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THE CARL F. NORBERG RESEARCH CENTER

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HEAT STERILIZABLE IMPACT RESISTANT CELL DEVELOPMENT

JET PROPULSION LABORATORY
CONTRACT NO. 951296

REPORT FOR FOURTH QUARTER, 1968
OCTOBER 1 TO DECEMBER 31, 1968

"This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100."

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May 9, 1969

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ABSTRACT

Further data were accumulated during this Quarter which exonerated the separators SWRI-GX, RAI-110, and RAI-116; the absorber EM-476; and polyphenylene oxide PPO 531-801 or PPO 534-801 from responsibility in causing low capacity or gassing during formation. However, the presence of excessive vapors of Catalyst 11 (sometimes used for curing epoxy resins) reduced the amount of current which could be withdrawn at higher rates of discharge. In the case of cells sealed with DEN438 EK85/Hardener 927, some sensitivity to resin/catalyst ratio seemed to appear. The most severe effects were caused by the presence of a heat shrinkable polyolefin tubing used as insulation on plate leads. It is thought that a flame retardant or a stabilizer added to this tubing is the culprit. In any case, replacement of the tubing with Teflon has corrected the problem.

Work has continued on cycling prior to heat sterilization but no specific recommendations are made at this time.

The emphasis of the contract has been redirected from battery to cell development. Cell performance after 72 or 100 hours of sterilization in the wet and sealed condition has improved to the extent that the following characteristics have been achieved during the first discharge after formation:

Model No.	Capacity AH to 1.25V	Mean Voltage (Volts)	Energy Watt-Hours	Energy Density Rate WH/lb.	Amps.
281	11	1.49	16.4	43	3.3
172	34	1.49	51	49	8.0
364	89	1.49	133	52	20.0

Wet life as a function of separator wet thickness has been estimated. The cycle life of 24 amp-hr cells after heat sterilization is now limited by AgO penetration. An increase in the number of layers of SWRI-GX separator from 6 to 9, an increase in ZnO/Ag ratio, and the use of sintered Teflonated negatives in more recently constructed cells are changes directed toward attaining ninety 50% DOD cycles in 18 months of wet charged life with or without 4000 g shock resistance.

TABLE OF CONTENTS

ELECTROCHEMISTRY

FABRICATION AND TESTING OF CELLS

LIST OF TABLES

LIST OF FIGURES

ELECTROCHEMISTRY

I. VARIATION IN CAPACITY AND PRESSURE OF CELLS

A. Introduction

The ability to build cells producing about 0.35 amp-hrs/g Ag and no pressure on a consistent basis has been the objective of the Fourth Quarter of 1968. When cells are constructed in Teflon inserts and sealed in nickel bombs prior to sterilization, the capacity and pressure were reproducibly good. However, when the cells were constructed in polyphenylene oxide cases and sealed with various epoxy systems prior to sterilization, the capacity varied from 0.25 to 0.38 amp-hrs/g Ag. In addition, the cells with low capacity developed gas pressure. The following discussion continues the work described in previous quarterly reports which had been predicated on the assumption that some organic material caused the undesirable effects.

B. Effect of Organic Components

In order to examine the effect of organic components on the capacity of cells following sterilization in the sealed condition, a number of experiments have been conducted in containers consisting of Teflon inserts sealed in nickel bombs. The design is shown in Figure 1, which was inadvertently omitted from previous quarterly reports. The nickel cap, not shown on the drawing, is caused to form a good seal by wrapping the threads of the lower portion of the bomb with Teflon tape. The cap also has attached to it a pressure gage. Leads from the electrodes are brought over the top of the Teflon insert, down the grooves, and attached to the electrical feed-through which is insulated from the bomb.

The data of this study are shown in Table I. Except for the first three cycles of one cell, 4B, containing the separator SWRI-GX alone (out of a total of five such cells), and one of the cells, 15B, containing Catalyst DMP-30, the capacity of the cells whether sterilized or not was around 0.35 amp-hrs/g Ag. The reason for the low initial capacity of cell 4B is not obvious, but by the end of four cycles, it had a capacity of 0.36 amp-hrs/g Ag, and the fact that other cells containing GX separator performed well indicate that the GX component did not reduce the cell capacity. On the other hand, the data for DMP-30, when interpreted along with other data which will be presented later, indicate that this catalyst could affect cell capacity.

Another effect which is not obvious from Table I is the rate at which the capacity was obtained from the cells. Usually, about 5.5 amp-hrs of the capacity is removed during the first stage of discharge which is a higher rate discharge (2.0 amps), whereas only about 1 amp-hr is obtained at

FIGURE 1

Ni Bomb With Teflon Insert

NOTE:

Electrical feed through not shown on back side

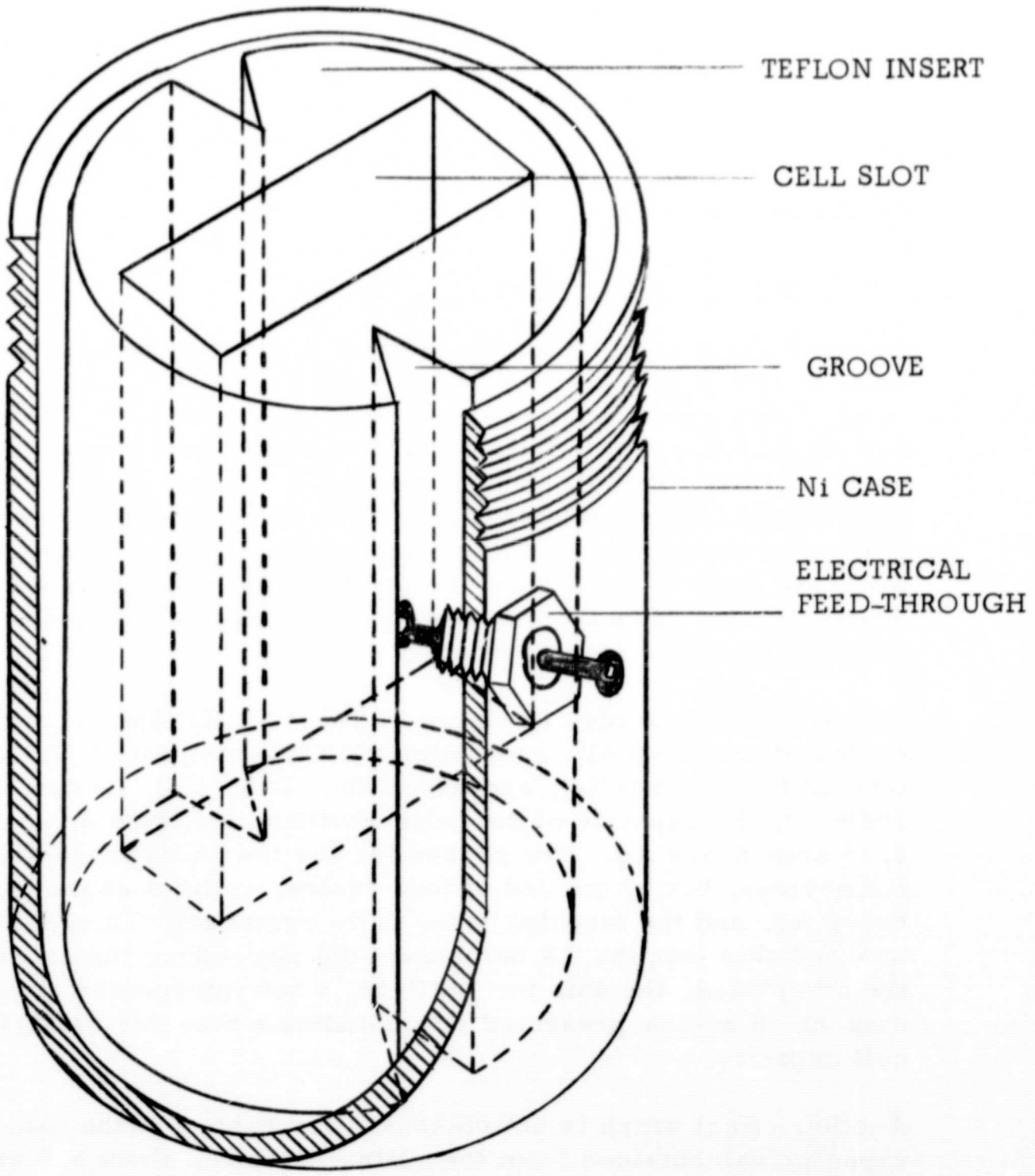


TABLE I

Summary of the Sterilization Effects of Organic Compounds on Cell Capacity
(Experiments in Teflon Inserts in Nickel Bombs)

Excess Head Space	Capacity (AH/g Ag) 1st Dischg.		2nd Dischg.		3rd Dischg.		4th Dischg.	
	A	B	A	B	A	B	A	B
(1) GX, 476 Unster.	.34	.32	.33	.30	.33	.31	.34	.30
(2) GX, 476 Ster. *	.33	.33	.33	.32	.35	.35	.36	.36
Limited Head Space								
(3) GX alone. Unster.	.39	.40	.35	.39	.37	.37	.37	.37
(4) GX alone ster.	.39	.24	.39	.26	.39	.30	-	.36
(4a) " " "	.35	.36	.32	.37	.35	.35	-	-
(4b) " " "	.38		-		-		-	
(5) GX, 531-801 ster.	.34	.33	.36	.35	.37	.35	-	-
(6) GX, cured DEN.../ DMP30 Ster.	.35	.40	.35	.35	.35	.37	-	-
(7) GX alone; cell heated at 160°F for 16 hrs. in N_2 before activa. and ster.	.36	-	.35	-	-	-	-	-
(8) GX, 534-801 ster.	.35	.34	.35	.34	.35	.35	.35	.33
(8a) " " "	.39	.40	-	-	-	-	-	-
(9) GX, DEN etc. cured in activated and sealed bomb before ster.	.35	.34	.35	.34	.35	.33	.34	.32
(10) RAI-110 alone ster.	.37	.39	.37	-	.37	-	.36	-
(11) RAI-116 alone ster.	.36	.40	.35	-	.37	-	.36	-
(12) GX, PPO, and uncured epoxy ster.	.40	.39	-	-	-	-	-	-
(13) GX, cell heated at 160°C for 16 hrs. in air before activa. and ster.	.40	.40	-	-	-	-	-	-
(14) GX, with no allowance for expansion, ster.	.40	.40	-	-	-	-	-	-

* All cells sterilized at 135°C for 120 hours.

