HEAT STERILIZABLE IMPACT RESISTANT CELL DEVELOPMENT

JET PROPULSION LABORATORY
CONTRACT NO. 951296

REPORT FOR THIRD QUARTER, 1969
JULY 1 TO SEPTEMBER 30, 1969

ESB, INCORPORATED
THE CARL F. NORBERG RESEARCH CENTER
Yardley, Pennsylvania

EXIDE MISSILE AND ELECTRONICS DIVISION
Raleigh, North Carolina

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ABSTRACT, CONCLUSIONS AND RECOMMENDATIONS

Electrochemical studies during the third quarter of 1969 covered three areas: the embrittlement of silver grids, life cycle testing of cells, and tear-down inspection of failed cells. Grid embrittlement of both positive and negative grids is related to the redistribution of negative active material with cycling. The positive grid becomes brittle in the center probably because the negative active material accumulates opposite it and works that portion of the silver electrode to the extent that some of the grid is converted to active material. The negative grid is embrittled by this redistribution of zinc probably because the mercury appears to follow it. Thus, only that portion of the grid covered with active material is brittle. For cells that have been cycled a limited number of times the grids appear to remain flexible if the cells are left in the charged condition either on stand or float for several weeks or longer. This could be due to the partitioning of available mercury between the small mass of the silver grid and the large mass of charged zinc. Cells in the discharged condition have little zinc to hold the mercury and thus more mercury is available to embrittle the silver.

At the beginning of the quarter cells on life cycle included those with pressed powder negatives made with and without Teflon powder, those with negatives made with lead plated negative grids, those with negatives made from sheets of MPR active material, and those made with normal cell packs inserted in cases with differently shaped cavities. The cells with pressed powder negatives are still on test. Of the others lead plating had little effect on cycle life as did the use of MPR active material (plastic bonded zinc electrodes). The MPR electrodes, however, held their shape very well. The exaggerated shapes of the cell cavity were without effect on cycle life, but the results of tear-down inspection indicated that the normal redistribution of zinc to the bottom of the electrode may be due more to the case being tighter at the bottom than to the effect of gravity. A case which was smaller at the top than at the bottom caused the zinc to accumulate at the top. Tapered sleeves or shims inserted into regular cases could be used to maintain uniform distribution of active material.

ABSTRACT, CONCLUSIONS AND RECOMMENDATIONS (continued)

Five AH cells, having a 6L GX separator system, sterilized in a bomb then sealed, were floated in parallel for 17 months at 1.97 volts after which discharge efficiency was 0.30-0.37 at the 3-hour rate of discharge. Similar cells with 8L GX, some cycled before heat sterilization, some after HS, and others before and after HS, were stored on charged stand at 25°C for 7-10 months. Capacity losses ranged from 3.4 to 4.1% per month and were lower for cells with negatives containing compound 232-43. Float storage is preferred over charged stand.

Ten AH cells having 6L GX were heat sterilized sealed, then cycled at 50% DOD on a 21 hour charge/3 hour discharge at 25 ± 4°C to failure of 4 of 6 cells. Cause of failure was growth of zinc up non-insulated lead wires. Cycle life was 74-83 cycles in 5.5-6.5 months. No less than 8L GX appear necessary for a reliable 90 cycles after interplanetary travel of 8-9 months. Real time mission testing will be essential to verify designs should a contract stretch-out occur.

Tensile yield strength of unannealed silver sheet, normally 45-52 ksi, is decreased to 25 ksi by heat sterilization 72 hours at 135°C and to 14 ksi by sintering one hour at 325°C. Amalgamation has no significant effect on yield strength at a level of 0.1 mil in 10 mils of thickness.

Sixteen AH cells sterilized 100 hours at 135°C and cycled at 100% DOD for 16 cycles exhibit increasingly greater capacity loss as the ZnO/Ag active material weight ratio decreases from 1.5 to 0.9. Ratios above 1.2 do not at this cycle life appear warranted.

Seventy AH cells of prototype design have been delivered to JPL for environmental shock, vibration, and acceleration tests. Typical discharge performance at rates from 2 amps to 70 amps is included.

Twenty-five AH cells of medium cycle life design have been tested at 50% DOD to failure on a 10-hour charge/2-hour discharge routine in five different designs. Best cycle life after heat sterilization was 168 cycles in the design having a separator system of 1L Pellon 2530W, 7L GX membrane, a positive wrap, and high density negative plates. Cells having a pretest of 3 100% DOD cycles before and after heat sterilization 72 hours at 135°C failed at 83-98 cycles. It is recommended that pretest discharges be limited in depth and frequency unless this apparent degradation of cycle life with pretest can be eliminated.

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I. INTRODUCTION

The major portion of time during the third quarter of 1969 was spent on studying the embrittlement of grids, cells on life cycle and tear-down inspection of failed cells. Mercury and hence grid embrittlement appeared to follow the redistribution of zinc active material during cycle life. It was found that even the grid of the silver electrode was weakened by this redistribution. Negative grids appeared to be flexible when cells were stored for several weeks in the charged condition on either stand or float.

Cells on life cycle, described in earlier reports, included those with negative electrodes made by the pressed powder technique with and without Teflon powder; those with negative electrodes made on lead plated grids, and those with negative electrodes made by hot pressing sheets of MPR active material onto the silver grids. Another series of cells on life cycle consisted of normal cell packs inserted in cases of three different shapes to determine the effect of the shape of the cell case cavity on cell parameters.

Most of the above mentioned cells have now failed and tear-down inspection has yielded additional information on these systems. Inspection of the grids, both positive and negative, of all cells has helped to clarify the grid embrittlement problem.

II. SILVER EMBRITTLEMENT

The purpose of this study was to determine the conditions under which mercury embrittles silver. The major variables considered were: time, cycle, formation charge, sterilization and amalgamation. In conducting this study two different experiments were performed. The first was done using sheet silver where as the second was with silver grids taken from negative electrodes.

A. Silver Sheet Study

In this phase of the study silver sheet was used to investigate amalgamation effects. Sheet was used rather than expanded grid for two reasons. First, the sheet is more adaptable to an overvoltage study to tie in overpotential with phase changes and secondly, it is easier to determine phase changes in a flat sheet using x-ray diffraction techniques.

The amalgamated sheet prepared by the electrodeposition of Hg from a HgI_2-KI solution was used in the determination of the phases present after amalgamation, after sterilization and after reamalgamation such as might take place in a preamalgamated grid which had been heat treated (sterilized) and preformed.

The data are presented in Table I. It can be seen that the γ phase which forms on amalgamation disappears following sterilization and an α phase takes its place. However, reamalgamation of the sterilized sheet produces additional γ phase material. This would indicate that sterilization should follow the formation discharge so as to develop as little γ phase as possible on the next cycle. The difficulty here is that brittleness has not yet been associated with any phase change. None of these silver sheets were brittle. This suggests that only the silver grid, which may be more cold worked, gets brittle. If this can be demonstrated, it may mean that sheet silver backbones and grids prepared by etching silver sheet may not become as brittle as expanded silver grids when they are amalgamated.

