

A STUDY OF THE OXIDATION OF $4\text{PbO}\cdot\text{PbSO}_4$ CRYSTALS IN CURED PASTE TO PbO_2 AGGLOMERATES DURING FORMATION OF POSITIVE PLATES FOR LEAD/ACID BATTERIES

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Introduction

The capacity and cycle life of the positive active mass of a lead/acid battery both depend on its structure. It has been established that the most stable PbO_2 structure is obtained when the positive active mass is derived from the oxidation of tetrabasic lead sulphate ($4\text{PbO}\cdot\text{PbSO}_4$) pastes [1 - 5]. Apparently, the active mass structure 'remembers' its origin. Burbank [1] was the first to claim that this 'memory effect' originates because the oxidation of $4\text{PbO}\cdot\text{PbSO}_4$ crystals proceeds via a metasomatic process. Similar transfer of the crystal morphology of $4\text{PbO}\cdot\text{PbSO}_4$ pastes through to the PbO_2 active mass was also observed by Hugel and Hammar [6], Pierson [7], Yarnell and Weeks [5], etc.

Pavlov and Papazov [4] have studied the active mass obtained from $4\text{PbO}\cdot\text{PbSO}_4$ pastes at high magnification, and have found that when a $4\text{PbO}\cdot\text{PbSO}_4$ crystal is oxidized, a great number of small PbO_2 particles are formed and are gathered into a porous agglomerate. The latter repeats the shape of the $4\text{PbO}\cdot\text{PbSO}_4$ crystal.

A model for the structure of the PbO_2 active mass has been developed by the present authors [8, 9]. According to this model, the smallest building block of the active mass structure is the PbO_2 particle. Numerous PbO_2 particles are grouped into microporous PbO_2 agglomerates (microstructural level). The agglomerates form a skeleton with macropores in between (macrostructural level). The above organization is most evident in active masses obtained from $4\text{PbO}\cdot\text{PbSO}_4$ pastes. The agglomerates are formed from $4\text{PbO}\cdot\text{PbSO}_4$ crystals. The size of the macropores in the active mass is determined by the paste density. Thus, by varying the paste density, definite ion-transport systems can be established in the active mass. Similarly, by varying the conditions of $4\text{PbO}\cdot\text{PbSO}_4$ crystal formation, definite sizes and shapes of PbO_2 agglomerates can be produced. Furthermore, the interconnection of the agglomerates and, hence, the strength of the skeleton as a whole can be influenced through regulation of the curing conditions.

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It is technologically important to understand the mechanism by which $4\text{PbO}\cdot\text{PbSO}_4$ crystals are oxidized to PbO_2 agglomerates during battery-plate formation, *i.e.*, to determine the processes of formation at the microstructural level. A survey of the literature reveals that this mechanism has yet to be studied in detail. It is well established, however, that the formation of $4\text{PbO}\cdot\text{PbSO}_4$ pastes proceeds at a very slow rate. Obviously, some of the elementary reactions of the oxidation mechanism are greatly hindered and thus cause plate formation to be a lengthy process, a feature that is technologically inconvenient. On the other hand, if the process of active mass formation is deliberately shortened, then $4\text{PbO}\cdot\text{PbSO}_4$ crystals cannot be fully oxidized to PbO_2 and the resulting plate will exhibit a low initial capacity that will most probably be below the required nominal value. These disadvantages have greatly restricted the application of $4\text{PbO}\cdot\text{PbSO}_4$ pastes in the battery industry.

The present paper reports some new aspects of the mechanism of oxidation of $4\text{PbO}\cdot\text{PbSO}_4$ crystals to PbO_2 agglomerates.

Experimental

Preparation of plates with $4\text{PbO}\cdot\text{PbSO}_4$ paste

Five kilogrammes of commercial leady oxide (70 wt.% PbO) was mixed in a laboratory mixer: first with a definite amount of water, then with H_2SO_4 (sp. gr. = 1.4) in an amount that was 6% with regard to the PbO contained in the leady oxide. The temperature was raised to 80 °C and paste mixing was continued for 1 h. The resulting paste had a density of 4.2 g cm⁻³ and was spread manually over automotive battery grids prepared from Pb-6wt.%Sb-0.1wt.%As-0.1wt.%Sn alloy. The plates were subjected to curing for 72 h at 40 °C and 100% humidity.

