The influence of different negative expanders on the performance of VRLA batteries

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Abstract

The behaviour of different novel expander additives and negative plate formulations has been investigated in cylindrical VRLA batteries under different electric (EV) and hybrid (HEV) vehicle service conditions, using negative active mass (NAM) compositions previously optimised in 2 V VRLA cells. The most interesting results are related to the cycling behaviour under both EV and HEV specifications, where up to 900 cycles and more than 180,000 cycles have been achieved, respectively, depending on the NAM additive used. Other interesting battery characteristics, such as charge acceptance at low temperatures, have been also improved by introducing an appropriate NAM formulation.
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1. Introduction

Within the project "Strategies for the further improvement of performance and life of lead-acid batteries for electric vehicle applications" and with the objective to improve the performance and prevent the degradation of the negative plates of VRLA batteries under electric (EV) and hybrid (HEV) vehicle service conditions, work has been carried out to develop organic expander additives for the maintenance of the required open structure in the negative active mass (NAM), since there are indications that at high rates of charge and discharge, the negative plate may limit battery performance.

The first step was focussed in a previous selection by different electrochemical techniques (cyclovoltammetry, potentiostatic transients and impedance measurements) of the best candidates from 19 potential expanders [1]. In accordance with the results obtained, since the materials that produced a higher capacity in discharge, lead also to a higher cathodic peak polarisation, which indicates a lower charge acceptance, it was necessary to trade-off between these two parameters, selecting ultimately a group of seven organic additives for further testing in 2 V VRLA prismatic cells [2]. These cells were submitted to initial and cycle life

tests under the ECE 15L specification showing remarkable differences in the performance and number of cycles fulfilled by each formulation. In addition, it was observed that an increase in carbon black concentration into the NAM usually improved the ECE 15L cycle life, as well as that a decrease in $BaSO_4$ concentration adversely affected the cycle life performance.

However, although the power requirements of the ECE 15L specification demonstrated to be too hard for this prismatic cell design, the four best expander formulations were included in a complete test programme to be performed on 12 V VRLA batteries with cylindrical cells. The cylindrical design is considered to be more adequate than the flat plate design for high rate duties like those specified by EUCAR for electric and hybrid vehicles, mainly due to the thin plate design and high separator compression maintained throughout the life of the battery [3].

In this paper, the influence of the different expanders on cycle life according EUCAR specifications as well as on other important performance characteristics of the batteries is reported.

2. VRLA batteries with different expander formulations

Taking into account the entire results obtained from the initial electrochemical characterisation [1] and the electrical

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Table 1
Composition of NAM in cylindrical VRLA batteries

Batch	Organic expander	BaSO$_4$ (%)	Carbon black (%)
N1	Sodium oxylignin	1	0.2
N2	Sodium oxylignin	1	1
N3	Sodium lignosulphonate	1	0.2
N4	Kraft lignosulphonate, condensed naphthalene sulphonate blend	1	0.2
N5	Synthetic condensation product from naphthalene sulphonic acid	1	0.2

Table 2
Initial performance of VRLA batteries EN 50342

Prototype	C$_{20}$ (Ah)	Cold cranking time 480 A/−18 °C/6 V (s)	Charge acceptance 14.4 V/0 °C (A)
N1	46.7	98	14.0
N2	47.3	99	13.5
N3	47.2	103	7.5
N4	47.5	103	11.5
N5	46.6	107	9.8

tests of the prismatic 2 V cells [2], the three best expander formulations were introduced in cylindrical VRLA batteries at a concentration of 0.2%, as well as a new synthetic expander derived from naphthalene sulphonic acid. Also, a further batch where the NAM carbon black content is increased five times with respect to the standard formulation was manufactured in order to reverse the sulphation produced during partial-state-of-charge working conditions. Similar approaches have been reported elsewhere using carbon-based additives [4]. The NAM composition of the five battery batches, labelled as N1–N5, is indicated in Table 1.

The prototypes were manufactured using a high density formulation in both the negative and positive active materials, which has also demonstrated an impressive behaviour in deep cycle applications [3]. The curing, assembly and charging processes were performed according to the same standard procedures for all batches. Once manufactured, the different battery groups were submitted, analogously to the single cells, to initial and performance electrical tests. At this point, it is important to remark that for these cylindrical batteries, no limitation in the negative plate has been imposed by design, as was the case of the prismatic cell design. For that reason, the interpretation of the electrical results will be more complex, since the influence of other parameters, e.g. the positive active material condition throughout the electrical testing or the available amount of sulphuric acid, can determine in some cases the electrical behaviour of the batteries.

In order to carry out a preliminary characterisation of the prototypes, three modules of each batch were submitted to initial tests according to the EN 50342 specification [5]. Table 2 summarises the average values obtained.

In these preliminary tests, although the initial capacity values were very similar, when the prototypes were submitted to the charge acceptance test at 0 °C, significant differences were found depending on the expander formulation used (Fig. 1). Thus, the lower values of charge acceptance correspond to the expanders that showed higher cathodic peak polarisation (batches N3–N5), as was previously observed in cyclovoltammetry and other electrochemical tests [1]. On the other hand, the batches containing sodium oxylignin as expander material (N1 and N2), gave the higher values of charge acceptance. Inversely, the behaviour of prototypes
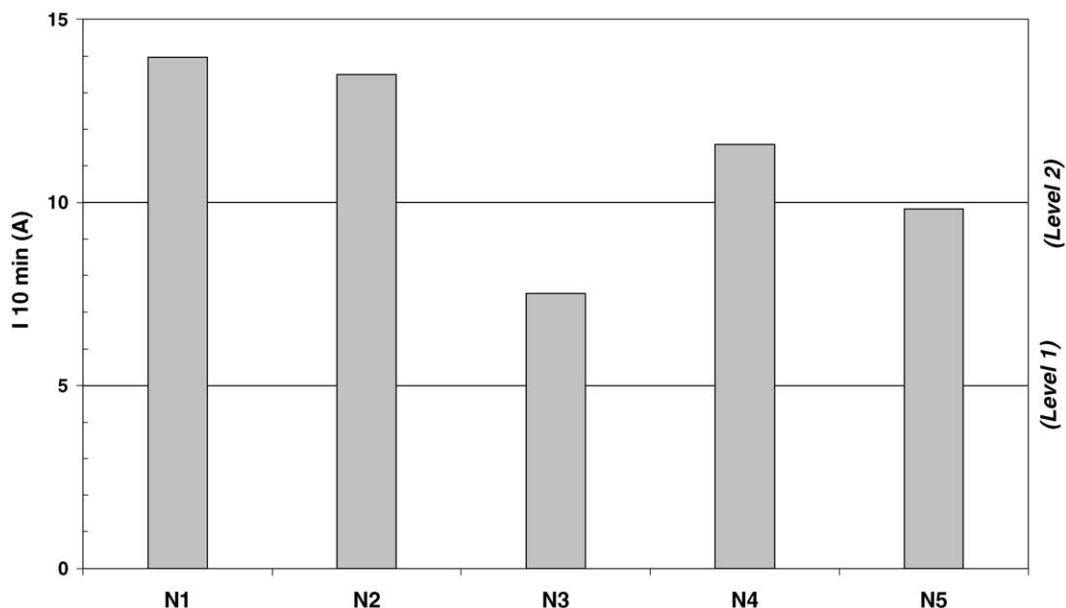

