Influence of the size of PbSO₄ crystals on their solubility and the significance of this process in the lead-acid battery

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When the PbO_2 plate of the lead–acid battery is discharged, small $PbSO_4$ crystals are initially formed which subsequently undergo recrystallization. In this paper the driving forces of the $PbSO_4$ recrystallization process are established. The change in solubility of the small $PbSO_4$ crystals with time in 1 M and 0.1 M H_2SO_4 is determined. Initially the solubility is high and decreases with time to reach a steady value, in agreement with that in the literature. SEM observations indicate that this process is associated with an increase in the volume of the $PbSO_4$ crystals. The surface free energy of $PbSO_4$ is estimated and a scheme for the recrystallization process at the PbO_2 active mass is proposed.

1. Introduction

The discharge of the lead–acid battery PbO_2 plate passes through a sequence of elementary processes that can be classified into two distinct stages [1].

(i) Reaction stage. During this stage the electrochemical and chemical reactions proceed. These can be expressed by the general equation:

$$PbO_2 + H_2SO_4 + 2H^+ + 2e$$
$$= (PbSO_4)^0 + 2H_2O$$
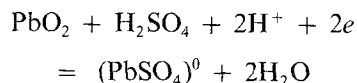
where $(PbSO_4)^0$ represents the initially formed lead sulphate crystals. No $PbSO_4$ crystals have been distinguished when scanning the active mass under an electron microscope during the first 1 or 2 h of the plate discharge [2]. This is due to the fact that the initially formed $(PbSO_4)^0$ crystals are very small and similar in shape and appearance to that of PbO_2. Also, many of the $PbSO_4$ crystals are formed in the micropores of the agglomerates of which the active mass is comprised.

(ii) Recrystallization stage. If the discharge process proceeds for a longer period of time or the discharged plate is left at open circuit, a recrystallization process takes place. This can be represented as follows:

$$(PbSO_4)^0 \longrightarrow (PbSO_4)^i$$
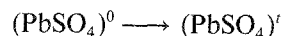
The aim of this paper is to determine why the process of recrystallization of $PbSO_4$ takes place in a discharged positive plate.

2. Experimental details

2.1. Formation of fine PbSO₄ crystals

We have tried to find a method for the formation of $PbSO_4$ crystals with sizes of approximately 0.1 μm or smaller. This is the order of magnitude of the $PbSO_4$ crystals formed during the reaction stage of the discharge. Small crystals can be obtained when the rate of nucleation is much higher than that of crystal growth. They are produced via mixing of concentrated solutions of Pb^{2+} and SO_4^{2-} ions. We found that $PbSO_4$ crystals of the required size and appearance can be obtained by treating basic lead sulphate crystals ($3PbO \cdot PbSO_4 \cdot H_2O$ or $4PbO \cdot PbSO_4$) with highly concentrated sulphuric acid (specific gravity 1.6) with continuous stirring. The $PbSO_4$ molecules in the basic sulphates serve as a nuclei,
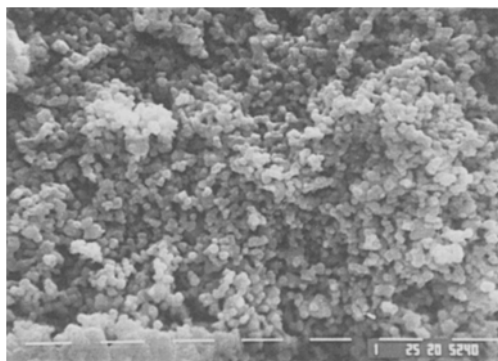
Fig. 1. PbSO$_4$ crystals. Scale bar: 1 μm.

while the constant PbO/PbSO$_4$ ratio in them ensures the growth of equal-sized PbSO$_4$ crystals. The sulphation process was carried out at room temperature to keep the crystal growth at a low rate. After the complete transformation of the basic lead sulphate into PbSO$_4$ the deposit was filtered, washed, and dried at 105° C. To check the purity of PbSO$_4$ thus obtained, the deposit was subjected to X-ray and electron diffraction analyses.

