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The effect of organic expander materials on the performance, life, surface area and crystal structure of negative electrodes in valve regulated cells

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Abstract

Valve regulated cells containing lignosulfonates and synthetic organic additives in their negative plates have been evaluated to determine their effect on capacity and cycle life. The negative active material was examined throughout cycle life to determine the effect of the additives on surface area and crystal morphology.

Capacity tests were conducted over a range of current densities at ambient temperature and -18°C on cells containing the additives at various levels. All of the materials increased the capacity but considerable differences were observed in the capacity/dosage level responses. All of the organic materials increase the surface area of the active material, and the surface area increases with concentration. The additives produce a morphology composed of small equiaxial grains with high porosity and surface area. During cycling a progressive reduction in surface area takes place which eventually produces a dense structure with low porosity.

The capacity and cycle life data show that each additive has a different optimum concentration in the plate. There are also indications that considerably higher concentrations of organic additives can be used in valve regulated batteries than is customarily used in flooded systems.

Keywords: Lead–acid batteries; Negative electrodes; Additives; Expanders; Capacity; Cycle life; Surface area; Crystal morphology

1. Introduction

Expanders are an essential component of the negative plate of lead–acid batteries. Without them the capacity and life of these batteries would be significantly impaired. Lignosulfonates are a principle ingredient of expanders. These are produced by chemical treatment of softwood lignin and contain methoxyl, carboxyl, ketonic and other functional groups. The lignin may also be sulfonated to various degrees. In addition to lignosulfonates synthetic organic materials have been used [1] that are derived from Syntans (a product of tanning) treated with formaldehyde.

Although the exact mechanism of how these organic molecules affect the behavior of negative active material is not known, they are known to exert a significant effect on the surface area and crystal morphology [2–6]. They are also strong rheological modifiers and affect the fluidity and pasteability of the negative paste.

Traditionally, expander and battery manufacturers have chosen the organic component, and its dosage level, based on trial and response testing. This is an expensive and time-consuming process and it would clearly be advantageous if the effects of the organic materials on the negative active material could be predicted from its effect on surface area and crystal morphology. Pavlov et al. [7] have attempted to correlate expander performance with the content of different structural groups and the molecular weight of lignosulfonates. They found that the strongest beneficial effect on battery performance was obtained with materials having low average molecular weight. They also found a correlation between capacity and the content of carboxyl groups in the molecule. High carboxyl contents favored improved capacity and a reduced rate of self-discharge. Increasing the percentage of methoxy groups in the molecule had an adverse effect on cold cranking behavior while increasing the organic sulfur content increased the rate of self-discharge. A complex relationship was found between the percentage of phenolic groups and the cycle life with negative effects on self-discharge and charge acceptance, and a positive effect on cycle life.

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The purpose of the present work was to examine the effects of various lignosulfonates and synthetic organic materials on the surface area and crystal morphology of negative active material (NAM) and to determine how these effects contributed to the capacity and cycle life of valve regulated cells.

2. Experimental

The organic materials that were investigated are shown in Table 1. Three of these (Vanisperse A, Maracell XC-2, Lignotech D-1380) are oxylignins, two (Kraftplex, Indulin AT) are kraft lignins and three (Lomar B, BNF, GKD) are synthetic materials. These materials were blended with barium sulfate (Solvay HD-80) and carbon black (Shawinigan acetylene block 334-7B, 100% compressed) and were added to the negative active material in the amounts and the ratios shown in Table 2. These blends were chosen since they represent a range of organic loading in the plate varying from the lowest to the highest concentrations normally used in lead–acid batteries. The blend with no organic additive (blend 0) was used as the control. The ''total amount in plate'' is the percentage in the dry oxide before water and acid are added.

The test fixture is shown in Fig. 1. This can hold the cell element either under a fixed compressive load (provided by springs and a floating plate) or hold it at a fixed spacing. Ports are provided for reference electrodes, thermocouples, pressure transducers and for gas sampling. In the present work, mercury/mercurous sulfate reference electrodes were used and the spring pressure was used to maintain the cell stack under a pressure of 60 kPa.

Cell testing consisted of initial capacity measurements, the United States Advanced Battery Consortium Dynamic Stress Test (DST) and cycle life to failure (80% of the initial capacity).

2.1. Initial capacity

The cells (five replicates) were discharged at ambient temperature at the 1, 3 and 5 h rates (1.98, 0.78, 0.52 A) to a cut-off voltage of 1.70 after 1 h on open circuit following charging.

Table 2
Expander formulations and loading

	Blend no. 0	Blend no. 1	Blend no. 2	Blend no. 3
Blend formulation				
Organic material (%)	0%	20%	33%	42%
Shawinigan carbon black (%)	21%	17%	14%	12%
Blanc fixe (HD-80) (%)	79%	63%	53%	46%
Total amount (%)	100%	100%	100%	100%
Loading in plate				
Organic material (%)	0%	0.25%	0.50%	0.75%
Shawinigan carbon black (%)	0.22%	0.22%	0.22%	0.22%
Blanc fixe (HD-80) (%)	0.80%	0.80%	0.80%	0.80%
Total amount in plate (%)	1.02%	1.27%	1.52%	1.77%

2.2. Dynamic stress test

Each cell (five replicates) was tested at ambient temperature and −18°C (0°F). The low temperature was chosen to accentuate the differences between the various organic additives. The current densities were normalized by weight to reflect the power density requirements of a full sized EV battery in the DST test, which has a requirement of 150 W/kg. This resulted in a maximum negative electrode current density of 16.3 mA cm^{-2}.

2.3. Life cycling

The cells were cycled at a discharge rate of 1.50 A. They were discharged to 1.70 V and recharged at 2.45 V with a current limit of 5 A. Recharge was terminated at 5 h. The cycle life test was conducted at ambient temperature and 40°C. Cells were removed from cycling at 0, 100 cycles and at failure. The negative active material was removed from the plate, washed, dried and subjected to examination by a

Table 1
Organic expander materials selected for cell testing

Additive	Chemical description	Comment
Vanisperse A, Maracell XC-2, Lignotech D-1380	Sodium salt of partially desulfonated, oxidized and purified lignosulfonates	Lignotech, USA, 100 highway 51 South, Rothschild, WI 54474-1198, USA
Kraftplex, Indulin AT	Sulfonated, modified kraft lignins	Westvaco Chemical Division, P.O. Box 70848, Charleston Heights, SC 29415-0848, USA
Lomar B	β-Napthol/formaldehyde condensates	GEO Specialty Chemicals Inc., 300 Brookside Avenue Ambler, PA 19002-3498, USA
GKD, BNF		Aidar Corporation, 3305 W. Spring Mountain Road, Las Vegas, NV 89102, USA
None	Lignin omitted from expander	Control

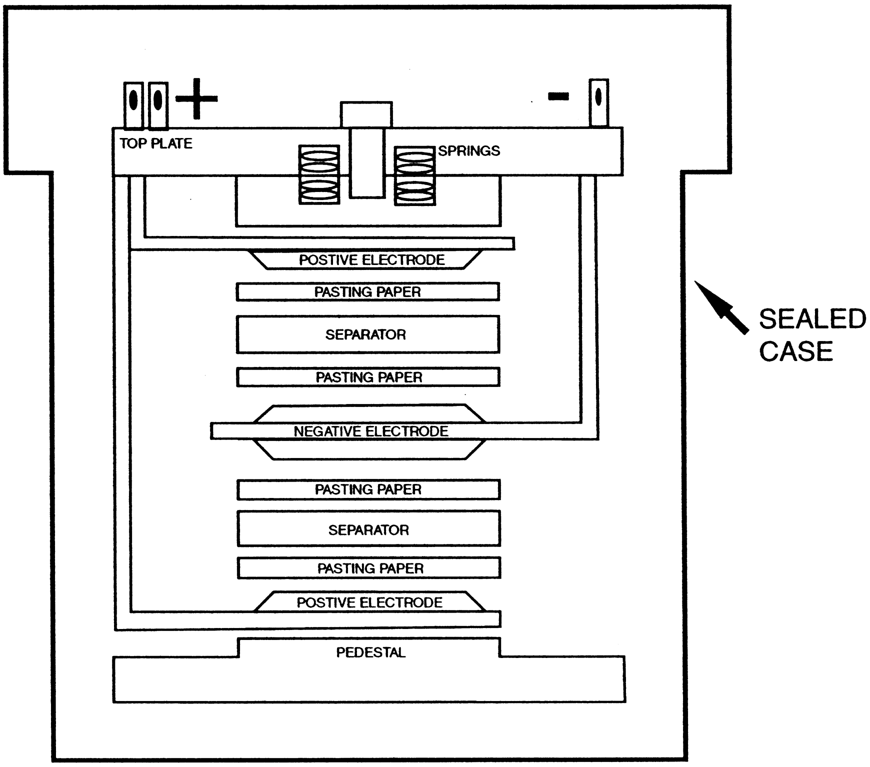


Fig. 1. Schematic of test cell assembly.

scanning electron microscope (SEM) and its BET surface area determined.

