Processes in positive lead/acid battery plates during soaking prior to formation

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Abstract

Before switching on the current for formation of the active mass of lead/acid batteries, cured plates stay for a certain period of time in H_2SO_4 solution at open circuit. This period is called 'soaking' or 'pickling'. The cured paste consists of PbO ($\alpha + \beta$) and basic lead sulfates (3BS or 4BS). They are unstable in H_2SO_4 solution and, hence, the chemical reactions of sulfation proceed. This work reports a study of these chemical processes for 3BS pastes through chemical and X-ray phase analysis and scanning electron microscopic observations. Sulfation has been studied during soaking in H_2SO_4 solutions of three concentrations (sp. gr. 1.05, 1.15 and 1.25) for 8 h. Soaking was performed in batteries assembled with cured plates. It is established that soaking in H_2SO_4 of sp. gr. 1.05 results in the formation of 3BS, 1BS and, after 4 h, small amounts of $PbSO_4$. In more concentrated H_2SO_4 solutions (sp. gr. 1.15 and 1.25), $PbSO_4$ predominates. Capacity, cold-cranking and cycle-life tests have been performed with batteries soaked in the three H_2SO_4 concentrations for different periods of time. It is established that, depending on the acid concentration and the duration of soaking, the battery capacity may be increased by 10%, and the time of high-rate discharge at -18 °C may be prolonged by about 1 min. Battery life may also be improved. These results indicate that soaking should be introduced as a separate technological procedure under constant control in order to ensure good and stable battery performance characteristics.

Introduction

The performance of lead/acid battery positive plates depends strongly on the structure of the lead dioxide active mass. The latter consists of a skeleton, built up of agglomerates and macropores. Agglomerates, in their turn, comprise particles and micropores [1].

The production technology aims at forming the optimum structure of the positive active material (PAM). As a rule, the following technological procedures are included in battery production:

(i) Paste preparation. Through mixing of leady oxide with H_2O and H_2SO_4 solution basic lead sulfate pastes are prepared. When the temperature of mixing is below 65 °C, $3PbO \cdot PbSO_4 \cdot H_2O$ (3BS) is obtained, while above 70 °C the obtained paste contains $4PbO \cdot PbSO_4$ (4BS). These pastes are pasted over plate grids.

(ii) Plate curing. Pasted plates are put into a curing chamber set at definite temperature and humidity. If curing is conducted at a temperature higher than 70 °C, 4BS pastes are obtained. Basic lead sulfates and lead oxide recrystallize and are interconnected into a skeleton. The metal surface is oxidized and the resulting corrosion layer is bonded to the paste skeleton.

(iii) Plate formation. PbO and mPbO $\cdot$ PbSO$_4$ crystals are oxidized to PbO_2 through metasomatic processes. Owing to the latter, the skeleton matrix of the cured paste is

transferred on to the structure of the active mass. The 3BS and 4BS crystals are converted into agglomerates of PbO_2 particles.

Prior to formation, the plates are arranged in tanks that contain H_2SO_4 solution, or positive and negative plates are assembled into cells that are flooded with H_2SO_4 solution. There is a certain period of time during which the plates soak in H_2SO_4 solution with no electric current passing. This period is called 'soaking' or 'pickling'. Its duration is usually from several minutes to several hours. During this period, PbO and $mPbO \cdot PbSO_4$ react with H_2SO_4 and the processes of sulfation of the plate start. These processes cause the structure and morphology of the crystals in the cured paste to change.

Lam et al. [2] report that on soaking of 4BS plates in H_2SO_4 of sp. gr. 1.25 for 35 h, a considerable part of the cured paste is converted into $PbSO_4$. The 4BS and PbO crystals are covered by a $PbSO_4$ layer which, after 25 h of soaking, may reach up to 3 μm in thickness. During formation, oxidation of $PbSO_4$ proceeds at a higher rate than that of 4BS.

Only a limited amount of information is available on the processes of soaking. The aim of the present work is to investigate these processes at different H_2SO_4 concentrations and at different paste/electrolyte ratios that correspond to the conditions of real battery production.

Experimental

Plate preparation

Through mixing of leady oxide with H_2O and H_2SO_4 solution (sp. gr. 1.40) in a ratio of 4.5% H_2SO_4/PbO at 40 °C, pastes were prepared with a density 4.1 g cm^{-3} and a phase composition of 3BS, α-PbO and β-PbO. Automotive grids made of Pb–1.6wt.%Sb–0.2wt.%As–0.2wt.%Sn alloy were pasted with the pastes. The plates were subjected to curing at 30 °C and 95–100% r.h. for 72 h. All investigations of the soaking process were performed with these plates.

Technology of the soaking investigation

Cells with four positive and five negative unformed plates, separated by polyethylene separators, were subjected to soaking in H_2SO_4 of sp. gr. 1.05, 1.15 and 1.25. One cm^3 of electrolyte per 1.423 g of paste (both positive and negative) was added. The ratios g H_2SO_4/kg paste for all three H_2SO_4 concentrations are given in Table 1.