TABLE I (continued)
Summary of the Sterilization Effects of Organic Compounds on Cell Capacity
(Experiments in Teflon Inserts in Nickel Bombs)

Excess Head Space	Capacity (AH/g Ag) 1st Dischg.		2nd Dischg.		3rd Dischg.		4th Dischg.	
	A	B	A	B	A	B	A	B
(15) GX, DMP-30 ** alone ster.	.35	.31	.33	.31	.34	-	.36	-
(16) GX, DEN438 EK85 ** alone ster.	.37	.38	.35	.38	.35	-	.35	-
(17) GX, Catalyst 11 ** alone ster.	.37	.37	.39	.39	-	-	-	-
(18) GX, EM-476 alone ster.	.38	.38	.37	.38	.37	.37	.37	.36

** DMP-30, DEN438 EK85, and Catalyst 11 were contained in the annular space between the Teflon insert and the nickel bomb.

an ensuing lower rate (0.40 amp). For cells 17A and B which contained Emerson and Cumings Catalyst 11 vapors, about 3.00 amp-hrs were obtained at each stage of discharge. The long second stage discharge may be related to surface films which create high cell resistance. As measured by the Wayne-Kerr bridge, resistances of cells 17A and B were higher than those of normal cells. Experiments are being conducted to determine if a relationship exists between cell impedance and discharge rates.

The final conclusion from the data on organic components is that the materials studied when used properly are not responsible for the capacity loss nor the gas pressure developed in cells sealed then sterilized. However, an excess of either the epoxy resin DEN438 EK85 or the catalyst Hardener 927 may affect the performance of the cells as shown in Table II.

Cells 89-1 and 2-2 having the smallest and the largest ratio of catalyst/resin respectively had lower capacities than the cells having formulations approaching the recommended ratio of 15:100. There was also an effect on the rate at which the capacity could be obtained for cell 89-1.

II. STERILIZATION OF CYCLED CELLS

The use of Compound 323-43 has been shown in previous studies to be essential for heat sterilized cells. Recently, consideration has been given to the possibility of sterilizing the cell after cycling. Cycling before sterilization of the cells is a desirable technique because it would permit the matching of cells before they are assembled as batteries and mounted on the spacecraft. Moreover, by cycling the cells before sterilization, metallic mercury is present during sterilization. Thus, HgO could be used in the negative mix. Table III shows some performance data of cells sterilized after cycling. All five cells had 3% HgO rather than Compound 323-43, but cells 6-4 and 6-5 had silver electrodes which were pretreated with a solution containing a variation of Compound 323-43. The three cells, 6-1, 6-2, and 6-3 which were untreated lost capacity after sterilization whereas the two that were pretreated maintained good capacity. Further testing along this line is planned.

III. LONG CYCLE LIFE DESIGN

A preliminary cell design including some features for long cycle life was evaluated. The features included were as follows: (1) One layer of polypropylene EM-476 was placed adjacent to the silver electrode; (2) ten layers of GX separator; and (3) a ratio of ZnO/Ag greater than 1. For easier insertion of the elements into the cell jar, the silver electrodes were wrapped, these being slightly smaller than the zinc electrodes.

The theoretical capacity ratio of 1.2:1 for zinc oxide to silver may be increased for future life studies. The results of the evaluation are shown in Table IV. The capacities of about 0.33 amp-hrs/g Ag were acceptable.

TABLE II

Effect on Performance of Sealed Sterilized Cells Caused by Variation of Epoxy Resin/Catalyst Ratio
Resin: DEN438 EK85; Catalyst: Furane Plastic Hardener 927

Cell Number	89-1	99-1	100-1	2-1	2-2
Catalyst/Resin ratio	11.7:100	14:100	17.5:100	16.4:100	20:100
Formation Charge:					
Amp. hrs. Step 1	4.21	3.82	3.87	4.18	3.76
Amp. hrs. Step 2	0.73	1.60	1.25	1.38	1.19
Amp. hrs. Total	4.94	5.42	5.12	5.56	4.95
Amp. hrs/gm Ag	0.336	0.368	0.348	0.378	0.336
Discharges:					
First - Step 1 (100 ma/sq. in)	2.01	4.41	4.02	4.02	3.69
Step 2 (20 ma/sq. in)	2.10	0.60	0.78	0.80	0.81
Amp. hrs., Total	4.11	5.01	4.80	4.82	4.50
Amp. hrs/gm Ag.	0.279	0.340	0.326	0.327	0.306
Second - Step 1	2.55	4.41	4.02	4.02	3.69
Step 2	1.76	0.60	0.78	0.80	0.81
Amp. hrs. Total	4.31	5.01	4.80	4.82	4.50
Amp. hrs/gm Ag	0.293	0.340	0.326	0.327	0.306
Third - Step 1	3.00	4.41	4.29	4.11	3.99
Step 2	1.45	0.60	0.71	0.84	0.72
Amp. hrs., Total	4.45	5.01	5.00	4.95	4.71
Amp. hrs/gm Ag	0.300	0.340	0.340	0.336	0.320
Fourth - Step 1	3.33	4.35	4.38	4.11	3.93
Step 2	1.23	0.60	0.60	0.65	0.58
Amp. hrs., Total	4.56	4.95	4.98	4.76	4.51
Amp. hrs/gm Ag	0.310	0.336	0.338	0.323	0.307

TABLE II (continued)

Effect on Performance of Sealed Sterilized Cells Caused by Variation of Epoxy Resin/Catalyst Ratio

Resin: DEN438 EK85; Catalyst: Furane Plastic Hardener 927

Cell Number		89-1	99-1	100-1	2-1	2-2
Catalyst/Resin ratio		11.7:100	14:100	17.5:100	16.4:100	20:100
Discharges:						
Fifth -	Step 1	3.15	4.17	4.44	4.05	3.99
	Step 2	1.43	0.60	0.42	1.02	0.71
	Amp. hrs., Total	4.58	4.77	4.86	5.07	4.70
	Amp. hrs/gm Ag	0.311	0.324	0.330	0.344	0.319
Load Voltages: 100 ma/sq. in - first discharge						
	After 30 min.	1.432	1.528	1.557	1.454	1.470
	After 60 min.	1.330	1.438	1.416	1.417	1.410
	After 90 min.	-	1.420	1.393	1.393	1.383
	After 120 min.	-	1.380	1.331	1.344	-

TABLE III

Performance of Ag-Zn Cells, Sterilized Following Cycling

Cell Number	6-1	6-2	6-3	6-4	6-5
Positives	Std	Std	Std	Treated (see Text)	Treated (see Text)
Additive to Negative, Percent	HgO, 3	HgO, 3	HgO, 3	HgO, 3	HgO, 3
Formation Charge					
Step 1, Amp hrs	4.95	4.98	4.91	5.39	5.07
Step 2, Amp hrs	0.51	0.48	0.42	0.15	0.29
Amp. hrs., Total	5.46	5.46	5.33	5.54	5.36
Amp. hrs/gm Ag	0.371	0.371	0.362	0.377	0.364
Discharges - before sterilization:					
First - Step 1, 100 ma/sq in.	4.92	4.95	4.77	4.74	4.38
Step 2, 20 ma/sq in.	0.25	0.29	0.31	0.29	0.46
Amp hrs Total	5.17	5.24	5.08	5.03	4.84
Amp. hrs/gm Ag	0.351	0.356	0.345	0.342	0.329
Amp. hrs/gm					
After sterilization:					
Second - Step 1, 133 ma/sq in.	2.44	0.60	2.28	3.28	0.88
Step 2, 20 ma/sq in.	1.46	3.11	1.41	1.18	4.28
Amp. hrs, Total	3.90	3.71	3.69	4.46	5.16
Amp. hrs/gm Ag	0.265	0.252	0.251	0.303	0.351
Third - Step 100 ma/sq in.	4.05	3.66	3.16	3.99	3.96
Step 2 20 ma/sq in.	0.76	1.05	0.79	0.91	1.32
Amp hrs. Total	4.81	4.71	4.45	4.90	5.28
Amp hrs/gm Ag	0.327	0.320	0.302	0.333	0.359

TABLE III (continued)
Performance of Ag-Zn Cells, Sterilized Following Cycling

Cell Number	6-1	6-2	6-3	6-4	6-5
Discharges:					
Fourth - Step 1	3.99	3.75	3.51	3.99	3.66
Step 2	0.90	1.12	0.96	0.90	1.59
Amp. hrs, Total	4.89	4.87	4.47	4.89	5.25
Amp. hrs/gm Ag	0.332	0.331	0.304	0.332	0.357
Load Voltages - Before sterilization - First Discharge - 100 ma/sq. in.					
After 30 min.	1.432	1.436	1.436	1.439	1.421
After 60 min.	1.441	1.443	1.443	1.449	1.429
After 90 min.	1.442	1.443	1.442	1.448	1.424
After 120 min.	1.435	1.435	1.434	1.435	1.397
After 150 min.	1.397	1.399	1.390	1.349	-
Load Voltages - After sterilization - Fourth discharge - 100 ma/sq. in.					
After 30 min.	1.500	1.439	1.462	1.481	1.503
After 60 min.	1.421	1.369	1.407	1.434	1.396
After 100 min.	1.414	1.355	1.372	1.421	1.378
After 120 min.	1.393	1.332	-	1.382	1.333

