ELSEVIER

Journal of Power Sources 95 (2001) 191–202

JOURNAL OF POWER SOURCES

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Semi-suspension technology for preparation of tetrabasic lead sulfate pastes for lead-acid batteries

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Abstract

A new technology for production of 4BS pastes for the positive (lead dioxide) plates of lead-acid batteries has been developed based on an Eirich Evactherm® mixer. The basic principle of this new technology is that 4BS crystals with dimensions between 20 and 25 μm are formed first from a semi-suspension at a temperature higher than 90°C and then the excess water is removed from the semi-suspension under vacuum until the desired paste density is obtained. During the vacuum treatment the temperature of the paste decreases and small 4BS and PbO crystals are formed. During the paste formation procedure, the large 4BS crystals build up the PbO_2 skeleton of the PAM, whereas the small crystals form the energetic PbO_2 structure, which participates in the charge–discharge processes on cycling of the battery. It has been found, through XRD and thermogravimetric analysis, that the 4BS particles comprise crystal and amorphous zones. The crystal zones contain water molecules, part of which can be easily removed from the particles under vacuum treatment and curing as a result of which the crystallinity of the 4BS particles decreases. Another part of the bound water remains in the 4BS particles after curing of the pastes and can leave them only after heating to 250°C. The ability of water to leave the particles depends on the density of the semi-suspension used for preparation of the paste. Experimental tests have shown that the highest battery performance is obtained when the paste is prepared under the following conditions: degree of lead oxidation in the leady oxide (LO) 85% PbO/LO, H_2SO_4/LO ratio 5–6%, liquid content ($H_2SO_4 + H_2O$) in the semi-suspension 240–260 ml/kg LO, temperature of the semi-suspension equal to or higher than 90°C, duration of paste mixing about 15 min. The new semi-suspension technology of 4BS paste preparation facilitates the formation of stable PAM structure that ensures high capacity and long cycle life of the positive plates of lead-acid batteries. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrated tetrabasic lead sulfate; Lead-acid battery paste; Lead dioxide active mass structure; Lead-acid battery technology

1. Introduction

The main component of every battery paste is basic lead sulphate. It is formed as a result of a chemical reaction between the H_2SO_4 solution and leady oxide. The reaction is exothermic and proceeds in a paste mixer. When the paste preparation is conducted at temperatures higher than 70°C, tetrabasic lead sulphate (4BS) is formed, whereas at lower temperatures tribasic lead sulphate (3BS) is obtained [1–3]. Most of the battery plants use 3BS pastes. In order to keep the temperature in the mixer below 70°C, the latter has to be cooled down. Until recently, this was done through blowing air into the mixer. Lately, the German company Maschinenfabrik Gustav Eirich has adopted a new method of temperature control, namely through evaporation of the water under vacuum [4]. This technology was called the Evactherm® technology. Having analysed carefully the Evactherm® technology, we have established that it has a much greater technological potential than simply to control the temperature of paste preparation.

One of its potential features is that it allows the reaction between the lead oxide and H_2SO_4 to proceed in a semi-suspension state (i.e. at densities between 3.2 and 3.5 g/cm^3). On completion of the crystallization of the basic lead sulphate the semi-suspension can be concentrated through evaporation (removal) of the excess water under vacuum, until a paste of a desired density is obtained.

The semi-suspension has a much lower viscosity than that of the paste. This would allow the chemical reaction between H_2SO_4 and PbO to proceed uniformly throughout the whole volume of the mixer. This, in turn, would yield a homogeneous paste. Secondly, the ion transport between the PbO and the growing basic lead sulphate crystals is much faster in the semi-suspension than in the paste and hence the chemical reaction could be facilitated, which would reduce the time for preparation of high-quality pastes. This, in turn, would improve the performance of the lead-acid batteries.

The aim of the present work was to verify the beneficial effect of the semi-suspension technology on the actual

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PII: S0378-7753(00)00643-1

performance characteristics of the batteries. We studied the influence of: (a) water content in the semi-suspension, (b) degree of oxidation of the leady oxide and (c) H_2SO_4/PbO ratio on the performance of the batteries. The effect of semi-suspension density on battery performance was announced earlier [5]. The present paper summarizes the results of the above mentioned investigations and discloses the structure of the 4BS pastes prepared using the semi-suspension technology.

2. Experimental

2.1. Method of paste preparation

This paper treats the production of tetrabasic lead sulphate pastes. The investigation was performed using a laboratory paste mixer Evactherm®, a product of Maschinenfabrik Gustav Eirich (Germany). The temperature of paste preparation was higher than 90°C. This was possible as the Eirich vacuum paste mixer is a closed system and no water is lost during the paste preparation process.

The paste density depends on the ratio liquid/solid phases. The liquid phase consists of H_2SO_4 solution and water. It has been established from the battery practice that to obtain pastes with densities from 3.9 to 4.1 g/cm^3 the total volume of H_2SO_4 solution and water should be between 190 and 216 ml per 1 kg LO. Let us assume the upper limit value (216 ml) as the base volume of $H_2SO_4 + H_2O$ for paste preparation (denoted as V_0). 5 kg batches of each paste were prepared using a H_2SO_4/LO ratio = 6%. First, the leady oxide was fed into the paste mixer. Then the total amount of H_2SO_4 solution and water pre-heated to a temperature higher than 70°C was added for about 2 min. The heat released by the chemical reaction between PbO and H_2SO_4 increased the temperature further to 88–92°C and the semi-suspension was stirred at this temperature for about 15 min. Then, vacuum was applied as a result of which the paste density increased and the temperature dropped down to 30°C. Water was removed from the semi-suspension in an amount as to obtain a paste of the desired density.

In order to determine how does the semi-suspension technology affect the nature of the 4BS crystals, we examined, through X-ray diffraction (XRD) and thermogravimetric analysis, the structure of the 4BS crystals. The crystal morphology of the 4BS particles in the paste, before and after curing, was observed through scanning electron microscopy at different magnifications.

The thus prepared pastes were pasted onto SLI grids and the plates were subjected to high-temperature curing and then to formation. These plates were assembled into 12 V/48 A h batteries and set to cycling tests employing different algorithms.

2.2. Preparation of pastes from semi-suspensions with various water content

For this series of experiments, the base liquid volume ($H_2SO_4 + H_2O$) was $V_0 = 216$ ml/kg LO. The H_2SO_4 concentration in this volume was 1.17 g/cm^3. Right after the above volume of H_2SO_4 solution and water (pre-heated to 70–75°C) was poured into the paste mixer containing the leady oxide, we introduced additional quantities of water heated at 70–75°C. The data in Table 1 show these additional amounts of water, expressed in both ml/kg LO and in % versus the base volume V_0. The water content in the semi-suspensions varied between 11 and 44%.

When the formation of the 4BS crystals was completed, vacuum was applied to allow the water to evaporate, as a result of which the paste temperature cooled down to 30°C. The volume of the removed water is also given in the table. All pastes had a density of 4.1 g/cm^3. Besides the density of the pastes we also measured their penetration and the values obtained are given in Table 1 in the column marked "Pen". The pastes with higher water content (33 and 44%) had to be heated additionally during the vacuum treatment to accelerate the water evaporation and remove the excess water from the semi-suspension. Hence, 260 ml of $H_2SO_4 + H_2O$ solution per 1 kg LO is the technological upper limit for the semi-suspension method at which no heating of the paste mixer is necessary.

