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The curing reaction study of the active material in the lead-acid battery

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Abstract

A study of the curing reaction involved in the positive plate of the lead-acid battery has been undertaken. The variation of the different parameters of the curing reaction has shown the possibility of changing the 4BS needles dimensions. In particular, the addition of a surfactant agent, namely the polyvinylpyrrolidone, to the reagents allows the obtention of tailor-made 4BS particles useable in the industrial preparation of the positive plates.

Keywords: Lead-acid batteries; Lead sulphates; Polyvinylpyrrolidone; Morphology control; Curing

1. Introduction

The Faure's process is a well-known industrial process used to prepare the positive plate in the lead-acid batteries. It consists of a mixing, a curing and a soaking-formation of the plates. The first step consists in mixing PbO with sulphuric acid in order to obtain a suitable paste density. Under usual experimental conditions ($T < 80°C$) only the tribasic lead sulphate (denoted as 3BS) forms. The mixing result is a paste made of PbO and 3BS that is applied onto a lead alloy grid, prior to be left in a highly humid atmosphere, between 60–80°C to perform the curing step. This step mainly allows the transformation of the mixture into 4BS, whose morphology strongly depends on the degree of humidity, standing time and temperature. Finally, during the soaking-formation step the 4BS is chemically transformed into $PbSO_4$ (soaking), and then electrochemically transformed into PbO_2 (formation). A good control of these different steps to obtain a 4BS of well-defined morphology is important not only for the plates rigidity but also for their electrochemical behaviour.

The cured basic 4BS sulphate particles, usually needle shaped are 10 μm × 100 μm in size. We have previously [1] shown that such needles, during the soaking-formation process, were not completely transformed into PbO_2 contrary to the other basic sulphates. Only a crust of 1.5 μm maximum thickness was transformed leaving the core of the needle untouched. Based on these results Torcheux et al. [2] have performed modelling calculations with the main result that the 4BS needles should have an improved geometry for an optimized electrochemical efficiency of the positive plate, namely 5–7 μm width and 50–100 μm length. To control the 4BS particles size, the curing reaction parameters have to be studied. Many investigations have been undertaken [3–7] showing that the chemical composition of the cured plates is largely dependent on the temperature and humidity conditions applied during the process. But, to our knowledge, no author has studied the influence of these parameters on the particle size control. Herein, we first determine which parameters affect the 4BS morphology during the curing process, and then show the possibility of controlling the size of the 4BS particles by means of soft chemistry.

2. Experimental

Our experiments were designed to be the closest to the industrial process while maintaining the ability to precisely control the different parameters of the curing step such as the reaction temperature, the nature of the precursors (3BS, 1BS, $PbSO_4$), the reaction stoichiometry and the effect of additives. Curing simulation experiments were performed on pure phase material in an oven. Mixtures of PbO and lead sulphates or basic sulphates were heated in water under reflux. The total mass of the mixture (usually 2 g) was placed in a Teflon balloon with 50 ml of water during

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16 h maximum. The product of the reaction was washed with acetone in an ultrasonic tank in order to remove by sedimentation the 0–10% of 3BS or PbO left, then analysed by X-ray diffraction, and the particles morphology controlled by Scanning Electron Microscopy. The needles size was determined as an average from at least three micrographs representative of the samples.

The precursor sulphates used, namely $PbSO_4$, the lead mono (1BS) and tribasic (3BS) sulphates were homemade. They were obtained by different synthesis methods. $3PbO \cdot PbSO_4 \cdot H_2O$ (3BS) was synthesized by Bode's method, [8] which consists in adding a lead acetate aqueous solution to a solution of ammonium sulphate. In the case of 3BS the pH is maintained between 8 and 13 by adding a 32% NH_3/H_2O mixture. $1PbO \cdot PbSO_4$ (1BS) and $PbSO_4$ were synthesized by adding PbO to an ammonium sulphate solution with a stoichiometric ratio PbO/SO_4^{2-} at 60°C. $PbSO_4$ was also synthesized by the soaking of lead basic sulphates. These two different syntheses led to two different morphologies in the case of $PbSO_4$.

3. Variation of reaction parameters

3.1. Stoichiometry

In the industrial process the curing occurs after the lead basic sulphate 3BS obtention by mixing, the reaction involved is:

$$3PbO \cdot PbSO_4 \cdot H_2O + PbO \rightarrow 4PbO \cdot PbSO_4.$$

Our experiments showed that the change in 3BS/PbO ratio does not alter the morphology of the 4BS needles, but affects the reaction output. To obtain a pure 4BS phase, the SO_4^{2-}/Pb ratio must be equal to 0.2, according to the stoichiometric ratio of the above reaction.