TABLE IV

Evaluation of Design for Extended Cycle Life

Cell Number	5-1	7-1
Number of silver electrodes, gas active material	4, 19.6	4, 19.6
Number of zinc oxide electrodes, gas ZnO	5, 18.2	5, 18.2
Number of separator layers (GX)	10	10
Electrolyte concentration, (before ZnO addition)	42% KOH	42% KOH
Absorber adjacent to silver electrode	EM-476	EM-476
Type of construction	U-wrap, silver electrodes	U-wrap, silver electrodes
Formation charge:		
Amp. hrs, Step 1	4.40	4.61
Amp. hrs, Step 2	2.48	1.63
Amp. hrs, Total	6.88	6.24
Amp hrs/gm Ag	0.351	0.318
Discharges:		
First - Step 1 (100 ma/sq. in)	5.70	5.04
Step 2 (20 ma/sq. in)	0.96	0.78
Amp. hrs. Total	6.66	5.82
Amp. hrs/gm Ag	0.340	0.300
Second - Step 1	6.04	5.60
Step 2	0.60	0.76
Amp. hrs, Total	6.64	6.36
Amp. hrs/gm Ag	0.340	0.324
Third - Step 1	3.96	5.68
Step 2	2.64	0.84
Amp. hrs, Total	6.60	6.52
Amp. hrs/gm Ag	0.336	0.332
Fourth - Step 1	5.96	5.60
Step 2	0.68	0.85
Amp. hrs, Total	6.64	6.45
Amp hrs/gm Ag	0.340	0.329
Load Voltages 100 ma/sq. in.		
After 30 min.	1.504	1.453
After 60 min.	1.395	1.408
After 90 min.	1.392	1.390
After 120 min.	1.380	1.322

FABRICATION AND TESTING OF CELLS

I. HEAT STERILIZABLE - HIGH IMPACT 5.0 AH AND 25 AH BATTERIES TASK 9

A. Objectives and Past Work. - This task has been redirected[1] from 18-cell battery development to development of cells meeting the requirements of JPL Specification GMP-50437-DSN-C, a shock level of 2,800 ± 200 g at 115 ± 3 ft/sec., and JPL Engineering Memorandum 342-70. Thirty (30) cells each of the 5 AH and 25 AH design are to be delivered to JPL by December 1969.

B. Non-High Impact Test Cells. - Previous test cells (Model 281) were designed and constructed in 5.0 AH size to determine the reason for a 23-59% capacity loss resulting from wet sealed heat sterilization for 120 hours at 135°C and hydrogen evolution during the early stages of formation charge. Two separator systems, SWRI-GX and RAI-116, two cell case materials PPO 531-801 and PPO 534-801, and two epoxy sealants DEN438EK85/DMP30 and Isochem 811B/A were tested, but no variable was found to account completely for the capacity losses or pressure rise.[2]

Two additional groups of cells were assembled to test three epoxy sealants, alternative curing techniques, and another formation charge technique. The test groups and formation charge results are given in Table V. The cause of gassing was common to all 16 cells since all 16 cells bulged in excess of 100 mils, and no significant improvement in formation charge acceptance was observed for the alternative cure method or sealing after the preformation charge.

(1) JPL Contract 951296 Modification 18.

(2) Report for Second and Third Quarter 1968, p24, 12-20-68.

TABLE V

EFFECT OF CELL SEALANT AND CURE METHOD ON
FORMATION CHARGE ACCEPTANCE
AFTER 120 HOUR HEAT STERILIZATION AT 135°C

Group I 6 Cells S/N 47 through 52		Group II 10 Cells S/N 53 through 62	
Test Sealants:		Test Sealants:	
2 - Epocast 221/927 Ratio	100:8	2 - Epocast 221/927 Ratio	100:8 *
2 - DEN438EK85/Cat. 11	100:18	2 - Epocast 221/927 Ratio	100:8 **
2 - DEN438/Cat. 11	100:18	2 - DEN438EK85/Cat. 11 Ratio	100:8
		2 - DEN438/Cat. 11 Ratio	100:8
		2 - DEN438EK85/DMP30 Ratio	100:5 ***
Cure Condition:		Cure Condition:	
2 Cycles 16 hours at 71°C Dry Heat		16 hours at 100°C, cells activated, in sealed bomb	
Other: 6L GX + 1L GX retainer pressed powder negatives		Other; 6L GX + 1L GX retainer and pressed powder negatives except -	
		• EM476 between GX layers	*
		• Sintered negatives	**
Preformation Activated and sealed before preformation		Preformation: Preformed vented, then sealed.	
Heat Sterilization Wet Sealed		Heat Sterilization Wet Sealed	
Formation Charge Results		Formation Charge Results	
• 0.22 to 0.27 AH/gm Ag		• Input .24-.31 AH/gm Ag.	*
		Input .27-.31 AH/gm Ag.	**
		Input .27-.31 AH/gm Ag.	***
		All others .22-.25 AH/gm Ag.	
• All cells bulged greater than 100 mils.		• All cells bulged 100 mils or more	

A third group of cells was assembled to investigate the common design factors used in cell assembly -

- Calgonite detergent wash of plastic parts
- Heat shrinkable polyolefin tubing on plate leads
- Sandblasting of sealing surfaces
- Electrolyte purity

The first 3 cells tested the electrolyte purity effect and by omission the detergent, tubing, and sandblasting factors. All three cells accepted .40 - .41 AH/gm Ag with no pressure rise in excess of 3 mils of sealed cell bulge. Charge acceptance of 80% of theoretical and pressure bulging of 1-3 mils on formation charge after 72 hours heat sterilization at 135°C is considered excellent performance. The next 3 cells identified the gassing agent to be the heat shrinkable polyolefin tubing used as plate lead insulation. Samples of the tubing exposed in hot caustic did not create gas by decomposition, but when exposed in direct contact with zinc metal powder in hot caustic, the hydrogen gassing rate of the zinc more than doubled. One or more additives in the tubing - a flame retardant and a stabilizer, both proprietary to the vendor - apparently vaporize during heat sterilization and accelerate negative gassing after charge. Work on another contract[3] shows exposure at 140°F for 2-3 days gives a similar response in wet charged Ag-Zn sealed cells. Substitution of teflon heat shrinkable tubing for polyolefin tubing has resolved this problem.

The Model 281 test cell now delivers on formation discharge no less than 11.0 AH at 3.3 amps to 1.25 volts per cell, 16.4 watt-hours at an

(3) C. D. Farris - JPL Contract 951927, Development of Improved Sealed Ag-Zn Battery for Mariner 1969, Part II, p.10.

average voltage of 1.49 volts, and 43.0 WH/lb. of cell at a wet sealed weight of 0.38 lb. Figure 2 gives the formation discharge of cells S/N 66, 67, and 68 as an example of voltage regulation at the C/3 rate.

C. High-Impact Cell. - Preliminary drafting work on the 5 AH high shock cell design to meet 4,000 "g" impact has been completed. Positive plates are reinforced with zirconium sheet for the impact test. Initial tests have shown that cell capacities are reduced 15-20% by the zirconium core in the positive plate but no gassing pressures have been observed during heat sterilization or later cycling. Negative plates are being supported by chemically etched pure Ag grid structures. Four 5.0 AH cells are being fabricated for design proofing tests at 4,000 "g" during the first quarter of 1969.

The 25 AH cell design differs from the 5.0 AH design only in the number of plates in the cell. Drafting for this design is in an advanced state. See Task 12 for detailed design description.

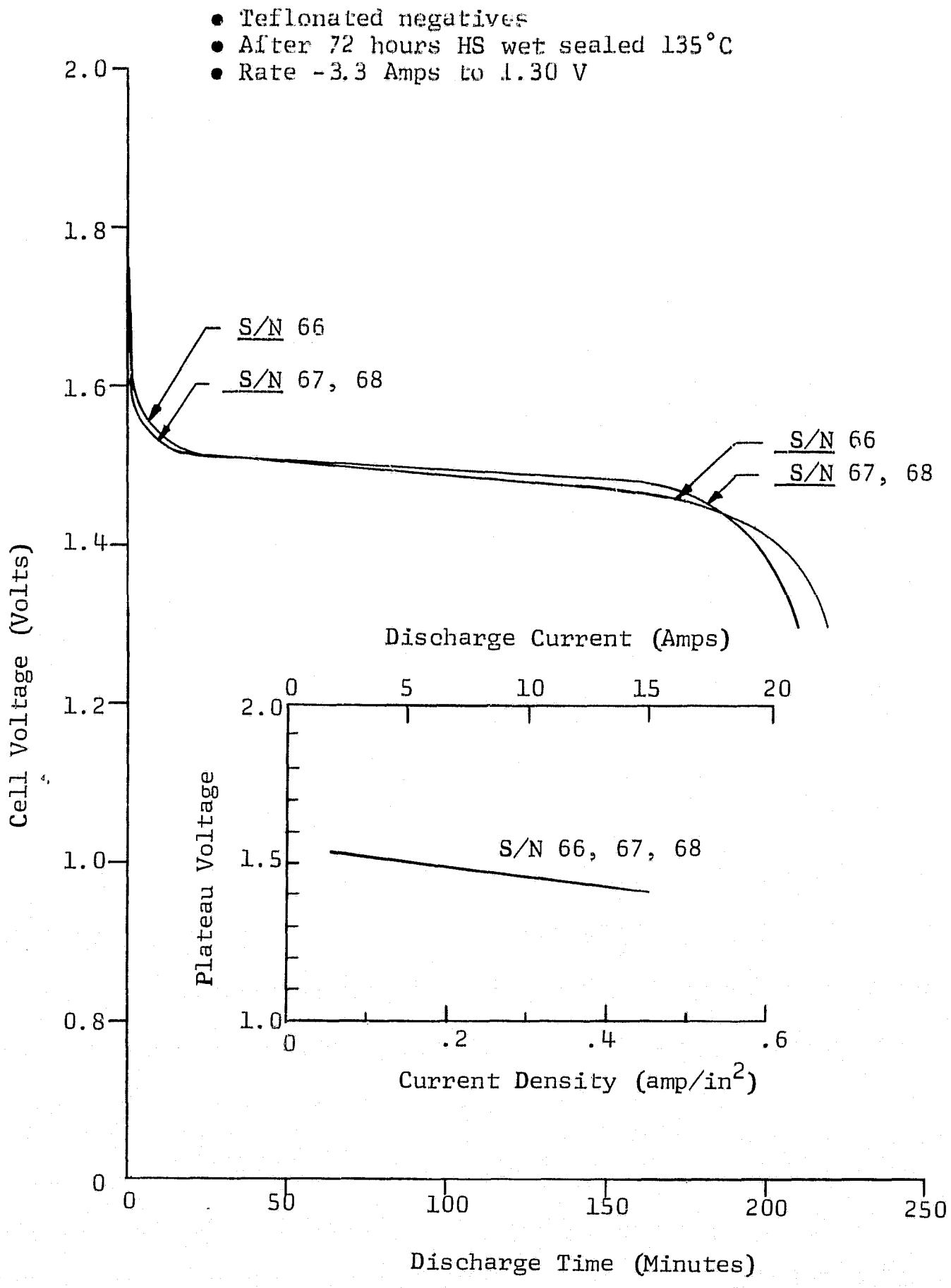
II. DEVELOPMENT OF 48 AH HIGH CYCLE LIFE, HEAT STERILIZABLE CELL TASK 10

A. Objectives and Past Work. - This task has been redirected to eliminate all battery design and development to allow concentration of all effort on cell development. Cell performance requirements are governed by JPL Specification GMP-50436-DSN-B and may be summarized -

