



The use of a Polymat material to reduce the effects of sulphation damage occurring in negative electrodes due to the partial state of charge capacity cycling of lead acid batteries[☆]

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ABSTRACT

A conventional lead acid cell that is exposed to a high rate partial state of charge capacity cycling (HRPSoCCC) would show the results of irreversible negative electrode damage due to excessive PbSO₄ formation that can be visually seen by the “Venetian Blinds” effect of the active material. This displays the loss of adhesion of the active material with the electrode’s grids thereby making large sections of the material ineffective and reducing the cells useful capacity during high current applications. The use of a commercial lightweight polyester non-woven material that was referred to as “Polymat” was placed on both sides of the negative electrode, has demonstrated a better physical adhesion of the active material thereby maintaining the active material’s physical integrity. This however does not reduce the sulphation effect due to the HRPSoCCC test but only reduces the physical damage due to the irreversible active material “Venetian Blinds” effect. The study looked at the effect the Polymat has on the battery’s cold cranking ability (CCA) at -18°C , the HRPSoCCC and its active material utilization. Typical flooded nominal 8 Ah test cells were assembled with 3 positive and 2 negative plates with and without Polymat. The study showed that there was little or no difference of cells made with the Polymat on the CCA and HRPSoCCC capabilities when compared to cells without the Polymat, with significant improvement in active material’s adhesion and integrity to the grid wire. Partial recovery of the cell’s discharge capacity made with the Polymat could be achieved after the “failed” cells were subjected to a simple pulse recharge sequence.

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1. Introduction

Over the last few years, the demands on the Pb-acid battery as an energy storage device by automotive manufacturers have increased considerably with requirements for the battery to work at a partial state of charge. This ranges from typical “Start Stop” applications to hybrid and full electric vehicles [1,2]. These new demands often requires the battery to capacity cycle in a variety of states of charges (SoC), which is not favorable towards the internal discharge and charge electrochemistry of the active electrode material. The fully charged electrodes’ material of Pb and PbO₂, respectively can be considered as conductive which discharges to a relatively non conductive PbSO₄ material on both electrodes. Subsequently, a battery that is subjected to a partial state of charge for prolonged periods of time, especially when subjected to capacity cycling applications

without being allowed to fully recharge; is believed to accumulate the PbSO₄ primarily on the negative Pb electrode which would result in irreversible “sulphation” and electrode damage [3]. This electrode damage would be observed by the formation of large non conducting PbSO₄ crystals, and due to the changes in the crystal’s unit cell volume between the Pb and PbSO₄ material, a considerable change in the physical morphology of the active electrode material. This is usually seen by the effects of active material “blistering” where the active material physically detaches itself from the electrodes’ grid current collector. This is also known as the “Venetian Blind” effect. In order to reduce the effect of sulphation in the negative electrode, extensive research was done in including additives to the paste mixture such as different graphites [4]. Other studies consider changes to the physical cell design in order to reduce the effect of sulphation. These include electrode grid designs [5] and the addition of a capacitor type material into the cell design of the Ultra battery [6]. A number of laboratory test procedures are used to simulate the accelerated capacity cycling testing of cells that are made with a range of different additives under high rate partial state of charge capacity cycling (HRPSoCCC). This is done in order to show if improvements can be achieved in batteries made with

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new electrode designs and additives over a relatively short period of testing time under controlled conditions [7].

Pb-acid battery manufacturers have made use of an inert polymer based material, known as Polymat, to cover the electrode surfaces as part of their continuous electrode pasting process. It is made from a non-woven polyester fiber that is applied to the pasted electrodes during the continuous pasting process. The pasting process normally makes use of thin sheets of porous tea bag type filter paper that prevents the electrodes from sticking and snaring together once pasted and stacked for the curing process. The paper also aids the physical handling of the electrodes that are subsequently assembled into the battery cases. The thin paper sheet would then easily dissolve from the electrode surface during the formation process and disintegrate in the strong sulphuric acid electrolyte. The Polymat was introduced and used in combination with a polyethylene separator that formed part of the plate assembling process. The main purpose was to ensure that the active material on the pasted plates was kept in place with the grid support to reduce its shedding from the grid during high temperature and heavy capacity cycling applications. The initial idea was to attach the Polymat to the surface of the electrodes and possibly replace the use of a polyethylene separator completely. This never proved to be possible and instead, the Polymat was shown to be more useful in retaining the active material and give support and structural integrity during capacity cycling on both the negative and positive electrodes. In this study, the use of the Polymat material was shown to reduce the physical damage of the negative active material due to sulphation that occurred during high rate partial state of charge capacity cycling conditions.

