

LEAD/ACID BATTERY POSITIVE PLATES MANUFACTURED FROM $4\text{PbO}\cdot\text{PbSO}_4$ PASTES PREPARED FROM LEADY OXIDE AND RED LEAD

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Introduction

The service life of lead/acid batteries is often limited by disintegration of the positive active mass (PAM) structure. It is known that the latter depends on the phase composition, crystal morphology and density of the initial paste [1 - 6]. Experimental data show that active masses prepared from $4\text{PbO}\cdot\text{PbSO}_4$ pastes have longer cycle lives than those obtained by 'classical' technology based on $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ [1 - 6]. An example of this behaviour is given in Fig. 1 for 12 V/55 A h batteries [5]. The results show that although batteries using plates obtained from $4\text{PbO}\cdot\text{PbSO}_4$ paste exhibit 30% longer cycle life, their initial capacity is about 20% lower than the rated value. Indeed, 20 - 50 cycles are required for the battery to reach its rated capacity. The poor initial capacity is due to incomplete oxidation of $4\text{PbO}\cdot\text{PbSO}_4$ to PbO_2 during plate formation. The oxidation reaction is so slow that it cannot be completed within a practical time. According to Bell Telephone Company [2], the formation process of $4\text{PbO}\cdot\text{PbSO}_4$ pastes lasts for more than 200 h. These shortcomings have limited the application of $4\text{PbO}\cdot\text{PbSO}_4$ pastes in battery manufacture.

The following three methods have been suggested for $4\text{PbO}\cdot\text{PbSO}_4$ paste preparation in the production of positive battery plates.

(i) From a slurry of lead oxide in water to which H_2SO_4 is added slowly in stoichiometric quantities with regard to the oxide; for the most part, $\beta\text{-PbO}$ (also known as orthorhombic-PbO) is used and the temperature of stirring is 80°C [1, 2].

(ii) By paste preparation from leady oxide and H_2SO_4 solution, mixed at 80°C for more than 30 min [3, 7 - 9].

(iii) By curing $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ pastes at temperatures above 70°C [10]. The conversion of $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ to $4\text{PbO}\cdot\text{PbSO}_4$ takes tens of hours. Plates prepared by this method are difficult to form and exhibit low initial capacity. In order to avoid these latter, unfavourable properties, an upper temperature limit of 65°C has been adopted for the curing process. Under

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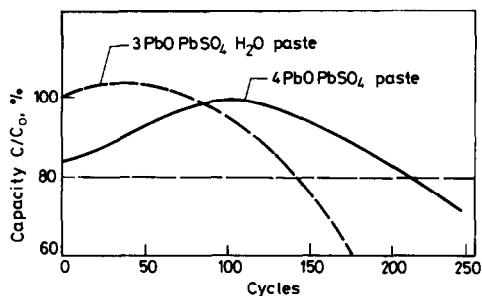


Fig. 1. Capacity performance of batteries manufactured with either $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ or $4\text{PbO}\cdot\text{PbSO}_4$ paste.

such conditions, however, the curing stage is slow and requires about 36 - 48 h for completion.

The starting materials in all the above methods for the preparation of $4\text{PbO}\cdot\text{PbSO}_4$ positive plates are: lead oxide ($\alpha\text{-PbO}$ (also known as tet-PbO) and $\beta\text{-PbO}_2$, or a mixture of the two) or leady oxide containing 60 - 80% $\alpha\text{-PbO}$ and 20 - 40% fine (unreacted) lead particles (so-called 'free lead').

Experience gained in battery manufacture has shown that plates prepared from $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ pastes obtained from a mixture of leady oxide and Pb_3O_4 are formed more quickly and have higher initial capacity. For this reason, an attempt has been made to manufacture $4\text{PbO}\cdot\text{PbSO}_4$ pastes also from a mixture of leady oxide and Pb_3O_4 [11 - 13]. The development of a suitable method posed two questions. First, what is the influence of Pb_3O_4 on the formation of $4\text{PbO}\cdot\text{PbSO}_4$ crystals? Second, can Pb_3O_4 increase the initial capacity of $4\text{PbO}\cdot\text{PbSO}_4$ positive plates without affecting their cycle life? To answer these questions, the reactions taking place during $4\text{PbO}\cdot\text{PbSO}_4$ paste preparation had to be determined.

