Plates soaking prior formation and its influence on positive active material phase composition and battery performance

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ABSTRACT

In the present work, we studied the behaviour of 3BS and lead oxide paste as a function of soaking time in two sulfuric acid solutions respectively with 1.05 and 1.20 g cm^{-3} specific gravity. The study was based on X-ray diffraction analysis (XRD), thermogravimetry (TG), differential scanning calorimetry (DSC) and chemical analysis. The results showed that during plates soaking, 3BS and PbO are converted to monobasic lead sulphate (1BS) and lead sulphate (PbSO$_4$). During plate formation in 1.05 s.g. H$_2$SO$_4$ solution, these compounds are oxidized to PbO$_2$, the XRD patterns showed that the longer is the time of plates soaking prior formation the lower is α-PbO$_2$ content in positive active material. On forming, PbSO$_4$ crystals convert to β-PbO$_2$ whereas α-PbO$_2$ is a result of 3BS oxidation. The capacity and cycle life of PAM decrease with soaking time, the concentration of the H$_2$SO$_4$ solution during soaking exerts stronger influence than the duration of soaking.

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1. Introduction

The positive active material of lead/acid battery plates consists of a mixture of two PbO$_2$ modifications: orthorhombic α-PbO$_2$ and tetragonal β-PbO$_2$ [1,2]. The formation mechanism of the two crystalline phases of lead dioxide has been well documented. Orthorhombic α-PbO$_2$ is the product of cured battery plate electroformation at high pH, and tetragonal β-PbO$_2$ is formed by oxidation of cured battery plate at low pH [3–9]. Discharge capacities of both modifications have been measured and it has been found that the capacity of α-PbO$_2$ is lower than that of β-PbO$_2$ [2,10,11]. Lead dioxide active mass is a gel-crystal system with proton and electron conductivity [12]. It's the main component of the positive plate. Paste preparation is a key step in the production of active materials that determine the design life and performance characteristics of lead-acid batteries. The paste is generally prepared by mixing leady oxide with water and sulfuric acid solution. This leads to the formation of basic lead sulfates, the nature of basic sulfates obtained depends on the conditions of paste preparation. The amount of H$_2$SO$_4$ with respect to leady oxide determines the phase composition during mixing. Up to 5% H$_2$SO$_4$, 3BS is present in the paste with high proportion in addition of free PbO and Pb. Above 5% H$_2$SO$_4$,

these compounds react with sulfuric acid and becomes 1BS and PbSO$_4$. On forming, the total mass is oxidized to α and β-PbO$_2$. In our previous papers [9,13], it has been demonstrated that 3BS crystals play an important role in the mechanism of paste conversion to PAM.

During the production of lead-acid batteries and before formation, the plates remain in H$_2$SO$_4$ solution at open circuit (i.e. soaked) for a certain period. 3BS and lead oxide are unstable and react chemically with H$_2$SO$_4$ whereby the paste is sulfated.

The processes during soaking of 3BS and 4BS plates have been investigated by some authors [7,14–19]. It has been established that the sulfation of the plates is mainly influenced by the phase composition of the cured plate, H$_2$SO$_4$ concentration and soaking time.

The main objective of the present paper is to determine the effect of plates soaking and heating prior formation on their phase compositions in the cured and formed states and its influence on battery capacity and cycle life.

2. Experimental

2.1. Plates preparation

All experimental investigations were carried out using industrial plates. The paste was prepared in a mixer at 35 °C from leady oxide (72% PbO). The XRD pattern of the starting material showed the

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presence of tetragonal PbO and Pb. Leady oxide (LO) was mixed with water and 1.40 s.g. H_2SO_4 in a ratio equal to 5% H_2SO_4/LO. Grids cast from Pb–5% Sb alloy were pasted and cured.

2.2. Plates pre-treatment

In the present study we investigate the effect of plates soaking as well as plates heating prior formation on the phase compositions of the paste before and after formation. For this purpose the following experiments were carried out:

-cured plates were placed in a battery cell box with 1.05 and 1.20 s.g. H_2SO_4 solutions for a period of time varying from 0.25 to 24 h. The plates were taken out from the box, washed in running water and dried at 110 °C.

2.3. Plates formation

Pre-treated plates of dimensions 124 mm × 134 mm × 1.8 mm were formed in 1.05 s.g. H_2SO_4 solution according to the following schedule: 4 h 1.25 A; 10 h 1.6 A; 3 h 1 A; 7 h 0.75 A.