3. Results and discussion

3.1. Capacity

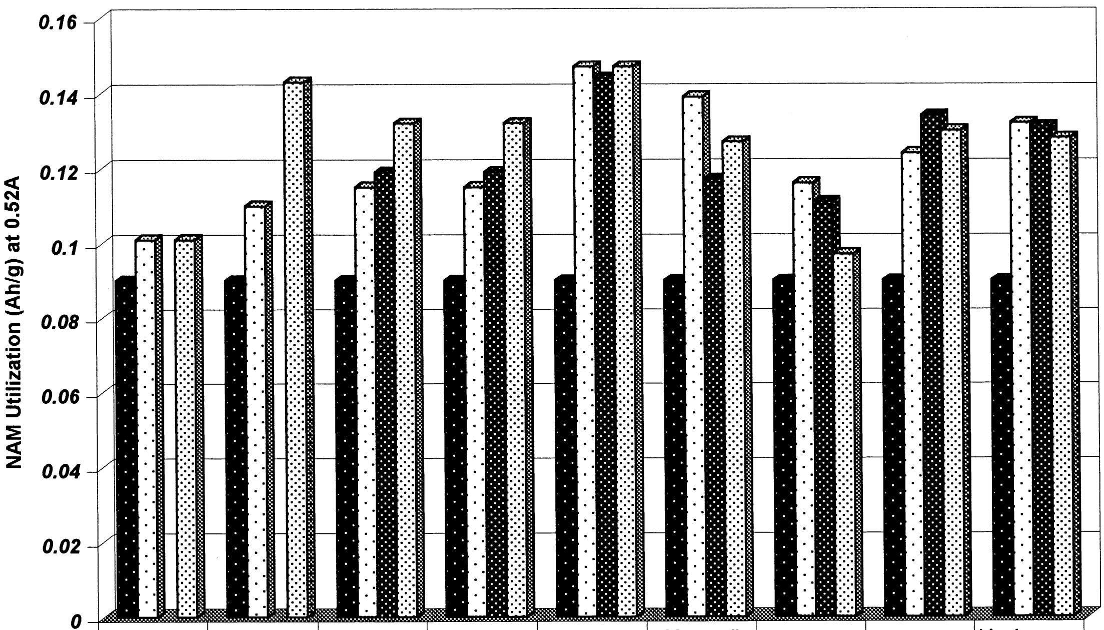
The results of the capacity testing are shown in Figs. 2–4 for the three discharge rates. These represent the average of five cells. Since cell-to-cell variation was small, the differences are believed to be significant. The data are expressed as ampere-hours per gram of formed negative active material to normalize the data and to eliminate the effects of small variations in active material weights among the cells.

All of the additives increased the NAM utilization to varying degrees compared to the cells with no organic material, however significantly different dosage responses are seen. This behavior suggests that each additive exerts a unique effect on the negative active material. Indulin AT and Kraftplex (both kraft lignins) gave increased active material utilization as the concentration in the active material is increased. This suggests that high dosage levels of these materials should be used. Lignotech D-1380 also showed improved capacity as the dosage is increased. Maracell XC-2 and Vanisperse A showed an initial increase in capacity at the 0.25% dosage level with very little further change as the concentration is increased. Over the range of concentrations studied the highest active material utilizations in decreasing order were

Additive	Concentration (%)	NAM utilization (A h/g)
Lomar B	0.25	0.147
Lomar B	0.75	0.147
Kraftplex	0.75	0.143
Maracell XC-2	0.25	0.139
GKD	0.50	0.134
Vanisperse A	0.25	0.132

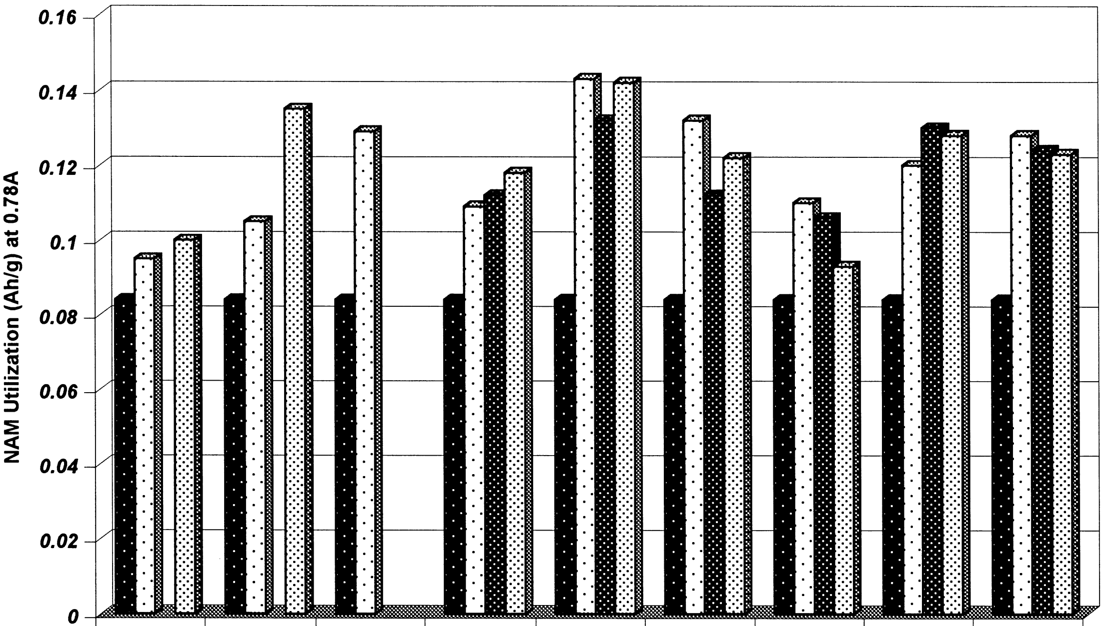
The data show that the interaction between the additive and the active material is complex. Each candidate influences the active material in a different way which may depend on such factors as molecular weight, degree of saturation, degree of sulfonation, percentage of methoxy groups, etc.

The results of the Dynamic Stress Test at ambient temperature and −18°C are shown in Fig. 5. Considerably higher active material utilization is obtained with all of the organic additives compared to the control cells. As was observed with constant current discharge, the initial improvement in utilization by the addition of 0.25% additive was significantly greater than the subsequent increase as the dosage level was increased to 0.50% and then 0.75%. A considerable reduction in NAM utilization is observed at −18°C as expected. However, with few exceptions, those candidates that performed best at ambient temperature also



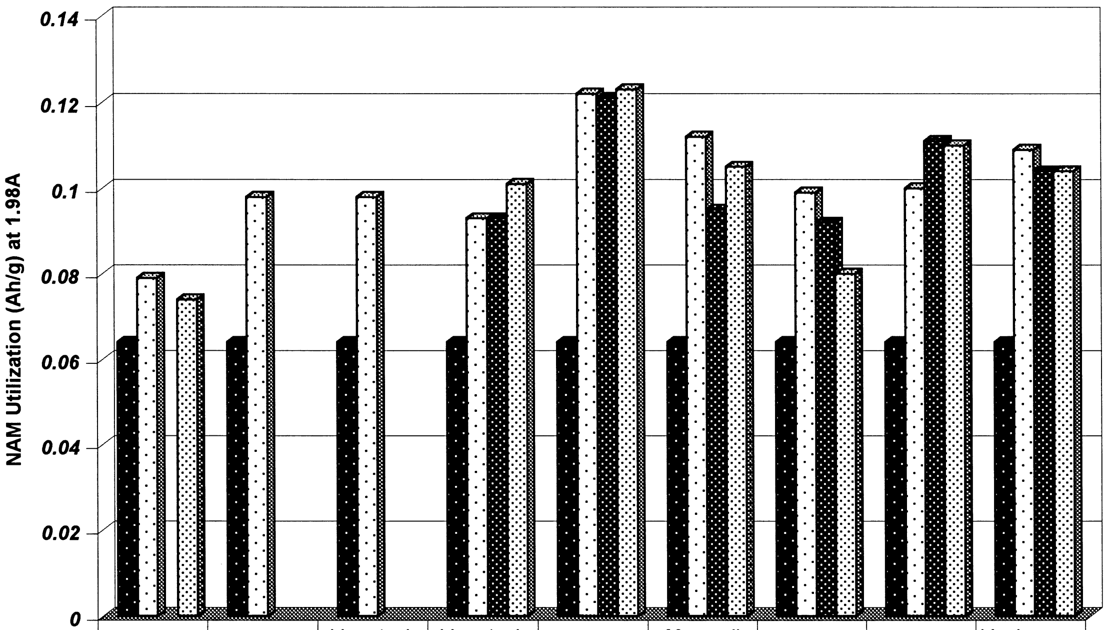
	Indulin AT	Kraftplex	Lignotech D-1271	Lignotech D-1380	Lomar B	Maracell XC-2	BNF	GKD	Vanisperse A
■ 0.00%	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
□ 0.25%	0.101	0.11	0.115	0.115	0.147	0.139	0.116	0.124	0.132
▩ 0.50%			0.119	0.119	0.144	0.117	0.111	0.134	0.131
⊡ 0.75%	0.101	0.143	0.132	0.132	0.147	0.127	0.097	0.13	0.128

Fig. 2. Negative active material utilization at 0.52 A.



	Indulin AT	Kraftplex	Lignotech D-1271	Lignotech D-1380	Lomar B	Maracell XC-2	BNF	GKD	Vanisperse A
■ 0.00%	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084	0.084
□ 0.25%	0.095	0.105	0.129	0.109	0.143	0.132	0.11	0.12	0.128
▩ 0.50%				0.112	0.132	0.112	0.106	0.13	0.124
⊡ 0.75%	0.1	0.135		0.118	0.142	0.122	0.093	0.128	0.123

Fig. 3. Negative active material utilization at 0.78 A.



	Indulin AT	Kraftplex	Lignotech D-1271	Lignotech D-1380	Lomar B	Maracell XC-2	BNF	GKD	Vanisperse A
■ 0.00%	0.064	0.064	0.064	0.064	0.064	0.064	0.064	0.064	0.064
□ 0.25%	0.079	0.098	0.098	0.093	0.122	0.112	0.099	0.1	0.109
▨ 0.50%				0.093	0.121	0.095	0.092	0.111	0.104
⊡ 0.75%	0.074			0.101	0.123	0.105	0.08	0.11	0.104

Fig. 4. Negative active material utilization at 1.98 A.

