

Influence of cycling on the nature of the positive active mass of lead/acid batteries and effect of CaSO_4 on the behaviour of the positive plates

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Abstract

Through cycling of tubular powder electrodes filled with positive active mass (PAM) powder obtained from positive SLI plates with pure-lead grids, it has been established that during cycling PAM loses its ability to restore its skeleton structure. X-ray diffraction investigations have shown that the crystallinity of PAM increases on cycling. This is probably the reason for the loss of PAM's ability to restore its skeleton structure. This ability is influenced by some metal ions called binders. The results of the present investigation indicate that Sn^{2+} ions do not act as binders in contrast to Ca^{2+} ions, which have a notable binder action. They facilitate the rebuilding process of the disintegrated PAM structure during discharge and, thus, improve the cycle life of positive plates with pure-lead grids. This effect of Ca^{2+} ions is most pronounced when the positive paste contains 0.8% of CaSO_4 . Besides, Ca^{2+} ions reduce the crystallinity of PAM particles and, hence, their proportion of gel (hydrated) zones increases. This yields a flexible skeleton structure of PAM. The effect of Ca^{2+} ions on the properties of PAM is explained by the phenomena that occur in the gel/crystal structure of the PAM as a result of the electrochemical, chemical and crystallization processes.

Keywords: Lead/acid batteries; Positive active mass; Calcium sulfate; Cycling

1. Introduction

The positive plates of lead/acid batteries consist of lead alloy grids and lead dioxide active mass (PAM). As a result of oxidation of the lead alloy, a corrosion layer (CL) is formed between the above two components. The parameters that determine battery life are: (i) rate of grid corrosion; (ii) rate of PAM disintegration, and (iii) changes in the electric properties and the structure of the corrosion layer/PAM interface [1]. The above processes are influenced by the plate production technology and the additives introduced into the grid alloy and/or into the paste as well as by the current profile on battery operation.

The PAM structure comprises interconnected agglomerates which form a continuous skeleton. The latter acts as a current collector in the plate. During deep-discharge, between 30 and 50% of the skeleton can be reduced and converted into PbSO_4 generating electric current. The skeleton organization is preserved to some extent during this process. During charge, the skeleton structure is completely restored. Thus PAM maintains the capacity of the plate for hundreds of cycles.

It has been established that some additives such as Sb, As and Bi do not only affect the electric conductivity of the

corrosion layer, but also facilitate the formation of a strong PAM skeleton [2,3]. During charge, these additives have a beneficial effect on the reversible restoration of the skeleton. They play the role of binders in this process. Their effect is of particular importance for ensuring long life of the positive battery plates. This role of binders has been established by a model tubular powder electrode (TPE) [2]. The technology for preparation of the TPE is as follows: after three deep charge/discharge cycles the active mass of positive SLI battery plates is taken off the grid, washed with water and dried, and then ground to powder. A definite amount of this powder is filled into tubular electrodes (of a definite volume comprising woven polyester tubes with Pb spines in the middle to serve as current collectors. This electrode construction allows for investigation of the effect of various parameters on the restoration processes of the PAM skeleton.

The present experimental study has two basic aims:

(i) To establish whether the nature of PAM changes on battery cycling thus making it a capacity limiting and hence life-limiting factor. An answer to the following question is sought for: 'Does PbO_2 at the end of service life of the positive plates preserve its ability to rebuild the PAM skeleton during recharge?'

(ii) Lead alloys containing Ca have been increasingly used in the battery industry. The effect of Ca^{2+} ions on the build-

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ing-up processes of the PAM structure has not been investigated yet. To elucidate the influence of Ca^{2+} ions on the structural processes in the PAM is the second aim of this investigation.

2. Experimental

The experimental setup is schematically presented in Fig. 1. It consists of two stages:

(i) the first stage involves preparation of PAM powder with definite properties, and

(ii) the second stage comprises investigation of the properties of the PAM powder through the fabrication and cycling of a tubular powder electrode.

