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LONG LIFE STABLE ZINC ELECTRODE FOR ALKALINE SECONDARY BATTERY

SEVENTH QUARTERLY REPORT

BY

J. McBREEN

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1. ABSTRACT

Cells made with 5% Teflon, contoured negatives and extended edges gave more than 400 62½% depth of discharge 6 hour cycles before shorting. Failure occurred by shorting as the result of disintegration of the cellophane separators at the top. Oxidative attack was severe, due perhaps to unusually high temperature resulting from external potting.

Non-oxidizable separator is needed. The results show that Teflonation, extended edges and contouring are effective in lengthening the life of the negative.

Cells were stored in the formed but discharged condition; other cells were stored green and wet down with zincate. After standing for one year the cells were cycled on a 40% depth of discharge, 6 hour regime. There was little difference between the two groups, but cycle life was lower than for cells cycled without wet shelf.

A statistically designed experiment with mercury content, depth of contours and superpressed edges as the parameters has been started. Results up to cycle 136 indicate that increased depth of contour is the most significant of the three parameters.

Construction of the ten cells for delivery to ECOM is under way.

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2. BACKGROUND

The purpose of this program is the development of a stable zinc electrode capable of cycling over a variety of current densities to fairly deep depths (62.5% D.D.) over long periods. The ultimate goal of the program is an electrode capable of 500 cycles to 60% of the cell's rated capacity at the C/5 discharge rate, at 80°F. The design goal is an electrode of this type, capable of 750 cycles.

The energy density of the silver-zinc battery constructed with this electrode should be:

Rate	Temperature (°F)	Wh/lb	Wh/in^3
C/5	80	40	3.5
C/5	-20	8.5	0.75
2C	80	35	3.1

In addition to the operational characteristics, the battery should have a charge retention, after 7 days, of 100% of rated capacity at C/5, for storage at 80°F, and 75% of rated capacity at C/5, for storage at 160°F.

3. SUPER-PRESSED ELECTRODE 10 AH CELLS

To check the consistency of cells cycled to date three 10 AH cells were constructed. These cells had sculptured zinc electrodes. The zinc plates consisted of the following mix: 94% ZnO + 5% Teflon + 1% HgO. The cells were wet down with 42% KOH which contained 80 mg ZnO/ml KOH. The cells were formed at the 20 hour rate and were given two hours of overcharge after the cell voltage reached 2.05. The cells were cycled on a six hour regime, consisting of a 3.5 hour charge at 1.9A to a 2.05V cut-off, followed by a discharge at 2.5A for 2.5 hours. The cells were discharged periodically at 5 A to 1.0 volts/cell to establish capacity. The capacity data for these cells are shown in Table 1 and Figure 1.

TABLE 1

Discharge Capacities for Cells Containing Contoured Zinc Electrodes

Nominal 10 AH 6 hour, 62.5% D.D. Regime

Cycle No.	Capacity (Ah) for Cell Number		
	120	121	122
30	12.5	12.5	15.0
58	12.5	10.0	15.0
82	11.9	8.3	13.3
130	10.5	7.8	12.7
187	9.8	7.5	11.9
230	9.4	7.5	11.0
258	8.0	6.0	10.0
281	6.9	6.9	8.7
310	8.1	8.1	8.8
338	8.0	6.5	8.75
380	6.7	6.7	8.0
418	7.0	7.0	8.6

Cell #122 shorted at Cycle #419, cell #121 at cycle #436 and cell #120 at cycle #456. A teardown analysis was made of these cells. In all cases it was found that considerable attack occurred at the top of the separator folds. The separator in this region was weakened by oxidation. This decomposition of the cellophane caused shorts to occur at the top of the cell plates. Shape change was not severe and the usual thickening of the zinc plates towards the center did not occur.

Since there was some difficulty with cell cases cracking during the early part of this program these cells had been inserted in a larger case and potted in with clear epoxy. Apparently this potting reduced heat dissipation by the cells. The result was that the cells ran hotter than usual during cycling. Hence, oxygen attack on the top of the separator folds was accelerated. This adiabatic condition is more representative of battery operation than of single cell operation.