Samples of the thus prepared paste were taken for XRD determination of its phase composition and SEM examination of the crystal morphology. These pastes were then used for the preparation of plates and batteries (12 V/48 A h). The batteries were set to cycling tests employing the algorithm presented in Table 2.

The end-of-life criterion was when the battery reached an end-of-discharge voltage of 9.0 V for 1 h of discharge at 50% DOD.

Table 1
Quantity of water added to or removed from the semi-suspension during paste preparation[a]

Paste #	V_{H_2O} in (ml/kg LO)	V_{H_2O} in (% V_0)	V_{H_2O} out (ml/kg LO)	d (g/cm^3)	Pen (mm)
0	0	0	0	4.1	32
11	24	11	18	4.1	29
22	48	22	40	4.1	27
33	72	33	62	4.1	31
44	96	44	94	4.1	28

[a] $V = 216 + V_{H_2O}$ (ml/kg LO).

Table 2
Test algorithm employed for testing of batteries with positive pastes prepared using various water content in the semi-suspension

Test procedure	Parameters
Initial performance characteristics	
Capacity C_{20} (three tests)	25°C, $I = 0.05\ C_{20}$ A
CCA (two tests)	-18°C, $I = 5\ C_{20}$ A
Peukert dependence	From 5 to 65 A/kg PAM
Cycle life test	
Charge	$I_1 = 0.5\ C_{20}$ A up to 14.8 V $U_2 = 14.8$ V for 24 h $I_3 = 0.1\ C_{20}$ A for 1 h
Discharge	$I = 1\ C_2$ A down to 50% DOD Voltage after 1 h discharge was determined

2.3. *Preparation of pastes using leady oxides with various degrees of oxidation*

We produced pastes using leady oxides with different degrees of oxidation: 72, 84 and 96%. The semi-suspensions were prepared with the maximum water content that allowed production of pastes with no additional heating. Thus, the total liquid content was 240, 250 and 275 ml/kg LO, respectively. All pastes had the same density of 4.1 g/cm^3. The measured penetration values are given in the column of the table marked ‘‘Pen’’. The basic characteristics of the three types of pastes are summarized in Table 3.

The amount of water evacuated from the cells under vacuum was a bit greater than that of the first series of experiments. The condition for equal paste density was important for determining the amount of water removed from the pastes.

The pastes were used for pasting grids and the thus produced plates were cured at high temperature and formed for 20 h employing an algorithm developed at CLEPS.

These plates were then assembled into 12 V/48 A h batteries, which were set to an accelerated test as presented in Table 4.

2.4. *Preparation of pastes using various H_2SO_4/LO ratios*

We also investigated the influence of the H_2SO_4/LO ratio on the performance of the battery. The pastes were prepared under the optimum conditions: 260 ml of H_2SO_4 solution were used per 1 kg of LO, the PbO/LO ratio was 84%, the temperature of paste preparation was higher than 90°C and the H_2SO_4/LO ratio was 4, 5, 6 and 7%, respectively. Commercial Pb-low Sb grids were pasted and the plates were assembled into 12 V/46 A h batteries at 54% utilization of the positive active mass (PAM). These batteries were set to deep-discharge cycling tests. The employed test algorithm is presented in Table 5. After every 25 charge–discharge cycles, a CCA test was conducted.

Table 4
Test algorithm employed for testing of batteries produced with positive pastes containing leady oxides with various degrees of oxidation

Test procedure	Parameters
Capacity C_{20} (three tests)	25°C, $I = 0.05\ C_{20}$ A
CCA (two tests)	-18°C, $I = 5.0\ C_{20}$ A
Peukert dependence	From 5 to 65 A/kg PAM

Table 5
Test algorithm employed for testing of batteries produced with positive pastes prepared using various H_2SO_4/LO ratios

Test procedure	Parameters
Initial performance tests	10 cycles C_{20} CCA: $I = 5.0\ C_{20}$, $t = -18$°C
Peukert dependence	From 5 to 65 A/kg PAM
Cycle life tests	
Charge	$I_1 = 0.5\ C_{20}$ up to 14.8 V $U_2 = 14.8$ V for 24 h $I_3 = 0.1\ C_{20}$ for 1 h
Discharge	$I = 0.05\ C_{20}$ down to 1.75 V/cell DOD = 100%

The end-of-life criterion was assumed to be when the capacity of the battery declines below 70% of the rated value and the CCA time reaches 90 s.

3. Experimental results

3.1. *Batteries prepared using semi-suspensions with various water content*

3.1.1. *Diffraction patterns of the pastes before and after vacuum treatment and curing*

Fig. 1 shows segments of the diffraction patterns (featuring the strongest characteristic diffraction peaks for 4BS with inteplanar distance $d = 0.321$ nm) for the pastes before

Table 3
Liquid content ($H_2O + H_2SO_4$) per 1 kg LO in semi-suspensions prepared with leady oxides with various degrees of oxidation

Supplier	PbO/(PbO + Pb) (%)	$V_{H_2SO_4} + V_{H_2O}$ (in semi-suspension) ml/kg LO	$(V_{H_2SO_4} + V_{H_2O})_{end}$ (in the paste) ml/kg LO	Density (g/cm^3 LO)	Pen (mm)
A	72	240	198	4.10	30
B	84	250	200	4.10	28
C	96	275	210	4.10	20

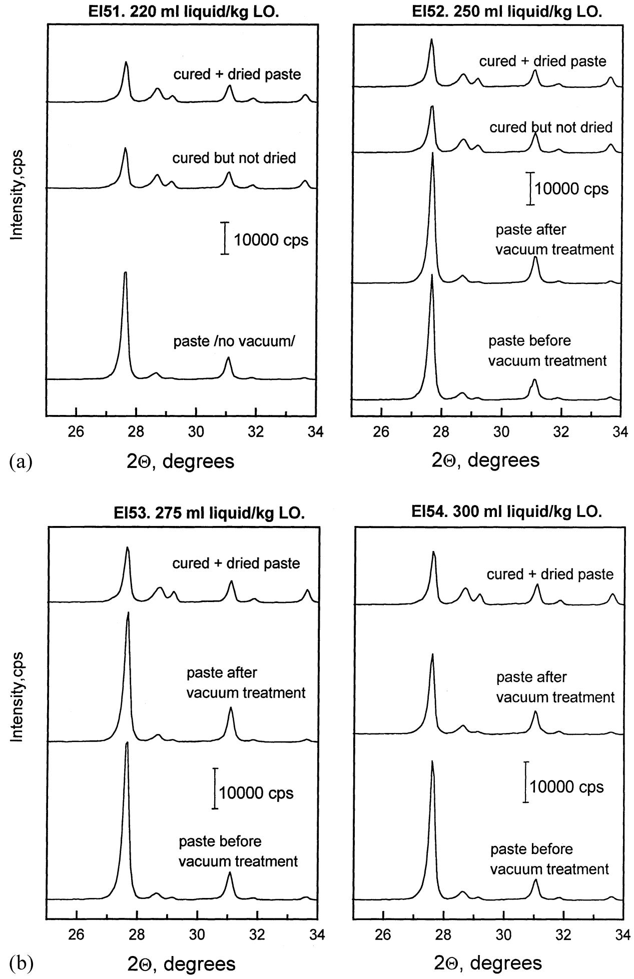

Fig. 1. Segments of the XRD patterns for 4BS pastes prepared by the semi-suspension technology using 220, 250, 275 and 300 ml of liquid ($H_2SO_4 + H_2O$) per 1 kg of LO. The XRD patterns are recorded before and after vacuum treatment of the semi-suspensions as well as before and after drying of the cured pastes.