After filling the cells with H_2SO_4 solution, the specific gravity was measured every hour and samples were taken from two of the positive plates (both situated in the centre of the cell) to determine the phase composition of the paste. After soaking for 1, 2, 5 and 8 h, samples were taken for chemical analysis and scanning electron microscopic (SEM) observations of the paste structure and crystal morphology.

Determination of battery performance

Twelve 12-V/46-Ah batteries were assembled. Four batteries were subjected to soaking at each of the three H_2SO_4 concentrations. After 0, 2, 5 and 8 h of soaking,

TABLE 1

Acid/paste ratios for test cells

H_2SO_4 sp. gr.	1.05	1.15	1.25
g H_2SO_4/kg paste	56.8	172.8	297

the current was switched on and the batteries were subjected to formation in the same solution for 24 h by application of the standard cyclogram developed in the authors' laboratories. After formation, the H_2SO_4 solution was poured out and the batteries were filled with new H_2SO_4 solution that, in every case, was adjusted to a sp. gr. of 1.28. The batteries were then subjected to testing under the DIN 43539/2 schedule. Three capacity measurements, two cold-cranking and cycle-life tests (for some of the batteries) were performed.

Results

Acid concentration during soaking

Figure 1 presents the changes in specific gravity of the electrolyte during soaking of the cells at the three H_2SO_4 concentrations.

At all three concentrations, the highest rate of sulfation is observed during the first hour of soaking. After that, it gradually decreases until the fifth hour. Thereafter, the changes in concentration become very small. After 8 h of soaking in H_2SO_4 of sp. gr. 1.05, 78% of the H_2SO_4 has reacted with the positive and negative plates. When soaking is performed in H_2SO_4 of sp. gr. 1.15, the amount of reacted H_2SO_4 is 71%, and in 1.25 sp. gr. it is 52%.

Chemical composition of paste during soaking

Figure 2 illustrates the changes in PbO and $PbSO_4$ content in the paste during soaking of the positive plates in the three H_2SO_4 concentrations. The rate of sulfation is highest in the first hour of soaking. After 8 h of soaking, the amount of $PbSO_4$ in the positive paste increases by 22, 47 and 60% for acid of 1.05, 1.15 and 1.25 sp. gr., respectively.

Phase composition of paste during soaking

It was established that the cured paste contains α-PbO, β-PbO and 3BS. During soaking, $PbO \cdot PbSO_4$ (1BS) and $PbSO_4$ are formed. Figure 3 presents the changes in intensity of the characteristic diffraction lines for the above phases during soaking. It can be seen that during the first 10 min, the content of α-PbO and 3BS decreases
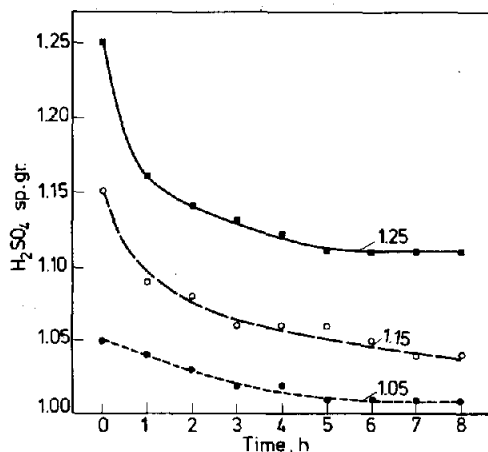

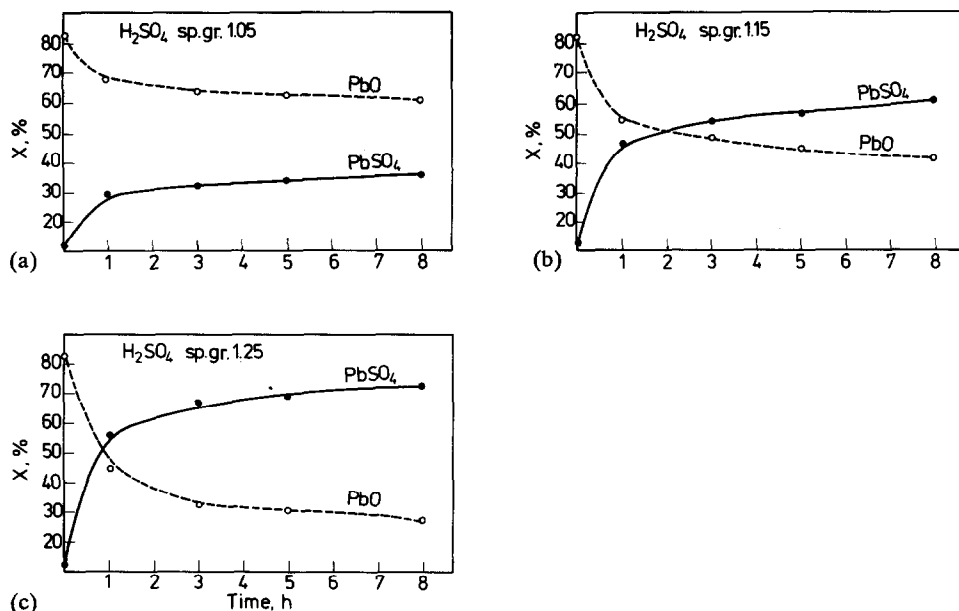Fig. 1. Changes in electrolyte sp. gr. in cells during soaking.