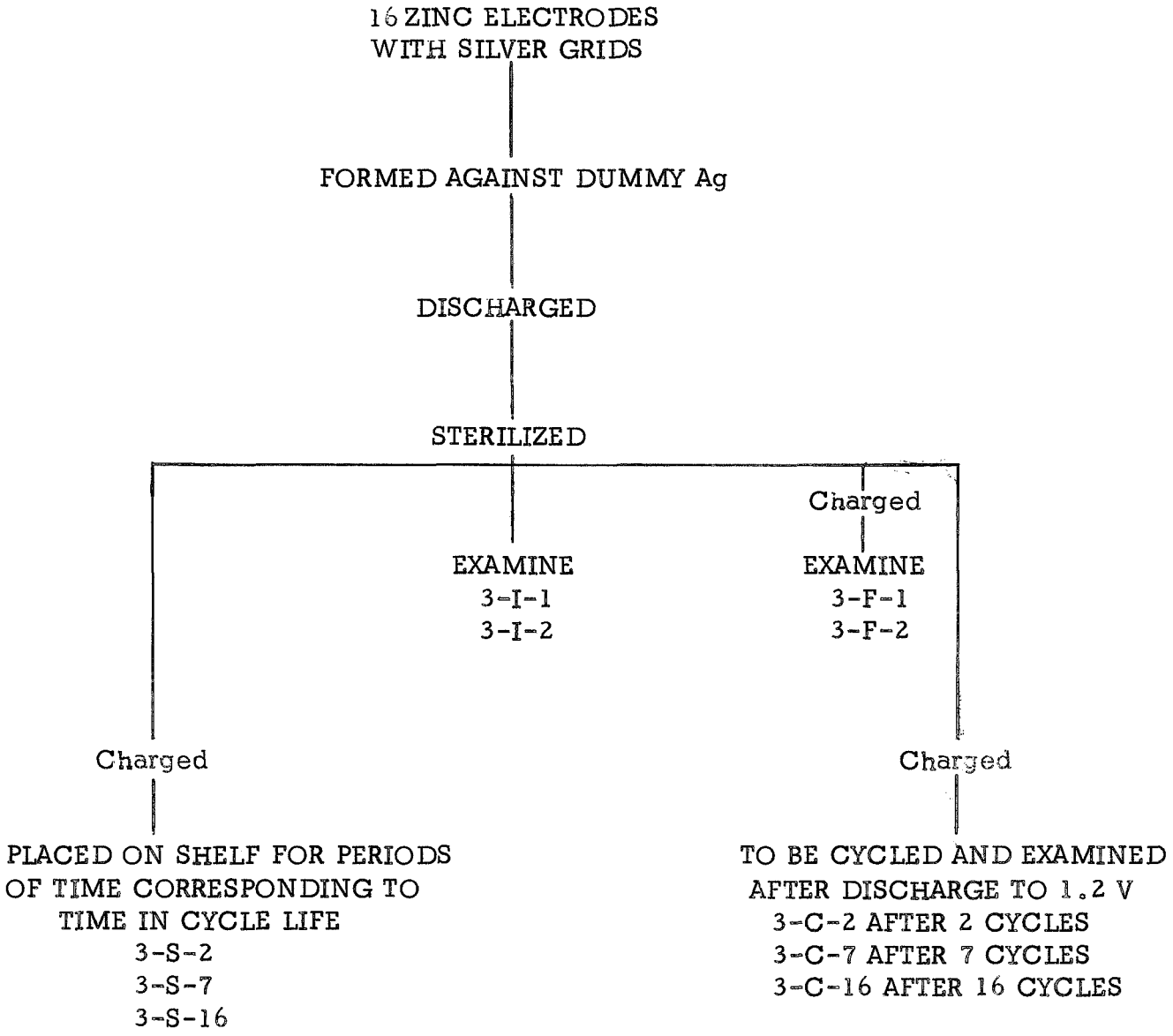
TABLE I

Grid Studies, X-Ray Analysis

Consecutive Treatment	Silver Sheet Sample 1	Silver Sheet Sample 2
Amalgamated	yes	yes
Sterilized	yes	no
X-rayed	yes	yes
α Phase	yes	no
β Phase	yes	yes
γ Phase	no	yes
Reamalgamated	yes	yes
X-rayed	yes	yes
α Phase	yes	no
β Phase	yes	yes
γ Phase	yes	yes

B. Grid Studies

Since silver grid material may respond differently than silver sheet to the embrittling effects of mercury, a second experiment was conducted to investigate the effects of formation charge, cycling, and stand on silver embrittlement. For this study 16 zinc electrodes (93% ZnO and 7% 323-43) were prepared. These were made into eight-3 plate cells using silver antipodes, SWRI-GX separation and 40% KOH nearly saturated with ZnO. These cells were charged by first converting the mercury with a long slow charging rate and then forming at 5.6 ma/in^2 to a cut-off of 2.05V. After discharging completely they were sterilized for 72 hours at 135°C. After sterilization one cell was disassembled and the two zinc electrodes submitted for analysis. The remaining cells were recharged and treated as shown in Figure 1.



Note: Each Sample Title
is Two Silver Grids
for S and C Series.

FIGURE 1

SECOND GRID EMBRITTLEMENT EXPERIMENT

Analysis consisted of x-ray diffraction which was used to see if there were any phases present which could be associated with brittleness. The center portion from all grids was examined by x-ray diffraction because embrittlement occurred there most often. The generally flexible area surrounding the brittle center portion was also examined by x-ray diffraction for comparison. Whenever the center portion was found to be flexible, the boundary area was not x-rayed.

Samples of the grid, both brittle center portions and flexible edge areas, were submitted for examination by light microscopy. Remaining pieces constituting a nearly total grid were submitted for chemical analysis. The nearly whole grids were analyzed for metallic zinc and total mercury after treatment with hot dilute ammonium chloride. The ammonium chloride treatment was necessary in order to remove any adhering zinc oxide.

Electrodes for grid analysis and inspection were taken from the cells in either the charged or discharged condition as indicated in Figure 1. In general electrodes from cells to be cycled 0, 2, 7, and 16 times were sampled in the discharged condition, whereas those on stand for similar periods of time were sampled in the charged condition. The active material was removed and the grids analyzed.

No correlation was found between brittleness of the grid and phases detected either by x-ray diffraction or light microscopy. Also there was no correlation with total mercury in the grid. This may be due to the method of analysis which solubilized both the silver grid and any tightly adhering metallic zinc which had plated out on the grid. The mercury determined, therefore, was a composite of that amalgamated with the zinc layer as well as that amalgamated with the silver.

An apparent correlation between brittleness and treatment of the grid was observed. In Figure 1 it may be reasoned that the F series is zero time for the S series and the I series is zero cycles for the C series.

Brittleness seemed to increase with cycling. Sample 3-I-1 was not brittle whereas 3-I-2 was. Sample 3-C-2 had a slightly brittle center, 3-C-7 a brittle center, and 3-C-16 a brittle center with a slightly brittle edge. The duplicate for 3-C-16, however, had a slightly brittle center.

Brittleness seemed to decrease with stand. Samples 3-F-1 and 2 had brittle centers whereas with samples of 3-S-2, one had a brittle center and the other had not. All samples of 3-S-7 and 3-S-16 had flexible center areas and edges.

The decrease of brittleness with stand time appears to be in the proper order but the sample size is rather small to form a sound conclusion. However, these findings have been substantiated for grids of cells which have been on charge-float for up to two years.

The working hypothesis which emerged as a result of this study is one involving the diffusion of mercury. When the zinc electrode is in the charged state the mercury is partitioned between the small mass of the silver grid and the large mass of the charged zinc. With a cell early in its life cycles the level of mercury in its grids is evidently not sufficient to cause brittleness. As the electrode is discharged the mercury does not discharge but stays with the metallic zinc and recedes toward the grid as the zinc is oxidized. This raises the concentration of mercury in the remaining zinc. The partition of the mercury between the grid and the remaining zinc is shifted so that the mercury concentration in the silver grid now is sufficient to embrittle it.

This same picture fits the observation made during tear-down inspection for the redistribution of zinc at the end of cycle life. As zinc accumulates in the center and lower half of the electrode the mercury recedes to follow the zinc mass. The edges and top half of the grid which is free of active material is flexible. Because much zinc is lost from the electrode by falling to the bottom of the case, the concentration of mercury is increased in the zinc which remains. Again, it is an observed fact that this portion of the grid is brittle especially when the electrode is in the discharged state.

If this picture of grid embrittlement be correct, then it would follow that for maximum grid ductility the cell should have negatives containing a minimum of mercury, should be early in its cycle life and should be maintained in a charged condition.

III. LIFE TESTING OF CELLS

During this quarter no new cells have been added to the data acquisition system for life cycle testing. Those that were on test at the beginning of the quarter covered four areas of interest, namely: cells with pressed powder negatives, cells with lead plated negative grids, cells with MPR negative electrodes, and cells of the usual construction placed in three differently shaped cavities.

Cells with pressed powder negatives were of two types: with and without Teflon powder. Those without consisted of five 9-plate cells of the 281 type which contained 4% 323-43. After the cells had completed three two-stage

cycles to characterize them, they were placed on life cycle at a 50% depth of nominal (4.5 AH) capacity. These cells have now completed 125 cycles except for cell 566-57-19 which failed after 83 cycles. Characterization data shown in Table II indicate a capacity decrease of the cells in the second cycle which also prevailed into the third cycle with the exception of cell 566-57-22. This cell improved in capacity (0.30 AH/g Ag) sufficiently to recover the second cycle loss.

Those cells with Teflon were constructed with the same parameters as those without except that the negative electrodes contained 2% Teflon powder. After the characteristics of these five cells were established by two two-stage cycles, they were placed on automatic cycle equipment at 50% d.o.d. They have now completed 90 cycles of nine hours charge and three hours discharge.

The two 7-plate cells containing lead plated grids which were described in the last quarterly report (Report for the Second Quarter of 1969, JPL contract 951296) have failed after 143 and 165 50% d.o.d. cycles. Of the two control cells one failed after 124 cycles whereas the other is still cycling after 190 cycles. In this limited test it would appear that the lead plating had little effect on cycle life. It did, however, cause initial low capacity which improved with cycling.

The MPR negative electrodes (plastic bonded zinc electrodes) were constructed and tested in six 7-plate cells as described in the Second Quarter report. Cells 1, 2 and 3 were sterilized whereas the others were not. The best cells (3,5 and 6) had a cycle life of about 105 cycles at 100% d.o.d. This life is about normal as compared with pressed powdered electrodes cycled similarly. Additional information may be found under IV, Tear-Down Inspection.

The 7-plate cells with tapered cell cavities, also described in the Report for the Second Quarter, have failed after about 185 cycles at 100% d.o.d. based on a nominal capacity of 0.21 AH/g Ag. This nominal value was chosen because all cells in this group developed low capacities while on stand awaiting space on the automatic cycler and the use of the nominal value of 0.25 AH/g Ag would be unrealistically high.

The impedance values taken at the end of charge of these cells have not changed from the original values which averaged about 0.05 ohms.

IV. TEAR-DOWN INSPECTION

Since this work under electrochemistry is drawing to a close, cells which had been set aside for inspection and cells which failed on life cycle were post

TABLE II

Cycle Data of Sterilized Then Sealed Ag-Zn Cells (1)

	566-57-18	566-57-19	566-57-20	566-57-21	566-57-22
Cycle No. 1					
AH/gram Ag Input	.41	.40	.41	.41	.38
AH/gram Ag Output	.32	.31	.31	.31	.29
Cycle No. 2					
First Stage Charge Capacity (AH)	4.82	4.70	4.88	4.82	4.64
Second Stage Charge Capacity (AH)	2.01	2.06	1.83	1.99	1.82
Net Charge Capacity (AH)	5.76	5.69	5.64	5.74	5.50
First Stage Discharge Capacity (AH)	4.09	3.94	3.99	4.02	3.86
Midvoltage	1.44	1.44	1.44	1.44	1.42
Second Stage Discharge Capacity (AH)	.55	.35	.65	.19	.54
Total Discharge Capacity (AH)	4.64	4.29	4.64	4.21	4.40
Output/Input	80%	75%	82%	74%	80%
AH/gram Ag Discharge	.26	.24	.26	.24	.25
Cycle No. 3					
First Stage Charge Capacity (AH)	4.39	4.12	4.57	4.07 (2)	4.48
Second Stage Charge Capacity (AH)	2.14	2.06	1.67	-	1.68
Net Charge Capacity (AH)	5.14	4.79	5.18	2.68	5.20
First Stage Discharge Capacity (AH)	4.50	4.54	4.35	1.50	4.92
Midvoltage	1.43	1.43	1.43	1.40	1.41
Second Stage Discharge Capacity (AH)	.17	.13	.22	.11	.28
Total Discharge Capacity (AH)	4.67	4.67	4.57	1.61	5.20
Output/Input	91%	98%	88%	-	100%
AH/gram Ag Discharge	.26	.26	.26	-	.30

(1) Cells contained 4% Compound 323-43, and 8 layers of SWRI.