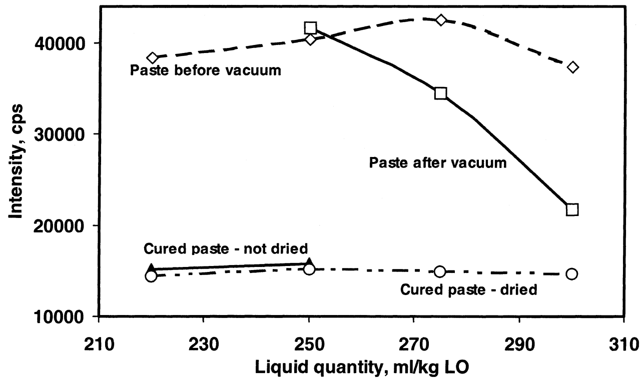

Fig. 2. Intensity of the characteristic diffraction peak ($d = 0.321$ nm) as a function of liquid content in the semi-suspension. The peak intensity reflects the crystallinity of the 4BS particles in the pastes before and after the vacuum treatment as well as before and after drying of the cured pastes.

and after vacuum treatment as well as for the cured paste before and after drying.

Curing of the plates was performed in two stages: (a) curing at 90°C and 98% relative humidity (RH) for 6 h, and (b) drying at 60°C and 10% RH for 10 h and then at 40°C and 10% RH for 8 h. Samples were taken from the pastes after curing and drying. All pastes were prepared using H_2SO_4/LO ratio equal to 6% and ($H_2SO_4 + H_2O$) volume 220, 250, 275 and 300 ml/1 kg LO.

The following conclusions can be drawn from the figure:

1. The 4BS crystallinity depends very strongly on the stages of paste preparation (before or after vacuum treatment) as well as on the curing conditions.
2. The crystallinity of the fresh paste depends on the total liquid volume used for its preparation. The intensity of the characteristic diffraction line for 4BS with $d = 0.321$ nm was used to determine this dependence of the paste crystallinity. The peak maximum was expressed in counts per second. Fig. 2 shows the measured intensities of the characteristic peak with $d = 0.321$ nm before and after the vacuum treatment (the paste with 220 ml/kg LO was not subjected to vacuum treatment) as well as after curing and drying of the cured pastes.

The 4BS crystallinity in the fresh paste is very high and it increases slightly with increase of the liquid content in the semi-suspension until 275 ml of liquid per 1 kg LO is reached. On further increase of the liquid content, the crystallinity of 4BS decreases slightly. When vacuum is applied, its crystallinity decreases if the liquid content in the semi-suspension is higher than 250 ml/kg LO. The greater the liquid content, the greater the decrease in crystallinity of the 4BS.

The above results indicate that the 4BS particles comprise crystal zones (with H_2O) and amorphous zones (without or with small quantities of H_2O). The ratio between the two types of zones depends on the amount of liquid used for paste preparation (i.e. the water content or the concentration of the H_4SO_4 solution used). It can be assumed that the water content in the 4BS particles determines their crystallinity. During vacuum treatment, part of the water leaves the particles as a result of which their crystallinity decreases.

Secondly, the mobility of the water in the 4BS particles depends on the density of the semi-suspension. The lower the semi-suspension density (i.e. the greater the $H_2SO_4+H_2O$ volume per 1 kg of LO) the easier the water leaves the 4BS particles and hence the amorphous zones in them increase in volume. On curing of the plates at 90°C in saturated water vapours this process proceeds at the highest rate and the crystallinity of the 4BS particles decreases from 38370 cps for the fresh paste prepared with 220 ml/kg LO to 15045 cps for the cured paste before drying. The difference in intensity of the 4BS characteristic diffraction line ($d = 0.321$ nm) for the cured paste before and after drying

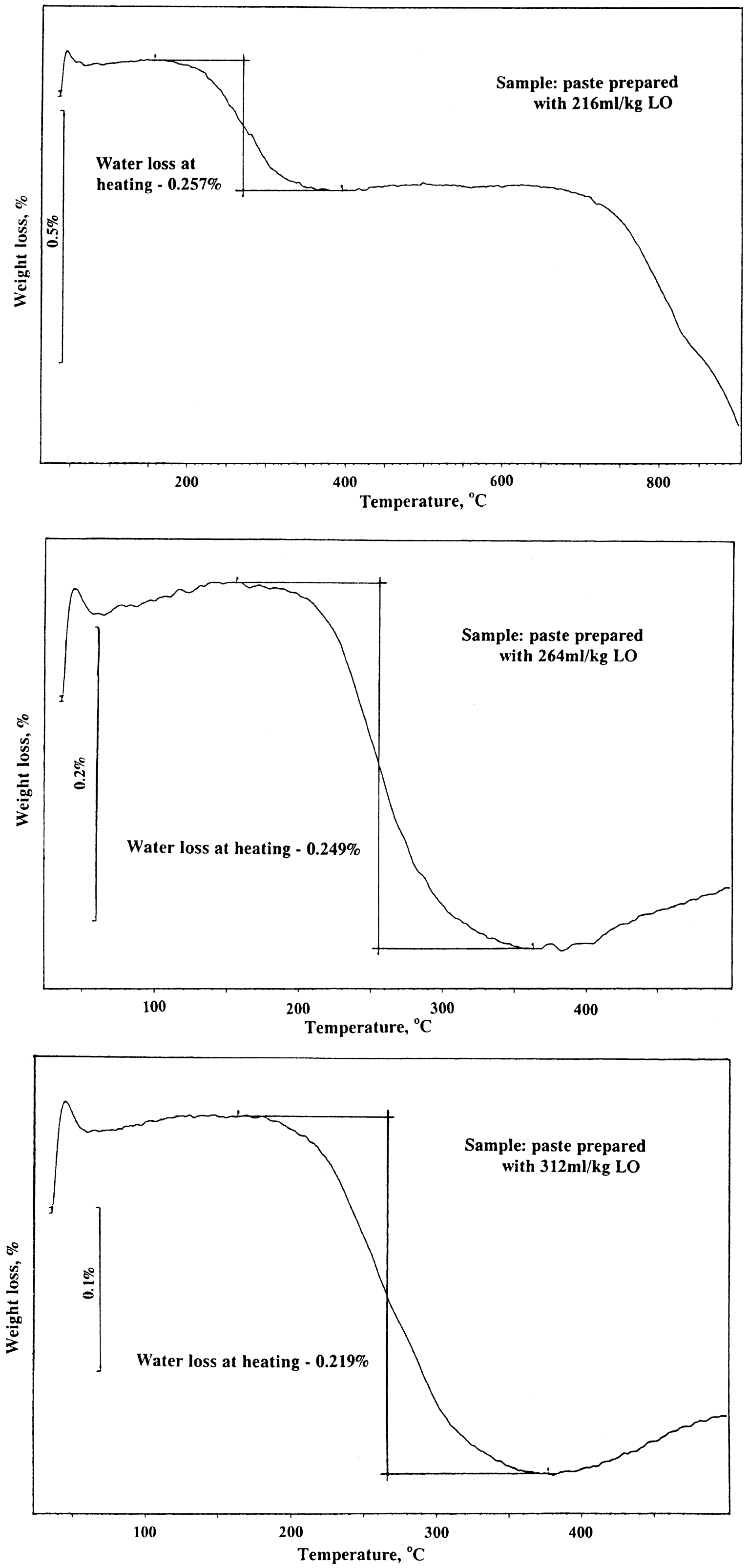

Fig. 3. Thermogravimetric curves for cured pastes prepared from semi-suspensions containing 216, 264 and 312 ml ($H_2SO_4 + H_2O$)/kg LO.

is within the range of the experimental error. Practically, the crystallinity of the cured paste does not change on drying as water is removed from the paste only during the curing proper (90°C and 98% RH). Similar results are also observed with the paste prepared with 250 ml/kg LO.