Fig. 2. Changes in chemical composition of the paste during soaking in three H_2SO_4 concentrations (a) sp. gr. 1.05; (b) sp. gr. 1.15; (c) sp. gr. 1.25.

rapidly, while β-PbO undergoes sulfation more slowly. After that, the rate of the sulfation reactions decreases.

On soaking in H_2SO_4 of sp. gr. 1.05, the principal products of sulfation are 1BS and 3BS, with small amounts of $PbSO_4$ formed after 4 h. The 1BS is formed at the beginning of soaking and the 3BS 2 h later. Probably, 3BS crystals in the surface layers undergo faster sulfation due to the lower pH of the solution in their pores. As H_2SO_4 is consumed, its concentration in the plate interior decreases and the pH increases to reach the region of the thermodynamic stability of 3BS. The PbO is sulfated to 3BS. That is why, after 2 h of soaking, the content of 3BS in the paste is increased, especially if soaked in H_2SO_4 of sp. gr. 1.05. After 5 h of soaking, the amount of 1BS is the same for all three H_2SO_4 concentrations. This is not the case with $PbSO_4$, however. The higher the H_2SO_4 concentration the greater the amount of $PbSO_4$ formed in the paste.

Paste structure and crystal morphology

Figures 4 to 6 present electron micrographs of paste crystals and structure after 1, 3 and 8 h of soaking in the three H_2SO_4 concentrations. The paste structure at the surface and in the interior of the plate is shown.

When soaking is performed in H_2SO_4 of sp. gr. 1.05 (Fig. 4), needle-like crystals typical of 1BS are formed at the surface of the plate during the first hour. The 1BS crystals in the plate interior are much smaller in size. After 3 and 8 h of soaking, small prismatic crystals characteristic of 3BS are also observed.

Figure 5 shows that 1BS crystals formed in H_2SO_4 of sp. gr. 1.15 are considerably smaller in size than those obtained in H_2SO_4 of sp. gr. 1.05. At the end of soaking, well-formed $PbSO_4$ crystals are also observed at the plate surface. These have resulted from recrystallization processes. The crystals are situated in and over a shapeless mass
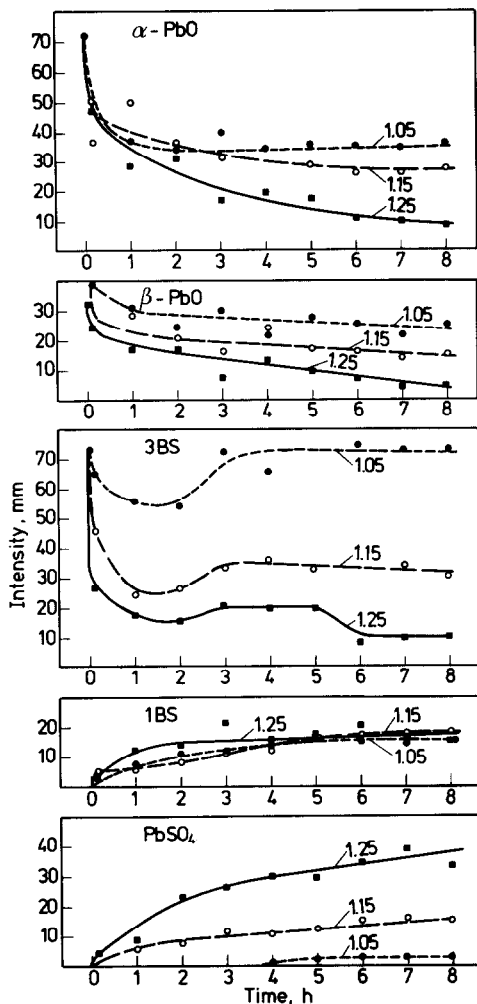
Fig. 3. Changes in intensity of characteristic X-ray diffraction lines for different phases in the paste during soaking in three H_2SO_4 concentrations.

(probably consisting of amorphous $PbSO_4$) in which nuclei of $PbSO_4$ crystallites are also detected. After 8 h of soaking, well-shaped $PbSO_4$ crystals are observed in the interior of the plate only in some of the micrographs.