3.2. Temperature

3BS and PbO Stoichiometric mixtures were subjected to curing at different temperatures in the 80–110°C range as described in Section 2, leading to a pure 4BS phase. The SEM micrography shows needle particles whose sizes are of the same order of magnitude as those observed for the industrially cured 4BS needles. The width of the particles ranges from 10 to 16 μm (Fig. 1), with no obvious dependence on temperature. However, the temperature seems to have an effect on their length. For $T < 95$°C the particles remain below 100 μm, with a narrow size distribution of 30 μm, and for higher temperatures their lengths become greater than 100 μm, with a spread of the distribution (50–60 μm).

3.3. Precursors

The choice of the above curing precursor (3BS) is purely economical, however we have tried to achieve the

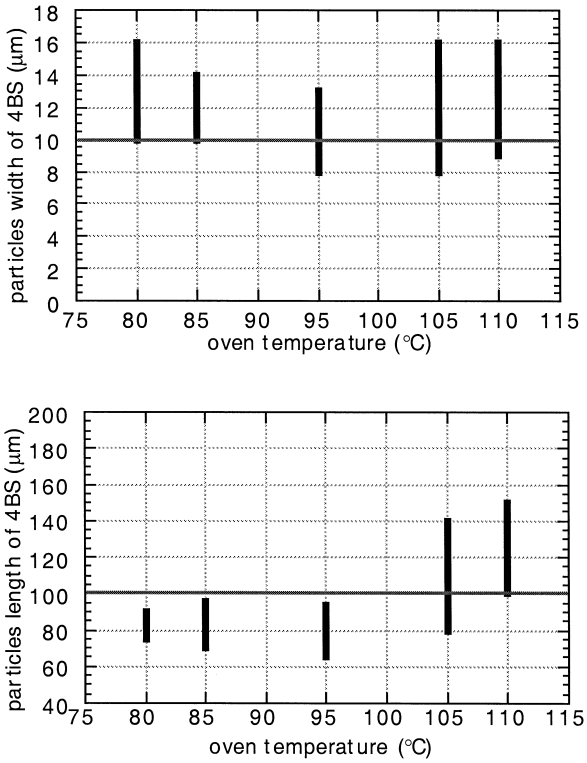

Fig. 1. 4BS particles widths and lengths are plotted as a function of the oven temperature.

4BS synthesis by curing from different lead sulphates, whose morphologies are illustrated in Fig. 2a–c. Depending on the lead sulphate/PbO reaction, the following reactions are expected:
From $PbSO_4$:

(a) $PbSO_4 + PbO \rightarrow PbO \cdot PbSO_4$ (1BS)

(b) $PbSO_4 + 3PbO \rightarrow 3PbO \cdot PbSO_4 \cdot H_2O$ (3BS)

(c) $PbSO_4 + 4PbO \rightarrow 4PbO \cdot PbSO_4$ (4BS).

Or from 1BS:

(d) $PbO \cdot PbSO_4 + 2PbO \rightarrow 3PbO \cdot PbSO_4 \cdot H_2O$ (3BS)

(e) $PbO \cdot PbSO_4 + 3PbO \rightarrow 4PbO \cdot PbSO_4$ (4BS).

X-ray diffraction analyses of the final cured samples confirm that the reaction product depends on the stoichiometric ratio. It must be pointed out that the PbO amount also plays a role in controlling the curing pH. As shown in Table 1 [9] there is a domain of pH separating the stability range of 3BS and 4BS from 1BS. This explains why reactions (b) and (c) do not yield 1BS as an intermediary reaction product. Indeed, the PbO dissociation leads to a pH of 8.9, far from the stability range of 1BS.

The 4BS samples prepared following reactions (c) and (e) were characterized by Scanning Electron Microscopy. Note that the particles width (Fig. 3), which ranges between 9 and 16 μm, is independent of the nature of the precursor with, however, a maximum value that is slightly lower when $PbSO_4$ is used as a precursor. The particle