Fig. 2 shows also that the crystallinity of the cured paste does not depend on the density of the semi-suspension. The latter affects only the mobility of the water in the 4BS particles, whereby the greater the water content in the semi-suspension, the greater the changes in crystallinity of the 4BS particles. It can be expected that this high mobility of the water in the 4BS particles (i.e. the dynamics of the structure of 4BS particles) will facilitate the conversion of the large 4BS particles into PbO_2 aggregates during formation of the positive active mass.

A series of three types of pastes prepared with different liquid content in the semi-suspension were set to thermogravimetric analysis after curing and drying. Fig. 3 presents the obtained TGA curves.

Between 150 and 300°C, the 4BS particles lose weight. Within this temperature range water leaves the structure of the particles. The figure shows that, though cured and dried, the paste "remembers" the density of the semi-suspension from which it was prepared. With increase of the liquid volume in the semi-suspension ($H_2SO_4 + H_2O$ per 1 kg of LO) the amount of water in the 4BS crystals decreases. If we assume that H_2O is bound to the PbO molecules in the 4BS particles, we can calculate the chemical formula of the 4BS particles for the three types of pastes. The results from these calculations are presented in Table 6.

The lower the density of the semi-suspension the smaller the hydrated part of the 4BS particles. As evident from Fig. 2, the water leaves readily the 4BS particles thus increasing the amorphous zones in them. Hence, the chemical formula $4PbO–PbSO_4$ generally used in the literature needs a certain correction in order to reflect adequately the water content in the 4BS particles. It follows from the present investigations that the characteristic diffraction pattern for 4BS particles refers to hydrated 4BS. The question arises why does the crystallinity of 4BS particles decrease with increase of the water content in the semi-suspension? It is logical to expect the reverse relationship. The rate of 4BS crystal growth should increase with decrease in semi-suspension density, i.e. increase of H_2O content in the semi-suspension. The process of water incorporation into the 4BS crystal lattice seems to be a slow process. The accelerated growth of 4BS particles in the semi-suspension does not allow the water molecules to fill in the respective vacancies in the 4BS crystal structure as a result of which a great number of highly defective (amorphous) zones are formed in the 4BS particles.

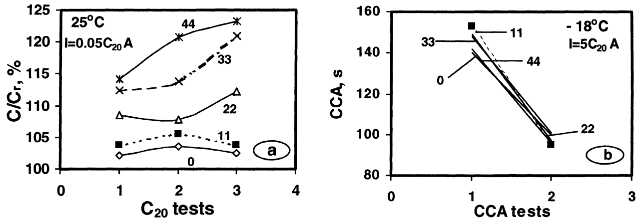

Fig. 4. Initial capacity and cranking time on CCA tests (with $I = 5\ C_{20}$ and $t = -18°C$) of batteries produced using semi-suspensions with various densities. The numbers 11, 22, 33 and 44 give the water content (in %) in the semi-suspension vs. the initial paste (#0) with basic liquid content 216 ml ($H_2SO_4 + H_2O$)/kg LO.

3.1.2. Influence of water content in the semi-suspension on battery performance

Fig. 4 illustrates the results from the initial three capacity and two CCA tests of batteries with positive plates prepared with pastes obtained from semi-suspensions with various densities. The numbers 0, 11, 22, 33 and 44 give the amount (in %) of the additional water added to the paste with H_2SO_4 solution volume $V_0 = 216$ ml/kg LO.

It can be seen that with increase of the water content in the semi-suspension the capacity of the plates increases. The CCA performance of all batteries under test is the same as it was limited by the negative plates.

The next test was determination of the Peukert dependences. The obtained curves are presented in Fig. 5.

It is evident that with increase of the water content in the semi-suspension, the Peukert curves shift towards higher specific capacity values.

And finally, the batteries were set to cycle life tests. The discharge was conducted with a current equal to 2 h rate of discharge down to 50% DOD. The voltage after 1 h of discharge was measured. Fig. 6 shows the end-of-discharge voltage as a function of the number of cycles.

The reference battery reached its end-of-life after 28 cycles. The batteries produced with semi-suspension pastes have more than twice longer cycle life.

The obtained results evidence that the vacuum semi-suspension technology affects the performance of the positive plates improving their service parameters.

Table 6
Formulae of hydration of 4BS particles as calculated from the water loss on heating

$H_2SO_4 + H_2O$/kg LO (ml/kg LO)	Water loss on heating (%)	Calculated formula of hydration of 4BS particles
216	0.257	$3.815PbO–0.185Pb(OH)_2–PbSO_4$
264	0.249	$3.821PbO–0.179Pb(OH)_2–PbSO_4$
312	0.219	$3.843PbO–0.157Pb(OH)_2–PbSO_4$

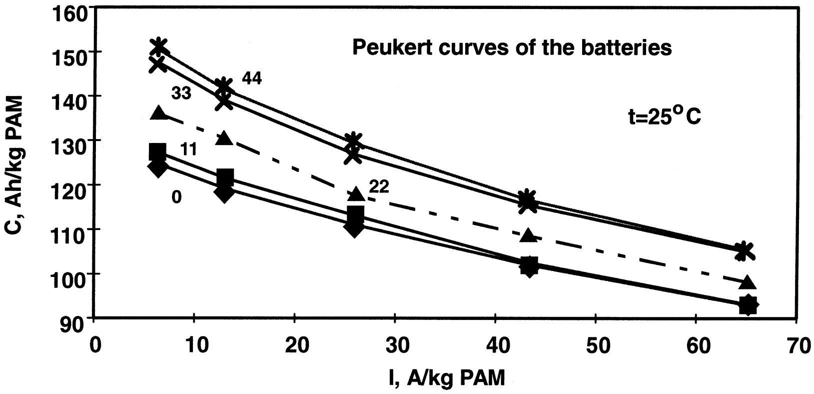

Fig. 5. Peukert curves for batteries with positive plates produced with 4BS pastes prepared by the semi-suspension technology. The numbers 11, 22, 33 and 44 give the water content (in %) in the semi-suspension vs. the initial paste (#0) with basic liquid content 216 ml ($H_2SO_4 + H_2O$)/kg LO.

