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Improved silver/zinc secondary cells for underwater applications

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Abstract

Performance improvements in silver/zinc technology have been achieved with new developments in additives and separator coatings. These improvements, aimed at increasing the cycle life and energy density of silver/zinc cells, were realized through advances in the state-of-the-art of the zinc electrode and of the separators, which are the major limitations to this electrochemical couple. To achieve these objectives, two basic approaches were employed: (i) the introduction of a new class of materials known as electro permeable membranes (EPM); (ii) the use of bismuth oxide (Bi_2O_3) as an additive to the negative electrode. The EPMs are applied to the separator to provide a barrier to silver penetration without impairing performance. This allows the use of very thin separators and/or a reduction in the number of layers required. This provides an increase in the available volume for active materials with a consequent improvement in volumetric energy density. The effect of the additives to the negative electrode is to inhibit shape change and increase the conductivity of the zinc. The general approach utilized in this program was to incorporate the performance enhancing improvements into a baseline cell design. The baseline has been configured to fit two underwater vehicles currently in use by the US Navy. The development approaches and specific cell configurations are presented along with current performance data. An analysis and critique of the data coupled with conclusions and recommendations for future development activities are also presented.

Keywords: Zinc/silver oxide secondary batteries; Applications/underwater vehicles

1. History

The silver/zinc system has the highest gravimetric energy density (watt-hour per kilogram Wh g^{-1}) and the highest volumetric energy density (watt-hour per liter Wh dm^3) of all rechargeable batteries in wide use today. The limitations of the system are its relatively short cycle life and short calendar life. These limitations are manifested principally in separator penetration and zinc electrode shape change. The need to reduce silver penetration and inhibit shape change in the silver/zinc system has been the ongoing objective of many research and development efforts.

2. Discussion of the problem

The two features addressed in these development efforts were improvements to the zinc electrode and separator system(s).

2.1. *The zinc electrode*

The zinc electrode is responsible for the cycle life limitation in silver/zinc cells. The primary reason is shape change. A secondary mode of cycle life limitation occurs if the cells are overcharged which causes the formation of zinc dendrites. These conditions are briefly described in the following paragraph.

2.2. *Shape change*

It is well known that the zinc electrode loses active zinc material during cycling of the cell. Shape change is a phenomenon whereby zinc oxide, formed during the discharge, is partially dissolved in the electrolyte and redeposited during recharge in a location different from where it originated. The zinc is lost preferentially at the top and sides of the electrode. This results in a gradual depletion of the active material. Attempts at reducing shape change through the use of excess zinc over the stoichiometric equilibrium, the use of oversized negatives and the inclusion of special additives and binders have been only partially successful.

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2.3. *Zinc dendrites*

These are a sharp, needle-like crystalline form of the metal that are produced during overcharge. Dendrites have a tendency to puncture the separators, causing cell failures by internal short circuits. There are several ways to minimize the formation of dendrites:

(i) careful charge control, coupled with individual cell voltage monitoring;

(ii) the use of excess zinc so that the negative is not overcharged;

(iii) non-conventional charging (i.e. pulse charging).

2.4. *The separators*

Regenerated cellulose, as plain or treated cellophane or fiber-reinforced sausage casing, has been used as the main separator for silver/zinc cells since Professor Andre developed the system. This separator, however, has a singular weakness — limited resistance to oxygen and the aqueous electrolyte. These factors limit the life of silver/zinc cells to 2–3 years. Other separators that have been tried include grafted and cross-linked polyethylene films and microporous polypropylene. The latter offers some distinct advantages over the cellulosics since they have lower electrolytic resistance and a high resistance to oxidation. In addition, they are very thin, allowing improvement in energy density by creating more volume for active materials. However, microporous polypropylene does not prevent migration of heavy ions and molecules, such as silver, zinc or their oxides. For this reason they must be coated for effective use in silver/zinc cells. The coating of microporous polypropylene with electro permeable membranes (EPMs) [1], in combination with improved negative electrodes developed at Yardney, has resulted in significantly improved wet life and cycle life.

The subject and content of this paper is a summary of several development initiatives which were extensive in nature and format. Therefore, the discussion shall be limited to the most important tasks leading to the technical objectives of improving the cycle life and energy density of the silver/zinc system.