(2) Cell No. 566-57-21 was not recharged after the 20% mid stage discharge.

mortemed with emphasis on the condition of the negative grids and past history of the cell. The main parameters investigated were the degree of embrittlement and the shape change effect. Several trends have been observed but the data are not without contradiction. Rather than present several tables of data that do not lead to clear cut results, the salient features of the more than 100 cells examined will be discussed.

Cells with Tapered Cavities

The five cells with different shaped cases all failed around 185 cycles at 100% d. o. d. Therefore, no effect on cycle life could be discerned by the use of the different shapes. However, on post mortem several interesting differences were obvious. The most striking of these was the shape change of the negative plate. The usual observation with pressed powder electrodes after cycling is that the active material is missing at the top and most of the active material accumulates in the lower half of the electrode. For the first time as shown in Figure 2A for the cell with the narrow top, the position of the active material is exactly reversed. The active material accumulated at the top and not at the bottom. The failure of this cell was due to the loss of Ag capacity as can be seen by the fact that the Ag electrode was not discharged. This lack of ability for the Ag to be cycled seems to be related to the amount of pressure or tightness of the parts of the cell. Where there is good pressure between the positive and the negative electrode, the active materials tend to cycle; whereas in those regions where insufficient pressure exists, the active materials do not cycle.

A further observation is that contrary to what is commonly believed, the washing of the active zinc material may not be due solely to the effect of gravity, but as shown in Figure 2A, can be offset by appropriate pressure at the top of the electrodes. From these observations it is suggested that the shape change of zinc electrodes could be reduced by increasing the pressure at the top of the electrodes by the insertion of a sleeve which is tapered so as to counteract the normal tapering required when cell cases are molded. The cells used in the present experiment were exaggerated with respect to tapering and perhaps created other problems such as lack of uniform current density on the surface but the results clearly indicate that the concept of the shape of the case must be considered for a better understanding of the shape change of a zinc electrode.

Grid Embrittlement

No clear cut explanation for the embrittlement of Ag grids is available at this time; however, the recent post mortem of cells revealed several interesting trends. The first of these is that the embrittlement appears to be

greatest wherever the largest amount of active material and consequently, the highest concentration of Hg accumulates. For example, examination of grids shows that embrittlement follows closely the shape change. Usually when a Ag-Zn cell is cycled the Zn electrode erodes as shown in Figure 2B. The edges of the electrodes where the active material has been washed away are not as brittle as the center and lower portions where the active material has remained.

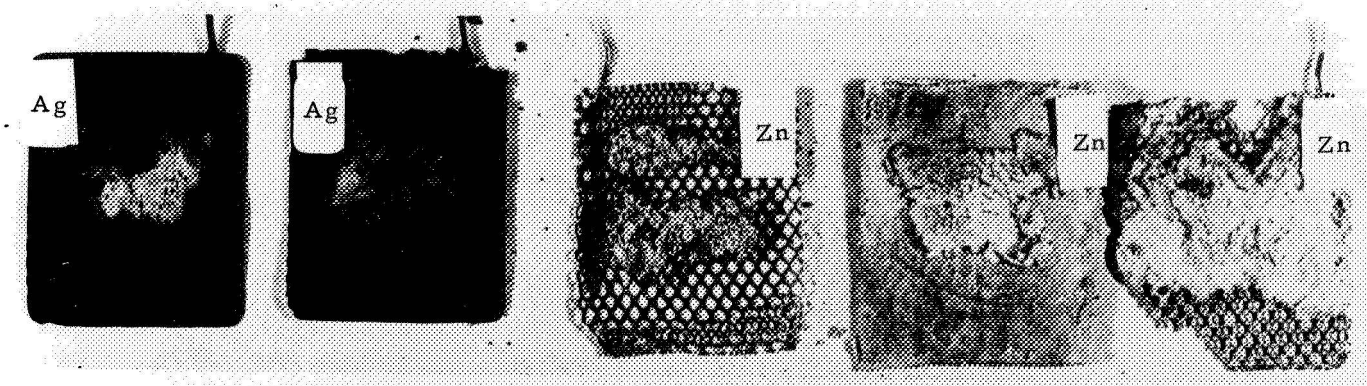
Post mortem of cells with grids that were lead plated showed that this did not solve the problem of grid embrittlement. However, these cells lasted as long as other cells on cycle life and consequently showed no bad effect of having lead present. This observation again points to the use of a mixture of lead and mercury for over voltage protection as a means of cutting down on the amount of mercury present. In other words, the post mortem of the lead plated cells showed no embrittlement of the Ag grid due to lead in those areas where there was no large build up of mercury and cell failure was due to loss of capacity rather than shorting due to Pb.

Another interesting observation as a result of the post mortem of the cells is one that has to do with the embrittlement of the Ag grid in the positive electrode. Again, the embrittlement tends to follow the pattern of the active material of the negative electrode. This phenomenon can be explained in a very simple way. The area of the positive electrode that cycles best is the area directly opposite to the negative active material. Hence when the active material of the zinc electrode concentrates in the lower half, the ratio of zinc to Ag is high at that area and hence forces the grid of the positive electrode to oxidize in trying to match the zinc capacity. Consequently, the positive grid has regions that have been converted to active material and hence is weak in structure.

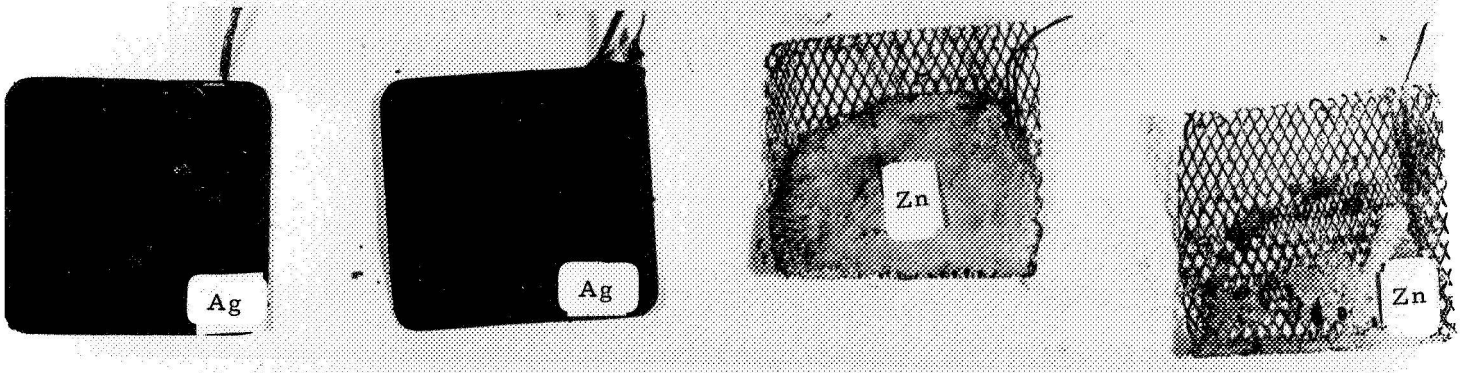
MPR Electrodes

The MPR electrodes were cycled at the same rate as other electrodes but they did not suffer any shape change. Typical electrodes after about 105 cycles at 100% d. o. d. are shown in Figure 2C. The zinc electrodes are in excellent shape, and judging from the appearance of the silver electrode zinc oxide is well enough distributed on the negative electrode to work the silver at the top.

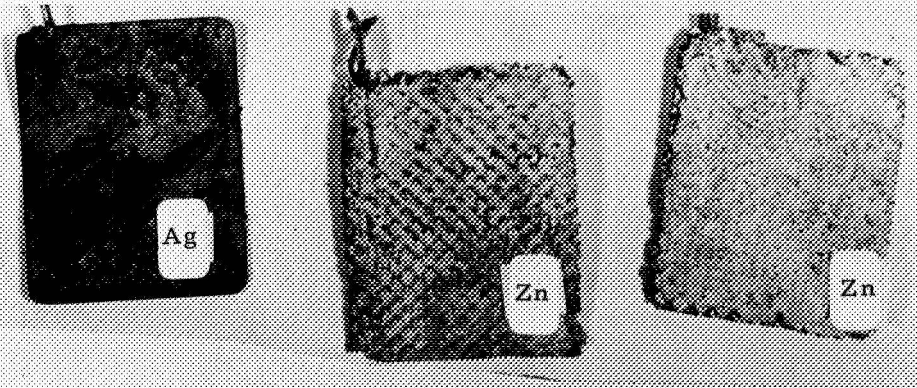
Admittedly these electrodes did not cycle as long as other electrodes but the formulation of the active mix had not been optimized. The mode of failure was loss of capacity which appeared to be due to islands of undischarged metallic zinc. This problem should be overcome by the addition of conducting materials, such as finely divided silver or graphite to the active mix. The MPR electrode deserves further consideration, if present electrodes do not meet the 400 cycle requirement.



