

Short communication

Dynamics of the composition of positive plates during the preformation period

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Abstract

The soaking step of battery formation, was investigated after the addition of 181 ml of sulfuric acid solution to plates that were allowed to rest for 5, 10, 15 and 30 min and then removed and dried. The same procedure was repeated three more times with new plates and allowed to rest in sulfuric acid solution for minutes. The results indicate plates with a higher content of sulfate display a final monobasic lead sulfate content larger than displayed by plates with smaller amounts of sulfate. Crystal sizes were also followed as a function of time during the soaking period, demonstrating the possibility of extending the use of X-ray diffraction in the observation of crystal sizes of lead compounds in this and any other step of battery production.

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1. Introduction

The final stage in battery production is the electrochemical conversion of the cured plates to active material (PbO₂ in the positive and Pb in the negative plate). This initial charging, known as formation, is usually preceded by a soaking period in sulfuric acid solution which may range from several minutes to a couple of hours [1,2]. During this period reactions take place that are accompanied by heat evolution [1]. These reactions are of fundamental importance to the subsequent process [3]. Initially sulfuric acid reacts with oxides and basic sulfates causing density changes in solution and in the plate, whose extent depends on the initial concentration of sulfuric acid, the initial plate composition and the extent of soaking. The different products of these reactions behave differently during the electrochemical charging step. Consequently it would be very useful to know more precisely how these soaking period reactions proceed with time in order to optimize formation and battery performance.

2. Experimental

Aiming to investigate the process of immersion of positive plates in sulfuric acid solutions (1.14 g/ml) prior to the charging process, two types of cured plates with the initial composition given in Table 1 were used.

The first type (low density) is characterized by similar amounts of tribasic (3BS) and tetrabasic (4BS) lead sulfates with a lower amount of oxide. The high density plate has a much higher 4BS content as well as a higher oxide percentage due to the lower amount of sulfuric acid solution used in the preparation of this plate.

To simulate container formation a cell consisting of one positive plate inside a polyethylene separator, between two negative plates was placed inside a small Plexiglas box of 154 mm × 115 mm × 16 mm (length × height × width). Each cured plate has 72 g of dried active material. After the addition of 181 ml of sulfuric acid solution the plates were allowed to rest for 5 min and then removed and dried. The same procedure was repeated three more times with new plates and allowed to rest in sulfuric acid solution for 10, 15 and 30 min. The dried plates were then prepared for powder X-ray diffraction analysis. X-ray intensities were collected with Cu K α radiation in a Siemens D 5000 Diffractometer, in the range of 5–60°. Steps of 0.02° and 1.0 s were employed

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Table 1
Initial composition of cured plates

	3BS (%)	4BS (%)	1BS (%)	α -PbO (%)
Low density plate	39.5	40.3	3.0	17.3
High density plate	5.7	61.7	0.0	32.6

for width and counting time, respectively. Quantitative analysis was carried out by means of the software PEAKS [4]. Crystal sizes were determined by profile fitting of the following phases: 1BS ($2\theta = 26.65^\circ$), 3BS ($2\theta = 9.03^\circ$), and 4BS ($2\theta = 10.70^\circ$).

3. Results and discussion

The dynamics of the composition of cells prepared with the high density plate that has a much higher 4BS content is shown in Fig. 1 and the results of phase composition versus time of the low density plate characterized by similar amounts of tribasic (3BS) and tetrabasic (4BS) lead sulfates is shown in Fig. 2.

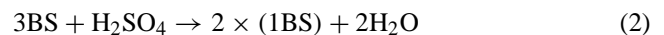
It can be seen that in low density plate there is a large increase in 1BS percentage whereas PbSO_4 changes significantly only in the end of the experiment. A significant decrease in 4BS can also be observed. On the other hand, high density plate displays a smaller increase in 1BS and a much larger variation in PbSO_4 than the previous plate. The initial behavior of 3BS in high density plate (increase) is opposite of that observed in low density plate (decrease). The other phases behave similarly in both plates:

no significant variation in β -PbO, and gradual decrease in α -PbO.

From the X-ray data it was also possible to obtain estimates of crystal dimensions. The results of crystal dimensions versus time for each phase in both plates are shown in Figs. 3 and 4.