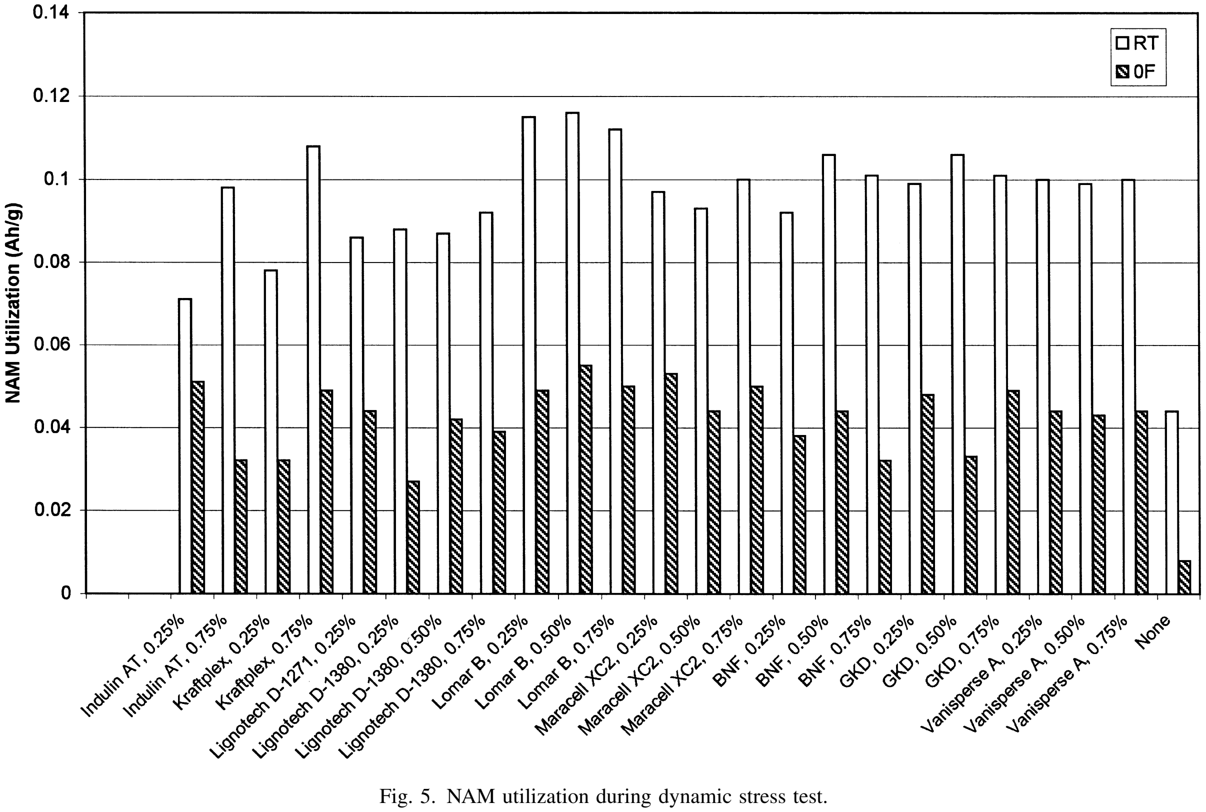


Fig. 5. NAM utilization during dynamic stress test.

performed best at low temperature. The best overall performance was obtained from the following cells.

Additive	Concentration (%)	NAM utilization (A h/g)
Ambient temperature		
Lomar B	0.50	0.116
Lomar B	0.25	0.115
Lomar B	0.75	0.112
Kraftplex	0.75	0.108
GKD	0.50	0.106
GKD	0.75	0.101
Maracell XC-2	0.75	0.100
Vanisperse A	0.25	0.100
Vanisperse A	0.75	0.100
−18°C		
Lomar B	0.50	0.055
Maracell XC-2	0.25	0.053
Indulin AT	0.25	0.051
Lomar B	0.75	0.050
Maracell XC-2	0.75	0.050
Kraftplex	0.75	0.049
Lomar B	0.25	0.049
GKD	0.25	0.049
GKD	0.25	0.048

Expanders with the greatest benefit on active material utilization reach their optimum performance at a low concentration in the plate, while those that do not initially perform as well improve as their concentration is increased. This suggests that there exists a point at which maximum surface adsorption takes place above which little, if any, benefit is obtained by further increases in concentration. This hypothesis suggests that further increases in the concentrations of several of the organic materials may yield greater active material utilization. It also illustrates the futility of comparing the performance of organic materials at a constant dosage level because of the specificity of the organic/active material interaction.

3.2. Cycle life

Tables 3 and 4 show the average cycle life of the cells at ambient temperature and at 40°C. These tables show the average cycle lives of the cells and the initial active material utilization. The active material utilization was in general greater at the higher temperature but not significantly so as shown in Fig. 6. The greatest NAM utilization at ambient temperature was obtained from Lomar B (0.75%), Vanisperse A (0.50%) and Kraftplex (0.75%). At 40°C Indulin AT (0.75%), GKD (0.75%) and Maracell XC-2 (0.75%) gave the best results.

The point at which the negative active material utilization fell by 0.020 A h/g from its initial value determined the number of cycles. The cells containing no organic additive in the expander showed very poor cycle life, 70 and 115 cycles being obtained at ambient temperature and 40°C, respectively. All the organic additives improved cycle life, but to different degrees.

Table 3
Cycle life of cells containing various organic additives, ambient temperature

Additive	Concentration (%)	Mean cycles	Initial active material utilization
None	0	70	0.058
Indulin AT	0.25	25	0.080
	0.75	200	0.090
Kraftplex	0.25	50	0.085
	0.75	250	0.110
Lignotech D-1271	0.25	40	0.084
Lignotech D-1380	0.25	80	0.092
	0.50	150	0.099
	0.75	150	0.103
BNF	0.25	25	0.087
	0.50	50	0.095
	0.75	370	0.090
GKD	0.25	40	0.097
	0.50	100	0.108
Vanisperse A	0.25	680	0.100
	0.50	220	0.110
	0.75	1000	0.106
Maracell XC-2	0.25	200	0.107
	0.50	220	0.103
	0.75	180	0.108
Lomar B	0.25	190	0.092
	0.50	175	0.103
	0.75	510	0.110

Additive	Concentration (%)	Cycle life (cycles)
The longest life obtained at ambient temperature		
Vanisperse A	0.75	1000
Vanisperse A	0.25	680
Lomar B	0.75	510
BNF	0.75	370
Best performing organic additives at 40°C		
Vanisperse A	0.75	500
GKD	0.5	480
Lignotech 1380	0.75	460
Maracell XC-2	0.75	420

An interesting aspect of these data is that some of the additives showed an increase in cycle life at the higher temperature. This is contrary to expectations since increased decomposition of the organic material is expected to take place at higher temperature. To test this hypothesis the

Table 4
Cycle life of cells containing various organic additives, 40°C

Additive	Concentration (%)	Mean cycles	Initial active material utilization (A h/g)
None	0	115	0.070
Indulin AT	0.25	360	0.077
	0.75	250	0.120
Kraftplex	0.25	208	0.090
	0.75	270	0.110
Lignotech D-1271	0.25	200	0.090
Lignotech D-1380	0.25	180	0.098
	0.50	440	0.105
	0.75	460	0.110
BNF	0.25	120	0.092
	0.50	90	0.093
	0.75	320	0.100
GKD	0.25	125	0.108
	0.50	480	0.110
	0.75	340	0.120
Vanisperse A	0.25	110	0.110
	0.50	390	0.110
	0.75	500	0.104
Maracell XC-2	0.25	320	0.100
	0.50	400	0.110
	0.75	420	0.118
Lomar B	0.50	120	0.102
	0.75	390	0.102

Table 5
Decomposition of organic additives in hot sulfuric acid[a]

Additives whose cycle lives increased at 40°C	Additives whose cycle life decreased at 40°C	Weight percent decomposed in sulfuric acid
Indulin AT		3.0
Kraftplex		17.0
Lignotech D-1380		2.5
Maracell XC-2		12.0
GKD		2.0
BNF		2.0
	Vanisperse A	22.0
	Lomar B	18.0

[a] The additive was soaked in 40% sulfuric acid at 60°C for 5 days.

organic additives were soaked in 40% sulfuric acid at 65°C for 5 days after which the residue was weighed to determine the extent of decomposition. The results are shown in Table 5.

Those additives that showed improved cycle life at the higher temperature showed the greatest sulfuric acid stability.

There may be an additional explanation for the increased cycle life at the higher temperature. At a constant end of charge voltage the negative plate polarization increases with temperature [8]. This will improve the charge acceptance and reduce the tendency towards self-discharge. Under conditions of 100% oxygen recombination charging of the negative plate is assured if the positive grid corrosion

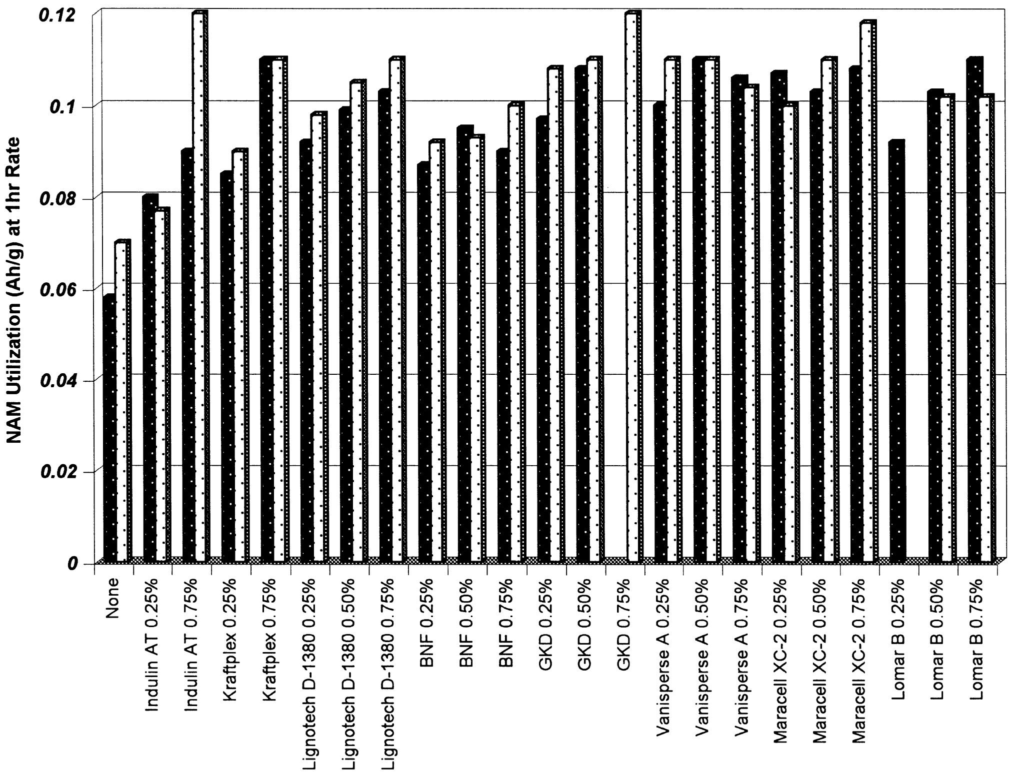


Fig. 6. NAM utilization at ambient temperature and 40C, 1 h rate.

current is greater than the Tafel intercept. When the oxygen recombination is less than 100% the current available to charge the negative is

$$C = I_c + (I_f - I_o)$$

where C denotes the charge current, I_c the corrosion current, I_f the float current and I_o the oxygen reduction current.

