

Processes during preparation of lead/acid battery positive plates from tetrabasic lead sulfate (4BS) pastes

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Abstract

The processes studied during this investigation were paste mixing and curing. Tetrabasic lead sulfate 4BS pastes were prepared by solution and paste methods both from α -PbO and mill oxides, and the development of 4BS was carried out already during the paste mixing stage. The 4BS pastes were characterized by SEM, TEM, XRD and wet-chemical methods, and the results were compared with those obtained from the characterization of corresponding tribasic lead sulfate (3BS) pastes. The preparation method was found to be one dominating factor affecting both the morphology and structure of 4BS active masses. The selection of raw material gave an additional effect on the morphology. Additionally, some differences in the behaviour between 3BS and 4BS pastes were observed. One should take them into account when planning a production line for 4BS pastes.

Introduction

Burbank [1] found that tetrabasic lead sulfate $4\text{PbO} \cdot \text{PbSO}_4$ (4BS), formed in the lead/acid battery positive active mass during the mixing and/or curing stage of the manufacturing process, undergoes a metasomatic conversion to PbO_2 . The 4BS crystals are significantly larger than $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ (3BS) crystals and this results in a mechanically stronger lead dioxide structure than that obtained in 3BS-based applications. Although 4BS-based positive plates are cycleable and have a long cycle life, large 4BS crystals require a very long formation time for complete oxidation to PbO_2 in order to obtain plates with sufficiently high initial capacity. Therefore, the presence of large amounts of 4BS in positive automotive-battery plates has been considered undesirable, at least until quite recently [2–5].

Additionally, an unambiguous explanation for the long cycle life of 4BS-based plates has not yet been given, although two different theories have been presented. One theory argues that the large PbO_2 crystals formed from 4BS make the plates durable [1], whereas the other states that 4BS is the source of α - PbO_2 , which forms a mechanically stronger structure in the plates [6]. Regarding the former theory, Culpin [7] has noted that very few investigations have dealt with the length of the time that

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the original structure is maintained during cycling. In addition, he showed an inconsistency between the latter explanation and the fact that 4BS can be converted to either α - or β -PbO₂ depending on the choice of the conditions.

Recently, methods for the production of 4BS-based positive automotive-battery plates, where no significant electroformation problems existed, have been reported. The basic idea of these methods is the partial substitution of leady oxide by red lead as the raw material [8, 9]. One significant advantage of these methods is the disappearance of the normal temperature limit for the curing stage. Therefore, the curing — a bottleneck stage in the manufacturing process — can be carried out at higher temperatures and, consequently, at faster rates than in automotive-battery applications using 3BS-based plates [10].

The new 4BS methods have opened up possibilities to produce long-life positive, automotive-battery plates with a sufficiently high initial capacity. Nevertheless, the economical and technological aspects of the new technology will mainly determine whether the lead/acid battery industry is anxious to replace the traditional automotive-battery technologies with the new 4BS technology or not. Furthermore, effective characterization methods of the active material are required in order to introduce the new technology as a full-scale industrial process. One important task of such work will be to clarify the differences between 3BS and 4BS and to evaluate their influence on each stage of the production process. Also, it is important to characterize 4BS prepared by different methods and to look for structural dissimilarities by which the deviations in the performance (e.g., initial capacity) can be explained. Our studies have concentrated on the processes during paste mixing and curing [11–13]. The results are reported in this paper.

Experimental

Most of the syntheses were performed in a simple laboratory mixer system consisting of a beaker, a mechanical stirrer, a hot plate and a water bath. Mill oxide from a battery plant, and α -PbO (Merck Art. 7405), distilled water and sulfuric acid solutions were used as raw materials in the production of the active masses. The mixing and curing procedures for 4BS pastes were carried out at 80 °C, and those for 3BS pastes at temperatures below 65 °C. The paste-method material was prepared as in the factory, except that the batches contained only 200 g of leady oxide. The solution-method pastes were prepared according to the technique described by Burbank [1]. Additionally, a 25 kg batch of 4BS paste prepared with a pilot-scale mixer and a 3BS-based automotive-battery paste from a battery plant (700 kg batch) were studied [11–13].