It is seen that 1BS has the smallest dimensions among the basic sulfates and remain essentially unchanged during the period investigated. On the other hand, for plates with low density (and lower 4BS content) there is a clear decrease in dimensions for the 4BS phase, which may indicate a dissolution process with conversion to 3BS. In the case of high density plates (and higher 4BS content) there is no clear tendency. It seems that 4BS dimensions increase slightly which may be due to the preferential dissolution of the smaller crystals and retention of the larger ones, since the values obtained from X-ray diffraction are average sizes.

Based on these observations and on the most probable chemical processes, the following routes can be proposed for the reactions taking place:



Two routes produce 3BS: 1 and 4. The observation of initial increase in 3BS and PbSO_4 is used to support this proposition. The disappearance of α -PbO by another route, e.g. producing 1BS, could not explain the smaller increase in 1BS in a plate with higher initial α -PbO.

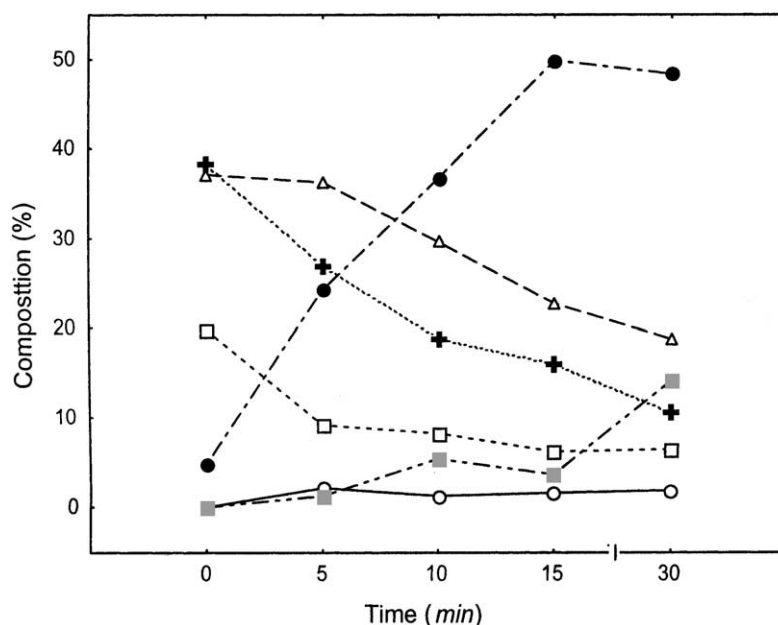


Fig. 1. Composition vs. time for low density plate. (\square) α -PbO; (\circ) β -PbO; (\bullet) 1BS; (\triangle) 3BS; (\blackplus) 4BS; (\blacksquare) PbSO_4 .

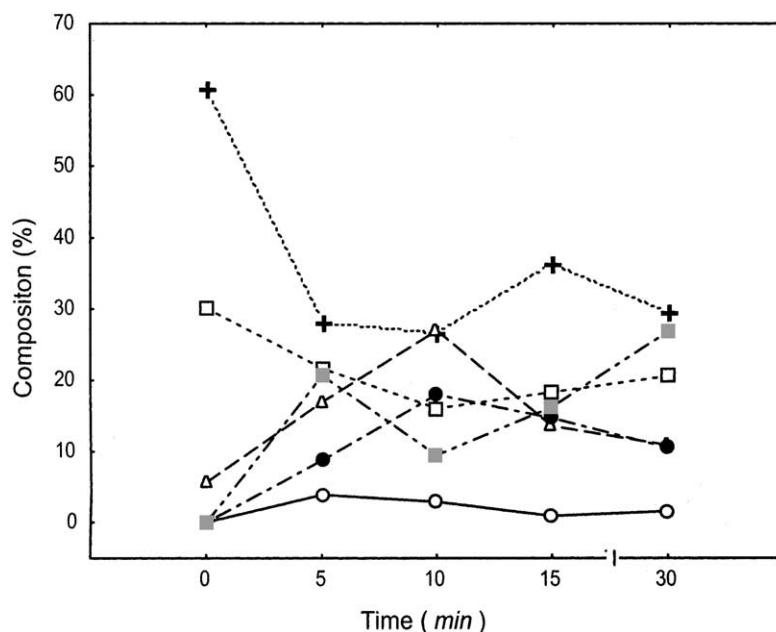


Fig. 2. Composition vs. time for high density plate. (□) α -PbO; (○) β -PbO; (●) 1BS; (△) 3BS; (⊕) 4BS; (■) PbSO₄.

