

The effect of the expander upon the two types of negative active mass structure in lead–acid batteries

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Received 19 October 1983; revised 24 January 1984

The active mass of the negative plate in the lead–acid battery is organized in a skeleton (primary) and energetic (secondary) structure. With the aid of electrochemical measurements and SEM observations the effect of the expander upon these structures is investigated both during their formation and during the cycling of the cell under service conditions.

It is established, that in the absence of an expander, an active mass with dendritic secondary structure is formed, which ensures a relatively low capacity of the plates. In active masses containing an expander no dendrites are formed. The expander enhances the formation of a secondary structure containing separate lead crystals deposited on the surface of the skeleton. The morphology and size of these crystals depend on the nature of the expander. Plates containing expander display a higher capacity and a longer life. The effect of the expander upon the primary structure is clearly revealed during the service life of the battery under deep charge–discharge cycling conditions. Plates with no expander show a contraction of the skeleton and the active mass becomes more compact. A reverse effect is observed in the presence of a highly efficient expander, the skeleton structure becomes more loose and the plates become thicker. This is evidence that the skeleton partially participates in the cycling process and that its branches are oxidized, being formed again later at a different site, thus changing the density of the skeleton structure. This process is affected by the expander.

It is also established that the skeleton structure of the active mass is built either from compact, shapeless, interconnected crystals, or linked agglomerates of scale-form lead crystals.

1. Introduction

In a previous paper [1] we had established that the active mass of the negative plates is composed of:

(a) a primary (skeleton) structure built during the first formation stage when the lead oxide and the basic lead sulphates are reduced to lead [1, 2]. It acts as a mechanical skeleton and current conductor from the grid bars to every site in the active mass and

(b) a secondary lead structure composed of separate lead crystals which are superimposed on the skeleton surface. The secondary structure appears during the second formation stage, when PbSO_4 crystals are reduced to lead [1, 2].

During the discharge, the secondary lead crystals are oxidized, and reduced again at charging.

Basically, they are the plate capacity determining factor, therefore the secondary crystals were denoted as the ‘energetic’ structure.

The negative active mass comprises the expander. The latter is a formulation containing 0.2–0.3% BaSO_4 , 0.2–0.3% carbon black, and 0.3–1.5% salts of the lignosulphonic or humic acids, or natural or synthetic tanning substances. The organic part of the expander formulation is the most active component. It has been established experimentally, that the expander increases the capacity of the negative plate, the effect becoming more pronounced at low temperatures and heavy drains. Another beneficial effect of the expander is that it helps to retain the capacity of the plate during continuous cycling, thus increasing the life of the battery. According to the proposed model for the structure of the active mass [1], the capacity of the

plate is determined mainly by the energetic structure, hence the expander should affect this structure.

Simon *et al.* [3–5] have shown, that the organic component of the expander enhances the formation of small spherical or needle-shaped lead crystals. Burbank *et al.* [6] have explained the variety in the shape of the crystals in formed negative plates by the different technology used by the respective manufacturers.

The present work is aimed at the determination of the effect exerted by the expander upon the skeleton and energetic active mass structures, and to establish the alternations which these structures undergo during cycling of the battery. This was attained by parallel forming and cycling of cells with negative plates containing an expander, and plates with no expander as a blank test reference.

2. Experimental procedure

2.1. Preparation of the plates

The studies were carried out with conventional 11 Ah SLI battery negative plates, the grids were cast from a Pb–6% Sb alloy and the paste was prepared using a 65% oxidized lead powder. Two types of plate were prepared with paste containing 4.5% H₂SO₄ only, or with 4.5% H₂SO₄ and 1% lignosulphonic expander A-72. Special care was taken during the preparation of the expander-free plates, so that they were not contaminated with organic compounds. Curing was carried out for 72 h in a chamber. The changes during the formation and cycling of both types of plate were checked with cells prepared from two negative and three positive plates.

2.2. Investigation of the changes in microstructure during formation

The formation of the negative plates was carried out in a 1.05 s.g. H₂SO₄ solution for 20 h at a current density of 5 mA cm⁻². The following parameters were checked during formation: (a) the potential of the plates vs a Hg/Hg₂SO₄ reference electrode; (b) the chemical composition of the paste (active mass) by routine chemical analysis; (c) the phase composition of the paste (active

mass) by X-ray diffraction techniques; (d) the morphology of the crystals in the formed parts of the plate by SEM observations.

The samples for the phase and the chemical analyses and SEM observations were taken from the four corners and the centre of the plates. They were washed in distilled and degassed water for 30 min and dried in an argon gas flow at 120° C. For SEM observations lumps of the active mass were used. Each lump was broken into two pieces. One of the pieces was boiled in a solution of NH₄CH₃COO for 30 min so that all divalent lead compounds dissolved and only lead crystals remained. The other piece was observed without any chemical pretreatment. The SEM observation was carried out at two magnifications: high for the morphology of the crystals and low for the structure of the active mass.

2.3. Determination of alternations in energy parameters and crystal morphology of negative plates during cycling

Six identical cells prepared from the two types of negative plate were subjected to cycling tests, under the following conditions: duration of charge 5 h; duration of discharge 1 h; depth of discharge 65% of the rated capacity of the negative plates assuming a 40% utilization of the active mass.

After every 25 cycles the five hour capacity (C₅) of the negative plates was checked. The cells were charged to a defined charged state. The capacity was determined by the time required for the negative half block to reach – 600 mV vs Hg/Hg₂SO₄ reference electrode during discharge with current 0.2 C₅ A. Then the cells were charged again to a defined charged state and the high rate discharge ability was tested at a discharge current $i = 3 C_5$ A until a cut-off potential of the negative plates, – 300 mV, was reached. Test samples were taken from both types of cell after 1, 20 and 100 cycles.

3. Results

3.1. Formation of plates with and without expander

3.1.1. Electrochemical behaviour of the negative plates. The changes in the electrode potential and

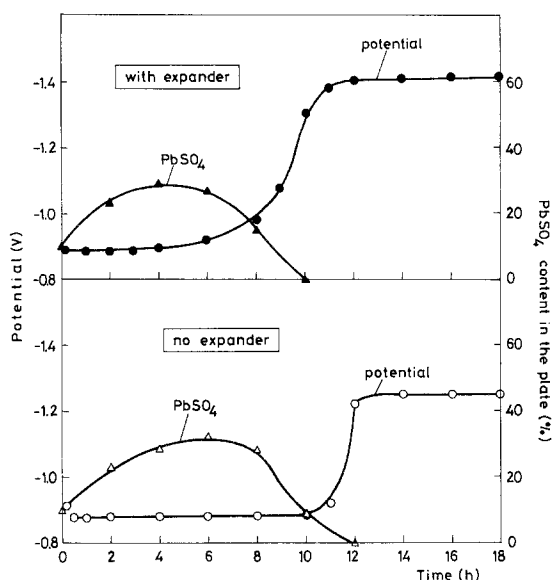


Fig. 1. Changes of the potential vs $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode and PbSO_4 content in the plate during formation.

PbSO_4 content observed in the two types of plate are shown in Fig. 1. The potential of negative plates with no expander is slightly increased during the second stage between 6 and 10 h when PbSO_4 is reduced to Pb. Only after 10 h have elapsed and the PbSO_4 content has dropped below 10% does the potential start to increase rapidly and then hydrogen is evolved intensively. At the current density used during the tests, the hydrogen evolution potential is approximately -1250 mV. In the case of plates containing an expander, the first formation stage is over after 4 h, and the PbSO_4 content starts decreasing. Simultaneously the potential of the electrode is increased. After 10 h, the plate is formed completely and the hydrogen evolution potential has a value of -1410 mV. If the types of cell are juxtaposed, it can be seen that the expander increases the hydrogen evolution overvoltage by 160 mV (at the formation current density). This fact has been observed previously by Jampolskaja *et al.* [7].

