

Naval Surface Warfare Center Carderock Division

West Bethesda, MD 20817-5700

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Survivability, Structures, and Materials Directorate
Technical Report

DEVELOPMENT OF SILVER-ZINC CELLS OF IMPROVED CYCLE LIFE AND ENERGY DENSITY

By ROBERTO SERENYI (YARDNEY TECHNICAL PRODUCTS, INC.)
EDITED AND REVIEWED BY DR. STANLEY D. JAMES (NSWCCD)

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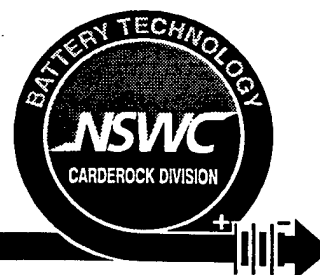
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13. ABSTRACT (Maximum 200 words) This document describes a Small Business Innovative Research (SBIR) Phase II program. The research was designed to improve the cycle life and energy density of silver-zinc cells, particularly those used in naval propulsion systems, by advancing the state-of-the-art of the negative electrode and the separator, which are responsible for most of the shortcomings of this electrochemical couple. Yardney relied on a new class of materials, known as Electro-Permeable Membranes, which were used as additives and/or coatings for the negative electrodes and also as coatings for conventional separator materials, such as cellophane and Celgard (microporous polypropylene). In addition, the use of bismuth oxide in conjunction with other additives to the negative electrode was shown to have a beneficial effect on cycle life and to reduce the hydrogen gassing of charged cells by up to 70%.				
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PREFACE

This report describes a Small Business Innovative Research (SBIR) Phase II program sponsored by the Office of Naval Research. It was conducted under Contract Number N60921-93-C-0062, which was awarded to Yardney Technical Products, Inc., by the Naval Surface Warfare Center Carderock Division's (NSWCCD's) White Oak Detachment in Silver Spring, Maryland. The work was performed during the period from 16 July 1993 through 31 March 1996, under the direction of the principal investigator and author of this document, Mr. Roberto Serenyi. NSWCCD's Dr. Stanley James of the Electrochemistry Branch (Code 683) served as the Contracting Officer's Technical Representative and also edited this report.

The author wishes to thank his colleagues: Dr. Thomas Reddy and Mr. James Skelton for their valuable technical suggestions and for editing this report; Mr. Jerry Kuklinski for developing methods of negative electrode manufacture; and Mr. Fred Thompson for directing the cell tests. A special recognition is due to Drs. Stanley James, Patricia Smith and Charles Fleischmann of NSWCCD, for their continued support and assistance in carrying out this program.

CHAPTER 1

INTRODUCTION

This research effort was designed to improve the cycle life and energy density of silver-zinc cells, particularly those used in naval propulsion systems, by advancing the state-of-the-art of the negative electrodes and the separators, which are responsible for most of the shortcomings of this electrochemical couple. To achieve those objectives, Yardney relied on a new class of materials, known as Electro-Permeable Membranes (EPMs).¹ These materials were used as additives and/or coatings for the negative electrodes and also as coatings for conventional separator materials, such as cellophane and Celgard microporous polypropylene. In addition, the use of bismuth oxide in conjunction with other additives to the negative electrode was shown to have a beneficial effect on cycle life.

The feasibility of substantial increases in the cost effectiveness and range of naval underwater vehicles, by virtue of advances made in silver-zinc propulsion batteries, was demonstrated during Phase I of this SBIR program. The increases, which can be applied to silver-zinc batteries in general, translate into a 70 percent longer vehicle run time, and 84 percent more vehicle missions before the batteries must be replaced.

BACKGROUND

Present state-of-the-art silver zinc cells offer the following: the highest power density among commercially available rechargeable batteries (up to 800 W/kg for continuous discharges and 3,000 W/kg for short duration pulses); very high energy density (up to 250 Wh/kg); a low self-discharge rate; and a flat voltage during most of the discharge. However, they have two limitations:

- A relatively short wet life (2-3 years, maximum)
- A fairly rapid capacity degradation, which reduces the number of useful deep discharges to 5-75, depending on use conditions (rate of charge and discharge, temperature, etc.).

These shortcomings are due to deficiencies of two of the cell's major components: the zinc electrode and the separators. The following paragraphs present a discussion of these two components.

The Zinc Electrode

This component is responsible for the cycle life limitation described above. The reasons are shape change and zinc dendrite formation.

Shape Change. 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 result is a gradual depletion of the active material at the top and edges of the electrode. Past attempts at reducing shape change, such as the use of excess zinc over the amount required for stoichiometric equilibrium with the active silver (still prevalent), the use of oversized negatives, the inclusion of special additives and binders (e.g., Teflon, neoprene, potassium titanate fibers), have been only moderately effective.

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

- Careful charge control, including individual cell voltage monitoring.
- Use of excess negative material so that the negative electrodes are not overcharged. However, as cycling progresses, this excess is depleted. From this time on, the risk of dendrite formation is high.
- Nonconventional charge methods (e.g., pulse charging).

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 André developed the system in the 1940's. Indeed, it is nearly ideal in many respects, but it suffers from one serious weakness--limited resistance to oxidation by silver oxides, by oxygen, and by the electrolyte. As a result, the life of silver-zinc cells is practically limited to about two to three years.

Other separators that have been tried in the intervening years include grafted and crosslinked polyethylene films, and microporous polypropylenes. The latter offer some distinctive advantages over the cellulose. They have lower electrolytic resistance and a high resistance to oxidative degradation and they are very thin, allowing for significant gains in energy density by creating more space for active materials. However, microporous polypropylene films alone are not good stoppers of large metallic ions, such as silver, zinc, and their oxides. For this reason, they must be coated for effective use in silver-zinc cells.

The coating of microporous polypropylene with EPMS, in combination with the improved negative electrodes developed in this program, promises to end the aforementioned limitations to wet life and cycle life.

PHASE I WORK

A brief summary of the Phase I work follows. For a more comprehensive description, see References 2 and 3.

Cell Design

Four cells of each of nine different variations were designed to fit into Yardney's standard 12 Ampere-hour cell case. All cell packs occupied the entire depth of the cases. As a result, and since separator systems of different thickness were used, the amount of active materials varied and the cells were judged both in terms of overall capacity and capacity per gram of active silver. The main design parameters of six of these variations are listed in Table 1-1. (Note: the variations excluded are of no interest for the purposes of this program).

TABLE 1-1. PHASE I CELL DESIGN SUMMARY (6)

Variation No.	Negative Electrode	Main Separator (1)	Active Silver (g)
V1	Standard (1% HgO)	5T C-19 (2)	27.7
V2	4% EPM No. 17k (3)	3T Coated Celgard (5)	34.0
V3	8.5% EPM No. 2029 (4)	3T Coated Celgard (5)	34.0
V4	Coated with EPM No. 2029	5T C-19	27.7
V5	Coated with EPM No. 2029	3T Coated Celgard (5)	34.0
V6	10% Bi ₂ O ₃	5T C-19	27.7

- Notes: (1) T means turns or layers
 (2) C-19: Yardney's silver treated cellophane
 (3) Nos. 17k and 2029 are solvent-based EPMs
 (4) Also coated with EPM No. 2029
 (5) Celgard microporous polypropylene
 (6) Other details (common to all variations)
 Number of plates : 4 (+)/5(-) Half end negatives
 Dimensions (in) : 1.50w X 2.25h

Cell Tests

After filling, formation and two test cycles, the cells were divided into two groups of 18 cells each (two per variation):

- Group A: These cells were cycled continuously on a computer controlled test station at 50% depth of discharge, based on nominal capacity, with one full capacity discharge every 15 cycles, until no longer capable of delivering their shallow cycle capacity.
- Group B: These cells were given a series of characterization cycles to measure the following parameters:

- gas evolution during charged stand at 38°C and during discharge,
- low temperature discharge (0°C and -20°C), and
- high rate discharge (8.0 and 12.0A).

Test Results

Only the results on V1 (the standard cells) and V2 (the best performing of the cells with EPMS) are shown. The V6 variation with 10% Bi₂O₃, without any other additive, performed poorly.

- The Group A results are shown in Table 1-2, in terms of total outputs and capacity per gram of silver. The number of cycles to failure for each cell was:

Cell No.	:	1	2	5	6
Variation No.	:	V1	V1	V2	V2
Failed Cycle No.	:	94	96	159	162

All cells failed because of low capacity, i.e., failure to deliver 50% of their nominal capacity. As may be seen, the cells with EPMS outlasted the standard cells by an average of 69%.

- The results of Group B tests showed that the rate of gas evolution of the cells with EPMS was approximately 37% that of the standard cells on charged stand at 38°C and only 30% during discharge at 4.0A.

In other Group B tests, including high rate and low temperature discharges, the cells with EPMS performed comparably to the standard cells.

