



# Synthesis and electrochemical performances of tribasic and tetrabasic lead sulfates prepared by reactive grinding

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Received 12 May 1997; revised 24 July 1997

## Abstract

Tribasic lead sulfate (3BS) and tetrabasic lead sulfate (4BS), used as precursors of the positive active material in the lead/acid batteries, were prepared by a new method: reactive grinding. The effects of various experimental parameters (stoichiometry, hygrometry of the starting compounds, duration of mechanical treatment) upon the nature and morphological features of the resulting phase were investigated. Among them, hygrometry turned out to be the most critical one. With water in excess, only 3BS was produced while dry reagents led to 4BS. In both cases, samples with a small particle size and high reactivity were obtained. In order to evaluate the influence of the morphology upon the electrochemical performances of such grinding produced samples, the capacity was measured and compared with that of traditional 3BS and 4BS samples. © 1998 Published by Elsevier Science S.A.

*Keywords:* Lead sulfate; Performances; Reactive grinding

## 1. Introduction

During the last thirty years, mechanochemistry has become a topic in the established field of reactivity of solids. The application of a mechanical energy to powder compounds leads generally to phase transitions or chemical reactions. For instance, by ball milling a pure solid phase, the energy transfer may cause the transition from the crystalline to the amorphous state. For several solid phases of powder compounds ground together, chemical reactions may be initiated inside the ball mill although they usually take place at very high temperature leading to the so-called 'reactive grinding'. The best known examples of reactive grinding are found in the field of 'mechanical alloying' (MA). MA produces finely divided powder alloys by grinding mixtures of pure metallic elements. Although the process is very simple, the mechanisms involved in reac-

tive grinding are rather complicated and are still the subject of many studies and discussions [1–5]. In a first approach, reactive grinding may be regarded as a process that considerably increases the reactivity of precursors by generating new interfaces and many defects inside the particles while providing heat to the system. As a consequence, an equilibrium between heat generation and defect storage is reached, which makes possible the diffusion of species through defects at temperatures lower than those required for other solid state chemical reactions [5]. The temperature measured at the macroscopic scale is around 60 °C inside the grinding container. The local temperature during the grinding interactions is certainly much higher (several hundred degrees) but cannot be evaluated accurately.

In the manufacturing process of lead/acid batteries,  $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$  and  $4\text{PbO} \cdot \text{PbSO}_4$  (designated as 3BS and 4BS), which are the precursors of the positive active material  $\text{PbO}_2$ , are produced by mixing leady oxide ( $\alpha$ - and  $\beta$ -PbO with free lead), sulfuric acid and water. The transposition of the industrial process to laboratory scale reveals that kinetics limitations prevent the formation of

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pure tri- and tetra-basic lead sulfates even if stoichiometric  $\text{PbO}/\text{SO}_4$  ratios are chosen for the synthesis [6]: for instance, during the 3BS preparation, the heterogeneous nucleation of 3BS takes place at the oxide surface leading to the coating of the small grains of  $\text{PbO}$  by the basic lead sulfate phase. Encapsulated  $\text{PbO}$  grains cannot react with the sulfate ions of the solution due to the very slow diffusion of these ions across the 3BS barrier. This mechanism explains why unreacted  $\text{PbO}$  always remains in small amounts even after several days of mixing. These results forced us to look for alternative synthesis routes, like mechanochemistry for which the kinetically limiting step can be avoided through the use of finely divided and reactive ground precursors to prepare both 3BS and 4BS powders. In this paper will be discussed: (i) the new synthesis route for 3BS and 4BS phases and the morphological and textural features of the resulting materials in relation to the experimental conditions; (ii) the electrochemical behaviour of  $\text{PbO}_2$  active materials prepared from such precursors with the usual active materials prepared by the standard chemical routes.

## 2. Preparation of basic lead sulfates by reactive grinding

### 2.1. Experimental

In order to prepare the basic lead sulfates 3BS and 4BS, lead oxide ( $\text{PbO}$ ) was ground with either lead sulfate ( $\text{PbSO}_4$ ) or monobasic lead sulfate ( $\text{PbO} \cdot \text{PbSO}_4$  designated as 1BS) in a SPEX mixer mill model 8000. The mixtures were introduced in cylindrical stainless-steel vials (length: 2.5 cm, diameter: 1.27 cm) with one steel ball. For each experiment, the weight ratio steel ball to powders ( $R$ ) was 0.15.