Scanning (SEM) and transmission (TEM) electron micrographs were obtained with a JEOL JSM-840A scanning electron microscope and a JEOL JEM-1200EX-II transmission electron microscope, respectively. SEM samples were coated with a thin layer of carbon, followed by a thin layer of gold. For TEM analysis, the active-mass particles were embedded in epoxy resin and thin sections were cut from the cured block by an ultramicrotome. The sections were coated with a thin layer of carbon prior to TEM analysis. X-ray powder diffraction analyses (XRD) were performed with a Siemens Diffrac 500 diffractometer and the patterns were interpreted with the help of JCPDS data base. Traditional wet-chemical analyses were employed in the chemical analyses of the masses.

Results and discussion

Influence of preparation method and long mixing time on 3BS and 4BS

The first task of these studies was to produce 3BS and 4BS masses that were as pure as possible from leady oxide by both the solution and paste methods. Next, an evaluation was made of the differences between 3BS and 4BS pastes, as well as of the differences due to the production method within the same basic lead sulfate. In order to complete the reaction between H_2SO_4 and leady oxide, as well as to facilitate the observation of the dissimilarities, the mixing period was prolonged to 4–5 h and the H_2SO_4 contents of the pastes were empirically optimized to give a maximum content of the desired basic lead sulfate in the reaction mixture. Moreover, one purpose was to use the materials synthesized as standard materials in the quantitative XRD analysis of active masses. The phase composition of the reaction mixtures as a function of mixing time was monitored by XRD. The completion of the reaction was checked after both mixing and curing by wet-chemical analyses and the morphology of the cured pastes was analysed by SEM.

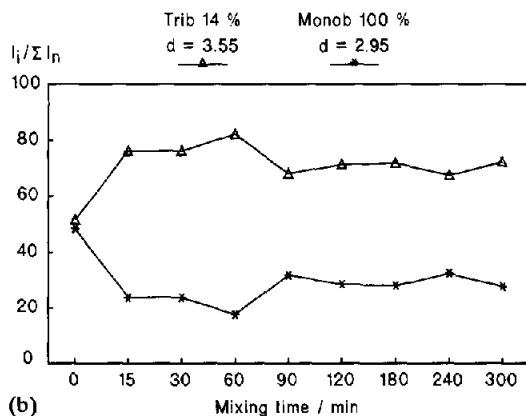
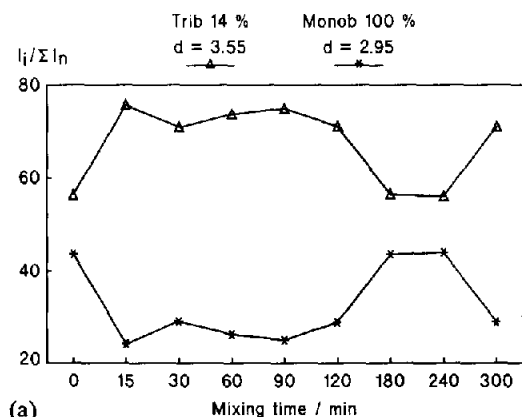
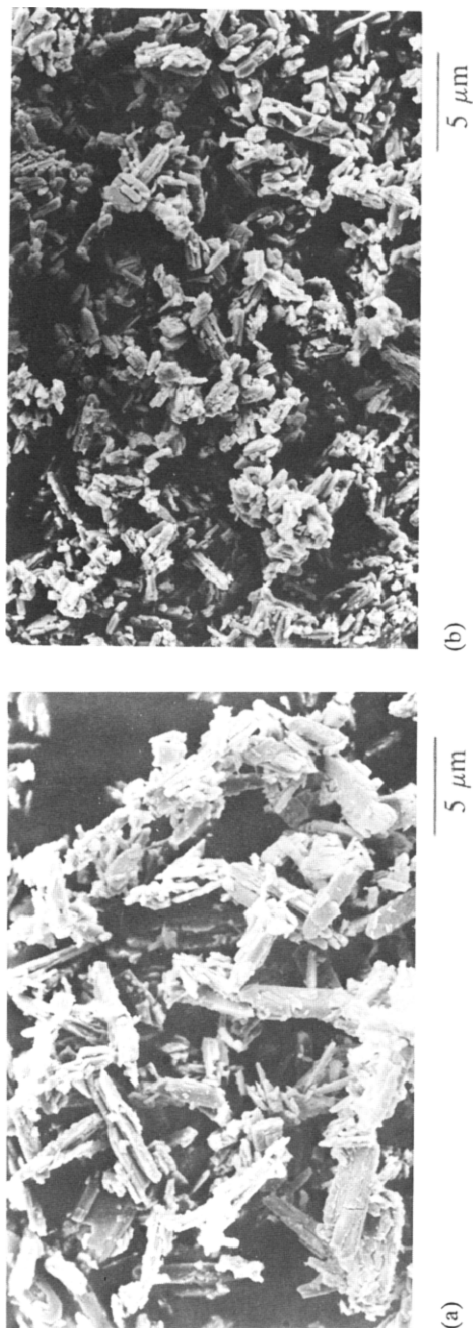


Fig. 1. Changes in the XRD phase composition of 3BS masses as a function of mixing time: (a) solution method; (b) paste method.