The temperature was maintained at 30 °C. After complete oxidation the plates were taken out of the box, washed in running water for several hours to remove excess H_2SO_4 and dried at 110 °C.

2.4. Investigations of the processes during plates soaking and heating

To investigate the effect of the plates pre-treatment prior formation on the phase compositions of cured and formed plates, samples were taken close to the four corners and from the middle portion of the plate and homogenized in a mortar. A part of the material was removed from the grids and ground to powder. This powder was placed in a glass flask and then set to X-ray diffraction, thermal and chemical analyses. The material was characterized by XRD analysis using an APD-15 Philips 2134 diffractometer. The relative intensity of the X-ray characteristic diffraction lines was adopted as a measure of the phase changes in the paste and in the positive active material. 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.

Thermogravimetric analysis (TGA) is a technique, which measures the mass of substances as a function of temperature increase. Differential scanning calorimetry (DSC) is an analytical method by which the difference in energy inputs into a substance and a reference material is measured as a function of temperature, whilst the substance and reference material are subjected to a controlled temperature programme. These two techniques were used to measure the water contents in the pastes and their corresponding energies of dehydration. All tests were performed using instruments supplied by Mettler Toledo: DSC 822e and TGA/SDTA 851e. All measurements were carried out in Nitrogen atmosphere at a gas flow-rate of 80 cm^3 min^{-1} for DSC and 50 cm^3 min^{-1} for TGA at constant heating rate of 2 K min^{-1}. The samples were dried at 60 °C to evaporate the surface absorbed water. Pb and $PbSO_4$ contents respectively in the paste and in the positive active material were determined by chemical analysis.

2.5. Discharge capacity tests

Electrochemical investigations were performed on small positive electrodes cut from the formed plates. The electrodes were discharged at a constant cathodic current of −20 mA and the potential versus capacity was recorded using an Hg/Hg$_2$SO$_4$/saturated K$_2$SO$_4$ reference electrode. Two large platinum foils were used as

negative electrodes. All experiments were carried out at room temperature in 1.28 s.g. H_2SO_4 solution.

3. Results and discussions

3.1. Changes in phase composition during plates soaking in H_2SO_4 solutions

XRD patterns of the different samples during plates soaking in H_2SO_4 solutions were recorded. The following characteristic reflections were used: $d = 3.12$ Å for tetragonal PbO; $d = 3.08$ Å for orthorhombic PbO; $d = 3.26$ Å for tribasic lead sulfate (3BS); $d = 2.95$ Å for Monobasic lead sulfate (1BS) and $d = 3.00$ Å for $PbSO_4$. The cured plate is initially composed of tetragonal and orthorhombic PbO, 3BS and 1BS. In addition, a small quantity of metallic lead was detected in the paste by chemical analysis.

Fig. 1 presents the changes in phase composition during plate soaking in 1.05 s.g. H_2SO_4 (Fig. 1-a) and 1.20 s.g. H_2SO_4 (Fig. 1-b). In acid medium, free PbO in its two forms and 3BS crystals are unstable. As the time of soaking increases, they react with H_2SO_4 giving first 1BS then $PbSO_4$. The rate of 3BS decreasing is more important when the concentration of H_2SO_4 solution is high as shown in Fig. 2.
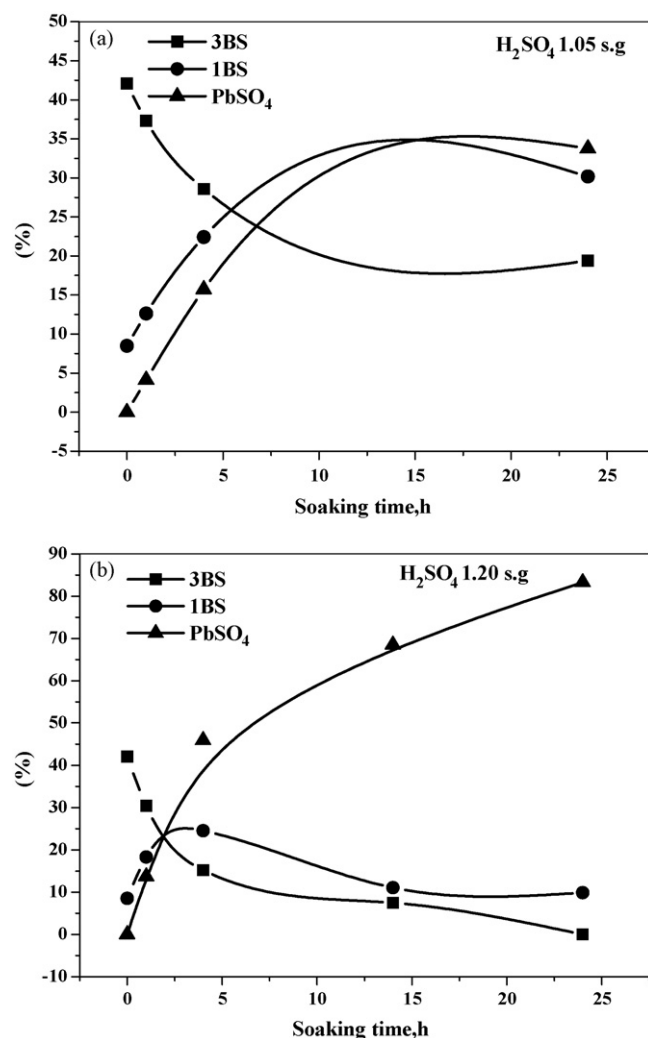