Plate formation

A series of battery cells was assembled with 3 positive and 4 negative plates. Formation was carried out in H_2SO_4 of sp. gr. 1.05 at a current density of 5 mA cm⁻² and a temperature of 30 - 40 °C for 30 h. At given intervals, one plate was removed and subjected to both phase analyses and examination in a scanning electron microscope. Changes in phase composition of the plate during formation were followed by X-ray diffraction (XRD) analysis; the chemical composition of the paste was determined by wet chemical analysis. The total pore volume and its distribution as a function of pore radius were assessed by mercury porosimetry. The BET method with low-temperature nitrogen adsorption was used to measure the specific surface area.

The crystal morphology, as well as the structure of the paste and the active mass, were examined by scanning electron microscopy. To establish the formation of PbO_2 agglomerates, small samples of the plate were put into saturated ammonium acetate solution and heated at 70 °C for 30 min. During this treatment, the unoxidized $4\text{PbO}\cdot\text{PbSO}_4$ is dissolved and the PbO_2

agglomerates remain unaffected. A further specimen of the plate was immersed for 16 h in a solution of H_2O_2 and HNO_3 maintained at 50°C . The specimen was then removed, washed with water, and dried at 50°C for 3 h. By this process, PbO_2 particles are preferentially dissolved and leave the unoxidized divalent lead compounds ($4\text{PbO}\cdot\text{PbSO}_4$, PbO , PbSO_4) unaffected. The shape and type of the latter compounds were used to derive information about the oxidation processes taking place in the crystal.

Results

Changes in phase and chemical composition of paste and active mass during plate formation

Figure 1 shows the changes in the phase and the chemical composition of the paste during formation of the active mass. The phase composition data are determined from the relative intensities of the characteristic diffraction lines of the individual phases. Unfortunately, some of these lines coincide.

The following conclusions can be drawn from the information presented.

(i) The initial composition of the cured paste consists of $4\text{PbO}\cdot\text{PbSO}_4$, tet-PbO (beside the 3.12 \AA line, the 2.79 \AA line is also clearly distinguishable), orthorhomb-PbO (both the 3.07 and 2.95 \AA lines are present). After curing of the plates, the lead content in the paste was $< 1\text{ wt.}\%$.

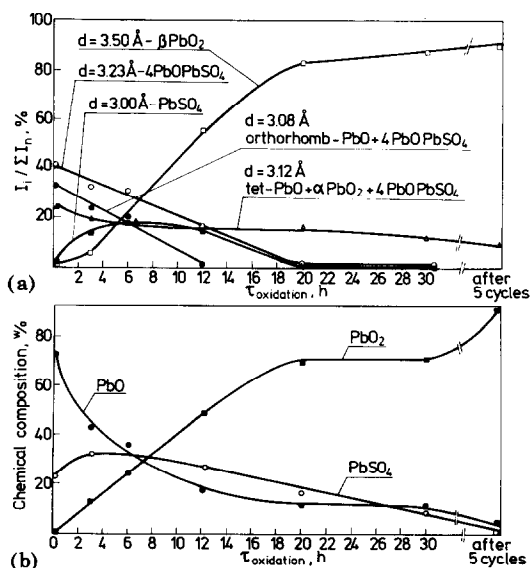


Fig. 1. Changes in (a) phase and (b) chemical composition of paste during formation of active mass.

(ii) The basic product of the electrochemical reaction is β - PbO_2 . Taking into account the results of the chemical analysis, as well as the XRD data for β - PbO_2 , it can be seen that oxidation of the paste to PbO_2 proceeds at a fairly rapid rate until the PbO_2 content reaches ~ 70 wt.%, and then slows down.

