different samples: (a) $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ (a commercial basic lead sulfate); (b) $\text{PbSO}_4 \cdot \text{H}_2\text{O}$ prepared by acetic attack of basic lead sulfate; (c) $\text{PbSO}_4 \cdot \text{H}_2\text{O}$ prepared by acetic attack of an unformed lead acid battery paste; (d) PbSO_4 prepared by heating sample B at $400\text{ }^\circ\text{C}$; (e) PbSO_4 prepared by soaking a manufactured lead/acid battery paste in H_2SO_4 (sp.gr. 1.05) for 10 days at room temperature.

(ii) during the second period, as a result of an acid/base reaction tet-PbO and $\text{PbSO}_4 \cdot \text{H}_2\text{O}$ produce $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ according to:



So we can assume that basic lead sulfate ($3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$) is a complex salt containing 3 moles of tet-PbO and 1 mole of monohydrated lead sulfate ($\text{PbSO}_4 \cdot \text{H}_2\text{O}$) obtained by a global reaction which takes place in basic regions according to the following:



Taking into account the X-ray diffraction results already obtained, we can assume that the process of formation can be divided in two stages:

(i) First stage (prior to the 10th h) according to the low pH value at the paste–electrolyte interface and the E/pH diagram of lead/sulfuric acid system, given by Rüetschi and Angstadt [18], it is obvious to remark that tet-PbO and $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ crystals yield lead sulfate. $\text{PbSO}_4 \cdot \text{H}_2\text{O}$ with basic character is oxidized to $\alpha\text{-PbO}_2$, while PbSO_4 with acid character leads partially to $\beta\text{-PbO}_2$.

(ii) Second stage (after the 10th h), the amount of $\alpha\text{-PbO}_2$ remains constant and lead sulfate (with acid character) continues to be oxidized to $\beta\text{-PbO}_2$ form. At the end of the formation the amount of $\alpha\text{-}$ and $\beta\text{-PbO}_2$ in the plate correspond to the quantities of metallic lead and lead oxide initially present in the lead powder, respectively.

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