The influence of the raw material and production method on the morphology, microstructure, chemical and phase composition of tetrabasic lead sulfate pastes

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Abstract

Tetrabasic lead sulfate (4BS) produced by two different methods (solution and paste) and from two different raw materials (tetragonal PbO and leady oxide) were characterized by different analytical techniques. The techniques applied were wet-chemical methods, scanning electron microscopy, transmission electron microscopy and X-ray powder diffraction. The preparation method was observed to be the most decisive factor influencing the structure and the morphology of the 4BS pastes in this study.

Introduction

Tetrabasic lead sulphate, $4PbO \cdot PbSO_4$ (4BS) is formed in the lead/acid battery active mass during the mixing and/or curing stage of the manufacturing process. The production of 4BS during the mixing stage occurs in 0.5–1.0 h at temperatures above approximately 70 °C. The chemical formation of 4BS at ambient temperature, however, is a very slow process. The formation of 4BS occurs through tribasic lead sulfate, $3PbO \cdot PbSO_4 \cdot H_2O$ ($= 3BS$), as an intermediate. In addition to an elevated temperature, which accelerates the 3BS/4BS conversion, a sufficiently high water content is required for the development of 4BS in the paste. Both 3BS and 4BS exist in the form of elongated prismatic crystals in the active mass, but 4BS crystals are considerably larger due to high crystal growth rate and a rather low nucleation rate [1–6].

Initially Burbank [1], followed by other researchers, found that 4BS undergoes an anodic conversion to PbO_2 while maintaining the original morphology of the 4BS. This so-called metasomatic conversion produces PbO_2 crystals, which results in long-life and cyclable lead/acid battery positive plates. The reason for the long cycle life of the 4BS-based plates is not yet clear. There are two main theories presented. One explanation is that the large PbO_2 crystals in such plates makes them durable [1]. The other is that 4BS is the source of α-PbO_2, which forms a mechanically stronger structure in the plates [7]. Concerning the former theory, Culpin [6] has noted that very little has been published on the length of the time that the original structure is

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maintained during cycling. He has also pointed out that there is a disagreement between the latter theory and the open literature, where it has been reported that 4BS can be converted to either α- or β-PbO_2 depending on the conditions.

The active masses are complex systems of several parameters, and the creation of a comprehensive theory is inevitably difficult. However, by considering the active mass as a two level system, containing micro- and macrostructures [8, 9] and by analysing the effects of different production parameters on both levels, one may obtain some new pieces to the unsolved parts of the lead/acid battery 'puzzle'.

Until quite recently, the presence of large 4BS crystals, at least in higher amounts, in the positive plates of starter batteries has been considered undesirable. The reason for that is the long electroformation time required to achieve a complete oxidation of 4BS to PbO_2 and thus to obtain 4BS-based plates with the initial capacity high enough [1, 6–8, 10–12].

Recently, however, Pavlov and Kapkov [13, 14] have reported a paste preparation technique by which the production of positive battery plates from 4BS is possible without the main disadvantage mentioned above. Their basic idea to overcome the problem is a partial substitution of the leady oxide by red lead as a raw material of 4BS paste. Altogether, they have presented three different 4BS paste preparation methods, in which the conversion of 3BS to 4BS proceeds at the stage of paste mixing. One important advantage of the methods presented is the disappearance of the upper temperature limit (about 65 °C) for curing [15]. Therefore, the curing of the plates can be carried out at higher temperatures and consequently in a shorter time than with the conventional 3BS technology.

These new methods are very promising, offering possibilities to produce long-life positive battery plates without the traditional electroformation problems, as well as reducing the curing time, which is a bottle-neck stage of the battery manufacturing process. However, one should not forget the economical aspects and the requirements for industrial processes of new technology. If the new methods for 4BS technology prove to be advantageous on the grounds of both economical and technological considerations, a new outlook for battery production will be opened up. In contrast to the general idea that 4BS gives cycling capacity and is therefore appropriate to industrial batteries, easily oxidizable 4BS could be used as a raw material of positive plates in order to improve cycle life of automotive batteries too, and without any loss of the initial capacity. If that is the case, effective characterization methods of the active material will play an important role in comparing different production technologies as well as in transferring the technology from laboratory to industrial scale.