(a)

(b)

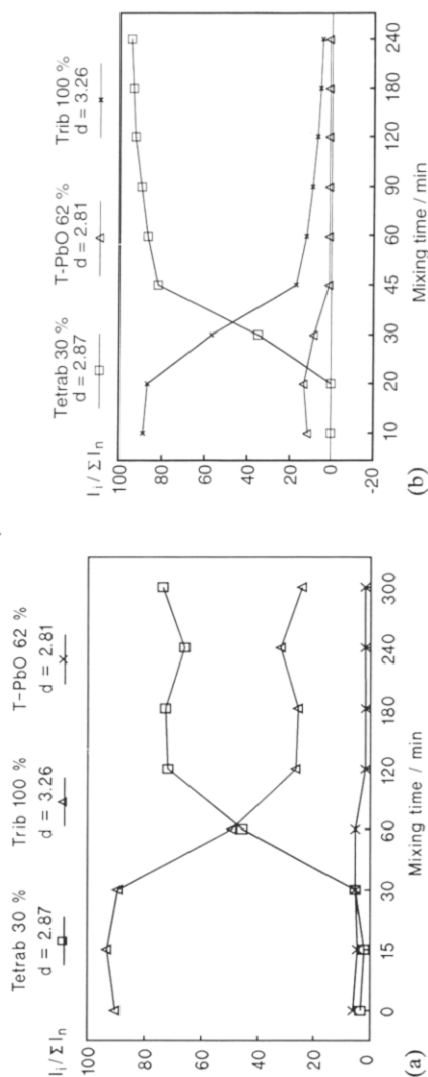


Fig. 2. Scanning electron micrographs of cured 3BS masses prepared by: (a) solution method; (b) paste method.

Fig. 3. Changes in the XRD phase composition of 4BS masses as a function of mixing time: (a) solution method; (b) paste method.

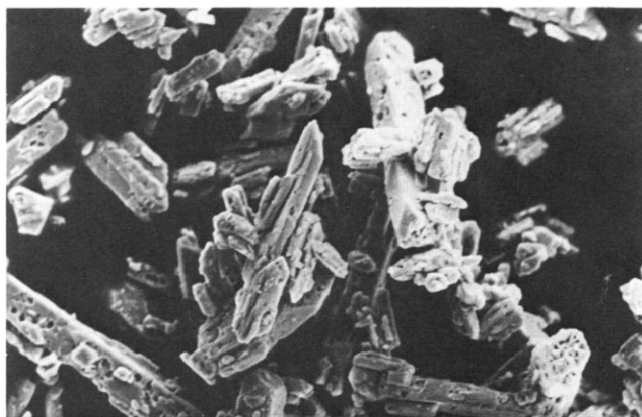
The XRD phase composition of 3BS masses as a function of mixing time are presented in Fig. 1. Despite the differences between the paste and solution methods during the course of the reaction, the composition of these two pastes at the end of the mixing was similar. SEM micrographs of the cured masses, however, revealed that 3BS crystals prepared by the solution method were significantly larger than those produced by the paste method (Fig. 2).

The production of 4BS by the paste method deviated from that obtained by the solution method. The development of the 4BS in the paste method started earlier and proceeded with a higher rate (Fig. 3). In addition, the XRD phase composition at the end of the mixing was slightly different with the two procedures.

SEM micrographs of the cured 4BS masses (Fig. 4) revealed a dissimilarity in the morphology of the material formed by the two preparation methods. Paste-method product was composed of porous irregular crystal agglomerates (Fig. 4(b)), whereas



(a)

5 μm 

(b)

5 μm

Fig. 4. Scanning electron micrographs of cured 4BS masses prepared by: (a) solution method; (b) paste method.