Advances in the state-of-the-art of the negative electrodes and separators have been achieved through two means:

(i) reliance on a new class of materials called EPMs;

(ii) the use of bismuth oxide Bi_2O_3 as an additive to the negative electrodes, in conjunction with other additives.

EPMs are a mixture of two polymers. One of the polymers is a long chain hydrogel while the other is a common plastic such as polypropylene, polyvinyl chloride (PVC) or polyvinylidene fluoride (PVDF). Three methods of application were tested in this study. First as an additive to the negative electrode, secondly as a coating on the negative electrode and finally as a coating on the separator.

The use of bismuth oxide as an additive to the zinc negative was previously reported by scientists at Brookhaven National Laboratory [2].

Initial studies were conducted with 12 Ah cells which were discharged at the $C/3$ rate and charged at the $C/24$ rate and showed that cells using 4% EPM added to the negative electrodes and three turns of EPM-coated Celgard as the main separator resulted in a 69% increase in cycle life.

The second phase of this work emphasized continuing efforts to enhance cycle life through the use of EPMs and bismuth oxide in conjunction with other additives [3].

Procedures were developed for the manufacture of composite negative electrodes containing EPMs or bismuth oxide and for the coating of separators with EPMs [4].

The coating of Celgard with EPMs was initially performed by hand. However, problems were encountered in cell performance which was ultimately traced to lack of uniformity in thickness or air entrapment in the coating. Because of these problems, a coating subcontractor was employed to coat the separator using automatic applicating rollers. Coating was performed using a continuous process with thicknesses controlled to less than 0.025 mm (one mil).

3. Test matrix

During the second phase of the program, two groups of cells were manufactured and tested. A matrix was designed to have a test iteration to evaluate coating and additives independently. These were designated as Groups 1A and 1B. Group 1A cells were dry unformed while Group 1B cells were dry charged. Control cells were included in each group. Tables 1 and 2 contain the salient design features of the cells.

3.1. *Group 1 cell tests*

The 60 cells of Groups 1A and 1B were tested for cycle life only. The Group 1A 'dry unformed' cells were tested as follows:

(1) Fill with 23 ml of
40% KOH
(2) Soak for 72 h,
minimum

Table 1
Group 1A cells

Variation no.	Negative electrode additive/coating	Separator
-X1	1% PbO, 2% CdO/none	5T C-19
-X2	1% PbO, 2% CdO, 5% Bi_2O_3/none	5T C-19
-X3	not built	
-X4	4% EPM/none	3T Celgard
-X5	4% EPM/none	3T Celgard
-X6	1% PbO, 2% CdO/none	1T Celgard
-X7	4% EPM/none	3T Celgard
-X8	4% EPM/none	2T Cellophane
-X9	4% EPM/none	2T Cellophane
-X10	1% PbO, 2% CdO/none	1T Cellophane
-X11	4% EPM/none	1T Cellophane
-X12	14% EPM/none	5T C-19

Table 2
Group 1B cells

Variation no.	Negative electrode additive/coating	Separator
DC-X1	1% PbO, 2% CdO/none	5T C-19
DC-X1A	1% HgO/none	5T C-19
DC-X2	1% PbO, 2% CdO, 5% Bi_2O_3/none	5T C-19
DC-X3	4% EPM/none	3T Celgard
DC-X4	4% EPM/none	3T Celgard
DC-X5	1% PbO, 2% CdO/none	1T Celgard
DC-X6	4% EPM/none	2T Cellophane
DC-X7	4% EPM/none	1T Cellophane
DC-X8	4% EPM/none	1T Celgard

(3) Cycle F-1 Charge: 0.50 A to 2.08 V
Discharge: 4.25 A to 1.10 V
(4) Cycles F-2 and F-3 Charge: 0.60 A to 2.05 V
Discharge: 4.25 A to 1.10 V
(5) Cycles 1 and 2 Charge: 0.75 A to 2.05 V
Discharge: 4.25 A to 1.10 V
(6) Cycles 3–14, 16–29, 31–44, etc. Charge: 0.75 A to 2.05 V
Discharge: 4.25 A for 1.00 h [a]
(7) Cycles 15, 30, 45, 45, etc. [a] Charge: 0.75 A to 2.05 V
Discharge: 4.25 A to 1.10 V

[a] Testing is terminated when the cells are no longer able to deliver 4.25 Ah.