Pavlov *et al.* [16] have investigated the hydration and amorphization of active mass PbO_2 particles by transmission electron microscopy methods including electron microdiffraction. They found that individual PbO_2 particles are composed of high-density crystalline and low-density amorphous zones. Their active mass for that study was prepared from 3BS paste.

The aim of the present paper is to clarify how 4BS-rich cured positive active mass and mass particles can be characterized by some widely used methods of analysis. The techniques applied are wet-chemical analysis, X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). By means of the abovementioned analysis techniques, attempts were made to observe the major differences between three 4BS samples. The samples were: (a) 4BS prepared by paste method from leady oxide; (b) 4BS prepared by solution method from leady oxide, and (c) 4BS prepared by solution method from tet-PbO.

Experimental

The synthesis of 4BS were carried out in a small laboratory-scale mixer system consisted of a beaker, a mechanical stirrer and a simple cooling/heating system. The raw materials used were distilled water, sulfuric acid solution (sp.gr. = 1.4 in the paste method and 1.25 in the solution method), tetragonal PbO (Merck Art. 7405) and leady oxide from a battery factory. The batch size in the past method syntheses was limited to 200 g of lead(y) oxide in order to maintain effective mixing.

The solution method products were prepared according to the method described by Burbank [1]. The solid precipitates were filtered, then cured for 24 h at 80–85 °C and in 100% relative humidity, and finally dried.

The 4BS prepared by the paste method was synthesized by weighing first 200 g of lead(y) oxide into the beaker, then starting the mixing. Following the start of the mixing, about one half of the total water amount was introduced to the beaker, then the sulfuric acid solution was dropped into the reaction vessel in 10 min and finally the other half of the water was introduced. The total mixing time was 2 h. The synthesis temperature in preparation of 4BS pastes was 80–85 °C. The final adjustment of the density of the paste to 4.2 with water was performed at the end of the mixing, because of the continuous water evaporation during the mixing. The pastes were cured for 24 h at 80–85 °C and in 100% relative humidity after mixing and then dried. The cured and dried 4BS pastes were then subjected to the analyses.

In order to prepare paste samples for SEM analysis they were coated with a thin layer of carbon followed by a thin layer of gold. For TEM analysis cured and dried 4BS paste samples were cast into an epoxy resin and thin sections were cut from the sample/epoxy rods by an ultramicrotome. The preparation of thin transparent sections from the epoxy block by ultramicrotome was rather complicated, because dried 4BS was brittle material. A very thin layer of carbon was evaporated on the sections prior to TEM runs.

The electron micrographs were obtained on a JEOL JSM-840A scanning electron microscope and a JEOL JEM-1200EX-II transmission electron microscope and the powder diffraction patterns on a Siemens Diffrac 500 diffractometer. The interpretation of the diffractograms was performed with the help of JCPDS reference data. Wet-chemical methods were employed in the chemical analyses of the 4BS pastes.

Results and discussion

The SEM micrographs taken from the cured products (Figs. 1(a)–(d)) showed that there are differences in sizes and shapes of the three different 4BS investigated. The paste method crystals (Fig. 1(a)) were clearly smaller and looked more porous than the solution method crystals (Figs. (1(b)–(c)) and they were composed of irregular crystal agglomerates. On the contrary, 4BS crystals prepared by the solution method from both leady oxide and tet-PbO were large single crystal-like particles with approximately regular shapes. In the solution method preparation, however, 4BS prepared from tet-PbO (Fig. 1(c)) has smoother edges and seemed to have higher crystallinity than the one synthesized from leady oxide (Fig. 1(b)). Among the 4BS needles prepared from tet-PbO some clearly distinguishable spherical particles (Fig. 1(d)) could be seen, presumably due to the incomplete chemical formation of 4BS.

