Effect of soaking time on the positive active material and performance of the valve regulated lead/acid battery

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Abstract

During valve regulated lead/acid (VRLA) battery production bottlenecks occurring on the production line can result in varying delays between the different stages of production thus acting as a source of inconsistencies between batches. This paper describes a study conducted to determine the effects of different soaking times between the 'acid fill' and 'formation' stages of production. X-ray diffraction (XRD), BET surface area analysis, scanning electron microscopy (SEM) and electrical testing have been used to study the compositional and morphological aspects of the positive active material just prior and after formation. Results indicate that paste compositions are effected by the time period between acid fill and formation. However, electrical test results and SEM examination of formed pastes suggest that soaking time is unlikely to affect the resulting battery performance. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The manufacture of a valve regulated lead/acid (VRLA) battery involves a number of stages which are carried out in succession as a batch process. However, a disadvantage of this is that bottlenecks can occur between different stages in the production process resulting in delays, which are variable between different batches. This is of concern as it is a potential source of inconsistencies between the same model batteries from different batches.

Two key stages where bottlenecks can occur are apparent, namely the drying of the pasted plates and formation of the assembled monoblocs. Study of the application and duration of heat and humidity on the active materials has been widely reported [1,2] mainly due to its relevance to curing processes. Pre-formation stand time, or soaking time, has received attention in a number of previous publications [3–6]. In this paper, the effect of soaking time, prior to formation, on the active material and performance of the final product is investigated for the batteries tested.

Before the formation reactions can occur, it is essential that the electrolyte penetrates and completely fills the pores within the structure of the active material. This normally occurs within minutes due to the capillary forces. Once penetration of the active material by the electrolyte has taken place the sulphuric acid in the electrolyte will react with the lead monoxide within the active material to form lead sulphate and water. The lead sulphate then reacts further with lead monoxide to form basic sulphates [7].

2. Experimental methods

Several different experimental techniques were used to determine the structure and composition of the samples in this study. Details of the procedures followed for each of these is given in the sections later.

2.1. Sample production (manufacture)

Twenty-four 40 Ah VRLA batteries were constructed with a red lead containing positive paste and a 100% grey oxide negative paste. X-ray diffraction (XRD) data obtained for the red lead revealed that it contained ∼52% α-PbO. Standard production procedures, details of which are of necessity confidential, were followed until acid fill. Acid fill was conducted using acid of specific gravity, 1.290 at 15.5 °C. This is the standard acid concentration used for the

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manufacture of the commercial batteries that the tests were based on. The significance of using concentrated acid has been set out previously by Pavlov [5]. After this stage, the batch was split into four groups of six. Each group was left for a specified duration (2, 6, 12 or 24 h). One battery from each group was taken for inspection and the remaining monoblocs were then formed in series using an input of ~196 Ah.

2.2. Electrical testing

After formation, one monobloc was removed from each group for investigation. The performance of the remaining monoblocs was evaluated by subjecting each to a C1 rate discharge/charge cycle using end-of-line Digatron test equipment.

2.3. X-ray diffraction

Compositional analysis of the active materials was determined using X-ray diffractometry. Samples removed from batteries were rinsed using distilled water and subsequently dried before grinding into a fine powder. The rinsing stage was omitted in the case of material not removed from a battery. Grinding times were restricted to a maximum of 10 min to keep the conversion of α to β lead dioxide to a minimum. Powders were placed into a standard aluminium glass-slide-back sample holder. A Phillips 1830 diffractometer was used with Cu Kα radiation. Scans were conducted in the 2θ range of 20–60°, with a scan time of 3 s per degree and a step size of 0.005°. Phases were identified by comparison of patterns with standard data obtained from the Joint Committee for Power Diffraction Studies (JCPDS) files.

2.4. Scanning electron microscopy

Scanning electron microscopy (SEM) was used to obtain images of the active material samples. Formed active material samples were prepared by gluing dried pieces to a planchett using conducting cement. Samples of fine powders were produced by dispersion of the powder in isopropanol and then allowing a drop of the mixture to evaporate from a SEM stub, leaving the particles bonded to the stub.