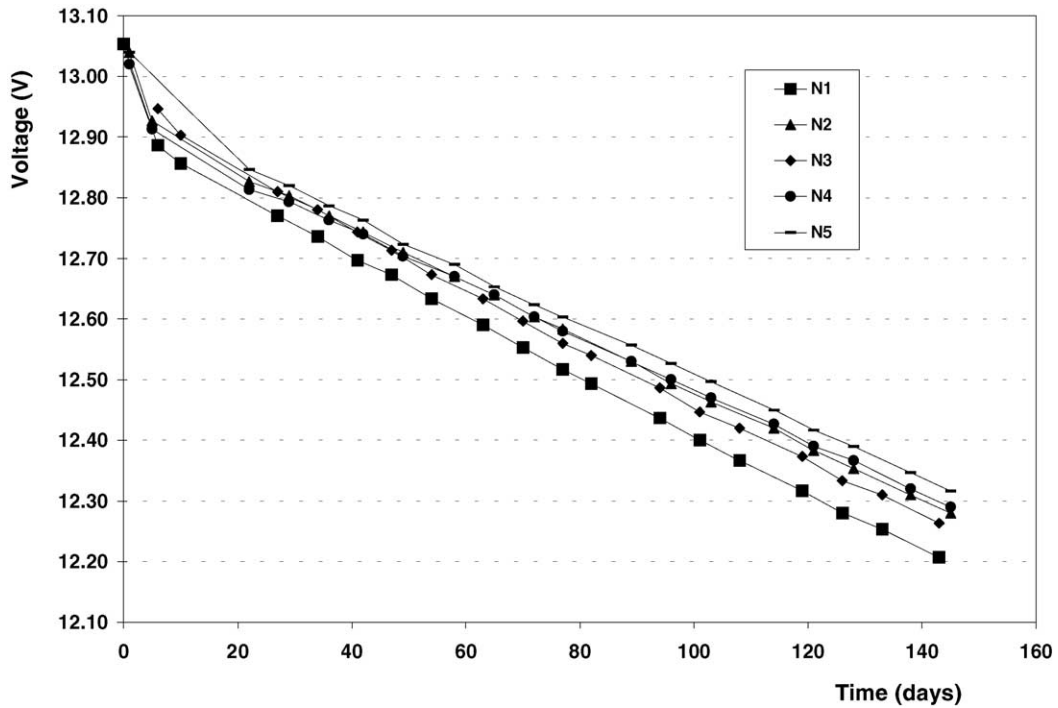Fig. 1. Charge acceptance according to EN 50342 (14.4 V, 0 °C, 50% SoC).

Fig. 2. Self-discharge at 40 °C.

containing N3–N5 expanders is better in the cold cranking test (Table 2). Assuming the indications that at high discharge rates the battery performance can be limited by the negative plate, these cold cranking results correlated well (except for the expander N3) with the observations made in the cyclovoltammetric tests, where the anodic peak area

(i.e. capacity in discharge) was higher for the expanders N4 and N5 when it was compared with the oxylignin additive (N1 and N2 batches).

Another test was carried out in order to know the effect of the expanders on the self-discharge. Three fully charged batteries of each group were introduced into a temperature-
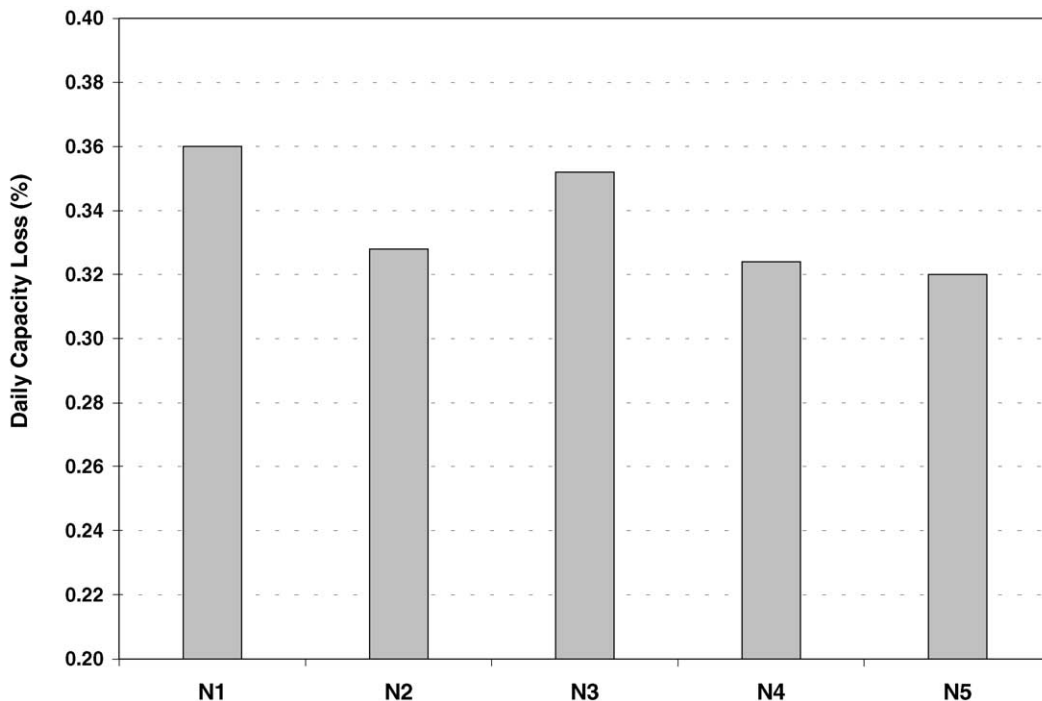