First, a battery was assembled using six cells with identical positive plates. The positive plates were prepared using Pb grids and positive paste with no additives. After three deep-discharge cycles, the positive plates of three of the cells were taken out, washed with water, dried and the PAM was ground to powder. The other three cells were cycled down to 50% of their rated capacity (end of battery life). Then the positive plates of these cells were taken out and subjected to the above processing. The two types of PAM powder were filled into

tubular electrodes with spines of Pb, Pb–0.6%Sn and Pb–6%Sn, and the electrodes were set to cycling. The PAM density in the tubular electrodes was 4.15 g/cm^3 . The changes in specific capacity (in Ah/g PAM) on cycling of the TPE with a current of 9 mA/g were followed.

3. Results and discussion

3.1. Influence of cycling on the properties of PAM

Fig. 2 summarizes the results from cycling of the TPE electrodes. The curves marked with (1) present the changes in specific capacity of TPE filled with PAM taken from the positive plates at the beginning of battery cycling. γ_{plate} is the value of the specific capacity of the battery plates (at 50% PAM utilization). The curves denoted with (2) give the specific capacities of TPE filled with PAM taken from the positive plates at the end of battery cycle life.

TPE electrodes filled with PAM, taken off the plates after three charge/discharge cycles, restore their capacity almost completely in electrodes with Pb and Pb–0.6%Sn spines, and those with Pb–6%Sn spines restore their capacity completely. On completion of cycling, the tubes were cut. The PAM

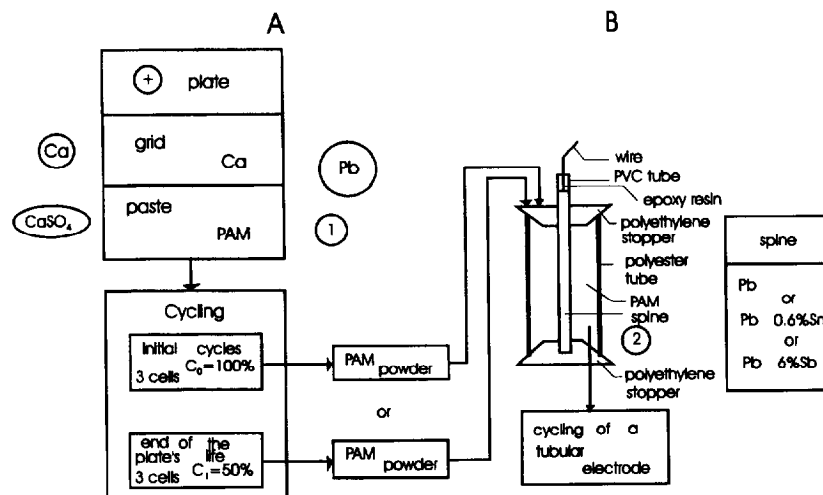


Fig. 1. Experimental setup.

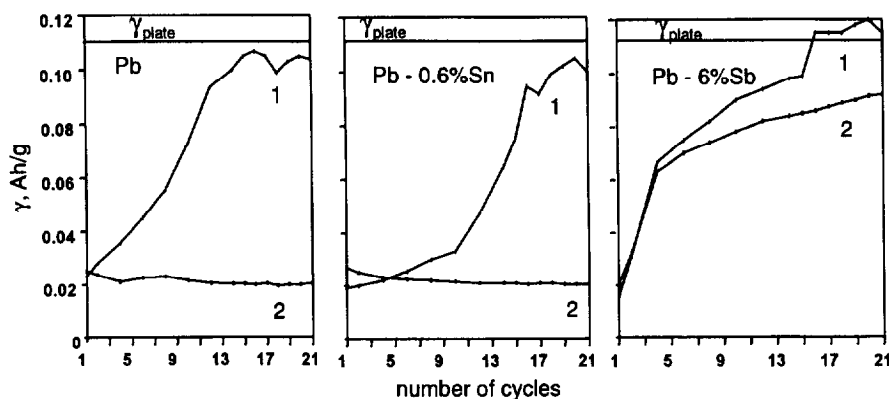


Fig. 2. Specific capacity of the TPE as a function of the number of cycles: (1) PAM taken off at the beginning of plate cycling, and (2) PAM taken off the plates at the end of their cycle life.