The voltage-current relationship of the plates was traced in an effort to determine the effect of the expander upon the electrochemical reduction processes of the Pb^{2+} ions during the first and second formation stages. For the first stage the measurements were carried out, after the second hour, while in the second stage tests the

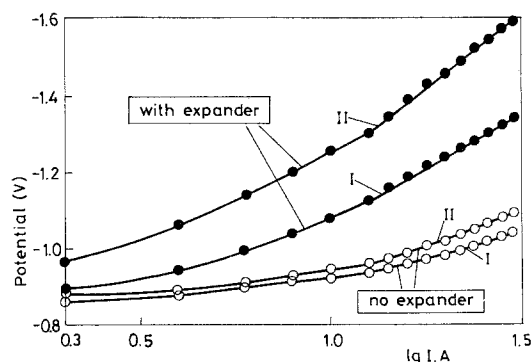


Fig. 2. Polarization curves traced at the second hour (first stage) and the seventh hour (second stage) of formation.

polarization curve was traced after 7 h when the contribution of hydrogen evolution processes to the overall current is still relatively small, and the reduction of PbO and the basic lead sulphates is over, as shown by the X-ray analyses. Fig. 2 presents the results of the polarization measurements. During the two periods the area of the electronically conductive surface is different. Some basic tendencies are clear:

- at both types of plate during the first and the second stage, current regions exist where the Tafel relationship is valid;
- the PbO and basic sulphate electrochemical reduction processes proceed with a lower polarization compared with that of the lead sulphate reduction. This is especially pronounced in the case of expander containing plates;
- the expander hinders the reduction processes during both formation stages. Therefore the polarization of expander-containing plates is substantially higher than that of expander-free ones.

3.1.2. Crystal morphology of the two types of active mass. The morphology of the crystals in the plate at the end of the first stage is shown in Fig. 3. In plates with no expander well-shaped PbSO_4 crystals are observed of size $1-2 \mu\text{m}$. In plates with expander PbSO_4 crystals of different dimensions and imperfect crystal shape are present.

After the dissolution of the PbSO_4 crystals, the skeleton structure of plates with and without expander was checked. The micrographs are shown

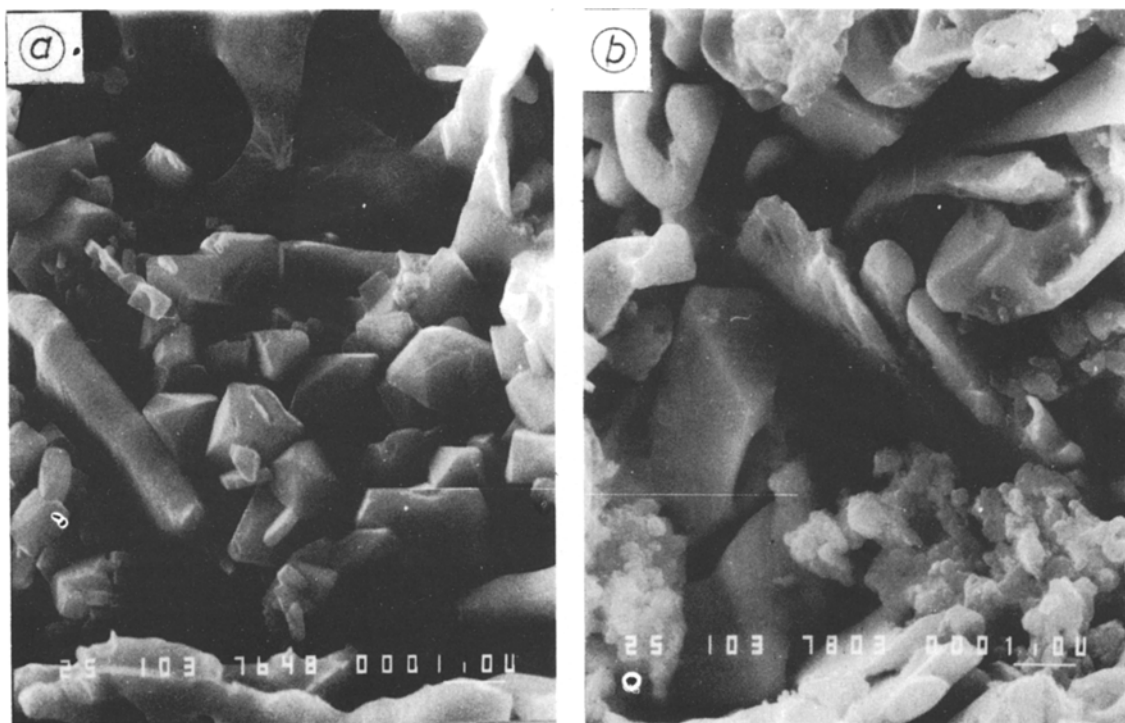


Fig. 3. Micrographs from the Pb-PbSO₄ parts of the plate; (a) no expander; (b) with expander. The white line corresponds to 1 μ m.

in Fig. 4. Both types of plate contain a skeleton structure of similar shape. A more pronounced roughness of the skeleton surface in expander-containing plates is observed.

The secondary lead structure of completely formed plates with and without expander is shown in Fig. 5. In plates with no expander, the secondary lead is in the form of coral-shaped interconnected dendrites. The secondary lead structure of expander containing plates (Fig. 5b) is composed of separate, individual lead crystals located upon the skeleton structure.

In an effort to determine whether the type of the expander affects the morphology of the secondary crystals, plates containing two different types of expander Eze - Skitan (GDR Trade mark) or lignosulphonates were subjected to formation. Fig. 6 presents the micrographs of the lead crystals of the secondary structure.

It is noted, that Eze - Skitan increases the rate of lead crystal nucleation much more than sodium lignosulphonate. When the latter is used as an expander, the secondary lead crystals are rather coarse and with imperfect shapes.

3.2. Change of structure of negative plates during cycling

3.2.1. Dependence of the capacity on the number of charge discharge cycles. Fig. 7 shows the changes in capacity of two types of cell measured at current $i = 0.2 C_5 A$ and $i = 3 C_5 A$ during cycling. The beneficial effect of the expander upon the capacity is very pronounced in both discharge tests. During the short discharges the effect of the expander is already impressive during the initial cycles. In the case of 5 h discharge runs of expander-containing cells, capacity is increased during the initial 50 cycles and then it slowly decreases. Cells with plates without expander display initially a pronounced loss of capacity, which afterwards decreases linearly.

3.2.2. Morphology of crystals and structure of the active mass after the first charge-discharge cycle. Fig. 8 shows the structure of the charged active mass with no expander after the first discharge-charge cycle. Two types of lead dendrite are observed. The first type are long, parallel,