Figure 6 presents micrographs of a paste that has undergone soaking in H_2SO_4 of sp. gr. 1.25. Needle-like crystals of 1BS are detected at the surface of the paste only during the first hour. These disappear after 3 h and are converted into well-pronounced $PbSO_4$ crystals. Shapeless crystals and amorphous mass are formed in the interior of the plate which recrystallize later into well-shaped $PbSO_4$ crystals (8th h).

These results are in good agreement with the X-ray patterns that represent the phase composition of the pastes. The electron micrographs, however, show the formation of a shapeless mass in H_2SO_4 of sp. gr. 1.25, which may be assigned to amorphous character. It is known that often an amorphous species of $PbSO_4$ is formed first and
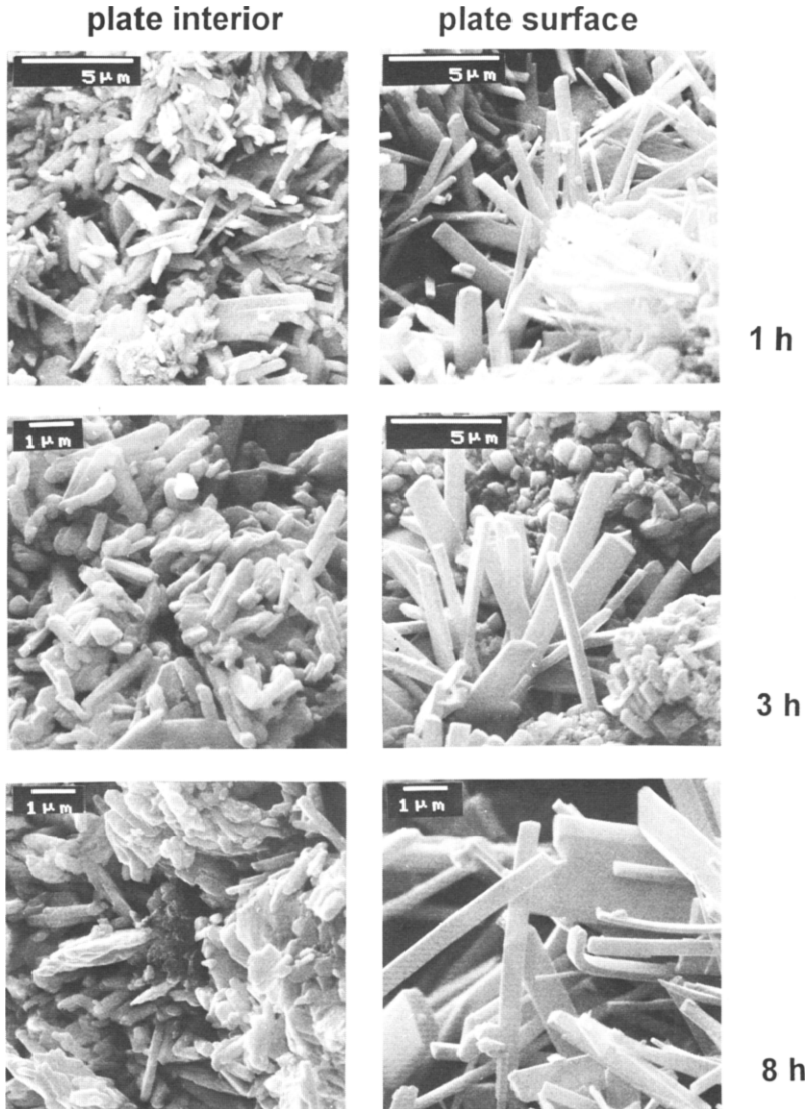
plate interior   plate surface

1 h

3 h

8 h

Fig. 4. Electron micrographs of paste structure and crystal morphology at the surface and in the interior of a plate soaked in H_2SO_4 of sp. gr. 1.05.

then, through recrystallization, well-shaped $PbSO_4$ crystals are formed with pronounced walls, edges and corners. This process depends on the concentration of H_2SO_4.