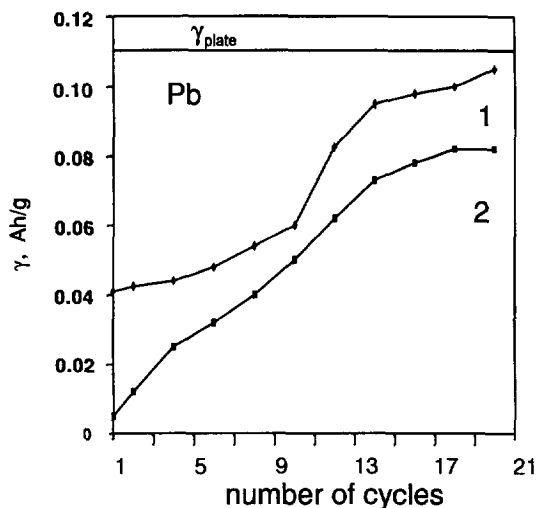


Fig. 3. Changes in specific capacity of TPE with Pb spines on cycling. PAM was obtained from positive plates with Pb–2%Sb grids: (1) PAM taken off the plates at the beginning of cycling, and (2) PAM taken off the plates at the end of their cycle life.

preserved its cylindrical shape. This means that the skeleton of PAM has been fully restored, and that PAM is a porous mass.

Electrodes with Pb and Pb–0.6%Sn spines and PAM taken off the plates after they have reached their end of life exhibit a capacity of about 0.2 Ah/g and this value remains unchanged on cycling. On completion of cycling of the TPEs the tubes were cut. The PAM in them looked like a mash. The PAM skeleton of these tubular electrodes has not been built. Hence, on cycling of the positive plates with pure-Pb grids, the degradation of the PAM skeleton is irreversible. This implies that on cycling of the batteries the nature of PAM changes and it loses its ability to rebuild its skeleton. Tin does not affect this process (Fig. 2(b)). It is therefore not a binder.

The behaviour of TPEs with Pb–6%Sb spines is totally different from that of the above-described electrodes. Fig. 2 shows that when the spine contains Sb, the TPE restores its skeleton structure and hence its capacity. As established in our previous investigations [2], Sb acts as a binder.

Fig. 3 presents the results from cycling of tubular electrodes with pure-Pb spines and PAM obtained from plates with Pb–2%Sb grids.

On cycling of the tubular electrodes Sb affects the formation processes of the PAM skeleton of the TPEs when filled with PbO₂ powder taken from the positive plates either at the beginning of cycling or at the end of battery cycle life. In the latter case, however, the degree of restoration of the PAM skeleton is lower (curve (2) in Fig. 3). Probably, a part of the Sb has been deposited on the negative plate, thus reducing the Sb content in PAM. The remaining amount of Sb in PAM is sufficient for almost 80% restoration of its skeleton.

3.2. Influence of Ca on the formation processes of the tubular powder electrodes structure

Positive plates with Pb–0.1%Ca grids were subjected to cycling. PAM from these plates, taken at the beginning of cycling and at the end of their cycle life, was filled into tubular electrodes with spines of Pb or Pb–0.6%Sn or Pb–6%Sb. Fig. 4 presents the obtained results.

The TPE prepared with PAM taken off the positive plates at the end of their cycle life restore their PAM skeleton within about 20 cycles and reach 50% utilization of the active mass on discharge. On comparing these results with the data presented in Fig. 2 it becomes evident that Ca from the grid alloy of the plates exerts a beneficial effect on rebuilding the structure of the tubular powder electrodes with Pb and Pb–0.6%Sn spines. On cycling of the positive plates, Ca is oxidized and enters the solution in the pores of the PAM, thus penetrating into the PAM itself and influencing the processes of skeleton restoration. Obviously, Ca acts as a binder.

In order to verify this effect of CaSO₄ on the PAM properties, 0.1% of CaSO₄ was added to the paste, used for preparation of the positive plates. Then, PAM samples were taken off the plates at the beginning and at the end of plate cycling, and used for preparation of tubular electrodes with the three types of spine. These electrodes were set to cycling. The obtained results are presented in Fig. 5.