2. Experimental

2.1. Electrodes and cells assembly

All electrodes (both anode and cathode) used in the study were received in their cured condition from a local commercial automotive battery manufacturing facility. The electrodes had a thickness of 1.6 mm for the positive and 1.3 mm for the negative electrodes made by the continuous casting type process with the grid alloys being typically Ca based alloy for the anode and Ca–Sn–Ag alloy for the cathode. The paste density for the electrodes used in the study was approximately 4.1 g cm^{-3} and 4.4 g cm^{-3} for both the cathode and anode electrodes, respectively. The negative electrodes active material was made with the standard addition of fine BaSO_4 , vanisperse and carbon lamp black with no additional graphite. Two sets of anode and cathode electrodes were pasted with the Polymat (14 g m^{-2} and 0.19 mm thick) and tea bag paper (12.5 g m^{-2}), respectively. The Polymat was made from non-woven 0.01 mm polyester fibers. The cured electrodes were cut to size ($62 \text{ mm} \times 109 \text{ mm}$) and assembled into a formation bath containing sulphuric acid (1.160 SG). The electrodes were formed at a relatively low constant current for 91 h to ensure complete formation. They were subsequently washed with water and positive electrode was dried at 100°C for 24 h and negative electrode at 60°C for 4 h under nitrogen gas. The mass of the dry formed negative active mass was determined by subtracting the pre-weighed grid mass. This mass would subsequently be used in determining the cell's material utilization (%) at the various discharge rates relative to the expected theoretical capacity of the available active mass of the negative electrodes. The formed negative and positive electrodes were assembled into a 5 plate cell design (3 positives and 2 negatives) with AMER-SIL standard porosity calendared ribbed industrial type separators (2.40 mm in thickness) that were cut to size ($62 \text{ mm} \times 109 \text{ mm}$). The assembled cells were placed into a polycarbonate cell container and filled with 1.28 SG sulphuric acid.

2.2. Standard capacity testing and Peukert relationship

The theoretical capacity of the two negative plate cells was estimated to be about 8 Ah at the C_{20} rate. Discharge current rates of 0.4 A, 0.8 A, 1.6 A, 2.4 A, 3.2 A, 6 A and 8 A were used, respectively followed by a standard recharge step between each discharge step. The recharge step was kept the same for all studies done, except for the cells subjected to the pulse recharge steps described in Section 2.5. This ensured that sufficient capacity returned to the discharged cell with a suitable upper voltage to limit excessive water electrolysis and positive grid corrosion. The charge profile would be an 18 h charge at a voltage limit of 2.4 V followed by an 800 mA charge for 1 h with no voltage limit.

The Peukert relationship for the cells discharged at the various current rates was determined by plotting the log time (t) vs. log current (I) and from the slope and intercept, the respective true C_1 and C_{20} capacity and currents relative to the actual negative formed material were determined.

2.3. Cold crank test (CCA)

The CCA test was done at $-18 \pm 1^\circ\text{C}$ by placing them in a freezer for 24 h before testing. Since the study was comparative in nature for the size and configuration of the batteries made, a relationship was determined between the actual C_{20} capacity of a particular cell and the expected CCA current according to the DIN European specification. The specification shows that there is a relationship between the C_{20} rated capacity of a battery type to the CCA current that is expected from the battery type and size. This relationship can be expressed as a linear relationship between the CCA (A) to the rated C_{20} capacity (Ah) as $\text{CCA} = 4.2 C_{20}$. This would allow for comparatively high current testing to be done of small cell designs where the current used would depend on the actual C_{20} capacity achieved for a cell. In using this relationship for the small cell assembly, an indication of the cell to manage high currents under low temperature conditions can be studied. The currents ranged between 40 and 55 A depending on the cell's actual C_{20} capacity and were discharged to a lower voltage limit of 1 V followed by a standard recharge sequence at room temperature.

