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Influence of temperature on expander stability and on the cycle life of negative plates

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Abstract

The influence of temperature and the type of expander on the cycle life of negative lead–acid battery plates set to cycling tests following the requirements of the ECE-15 test protocol has been investigated. The plates prepared with the currently used expanders Vanisperse (Vs) or Indulin (In) alone have a considerably shorter cycle life than negative plates produced with a blend of the two expanders. The new experimental products UP-393 and UP-414 of Borregaard LignoTech (Norway) ensure much better cycle life performance when used for EV battery applications.

Investigations on the influence of temperature on battery cycle life have evidenced that with increase of temperature the cycle life of the battery features a maximum at 40 °C (UP-393, Indulin + Vanisperse). At 60 °C almost all expanders disintegrate and the cycle life of the batteries decreases, though the plates with UP-393 and UP-414 have better cycle life performance than those with other expanders.

A gradual degradation of the NAM structure is observed with batteries set to EV cycling. The energetic structure of NAM, which is built up of small crystals with large surface area, is converted into skeleton structure at the end of battery life, which comprises large crystals with small surface area yielding low battery capacity. On cycling at temperature about 60 °C, the NAM is converted into a well-developed network of thin lead branches with large pores in between. On discharge, some of these branches are oxidized more quickly, thus, excluding part of NAM from the current generation process, which consequently reduces the capacity of the negative plates.

Keywords: Expanders; Negative plate; NAM structure; ECE-15 test; NAM degradation

1. Introduction

Organic expanders are a very important component of the lead–acid battery negative plate. These substances regulate the processes involved in the formation of the negative active mass structure and exert a strong influence on the crystallization processes of Pb and $PbSO_4$ crystals during charge and discharge, as well as on the hydrogen evolution [1–14]. The efficiency of the expanders and their stability determine the capacity and the cycle life of the negative lead–acid battery plates.

In VRLA batteries, the expander contained in the negative active mass is subjected to oxidation by the oxygen evolved at the positive plate. Also, the high operating temperature has destructive influence on the expander [15–18]. Because of the specific conditions of EV battery operation it is important to investigate the influence of expander and temperature on the cycle life of negative plates for EV battery applications.

The structure of the active material of the negative plate consists of: (a) skeleton connected to the grid and built up of interconnected shapeless lead crystals, and (b) individual lead crystals that have grown over the skeleton surface [1,2]. The individual lead crystals participate in the charge–discharge processes and form the energetic structure of the NAM.

On battery cycling the NAM structure undergoes some changes as follows: (a) The lead branches of the skeleton are gradually converted into crystals of the energetic structure, whereby the volume of NAM increases. Consequently, the contact between the skeleton branches is impaired (or even lost) and the capacity decreases, despite the large surface area of the NAM. This phenomenon occurs when the expander content is too great. (b) The crystals of the energetic structure are converted into skeleton ones, whereby the NAM shrinks in volume, its surface area decreases and so does the capacity and the cycle life of the plate. This occurs when the amount of the expander is too little or when the expander degrades. These two types of conversion depend both on the mode of battery operation (rate and mode of charge and discharge) and

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on the activity and stability of the expander(s) used, on temperature, and on the battery type (VRLAB or flooded). Because of the specific conditions of EV battery operation (high rates of charge and discharge, pulse discharge, high temperature, etc.) it is important to investigate the influence of expander and temperature on the cycle life of negative plates as well as the nature of the phenomena leading to degradation of the structure of NAM as depending on the EV mode of battery operation and temperature.

Table 1
Expanders used in the investigation

Expanders	Amount (wt.%)
Vanisperse A	0.1, 0.2, 0.4
Indulin + Vanisperse A	0.15 + 0.08
UP-393	0.2
UP-414	0.2
Indulin + Vanisperse A + UP-393	0.1 + 0.1 + 0.1
Indulin + Vanisperse A + UP-414	0.1 + 0.1 + 0.1

2. Experimental

2.1. Pastes for the negative plates prepared with various expanders

For the purpose of these investigations, pastes for negative plates were prepared using a variety of the most efficient expanders currently used on a worldwide basis such as Indulin (In) and Vanisperse A (Vs), as well as a mixture of Indulin and Vanispesrse A. Tests were also performed with the new experimental expander products UP-393 and UP-414, produced by Borregaard LignoTech (Norway).

The paste formulation for all types of negative pastes was as follows:

Leady oxide (kg)	1
Sulfuric acid (s.g. 1.40; ml)	65
Water (ml)	110
$BaSO_4$ (g)	4
Carbon black expander (g)	2

The various expander concentrations used in the present investigations are summarized in Table 1.

The paste density of all experimental pastes was 4.15–4.20 g/cm^3.

Fig. 1 presents an XRD pattern showing the phase composition of the negative paste. All pastes comprise 3BS and tetragonal and orthorhombic lead oxides, irrespective of the type of expander used. The X-ray diffractograms for all negative pastes are similar.

The positive plates for all experimental batteries were prepared using the same paste with the following formulation:

Leady oxide (72% PbO; kg)	1
Sulfuric acid (s.g. 1.40; ml)	65
Water (ml)	115

The positive paste density was 4.10–4.15 g/cm^3.