The active mass taken off the plates, after the third battery cycle as well as that taken off at the end of battery cycle life when ground to powder and filled into the TPE, restores its skeleton structure on cycling of the TPEs with all three types of spine. Hence, CaSO₄ has a beneficial binder effect on the

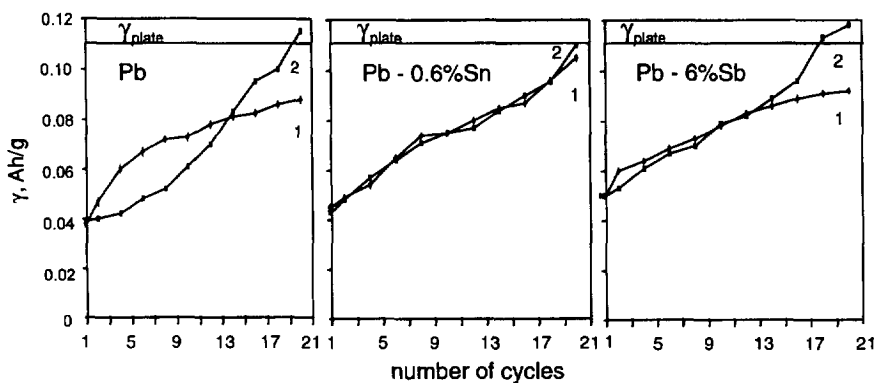


Fig. 4. Changes in specific capacity of TPE on cycling. PAM was obtained from positive plates with Pb–0.1%Ca grids: (1) PAM taken off the plates at the beginning of cycling, and (2) PAM taken off the plates at the end of their cycle life.

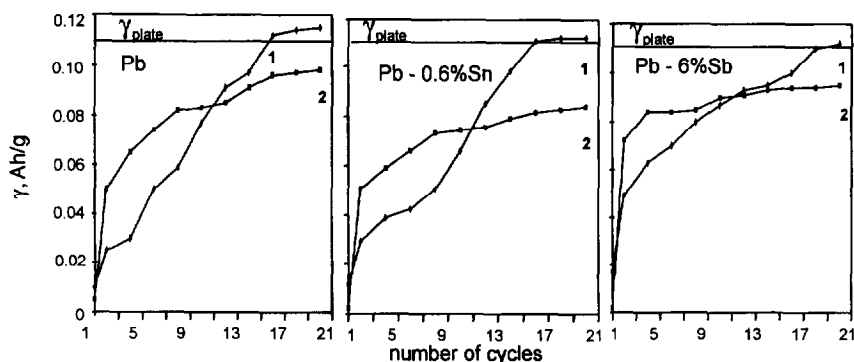


Fig. 5. Changes in specific capacity of TPE on cycling. PAM was obtained from positive plates with Pb grids and 0.1% CaSO_4 added to the paste: (1) PAM taken off the plates at the beginning of cycling, and (2) PAM taken off the plates at the end of their cycle life.

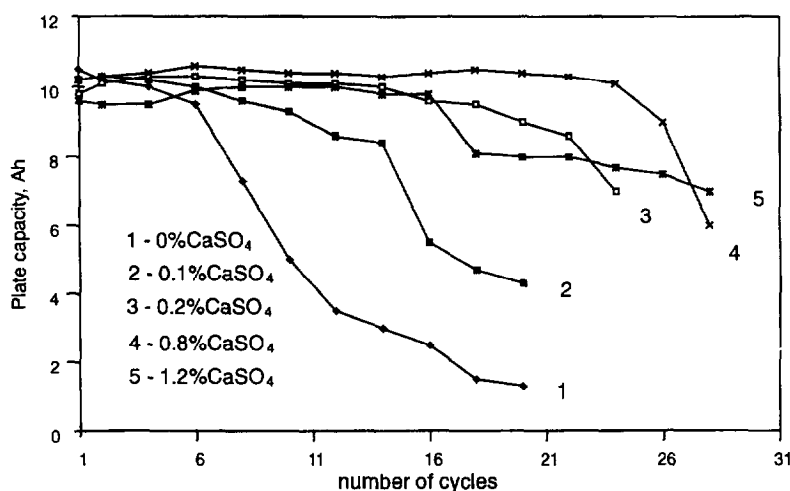


Fig. 6. Changes in specific capacity of positive plates with various CaSO_4 contents on cycling.

formation processes of the PAM structure on electrode cycling.