- One year prelaunch storage followed by heat sterilization for 120 hours (now reduced to 72 hours) at 135°C;
- Charge, 9-month interplanetary travel;
- Flight, entry, and landing environments of 200 "g" for 0.7 ± 0.2 msec, 100 "g" deceleration for 10 minutes, and 35 "g" rms maximum vibration 100 to 2000 cps;

FIGURE 2

DISCHARGE CHARACTERISTICS - MODEL 281 CELLS



- 400 cycles, 50% depth, 12-hour maximum charge time, discharge rates C/10 to C/3 delivering 24 AH at operating temperatures in the range 10°C to 50°C.

Half size 24 AH cells have been designed and tested through one year uncharged stand (the Model 345), through 80 cycles (the Model 172), but in no case to date the combination.

B. Effect of Heat Sterilization, Negative Additive, and Absorber on Cycle Life. - With the Model 172 24 AH cell as the basic test cell design five groups of 3 cells each were assembled and then cycled to determine the effect on cycle life of -

- heat sterilization 120 hours at 135°C vs no sterilization
- percentage of Compound 323-43 in the negative plate active material (3, 5, and 7%)
- Pellon 2530W absorber vs no absorber

Table VI summarizes measured 100% depth of discharge capacity during 80% and 60% DOD cycling on a 21 hour modified CP charge and a 3 hour constant resistance discharge giving a total cycle life of -

6	100%	DOD cycles plus
34	80%	DOD cycles (6.4 amps, 3 hrs.), plus
44 max.	60%	DOD cycles (4.8 amps, 3 hrs.).
84	total cycles in 5-6 months wet life	

Figure 3 shows the decay of capacity for the control non-heat sterilized cells (0.33 AH/cycle) vs the four test designs. Pellon 2530W used as a positive plate absorber gave an abrupt initial capacity loss but maintained this capacity for 50 cycles before beginning to decay at the control group rate. The decay in capacity corresponded to negative plate

TABLE VI

MODEL 172 CELLS ON AUTOMATIC CYCLING

Sterilized	No			Yes			Yes			Yes			Yes		
Absorbers	None			None			Pellon 2530W			None			None		
Percent 323-43	7			7			7			5			3		
S/N	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Cell Shorted	No	No	No	Yes	Yes	No	Yes	No	No	Yes	No	Yes	Yes	Yes	Yes
Date Shorted				12/16	12/16		12/17			12/17		11/26	11/26	11/26	11/26
Cycles to Date	78	78	78	70	70	70	74	74	40	70	70	60	60	60	62
Mean Cycle Life		78			70			74			67			61	
Wet Life, Mos.	6.6	6.6	6.6	6.1	6.1	6.6	6.1	6.6	6.6	6.1	6.6	5.5	5.5	5.5	5.5
Full Capacity[1] discharge, AH	16.0	17.1	16.0	17.7	17.2	16.0	16.7	18.6	25.1	18.6	20.1	16.4	24.0	21.3	22.0
Cycle at which disch. performed	64	64	64	64	64	64	64	64	50	61	61	42	42	42	61
Last Auto-cycle[4]	82	82	82	70	70	70	74	84S	50	70	70	60	60	60	62

Automatic Cycling

- Discharge

3 hours at 6.4 amps (80% depth)	S/N 1-8, 10-15 (cycles 1-49) S/N 9 (cycles 1-15)
3 hours at 4.8 amps (60% depth)	S/N 1-8 (cycle 50-failure) S/N 10-15 (cycle 49-failure) S/N 9 (cycles 16-40)

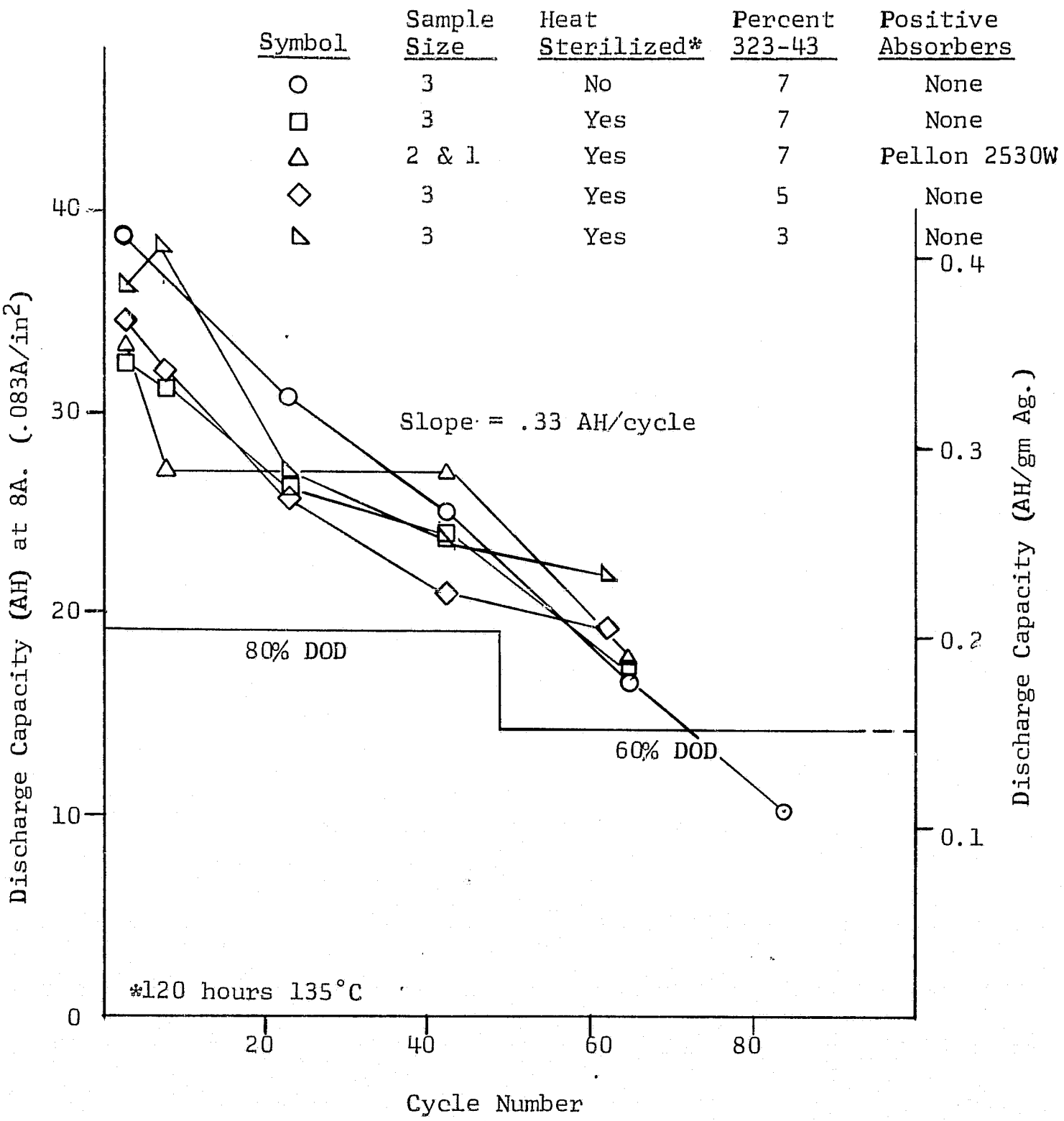
- Charge

CP for 21 hours (0.96 amp. max.)	S/N 1-8, 10-15 (cycles 1-49) S/N 9 (cycles 1-15)
CP for 21 hours (0.72 amp max.)	S/N 1-8 (cycle 50-failure) S/N 10-15 (cycle 49-failure) S/N 9 (cycles 16-40)

NOTES: (1) Discharge profile: 8.0 amps to 1.25 volts.
(2) Active silver in cell - 96.6 grams - nominal capacity 24 AH.
(3) Activation date (all cells) - 6/12/68. Last auto-cycle 12-31-68 and continuing.
(4) S = Shorted Cell.

FIGURE 3

EFFECTS OF ABSORBER AND NEGATIVE ADDITIVE ON
CAPACITY DURING AUTO-CYCLING OF MODEL 172 (24-AH) CELLS



erosion as determined by post-mortem analysis. All cells failed first, however, from Ag penetration through the 6L Southwest Research Institute GX membrane system. The three control non-sterilized cells gave at least 30-40% more cycles to end of life and failed by negative plate erosion.

As the result of the experiment above the following design changes were made the 24 AH cell.

- Compound 323-43 reduced from 7% to 4%.
- Layers GX increased from 6 to 7, 8, or 9.
- Ratio ZnO/Ag increased.
- Negative plate process changed to a sintered teflonated active material.

The newer 24 AH cell designs are described as either the Model 379 cell of Task 13 or the Model 380 cells constructed for the factorial design.