Fig. 3. Daily capacity loss at 40 °C after 150 days self-discharge.
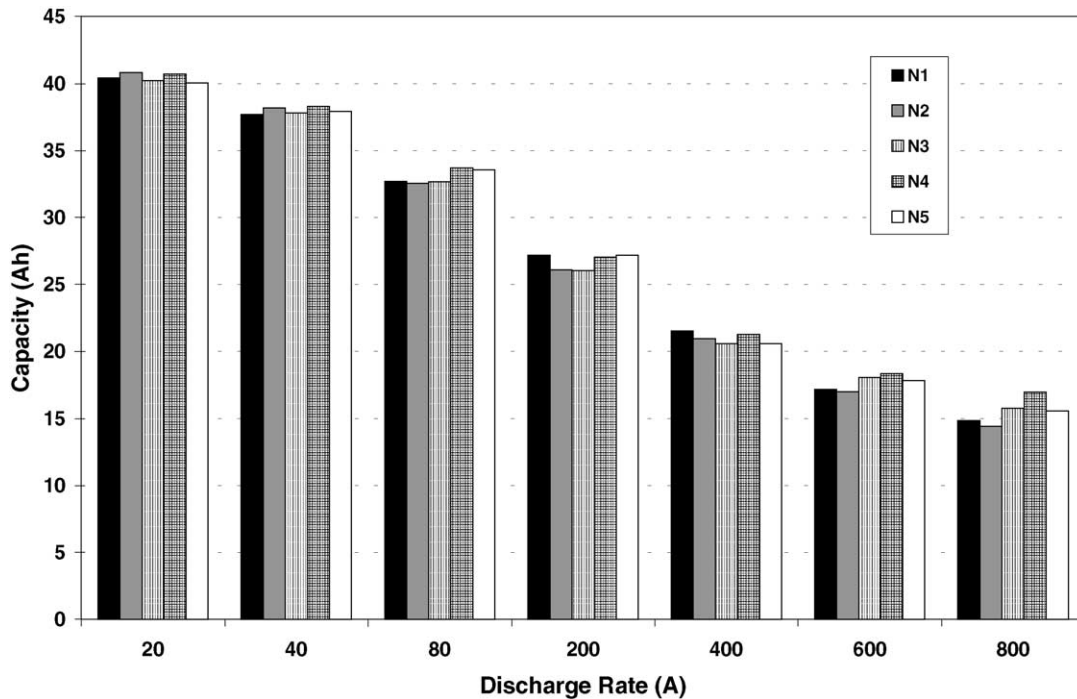
Fig. 4. Capacity at different discharge rates (25 °C) according to EUCAR specification for HEV.

controlled chamber at 40 °C for 150 days. As can be observed in Fig. 2, the more pronounced self-discharge is observed in the oxylignin batteries N1, whereas the best charge retention occurs in batteries with the synthetic condensation product (N5) and kraft lignin naphthalene sulphonate combination (N4) as expanders, although there is only a slight difference with the other groups.

In order to confirm this behaviour, the remaining capacity of the prototypes after the self-discharge was determined and, as expected, the best charge retention corresponds to the prototypes N5 and N4, respectively. Fig. 3 shows the values expressed as daily capacity loss.

It seems to be clear that the aforementioned results could be related to the expander nature of each batch, as
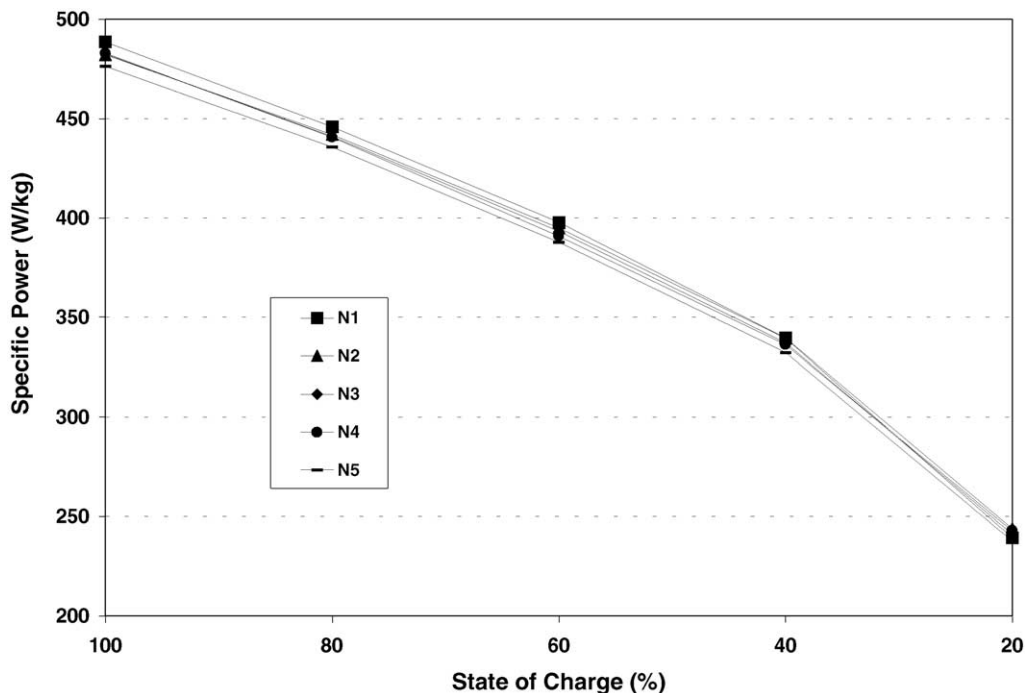

Fig. 5. Specific power at different SoCs (10 s high current discharges, 25 °C).

the self-discharge of batteries is usually determined by the hydrogen evolution rate at the negative electrode and organic additives are assumed to increase the hydrogen overvoltage to a greater or lesser extent (decreased hydrogen evolution at the negative electrode) [6]. In this way, the best charge retention is produced in the batteries containing the synthetic condensation product (N5) and kraft lignin naphthalene sulphonate combination (N4), the former being the expander that presents more cathodic polarisation in cyclovoltammetric experiments. On the other hand, the batteries manufactured with sodium oxylignin (N1) have slightly lower charge retention on storage, an expected behaviour taking into account the intermediate-low value of cathodic polarisation of this organic additive measured after running the same electrochemical test.

2.1. EUCAR test for HEV

Due to the growing interest of VRLA batteries in hybrid vehicle applications, further tests according to EUCAR specification [7] were made to know the influence of the different expanders on the prototype performance and cycle life of VRLA batteries, and ultimately with the aim of selecting an optimum formulation to be applied in real use.

Firstly, the capacity at different discharge rates was determined for all batches (hereinafter, after every electrical test, unless otherwise indicated, all the batteries are charged in accordance with the EN 50342 specification, that is, 20 h at 14.4 V (12.5 A limited) + 4 h at 1.25 A). The results are included in Fig. 4.