The precursors subjected to grinding were commercial STREM  $\text{PbO}$  (mixtures of  $\alpha$ - and  $\beta$ - $\text{PbO}$ ), commercial PROLABO lead sulfate, and pure  $\text{PbO} \cdot \text{PbSO}_4$  prepared by reaction of 5.62 g  $\text{PbO}$  with 3.01 g  $\text{H}_2\text{SO}_4$  and 172 g  $\text{H}_2\text{O}$  at room temperature. Scanning electron microscopy (SEM) graphs reveal the presence of 3  $\mu\text{m}$  diameter flake particles for  $\text{PbO}$  (Fig. 1(a)), nodular particles (diameter comprised between 0.5 and 3  $\mu\text{m}$ ) for Prolabo lead sulfate (Fig. 1(b)) and needles (1  $\mu\text{m} \times 0.1 \mu\text{m}$ ) for  $\text{PbO} \cdot \text{PbSO}_4$  (Fig. 1(c)). The  $\text{PbO}/\text{PbSO}_4$  ratio was set to 4 or 5 depending on the experiment set-up.

The influence of water in the medium was investigated. Some experiments were carried out from products dried several hours under vacuum in order to eliminate adsorbed water, while others were conducted by using starting materials which were allowed to stand several hours under 100% of relative humidity atmosphere. In other cases, even liquid water ( $\sim 0.2$  ml) was added to the vial.

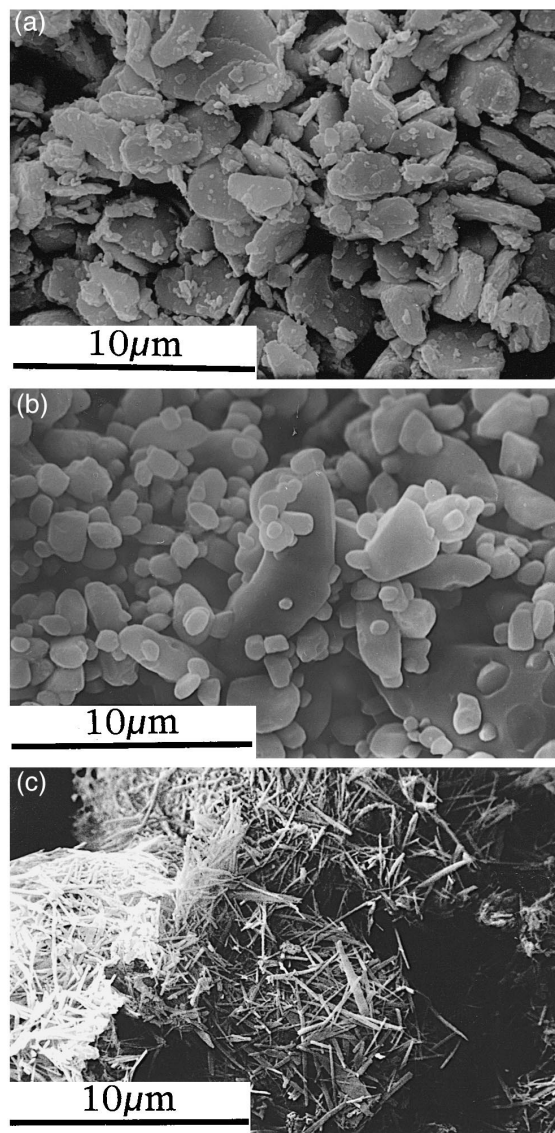


Fig. 1. SEM micrographs of the starting materials: (a) commercial STREM  $\text{PbO}$ ; (b) commercial PROLABO  $\text{PbSO}_4$ , and (c) monobasic lead sulfate ( $\text{PbO} \cdot \text{PbSO}_4$ ).

Powders ground for 30 min to 10 h were characterized by X-ray powder diffraction (Philips diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 15418 \text{ \AA}$ )), SEM (Philips 505), and transmission electron microscopy (Philips STEM CM12).

### 2.2. How to control the synthesis?

Pure samples of 3BS can easily be prepared by grinding stoichiometric mixtures of  $\text{PbO}$  and  $\text{PbO} \cdot \text{PbSO}_4$  or  $\text{PbSO}_4$  during less than 1 h providing that the  $\text{PbO}/\text{PbSO}_4$  ratio is 4 and water molecules are present (either as liquid or adsorbed at the grain surface). Fig. 2(a) gives the XRD pattern of a sample obtained by this method revealing the complete absence of  $\text{PbO}$  in the final product in contrast to the paste mixing preparation way. SEM micrograph (Fig.