Fig. 1. Average phase composition of the pastes after soaking a) in 1.05 s.g. H_2SO_4, and b) in 1.20 s.g. H_2SO_4.
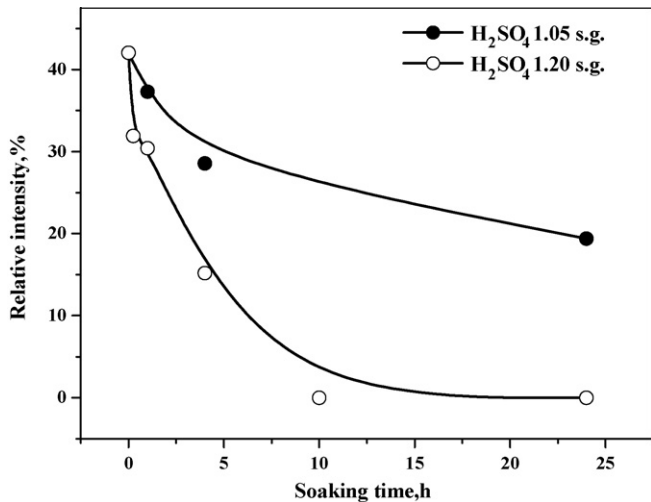
Fig. 2. Changes in 3BS content in the pastes during plate soaking in H_2SO_4 solutions.

3.2. Investigation of thermal behaviour of the pre-treated plates

Fig. 3 presents the weight losses of the plates previously soaked in 1.05 (Fig. 3-a) and 1.20 s.g. H_2SO_4 (Fig. 3-b) as a function of temperature. The cured plate shows two plateaus, the first one in the range of temperature comprised between 25 and 330 °C corresponding to the evaporation of water bonded in 3BS crystals, the second one appears for the temperatures higher than 330 °C relative to the thermal decomposition of hydrocerussite. This compound is a result of a reaction between the paste and CO_2 of the atmosphere as our samples were not immediately analyzed. As far as the time of soaking increases the weight loss decreases, the rate of decreasing is important for the plates soaked in concentrated H_2SO_4 solution. This is mainly due to the fast conversion of hydrated 3BS crystals to anhydrous 1BS and $PbSO_4$.

