

Conversion of tribasic lead sulfate to lead dioxide in lead/acid battery plates

1. Relationship between the phase compositions of plates in the cured and formed states

L. Zerroual, N. Chelali and F. Tedjar

Laboratoire d'Energétique et d'Electrochimie du Solide, Université de Sétif, Sétif 19000 (Algeria)

J. Guitton

Laboratoire d'Ionique et d'Electrochimie du Solide (LIES), BP 75, Domaine Universitaire, 38402 Saint-Martin-d'Hères Cedex (France)

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Abstract

The influence of the initial amount of H_2SO_4 added to lead powder on the phase compositions of plates in the cured and formed states has been studied. IR spectra, X-ray diffraction, scanning electron microscope observations, and wet-chemical analysis are used as techniques of investigation. It was found that the phase composition of the paste depends on the H_2SO_4 :oxidized lead powder ratio. In addition, it is found that α - and β - PbO_2 are formed in the lead/acid battery positive plate from $3PbO \cdot PbSO_4 \cdot H_2O$. The amounts of these two compounds were strongly affected when varying the quantity of H_2SO_4 with respect to the lead powder.

Introduction

It has been shown that variations in the nature of positive active material can have a great effect on the behaviour of positive plate in lead/acid battery [1]. During formation lead oxide and basic lead sulfates turn into α - and β - PbO_2 . The amounts of these polymorphs depend on the following conditions: (i) concentration of the formation H_2SO_4 electrolyte; (ii) formation current density; (iii) phase composition of the cured paste; (iv) paste density, and (v) temperature. In addition, the nature and morphology of the phases in the cured plate are of a considerable importance.

Previous studies [2–12] were aimed at determining the influence of the aforementioned conditions on the phase compositions of the active material in the cured and formed states. Many studies were aimed at the determination of the mechanism of PbO_2 formation in lead/acid battery positive plate. It is considered [12–15] that large crystals of tetrabasic lead sulfate, $3PbO \cdot PbSO_4$, convert via a metasomatic process to α - PbO_2 . Thus, it has become common place to accept that tetrabasic lead sulfate favours the formation of α - PbO_2 and, by analogy, that tribasic lead sulfate yields the β - PbO_2 phase.

In studying the conversion of tetrabasic lead sulfate to lead dioxide in lead/acid battery positive plates, however, Lam *et al.* [16] demonstrates that the surface of tetrabasic lead sulfate crystals is chemically converted to a dense layer of lead sulfate

that, in turn, is electrochemically oxidized to β -PbO₂ during the subsequent formation stage. In a previous paper [17] it was also shown that β -PbO₂ originates as a result of anodic conversion of an anhydrous form of lead sulfate, whereas PbSO₄·H₂O, a monohydrated lead sulfate phase, initially bonded in tribasic lead sulfate, yields α -PbO₂.

It is well known that 3PbO·PbSO₄·H₂O is one of the main compounds which is formed in the paste. As reported in previous studies [18, 19], in the presence of H₂SO₄, this compound reacts and converts to monobasic lead sulfate, PbO·PbSO₄, and/or lead sulfate, PbSO₄.

The present work aims to find the conditions under which 3PbO·PbSO₄·H₂O is formed and to detect the relationship between the phase compositions of plates in the cured and formed states. IR spectra, X-ray diffraction technique (XRD), scanning electron microscopy (SEM), and wet-chemical analysis were used in this study.

Experimental

The pastes were prepared from industrial lead powder (72% PbO). The XRD pattern of the powder showed the presence of tetragonal PbO and Pb. Pastes were prepared in a laboratory mixer at 40 °C with H₂SO₄ varying from 2 to 15 wt.% with respect to the lead powder.

The components were introduced in the following sequences: lead powder, water, H₂SO₄ solution. Mixing was continued for 45 min, then the paste was cooled down to room temperature and homogenized in a mortar. The phase composition was determined by XRD technique. The crystal structure was observed by SEM. IR spectra were recorded using a PYE UNICAM SP3-300 infrared spectrophotometer.