TABLE 1-2. PHASE I/CELL CAPACITY IN DEEP CYCLES ⁽¹⁾

Variation No.		V1	V2
Baseline Capacity ⁽²⁾	Ah mAh/g ⁽³⁾	9.71 351	12.53 369
<i>Deep Cycle Capacity</i>			
CY 15	Ah mAh/g ⁽³⁾	7.75 280	10.84 319
CY 30	Ah mAh/g ⁽³⁾	6.65 240	9.76 287
CY 45	Ah mAh/g ⁽³⁾	5.96 215	9.04 266
CY 60	Ah mAh/g ⁽³⁾	5.12 189	8.47 249
CY 75	Ah mAh/g ⁽³⁾	4.71 170	7.75 228
CY 90	Ah mAh/g ⁽³⁾	4.29 155	7.28 214
CY 105	Ah mAh/g ⁽³⁾		6.73 198
CY 120	Ah mAh/g ⁽³⁾		6.29 185
CY 135	Ah mAh/g ⁽³⁾		5.78 170
CY 150	Ah mAh/g ⁽³⁾		5.34 157

- Notes: (1) All data points represent the average of two cells
 (2) Average capacity of cycles 1 and 2
 (3) Milliampere-hours per gram of active silver

CHAPTER 2

PHASE II WORK

The technical objective of the program, i.e., the advancement of the state-of-the-art of the silver-zinc system, through improvements to the negative electrode and the separators remained unchanged during Phase II. However, the Phase II effort was much more extensive, and some of the best results obtained so far could not have been predicted from the Phase I work, particularly those involving bismuth. In Phase II, YTP resorted to two basic approaches to achieve this objective: (1) reliance on a new class of materials, known as Electro Permeable Membranes, henceforth referred to as EPMs and (2) Use of bismuth oxide, Bi_2O_3 , as an additive to the negative electrodes.

MATERIALS

Electro Permeable Membranes (EPMs)

EPMs are the analog of biological membranes that can keep two different solutions or electrolytes separated indefinitely, yet can freely transfer selected ions. They have been described as ionic semiconductors and are the ionic analog of electronic semiconductors. EPM material consists of a two-polymer blend. One of the polymers is a long chain hydrogel, such as used to thicken solutions or to form gels, while the other polymer is a supporting material and can be one of the common plastics such as polypropylene, polyvinyl chloride (PVC), or polyvinylidene fluoride (PVDF).

Several formulations of EPMs were tested for use in silver-zinc cells in three different capacities:

- as an additive to the negative electrode
- as a coating to or reinforcement of the negative electrodes, and
- as a coating to the separators.

Bismuth Oxide (Bi_2O_3)

Bi_2O_3 alone was previously reported as effective by scientists at the Brookhaven National Laboratory.⁴ The task in this program was to establish a working formulation in combination with other additives.

APPROACH

During Phase II of this program, three groups of cells were designed, manufactured and tested. Each iteration incorporated the best features of the previous one. The first two groups consisted of 8.5Ah nominal cells and were built into the same 12Ah case as the Phase I cells. Groups 1 and 2 comprised 60 and 40 cells respectively. The third group consisted of 32, 190Ah cells.

Manufacturing Procedures

Procedures were developed for the manufacture of composite zinc oxide and zinc electrodes with EPMs or Bi_2O_3 , and for the coating of separators with EPMs.

- Composite negative electrodes, with solvent-based EPM, were made by mold pressing. The plates so obtained were mechanically strong and of uniform weight and thickness. However, this method is labor intensive, and adequate only for small scale production, such as required for the Phase I cells, and for some 8.5Ah cells used in Phase II.
- The manufacture of composite zinc oxide/water based EPM electrodes can also be done by mold pressing; however, after several attempts, Yardney was able to produce these electrodes by pasting, which is a mass production method, also used for standard zinc oxide electrodes.
- The manufacture of zinc oxide electrodes with bismuth oxide additive was also accomplished by pasting, as described above.
- All of the described above methods apply to the so called "dry unformed" cells, i.e., those consisting of silver and zinc oxide electrodes. For the manufacture of "dry charged" cells, consisting of silver oxide and zinc electrodes, Yardney was able to electroform the zinc oxide, a method consisting of electrochemically reducing the zinc-oxide from pasted strips with EPMs or Bi_2O_3 . Electroforming of zinc-oxide strips is routinely used at Yardney as a mass production technique.
- The coating of Celgard with EPMs was initially performed by hand, with rollers, a primitive and time consuming operation, which seemed adequate for small-scale production such as that required to build the 8.5Ah cells for cell Groups 1A, 1B and 2, as explained later. However, problems were experienced with Groups 1A and 1B cells and, to a lesser degree, with Group 2 cells which were traced to coating imperfections such as (1) lack of uniformity in thickness and (2) entrapment of air bubbles.

Because of those problems, Yardney investigated the use of automatic coating equipment and contracted the services of Coating Sciences, Windsor, CT to secure enough material for the manufacture of the 190Ah nominal Group 3 cells. Coating was done as a continuous process and its thickness was controlled to ± 0.05 mils.

8.5Ah Group 1 Cell Design

The control cells for Groups 1 and 2 were identical to each other; their main design parameters are shown below.

Positives

Number	6
Size	1.50" W x 2.50" H x 0.0185" Thk
Collector	Exmet No. 5 Ag 14-1
Mass of active silver	29.9g

Negatives

Number	7 (5 full and 2 half ends)
Size	1.50" W x 2.50" H x 0.0345/0.019" Thk
Collector	Exmet No. 5 Ag 7-3/0
Additives	1% PbO + 2% CdO
Zn to Ag capacity ratio	1.43:1.00

Separators

Positive interseparator	1 turn of 2.5 mil woven nylon
Main	5 turns of C-19
Negative interseparator	none

Electrolyte type	40% KOH
-------------------------	---------

Group 1: The cells of this group included 33 "dry unformed" cells (3 each of 11 variations, designated as Group 1A) and 27 "dry charged" cells (3 each of 9 variations, designated as Group 1B). The test cells were built to retain the parameters of the controls, except those that were intentionally varied.

It should be noted that some cell variations had thinner separator systems than the controls. These were fitted with acrylonitrile-butadiene-styrene (ABS) shims to occupy the extra space, to ensure that all cell packs were under approximately the same pressure, which is required for meaningful performance comparison.

This procedure is different from what was done in Phase I, where the additional space available was filled with active materials, and capacity data was expressed both in terms of total ampere-hours and ampere-hours per gram of active silver. For Phase II, as stated in Yardney's technical proposal, the amount of active material was constant to avoid possible mistakes, given the large number of cells assembled at the same time. However, for a fair comparison, both the actual and the potential capacity (that which would be available had the entire cell cavity been used) are tabulated and plotted in this chapter.

Tables 2-1 and 2-2 contain the most important design parameters of the Group 1A (LR8.5-X) and Group 1B (LR8.5DC-X) cells, respectively.

TABLE 2-1. LR8.5-X CELLS (GROUP 1A)

Variation No.	Negative Electrode Additive (1)/Coating	Main Separator	C.F.(6)
-X1	1% PbO, 2% CdO/none	5T C-19	1.00
-X2	1% PbO, 2% CdO, 5% Bi ₂ O ₃ /none	5T C-19	1.00
-X3	Not Built	-	-
-X4	4% EPM 17k (2)/none	3T Celgard (4)	1.35
-X5	4% EPM 1718 (3)/none	3T Celgard (4)	1.35
-X6	1% PbO, 2% CdO/(5)	1T Celgard (4)	1.25
-X7	4% EPM No. 2518 (3)/none	3T Celgard (4)	1.35
-X8	4% EPM No. 17k (2)/none	2T Cellophane (4)	1.33
-X9	4% EPM No. 1718 (3)/none	2T Cellophane (4)	1.33
-X10	1% PbO, 2% CdO/(5)	1T Cellophane (4)	1.20
-X11	4% EPM No. 2518 (3)/(5)	1T Cellophane (4)	1.20
-X12	4% EPM No. 1718 (3)/none	5T C-19	1.00

- NOTES: (1) Variations -X4, -X8 and -X12 were mold pressed; all others were pasted.
 (2) Solvent-based.
 (3) Water-based.
 (4) Coated with EPM No. 1718 (one side only).
 (5) Reinforced with EPM No. 1418 on a PVA paper substrate.
 (6) Factor to calculate potential capacity

TABLE 2-2. LR8.5DC-X CELLS (GROUP 1B)

Variation No.	Negative Electrode Additive (1)/Coating	Main Separator	C.F.(4)
DC-X1	1% PbO, 2% CdO/none	5T C-19	1.00
DC-X1A	1% HgO/none	5T C-19	1.00
DC-X2	1% PbO, 2% CdO, 5% Bi ₂ O ₃ /none	5T C-19	1.00
DC-X3	4% EPM No. 2518/none	3T Celgard (2)	1.35
DC-X4	4% EPM No. 1718/none	3T Celgard (2)	1.35
DC-X5	1% PbO, 2% CdO/(3)	1T Celgard (2)	1.25
DC-X6	4% EPM No. 2518/none	2T Cellophane (2)	1.33
DC-X7	4% EPM No. 2518/(3)	1T Cellophane (2)	1.20
DC-X8	4% EPM No. 2518/(3)	1T Celgard (2)	1.25