All samples were sputter coated with a thin layer of gold, ~10 nm in thickness, to reduce charging and improve image quality. Examination was carried out in a Camscan 3 SEM using a working distance of 24 mm, a spot size of 4 or 5, and an electron beam voltage of 20 kV.

2.5. Surface area analysis

Surface areas were obtained using the BET method. Samples were removed from the battery and dried in the same way as for XRD. Perkin-Elmer BET surface area measuring equipment was used. Sample degassing, prior to measurement, was carried out under 2–3 atmospheres of nitrogen gas at 120 °C for 17–19 h.

3. Initial observations

A visual inspection of the ground positive pastes prepared for XRD analysis revealed the following features.

3.1. Unformed materials

A graduated colour change from the orange 2 h sample to a brown 24 h sample was observed. A white material was also interspersed within the paste, giving the powder a 'milky' appearance. The colour changes are believed to indicate the compositional differences between the pastes. Subsequent analysis identified the white material as lead sulphate.

The colour change of the paste from orange to brown can be explained by a reduction in Pb_3O_4 levels which produce the orangey-red appearance of red lead based powders. This hypothesis is supported by the compositional analyses, which show a decline in the Pb_3O_4 content of unformed pastes for longer stand-time durations.

3.2. Formed materials

No detectable colour change was observed in the formed samples, which were all dark brown/black. White material was not observed indicating that sulphate levels were much lower than in unformed pastes.

4. Phase analysis

4.1. Unformed pastes

After 2 h, significant formation of $PbSO_4$ and hydrated tribasic lead sulphate ($3BS·H_2O$) had occurred, however α-PbO remained the major phase present. No tribasic lead sulphate (3BS) or tetrabasic lead sulphate (4BS) was apparent at this stage. After 6 h, the formation of 3BS and 4BS was evident and the amount of $3BS·H_2O$ had increased. The proportion of $PbSO_4$ also increased and the lead monoxide (α-PbO) content was reduced accordingly.

The $PbSO_4$ content continued to rise after 12 h soaking time and the formation of monobasic lead sulphate (1BS) became evident. The relative quantity of the other basic sulphates decreased which suggested that soaking times shorter than 12 h can be recommended. After 24 h, the composition was similar to that obtained after 12 h except that further $PbSO_4$ and 1BS formation has occurred to the detriment of the tri- and tetrabasic lead sulphate content. Increase in $PbSO_4$ content was confirmed by the visual observation that the unformed powders had an increasingly 'milky' appearance.
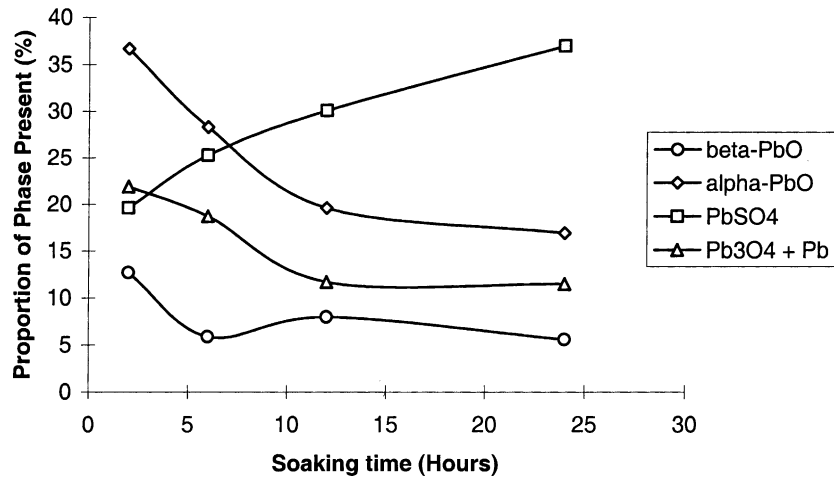
Fig. 1. Main constituents of the unformed pastes.

4.2. Effect of soaking time on the composition of unformed pastes

The compositional variation of unformed pastes is shown in Fig. 1, the basic sulphates are shown separately in Fig. 2. From the figures, it can be seen that as the stand time duration increases, α-PbO, Pb_3O_4, and Pb are all gradually sulphating. The rate of conversion appears to decrease after a 12-h stand-time. The minimum observed in the β-PbO line could result from a slight inhomogeneity of the paste. This was also observed in the 12-h sample which has a lower free lead content compared to the 24-h sample. However, there may be some reduction of Pb_3O_4 to the orthorhombic phase, leaving an oxygen ion free to combine with two H^+ ions forming water. The rate of conversion of the β-PbO phase appears to slow at an earlier stage, after 6 h, which is in agreement with its metastable characteristics.