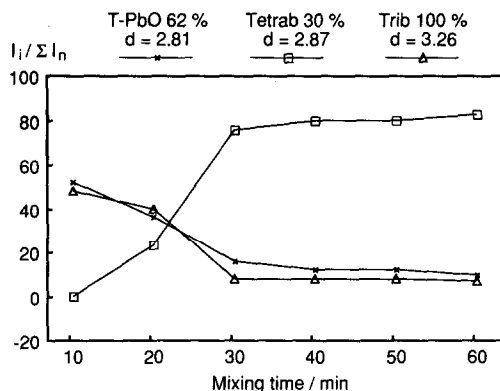


Fig. 5. Changes in the XRD phase composition of 4BS mass prepared by the paste (tetrabasic) method in a pilot-scale mixer as a function of mixing time.

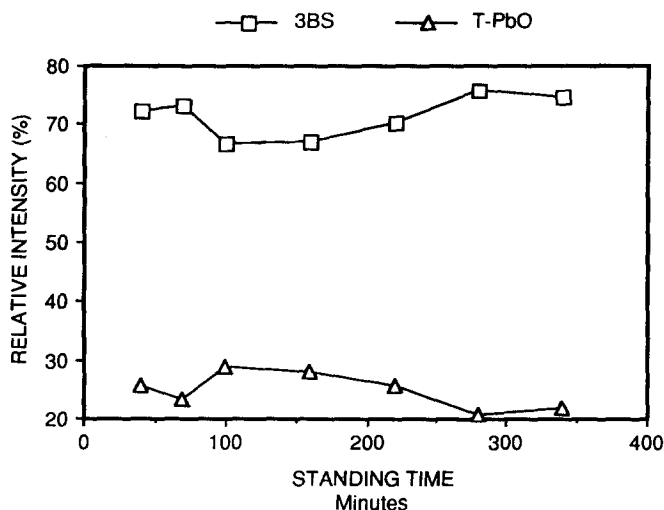


Fig. 6. Changes in the XRD phase composition of a 3BS-containing automotive battery factory paste as a function of stand time. Mixing time 20 min.

solution-method particles were more compact with larger single crystals (Fig. 4(a)). By comparing Figs. 2 and 4, the dissimilarities between 3BS and 4BS can be seen. The particle size in 4BS masses is larger than in 3BS masses due to the higher crystal growth rate of 4BS.

The results from the chemical analyses of mixed and cured 3BS and 4BS masses can be seen in Tables 1 and 2. The very low metallic lead contents of the masses indicate that this component has already oxidized and reacted with sulfuric acid during the mixing stage.

When comparing laboratory-scale and pilot-scale production of 4BS by the paste method (Figs. 3(b) and 5), it was observed that the development of 4BS occurred at a 50% higher rate in the pilot-scale mixer (batch size approximately 25 kg) than in a small laboratory mixer.

TABLE 1

Results from chemical analyses of 3BS and 4BS pastes prepared by paste and solution methods after an extended period of mixing. The values are given as wt.% and the added H₂SO₄ content as wt.% with respect to the leady oxide

Paste type	Preparation method	H ₂ SO ₄	Free lead	SO ₄ ²⁻ (wet-chemical analysis)
3BS	Solution	10.1	0.39	10.0
3BS	Paste	10.1	0.40	9.3
4BS	Solution	7.1	0.41	7.1
4BS	Paste *	7.1	0.31	7.1

TABLE 2

Results from chemical analyses of cured 3BS and 4BS pastes prepared by paste and solution methods with an extended mixing period. The values are given as wt.% and the added H₂SO₄ content as wt.% with respect to the leady oxide

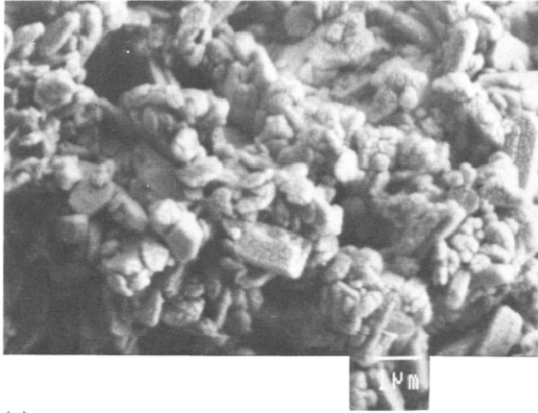
Paste type	Preparation method	H ₂ SO ₄	Free lead	SO ₄ ²⁻ (wet-chemical analysis)
3BS	Solution	10.1	0.38	10.0
3BS	Paste	10.1	0.29	9.2
4BS	Solution	7.1	0.39	7.0
4BS	Paste	7.1	0.30	7.0

