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Alternative separation evaluations in model rechargeable silver–zinc cells

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Abstract

Several varieties of standard and reinforced, cellulose-based, sausage casing films derived from wood pulp have been evaluated in model (nominal 28 A h) rechargeable silver–zinc cells. The cell performance data for both cycle life and wet stand life have been compared with cells equipped with conventional 1 mil (0.025 mm) cellophane. Although shorting was the most common failure mode in the cells with sausage casing separation, remarkably good cycle and wet life were obtained when the separation wrap also included PVA film. This paper reports the cycle and wet life comparison data for these substitute separators, with respect to conventional cellophane separation, as well as separation physical property data and silver migration rates in the cells as a function of cell life. © 1999 Elsevier Science S.A. All rights reserved.

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1. Objective

To determine whether cellulosic tubular casing could be used in place of cellulosic cellophane film as a separation in the rechargeable alkaline silver–zinc electrochemistry, in order to provide improved cell cyclability, wet life, resistance to shorting failure, and improved discharge capacity.

2. Introduction

Anecdotal information has suggested that when fibre-reinforced tubular casing was used as the separation in batteries of this chemistry in the 1970s, cell performance was superior to that of cells which used cellophane film as the separator. However, the lower cost of cellophane coupled with the switch from a materials specification for Navy applications, to a performance specification, allowed the battery industry to change over to,it was claimed, the eventual detriment of cell performance. In addition, the availability of several modifications in the types of tubular casing and the addition of a plastic film with exceptional barrier properties to silver migration, appeared to give promise of improved cell performance in comparison to the older fibre-reinforced casing.

Therefore, a study was constructed to evaluate these materials in comparison to the standard cellophane film currently used in batteries.

3. First experiment

Initially, five sets of model cells (nominal 23 A h, six cathodes and seven anodes) with 13 cells in each set, were constructed by Eagle Picher Industries for evaluation of separations. These were as follows:

Set 1: 1 × 2-mil Webril, 6 × 1-mil Flexel cellophane//1 × 4.2-mil Viskon
Set 2: 1 × 2-mil Webril, 1 × 1-mil Flexel cellophane, 3 × 2.3-mil Viskase casing//1 × 4.2-mil Viskon
Set 3: 1 × 2-mil Webril, 2 × 5.9-mil cellulose fibre-reinforced Viskase casing//1 × 4.2-mil Viskon

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Table 1
Dry and wet thicknesses and tensile strengths

Film	Thickness (mil)		Tensile strength (lb)			
	Dry	24 h soak	Dry		24 h soak	
			MD	TD	MD	TD
Flexel 1 mil	1.19 ± 0.04	3.01 ± 0.04	5.35 ± 0.21	3.44 ± 0.19	0.80 ± 0.06 (0.27)	0.42 ± 0.05 (0.14)
Visk 1 mil	1.02 ± 0.02	2.95 ± 0.14	4.93 ± 0.37	2.50 ± 0.16	1.53 ± 0.16 (0.51)	0.40 ± 0.05 (0.13)
Visk 1.75 mil	2.29 ± 0.00	7.24 ± 0.02	5.14 ± 0.39 (2.83)	3.19 ± 0.11 (1.39)	2.37 ± 0.19 (0.33)	1.75 ± 0.06 (0.24)
Visk 3 mil FR	5.91 ± 0.71	7.81 ± 0.09	13.26 ± 0.41 (2.24)	8.56 ± 0.41 (1.45)	4.62 ± 0.20 (0.59)	3.26 ± 0.12 (0.42)
Visk 3 mil PAF × 1	5.00 ± 0.18	5.95 ± 0.39	7.24 ± 0.32 (1.45)	4.37 ± 0.26 (0.87)	5.38 ± 0.17 (0.90)	3.23 ± 0.12 (0.54)
Visk 3 mil PAF × 2	4.59 ± 0.19	7.00 ± 0.38	7.27 ± 0.16 (1.58)	4.32 ± 0.18 (0.94)	4.37 ± 0.14 (0.62)	1.71 ± 0.19 (0.24)

MD is machine direction.
TD is transverse.
FR is fibre-reinforced.
PAF is polyamide fibre-reinforced.
×1 is single-coated.
×2 is double-coated.
The 24-h soak was in 45% KOH. The values in parentheses are normalized to 1 mil thickness. All values are from six measurements.