2.4. Capacity cycling test (HRPSOCCC)

In this study, the high rate partial state of charge capacity cycling was done by discharging the respective cells at the C_1 rate to 50% of the C_1 capacity. This is followed by respective 1 min charge and 1 min discharge steps at the C_1 rate with the recharge step in the loop sequence having no upper voltage limit. This was repeated until the cell reached a lower discharge voltage of 1.75 V. This was followed by a standard recharge step described previously and the number of cycles achieved would be described as those within one loop cycle sequence. After the cell was recharged, the loop sequence test would be repeated two or three times until the cells indicated that it no longer was able to maintain the C_1 rate of discharge to 50% DoD or until the number of cycles within a loop count was below 3 cycles. The experiment for this cell would then be terminated and the cause of cell failure would then be determined by disassembling the cell electrodes analyzing the active material on the negative electrode by powder X-ray diffraction (PXRD), optical microscopy and scanning electron microscopy (SEM) to determine the extent of the sulphation.

2.5. Pulse recharge

Selected cells with Polymat that showed limited active material damage after the HRPSOCCC testing were subjected to a "pulse charge" recharge step similar to the work published by James et al.

[8]. The sequence steps required the charge of the cell 5 A with a voltage limit of 2.67 V for 5 s, followed by 1 s discharge at 5 A with a lower voltage limit of 1.75 V. The recharge pulse sequence was repeated for 14 h ensuring that at least 110% of the actual C_1 capacity had been returned to the cell during charge. This was done in order to show if the cells with the Polymat could partially recover its capacity.

2.6. Powder X-ray diffraction and scanning electron microscope

Phase identification of a crystalline material was determined by X-ray powder diffraction (PXRD) using a Bruker D8. Phase quantification was done by Rietveld refinement using Topas V3.1. A scan range of 5–70° was used at 1 s/0.2° steps for all PXRD analysis. For formed active material taken from the electrodes, samples were ground using a mortar and pestle and the powder mounted in standard polycarbonate sample holders. Scanning electron microscope (SEM) was done using a Joel JSM 6380. Samples were prepared by placing a small amount of electrode active material onto the sample holder using a carbon paste and subsequently gold sputter coating it to increase its conductivity.

3. Results

A summary of the comparative electrochemical study of lead acid cells made with electrodes that were assembled with and without Polymat are shown in Table 1. The analysis was done on 7 cells of each build type to show the repeatability of the responses.

The results showed that there were no significant differences in terms of the cell's C_1 and C_{20} capacity between the electrodes made with and without the Polymat. In particular, the time taken to reach 1 V at the CCA rate, the use of the Polymat material to the cell electrode would not negatively influence the high current discharge ability at low temperatures. Concern was expressed that the addition of an inert fibrous material to the surface of the electrodes could reduce the diffusion ability of the acid into the porous structure of the electrodes during high discharge and low temperature applications. This was not observed to be the case in this study.

Another important parameter to consider when comparing cell types that contain different configurations or build is the capacity that can be obtained at different rates. The results showed that there was a slight difference in the active material masses between the two negative electrodes types made with and without Polymat (Table 1). The electrodes made with the Polymat showed to have a slightly higher active material mass that was not necessary due to the mass of the Polymat, since the electrode, grid and Polymat masses were subtracted from the final electrode mass. Hence, the respective C_1 , C_{20} and CCA capacities were slightly higher, but when considering the % mass utilization at the C_1 , C_{20} and CCA rates, there were no significant differences within the 95% confidence interval between the cells made with and without Polymat. This was also seen by the fact that there were no significant differences between the Peukert constant (n) determined for the cells made with and without the Polymat.