Influence of standing

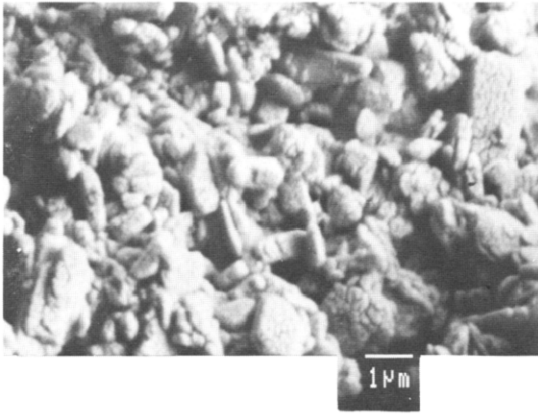
For the planning of the process stages subsequent to the paste mixing, it is important to know what reactions occur in the 4BS pastes during standing and whether the processing properties of 4BS mass deviate from those of 3BS mass. Therefore, the changes in the morphology and phase composition of the 4BS masses due to standing were studied and compared with the corresponding properties of a 3BS-based automotive-battery factory paste.

The changes in the XRD phase composition of the 3BS-based factory paste (700 kg batch) as a function of stand time are given in Fig. 6. This reveals that the phase composition remained practically constant for several hours. SEM micrographs of the paste taken after 40, 110 and 280 min of standing (Fig. 7) showed, however, that the crystallization and growth of 3BS crystals continued during the whole stand time of over 5 h.

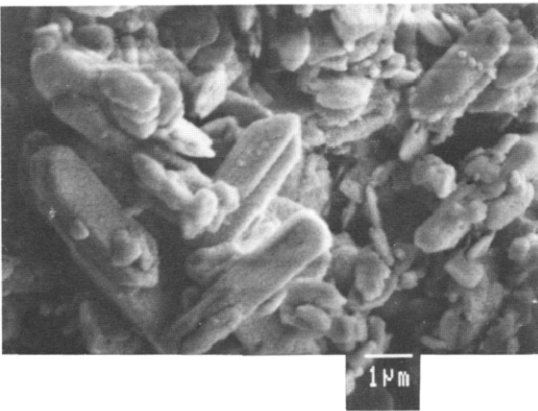
The XRD phase composition of the mixed 4BS paste also remained virtually constant after standing for nearly 5 h (Fig. 8). The slight changes in the relative intensities of the 4BS diffraction lines evidently indicate variations in crystal orientation. By contrast, the morphology of the 4BS paste particles changed remarkably during the first hour of standing. This can be clearly seen in SEM micrographs taken from 4BS pastes at standing times of 0, 60 and 285 min (Fig. 9). In fact, the rather fast growth of 4BS crystals terminated after the first hour of standing.



(a)



(b)



(c)

Fig. 7. Scanning electron micrographs of a mixed 3BS-containing automotive battery factory paste. Stand time: (a) 40 min; (b) 110 min; (c) 280 min.

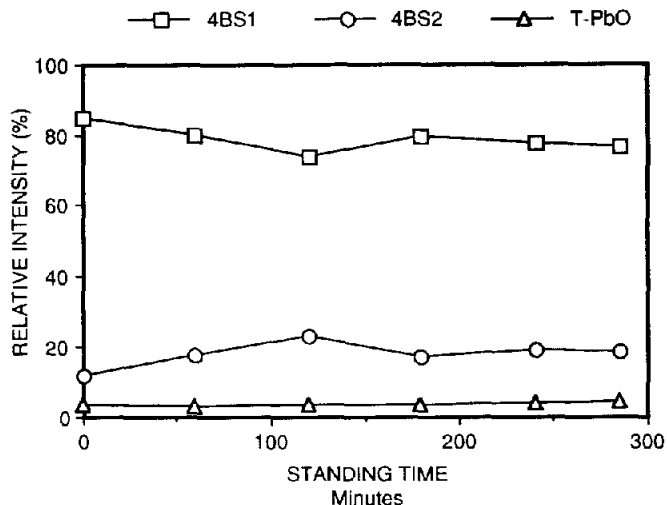


Fig. 8. Changes in the XRD phase composition of a 60 min mixed 4BS paste as a function of stand time. Mixing time 60 min. 4BS1 and 4BS2 correspond to diffraction lines at 27.58 and 30.99° (2θ), respectively.