2.2. Morphology and structure of the PbSO$_4$ crystals obtained by sulphation of 4PbO · PbSO$_4$

SEM observations of crystals obtained by sulphation of 4PbO · PbSO$_4$ suggest that they consist of small, equal-sized grains of PbSO$_4$ gathered in porous agglomerates (Fig. 1). The

same is also true for PbSO$_4$ obtained from 3PbO · PbSO$_4$ · H$_2$O.

2.3. Determination of solubility of PbSO$_4$ crystals

The solubility of PbSO$_4$ crystals at different solid phase–solution ratios was determined (1.5 g PbSO$_4$ in 100, 150 and 200 ml of 1 M H$_2$SO$_4$ solution). The values varied within a range of 6% which is the relative error of the experiment. Subsequently, all experiments were carried out with 1.5 g PbSO$_4$ in 150 ml H$_2$SO$_4$.

The cell was closed and put in a thermostat at 30° C. Stirring was performed by sparging with argon which was presaturated in saturating vessels containing an H$_2$SO$_4$ solution of the same concentration as the solution in the cell.

Samples were taken both from the solution and the deposit at fixed intervals. After filtration the sample from the solution was diluted to 50 ml. The lead content was determined via atomic absorption analysis at $\lambda = 283.3$ nm. Samples from the deposit were washed and dried and the morphology of the crystals was determined by SEM.

2.4. Literature values of the solubility of PbSO$_4$

Table 1 presents literature values of PbSO$_4$ solubility at 30° C and the method for its determination.

Table 1. Literature values of PbSO$_4$ solubility at 30° C

|	C$_{PbSO_4}$ (mg dm^{-3}) at 30° C			
	1 M H$_2$SO$_4$	0.1 M H$_2$SO$_4$	Method of determination	Reference
Afifi et al. (28° C)	6.6	–	No information	[3]
Dawkins and Weldon	10.5	7.1	Titration with Na$_2$S$_2$O$_3$ after precipitation from CH$_3$COONH$_4$ solution as chromate	[4]
Kamayama and Fukumoto	7.5	–	Colourimetric in which brown solution of PbS is formed	[5]
Huybrechts and Ramelot	9.55	7.13	Colourimetric in which sulphate is converted to colloidal sulphur	[6]
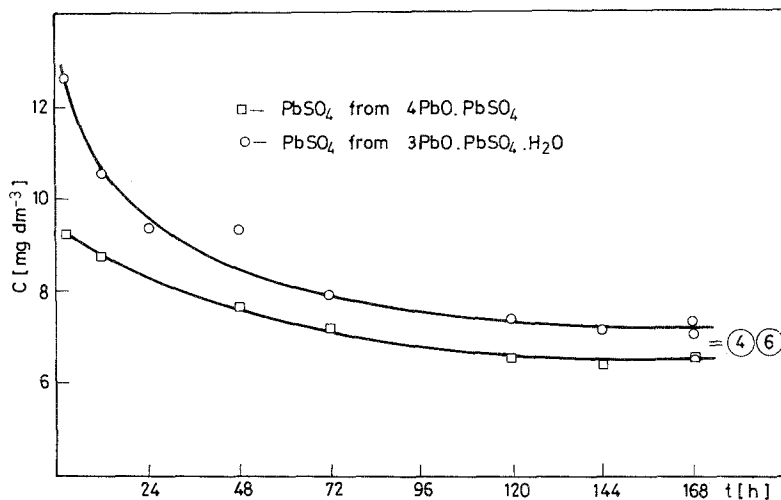
Fig. 2. Changes of the concentration of $PbSO_4$ in the solution during the time of stay of $PbSO_4$ crystals in $0.1\,M$ H_2SO_4. Encircled numbers represent the solubility data presented by the authors as indicated in Table 1.