Fig. 2 reveals that the higher basic sulphates, $3BS \cdot H_2O$ and 4BS, form preferentially in the early stages. This is most probably due to the relatively high concentration of PbO compared to the sulphate ions. This ratio reduces over time as more acid reacts with the paste, leading to the formation of 1BS. Formation of $3BS \cdot H_2O$ reaches a maximum at around 6 h duration. The graph suggests that a significant quantity of $3BS \cdot H_2O$ is converted to 1BS after a stand-time duration of between 6–12 h. The rate of formation of 4BS also slows after 6 h, which may also be due to the conversion from 4BS to 1BS. Definite conversion of 4BS to an alternative phase is not apparent until the stand-time duration exceeds 12 h. Since the rate of formation of 1BS slows after 12 h to approximately the same rate as the reduction in 4BS and there is no overall increase in the basic sulphate content, this would appear to suggest that direct conversion of the tetra to monobasic sulphate is taking place.

4.3. Formed pastes

The most abundant phases identified in all post-formation pastes were β-PbO$_2$, α-PbO$_2$, $PbSO_4$ and various basic lead sulphates.

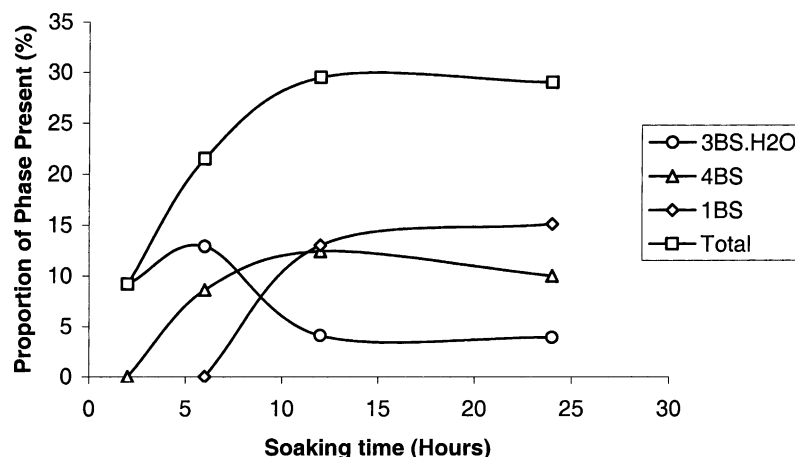Fig. 2. Effect of soaking time on sulphate composition in unformed pastes.

The 2-h sample contains the greatest proportion of $\sim$10% α-PbO$_2$, $\sim$6% PbSO$_4$ and 3BS, and $\sim$5% 4BS. A small proportion of 1BS was also identified.

The 6-h sample had a slightly lower β-PbO$_2$ and α-PbO$_2$ content. Residual α-PbO was also evident. Lead sulphate levels were slightly higher than the previous sample at $\sim$15%. Small quantities of 3BS and 1BS were identified, but 4BS did not appear to be present.

The β-PbO$_2$ content in the 12-h sample appears to be similar to that of the 2-h sample, however, the α-PbO$_2$ content has decreased further to only $\sim$2%. Residual α-PbO has increased to $\sim$9%, indicating that the formation at longer stand-times may be less efficient. PbSO$_4$ levels are slightly lower than in the 6-h sample ($\sim$11%).

The fourth sample, 24 h, has the highest level of β-PbO$_2$, at 72%. The XRD pattern indicated the possibility of some

residual Pb$_3$O$_4$. Unfortunately, it was impossible to resolve whether α-PbO$_2$, or α-PbO was present, since the main peaks of these two phases are very similar. Compositional trends, and the appearance of residual Pb$_3$O$_4$, indicate that α-PbO was the most likely phase. The level of PbSO$_4$ was $\sim$13% and both 4BS and 1BS were identified at a concentration of $\sim$4%.