- NOTES: (1) All variations were pasted and electroformed, except DC-X3, which was mold pressed. All EPMs were water-based
 (2) Coated with EPM No. 1718 (one side only)
 (3) Reinforced with EPM No. 1418, on a PVA paper substrate
 (4) Factor to calculate potential capacity

8.5Ah Group 1 Cell Testing

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 cc's of 40% KOH
- (2) Soak for 72 hours, minimum
- (3) Cycle F-1
 - Charge: .500A to 2.08V
 - Disc.: 4.25A to 1.10V
- (4) Cycles F-2 and F-3
 - Charge: .600A to 2.05V
 - Disc.: 4.25A to 1.10V
- (5) Cycles 1 and 2
 - Charge: .750A to 2.05V
 - Disc.: 4.25A to 1.10V
- (6) Cycles 3-14, 16-29, 31-44, etc.
 - Charge: .750A to 2.05V
 - Disc.: 4.25A for 1.00 hr.*
- (7) Cycles 15, 30, 45, 60, etc.*
 - Charge: .750A to 2.05V
 - Disc.: 4.25A to 1.10V

(*) Testing is terminated when the cells are no longer able to deliver 4.25 ampere-hours.

The Group 1B cells were tested the same way as Group 1A, except for the procedures that are normally different for “dry charged” cells, i.e.:

- Steps (3) and (4) were omitted.
- The charge portion of step (5), cycle 1 was replaced with a top-off charge (.400A to 2.10V).

Group 1A Test Results. The results of the full-capacity discharges for the best performing Group 1A cells and that of the standard cells (LR8.5-X1) are shown in Table 2-3 and Figure 2-1.

TABLE 2-3. FULL-CAPACITY DISCHARGES AT 4.25A (GROUP 1A)

Variation No.	LR8.5-X1 (2)	LR8.5-X2	LR8.5-X12
Minimum Voltage (1)	1.501	1.501	1.505
Output (Ah) (1)			
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 (4)
CY 75	5.22	5.85	6.33
CY 90	6.79 (3)	7.36 (3)	5.96
CY 105	4.85	6.12	5.36
CY 120	(5)	5.05	(5)
CY 135		4.72	
CY 150		4.58	
CY 165		(5)	

- NOTES:
- (1) All data points represent the average of three cells
 - (2) These are the control cells
 - (3) Overcharged by 4.0Ah, cycle 86
 - (4) Overcharged by 4.0Ah, cycle 48
 - (5) < 4.25Ah

The average number of cycles to failure for each variation, and the corresponding failure mode for the Group 1A cells, are shown in Table 2-4.

TABLE 2-4. NUMBER OF CYCLES TO FAILURE* (GROUP 1A)

Variation Number	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

*Defined as the number of cycles delivering more than 4.25 Ah (50% of nominal)

At least one cell of each variation was dissected after failure. The findings were as follows:

- Variations 1, 2 and 12: 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: the separators (C-19) were wet and pliable, there were no internal shorts, and the silver penetration was only moderate.
- Variations -X6, -X10 and -X11: All the cells of these variations experienced internal short circuits due to the fact that the heat sealed polyvinyl alcohol (PVA) bags placed around the negative electrodes opened up at the edges.
- None of the cells of the other variations (Nos. -X4, -X5, -X7, -X8 and -X9) had internal shorts; however, they lost capacity fast, failing to deliver 4.25Ah within 29 to 43 cycles.
- Although there were differences between cells of these variations, all of them shared the following characteristics:
 - Extensive shape change: approximately 30% to 50% of the negative area was lost.
 - The negative electrodes were very dry, in spite of the fact that there was plenty of free electrolyte in the cells.
 - Some imperfections in the coating of the separators were noted at the time of cell -dissection, including partial delamination of the coating.

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 2-5 and Figure 2-2.

TABLE 2-5. FULL-CAPACITY DISCHARGES AT 4.25A (GROUP 1B)

Variation No.	LR8.5DC-X1	LR8.5DC-X1A	LR8.5DC-X2
Minimum Voltage (1)	1.496	1.494	1.496
Output (Ah) (1)			
CY 1-2	11.47	11.45	
CY 15	9.71	9.64	11.43
CY 30	9.05	8.94	10.09
CY 45	8.52	8.41	9.75
CY 60	7.99	7.90	9.23
CY 75	7.33	7.27	8.62
CY 90	6.46	6.40	8.17
CY 105	5.89	5.71	7.62
CY 120	5.16	4.98	7.00
CY 135	4.42	4.27	6.43
CY 150	(2)	(2)	5.85
CY 165			5.41
CY 180			4.82
CY 195			4.48
			(2)

NOTES: (1) All data points represent the average of three cells
 (2) < 4.25Ah

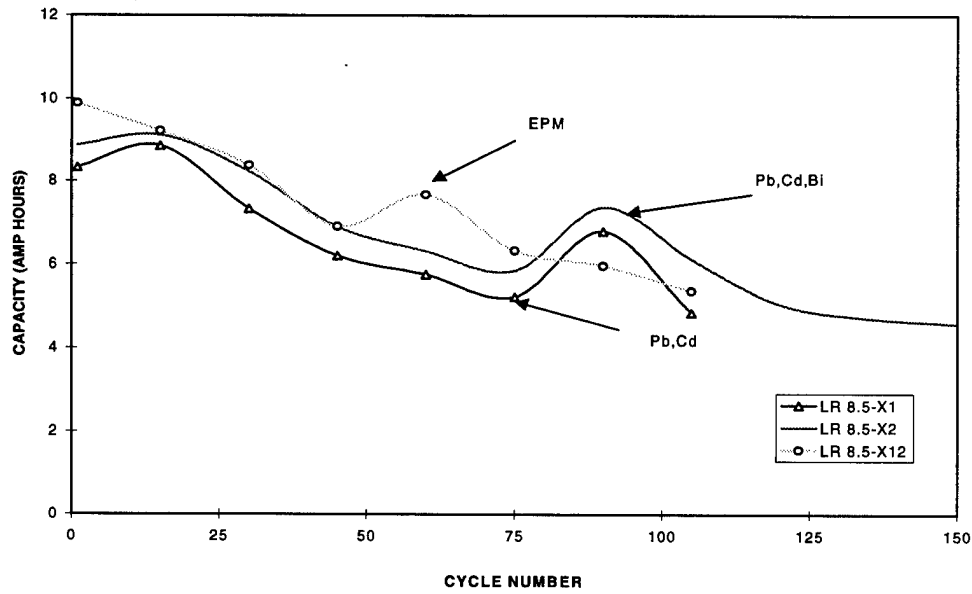
The average number of cycles to failure and the failure mode for each of the Group 1B cells are shown in Table 2-6.

TABLE 2-6. NUMBER OF CYCLES TO FAILURE* (GROUP 1B)

Variation Number	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 Short

*Number of cycles delivering over 4.25 Ah (50% of nominal)

a. GROUP 1A, DRY UNFORMED



b. GROUP 1B, DRY CHARGED

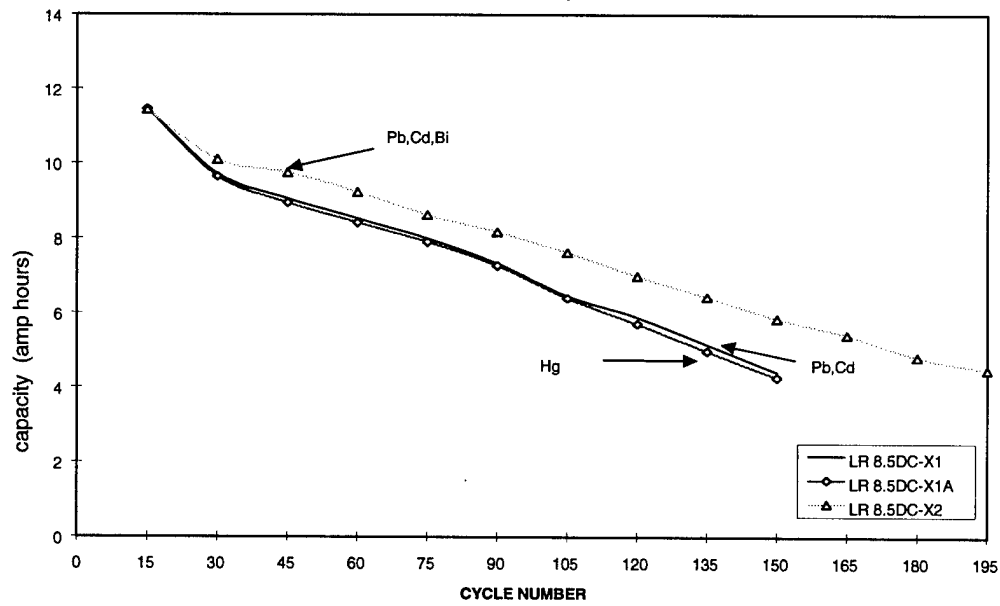


FIGURE 2-1: 8.5 AH CELLS FULL-CAPACITY DISCHARGES AT 4.25 A, GROUP 1

As done 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 extra precautions were taken 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 run 36% more cycles to reach that stage.