The Group 1B cells were tested the same way as Group 1A, except for steps (3) and (4). Formation cycles are not required on dry charged cells. Therefore, these steps were omitted and the charge portion of step (5) was replaced with a top-off charge (0.40 A to 2.10 V).

3.2. Group 1 test results

The results of the full capacity discharges for the best performing Group 1A cells and that of the standard cells are shown in Table 3.

The average number of cycles to failure for each variation, and the corresponding failure mode for the Group 1A cells are shown in Table 4.

The dissection results of cells from X1, X2 and X12 variations are as follows.

Variations X1, X2 and X12: cells of these variations presented characteristics common to aged cells, especially extensive shape change of the negative electrodes. The cells of variation -X1 and -X2 lost about 60% of the active area, mostly at the top and edges. Cells of variation -X12 had significantly less shape change (only about 40% area loss). Otherwise, the cells were in good condition, considering their cycle life.

Table 3
Full capacity discharges at 4.25 A, Group 1A

Variation no.	X1 [b]	X2	X12
	Minimum voltage [a]		
	1.501	1.501	1.505
	Output (Ah) [a]		
CY 1-2	8.33	8.86	9.88
CY 15	8.85	9.11	9.21
CY 30	7.32	8.22	8.37
CY 45	6.20	6.89	6.90
CY 60	5.75	6.31	7.67 [d]
CY 75	5.22	5.85	6.33
CY 90	6.79 [c]	7.36 [c]	5.96
CY 105	4.85	6.12	5.36
CY 120	[e]	5.05	[e]
CY 135		4.72	
CY 150		4.58	
CY 165		[e]	

[a] All data points represent the average of three cells.
[b] These are the control cells.
[c] Overcharged by 4.0 Ah, cycle 86.
[d] Overcharged by 4.0 Ah, cycle 48.
[e] < 4.25 Ah.

Table 4
Number of cycles to failure (Group 1A)

Variation no.	No. of cycles to failure	Failure mode
-X1	111	low capacity
-X2	151	low capacity
-X4	38	low capacity
-X5	40	low capacity
-X6	16	internal shorts
-X7	41	low capacity
-X8	35	low capacity
-X9	31	low capacity
-X10	19	internal shorts
-X11	23	internal shorts
-X12	113	low capacity

3.3. Group 1B test results

The results of the full capacity discharges for the best performing Group 1B cells and those of the standard cells (LR8.5DC-X1 with 1% PbO/2% CdO and LR8.5DC-X1A with 1% HgO) are shown in Table 5.

The average number of cycles to failure and the failure mode for each of the Group 1B cells are shown in Table 6.

As with Group 1A, a minimum of one cell per variation was dissected. The findings were similar to those described for Group 1A.

Variations DC-X1 and DC-X2: these cells performed better than the corresponding cells of Group 1A by over 25%. The most likely reason for this improvement was that mixing was enhanced to ensure the uniform distribution of the additives within the negative electrodes. The reason for their eventual failure was shape change of the negatives, with a loss of active area of about 60%. However, it should be noted that the DC-X2 cells took 36% more cycles to reach that stage. The cells with 1% HgO (DC-X1A) showed no significant difference in performance, or during dissection, when

Table 5
Full capacity discharges at 4.25 A, Group 1A

Variation no.	X1	X1A	X2
	Minimum voltage [a]		
	1.496	1.494	1.496
	Output (Ah) [a]		
CY 1-2	11.47	11.45	11.43
CY 15	9.71	9.64	10.09
CY 30	9.05	8.94	9.75
CY 45	8.52	8.41	9.23
CY 60	7.99	7.90	8.62
CY 75	7.33	7.27	8.17
CY 90	6.46	6.40	7.62
CY 105	5.89	5.71	7.00
CY 120	5.16	4.98	6.43
CY 135	4.42	4.27	5.85
CY 150	[b]	[b]	5.41
CY 165			4.82
CY 180			4.48
CY 195			[b]

[a] All data points represent the average of three cells.
[b] <4.25 Ah.