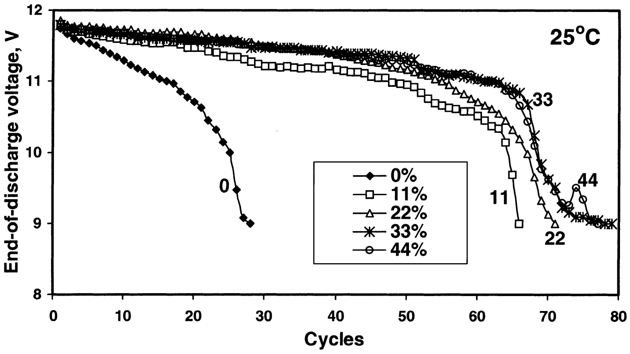

Fig. 6. End-of-discharge voltage at 50% DOD reached for 1 h as a function of the number of cycles. The numbers 11, 22, 33 and 44 give the water content (in %) in the semi-suspension vs. the initial paste (#0) with basic liquid content 216 ml ($H_2SO_4 + H_2O$)/kg LO.

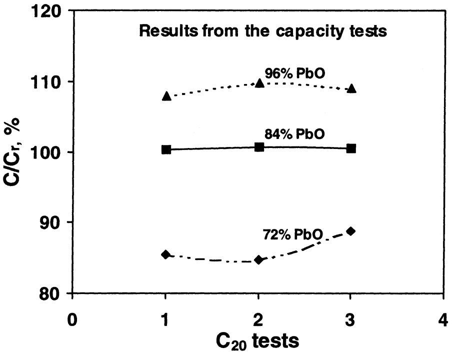

Fig. 7. Initial capacity of batteries with positive pastes prepared by the semi-suspension technology using leady oxides with three different degrees of oxidation.

3.1.3. *Influence of the degree of leady oxide oxidation on the performance of batteries with positive plates prepared using the semi-suspension technology*

The leady oxide used in the current production practice has a degree of oxidation between 65 and 85%. In order to establish the most efficient degree of LO oxidation for the semi-suspension technology, we investigated leady oxides with 72, 84 and 96% PbO/LO ratios.

Fig. 7 shows the capacity curves for the batteries with positive plates produced with the above three types of pastes.

The increase of the degree of oxidation of the LO leads to an increase in plate capacity. An almost constant capacity value is maintained during the three cycles.

Fig. 8 presents the CCA voltage after 30 s of discharge and the time of discharge with a current equal to 5 C_{20} for two measurements.

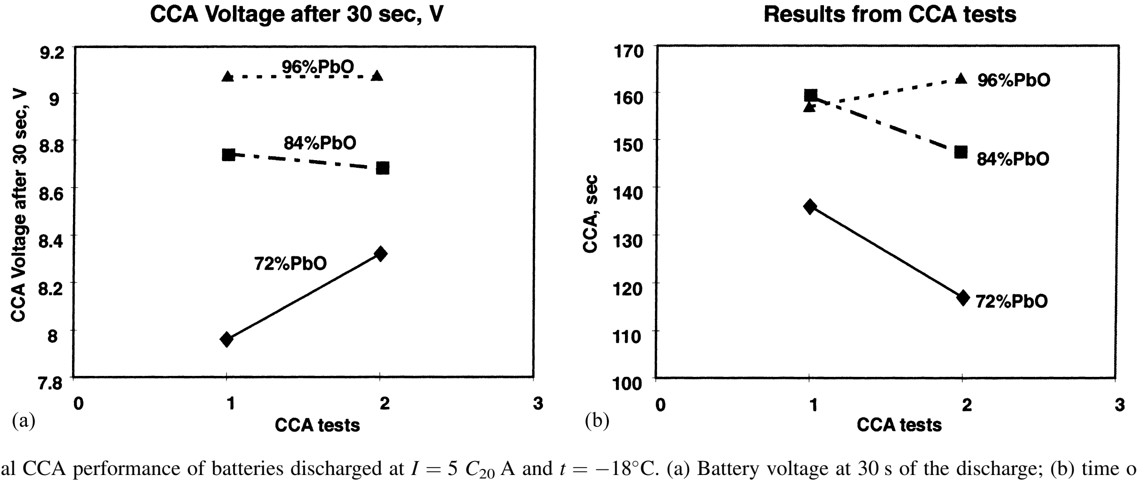

Fig. 8. Initial CCA performance of batteries discharged at $I = 5\ C_{20}$ A and $t = -18°C$. (a) Battery voltage at 30 s of the discharge; (b) time of discharge.

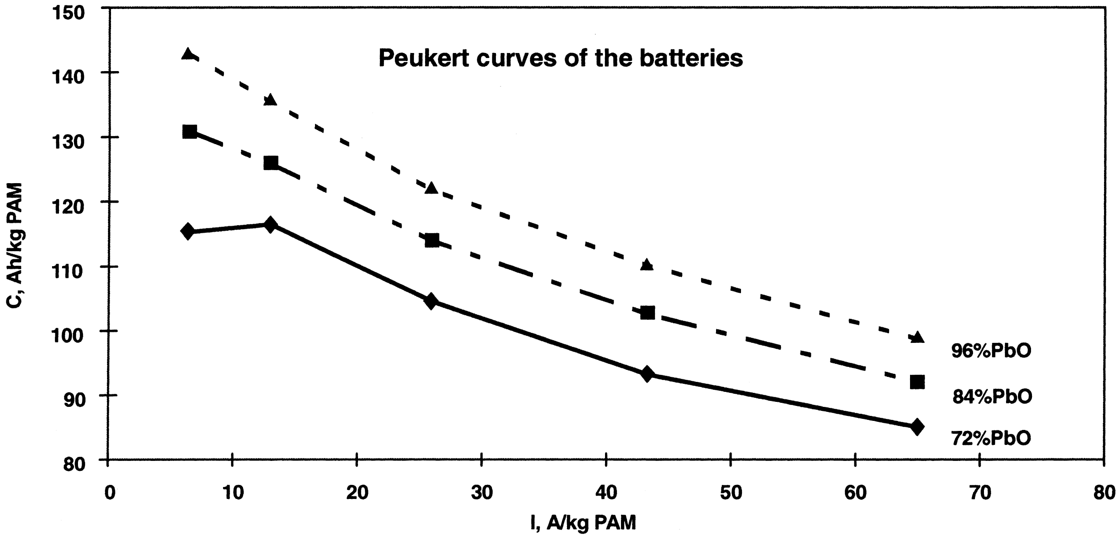

Fig. 9. Peukert dependence of the batteries with positive pastes prepared by the semi-suspension technology using leady oxides with three different degrees of oxidation.