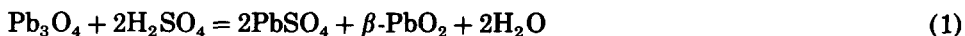
The formation of $4\text{PbO}\cdot\text{PbSO}_4$ during paste preparation has one important advantage — the need for an upper temperature limit for curing is removed. The temperature of curing may therefore be raised above 65°C , thereby accelerating the processes involved and shortening the curing period.

The aim of the present work is to determine, in general, the phenomena occurring during plate preparation from $4\text{PbO}\cdot\text{PbSO}_4$ pastes obtained from mixtures of leady oxide and Pb_3O_4 .

Experimental

The following processes can take place when leady oxide is mixed with Pb_3O_4 , H_2SO_4 solution and water:

(i) Pb_3O_4 reacts with H_2SO_4 according to:



(ii) The free lead (~ 22 wt.%) in leady oxide reacts with Pb_3O_4 via the following redox process:



Besides these two processes, the formation of $4\text{PbO}\cdot\text{PbSO}_4$ can also take place. Which of the reactions involving Pb_3O_4 actually occurs, and to what extent, depends on the procedure used to mix the three initial components.

In addition to the preparation of 'classical' $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ paste, three different methods were used to make $4\text{PbO}\cdot\text{PbSO}_4$ paste. In each method, 5 kg of paste were prepared using 1.25 kg Pb_3O_4 and 3.75 kg leady oxide. The amount of H_2SO_4 (1.4 sp. gr.) was 6% *versus* the total quantity of PbO contained in Pb_3O_4 and the leady oxide. A certain amount of water was also added to obtain a paste density of 4.2 g cm^{-3} . In detail, the procedures were as follows:

Method (a). A classical paste with $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ as the main component was first prepared as a benchmark. The procedure involved mixing leady oxide with water and H_2SO_4 (4.5% *versus* PbO in the leady oxide) and stirring the paste for 15 min at 40°C .

Method (b). $4\text{PbO}\cdot\text{PbSO}_4$ was prepared from leady oxide and H_2SO_4 according to the method described in ref. 7. Then Pb_3O_4 and H_2O were added to the paste containing $4\text{PbO}\cdot\text{PbSO}_4$, PbO and Pb in the correct amounts to give the required paste density. The paste was mixed for 15 min. By this method, Pb_3O_4 does not react with H_2SO_4 , and, hence, does not take part in the growth of $4\text{PbO}\cdot\text{PbSO}_4$ crystals. Rather, Pb_3O_4 initially reacts with Pb (via reaction (2)).

Method (c). Leady oxide and Pb_3O_4 were mixed and then H_2SO_4 solution was added. The paste was stirred at 80°C for 1 h. By this method, reactions (1) and (2) of Pb_3O_4 with, respectively, H_2SO_4 and Pb proceed simultaneously.

Method (d). Pb_3O_4 was first decomposed with H_2SO_4 solution to PbSO_4 and PbO_2 . To the suspension thus obtained, leady oxide was added. The temperature was raised to 80°C and the paste was stirred at that temperature for 1 h. At this stage, the reaction between PbO_2 and Pb commenced. By this method the products of Pb_3O_4 decomposition participate in the formation of $4\text{PbO}\cdot\text{PbSO}_4$ crystals.

All the pastes were manually spread over 2 mm thick SLI grids. The resulting plates had a rated capacity of 11 A h, which was equivalent to 43% utilization of the active material.

Plate curing

Two regimes of plate curing were applied. One followed the classical technology — at 40°C and controlled relative humidity for 72 h — while the other was conducted at $93\text{--}95^\circ\text{C}$ in the presence of water vapour. The duration of curing in the latter regime was 8 or 21 h.