Although the differences in capacity were not very significant at low and medium discharge rates, the prototypes

N3–N5 showed a better behaviour at high current rates, the latter having up to 14% better performance than the prototypes containing sodium oxylignin. As previously set forth, if the negative plate limits the battery capacity at high currents of discharge, the results obtained correlated again with the increase of the anodic peak area (i.e. capacity in discharge) observed in the cyclovoltammetric tests for N3–N5 additives when compared with the sodium oxylignin contained in groups N1 and N2.

The power performance as a function of the state of charge (SoC) is an important issue in HEV systems. Therefore, it was also determined in new prototypes to see if there is any influence of the different NAM composition on this parameter, when high power peaks would be demanded. As can be seen in Fig. 5, all the prototypes showed quite similar values of specific power in the range tested from 100 to 20% SoC (500 W/kg to about 250 W/kg, respectively). Unexpectedly, not even the presence of an increased amount of carbon black (five times the standard formulation) enhanced the performance of the prototypes N2 at a low SoCs. Therefore, more work should be done in this direction, either increasing the amount of the current carbon blacks or choosing an improved carbon-based conductive filler, to overcome the problems that arise in the negative plate when the $PbSO_4$ predominates.

After the completion of the initial characterisation tests described above, and within the scope of the EUCAR testing for HEV, one battery of each group was selected to perform the power assist cycle life test according the EUCAR specification [7], where the prototypes are cycled around a specific SoC. This test simulates the load for the battery in a power assist hybrid, to assist the engine during acceleration and to recover energy during braking.
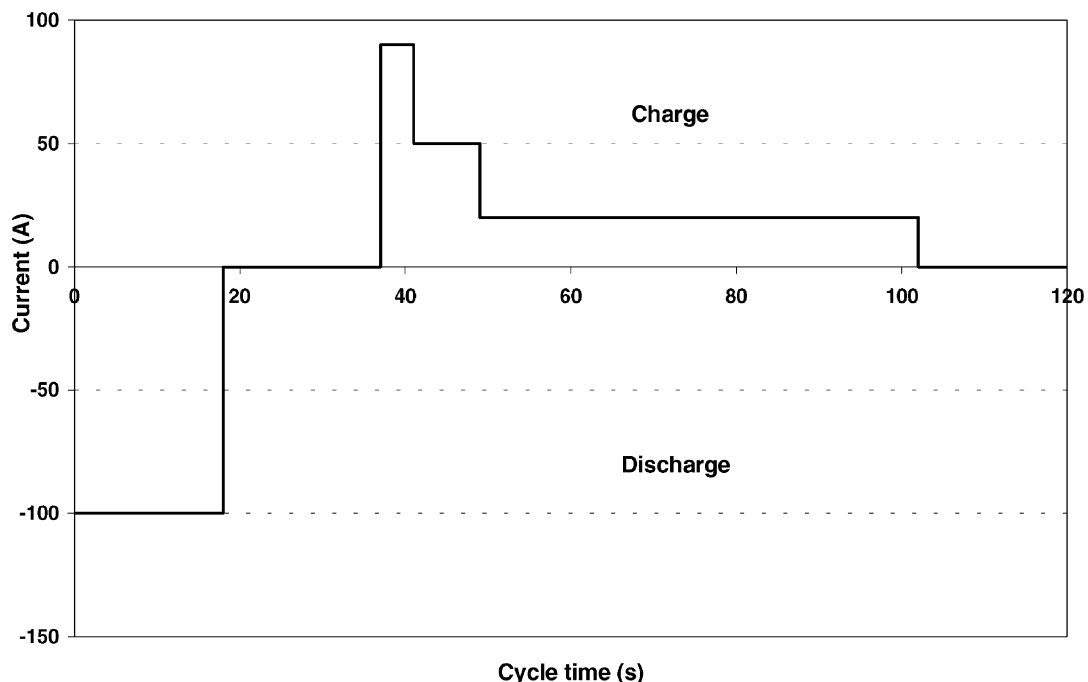

Fig. 6. Power assist profile for cycle life testing according to EUCAR specification for HEV. The batteries are previously discharged to 60% SoC.
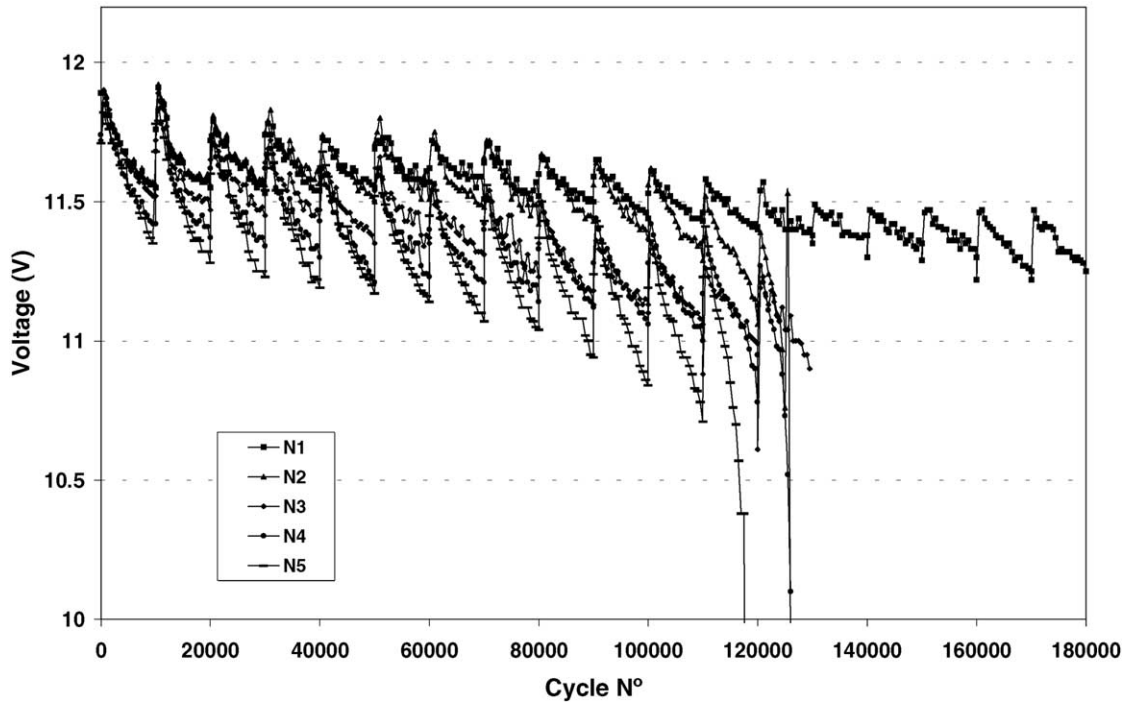
Fig. 7. Power assist test at 60% SoC. End of discharge voltage vs. cycle number.