4.4. Effect of soaking time on the composition of formed pastes

Overall the delay in formation appears to have less effect on phase abundance in the formed pastes than the unformed pastes examined previously. Fig. 3 shows the trends observed for the main constituents of the positive pastes. The sulphate content shown is the sum of all the sulphated material, which is shown in detail in Fig. 4.
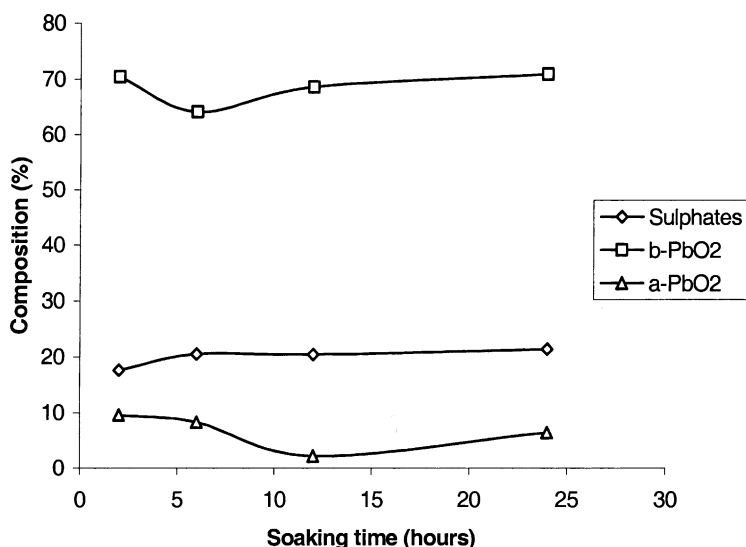

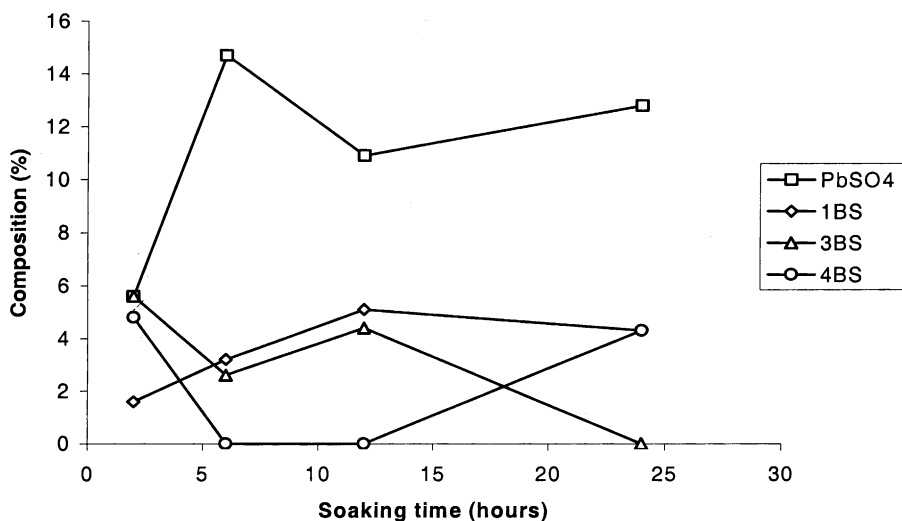Fig. 3. Effect of soaking time on the composition of formed pastes.

Fig. 4. Effect of soaking time on sulphate formation in formed positive pastes.
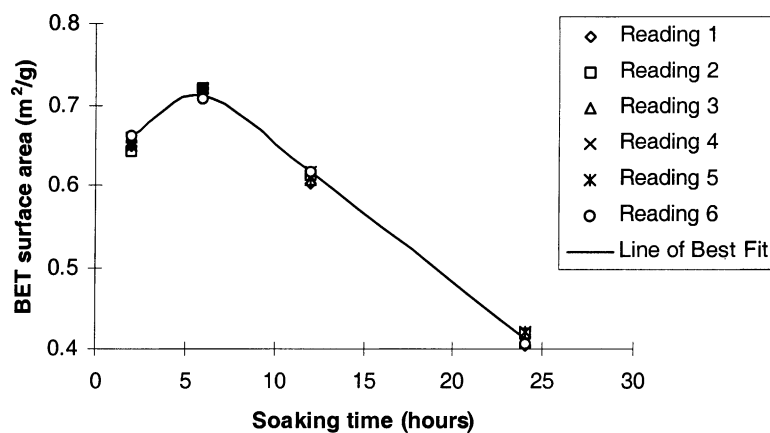
Fig. 5. BET specific surface area values versus soaking time for unformed samples.

