ELSEVIER

Journal of Power Sources 95 (2001) 174–190

JOURNAL OF POWER SOURCES

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The influence of different negative expanders on the performance of VRLA single cells

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Abstract

In the first part of the present project, electrochemical characterisation techniques for several expander materials were developed and applied to a total of 19 potential expander candidates, selected from various different sources: conventional and novel expanders, new synthetic products, and natural substances. From the obtained results, seven most effective candidates were selected for further testing in real VRLA single cells. In these tests, all the candidates have been tested at the 0.2% concentration level in the paste, and for three selected candidates, alternative levels of the expander, carbon black and barium sulphate have been additionally tested. After the cell formation, initially a series of preliminary discharges at different discharge rates were carried out in order to characterise the initial performance of each formulation. Then, the single cells were submitted to the initial tests previous to the EUCAR ECE15L cycling specification for electric vehicles and then to the ECE15L cycle life test at 80% depth-of-discharge (DoD). The results of the preliminary discharges showed that differences up to 10–13% can be found in the initial capacity delivered by the different formulations at the test rates. The results of the cycle life tests showed that all the tested variables (type/concentration of the expander, concentration of carbon black and concentration of barium sulphate) usually caused a variation in the cycle life behaviour, although the amount of this variation was strongly dependent on the considered expander. The most significant effect was observed when the carbon black level was increased, producing remarkable improvements both in the initial discharge capacities and in the cycle life performance.

Keywords: Expanders; Lead–acid batteries; VRLA; Electrical testing

1. Introduction

The present project is aimed to obtain a negative active material formulation optimised for EV working regime. This has been carried out through the investigation of the characteristics and performance of negative pastes produced using different organic expanders, as well as the effect of variations in the concentration of either the expander, the carbon black or the barium sulphate compounds, under an EV working regime such as the EUCAR ECE15L specification for electric vehicles. During the first year of the project, several electrochemical characterisation techniques for expander materials were developed and applied to a total of 19 potential expander candidates, selected from different sources: conventional and novel expanders, new synthetic products, and natural substances [1]. These techniques included potentiostatic transients, impedance plots and cyclic voltammetry techniques, which have been widely used in the past to characterise battery active materials [2–7]. From the results obtained in these electrochemical techniques, the seven most effective additives were selected for further testing in VRLA single cells. The description given by the manufacturer of each one of these selected compounds is shown in Table 1.

Following that, during the second year of the project, different negative formulations for testing in VRLA cells were defined, including each one of the above expanders at a fixed concentration, as well as several additional experiments with alternative concentrations of either the expander, carbon black or barium sulphate for three selected candidates. Then, the cells were formed and their initial performance at different rates, as well as under the ECE15L regime, were obtained. Finally, the cells were submitted to cycling tests using the EUCAR ECE15L specification for electric vehicles. This study is part of a larger project aimed to improve the overall performance of valve-regulated lead–acid battery for electric vehicle applications. An outline of the results of these investigations can be found in [8,9].

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0378-7753/01/$ – see front matter
PII: S0378-7753(00)00617-0

Table 1
Description of the selected expanders

Expander (abbreviation)	Description
Kraftperse DD5 (DD5)	Blend of kraft lignin + condensed naphthalene sulphonate
Kraftperse DD8 (DD8)	Blend of sodium lignosulphonate + condensed naphthalene sulphonate
Kraftplex (KRA)	Modified kraft sodium lignosulphonate
Calder N17 (N17)	Sodium lignosulphonate
Calder S004 (S04)	Sodium lignosulphonate
Borregaard UP414 (UP4)	Experimental product derived from Van A
Vanisperse A (VAN)	Sodium oxylignin

2. Description of the cell tests

A motorcycle-type battery size was chosen to carry out the cell tests due to the intermediate size of these batteries, which allowed the assembly of an appropriate number of single cells with just one paste mixing made in our laboratory mixer, and to their container and lids made of ABS material, which allowed the sealing of these pieces just with a glue, so that a thermal welding was not necessary. The mixing tests were carried out using an Eirich laboratory mixer of 12 kg oxide capacity. The employed formulation is shown in Table 2.

The duration of the mixing process was approximately 30 min. Following this, the density of the active material was measured, resulting in a wet mass density of about 4.2 g/cm^3 (with small variations from test to test, depending on the expander) and plasticity and penetration values adequate for manual pasting. For all components, the chosen concentration in this recipe has been taken from typical values in commercial batteries, except for the barium sulphate, which is somewhat higher than the usual (about 0.5%) concentration. This is due to the fact that a high $BaSO_4$ concentration (about 1.0%) is being claimed in recent years to improve the cycle life behaviour of the negative active material [10–12]. For this reason, 1.0% concentration has been chosen as reference concentration for this component. However, in order to assess the effect of this increased concentration, further experiments have been carried out with a reduced $BaSO_4$ concentration (0.5%).

Table 2
Recipe used in the reference formulation (formulation A)

Component	Amount (kg)	Concentration (related to oxide) (%)
Lead oxide	10	100
Total water	1.350	13.5
Sulphuric acid (d = 1.40 g/cm^3)	0.84	8.40
Fibre	0.007	0.07
Carbon black	0.028	0.28
Barium sulphate	0.100	1.00
Expander	0.020	0.20
Total	12.3	

After the mixing process, the active mass was manually pasted onto Pb/Ca grids. Then, after the pasting process, the plates were subjected to a typical curing process in a laboratory curing chamber. This process had the following steps:

- 24 h at 55°C and 100% relative humidity;
- at least 6 h at 60°C and 20% relative humidity.

The different amounts of components were adequately chosen so that a limitation in the negative half-cell was ensured. Thus, the differences in performance of the different cells would be due to the different performance of the negative plates. Therefore, the following cell design was defined:

- two positive plates per cell with 73 g positive formed mass per plate;
- one negative plate per cell with 50 g negative formed mass per plate.

The plates were carefully selected in order to have the same mass and grid weight throughout all the different tests. In order to avoid a too large excess of acid, the void space inside the cell was filled with polypropylene spacers. The cast-on-strap welding was carried out with a manual welding device for battery prototypes. Once the positive and the negative groups had been welded, the cells were inserted in the container and the cell lid was placed and sealed. Then, the formation process was carried out at a constant current of 0.55 A during 24 h, using thermoregulated baths at 45°C and 130 ml per cell of 1.300 g/cm^3 density formation acid.

3. Physico-chemical characterisation

Therefore, the following experiments were carried out using the reference formulation.

Test 1 0.2% DD5
Test 2 0.2% DD8
Test 3 0.2% Kraftplex
Test 4 0.2% N17
Test 5 0.2% S-004
Test 6 0.2% UP414
Test 7 0.2% Vanisperse A

These tests, where the reference formulation is used (i.e. including the organic at the 0.2% level) is known throughout this paper as formulation A. In addition to these tests, three of the expanders (DD5, N17 and VAN) were selected for additional testing with the following variations.

Tests 8–10 Increase the expander concentration to 0.4% (formulation B)
Tests 11–13 Increase the carbon black concentration to 0.56% (formulation C)
Tests 14–16 Reduce the barium sulphate concentration to 0.5% (formulation D)
Test 17 Increase the carbon black concentration to 2.8%, i.e. 10 times higher than in the reference formulation (only for Vanisperse A) (formulation E)

The reason for the testing of increased carbon black concentrations is based on the research of Shiomi [13] among other authors. This author found remarkable improvements in the formation of lead sulphate pastes when the carbon black concentration used was three times higher than the standard amount, due to the formation of a conductive network around the lead sulphate crystals.

All materials were exhaustively analysed before their use, verifying their adequacy for the application. The results of the analysis were:

- positive plates:
  - grid alloy: 0.091% Ca, 1.05% Sn;
  - formed mass:
    - composition: 87.9% PbO_2, 5.0% $PbSO_4$;
    - porosity: 52% (Hg porosimetry);
    - apparent density: 4.1 g/cm^3 (Hg porosimetry);
    - mean pore size: 0.82 μm (Hg porosimetry);
    - specific surface: 2.15 m^2/g (BET);
    - impurities: free of detectable impurities (atomic absorption);
    - X-ray diffraction: α-PbO_2: 43%, β-PbO_2: 57%.

The same positive plates were used for all the experiments:

- negative plates:
  - grid alloy: 0.12% Ca, 0.22% Sn;
  - formed mass: depends on the formulation (see Table 3).

The physico-chemical characteristics of the different masses varied slightly from test to test, within the expected experimental error. The results obtained by the different initial mixing/pasting tests were those settled in Table 3. Only small differences can be observed in the main physico-chemical parameters among the different cured masses.

4. Results and discussion

After the formation of the cells, they were submitted to the designed planning of electrical tests. This planning consists of the following tests.

1. Preliminary characterisation tests:
   - discharge at 25 A (approximately 5 C);
   - discharge at 10 A (approximately 2 C);
   - discharge at 5 A (approximately 1 C).
2. Initial tests previous to the ECE15L cycling:
   - 5-h capacity (C_5);
   - ECE15L at 100% depth-of-discharge (DoD);
   - 5-h capacity (C_5);
   - ECE15L at 100% DoD;
   - 5-h capacity (C_5);
   - ECE15L at 100% DoD.
3. ECE15L cycling at 80% DoD.