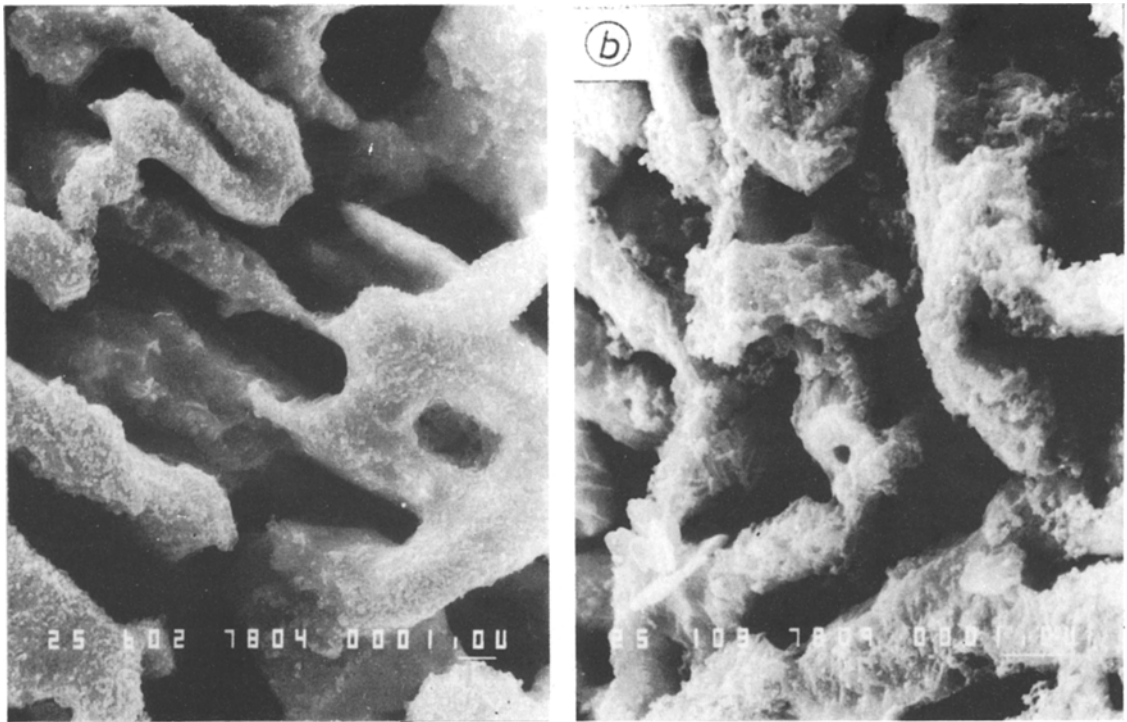


Fig. 4. Skeleton structure of the active mass formed during the first formation stage in the plates; (a) no expander; (b) with expander. The white line corresponds to 1 μm .

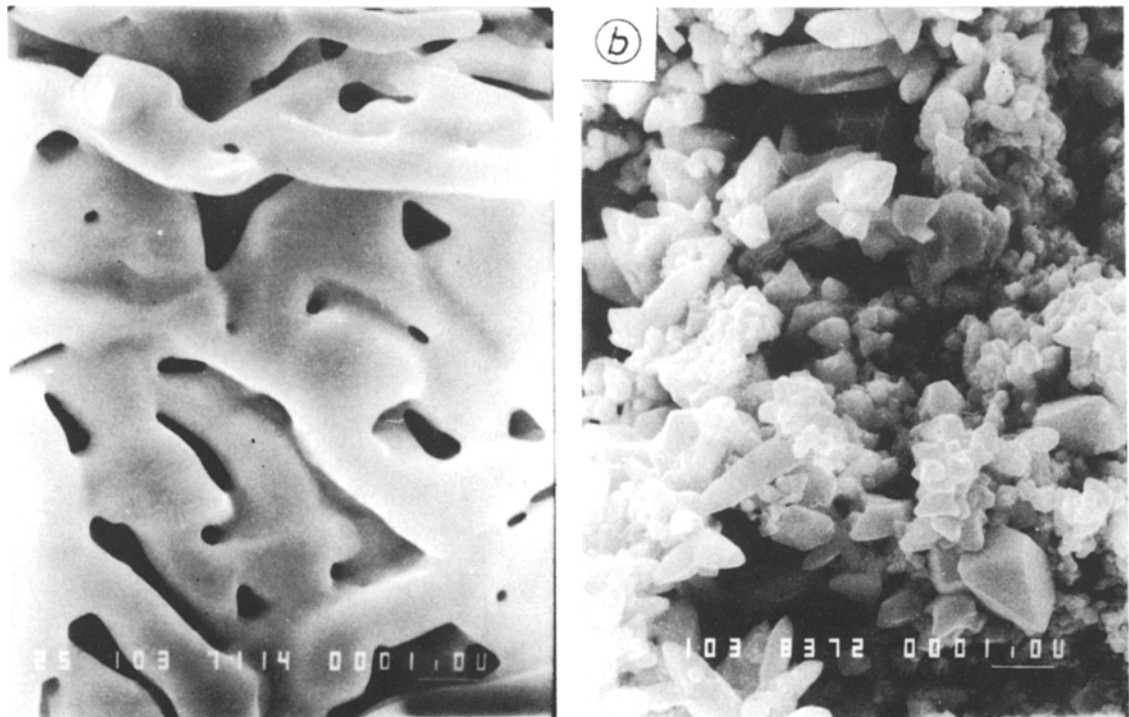


Fig. 5. The morphology of the crystals of the secondary lead structure formed in the plates during the second formation stage: (a) no expander; (b) with expander. The white line corresponds to 1 μm .

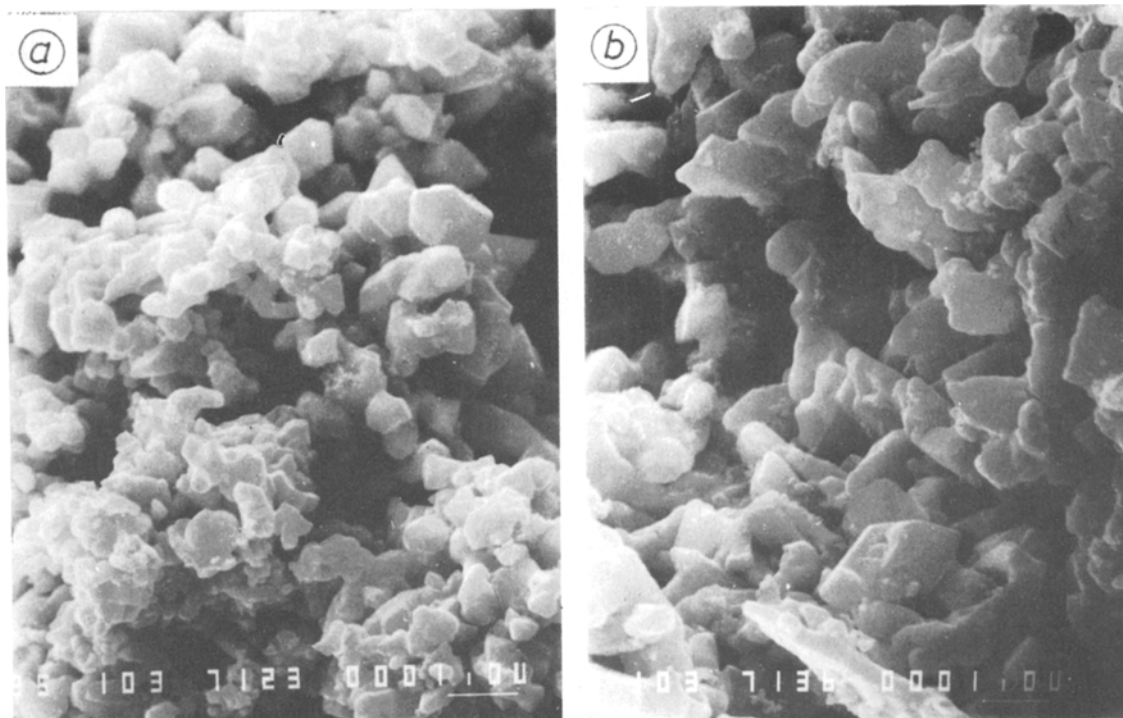


Fig. 6. The morphology of the crystals of the secondary lead structure with expander: (a) 1% Eze-Skitan; (b) 1% sodium lignosulphonate. The white line corresponds to 1 μm .

interconnected, round-edged dendrites (Fig. 8a), while the other shape comprises heavily broken dendrites with many knees (Fig. 8b). It appears reasonable that this variety in the shape of the secondary lead structure is due to the different density of the active mass.

Fig. 9 presents the structure of the charged active mass of plates containing an expander. The micrographs are shot at the plate surface (Fig. 9a) and in the bulk of the plate (Fig. 9b). It can be seen clearly that the secondary structure is composed of well-shaped, singular, needle-form (Fig. 9a), or prismatically shaped (Fig. 9b) crystals positioned on the skeleton. A comparison of Figs. 8 and 9 shows the expander affects on the crystallization processes of the secondary lead crystals, enhancing the formation of separate small crystals, i.e. accelerating nucleation and decreasing the crystal growth rate of the secondary crystals.