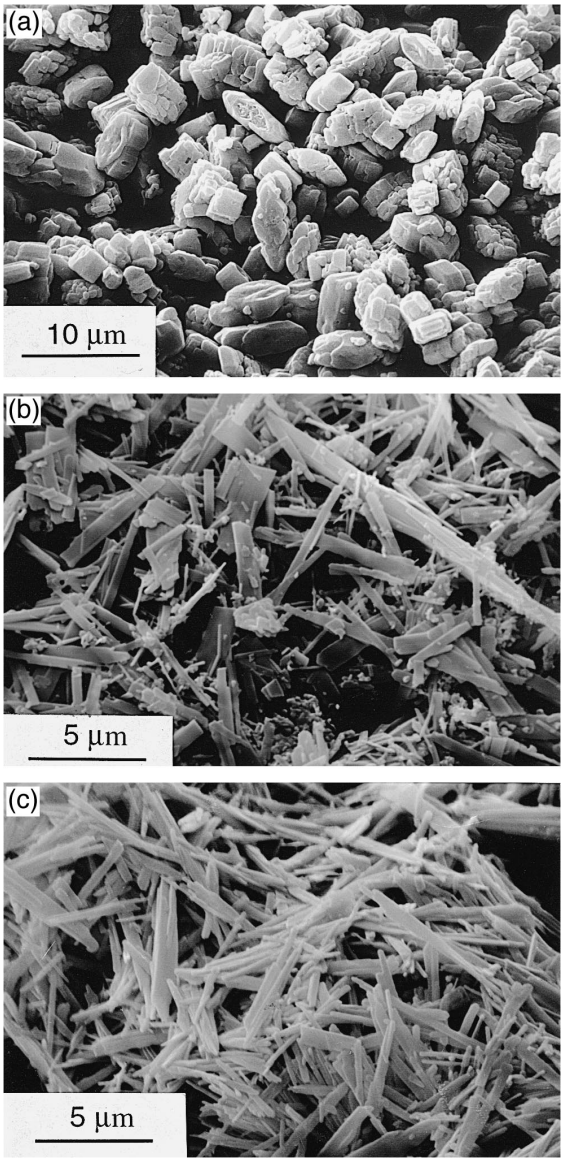

Fig. 2. Scanning electron micrographs of the various lead sulphate precursors used for the curing reaction (a) $PbSO_4$, (b) $PbO \cdot PBSO_4$ and (c) $3PbO \cdot PbSO_4 \cdot H_2O$.

length, in contrast, seems to be more sensitive to the precursor nature. The lengths increase when $PbSO_4$, 1BS and 3BS are used as precursors with a minimum value around 50 µm for $PbSO_4$, and a maximum value around

Table 1
pH domains of lead oxide and sulphates stability in solution [9]

Solid material in equilibrium with the solution	pH value
$PbSO_4$	< 6.28
$PBSO_4$ / $PbO \cdot PBSO_4$	6.28
$PbO \cdot PBSO_4$	6.28–7.31
$PbO \cdot PBSO_4$ / $3PbO \cdot PBSO_4 \cdot H_2O$	7.31
$3PbO \cdot PBSO_4 \cdot H_2O$	7.31–8.99
$3PbO \cdot PBSO_4 \cdot H_2O$/PbO	8.99
PbO	> 8.99

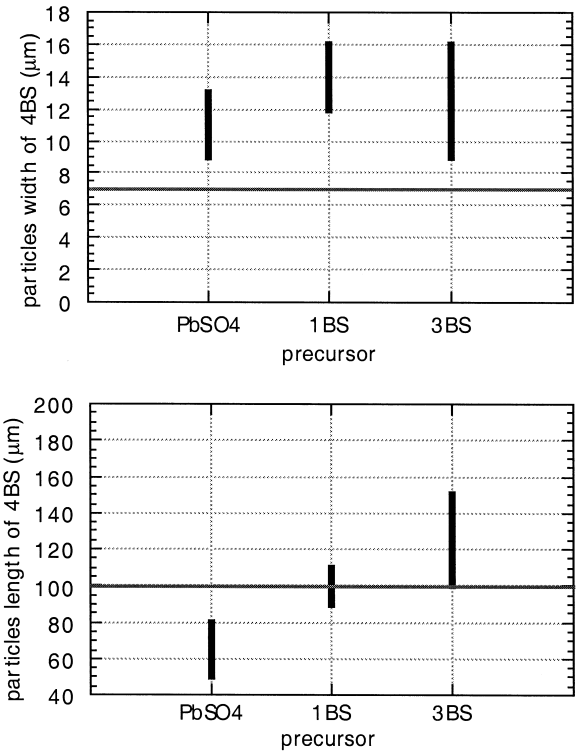

Fig. 3. Influence of the precursor's nature on the width and length of 4BS particles.