(iii) At the beginning of formation, it is virtually impossible to prove the presence of α - PbO_2 by XRD phase analysis. This is because the characteristic diffraction lines of α - PbO_2 coincide with those of other lead compounds. After 30 h of formation, however, the 3.12 \AA line is quite well expressed and, therefore, it can be concluded with confidence that the line denotes the presence of α - PbO_2 .

(iv) During plate formation, H_2SO_4 reacts with PbO and $4\text{PbO}\cdot\text{PbSO}_4$ to yield PbSO_4 . The amount of PbSO_4 reaches a maximum after ~ 6 h of formation and then slowly decreases. After 20 h, wide peaks appear at interplanar distances of 3.00 \AA and 3.33 \AA that differ slightly from the noise signal. This suggests that the PbSO_4 is most probably present in the form of very fine crystals.

(v) The amount of $4\text{PbO}\cdot\text{PbSO}_4$ decreases gradually during formation and, after 20 h, the 3.23 \AA line is very wide and little different from the noise signal.

(vi) Both the tet- PbO and orthorhomb- PbO contents decrease as the formation proceeds. The orthorhombic modification is totally converted within 12 h, but tet- PbO remains unoxidized until 20 h have elapsed.

Changes in pore volume and BET surface during plate formation

Oxidation of both $4\text{PbO}\cdot\text{PbSO}_4$ and PbO to PbO_2 leads to a decrease in volume of the solid phase in the plate because the molar volumes of the former compounds are larger than that of PbO_2 . Figure 2 presents changes in the pore volume and the specific surface-area of the plate during formation.

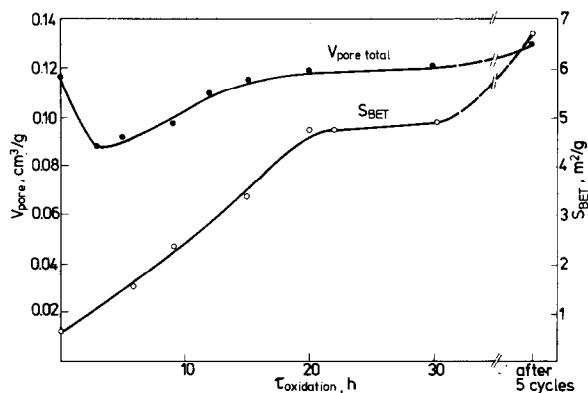


Fig. 2. Changes in volume and surface of active mass pores during formation.

According to Fig. 1, the parallel processes of PbSO_4 and PbO_2 formation proceed relatively rapidly during the first 3 h. On the other hand, the pore volume decreases (see Fig. 2); this indicates that lead sulphate production (*i.e.*, 'sulphatation') is the major reaction. After this period, the pore volume grows, indicating that the electrochemical reaction of PbO_2 formation is dominant.

Since the volume of PbO_2 particles is smaller than that of either $4\text{PbO}\cdot\text{PbSO}_4$ or PbSO_4 crystals, it follows that when PbO_2 particles are formed the plate BET-surface-area will increase. This is confirmed by the data given in Fig. 2. The growth of the BET surface is almost proportional to the formation of PbO_2 . By contrast, the molar volume of the PbSO_4 crystals formed at the beginning of formation have a negligible effect on the specific surface area of the plate. The formation process slows down after 20 h and, accordingly, so does the increase in the BET surface area.

SEM observations of crystal morphology of paste and active mass during formation

Initial paste

The morphology of the paste crystals prior to formation is illustrated in Fig. 3. It can be seen that the $4\text{PbO}\cdot\text{PbSO}_4$ crystals are prismatic in shape with a length of 15 - 20 μm and a width of 2 - 4 μm . The smaller crystals are tet-PbO and orthorhomb-PbO.

After 3 h of formation

Two zones can be distinguished in the plate cross-section. One zone is dark brown in colour and is due to completion of the formation process; the other zone has the same colour as the paste and has been unaffected by the formation process. An electron micrograph of the former (dark brown) zone is given in Fig. 4. It is evident that only part of the crystals has been oxidized.