Set 4: 1 × 2-mil Webril, 1 × 1-mil Flexel cellophane, 2 × 5-mil PAF-reinforced Viskase casing//1 × 4.2-mil Viskon
Set 5: 1 × 2-mil Webril, 1 × 1-mil PVA film, 2 × 2.3-mil Viskase casing//1 × 4.2-mil Viskon

Webril® is a nonwoven polypropylene film and Viskon® is a rayon film. PAF is polyamide fibre and PVA is polyvinyl alcohol. The notation is from the cathode to the anode. The cells were built using the same sizes of cell hardware to provide a constant internal stack pressure. The total wet thickness of the cell pack was 800 mil (20 mm).

However, it was found subsequently that Set 2 had a wet thickness of 847 mil (21.2 mm), Set 3 was failing early in cycle life because the separation, too rigid at the plate corners, was splitting and allowing zinc penetration, while Set 4 was too porous, allowing for easy zinc penetration. Therefore, Sets 2, 3, and 4 were rebuilt, as:
Set 2A: 1 × 2-mil Webril, 1 × 1-mil Viskase casing, 2 × 2.3-mil Viskase casing//1 × 4.2-mil Viskon
Set 3A: 1 × 2-mil Webril, 1 × 1-mil Viskase casing, 2 × 5.9-mil cellulose fibre-reinforced Viskase casing//1 × 4.2-mil Viskon
Set 4A: 1 × 2-mil Webril, 1 × 1-mil Viskase casing, 2 × 4.6-mil PAF-reinforced Viskase casing//1 × 4.2-mil Viskon

Set 4A had Viskase casing that was coated on both sides (inside and out) with polyamide fibre emulsion, rather than just on the outside as in Set 4. The problems with rigidity at the cell pack corners due to the separation thickness were solved by making the cell cases slightly wider. Set 2, in spite of the excessive wet thickness for these cell cases relative to Set 1, continued to perform fairly well, so its testing was continued to failure for all cells. Sets 3 and 4 were withdrawn from test because of the preponderance of short failures in early cycle life, and no cells were put on wet life test.

All cells, which were delivered dry and uncharged, were filled with 45% KOH and initially formed by five cycles of charge: 1 A to 1.98 V + 0.5 A to 2.03 V, discharge at 2 A.

After this, one of the 13 cells in each group was withdrawn for baseline property analysis; of the remainder, seven cells were put on a cycle life regime, the other five for wet life evaluation. The test regime was based roughly on the Lot Acceptance test for Mk89 cells [1].

Initially, in the cycle life study, each cell cycled through a C/15 charge and a C/5 discharge (100% DOD), but after a few cycles it was determined that the cells were not accepting charge very well, so the charge regime was changed to the formation charge regime while discharges were maintained at C/5. At this point, all cells recovered

Table 2
Average discharge capacities in ampere hours during cycle life

Cell/cycle	20	25	30	35	40	45	50	55	60	65	70	75
Set 1	19.2 (7)	22.3 (7)	22.0 (7)	23.9 (7)	22.6 (7)	21.6 (7)	20.7 (7)	20.2 (6)	19.2 (6)	19.2 (4)	17.9 (4)	16.7 (4)
Set 2	22.8 (7)	20.7 (6)	19.8 (6)	18.7 (6)	17.6 (3)	17.0 (3)	14.1 (3)	14.8 (2)	13.6 (2)	None		
Set 2A	20.6 (7)	18.9 (7)	17.0 (7)	15.9 (6)	15.1 (6)	15.2 (4)	14.0 (4)	13.0 (3)	12.8 (3)	10.6 (1)	10.2 (1)	None
Set 3A	22.2 (7)	20.5 (7)	18.2 (7)	16.8 (6)	14.7 (6)	15.2 (4)	14.7 (1)	None				
Set 4A	22.2 (7)	19.7 (6)	17.1 (5)	12.7 (1)	None							
Set 5	21.2 (7)	20.2 (7)	18.7 (7)	16.6 (7)	16.1 (7)	14.8 (7)	13.7 (7)	12.9 (6)	12.5 (6)	11.3 (6)	10.4 (6)	10.2 (6)

The numbers in parentheses are the cells still on test at that point. One cell was removed from each surviving at cycle 50 for analysis.