2.2. Manufacture of plates and assembly of test cells

The negative and positive pastes were pasted on grids cast from a lead–calcium–tin alloy (Pb–0.097% Ca–0.28% Sn). The negative plates were set to curing in a chamber (at 40 °C) for 72 h. The plates thus produced were assembled in cells with one negative and two positive plates and AGM separators were used between the plates at 30% compression of the active block. After formation of the plates, three cells with each type of expander were set to test.

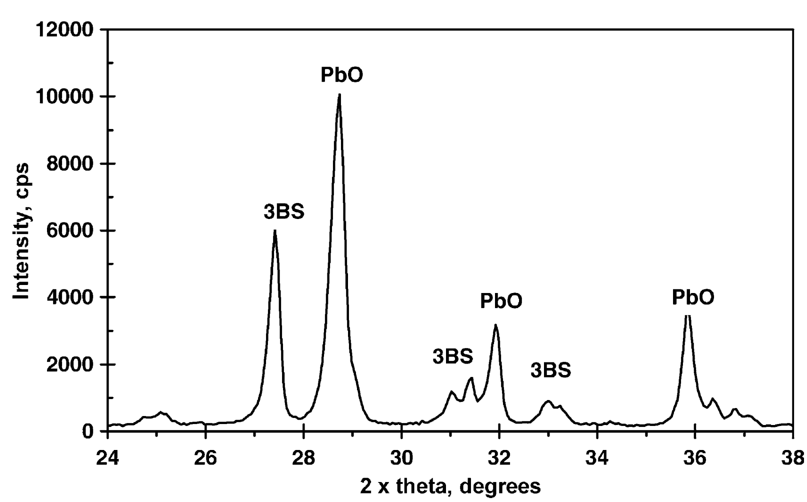

Fig. 1. Phase composition of the negative paste.

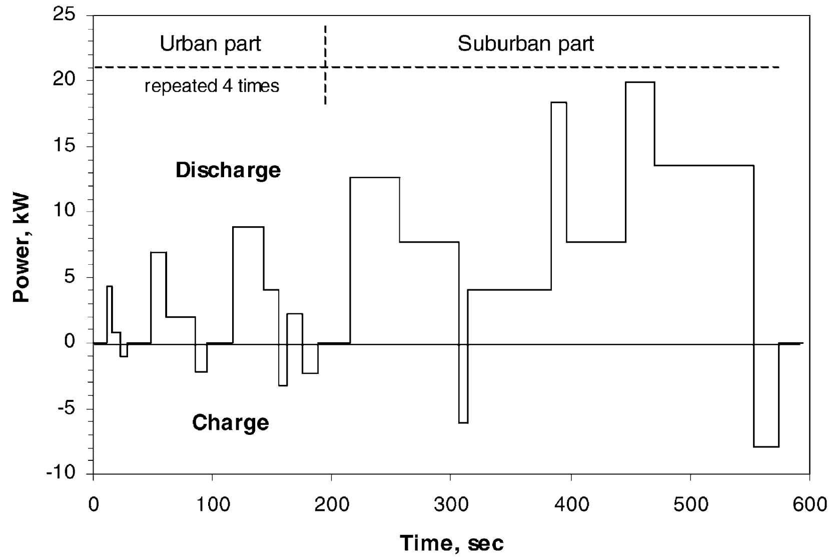

Fig. 2. ECE-15 test profile [19].

2.3. Test procedure

All tests were performed following the requirements of the ECE-15 cycling test procedure for electric vehicle batteries [19]. ECE-15 (Fig. 2) is based on a standard European test cycle, speed versus time, and the battery power profile has been calculated using a EUCAR reference vehicle.

Each cycle consists of two parts, one urban part which is repeated four times without rest periods, followed by one suburban part. The total cycle is 1180 s long and is repeated without rest periods until the end of discharge is reached. The end-of-life criterion is when the battery fails to deliver 80% of its useful capacity, which is the average capacity of the first three ECE cycles. Our experiments have evidenced that when the cells reach 80% of their useful capacity, they continue to deliver capacity for a considerable number of cycles more and then an abrupt capacity decline follows when about 60% of the useful capacity is reached, i.e. the cells have reached their end-of-life due to irreversible degradation of the negative active mass. That is why all cycle life data are presented with regard to two end-of-life criteria: 80 and 60% of the useful capacity.

The test results are presented in terms of relative ECE capacity versus cycle number, the relative ECE capacity of the cells being determined as the ratio between the discharge capacity on ECE-15 cycling and the useful ECE capacity.

2.4. Changes in NAM structure on cycling

The aim of this work was to investigate the influence of expanders on the energetic and skeleton structures of NAM and on the degradation which occurs when negative plates are cycled following the cycling profile of the ECE-15 EV battery test protocol. For the purpose of the investigation, samples were taken from NAM after plate formation and at the end-of-life of the negative plates and these samples were examined by scanning electron microscopy to determine both structures of NAM [1,2].

To prevent oxidation of the spongy lead, small samples of the formed active mass were washed thoroughly with water and then with alcohol. After that the samples were treated with ether and then air dried. The samples were subjected to SEM observation. to see the energetic structure. Then the plates were discharged for 10 h. Samples were taken from the fully discharged active mass and these samples were treated with a saturated solution of ammonium acetate at 90 °C for 30 min. Under such conditions the lead sulfate formed during the discharge dissolves and the metal lead that has not taken part in the discharge process remains undissolved, which presents the NAM skeleton. The skeleton was treated with water, alcohol and ether, as described above, and then the samples were set to scanning electron microscopy examinations.