4.1. Preliminary characterisation tests

As a first stage of the electrical testing, initially a series of characterisation discharges at different rates were carried out on the cells. The goal of these tests was to monitor eventual differences in the initial performance among all the groups tested at different discharge rates. Therefore after formation, the cells were subjected to the following tests.

1. Discharge at 25 A (approximately 5 C) until $V < 1.0$ V.
2. Recharge at 2.4 V per cell until 105% of the previous capacity has been recharged and then 2 h at 0.25 A (constant current).
3. Discharge at 10 A (approximately 2 C) until $V < 1.5$ V.
4. Recharge (same as before).
5. Discharge at 5 A (approximately 1 C) until $V < 1.5$ V.
6. Recharge (same as before).

Table 3
Physico-chemical characteristics of the different obtained masses

Sl. No.	Expander (formulation)	Free lead (%)	Porosity (%)	Mean pore size (μm)	Specific surface (m^2/g)
1	VAN (A)	2.5	49	0.38	1.53
2	KRA (A)	3.3	47	0.37	1.26
3	N17 (A)	3.6	44	0.31	1.37
4	DD5 (A)	2.9	45	0.30	1.32
5	S04 (A)	2.2	45	0.32	1.35
6	UP4 (A)	2.4	46	0.33	1.51
7	DD8 (A)	2.1	44	0.34	1.31
8	VAN (B)	3.1	45	0.25	1.76
9	DD5 (B)	1.2	46	0.30	1.76
10	N17 (B)	2.2	42	0.34	1.15
11	VAN (C)	1.1	45	0.28	1.65
12	DD5 (C)	1.2	46	0.30	1.40
13	N17 (C)	1.2	47	0.38	1.38
14	VAN (D)	3.5	42	0.30	1.81
15	DD5 (D)	2.3	43	0.32	1.52
16	N17 (D)	2.5	45	0.43	1.62
17	VAN (E)	1.4	41	0.25	1.62

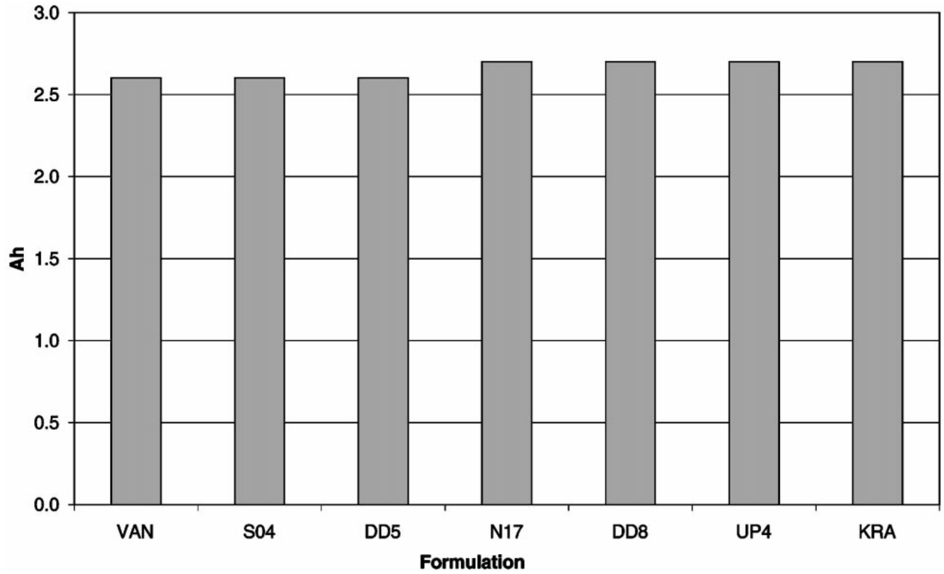

Fig. 1. Formulation A (expanders at 0.2%): discharges at 5 C rate (25 A).

Between three and six cells of each formulation were tested in every experiment at each rate, so that the values shown in the figures and tables throughout this paper correspond to *average values* over three or six cells for each test. One cell was monitored in each group using a cadmium reference electrode in order to assess which plate was responsible for the end of the discharge. In these experiments, a clear limitation of the negative plate was found in nearly all cases (data not shown). Therefore, the differences in the obtained results are due exclusively to differences in the negative plate performance, and since the plate weights were carefully chosen so that there was exactly the same paste weight in every case, the results are directly comparable.

4.1.1. Expanders at 0.2% concentration (formulation A)

The average capacity values for each one of the seven expanders tested using formulation A are shown in Figs. 1–3. At the highest rate (5 C), all the expanders produced closely similar results. Then, at 2 C (10 A), a somewhat higher difference among the seven expanders was found: about 0.4 A h difference from the best to the worst product, which represents around 10% difference in capacity at this rate. And finally, at the lowest rate, equivalent to 1 C (5 A), a maximum difference of about 0.6 A h was found in the average values, i.e. approximately a 13% increase in capacity at this rate between the maximum and the minimum values. Therefore, slight but significant differences have been found in the initial

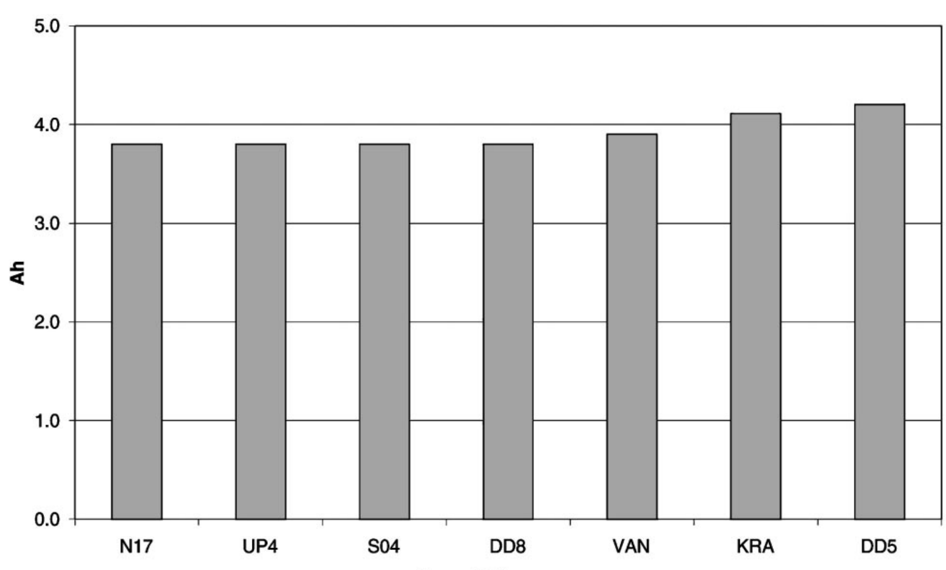

Fig. 2. Formulation A (expanders at 0.2%): discharges at 2 C rate (10 A).

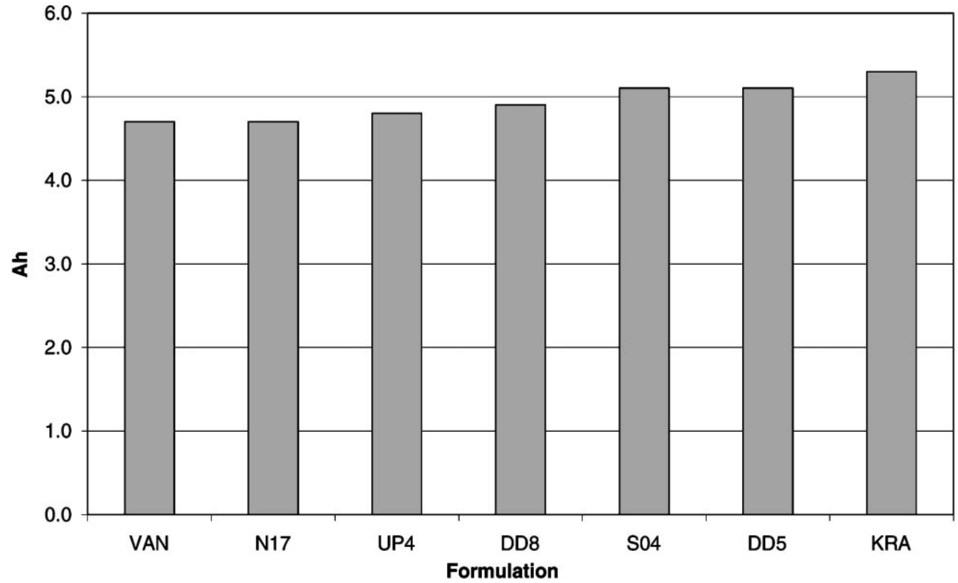

Fig. 3. Formulation A (expanders at 0.2%): discharges at 1 C rate.

characterisation tests, especially at low rates, while at high rates the differences are marginal. According to this ranking, DD5, DD8, KRA and S04 produce a somewhat higher initial performance than the other products at the test rates.

4.1.2. Expanders at 0.4% concentration (formulation B)

The percent variation in the average capacity values produced by the three expanders tested using formulation B in relation to the equivalent values obtained in formulation A, can be observed in Table 4.