Table 3
Average discharge capacities in ampere hours during wet life (1 month stand between each charge/discharge cycle)

Cell	Time into test (months)					
	3	6	9	12	15	18
Set 1	22.5 (5)	26.9 (5)	27.0 (4)	26.0 (4)	24.8 (3)	23.2 (3)
Set 2	15.8 (5)	24.3 (3)	22.4 (2)	17.6 (2)	24.3 (1)	21.8 (1)
Set 2A	19.4 (5)	23.1 (5)	None			
Set 3A	17.5 (5)	21.5 (5)	None			
Set 4A	19.1 (5)	23.2 (1)	None			
Set 5	21.3 (5)	21.9 (5)	20.0 (4)	20.1 (4)	18.5 (3)	16.4 (3)

The numbers in parentheses are the cells still on test. One cell was removed from each set at 6 and 12 months for analysis.

to ~90% theoretical discharge capacity. The wet life regime was identical in the charge and discharge procedures, but with a 30-day stand at full charge between each 100% DOD discharge and recharge. The cell failure criteria were either a short, whereby the cell could not be recharged, or a discharge capacity less than 50% of the initial discharge capacity which was generally about 38 A h.

3.1. Results and discussion for the first experiment

The initial physical properties for the various separations are presented in Table 1.

It is evident from the data in Table 1 that on a normalized basis, all the casings are stronger after a 24-h soak in 45% KOH, some considerably, than ordinary 1 mil cellophane film. It is also curious that double-coating the casing with polyamide emulsion decreases the apparent wet strength of this casing material.

In Table 2 are presented the data for average discharge capacities during cycle life, at five cycle intervals beginning at cycle 20.

It is evident from these data that in terms of discharge capacity, Set 1 (1 mil cellophane film) performed the best, while Set 5 had the fewest cell failures due to shorting (actually none). Sets 2 and 3A lost significant numbers of cells to shorting failures after cycle 40 while Set 4A lost cells after cycle 30. These short failures were traced during subsequent dissection to splitting of the separation at the bottom of the U-fold around the cathodes, allowing zinc to penetrate and provide a shorting path.

In Table 3 are presented similar data from the wet life study. As with the life-cycling test, the cells with 1 mil cellophane performed in a superior manner to the casing cells and again, serious shorting losses were observed in Sets 3A and 4A. These shorts were again found to be the result of separation splitting at the bottom of the U-fold on the cathode.

Finally, in Table 4 are presented the data on rates of silver migration by layer of separation as found during the cycle life study for the various cell sets.

Using just the data taken at 50 cycles (or the closest to that if no cells in a given set reached this cycle number), it appears that the separation combination in Set 5 was the best at stopping silver migration, followed by the polyamide reinforced casing of Set 4A. The 1 mil cellophane (Set 1) and the 1.75 mil casing (Set 2) were the worst.

3.2. Conclusions from the first experiment

From this data, it would appear that no cellulosic casing material currently available is, on its own, superior in

Table 4
Silver content by layer in mg cm^{-2} and the total in milligram for each separation pack

Cell	Cycles to failure	Webril	Layer 1	Layer 2	Layer 3	Layer 4–6	Total	Pack
Set 1	6, baseline	0.143	0.766	0.138	0.016	0	1.062	171
Set 1	50, dissection	0.186	3.652	1.369	0.282	0.008	5.489	925
Set 1	88, capacity	0.408	5.377	2.564	1.100	0.360	9.810	1680
Set 2	6, baseline	0.123	0.391	0.114	0.002	0.002	0.630	120
Set 2	50, dissection	0.241	2.408	2.955	0.087	0.006	5.697	1005
Set 2	64, capacity	0.715	2.091	2.320	0.143	0.002	5.270	877
Set 2A	6, baseline	0.172	0.544	0.067	0.004	NA	0.787	129
Set 2A	50, dissection	0.258	2.073	0.983	0.003	NA	3.317	542
Set 2A	70, capacity	0.146	1.671	1.089	0.032	NA	2.929	481
Set 3A	6, baseline	0.322	1.094	0.048	0	NA	1.463	231
Set 3A	48, capacity	0.311	2.336	0.266	0.002	NA	2.915	459
Set 4A	6, baseline	0.143	0.766	0.138	0.016	NA	1.063	174
Set 4A	36, short	0.093	1.392	0.196	0.007	NA	1.688	275
Set 5	6, baseline	0.111	0.783	0.006	0	NA	0.908	162
Set 5	50, dissection	0.224	0.747	0.110	0.122	NA	1.204	191
Set 5	191 cycles	0.248	3.324	0.236	0.045	NA	3.850	665

Total refers to the total mg cm^{-2} found in all layers.
Pack to the milligram of silver in the separation pack.
The term capacity refers to a capacity failure, where the discharge capacity fell below the 50% requirement.

resisting the development of shorts or in discharge capacity performance to 1 mil cellophane.