A. Electrodes from Cell Shaped Like ⏢



B. Electrodes Showing the Usual Shape Change



C. Typical MPR Zinc Electrodes with Silver Antipode

FIGURE 2. DISCHARGED ELECTRODES AFTER CELL FAILURES

V. CELL TESTS BY ESB PERSONNEL AT JPL (TASK 1)

A. Long Term Float Tests.

Twelve 5 AH cells, sterilized in a bomb and then sealed in 1967, completed 17 months of parallel float at 1.97 volts at 25°C. Total float current was 5-10 ma for the 12 cells at time float was terminated. Table III summarizes the results. It may be concluded that parallel float 1.97 volts for 17 months followed by discharge efficiencies of .30 - .37 AH/gm Ag are feasible at the 3 hour rate. No cell shorts have occurred to date. Maximum pressure of 37 in. Hg was observed during entire test period.

B. Charged Stand Tests.

A group of 26 sealed-sterilized cells, some cycled before sterilization, some cycled after sterilization, and some cycled both before and after sterilization, were placed on charged stand for 7-10 months at 25°C and then cycled. Table IV summarizes the data showing mean capacity loss rates ranging from 3.4 to 4.1 percent per month at 25°C, values reasonably independent of whether cycling occurred before, after, or both before and after sterilization. These results are promising, - suggesting that pretesting cells will not adversely affect charged stand life.

C. Preliminary Cycling Tests.

Nine 5 AH cells representing three negative active material compositions, two separator systems (8 or 9 layers SWRI-GX, no absorber) three electrolyte compositions (41, 42, 44% KOH saturated with ZnO), and ZnO/Ag weight ratios varying from 1.05 to 1.17 were cycled after heat sterilization sealed for 72 hours at 135°C. Each cycle consisted of charge for 21 hours at 1.93 volts per cell in a series string with the current limited to C/20 and a 2.7 AH discharge in 3.0 hrs. through a constant resistance at 25°C. Prior to heat sterilization each cell had been cycled at least one 100% DOD cycle and let down. Capacity measurements made at intervals have revealed capacity losses on cycling as follows to date:

Cycle Number	Capacity, % of Original minimum (median) maximum
60	80 (93) 113
61	83 (91) 111
92	75 (78) 90
103	71 (80) 88

On the basis of these results additional cells have been constructed for cycling tests by JPL personnel as 10-cell batteries.

TABLE III
LONG TERM FLOAT TESTS ON 5 AH CELLS, 25°C

	Test Parameter	Test Data by Test Group		
1.	Group electrolyte concentration, %KOH	35	40	42
2.	Number cells	4	2	6
3.	Number of days on float in parallel at 1.97v	509-521	521	509-521
4.	Wet life in days after formation to end of float	594-603	604	594-612
5.	Open circuit voltage, volts 8 days after end of float	1.857-1.860	1.858-1.859	1.859-1.860
6.	Discharge capacity, AH, 3 hr. rate			
	before float: 1.30 volt TEV	6.11-6.33	6.21-6.76	6.22-7.15
	after float: 1.25 volt TEV	6.32-7.71	7.16-7.20	6.37-6.80
7.	Loaded voltage, 3 hr. rate, at 1.5 hr. - before float	1.38-1.42	1.37-1.40	1.36-1.41
	- after float	1.35-1.41	1.39-1.40	1.32-1.36
8.	Recharge capacity, AH at 0.1 ampere to 2.04 volts	7.45-6.09	7.13-6.46	6.65-6.11
9.	Discharge capacity, AH			
	• 1.8 amps to 1.25 volts	6.51-5.40	6.69-6.12	5.97-5.37
	• 0.4 amps to 1.25 volts	.44-1.19	.30- .43	.64-1.10
	Total: both rates	6.42-7.13	6.42-7.12	6.21-6.78
10.	Highest pressure during float and cycling, in Hg	25	13	37
11.	Efficiency after 17 months float, AH/gm Ag			
	3 hr. rate	.30- .37	.34- .37	.30- .33
	12 hr. rate	.36- .40	.36- .40	.35- .38

Notes: (1) 18g Ag each cell; 20g negative mix
(2) 8-10 100% depth cycles before float
(3) Separation: 6 layers SWRI-GX membrane
(4) Negative mix contained 7% Compound 323-43

TABLE IV
CHARGED STAND TESTS ON SEALED STERILIZED CELLS
25°C

Test Parameter	Cell No.	Cycled Before Heat Sterilization		Cycled After Heat Sterilization	Cycled Both Before & After Heat Sterilization
		Standard Negative	Negative with Compound 323-43		
Charged Wet Stand Period-days		319-329*	317-323	235	343
Capacity Before Stand	1	5.40	3.56	4.50	4.88
	2	5.23	3.60	4.51	4.73
	3	5.38	3.48	4.65	4.86
	4	5.48	2.83	4.72	5.37
	5	4.50	3.04	3.41	
	6	4.38	2.79	4.03	
	7			5.02	
Decrease in Capacity, %/day	1	.13	.19	.093	.16
	2	.10	.20	.059	.18
	3	.082	.16	.093	.050
	4	.13	.034	.12	.057
	5	.29	.11	.17	
	6	.085	.070	.17	
	7			.12	
Mean Loss at 25°C %/day		.14	.13	.12	.11
%/month		4.1	3.8	3.5	3.4

* Separator system: 8L SWRI GX, no absorber, no retainer

FABRICATION AND TESTING OF CELLS

I. DEVELOPMENT OF HIGH IMPACT 5.0 AH CELLS, TASK 9

A. OBJECTIVE AND PAST WORK

This task requires the development of 5.0 AH cells meeting the requirements of JPL Specification GMP-50437-DSN-C, high impact of 2,800 ± 200g from 115 ± 3 ft/sec., and JPL Engineering Memorandum 342-70. Thirty (30) cells for an 80 watt-hour battery are to be delivered in December 1969.

Non-high impact cells have delivered 11.0 AH at 3.3 amperes to 1.25 volts at 43 watt-hours per pound of sealed cell after 72 hours heat sterilization at 135°C. One high impact cell design with only Ag sheet plate structure survived 2400 "g" when assembled as a 12-cell battery by JPL into the C-SAD experimental spacecraft and drop tested in the desert. Zirconium positive plate cores and massive etched Ag grids have been proved necessary by stress analysis and shock tests to survive 2800 ± 200 "g" impact forces.

B. MODEL 281 CELLS ON AUTOMATIC CYCLING

Six 10 AH cells (non-high impact) were cycled in series at 50% depth of discharge on a 21 hour charge/3 hour discharge at room ambient to failure of the first 4 cells. The failing cells gave 74 to 83 total cycles in a wet life of 5.5 to 6.0 months. The cause of failure was found to be cell shorting through zinc moss growing up negative plate leads which were not insulated with tubing. Negative active material was 40-60% eroded from plate edges toward the center of the plates and toward the negative plate leads. Sintered teflon substrates were still intact over the entire plate area. A summary of the processing steps varied in manufacture and cycle life is presented below:

Cell S/N	Process Variable	Number of Cycles and Type			Wet-Life Months
		100% DOD	50% DOD	Total	
66	NT, NSB, NP	9	74	83	7.0
67	NT, NSB, NP	9	65	74	6.0 (S)
68	NT, NSB, NP	9	74	83	6.5 (S)
70	NT, SB, NP	5	74	79	6.5
72	NT, NSB, NP	5	74	79	6.0 (S)
73	NT, NSB, P	3	74	77	5.5 (S)

S = Cell short
NT = No plate lead tubing (RFN = 100 tubing caused gassing)
NSB = No sand blasting of seal areas; SB = sandblasted areas
NP = No platelock; P = 2.0 cc Epocast 221/927 epoxy platelock

It was concluded that plate lead tubing is vital to long cycle life to prevent zinc mossing up negative leads from shorting cell; also, sandblasting and the epoxy platelock do not reduce life significantly.

C. MODEL 281 CELLS WITH ZIRCONIUM REINFORCED POSITIVES

Two cells were constructed with positive plate cores of 10-mil zirconium sheet. Special care was taken to assure proper contact between silver active material and positive plate lead wires. No dependence upon zirconium as an electron conductive path was assumed. The two cells were preformed vented, sealed, heat sterilized 72 hours at 135°C and then given three 100% DOD cycles.

Cycle No.	Test Parameter	S/N78	S/N79
1	Charge Input, AH	8.66	8.76
	Discharge Output, AH	7.97	8.36
	AH/gm Ag	.34	.36
	Midpoint Voltage, volts at 3.3A	1.46	1.44
2	Recharge Input, AH	7.92	8.34
	Discharge Output, AH	7.84	8.34
	Midpoint Voltage, volts at 3.3A	1.46	1.43
3	Recharge Input, AH	8.01	8.49
	Discharge Output, AH	7.31	7.87

Discharges were 2 step: 3.3 amps to 1.25 volts, then 0.7 amp to 1.25 volts. On cycle 3 the low rate step was omitted; however, the higher rate capacities increased over the three cycles from a minimum 6.86 AH on first cycle to 7.87 on the third cycle.

No gassing was observed during heat sterilization or cycling. The use of zirconium reinforced positives therefore appears to be acceptable.