In order to study the processes taking place during paste preparation and plate curing, samples were removed periodically and subjected to:

- (i) X-ray diffraction phase analysis;
- (ii) SEM investigations of crystal morphology and active-mass structure;
- (iii) mercury porosimetric determination of pore volume and surface distribution by radius.

Formation was carried out under classical conditions, *i.e.*, H_2SO_4 solution of 1.05 sp. gr., current density 5 mA cm^{-2} , temperature 35°C , and duration 20 h. The formed plates were used for the manufacture of 12 V/55 A h batteries which were cycled under the regime: 3 h discharge (up to 80% DOD) and 9 h charge (with 15% overcharge). Cycle-life testing of batteries was continued until the capacity decreased to 80% of the rated value (calculated at the C/5 discharge rate). Capacity measurements were performed at the C/5 rate.

Results and discussion

Method (a): Classical $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ paste cured at 40°C and at 93°C

The processes taking place during paste preparation, plate curing, and formation have been discussed in refs. 7 and 14. Figure 2 presents: (a) an

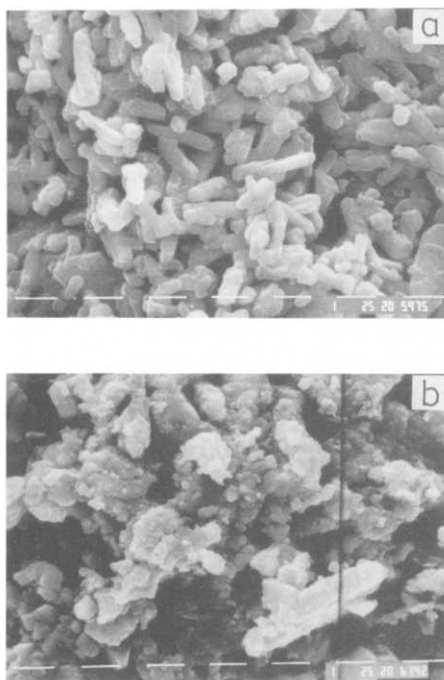


Fig. 2. Electron micrographs of: (a) crystals of cured paste, (b) agglomerates of formed active mass. Paste contains $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ and was cured at 40°C for 72 h. White line = $1 \mu\text{m}$.

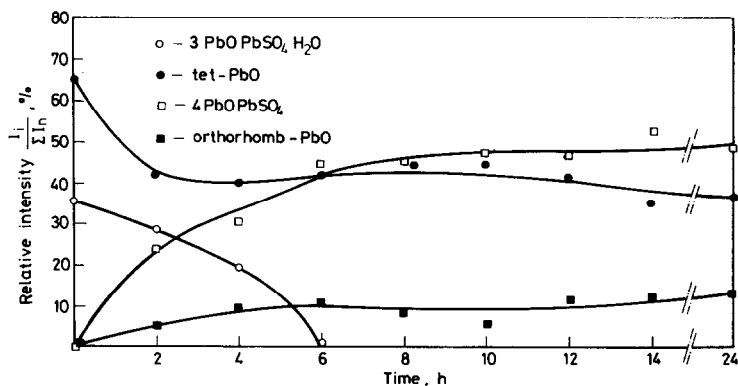


Fig. 3. Changes in phase composition of a paste during curing at 93 °C with water vapour. (Taken from ref. 12.)

electron micrograph of the morphology of the crystals and the structure of the paste cured at 40 °C for 72 h, and (b) a micrograph of the PbO_2 active mass after formation. The cured paste has a homogeneous structure comprised of approximately equal-sized crystals. The PAM consists of rounded PbO_2 particles interconnected into agglomerates.

Figure 3 shows the change in phase composition of the paste during curing at 93–95 °C in the presence of water vapour, as determined by the relative intensity of the characteristic X-ray diffraction lines of the phases. It can be seen that conversion of $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ to $4\text{PbO}\cdot\text{PbSO}_4$ starts soon after the onset of curing; the process is completed within 6 h. The cured paste also contains unreacted α -PbO and produced β -PbO.

