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DEVELOPMENT AND TESTING OF A FIVE AH SILVER ZINC CELL

SUMMARY REPORT COVERING PERIOD
JULY 1967 THROUGH JUNE 1968
UNDER CONTRACT NAS 3-10924

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SUMMARY REPORT

DEVELOPMENT AND TESTING OF
A FIVE AH SILVER-ZINC CELL

by

A. Himy

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

July 1968

CONTRACT NAS 3-10924

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CONTENTS

Section 1	INTRODUCTION	1
Section 2	SUMMARY	3
Section 3	WORK PERFORMED	5
	3.1 Task I: Selection of Improved Cell Components	5
	3.2 Task II: Finalized Design, Preliminary Cell Testing	89
	3.3 Task III: Fabrication, Test and Delivery of Cells	102
Section 4	COMMENTS AND CONCLUSIONS	129
	REFERENCES	131
Appendix A	ENVIRONMENTAL TESTS	133

FIGURES

1	Discharge Curves at 1 A	8
2	Cycling Performance of Cells on the 90 Minute Regime	10
3	Cycling Curves of Cells With and Without PbO	11
4	Cycling Curves of Cells With and Without PbO	12
5	Cycling Curves of Cells With and Without PbO	13
6	Discharge of Curves of Cells With Two Different Sizes of Positive Electrodes	17
7	Text Fixture for Case-to-Cover Seal	20
8	Water Weight Loss After 120 Hours Through Plastic 5 AH-Cell Case	24
9	Ultrasonic Welding of Cover to Case	27
10	Pressure Testing of Cell After Welding	28
11	Electrode Lead Attachment to Cell Terminal	29
12	Cycling Curves of Cells With 5 Ag-14-1/0 Exmet	34
13	Cycling Curves of Cells With 5 Ag-14-1/0 Exmet	
14	Discharge Curves of Cells With Various Concentrations of KOH	38
15	Group ZL-32 Typical Cycling Curves	44
16	Group ZL-32 Typical Cycling Curves	45
17	Group ZL-32 Typical Cycling Curves	46
18	ZL-32 Cell Electrode Set After 1632 Cycles	49
19	First Concept for Epoxy Separator Bond Shear Test	54
20	Second Concept for Epoxy-Separator Bond Shear Test	58
21	Gassing Test Set-up	65
22	Gassing vs. Cycle	68
23	Average Gassing Rate of Free Venting Cells (DA-5) on Cycling at 25°C	70
24	Average Open Circuit Gas Evolution of Free Venting Cells (DA-5) After End of Charge, on Stand at 25°C	71

25	Gassing Rate of Cells on Cycling	75
26	Gassing Rate of Cells on Open Circuit Stand at 25°C	76
27	Gassing Rate of Cells on Cycling	78
28	Gassing Rate of Cells on Open Circuit Stand at 25°C	79
29	Average Gassing Rate of Free Venting Cells (DA-5) on Cycling	83
30	Average Gassing Rate and Gas Composition of Free Venting Cells on a 24-Hour Cycle	85
31	Cycling Curve of Free Venting DA-5 Cell on 24-Hour Regime	86
32	Cycling Curve of Pressurized DA-5 Cells on 24-Hour Regime	87
33	Average Gassing Rate of Cells on Open Circuit Stand	88
34	Gassing Rates at 25°C and 40°C on the 2 Hour-Period Regime	91
35	OCV Drop at 100°C of Charged 5 Ah-Cells	96
36	Capacity Retention on Charged Stand Over a 3-Month Period at 25°C	98
37	Typical Voltage-Current Relationship During Cycling	101
38	Group A (Environmental Test) Typical Cell	106
39	Group A (Environmental Test) Typical Cell	107
40	Group B (Control) Typical Cell	111
41	Group B (Control) Typical Cell	112
42	Group C (Pressure Gauge) Typical Cell	116
43	Group C (Pressure Gauge) Typical Cell	117
44	Group D: Repeat of Controls With Higher Voltage Limit	121
45	Group D: Repeat of Controls With Higher Voltage Limit	122
46	ZL-40-1 Cell: Condition of Electrodes After 557 Cycles at 45% Depth of Discharge of Rated Capacity	124
47	Silver-Zinc Cells of Final Design for Task III	128