In order to study the phase compositions of the three 4BS pastes, they were analysed by XRD. The results of the XRD analyses are presented in Table 1. The
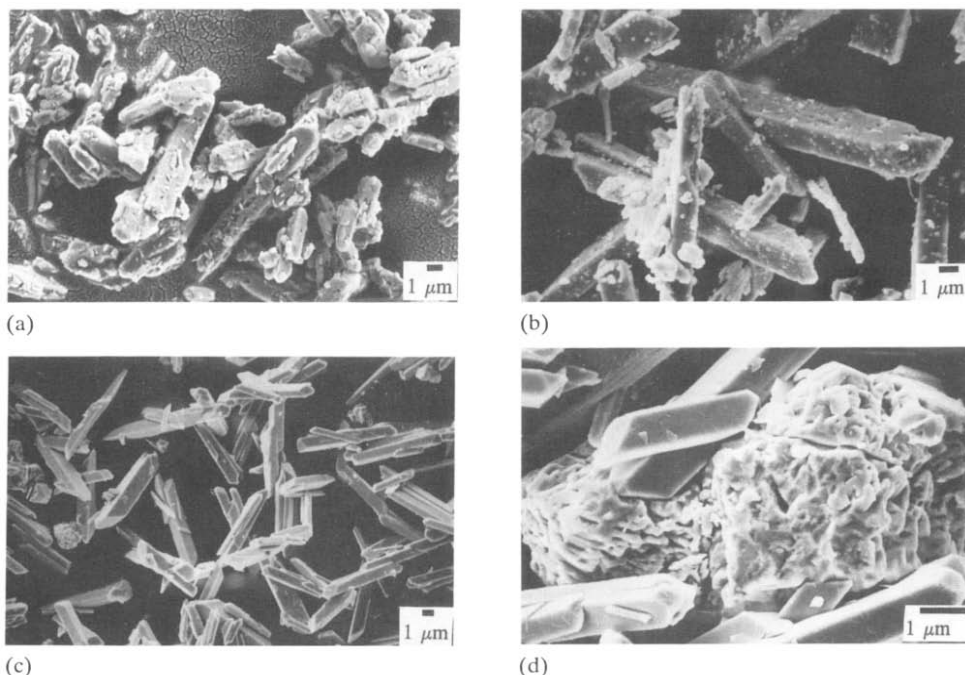
Fig. 1. Scanning electron micrographs of 4BS prepared (a) by paste method from leady oxide, (b) by solution method from leady oxide, (c) and (d) by solution method from tet-PbO.
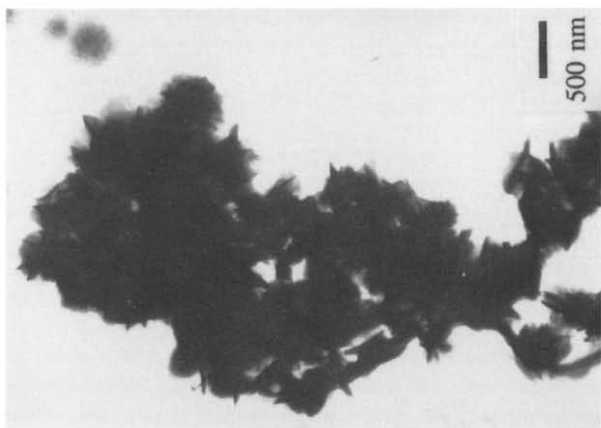
TABLE 1

The phase composition of different 4BS pastes by X-ray diffraction. The values are given as relative diffraction intensities

Method	Raw material	4BS	3BS	tet-PbO
Paste	leady oxide	94.6	0.9	4.5
Solution	leady oxide	91.3	5.7	2.0
Solution	tet-PbO	94.3	1.6	4.1

relative diffraction intensities of 4BS, 3BS and tet-PbO were calculated from intensities of peaks with d-values 2.87, 3.26 and 2.81, respectively. The results obtained showed that there was some 3BS and tet-PbO present in all the 4BS synthesized, but their relative concentrations varied according to the production method. On the basis of XRD, the paste method product and the 4BS prepared from tet-PbO by the solution method had very similar phase composition although SEM pictures showed their morphologies to be rather different.