A typical HRPSoCCC sequence capacity cycle test over 3 loop sequences is shown in Fig. 1. The results showed that for most cells studied, there were more partial state of charge capacity cycles within the 2nd loop sequence than in the preceding 1st loop sequence (Fig. 2). Particularly when comparing the averages of the number of cycles achieved for the 7 cells per group used in this study of cells that were made with and without the Polymat, there were more cycles within the 2nd loop sequence. However, there were also larger statistical standard deviations shown for the group of results for the cycles achieved in the 2nd loop sequence (Fig. 2). This implied that within these types of capacity

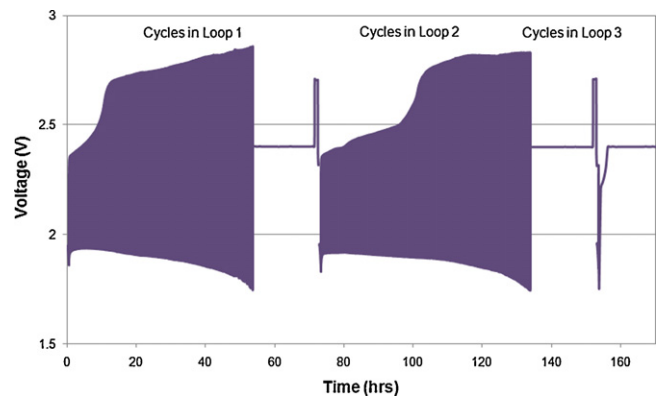


Fig. 1. HRPSoCCC sequence of a cell that was made with Polymat.

performance cycling tests, the standard deviations in achievable cycles should be taken into consideration for a number of similar cells that were subjected to the same testing sequence. One could only imply from these results that the method gave an indication that a particular group of cells are better or worse if their loop cycle counts are significantly outside the confidence intervals shown. Results based on the averages only could imply that the cells made with Polymat performed worse than those made without but when considering the large spread of results within the confidence interval shown for the two sets of cell types, their cycling performance are similar. The results also showed that none of the cells were able to achieve any significant number of cycles within the 3rd loop sequence. All cells showed failure within the first 3 cycles after being recharged once having completed the 2nd loop cycle test. The main contribution to the failure of the cells could be attributed to the sulphation of the negative active material.

The results in Fig. 1 showed that as the cycle number would increase in the 1st loop sequence, the end of charge voltage within the recharge step would relatively quickly increase to about 2.7 V. As the capacity cycling continued, the charge voltage would gradually continue to increase up to 2.9 V, after which the corresponding discharge voltage would notably decrease until 1.75 V was reached, indicating the end of the loop sequence test. This is an indication that the internal resistance of the cell would gradually increase upon cycling, allowing for most of the current on the recharge steps to contribute to cell gassing. This in turn would continue to increase the internal resistance, since the cell would be limited in its active material recharge, thereby gradually depleting the available cell's capacity. At this point, a simple recharge step of charging at a constant voltage of 2.4 V for 18 h allowed the cell to recover significantly in order to allow for a 2nd loop sequence testing to commence. The capacity cycling characteristics of the 2nd loop sequence was notably different in that the maximum recharge

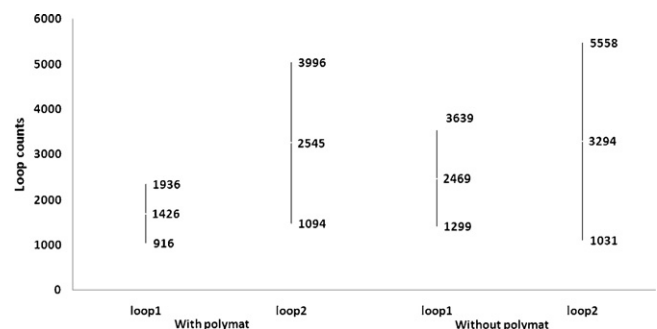


Fig. 2. Average number of loop cycles in each loop sequence with the 95% confidence interval.