150 µm for 3BS. This difference is possibly due to the existence of intermediary species when the reaction is done with $PbSO_4$ and 1BS. Indeed the 3BS formation is observed in these two cases during the first half-hour of the curing reaction. To check the influence of this reaction intermediate on the 4BS particle size, the mixture 'precursor ($PbSO_4$ or 1BS) + PbO + H_2O' was subjected for five minutes to an ultrasonic source with frequency of 20 kHz. The use of ultrasound led to the mixture of 3BS + PbO as the end product. Needle-shaped 3BS particles (0.3×3 µm) are obtained (Fig. 4) whatever the precursor ($PbSO_4$ or 1BS). When curing is performed starting from

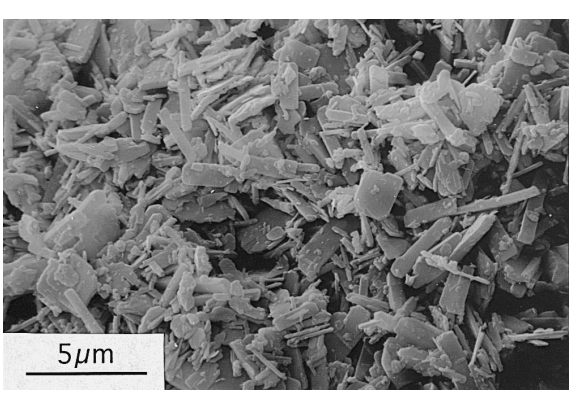

Fig. 4. Scanning electron micrography of the 3BS + PbO mixture obtained after ultrasonic treatment. 3BS needles size are much smaller than those on Fig. 2c.

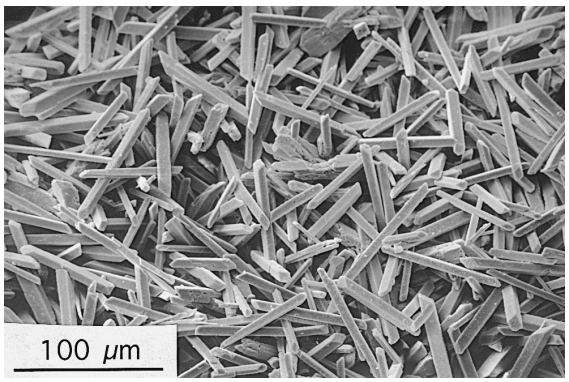

Fig. 5. Scanning electron micrography of the 4BS obtained from the curing of the 3BS + PbO mixture prior to being subjected to an ultrasonic source.

these small 3BS particles, the resulting 4BS phase shows particles 40–80 μm in length and 3–7 μm in width (Fig. 5). These values are one half those obtained when an ultrasonic source was not used. This behaviour suggests that the precursor morphology influences the dimensions of the cured 4BS phase. In Section 3.4, we focus on the role of the precursor morphology and crystallinity.

3.4. Morphology and crystallinity of the precursor

An experiment has been conducted using two lead sulphates ($PbSO_4$) differing by the size of their particles. In addition to that previously used for all the reactions described above, and having polyhedral particles of 1 to 10 μm, $PbSO_4$ obtained from the soaking of 3BS or 1BS was used. In the latter case the particles have no particular shape and their sizes are less than 1 μm (Fig. 6). The dimensions of the two sulphates differ by a factor of approximately 10 × and the results of the curing also show a difference in the 4BS dimension as indicated by the micrographs on Fig. 7.

In both cases the needles lengths are identical (an average range of 50 to 80 μm) but the width values are smaller when $PbSO_4$ from the soaking is used. Their range is, according to the previous experiments, 8–13 μm, and

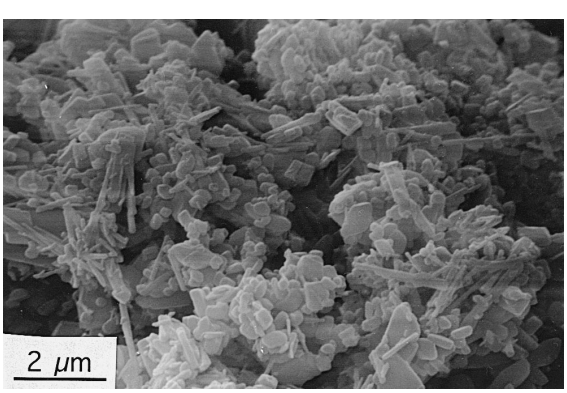

Fig. 6. Scanning electron micrography of $PbSO_4$ synthesized by soaking.