3. Experimental results

3.1. Correlation between cycle life and amount of Vanisperse

The results of the ECE-15 cycling tests for cells with 0.1, 0.2 and 0.4 wt.% Vanisperse are presented in Fig. 3.

The concentration of 0.2 wt.% is the optimum content of Vanisperse to be used for the production of negative plates for EV battery applications. However, even when used in this optimum concentration, Vanisperse alone yields but a short EV battery cycle life. Vanisperse is one of the best expanders for SLI batteries. However, it does not seem to be sufficiently efficient for VRLA batteries for EV application and should, therefore, be blended with some other expander product(s).

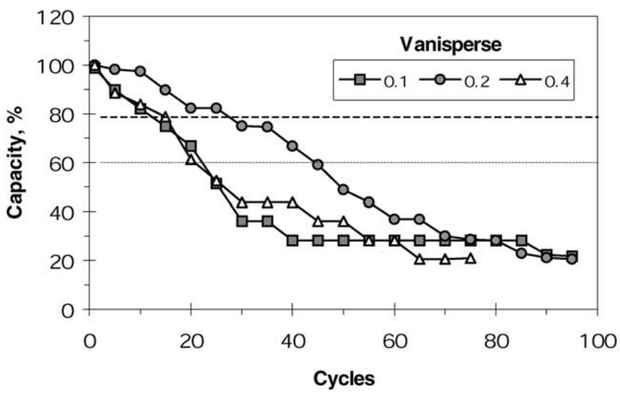

Fig. 3. Capacity changes on cycling of the cells with 0.1, 0.2 and 0.4% Vanisperse.

3.2. Influence of compression on the cycle life

For this investigation we used negative plates with 0.2 wt.% Vanisperse, which were assembled into cells with 10 and 30% compression of the AGM separators, respectively. The test results are presented in Fig. 4.

It can be seen from Fig. 4 that a rapid decrease in capacity is observed within the first 10–15 cycles. Following this initial decline, the capacity of both cells under test decreases slowly until the end-of-life is reached. The data in the figure show that the cell with 10% compression has a cycle life of 40 cycles, whereas that with 30% compression endures 100 cycles (at 60% end-of-life).

3.3. Influence of temperature on the cycle life of negative plates

To investigate the influence of temperature on the cycle life of VRLA cells negative plates with 0.2 wt.% Vanisperse were used at 30% compression of the AGM separators. Fig. 5 presents the capacity curves obtained on ECE-15 EV cycling of the cells at three different temperatures.

The shortest cycle life (70 cycles) was measured for the batteries tested at 60 °C against 100 cycles for those cycled at 25 °C. When the test was performed at 40 °C the cell capacity was higher throughout the test and the plates reached their end-of-life after 200 cycles, which indicates that the temperature of 40 °C has the most beneficial effect

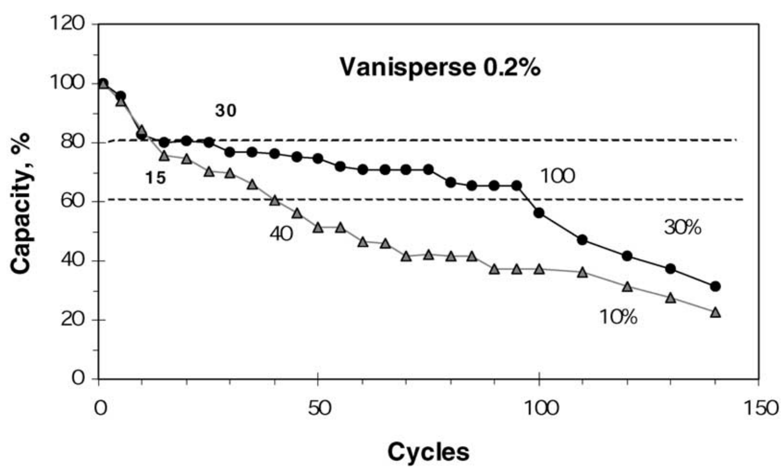

Fig. 4. Capacity changes on cycling of cells with different compression.

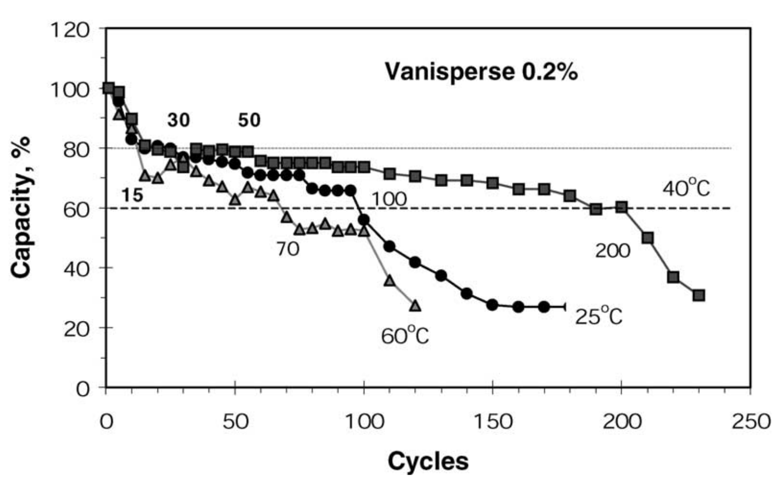

Fig. 5. Capacity changes on cycling of the cells at different temperatures.