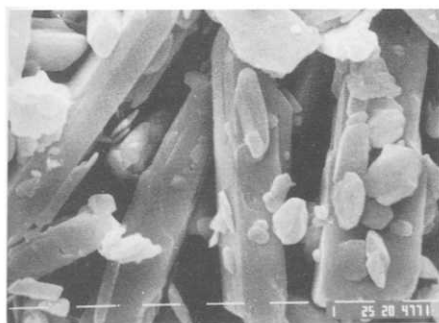


Fig. 3. Electron micrograph of $4\text{PbO}\cdot\text{PbSO}_4$ crystals in cured paste. Magnification bar = 1 μm .

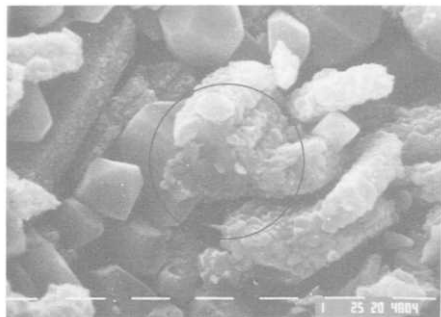


Fig. 4. Electron micrograph of crystals in dark-brown zones after 3 h of formation. Magnification bar = 1 μm .

Judging by their shape, these are $4\text{PbO}\cdot\text{PbSO}_4$ crystals. The latter are covered by a layer of small, grain-shaped PbO_2 particles. Numerous small pores can be distinguished between these particles. The process of oxidation passes from one crystal to the next at the points of contact. The $4\text{PbO}\cdot\text{PbSO}_4$ crystal marked by a circle has been broken off and its cross-section is clearly seen. Only the surface of the crystal has been oxidized: the interior is smooth and still unaffected by the oxidation process. The reaction layer where the electrochemical and chemical processes take place is at the interface between the surface PbO_2 layer and the unoxidized inner volume of the $4\text{PbO}\cdot\text{PbSO}_4$ crystal. Pores are also clearly visible.

It can be assumed that the conversion of $4\text{PbO}\cdot\text{PbSO}_4$ pastes to PbO_2 proceeds in two directions. First, the oxidation process spreads over adjoining crystals. There is a movement in the plate volume as a result of which zones of different phase composition are formed. These processes are called zone processes [10] and are responsible for the development of the macrostructural level of the active mass. In the second direction, oxidation proceeds inwards from the surface of the $4\text{PbO}\cdot\text{PbSO}_4$ crystals. During this process, the microstructural level is formed.

Relatively large crystals with well-defined walls, edges and apices can also be observed in Fig. 4. These crystals are not present in the initial paste. It follows, therefore, that they have grown during the process of formation. The XRD pattern of their phase composition suggests that these are PbSO_4 crystals. They result from the chemical reactions of PbO sulphatation. Their well-defined crystal shapes imply that the processes of PbSO_4 crystal growth proceed through the solution. Probably a certain part of the $4\text{PbO}\cdot\text{PbSO}_4$ crystals also undergoes sulphatation.

After 6 h of formation

An examination was made of the newly-formed PbO_2 agglomerates. For this purpose, samples of the plate were treated with ammonium acetate solution. Electron micrographs of the PbO_2 agglomerates are shown in Fig. 5.

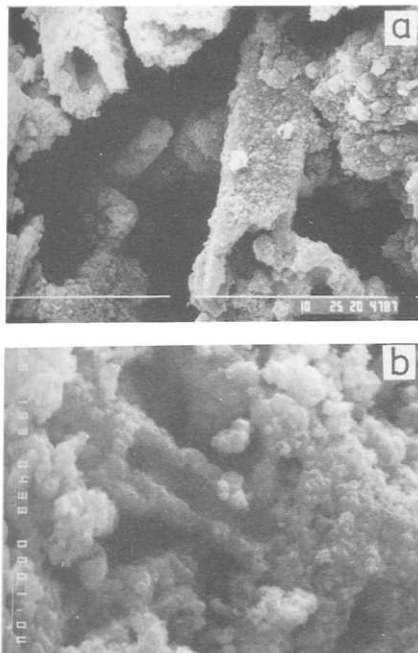


Fig. 5. Electron micrographs of PbO_2 agglomerates after 6 h of formation. Magnification bar: (a) $10\ \mu\text{m}$; (b) $1\ \mu\text{m}$.