At the higher temperature the corrosion current will be increased thereby increasing the negative charging current. It is probable, therefore, that the negative plates were being charged more effectively at the higher temperatures. The cycle life, therefore, is probably governed by a combination of the effect of the additive on the charge reaction and its stability in sulfuric acid. The access of oxygen to reaction sites on the negative plate is not uniform but takes place preferentially at the top of the plate and through pores in the separator that are not filled with electrolyte. This will lead to microscopic hot spots on the surface of the negative plate where accelerated thermal decomposition can take place.

3.3. Effects of organic additives on the surface area

During the cycle life tests, some of the fully charged cells were removed from the circuits at 0, 100 cycles and the end of life. These cells were autopsied, the negative plates washed and dried and the surface area of the NAM determined by nitrogen BET. They were also analyzed for residual lead sulfate. The data are shown in Tables 6–8 for 0.25, 0.50 and 0.75% dosage levels.

All of the organic additives produced an increase in BET surface area of the negative active material compared to the control cells. Fig. 7 shows the initial surface area data for the eight additives and the electrodes without an organic additive. With some of the additives, surface area increased with the concentration in the NAM (Vanisperse A, Kraftplex, Indulin AT, BNF, GKD) while with others a peak surface area was reached followed by a decline as the concentration was further increased (Maracell XC-2, Lignotech D-1380). The maximum surface area with Lomar B was achieved at the lowest dosage level. There was no correlation between surface area and initial capacity as shown in Fig. 8 indicating that the effect of the organic additive on the active material is complex and that surface area is a poor indicator of the effect of the additive on capacity.

As the cells were cycled the surface area progressively decreased indicating that the organic additive was being deactivated. The reduction in surface area takes place faster at 40°C, an observation that is congruent with the suggestion made earlier that cycle life is dependent on the stability of the organic material in hot sulfuric acid. It is noteworthy that the surface area of NAM containing Lomar B changes very little with cycling. The reasons for organic expander deactivation at this time can only be speculative since work still needs to be done to determine its mechanisms. However, four possible mechanisms are suggested: chemical degradation, burying of the organic additive under the active material [9], deactivation by formation of organo-lead compounds, dissolution at areas of high pH with subsequent migration to the positive electrode and oxidation.

It is also evident from the examination of failed NAM that high levels of lead sulfate are present in many of the samples. It is believed that there are two possible

Table 6
BET surface area and lead sulfate concentrations in NAM following cycling[a]

Additive	0 cycles		100 cycles		End of life	
	Surface area ($m^2 g^{-1}$)	$PbSO_4$ (%)	Surface area ($m^2 g^{-1}$)	$PbSO_4$ (%)	Surface area ($m^2 g^{-1}$)	$PbSO_4$ (%)
Ambient temperature data						
None	0.20	10	0.21	2	0.22	4
Indulin AT	0.67	2	0.16	9	0.13	0
Kraftplex	0.58	3	0.46	4	0.44	3
Lignotech D-1380	0.55	2	0.51	0	0.28	81
BNF	0.42	4			0.39	3
GKD	0.45	4	0.43	2	0.32	5
Vanisperse A	0.3	6	0.53	2		
Maracell XC-2	0.52	4	0.49	3	0.49	3
Lomar B	0.43	3	0.4	2		
Data at 40°C						
None	0.2	10	0.21	0	0.22	4
Indulin AT	0.67	2				
Kraftplex						
Lignotech D-1380	0.73	2	0.45	3	0.46	3
BNF	0.67	4	0.33	4	0.19	35
GKD	0.61	4	0.1	6	0.32	5
Vanisperse A	0.77	6	0.44	8	0.26	51
Maracell XC-2	0.79	4	0.41	9		
Lomar B	0.41	3	0.38	15		

[a] Additive concentration is 0.25%.

Table 7
BET surface area and lead sulfate concentrations in NAM following cycling[a]

Additive	0 cycles		100 cycles		End of life	
	Surface area ($m^2 g^{-1}$)	$PbSO_4$ (%)	Surface area ($m^2 g^{-1}$)	$PbSO_4$ (%)	Surface area ($m^2 g^{-1}$)	$PbSO_4$ (%)
Ambient temperature data						
None	0.2	10	0.21	2	0.22	4
Indulin AT						
Kraftplex						
Lignotech D-1380	0.73	8	0.53	2	0.28	81
BNF	0.67	9	0.52	2		
GKD	0.61	8	0.53	2	0.29	41
Vanisperse A	0.77	9	0.73	5	0.42	17
Maracell XC-2	0.79	9	0.79	2	0.55	10
Lomar B	0.41	5	0.53	2	0.41	12
Data at 40°C						
None	0.2	10	0.21	0	0.22	4
Indulin AT						
Kraftplex						
Lignotech D-1380	0.73	8	0.45	3	0.25	69
BNF	0.67	9	0.46	5	0.19	35
GKD	0.61	8	0.18	30		
Vanisperse A	0.77	9	0.57	4	0.3	57
Maracell XC-2	0.79	9	0.54	2	0.32	41
Lomar B	0.41	5	0.43	2	0.32	10

[a] Additive concentration is 0.5%.

explanations for this; deactivation of the additive results in changes to the morphology of the NAM thereby reducing the charge efficiency. There is an evidence for this in the SEM images that are discussed later. Alternatively, the growth of lead sulfate could be a result of insufficient NAM polarization resulting from a high efficiency of oxygen recombination causing self-discharge. Fig. 9 shows the relationship between charge and discharge ampere-hours and positive and negative electrode polarizations for a cell with Vanisperse A in the expander. Similar behavior was displayed by many of the cells in the study. It can be seen that the positive plate polarization increases and the negative

Table 8
Surface area and lead sulfate concentrations in NAM following cycling[a]

Additive	0 cycles		100 cycles		End of life	
	Surface area ($m^2 g^{-1}$)	$PbSO_4$ (%)	Surface area ($m^2 g^{-1}$)	$PbSO_4$ (%)	Surface area ($m^2 g^{-1}$)	$PbSO_4$ (%)
Ambient temperature data						
None	0.2	10	0.21	2	0.22	4
Indulin AT			0.66	4	0.52	19
Kraftplex	0.59	4	0.66	2	0.56	3
Lignotech D-1380	0.68	20	0.73	2	0.8	2
BNF	0.83	40	0.65	2	0.61	3
GKD	0.64		0.51	3	0.43	10
Vanisperse A	0.85	15	0.92	1	0.32	41
Maracell XC-2	0.72	15	0.52	2	0.56	2
Lomar B	0.43	0	0.39	3	0.39	12
Data at 40°C						
None	0.2	10	0.21	4	0.22	4
Indulin AT			0.34	30	0.26	41
Kraftplex	0.59	4			0.25	32
Lignotech D-1380	0.68	20	0.65	3	0.29	74
BNF	0.83	40	0.47	2	0.24	49
GKD	0.64		0.49	3	0.39	12
Vanisperse A	0.85	15	0.81	2	0.31	68
Maracell XC-2	0.72	15	0.78	2	0.42	63
Lomar B	0.43	0	0.43	2	0.41	12

[a] Additive concentration is 0.75%.