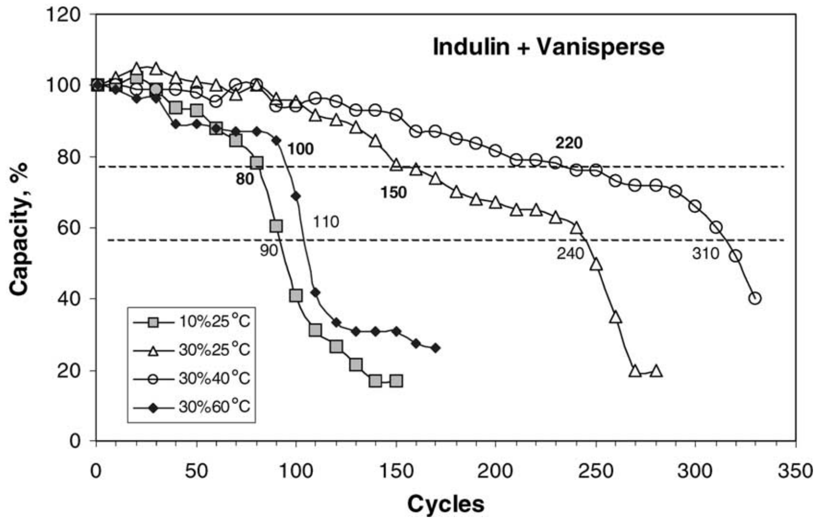

Fig. 6. Capacity changes on cycling of cells with a blend of Vanisperse and Indulin.

on the performance of the batteries when cycled according to the ECE-15 EV test procedure.

3.4. Cycle life tests of negative plates prepared with a mixture of Vanisperse and Indulin

A series of cell tests were performed with negative plates prepared with a blend of Indulin and Vanisperse. The results of the ECE-15 tests of the above cells are presented in Fig. 6.

No initial capacity decline down to 80% of the useful capacity was observed with the cells containing this expander blend as it was established in Figs. 3–5 for cells with Vanisperse. The cells with low compression (10%) had a cycle life of 90 cycles, whereas those tested at high temperature (60 °C) endured 110 cycles before reaching their end-of-life. The cells with 30% compression had a cycle life of 240 cycles when cycled at 25 °C and the best cycle life performance (310 cycles) was observed for the cells with 30% compression at 40 °C. Fig. 6 shows also that the capacity performance of the cells under test is fairly stable within the capacity range 80–60% of the useful capacity and they can undergo about 100 cycles more before their capacity falls below 60%. Fig. 7 presents the cycle life data for the cells under test at different end-of-life criteria (60 and 80% of the useful capacity).

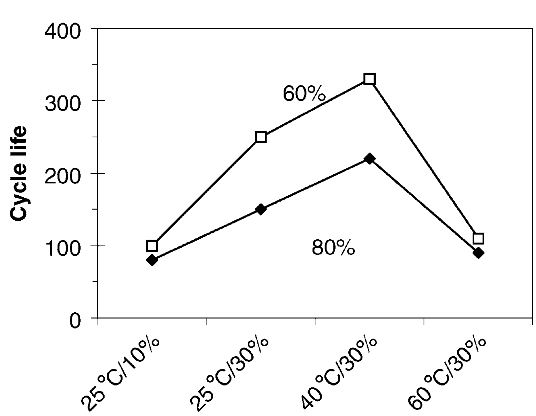

Fig. 7. Cycle life of the cells under test.

Analyzing the data in Figs. 6 and 7, it seems a real challenge to improve the capacity performance of the negative plates to above 80% of their useful capacity. One possible way of achieving this would be to optimize the charge mode of the negative plates.

Fig. 7 illustrates also the effect of AGM compression on the cycle life of negative plates cycled at 25 °C. It can be seen that with increase of the compression from 10 to 30% the cycle life of the plates increases considerably.

Fig. 7 shows that the plates with 10% compression have almost the same cycle life for both end-of-life criteria (60 and 80% of the useful capacity). This is not the case at 30% compression. Here the cycle life performance differs substantially when one or the other end-of-life criterion is adopted. Probably, the nature of the negative plate/AGM contact interface plays an important role in the processes that take place in the negative plate and, thus, influences its cycle life performance.

3.5. Cycle life tests of negative plates with the new expanders UP-393 and UP-414

The new expanders UP-393 and UP-414 are experimental products of Borregaard LignoTech (Norway). The results of the ECE-15 tests of the cells with UP-393 expander are presented in Fig. 8.

The cells cycled at 60 °C have the shortest cycle life of only 160 cycles, whereas those cycled at 25 and 40 °C endure 360 and 390 cycles, respectively. Another interesting finding is that almost all cells maintain a capacity performance of about 80% of the useful capacity for a fairly long period of time and then their capacity decreases rapidly as a result of some irreversible processes that cause degradation of the NAM.