TABLES

I	Cells With and Without PbO Additive	7
II	Voltage at End of Discharge Period	9
III	Failure Analysis of ZL-11 Series	14
IV	Capacity on Formation	16
V	Effect of KOH on KT Interseparator Measured by Variation of Contents (g/l) of Free KOH and Carbonate	19
VI	Hot-Gas Welding Test	21
VII	Water Weight Loss Through Sealed Cases After 120 Hours	23
VIII	Weight Loss of Sealed Cases Partially Filled With KOH and Submitted to 135°C for Indicated Time	26
IX	Five-Ah Cell Performance Data	32
X	Voltage at End of Discharge Period	33
XI	Group ZL-1 Cycling Data Summary	36
XII	Formation With Different KOH Concentrations	37
XIII	Formation of Standard Cells With 40% KOH Electrolyte	40
XIV	Uniformity Study	41
XV	Uniformity Study	42
XVI	Uniformity Study	43
XVII	Group ZL-32 Capacity Check During the 90-Minute Cycling	47
XVIII	Group ZL-32 - Test Summary	48
XIX	Material Tests	50
XX	Separator 3420-09 Physical Characteristics	53
XXI	Shear Strength of Bonded Separators	56
XXII	Shear Strength of Bonded Separators Submitted to KOH at 135°C for Indicated Hours	59
XXIII	Average Test Data Over 30 Days - Valve A	62
XXIV	Average Test Data Over 30 Days - Valve B	62
XXV	Average Data for Valve C	63

XXVI	Average Test Data Over 30 Days - Valve AA	63
XXVII	Gassing Tests	66
XXVIII	Gassing Tests	67
XXIX	Comparison of Amounts of Gas Collected and Gas Equivalent of Electrolyte Consumed During the Entire Testing Period	72
XXX	Tests Run After Completion of 360 Cycle Gassing Test	73
XXXI	Formation of Cells With New 3420-09	77
XXXII	Gassing Tests	80
XXXIII	Gassing Tests	82
XXXIV	Oxygen Evolution During the Course of a Cycle	84
XXXV	Gas Composition and Gassing Rate of Free Venting Cells on 27th Cycle	84
XXXVI	Gassing Tests	90
XXXVII	Status of Cells After Gassing Test at 40°C	92
XXXVIII	100°C Wet Stand Test Data	94
XXXIX	100°C Wet Stand Test Averages of 8 Cells	95
XL	25°C Wet Stand Test	97
XLI	Uniformity Study	103
XLII	Uniformity Study	104
XLIII	Uniformity Study	105
XLIV	Uniformity Study	108
XLV	Uniformity Study	109
XLVI	Uniformity Study	110
XLVII	Uniformity Study	113
XLVIII	Uniformity Study	114
IL	Uniformity Study	115
L	Uniformity Study	118
LI	Uniformity Study	119
LII	Uniformity Study	120
LIII	Group ZL-40 - Test Summary	123
LIV	Task III - Cell Test Distribution	125
LV	Task III - Correlation of Variables	127

Section 1

INTRODUCTION

The conventional silver-zinc cell is restricted in operation because of its limited cycle life. Improvement of the cycle life would qualify this energy source for many applications for which less energetic systems are now used, like the synchronous orbit satellite.

The key to improved life lies in developing a nonreactive separator to eliminate most of the factors that cause degradation and early failure.

Laboratory cells using a Douglas Aircraft Company inorganic separator on contract NAS 3-7639 (Reference 1) shown stability, improved cycle life, and the ability to operate over a wide temperature range. Multiplate cells were designed and tested. Additional work is required on the present contract to provide a refined sealed cell design suitable for extensive characterization.

Six lots of 25 cells each will be delivered to NASA for testing.

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Section 2

SUMMARY

The present report presents a summary of the work performed in the first year of this program. The program consists of three tasks. Two were completed; the third one will be completed in six months and covers the fabrication, test and delivery of the final approved cell design.

The first two tasks cover the selection of improved cell components and the testing of the cell design incorporating all the improvements.

Task I was a study of all cell components with particular emphasis on the sealing; 40 psig pressure relief valves were adapted to the cell for cycling tests and gassing rate characteristics were investigated in free-venting and pressurized cells on three different cycling periods and temperature combinations.

Task II was concerned with the preliminary cell testing of the approved design incorporating all improvement features of the previous task.

Wet stand tests were run at 100°C and 25°C over a three-month period. The more useful data were at 25°C and showed an 84% residual capacity retention after a three-month stand.