There are data reported by Ramanathan [4] evidencing that CaSO_4 added to the paste of positive electrodes improves the cold-cranking ability of starter batteries. In addition, Lorenz [5] reports that ' CaSO_4 has no deleterious effect on the life of the positive plates'.

We investigated the effect of CaSO_4 additions to the paste on the life of positive plates. Positive SLI plates with pure-Pb grids and pastes containing from 0.1 to 1.2% CaSO_4 were prepared. Fig. 6 shows the results from the cycle-life tests of batteries assembled with the above-mentioned plates. It can be seen from the figure that the positive plates containing CaSO_4 exhibit longer cycle life than those with no CaSO_4 additions. The most stable capacity on cycling was observed with the plates containing 0.8% CaSO_4 .

3.3. Changes in the structure of $\beta\text{-PbO}_2$ on cycling and under the influence of CaSO_4

The structure of PAM at the beginning and at the end of cycling of the positive plates with pure-Pb grids was determined through X-ray diffraction (XRD) analysis. After three cycles the charged PAM comprised mainly $\beta\text{-PbO}_2$. The content of $\alpha\text{-PbO}_2$ was negligibly small as compared with that

of the $\beta\text{-PbO}_2$ species. Table 1 summarizes the peak heights of the characteristic diffraction lines for $\beta\text{-PbO}_2$ at the beginning and at the end of cycle life of the positive plates.

The skeleton of PAM consists of crystal ($\beta\text{-PbO}_2$) and amorphous zones [6,7]. The data in Table 1 show that on battery cycling, the amount of the crystal $\beta\text{-PbO}_2$ zones increases by about 18%. Such an increase in crystallinity of $\beta\text{-PbO}_2$ on cycling has also been observed by Yamashita et al. [8].

The XRD method was also used to study the influence of CaSO_4 on the PAM structure both in charged and discharged state. Table 2 summarizes the intensities of some of the characteristic diffraction lines for $\beta\text{-PbO}_2$ and for PbSO_4 .

The following conclusions can be drawn from the data in Table 2:

Table 1
Intensities of the XRD lines for $\beta\text{-PbO}_2$ at the beginning and at the end of cycle life of the positive plate

| d spacing (\AA) | I_b at the beginning of cycling (mm) | I_e at the end of cycle life (mm) | $(I_e - I_b)/I_b$ (%) |
|------------------------------|--|-------------------------------------|-----------------------|
| 3.50 | 160 | 190 | 19 |
| 2.78 | 188 | 221 | 18 |
| 2.47 | 63 | 73 | 16 |

Table 2
Intensities of the XRD lines for β -PbO₂ and for PbSO₄ vs. CaSO₄ content in the paste ^a

| CaSO ₄ in paste (%) | 3.50 Å β -PbO ₂ | | $(I_{\text{ch}} - I_{\text{disch}})/I_{\text{ch}}$ (%) | 2.80 Å β -PbO ₂ | | $(I_{\text{ch}} - I_{\text{disch}})/I_{\text{ch}}$ (%) | I _{PbSO₄} | | |
|--------------------------------|----------------------------------|--------------------|--|----------------------------------|--------------------|--|-------------------------------|--------|--------|
| | I_{ch} | I_{disch} | | I_{ch} | I_{disch} | | 3.33 Å | 3.21 Å | 3.00 Å |
| | 0.00 | 162 | 121 | 25 | 194 | 135 | 30 | 29 | 25 |
| 0.10 | 142 | 92 | 35 | 190 | 108 | 43 | 37 | 31 | 45 |
| 0.80 | 154 | 100 | 34 | 185 | 116 | 37 | 34 | 41 | 48 |
| 1.20 | 152 | 105 | 31 | 181 | 120 | 34 | 41 | 35 | 58 |

^a I_{ch} = intensity of the XRD lines for charged PAM (in mm); I_{disch} = intensity of the XRD lines for discharged PAM (in mm).