Table 1

Statistical summary of electrochemical results obtained from cells made with and without Polymat. Capacity values are with respect to the active materials on the negative electrodes.

	With Polymat		Without Polymat	
	Average	Standard deviation	Average	Standard deviation
Peukert constant and capacity				
<i>n</i>	1.05	0.025	1.06	0.021
<i>C</i> ₁ (Ah)	8.28	0.546	7.54	0.28
<i>C</i> ₂₀ (Ah)	9.22	0.227	8.5	0.25
CCA				
Time at 1 V (s)	196.77	3.85	198.56	23.31
Material utilization				
Active material mass (g)	56.76	1.13	52.86	1.44
% Util <i>C</i> ₂₀	62.83	2.08	62.18	1.08
% Util <i>C</i> ₁	56.45	4.12	55.17	2.62
% Util CCA	14.38	2.61	14.40	1.65
HRPSoCCC				
Loop 1 (cycles)	1426	552	2469	1265
Loop 2 (cycles)	2545	1569	3294	2447
Loop 3 (cycles)	2	–	2	–

voltages in the cycles seemed to plateau at just below 2.5 V for a significant number of initial cycles, before gradually increasing to 2.8 V after which it then increased to 2.9 V. At this point, during the discharge step, the corresponding discharge voltage decreased before quickly reaching the lower voltage limit of 1.75 V, after which the testing stopped. This phenomenon of observing the recharge voltage to initially plateau during the first few cycles in the 2nd loop sequence could be a reason for some cell achieving more cycles when compared to the 1st loop sequence.

It must be remembered that the cells were recharged after each loop sequence using only a standard 18 h 2.4 V constant voltage step. This charge step was not sufficient after the 2nd loop cycle testing to restore the cells capacity in order to allow for another partial state of capacity cycling sequence.

Upon disassembling the cells and analyzing the active material on the negative electrode, the PXRD results showed that the active material of the negative electrode contained between 50% and 60% PbSO₄ (Fig. 3). The PbO observed in the diffraction pattern was due to the oxidation of the Pb that occurred during sample preparation.

More significant were the visual observations of the negative electrodes after HRPSoCCC testing in terms of their physical appearances (Figs. 4 and 5). The negative electrodes made without Polymat (Fig. 5) showed the typical blistering of the active material that was also referred to as the “Venetian Blind” effect where the active material had separated from the current collectors which would result in irreversible electrode damage. By comparison the electrodes made with the Polymat showed that fibrous material still adhered to the active material and the current collectors. The only

noticeable difference was that in some places, the Polymat material on the plates that had capacity cycled had separated slightly from the surface of the active material. The Polymat material seemed to reduce the physical electrode surface damage that occurs due to excessive sulphation that results in the expansion of the active material resulting in a loss of electrode structural integrity. Hence, the loss of contact between the active material and current collectors would be considered as physical plate damage which is irreversible. The cells with the Polymat showed a lesser degree of physical damage, but still showed the chemical effect of the lead sulphate crystals formed during the HRPSoCCC cycling. Hence the cells with the Polymat still suffered from capacity loss due to the excessive sulphation thereby reducing the effective capacity cycle life time of the cell in this type of application. By comparison, if one would consider the number of cycles achieved within Loop sequences (Table 1), the cells made with the Polymat achieved fewer cycles than the ones made without Polymat. However, the physical damage observed on the negative electrodes without Polymat was comparatively more severe than those without.

Upon closer inspection of the active materials by SEM, the negative active material with Polymat showed the typical fibers of the Polymat with slightly different active material characteristics to that of the active material without Polymat (Figs. 4d and 5d). The Pb crystals in the sample without Polymat shows typical plate like structures (Fig. 5d), whereas the ones with Polymat had finer needle shaped crystals (Fig. 4d). After HRPSoCCC testing, the PbSO₄ crystals are scattered amongst the plate like crystals of the negative active material. The samples after cycling showed significantly