Micrographs of cured and formed paste crystals are shown in Fig. 4(a) and (b), respectively. The cured paste consists of large, ill-defined crystals of $4\text{PbO}\cdot\text{PbSO}_4$ together with smaller crystals of PbO and Pb (Fig. 4(a)). The material is very heterogeneous. The formed active mass has a very similar structure (Fig. 4(b)). A $4\text{PbO}\cdot\text{PbSO}_4$ crystal (broken) after formation, is shown in Fig. 4(c). It can be seen that the surface layers of this crystal (right-hand side of the micrograph) have been oxidized, and rounded PbO_2 particles have been formed. By contrast, the inner parts of the crystal (smooth surfaces) have remained unaffected by formation. It has been established by chemical analysis that the amount of PbO_2 in plates cured at 40 and 93 °C is 88 and 43% PbO_2 , respectively. The capacity of the latter plates is below 50% C/5.

Method (b): Pastes prepared from a mixture of $4\text{PbO}\cdot\text{PbSO}_4$ and Pb_3O_4

The processes occurring during preparation of $4\text{PbO}\cdot\text{PbSO}_4$ pastes have been described in ref. 7. When Pb_3O_4 is added to a $4\text{PbO}\cdot\text{PbSO}_4$ paste that has been made from leady oxide containing Pb and PbO, reaction (2) proceeds between Pb and Pb_3O_4 . The lead content in the paste during the stages of its preparation was determined by wet chemical analysis. The experimental data



Fig. 4. Electron micrographs of: (a) crystals of the cured paste (refer Fig. 3), white line = 10 μm ; (b) agglomerates of active mass, white line = 100 μm ; (c) broken $4\text{PbO}\cdot\text{PbSO}_4$ crystal, white line = 10 μm . (Taken from ref. 12.)

show that the content of Pb in the paste is reduced from 18 to 8 wt.% as a result of its interaction with Pb_3O_4 . X-ray diffraction patterns revealed that Pb_3O_4 does not react completely. Thus, small amounts (several percent.) of Pb and Pb_3O_4 remain in the cured paste. This is probably due to the larger Pb and Pb_3O_4 particles becoming covered by an oxide layer that hinders further reaction.

Electron micrographs of the cured paste and the formed active mass are given in Fig. 5(a) and (b), respectively. The large prismatic crystals in Fig. 5(a) are $4\text{PbO}\cdot\text{PbSO}_4$; the small ones are PbO. The agglomerate consisting of numerous small particles on the left-hand side of the micrograph is unreacted Pb_3O_4 . The PbO_2 agglomerates produced during paste formation repeat the

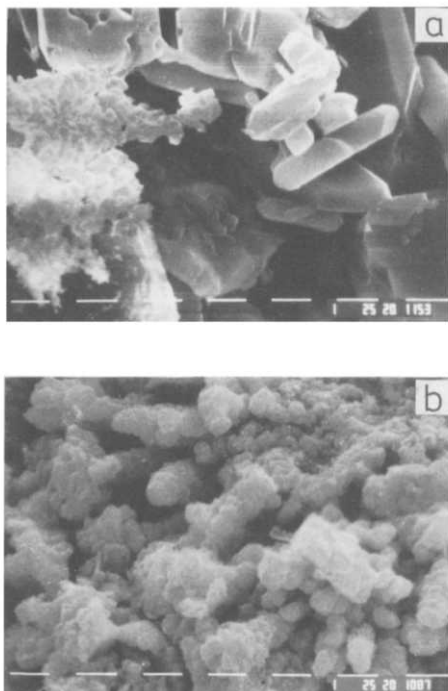


Fig. 5. Electron micrographs of: (a) crystals of cured paste, white line = 10 μm ; (b) agglomerates of active mass, white line = 1 μm .

shape of the initial paste crystals (Fig. 5(b)). The degree of formation of the paste is 85% PbO_2 . This method of paste preparation, however, involves too many procedures and is therefore commercially impracticable.