2(b)) of the resulting powder shows regular needles which are  $1\ \mu\text{m}$  long and  $0.5\ \mu\text{m}$  thick. This morphology has been previously reported for a sample prepared according to the Bode and Voss method at  $40\ ^\circ\text{C}$  with, in this condition, needle size of  $1\ \mu\text{m} \times 10\ \mu\text{m}$  (cited in Ref. [7]).

With a ratio  $\text{PbO}/\text{PbSO}_4$  equal to 5, 4BS can be obtained either from water-free reactants or from powders saturated with water. It is interesting to note that the 4BS samples show various textural features depending on the experimental conditions. If 4BS is prepared from dry powders, the XRD pattern of the corresponding phase after 5 h of grinding shows very broad Bragg peaks (Fig. 3(a)), with some missing due to the overlapping with background. This indicates a small crystallite size probably associated with internal strains. The Williamson and Hall method allows a separate evaluation of crystallite size and internal strain effects [8]. However, such a method cannot be applied to the present 4BS patterns due to anisotropy and lack of multiple reflections. As a first approximation, the Scherrer equation was used to evaluate the mean crystallite size of the particles, giving values around  $100\text{--}250\ \text{\AA}$ . By contrast, powders saturated with water led to samples with sharper lines (Fig. 3(b)) for which the width

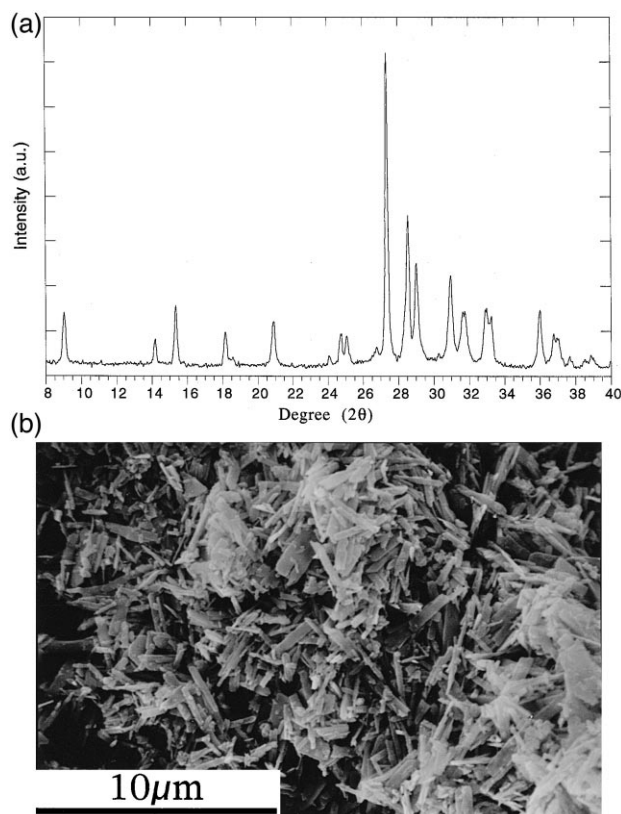


Fig. 2. Characterization of 3BS phase prepared by reactive grinding with liquid water and a  $\text{PbO}/\text{PbSO}_4$  ratio equal to 4: (a) XRD pattern showing the rather good purity of the ground sample, and (b) SEM micrograph showing the needle-shape particle ( $0.5\ \mu\text{m} \times 1\ \mu\text{m}$ ).