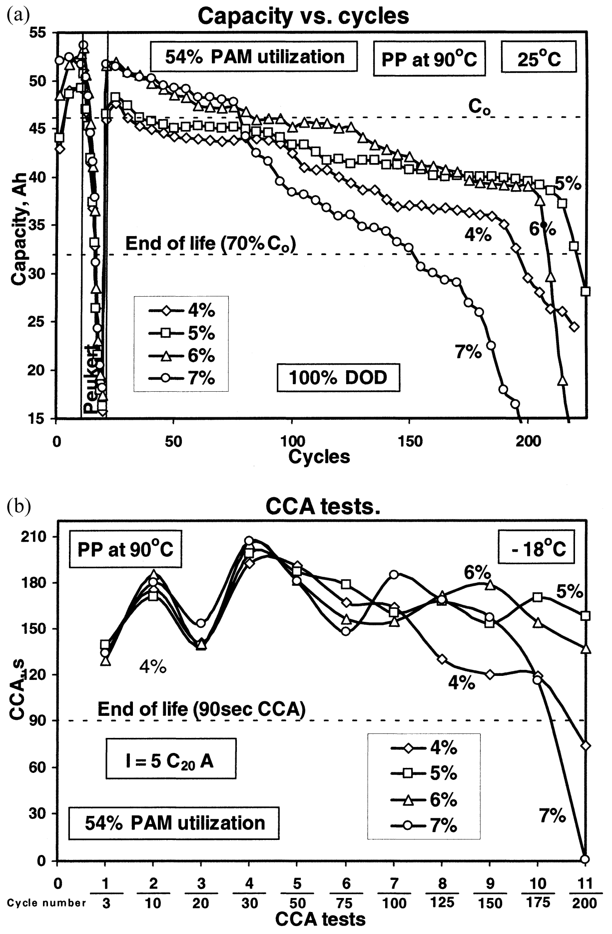

Fig. 10. Summary of the test results for batteries with positive plates produced using the semi-suspension technology of paste preparation using H_2SO_4/LO ratios: 4, 5, 6 and 7%. (a) Capacity curves on deep-discharge; (b) time of discharge at CCA test as a function of number of cycles.

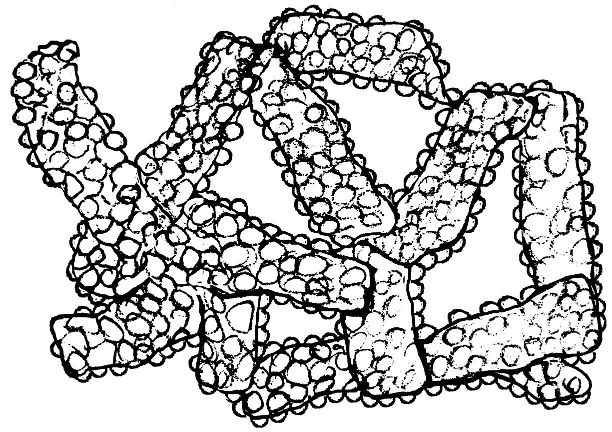

Fig. 11. Schematic representation of the structure of PAM.

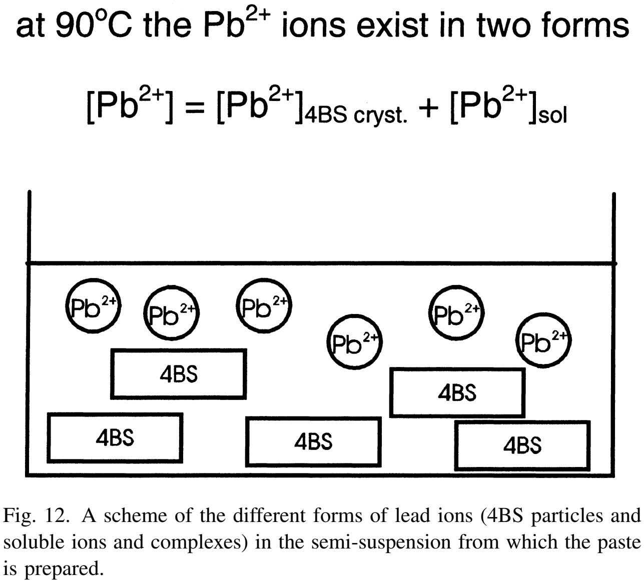

Fig. 12. A scheme of the different forms of lead ions (4BS particles and soluble ions and complexes) in the semi-suspension from which the paste is prepared.

In this series of tests, the batteries had such a ratio between the positive and negative active masses that the time of discharge was limited by the positive plates. It can be seen that the increase of the degree of oxidation of the LO yields an increase in both parameters of the CCA test.

Fig. 9 presents the Peukert curves obtained for the three types of batteries. It is evident that with increase of the degree of oxidation of the LO, the Pukert curves shift towards higher values of the specific capacity.

3.1.4. Influence of the ratio H_2SO_4/LO on the performance of batteries with positive plates prepared using the semi-suspension technology

In this series of tests, the positive pastes were prepared using H_2SO_4/LO ratios 4, 5, 6 and 7%. Fig. 10 presents a summary of the test results obtained for all four batteries.

It can be seen that with increase of the H_2SO_4/LO ratio the initial capacity of the batteries increases, too. The CCA and Peukert dependences are very close for all batteries under test.