The batteries were discharged to 60% SoC and cycled according to the profile showed in Fig. 6, which has been adapted to the lead-acid test equipment capability, adjusting the charge efficiency to 101%. In summary, the prototypes were cycled at 1.25% DoD after extracting previously 40% of the nominal capacity. The cylindrical batteries were refrigerated with forced air (25 °C) through the inter-cell cooling channels, specially designed to this end, to avoid an excessive temperature increase. The temperature of the batteries measured inside the cooling channels varies in a range of about 31 ± 3 °C throughout cycle life.
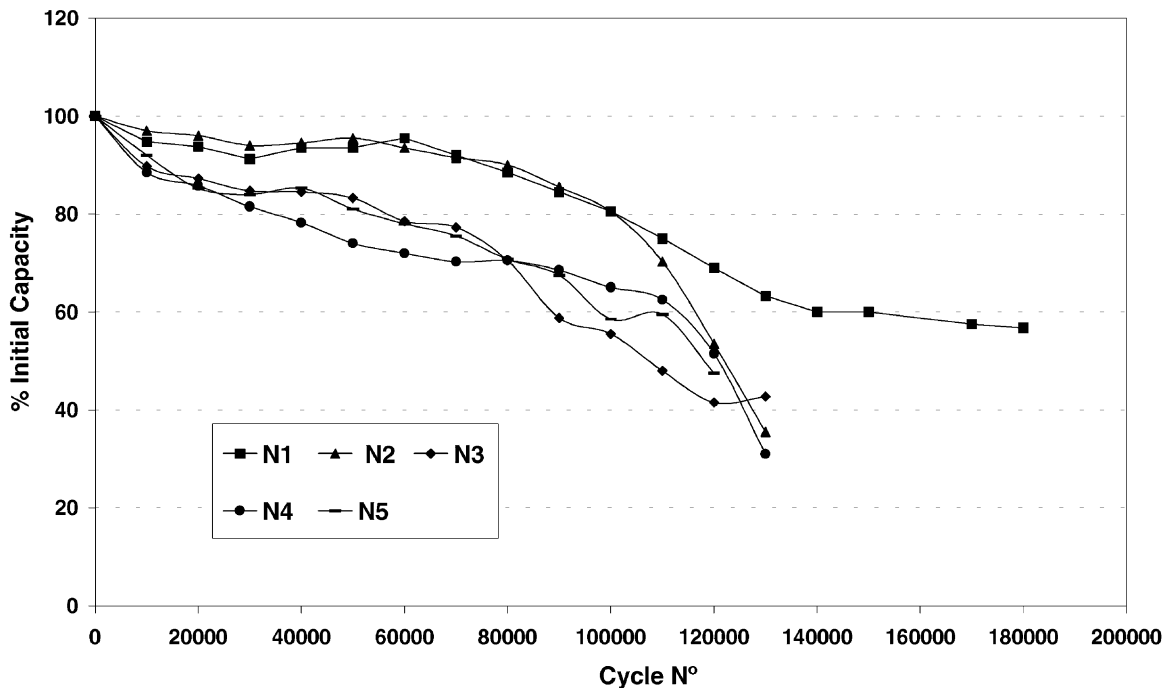

Fig. 8. Power assist test. Evolution of C_2 capacity control every 10,000 cycles.

Table 3
Tear-down analysis of negative plates after the end-of-life

Batch	Cycles fulfilled	PbO (%)	PbSO$_4$ (%)	BET (m^2/g)
Negative plate analysis				
N1	180,000	1.7	36.3	0.38
N2	130,000	3.8	3.1	0.48
N3	130,000	4.2	9.3	0.40
N4	130,000	2.9	10.2	0.33
N5	120,000	2.7	6.4	0.30

Every 10,000 cycles a control capacity test was carried out to check the state of health of the batteries, after which the prototypes were completely recharged (EN 50342). However, the end-of-life criterion was established when the batteries reached a minimum voltage of 10 V during the 100 A discharge step.

As can be observed in Fig. 7, where the relationship between the end of discharge voltage and the cycle number is represented, significant differences have been found among the five groups, more acute at the end of the cycle life. Interestingly, as shown also in Fig. 8, only the prototype containing the sodium oxylignin as expander (N1) has exceeded 130,000 cycles, having reached up to 180,000 without failure, that means a capacity turnover of 2250. Although evaluating the contribution of the different components and parameters of a battery in its behaviour and failure mode is many times a very complex issue, in this particular case a strong influence of the nature of the selected organic additive in the cycle life of the corresponding prototype can be seen. As previously mentioned, the rest of the composition (PAM, NAM except for the additives, etc.) and manufacturing parameters were the same for all the groups.

In order to know the failure mode of the batteries after the power assist test, the batteries were torn-down and analysed, including the still healthy prototype N1. The most representative results concerning the negative plate are shown in Table 3, since the analytical data of positive plates indicate that the PAM as well as the grids are in relative good condition (more than 96% PbO$_2$ content in the five groups). The batteries, also, have enough acid in the separator to support the electrochemical reactions.

However, the negative plate analysis shows some results that can explain the different behaviour among the groups in this power assist test. The main data are summarised in Table 3.

First, the sulphate content of the negative plates in groups N2–N4 is too low <11% to explain the capacity loss (>50%) of the batteries after the failure, as can be seen in Fig. 8. On the other hand, the surface area, under 0.40 m^2/g in batches N3–N5 indicates a degradation of the NAM, probably due to the loss of activity of the organic additives (in a cylindrical battery newly formed of this type, the surface area of NAM is about 0.80 m^2/g). However, this failure mode

cannot be assigned to batteries N2 (containing sodium oxylignin as N1 batch), wherein the sudden increase of internal resistance and loss of performance around cycle number 110,000 was observed, probably due to a higher corrosion rate of this particular battery. Further tests would be performed to validate the possible effect of increased carbon content.

With respect to the battery N1, the analytical results should not be compared to the previous ones, since this prototype reached, without failure, 180,000 cycles. Even with a high PbSO$_4$ content in the negative plates (about 36%) that in this case also contributes to decrease the surface area, the capacity control exceeded 50% of the nominal value (Fig. 8).

Failure seems to be related with the decrease in specific surface area due to the degradation of the expander, but sodium oxylignin, which seems to be highly effective in maintaining an open structure in the negative plate. This can be seen in both prototypes N1 and N2. Prototypes N2, with the same number of cycles fulfilled as prototypes N3–N5, shows a specific surface area remarkably higher. The same can be said for prototype N1. In this case, even with a very high sulphate content (36%) that leads to a decrease in BET area due to the higher molar volume of PbSO$_4$ versus Pb, they show a similar or higher BET area than prototypes N3–N5. All the previous data make the sodium oxylignin additive as well as the negative formulation promising for the PSOC application.