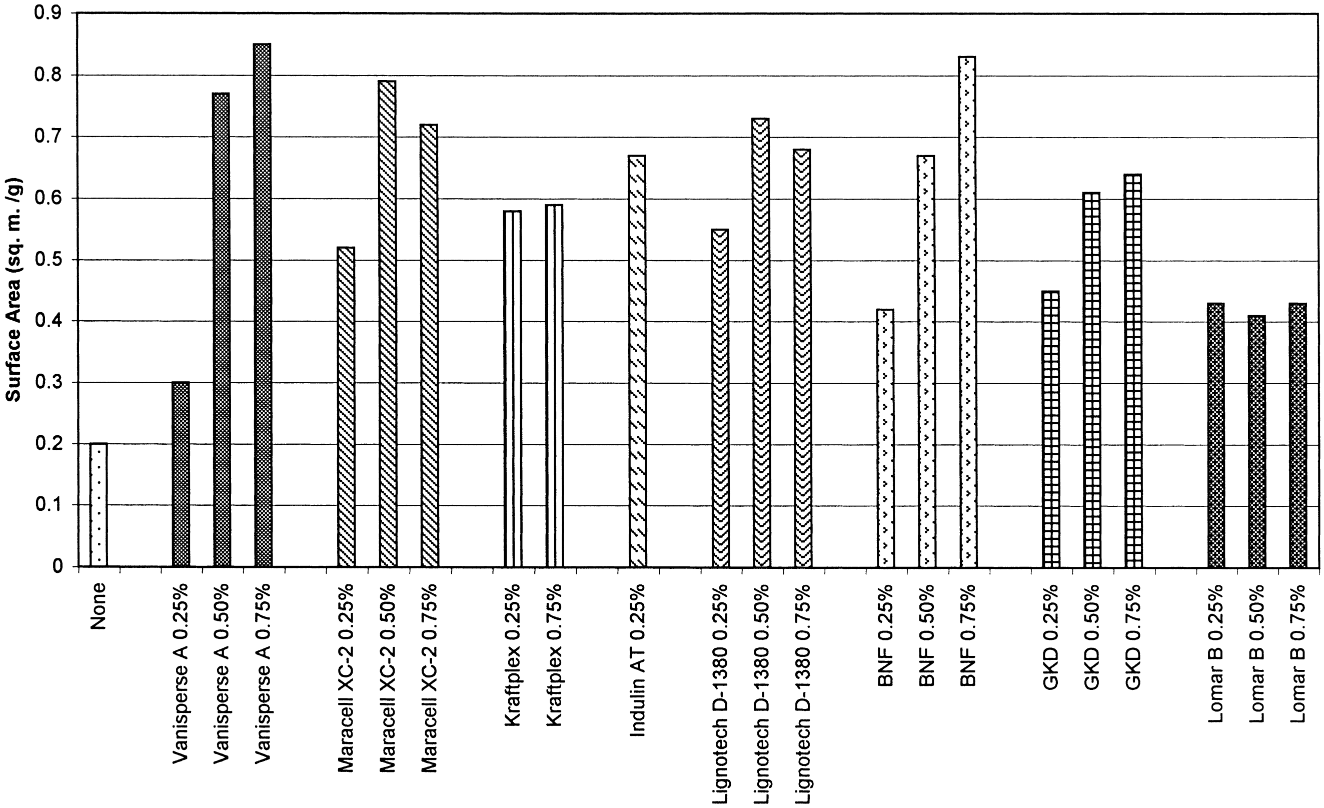


Fig. 7. BET surface area of negative active material with various organic additives.

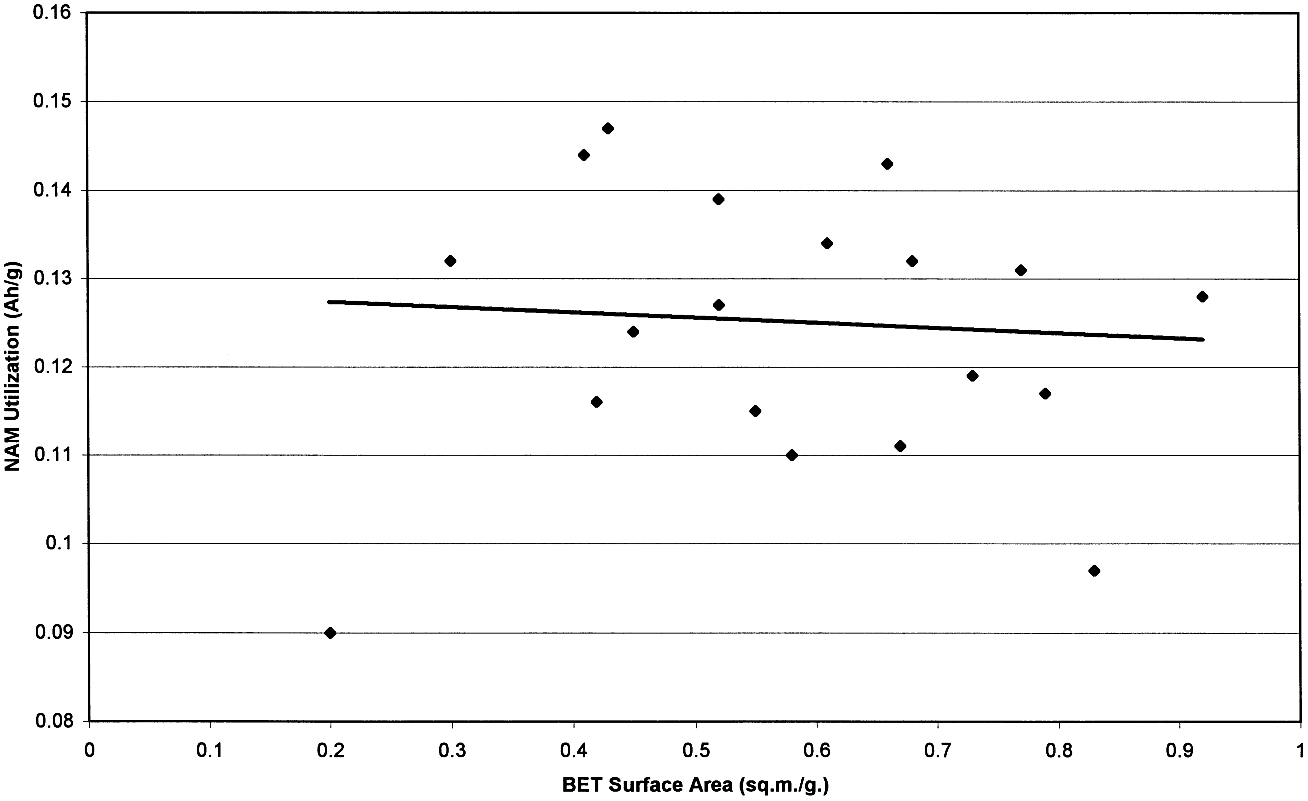


Fig. 8. Initial capacity vs. BET surface area ($C/5$).

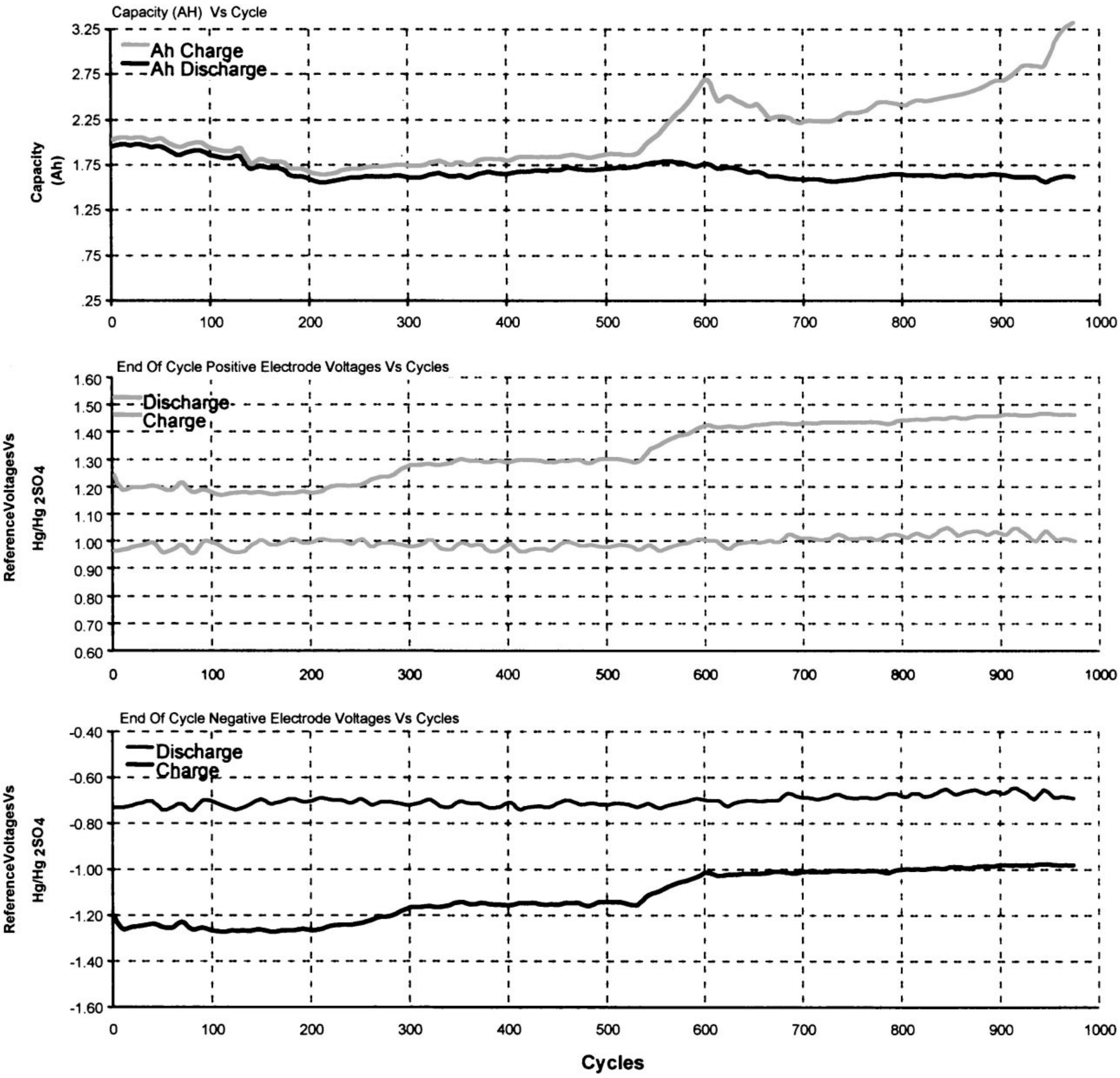


Fig. 9. Positive and negative electrode potentials during cycling Vanisperse A, 0.75%, *RT*.

plate polarization decreases as cycling progresses. Under these conditions it is probable that the negative electrode is insufficiently polarized to maintain its charge. Fig. 10 shows similar behavior from a cell containing Lomar B.

The effect of lignosulfonates on the recharge behavior of negative plates is well known and it has been observed that various organic materials affect the charge acceptance and the polarization in different ways. This may require each organic additive to have a unique charge algorithm to optimize its performance. In the present work, all cells were charged with the same algorithm and no attempt was made to optimize the recharge behavior. It is possible, therefore, that different cycle lives would have been obtained with a different charge algorithm. These problems are not seen in flooded cells since oxygen recombination does not occur and the negative plate is sufficiently polarized to ensure its full charge. The cycle lives obtained from these materials therefore may have been considerably different in flooded cells.