The cells with 1% HgO (DC-X1A) showed no significant difference in performance, or during dissection, when 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.

8.5Ah Group 2 Cell Design

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 mediocre results obtained with cells containing EPMS, these were redesigned entirely:

- The practice of reinforcing the negatives with EPM coated PVA paper was discontinued.
- 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). Again, some variations had thinner separator systems than the controls and were fitted with ABS shims. For these variations both the actual and potential capacity (as defined when referring to Group 1 cells) are shown in this chapter.

Four cells of each of five variations of “dry unformed” cells, designated as LR8.5-Y, and five identical variations of “dry charged” cells, designated as LR8.5DC-Y, were designed and manufactured. The most important parameters of these cells are listed in Table 2-7.

TABLE 2-7. LR8.5 AND LR8.5DC CELLS (GROUP 2)

Variation No.	Negative Electrode Additive	Separator	C.F.(2)
Y1	1% PbO + 2% CdO	5T C-19	1.00
-Y2	1% PbO + 2% CdO + 5% Bi ₂ O ₃	5T C-19	1.00
-Y3	1% PbO + 2% CdO	1 bag of Celgard coated with EPM #1718A/1 bag of non-woven nylon (1)	1.17
-Y4	4% EPM	same as -Y3	1.17
-Y5	1% PbO + 2% CdO	same as -Y3, but with EPM #1735	1.17
DC-Y1	Dry charged version of -Y1	same as -Y1 and -Y2	1.00
DC-Y2	Dry charged version of -Y2	same as -Y1 and -Y2	1.00
DC-Y3	Dry charged version of -Y3	same as -Y3 and -Y4	1.17
DC-Y4	Dry charged version of -Y4	same as -Y3 and -Y4	1.17
DC-Y5	Dry charged version of -Y5	same as -Y5	1.17

NOTE: (1) Each plate, (+) and (-), is wrapped individually
 (2) Factor to calculate potential capacity

8.5Ah Group 2 Cell Testing

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 LR8.5-X cells of Group 1A.

The "dry charged" cells, DC-Y1 through DC-Y5, were tested in exactly the same way, as the LR8.5DC-X cells of Group 1B.

Testing of each cell was terminated when it could no longer deliver 60 min. at 4.25A.

The results of the continuous cycling test (set A) are shown in Tables 2-8, 2-9, 2-10 and Figures 2-2 (a. and b.).

TABLE 2-8. LR8.5 AND LR8.5DC CELLS (GROUP 2)

Variation #	Minimum Voltage @4.25A	Average Output (Ah)												
		Cycle #												
		1-2	30	60	90	120	150	180	210	240	270	300	330	360
-Y1	1.505	10.44	10.23	8.50	6.68	6.01	5.62	4.81	(2)	-	-	-	-	-
-Y2	1.505	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 (4)
-Y3	1.497	10.81	9.93	8.63	7.69	7.00	-	-	-	-	-	-	-	-
-Y4	1.490	10.76	7.09 (3)	7.67	6.12	(2)	-	-	-	-	-	-	-	-
-Y5	1.510	10.34	9.90	9.59	8.67	8.23	(2)	-	-	-	-	-	-	-
DC-Y1	1.510	10.77	10.39	7.43	6.42	5.83	5.30	(2)	-	-	-	-	-	-
DC-Y2	1.499	11.59	10.92	9.39	8.27	7.42	6.99	6.14	5.72	(1)	-	-	-	-
DC-Y3	1.505	10.47	9.99	9.72	8.55	8.35	7.27	(1)	-	-	-	-	-	-
DC-Y4	1.489	10.00	5.97	4.68	(2)	-	-	-	-	-	-	-	-	-
DC-Y5	1.496	10.22	10.15	(1)	-	-	-	-	-	-	-	-	-	-

- NOTES: (1) Slow Short
 (2) Low Capacity (<4.25Ah)
 (3) One cell removed after cycle 47, capacity <4.25Ah
 (4) Cells discontinued after 348 and 383 cycles, capacity <4.25

TABLE 2-9. POTENTIALLY AVAILABLE CAPACITY (GROUP 2)
LR8.5 AND LR8.5DC CELLS

Variation No.	Average Potentially Available Capacity(Ah)													
	Cycle No													
	1-2	30	60	90	120	150	180	210	240	270	300	330	360	
-Y1	10.44	10.23	8.50	6.68	6.01	5.62	4.81	-	-	-	-	-	-	
-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	12.65	11.62	10.10	9.00	8.19	-	-	-	-	-	-	-	-	
-Y4	12.59	8.30	8.97	7.16	-	-	-	-	-	-	-	-	-	
-Y5	12.10	11.58	11.22	10.14	9.63	-	-	-	-	-	-	-	-	
DC-Y1	10.77	10.39	7.43	6.42	5.83	5.30	-	-	-	-	-	-	-	
DC-Y2	11.59	10.92	9.39	8.27	7.42	6.99	6.14	5.72	-	-	-	-	-	
DC-Y3	12.25	11.69	11.37	10.00	9.77	8.51	-	-	-	-	-	-	-	
DC-Y4	11.70	6.98	5.48	-	-	-	-	-	-	-	-	-	-	
DC-Y5	11.96	11.88	-	-	-	-	-	-	-	-	-	-	-	

TABLE 2-10. NUMBER OF CYCLES TO FAILURE* (GROUP 2)

<u>Variation Number</u>	<u>Avg. Number of Cycles to Failure</u>	<u>Failure Mode</u>
-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

NOTE: *Number of cycles delivering over 4.25 Ah (50% of nominal)

- Set B: characterizations tests. These consist of a series of cycles to measure the following parameters:
 - Gas evolution on charged stand
 - Low temperature discharge (0 and -20°C)
 - High rate discharge (12 and 24A)
 - High rate charge
 - Capacity after 90 days stand

The results of the characterization tests (set B cells) are shown in Tables 2-11 to 2-14.

- Gas Evolution: This test was performed during cycle 3, with the cells in the charged condition, and stabilized at 37.8°C. The gas evolution was measured hourly during the last 8 hrs of the 24 hr stabilization period. The results are shown in Table 2-11.