Fig. 4a and b presents the DTG curves giving the differential weight losses on temperature increase respectively for plates soaked in 1.05 and 1.20 s.g. H_2SO_4. The DTG curve for the cured plate features two characteristic peaks at 240 and 278 °C. These correspond to two types of water bonding in the 3BS crystals present in the paste. As the time of soaking increases, the characteristic peak of 3BS decreases in intensity and progressively disappears after 24 h of soaking in H_2SO_4. The decrease in peak intensity is more prominent
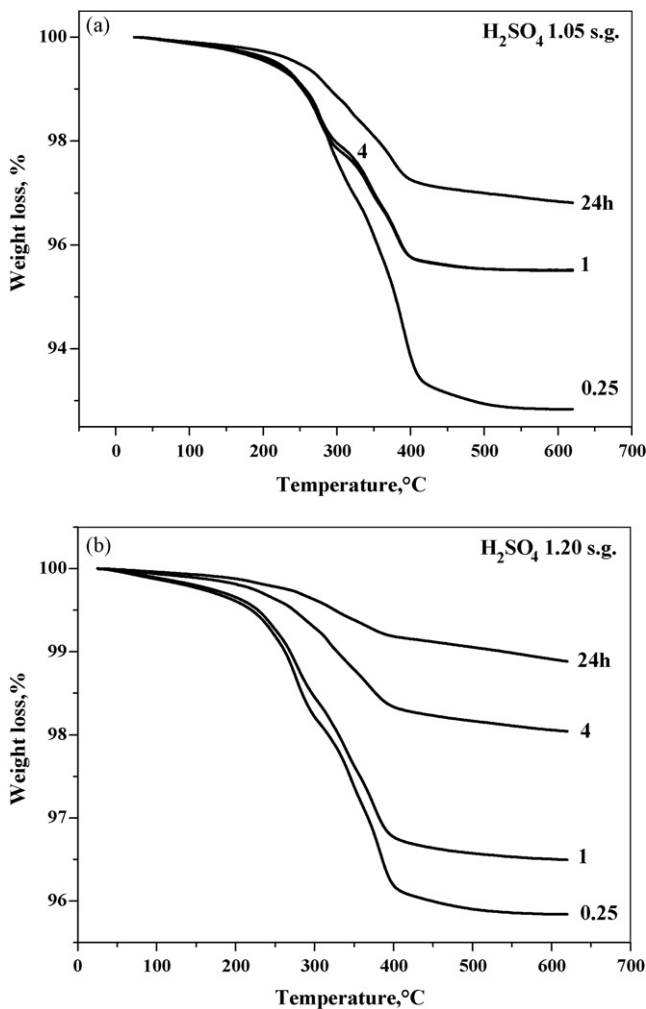

Fig. 3. TG curves of the pastes during plates soaking. a) in 1.05 s.g. H_2SO_4, and b) in 1.20 s.g. H_2SO_4.
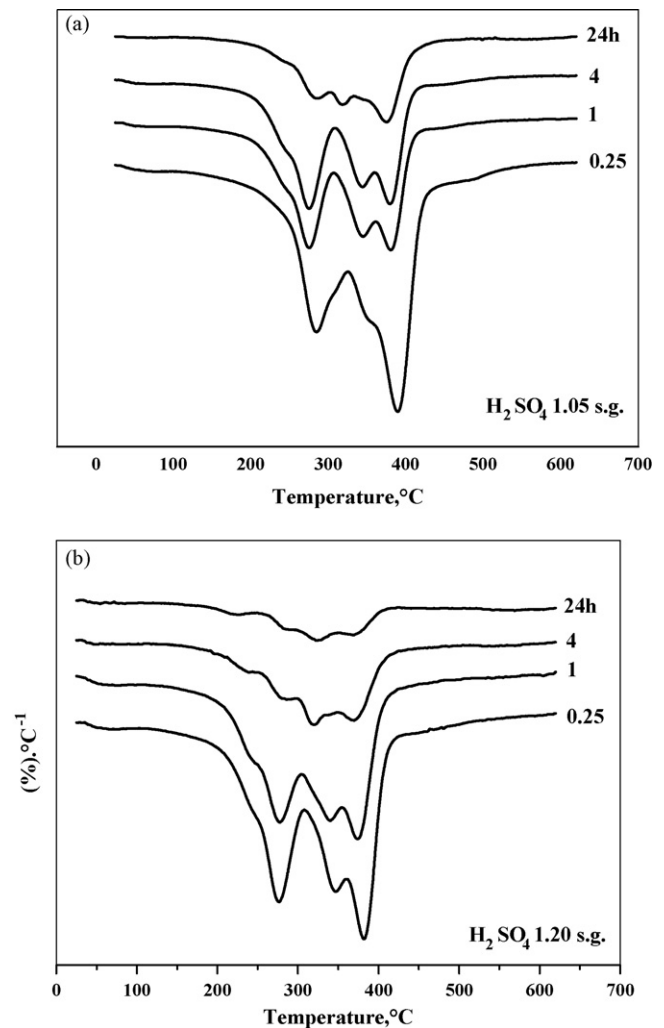
Fig. 4. DTG curves of pastes during plates soaking. a) in 1.05 s.g. H_2SO_4, and b) in 1.20 s.g. H_2SO_4.

for samples soaked in concentrated H_2SO_4 solution. This indicates that 3BS particles are more affected by sulfation. The higher is the concentration of H_2SO_4 solution; the lower is the 3BS content in the paste.