D. EFFECT OF HEAT TREATMENT AND AMALGAMATION ON STRENGTH OF SILVER SHEET

To survive 4,000 g shock, adequate tensile and buckling strength must be maintained in silver sheet plate reinforcements through all treatments prior to the landing shock. An experiment was conducted to measure the effect on the tensile strength of 10-mil Ag sheet of --

- mercury amalgamation (.0001 inch layer)
- sintering at 325°C for 1 hour dry
- heat sterilization at 135°C for 72 hours

Test specimens were machined to a tensile paddle configuration and then, after the specified treatment, pulled to failure on a Dillon tensile tester at a strain rate of 0.25 inch per minute. Table V data reveals the worst to least reduction in strength is attained from the treatments:

sintering > sterilization > amalgamation.

Electroplating a mercury coating of 0.1 mil (total for both sides) in 10-mil did not decrease silver sheet tensile strength significantly from pure Ag controls. It was concluded that a non-sintered negative process would have to be used in the high impact negative plates and that designs should include a maximum Ag yield strength of 34,000 psi.

TASK IX
TABLE V

STRENGTH OF TREATED SILVER SHEET TENSILE SPECIMENS

Sample No.	Treatments Before Test	Force to Yield (Lbs.)	Force to Failure (Lbs.)	Yield Strength (ksi)	Ultimate Strength (4) (ksi)
1	Controls-Material as received	225	225	45	45
2		250	250	50	50
3	Heat Sterilized (1)	130	170	26	34
4		125	155	25	31
5		125	165	25	33
6	Mercury Amalgamation only (2)	260	260	52	52
7		245	245	49	49
8	Mercury Amalgamation and Heat Sterilized	125	170	25	34
9		125	170	25	34
10		125	170	25	34
11	Mercury Amalgamation plus Sintered (3) plus Heat Sterilized	70	150	14	30
12		70	120	14	24

NOTES:

(1) All heat sterilization at 275°F for 72 hours.
(2) Amount of amalgamation = 0.0001 inch thick layer.
(3) Sintered dry in oven at 325°C for 1 hour.
(4) Ultimate strength based on original cross-section.

E. PROTOTYPE CELLS AND FUTURE WORK

Design and drawings for the Model 361 5AH high impact cells are complete. Molded parts are scheduled for delivery October 10. Negative plate etched grids are to be delivered October 6. After completion of acceptance tests on all parts, cell assembly will be released for 15 prototype units. Acceptance tests will include gassing studies on non-sintered negative plates after heat sterilization and preamalgamation.

II. DEVELOPMENT OF HIGH CYCLE LIFE 48 AH CELLS TASK 10

A. OBJECTIVES AND PAST WORK

This task requires development of wet heat sterilizable 48 AH cells meeting the requirements of JPL Specification 50436-DSN-B and delivery of 100 cells by April 30, 1970. Operational requirements include one year prelaunch storage, heat sterilization 72 hours at 135°C, launch, interplanetary cruise 9-months, landing (soft), plus 400 cycles of 50% depth of discharge with a 12-hour charge and discharge rates from C/10 to C/3. A factorial experiment has been initiated to optimize the design factors ZnO/Ag ratio, wet thickness of separator, teflonation level, and electrolyte composition.

B. FACTORIAL DESIGN CELL TEST

Twenty-seven 9 plate cells, each rated at 16 AH, were constructed using one lot of positive plates. Negative plate composition and thickness was varied to give ZnO/Ag weight ratios of 0.9, 1.2, or 1.5. Teflonation was varied at three levels: 5, 7, or 9%. PP0534-801 shims were inserted to control the mean SWRI-GX separator wet thickness after heat sterilization to 2.0, 2.4, or 2.8 mils per layer. Specific design factors allotted each cell were given in an earlier report.[1] All cells contained nine layers of GX wrapped in "U" fold array on the four full negative plates of each cell. During this quarter 16 cycles at 100% depth were completed. After heat sterilization for 100 hours at 135°C, discharge capacity data was analyzed for statistically significant effects appearing to date. The analysis performed by the School of Statistics, North Carolina State University in Raleigh is included as Appendix I. Significant effects were --

- Decrease in capacity measured by the formation discharge capacity minus the mean discharge capacities of cycles 4, 5, and 6 increased with decreasing ZnO/Ag weight ratio.
- The change in capacity from cycle 5 (mean of 4, 5, and 6) to cycle 15 (mean of 14, 15, and 16). Both effects may be summarized:

ZnO/Ag Ratio	CI-AV5 (AH)	AV5-AV15 (AH)
1.5	3.83	1.35
1.2	4.15	-.28
0.9	5.66	.89

C. FUTURE WORK

Cycling will continue through the next quarter. A second analysis will be performed at the 30-35 cycle point. Design decisions will then be made for the 48 AH full size cell.

III. DEVELOPMENT OF RECHARGEABLE PRIMARY 70 AH CELLS - TASK 11

A. OBJECTIVES AND PAST WORK

In this task wet heat sterilizable 70 AH Cells are being developed to meet the requirements of JPL Engineering Memorandum 342-71. The ESB Model 364 cell, now developed to the prototype stage, has been released for environmental tests at JPL to confirm capability for surviving after heat sterilization and formation cycling:

- Shock: five 200 g 0.7 ± 0.2 msec each direction three orthogonal axes (30 tests)
- Vibration: sweeping sine 1/2 octave per minute; 5 g 17 to 50 cps; 15 g, 50 to 100 cps; 35 g, 100 to 2000 cps.
- Vibration: random, 25 grms, 9 minute duration band limited 20 to 2000 cps
- Acceleration: 100g, 10 minutes, each of six directions

B. PROTOTYPE CELL TESTS

Cycling Before Heat Sterilization

Nine Model 364 prototype cells were constructed. Three were cycled with no heat sterilization through four cycles - charging at 1.5 amperes to 2.00 volts per cell and discharging at 2, 20, 35, and 70 amperes to 1.25 volts per cell. Figures 3A and 3B give typical discharge voltages and capacities for these cells before heat sterilization.

Effect of Heat Sterilization

Six cells were heat sterilized sealed for 72 hours at 135°C, then given a formation charge at 0.9 amp to 1.97 volts, a partial discharge, then recharge to fully form the plates, and finally a 100% depth discharge at 20 amperes to 1.25 volts. Individual cell data for the nine cells is given in Table VI. The effect of heat sterilization in formation cycle capacity is --

Test Parameter	Unit	Non-Sterile	Sterile
Mean Formation Charge Capacity	AH	104.7	99.7
n		3	6
s		3.66	3.86
Mean Discharge Capacity	AH	101.3	93.8
3		3.86	4.76

Student t tests for significances of the 4.8% decrease of charge input and the 7.4% decrease in discharge output show that only the difference in mean output is significant at the 95% level of confidence.

The six sterile cells were then recharged, potted into an aluminum chassis with Emerson-Cuming Epocast 1090 epoxy, and shipped to JPL for full environmental testing. The results of this testing will be available during the next quarter.