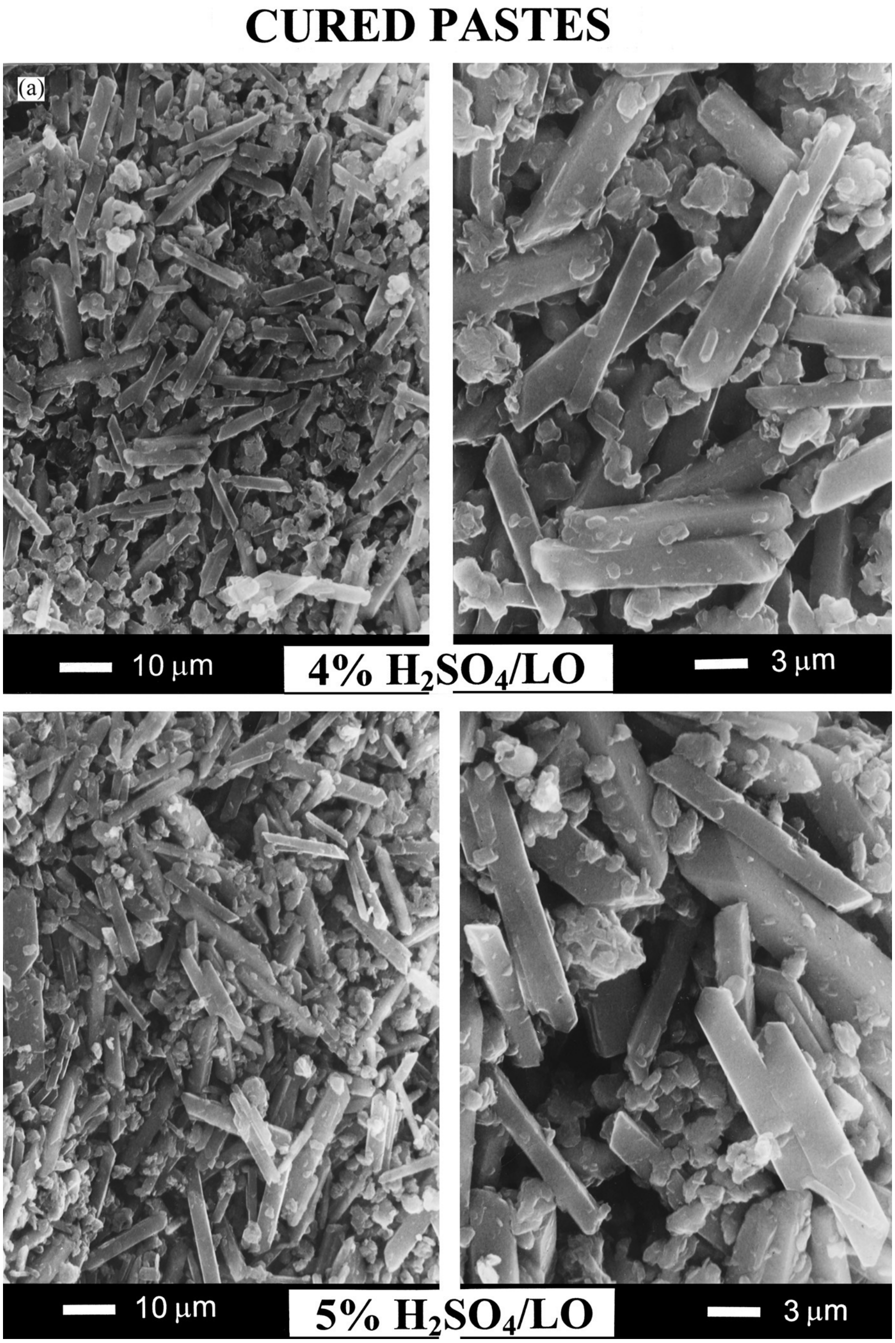

Fig. 13. (a) SEM micrographs of the cured pastes prepared by the semi-suspension technology using H_2SO_4/LO ratios 4 and 5%; (b) SEM micrographs of the cured pastes prepared by the semi-suspension technology using H_2SO_4/LO ratios 6 and 7%.

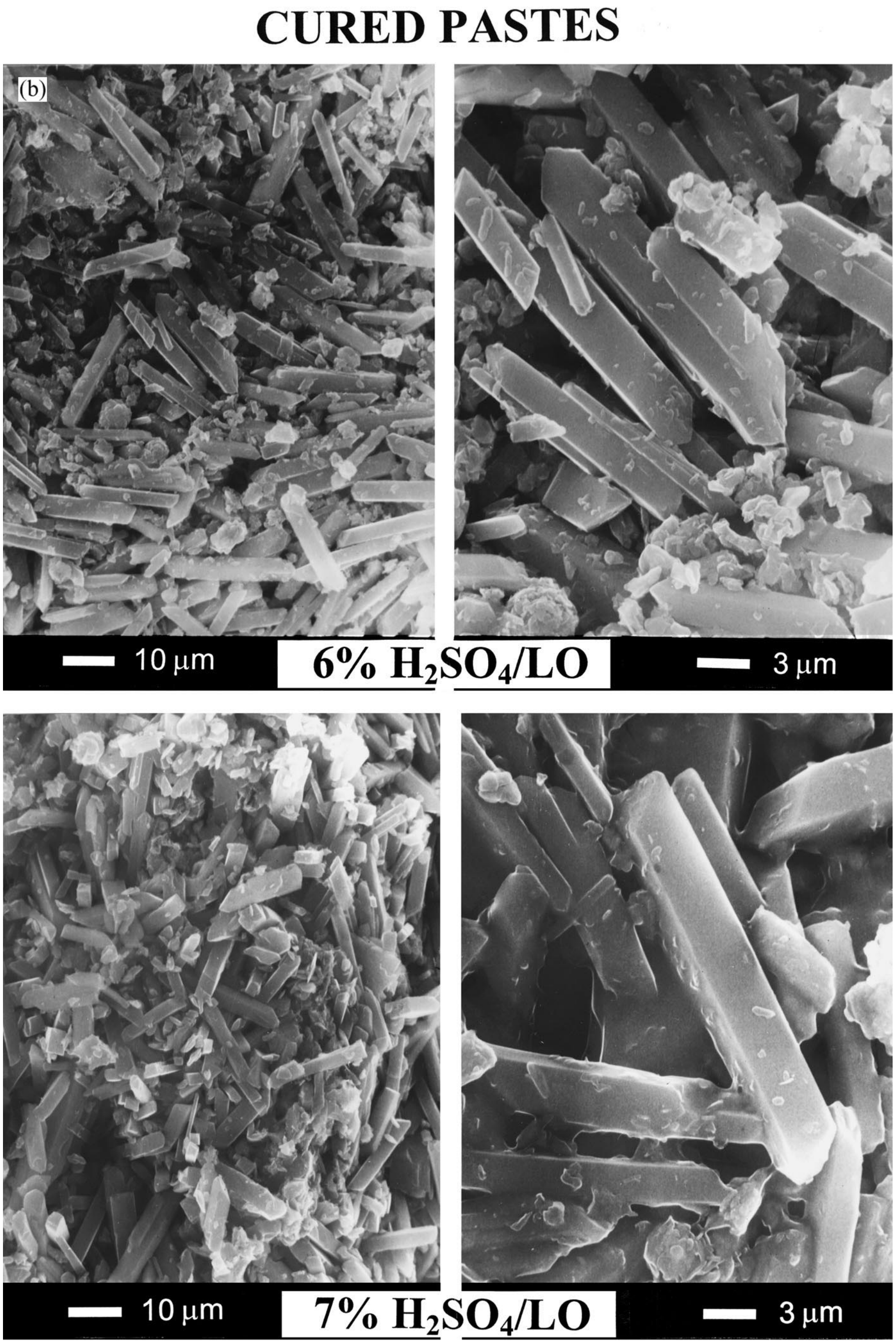

Fig. 13. (*Continued*).

Batteries with H_2SO_4/LO ratio equal to 4 and 7% have shorter cycle life and have endured 10 CCA tests, whereas the batteries with 5 and 6% H_2SO_4/LO ratio have longer cycle life (more than 200 deep-discharge cycles) and they have endured more than 11 CCA tests. Hence, the optimum H_2SO_4/LO ratio in the paste is 5–6%, which ensures the optimum amount of 4BS crystals in the paste. This finding indicates that the optimum structure of PAM should contain a certain, not great, amount of PbO that would make the structure of the positive plates stable and ensure the longest cycle life on deep-discharge cycling.

4. Discussion of results

The results from our investigations have raised the following question. Why does the vacuum semi-suspension technology affect the performance of the positive lead-acid battery plates?

It has been found that the performance of the positive and negative LAB plates is determined by the structure of their active masses [6].

The positive active mass (PAM) is built of:

1. Skeleton that conducts the electric current and provides mechanical support to the PAM and also ensures its contact with the grid.
2. Energetic structure that takes part in the charge–discharge processes.

This structure is presented schematically in Fig. 11.

The capacity of the positive plates depends on the amount of the energetic structure, which can be reduced during discharge. The cycle life of the positive plate depends on the stability of the skeleton and its contact with the current collector.

Lead ions exist in the semi-suspension in two forms: bound in 4BS and PbO particles, and soluble ions or soluble complexes in the solution. A diagrammatic presentation of the above two forms of Pb ions is given in Fig. 12.