It is found that, in all cases, the differences have a negative sign, i.e. the capacity decreases when the organic concentration is increased from 0.2 to 0.4%. It can be also observed that, again in these tests, at the 5 C rate the differences are marginal, but these differences increase at the 2 C rate for the three expanders tested, and later again at the lowest 1 C rate. Additionally, it can be observed that, for these three expanders, the decrease in the initial performance is different, depending on the expander considered, whereas for N17 the differences are small at all the tested rates, for DD5 the differences are much higher, especially at low rates. Therefore, for these expanders a general tendency can be observed: an increase in the organic content causes a decrease in the initial capacity, but the extent to which this variation occurs depends strongly on the expander considered.

Table 4
Percent variation in initial capacity using formulation B respect to formulation A

Expander	Rate (1 C) (%)	Rate (2 C) (%)	Rate (5 C) (%)
VAN	−12	−11	−4
DD5	−21	−17	−4
N17	−7	−9	−8

4.1.3. Expanders at 0.2% concentration plus 0.56% carbon black (formulation C)

The variations in the average capacity values for the three expanders tested using formulation C in relation to formulation A can be found in Table 5. In this case, all the figures are positive, so that the observed effect is in the opposite direction to the previous case. When the carbon black content is increased from 0.28 to 0.56% in the formulation, a slight increase in capacity is usually obtained.

Therefore, again a general rule can be observed for these expanders: an increase in carbon black causes a slight increase in capacity, but once more, the extent of this variation depends strongly on the expander considered. While N17 is the most insensitive expander to this parameter, for DD5 and particularly for VAN, the effects are stronger, especially at high rates. This can be explained by the increased paste conductivity at higher carbon black loadings, which are specially useful near to the end of the discharge, when most of the active material is lead sulphate and the carbon black provides a conductive network which helps to sustain the discharge.

4.1.4. Expanders at 0.2% concentration plus 0.5% barium sulphate (formulation D)

The respective variations in the average discharge values for the tested compounds using formulation D with respect to formulation A can be observed in Table 6.

Table 5
Variation in initial capacity using formulation C respect to formulation A

Expander	Rate (1 C) (%)	Rate (2 C) (%)	Rate (5 C) (%)
VAN	11	8	12
DD5	2	0	12
N17	0	3	4

Table 6
Variation in initial capacity using formulation D respect to formulation A

Expander	Rate (1 C) (%)	Rate (2 C) (%)	Rate (5 C) (%)
VAN	4	−3	0
DD5	−4	−8	−4
N17	−12	−12	−8

In this case, when the barium sulphate concentration is reduced from 1.0 to 0.5%, in nearly all cases, a decrease in the initial capacity is obtained. For VAN and DD5 these differences are small, and cannot be considered significant, but expander N17 suffers higher variations. Curiously, this latter expander, which was the most insensitive compound to variations both in the organic content and the carbon black content, turns out to be the most sensitive one to the $BaSO_4$ content. This reflects the fact that the different expanders tested, with different chemical composition, behave in a different way under different working conditions.

Therefore, again a general rule can be obtained for these expanders: a decrease in $BaSO_4$ from 1.0 to 0.5% causes typically a small reduction in capacity, and once more, the effect depends strongly on the expander considered. In the present tests, N17 is the most sensitive expander to this parameter, while the other two compounds are not significantly affected.

4.1.5. Vanisperse A at 0.2% concentration plus 2.8% carbon black (formulation E)

In the tests using formulation E, only one expander (VAN) was tested at 0.2% level using 10 times the carbon black content of the reference formulation, i.e. 2.8%, in order to observe whether further increases in this component lead to additional increases in performance. The results obtained in this test, in comparison to those from the reference formulation, are summarised in Table 7.

These results are of the same order, or even slightly lower, than those obtained using formulation C. Therefore, it can be concluded that, for these expanders, similar or lower increases in the initial performance are obtained when the carbon black content is increased to 2.8% in comparison to the 0.28% base level.

4.1.6. Conclusions of the preliminary tests

The following general conclusions can be drawn from the previous experiments.

- The cell design is correct: the negative plate limits the cell discharge.
- The different expanders deliver up to about 10–13% different initial capacity at low rates (1 C or 2 C). At higher rates (5 C), the differences become negligible.
- Expanders DD5, DD8 and KRA produce slightly better initial results than the rest of compounds.
- For the three expanders which were tested including variations in the expander/carbon black/$BaSO_4$ content, it was found that, in general terms:
  - by increasing the expander loading from 0.2 to 0.4%, the initial capacity at low rates (1 C) was reduced, while no significant effect was found at high rates (5 C);
  - by increasing the carbon black loading from 0.28 to 0.56%, the initial capacity was not influenced at low rates, but it increased slightly at high rates. If this loading is further increased to 2.8%, there are no significant changes respect to 0.28% content;
  - by decreasing the $BaSO_4$ loading from 1.0 to 0.5%, the initial capacity is more or less slightly reduced, depending on the expander.
- In all cases, the extent of the respective effect depends strongly on the expander considered.

Table 7
Variation in initial capacity using formulation E respect to formulation A

Expander	Rate (1 C) (%)	Rate (2 C) (%)	Rate (5 C) (%)
VAN	6	5	8

4.2. Initial tests previous to the ECE15L cycling

Following that, the groups started the initial testing program under the ECE15L specification for lead–acid batteries. According to this specification, the cells are submitted to repetitive series of constant power charges, discharges and rest periods. The basic ECE15L unit is comprised by four sub-units, referred to as the 'urban part', performed successively, which have lower and shorter power peaks, and one additional sub-unit, referred to as the 'suburban part', with higher and longer power peaks. These five sub-units are executed consecutively, and they conform the ECE15L discharge profile. This profile is repeated indefinitely until the cells fail due to reaching the lower voltage limit. One of this ECE15L discharge tests at 100% DoD is shown in Fig. 4.

The failure in this test typically occurs during the high power discharges applied in the course of the suburban part of the ECE15L unit. Therefore, the following initial tests have been carried out according to the ECE15L specifications, and previously to the cycle life testing.

1. Standard discharge (5-h capacity, C_5).
2. ECE15L at 100% DoD.
3. Standard discharge (C_5).
4. ECE15L at 100% DoD.
5. Standard discharge (C_5).
6. ECE15L at 100% DoD.

From the average capacity values of the three ECE15L discharges at 100% DoD both the useful capacity and the useful energy are calculated. These values will be used to calculate the DoD in each cycle during the cycling stage.

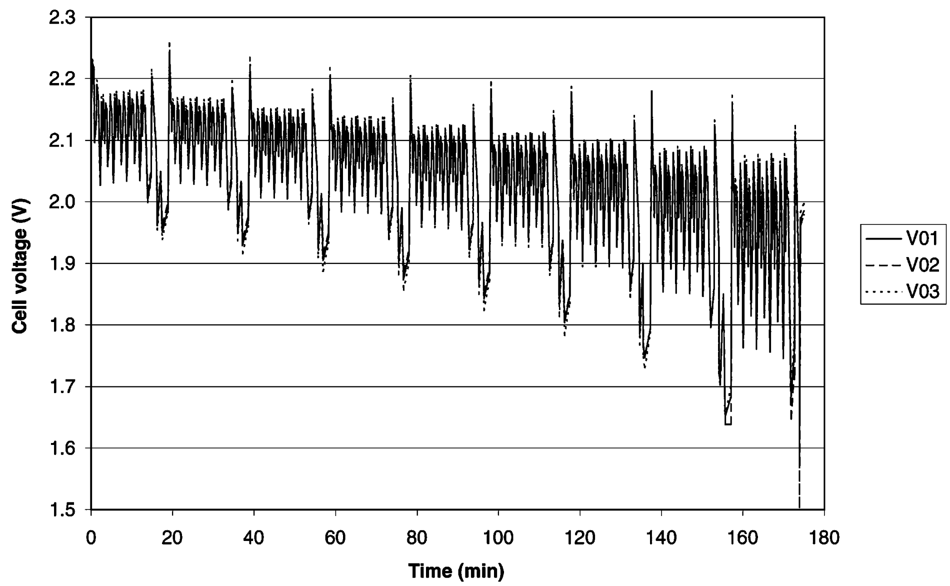

Fig. 4. Evolution of single cell voltage in one ECE15L initial discharge.

4.2.1. Expanders at 0.2% concentration (formulation A)

The results of the initial C_5 standard discharges are represented in Fig. 5. Except for DD5, in all cases the capacity value ranges between 6 and 7 A h, with rather small deviations from test to test, even taking into account that the three tests have been carried out alternated with a quite different kind of discharge test (the ECE15L profile). In comparison to the preliminary characterisation tests, it can be observed that still DD8 and KRA show a slightly better performance than the other expanders.