C. Advanced Design 24 AH Test Cells. - Special plates were constructed to test scale up of sintered teflonated negative plates from 5 AH size to 24 AH size. Shedding around plate edges was encountered with physical deterioration varying with plate thickness -

Plate Thickness Mils	Physical Description After Sintering
20-22	Smooth, intact
34-38	Cracked, shedding on edges
58-63	Cracked, shedding on edges and corners
75-78	Delaminated

Grids of greater expanded thickness appeared to be necessary to achieve greater dry unformed strength. A study of grid types was initiated to improve strength without an increase in true negative active material density. See Task XI. Two 3/0 expanded Ag grids spotwelded together with grids crossed gave the best overall result for the 24 AH cell.

Two teflon powders were evaluated: particle size 35 micron and 8 micron. The larger particle size gave the best green strength and sintered structure. A 6 gram metal ball was dropped from a predetermined height of 32 inches onto the dry unformed sintered plates. The plate with larger teflon particle size shed only one-third as much active material.

Four 24 AH cells were constructed using: 7 double-grid, sintered-teflonated negatives; 6 DP positives 69 gm/in^3; a 29% ZnO capacity reserve at full float charge; 96 in^2 active plate area; and 6 layers GX membrane as a separator system.

After 72 hours sterilization at 135°C in nitrogen, the cells were formation charged at the 50 hour rate and then discharged at 8.0 amps (C/3) to 1.25 volts per cell. A formation charge and discharge data summary is presented below:

Test Parameter	Unit	Observations and Cell No.			
		16	17	19	20
• Formation Charge Input (to 2.00 v/c)	AH	42.8	44.7	42.5	43.6
• Formation Discharge Output (to 1.25 v/c)	AH	34.1	36.8	41.2	41.2
• Midpoint Voltage,	Volts	1.492	1.510	1.502	1.505
• Energy Density, (Cell weight 1.08 lb.)	WH/lb.	48.5	52.8	56.2	57.0

Figure 4 summarizes voltage vs discharge current for the previous 5 experimental design types and the most recent design. A significant increase in voltage has been obtained in this progression at all discharge rates. Figure 5 gives an overall schematic of the cell design with dimensions and sealing technique. Burst pressures of the cell jars range from 175-195 psi water pressure.

FIGURE 4

MODEL 172 CELL VOLTAGE VS PULSE DISCHARGE

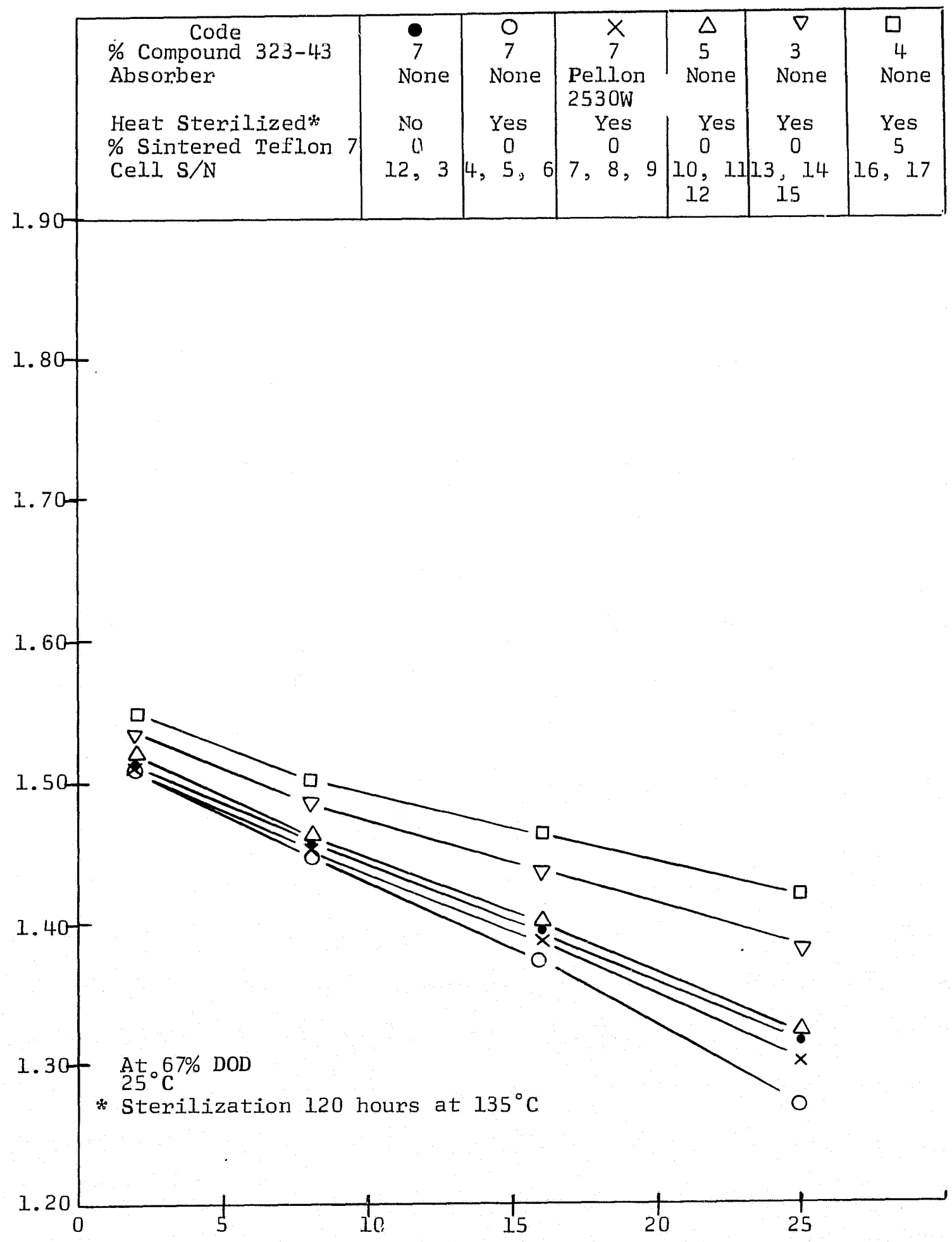
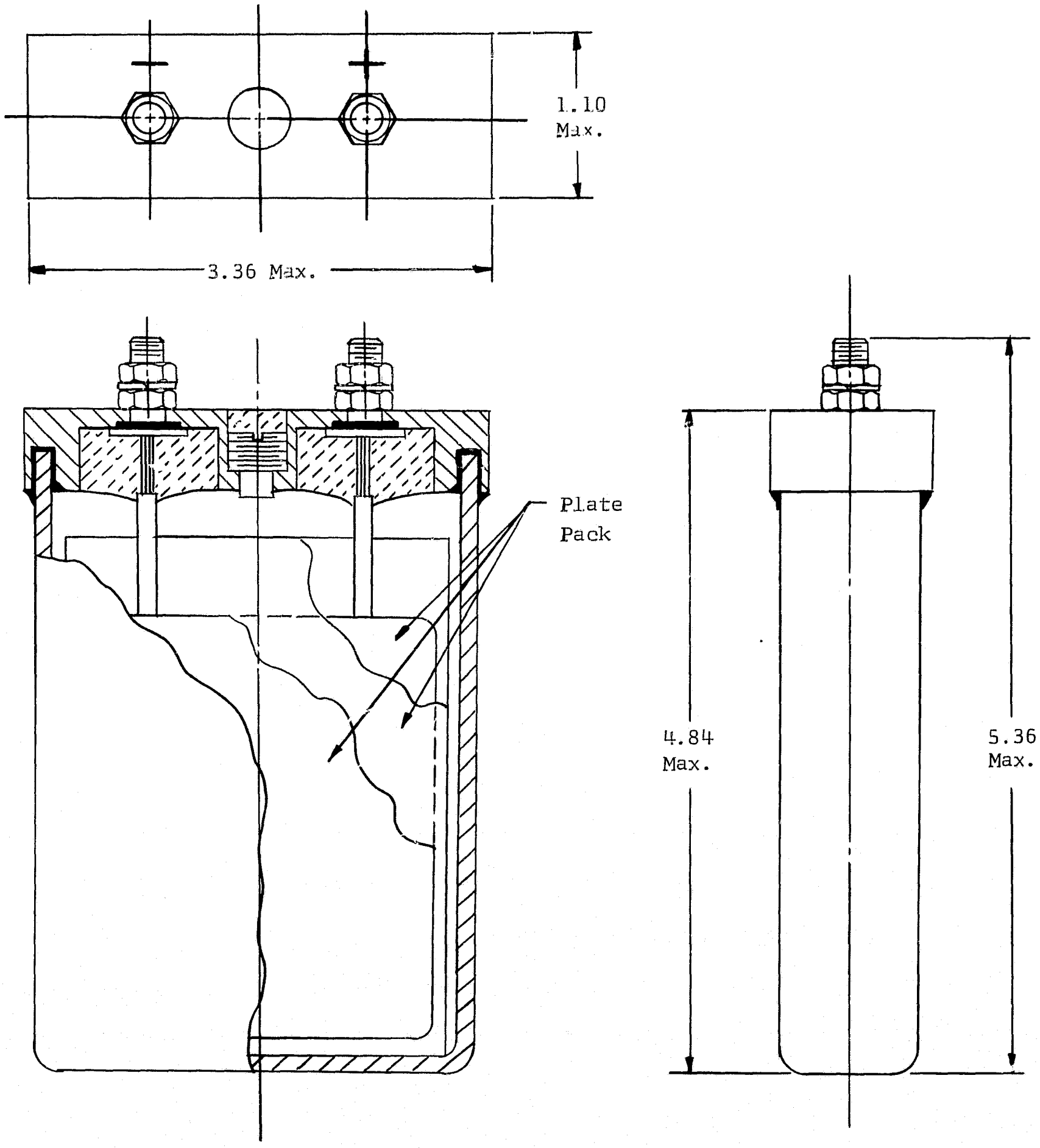


FIGURE 5

MODEL 172 (379) CELL DIMENSIONAL AND CUT-A-WAY VIEW



The four cells are now on automatic cycling routines: two on 9-hour charge/3-hour discharge at 50% DOD and two on 21 hour charge/3hour discharge at 80% depth of discharge.

D. Factorial Experiment. - Twenty-seven 24-AH cells have been designed and released for construction to test the following variables and levels on 100% depth of discharge after 72 hours wet sealed sterilization at 135°C.