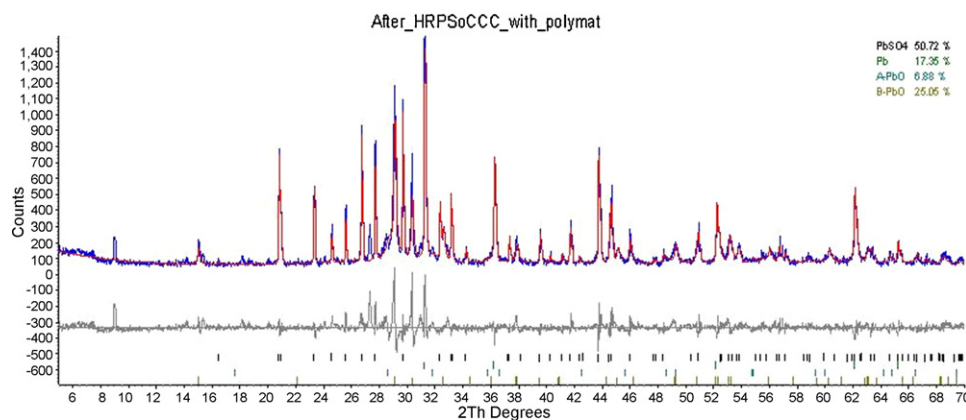


Fig. 3. XRD spectrum of a negative electrode made with Polymat after HRPSoCCC testing.

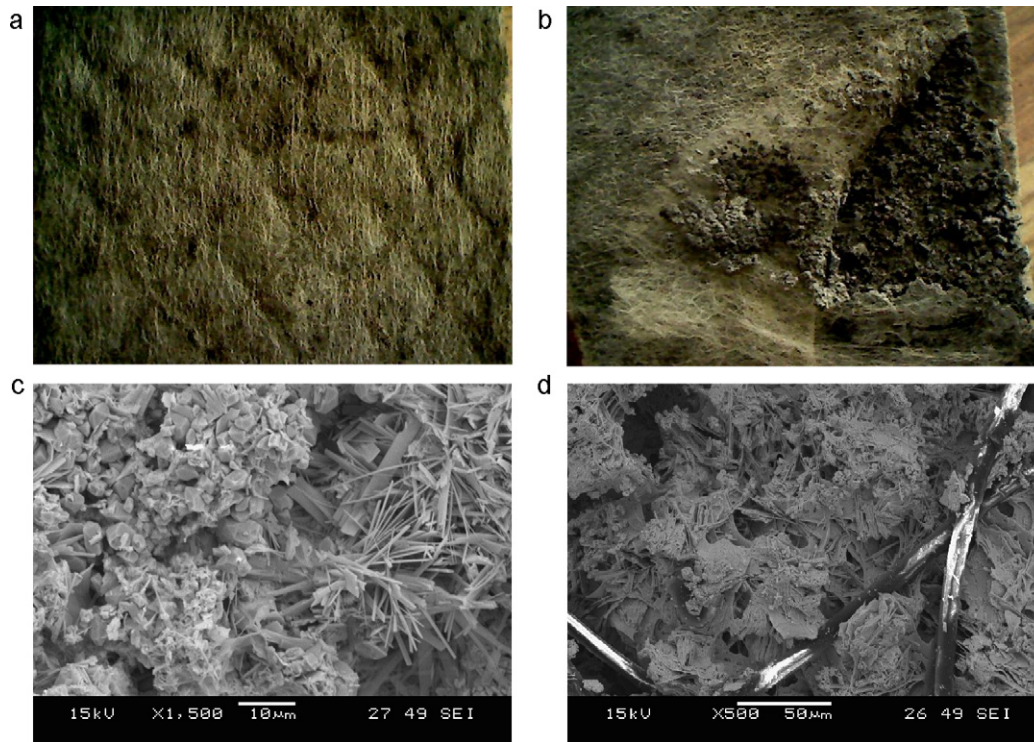


Fig. 4. SEM and photograph images of negative electrodes with Polymat.

larger PbSO_4 crystallites interspersed amongst the plate like crystals of the Pb active material from the electrode made without Polymat. Whereas the one with Polymat showed finer PbSO_4 crystallites distributed amongst the needle shaped active phase.