Scanning electron microscope (SEM) images for several of the additives are shown in Figs. 11–19. These show that without an organic additive the NAM is composed of dense overlapping shingle-like crystals with low porosity. All of the organic additives changed the morphology to a small equiaxial crystal form with increased porosity. In good agreement with the surface area studies, those additives that gave the greatest surface area also created the finest grained, most porous structure. Comparison of the plates at 50 and 100 cycles showed little change in morphology, however, there were indications of loss of surface porosity compared to the interior. At the end of life, the SEM images showed that the active material had become denser and contained a considerable amount of lead sulfate. The large size of these

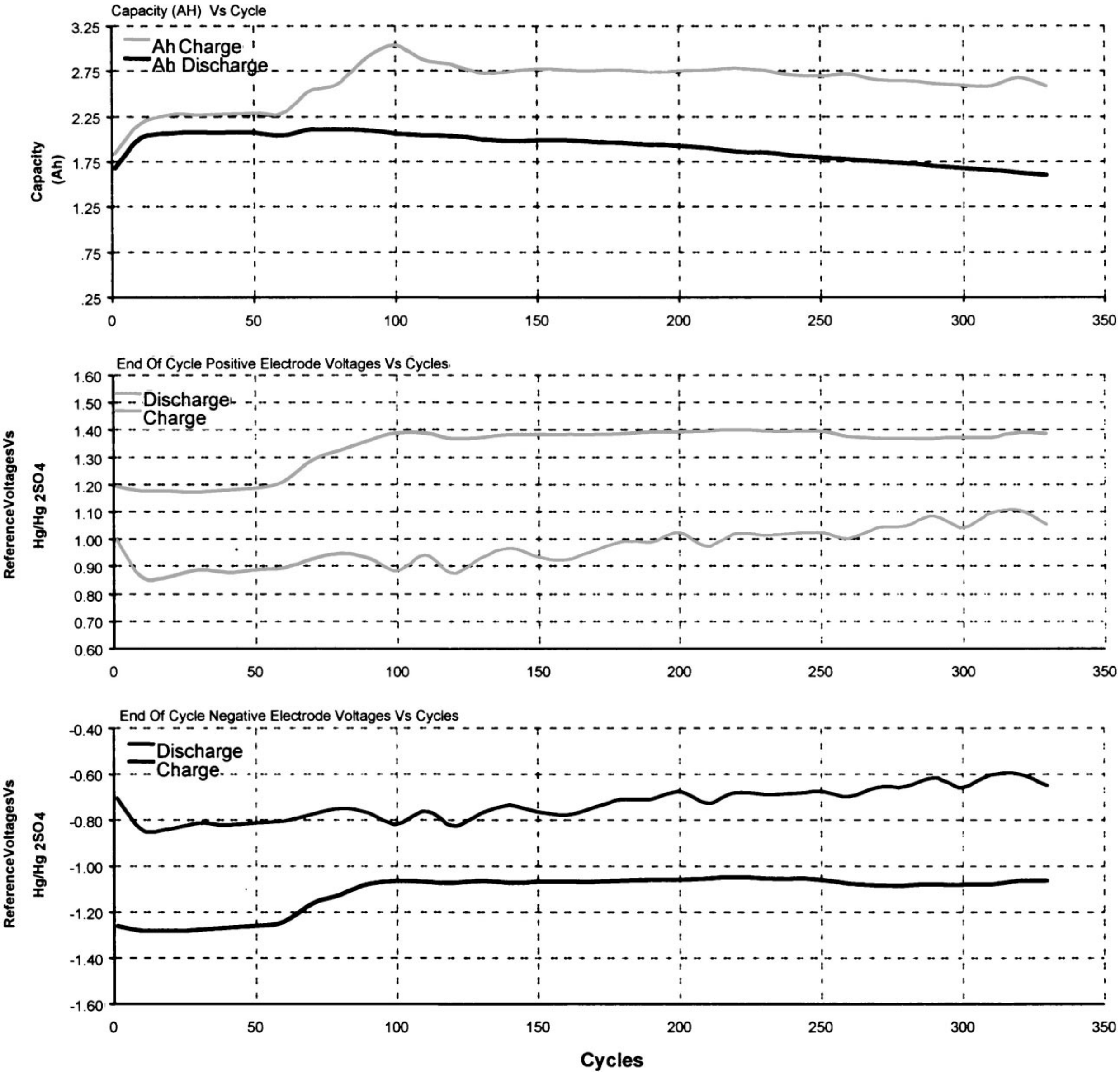


Fig. 10. Positive and negative electrode potentials during cycling Lomar B, 0.75%, *RT*.

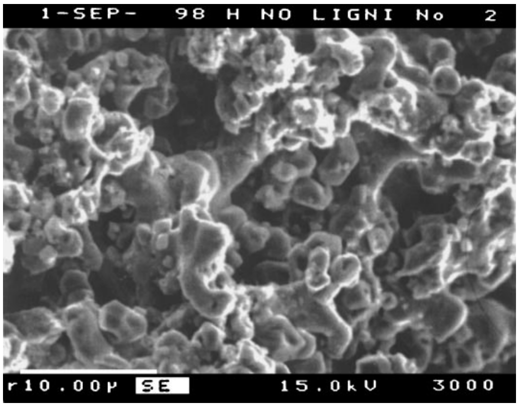


Fig. 11. SEM image. No organic additive, 0 cycles. $PbSO_4 = 10\%$, surface area = 0.2 m^2/g.

crystals is consistent with slow growth giving support to the idea that self-discharge is responsible for at least part of the capacity loss during cycling.

4. Conclusions

All of the organic additives tested gave both improved capacity and cycle life compared to NAM containing no organic additive. With respect to active material utilization, Lomar B gave the best performance, 0.147 A h g^{-1}, at a dosage level of 0.75%. We were able to increase the dosage level of the organic additive to approximately double the level normally used in flooded cells without any adverse effects. This is presumably due to the restraining effect of the

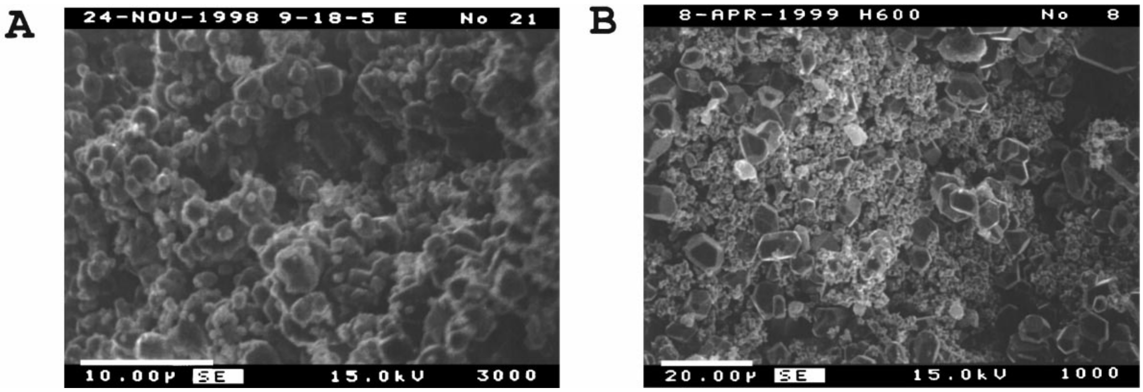


Fig. 12. SEM imges: (A) Indulin AT, 0.75%, 0 cycles, $PbSO_4 = n/a$, surface area $= n/a$; (B) 324 cycles, $PbSO_4 = 19\%$, surface area $= 0.52\ m^2/g$.

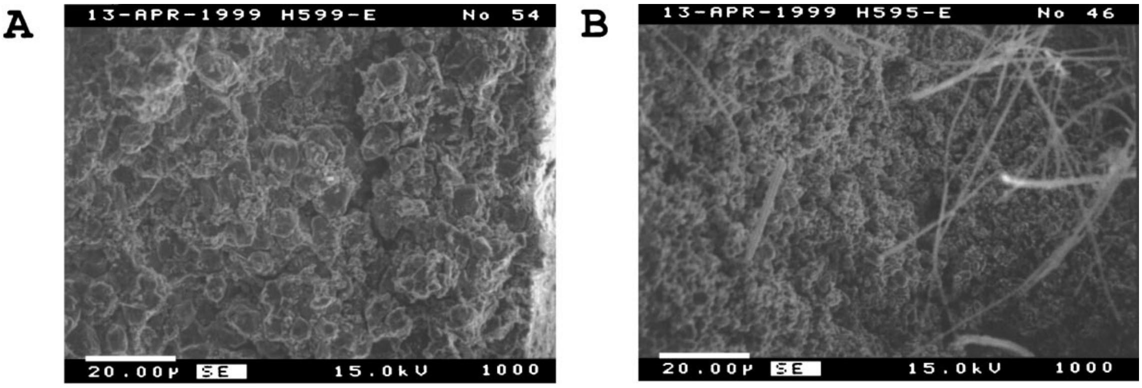


Fig. 13. SEM images: (A) Kraftplex, 0.75%, 283 cycles, $PbSO_4 = 32\%$, surface area $= 0.25\ m^2/g$; (B) 307 cycles, $PbSO_4 = 3\%$, surface area $= 0.56\ m^2/g$.