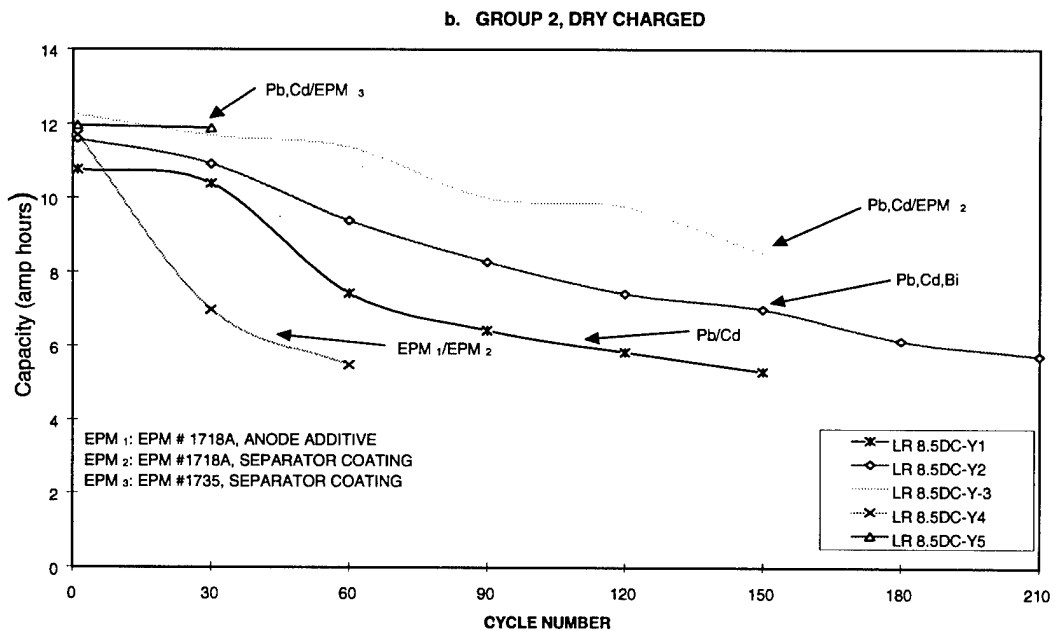
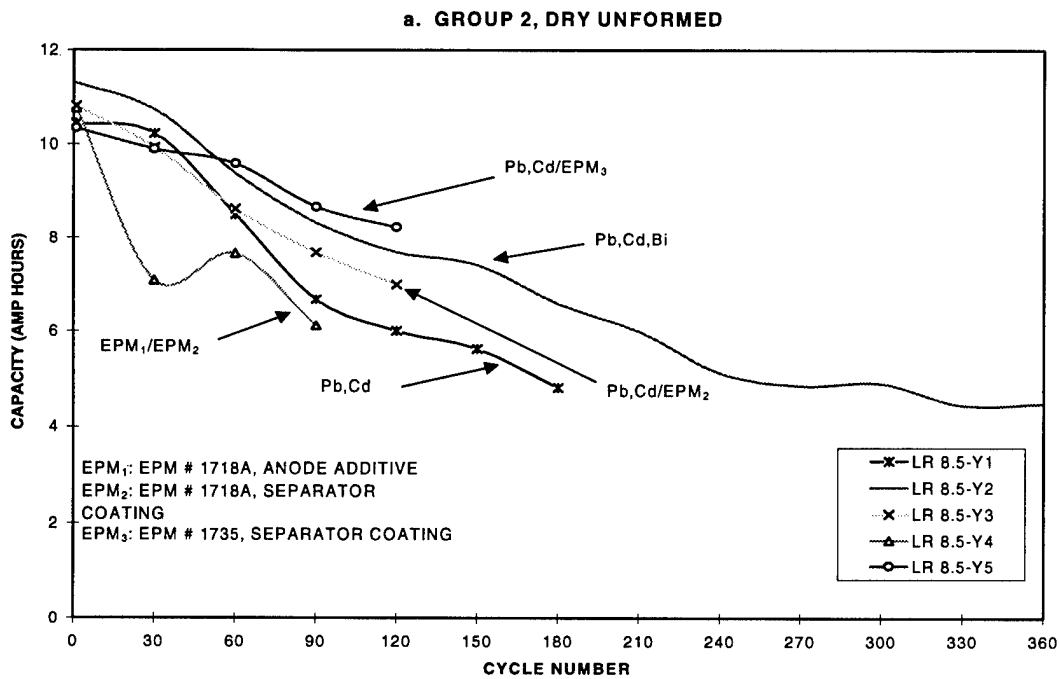


FIGURE 2-2. 8.5 AH CELLS FULL-CAPACITY DISCHARGES AT 4.25 A,
GROUP 2

TABLE 2-11. GAS EVOLUTION, CHARGED, AT 100°F (GROUP 2)

Variation No.	Avg. gassing rate (cm ³ /hr)	Avg. gassing rate (cm ³ /hr ÷ gZn)
-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 discharges: These were done at 4.25A during cycles 4 (0°C) and 12 (-20°C). The results (see Table 2-12) indicate no major differences in capacity of voltage between variations, except for -Y4 and DC-Y4, which were considerably lower.
- High rate discharges: These were done at 12A (cycle 6) and 24A (cycle 8). Again, there were only minor differences between variations, except for -Y4 and DC-Y4. (see Table 2-13)

TABLE 2-12. LOW TEMPERATURE DISCHARGES AT 4.25A (GROUP 2)

Variation No.	0° C Discharge		-20°C Discharge	
	V min	Aho	V min	Aho
-Y1	1.439	8.75	1.344	6.85
-Y2	1.433	9.88	1.329	7.54
-Y3	1.406	9.91	1.285	7.61
-Y4	1.410	9.27	1.267	5.17
-Y5	1.438	9.10	1.336	8.83
DC-Y1	1.420	9.37	1.312	7.90
DC-Y2	1.418	9.36	1.277	7.87
DC-Y3	1.412	9.49	1.270	8.89
DC-Y4	1.417	7.02	1.234	4.14
DC-Y5	1.437	9.39	1.331	8.00

TABLE 2-13. HIGH-RATE DISCHARGES (GROUP 2)

Variation #	12A Discharge		24A Discharge	
	V min	Aho	V min	Aho
-Y1	1.466	9.19	1.316	8.59
-Y2	1.467	9.33	1.345	8.87
-Y3	1.436	8.31	1.306	7.73
-Y4	1.441	8.14	1.308	7.38
-Y5	1.474	9.46	1.369	7.78
DC-Y1	1.455	8.50	1.305	6.64
DC-Y2	1.443	8.98	1.294	7.41
DC-Y3	1.436	8.99	1.273	7.23
DC-Y4	1.438	5.58	1.262	5.42
DC-Y5	1.468	8.89	1.293	7.06

Capacity after 90 days charged stand: After the 14th cycle charge, the cells were allowed to stand for 90 days at room temperature ($25 \pm 3^\circ\text{C}$) prior to discharge. The results of this test are shown in Table 2-14.

TABLE 2-14. CAPACITY AFTER 90 DAYS CHARGED STAND AT $25 \pm 3^\circ\text{C}$ (GROUP 2)

Variation #	Charge (Ah)	Discharge (Ah)	Capacity Loss (%)
-Y1	8.52	7.21	15.4
-Y2	9.08	8.15	10.2
-Y3	8.25	7.52	8.8
-Y4	8.33	4.93	40.8
-Y5	8.95	(1)	100
DC-Y1	8.99	7.76	13.7
DC-Y2	9.48	8.54	9.9
DC-Y3	8.74	7.94	9.1
DC-Y4	8.17	5.34	34.6
DC-Y5	8.70	(1)	100

(1) Cells developed internal shorts

190Ah Group 3 Cell Design

As stated in YTP's Technical Proposal for Phase II of this SBIR program, a total of thirty-two 190Ah cells were built and tested. Based on the test results on Group 1 and 2 cells, and after consulting with NSWCCD technical personnel, it was decided to manufacture cells of three different designs:

1. Eight (8) LR190DC-X1 cells, identical to YTP's standard LR190DC-1, except that a mix of 1% PbO and 2% CdO was substituted for 1% HgO, as the negative electrode additive.
2. Ten (10) LR190DC-X2 cells, same as above, except that the negative electrode additive was 1% PBO, 2% CdO and 5% Bi₂O₃.
3. Fourteen (14) LR190DC-X3 cells, of a significantly different design, featuring the same separator system used for the Group 2 LR8.5-Y3 and LR8.5DC-Y3 cells, i.e., all positive and negative electrodes were individually wrapped with one layer of Celgard coated with EPM No. 1718A and one layer of non-woven nylon. The -X3 cells were built with ~ 17% more active materials than the -X1 and -X2s, taking advantage of the extra room made available by the thinner separator (distance between electrodes reduced from 18.5 mils to 9.2 mils). This is one significant advantage of using EPM coated separators, which is accentuated for high rate cells with a large number of electrodes. For instance, a cell with the same external configuration as the LR190's, but with 20 positive and 21 negative electrodes would accommodate 59.5% more active materials by substituting EPM coated Celgard for conventional separators. The most important design parameters of the Group 3 cells are shown below.

	LR190DC-X1/-X2	LR190DC-X3
Positives		
Number	10	10
Size (in)	5.25w x 4.375 x .033	5.25w x 4.375 x .038
Collector	Exmet No. 5Ag8-1/0	Exmet No. 5Ag8-1/0
Mass of active silver	559.8 g	657.2 g
Negatives		
Number	11 (1)	11 (1)
Thickness	.060/.032	.070/.037
Collector	1.5 mil perf. Ag foil	1.5 mil perf. Ag foil
Additives	(2)	1% PbO + 2% CdO
Zn to Ag capacity ratio	1.45:1.00	1.39:1.00
Separator		
Positive	1T woven nylon	1 bag non-woven nylon
Main	5T C-19	(3)
Negative	none	1 bag non-woven nylon
Electrolyte Type	45% KOH	45% KOH

- Notes:
- (1) Nine (9) full center and two (2) half end electrodes.
 - (2) 1% PbO + 2% CdO for -X1; 1% PbO + 2% CdO + 5% Bi₂O₃ for -X2.
 - (3) Individual single layer EPM coated Celgard 3401 bag.

190Ah Group 3 Cell Testing

The cells of this group are being tested on automated, computer-controlled test stations. The basic regime consists of low-rate, continuous 67.5% depth of discharge (DOD) cycles, performed as follows:

charges: 6.0A to 2.05V
discharges: 32.0A for 4 hrs. (128Ah output) with deep discharges (32.0A to 1.28V) on cycles 1, 5, 10 and every 10 cycles thereafter.

Additions and exceptions to the basic regime include:

- Four of the -X3 cells were discharged at 37A, instead of 32A, to take into account the greater amount of active materials in this design (37A corresponds to 67.5% DOD, while 32A represents only 58.4%).
- All cells were subjected to the following special tests:

- (1) gas evolution measurement, 24 hrs. in the charged condition, at room temperature,
- (2) one low-temperature discharge, at 0°C, and
- (3) one brief high-rate discharge (185A for 3 minutes).