3. Results

3.1. Changes in the solubility of PbSO₄ crystals in H₂SO₄ solution

Fig. 2 presents the change in the concentration of $PbSO_4$ in the solution during the stay of $PbSO_4$ crystals in $0.1\,M$ H_2SO_4. The solubility data from papers [4] and [6] are encircled. Initially the solubility of $PbSO_4$ obtained from $3PbO \cdot PbSO_4 \cdot H_2O$ is higher (by 64%) than the literature value, while for $PbSO_4$ obtained from $4PbO \cdot PbSO_4$ the difference is 41%. The solubility decreases with time and after about 120 h it reaches a steady value for both types of

$PbSO_4$. Evidently, the difference between the solubility curves at the beginning is due to the origin of the $PbSO_4$ crystals.

Fig. 3 presents the change in solubility of $PbSO_4$ crystals during their stay in $1\,M$ H_2SO_4. Here also the initial solubility is very high and decreases with time reaching a steady value which is almost equal to that given in [4] and [6]. The value given in [5] is somewhat lower. At this H_2SO_4 concentration the solubility of $PbSO_4$ obtained from $4PbO \cdot PbSO_4$ is initially lower than that of $PbSO_4$ obtained from $3PbO \cdot PbSO_4 \cdot H_2O$. However, in only 24 h this difference disappears and the steady value is reached by the 96th h. On comparing Figs 2 and 3 it is
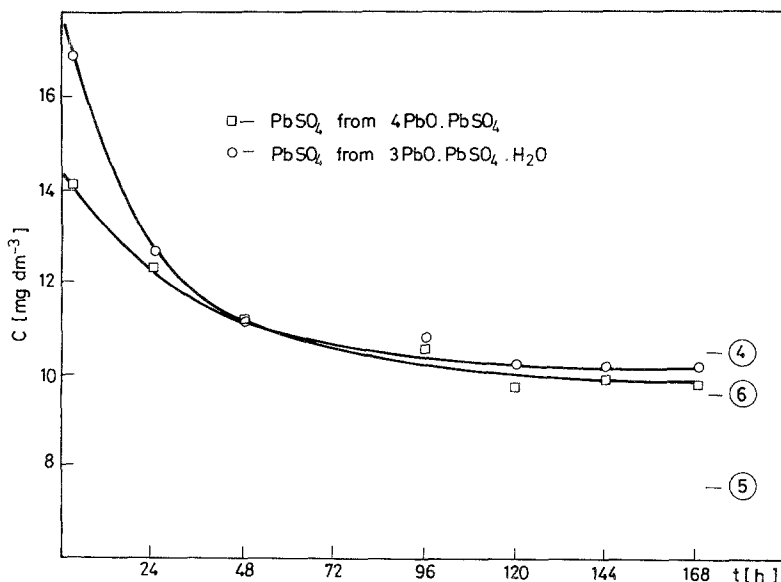

Fig. 3. Changes of $PbSO_4$ concentration in the solution during the time of stay of $PbSO_4$ crystals in $1\,M$ H_2SO_4. Encircled numbers represent the solubility data presented by the authors as indicated in Table 1.

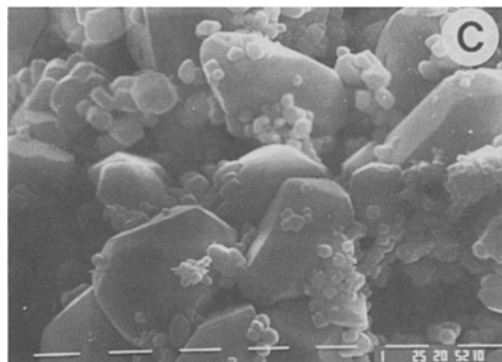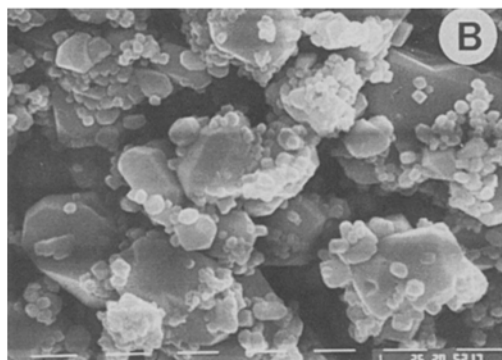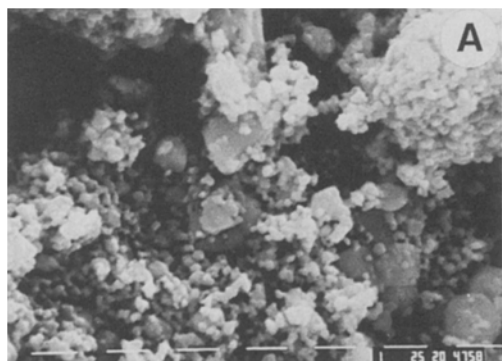Fig. 4. SEM micrographs of $PbSO_4$ crystals at (A) the 6th, (B) the 72nd, (C) the 192nd h of their time in 0.1 M H_2SO_4. The $PbSO_4$ crystals were obtained from $4PbO \cdot PbSO_4$. Scale bars: 1 μm.