Fig. 10 shows the morphology of the crystals of the two types of active mass after discharge. On the plates with no expander one can observe large, coalescent PbSO_4 crystals, while in the

presence of an expander, small, well-shaped crystals with quite perfect prismatic and pyramidal planes are seen. Upon many of the PbSO_4 crystal planes small PbSO_4 nuclei at different growth stages are observed. Obviously the expander

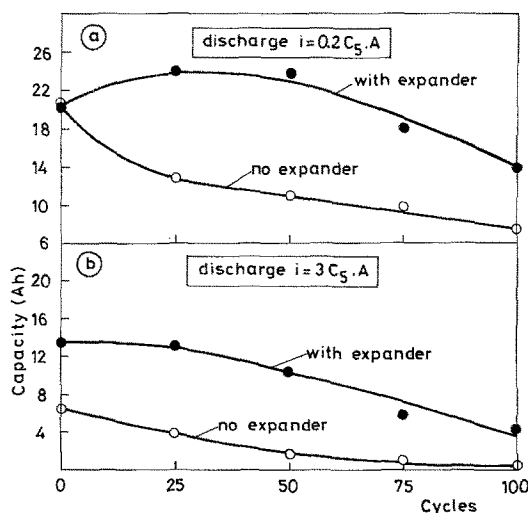


Fig. 7. Change of the capacity during deep charge-discharge cycling.

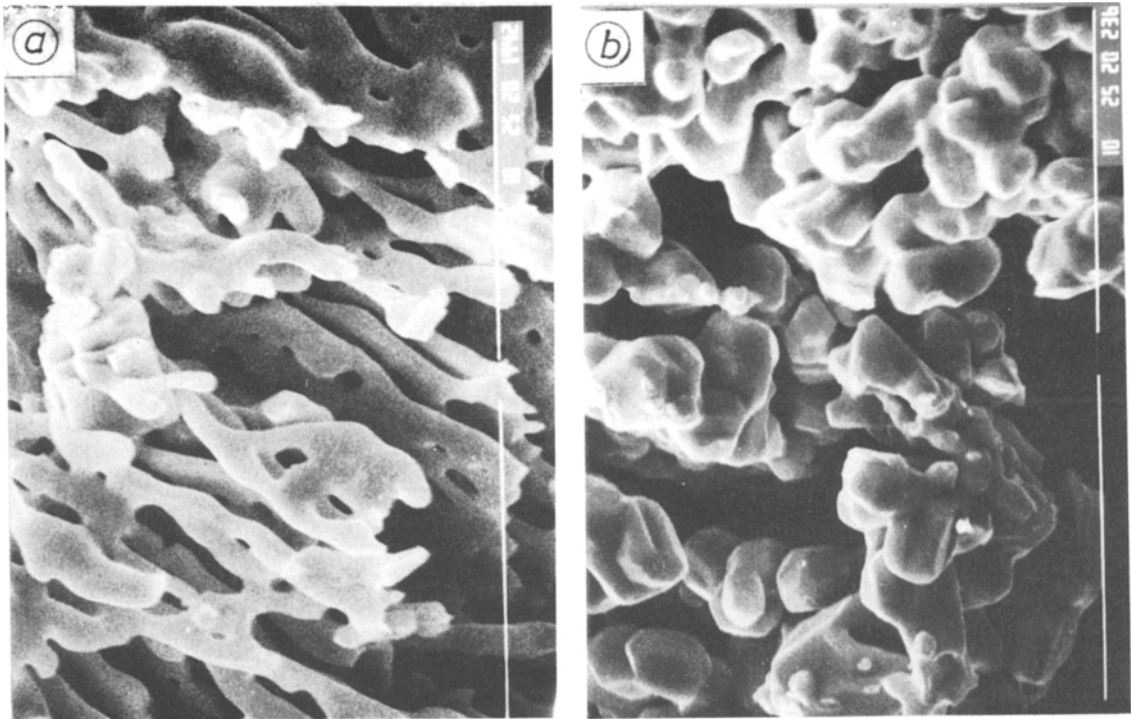


Fig. 8. Morphology of the secondary lead crystals of the active mass without expander after the first discharge-charge cycle. White line corresponds to 10 μm .

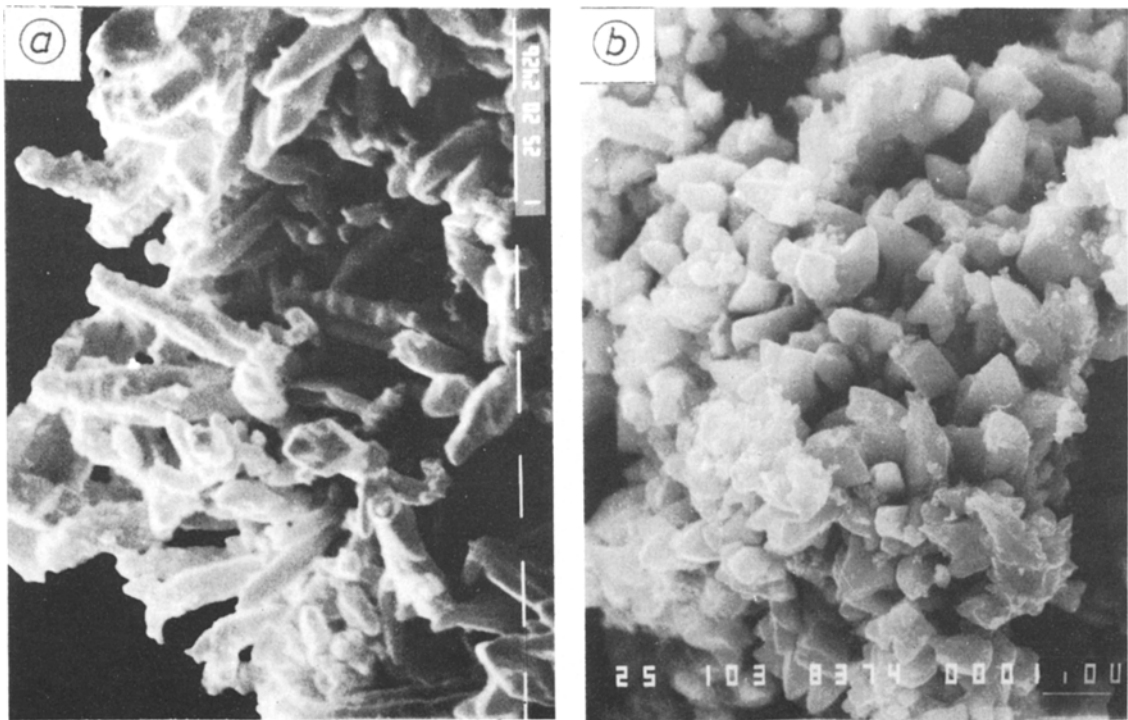


Fig. 9. Morphology of the secondary lead crystals at the surface (a) and the bulk (b) of the plate with active mass containing expander after the first discharge-charge cycle. White line corresponds to 1 μm .