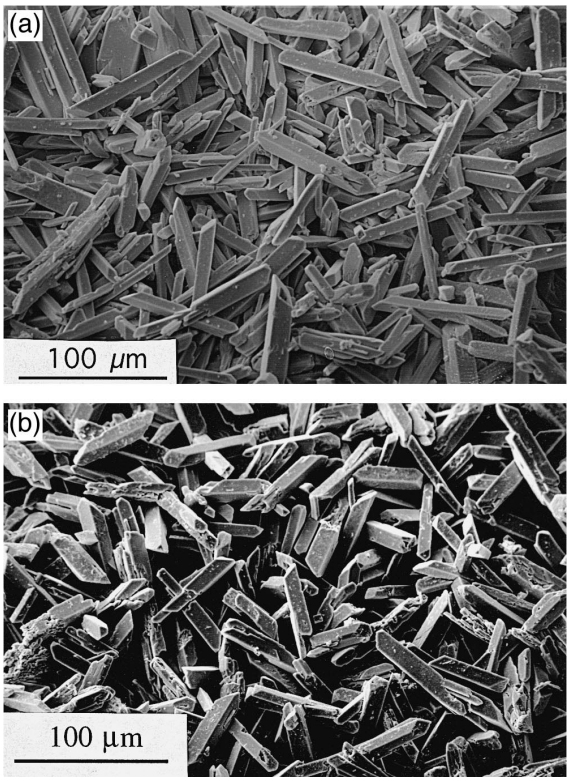

Fig. 7. Scanning electron micrographs of the 4BS obtained from curing of two different $PbSO_4$ samples. (a) precursor prepared from soaking (< 1 μm), (b) precursor prepared from PbO and an ammonium sulfate solution (1–10 μm).

with the use of the smallest $PbSO_4$, 5–12 μm. The average being 11 and 8.4 μm with a standard deviation of 1.8 μm. Another experiment has been conducted with two different 3BS morphologies, the one synthesized by Bode's method (1×10 μm), and the other obtained from an ultrasonic process (0.3×3 μm). Contrary to the $PbSO_4$ precursor case, the 3BS morphology influences both dimensions. The 4BS average dimensions are $(14.7 \pm 3.6) \times (131 \pm 27)$ μm from Bode's 3BS, and $(5.8 \pm 1.3) \times (64 \pm 12)$ μm for the other. Finally, to check the influence of the

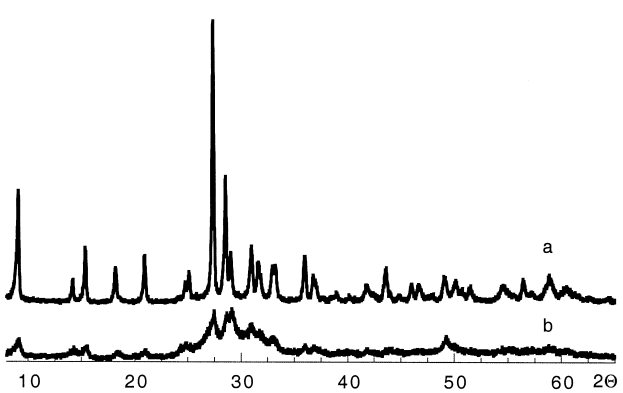

Fig. 8. X-ray powder diffraction diagrams of (a) tribasic lead sulphate and (b) after five hours grinding.

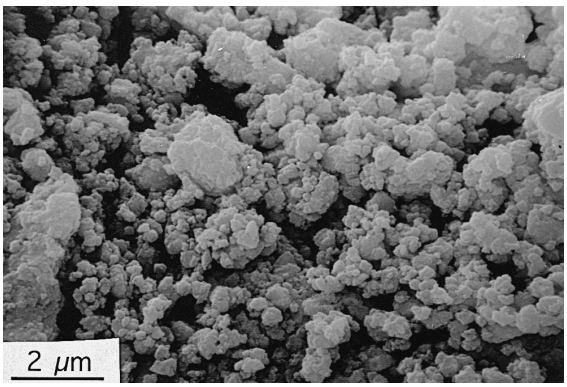

Fig. 9. Scanning electron micrography of the 3BS ground for five hours.

precursor crystallinity, an experiment has been conducted from a mechanically ground 3BS, whose structural disorganization is portrayed by the X-ray powder diffraction diagram shown in Fig. 8. SEM micrograph shows that the ground 3BS particles are pseudo-spherical with a size below 1 μm (Fig. 9). The curing of these particles leads to 4BS needle particles with a width between 0.5 and 2.5 μm and a length between 5 and 30 μm (Fig. 10).

From the above results we have seen that it is possible to modify the 4BS particle sizes using either physical means (ultrasonic source) or chemical means (another lead sulphate precursor). The implementation of these findings to the industrial scale seems to be, however, difficult for economical reasons. As an attempt to modify the needle width without changing the operating mode of the Faure's process, we introduced, based on our own experience, a surfactant agent (polyvinylpyrrolidone) into the reacting mixture.