Fig. 5. SEM micrographs of $PbSO_4$ crystals at (A) the 6th, (B) the 24th, (C) the 96th h of their time in 1 M H_2SO_4. The $PbSO_4$ crystals were obtained from $3PbO \cdot PbSO_4 \cdot H_2O$. Scale bars: 1 μm.

evident that the rate of $PbSO_4$ recrystallization in 1 M H_2SO_4 is higher than that in 0.1 M solution.

3.2. Changes in the morphology of $PbSO_4$ crystals in H_2SO_4 solution

Fig. 4 presents a series of SEM micrographs of the $PbSO_4$ crystals at the 6th, 72nd and 192nd h of their stay in 0.1 M solution. These $PbSO_4$

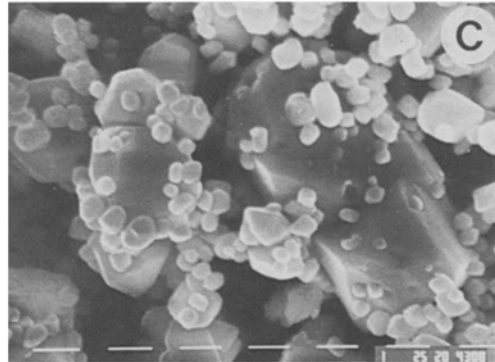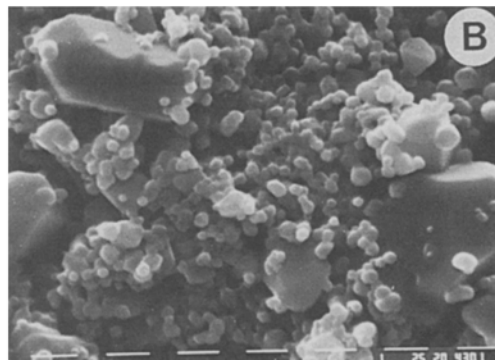crystals were obtained from $4PbO \cdot PbSO_4$. It is evident that $PbSO_4$ crystals grow with time to reach sizes which are almost one order of magnitude bigger than the initial sizes.

Fig. 5 presents a series of SEM micrographs of $PbSO_4$ crystals at the 6th, 24th and 96th h of their stay in 1 M H_2SO_4. These $PbSO_4$ crystals were obtained from $3PbO \cdot PbSO_4 \cdot H_2O$. Again, a similar trend to that seen in Fig. 4 is observed.
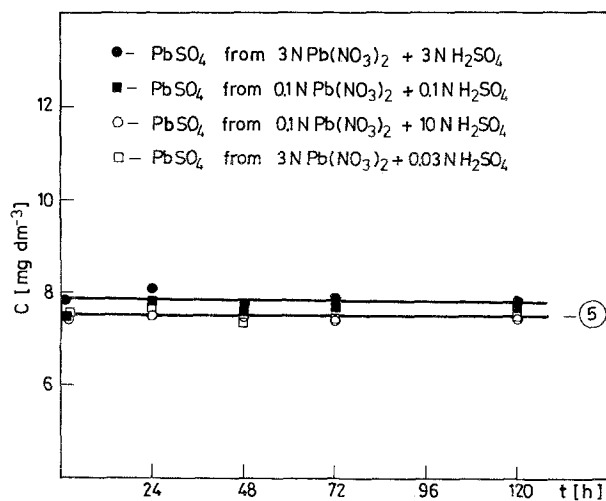
Fig. 6. Concentration of PbSO₄ in the solution, C (mg dm^{-3}) versus time, t (h) in 1 M H₂SO₄. The PbSO₄ crystals were obtained from different combinations of Pb(NO₃)₂ and H₂SO₄ as indicated in Table 2.