For a more detailed test program, see Appendix A.

The results of the continuous cycling test are included in Table 2-15 and Figure 2-3 (Capacity in Deep Cycles) and Table 2-16 (Number of Cycles to Failure).

The results of the special tests described in the preceding paragraph and in Appendix A are shown in Tables 2-17 (Gas Evolution), 2-18 (Low Temperature) and 2-19 (High Rate).

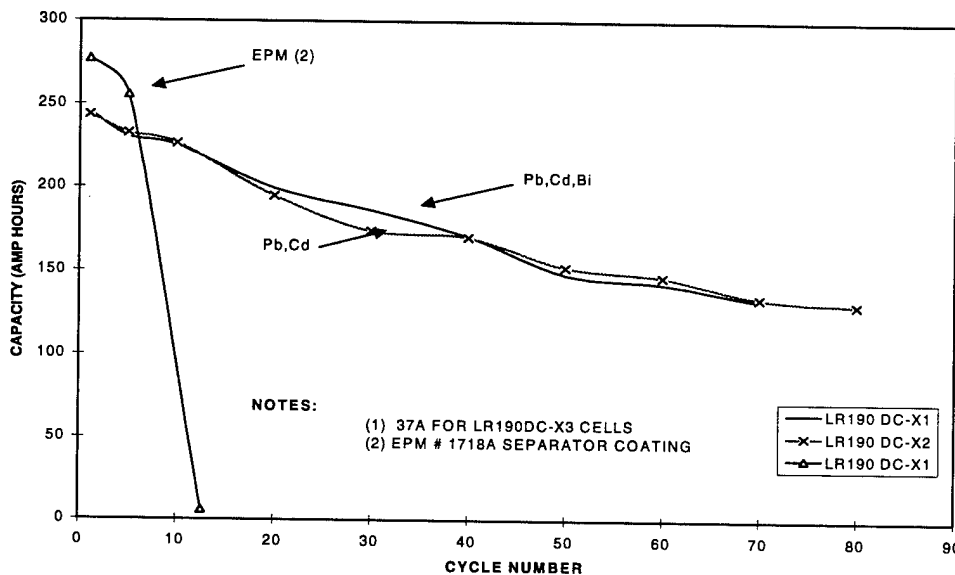


FIGURE 2-3. LR 190DC CELLS FULL-CAPACITY DISCHARGES AT 32 A (1), Group 3, DRY CHARGED

TABLE 2-15. DEEP DISCHARGES AT 32 AND 37 A (Group 3)

Cell #	Dash #	Outputs (Ah) for cycle number									
		1	5	10	20	30	40	50	60	70	80
1	X1	241.0	232.1	226.6	196.5	182.2	166.3	143.4	137.2	(5)	-
2		245.0	227.4	222.6	200.0	185.7	171.3	148.3	141.5	128.1	(6)
3		247.4	234.1	224.2	200.2	188.2	168.0	149.5	144.2	131.4	(7)
4		246.6	232.3	225.3	191.0	174.3	159.5	135.4	129.1	(4)	-
5		250.3	233.7	225.8	207.2	191.7	175.8	148.8	143.1	131.2	(9)
6		242.5	230.5	226.3	205.2	193.9	182.4	161.5	156.9	142.4	(10)
7		243.6	235.7	229.3	194.4	185.1	170.3	146.1	141.3	130.3	(7)
8		242.4	216.5	219.3	200.8	188.5	170.8	150.0	145.5	130.9	(7)
Avg-X1 at 32A		244.9	230.3	224.9	199.4	186.2	170.6	147.9	142.4	132.4	-
9	X2	246.9	233.9	227.6	194.7	176.5	169.1	148.6	143.7	131.9	(8)
10		244.0	235.4	229.3	197.3	176.0	169.9	150.2	146.0	132.3	(8)
11		241.8	235.1	228.1	193.7	174.6	171.4	153.7	146.7	135.7	(10)
12		243.0	233.6	224.1	187.4	166.0	162.1	142.2	139.7	129.9	(7)
13		243.5	231.5	227.1	200.3	178.8	171.4	150.6	142.4	130.7	(7)
14		239.0	225.6	221.5	188.6	169.2	161.0	152.5	(3)	-	-
15		243.2	229.0	219.4	184.8	164.0	162.9	143.5	138.9	128.3	(7)
16		244.5	234.4	230.2	203.7	181.8	180.4	164.7	157.5	143.3	128.1 (11)
17		242.4	234.2	227.3	197.7	175.6	180.8	164.6	158.2	143.7	132.5 (12)
18		245.9	232.6	226.2	199.2	174.5	173.4	152.9	145.8	129.9	(9)
Avg-X2 at 32A		243.4	232.5	226.1	194.7	173.7	170.2	152.4	146.5	134.0	130.3
19	X3	256.0(1)	251.6	249.9	(2)	-	-	-	-	-	-
20		256.0(1)	253.7	(2)	-	-	-	-	-	-	-
21		256.0(1)	250.7	247.5	(2)	-	-	-	-	-	-
22		256.0(1)	264.0	(2)	-	-	-	-	-	-	-
23		256.0(1)	252.4	(2)	-	-	-	-	-	-	-
24		256.0(1)	260.6	(2)	-	-	-	-	-	-	-
25		256.0(1)	(2)	-	-	-	-	-	-	-	-
26		256.0(1)	262.2	(2)	-	-	-	-	-	-	-
27		256.0(1)	(2)	-	-	-	-	-	-	-	-
28		256.0(1)	257.9	250.8	(2)	-	-	-	-	-	-
Avg-X3 at 32A		256.0(1)	256.6	249.4	-	-	-	-	-	-	-
29	X3	285.0	260.8	255.8	(2)	-	-	-	-	-	-
30		283.3	255.4	(2)	-	-	-	-	-	-	-
31		272.8	253.2	(2)	-	-	-	-	-	-	-
32		268.0	253.5	251.2	(2)	-	-	-	-	-	-

Notes: (1) Discharge stopped at 8 hrs. (=256 Aho) due to a computer programming error.
 (2) Cell developed an internal short.
 (3) Cell dissected
 (4) Failed, cycle 62, capacity < 128Ah
 (5) Failed, cycle 68, capacity < 128Ah
 (6) Failed, cycle 71, capacity < 128Ah

(7) Failed, cycle 72, capacity < 128 Ah
 (8) Failed, cycle 73, capacity < 128Ah
 (9) Failed, cycle 74, capacity < 128 Ah
 (10) Failed, cycle 77, capacity < 128 Ah
 (11) Failed, cycle 81, capacity < 128Ah
 (12) Failed, cycle 83, capacity < 128Ah

TABLE 2-16. NUMBER OF CYCLES TO FAILURE* (GROUP 3)

Cell Number	Dash Number	Number of Cycles to Failure	Failure Mode
1	X2	68	Low capacity
2		71	Low capacity
3		72	Low capacity
4		62	Low capacity
5		74	Low capacity
6		77	Low capacity
7		72	Low capacity
8		72	Low capacity
Average, -X1		71	
9	X2	73	Low capacity
10		73	Low capacity
11		77	Low capacity
12		72	Low capacity
13		72	Low capacity
14			See note (1)
15		72	Low capacity
16		81	Low capacity
17		83	Low capacity
18		74	Low capacity
Average, -X2		75	
19	X3	12	Internal Short
20		8	Internal Short
21		12	Internal Short
22		6	Internal Short
23		7	Internal Short
24		8	Internal Short
25		4	Internal Short
26		7	Internal Short
27		5	Internal Short
28		11	Internal Short
29		12	Internal Short
30		9	Internal Short
31		8	Internal Short
32		11	Internal Short
Average, -X3		9	

Notes: * Defined as the number of cycles delivering more than 128 Ah (67.5% of nominal)
 (1) Cell dissected after 58 cycles

Gas Evolution at Room Temperature ($25 \pm 3^\circ\text{C}$)

Two cells of each variation were tested:

- X1: Nos. 1-2
- X2: Nos. 9-10
- X3: Nos. 19-20

- The cells were allowed to stand in the fully charged condition for 24 hrs at RT ($75 \pm 2^\circ\text{F}$). (Running the test at 75°F , instead of 100°F , as done with the LR8-5 Group 2 cells, reduces the gassing rate by approximately 50%.)
- During the last 8 hrs of that period the amount of gas generated was measured. The results were as follows:

TABLE 2-17. GAS EVOLUTION (GROUP 3)

Variation No.	Cell No.	Gas Evolved	
		cc/hr	cc/(hr x g Zn)
-X1	1	23.5	.045
-X1	2	28.7	.055
AVG -X1		26.1	.050
-X2	9	13.1	.025
-X2	10	9.9	.019
AVG -X2		11.5	.022
-X3	19	9.0	.016
-X3	20	7.6	.014
AVG -X3		8.3	.015

TABLE 2-18. 0°C DISCHARGE (GROUP 3)