In addition to XRD analysis the 4BS pastes were analysed by wet-chemical methods. The results obtained can be seen in Table 2. The sulfuric acid amount added in preparation of each batch is reported there with respect to the lead(y) oxide and the other values in Table 2 are concentrations in the dried paste. The metallic lead concentrations from wet-chemical analyses indicate that metallic lead present in leady
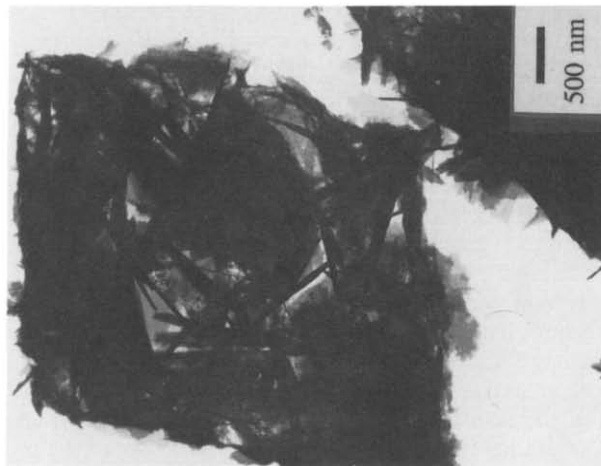
Fig. 2. Transmission electron micrographs taken from 4BS pastes prepared (a) by paste method from leady oxide, (b) by solution method from leady oxide and (c) by solution method from tet-PbO.

TABLE 2

The results from chemical analyses of the cured and dried 4BS pastes, values given as wt.%

Method	Raw material	H_2SO_4 (add.)	Pb (wet.chem.)	SO_4^{2-} (wet.chem.)
Paste	leady oxide	7.2	0.29	7.0
Solution	leady oxide	7.2	0.36	6.8
Solution	tet-PbO	7.3		6.9

oxide has oxidized nearly completely during mixing and curing. In addition, sulfate results prove that the majority of the sulfuric acid added has attacked the raw material.

Although 4BS crystals, especially those prepared by the solution method and from tet-PbO, were, on the grounds of SEM pictures, very much like single crystals, there is, in practice, a microstructure inside these needle-shaped crystals composed of smaller crystallites. In many cases the size and shape of the crystallites have a remarkable influence on the physical properties of materials. Therefore, it is important to somehow try to characterize the microstructure of the 4BS particles. In order to characterize this fine structure, the TEM technique was applied. The TEM micrographs of the three 4BS pastes can be seen in Fig. 2.

The TEM pictures showed that the two solution method products had a different microstructure than the paste method product. 4BS 'rods' prepared by the solution method (Figs. 2(a)–(b)) were composed of clearly defined crystalline needles of varying sizes, whereas 4BS crystals prepared by the paste method consisted of material of lower crystallinity and less well-defined shapes (Fig. 2(c)).

Conclusions

In this study, the preparation method was found to be one decisive factor affecting the morphology of the 4BS crystals. The preparation of 4BS from solution allows paste particles to grow and to form large 4BS rods composed of needle-shaped crystallites. In addition, the choice of raw material oxide had an additional effect, primarily on the regularity of the crystals of the solution method preparation. In the paste method preparation of 4BS the particle size, morphology and crystallite structure of the product were totally different than in the solution method 4BS due to the different process conditions such as pH, the contact between paste particles, water content, etc.

The results obtained from the characterization of the 4BS laboratory pastes were so encouraging that it would be interesting to continue the investigations. First, the traditional 3BS and 4BS pastes as well as the red lead 4BS paste should be compared in order to find differences between them prior to formation stage. Then, these pastes should be monitored during cycling in order to observe if there are any permanent differences that explain the mechanical strength of 4BS paste and the ease of the electroformation of the 4BS plates produced by the red lead techniques. To ensure the applicability of the results to real-life systems further investigations should be carried out using either a large laboratory or a pilot-scale mixer.

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