3.3. Changes in H_2O content in the paste and dehydration energy during plate soaking in H_2SO_4 solutions

Fig. 5 illustrates the average weight losses, obtained from TG curves of Fig. 3, as a function of the soaking time in 1.05 or 1.20 s.g. H_2SO_4. When the plates are soaked in 1.05 s.g. H_2SO_4 solution, the weight losses decrease with the increase of soaking time. This indicates that in contact with H_2SO_4 solution hydrated 3BS crystals undergo chemical reaction to convert to 1BS and $PbSO_4$. Consequently less hydrated particles are present in the paste and a decrease in water content is recorded. In the case of samples soaked in 1.20 s.g. H_2SO_4, the rate of 3BS conversion to 1BS and $PbSO_4$ is higher and an important decrease in weight loss is observed during the first 4 h of soaking. The water content in the paste is less than 0.55%.

Fig. 6a and b presents the DSC curves for the plates soaked in 1.05 and 1.20 s.g. H_2SO_4. The characteristic endothermic peaks of 3BS dehydration appear at 240 and 278 °C. A broad double peak relative to hydrocerussite decarbonation is recorded between 350 and 450 °C. As the time of soaking increases, the peak intensity decreases and almost disappears after 24 h of soaking. When the plates are soaked in 1.20 s.g. H_2SO_4 solution the acid attack is higher and the conversion of 3BS to anhydrous particles is faster and consequently the paste is completely sulfated. Thus no endothermic peak of 3BS dehydration is recorded after the first 4 h of soaking.

Fig. 7 presents the dehydration energy as determined from the DSC curves versus the soaking time. This was expressed in joule per gram and calculated by integrating the surface area of the endothermic peak that corresponds to 3BS decomposition. When the plates are soaked in 1.05 s.g. H_2SO_4 solution, the dehydration energy decreases almost linearly with soaking time as the conversion of 3BS crystals to 1BS and $PbSO_4$ is progressive. In contrast, when the plates are soaked in 1.20 s.g. H_2SO_4 solution, the dehydration energy decreases abruptly and reaches a value of 0.7% after 4 h of soaking in H_2SO_4 solution. This can be explained by the fact that when the concentration of acid increases
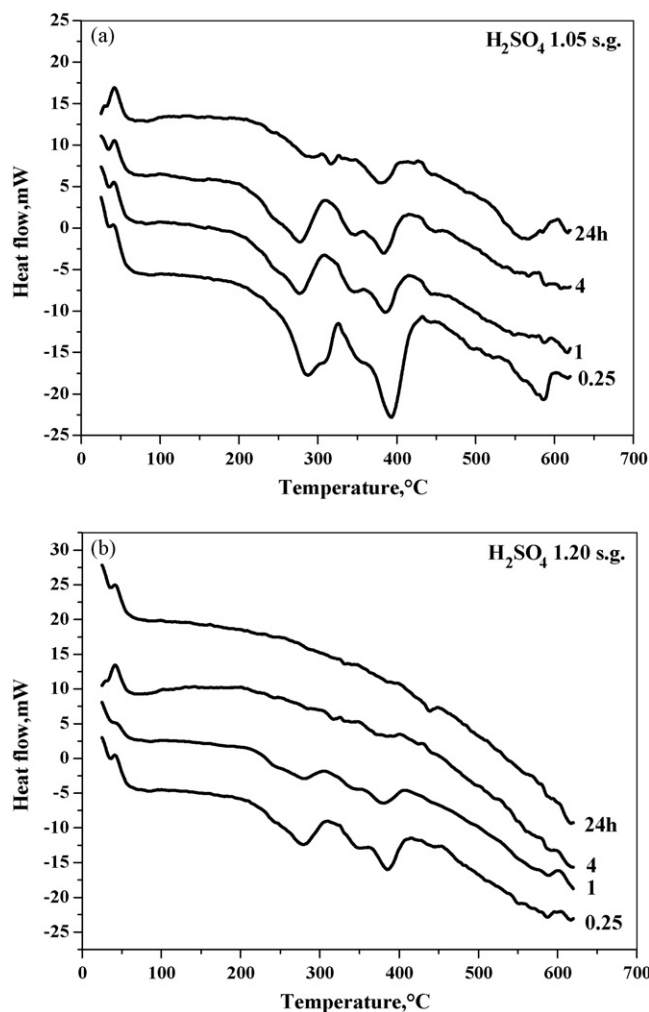