Battery test results

Capacity tests

Figure 7 presents the results from the three capacity measurements for batteries with plates that have been soaked in H_2SO_4 solution of all three concentrations for 0, 2, 5 and 8 h, respectively. The utilization of the positive active mass was 50% in
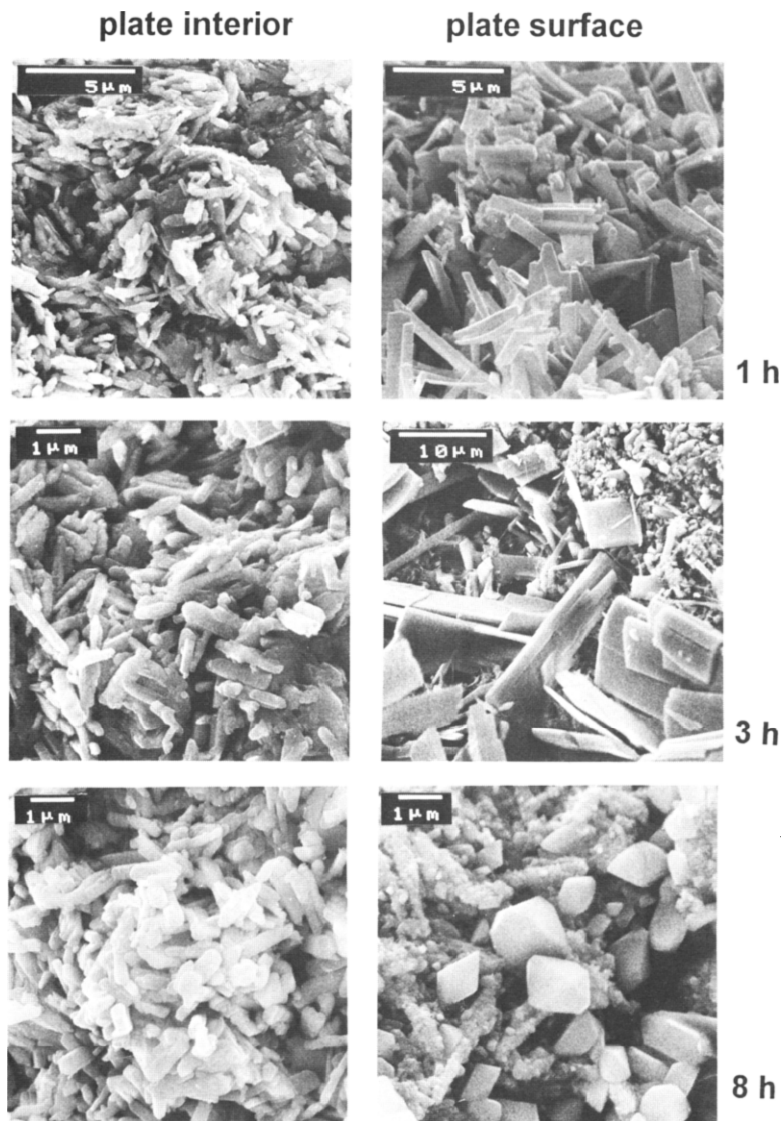
Fig. 5. Electron micrographs of paste structure and crystal morphology at the surface and in the interior of a plate soaked in H_2SO_4 of sp. gr. 1.15.

all tests. The capacity measurements were performed at 20-h rate of discharge and 25 °C.

When soaking is performed in H_2SO_4 of sp. gr. 1.05, the first capacity measured is always low, irrespective of the time of soaking. Only on the second measurement the value is close to and over 100%. The third capacity measurement does not differ substantially from the second. The difference between the values of the first and the third capacity measurements is most significant at the beginning of soaking. This difference may be related to the phase composition of the paste. Figure 3 shows that the phase composition is stabilized between the 5th and 8th h of soaking, and
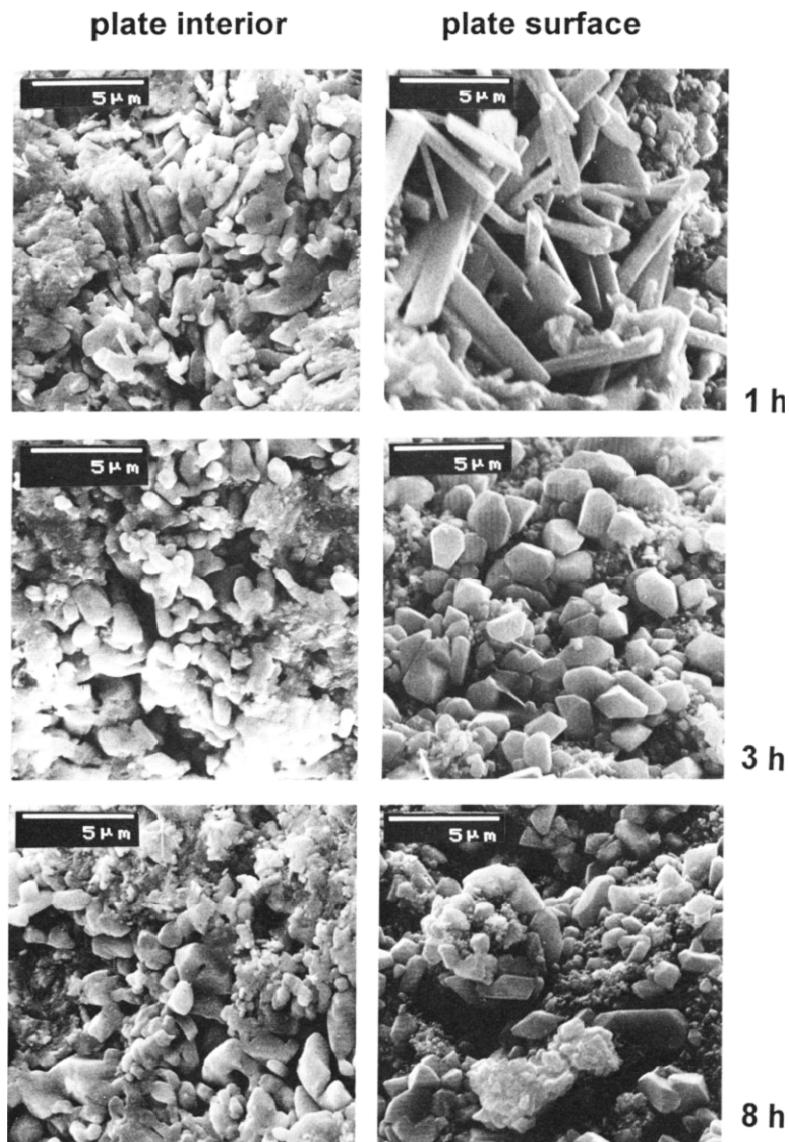
plate interior   plate surface