These results point clearly to the necessity for use of a non-oxidizable separator since at this point the zinc electrode is no longer the limiting factor in the life of the cell.

When a teardown analysis was made of cell #121, it was found that two of the negatives in the cell pack center were shifted upwards. This apparently occurred during cell fabrication. This misalignment of positives and negatives accounts for the low capacity of cell #121 throughout cycling. The capacity-cycle data for cell #120 were essentially the same as those found for cells #76A and #76B, while cell #122 had somewhat higher capacity. These results indicate that the various modifications in zinc electrode construction made to date, i.e., Teflonation, extended edges and contouring have resulted in significant reproducible improvements in zinc electrode performance.

3.1 Long Term Wet Stand Study

As part of this program, a limited long term wet stand study was made. Four 16 AH cells were constructed for this purpose. These cells were of a tall design. The positive and negative plate lateral dimensions were 1-29/32" x 3-1/8". The cell pack consisted of six positives and seven negatives. The positives were bagged in one layer of 0.005" Pellon interseparator. The main separator was five turns of silver treated PUDO-300 (DuPont). All cells were filled with 40 cc of 42% KOH which contained 80 mg/ml ZnO. The negatives used in these cells did not have extended edges and were not contoured but were Teflonated. Two of the cells were given three formation cycles and then discharged to zero voltage. The other two cells were left in the "green" condition. All cells were fitted with Bunsen valves and stored for one year at room temperature. During storage one of the formed cells cracked due to crazing of the plastic cell case. At the end of one year the remaining three cells were put on a six hour cycling regime consisting of a 1.9 A charge for 3.5 hours and a 2.5 A discharge for 2.5 hours. This regime amounted to about a 40% D.D. discharge regime. The capacity-cycle data for these cells are given in Table II and Figure 2. Cells 7 & 8, stored unformed, gave better results than cell 6 through the cycling period. However, the data are inadequate for judgment as to preference for either method of storage.

Although these cells are being cycled on a shallow depth regime, their capacity maintenance is only fair. Furthermore the end electrodes appear to have undergone considerable shape change. In comparing performance of these cells with other cells constructed later on in this program the advantages of squat design, extended edges and contoured negatives become apparent.

TABLE II

Capacity Cycle Data for Cells in Wet Stand Study

Cycle No.	Capacity in Ah			
Cell No.	5	6	7	8
Stored	Formed	Formed	Green	Green
Formation Cycle 2	---	---	12.0	12.0
Cycle 2	18.0	18.0	---	---
21	12.5	17.0		17.0
50	Cell	16.5	20.0	20.0
91	Case	15	17.5	17.5
	broke			
130	during	13	15.0	16.7
151	stand	12.5	14.5	16.7
176		13	14.3	17.0
207		10	10.5	15.0
231		9.2	9.8	13.8
256		10.7	9.1	13.7

3.2 The Contour-Superpress-Mercury (CSM) Experiment

As a final evaluation of the best combination of factors that have shown promise during the course of this work the following statistical equipment was set up. The variables under investigation are the following: degree of amalgamation, depth of depression in contoured electrodes, and superpressing of contoured electrodes. Table III

TABLE III

CSM Experiment-10Ah Cells

Design	A	B	C	D	Parameters
HgO Content	-	+	-	+	+1% -0.5%
Contour Depression Depth	-	-	+	+	+0.047" -0.027"
Superpress	+	-	-	+	+yes -no

gives the designs and the numerical values of the parameters that were varied. The positives, the amount of edge-extension of the negatives and the separator system were kept constant and were similar in construction to other 10 Ah cells cycled in this program.

Table IV and Figure 3 give the cycle capacity history for these cells. The results to date indicate that the most important parameter is the depth of the depression. The deeper depressions give higher capacity plateaus.