On the other hand, the results of the initial ECE15L discharges at 100% DoD show a different tendency. At this EV regime (Fig. 6), the initial capacity of all the expanders is around 5.5 A h, except for UP414. Nevertheless, this latter product is not a commercial product but a development product from Borregaard, and should be considered as an experimental expander. In any case, during the first ECE15L discharge, and usually again in the second discharge, the capacity values maintain a quite constant value, but in nearly all cases, at the third discharge a marked decrease in capacity is obtained. This decrease is even more clearly observed in the discharged energy drawing (Fig. 7). From the first to the second and to the third test, there is a marked decrease in performance at the ECE15 regime, which amounts up to around 15–20% in Watt hour. Clearly, this decrease is more closely related to the power requirements of the ECE15L

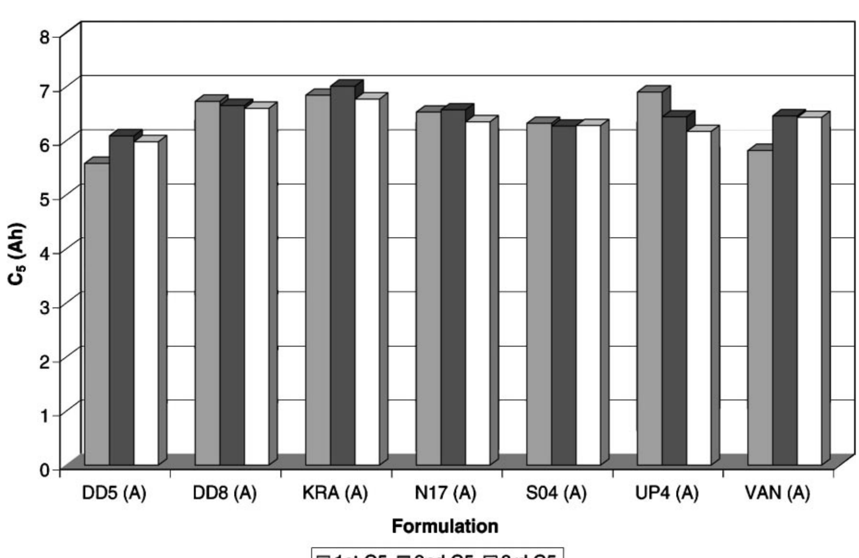

Fig. 5. Formulation A: C_5 initial capacities.

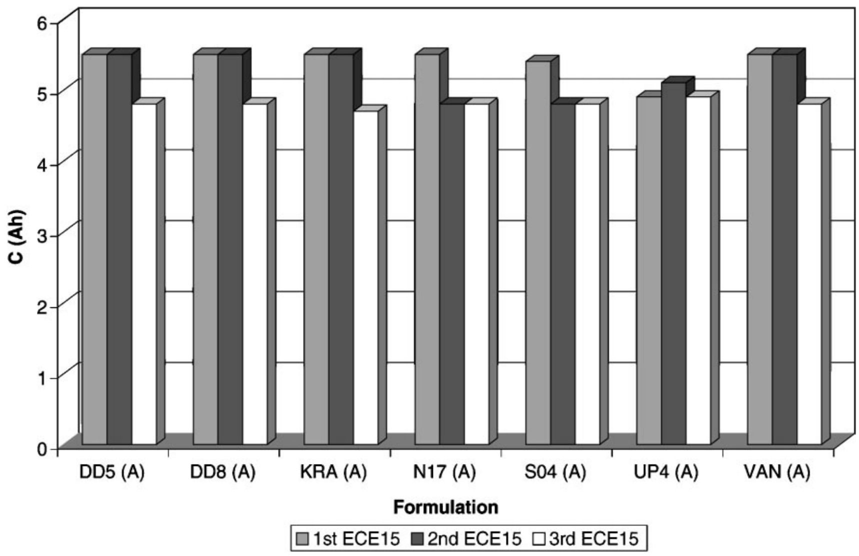

Fig. 6. Formulation A: ECE15L (100% DoD) initial capacities.

regime and its influence on the present cell design than to the real conditions of the cells, since the C_5 tests, which are carried out alternated with the ECE15L discharges, maintain their values in a quite constant mode.

4.2.2. Expanders at 0.4% concentration (formulation B)

The average values produced by the three expanders tested using formulation B in comparison to formulation A can be found in Figs. 8–10. From the previous figures, it can be concluded that the earlier observations made during the comparison of formulations A and B at the preliminary tests (Section 4.1.2) are still valid here both for the C_5 and the ECE15L regimes. For the three expanders tested in these conditions, an increase in the expander loading from 0.2 to 0.4% produces a slight decrease in the initial discharges, especially at the ECE15L regime, both in capacity and in energy. However, in this case the effect is more clearly observed at higher rates (ECE15L) than at lower rates (C_5).

4.2.3. Expanders at 0.2% concentration plus 0.56% carbon black (formulation C)

The values of the initial tests both under C_5 and ECE15L regimes for the three expanders tested in these conditions can be observed in Figs. 11–13. Again, the same remarks can be made as in the preliminary discharges. When the concentration of carbon black is increased from 0.28 to 0.56%, the values of the initial discharges increase slightly, especially at the ECE15L rate. The effect is again more clearly

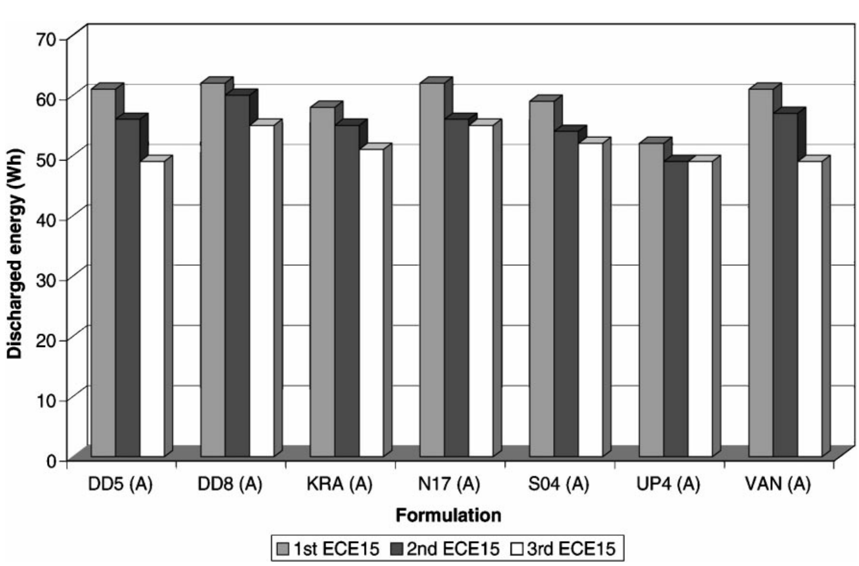

Fig. 7. Formulation A: ECE15L (100% DoD) initial discharged energy.

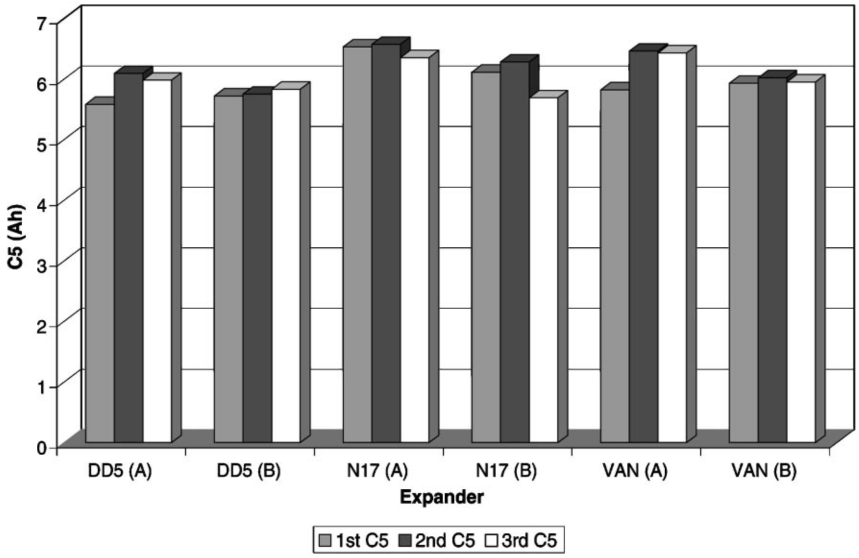

Fig. 8. Comparison of formulations A and B: C_5 initial capacities.

observed in the discharged energy drawing (Fig. 13). Also, once more, the C_5 tests produce quite similar capacity values, but the ECE15L tests show a marked decrease at the second or third discharge.

4.2.4. Expanders at 0.2% concentration plus 0.5% barium sulphate (formulation D)

The results obtained by comparing the discharge values both at the C_5 and ECE15L regimes using formulation A with those using formulation D can be observed in Figs. 14–16. Once again, the conclusions are similar to those obtained in the preliminary tests. For the three expanders tested, when the $BaSO_4$ content is reduced from 1.0 to 0.5%, in general terms the initial discharges are slightly reduced, but the extent of this effect depends strongly on the expander. Whereas this effect is quite strong for expander N17, for the other two compounds, the variations (either positive or negative) are rather low, and cannot be considered significant. This is true for high discharge rates (ECE15L); for C_5 discharges, the effects are different, depending on the expander. For DD5 and VAN, the C_5 increases slightly, while for N17, the C5 decreases slightly.