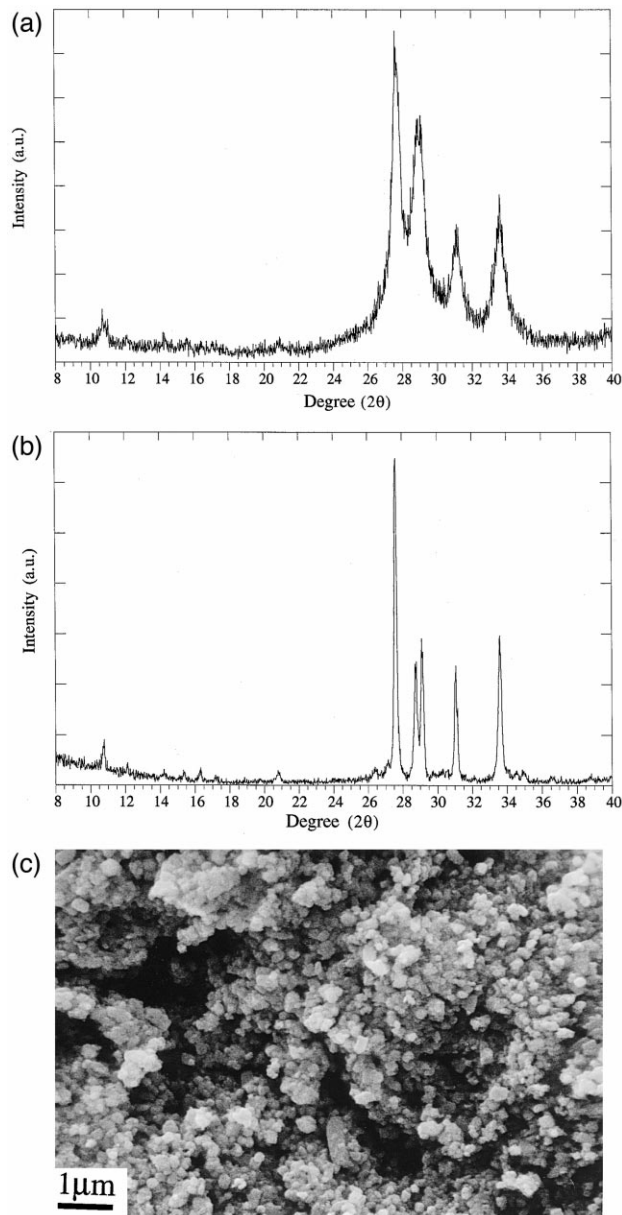


Fig. 3. Characterization of pure 4BS phases obtained by grinding of  $\text{PbO}$  and  $\text{PbSO}_4$  or  $\text{PbO}$  and  $\text{PbO} \cdot \text{PbSO}_4$  mixtures with a  $\text{PbO}/\text{PbSO}_4$  ratio equal to 5: (a) XRD pattern of the sample prepared from dry powders ( $\text{PbO}$  and  $\text{PbSO}_4$ ) after 3 h of grinding; (b) XRD pattern of the sample prepared from saturated water powders, and (c) typical SEM micrographs of ground 4BS samples.

at half-maximum intensity corresponds to the instrumental width, so we can consider that in this case the crystallite size exceeding  $1000\ \text{\AA}$ .

### 2.3. Discussion

The results showed that mechanochemistry can be used as a suitable new route to synthesize the 3BS and 4BS with a rather good purity level. In fact contamination from the grinding container is negligible.

Table 1

Synthesis of 3BS and 4BS compounds by reactive grinding: influence of the experimental conditions upon the structural and textural features of the resulting ground powders

Case number	PbO/PbSO <sub>4</sub> ratio	Starting materials	Hygrometry weighed (%)	Grinding time (h)	Results	Crystallite size (Å)
1	5	3BS + PbO	0	3	4BS	> 1000
2	5	PbSO <sub>4</sub> + PbO or 1BS + PbO	0	2	starting compounds	XRD lines broadening
3	5			5	4BS	150 to 250
4	5			8	4BS	400
5	5		< 5	1	**	
6	5				PbSO <sub>4</sub> , PbO 4BS, 3BS if starting sulfate is PbSO <sub>4</sub>	
7	5			3	4BS	> 1000
8	5		> 30	1	3BS, PbO mixture	
9	4	PbSO <sub>4</sub> + PbO or 1BS + PbO	0	1	starting compounds	XRD lines broadening
10	4			10	4BS $\epsilon$ + 1BS or PbSO <sub>4</sub>	~ 200
11	4		< 5	1	3BS	> 1000
12	4		> 30	0.5	3BS with 1BS as an intermediate phase from PbSO <sub>4</sub>	> 1000

However, two questions arise from our experiments:

1. What are the driving forces leading to each basic salt in the grinding experiments?
2. Why are various textural features observed for the 4BS phase depending on the starting material hygrometry?

To get further insight into these questions, we have summarized in Table 1 the structural and textural features of the ground final powder as a function of the experimental conditions (PbO/PbSO<sub>4</sub> ratio, starting materials, hygrometry and duration of the grinding).