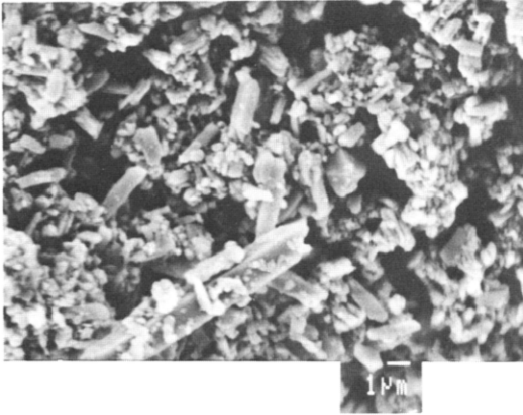
Influence of the raw materials and production method

While developing a proper set of analytical methods for the characterization of 4BS masses, the influence of the raw materials and production method on the morphology, microstructure, chemical and phase composition of 4BS masses were investigated. Three cured 4BS masses produced by paste and solution methods from leady oxide and α -PbO were characterized to find the major differences between them.

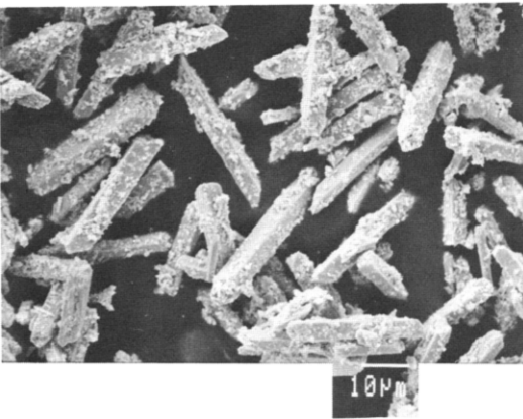
The XRD phase composition of the three cured 4BS pastes, calculated on the basis of the relative XRD peak intensities, can be seen in Table 3. The relative peak intensities of 4BS, 3BS and α -PbO are calculated from peaks with d values of 2.86, 3.26 and 2.81, respectively. The results of the chemical analysis of the 4BS masses can be seen in Table 4.

In spite of rather small differences in the XRD phase composition and the chemical analyses, there were very large variations in the morphology of the three 4BS masses. The differences in the morphology can be seen in the SEM micrographs of the masses (Fig. 10). The paste-method crystals prepared from leady oxide were composed of crystal agglomerate (Fig. 10(a)); they were smaller and more porous and irregular than the solution-method crystals (Fig. 10(a)). Conversely, the solution-method crystals prepared both from leady oxide and α -PbO were large, single, crystal-like particles with more regular shapes (Figs. 10(b), (c)). Additionally, 4BS crystals produced from α -PbO (Fig. 10(c)) had smoother edges and evidently higher crystallinity than those prepared from leady oxide (Fig. 10(b)). Among the 4BS crystals produced by the solution method from α -PbO, some spherical particles, presumably due to the incomplete development of 4BS, were seen (Fig. 10(d)).

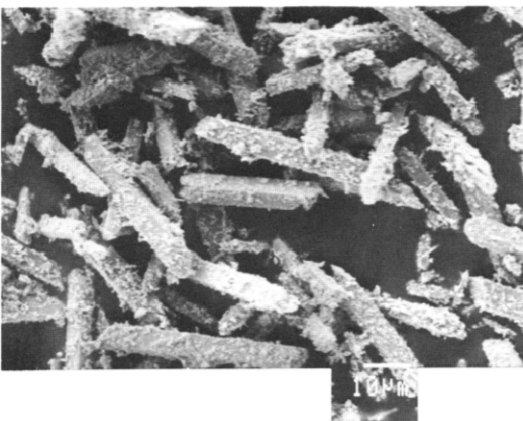
The selection of the production method has an influence not only on the morphology of the resulting 4BS masses, but also on the microstructure of the individual 4BS paste particles. This can be seen in TEM micrographs of three 4BS masses (Fig. 11).



(a)



(b)



(c)

Fig. 9. Scanning electron micrographs of a 60 min mixed 4BS paste after standing for: (a) 0 min; (b) 60 min; (c) 285 min.