Initially, between 2 and 6 h of soaking time, the overall sulphate content increases slightly, corresponding to decreases in both the lead dioxide modifications. The sulphate content does not appear to be affected by longer stand-times, however, the α-PbO$_2$ content remains low. The slight increase in α-PbO$_2$ observed after 12 h may be due to an inconsistency with the results, caused by peak overlap between α-PbO$_2$ and α-PbO, thus giving an overestimation of the total lead dioxide content.

Fig. 4 reveals the relative abundances of the sulphated species. The major constituent of the sulphate phase is PbSO$_4$, which reaches a maximum level in the 6-h sample. A sudden drop in PbSO$_4$ in the 12-h sample matches, an increase in 1BS and 3BS formation. The 4BS content becomes negligible for both 6 and 12-h stand-times. The 4BS formation is desirable in the positive paste [4], and it would therefore appear that the shortest stand-time of 2 h, produces the best paste in terms of composition, since it has a combination of the highest concentration of 3BS and 4BS and the lowest PbSO$_4$ and 1BS contents.

5. Morphology

5.1. Morphology of the unformed samples

BET surface area results indicated that the maximum surface area occurs when the batteries are left to soak in acid for between 2 and 6 h. Specific surface area then declines for increasing stand-times in excess of 6 h. Since surface area is inversely proportional to the apparent particle diameter, the 6-h sample must also, on average, contain the finest sized particles compared to the other groups. Although there may be a link to the relative particle sizes of the different phases present, it is more likely that this trend reflects the nucleation and growth of sulphate species. After only 2 h, sulphate crystals are beginning to nucleate and grow. Nucleation reaches a maximum between 2 and 6 h, leading to a maximum in the number of fines recorded after 6 h stand-time.

After this point, the growth of the sulphate crystals leads to a gradual increase in particle size, corresponding to the decrease in surface area observed in Fig. 5.

SEM observations of the unformed pastes indicate that the particle sizes are affected by the soaking time. Figs. 6 and 7 show dispersed particles from the 2 and 6 h samples, respectively. The magnifications of the two micrographs are approximately the same. It is observed that the particle sizes of the 6-h sample are not significantly finer than the 2-h sample. However, observations at higher magnifications have shown that these particles are themselves coated with tiny acicular crystal growths. Even at high magnifications, the crystals are not well defined giving the particles a non-distinct appearance. Fig. 8 shows that these crystals are also present after longer durations. Crystal growth appears to have occurred between the 6 and 12-h samples allowing the crystals to be photographed; the crystals on the surface mask the morphology of the underlying particles.
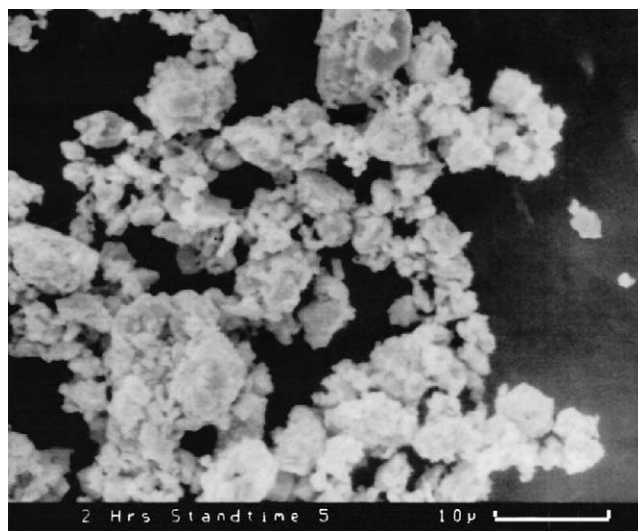