From Table 1, it appears that the role of water is important and governs the reaction pathway. Indeed, the 3BS synthesis definitely requires the presence of water. If water is eliminated by drying the powders under vacuum, the main final compound is 4BS even if the stoichiometry corresponds to 3BS. However, just a small amount of adsorbed water is sufficient to produce 3BS. The relatively short reaction time (less than 1 h) and the well-defined morphology of the resulting 3BS phase (needle) suggest that the reaction probably proceeds with a partial dissolution and diffusion of species through the adsorbed water layer. It can be concluded that the effect of grinding in this case just allows an intimate mixing of the components and avoids the PbO encapsulation observed for other synthesis routes [6] similar to paste mixing. By using liquid water in the grinding container, the reaction rate is higher, enhancing the hypothesis of a mass transfer promoted by water.

By contrast, 4BS is never obtained when liquid water is present in the vial. In these conditions, if the stoichiometry corresponds to 4BS, a mixture of 3BS and PbO is obtained instead of the expected 4BS phase. Starting from dried or containing adsorbed water materials, it is possible to form 4BS with very small particle size (< 1  $\mu\text{m}$ ) (Fig. 3(c)).

The very small size of the crystallites observed when dried powders are used as the starting materials (PbSO<sub>4</sub> or 1BS) can be explained as follows: without water, the

reaction involves only the solid phases of the powders. As shown by XRD line broadening, grinding induces in a first stage a decrease in crystallite size and/or an increase in internal strain so that the reagents become more reactive. Moreover, the heat release induced by grinding favours the diffusion of the species. All these grinding effects allow the crystallization of 4BS in small nuclei. However, for very long grinding times, the excess of heat causes the growth of crystallites from 200 to 400 Å. Finally, a balance between the defect formation and the heat release stabilizes the crystallite size. 4BS prepared by this method is very reactive (just adding water to it leads to the formation of 3BS).

A completely different behaviour is observed when water saturated starting materials are used for the 4BS synthesis. As for the 3BS formation, adsorbed water favours the diffusion of species and promotes the particle growth from the solution so that shorter grinding times are required and large crystallite sizes can be reached (~ 1000 Å).

However, such a mechanism does not explain why starting from dry 3BS/PbO mixture, the 4BS phase shows large crystallites, only in the case we consider that the structural water molecules from 3BS (3PbO · 1PbSO<sub>4</sub> · 1H<sub>2</sub>O) are released during grinding, thus playing the role of adsorbed water. Another explanation based on structural considerations may be proposed to account for the formation of large crystallite 4BS in such conditions. Crystallites greater than 1000 Å are observed when 3BS is either the starting or the intermediary reaction compound. If structural relationships exist between 3BS and 4BS, the reaction requires less energy to occur, compared with other sulfates (1BS, PbSO<sub>4</sub>). This hypothesis is supported by the fact that shorter reaction times are observed with 3BS (see Table 1). As a consequence, the defect level reached at the end of reaction is probably lower, favouring a large coher-

ence length. At the present, the two possibilities are difficult to be distinguished.

### 3. Capacity measurements

As seen above, reactive grinding showed to be a powerful and new method for producing 3BS and 4BS with specific morphological features. In view of their potential application as the positive electrode materials of lead/acid batteries, electrochemical measurements were carried out on such materials and the results compared with other standard 3BS and 4BS samples prepared by the usual chemical processes.

#### 3.1. Experimental

##### 3.1.1. Starting materials

The samples nos 1, 4 and 12 in Table 1 were selected for the electrochemical tests. Similar capacity measurements were carried out from two other samples: (i) a standard 3BS phase prepared by the Bode and Voss method [7,9], and (ii) a 4BS phase synthesized by curing a 3BS/PbO mixture. The 3BS samples show needle-shape particles but the 3BS<sub>br</sub> particles are twice smaller than the standard sample prepared by the Bode and Voss method. By contrast, the morphology of the cured 4BS sample completely differs from that of the 4BS phases prepared by reactive grinding (needle with sizes of 10 μm × 100 μm (Fig. 4) versus nodular submicronic particles (Fig. 3(c)).

##### 3.1.2. Electrochemical tests

The basic lead sulfate powder (200 mg) was packed with the current collector at a pressure of 3 ton/cm<sup>2</sup>. The positive electrode was then put into a small polytetrafluoroethylene (PTFE) cell (Swagelok type) described in a previous paper [10], with 0.5 ml of sulfuric acid (sp. gr. 1.23), a fiber glass separator and a pure lead counter electrode.