TABLE 3

XRD phase composition of cured 4BS masses prepared by different methods and with different raw materials. The values given are relative diffraction intensities of the corresponding phases

Preparation method	Raw material	4BS	3BS	α -PbO
4BS paste	Lead oxide	94.6	0.9	4.5
4BS solution	Lead oxide	91.3	5.7	2.0
4BS solution	α -PbO	94.3	1.6	4.1

TABLE 4

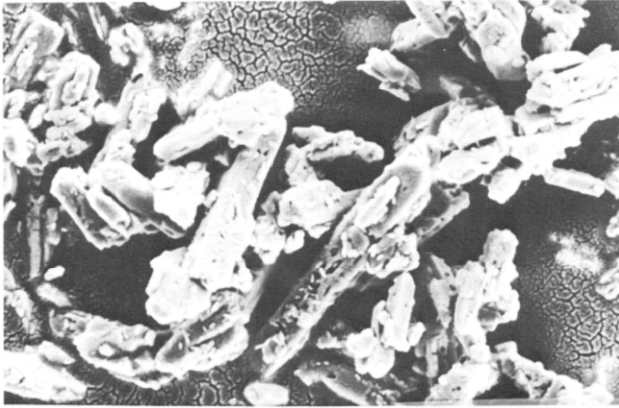
Results from wet-chemical analyses of the cured 4BS masses. The values are given as wt.% and the added H_2SO_4 content as wt.% with respect to the raw material oxides

Preparation method	Raw material	H_2SO_4	Free lead	SO_4^{2-}
4BS paste	Lead oxide	7.2	0.29	7.0
4BS solution	Lead oxide	7.2	0.36	6.8
4BS solution	α -PbO	7.3		6.9

The solution-method particles (Figs. 11(b), (c)) were composed of clearly defined needle-shaped crystallites, whereas the paste-method particles consisted of material with less well-defined shapes and evidently lower crystallinity (Fig. 11(a)).

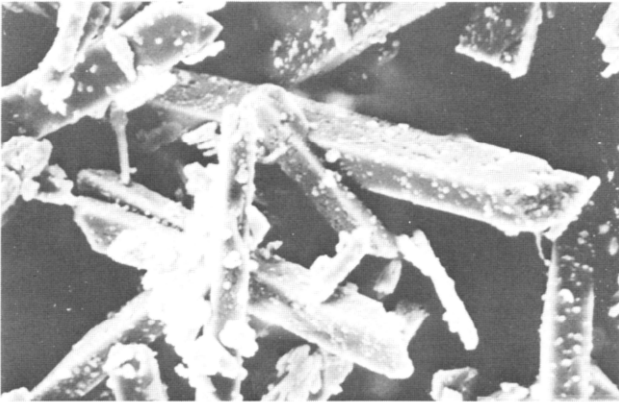
Conclusions

The preparation method was found to be one dominating factor affecting the morphology and structure of 4BS active masses. The solution-method paste particles were large single crystal like rods, whereas the paste method products were crystal agglomerates of smaller size and more regular shape. Additionally, the selection of raw material oxide gave another effect on the morphology. When α -PbO was used as raw material in the solution method, the 4BS crystals produced were of higher regularity and had smoother edges than lead oxide. In solution-method production, however, both α -PbO and lead oxide resulted in a similar 4BS microstructure that was composed of large, needle-shaped crystallites. Conversely, the paste method gave a 4BS microstructure consisting of small crystallites and material of evidently low crystallinity. The microstructure of individual 4BS-paste particles will have an influence on the physical, and presumably the electrochemical, properties of the corresponding active mass. Therefore, TEM is a powerful tool in the characterization of 4BS pastes. Despite the remarkable differences in the macro- and microstructure of the 4BS masses, the XRD phase composition of the masses was rather similar.



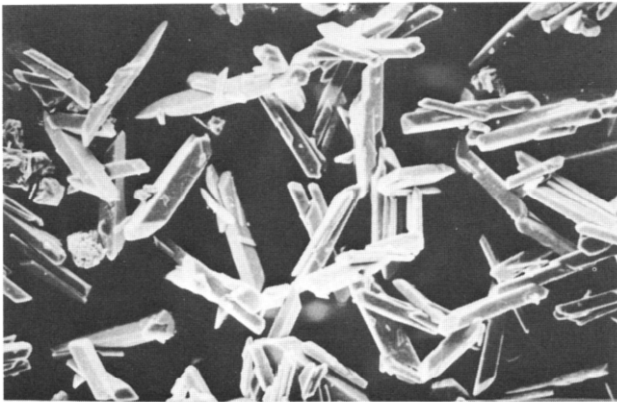
(a)

1 μm



(b)