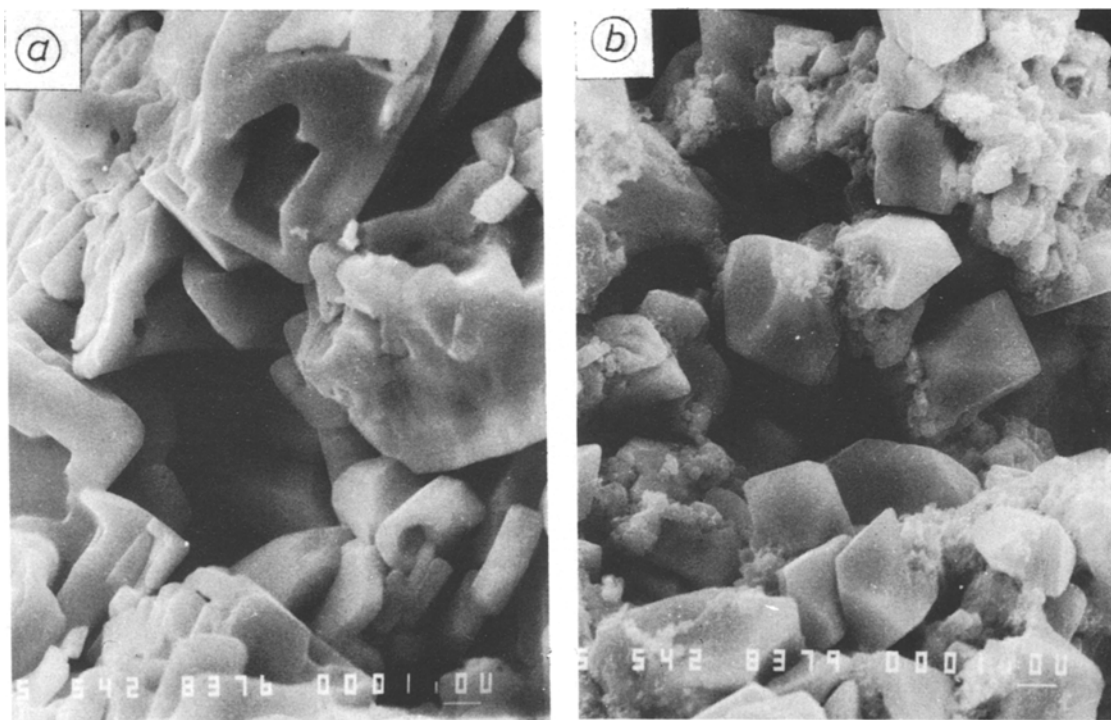


Fig. 10. Morphology of the PbSO_4 crystals of discharge plates after the first cycle with active mass containing: (a) no expander; (b) with expander. White line corresponds to $1\ \mu\text{m}$.

affects both the nucleation and growth of PbSO_4 crystals.

Figs. 11a, b presents the skeleton structure of the active mass with no expander at different magnifications. The skeleton structure is very distinct and is composed from compact branches (Fig. 11c). In many parts of the active mass interconnected agglomerates comprising flake shaped crystals are observed (Figs. 11a, b).

The skeleton structure of an expander-containing active mass is shown in Figs. 12a, b. The skeleton consists either of continuously interconnected, shapeless dense crystal formations (Fig. 12a) or linked agglomerates of scale-shaped crystals (Fig. 12b). If Figs. 12 and 11 are juxtaposed, it can be seen that the expander affects the shape of the crystals of the skeleton less. A qualitative difference between the skeleton of the two types of plates is not observed as in the case of the secondary structure.

3.2.3. Morphology of the crystals and structure of the active mass after 100 charge-discharge cycles of the cells. Fig. 13a, b shows the mor-

phology of the lead crystals (Fig. 13a), and the structure of the charged active mass (Fig. 13b) with no expander, in plates after 100 charge-discharge cycles. The micrographs display shapeless, interconnected in-a-network lead crystals (Fig. 13a). This network is fairly dense (Fig. 13b). No long lead dendrite structures as seen in Fig. 8a were encountered in the active mass.

Fig. 14 shows the morphology of the lead crystals (Fig. 14a) and the structure of the active mass containing an expander after 100 charge-discharge cycles. The lead crystals contain many defective planes and edges, and are not so distinctly differentiated. This is probably due to the decrease of the effect exerted by the expander which disintegrates during cycling.

Fig. 15 presents micrographs of the PbSO_4 crystal morphology after a discharge of the active mass with an expander (Fig. 15b) and with no expander (Fig. 15a), of plates which have been subjected to 100 charge-discharge cycles. If the size of the PbSO_4 crystals in the plates with no expander is compared with that in Fig. 10a, a decrease in their volume is observed. After 100

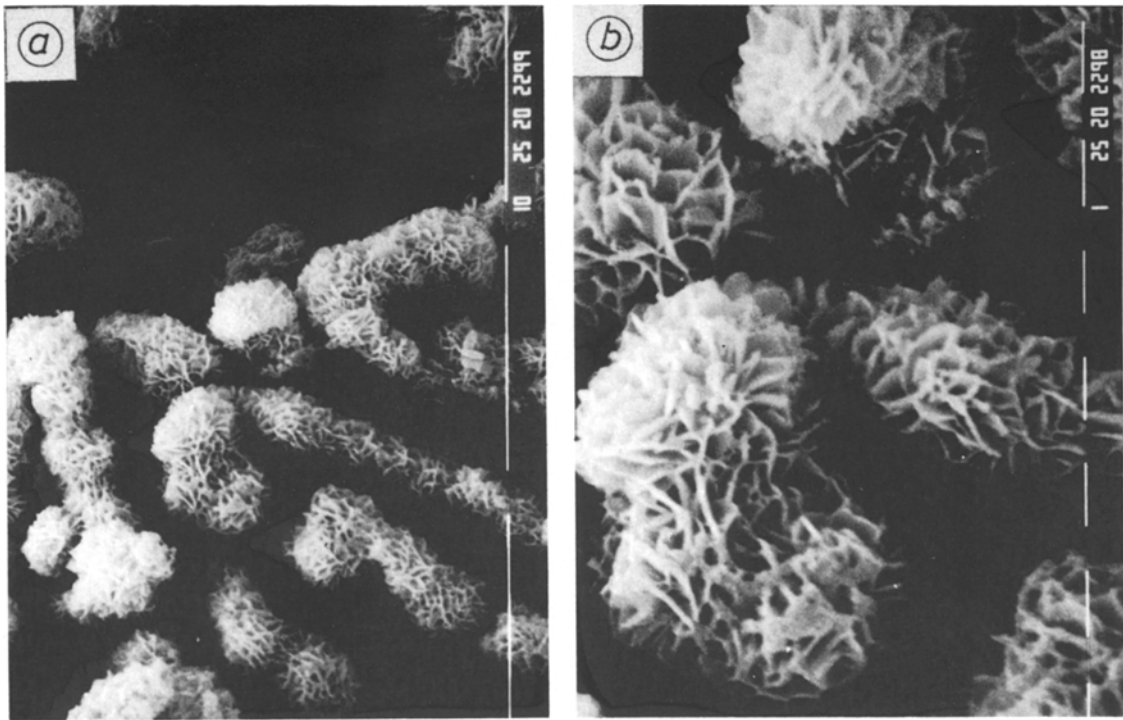
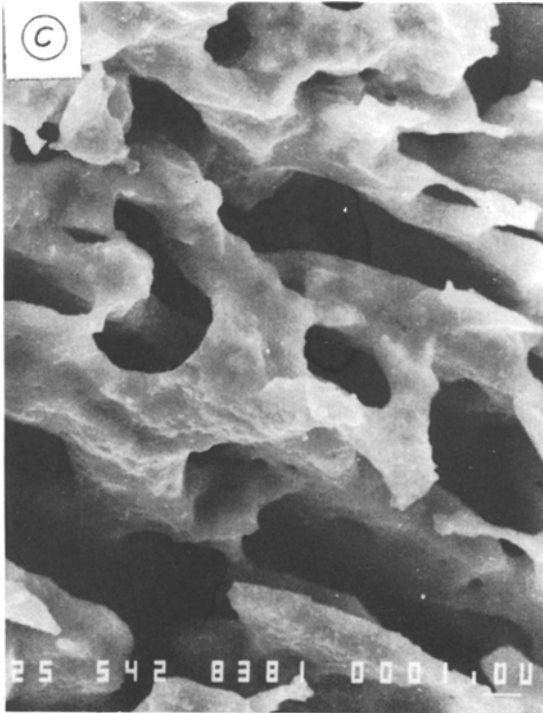


Fig. 11. Skeleton structure of the active mass without expander after the first cycle. White lines correspond to: (a) 10 μm ; (b, c) 1 μm .



the morphology of the PbSO_4 crystals in the two types of plate becomes less pronounced during cycling.