The 1 mil casing material cannot at present be produced in a diameter which would allow plate wrapping in a manner similar to 1 mil cellophane film, and not even in a diameter which would be useful for the plate sizes currently in use for US Navy applications. However, the Set 5 data are intriguing because these cells actually ran for over 200 cycles without a shorting failure, even though their average discharge capacity fell below the 50% failure criterion by cycle 55. In the more important criterion for Navy applications, that is wet stand life, no cells from Set 5 shorted or fell below the capacity requirement after 18 months, although their average discharge capacity was only 70% of that of the control—Set 1.

These latter observations implied that, if the discharge capacity decline in Set 5 could be remedied (it may be just an internal impedance problem), then the 1.75 mil casing separation might indeed be superior to 1 mil cellophane film. To evaluate this possibility, a second experiment was devised.

4. Second experiment

In the second phase of this study, two sizes of cells were built. One size is in the Mk89 LR360 hardware, nominally a 360 A h cell, while the second was, as in experiment 1, at the model cell level of 23 A h nominal. The separations in the Mk89 cells were designed as:

Set X: 1 × 3-mil Pellon, 6 × 1-mil Flexel cellophane//1 × 3-mil Pellon
Set Y: 1 × 3-mil Pellon, 1 × 1-mil PVA film, 2 × 2.3-mil Viskase casing//1 × 3-mil Pellon

while the model cells were designed with:

Set A: 1 × 3-mil Pellon, 3 × PVA-coated 2.3-mil Viskase casing//1 × 3-mil Pellon
Set B: 1 × 2-mil Webril, 1 × 1-mil Viskase casing, 1 × 2.3-mil Viskase casing//1 × 4.2-mil Viskon
Set C: 1 × 2-mil Webril, 1 × 1-mil Viskase casing, 1 × 1-mil PVA film, 1 × 2.3-mil Viskase casing//1 × 4.2-mil Viskon
Set D: 1 × 2-mil Webril, 6 × 1-mil Flexel cellophane//1 × 4.2-mil Viskon

Note that both the Mk89 cells and the additional model cells contain a standard Flexel cellophane set, and again, the notation is from the cathode (left) to the anode (right). The Mk89 sets are designed to evaluate, in Fleet-size hardware, the relative performance results from Sets 1 and 5, because Set 5 had shown long cycle and wet life, but with inferior capacity performance. The model cell sets (A–D) are designed to evaluate, first, the performance of one less layer of casing (to reduce internal impedance) with and without PVA film (Sets B and C vs. D), and second, the performance of PVA-coated casing (Set A vs. D). These modifications were attempts to take advantage of the extended cycle and wet life found in Set 5 of the first experiment while removing the impedance problems which yielded poor discharge capacity results. As in experiment 1, seven cells were put on life cycling, six on wet life tests.

Table 5
Average discharge capacities in ampere hours against cycle life for the nominal 23 A h cells containing Sets A and D

	Cycle number										
	10	15	20	25	30	35	40	45	50	55	60
Set A	27.3	25.5	23.2	22.9	20.7	19.6	19.0	17.4	19.3	16.8	16.1
Set D	27.3	24.9	23.6	22.2	20.6	15.2	18.3	17.6	17.1	16.7	16.3

No cells have been lost to shorts. Of the six cells originally in each set, one was removed after five cycles and one each at 25 and 50 cycles, all for baseline analysis.

4.1. Results and discussion for the second experiment

The data available at this time (late 1998) are somewhat preliminary in nature, because of several problems encountered in the cell constructions. In Table 5 are presented the discharge capacity data available so far for Sets A and D.

The cycling is not yet complete and so far, there is essentially no difference in capacity performance between these two cell sets. The capacity performance for both sets is slightly lower than that for Set 1 in Table 1 (which would be comparable to Set D in this experiment), and that is the reason for including a control set in every experiment.

In Table 6 are the data obtained so far for Sets X and Y.

These interim results suggest that the casing separation cells (Set Y) are performing at least as well as the control cells, although they started at slightly less capacity.

4.2. Conclusions from the second experiment

It is much too early in this second experiment to say whether any of the cell sets containing casing separation will be as good as or better than the control sets, however, we have succeeded in eliminating some of the problems

Table 6
Average discharge capacities in ampere hours against cycle life for the nominal 360 A h Mk89 cells containing Sets X and Y

	Cycle number				
	1	5	15	25	35
Set X	546	505	470	407	340
Set Y	526	470	438	408	353

No cells have been lost to shorts. Of the six original cells in each set, single cells were removed after 5 and 25 cycles for dissection and baseline analysis.

encountered in the first experiment, and at the time of the 1999 Symposium, more definite conclusions will be available, and will be presented as supplemental data and text.

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References

[1] SDV Mk89 Power Battery Specification, Rev. 6096-PS-007, 20 September 1995.