Fig. 6. Dispersed particles as observed in the unformed positive paste after a soaking time of 2 h (magnification: 1980×).
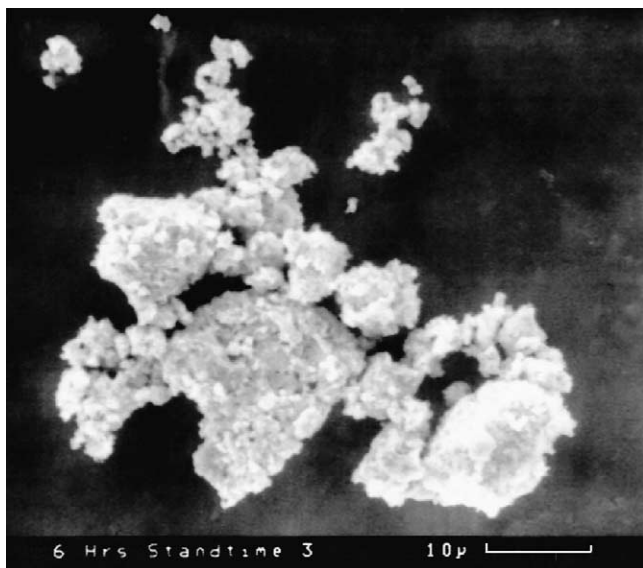
Fig. 7. Dispersed particles as observed in the unformed positive paste after a soaking time of 6 h (magnification: 1710×).

Fig. 9. Agglomerate surface as observed in the unformed positive paste after a soaking time of 6 h (magnification: 1980×).

Figs. 9–11 show the relative particle sizes as observed on the surface of an agglomerated particle. The samples shown are the 6, 12 and 24-h samples, respectively. Apparent particle sizes are increasing with increasing soaking time.

SEM examination at higher magnifications revealed that these particles may actually be present as small agglomerates. As shown in Fig. 12, particles with an apparent diameter of 3 μm are actually made up of a number of sub-micron particles. The appearance of the sub-micron media are not distinct, perhaps indicating that they are composed of still smaller crystals or that crystals are nucleating on the particle surface.

5.2. Morphology of the formed samples

The appearances of the formed pastes were very similar for different soaking times, probably due to the high proportion of β-PbO_2 in all the pastes. No evidence for the presence of the sulphate phases identified during compositional analysis was observed, although this may be due to the method of specimen preparation. A typical micrograph of dispersed particles and agglomerated particle surfaces is shown in Fig. 13. The particles shown are believed to be β-PbO_2, and are sub-micron in size, agglomerating to form aggregated particles ∼3 μm in diameter, which can also form larger agglomerates. The particle morphology is not well defined, but appears to be elongated.
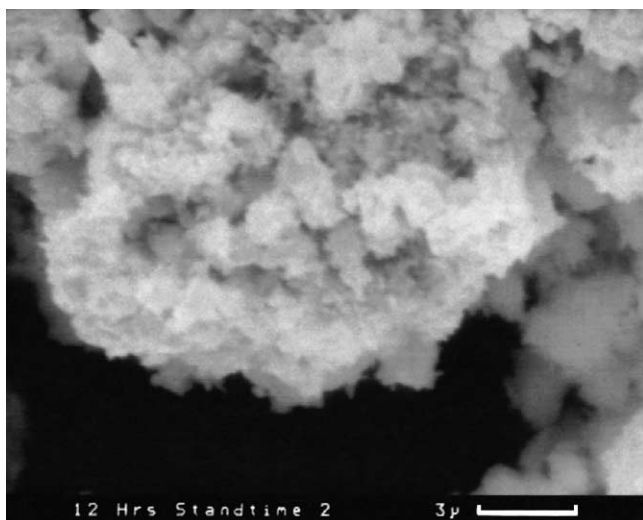