Variable	Level		
	-1	0	+1
A. Weight % teflon in sintered negative plate	5	7	9
B. SWRI-GX membrane wet thickness-mils	2.0	2.4	2.8
C. Weight ratio ZnO/Ag	0.9	1.2	1.5
D. Electrolyte concentration before 90% saturation	41	43	45

Molded covers for all cell jars have been procured. Two Model C-100 Automatic Battery Cycler and controllers and two Model CT-100 Current Time Integrators have been ordered from Electro-Mechanical Research, Inc., College Park, Maryland to perform the 100% depth cycling tests to begin during the next quarter.

III. DEVELOPMENT OF 1200 WATT-HOUR BATTERY CELLS TASK 11

A. Objectivesand Past Work. - The goal for this task has been redirected from an 18-cell 2000 watt-hour battery per JPL Specification GMP-50607-DSN to a 12-cell 1200 watt-hour battery cell meeting the requirements of JPL

Engineering Memorandum 342-71. One-hundred cells are to be delivered to JPL by June 1969. Table VII summarizes the old and new specification requirements on a cell and battery basis. The major impact of redirection on the previously developed Model 364 cell design will be due to:

- Increase in landing shock from 200 to 250 g each 0.7 ± 0.2 millisecond, 30 shocks total
- Entry deceleration increase from 100 to 250 g in any direction for 10 minutes.

B. Plate Grid Structure Development. - The Model 364 80 AH cell design met the discharge requirements after sterilization for 120 hours at 135°C at 44-59 watt-hour/lb. of sealed cell but failed the shock and vibration requirements when plate grid structures did not support impact or vibration forces. Plate grid structures have been reinforced by using double 3/0 expanded mesh with long mesh dimensions at 90° angles to each other and the edges framed with 1/4 inch Ag ribbon shaped into "U" form and spot-welded to the grids. A mechanical device has been designed and constructed to test the failure modes under varying vibrational loads.

The contribution of these framed grids to plate thickness was measured using the equation

$$T_p = T_G + \left(\frac{1}{d}\right) \cdot \left(\frac{W}{A}\right)$$

where T_p, the sintered plate thickness is plotted vs (W/A), the negative mix weight per unit area giving a slope (1/d), the reciprocal active material density, and an intercept at (W/A) = 0 equal to the effective grid thickness. Effective grid thicknesses measured for several grid types and combinations are given below.

TABLE VII

DESIGN REQUIREMENTS FOR 70 AH WET
HEAT STERILIZABLE CELL

Design Parameter	Unit	Specification Requirement*	Achieved To Date Model 364 Sterilized (1)
1. Energy (12 cell battery)	WH	1200	1200 est. (1)
2. Energy density (12 cell battery)	WH/lb.	35	35 est. (2)
3. Voltage, load	Volts	14.5-22.5	15.0-21.6
	Volts/cell	(1.21-1.87)	1.25-1.8
4. Voltage, charge, max.	Volts	25.0	24.2
5. Power, continuous	Watts	300	300 est.
6. Current, continuous, C/4	Amps	17 est.	20
7. Capacity, discharge, C/4	AH	69 est.	83
8. Cycle life, 100% DOD	ea.	4	4
9. Charge time, full	Hrs.	72	51 (3)
10. Operating temperature (30 days after landing)	°C	10 to 55	20 to 30
11. Storage			
Prelaunch, 0 to 25°C	Yr.	1	NT
Transit, -10 to 25°C (25 to 40°C, 10 days only)	Months	9	NT
12. Operating Pressure	Torr	10^{-12} to 800	NT
13. Heat sterilization			
Time	Hrs.	72 (1 Period)	120
Temperature	°C	135	135
14. Shock-launch & transit (30 shocks)		250g, 0.7±0.2 msec.	NT
15. Vibration-entry and landing			
Sine		35g rms, 100 to 2000 Hz	F
Random		25g rms, 20 to 2000 Hz	NT
16. Deceleration		25g, 20 seconds	NT

(1) Based on sterilized cell tests.
(2) Estimated from achieved 40 WH/lb/sterilized cell.
(3) Formation charge-discharge-charge cycle required 134 hours, 10 hours, 38 hours respectively.

(*) JPL Engineering Memorandum 342-71 (Task 11)

NT = Not Tested; F = Failed.

Grid Type	Nominal Thickness Mils	Weight gm/in^2	Effective Thickness Mils	Mix Density gms/in^3
2/0	17	.200	5.6	37.6
3/0	15	.244	2.8	38.3
2 X 2/0	34	.400	5.6	37.4
2/0 Distorted	26	.260	3.0	36.1
2 X 3/0	30	.488	5.7	35.7

C. Model 364 Cell Performance. - Development to date on the 80 AH cell has given the performance summarized in Figure 6. No significant difference was observed comparing 6 cells heat sterilized 120 hours at 135°C from 3 cells not sterilized during their first four 20 ampere discharge tests -

Test Parameter	Group Non-Sterile	Group Sterile 120 hrs. 135°C
Voltage, Initial, 20 Amp Load	1.73	1.73
Plateau	1.47	1.47
Average	1.49	1.49
Energy Delivered, Watt-Hours	136	133
Energy Density, WH/lb. Sealed Cell	53.6	52.3

Figure 6 also shows the 20-36% loss in discharge capacity which occurred in the non-sterile group on the sixth to 24th cycle when sterilized 120 hours at 135°C after five pretest cycles. This loss can now be eliminated by proper let down technique. See Task I. Figure 7 shows projected cell dimensions and weight with the new plate grid structures. New molded covers have been ordered and will be available for the next cell tests.

IV. DEVELOPMENT OF 400 WATT-HOUR 4,000 "G" IMPACT BATTERY CELLS TASK 12

A. Objectives and Schedules. - This task is a new task requiring the development and test of cells meeting the requirements of JPL memoramdum 342-68

FIGURE 6

MODEL 364 SEALED CELL CYCLE LIFE
DISCHARGE CHARACTERISTICS SEALED - STERILIZED

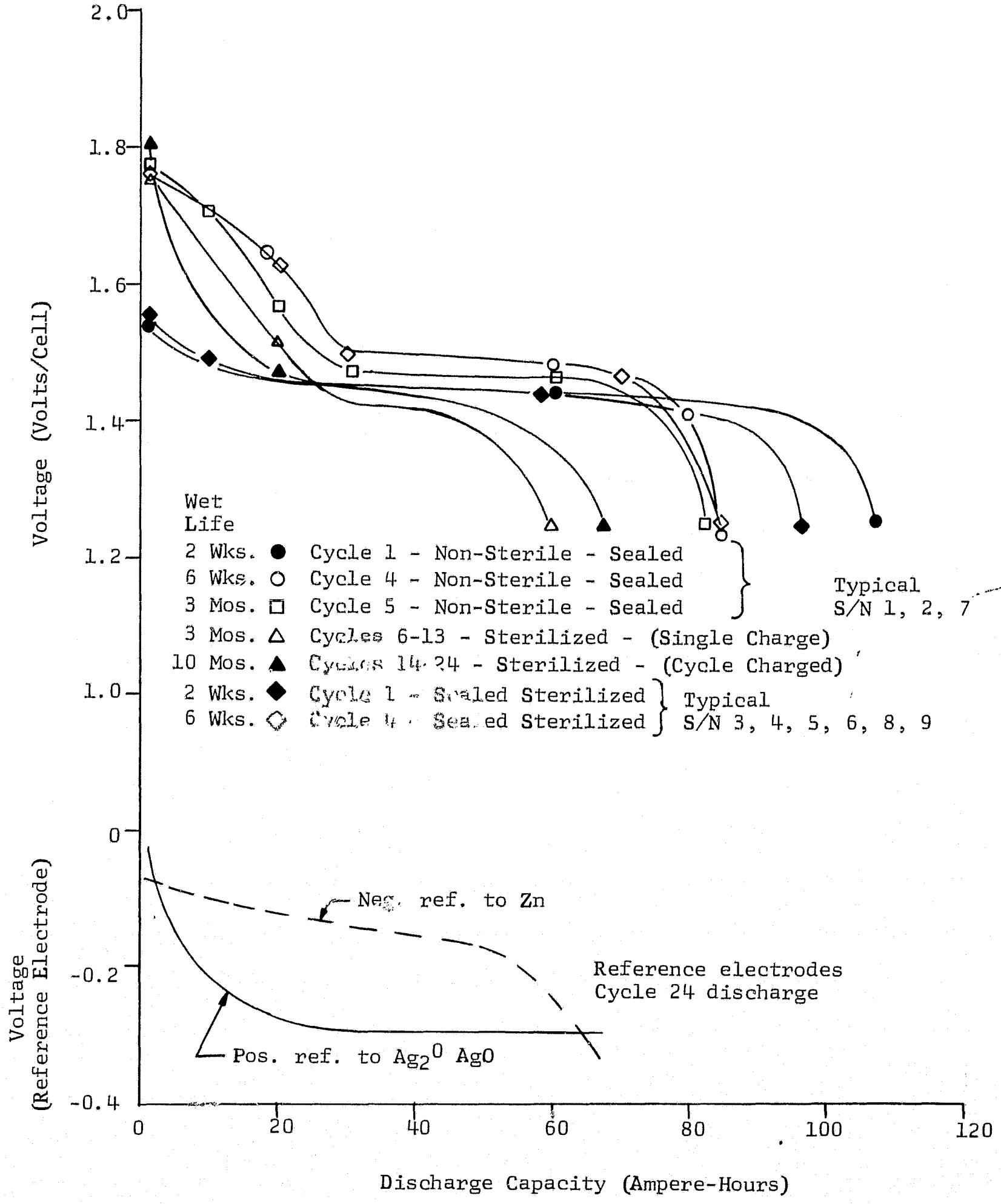
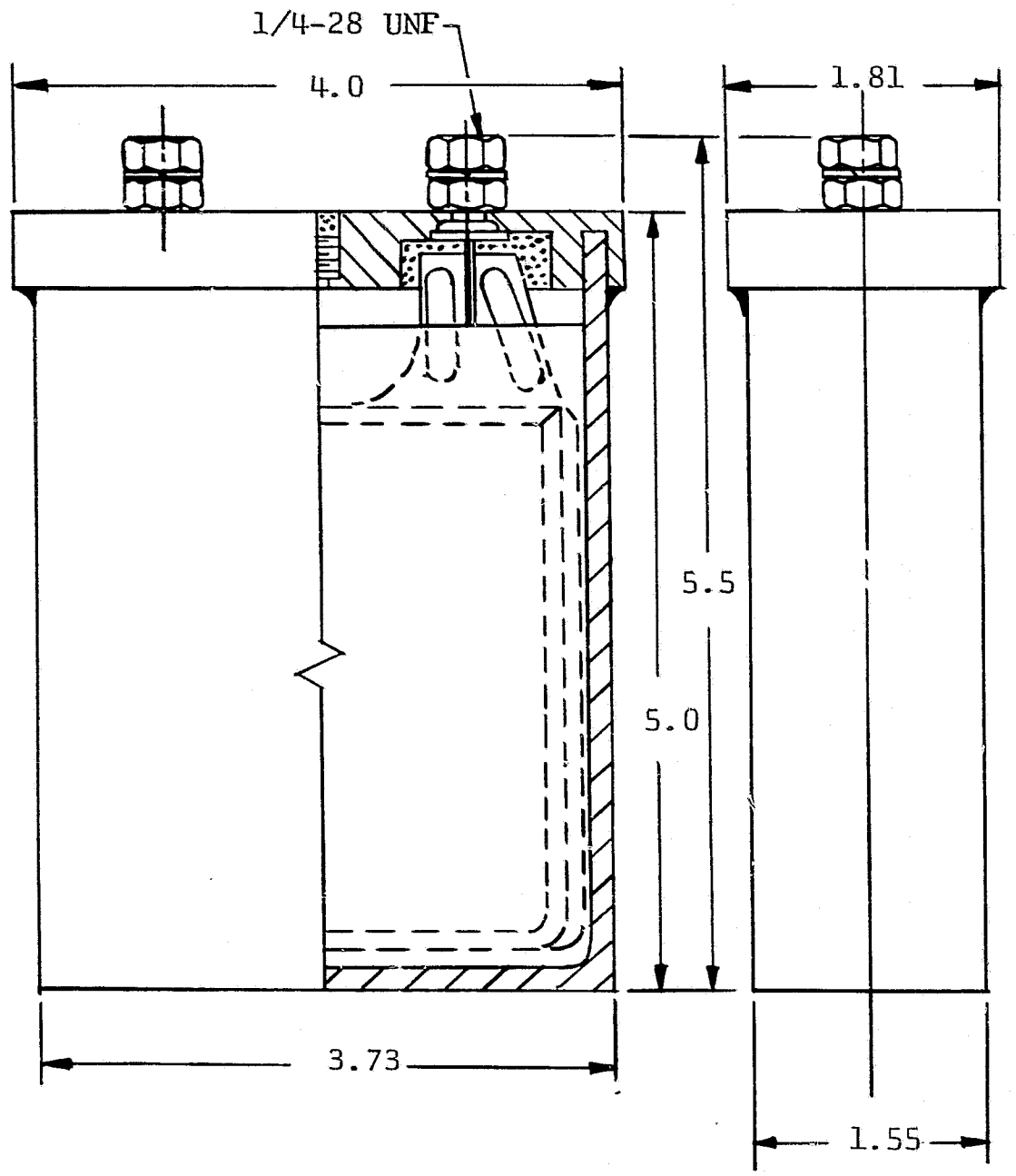