4.2.5. Vanisperse A at 0.2% concentration plus 2.8% carbon black (formulation E)

The results obtained in these tests by the three formulations including Vanisperse A at the 0.2% level with different amounts of carbon black are shown in Figs. 17–19. In

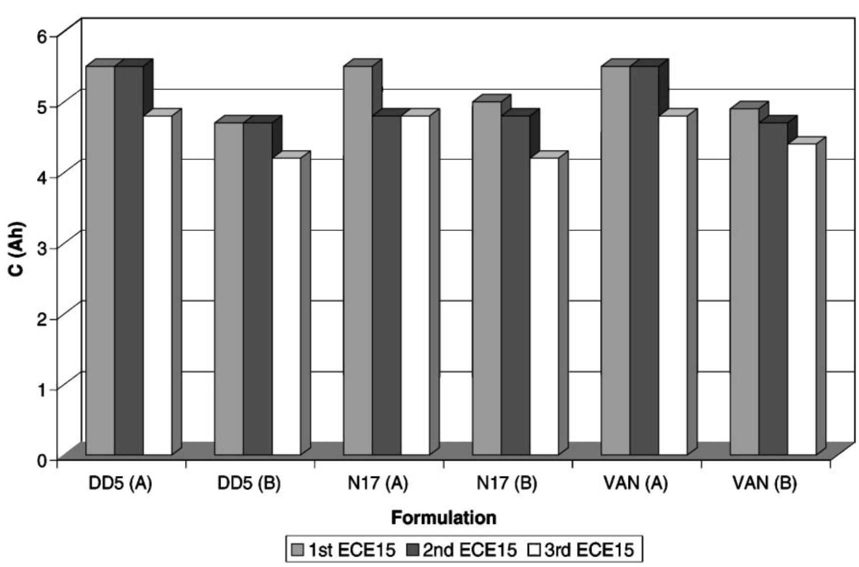

Fig. 9. Comparison of formulations A and B: ECE15L (100% DoD) initial capacities.

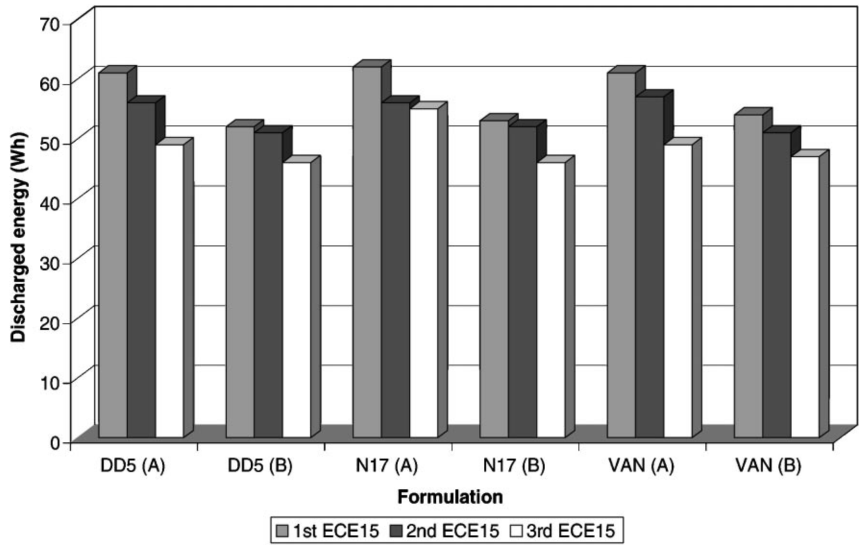

Fig. 10. Comparison of formulations A and B: ECE15L (100% DoD) initial discharged energy.

relation to the C_5 capacity (Fig. 17), the initial capacities when the carbon black content is increased from 0.28 to 0.56% show a slight increase. But, when this content is increased further to 2.8%, the C_5 tests showed values higher than in the reference formulation, but lower than in formulation C. Therefore, excessively high increments in the carbon black content can produce an adverse effect on the initial performance at the C_5 rate. Regarding to the ECE15L capacities, the Fig. 18 shows that, from formulation A to C, there is no significant variation in the initial discharges; nevertheless, when the carbon content is increased to 2.8% (formulation E), a decrease in the initial performance is obtained. This decrease in performance, even slight, can be more clearly observed in the discharge energy drawing (Fig. 19). The discharged energy increases slightly from 0.28 to 0.56% carbon black, but when the content is raised to 2.8%, the discharged energy falls even below the values obtained in the reference formulation. Therefore, in summary, a carbon content of 2.8% is excessively high for the initial performance and has an adverse effect on the initial capacities both at the C_5 and the ECE15L regimes.

4.2.6. Conclusions of the initial tests previous to the ECE15L cycling

The results obtained in the initial tests previous to the ECE15L cycling are similar to those obtained earlier in the preliminary characterisation tests, and can be summarised in the following statements.

- At the same organic loading (0.2%), all the expanders tested produce similar discharge values with DD8 and KRA performing slightly above the average.

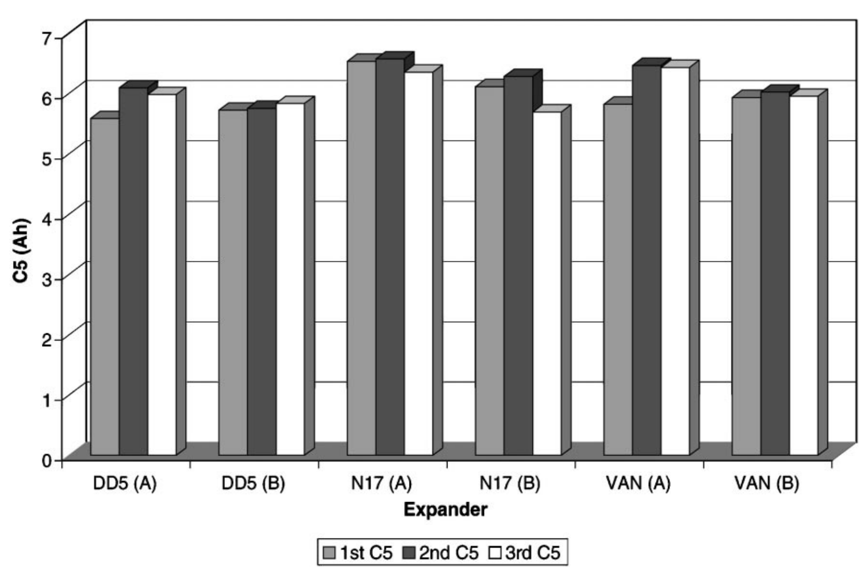

Fig. 11. Comparison of formulations A and C: C_5 initial capacities.

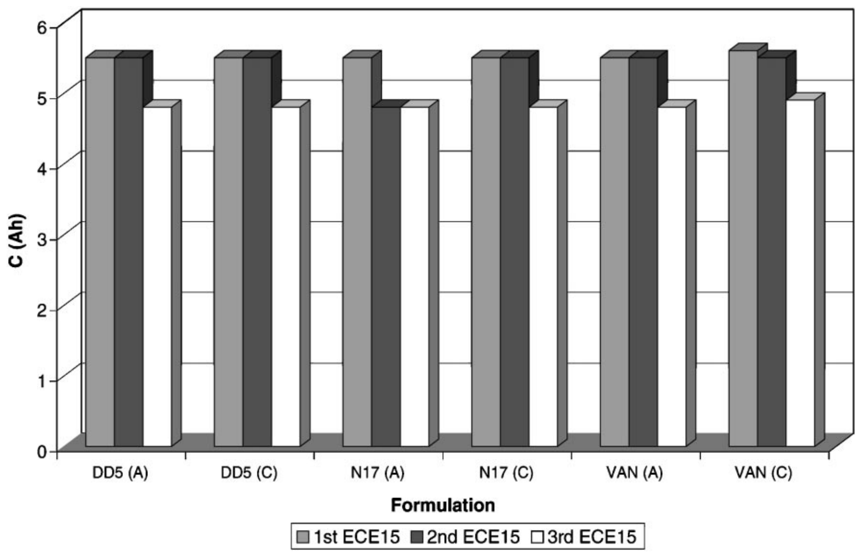

Fig. 12. Comparison of formulations A and C: ECE15L (100% DoD) initial capacities.

- For the three expanders tested with different additive contents, it has been observed that:
  - increasing the expander concentration reduces slightly the initial discharge values especially at high rate (ECE15L);
  - increasing the carbon black concentration increases slightly the discharge capacity especially at high regime (ECE15L). However, if this concentration is increased further (until 10 times the initial value), the obtained effect is adverse;
  - decreasing the $BaSO_4$ content from 1.0 to 0.5%, in general, has a very slight deleterious effect in the capacity at the ECE15L regime, but this effect depends strongly on the specific expander.
- In all cases, the extent of the effect of each variation depends heavily on the specific expander considered.
- The three consecutive initial C_5 capacities produce quite constant results, but the three alternated ECE15L capacities show a remarkable decline already since the beginning:
  - the power requirements required by the ECE15L specification are too severe for this cell design.