Fig. 16 shows the skeleton structure of the active mass with no expander at two different magnifications. During cycling the lead skeleton has become thicker, and the structure of the net more compact. Large caves are formed at separate sites (Fig. 16b).

Fig. 17a, b presents the skeleton structure of an expander containing active mass. Here also a slight increase in the thickness of separate branches of the skeleton are observed, but simultaneously the pores in the skeleton have increased dimensions, i.e. the structure has become more loose.

The above-mentioned conclusions are clear if the changes in the volume of the active mass of the plate are considered. The active mass of the plate with no expander is slightly contracted, and tends to detach from the grid at separate sites. The reverse effect is observed in the active mass of expander-containing plates which tend to swell. The initial thickness of the plate 1.6 mm

charge-discharge cycles plates with an expander still show the preference of PbSO_4 crystals with well-shaped planes and edges. The difference in

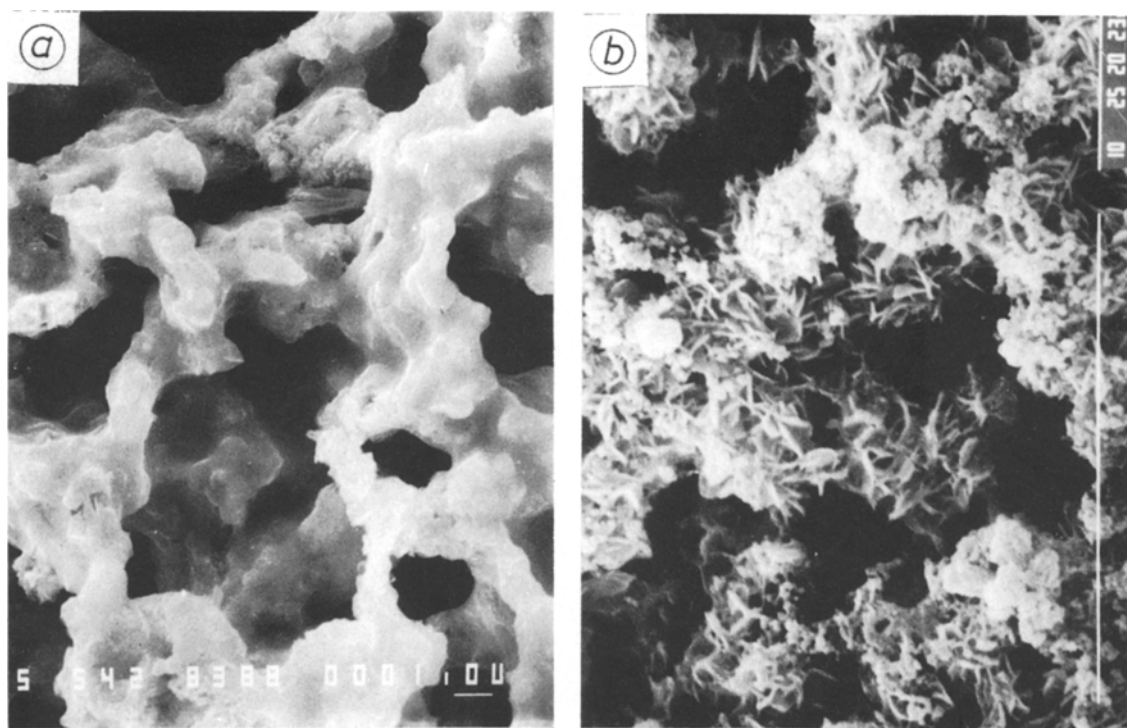


Fig. 12. Skeleton structure of the active mass with expander after the first cycle. White line corresponds to: (a) $1\ \mu\text{m}$; (b) $10\ \mu\text{m}$.

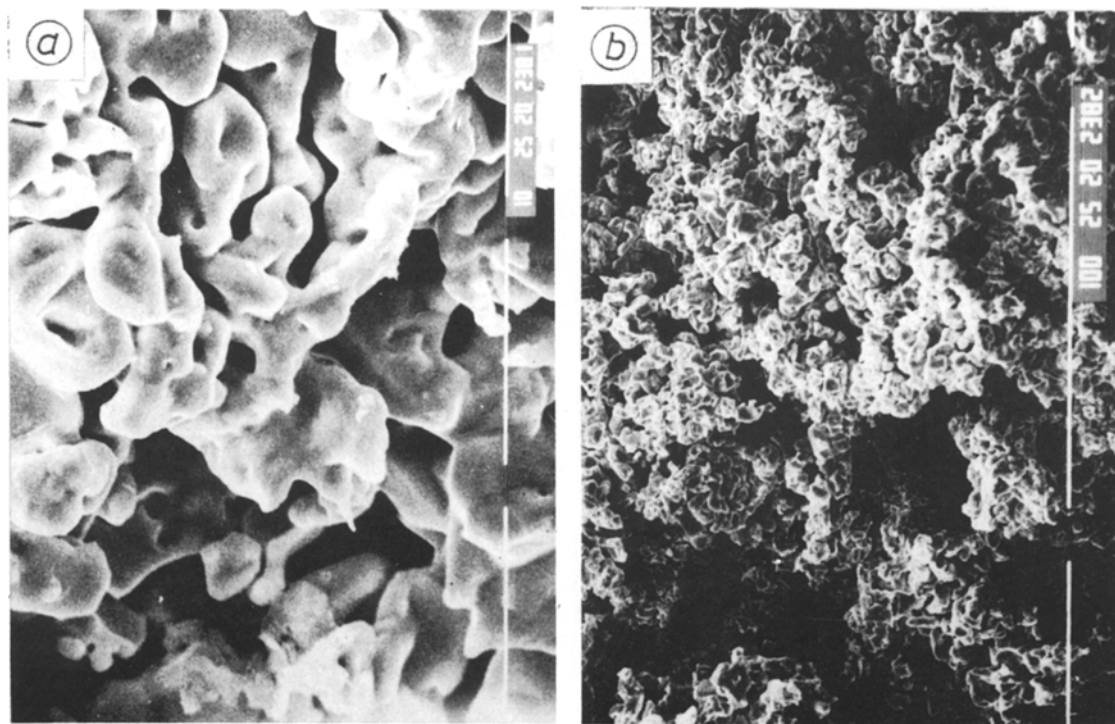


Fig. 13. Morphology of the lead crystals of charged active mass without expander after 100 cycles. White line corresponds to: (a) $10\ \mu\text{m}$; (b) $100\ \mu\text{m}$.