Cells submitted to environmental tests (shock, acceleration, vibration) as specified by the contract passed successfully while in the charged condition, maintained their OCV, and cycled afterwards along with cells destined for electrical tests.

Four groups of five cells each all cycled on a regime equivalent to 45% depth of discharge, based on rated capacity (5 Ah) on the 90-minute cycling regime in the medium range of 500 to 700 cycles. (Maximum reached 960 cycles, average 660 cycles.)

The main characteristics of the 5-Ah silver-zinc cell design (DA-5-1N) are as follows:

Electrode Pack Configuration: 5 positives, 4 negatives

Positives:

Dimensions: 1.6" x 1.6" x 0.022"

Silver Weight: 4.5 g

Interseparator: Pellon 2505 ML

Negatives:

Dimensions: 1.6" x 1.6" x 0.070"

Interseparator: KT (pressed in electrode)

ZnO mix: 6.0 g

HgO: 2%

Separators:

Inorganic, rigid, 3420-09

Thickness: 25 mils

Absorption: 10%

Assembly:

Negative electrode sandwiched between two oversized rigid separators forming a compartment sealed on 3 edges and open at the top

Electrolyte: 20 cm³ of 40% KOH

Case and Cover: Polysulfone P-1700

Cover to Case Seals: Ultrasonic weld and epoxy

Other: 40 psig pressure relief valve

Dimensions (plastic only): 3" h x 2.28" w x 1.04"

Weight (with electrolyte): 230 grams

Original Capacity: 7.5 to 8.0 Ah

Section 3

WORK PERFORMED

Work done on Contract NAS 3-7639 (Reference 1) has shown that a silver-zinc cell designed with the Douglas inorganic separator 3420-09 (rigid type) is capable of improved cycle life at temperatures as high as 100°C.

The present program requires that a refined 5-Ah cell design be provided suitable for extensive characterization. After a period of cell component improvement and final design selection, a number of identical cells of the approved design are to be delivered to NASA for independent testing in six lots of 25 cells each, fabricated at short intervals.

3.1 TASK I: SELECTION OF IMPROVED CELL COMPONENTS

The objective of this task was to improve various cell components and fabrication techniques and to incorporate these improvements into a 5-Ah cell design. The gassing characteristics were also to be investigated to provide information for the design of a fully sealed cell.

3.1.1 Electrodes

The positive and negative electrodes were essentially the same design as used on previous contract NAS 3-7639 (Reference 1). Minor modifications were tried on the negative and positive electrodes, but were not used on the majority of the tests.

3.1.1.1 Negative Electrode

The addition of 1% PbO to the zinc oxide mix of the negative electrode was tried once in a few test cells on contract NAS 3-8513 "Improvement of the Zinc Electrode" (Reference 2). This modification of the standard electrode was tested again on full 5-Ah cells. Five standard 5-Ah cells and five cells

using PbO additive were built and placed on test on the 1/2-hour discharge, 1-hour charge cycling regime at 20 mA/cm^2 at room temperature. Table I and Figure 1 show their original electrical performance. Table II gives their end discharge voltages at various cycles. Figure 2 and Table II give their failure cycles and failure analyses. Figures 3 to 5 show comparative typical cycling performance at various cycles.

Two control cells failed after 2212 cycles, one cell with PbO failed after 2554 cycles, but upon dissection of the three cells, it was found that the negative electrode wire leads were loose in the terminal with solder that was heavily corroded (these early cells used feed-through terminals). Two other cells (one control, one with PbO) failed to deliver their cycling capacity at cycles 2554 and 2720, respectively. The terminals showed the same corrosion signs and were tentatively crimped around the wires for better contact. After recharge, the cells were put back on cycling. However, the first one could not cycle more than 2575 cycles, whereas the other continued cycling. The cycle life ranged from 2212 cycles to 3194 cycles. Analysis of the data shows marginal differences that may be attributable to normal statistical distribution.

The cause of failure is primarily low capacity, close to the cycling capacity requirement (Table III), which makes the cell operate at 100% of the available capacity. However, when the cell stood in the charged condition, there was a slight decay of its OCV, which was also evidence of a slow short. Upon dissection, it was noticed that the separators were not cracked in many instances, the edge seals were good, and the electrodes were in good condition. The zinc electrodes did not slump nor lose shape for more than 10 to 15% at their top. However, some separators showed signs of zinc penetration.