When the unoxidized inner part of the $4\text{PbO}\cdot\text{PbSO}_4$ crystal is dissolved, channels are formed in the interior of the resulting PbO_2 agglomerate. During oxidation, grain-shaped $\beta\text{-PbO}_2$ crystals are formed and are separated by narrow pores.

It was considered instructive to examine the nature of the unoxidized inner part of the $4\text{PbO}\cdot\text{PbSO}_4$ crystals. This was achieved by treating a specimen of the active mass with a solution of H_2O_2 and HNO_3 , whereby the PbO_2 phase was dissolved. Only PbSO_4 and $4\text{PbO}\cdot\text{PbSO}_4$ were left. Electron micrographs of these crystals are given in Fig. 6.

The large crystals in the Figure are unoxidized parts of $4\text{PbO}\cdot\text{PbSO}_4$. The crystals with well-defined walls and edges are PbSO_4 . The oxidation process does not proceed uniformly throughout the $4\text{PbO}\cdot\text{PbSO}_4$ crystal. In some zones the oxidation results in the formation of steps, while in other parts, grains are formed. At some sites of the $4\text{PbO}\cdot\text{PbSO}_4$ crystal volume, the oxidation has reached deep into its interior, while other sites remain completely unaffected. This irregular progress of the oxidation process into the crystal inner volume may be due to:

- (i) a preceding chemical reaction;
- (ii) defects in the $4\text{PbO}\cdot\text{PbSO}_4$ crystal lattice;
- (iii) various ion transport hindrances through the PbO_2 layer.

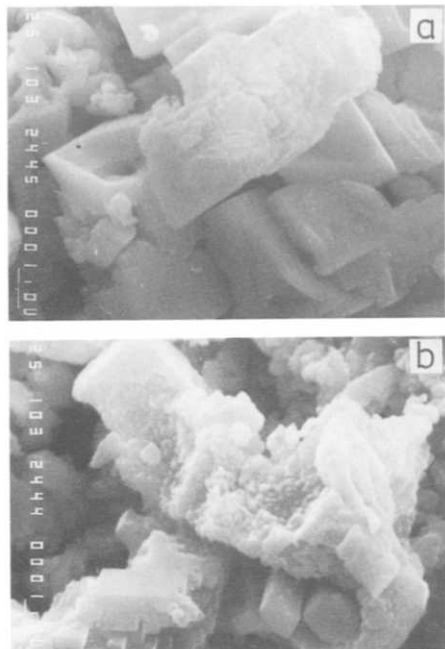


Fig. 6. Electron micrographs of unoxidized parts of $4\text{PbO}\cdot\text{PbSO}_4$ crystals and of PbSO_4 crystals after 6 h of formation. Magnification bar = $1\ \mu\text{m}$.

After 12 h of formation

Figure 7 presents an electron micrograph of crystals from the dark-brown zone of the plate. This zone comprises PbO_2 agglomerates and PbSO_4 crystals with rounded edges and apices. Obviously, oxidation of PbSO_4 has started and the crystal edges and apices have dissolved first. This indicates that the oxidation process passes through a stage of Pb^{2+} transfer through the solution in the pores.

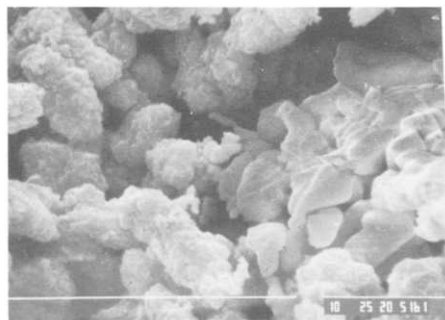


Fig. 7. Electron micrograph of crystals in paste and active mass after 12 h of formation. Magnification bar = $10\ \mu\text{m}$.