4.3. ECE15L cycling at 80% depth-of-discharge (DoD)

Once the previous discharge program has been completed, the cell modules started the ECE15L cycling test at 80% DoD. The evolution of the discharged capacity in one cycle is shown in Fig. 20. According to this profile, the cells are discharged first to 40% DoD, then a rest period of 30 min is introduced, and finally the discharge continues down to 80% DoD. The average values of the C_5 and ECE15L control

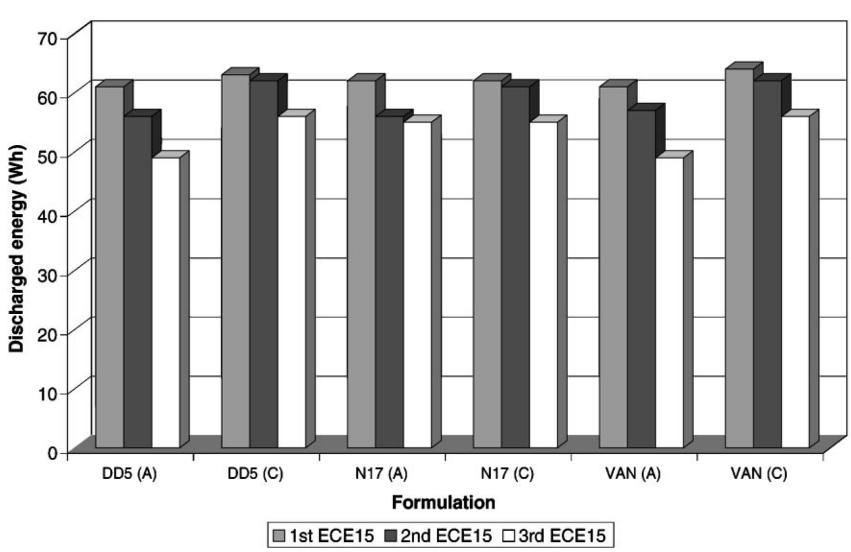

Fig. 13. Comparison of formulations A and C: ECE15L (100% DoD) initial discharged energy.

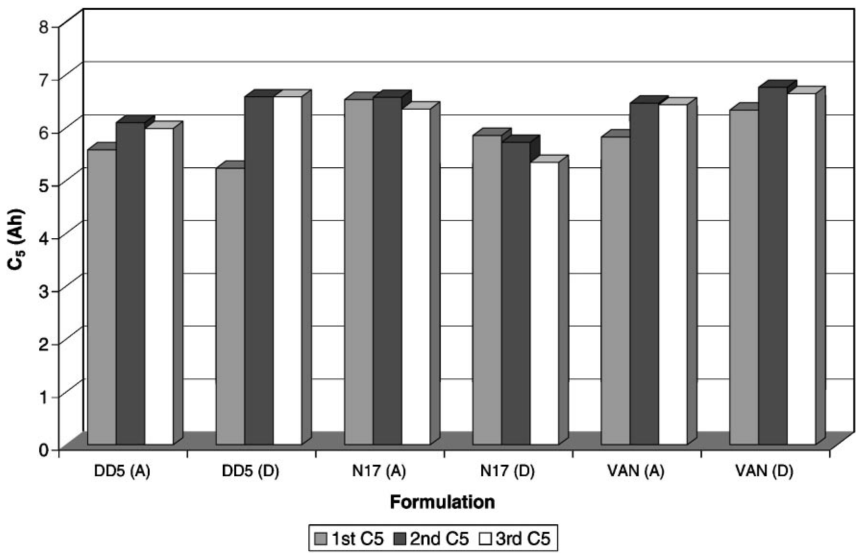

Fig. 14. Comparison of formulations A and D: C5 initial capacities.

discharges at the beginning (before the cycle life test) and after the end-of-life are shown in Figs. 21 and 22.

In these figures it can be observed that, in all cases, the ECE15L control discharges carried out after the end-of-life (according to the ECE15L criterion) are substantially lower than the initial values. Nevertheless, this is not the case for the C_5 controls, where the values obtained are quite close to the initial amounts. This indicates that the end-of-life criteria pointed out by the ECE15L specification do not match the C_5 criteria. While the cells are dead, according to the ECE15L discharge, on the other hand, they are still quite healthy according to the C_5 discharge. If the initial discharge values are normalised to 100%, it can be observed that, in all cases, the C_5 capacity after the end-of-life is substantially higher than 80%, value which is usually considered to be a limit above which the battery is still considered healthy. On the other hand, the end-of-life ECE15L controls produce values clearly lower than 80%, as expected. These evidences could question the real meaning of a test program based on each one of these criteria.

Finally, the results of the cycle life test according to the ECE15L specification at 80% DoD are shown in Fig. 23, for the seven expanders tested using formulation A (0.2% concentration). The figure shows that there are extremely different values for the different expanders. This is probably more closely related to their respective ability to withstand a high power discharge peak than their real life cycles until a truly dead cell.

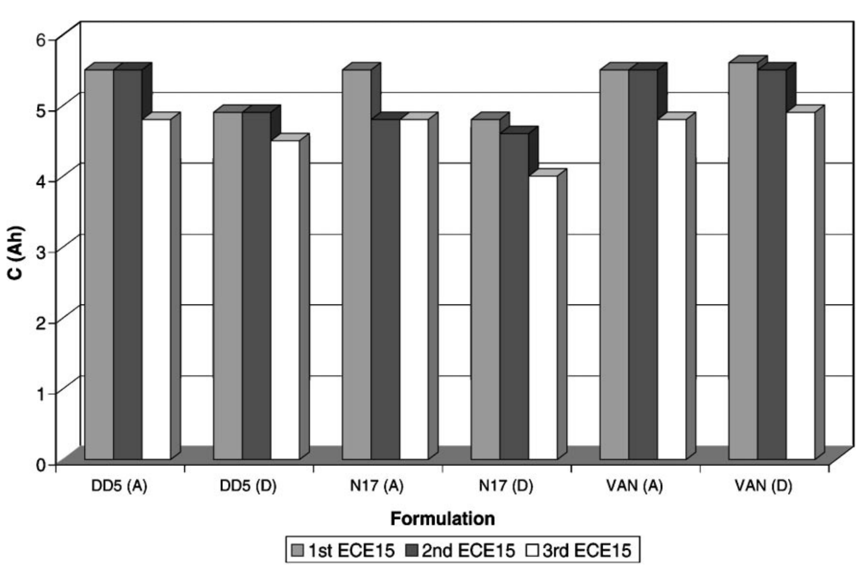

Fig. 15. Comparison of formulations A and D: ECE15L (100% DoD) initial capacities.

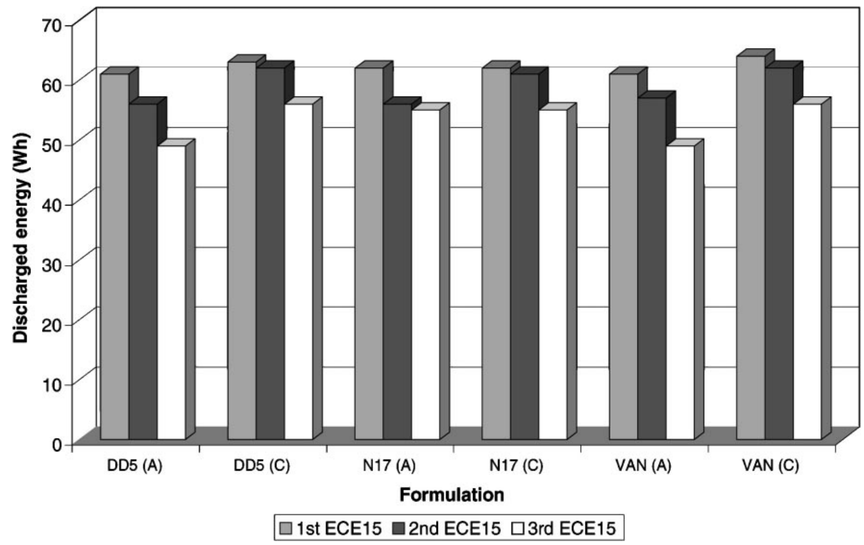

Fig. 16. Comparison of formulations A and D: ECE15L (100% DoD) initial discharged energy.

In any case, the expanders that have shown a better behaviour in the cycle life test at 0.2% expander loading and using the ECE15L regime, are:

- Kraftperse DD8;
- Vanisperse A;
- Kraftplex.

Therefore, these expanders have been selected for further testing in real VRLA batteries, during the last part of the project program. And, finally, regarding the results obtained with the three expanders tested using different additive contents (see formulations in Section 3), the results can be observed in Fig. 24.

The following observations can be obtained.

- Formulation B: whereas for DD5 the cycle life is increased when doubling the expander concentration, for N17 and VAN, the cycle life is decreased. Once more, the effect depends strongly on the expander considered.
- Formulation C: in this case, when the carbon black concentration is doubled, for N17 there is no significant variation observed, while for DD5 and VAN there is significant increase in the number of fulfilled cycles. This is probably due to the increased conductivity, especially close to the end of the discharge, which allows the

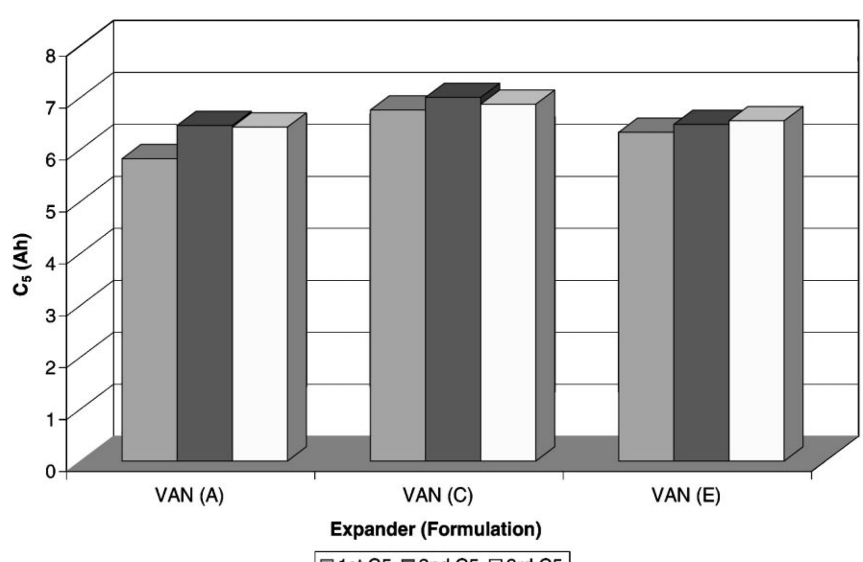

Fig. 17. Comparison of formulations A, C and E: C_5 initial capacities.