2.2. ECE 15L test for EV

Following a similar profile to that used for the VRLA cells [2], the prototypes were submitted to the ECE 15L test [8], specially designed for lead-acid batteries in electric vehicle applications. Firstly, useful capacity and useful energy were determined for the groups N1–N5 before the cycling starts:

- capacity control + standard charge (SCH);[1]
- ECE 15L at 100% DoD + SCH;
- capacity control + SCH;
- ECE 15L at 100% DoD + SCH;
- capacity control + SCH; and
- ECE 15L at 100% DoD + SCH.

From the standard discharge tests, the average initial capacity values were obtained and, from the ECE 15L tests at 100% DoD, the average initial capacity (useful capacity) and energy (useful energy) values at this regime were calculated. The ECE 15L tests were carried out by repeating the basic ECE 15L microcycle (Fig. 9) indefinitely until the batteries fail due to reaching the lower voltage limit (8.5 V).

The results of the initial capacity and ECE 15L discharges at 100% DoD, are indicated in Table 4 (as average of three batteries tested), and offered very similar values in useful

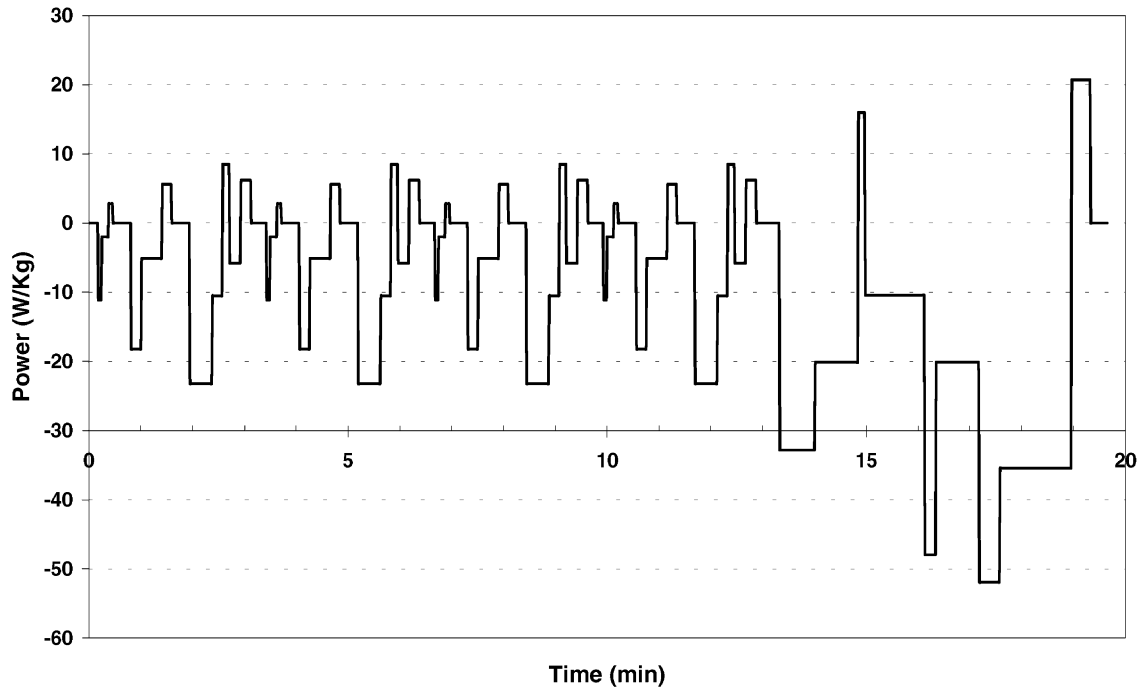[1] Standard charge: according to EN 50342 specification (20 h at 14.4 V + 4 h at 1.25 A).

Fig. 9. ECE 15L microcycle profile (urban and suburban parts).

Table 4
Capacity control and ECE 15L 100% DoD discharges

Prototypes	First		Second		Third	
	Capacity (C_5)	ECE 15L 100% DoD	Capacity (C_5)	ECE 15L 100% DoD	Capacity (C_5)	ECE 15L 100% DoD
N1 (Ah)	41.2	36.2	40.4	36.1	41.0	36.5
N1 (Wh)		427		426		433
N2 (Ah)	41.9	36.8	41.4	36.5	42.0	37.0
N2 (Wh)		435		432		439
N3 (Ah)	42.0	36.8	41.7	36.5	42.4	37.1
N3 (Wh)		434		432		439
N4 (Ah)	42.2	36.9	41.6	36.6	42.0	37.1
N4 (Wh)		436		432		439
N5 (Ah)	41.4	36.2	40.4	36.1	40.7	36.5
N5 (Wh)		428		427		432

capacity and useful energy for all the groups tested, since in this battery design the negative plate does not determine the capacity performance of the batteries at low discharge rates.

Once the previous discharge program was completed, the battery modules started the ECE 15L cycle life test at 80% DoD, with the same profile as that used when testing the single VRLA cells (Fig. 10).

Each discharge cycle (or macrocycle) is composed of microcycles as shown in Fig. 9. Every 50 macrocycles (or unit), a C_5 capacity control was carried out to check the state of health of the batteries. Two criteria were established as end-of-life criteria: a lower voltage limit of 8.5 V during the

Table 5
Number of cycles fulfilled according ECE 15L cycle life test

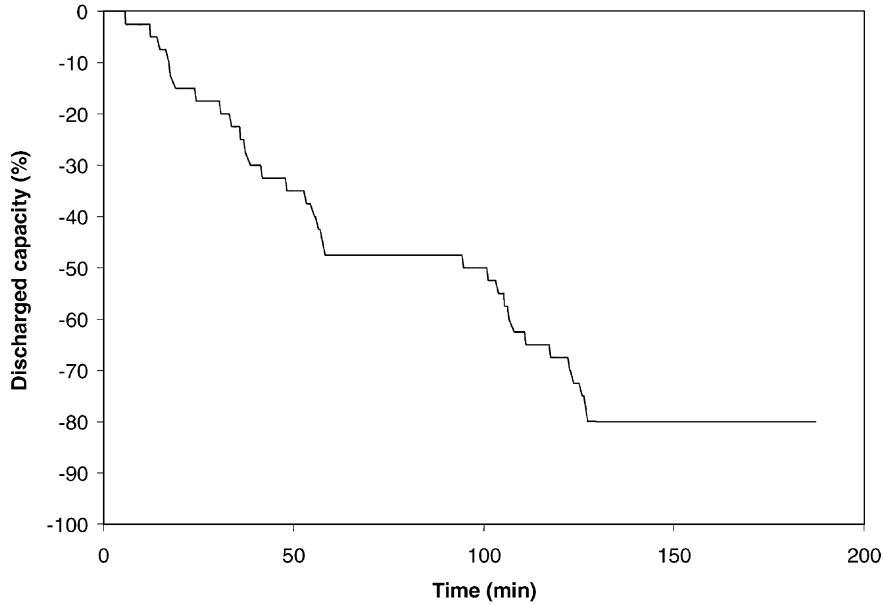| Batch	80% capacity control criterion			Cut-off voltage criterion		
	1	2	3	1	2	3
Number of ECE 15L cycles fulfilled						
N1	700–750	900	850–900	775	940	885
N2	700–750	750–800	700–750	800	825	800
N3	600	650–700	700–750	645	695	735
N4	700–750	700–750	700–750	735	740	735
N5	600	600–650	600–650	650	645	650