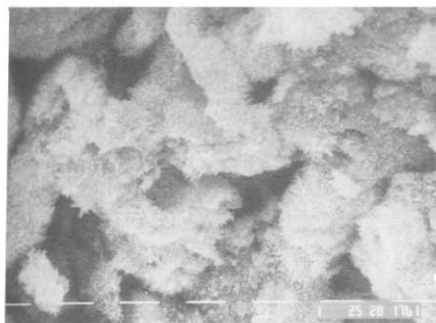


Fig. 8. Electron micrograph of PbO_2 agglomerates in active mass after 30 h of formation. Magnification bar = $1\ \mu\text{m}$.

After 30 h of formation

A micrograph of the formed active mass is shown in Fig. 8. Well-pronounced PbO_2 agglomerates are clearly seen. They reproduce the shape of $4\text{PbO}\cdot\text{PbSO}_4$ crystals. There are also agglomerates of different shape. These are probably formed as a result of PbSO_4 oxidation.

Data obtained from chemical analysis of the formed active mass showed that about 20% of the paste remained unoxidized. A sample of the active mass was treated with $\text{H}_2\text{O}_2 + \text{HNO}_3$ solution: it disintegrated into smaller, white grains. The structure of the latter is presented in Fig. 9. The contours of long, prismatic $4\text{PbO}\cdot\text{PbSO}_4$ crystals can be distinguished. It is worth noting that these crystals have the shape of interconnected grains. The latter may be due to the formation of a new phase. At some sites larger, smooth crystals are also found (circled areas). These are probably unoxidized parts of $4\text{PbO}\cdot\text{PbSO}_4$ crystals. These areas of the active mass were subjected to XRD phase analysis (Fig. 10).

Diffraction peaks for $4\text{PbO}\cdot\text{PbSO}_4$, PbSO_4 and $\beta\text{-PbO}_2$ can be clearly identified. The peaks are wide, implying that the residue is of fine crystals. It

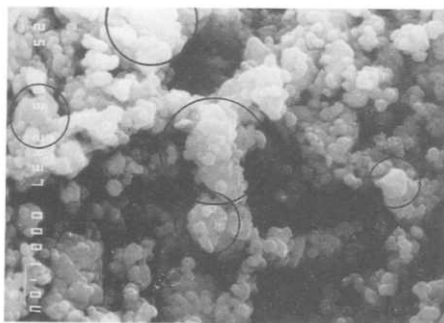


Fig. 9. Electron micrograph of non-formed parts of $4\text{PbO}\cdot\text{PbSO}_4$ crystals in inner volume of PbO_2 agglomerates after 30 h of formation. Magnification bar = $1\ \mu\text{m}$.

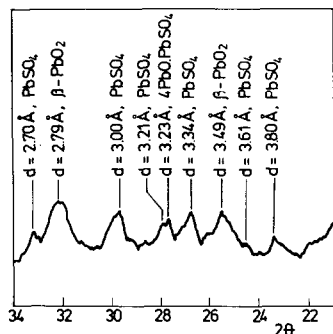


Fig. 10. XRD pattern of phase composition of non-formed, divalent lead compounds found in interior of PbO_2 agglomerates after 30 h of formation.

seems that $\beta\text{-PbO}_2$ has not been completely dissolved, while $4\text{PbO}\cdot\text{PbSO}_4$ crystals are not fully oxidized. The presence of PbSO_4 in the interior of the PbO_2 agglomerates can be explained if it is assumed that during $4\text{PbO}\cdot\text{PbSO}_4$ crystal oxidation a parallel chemical reaction of sulphatation proceeds in its interior. Probably the small, rounded crystals in Fig. 9 are PbSO_4 .