Fig. 6. Electron micrographs of paste structure and crystal morphology at the surface and in the interior of a plate soaked in H_2SO_4 of sp. gr. 1.25.

the difference between the three capacity measurements is the smallest within this time interval. It is well known that the capacity of the positive plate is determined by the structure of the active mass and the corrosion layer, as well as by the contact between them.

The most beneficial conditions for soaking are the following: H_2SO_4 of sp. gr. 1.15 and 2 to 5 h of soaking. The content of $(\alpha + \beta)$ PbO and 3BS in these pastes is almost half that in the cured plaste. 1BS and a considerable, though not excessive, amount of $PbSO_4$ are also formed (Fig. 3).
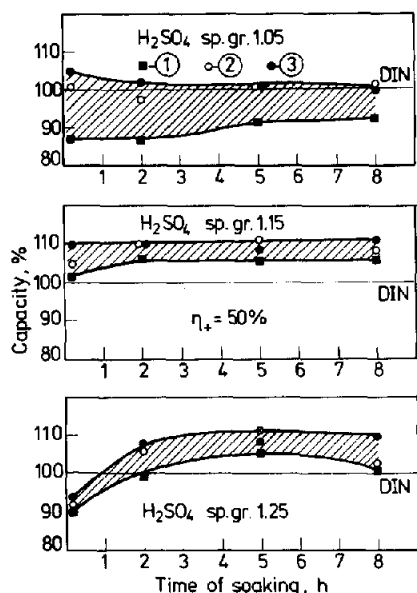
Fig. 7. Battery capacity vs. soaking time in three H_2SO_4 concentrations: (■) first, (○) second, (●) third capacity measurements, respectively, under DIN 43539/2 test.
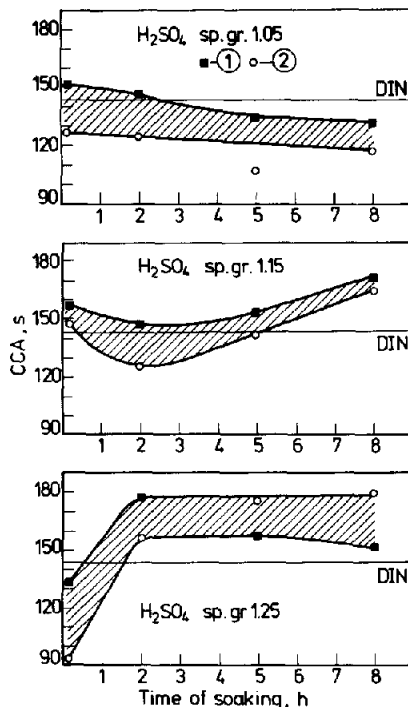
Fig. 8. Dependence of CCA on soaking time in three H_2SO_4 concentrations: (■) first, (○) second CCA test at -18 °C under DIN 43539/2 requirements.

When the current is switched on immediately after filling of the batteries with H_2SO_4 of sp. gr. 1.25 (0 h of soaking), all three of the capacity values are below 100%. H_2SO_4 reacts with the paste instantly, but the time is too short for the growth of sufficiently large crystals (Fig. 6) and the formation of an appropriate paste skeleton that has good contact with the corrosion layer. This is achieved after 2 h of soaking. The plate capacity in this case reaches values higher than 100%.

The small difference between the three capacity values measured for batteries soaked in H_2SO_4 of sp. gr. 1.15 and 1.25 indicates that plates sulfated under the above conditions have a stable structure. This means that $PbSO_4$ crystals, when of a definite size, ensure high plate capacity.

From the above results, it follows that through variation of the conditions of soaking, the capacity may be increased by about 10%.