1 μm

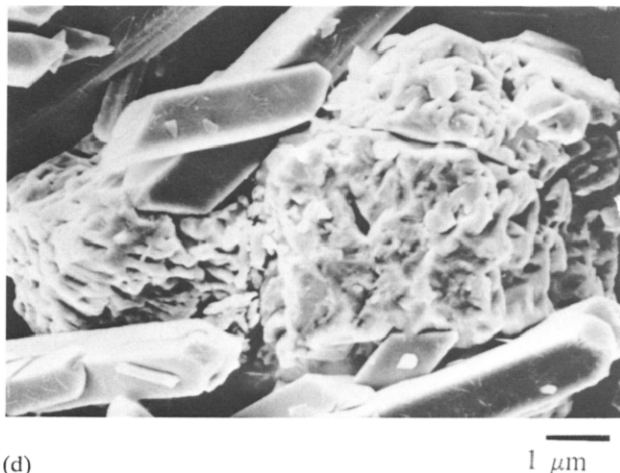


(c)

1 μm

Fig. 10.

(continued)



(d)

1 μm

Fig. 10. Scanning electron micrographs of cured 4BS masses prepared by: (a) paste method from leady oxide; (b) solution method from leady oxide; (c) and (d) solution method from α -PbO.

One essential difference in the behaviour of 3BS and 4BS pastes is a faster crystal growth rate of 4BS. This should be taken into account when planning an industrial production line for 4BS.

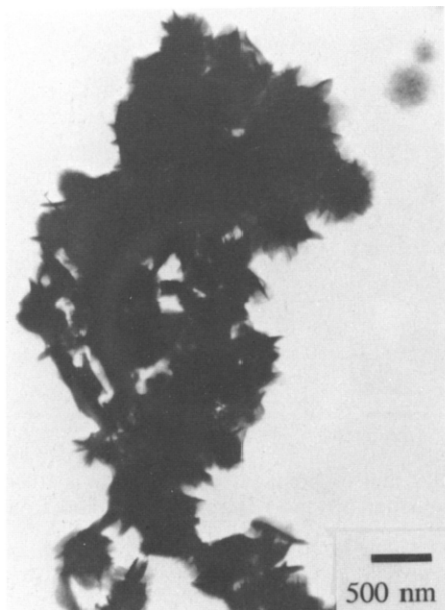
The introduction of the new 4BS technology to the automotive-battery manufacturing process depends largely on the result of considerations concerning the economical aspects and the requirements for the industrial processes. The implementation of the new technology requires a small increase in running costs due to the following changes in the production process.

(i) The present processes are using leady oxide as raw material and in the new 4BS process some of this oxide has to be supplemented with red lead. This creates a need for new storage facilities if the red lead is bought or, if the red lead is produced on site, an additional production unit. In any case, the red lead is a more expensive raw material than leady oxide.

(ii) The paste mixing is carried out at a higher temperature and it takes a significantly longer time than in traditional automotive-battery production.

(iii) Although, at high temperature, the curing of 4BS-based plates can be carried out at a rate that is three-times faster than in normal production, it is unclear whether the heat evolved from the oxidation of the residual lead is sufficient to heat the curing chamber to the desired temperature. Additional heating of the chamber would also increase the running costs.

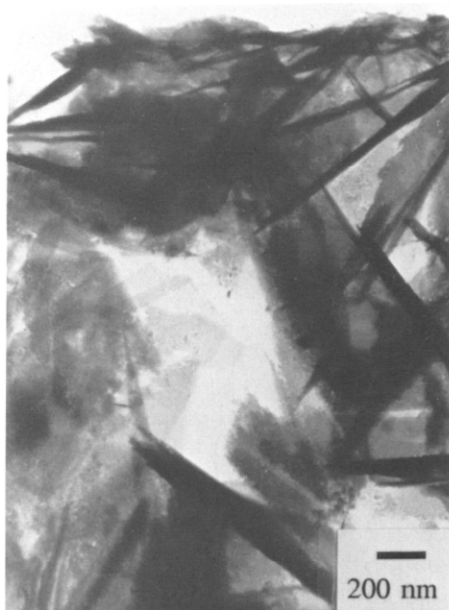
In spite of the somewhat higher production costs compared with traditional technology, the new 4BS method may improve the performance in certain automotive-battery applications, e.g., heavy-duty batteries, so much that the introduction of the new technology is advantageous. Therefore, a manufacturer should select carefully the automotive-battery applications in which to use the new technology. The near future will show whether this promising technology — first reported by Burbank in 1966 — will be adopted by the battery industry.



(a)



(b)



(c)

Fig. 11. Transmission electron micrographs of cured 4BS pastes prepared by: (a) paste method from leady oxide; (b) solution method from leady oxide; (c) solution method from α -PbO.

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