Fig. 6. DSC curves of pastes during plates soaking a) in 1.05 s.g. H_2SO_4, and b) in 1.20 s.g. H_2SO_4.

the rate of paste sulfation increases too and the paste becomes totally anhydrous. Consequently, the process of paste dehydration is stopped and the value of dehydration energy is almost zero.
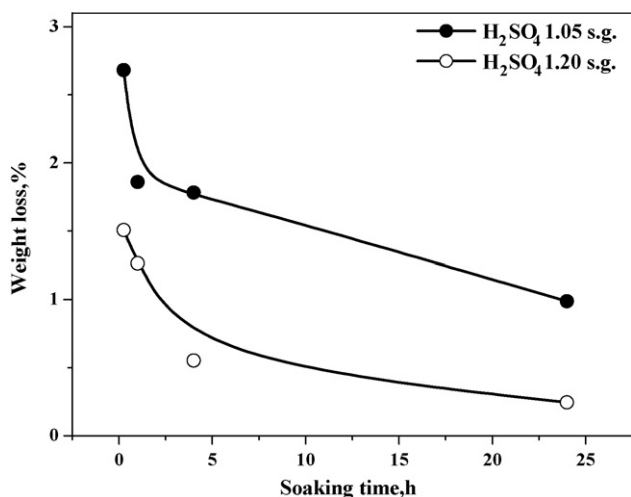

Fig. 5. Changes in water content in the pastes during plates soaking in 1.05 and 1.20 s.g. H_2SO_4.
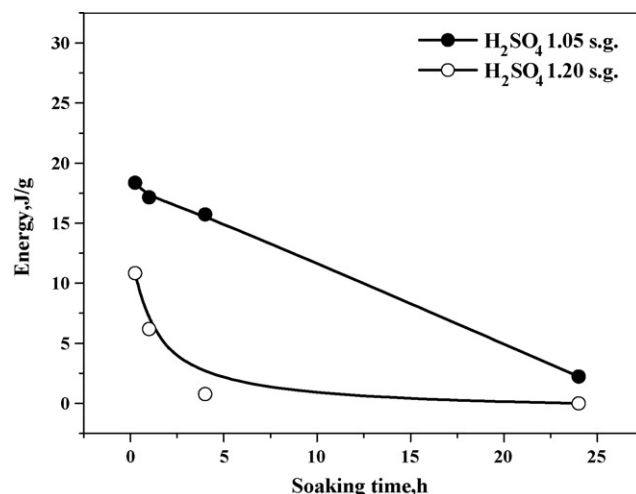

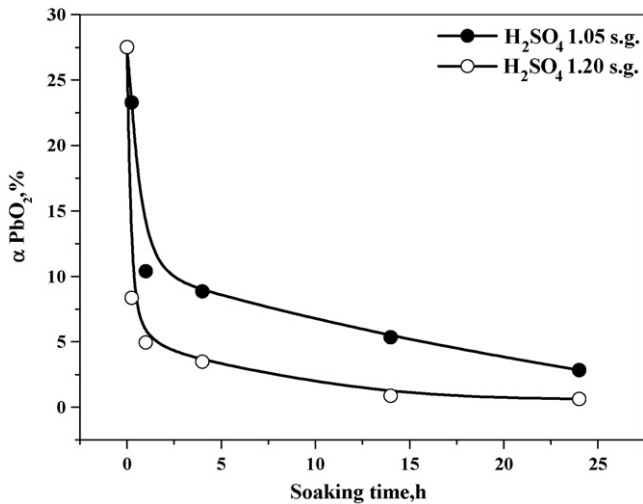**Fig. 7.** Average dehydration energy of pastes soaked in 1.05 and 1.20 s.g. H_2SO_4.

Fig. 8. average α-PbO$_2$ content in PAM versus time of plates soaking in 1.05 and 1.20 s.g. H$_2$SO$_4$.

3.4. Changes in X-ray diffraction patterns of PAM phase composition

Fig. 8 represents the changes in phase composition of PAM on soaking time in 1.05 and 1.20 s.g. H$_2$SO$_4$ solutions. The following characteristic reflections were used: $d = 3.50$ Å for tetragonal PbO$_2$ and $d = 3.12$ Å for orthorhombic PbO$_2$. The starting material (PAM obtained by oxidation of cured plate) consists of a mixture of α- and β-PbO$_2$. Chemical analysis data show the presence of small proportion of unconverted PbSO$_4$. As the time of soaking increases the amount of α-PbO$_2$ decreases. The rate of decreasing is important when the concentration of H$_2$SO$_4$ is high. In contrast, the amount of β-PbO$_2$ in the PAM increases.