In order to investigate the ability of the cells that were built with Polymat material to recover from sulphation damage due to

the HRPSoCCC testing, a set of cells made with the Polymat material were allowed to recharge with a slightly modified recharging step that could be considered as a pulse charging sequence. The aim of this study was not to optimize the pulse charging sequence, of which much had been published in the literature [8], but to rather show that the cells made with the Polymat could partially recover

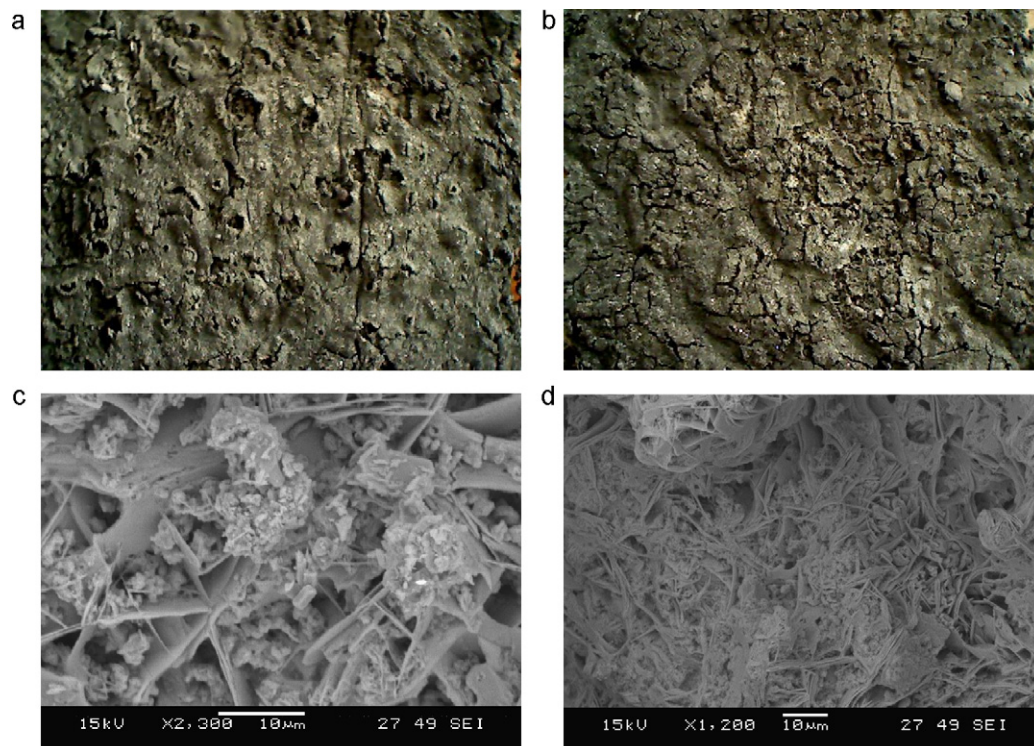


Fig. 5. SEM and photograph images of negative electrodes without Polymat.

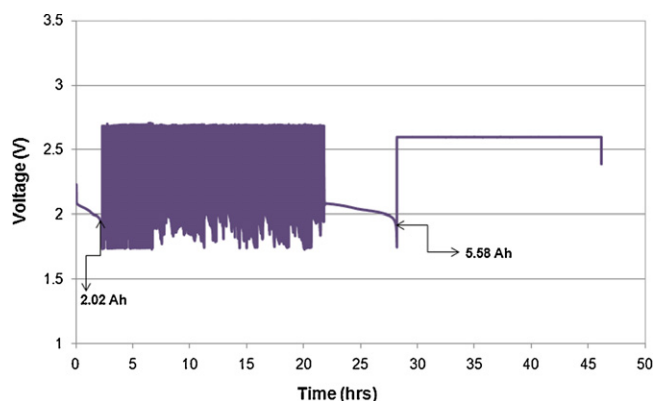


Fig. 6. Pulse recharging sequence of a cell made with Polymat.

in terms of their usable capacity since their physical damage was limited and the primary reason for capacity failure was sulphation which could be reversed electrochemically.