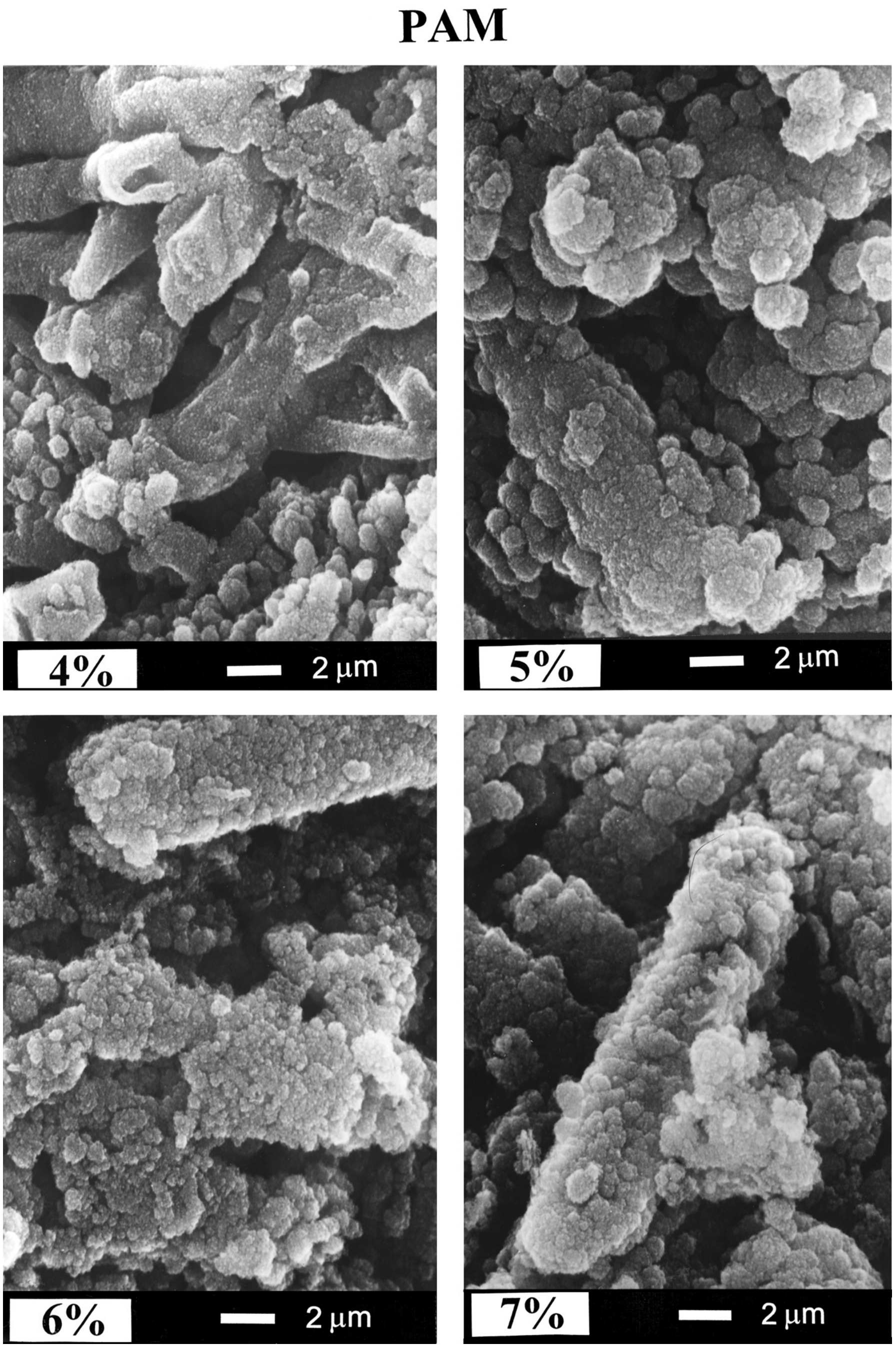

Fig. 14. SEM micrographs of the PAM obtained from pastes prepared by the semi-suspension technology using H_2SO_4/LO ratios 4, 5, 6 and 7%.

The amount of solid-phase bound ions is determined by the solubility of 4BS and PbO at the temperature of the semi-suspension and the H_2SO_4/LO ratio.

The amount of free lead ions and/or complexes in the liquid phase of the suspension depends on the solubility of the 4BS and PbO crystals, the volume of electrolyte in the suspension and the temperature of paste preparation.

At high temperatures, a great part of the PbO and 4BS crystals dissolve in the solution and only large 4BS crystals are formed. During the subsequent vacuum treatment, the semi-suspension concentrates, on the one hand, and on the other hand it cools down. These processes result in high oversaturations and formation of a great number of small-sized 4BS and PbO crystals. During vacuum treatment the temperature of the semi-suspension is reduced from 90 to 30°C and the density of the paste increases from 3.2 to 4.1 g/cm^3.

The large crystals formed in the semi-suspension at high temperature (90°C) will build up the skeleton of the PAM, which in turn affects the life of the battery. The small crystals in the paste will take part in the charge–discharge reactions and will determine the capacity of the plates. In order to verify the above inferences, samples of the fresh and cured pastes as well as of the formed lead dioxide active mass were subjected to SEM examinations. Fig. 13(a) and (b) shows SEM micrographs of the cured paste at two magnifications, and Fig. 14 presents SEM photos of the active mass.

The SEM micrographs show clearly the presence of large and small 4BS crystals in the cured paste. The small crystals often form bridges between the large 4BS crystals. The photos evidence also that the semi-suspension technology of 4BS paste preparation and high-temperature curing facilitate the formation of good contacts between the 4BS crystals thus yielding a stable PAM skeleton.

The SEM micrographs of PAM samples given in Fig. 14 show that the 4BS crystal matrices (mainly of the large ones) have been preserved during their conversion into PbO_2 aggregates. It can be seen clearly that the aggregates comprise agglomerates built up of small particles and they are fairly well interconnected into a skeleton. The matrices of the small crystals can also be distinguished at some places in the structure of PAM.

Hence, the Evactherm® technology allows pre-setting of the structure of PAM by the conditions of paste preparation. This is a great advantage of the Evactherm® technology as compared to the currently used conventional paste mixers. In fact, the Eirich vacuum mixer is a reactor in which the reaction of formation of the basic building elements of the structure of the cured paste and the PAM proceeds. These are large and small 4BS particles which during the subsequent formation process build up the skeleton and the energetic structure of the positive active mass.

5. Conclusions

1. A new technology of 4BS paste preparation has been developed based on Eirich Evactherm® paste mixer. A semi-suspension of the initial paste is prepared at temperatures above 90°C. In this semi-suspension, large 4BS crystals (up to 20–25 μm) grow. Then the excess water is removed under vacuum until the desired paste density is obtained. During the vacuum treatment, small crystals of 4BS and PbO are formed. On formation of the PAM the large 4BS crystals build up the skeleton of PAM and the small crystals take part in the charge–discharge reactions on cycling of the battery, thus building the energetic structure of PAM.
2. On preparation of 4BS pastes at 90°C and various semi-suspension densities, 4BS particles are formed that comprise crystal and amorphous zones. The crystal zones contain water molecules. On curing of the plates part of the water is lost and the crystallinity of the 4BS particles decreases. The more diluted the semi-suspension the more readily the crystallinity of the 4BS particles decreases on vacuum treatment of the semi-suspension or on curing of the paste.
3. In order to obtain a paste density of 4.1 g/cm^3 after the vacuum treatment without additional heating, the liquid volume ($H_2SO_4 + H_2O$) in the semi-suspension should not exceed 260 ml/kg LO. The duration of paste preparation is about 12–15 min and the obtained 4BS crystals are sized between 15 and 25 μm. The nature of these crystals allows them to be readily formed to PbO_2 and the structure of the resulting PAM preserves the matrix of the cured paste.
4. High initial capacity and long cycle life of the batteries can be achieved when the leady oxide with 85% degree of oxidation (PbO/LO) is used for preparation of the paste and the H_2SO_4 to LO ratio is within the range 5–6%.
5. The new technology can easily be introduced in the battery practice provided there is an Eirich Evactherm® paste mixer available.

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