FIGURE 3A
TYPICAL 70 AH CELL DISCHARGE CHARACTERISTICS

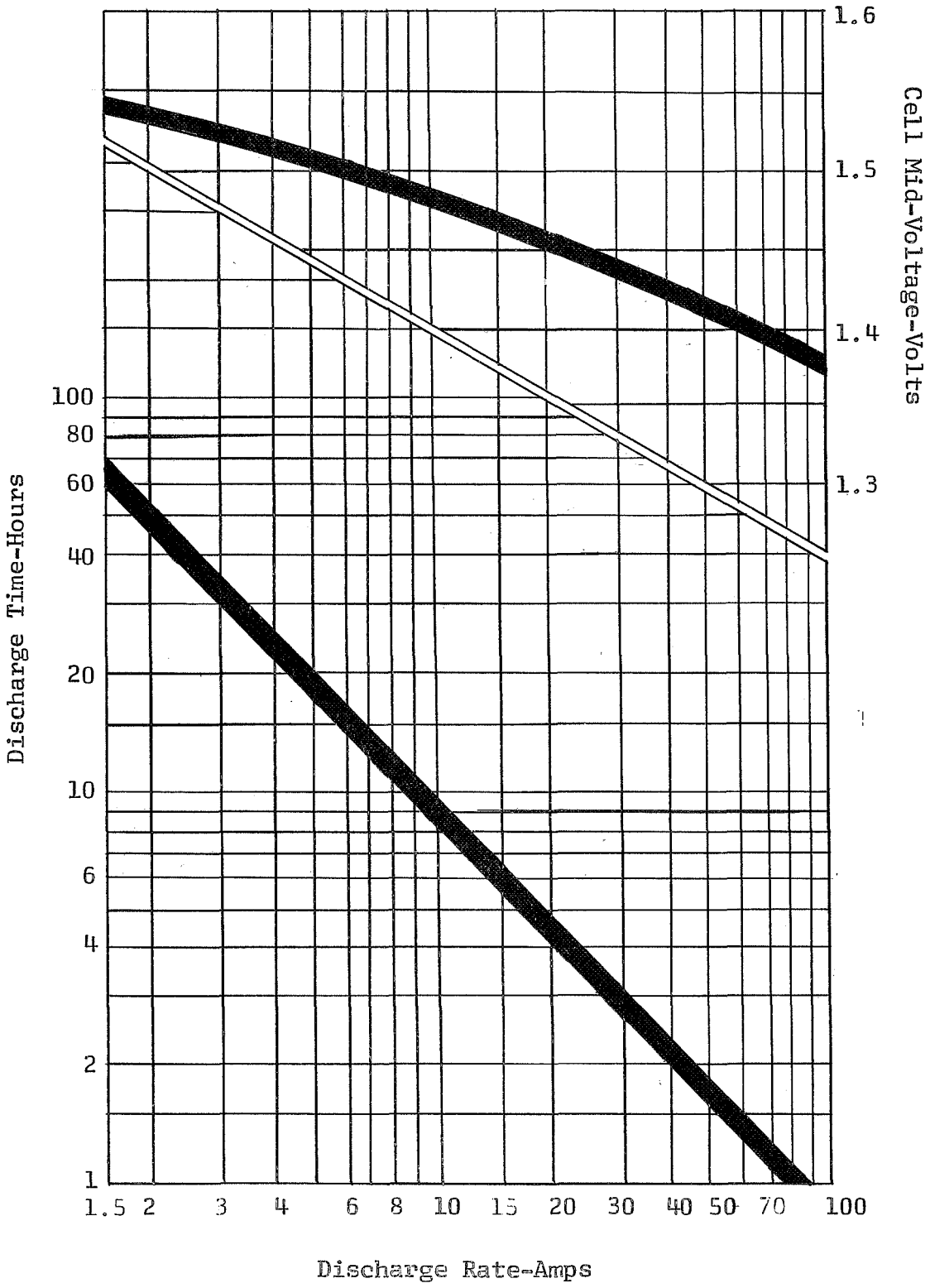


FIGURE 3B
TYPICAL DISCHARGE CHARACTERISTICS 70 AH CELLS
BEFORE HEAT STERILIZATION
ESB MODEL 364

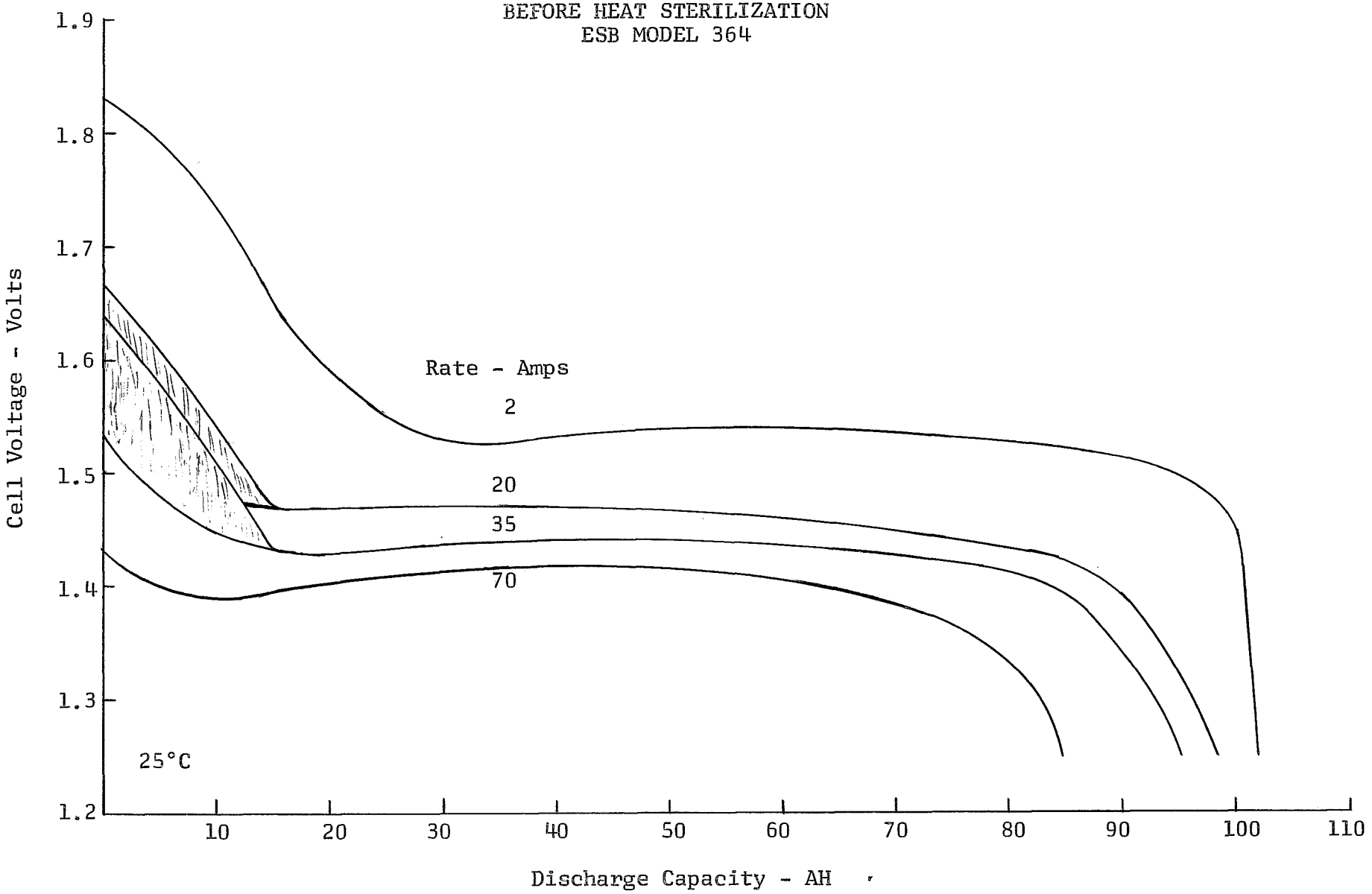


TABLE VI
CYCLING PERFORMANCE OF MODEL 364 PROTOTYPE CELLS

Test Parameter	Unit	Non-Sterile Cells			Sterilized Cells *					
		10	11	12	13	14	15	16	17	18
Cycle 1 (Formation)										
o Charge										
0.9 amp to 1.97 V	AH	88.0	88.9	88.9	71.8	75.4	75.4	88.0	75.7	75.7
Net Gain, Partial Cycle	AH	20.0	11.9	16.6	24.7	24.7	23.0	19.2	22.0	22.7
Total Input		108.0	100.8	105.5	96.5	100.1	98.4	107.2	97.7	98.4
Efficiency**	AH/g	0.435	0.405	0.425	0.384	0.403	0.396	0.432	0.393	0.392
Maximum Pressure		2	7	4	8	7	15	10	5	10
o Discharge										
20 amps to 1.25 V	AH	104.0	98.0	102.0	88.0	94.7	92.0	102.3	92.0	93.7
Efficiency	AH/g	0.419	0.396	0.411	0.354	0.381	0.370	0.412	0.370	0.377
Midpoint Voltage	volts	1.465	1.465	1.465	1.460	1.470	1.480	1.485	1.485	1.485
Cycle 2										
o Charge @ 1.5 amps to 2.01V	AH	99.4	99.4	97.6	82.3	92.3	92.3	86.0	82.3	82.3
o Discharge @35 amps to 1.25V	AH	95.5	95.5	94.5						
Efficiency	AH/g	0.384	0.384	0.380						
					Shipped to JPL for Environmental Testing 7-22-69					
Cycle 3										
o Charge @1.5 amps to 2.00V	AH	90.0	96.0	95.9						
o Discharge @2.0 amps to 1.25V	AH	96.2	102.0	102.0						
Efficiency	AH/g	0.387	0.410	0.410						
Cycle 4										
o Charge @1.5 amps to 2.00V	AH	91.5	91.5	91.5						
o Discharge @70 amps to 1.25V	AH	85.2	85.2	84.0						
Efficiency	AH/g	0.343	0.343	0.338						

* Heat sterilized 72 hours at 135°C sealed.
** Based on weight Ag active material in positions.

Sterilization After Cycling

The three non-sterile 70 AH cells were given a fifth cycle discharge at 20 amps to 1.25 volts, followed by a let-down through 0.4 ohms on each cell for 3 days. The let-down cells were then sterilized 72 hours at 135°C in clamps, simulating a battery chassis except that support was on broad faces only. Only one cell survived without leakage. One cell leaked around a polysulfone window cemented into a narrow wall for visual observation of electrolyte level. The other leaked through a crack which developed in a melt knit line in the PPO cell case. Electrolyte loss was 57 and 80 g in the leakers as compared to 1 g in the cell which survived the test. The leaks were repaired but only 80% of the lost electrolyte could be added to the cells. After reseal, the three cells were cycled again. Table VII summarizes the data of each treatment for the three cells.

The one cell of three which survived shows that cycling before let-down, followed by heat sterilization, is feasible, but the let-down procedure must be improved and rigidly controlled. The gain in capacity from the cell-balancing action of the let-down may off-set any loss due to sterilization. No leakage has been observed around cell terminals or the case to cover seal to the present wet life of 4.6 months confirming the capability of the prototype epoxy seals.

C. FUTURE WORK

All tooling needed for the manufacture of 100 production cells has been completed. Production release is dependent upon the successful completion of environmental tests at JPL of the six cell battery and a subsequent design review.

IV. DEVELOPMENT OF HEAT STERILIZABLE HIGH IMPACT 25 AH CELLS - TASK 12

A. OBJECTIVES AND PAST WORK

This task requires the development of wet heat sterilizable 25 AH cells capable of surviving 4000 "g" shocks in any axis and meeting the requirements of JPL Engineering Memorandum 342-68. A lot of 100 cells is to be delivered in December, 1969. Experimental cells were tested in Lucite jars at peak "g" levels of 4200 "g" and pulse durations of 1 msec. Plate strut failure occurred only in the terminals forward shock vector. Redesign was accomplished and all parts ordered for prototype cells. Gassing on formation charge was observed at the massive negative Ag grid to zinc metal interface and amalgamation studies were initiated to solve this problem.