Method (c): $4\text{PbO}\cdot\text{PbSO}_4$ paste prepared from a mixture of leady oxide and Pb_3O_4

First, water was added to a mixture of leady oxide and Pb_3O_4 , then H_2SO_4 solution was introduced. Figure 6 illustrates the changes in phase composition during preparation of the paste at 80 °C. Initially, $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ is formed. This is a very rapid process and is completed within a few minutes. In the early stages of mixing, $\beta\text{-PbO}$ also appears. After 5 - 15 min, the process of $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ conversion to $4\text{PbO}\cdot\text{PbSO}_4$ commences; this is completed by about the 50th minute.

Pb_3O_4 reacts with Pb during the first 5 min, whereby the content of Pb in the paste is reduced from 18 to 7 wt.% (determined by wet chemical analysis). Further oxidation proceeds slowly, and at the end of paste preparation only 5 wt.% of Pb remains in the paste. A small amount of unreacted Pb_3O_4 is also present in the final paste.

The paste thus prepared was used for the manufacture of battery plates that were subjected to curing at: (i) 93 - 95 °C for 21 h in the presence of water vapour; (ii) under the classical conditions of curing at 40 °C for 72 h.

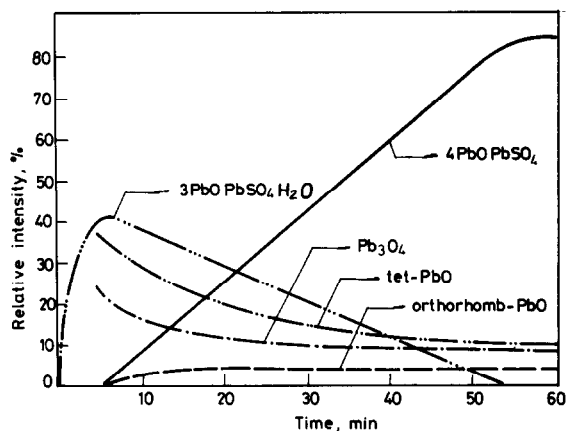


Fig. 6. Changes in phase composition of a paste during preparation by method (c).

Figure 7 presents an electron micrograph of the paste cured at 40 °C for 72 h. The paste consists of large, prismatic crystals of $4\text{PbO}\cdot\text{PbSO}_4$ with well-pronounced sides, edges and apices, together with small crystals, probably of $\alpha\text{-PbO}$. Crystals of a similar appearance are also found in the paste cured at high temperature and humidity. The X-ray pattern for the phase composition of the paste during high-temperature curing also remained unchanged. SEM observations did show, however, that during high-temperature curing the individual crystals were 'welded' together in the regions of contact. Thus, the structure of the cured paste is mechanically strengthened by high-temperature curing. The latter process needs between 8 and 21 h for completion at 95 °C in the presence of water vapour.

An electron micrograph of the formed active mass is given in Fig. 8. It can be seen that the active mass preserves the macrostructure of the initial

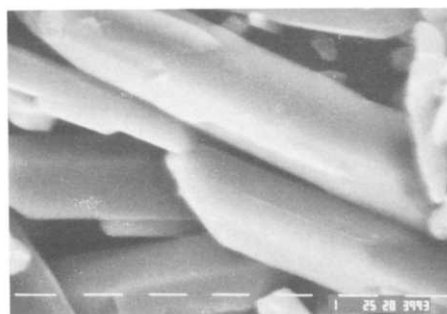


Fig. 7. Electron micrographs of crystals in cured paste (refer Fig. 6). White line = 1 μm .

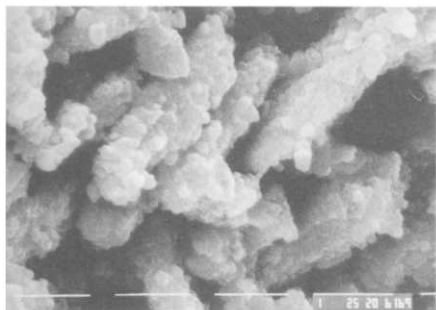


Fig. 8. Electron micrograph of agglomerates of active mass (refer Fig. 7). White line = 1 μm .

paste. In practice, $4\text{PbO}\cdot\text{PbSO}_4$ crystals are transformed into PbO_2 agglomerates consisting of rounded PbO_2 particles. The degree of formation was found to be 89% PbO_2 for both types of curing conditions.