3.5. Additives

The curing experiments were conducted with $PbSO_4$ as the sulphated precursor under the above experimental conditions. Various amounts of polyvinylpyrrolidone (PVP) were dissolved in water in the range of 0 to 40% in weight, in relation to the weight of the mixture (precursor PbO).

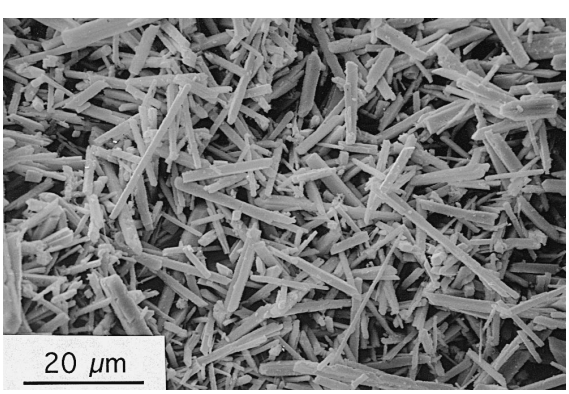

Fig. 10. Scanning electron micrography of the 4BS obtained from the mechanical milling of the 3BS.

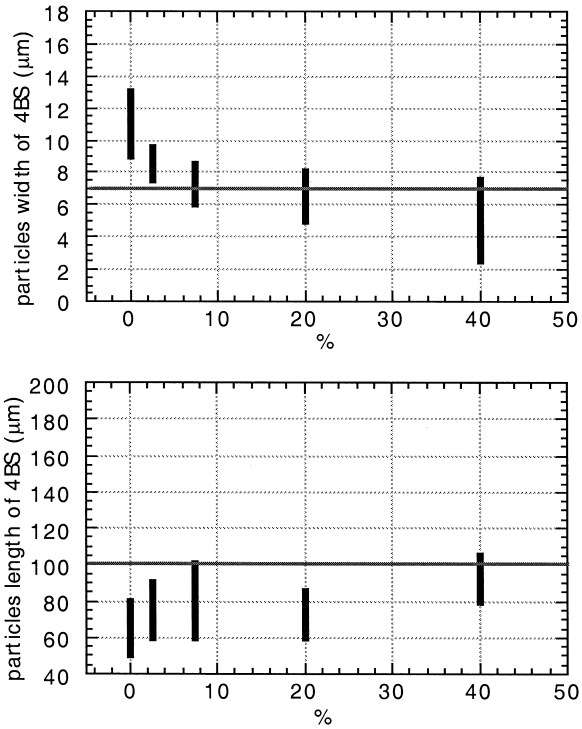

Fig. 11. Effect of the PVP percentage on the widths and lengths of the 4BS particles.

SEM investigations of the particles clearly indicate that the surfactant agent modifies the needle size. Only 2.5% of

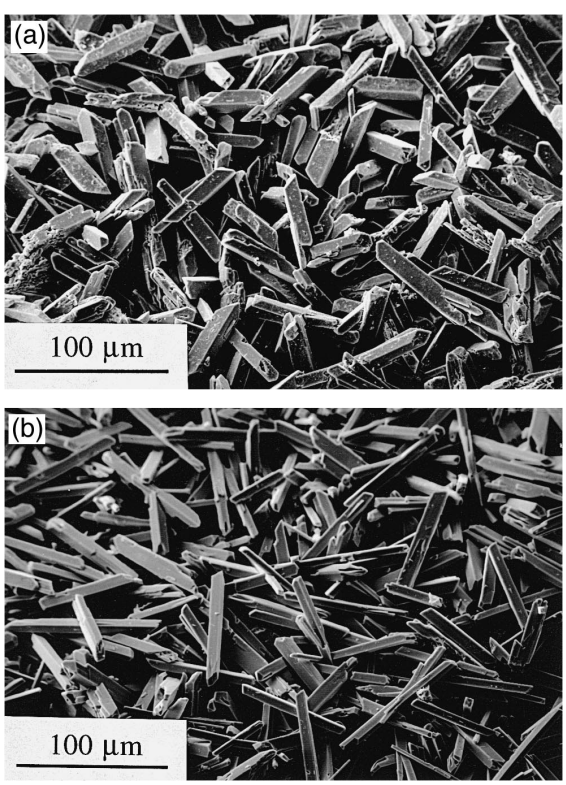

Fig. 12. Scanning electron micrographs of the 4BS with (a) no PVP and (b) 7.5% of PVP.