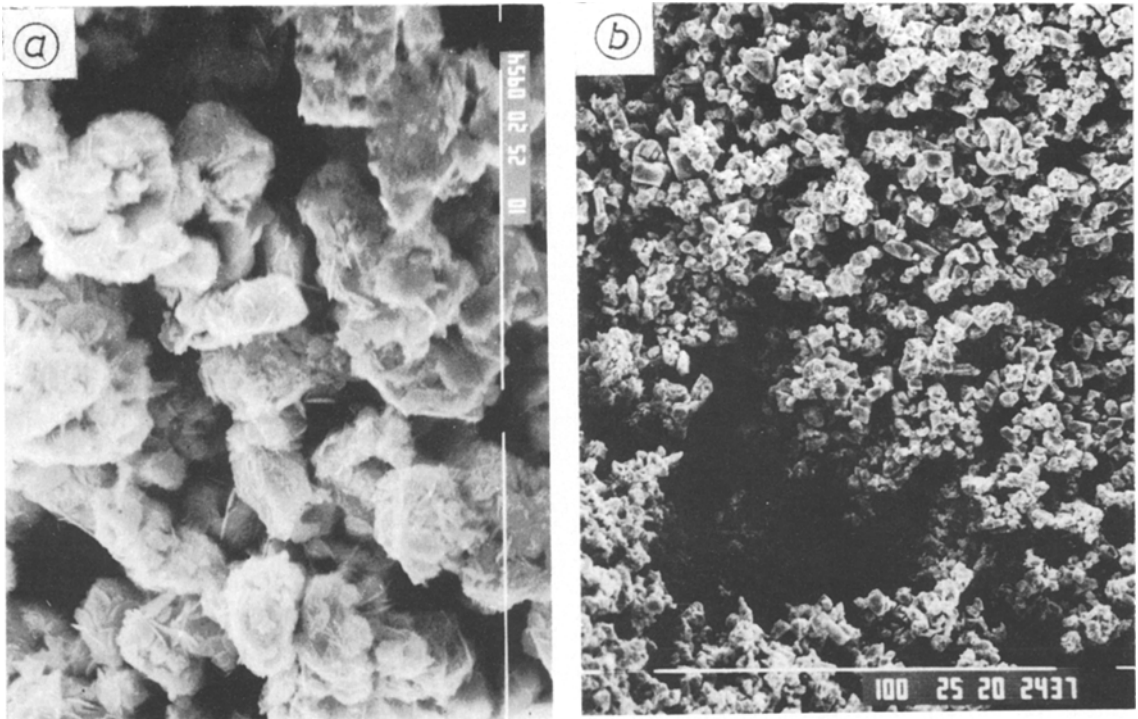


Fig. 14. Morphology of the lead crystals of charged active mass with expander after 100 cycles. White line corresponds to: (a) 10 μm ; (b) 100 μm .

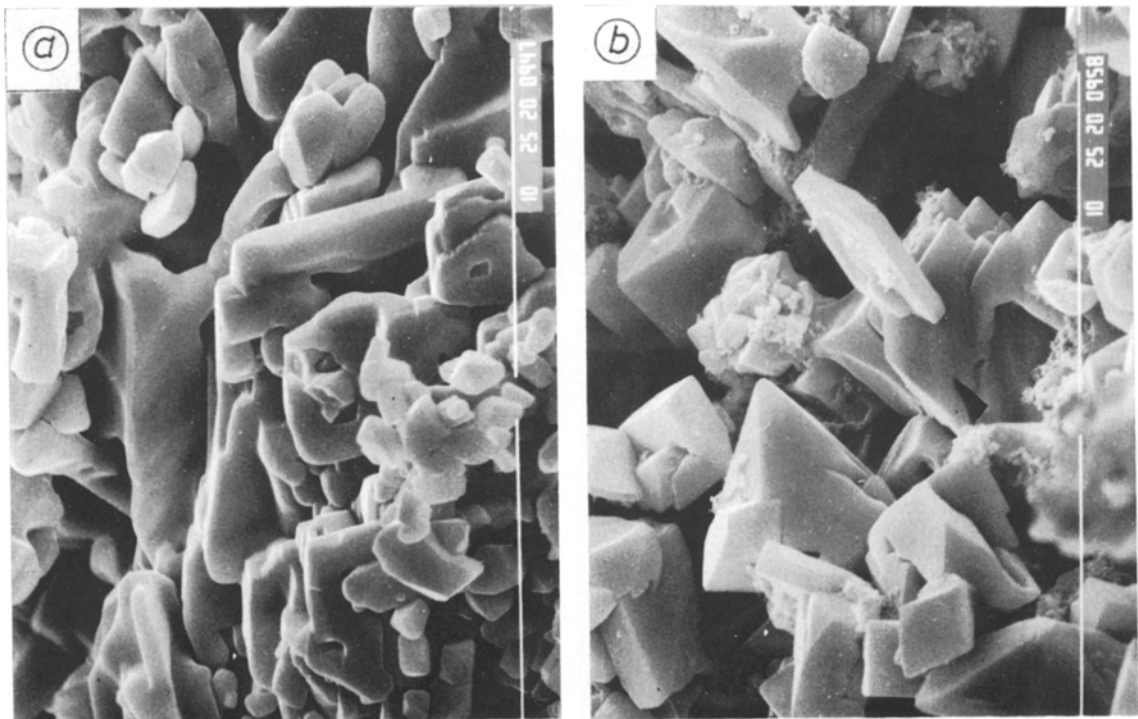


Fig. 15. PbSO_4 crystals of discharged plates after 100 cycles: (a) active mass with no expander; (b) active mass with expander. White line corresponds to 10 μm .

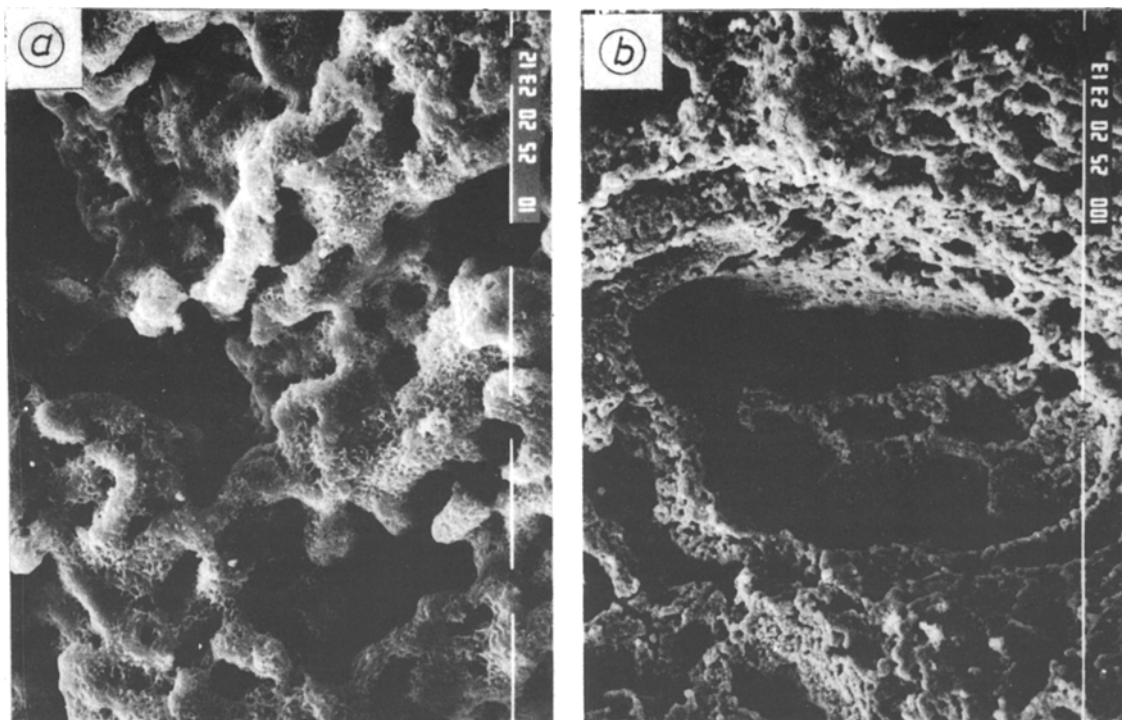


Fig. 16. Skeleton structure of the active mass without expander after 100 cycles: (a) morphology of the crystals; (b) macrostructure of the skeleton. White line corresponds to: (a) 10 μm ; (b) 100 μm .