On comparing the curves in Figs. 2, 5, 7 and 8, we can deduce that all these curves present almost the same profile. They exhibit respectively the quantity of 3BS in the paste, the water content in the paste, the energy of dehydration and the amount of α-PbO$_2$ in the PAM as a function of time of soaking in 1.05 and 1.20 s.g. H$_2$SO$_4$ solutions. This means that the longer is the time of soaking, the smaller is the amount of 3BS crystals in the paste and consequently the lower is the water content. In addition, lower is the average energy of dehydration and smaller is the quantity of α-PbO$_2$ in the PAM. In concentrated H$_2$SO$_4$ solution, the decrease of 3BS and water contents as well as the energy of dehydration and α-PbO$_2$ proportion in the PAM is more pronounced. In the contrary, the longer is the time of soaking, the higher is the quantity of PbSO$_4$ particles in the paste and consequently the higher the concentration of β-PbO$_2$ is in the PAM.

According to the literature tribasic lead sulfate (3BS) is a component that crystallizes in a triclinic system with one water molecule commonly written as 3PbO·PbSO$_4$·H$_2$O. Its DSC curve features two endothermic peaks respectively at 240 and 278 °C characteristic of two types of water bonding in the 3BS particles. In order to disclose the contribution of water in the mechanism of 3BS conversion to α-PbO$_2$, the following experiments were carried out:

- cured plates were heated during 8 h at 250 and 330 °C respectively and formed in 1.05 s.g. H$_2$SO$_4$.
- cured plates were soaked during 18 h in 1.40 s.g. H$_2$SO$_4$ solution and formed in 1.05 s.g. H$_2$SO$_4$.

Fig. 9 shows the XRD patterns of the different samples after formation in 1.05 s.g. H$_2$SO$_4$. The positive active material obtained by
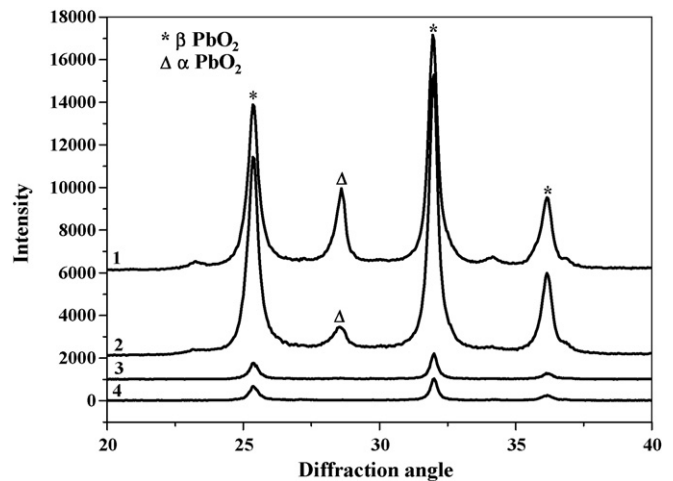

Fig. 9. XRD patterns of (1) PAM obtained by oxidation in 1.05 s.g. H$_2$SO$_4$ of cured plate. (2) PAM obtained by oxidation in 1.05 s.g. H$_2$SO$_4$ of cured plate heated at 250 °C. (3) PAM obtained by oxidation in 1.05 s.g. H$_2$SO$_4$ of cured plate heated at 330 °C. (4) PAM obtained by oxidation in 1.05 s.g. H$_2$SO$_4$ of cured plate soaked during 18 h in 1.40 s.g. H$_2$SO$_4$.

oxidation of cured plate is a mixture of α and β-PbO$_2$. When the paste is heated at 250 °C the corresponding XRD pattern shows a decrease in the intensity of the characteristic peak of α-PbO$_2$. For paste heated at 330 °C or long soaked in H$_2$SO$_4$ solution, β-PbO$_2$ constitutes the main phase of the PAM and the characteristic peak of α-PbO$_2$ disappears completely. On the light of these considerations we can deduce that the origin of α-PbO$_2$ is 3BS crystals whereas β-PbO$_2$ is the result of PbSO$_4$ oxidation. In addition, structural water bonded in 3BS crystals plays an important role in the determination of PAM phase composition in lead acid battery.