If Figs 2, 3, 4 and 5 are compared it becomes clear that the solubility of PbSO₄ crystals decreases as a result of their growth.

3.3. Effect of the concentration ratio of the Pb(NO₃)₂ and H₂SO₄ solutions on the morphology, size and solubility of PbSO₄ crystals

In the previous section we discussed the behaviour of small PbSO₄ crystals during their stay in H₂SO₄ solution. How do large PbSO₄ crystals behave under the same conditions? To find an answer to this question, PbSO₄ crystals were obtained by mixing Pb(NO₃)₂ and H₂SO₄ solutions of different concentrations. The concentration ratios are presented in Table 2.

PbSO₄ crystals were obtained by mixing equal volumes of Pb(NO₃)₂ and H₂SO₄ solutions with continuous stirring. To prevent recrystallization the deposit was immediately filtered, washed and dried. The solubility and morphology of the PbSO₄ crystals were then determined.

Table 2. Concentration ratios of Pb(NO₃)₂ and H₂SO₄ in solution

Combination	Pb(NO₃)₂ (N)	H₂SO₄ (N)
A	0.1	10
B	0.1	0.1
C	3	0.03
D	3	3

Fig. 6 gives the solubility of PbSO₄ crystals, obtained using the combinations indicated in Table 2, versus time in 1 M H₂SO₄. It can be seen that the solubility of the four types of PbSO₄ crystals remains almost unchanged. The solubility values determined coincide with those of Kamayama and Fukumoto [5].

Fig. 7 presents SEM micrographs of the morphology of dry PbSO₄ crystals obtained using the above combinations of concentrations of the initial solutions. It can be seen that in general the nucleation rate is considerably lower than that of the crystal growth. The nucleation rate is high only for combination D (Table 2) where both reacting solutions are highly concentrated; here, a large quantity of small-sized crystals is formed (Fig. 7D). Their size, however, is not smaller than 0.5–1 μm. On comparing them with those of Fig. 1 it becomes clear that comparatively large crystals are obtained on mixing solutions of Pb(NO₃)₂ and H₂SO₄.

For combinations A and C (Table 2) there is a great difference between the concentrations of the reacting solutions, and dendrites are formed upon mixing of the solutions. The length and width of the dendrites are from 5 to 25 μm and from 1 to 2 μm respectively (Fig. 7A, C). In the case $C_{Pb}^{2+} > C_{SO_4}^{2-}$ the dendrites are strongly branched (Fig. 7C). For combination B both reacting solutions have low concentrations and the dendrites obtained have a smaller cross-section and differ from one another in length quite significantly (Fig. 7B).
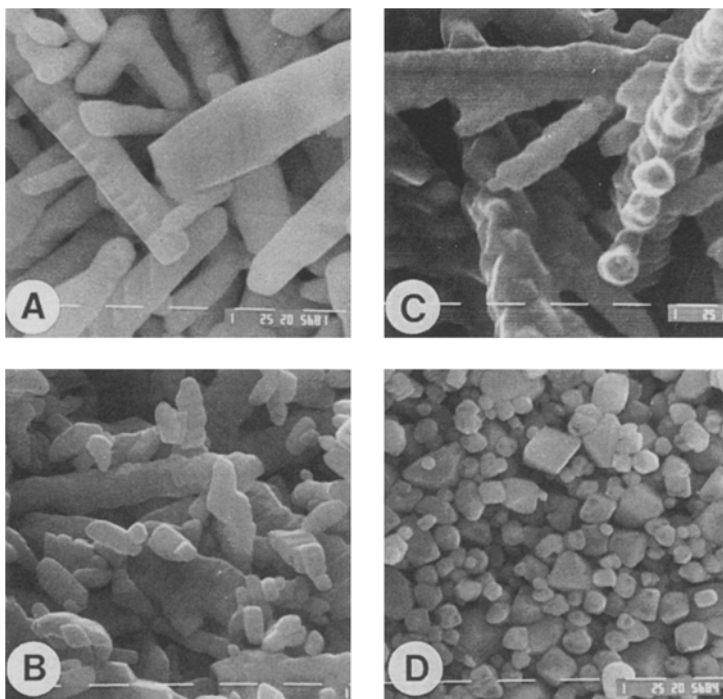
Fig. 7. SEM micrographs of PbSO$_4$ crystals obtained from different combinations of Pb(NO$_3$)$_2$ and H$_2$SO$_4$ as indicated in Table 2. Scale bar: 1 μm.