1, 2 and 3 are battery numbers.

Fig. 10. ECE 15L cycling profile. Typical evolution of the discharged capacity in one macrocycle.

macrocycle and less than 80% of the nominal capacity in the capacity control. Fig. 11 shows the evolution of the average capacity of the five groups of prototypes through the cycle life test, with at least 700 cycles to 80% DoD achieved (except for the batteries containing the synthetic expander, N5), according to the capacity control criterion. Anyway, a quite similar number of cycles has been obtained taking into account the cut-off voltage criterion (Table 5).

It is interesting to compare these results with those obtained previously when testing the expanders in the VRLA prismatic 2 V cells [2], where only about 30 ECE 15L cycles were obtained. Although an increase of carbon black improved substantially the cycle life (about double number of cycles using sodium oxylignin as organic additive), the prismatic configuration showed again a limitation when submitted to this EV cycle test.
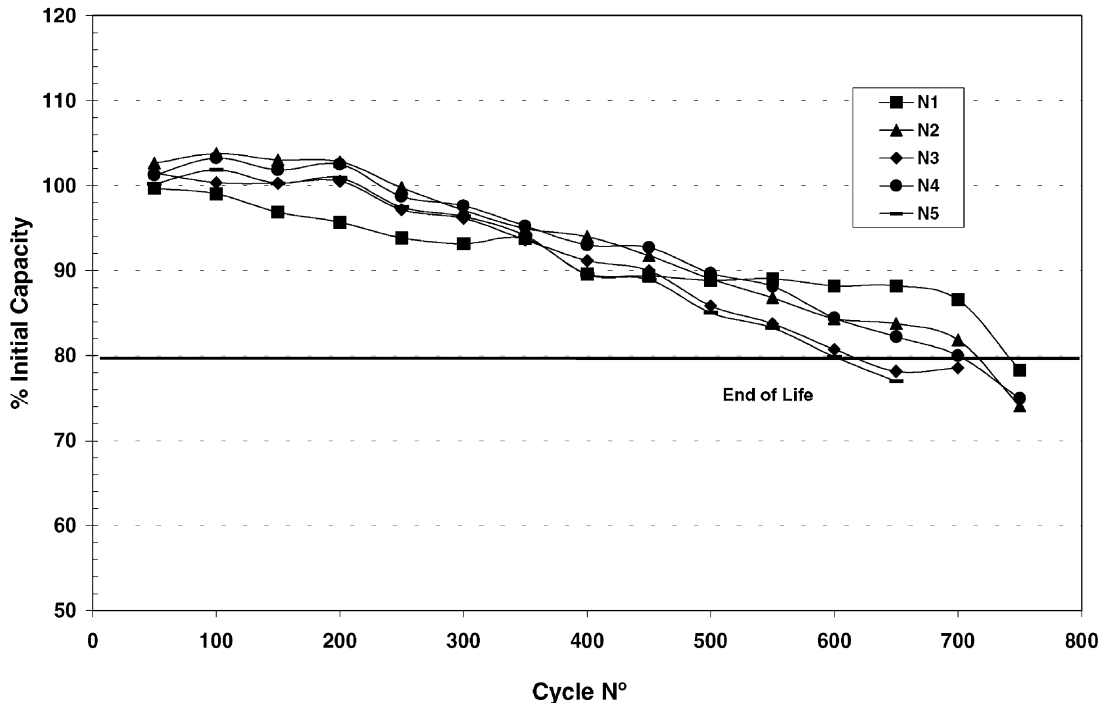

Fig. 11. ECE 15L cycle life test. Evolution of C_5 capacity control every unit (50 macrocycles).
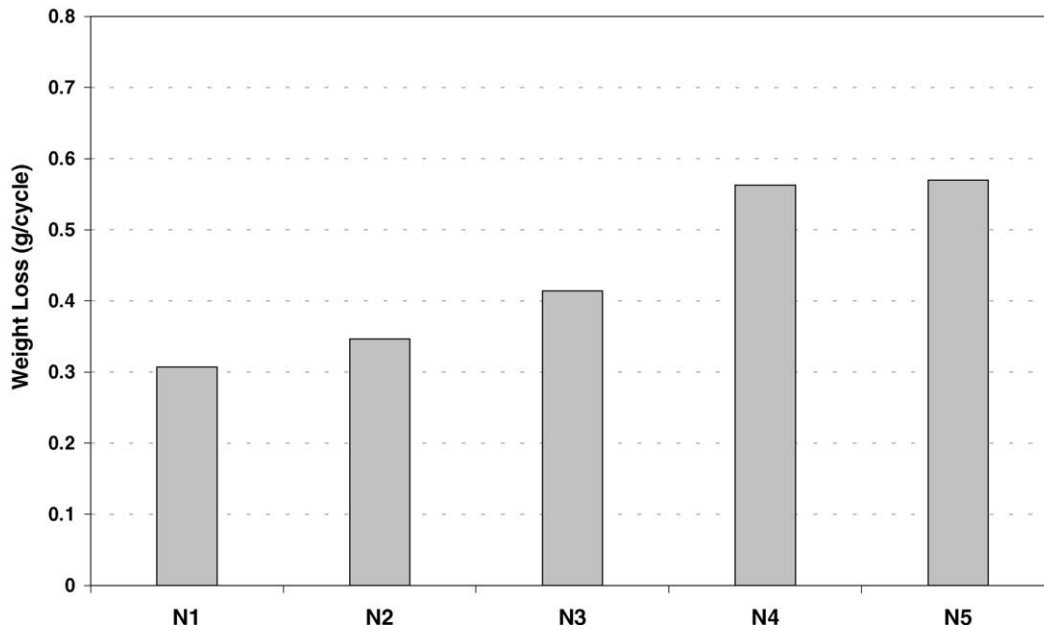
Fig. 12. ECE 15L cycle life test. Weight loss per cycle calculated after the end of life of the batteries.