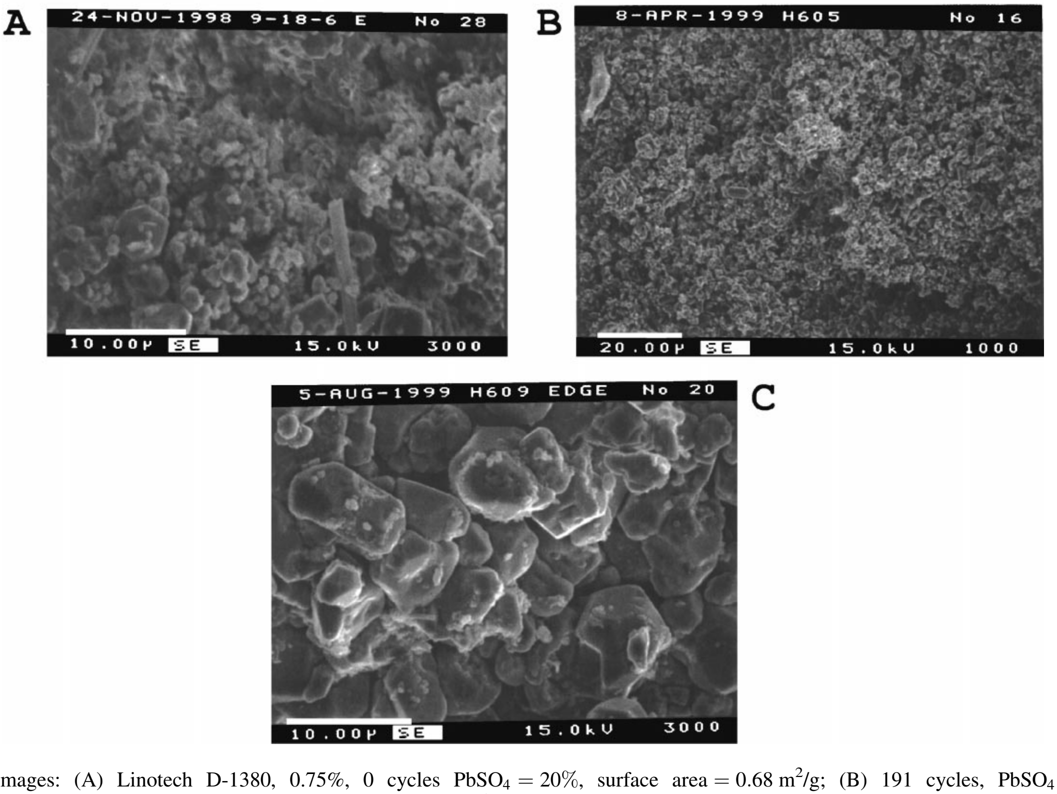


Fig. 14. SEM images: (A) Linotech D-1380, 0.75%, 0 cycles $PbSO_4 = 20\%$, surface area $= 0.68\ m^2/g$; (B) 191 cycles, $PbSO_4 = 2\%$, surface area $= 0.80\ m^2/g$; (C) 598 cycles, $PbSO_4 = 68\%$, surface area $= 0.42\ m^2/g$.

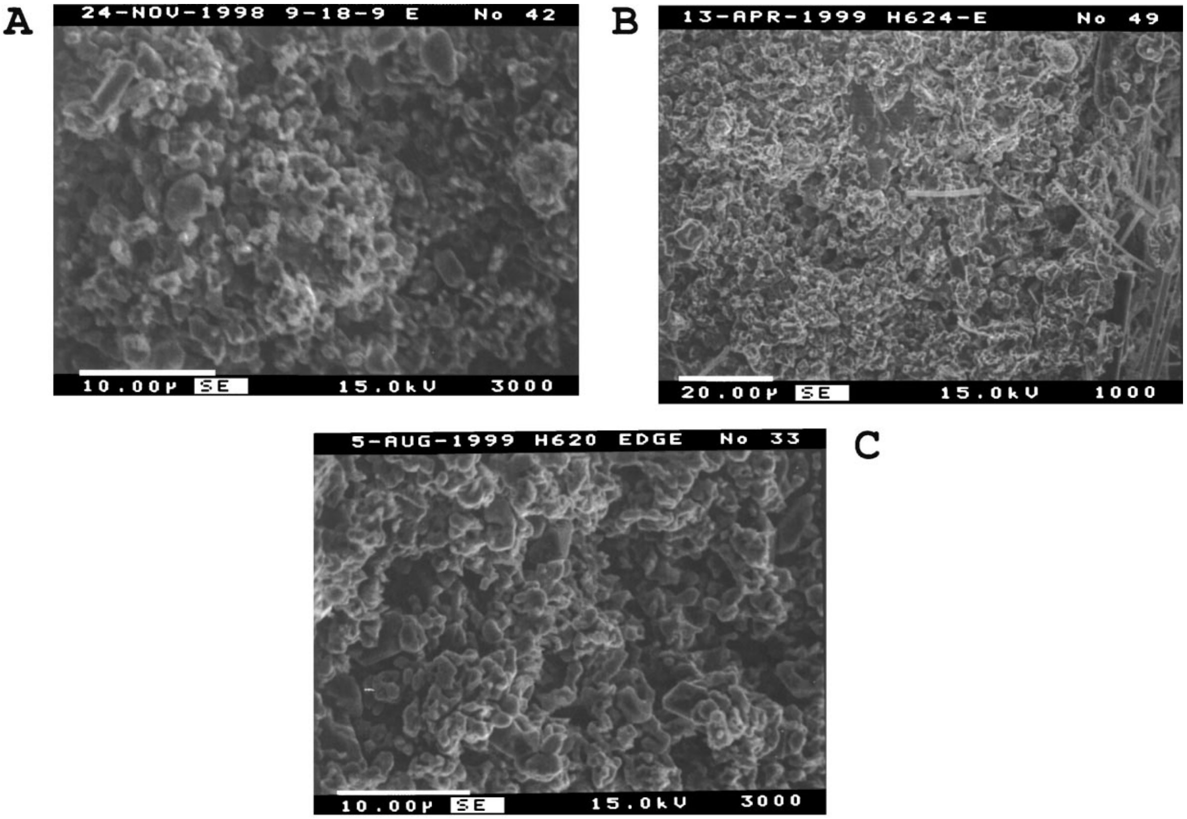


Fig. 15. SEM images: (A) Lomar B, 0.75%, 0 cycles, $PbSO_4 = 0\%$, surface area = 0.43 m^2/g; (B) 338 cycles, $PbSO_4 = 37\%$, surface area = 0.2 m^2/g; (C) 736 cycles, $PbSO_4 = 12\%$, surface area = 0.39 m^2/g.

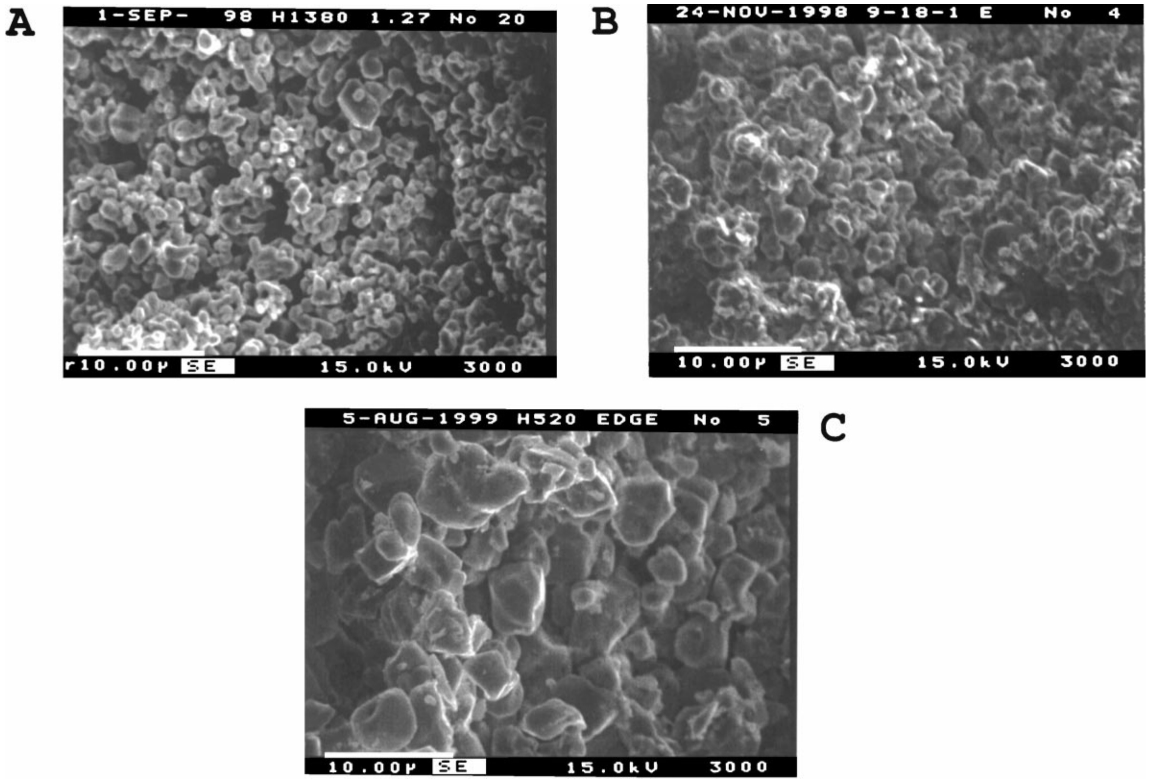


Fig. 16. SEM images: (A) Lignotech D-1380, 0.25%, 0 cycles, $PbSO_4 = 2\%$, surface area = 0.55 m^2/g; (B) 100 cycles, $PbSO_4 = 0\%$, surface area = 0.51 m^2/g; (C) 776 cycles, $PbSO_4 = 81\%$, surface area = 0.28 m^2/g.