Method (d): $4\text{PbO}\cdot\text{PbSO}_4$ paste prepared with Pb_3O_4 pre-decomposed with H_2SO_4 solution

The influence of H_2SO_4 concentration on the extent of Pb_3O_4 decomposition was studied. The reaction was examined by mixing 10 g of Pb_3O_4 with 100 ml of H_2SO_4 solution of various concentrations. Figure 9 shows the dependences of the amounts of PbSO_4 , PbO_2 and unreacted Pb_3O_4 on the concentration of H_2SO_4 . The concentrations of both PbSO_4 and PbO_2 were determined by wet chemical analysis, and the values were used to calculate the unreacted Pb_3O_4 concentration on the basis of reaction (1). Each phase analysis was performed after 40 min of mixing.

It was found that Pb_3O_4 reacts rapidly with H_2SO_4 solution. Although there was an excess of H_2SO_4 with regard to the stoichiometric quality, a certain amount of Pb_3O_4 remained intact. It can be seen that Pb_3O_4 decomposition occurs to a higher extent at lower H_2SO_4 concentrations. Hence, a dilute H_2SO_4 solution was used for paste preparation. The lowest possible concentration was obtained by diluting a calculated amount of 1.4 sp. gr. H_2SO_4 with water so that a paste density of 4.2 g cm^{-3} was achieved. To the suspension thus obtained (dark brown in colour) the required amount of leady oxide was introduced. The paste was then stirred for 1 h at 80°C . The changes in phase composition are shown in Fig. 10.

During formation of this type of $4\text{PbO}\cdot\text{PbSO}_4$ paste, the same processes occur as when $4\text{PbO}\cdot\text{PbSO}_4$ paste is prepared from a mixture of leady oxide and Pb_3O_4 . In the former case, however, the rates of these processes are considerably faster. The paste is light brown in colour although $\beta\text{-PbO}_2$ diffraction lines are not observed. Thus, the PbO_2 is probably in an amorphous state.

Figure 11(a) and (b) presents electron micrographs of $4\text{PbO}\cdot\text{PbSO}_4$ crystals in the paste and in the structure of the active mass, respectively. The

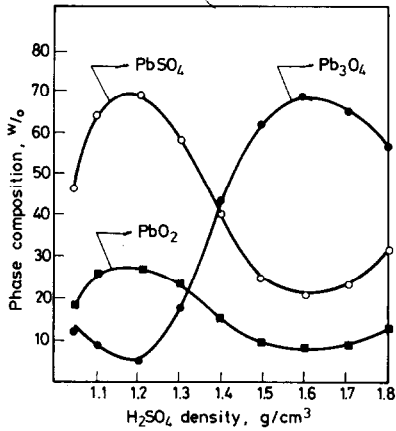


Fig. 9. Reactivity of Pb_3O_4 with H_2SO_4 — composition 40 min after mixing.

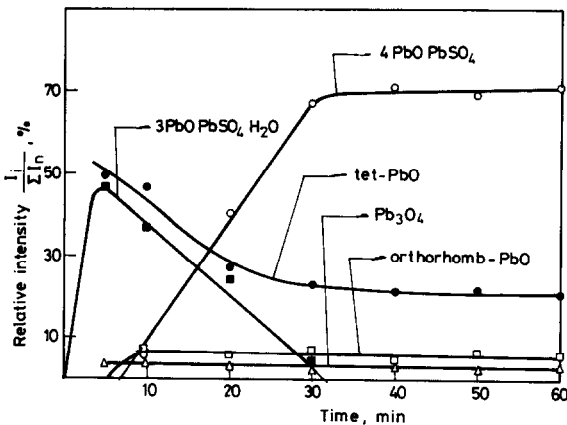


Fig. 10. Changes in phase composition during stirring of a paste prepared by mixing Pb_3O_4 suspension (partially decomposed with H_2SO_4) with leady oxide (method (d)).