Cell No.	Dash No.	Voltage at 32a (1) and 0°c				Output to 1.28v (Ah)
		Min	Peak	1 hr	2 hrs	
1	X1	1.438	1.483	1.453	1.476	218.3
2		1.438	1.486	1.452	1.475	214.1
3		1.438	1.492	1.456	1.482	220.2
4		1.435	1.488	1.452	1.476	221.4
5		1.433	1.492	1.455	1.482	220.0
6		1.433	1.491	1.453	1.480	220.0
7		1.436	1.487	1.455	1.478	223.6
8		1.437	1.481	1.448	1.473	210.4
AVG -X1		1.436	1.488	1.453	1.478	218.5
9	X2	1.430	1.485	1.449	1.477	222.7
10		1.433	1.490	1.453	1.481	221.1
11		1.436	1.491	1.455	1.482	218.5
12		1.440	1.491	1.456	1.482	220.2
13		1.407	1.490	1.453	1.482	219.1
14		1.440	1.490	1.455	1.481	214.2
15		1.437	1.486	1.452	1.478	218.2
16		1.434	1.483	1.449	1.476	220.0
17		1.432	1.486	1.448	1.478	219.2
18		1.424	1.493	1.454	1.482	225.3
AVG -X2		1.431	1.489	1.452	1.480	219.9
19	X3	1.440	1.478	1.456	1.476	250.9
20		(2)	-	-	-	-
21		1.437	1.474	1.455	1.473	255.8
22		(2)	-	-	-	-
23		1.435	1.472	1.453	1.470	255.8
24		1.438	1.474	1.454	1.471	257.5
25		(2)	-	-	-	-
26		1.430	1.466	1.450	1.466	256.7
27		(2)	-	-	-	-
28		1.432	1.469	1.452	1.468	254.9
29		1.430	1.465	1.450	1.463	250.2
30		(2)	-	-	-	-
31		1.429	1.464	1.449	1.464	252.4
32		1.429	1.463	1.449	1.462	254.3
AVG -X3 (3)		1.435	1.472	1.453	1.471	254.3

- NOTES: (1) 37 A for cells 29-32
 (2) Cell developed an internal short
 (3) Not including cells 29-32 because of the higher rate of discharge

TABLE 2-19. HIGH-RATE DISCHARGE (GROUP 3)

Cell #	Dash #	Voltage at 185A				
		15 SEC	30 SEC	1 MIN	2 MIN	3 MIN
1	X1	1.291	1.293	1.296	1.306	1.315
2		1.284	1.285	1.288	1.298	1.307
3		1.288	1.289	1.291	1.301	1.310
4		1.286	1.288	1.291	1.302	1.311
5		1.304	1.305	1.307	1.316	1.325
6		1.293	1.295	1.297	1.308	1.317
7		1.300	1.300	1.302	1.312	1.321
8		1.288	1.290	1.293	1.304	1.314
Average -X1		1.292	1.293	1.296	1.306	1.315
9	X2	1.307	1.307	1.306	1.312	1.320
10		1.301	1.300	1.300	1.307	1.316
11		1.302	1.301	1.301	1.309	1.317
12		1.308	1.307	1.307	1.313	1.320
13		1.298	1.297	1.297	1.303	1.312
14		1.320	1.320	1.319	1.322	1.327
15		1.307	1.306	1.306	1.312	1.319
16		1.297	1.296	1.296	1.303	1.311
17		1.302	1.301	1.301	1.307	1.315
18		1.309	1.309	1.308	1.312	1.319
Average -X2		1.305	1.304	1.304	1.310	1.318
19	X3	1.321	1.321	1.321	1.324	1.328
20		1.322	1.320	1.317	1.322	1.327
21		1.323	1.323	1.322	1.325	1.329
22		1.322	1.322	1.321	1.325	1.330
23		1.319	1.319	1.319	1.322	1.327
24		1.321	1.320	1.321	1.325	1.330
25 (1)		-	-	-	-	-
26		1.318	1.318	1.318	1.322	1.326
27		1.323	1.322	1.322	1.326	1.331
28 (1)		-	-	-	-	-
29		1.319	1.318	1.317	1.320	1.324
30		1.321	1.320	1.320	1.323	1.327
31		1.324	1.323	1.322	1.327	1.332
32		1.322	1.321	1.320	1.324	1.329
Average -X3		1.321	1.320	1.320	1.324	1.328

(1) Cell developed an internal short

CHAPTER 3

DISCUSSION OF PHASE II DATA

This chapter describes the effect of the two additives used in this work on the performance of silver-zinc cells.

BISMUTH OXIDE

The beneficial effects of bismuth oxide were not obvious until Phase II of the SBIR program, when it was found that a mixture of Bi_2O_3 with PbO and CdO would enhance the cycle life of the cells by what is believed to be a synergistic effect. Improvements to the manufacturing process, introduced during the construction of the Group 2 cells of Phase II, further added to their cycle life, to the point that these cells averaged 365 cycles before their capacity dropped below 50% of nominal (4.25 Ah).

Unfortunately, the Group 3 LR190DC cells with Bi_2O_3 did not perform as expected, outlasting the controls by only 5.6% (75 cycles vs. 71). Upon dissection, it was found that the concentration of Bi_2O_3 within the negative electrodes was not uniform, with some spots having up to 75% more than others in the same electrode. This lack of uniformity can be traced to non-ideal mixing of the additives with the zinc oxide during the electrode manufacture.

Table 3-1 shows a comparison of the cycle life of the cells with bismuth and the controls.

TABLE 3-1. CELLS WITH BISMUTH, # OF CYCLES TO FAILURE *

Type, group & construction		Nominal Capacity (Ah)	Controls	Cells w/ Bi_2O_3	% Difference
Phase I	LR8.5	8-10	96 (1)	<10 (2)	N/A
Phase II					
	LR8.5-X, group 1A	8.5	111	151	+36.0
	LR8.5DC-X, group 1B (3)	8.5	141	192	+36.2
	LR8.5-Y, group 2	8.5	199	365	+83.4
	LR8.5DC-Y, group 2	8.5	167	238	+42.5
	LR190DC-X	190	71	75	+5.6

NOTES: (*) Defined as the number of cycles delivering over 50% of nominal capacity (over 62.5% for LR190DC-X).

(1) With 1% HgO . All other control cells with 1% PbO and 2% CdO .

- (2) With 10% Bi_2O_3 and no other additive. All others 5% Bi_2O_3 + 1% PbO + 2% CdO .
- (3) The suffix "DC" indicates "dry charged." All others "dry unformed."

In addition, the cells with Bi_2O_3 generate gas at only about 50% the rate of the controls. Their high rate and low temperature performance are equivalent to that of the controls, as shown in Tables 2-12, 2-13, 2-18, and 2-19.

It should be emphasized that Yardney has introduced Bi_2O_3 in the negative electrodes of several long-life cells, the most notable being MR200DC-1. It was developed for use in the MK 30, Mod 2 torpedo target and LR30's proposed for the NASA astronaut's EMU (Extra-vehicular Mobility Unit) space suit, with excellent results, as shown in Appendix B.

EPMs

The results with EPMs were excellent at times, but lacked consistency because of several problems experienced during this program, which were never satisfactorily resolved. In summary, the following was observed:

- During Phase I, one variation of LR12 cells, with EPMs in the negative electrode (4%, solvent based), and 3 turns of coated Celgard, outlasted the standard cells by over 68% (160 cycles vs 95), and showed higher capacity through the entire test. Thus, by cycle 90, their capacity was 70% higher.
- Group 1A cells of Phase II did poorly, with just one variation (-X12) outperforming the standard cells, and only by the narrowest margin. The group 1B cells showed significant improvements over the corresponding cells of group 1A, but their performance remained below expectations.

Dissection of group 1A and 1B cells uncovered the following reasons for this disappointing performance: (1) the heat-sealed, EPM-coated polyvinyl alcohol (PVA) bags opened up at the edges, exposing the cells to premature internal shorts;

(2) excessive dryness of the negative compartment; (3) 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 under "Group 2 Cell Design." 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. Looking at Tables 2-8 and 2-9, we can see that certain variations outperformed the controls by a significant margin in terms of capacity; e.g., the cycle 90 results show:

1.	Dry unformed cells		<u>Actual (Ah)</u>	<u>Potential (Ah) (1)</u>
	-Y1 (control)	:	6.68	6.68
	-Y3 (w. EPMs)	:	7.69 (+15.1%)	9.00 (+34.7%)
	-Y5 (w. EPMs)	:	8.67 (+29.8%)	10.14 (+51.8%)
2.	Dry Charged cells		<u>Actual (Ah)</u>	<u>Potential (Ah) (1)</u>
	DC-Y1 (control)	:	6.42	6.42
	DC-Y3 (w. EPMs)	:	8.55 (+33.2%)	10.00 (+55.8%)

(1) As defined in Chapter 2 under "Group 1 Cell Design"

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 assumption was made for the Group 3 cells that a coating could be obtained with fewer defects by using a commercial single pass machine coating. It was also believed that a film of 0.001" would provide further protection. Unfortunately, the machine-coated Celgard failed faster than the earlier cells, which developed shorts. It might be argued that since the area of the total coated Celgard was much larger in the later cells that there might not be a significant increase in the number of defects per unit area since a larger area was sampled. In any event, the single machine coating was unsatisfactory.