Fig. 8. Indistinct surfaces of agglomerated particles due to the presence of very fine acicular crystal growths, as observed in the 12 h unformed paste (magnification: 5650×).
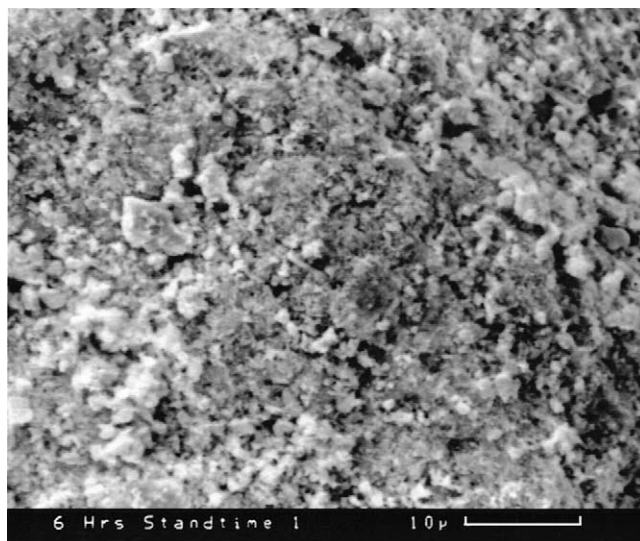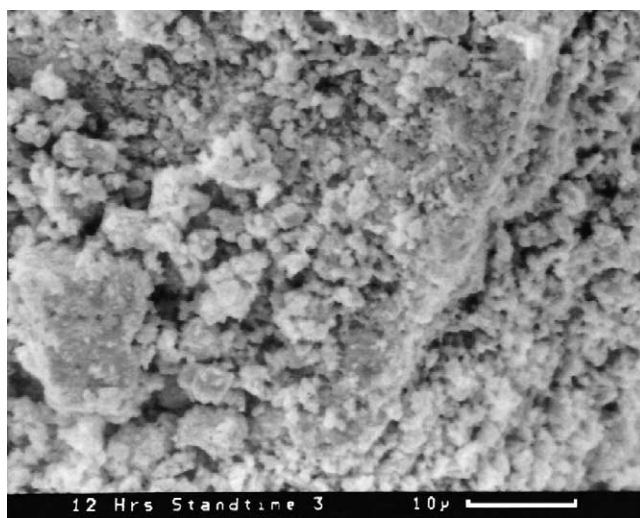

Fig. 10. Agglomerate surface as observed in the unformed positive paste after a soaking time of 12 h (magnification: 1980×).
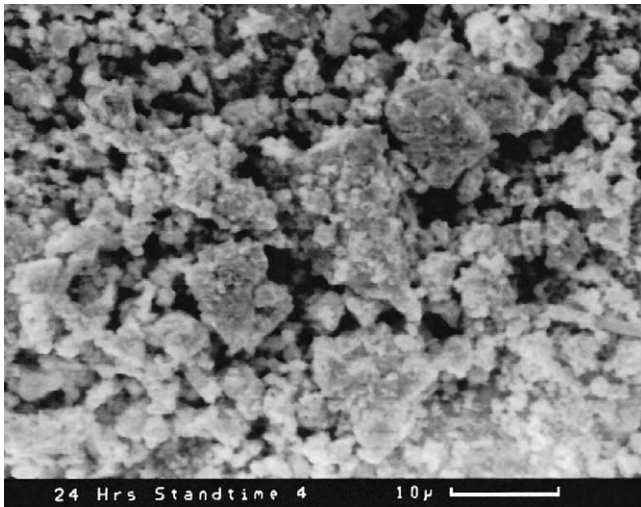
Fig. 11. Agglomerate surface as observed in the unformed positive paste after a soaking time of 24 h (magnification: 1970×).