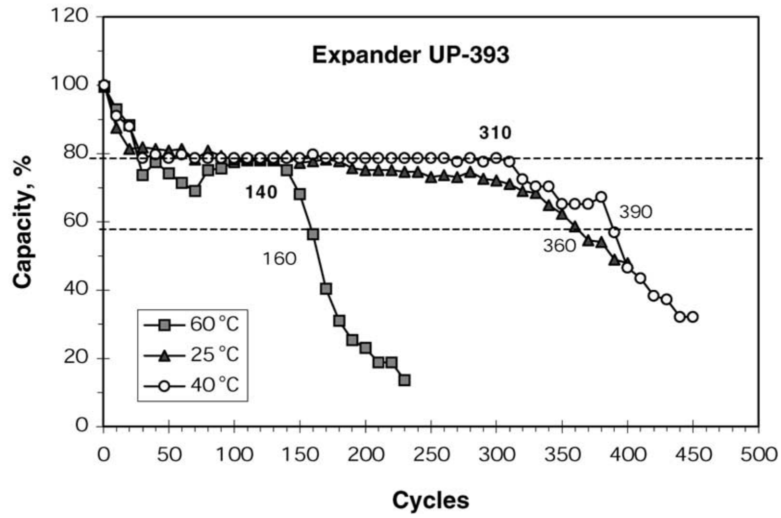

Fig. 8. Capacity changes on cycling of cells with UP-393 expander.

The results of the ECE-15 tests of the cells with UP-414 expander are presented in Fig. 9. In this case, too, the cycle life of the negative plates tested at 60 °C is the shortest (120 cycles). Until cycle 160, the cells tested at 40 °C have the highest capacity, which however falls below 80% of the useful capacity thereafter. The capacity of the cells cycled at 25 °C is constant and very close to 80% of the useful capacity for about 280 cycles and begins to decrease thereafter. The cycle life of these cells is 350 cycles.

These results indicate that the cells with expanders UP-393 and UP-414 have similar performance characteristics (capacity and cycle life) when cycled at 25 °C, but expander UP-393 is more stable than UP-414 at 40 °C and ensures the highest capacity at this temperature for 390 cycles.

If these results are compared with those obtained for the batteries with 0.2 wt.% Vanisperse it is evident that expanders UP-393 and UP-414 at 40 °C are much more stable than Vanisperse and ensure considerably longer cycle life of the negative plates for EV batteries.

3.6. Cycle life tests of negative plates with three-component expander blends: In + Vs + UP-393 and In + Vs + UP-414

In all tests discussed up to now the batteries were charged employing the IU charge algorithm (i.e. constant current—voltage limited charge). The current was $0.4C_{10}$, the voltage was limited to 2.5 V per cell and the charge factor was 108%. As has been established for positive plates, the increase in charging current leads to a linear increase of battery cycle life [20]. How does the higher charging current affect the performance of the negative plates? In order to find the answer to this question, we set six identical cells with negative plates with Indulin + Vanisperse + UP-393 to

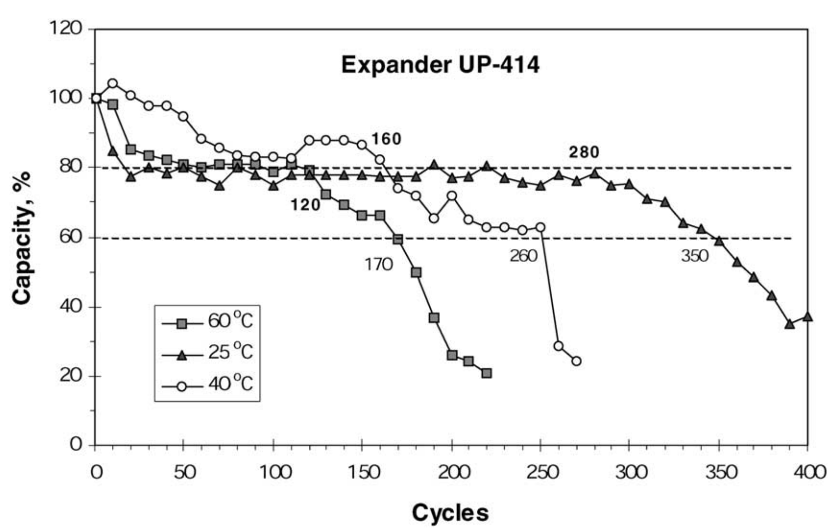

Fig. 9. Capacity changes on cycling of cells with UP-414 expander.

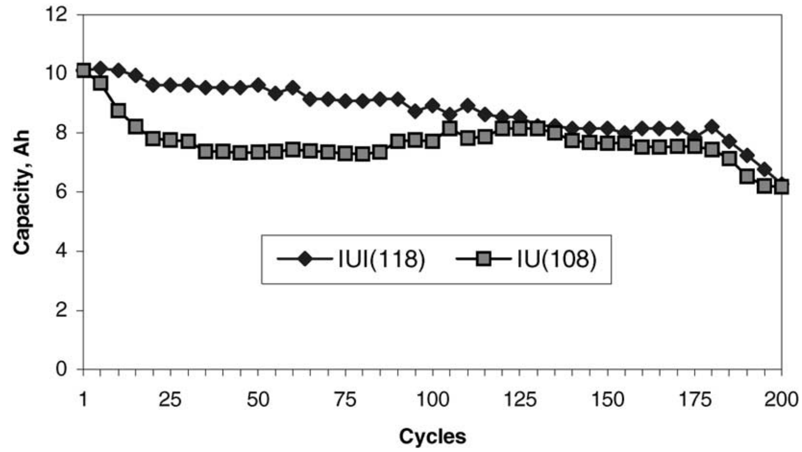

Fig. 10. Capacity changes on cycling with two different charge modes.