FIGURE 7

DEVELOPMENT MODEL 364
HEAT-STERILIZABLE
HSS80 Ag-ZnO CELL



Predicted cell performance at C/4 Discharge rate: (20A)

Voltage, Avg.- Volts	1.49
Capacity, AH	88
Energy, WH	133
Energy Density, WH/lb	49
Weight, lb.	2.7

which are given in Table VIII in abbreciated form. A lot of 100 cells are to be delivered to JPL in December 1969.

B. Experimental Nine Plate Cells. - Heat sterilization problems have been resolved in other tasks; thus, the major development emphasis will be on the 4,000 "g" impact plus the 90 50% depth cycles after shock. Figure 8 is a sketch of the cell design. Four positives, each reinforced with a central core of 17 mil zirconium sheet, will be inserted within the "U" folds of 8L SWRI-GX membrane. Five negatives, each having a pure Ag grid of full plate thickness chemically etched in precise pattern to retain active material, will be mounted in slots in the cell case, so that shock loads in all directions are carried by the cell case. Detailed design features of the ultimate cells are described by ESB Drawings 382-1000 for the 25 AH version and 361-1000 for the 5 AH version. The nine plate 5 AH test cell will verify electrochemical performance and shock capability prior to release of molded parts for procurement. Test cell parts will be machined from Lucite and cemented up with Lucite cement to give 1/2 inch thick jar walls. Ultimate parts will be molded in PPO 534-801 and sealed with epoxy. Liaison with the molder has established the critical flow points and compromises to favor the molder are in process.

First discharge shock tests are scheduled for the first quarter 1969.

V. DEVELOPMENT OF 400 WATT-HOUR SECONDARY BATTERY TASK 13

A. Objectivesand Past Work. - In this new task a 25 AH wet heat sterilizable cell will be designed, developed, and tested to the requirements of JPL Engineering Memorandum 342-68 except no 4,000 "g" impact test. Table IX summarizes the design requirements and data verification to date. High priority requires the delivery of 20 Type A cells in March, 20 Type B cells

TABLE VIII

DESIGN OBJECTIVES FOR 25 AH
4000 "G" IMPACT SECONDARY CELLS

Design Parameter		Units	Contract* Requirement
1.	Battery energy (12 cells)	WH	400
2.	Energy density, minimum	WH/lb.	20
3.	Voltage, load (12 cells)	Volts	14.5-22.5
4.	Capacity	AH	25
5.	Wattage (12 cells)	W	200
6.	Cycle life, 50% DOD	ea.	90
7.	Charge time, max.	hrs.	72 (full charge after heat sterilization)
8.	Cycle Charge, max. Discharge, min.	hrs.	 10 14
9.	Operating Temperature	°C	10 to 55
10.	Storage Life Prelaunch, 0 to 25°C In Transit, -10 to 25°C (10 days 25 to 40°C)		 1 year (uncharged) 9 months (charged)
11.	Operating Environment	Torr	10^{-12} to 800
12.	Heat Sterilization		3 each
13.	Shock-Launch and Transit		5 shocks X 6 250 g, 0.7 ±.2 msec.
14.	Vibration-Entry and Landing		30 g, 16 to 2000 Hz
15.	Deceleration - Entry		250 g, any axis for 30 secs.
16.	Shock-Landing		4000 "g" from 120 ft/sec.

(*) JPL Contract 951296 Engineering Memorandum 342-68.