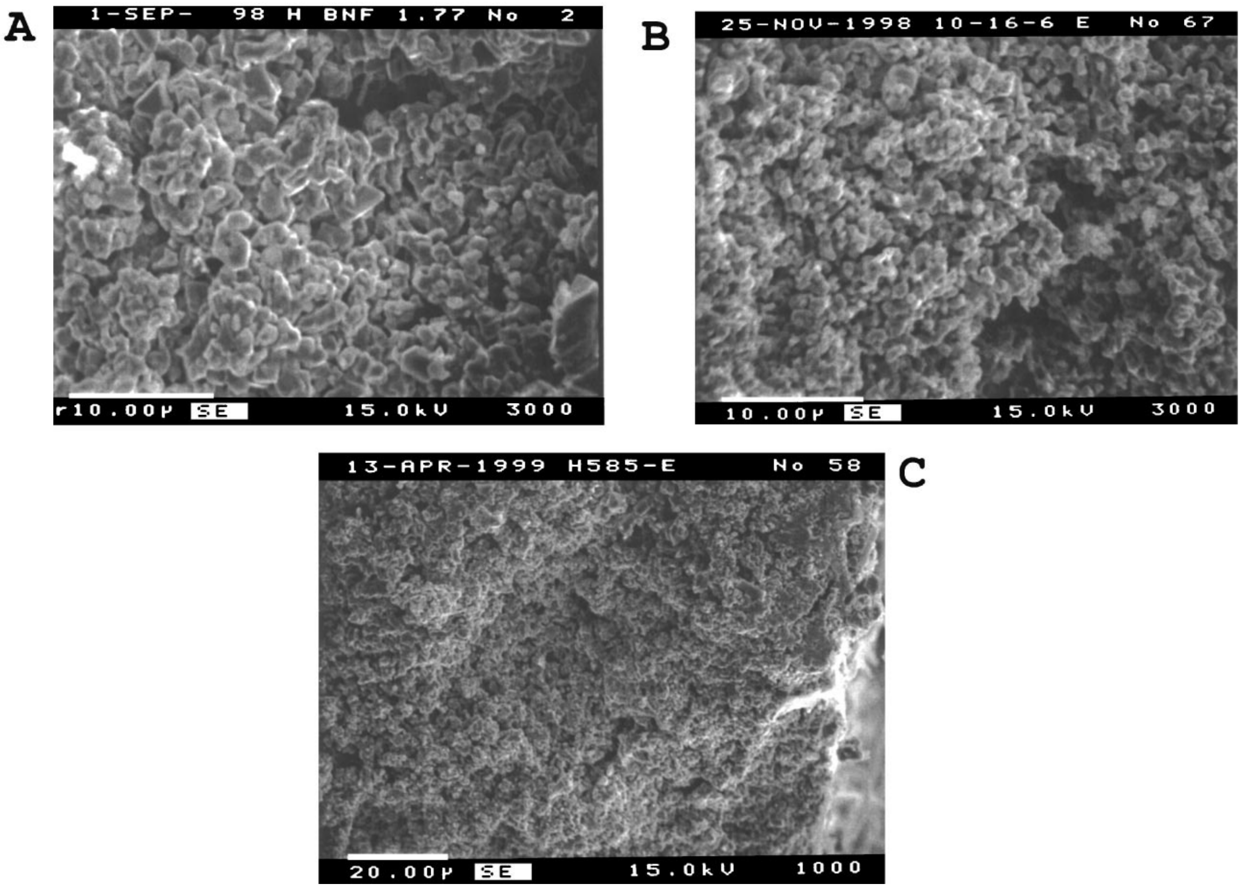


Fig. 17. SEM images: (A) BNF, 0.75%, 0 cycles, $PbSO_4 = 40\%$, surface area = 0.83 m^2/g; (B) 100 cycles, $PbSO_4 = 2\%$, surface area = 0.65 m^2/g; (C) 448 cycles, $PbSO_4 = 3\%$, surface area = 0.61 m^2/g.

VRLA design on NAM expansion. This suggests that even higher levels may be beneficial in VRLA batteries. Work is currently underway to investigate this.

The longest cycle life was obtained from cells containing Vanisperse A. This material also gave good active material utilization (0.132 $A\,h\,g^{-1}$). This is not surprising since Vanisperse A is the most widely used lignosulfonate used by the lead–acid battery industry. The cycle life appears to be limited by two phenomena: progressive deactivation of the additive by a mechanism as yet unknown, and insufficient NAM polarization at high oxygen recombination efficiencies permitting self-discharge to take place.

The synthetic materials were effective expanders but their durability was poor compared to Vanisperse A. Since the

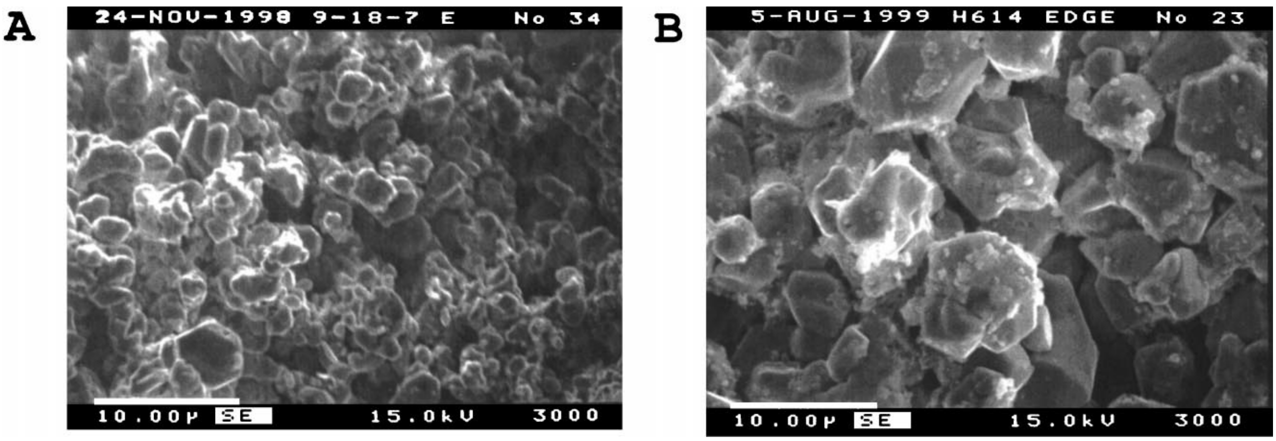


Fig. 18. SEM images: (A) Vanisperse A, 0.75%, 0 cycles, $PbSO_4 = 15\%$, surface area = 0.85 m^2/g; (B) 593 cycles, $PbSO_4 = 68\%$, surface area = 0.31 m^2/g.

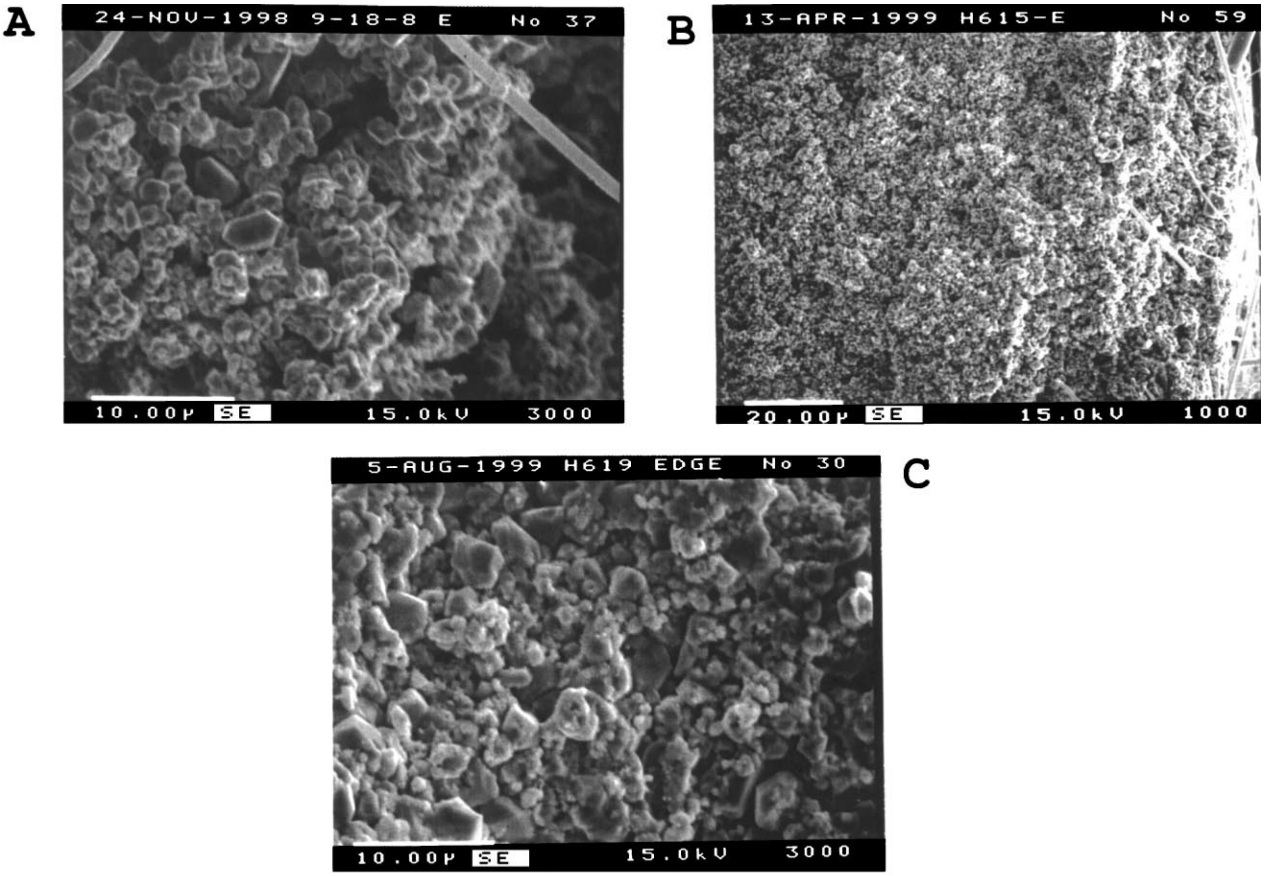


Fig. 19. SEM images: (A) Maracell XC-2, 0.75%, 0 cycles, $PbSO_4 = 15\%$, surface area = 0.75 m^2/g; (B) 253 cycles, $PbSO_4 = 2\%$, surface area = 0.56 m^2/g; (C) 606 cycles, $PbSO_4 = 66\%$, surface area = 0.42 m^2/g.

chemistry of the synthetic materials is more easily controlled than the natural products, it may be possible to improve their durability by modifications to the molecular structure.

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