ECE-15 cycling tests employing two different charge modes:

$$I_1 = 0.4C_5 \quad \text{up to} \quad U_2 = 2.50\,\text{V}, \quad U_2 = 2.50\,\text{V} \quad \text{until} \quad F_{ch} = 108\%. \tag{1}$$

$$I_1 = 1.2C_5 \quad \text{up to} \quad U_2 = 2.5\,\text{V}, \quad U_2 = 2.5\,\text{V} \quad \text{until} \quad F_{ch} = 108\%, \quad I_3 = 0.1C_5 \quad \text{until} \quad F_{ch} = 118\%. \tag{2}$$

The results of these tests are presented in Fig. 10.

The results obtained provide evidence that when the cells are charged with a current equal to $0.4C_5$ during the first charge stage, the negative plate capacity decreases to about 80% of the initial capacity within the first 15–20 cycles. If the cell is charged at constant current equal to $1.2C_5$ and then at $0.1C_5$ during the third charge stage with no voltage limit until a charge factor of 118% is reached, then there is no initial capacity decline during the first 20 cycles, no change in cycle life, and the capacity performance of the negative plates improves. Due to this increase in capacity, the energy delivered throughout the whole cycle life of the battery increases by more than 18%.

The experimental cells with three-component mixtures of expanders were set to cycling tests following the ECE-15 test protocol. The results are presented in Figs. 11 and 12.

As is evident from the figures, under the above charge conditions the cells have a stable capacity performance (about 100%) for about 150–200 cycles with no capacity decline at the beginning of cycling. The shortest cycle life (50–65 cycles) is exhibited by the negative plates cycled at 60 °C. When the tests are conducted at 25 and 40 °C the negative plates have a cycle life of 200 cycles for the blend In + Vs + UP-393 and 160–180 cycles for the blend In + Vs + UP-414, respectively. If these results are compared to those obtained for the plates with Indulin + Vanisperse (Fig. 6), UP-393 (Fig. 8) and UP-414 (Fig. 9), it becomes evident that the three-component expander blends yield shorter cycle lives.

3.7. Influence of temperature on the cycle life of negative plates

The temperature of cycling exerts a strong influence on the cycle life performance of negative plates by affecting

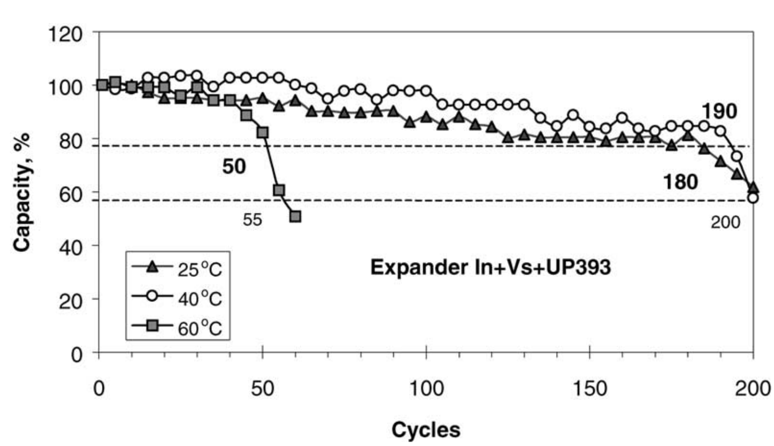

Fig. 11. Capacity changes on cycling of cells with the three-component expander blend In + Vs + UP-393.

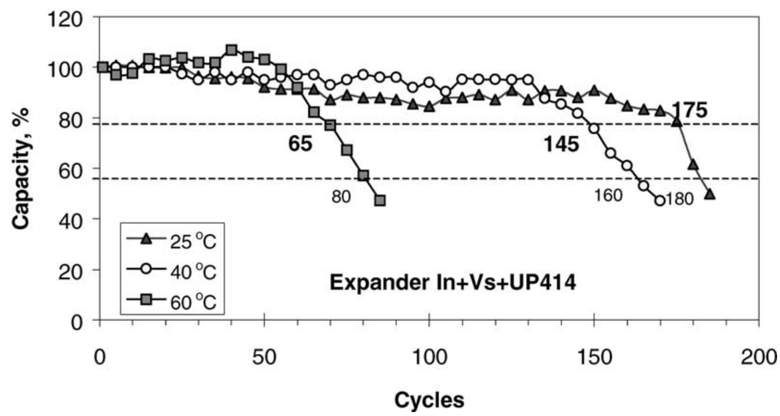

Fig. 12. Capacity changes on cycling of cells with the three-component expander blend In + Vs + UP-414.

both the stability and the rate of disintegration of expanders as well as the structure of the NAM, which in turn determines the capacity of the plate. The influence of temperature on the cycle life of negative plates containing the expanders discussed above is summarized in Fig. 13. As all the above tests were performed with VRLA cells, the effect of oxygen (during operation of the oxygen cycle) on the expander should also be added to the temperature effects.

The following conclusions can be drawn on the grounds of the data in the figure: the expanders UP-393 and In + Vs + UP-393 ensure the longest cycle life at 40 °C. The expander UP-414 can also be added to this group.