B. PROTOTYPE CELL PARTS PROCUREMENT

Cell case cover, jar, and shims have been ordered from the molder. Deliveries are now scheduled for early October. The first lot of etched silver negative grids was received. Of 109 pieces, 32 were over-etched (underweight) and 2 were under-etched (overweight). All pieces were

TABLE VII

PROPERTIES OF 70 AH CELLS HEAT STERILIZED AFTER CYCLING

	Test Observation	Unit	Cell Serial Number 10	11	12
1.	Net input after cycle 4 discharge	AH	8.9	7.0	8.0
2.	Cycle 5 recharge, 1.5 A to 2.00V	AH	80.5	91.0	87.0
3.	Discharge at 20A to 1.25V	AH	94.3	89.3	82.3
	Midpoint voltage	volts	1.46	1.47	1.47
4.	Let-down over .4 ohm for 3 days				
	• OCV after let-down	volts	.4	.1	.2
5.	Heat sterilization 72 hours 135°C				
	• OCV after sterilization	volts	.13	.17	.40
	• Electrolyte loss	g	80L	57L	1
	• Electrolyte replaced	%	80	79	NA
6.	Cycle 6 recharge, 1.64A to 2.02V, then .83A to 2.02V	AH	79.9	97.9	96.4
7.	Discharge at 20A to 1.25V	AH	65.2	74.5	86.6
	Midpoint voltage	volts	1.35	1.40	1.41
8.	Capacity (loss) gain from HS	AH	(29.1)	(14.8)	+4.3
9.	Cycle 7 recharge				
	• 1.64A to 1.97V	AH	46.7	46.7	54.5
	• 0.83A to 2.02V	AH	19.7	25.5	35.0
	• Total input	AH	66.4	72.2	89.5
10.	Total Wet Life (to date)	mos.	4.6	4.6	4.6

accepted, but the 34 out-of-tolerance parts were used in amalgamation studies.

C. AMALGAMATION OF ETCHED GRIDS

Chemically etched silver grids[2] were electrochemically amalgamated from a plating solution of 50 g potassium iodide, 5 g mercuric iodide, and 1000 g water. The grids were suspended from a metal bar (parallel connection) and then immersed in the plating solution between two vertical columns of pure mercury contained in a microporous PVC tube. Electroplating at 0.1 amp per grid was continued to a theoretical deposition of 0.5 mil. Weight analysis confirmed that deposition was quantitative. Visual inspection by microscope at 10x to 80x showed a matte finish over the entire grid surface including the etched out cavities.

D. WET GRID PASTING PROCESS

Task 9 tensile tests require deletion of the normal negative plate sintering process to prevent a significant reduction in grid strength. The plate process selected is one in which the active mix containing teflon is prepared as a wet paste and heated separately to 270°F to evaporate the water and to develop the teflon matrix. The moist crumbs thus prepared were then pasted into cavities of the etched grids to drawing weight and thickness tolerances. Plates have been charged and tested both for capacity and voltage with good results. Amalgamated grids pasted in this manner have not to date gassed hydrogen on formation charge prior to heat sterilization.

E. FUTURE WORK

During the coming quarter electrochemical characteristics of the wet pasted-amalgamated grids will be determined after heat sterilization for 72 hours at 135°C. Prototype cell assembly will be initiated after a final cell design review.

V. DEVELOPMENT OF MEDIUM CYCLE LIFE 25 AH CELLS, TASK 13

A. OBJECTIVES AND PAST WORK

In this task a 25 AH wet heat sterilizable cell will be designed, manufactured, and tested to the requirements of JPL Engineering Memorandum 342-68 less the 4,000 g shock. Five cells each of five cell designs were manufactured to evaluate two negative densities (42 and 49 gm/in^3), two separator systems (1L Pellon 2530W and 7L GX vs 9L GX), and positive or negative wrap. Each 5 cell group was divided into three test groups: Test 1 (no plate-lock, no pretest); Test 2 (with plate-lock); and Test 3 (with pretest of 3 cycles before heat sterilization). For Test 1 (n=3) cells were heat sterilized before cycling for 72 hours at 135°C, cycled for 3 100% depth cycles at 8A, 16A, and 2A to 1.30V, and then placed on automatic cycling -- 10 hour charge/2 hour discharge. The fifteen cells (3 each 5 designs) were cycled over a 4 month period to failure of 3 of the five designs at 74-84 cycles of 50% of rated capacity.[3]

B. AUTOMATIC CYCLING OF 25 AH CELLS

Model 379 cell types (-1) and (-2) continued on cycling at 50% depth of rated capacity on the routine 10-hour charge/2-hour discharge, 2 cycles per day. First cell failure of design (-1) occurred at 168 cycles in 6 months total wet life. First cell failure of design (-2) occurred after 5 months life at 118 cycles. Figure 4 summarizes graphically the cycle life of the Test Group 1 cells and gives the last 100% depth capacity monitored before failure. Each cell design group received 5 100% depth cycles, and two types of 50% depth cycles:

- Single step C/3 rate discharge
- Two step C/2 rate followed by C/20 rate

Energy delivered per cycle varied by design group. Table VIII summarizes the accumulated ampere-hour capacity for each cell during cycling and lists the average watt-hours of energy per DAS cycle (2-step) for each design group. Design group (-1) delivered 1920 ampere-hours in 168 cycles and six months wet life and represents optimum performance for the system-

- positive wrap (3"U" folds on 6 positive plates)
- 1L Pellon 2530W, 7L GX membrane separator system
- 49 gm/in^3 negative active material density

On the basis of comparison of mean accumulated capacity for all cycles to failure, the major experimental design responses were-

- Absorber > No absorber, Positive Wrap (Design 2 vs Design 3) — Capacity Increase 16%
- High negative density > low negative density With absorber and positive wrap (Design 1 vs Design 2) — Capacity Increase 22%

The major reason for an absorber at the positive plate is to maintain 100% of the positive plate wetted with electrolyte so that 100% of the negative plate area opposite the positives can continue to function. During cycling with more time for charge than discharge, electrolyte will tend to move toward the negative plates irreversibly leaving upper portions of positive plates charged and inactive above the cell electrolyte level. Table VIII shows that Designs (-4) and (-5) may actually have been more electrolyte limited (1.2 g electrolyte per g active silver in the positive plate vs 1.4 to 1.5 g electrolyte per g Ag for Designs (-1), (-2), and (-3).