In general, a pulse charging sequence has a short discharge step in the procedure that encourages the electrochemical regeneration of the “impenetrable” non conductive PbSO_4 to form the active Pb phase. No boost charge sequence during the HRPSoCCC testing was considered in this study, since these sequences for Pb-acid batteries can vary considerably in their nature where multiple pulse steps are often used, making their algorithm relatively complex. With the simple pulse charge sequence described, it was shown that the cells made with the Polymat that typically failed after 2 HRPSoCCC sequences could partially recover its discharge capacity (Fig. 6). The cell with the Polymat that had shown failure after 2 loop HRPSoCCC loop sequences was recharged using the standard constant voltage recharge sequence, followed by a C_{20} discharge step, resulting in a capacity of only 2.0 Ah. The cell was subsequently recharged with the simple pulse charge sequence followed by another C_{20} discharge that could achieve a capacity of 5.6 Ah. However, if the cells were discharged at the C_1 rate, no significant capacity could be achieved. This showed that the cell could only partially recover, and that additional steps are needed to reduce the sulphation effect by either changing the pulse recharge sequence and include additives such as graphite to the negative paste mixture. The cells made without the Polymat material were not subjected to the pulse sequence, since it was apparent that physical damage had occurred to the active material of the electrodes.

4. Conclusion

The statistical comparison study of the cells made with and without Polymat showed that the following electrochemical testing criteria were within certain statistical parameters for determining the characteristics and possible improvements of a cell’s performance.

- The Peukert relationship at various currents and the material utilization at the various discharge rates showed there were slight variations between cells made with and without Polymat. However, over the number of similar cells studied within a group, the statistical error showed that these variations were within experimental error and that there was no significant influence of the Polymat on the cells capacity behavior at various discharge rates.
- The use of the high current low temperature (CCA) test that was modified according to international acceptable DIN specifications showed to be a useful technique to determine the particular cells high current electrochemical performance. The criteria were selected of measuring the total time of discharge to achieve 1 V.

This test proved to be comparatively useful in showing the high current ability of small scale cells modified in this study with Polymat and that it had no significant influence on the cells ability to discharge at high rates at low temperatures.

- The use of the HRPSoCCC test procedure showed to be effective to obtain a relatively quick (within 3–5 weeks) accelerated capacity life cycle test of Pb-acid cells by showing that the main cause of failure in such cells was the sulphation of the negative electrode. However, the absolute number of cycles within each loop sequence was shown not to be a definitive indication that the subsequent electrode formula had improved without significant standard deviations between test cells subjected to the same test procedure. Only when a considerable number of additional cycles have occurred in a comparative loop sequence test or that additional loop sequences were achievable when compared to other cell designs can such conclusions be drawn that an improvement in cell design had been achieved to improve the HRPSoCCC applications.
- The SEM and microscope images showed that there was a distinctive crystal shape difference of the Pb active material between the electrodes that contained the Polymat and those that did not. The electrodes without the Polymat showed the typical sponge shaped crystals of the active material, whereas the ones that were formed with the Polymat showed a more needle/plate shaped crystals near the surface. Failure analysis of the cells made with and without Polymat showed that even though there were no significant differences in the number of achievable cycles with the HRPSoCCC testing, there was a notable difference in the final electrodes’ appearance. The material without the Polymat showed that the active material on the electrodes indicated the typical blistering (Venetian blind) effect that would cause the electrical integrity of the active material to lose contact with the current collectors. This was not observed for the electrodes that contained the Polymat. The Polymat material seemed to reduce the effect of the sulphation from expanding the active material and to lose its structural integrity. However, this effect does not reduce the fact that the lead sulphate crystals are still formed due to the HRPSoCCC cycling, thereby reducing the effective life time of the cell.
- The results of this study also showed that a cell that was subjected to capacity cycling (HRPSoCCC) could partially recover the cell lower rate discharge capacity by using a simple pulse charging sequence.

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