(i) CaSO₄, i.e. Ca²⁺ ions in particular, affect the structure of PAM decreasing the intensity of the diffraction peaks for β -PbO₂ by 6 to 12%, i.e. they cause the gel/crystal ratio in PAM to increase. This conclusion agrees well with the experimental data reported in Ref. [6].

(ii) On discharge of the plates with CaSO₄, a greater amount of PbSO₄ is obtained in PAM and the decrease in intensity of the diffraction lines for β -PbO₂ is more pronounced in plates containing CaSO₄ as compared with those with no CaSO₄ addition. This is in good agreement with the data in Fig. 6 showing that positive plates with CaSO₄ have higher capacity.

Fig. 7 presents scanning electron micrographs (SEM) of charged PAM without CaSO₄ additions (Fig. 7(a)) and with 0.8% CaSO₄ (Fig. 7(b)). It can be seen that Ca²⁺ ions yield

a fine PAM grain structure. Hence, Ca takes part in the building-up processes of the PbO₂ structure. This conclusion is in good agreement with the results from XRD of charged PAM (Table 2) indicating a decrease in PAM crystallinity on addition of CaSO₄. SEM graphs of discharged PAM without CaSO₄ are shown in Fig. 8(a), whereas Fig. 8(b) presents SEM graphs of discharged PAM with 0.8% CaSO₄. The addition of CaSO₄ refines the PbSO₄ crystal structure and causes the morphology of the crystals to change as well. Obviously, it increases the rate of PbSO₄ nucleation.

It is evident from the SEM graphs in Figs. 7 and 8 that CaSO₄ exerts a strong influence on PAM modifying the structures of both PbO₂ and PbSO₄, thus affecting the electrochemical behaviour of the positive plate.

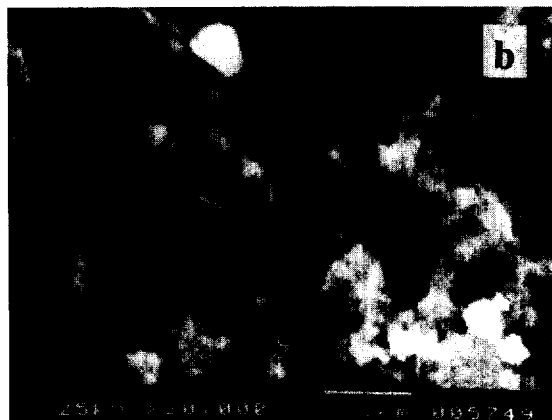


Fig. 7. SEM graphs of charged PAM: (a) without CaSO₄, and (b) with 0.8% CaSO₄ addition.

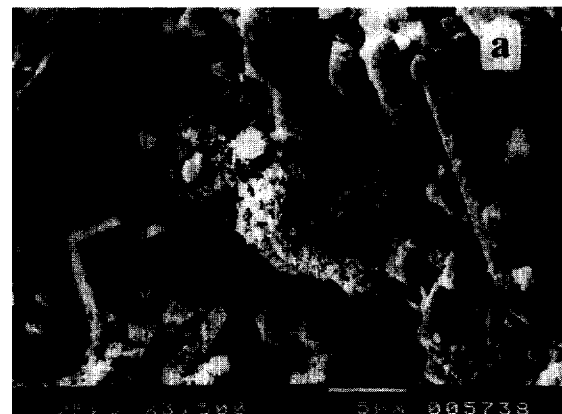
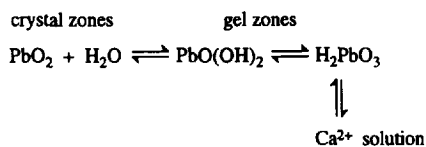


Fig. 8. SEM graphs of discharged PAM: (a) without CaSO₄, and (b) with 0.8% CaSO₄ addition.