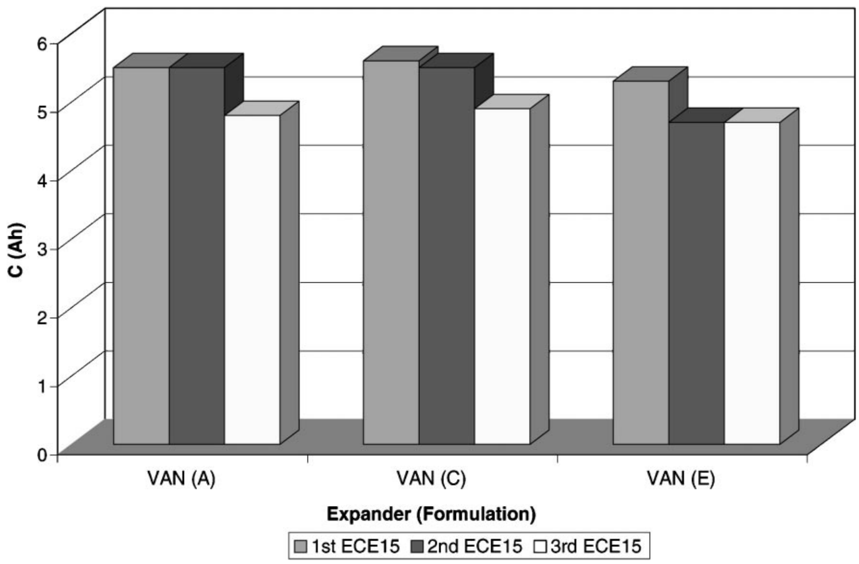

Fig. 18. Comparison of formulations A, C and E: ECE15L (100% DoD) initial capacities.

negative active mass to better withstand high power discharge peaks.

- Formulation D: both for N17 and VAN, the cycle life is clearly reduced when the $BaSO_4$ is reduced from 1.0 to 0.5%. This confirms the statements previously claimed by other authors to this respect. For DD5, the data were lost due to a malfunction in the test equipment, so that most of the final cycles were lost. Nevertheless, the initial cycles recorded showed the same tendency than N17 and VAN.
- Formulation E: finally, for formulation E (Vanisperse 0.2% plus 2.8% carbon black), the highest number of ECE15L cycles obtained throughout all the test program has been recorded. Therefore, a further increase in the carbon black content respect to formulation C produces remarkable further increases in the cycle life performance.

4.3.1. Conclusions of the ECE15L cycle life tests

The overall results are complex and the conclusions depend quite heavily on the specific expander considered. Nevertheless, several general rules can be identified, such as:

- the best expanders, at the 0.2% level, in the cycle life test according to the ECE15L specification, are: DD8, KRA, and VAN;
- an increase in expander concentration from 0.2 to 0.4% may increase or decrease the ECE15L cycle life, depending on the specific expander;
- an increase in carbon black concentration from 0.28 to 0.56% usually improves significantly the ECE15L cycle life. In the case of Vanisperse, if this loading is additionally increased up to 2.8%, the cycle life behaviour is markedly enlarged further;

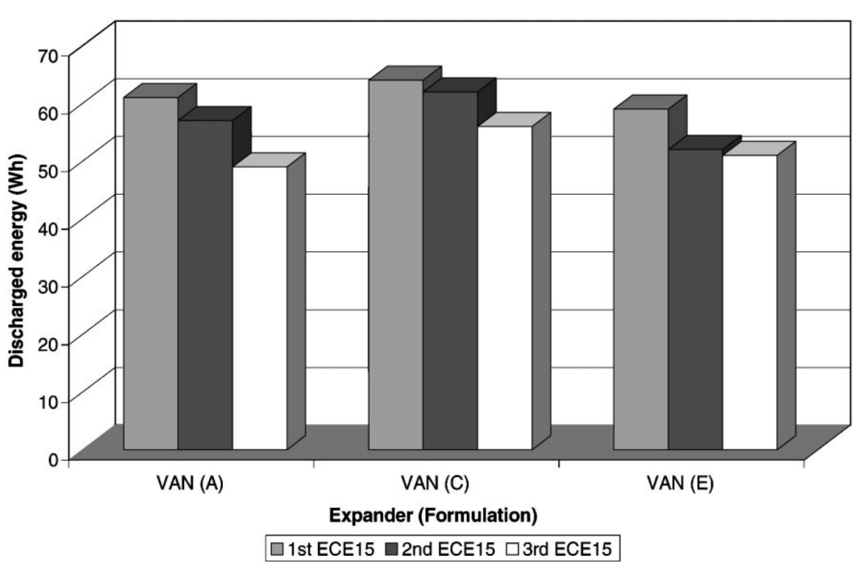

Fig. 19. Comparison of formulations A, C and E: ECE15L (100% DoD) initial discharged energy.

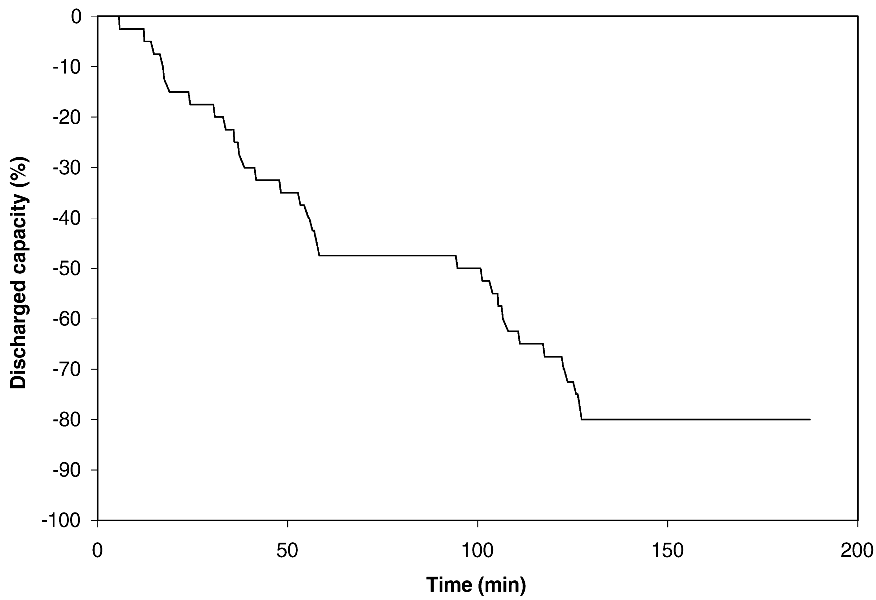

Fig. 20. ECE15L profile: evolution of discharged capacity in one cycle.

- a decrease in $BaSO_4$ concentration from 1.0 to 0.5% affects adversely the cycle life performance;
- at the end of the ECE15L cycling, the C_5 capacity is still >80%, but the ECE15L capacity is poor:
  - the power requirement asked by the ECE15L specification seems to be too severe for this cell design. Therefore, the power requirements of the specification are influencing the results of the tests.

4.3.2. Selection of formulations for battery testing

Therefore, as a final conclusion to all the above tests, the following formulations have been selected for further testing in VRLA batteries:

- VAN at 0.2% concentration (control);
- VAN at 0.2% concentration + increased carbon black concentration;
- DD8 at 0.2% concentration;
- KRA at 0.2% concentration.

5. Conclusions

During the first year of the project, a series of 19 potential expander candidates, proceeding from various different sources, were tested using several basic electrochemical techniques. From the results obtained in this pre-screening procedure, a list of seven expanders was selected for further testing in single VRLA cells.