When comparing Figs 6 and 7 it may be concluded that the solubility of PbSO$_4$ crystals becomes independent of their size for dimensions greater than 0.5 μm.

The PbSO$_4$ crystals have been observed after 100 h in 1 M H$_2$SO$_4$ solution. The crystals from all four combinations had undergone recrystallization and the grown crystals possessed well-delineated walls, edges and apices.

4. Discussion

4.1. Calculation of the surface free energy of PbSO$_4$ crystals

It is well known that the smallest particles determine the solubility of a deposit. The equilibrium ion concentration of the solution above the small crystals (C) is higher than that of the same ions above the large ones (C_∞). This difference predetermines the process of recrystallization during which the large crystals grow at the expense of the small ones. The inter-relation between the surface free energy (σ), the crystal radius (r) and the ion concentration above large and small crystals is expressed by the Ostwald—

Freundlich equation:

$$\ln \frac{C}{C_\infty} = \frac{2V_M \sigma}{RTr} \tag{1}$$

This equation is applicable to systems in equilibrium. The phenomenon under consideration is actually a process of recrystallization during which the small crystals are in a state of subsaturation, while the large ones are in a state of supersaturation. Figs 2 and 3 indicate that the process of recrystallization proceeds very slowly. This justifies our conjecture that the system is in a state of quasi-equilibrium.

Fig. 1 indicates that the size distribution of the initial PbSO$_4$ crystals is in a very narrow range and that the PbSO$_4$ crystals is in a very narrow range and that the PbSO$_4$ crystals have a near-spherical geometry. Thus we assume for the value of r the value of the arithmetic mean measured from the micrographs of the initially formed PbSO$_4$. Through a statistically significant number of measurements it was established that PbSO$_4$ crystals obtained from 4PbO · PbSO$_4$ have an average radius of 0.088×10^{-4} cm, while for those from 3PbO · PbSO$_4$ · H$_2$O the average is 0.098×10^{-4} cm.

On the basis of the above considerations we can assume the validity of Equation 1 and calculate the surface free energy of PbSO₄ crystals. We take for C the value determined at the second hour of the experiments. The period of 2 h is sufficiently long for the concentration to reach a steady value and is still insufficient for the progress of recrystallization leading to the emergence of great differences in the PbSO₄ crystal volumes. The other components of Equation 1 have the following meaning and values: V_M is the molar volume of PbSO₄ ($V_M = 47.96\,cm^3\,mol^{-1}$), T is the temperature in K ($T = 303\,K$), R is the gas constant ($R = 8.314\,J\,K^{-1}\,mol^{-1}$). Inserting values for V_M, R and T into Equation 1 gives

$$\sigma = 26.26r \ln C/C_\infty \qquad (2)$$

Substituting the experimental values of r, C and C_∞ into Equation 2 gives the σ values shown in Table 3.