AFTER HEAT STERILIZATION
72 HOURS 135°C
NO PRETEST, NO PLATE LOCK

TASK XIII
FIGURE 4

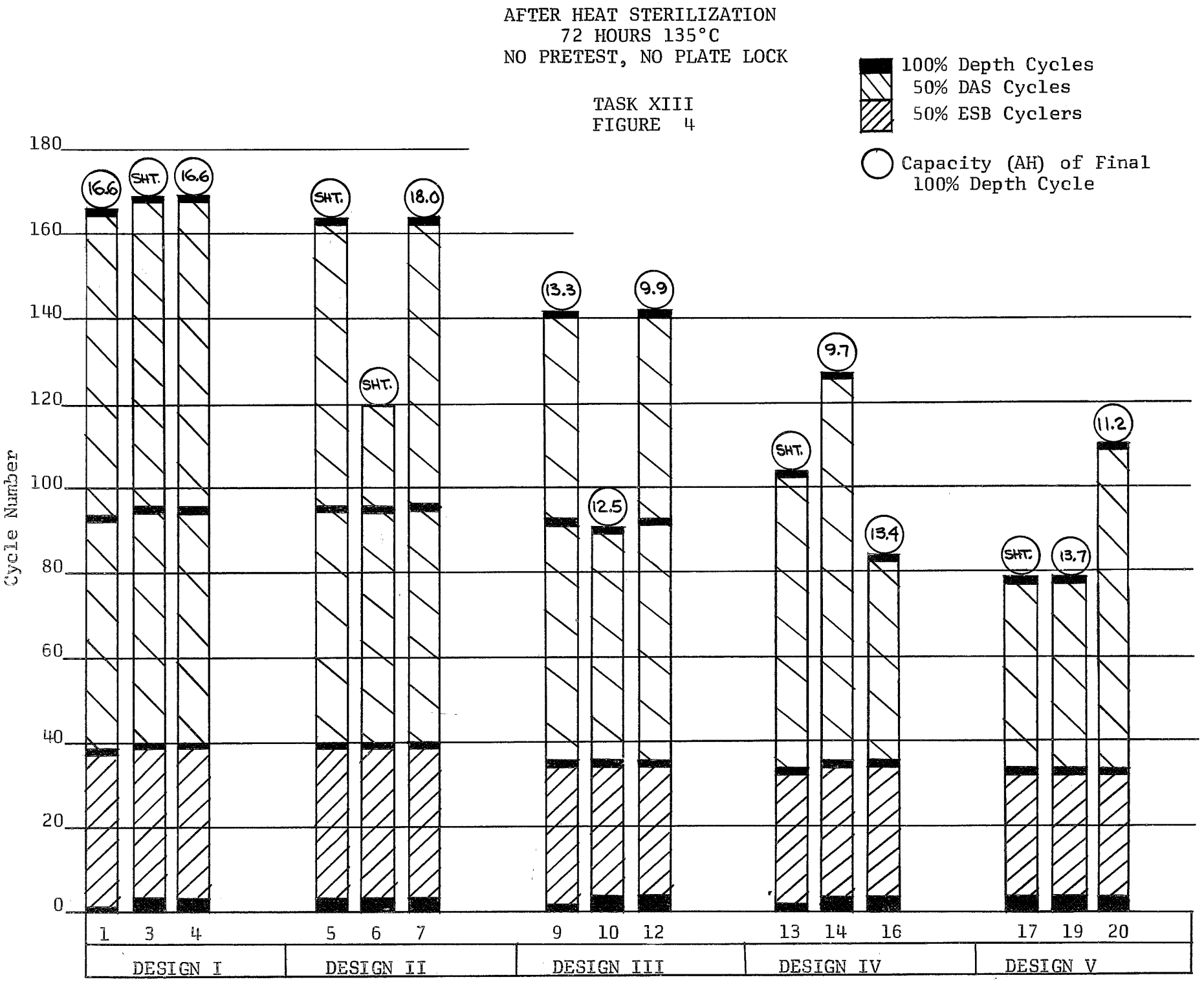


TABLE VIII

LOW IMPACT 25 AH CELL CYCLING TEST - CYCLES TO SEPTEMBER 30

Cell Design Variables						Number of Cycles, DOD				Capacity-Accumulated Output All Cycles AH	Output Energy** On DAS Per Auto-Cycle W-Hr.
Plate Wrap	Separation L/Type	Negative Density g/in^3	Electrolyte Weight g***	g/gAg	C Rating AH	100% Single Step	50% Single Step	50% Two Step Discharge	Total Cycles		
+	1L Pellon 2530 W 7L GX	49	123	1.40	22	5	36 (11.4AH)*	127 127 125	168 FS 168 166	1920 1920 1900	16.6
+	same	42	124	1.55	20	5	36 (9.8AH)	123 123 77	164 FS 164 118FS	1690 1690 1220	15.4
+	9L GX only	42	125	1.56	20	5	30 (9.7AH)	106 106 56-	141 141 91	1480 1480 960	14.9
-	same	42	124	1.29	24	5	30 (11.8AH)	69S 92 49	104FS 127 84	1270 1550 1040	17.6
	same	49	118	1.13	26	5	28 (12.2AH)	77 45 45	110 78 78FS	1440 1030 1030	19.3

* Discharge capacity per cycle at C/3 rate

** Includes energy of both discharge steps

*** 40% by weight as KOH

Test Group 2 cells (with no plate-lock, but cycled 3-100% depth cycles before heat sterilization) were auto-cycled only on the DAS 2-step routine at 50% depth. Table IX summarizes the cycle life history of these five pretest cells. Cell designs (-1), (-3), and (-4) failed by erosion of negative plates and low capacity at 88, 83, and 69 cycles respectively. Design (-2) shorted at 98 cycles. Design (-5) did not fail and was removed from test after 51 cycles at a measured residual capacity of 15.1AH. The marked decrease in cycle life to the 50% depth capacity cut-off indicates a possible interaction of the pretest before heat sterilization with cycle life and deserves additional investigation.

Test Group 3 cells with plate-lock were cycled after heat sterilization and then shipped to JPL for environmental tests to the requirements of JPL Memorandum 342-68.

Failure analyses or dissections of cells at the end of cycling tests are not complete; however, preliminary conclusions are -

- Erosion of negative plates caused capacity failures of cells. Erosion exceeded 50% of the plate area and was in a random pattern for cells having absorbers adjacent positive plates except those in the pretest group.

- Erosion was top to bottom in all other cells concentrating the active material in a dome shaped area in the lower half of the plate.

- Cells cycled before heat sterilization have considerably more silver trapped in the GX separator at the same cycle life.

C. FUTURE WORK

During the next quarter failure analyses will be completed and results summarized. Plate-lock cells will complete environmental tests at JPL and will be placed on cycling tests at ESB.

VI. QUALITY ASSURANCE ACTION

A full design review of the Model 379-1 25 AH medium cycle life cell was conducted on September 30 with JPL Quality Assurance and Engineering personnel in attendance. The review established the final design for this cell provided environmental tests at JPL are completely successful. Engineering drawings, process specifications, material specifications, and quality assurance documents were reviewed.

A post-mortem form was devised to standardize procedures and information recorded during failure analyses and dissections of cells. Post-mortem analyses were witnessed and reports approved for Model 379 cells S/N 3, 7, and 12.

TABLE IX

CYCLE LIFE OF PRETEST 25 AH CELLS

Plate Wrap	Separator System	Negative Density g/in^3	Cell S/N	Discharge Capacity 8A Rate 100% Depth* Cycle 1 Before HS	Cycle 4 After HS	Cycle 22 After HS	Cycle No. Last Capacity**	Test End Capacity AH
+	1L Pellon 2530W 7L GX	49	2	33.6	28.3	24.0	11.6 (88) FC	11.0
+	same	42	8	36.0	32.5	24.0	FS (98)	10.0
+	9L GX	42	11	34.4	32.2	20.1	9.7 (83) FC	10.0
-	same	42	15	36.4	32.0	26.1	12.1 (69) FC	11.0
-	same	49	18	44.3	30.4	27.7	15.1 (51) NF	12.0

* All cells cycled 3 100% DOD at 8, 16, and 2 amps to 1.30v before and after 72 hours heat sterilization at 135°C plus 2 capacity measuring cycles (8 amp to 1.30v) during automatic cycling. All automatic cycles were 10 hour charge/2 hour discharge, 2 cycles per day. Discharge was 2-step: C/2 followed by C/20.

** NF = no failure
FC = failure by low capacity
FS = failure by shorting

ferences: (1) First Quarterly Progress Report, JPL Contract 951296, January 1 to March 31, 1969, p31, Table XII.

(2) Second Quarterly Progress Report, JPL Contract 951296, April 1 to June 30, 1969, p43.

(3) IBID, Table XVIII, p55.

APPENDIX I

CAPACITY DATA FROM FIRST SIXTEEN CYCLES

Capacity data for the first sixteen cycles was available for 24 of the original 27 cells of the experimental design. A plot of capacity vs. cycle number was made for each cell so that general trends could be observed. Formation cycle capacities were quite variable ranging from about 16 amp - hrs to almost 26 amp - hrs. During the first four or five cycles all cells showed a sharp decrease averaging about 5 amp - hrs. Thereafter most of the curves leveled off falling slightly in the last two or three cycles. In a number of cases, however, the initial sharp decrease was followed by a subsequent increase of from 2 to 5 amp - hrs.

On the basis of the appearance of the capacity vs cycle number plots it was decided to analyze as dependent variables the following:

(1) CI = first cycle capacity
(2) AV5 = average capacity for cycles 4, 5 and 6
(3) AV15 = average capacity for cycles 14, 15 and 16
(4) CI-AV5 = change from cycle 1 to average 4, 5 and 6
(5) CI-AV15 = change from cycle 1 to average of 14, 15 and 16
(6) AV-AV15 = change from cycles 4, 5,6 to cycles 14, 15, 16
(7) AV_5_15 = combined average of cycles 4, 5, 6, 14, 15 and 16

For each of the above dependent variables a multiple regression analysis was run for each of the following two models in the independent variables based on the four factors varied in the cell construction.

LINEAR MODEL

$$\text{Dependent Variable} = b_0 + b_1 (TF) + b_2(TH) + b_3(R) + b_4(K)$$

where $$TF = \frac{\text{TEFLON} - 7}{2}$$

$$TH = \frac{\text{THICKNESS} - 2.4}{.4}$$

$$R = \frac{\text{Zn O/Ag} - 1.2}{.3}$$

$$K = \frac{\text{KOH} - 43}{2}$$

That is, TF, TH, R and K are coded values of the four factors. The coding reduces the three levels of each factor to -1, 0, +1.

QUADRATIC MODEL

$$\text{Dependent Variable} = b_o + b_1(TF) + b_2(TH) + b_3(R) + b_4 K + n_5(TF)^2 + b_6(TH)^2 + b_7 R^2 + b_8 K^2 + b_9(TF)(TH) + b_{10}(TF)(R) + b_{11}(TF)(K) + b_{12}(TH)(R) + b_{13}(TH)(K) + b_{14}(R)(K)$$

This model adds the square of each variable of the linear model plus all possible cross products of the variables two at a time. The cross product terms represent so-called two factor interactions.

RESULTS OF ANALYSES

All analyses were run through the North Carolina State University Computing Center on an IBM 360, Model 75 system. A standard multiple regression program was used.

The results of most of the analyses were negative, that is, with a few exceptions the influence of the independent variables included in the two models was not sufficiently strong or not consistent enough to be judged statistically significant at reasonable probability levels. The few exceptions were:

(1) The difference CI-AV5 is significantly influenced by R, the Zn O/Ag ratio. The average values of CI-AV5 by levels of Zn O/Ag are

Zn O/Ag	CI-AV5
.9	5.66
1.2	4.15
1.5	3.83

(2) By the routine analysis the difference AV5 - AV15 shows a statistically significant quadratic effect of R. The average values are

Zn O/Ag	AV5 - AV15
.9	.89
1.2	-.28
1.5	1.35

The middle level of R actually shows an increase in capacity from 5 to cycle 15. These differences, however, are influenced to a considerable extent by the several cells whose capacity increased markedly after cycle 5.

The net effect of decreases from CI to AV5 followed by increases (for some cells) from AV5 to AV15 is to obscure the effect of R in the overall change from CI to AV15.

(3) The (TF)(TH) interaction was statistically significant for both CI - AV15 and A5 - AV15. However, in both cases this conclusion is strongly influenced by three cells whose capacity increased markedly after the fifth cycle.

(4) Two other interactions, (TH)(R) and (TF)(K) come close to significance at the conventional 5% level in the CI - AV5 analysis.

(5) Though not supported by a test of significance it was noted that the several cells whose capacity increased after the fifth cycle were confined to the following three combinations of Zn O/Ag and KOH:

R = .9, K = 43 or R = 1.2, K = 41 or R = 1.2, K = 43.