Lead, lead oxide (free PbO plus PbO bonded in basic sulfates), and lead sulfate (free PbSO₄ and PbSO₄ bonded in basic sulfates) were chemically determined.

To express more clearly the dependence of the active material phase composition on the initial H₂SO₄ paste content, cured plates were soaked in 1.05 g cm⁻³ H₂SO₄ for 15 min and then formed at 40 °C according to the schedule described elsewhere [17].

After formation was completed, the plates were washed in running water for several hours followed by drying in an oven at 120 °C for 24 h. The PbO₂ and PbSO₄ contents were determined by wet-chemical analysis. XRD was used to identify the allotropic PbO₂ phases present in the formed active material. Specific area measurements were made according to the BET method, using nitrogen adsorption. The samples were degassed overnight at 120 °C.

Results

Unformed active material

The change in phase composition of the paste obtained after addition of H₂SO₄ was expressed by the change of the relative intensity of the reflections belonging to this phase, $I_i/\Sigma I_n$, where I_i denotes the intensity of the reflection belonging to the given phase and ΣI_n is the sum of the characteristic reflections belonging to all phases present in the paste.

The following characteristic reflections were used: $d=3.12$ Å for tetragonal PbO; $d=3.26$ Å for 3PbO·PbSO₄·H₂O; $d=2.84$ Å for Pb, and $d=2.95$ Å for PbO·PbSO₄ [17].

Figure 1 illustrates the change of the phase composition of the different pastes as a function of the amount of H_2SO_4 . Up to 5% H_2SO_4 , it is seen that the amounts of PbO and Pb decrease and undergo an acid-base reaction to $3PbO \cdot PbSO_4 \cdot H_2O$. The amount of this compound increases in proportion to the H_2SO_4 content and constitutes the major phase of the mixture.

Above 5% H_2SO_4 , $PbO \cdot PbSO_4$ increases while $3PbO \cdot PbSO_4 \cdot H_2O$ and PbO decrease to reach 20 and 21%, respectively, for a paste prepared with 15% H_2SO_4 . The amount of Pb remains almost constant. Figure 2 shows the changes in percentages of $PbSO_4$, PbO, and Pb determined by chemical analyses for the different pastes. It is seen that the amount of $PbSO_4$ ($PbSO_4$ bonded in $3PbO \cdot PbSO_4 \cdot H_2O$, and $PbO \cdot PbSO_4$) increases with increasing amount of H_2SO_4 , while PbO decreases and Pb remains almost constant at about 10%.

The room temperature transmittance spectra of pastes prepared respectively with 2, 5, and 15% H_2SO_4 are presented in Fig. 3. Note that for an increasing amount of H_2SO_4 with respect to the amount of lead powder, the lead-oxygen bands (region

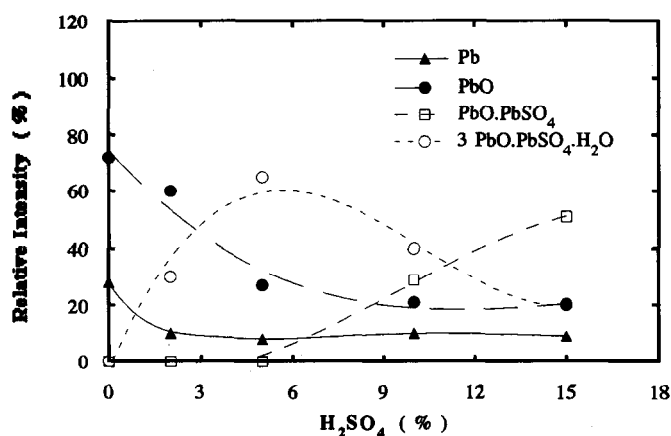


Fig. 1. Change of the phase composition of the paste vs. % H_2SO_4 ; X-ray diffraction analysis.