When the battery is cycled at 60 °C and is of the VRLA type, the expanders containing lignin and its derivatives disintegrate as a result of which the battery's cycle life is reduced by almost a factor of two. In order to improve the cycle life performance of the negative plates, the battery temperature should be kept equal to about 40 °C or other polymer substances should be sought for to be used as expanders.

3.8. Degradation of the structure of the negative plates

The second aim of this work was to investigate the influence of expanders on the energetic and skeleton structures of NAM and on the degradation which occurs when negative plates are cycled employing the cycling profile of the ECE-15 test protocol. Following the procedure, developed by Pavlov and Iliev [1], samples were taken from NAM after plate formation and at the end-of-life of the negative plates and these samples were examined by a scanning electron microscope to determine the structures of the NAM.

The left-hand photo in Fig. 14 shows the structure of charged negative active mass after formation of plates with expander blend In + Vs. It comprises individual small sized lead crystals obtained from the reduction of $PbSO_4$ during the second stage of formation or during the charge, and presents the energetic structure.

The right-hand micrograph presents the skeleton structure as observed after discharging the NAM and dissolution of

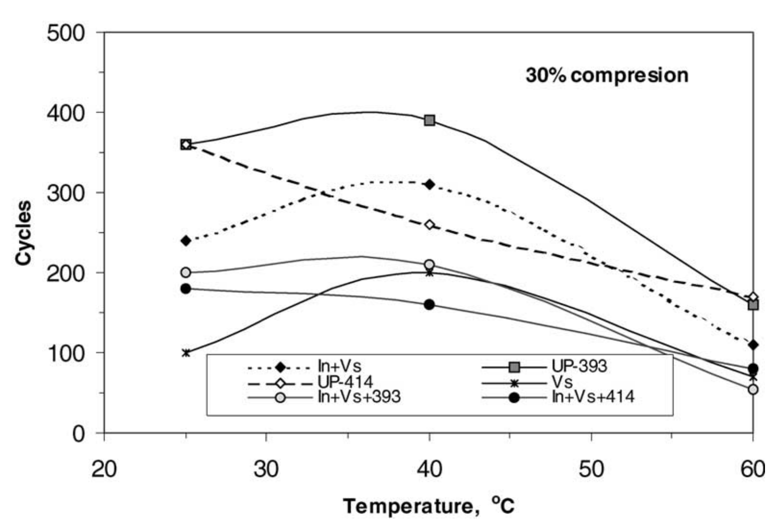

Fig. 13. EV cycle life for batteries with different expanders.

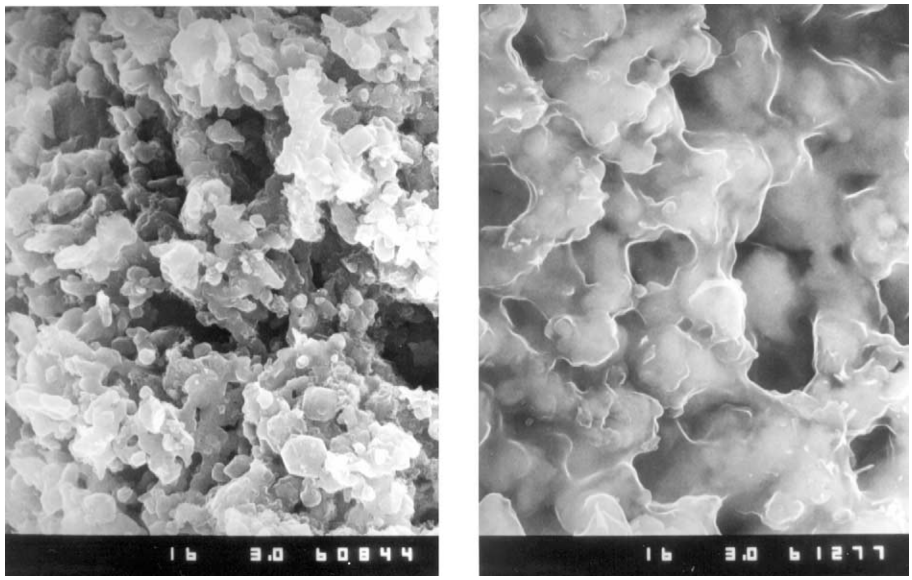

Fig. 14. Energetic and skeleton structure of NAM after formation. Magnification 3000×.

the lead sulfate crystals. The skeleton acts as a current collector for the whole plate and provides mechanical support to the lead crystals from the energetic structure.

Fig. 15 presents the energetic and skeleton structures at the end of battery life, when cycled at 25 °C. The lead crystals of the energetic structure have lost their initial crystal shape (Fig. 14a), they have grown in size and a great part of them have been converted into shapeless crystals of the skeleton structure. The changes in the skeleton structure are negligible. The conversion of the energetic structure into skeleton one is responsible for failure of the plates.

The negative plates are visibly in good health at the end-of-life. This may mislead us to conclude that the negative plates are good, while they have actually a very low capacity. Fig. 16 shows the energetic and skeleton structures of plates with the same expander blend at the end of battery life, when cycled at 60 °C. There is no difference between the two types of structure. If we compare the two micrographs in Fig. 16, it can be seen that the skeleton structure (as also the whole NAM structure) consists of thin branches interconnected into a highly porous mass. The NAM at the end-of-plate-life is very soft and highly expanded in volume.