Table 6
Number of cycles to failure (Group 1B)

Variation no.	No. of cycles to failure	Failure mode
DC-X1	141	low capacity
DC-X1A	137	low capacity
DC-X2	192	low capacity
DC-X3	39	low capacity
DC-X4	44	low capacity
DC-X5	46	low capacity
DC-X6	58	low capacity
DC-X7	26	internal shorts
DC-X8	23	internal shorts

compared to those with PbO/CdO. The cells with EPMs improved substantially in terms of integrity of the PVA bags and wetness of the negative electrodes, but their performance remained poor.

3.4. Group 2 cell design (Table 7)

The cells of this group were to be based on the best performing variations of Groups 1A and 1B. This was done for the cells with bismuth, which were essentially the same as the corresponding Group 1 cells, the only difference being the development of improved manufacturing procedures for the negative electrodes, to ensure the uniform distribution of all the additives within those electrodes.

However, in view of the poor results obtained with cells containing EPMs, these were redesigned entirely. The practice of reinforcing the negatives with EPM-coated PVA paper was discontinued and positive and negative electrodes were wrapped individually with one layer of EPM-coated Celgard 3401 and one layer of uncoated non-woven nylon.

As with the Group 1 cells, some key parameters were kept constant, and the design of the standard cells was the same (refer to Group 1 cell design). Four cells of each of five variations of 'dry unformed' cells and five identical variations of 'dry charged' cells were designed and manufactured.

3.5. Group 2 cell tests

The cells of this group were divided into two sets of 20 (2 cells of each variation per set) and tested as follows.

Set A: continuous cycling. The 'dry unformed' cells, -Y1 through -Y5, were tested in exactly the same way as the 'X' cells of Group 1A. The 'dry charged' cells, DC-Y1 through DC-Y5, were tested in exactly the same way as the 'DC-X' cells of Group 1B. Testing was terminated for each cell, when no longer able to deliver 60 min at 4.25 A.

3.6. Group 2 test results

The results of the continuous cycling test (set A) are shown in Tables 8 and 9.

Gas evolution tests were performed during cycle 3, with the cells in the charged condition, and stabilized at 37.8°C (100°F). The gas evolution was measured hourly during the last 8 h of the 24 h stabilization period. The results are shown in Table 10.

Table 7
Unformed and dry charged cells, Group 2

Variation no.	Negative electrode additive	Separator
-Y1	1% PbO+2% CdO	5T C-19
-Y2	1% PbO+2% CdO+5% Bi_2O_3	5T C-19
-Y3	1% PbO+2% CdO	1 bag of Celgard coated with EPM/1 bag of non-woven nylon [a]
-Y4	4% EPM	same as -Y3
-Y5	1% PbO+2% CdO	same as -Y3
DC-Y1	dry charged version of -Y1	same as -Y1 and -Y2
DC-Y2	dry charged version of -Y2	same as -Y1 and -Y2
DC-Y3	dry charged version of -Y3	same as -Y3 and -Y4
DC-Y4	dry charged version of -Y4	same as -Y3 and -Y4
DC-Y5	dry charged version of -Y5	same as -Y5

[a] Each plate, (+) and (-) is wrapped individually

Table 8
LR and LRDC cells, Group 2

Variation no.	Average output (Ah)												
	Cy1-2	Cy30	Cy60	Cy90	Cy120	Cy150	Cy180	Cy210	Cy240	Cy270	Cy300	Cy330	Cy360
-Y1	10.44	10.23	8.50	6.68	6.01	5.62	4.81	[b]					
-Y2	11.30	10.74	9.38	8.33	7.70	7.42	6.59	6.00	5.12	4.85	4.90	4.45	4.48
-Y3	10.81	9.93	8.63	7.69	7.00								
-Y4	10.76	7.09	7.67	6.12	[b]								
-Y5	10.34	9.90	9.59	8.67	8.23	[b]							
DC-Y1	10.77	10.39	7.43	6.42	5.83	5.30	[b]						
DC-Y2	11.59	10.92	9.39	8.27	7.42	6.99	6.14	5.72	[a]				
DC-Y3	10.47	9.99	9.72	8.55	8.35	7.27	[a]						
DC-Y4	10.00	5.97	4.68	[b]									
DC-Y5	10.22	10.15	[a]										

[a] Slow short.
[b] Low capacity (<4.25 Ah).