PVP is necessary for a 20% decrease in the needle width (Fig. 11) that can reach dimensions below 7 μm. But beyond 20% of surfactant the increase in its effect slows down the reaction kinetic. The PVP not only affects the width but also the particle length, that was found to increase from 80 μm without additive to 100 μm with additive. More specifically, the curing of $PbSO_4$ and PbO with the addition of 7.5% of PVP in solution allows 4BS needles of 5–7 μm in width and 50–100 μm in length to be realized (Fig. 12). These are the dimensions predicted [10] by a theoretical model to lead to optimized electrochemical use of the positive plates.

Since the precursor used in the experiments ($PbSO_4$) differs from that used in the industrial process, we decided to implement our approach consisting of the addition of PVP, under the same conditions, to curing experiments with 1BS and 3BS as precursors; the results are shown on Fig. 13. The surfactant agent acts similarly for all the sulphates: the main result being a decrease in the width and an increase in the length but differences appear depending on the precursor. The particle dimensions obtained from $PbSO_4$ are, however, consistently the smallest in both directions; furthermore the particle dimension distribution is narrower when $PbSO_4$ is used instead of 1BS or 3BS.

Among other common procedures to diminish the size distribution is mechanical stirring, however, this physical means is not directly applicable to the industrial curing process. The distribution of 4BS particles width, obtained from 3BS, is as narrow as that obtained without PVP but

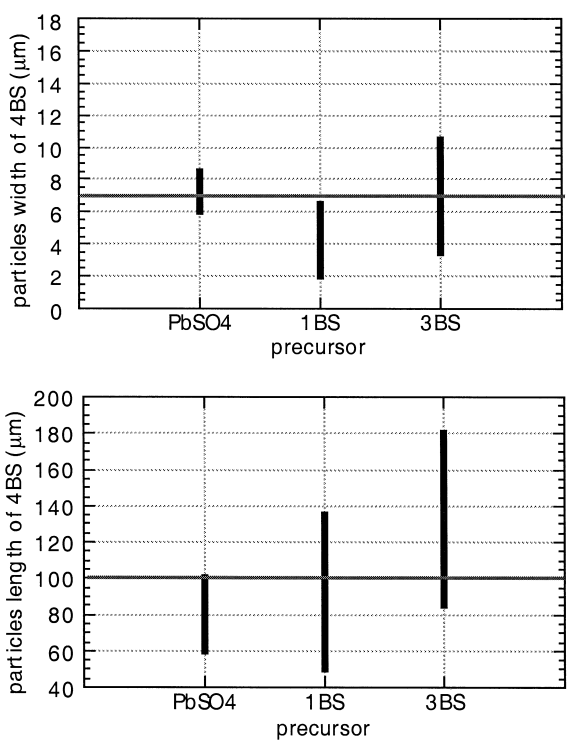

Fig. 13. Influence of the nature of the precursor with 7.5% of PVP on the width and length of 4BS particles.

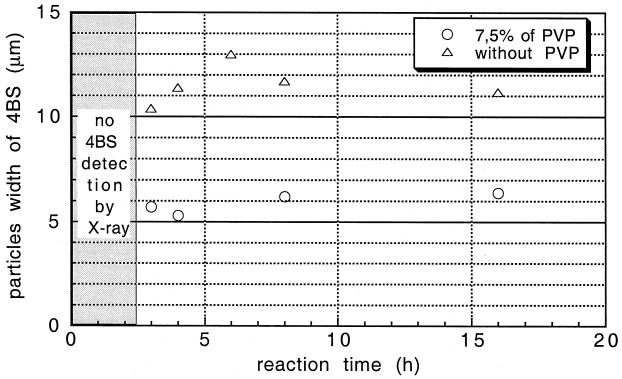

Fig. 14. Effect of the reaction time on the 4BS particles width.

the length distribution is more important. For 1BS the results show needle widths below 7 μm and an effect on the length comparable to the 3BS. Finally to throw more light on the role of PVP, kinetic studies of the curing reaction were undertaken.

3.6. Kinetic studies

We noted when using 3BS as precursor without and with 7.5% of PVP that 2.5 h were needed to detect the presence of 4BS (Fig. 14). No reaction slowdown was detectable, and the particle sizes in both cases reached their final state after a 4-h period.

4. Discussion

We experimentally demonstrated the possibility of controlling the 4BS particles size by adding PVP to the reaction vessel. However, one remaining question is the role played by such a surfactant agent, and how it influences the nucleation and growth processes.