Discussion

Reaction scheme for the formation of PbO_2 and PbSO_4

A scheme of chemical and electrochemical reactions is presented in Fig. 11 for the oxidation of $4\text{PbO}\cdot\text{PbSO}_4$. The symbol θ is used to signify those Pb^{2+} ions formed from each $4\text{PbO}\cdot\text{PbSO}_4$ molecule that take part in the electrochemical (2) and chemical (3) reactions of PbO_2 formation. $(1 - \theta)$ represents the remaining part of the Pb^{2+} ions that are involved in the formation of PbSO_4 . For the reactions of formation to proceed, an exchange of H^+ and SO_4^{2-} ion flows, as well as H_2O (i.e., N_{H^+} , $N_{\text{SO}_4^{2-}}$, $N_{\text{H}_2\text{O}}$), is necessary between the reaction layer and the bulk of the electrolyte. The flows of H^+ and SO_4^{2-} ions maintain the electroneutrality of the reaction

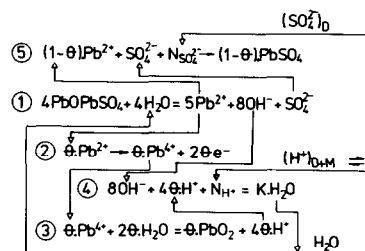


Fig. 11. Scheme for electrochemical and chemical reactions during formation of PbO_2 and PbSO_4 .

layer. Their transport hindrances may regulate the direction of the oxidation progress along the plate cross-section [10]. Since the product of reaction (3) is $\beta\text{-PbO}_2$ (Fig. 1), it may be concluded that the reaction proceeds in an acidic medium. The processes of oxidation and sulphatation of PbO have been discussed in previous work [10, 11], hence they will not be considered here.

Reaction scheme for PbSO_4 oxidation

The oxidation of PbSO_4 takes place at the same time as that of $4\text{PbO}\cdot\text{PbSO}_4$, but it probably occurs in other parts of the plate cross-section. The PbSO_4 oxidation processes have been studied earlier [11]; a reaction scheme is given in Fig. 12. Oxidation of PbSO_4 results in H_2SO_4 generation. The process occurs at relatively high potentials where the parallel electrochemical reaction of oxygen evolution takes place.

A reaction scheme for the oxidation of the interior of $4\text{PbO}\cdot\text{PbSO}_4$ crystals

When $4\text{PbO}\cdot\text{PbSO}_4$ crystals are covered with a layer of PbO_2 particles (PbO_2 agglomerate), the oxidation reactions proceed in the reaction layer at the interface between the agglomerate and the crystal surface. A characteristic feature of this stage is that there is no free movement of lead ions. The latter simply pass from the $4\text{PbO}\cdot\text{PbSO}_4$ crystal lattice to that of the nearest PbO_2 particle. The oxidation process can be presented by the reaction scheme given in Fig. 13.

For the individual reactions to proceed, flows of H_2O , H^+ ions and H_2SO_4 should pass through the PbO_2 layer covering the $4\text{PbO}\cdot\text{PbSO}_4$ crystals. These flows can be transported along the micropores between the particles.

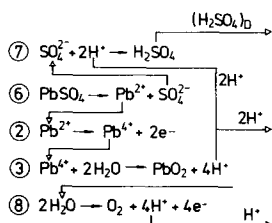


Fig. 12. Scheme for electrochemical and chemical reactions during PbSO_4 oxidation.

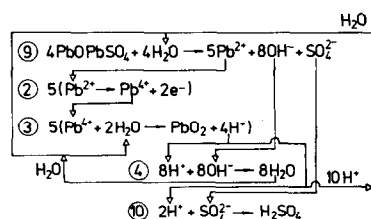


Fig. 13. Scheme for the reactions of oxidation of inner region of $4\text{PbO}\cdot\text{PbSO}_4$ crystals to PbO_2 agglomerates.