4. Phenomena proceeding in the gel/crystal structure of PAM under the action of Ca^{2+} ions and their effect on the capacity and cycle life of the positive plate

It can be expected that CaSO_4 would affect the crystallization processes of PbSO_4 . These two compounds, though not isomorphous, are slightly soluble salts of one and the same acid. It is hardly probable, however, that CaSO_4 (i.e. Ca^{2+} ions) would influence the lead dioxide properties. But this is what actually happens.

The effect of Ca^{2+} ions on the behaviour of PAM can be explained with the gel/crystal structure of PAM [6,7]. The following equilibria are established in PAM:



CaPO_3 is calcium plumbate. Recently, BaPbO_3 has been reported to have a beneficial effect when introduced into the positive plate [9,10].

The gel zones interconnect mechanically and electrically many of the agglomerates in PAM into a skeleton, particularly when a considerable part of the PbO_2 is reduced to PbSO_4 . Gel zones play also the role of 'hinges' in the skeleton structure, which dissipate the energy evolved by the mechanical tensions created in the plate during discharge [7].

The gel (hydrated) zones and the solution exchange ions. Ca^{2+} ions from the solution are exchanged with H^+ ions from the gel zones. The XRD data (Table 2) show that this interaction results in an increase of the proportion of gel zones in the PAM skeleton. Consequently, equilibrium (1) is shifted to the right. Larger PbO_2 gel zones and surface layers are formed in the PAM particles. The surface gel zones of adjacent PAM particles interact with one another interconnecting the particles into a continuous electrical network along which the electric current flows. In addition, as established in our previous investigations [7], the discharge reaction proceeds in the gel zones. This is probably one of the reasons for the beneficial effect of Ca^{2+} ions on the capacity and hence on the cycle life of positive plates with pure-Pb grids.

It can be expected that equilibrium (1) would also be affected by other ions present in the solution. These may displace the Ca^{2+} ions from the above equilibrium. Hence, the effect of Ca^{2+} ions cannot always be displayed in its pure form. This is probably the reason why the effect of Ca^{2+} ions, as well as of some other ions, on PAM has remained unnoticed up to now.

Through the gel/crystal concept of the structure of PAM particles we can also explain the loss of PAM's ability to restore its skeleton structure in positive plates with pure-Pb grids. XRD investigations of PAM taken off the plates at the beginning and at the end of cycling of the positive plates show that during cycling the crystallinity of PAM increases

(Table 1), i.e. there is a loss of gel zones interconnecting the individual particles. The connections crystal/crystal or agglomerate/agglomerate in PAM lose their flexibility. During discharge, the skeleton may crack (at the sites of thinning of its branches) under the influence of the newly formed PbSO_4 crystals and the flows running through the pores. As a result of this the electrical contact between the particles is impaired. Consequently, the capacity of the plate declines.

As established earlier [7] there is a certain ratio between the gel and crystal zones in PAM particles and agglomerates that ensures optimum capacity and cycle life of the positive plates. When this ratio decreases on cycling, i.e. the crystallinity of PAM increases, the contacts between the particles and agglomerates in PAM are impaired and PAM loses its ability to rebuild its skeleton structure on recharge. On the contrary, when gel zones prevail in PAM, the resistance of the skeleton increases considerably and certain parts of it are excluded from the current generation as a result of which the plate loses again its capacity. When PAM contains definite ions (binders) the latter maintain an optimum ratio between the gel and crystal zones and keep this ratio unchanged on cycling. Consequently, PAM preserves its ability to restore the structure of its skeleton on recharge. Through this effect, binders improve the cycle life of the battery. Thus, by shifting equilibrium (1) in one direction or the other we can affect the capacity and the cycle life of positive lead/acid battery plates.

5. Conclusions

1. At the end of cycle life of a battery, the PAM of plates with pure-Pb grids increases its crystallinity and loses its ability to restore its skeleton on recharge.
2. Sn ions do not act as binders of the PAM skeleton.
3. Ca^{2+} ions act as binders of the PAM skeleton. CaSO_4 improves the cycle life of plates with pure-Pb grids. Ca^{2+} ions increase the gel/crystal ratio in PAM and refine the structure of PbSO_4 crystals, thus influencing the processes of charge and discharge of PAM.

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