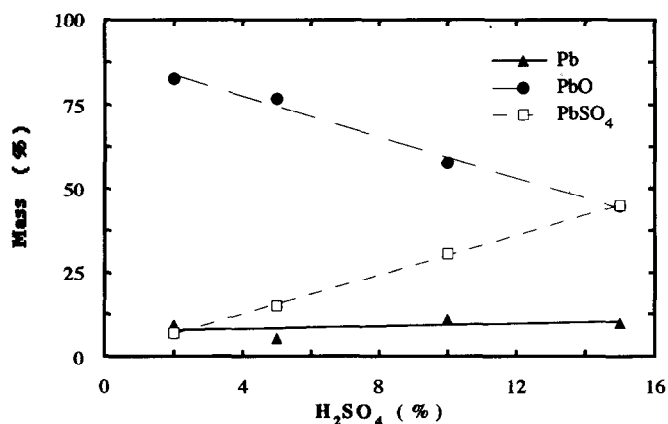


Fig. 2. Change of the phase composition of the paste vs. % H_2SO_4 ; chemical analysis.

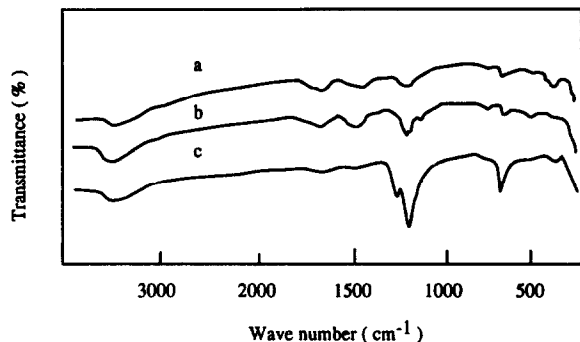


Fig. 3. Transmittance spectra of the different pastes, at room temperature, prepared with: (a) 2%; (b) 5%, and (c) 15% H_2SO_4 .

TABLE 1

Chemical and X-ray diffraction analysis of the formed active material

| H_2SO_4 (%) | PbSO_4 (%) | PbO_2 (%) | $\alpha\text{-PbO}_2$ (%) | $\beta\text{-PbO}_2$ (%) | BET surface area ($\text{m}^2 \text{g}^{-1}$) |
|--------------------------------|------------------------|-----------------------|------------------------------|-----------------------------|--|
| 2 | 7.73 | 92.27 | 18.45 | 73.82 | 6.50 |
| 5 | 4.90 | 95.10 | 22.50 | 72.60 | 5.10 |
| 10 | 10.59 | 89.41 | 15.51 | 73.90 | 5.60 |
| 15 | 25.39 | 74.61 | 6.79 | 67.82 | 5.20 |

between 200 and 600 cm^{-1}) disappear progressively, in contrast to the lead sulfate bands (region between 600 and 1200 cm^{-1}) which become more prominent. In addition to the large band detected at 3500 cm^{-1} which is relative to physisorbed water, two large bands indicating the presence of chemisorbed water (within $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ lattice) were recorded at 1400 and 1600 cm^{-1} for the samples prepared with 2 and 5% H_2SO_4 (Figs. 3(a) and (b)).

Similar bands, but less prominent, were observed in this region for the sample prepared with 15% H_2SO_4 (Fig. 3(c)). In Fig. 4 the SEM pictures of different pastes prepared with 0% (Figs. 4(a) and (b)), 5% (Figs. 4(c) and (d)), and 15% H_2SO_4 (Fig. 4(e)) are represented. From the micrographs we conclude that the addition of H_2SO_4 has strongly affected the material crystal structure. A great difference in the form and the size of the particles was observed. From Figs. 4(a) and (b) it is seen that lead powder is composed of particles identical in size and form.

After having added H_2SO_4 (5% with respect to lead powder), the sample obtained showed a mixture of the common needle particles of tribasic lead sulfate, and lead oxide (Figs. 4(c) and (d)). Figure 4(e) shows a sample prepared with 15% H_2SO_4 , with a group of assembled particles different in form and size with respect to PbO and $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ crystals.