Cold-cranking tests

The quantity of the negative active material in the batteries under test was chosen so that the negative plates would not affect the cold-cranking ability (CCA) at -18 °C. The CCA performance was determined only by the positive half-block. The CCA tests were performed with a current of $i = 5\ C/20$ A at -18 °C. Figure 8 presents the results obtained.

When soaking and formation are conducted in H_2SO_4 of sp. gr. 1.05, the resulting PAM structure does not ensure high power, especially at 5 to 8 h of soaking. Such batteries do not meet DIN requirements. After 0 and 2 h of soaking, only the first CCA test shows a discharge time that is longer than the required standard value.

When soaking and formation are performed in H_2SO_4 of sp. gr. 1.15 and 1.25, almost all the batteries meet DIN requirements. Obviously, sulfation exerts a beneficial influence on the CCA of positive plates. Only batteries soaked in H_2SO_4 of sp. gr. 1.25 exhibit a CCA performance that is lower than the required DIN value.

The above results show that through varying the conditions of soaking, the time of high-rate discharge at -18 °C can be prolonged by almost one minute.

Cycle-life tests

Cycle-life tests were performed with three batteries soaked for 2 h in H_2SO_4 of sp. gr. 1.05, 1.15 and 1.25. The period of 2 h is very close to the actual conditions of lead/acid battery production. After determining the capacity and the CCA, the batteries under test were subjected to cycle-life tests according to the requirements of the DIN 43539/2 standard.

The one-week test cycle involves 10 charge (at constant voltage)/discharge (with constant current) cycles at 40 °C. The end-of-discharge voltage is measured at the 10th cycle. A period of 65 h at open circuit and 40 °C follows, and then the CCA is measured at -18 °C and $i = 5$ $C/20$ A. The voltage at the 30 s is measured.

Figure 9 presents the end-of-discharge values measured at the 10th charge/discharge cycle, as well as the voltage after 30 s during the CCA tests for the three types of batteries. When soaking and formation are conducted in H_2SO_4 of sp. gr. 1.05, the batteries are only one cycle short of the standard requirements. On the other hand, batteries soaked and formed in H_2SO_4 sp. gr. of 1.15 and 1.25 meet these requirements.
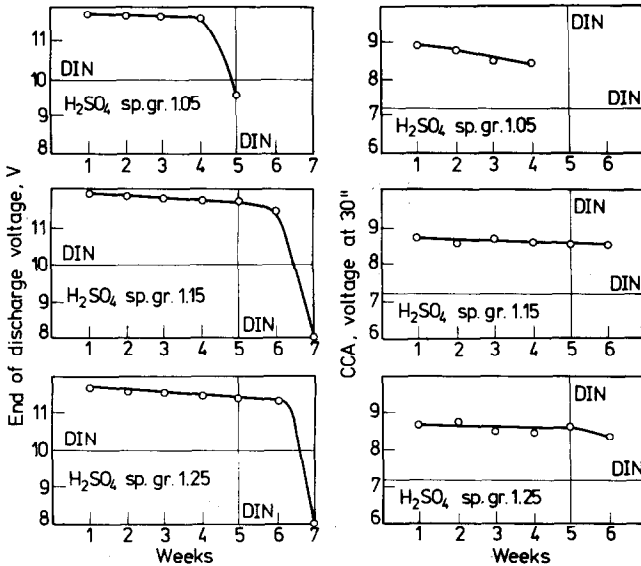

Fig. 9. End-of-discharge voltage (at 10th cycle) and voltage after 30 s during DIN 43539/2 CCA tests of batteries soaked for 2 h and formed in H_2SO_4 of sp. gr. 1.05, 1.15 and 1.25.

On completion of the tests, the batteries were disassembled and the positive plates examined. The grids were not affected by corrosion. The active mass in the upper-most parts of some of the plates had stuck to the separators and shed off in pellets from the grid. Most of the plates, however, appeared to be in good condition. On shaking of the plates, large pellets of the PAM were detached from the grids. Probably, the contact between the corrosion layer and the PAM had lost mechanical strength during cycling and, hence, electrical conductivity. The active mass skeleton was quite strong. It can be concluded, therefore, that the positive battery plates have been affected by the phenomena that cause premature capacity loss (PCL) [3].

Discussion

Bode and Voss [4] have studied the thermodynamic states of the system PbO/H_2SO_4/NaOH. In alkaline solution, lead takes the form of $HPbO_2^-$ ions, whilst in acid media, it is present as Pb^{2+} ions.

Figure 10 gives the solubility curves for both types of lead ions (Pb^{2+} and $HPbO_2^-$) at 25 °C. The least soluble compound is thermodynamically the most stable one. The diagram shows the stability regions of the lead compounds at $a_{SO_4^{2-}} = 1$. At lower activities of SO_4^{2-}, the stability regions shift to lower pH values and, vice versa. A three-coordinate representation of the above system (potential/pH/H_2SO_4 concentration) was suggested by Bullock [5].