3.5. Effect of soaking on the PAM capacity

Figs. 10 and 11 present the changes in PAM capacity versus time of soaking in 1.05 and 1.20 s.g. H$_2$SO$_4$. It can be seen that soaking time prior formation has a remarkable influence on the PAM capacity. The longer the soaking time in solution, the smaller is the capacity of the PAM. In addition, the concentration of H$_2$SO$_4$ solution during soaking exerts stronger influence with comparison to the time of soaking. This may be explained by the fact that plates soaked in weak H$_2$SO$_4$ solution contain more α-PbO$_2$ than those
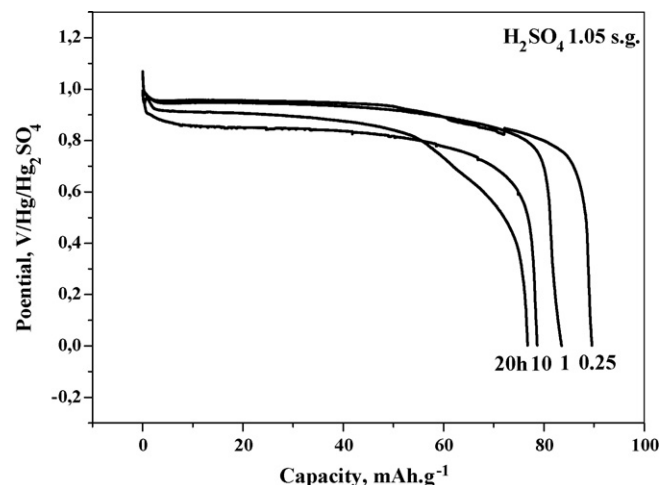

Fig. 10. Changes in PAM capacity versus time of soaking in 1.05 s.g. H$_2$SO$_4$.
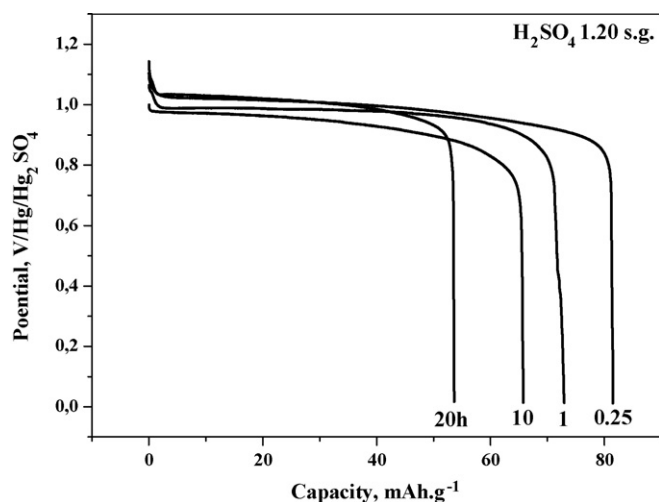
Fig. 11. Changes in PAM capacity versus time of soaking in 1.20 s.g. H_2SO_4.

soaked in strong H_2SO_4 solution, consequently their initial capacity is higher and exhibit longer cycle life. These results are in good agreement with the data published by Pavlov et al. [19].

4. Conclusions

Paste prepared by mixing leady oxide 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 leady oxide. Up to 5%, 3BS is the major phase that constitutes the paste. In the present work, the plates were placed in a cell box in 1.05 and 1.20 s.g. H_2SO_4 solutions prior formation to investigate the processes that take place during paste soaking. It has been established that 3BS and PbO are unstable; in contact with H_2SO_4 they undergo an acid base reaction to form 1BS and $PbSO_4$. The process of sulfation is greatly influenced by the concentration of H_2SO_4 and the phase composition of the paste. During soaking, the proportion of 3BS in the paste decreases and converts to anhydrous lead components. The thermal decomposition of the paste shows a decrease in the quantity of structural water and dehydration energy. At high concentration of H_2SO_4, the plate sulfation process is accelerated.

On forming, the different phases present in the paste convert to PbO_2 with different proportions of β and α -PbO_2. The former is a result of $PbSO_4$ conversion in the acid zones of the paste. The later originates from 3BS particles in the alkaline zones of the paste. The capacity and cycle life of PAM decrease with soaking time, the concentration of the H_2SO_4 solution during soaking exerts stronger influence than the duration of soaking.

These experimental findings should be taken into account in the technology of lead-acid battery manufacture, as the plate soaking in H_2SO_4 solutions prior formation greatly affects the PAM phase composition and determines the capacity and power performance of the battery.

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