$4\text{PbO}\cdot\text{PbSO}_4$ crystals are smaller in size than those obtained from a mixture of leady oxide and Pb_3O_4 (method (c), Fig. 8). Thus, it appears that the PbSO_4 crystals formed by the decomposition of Pb_3O_4 facilitate the nucleation of $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ and, in turn, the nucleation of $4\text{PbO}\cdot\text{PbSO}_4$ crystals.

No changes in phase composition were registered, neither during paste curing at 40°C for 72 h nor at 93°C for 21 h. A process of recrystallization was observed, however, for both $4\text{PbO}\cdot\text{PbSO}_4$ and $\alpha\text{-PbO}$. After curing, the plates were subjected to formation. The degree of active mass formation was 86% PbO_2 .

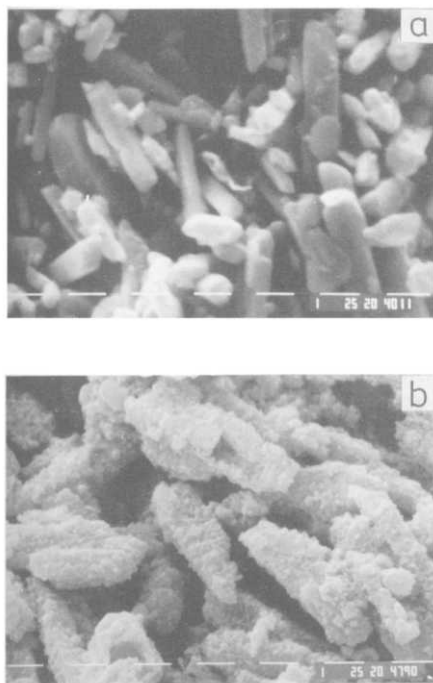


Fig. 11. Electron micrographs of: (a) crystals of cured paste; (b) agglomerates of active mass (refer Fig. 10). White line = 1 μm .

Plots of the plate potential during formation of the different pastes under investigation are superimposed in Fig. 12. It can be seen that Pb_3O_4 -containing pastes undergo a longer period of low polarization of the electrochemical reaction of PbO_2 formation. This suggests a possible participation of Pb_3O_4 , or its products. On the other hand, plates prepared with classical paste, but cured at 93°C , exhibit the fastest polarization during formation, and a greater amount of $4\text{PbO}\cdot\text{PbSO}_4$ remains unformed.

Differences in the crystal morphology and the active mass structure of the pastes prepared by the above techniques can be expected to bring about corresponding differences in active-mass porosity. Figure 13 presents curves of the pore surface (S) and volume (V) distribution by pore radius for the various active masses. The data show that active masses obtained from $4\text{PbO}\cdot\text{PbSO}_4$ have larger average macropore radius (determined by the inflection point of the porogramme) than the active masses derived from classical $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ paste. Similar results are to be found in the literature [7, 9]. The $4\text{PbO}\cdot\text{PbSO}_4$ crystals are larger in size, hence the pore surface is smaller in the active masses obtained from $4\text{PbO}\cdot\text{PbSO}_4$ pastes compared with those prepared by classical $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ technology.

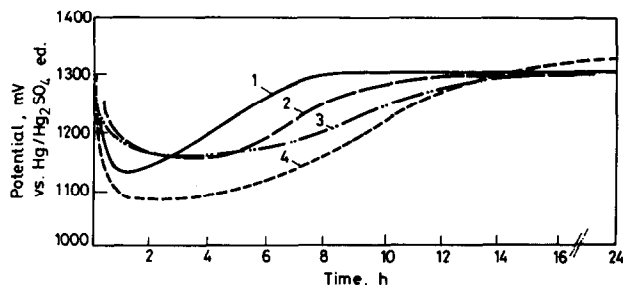


Fig. 12. Potential during plate formation. Active mass formed from: 1, method (a): $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ paste cured at 93°C ; 2, method (a): $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ paste cured at 40°C ; 3, method (d): $4\text{PbO}\cdot\text{PbSO}_4$ paste ($\text{PbSO}_4 + \text{PbO}_2$) + PbO cured at 93°C ; 4, method (c): $4\text{PbO}\cdot\text{PbSO}_4$ paste ($\text{PbO} + \text{Pb}_3\text{O}_4$) cured at 93°C .