Fig. 12. High magnification image of dispersed particles as observed in the unformed positive paste after a soaking time of 24 h (magnification: 5650×).
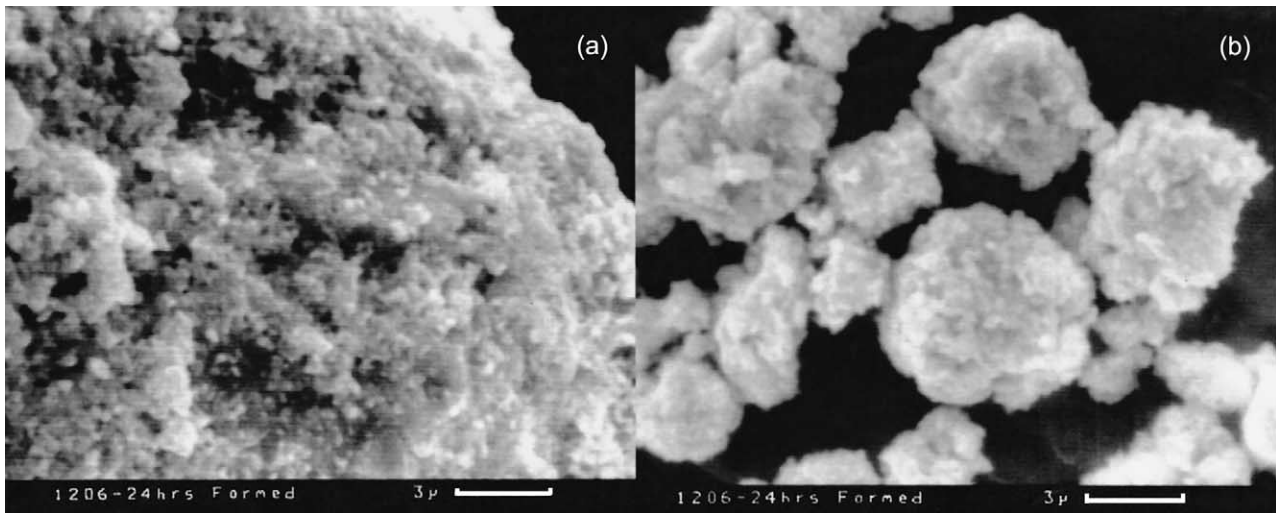

Fig. 13. Formed positive active mass, subjected to 24 h soaking time: (a) agglomerate surface (magnification: 5490×); (b) dispersed material (magnification: 5480×).

5.3. Electrical results

A series of electrical tests were carried out on the remaining four batteries from each batch. Descriptions of the various tests carried out are:

The electrical results shown in Table 1 suggest that the performance of the battery is not significantly affected by soaking time, despite a small change in the sulphate composition.

OCV (V)	Open circuit voltage.
Z (Ω)	Impedance.
1000 A 2 s test	A load of 1000 A is applied for a limited time of 2 s. Results are recorded as the final OCV (V).
5 min	A load of 155 A is applied to the battery and the time (in seconds) taken to reduce battery voltage to 10.2 V is then recorded. The time taken for this to occur should be at least 5 min.
C1 (h)	A load of 27.6 A is applied to the test battery. The recorded result is the time (in hours) taken to reduce the battery voltage to 10.2 V. This should take at least 1 h.
(1), (2) (h)	Different batteries were used for each test type, the first reading is a conditioning cycle therefore the second reading is more representative of the battery performance.

Table 1
Electrical test data for soaking time samples

	2 h	6 h	12 h	24 h
OCV (V)				
Average	12.982	13.002	13.006	12.999
S.D.	0.004	0.006	0.007	0.001
Z (Ω)				
Average	4.4	4.5	4.5	4.3
S.D.	0.1	0.2	0.3	0.1
1000 A 2 s (V)				
Average	7.574	7.361	7.450	7.660
S.D.	0.044	0.088	0.215	0.039
5 min (1) (s)				
Average	383.3	385.5	396.3	386.5
S.D.	10.3	10.7	17.1	14.4
5 min (2) (s)				
Average	366.1	365.2	378.0	373.4
S.D.	12.2	4.5	6.9	14.7
C1 (1) (h)				
Average	1.07	1.05	1.05	1.06
S.D.	0.01	0.01	0.03	0.02
C1 (2) (h)				
Average	1.09	1.08	1.08	1.07
S.D.	0.01	0.02	0.02	0.01

6. Conclusions

- The time period between acid fill and formation does have an effect on the composition of the unformed positive paste. It would appear that soaking times >2 h but <12 h produce the optimum unformed compositions, suggesting soaking times range between 4 and 8 h.
- Examination of XRD patterns of the formed pastes, however, indicates that levels of $PbSO_4$ and 1BS are increased after 6 h, and therefore soaking times should be kept to between 2 and 6 h.
- The two previous conclusions suggest an optimum stand-time of 4–6 h, however, both the electrical results and SEM examinations of the formed pastes suggest that optimisation of the soaking time is unlikely to affect battery performance.

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