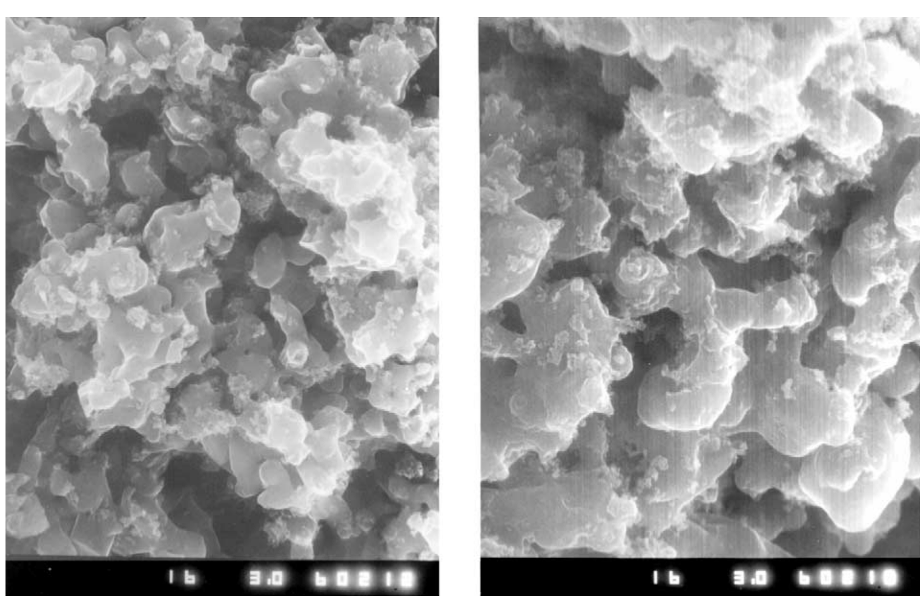

Fig. 15. SEM micrographs of NAM cycled at 25 °C. Magnification 3000×.

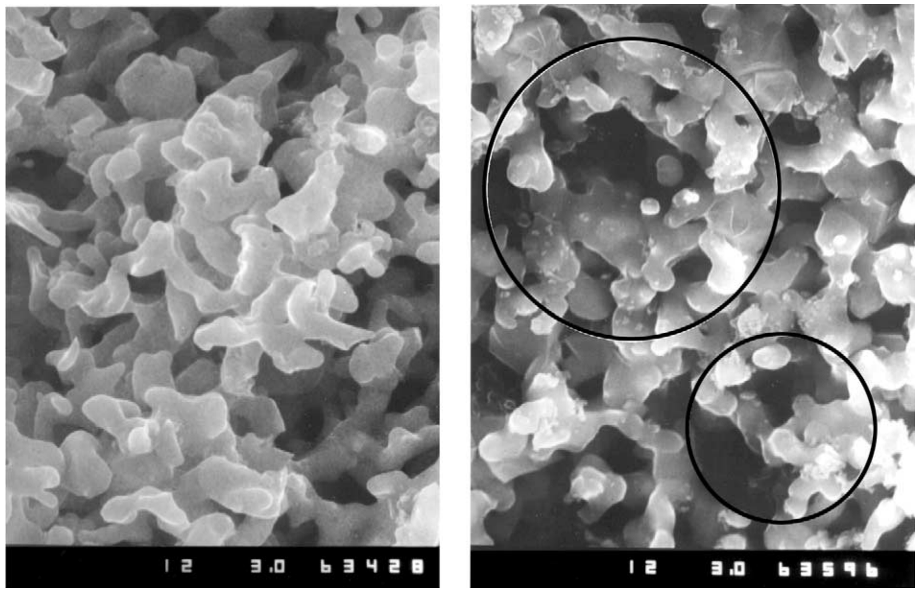

Fig. 16. SEM micrographs of NAM cycled at 60 °C. Magnification 3000×.

The thin branches increase the ohmic resistance of NAM (and, hence, the polarization of the plates), and the lead network is easily broken at some sites during discharge, thus, large parts of NAM are excluded from the current generation process. In this way, the lead network disintegrates into individual zones, which are often poorly connected electrically to the grid, which in turn results in capacity decline. Thus, on cycling of the cells at 60 °C the structure of NAM changes in terms of formation of a lead network of thin branches, which cannot be oxidized uniformly throughout the plate volume and consequently, the coefficient of NAM utilization, and hence, the plate capacity, decrease. These processes are illustrated in Fig. 16 by the large caverns (encircled zones).

4. Conclusions

When cycled according to the requirements of the ECE-15 test protocol at temperatures up to 40–50 °C the NAM structure changes. The small crystals of the energetic structure, which cover the skeleton of NAM and have a large surface area, are converted into large shapeless crystals similar to those that build up the skeleton structure. These latter crystals have a small surface area and consequently the negative plates have but a low capacity, which limits the cycle life of the battery. On cycling at temperatures about 60 °C, the NAM structure obtained during the formation process is converted into a network of thin lead branches, which can be easily broken. During discharge, these lead branches are rapidly oxidized at some sites, thus, excluding large parts of NAM from the current generating process, which leads to a decline in capacity of the negative plates.

Acknowledgements

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