Formed active material

For the determination of the active material phase composition the following characteristic reflections were considered: $d=3.12 \text{ \AA}$ for $\alpha\text{-PbO}_2$; $d=3.50 \text{ \AA}$ for $\beta\text{-$

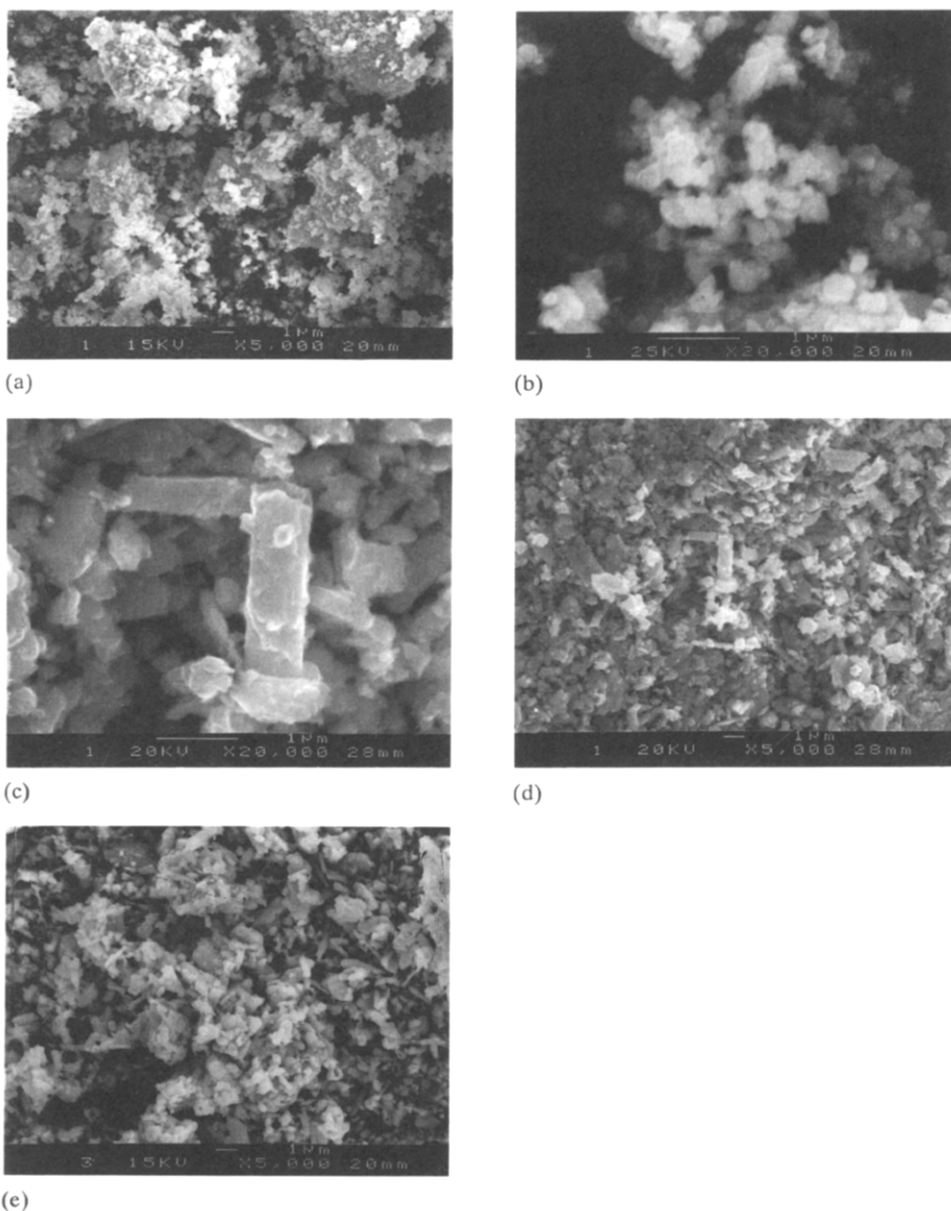


Fig. 4. Scanning electron micrographs of the different pastes prepared with: (a, b) 0%; (c, d) 5%, and (e) 15% H_2SO_4 .