SEM investigation performed on the particles withdrawn during the kinetic study (Fig. 15) shows that the 4BS particles growth seems to partially happen from the stacking of different particles. Based on this observation a schematic of the reaction mechanism can be proposed. Most likely the reaction rapidly occurs through coalescence of the particles (3BS or 4BS) leading to a preferential widthwise growth, the stacking of the particles favoring a 'welding' effect. This stage is followed by a lengthwise growth which can happen by mass transport formed by dissolution of the other particles.

When a PVP surfactant agent is used, the coalescence of the 3BS particles is reduced thus diminishing the width. Indeed the polyvinylpyrrolidone is an organic polymeric chain that is well known to coat the particles, modifying the interface thereby preventing the coalescence step. The precursor particle has a needle shape and the polymer coating is, probably, continuous on the prismatic faces

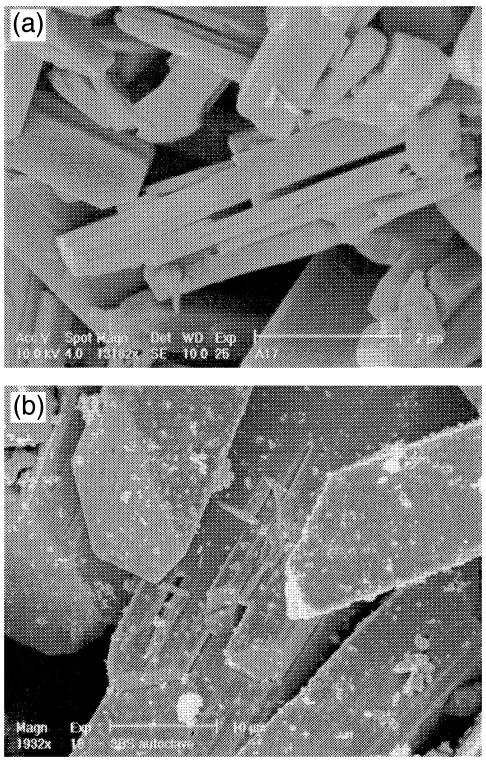

Fig. 15. Scanning electron micrographs of 3BS and 4BS particles during the curing reaction.

where it hinders the crystal growth, whereas it is defective on the extremities due to a steric obstruction. Thus, during particle growth the different species more easily diffuse towards the end than the needle faces, allowing a large length to width ratio.

When no surfactant agent was added we noted that differences in the 4BS dimension appeared depending on different factors. The temperature has an effect on the particles length, probably due to the enhancement of the species diffusion, in solution, with temperature. With different sulphate precursors the length varies, but this can be alleviated when an ultrasonic process is applied to the starting mixture. This indicates that the nature of the precursor is not the most important parameter to take into account for the variation of the 4BS dimension. Indeed, 4BS synthesis always originates from the 3BS, and the kinetic study has shown that after 30 min of curing reaction the presence of 3BS is detected, independently of the precursor used.

In contrast, the precursor morphology turns out to have also a significant effect on the 4BS dimension. This effect was illustrated by using two 3BS morphologies. Indeed the 4BS particles average size, resulting from the curing, can be doubled in both directions depending on the 3BS morphology used. It should be recalled that whatever the precursor used the 3BS is an intermediate product in the curing reaction. So controlling the 3BS morphology finally results in controlling the 4BS morphology. Besides the 3BS morphology, we note that its crystallinity can also alter the 4BS particles dimension, as demonstrated by the mechanical milling experiment.

In light of these experiments, a reactional path can be proposed to describe the curing. Starting from a mixture of lead sulphate, $PbSO_4$ or 1BS, and PbO, the local pH (at the solid–liquid interface) allows, at first, the synthesis of 3BS. In the next stage, the remaining PbO reacts with 3BS to form 4BS. The nucleation process occurs at the 3BS surface, and the 3BS → 4BS transformation takes place within the particle. Simultaneously, a coalescence phenomenon allows the rapid widthwise growth, except in the case where a surfactant agent is used. Finally, the lengthwise growth of 4BS needles takes place, due to the diffusion of lead species, supplied either by the dissolution of PbO or small basic lead sulphate particles, similar to an Ostwald ripening effect.

5. Conclusion

The curing reaction study at the laboratory scale has allowed to prepare tailor-made lead tetrabasic sulphate crystals by a precise control of various reaction parameters. In addition, we demonstrated that additives such as PVP can be used to rapidly and precisely control the 4BS particle size. This method presents the advantage of being easily implemented on the industrial scale. Electrochemical tests are presently being made to verify the importance of 4BS particle size on their electrochemical performance [10]; primary results confirm the importance of controlling the crystal size, and seem to validate the theoretical predictions.

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