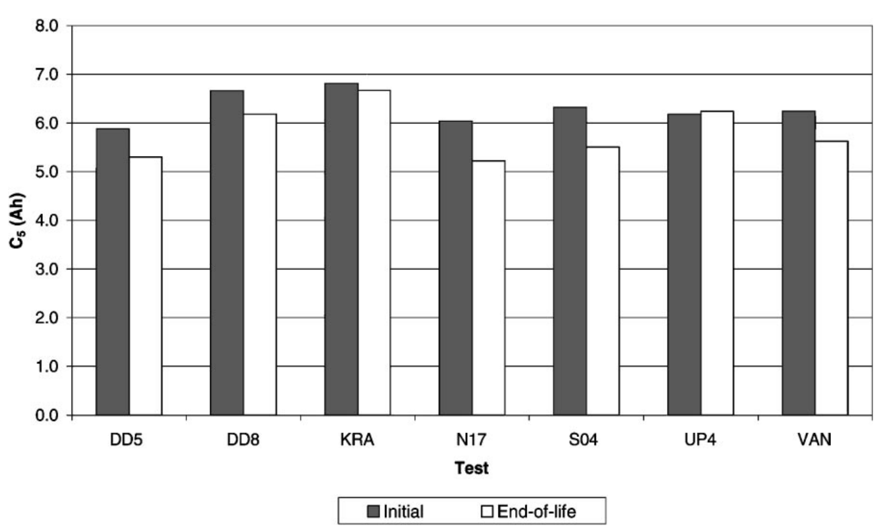

Fig. 21. ECE15L cycle life test: evolution of C_5 capacity controls.

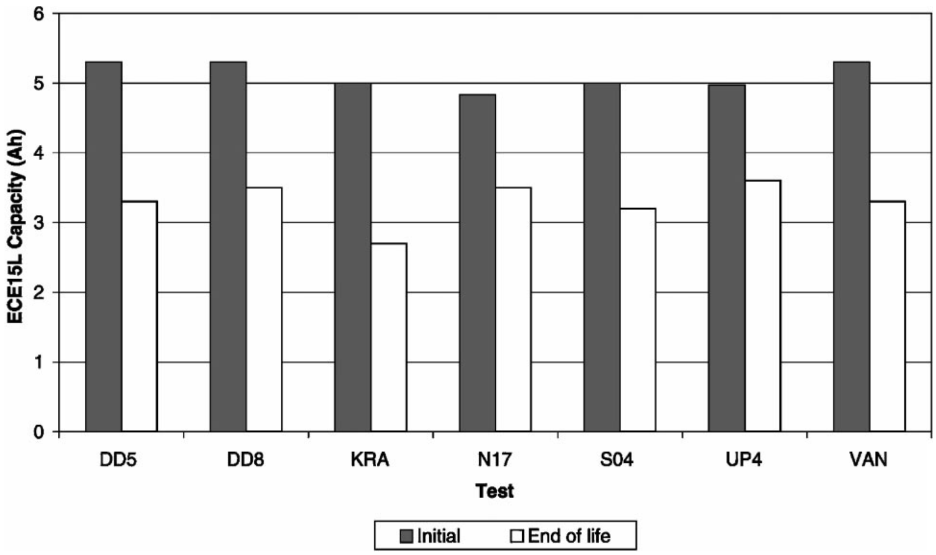

Fig. 22. ECE15L cycle life test: evolution of ECE15L capacity controls.

During the second year of the project, a formulation was designed for the testing of each expander in the negative plate in VRLA single cells, including, for three selected compounds, formulations with different concentrations of either the organic, carbon black or barium sulphate, and then the different plate formulations were mixed, hand-pasted, cured, assembled and formed. The preliminary electrical tests carried out at different rates showed that the different formulations delivered up to about 10–13% different initial capacity, depending on the rate. From these results, expanders DD5, DD8, S04 and KRA produced slightly better results in the initial discharges at the tested rates than the other compounds.

Then, during the initial tests previous to the ECE15L cycling, in general terms the C_5 capacities showed a quite constant behaviour, but the ECE15L capacities/discharge energies showed a marked decrease already along these three initial charge/discharge cycles. This declining tendency was later confirmed during the cycling tests performed using this specification. Therefore, it seems that the power requirements asked by the ECE15L profile to this cell design are too severe, so that the test results are

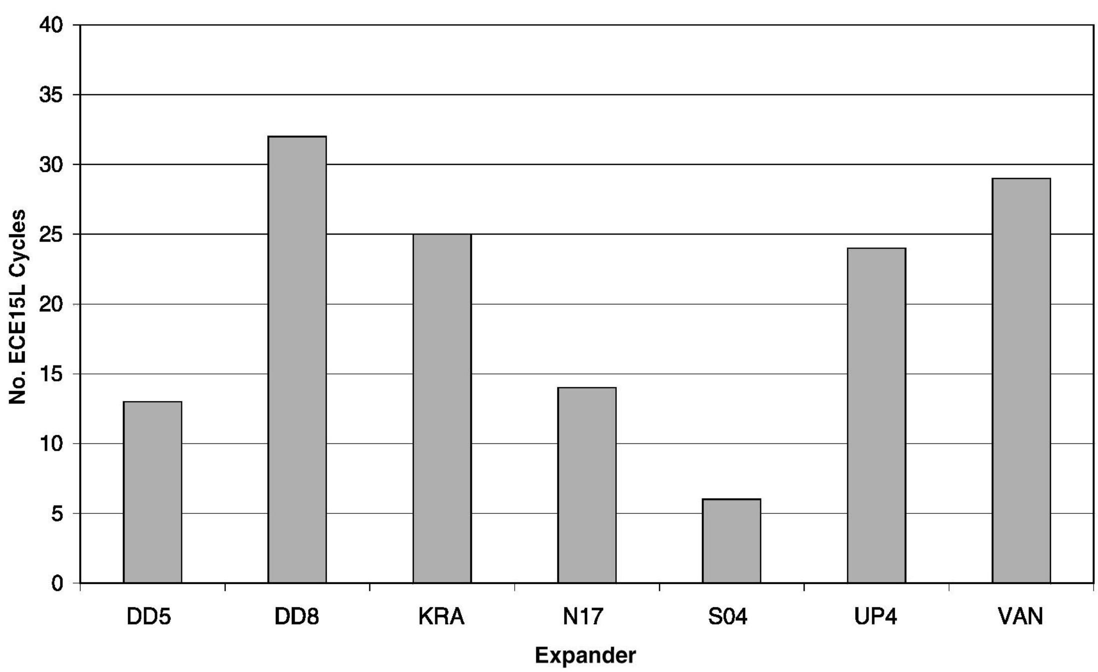

Fig. 23. Formulation A: ECE15L (80% DoD) cycle life test.

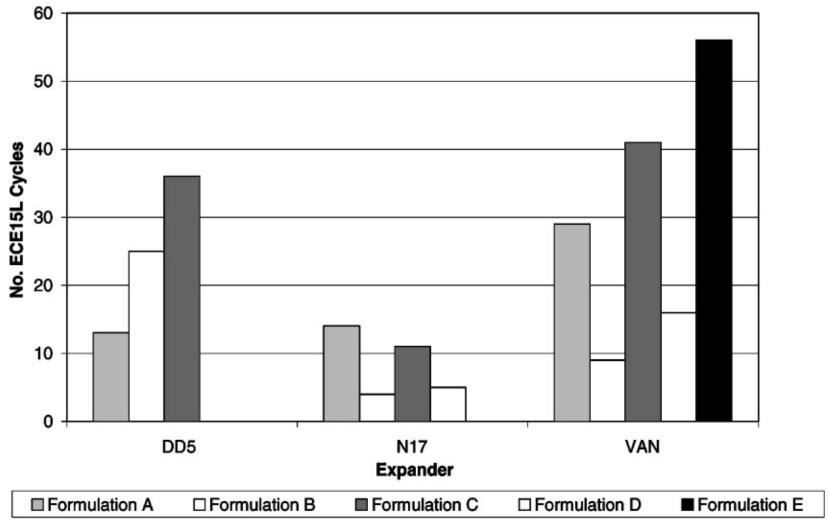

Fig. 24. All formulations: ECE15L (80% DoD) cycle life tests.

being strongly influenced by the power requirements of the specification.

The cycling tests according to the ECE15L regime showed remarkable differences in the number of cycles fulfilled by each formulation. However, these difference are more probably due to differences in the ability of each expander to withstand a high power peak than a real cycle life accounting until the cell is flat. Anyway, regarding to the cell tests carried out using the expanders at 0.2% level (formulation A), the most effective compounds have been Vanisperse, Kraftplex and Kraftperse DD8. Therefore, these three expanders have been selected for further testing in real VRLA batteries.

Finally, in relation to the expanders tested including different levels of additives (formulations B, C, D and E), the obtained results were complex and the conclusions depended quite heavily on the specific expander considered. Nevertheless, several general rules could be identified, such as:

- an increase in expander concentration from 0.2 to 0.4% may increase or decrease the ECE15L cycle life, depending on the specific expander;
- an increase in carbon black concentration from 0.28 to 0.56% usually improves the ECE15L cycle life. In the case of Vanisperse, if this concentration is additionally increased to 2.8%, the cycle life behaviour is markedly enlarged further. This is probably due to the increased electric conductivity, especially near to the end of the discharge, which allows the negative plate to better withstand high power peaks;
- a decrease in $BaSO_4$ concentration from 1.0 to 0.5% affects adversely the cycle life performance;
- at the end of the ECE15L cycling, the C_5 capacity is still >80%, but the ECE15L capacity is poor:
  - the power requirement asked by the ECE15L specification seems to be too severe for this cell design. Therefore, the power requirements of the specification are influencing the results of the tests.

Acknowledgements

The present study has been funded by the European Union under the Brite-Euramm Programm (Project BE97-4085) and the Advanced Lead Acid Battery Consortium (ALABC). Their support is fully acknowledged.

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