The 3BS-rich paste maintains the pH value in the pore solution within the range 9.6–10. On soaking, pH decreases due to the H_2SO_4 flow that enters the pores of the paste. In this way, 3BS and PbO ($\alpha + \beta$) move out of the region of their thermodynamic stability and, as a result, the reactions of sulfation start to promote the formation of 1BS and $PbSO_4$:
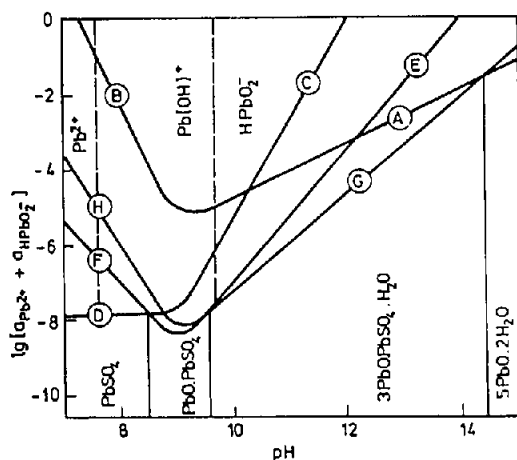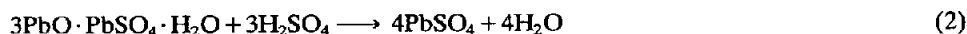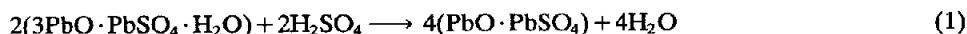
$$2(3PbO \cdot PbSO_4 \cdot H_2O) + 2H_2SO_4 \longrightarrow 4(PbO \cdot PbSO_4) + 4H_2O \tag{1}$$

$$3PbO \cdot PbSO_4 \cdot H_2O + 3H_2SO_4 \longrightarrow 4PbSO_4 + 4H_2O \tag{2}$$

$$4PbO + H_2SO_4 \longrightarrow 3PbO \cdot PbSO_4 \cdot H_2O \tag{3}$$

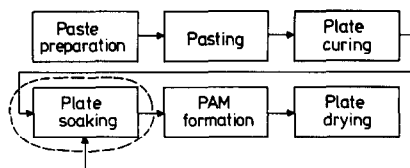Fig. 10. Solubility curves of phases in PbO/H_2SO_4/NaOH system vs. solution pH [4].

Fig. 11. Technological scheme for the production of positive lead/acid battery plates.

Depending on the solution pH, the phases 3BS, 1BS and $PbSO_4$ are formed in the pores in different ratios. Figure 3 shows that, when soaking is performed in H_2SO_4 of sp. gr. 1.05, up to the second hour, sulfation of both PbO and 3BS proceeds and yields 1BS and, probably, amorphous $PbSO_4$. As a consequence, the H_2SO_4 concentration is decreased and the pH in the pores of the paste increases and reaches the zone of 3BS stability. Sulfation of 3BS stops and its formation starts at the expense of PbO $(\alpha + \beta)$. Small amounts of $PbSO_4$ are detected only after 4 h of soaking. Probably these are at the surface of the plate, where the concentration of H_2SO_4 is the highest.

When soaking is performed in H_2SO_4 of sp. gr. 1.15, the concentration of H_2SO_4 in the pore solution is high enough to facilitate the formation of $PbSO_4$ crystals at the very beginning of soaking. The quantity and the size of these crystals grow slowly until the eighth hour. Figure 1 indicates that the sp. gr. of H_2SO_4 is 1.04 at the end of soaking, i.e., it is sufficiently high to maintain a low pH in the solution. In the bulk of the paste, however, the solution pH is higher and formation of 3BS is observed (though at a lower rate).

On soaking in H_2SO_4 of sp. gr. 1.25, the H_2SO_4 flow in the interior of the plate is intense and the rate of $PbSO_4$ formation from 3BS and PbO is the highest. Thus, after 8 h of soaking, $PbSO_4$ is the predominant phase in the paste.

On plate formation, the oxidation of basic lead sulfates, PbO and $PbSO_4$ to PbO_2 proceeds through metasomatic processes, whereby the matrix of the paste is transferred to that of the active mass. After curing, however, the structure of the cured paste undergoes significant changes during soaking. The latter changes significantly the phase composition and structure of the cured paste and these changes depend strongly on the concentration of H_2SO_4 and the duration of soaking. Hence, during formation, the structure of the soaked (and not cured) paste would be transferred to the matrix of the active mass. This would exert its effect on the capacity and the cycle life of the battery. That is why soaking should be considered as an autonomous technological procedure that plays an important role in determining battery performance and, therefore, should be controlled carefully (Fig. 11).

Thus, the technological procedures included in the production of positive battery plates are: paste preparation, pasting, curing, soaking, formation, and drying of the plates. Only when each of these procedures is under constant monitoring can the batteries produced be expected to have the desired performance characteristics.

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