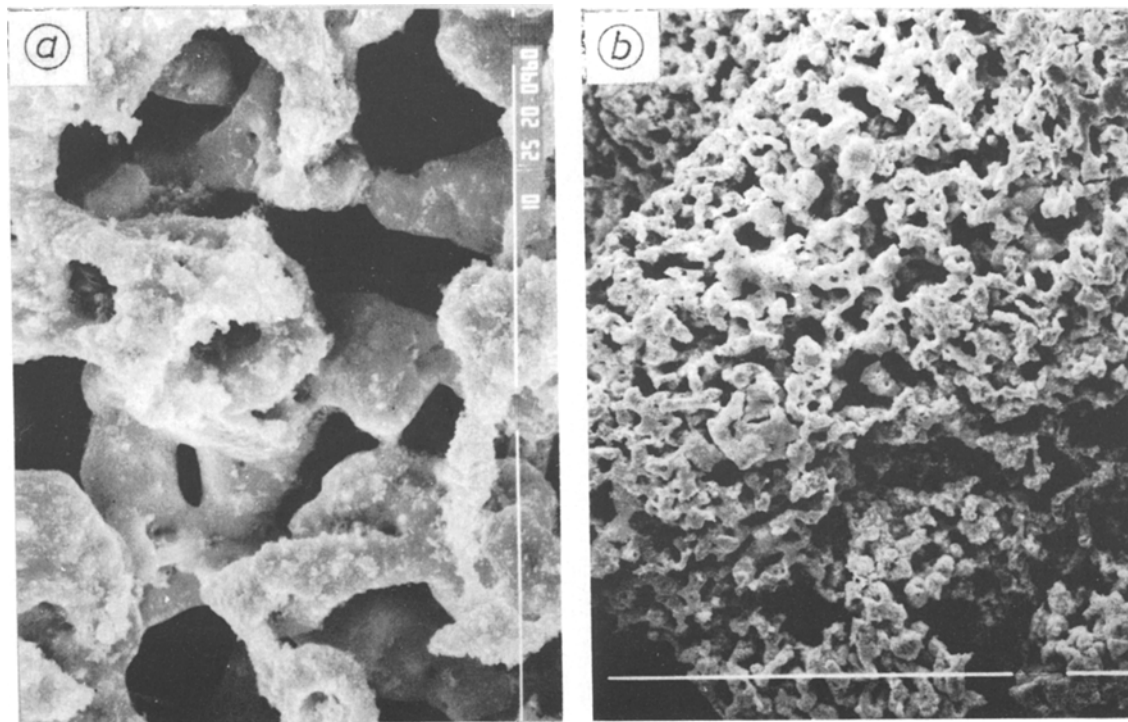


Fig. 17. Skeleton structure of the active mass with expander after 100 cycles; (a) morphology of the crystals; (b) macrostructure of the skeleton. White line corresponds to: (a) 10 μm ; (b) 100 μm .

is increased to 2.5 mm after 100 charge-discharge cycles, i.e. an increase of 50–60% is observed. But only part of the overall volume increase of the plate is due to the increased porosity of the skeleton structure. Numerous macro-pores, as well as separate large caves are observed in the active mass.

4. Discussion

4.1. *Effect of the expander upon the morphology of the secondary crystals*

The secondary lead structure of plates with no expander represents a network of long or broken lead dendrites (Figs. 5a, 8). The expander suppresses the growth of these dendrites and forms small lead crystals attached to the lead skeleton (Figs. 5b, 6, 9). This is confirmation that the expander controls the nucleation and crystal growth rates of the secondary lead crystals. This effect is of paramount importance for the electrochemical characteristics of the plate. A larger active surface is created and the capacity of the active mass is increased, as shown in Fig. 7. In fact that phenomenon is far more complex and sophisticated.

The expander also affects the shape of the PbSO_4 crystals, enhancing the formation of smaller crystals with more perfect planes and edges (Fig. 10b).

The effect exerted by the expander upon the crystallization processes of lead and lead sulphate can be related partially to its absorption on their surface. Sharpe [8, 9], Archdale and Harrison [10] and Mahato [11, 12] have shown that the expander is really adsorbed on lead and PbSO_4 . On the other hand, it has been established that the adsorption of the expander depends on the pH value of the medium [11, 13]. The pH value of the solution in the reaction layer of the plate, where the lead crystals are formed is quite different during the two formation stages [1, 2]. During this first stage the solution is either neutral or slightly alkaline, while during the second it becomes strongly acidic. On the other hand, it is well known that lignosulphonates are soluble in alkaline or neutral media. In this pH range the lignosulphonates are probably slightly adsorbed upon the lead surface of the skeleton,

which offers an explanation for their relatively less pronounced effect upon the crystallization processes during this stage. In acidic media lignosulphonates are slightly soluble. During the second stage the solution in the pores of the plate is strongly acidic and, as already pointed out, the adsorption of lignosulphonates upon the Pb and PbSO_4 surface is substantial [8–13]. This is shown in Figs. 1 and 2. The polarization curve of the plate with active mass containing an expander (Fig. 2) is much steeper than that of the plate with no expander. This increased polarization may be due to the adsorption layer which the expander forms on the lead and PbSO_4 surface, impeding the shift of Pb^{2+} ions and Pb atoms formed during their reduction, and thus affecting the nucleation and growth rate of the lead crystals.

4.2. *Participation of the skeleton structure in the charge-discharge processes*

It has been established during cycling that the active mass containing no expander contracts and the skeleton becomes more compact (Fig. 16). In expander-containing plates the active mass swells and the skeleton becomes more porous (Fig. 17). Evidently processes occur during cycling when part of the branches of the skeleton are oxidized during discharge, and new branches of the skeleton are formed during charge but situated at different locations as compared with the sites of oxidized branches. Thus the skeleton may become more compact or expand. The expander exerts a strong effect upon this process, determining its direction and rate. This ability of the expander to change the structure of the skeleton and the active mass during cycling directly affects the capacity and life of the battery.

Since the skeleton appears to differ in terms of design and functions from the secondary structure, the laws governing the behaviour of the two structures should be different. In order to improve the specific energy of the negative active mass during the service life of the battery it is necessary to elucidate the laws which govern the behaviour of both structures during the cycle life of the battery. Since these alternations depend on the expander, and the latter is introduced into the

battery during the preparation of the paste, it follows that the stability of both structures and their ratio is assigned by the respective technology used for the preparation of the plate. Naturally the behaviour of the negative plates is affected not only by the expander, but also by the phase composition and density of the negative paste, as well as the conditions of formation. However, manufacturing experience has shown that these factors exert a less important effect than the expander; they affect the behaviour of the positive plates more.

4.3. Morphology of the crystals of the skeleton structure

Figs. 11 and 12 shows that the skeleton structure is built by the formation of dense, shapeless interconnected crystals or linked agglomerates of scale-form lead crystals. Obviously the nucleation and growth rates of the skeleton crystals are quite different. Since both morphological types of crystal in the lead skeleton structure are present in active masses with and without an expander, it can be presumed that their appearance is determined by the properties of the paste and the conditions of the formation process.

4.4. Efficiency and stability of the expander action

The amount of expander in the plate and its efficiency and chemical stability are the basic factors which determine the rigidness of the two types of negative active mass structures. A highly efficient expander used in large quantities may cause a rapid expansion of the negative active mass during cycling. This will, in turn, cause a thinning of the branches of the skeleton structure, and as the latter are the electronic current conductors, the internal resistance of the plate will be increased. If the plate contains a smaller amount of an expander with inadequate efficiency, the porosity of the skeleton structure is decreased. As the porosity of the active mass is associated

with the ionic current conductor of the plate it determines the ionic resistance of the solution in it: when the porosity decreases the ionic resistance of the plate is increased resulting in a decrease of the capacity and energy delivered by the battery.

The second important factor through which the expander affects the battery is its chemical stability. If the expander rapidly disintegrates, e.g. is hydrogenized by the evolved hydrogen, or is oxidized on the positive plate after partial dissolution or by oxygen which diffuses to the negative plate, the battery will soon decrease its capacity due to restrictions imposed by the negative plate. Therefore the stability of the expander appears to be one of the indispensable conditions which ensures the long life of the battery.

Acknowledgements

The authors are grateful to M. Iosifova and A. Dimitrova for their valuable assistance in the preparation of SEM micrographs.

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