TABLE IV

Cycle Capacity Data for CSM Experiment Cells

	Cell Capacity							
Design	A		B		C		D	
Cell #	128	129	130	131	132	133	134	135
Cycle # 10	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
32	14.0	13.4	13.2	13.5	13.4	13.4	13.7	13.7
54	14.0	13.7	13.5	13.6	13.6	14.0	14.0	14.1
88	12.8	12.0	11.9	11.8	12.3	12.8	12.8	13.3
111	12.3	11.6	11.7	11.3	12.0	12.5	12.5	13.1
136	11.8	11.0	11.3	10.8	11.5	12.5	12.3	13.3

Calculation of F Ratio for the

Contour, Superpress, Mercury Test

Using the data of Table IV

C^- 44.9, S^- 46.1, M^- 46.8

C^+ 49.6, S^+ 48.4 M^+ 47.7

$(C^-)^2$2016.01, $(S^-)^2$2125.21, $(M^-)^2$2190.24

$(C^+)^2$2460.16, $(S^+)^2$2342.56, $(M^+)^2$2275.29

Σx 94.5, $\Sigma x^2$1121.25, $(\Sigma x)^2$ 8930.25

$\frac{(\Sigma x)^2}{8}$1116.28, SS_c2.76, SS_s0.66, SS_m0.10, SS_T4.97, SS_E1.45

Error $_{MS}$0.36

F Ratios	
C	7.63
S	1.82
M	.28

The 95% confidence point for $F_{.05}(1,4)$ is 7.71.. Only the ratio for the contour depth approaches this value. The 90% point is 4.54 and the 75% point is 1.81. Obviously, then, the capacity difference attributed to superpressing could occur once in four trials in a normal distribution.

The difference between C+ and C- indicates an advantage of about 10% for the deeper contour (.047). Superpressing appears to afford a 6% increase in capacity but as pointed out above, the increase may well be due to chance. Increasing the mercury content gives little if any advantage.

4. CONCLUSIONS:

Contouring, extension of edges and incorporation of 5% Teflon extend the life of zinc negatives beyond 400 cycles on a 6 hour, 62½% depth of discharge regime. The mode of failure, disintegration of the silver-treated cellophane separator at the top, shows that the zinc electrode is no longer the limiting factor in the life of the silver-zinc cell. It should be noted that the drawing of this conclusion is justified only for small electrodes on which the effect of contouring has been demonstrated. It is not known as yet whether contouring is feasible and advantageous for large electrodes.

The disintegration of the top of the silver-treated separator indicates that silver oxide is not the principal causative agent, though attack on the separator below the electrolyte surface shows that silver oxide is a major factor. These results point up the need for a more oxidation-resistant separator.

Sparse data on wet shelf for 1 year indicate little advantage for storage in unformed condition. The test consisted of 40% depth of discharge on a six-hour cycle. The extent of visible shape change on the end negatives and rate of loss of capacity were greater than for cells cycled immediately after wetting down.

Contouring of a 73 mil plate to a center depression of 47 mils is preferable to one of 27 mils so far as capacity retention is concerned. Superpressing may present some advantage in this respect but this is questionable. Capacity retention is not sensitive to the difference between mercury contents of 1% and 0.5%.