There are few experimental estimates of the value of σ for PbSO₄ in the literature. The number of experimentally determined σ values for BaSO₄, SrSO₄ and CaSO₄ in electrolytic solutions is considerably greater. These values may be classified into two groups. The first is within the 5×10^{-6} to $2 \times 10^{-5}\,J\,cm^{-2}$ range [7, 8] and the second comprises the range 4×10^{-5} to $2 \times 10^{-4}\,J\,cm^{-2}$ [9]. Nielsen and Sohnel [8] have determined the value of σ using data for crystal nucleation for a number of salts, including PbSO₄. They found that for PbSO₄, $\sigma = 1 \times 10^{-5}\,J\,cm^{-2}$.

The purpose of our investigations is to simulate the processes that take place in the porous active mass of the lead–acid battery positive plate, where PbSO₄ crystals are placed under similar conditions. It may be expected that this specific structure creates the necessary condi-

tions for the formation of crystal surface defects, especially at places where the crystals are attached to one another. These crystal defects affect the surface energy value. This is probably one of the main reasons why the σ data obtained in the present study are in the high value range.

Table 3 illustrates yet another fact, namely that the effect of H₂SO₄ concentration on σ is comparatively weak. Thus, a tenfold concentration increase leads to a change in σ of less than 10%.

There are also other equations in the literature treating the relation between surface energy, crystal radius and solubility [7, 10]. When calculating σ using the equations of Lifshitz and Slezov [7] or of Enustun and Turkevich [10] values for σ are higher than those obtained from the Ostwald–Freundlich equation.

4.2. Mechanism of the recrystallization process in the pores of the PbO₂ active mass

The structure of the PbO₂ active mass comprises two levels [1, 11].

(i) Microstructure. At this level the smallest element is the PbO₂ crystal. A huge quantity of PbO₂ crystals gather to form a microporous agglomerate. Micropores of the agglomerate have small volume and large surface area. The electrochemical reaction that takes place at this surface is responsible for the capacity of the plate.

(ii) Macrostructure. The porous agglomerates join together and form an intensively branched framework. Macropores are formed between the branches of the latter. They have a large volume and a small surface area. Macropores serve as a main transport system in which H^+ and SO_4^{2-} ions flow and water moves between the bulk of the electrolyte and the interior parts of the active mass.

In conformity with this model the results of the present investigation may be interpreted within the following scheme for the recrystallization stage of the positive active mass discharge. Nuclei and small PbSO₄ crystals are formed in the micropores of the agglomerates during the discharge reaction. This maintains a high concentration of Pb^{2+} ions and of PbSO₄ in the solution within the micropores of the

Table 3. Values of surface free energy obtained experimentally

Source of PbSO₄	$\sigma \times 10^{-7}\,(J\,cm^{-2})$	
	1 M H₂SO₄	*0.1 M H₂SO₄*
3PbO · PbSO₄ · H₂O	1310	1425
4PbO · PbSO₄	825	790

agglomerates. On the other hand, each macropore is connected with a large number of micropores that supply Pb^{2+} ions and $PbSO_4$ complexes. Sulphate ions coming from the bulk of the solution also flow easily within the macropore. This facilitates the formation and growth of large $PbSO_4$ crystals. The large $PbSO_4$ crystals maintain low concentrations of Pb^{2+} ions and of $PbSO_4$ complexes in the bulk of the solution in the macropores. In this way the concentration gradients of Pb^{2+} ions and of $PbSO_4$ complexes between the micro- and macropores emerge. Under the action of these gradients Pb^{2+} ions and $PbSO_4$ complexes move from the micro- into the macropores. This leads to the dissolution of $PbSO_4$ nuclei or small crystals in the micropores, while the $PbSO_4$ crystals in the macropores grow.

The molar volume of $PbSO_4$ is greater than that of PbO_2. The existence of this recrystallization stage is more or less one of the reasons for the prevention of blocking of the micropores by $PbSO_4$ crystals during the discharge. This enables PbO_2 crystals from the inside of the agglomerates to take part in the discharge. So the recrystallization stage of the discharge represents one of the conditions for the increase in the utilization coefficient of the PbO_2 active mass.

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