Table 9
Number of cycles to failure (Group 2)

Variation no.	Av. number of cycles to failure	Failure mode
-Y1	199	low capacity
-Y2	365	low capacity
-Y3	122	low capacity
-Y4	102	low capacity
-Y5	134	low capacity
DC-Y1	167	low capacity
DC-Y2	238	slow short
DC-Y3	160	slow short
DC-Y4	63	low capacity
DC-Y5	43	slow short

Table 10
Gas evolution, charged, at 37.8°C

Variation no.	Av. gassing rate ($cm^3 h^{-1}$)	Av. gassing rate ($cm^3 h^{-1}$/g of $zinc^{-1}$)
-Y1	2.50	0.096
-Y2	1.26	0.048
-Y3	0.83	0.032
-Y4	4.15	0.160
-Y5	0.94	0.036
DC-Y1	3.05	0.117
DC-Y2	1.35	0.052
DC-Y3	1.02	0.039
DC-Y4	4.93	0.190
DC-Y5	1.07	0.041

Low temperature discharge tests were done at 4.25 A during cycles 4 (0°C) and 12 (− 20°C). The results indicate no significant difference in capacity or voltage between variations, except for -Y4 and DC-Y4, which were significantly lower. High rate discharge tests were done at 12 A (cycle 6) and 24 A (cycle 8). Again, there were only minor differences between variations, except for -Y4 and DC-Y4.

The next phase of testing included cells with larger capacities and rate capabilities. The intent of this next phase was to validate the additives for inclusion in cells for underwater vehicles. These cells range in capacity from 40 to over 360 Ah. The configuration selected for initial testing was a cell that has a nominal capacity of 190 Ah. The performance results for this phase of testing were disappointing as they did not offer any additional cycle life over the current design. The cells with the EPMs failed very early in the cycle testing. By cycle 20 all the cells were below the pre-determined cut-off value. The cells with the bismuth oxide additive and the standard mercuric oxide cell performed the same. They both yielded about 50 cycles before reaching the 152 Ah cut-off value. All analyses showed that the EPM cells failed by internal shorting through the EPM separator. The reason for the shorting was determined to be a porous and non-uniform EPM coating.

The bismuth cell analysis indicated that the additive was mixed into the zinc oxide incorrectly and resulted in non-uniform distribution which caused increased gassing resulting in accelerated zinc loss and separator damage.

A study was initiated to investigate the cause(s) and remedial action necessary to correct the uneven additive distribution. As a result of these investigations, the mixing procedures were extensively revised.

These changes provided the necessary remedial actions to correct the distribution anomalies. Based on resolution of the mixing problems, investigations into the use of bismuth in higher rate cells were continued. Cells were manufactured to evaluate performance to existing specification requirements.

Cells with 30 and 210 Ah nominal capacities were manufactured with and without bismuth. The non-bismuth cells contained mercuric oxide, while the bismuth cells were a mixture of bismuth oxide, cadmium oxide and lead oxide. The 30 Ah cell was discharged at the *C*/6 rate and charged at the *C*/15 rate. The 200 Ah cell was discharged, essentially, at the *C* rate and charged at the *C*/16 rate. The results of these tests are shown in Figs. 1 and 2. These results graphically illustrate the dramatic improvement with the addition of bismuth.

Any testing with EPMs was discontinued until the problems with the non-uniform coating can be investigated and