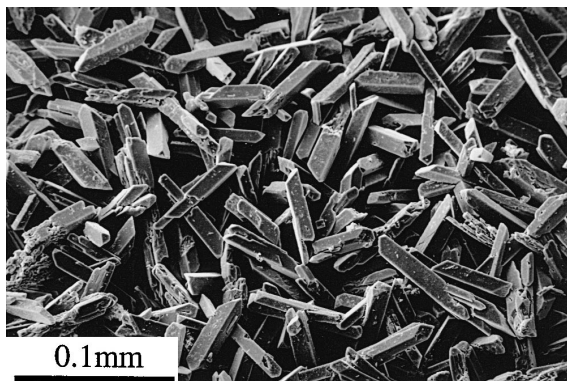


Fig. 4. SEM micrographs of a cured needle-shape 4BS samples.

Table 2

Comparison of capacities characterizing ground 3BS and 4BS samples and standard materials

Compounds	First capacity (Ah kg <sup>-1</sup> )	Second capacity (Ah kg <sup>-1</sup> )
3BS (standard sample)	125	128
3BS (grinding)	68	76
4BS (cured sample)	56	104
4BS <sub>br1</sub> (grinding, large crystallites size)	102	132
4BS <sub>br2</sub> (grinding, small crystallites size)	85	115

The first and second charges were conducted at room temperature at a constant current rate ( $C/20$ ) where  $C$  represents the theoretical capacity of the 4BS phase, i.e. 224 Ah kg<sup>-1</sup>. Such a current is maintained during 60 h, providing a total amount of charge equal to 672 Ah kg<sup>-1</sup>. Discharges were performed with the same galvanostatic rate ( $C/20$ ), until the positive cell voltage drops below 1 V versus the lead counter electrode.

#### 3.2. Results

The first and second discharge capacities are given in Table 2. This Table shows an increase in capacities between the first and second cycles. This trend, observed for all samples but more pronounced for 4BS, can be attributed to an activation procedure resulting from the increase in conductive material amount inside the electrode. At the beginning of the first charge, the electronic conductivity inside the pellet is very low as basic lead sulfates (3BS and 4BS) are poor electronic conductors. After the first cycle, conductive PbO<sub>2</sub> materials remain in the discharged state because this phase cannot be completely reduced into PbSO<sub>4</sub> by electrochemical procedures. This left-over PbO<sub>2</sub> phase improves the transport of electrons inside the electrode during the subsequent recharge, thereby increasing the charge efficiency and second cycle capacities.

Table 2 also stresses the fact that mechanical grinding can be used as a suitable preparation method to produce 4BS-type materials with a capacity higher than the usual cured 4BS materials; they are therefore of potential interest to thin metal foil technologies where fine divided powders are required. In contrast, this effect is the opposite in the 3BS phase. Mechanical grinding leads to performances lower than traditional preparation ways for 3BS.

Such a behaviour is not surprising, since 4BS cured samples are well known to exhibit a low formation efficiency due to their large crystal sizes (10 μm × 100 μm). By using mechanical grinding, we were able to reduce the

particle size below 1  $\mu\text{m}$  so that conversion into  $\text{PbO}_2$  during charge is complete, leading to capacities higher than for the cured 4BS counterpart. A small difference in capacities can be noticed for the two 4BS<sub>br</sub> samples. No straightforward explanation can be proposed here. Answers to these questions require further investigation to screen both the microstructural (crystallite size, defect level) and the macrotextural (agglomerate shape, porosity of the pellet)  $\text{PbO}_2$  features resulting from such 4BS samples. Such experiments are in progress in our laboratory but are beyond the scope of this paper.

The electrochemical behaviour of the 3BS samples can be also explained on the basis of morphological considerations. The 3BS<sub>br</sub> phase shows a capacity  $\sim 40\%$  lower than the standard 3BS sample. This difference is probably correlated with the particle morphology. Both the 3BS samples show needle-shape particles, but the particles are twice smaller for those of the 3BS<sub>br</sub> powder. The reduced particle size for 3BS<sub>br</sub> leads to a more compact pellet with a poor porosity, thereby preventing the electrolyte diffusion inside the electrode.

Finally, it results from this work that the particle size of the  $\text{PbO}_2$  made from 4BS or 3BS precursors plays a key role in governing the positive active material capacities. Thus, a compromise has to be found to optimize both the charge efficiency (the smaller the particle size, the higher the charge efficiency) and the electrolyte diffusion path (the biggest particles providing the better porosity). We are

presently addressing these issues and have succeeded in a better control of the basic lead sulfate particle morphology (size and shape) as will be described in a forthcoming paper.

### Acknowledgements

The authors thank the Agence De l'Environnement et de la Maitrise de l'Energie (ADEME) and CEAC for its financial support.

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