However, the cylindrical configuration of the VRLA batteries tested in this work provides a dramatic improvement of the ECE 15L cycle life, as most of the batteries have exceeded 700 cycles. For a better understanding of the failure mode under this test, after every capacity control (50 cycles), the batteries were also weighed to follow the water loss (Fig. 12) and the internal resistance was measured (Fig. 13).

Figs. 12 and 13 show the progressive increase of internal resistance and water loss during the cycles. As shown in Fig. 12 the water loss is higher in batteries N3–N5, this effect being more pronounced in the latter, in the opposite sense to the expected, since these expanders gave more cathodic polarisation in cyclovoltammetric experiments. The explanation could be found in the progressive degradation of the
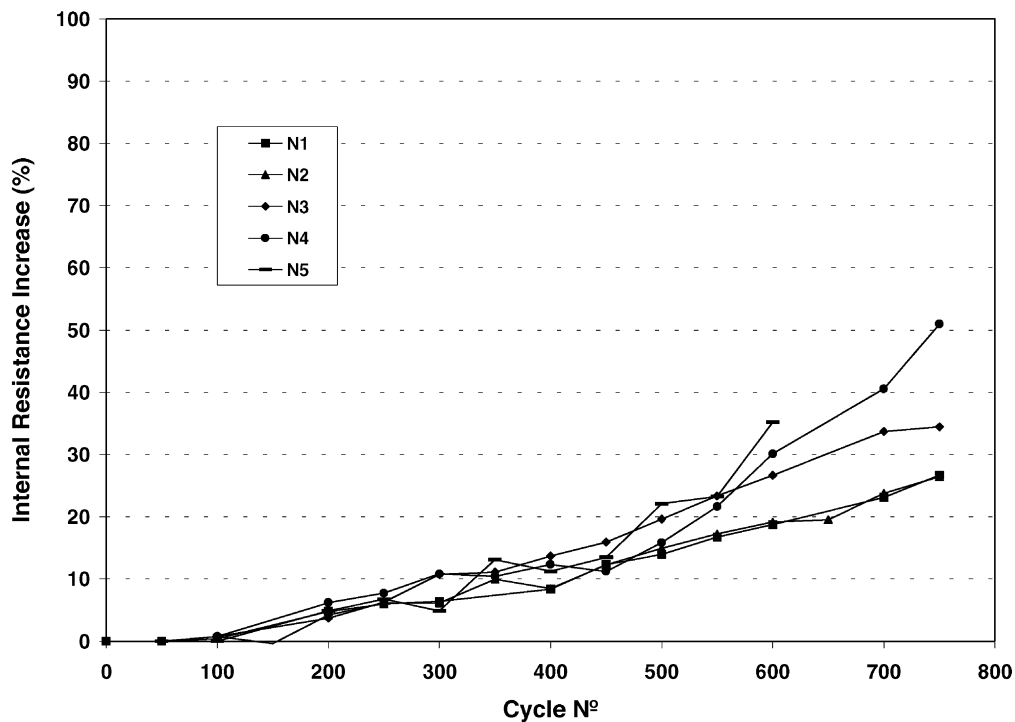

Fig. 13. ECE 15L cycle life test. Evolution of internal resistance with cycling.

Table 6
Tear-down analysis of negative plates after the end-of-life

Batch	PbO (%)	PbSO$_4$ (%)	BET (m^2/g)
Negative plate analysis			
N1	1.2	5.2	0.34
N2	1.4	3.5	0.37
N3	1.4	5.9	0.27
N4	1.4	11.3	0.30
N5	1.5	11.4	0.32

expander submitted to this high power specification, already observed in the power assist test.

On the other hand, the post-mortem tear-down analysis of the batteries allowed us to establish the contribution made by the negative and positive plates to the battery failure. Table 6 shows the lower specific surface area and higher sulphate content in the negative plates of batteries N3–N5.

Additionally, the analyses made on the positive plates have shown: (i) that the corresponding grids are in relative good condition; (ii) the softening of positive active material close to the grid; and (iii) a good cohesion of positive active material in the core of the pellets. These observations agree with those reported by CLEPS, where some structural changes were found by Pavlov in the PAM during the ECE 15L cycling [9]. He described that the active material layer that is in contact with the grid corrosion layer becomes crumbly during the cycle life, and consequently losses contact with the external working layer of the active mass. Therefore, considerable parts of the outer PAM layer are excluded from the current generation and accumulation processes and the capacity of the plate declines.

Therefore, taking into account the post-mortem analysis results, each expander seems to contribute in a different way to the ECE 15L cycle life, since there are significant differences in the number of ECE 15L cycles fulfilled by each group (200 cycles approximately between batteries containing sodium oxylignin N1 and the synthetic condensation product N5). However, it is necessary to consider also the progressive grid corrosion and degradation of the positive active material (softening next to the grid) subjected to this high power test.

3. Conclusions

The cyclovoltammetric method used in the first step of this work was a very useful tool to determine the electrochemical effects of the organic expanders on the negative plate behaviour. As a general rule, those materials which are the most efficient to increase the electrode capacity, polarise the negative plate producing a detrimental effect in the charge acceptance. A compromise has to be chosen or, whenever it is feasible, the expander composition can be another tool for the design of VRLA batteries as a function of the application. When a series of selected expanders were further tested in prismatic cells in a second step, it was found

that increasing the concentration of carbon black and barium sulphate (up to 1%) improved generally the initial performance and cycle life of VRLA cells which had been designed with negative plate limitation, but a further increase of the organic concentration (from 0.2 to 0.4%) had a detrimental effect in most cases.

The most effective expander formulations were finally tested very successfully in VRLA batteries with a cylindrical design, showing that this particular configuration is more useful than the flat plate cell design for high rate duties like those specified by EUCAR for electric and hybrid vehicles. Whereas the initial high rate performance and shelf-life are improved by new types of organic materials (like the N3–N5 batches), charge acceptance at low temperature is reduced. Importantly, it has been found, that the sodium oxylignin additive is capable of improving the cycle life in both EV and HEV specifications (up to about 900 ECE 15L cycles and more than 180,000 power assist cycles, respectively) with respect to the other formulations. On the other hand, whereas the addition of larger amounts (up to five times the standard) of carbon black to the negative plate does not enhance the performance of this type of batteries, it seems to reduce the lead sulphate content throughout life. Further tests with more conductive types of carbon-based materials (e.g. graphite) would be needed to asses the improved cycle life performance of spiral wound VRLA batteries under partial-state-of-charge conditions.

Acknowledgements

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