The large increase in 1BS observed on a plate with high initial 3BS is used as argument to support route 2. And, finally, route 3 is supported by the complementary behavior of 1BS and PbSO₄ observed in the figures.

Formation of 1BS from 3BS could occur also by: $3BS \rightarrow 1BS + 2PbSO_4$. However, this would cause a large increase in PbSO₄ not observed on a plate with 3BS initially high (low density plate).

Since in this experiment, after 30 min of soaking it seems that the composition remains relatively constant, formation

could start after that time. However, for low density plates the large amount of 1BS produced could be detrimental to plate integrity because of the known deleterious effects of this phase, associated with the crystal structure of 1BS. In such cases, formation should start immediately after addition of sulfuric acid solution. It seems also that 3BS should not be present in large amounts to avoid formation of 1BS. On the other hand it can be argued that the large increase in 1BS may be due to the initial presence of this phase in the cured plate, acting as a seed (or catalyst) for its production.

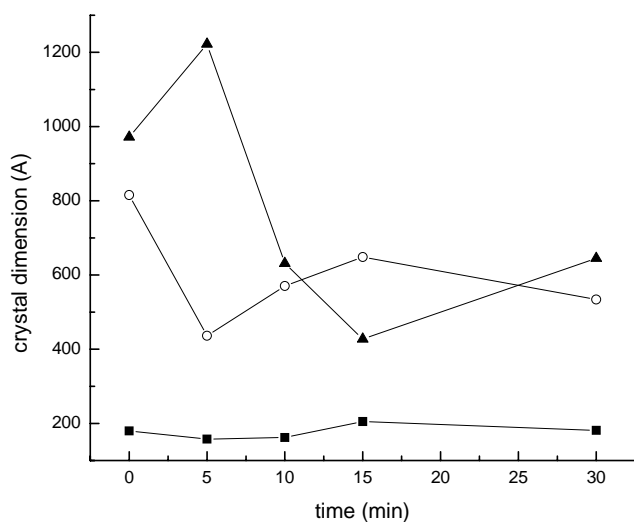


Fig. 3. Crystal dimension vs. time for low density plate. 4BS (▲), 3BS (○), 1BS (■).

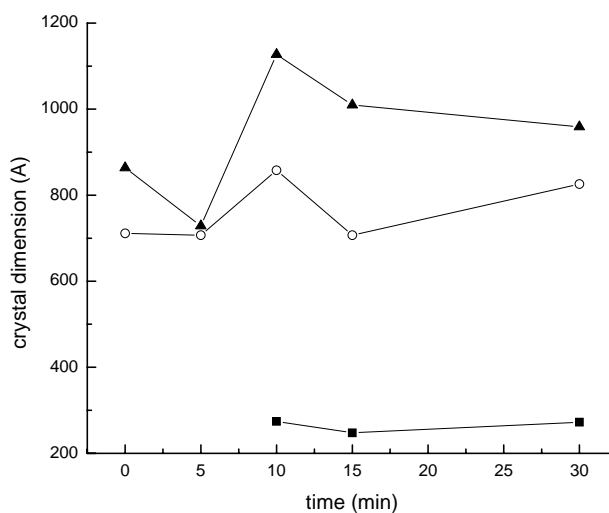


Fig. 4. Crystal dimension vs. time for high density plate (average of three measurements). 4BS (▲), 3BS (○), 1BS (■).

4. Conclusions

During the investigation of the soaking step in battery formation, it was observed that plates with a smaller content of sulfate display a final monobasic lead sulfate content bigger than those displayed by plates with smaller amounts of sulfate. In order to explain this behavior, two hypotheses are proposed: (a) 3BS could lead to monobasic sulfate crystallization; and (b) 1BS initially present in the plates could act as seeds for further crystallization. As to the crystal growth and dimensions, they are in agreement with results commonly found in the literature [5], demonstrating the possibility of extending the use of X-ray diffraction in the observation of crystal sizes of lead compounds in this and any other step of battery production.

Acknowledgements

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