PbO_2 , and $d=3.00 \text{ \AA}$ for PbSO_4 [17]. The chemical analysis and XRD results are summarized in Table 1.

The chemical analysis results showed that up to 5% H_2SO_4 paste content, the conversion of the unformed active material to PbO_2 is almost complete and the amount

of unreacted PbSO_4 is less than 8 and 5%, respectively, for pastes prepared with 2 and 5% H_2SO_4 .

Above 5% H_2SO_4 the pastes convert partially to PbO_2 and the amount of unreacted PbSO_4 increases in proportion to the H_2SO_4 paste content. The XRD results showed that when increasing the amount of H_2SO_4 with respect to that of oxidized lead powder in the paste, the quantity of $\alpha\text{-PbO}_2$ decreases. From Fig. 1 and Table 1 it is also seen that the larger the amount of $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ paste content, the larger will be the $\alpha\text{-PbO}_2$ amount in the formed active material. Regarding the BET specific surface area, we did not observe any relationship between the values obtained and the phase composition of the formed active material.

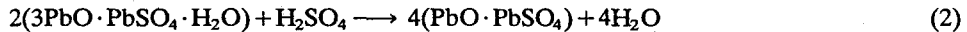
Discussion

Paste prepared by mixing oxidized lead powder with sulfuric acid solution leads to the formation of basic lead sulfates. The nature of the basic sulfate obtained depends on the amount of H_2SO_4 with respect to that of oxidized lead powder.

Up to 5% H_2SO_4 , $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ is the major phase which is formed in the paste according to the following equation:



Above 5% H_2SO_4 , this compound disappears progressively and becomes $\text{PbO}\cdot\text{PbSO}_4$ according to the following equation:



As we have mentioned elsewhere [17], $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ originates as a result of an acid-base reaction taking place into two stages.

During the first stage metallic lead contained in the lead powder becomes $\text{PbSO}_4\cdot\text{H}_2\text{O}$ in the presence of air and H_2SO_4 . During the second stage, tetragonal PbO reacts with $\text{PbSO}_4\cdot\text{H}_2\text{O}$ and gives $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$. So the presence of $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ in the paste can be associated with the stability of $\text{PbSO}_4\cdot\text{H}_2\text{O}$. In the light of these considerations we can conclude that the paste composition depends largely on the molar ratio between the lead powder and the sulfuric acid. At a H_2SO_4 concentration lower than 5%, $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ is formed and constitutes the major phase of the paste. But at H_2SO_4 concentrations higher than 5% this compound converts to $\text{PbO}\cdot\text{PbSO}_4$.

On forming, the different pastes convert to PbO_2 with different amounts of β - and $\alpha\text{-PbO}_2$. The latter seems to vary in proportion to the $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ paste content. In addition, large quantities of PbSO_4 remain unconverted when the amount of H_2SO_4 is higher than 5%. This can be explained by the fact that, on one hand $\text{PbO}\cdot\text{PbSO}_4$ constitutes the major phase of the paste, and on the other hand, $\text{PbO}\cdot\text{PbSO}_4$ converts with greater difficulty than $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$. According to the chemical and XRD analysis results of both unformed and formed active material, it seems that $\alpha\text{-PbO}_2$ is formed with high percentage in pastes prepared with H_2SO_4 concentration lower than 5%. With increasing H_2SO_4 concentrations, higher than 5%, the amount of $\alpha\text{-PbO}_2$ decreases.

Considering these results, we can deduce that when varying the H_2SO_4 content in the process of paste preparation, the phase compositions of the plates in the cured and formed states change also. These changes are due to the variation of the pH within the paste. This results in pastes containing different quantities of

$3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$. The analysis of the XRD data show that $\alpha\text{-PbO}_2$ is formed in proportion to $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$.

The study of the stability and reactivity of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ at another stage of the process of the lead/acid battery manufacture is in progress.

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