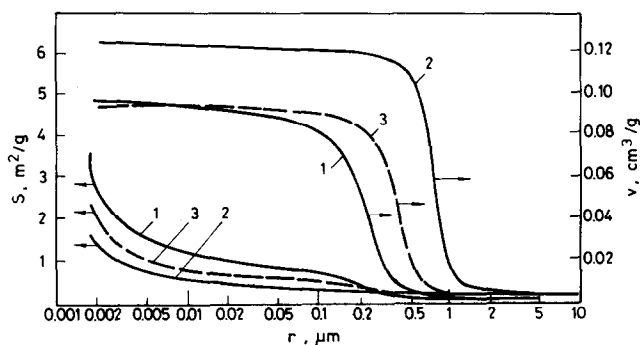


Fig. 13. Pore volume and surface distribution by radius for active masses prepared from: 1, $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ cured at 40°C for 72 h (method (a)); 2, $4\text{PbO}\cdot\text{PbSO}_4$ paste (prepared from a mixture of PbO and Pb_3O_4) cured at 93°C for 21 h (method (c)); 3, $4\text{PbO}\cdot\text{PbSO}_4$ (prepared from Pb_3O_4 pre-decomposed with H_2SO_4) cured at 93°C for 21 h (method (d)).

Initial capacity and cycle life of batteries

In order to make shedding of active mass the capacity-limiting factor, positive plates were separated from the separator by a 2 mm plastic grid. 12 V/55 A h batteries were manufactured and subjected to cycling tests. The results are presented in Fig. 14.

Batteries prepared with $4\text{PbO}\cdot\text{PbSO}_4$ pastes exhibited a capacity above the rated value within the first three cycles. Thus, by comparison of the data in Figs. 1 and 14, it can be concluded that Pb_3O_4 has a strong influence on initial plate capacity. At the same time, the cycle life of batteries manufactured with $4\text{PbO}\cdot\text{PbSO}_4$ pastes was about 30% longer than that of batteries prepared via the classical $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ technology. It follows, therefore, that the introduction of Pb_3O_4 into the paste removes the main disadvantage of $4\text{PbO}\cdot\text{PbSO}_4$ pastes, namely, slow formation and low initial capacity, without adversely affecting battery cycle life. This method of paste preparation opens up new possibilities for using $4\text{PbO}\cdot\text{PbSO}_4$ pastes in the manufacture of lead/acid batteries.

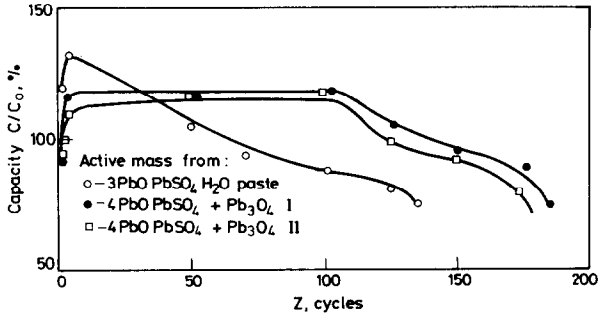


Fig. 14. Capacity performance of three types of paste. End-of-life = 80% $C/5$. Paste I = $4\text{PbO}\cdot\text{PbSO}_4$ prepared from a mixture of leady oxide and Pb_3O_4 (method (c)). Paste II = $4\text{PbO}\cdot\text{PbSO}_4$ prepared from Pb_3O_4 pre-decomposed with H_2SO_4 (method (d)). (Taken from ref. 12.)

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