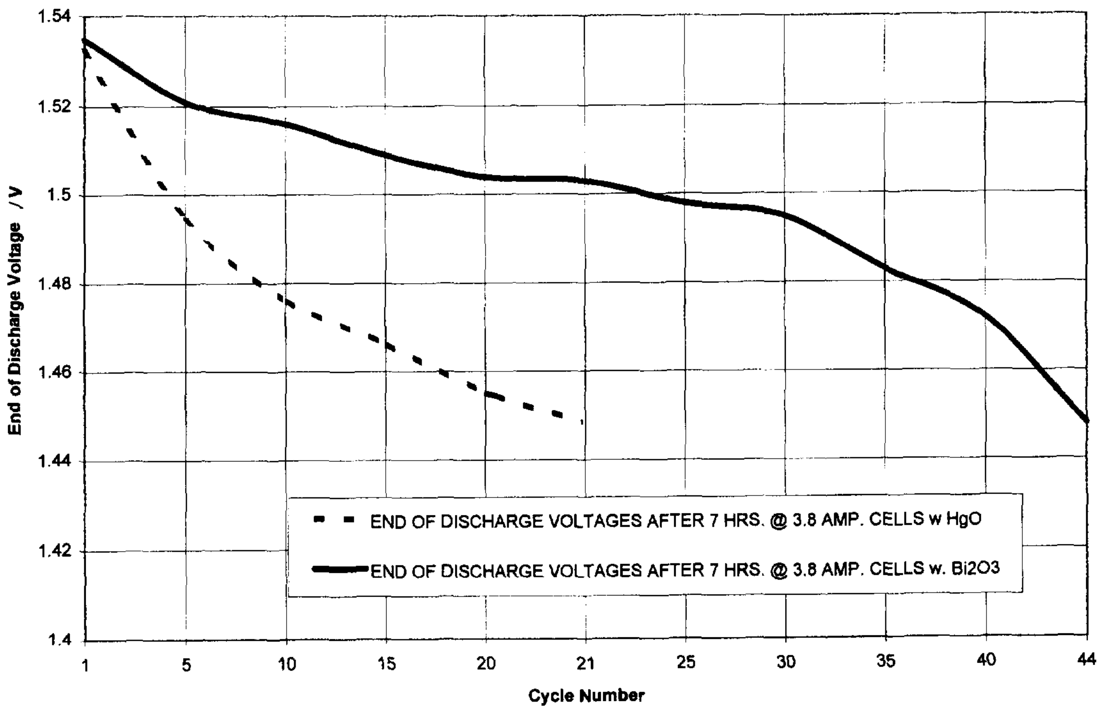

Fig. 1. 30 Ah cells with bismuth and mercury.

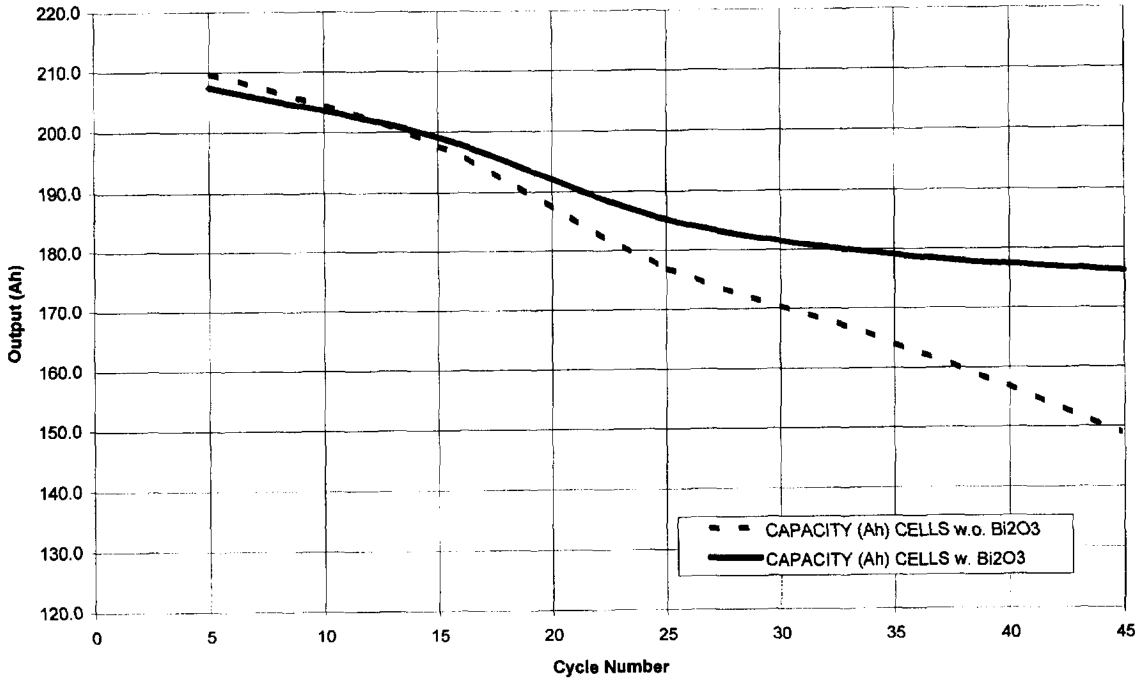

Fig. 2. 200 Ah cells with and without bismuth.

resolved. Attention is also being directed at mixing and uniform coating application.