Considerable experience was gained by using EPM films in Zn/Ag cells, which indicate that the EPM film can give better performance than other separators; and that the remaining problem is one of either reducing the number of defects in the coating or re-designing the cells to compensate for the presence of possible defects. Two possible approaches to solving this problem are outlined below:

1. The resistance of the EPM films is not a limiting factor and hence the thickness or the number of the films can be increased which would be similar to the old method of using multiple wraps of cellophane separators.
2. A further possibility would be to machine coat with multiple passes through the coater and dryer.

Of these two approaches, the most attractive in terms of cost would appear to be the second due to the relatively high cost of Celgard.

CHAPTER 4

CONCLUSIONS

SUMMARY

The objectives of the Phase II work, as defined in YTP's SBIR proposal (June 12, 1992), were twofold: (1) to build upon the Phase I improvements by resorting to advanced EPM formulations more easily adapted to large-scale production and by testing negative electrodes containing bismuth oxide and calcium hydroxide; (2) to extend such improvements to large cells, (those used in underwater vehicle propulsion).

8.5 Ah cells with EPMs did not perform as anticipated during the first year of the program. None of the formulations, tested as additives to the zinc electrode and/or as coating to the separators, lived up to the expectations created during the Phase I work. However, cells built with these materials used as a coating to the separators during the second year demonstrated improved performance.

8.5Ah cells with negative electrodes, containing 5% bismuth oxide (Bi_2O_3), used in combination with lead oxide (PbO) and cadmium oxide (CdO), performed very well. They outlasted the standard cells (with PbO and CdO or HgO additives) by 83% (365 cycles vs 199) in "dry unformed" Ag/ZnO cells and by 49% (238 cycles vs 160) in "dry charged" AgO/Zn cells. This is a welcome development, considering that Bi_2O_3 is nontoxic, and that it performed poorly in Phase I of this SBIR program, when it was used alone, at a higher concentration (10%).

Three variations of 190Ah cells, including the standard design (8 cells), those with 5% Bi_2O_3 (10 cells) and those with EPMs (14 cells) were tested during the last six months of the program (October 1995 - March 1996). The results of these tests were disappointing. The standard cells remained above 128 Ah (67.5% of nominal) for 71 cycles, on average, those with bismuth did the same for 75 cycles, on average and those with EPMs developed internal shorts in the range of 4 to 12 cycles. The cause of the unexpectedly poor performance in the case of cells with bismuth was surmised to be the observed, imperfect mixing of the bismuth additive within the zinc electrode. With the EPM cells, the cause was presumed to be observed defects in the separator coatings.

Based on the 8.5 Ah cell test results obtained in this program, YTP introduced bismuth into the 200 Ah cells used in the MK30 MOD 2, Torpedo Target Battery Development Program (BDP) and into the 30 Ah cells proposed for the NASA astronauts' space suits. In Phase 1 of the Torpedo Target Program, the effect of the bismuth additive was mixed, varying from an 80% increase in cycle life with one variation, to a decrease in another. More uniformly favorable

results were achieved later in the BDP. With the space suit cells, the results were favorable, showing a 62% gain in cycle life. (See Appendix B)

A chronic problem with the Zn/AgO system is the thermodynamic instability of zinc metal in aqueous media. Zinc anodes, especially in the fully charged state, react with water, venting potentially explosive hydrogen gas. A significant bonus of the bismuth and EPM additives is a reduction in hydrogen gassing. Gas evolution, measured during cycle 3 with cells in the fully charged condition, was cut by 56% with bismuth and by 68% with EPM. This applied to both 8.5 and 190Ah cells.

YTP was unable to evaluate calcium hydroxide $[\text{Ca}(\text{OH})_2]$ as an additive to the negative electrodes, as proposed, because of insurmountable manufacturing difficulties, even when the concentration was cut to 5%, which is half of the minimum amount cited in the literature as being effective.

RECOMMENDATIONS

Bismuth Oxide

Bismuth oxide, used as an additive to the negative electrode in conjunction with lead and cadmium oxides, has been shown to extend the life of silver-zinc cells by up to 80%. It remains to be demonstrated that an observed lack of reproducibility in bismuth's beneficial effect can be overcome by more uniform mixing of bismuth oxide into the anode precursor. Also recommended is a program to optimize the concentration of Bi_2O_3 , including life cycle and characterization tests on small cells (similar to the 8.5Ah cells used in the SBIR program) with variable amounts of bismuth (2-5%) in combination with other anticorrosive agents, preferably ones which are nontoxic.

Electro Permeable Membranes (EPMs)

The outlook for EPMs, as a coating to the separators, remains in doubt because several successful results were overshadowed by the persistent problem of cell shorting, caused by imperfections in the EPM coating. However, it must be noted that EPMs, when used as a coating to the separators, as in the case of the above 190Ah cells, allow for less separation between adjacent plates, thus creating more room for active materials and therefore, increases energy density by at least 15%. It is the opinion of the author that a program to test the approaches described in the preceding chapter is warranted.

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APPENDIX A
LR190DC DETAILED TEST PROGRAM

- 1) Number cells as follows:

LR190DC-X1	:	1-8
LR190DC-X2	:	9-18
LR190DC-X3	:	19-32

- 2) Weigh dry
 - Fill (315 cc, 45% KOH)
 - Weigh filled
 - Band
 - Soak (96 ± 8 hrs.)

- 3) Adjust electrolyte quantity, if required

- 4) Top charge : 3.0A to 2.08V

- 5) Standard Cycling
 - All charges: 6.0A to 2.05V
 - Discharges
 - All cells, excluding 29-32: 32A for 4 hrs, except 32A to 1.28V in cycles 1, 5, 10 and every 10 cycles thereafter.
 - Cells 29-32: same as above, but discharge at 37A
 - Rest periods: 2 hrs. after charge and 4 hrs. after discharge
 - Terminate testing of each cell when it can no longer deliver 4 hrs. at or above 1.28V.

- 6) Special tests
 - Gassing: At the end of cycle 2 charge, allow to stand at room temperature for 24 hrs. Measure gas evolution in cc's on cells 1, 2, 9, 10, 19 and 20, for the last 8 hrs. of the 24 hr. stand period.
 - Low-Temperature (Cycle 6 only): Discharge at 32A or 37A, as applicable, to 1.28V at 0°C, after a minimum of 16 hrs. stabilization at 0°C.
 - High-Rate (Cycle 3 only): Discharge as follows:
 - 60 min. at 32A (37A) +
 - 3.00 min. at 185A +
 - 163 min. at 32A (37A)
 - (Total output {Cells 1-28: 128.2Ah
 - {Cells 29-32: 146.8Ah

Note: Voltage readings on discharge

- (a) At 32 and 37A: 1 min., 15 min., 30 min. + every 30 min. thereafter
- (b) At 185A: 1 sec., 15 sec. + every 15 sec. thereafter

APPENDIX B

MR200DC AND LR30 TEST DATA

TABLE B-1. MR 200DC CELL PERFORMANCE DATA
Average deep discharge capacity at 16.25 A

Cell Dash No	Negative Additive	Separator Wrap	Capacity @ Cycle No					
			1(4)	15	25	35	45	Loss/cycle (5)
X1	PbO/CdO	Normal (1)	210.0	174.9	172.7	151.8	136.2	0.96
X6	PbO/CdO/Bi ₂ O ₃	Reverse (2)	210.0	188.5	182.0	177.7	166.1	0.52
X7	PbO/CdO	Split (3)	210.0	203.8	176.9	164.0	148.6	0.77
X8	PbO/CdO/Bi ₂ O ₃	Split (3)	210.0	199.2	185.3	179.1	176.2	0.39

NOTES:

- (1) Only the positive electrodes are wrapped
- (2) Only the negative electrodes are wrapped
- (3) Both positive and negative electrodes are wrapped
- (4) Cycle 1 capacity is estimated, based on the amount of silver per cell
- (5) Calculated for cycle No. 45

TABLE B-2. LR30 CELLS (1) NUMBER OF CYCLES TO FAILURE(2)

Cell type	LR30-P4	LR30-P5	% difference, -P5 vs -P4
Negative additive	1% HgO	1%PbO+2%CdO+5%Bi ₂ O ₃	
No of cycles to failure(3)			
Maximum	28	44	+57.1
Minimum	22	40	+81.8
Average	26	42	+61.5

NOTES :

- (1) : Proposed for use by NASA in the astronaut's space suits
- (2) : Defined as capacity below 26.6 Ah
- (3) : 35 cycles required

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