Another possibility also exists. The surfaces of the PbO_2 particles and parts of their inner volumes are hydrated [12, 13]. These hydrated layers can serve as channels along which the movement of H_2O and H^+ ions is realized. During electrochemical reactions (2) and (3), positive charges are formed (see Fig. 13). The latter have to be released out of the particles into the solution through the PbO_2 layer. For each oxidized molecule of $4\text{PbO}\cdot\text{PbSO}_4$, ten H^+ ions are liberated. They migrate through the PbO_2 layer along the above channels.

The oxidation of each $4\text{PbO}\cdot\text{PbSO}_4$ molecule is accompanied by the evolution of one molecule of H_2SO_4 . It may be expected that the movement of the large SO_4^{2-} ions through the PbO_2 layer will be greatly impeded when its thickness exceeds a certain value. Consequently, the PbO_2 layer plays the role of a semi-permeable membrane for SO_4^{2-} ions. This will cause H_2SO_4 to accumulate in the reaction layer and thereby interact with $4\text{PbO}\cdot\text{PbSO}_4$ to form PbSO_4 . The latter was detected by X-ray phase analysis (Fig. 10). It was assumed that the small, unoxidized crystals in the interior of the PbO_2 agglomerates consisted of PbSO_4 (Fig. 9). Oxidation of this PbSO_4 is greatly hindered. If the PbSO_4 layer is formed between the $4\text{PbO}\cdot\text{PbSO}_4$ surface and the layer of PbO_2 , further oxidation of $4\text{PbO}\cdot\text{PbSO}_4$ will stop or will proceed at a very slow rate. This can be seen in Fig. 1 after 20 h of formation. Deep cycling of the plate is necessary to disintegrate part of the PbO_2 agglomerates and thus facilitate the transport of H_2SO_4 from the crystal interior to the solution during charge.

The above reaction schemes show that the conditions of $4\text{PbO}\cdot\text{PbSO}_4$ crystal oxidation to PbO_2 agglomerates are significantly different at the surface and in the interior of the agglomerate. These differences will probably cause differences in the structure and properties of PbO_2 particles in different regions of the agglomerates which will, in turn, affect their reduction during discharge.

References

- 1 J. Burbank, *J. Electrochem. Soc.*, 113 (1966) 10.
- 2 R. V. Biagetti and M. C. Weeks, *Bell Syst. Tech. J.*, 49 (1970) 1305.
- 3 D. Pavlov, E. Bashtavelova and V. Iliev, in K. R. Bullock and D. Pavlov (eds.), *Advances in Lead-Acid Batteries, Vol. 84-14*, The Electrochem. Soc. Inc., Pennington, NJ, U.S.A., 1984, p. 16.
- 4 D. Pavlov and G. Papazov, *Electrochemical Power Sources*, Dum Techniky CVTS, Prague Zari, Czechoslovakia, 1975, p. 49.
- 5 C. F. Yarnell and M. C. Weeks, *J. Electrochem. Soc.*, 126 (1979) 7.
- 6 T. J. Hughel and R. H. Hammer, in D. H. Collins (ed.), *Power Sources 3*, Oriol Press, Newcastle upon Tyne, U.K., 1971, pp. 35 - 57.
- 7 J. Pierson, in D. H. Collins (ed.), *Power Sources 2*, Pergamon Press, Oxford, 1970, p. 103.
- 8 D. Pavlov and E. Bashtavelova, *J. Electrochem. Soc.*, 131 (1984) 1468.
- 9 D. Pavlov and E. Bashtavelova, *J. Electrochem. Soc.*, 133 (1986) 241.
- 10 D. Pavlov and G. Papazov, *J. Electrochem. Soc.*, 127 (1980) 2104.
- 11 D. Pavlov, G. Papazov and V. Iliev, *J. Electrochem. Soc.*, 119 (1972) 8.
- 12 D. Pavlov, E. Bashtavelova, V. Manev and A. Nasalevska, *J. Power Sources*, 19 (1987) 15.
- 13 D. Pavlov, I. Balkanov, T. Halachev and P. Rachev, *J. Electrochem. Soc.*, 136 (1989) 3189.