4. Evaluation of results and summary

The beneficial effects of bismuth oxide in conjunction with other additives did not materialize until the second phase of the program when it was found that a mixture of bismuth oxide, lead oxide and cadmium oxide would enhance the cycle life of the cells [5]. A comparison of the life of these cells is illustrated in Table 11.

In addition, the cells with Bi_2O_3 generate hydrogen gas at only about 50% the rate of the controls, which provides a justification for their superior cycle life. Their high rate and

Table 11
Number of cycles to failure of cells containing bismuth oxide

Test group	Controls	Cells with Bi_2O_3	% Improvement
First Phase	96 [a]	< 10 [b]	n/a
Second Phase			
Group 1A	111	151	36.0
Group 1B	141	192	36.2
Group 2, dry unformed	199	365	83.4
Group 2, dry charged	167	238	42.5

[a] With 1% HgO. All other control cells with 1% PbO and 2% CdO.
[b] With 10% Bi_2O_3 and no other additive. All others with 5% Bi_2O_3 and PbO/CdO.

low temperature performance are equivalent to that of the controls.

The results with EPMs were excellent at times, but lacked consistency because of several problems experienced during this program. In summary, the following observations were made.

(i) During Phase I, one variation of LR cells, with EPMs in the negative electrode (4%, solvent based), and three turns of coated Celgard, outlasted the standard cells by over 68% (160 cycles versus 95), and showed better capacity through testing. Thus, by cycle 90, their capacity was 70% higher.

(ii) Group 1A cells of Phase II did poorly, with just one variation (-X12) outperforming the standard cells, but only by the narrowest of margins. The Group 1B cells showed significant improvements over the corresponding cells of Group 1A, but their performance remained below expectations.

(iii) Dissection of Groups 1A and 1B cells identified the reasons for this disappointing performance:

(a) the heat sealed, EPM-coated polyvinyl alcohol (PVA) bags had opened up at the edges, exposing the cells to premature internal shorts;

(b) excessive dryness of the negative compartment;

(c) imperfections in the coating of the separators, including voids and partial delamination.

As a result of these problems, the Group 2 cells with EPMs were completely redesigned, as described in Section 3.4. In summary, EPMs were no longer used as additives to the negatives, but only as a coating to single layers of Celgard microporous polypropylene, used to wrap all the positive and negative electrodes. The results of Group 2 cells placed the EPMs back in contention in the effort to improve the cycle life and energy density of the silver–zinc cells. As seen in Table 8, certain variations outperformed the controls by a significant margin, e.g. the cycle 90 results show:

1. Dry unformed cells

-Y1 (control)	6.68 Ah
-Y3 (with EPMs)	7.69 Ah (+15.1%)
-Y5 (with EPMs)	8.67 Ah (+29.8%)

2. Dry charged cells

DC-Y1 (control)	6.42 Ah
DC-Y3 (with EPMs)	8.55 Ah (+33.2%)

The only remaining problems are imperfections to the coating of the Celgard, which causes the cells to short, or allows the zinc or zinc oxide to migrate outside of the Celgard bag, resulting in rapid capacity losses. The resolution of these problems continues to be investigated.

Work continues on formulation and testing of additives to the zinc electrode and on electro-permeable membranes. Yardney plans to introduce these additives into its standard line of cells where the application and end-use provide an economic and performance benefit to the cell's cycle life cost.

5. Conclusions

Bismuth oxide, used as an additive to the negative electrode in conjunction with lead and cadmium oxides, has been demonstrated to extend the life of silver/zinc cells by at least 35% [6].

Recent work, which includes not only cells tested on this program, but also higher capacity cells for underwater programs, points to even more significant improvements, in the order of 40 to 83%, through improved manufacturing procedures which ensure the homogeneous dispersion of the additives through the body of the negative electrodes.

The outlook for EPMs remains unclear at this point. The use of EPMs has proven to be beneficial but process problems may ultimately impact the large scale production use of this product.

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