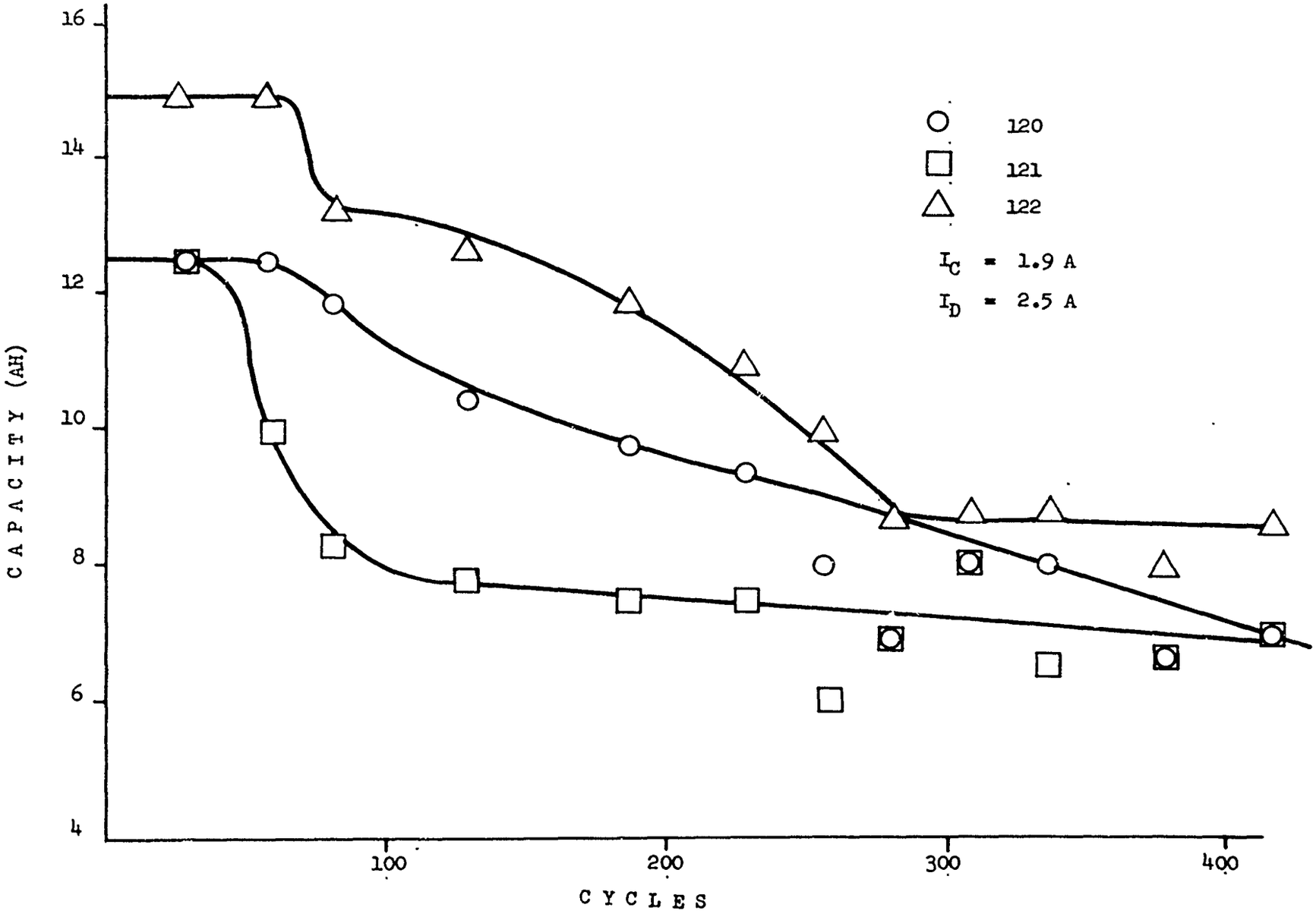

Figure 1. Capacity vs. Cycle Life for 10 AH Contoured Negative Cells

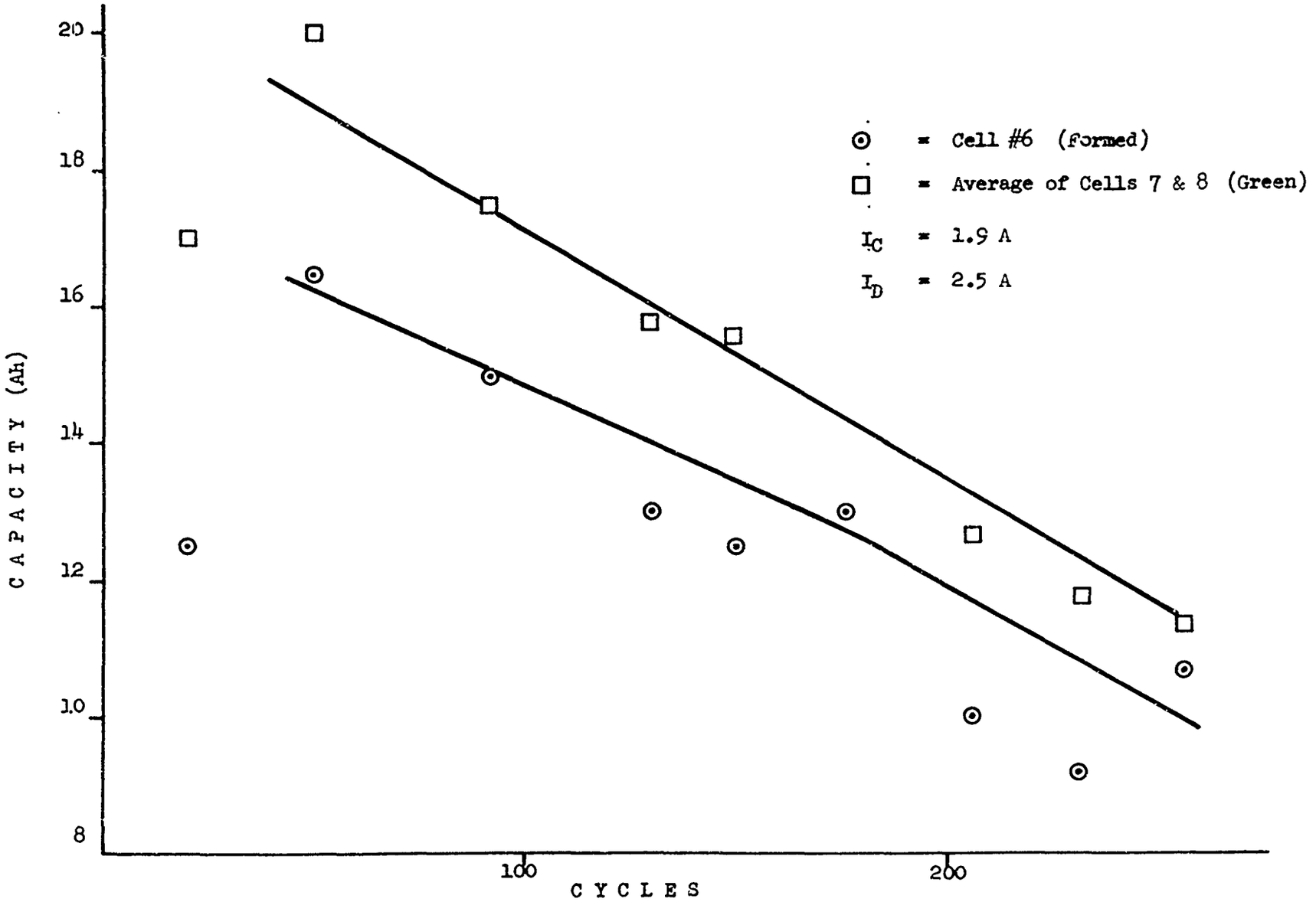

Figure 2. Capacity vs. Cycle Life for Wet Stand Study Cells

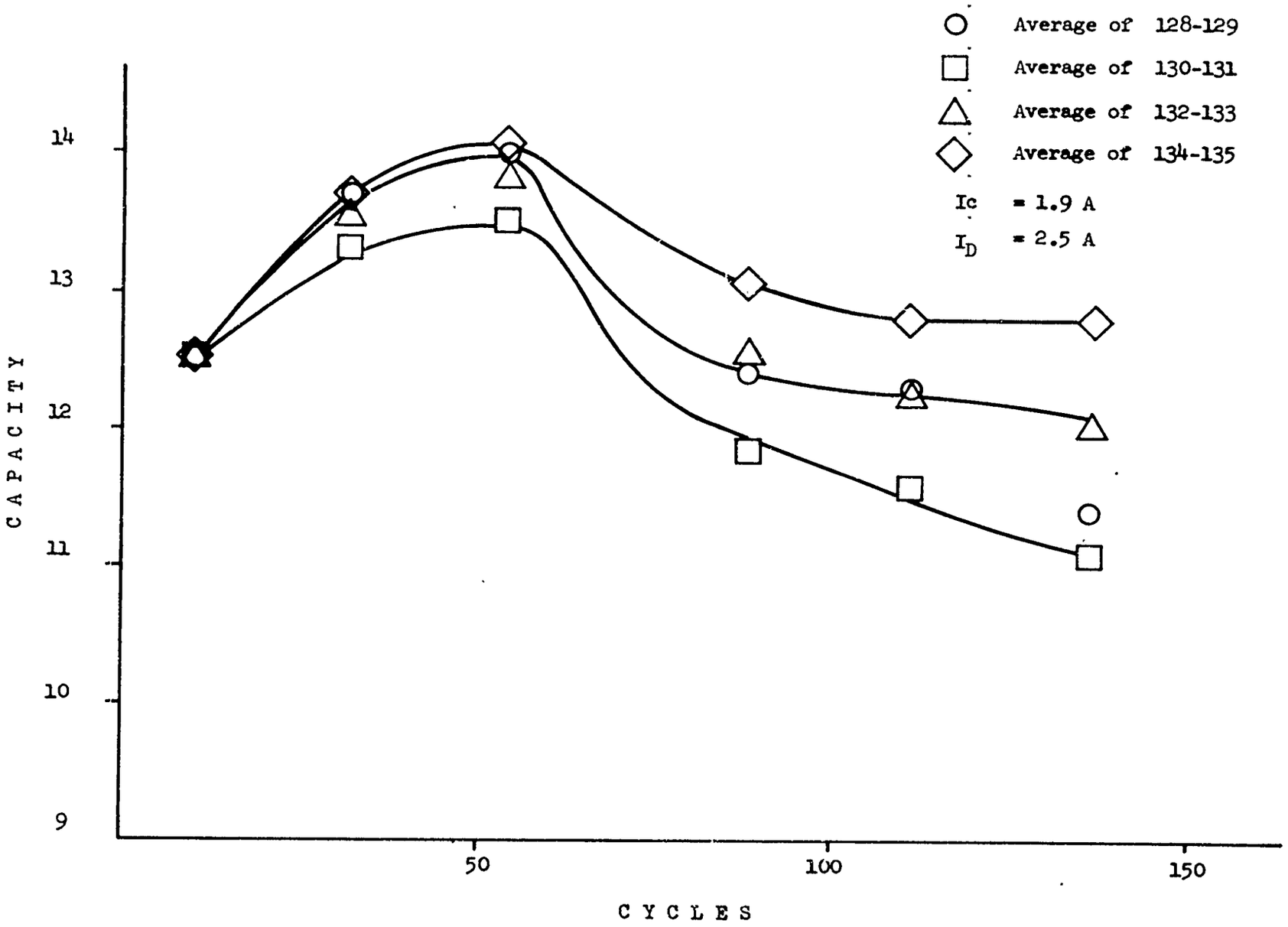

Figure 3. Capacity vs. Cycle Life for CSM Experiment Cells

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13. ABSTRACT

Cells made with 5% Teflon, contoured negatives, and extended edges gave more than 400 62½% depth of discharge, 6 hour cycles before shorting. Failure was due to disintegration of the cellophane separators at the top. Oxidative attack was severe, due perhaps to unusually high temperature resulting from external potting.

Capacity of one cell was lower than the others due to some misalignment of the plates.

Cells were stored in the formed but discharged condition; other cells were stored green and wet down with zincate. After standing for one year the cells were cycled on a 40% depth of discharge, 6 hour regime. There was no difference between the two groups, but cycle life was lower than for cells cycled without wet shelf.

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