FIGURE 8

NINE-PLATE EXPERIMENTAL CELLS FOR TESTING PLATES

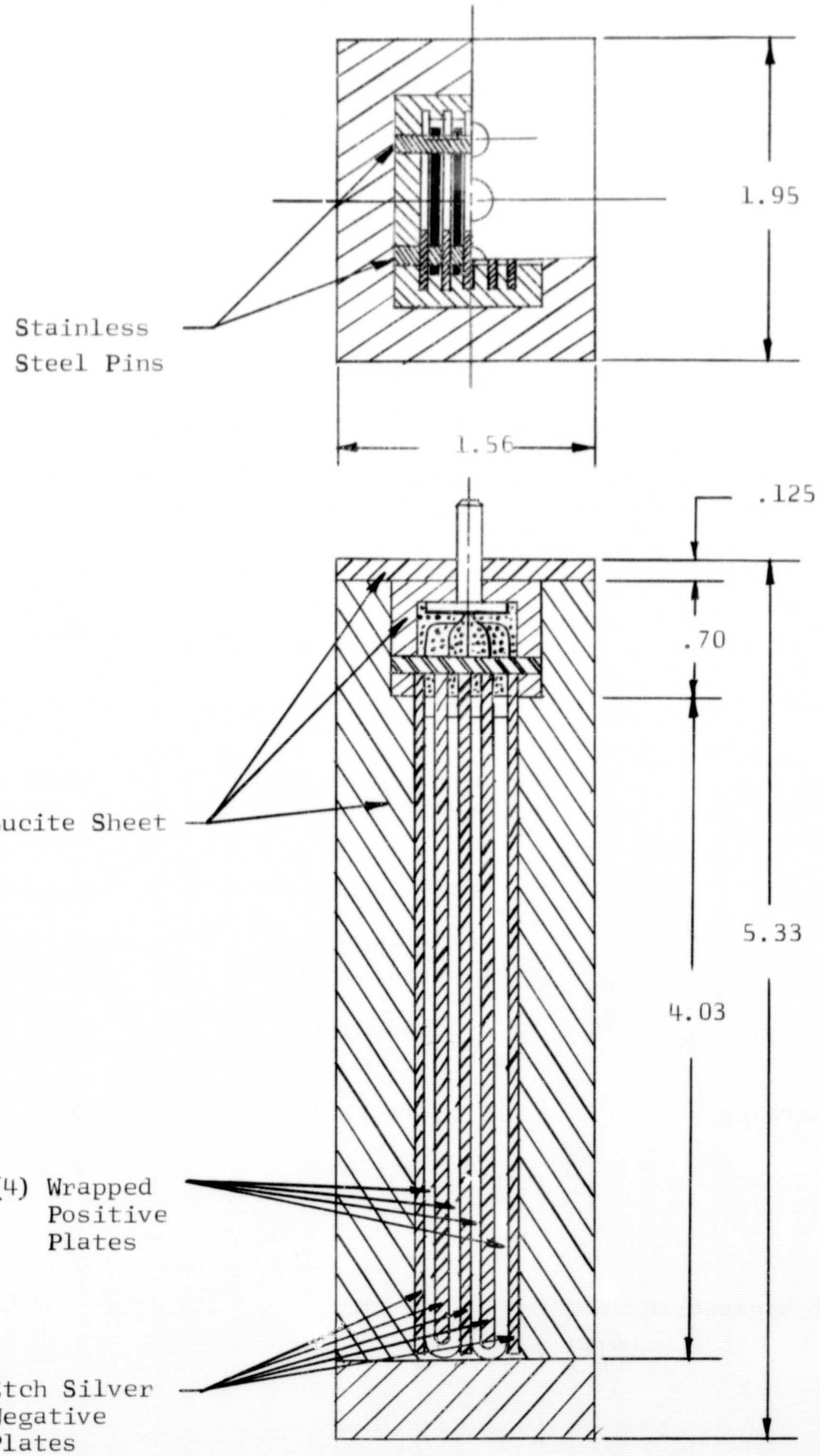


TABLE IX

DESIGN OBJECTIVES FOR 25 AH WET HEAT STERILIZABLE SECONDARY CELLS

Design Parameter	Units	Contract* Requirement	Achieved to Date (Model 172)
1. Battery energy (12 cells)	WH	400	618
2. Energy density, minimum	WH/lb.	20	52 on cells; 40 battery (est.)
3. Voltage, load (12 cells)	Volts	14.5-22.5	17.4 (C/3)
4. Capacity	AH	25	35.5
5. Wattage (12 cells)	W	200	420 (C/1)
6. Cycle life, 50% DOD	ea.	90	84
7. Charge time, max. (100%)	hrs.	72	60 - 88
8. Cycle	hrs.		
Charge, max.		10	N.T.
Discharge, min.		14	N.T.
9. Operating Temperature	°C	10 to 55	10 to 55
10. Storage Life			
Prelaunch, 0 to 25°C		1 yr. (uncharged)	1 yr. (Model 345)
In Transit, -10 to 25°C		9 month (charged)	12 months (Model 364)
(10 days 25 to 40°C)			(Not consecutive)
11. Operating Environment	Torr	10^{-12} to 800	Ambient
12. Heat Sterilization		3 each 24.5 hrs. at 135°C	120 hrs. 135°C
13. Shock-Launch and Transit		5 shocks X 6 250 g, 0.7 ±.2 msec.	N.T.
14. Vibration-Entry & Landing		30 g, 16 to 2000 Hz	N.T.
15. Deceleration-Entry		250 g any axis for 30 secs.	N.T.

(*) JPL Contract 951296 Engineering Memorandum 342-68.

in April, and 20 Type C cells will be delivered in August 1969. Basic cell design will be an advanced version of the 24 AH test cell of Task 10.

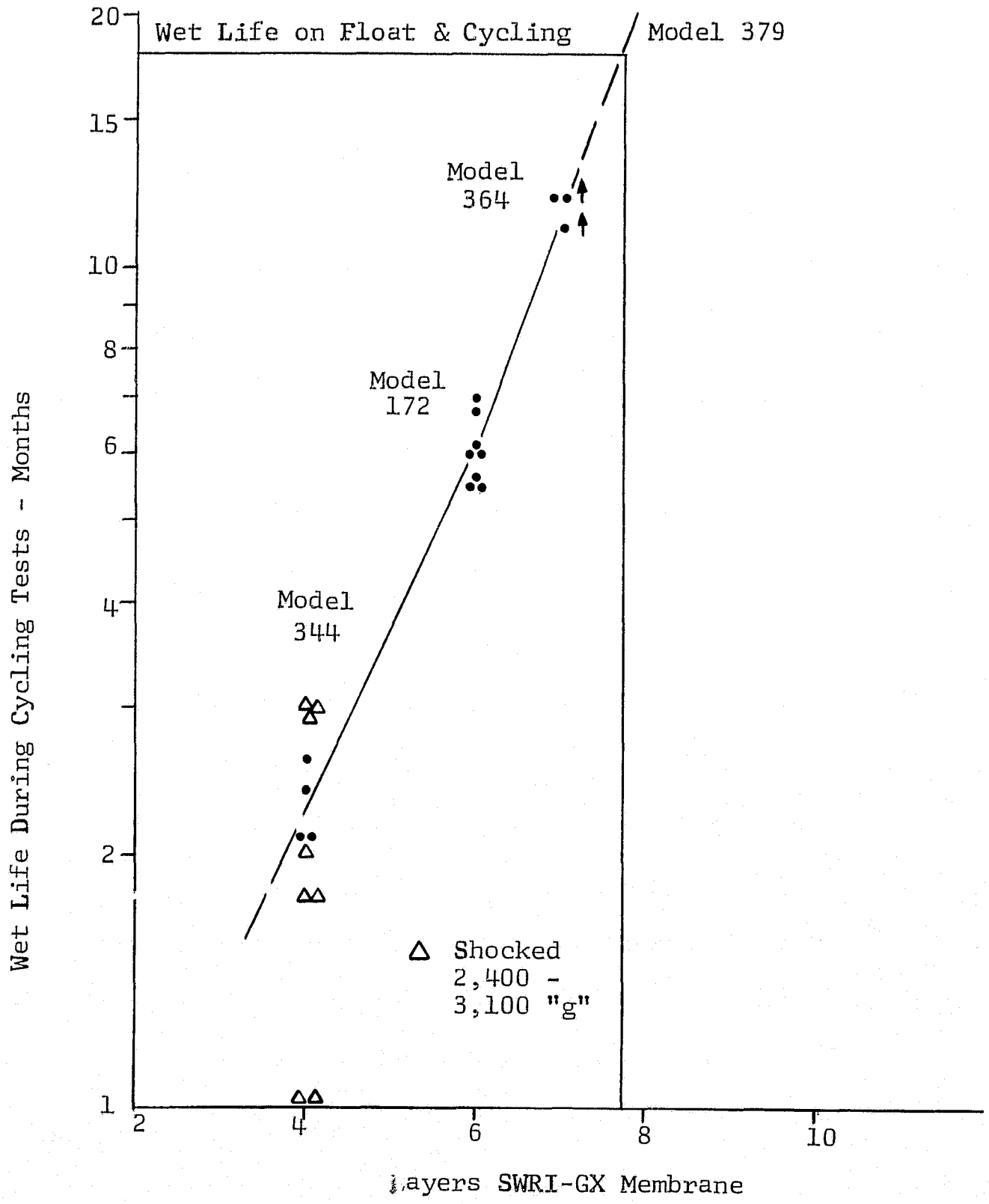
B. Cell Design. - Redesign of the Model 172 cell has been concentrated in three areas: (1) increased cycle life to give 90 50% depth of discharge cycles reliably; (2) increased wet life with an 18 month goal; (3) increased structure to meet the vibration and 250 g deceleration requirements. Selection of number of layers SWRI-GX separator was based on wet life data accumulated on previous cell types all designed for operation at a current density of approximately 0.1 amps/in^2 but having differing wet thicknesses of membrane. Figure 9 shows the extrapolation predicting that 8L GX separator should give at least 18 months wet life (combined charged stand and cycling). Twenty-five test cells are being assembled to test -

- 7L vs 9L GX membrane separator
- 42 vs 49 gm/in^3 active material density in sintered negative plates at a ZnO/Ag weight ratio of 0.8 to 1.0.
- Positive plate absorber (Pellon 2530W) vs no absorber.
- GX "U" fold on positives vs on negatives.
- Epoxy platelock vs no platelock to cement the bottom edges of exposed plates to the jar.

The cycle life achieved for the Model 172 cell (see Task 10) (6-100% DOD cycles, 34-80% DOD cycles, plus 20-44 50% DOD cycles) should be increased to the desired 90 50% DOD cycles (21 hour charge, 3 hour discharge) by the addition above of 2-4 layers GX, a 20% reserve of ZnO after full float charge, and by decreased plate erosion resulting from the sintered negative plate process. Test data will be available during the first quarter of 1969.

FIGURE 9

WET HEAT STERILIZED CELL LIFE VS NUMBER
OF LAYERS SWRI-GX MEMBRANE



VI. CONCLUSIONS AND RECOMMENDATIONS

A. Heat shrinkable polyolefin tubing, used as plate lead insulation in Model 281 test cells, has been found to accelerate hydrogen evolution from negative plates of heat sterilized Ag-ZnO cells on formation charge. Replacement of polyolefin with teflon tubing eliminated this major problem.

B. Model 281 test cells now deliver 11.0 AH at 3.3 amps to 1.25 volts at an average voltage of 1.49 volts, 16.4 watt-hours and 43.0 watt-hours per pound of sealed cell after sterilization wet sealed for 72 hours at 135°C.

C. Model 172 24 AH heat sterilized sealed cells have delivered 6 100% DOD, plus 34 80% DOD, plus 44 maximum 60% DOD cycles in 5-6 months of wet life. Failures occurred from Ag penetration. Non-sterile control cells exhibited failures at 84 total cycles from plate erosion but no cell shorts.

D. Model 172 24 AH sealed cells have delivered 34 AH at 8.0 amps to 1.25 volts, a midpoint voltage of 1.49 volts, and an energy density of 49 watt-hours per pound of sealed cell after 120 hours sterilization at 135°C.

E. Model 364 80 AH sealed cells have delivered a mean 4-cycle capacity of 89 AH at 1.49 volts at 20 amps to 1.25 volts, an energy of 133 watt-hours, and an energy density of 52 watt-hours per pound of sealed cell after sterilization 120 hours at 135°C.

F. Life to short data accumulated to date predicts 8 layers of GX separator should increase cell life after sterilization to 18 months. New cell designs are testing 7, 8, and 9 layers for verification.

PROJECT PERSONNEL

The experimental work presented herein has been performed by the following ESB Incorporated personnel.

At the Research Center -

Section Leader	- G. F. Nordblom
Scientist	- H. I. James
Technicians	- W. F. Kobie, F. J. Lewis

At Jet Propulsion Laboratory -

Scientist	- J. T. Arms

At Exide Missile and Electronics Division -

Project Leader	- A. M. Chreitzberg
Staff Consultant, Mechanical Design & Stress Analysis	- T. H. Purcell, Jr.
Senior Project Engineers: Tasks 4, 8, 9, 12 Task 11	 - A. W. Jordan - J. F. Szabo
Project Engineers Taks 10, 13	 - E. K. Woomer, C. D. Farris
Quality Assurance Engineer	- W. C. Rodgers