3.1.1.2 Shifting Positive Electrodes and Their Correction

Cells with Large Positive Electrodes

It was noticed that the silver electrodes may shift when cells are handled dry. In order to circumvent this undesirable shifting, the silver electrodes were made larger so as to occupy the full width of the case and touch the bottom.

TABLE I
CELLS WITH AND WITHOUT PbO ADDITIVE

(All cells charged at 0.350 A to 2.10 V
and discharged at 1.0A to 1.0V)

	Input	Output	Plateau Voltage
Control Cells			
ZL-11-1	8.4 Ah	7.3 Ah	1.42 V
ZL-11-2	8.4	7.2	1.42
ZL-11-3	8.4	7.4	1.42
ZL-11-4	8.4	7.2	1.42
ZL-11-5	<u>8.4</u>	<u>7.3</u>	<u>1.42</u>
Average	8.4 Ah	7.3 Ah	1.42 V
Cells with PbO			
ZL-11-6	10.7 Ah	8.6 Ah	1.43 V
ZL-11-7	10.7	8.7	1.43
ZL-11-8	10.7	8.5	1.43
ZL-11-9	10.7	8.5	1.43
ZL-11-10	<u>10.7</u>	<u>8.5</u>	<u>1.43</u>
Average	10.7 Ah	8.6 Ah	1.43 V

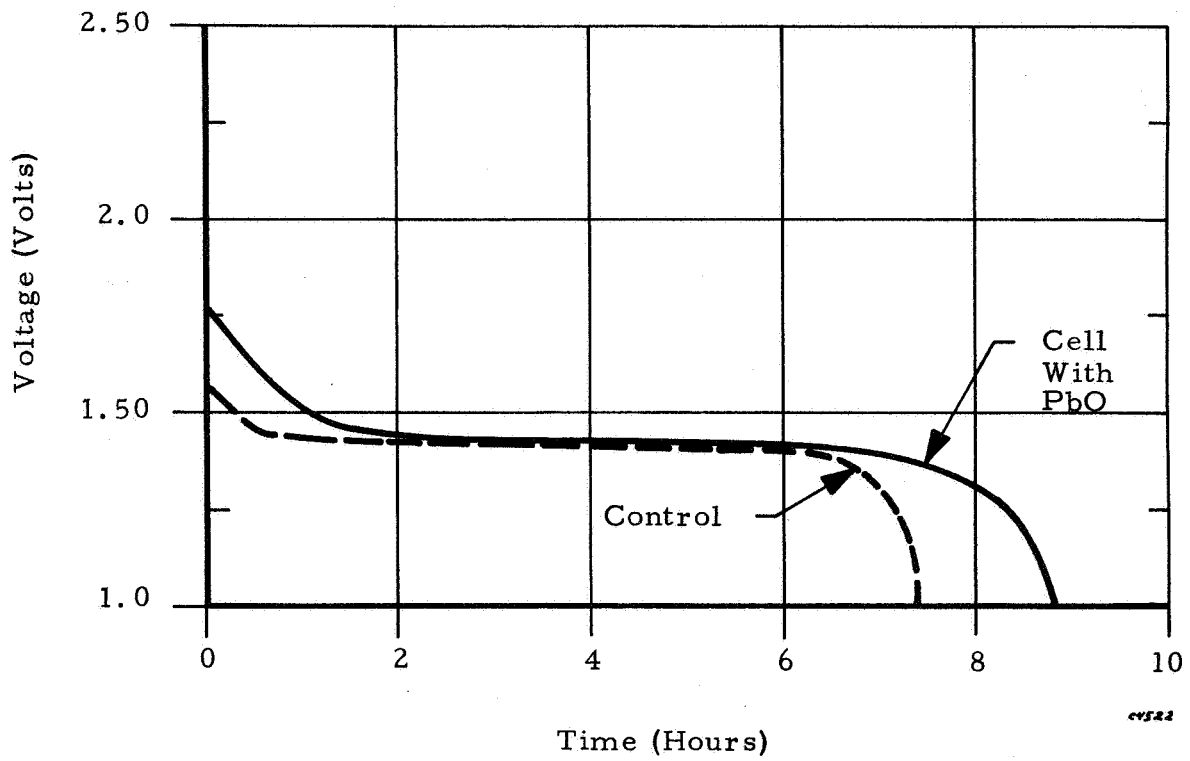


Figure 1. Discharge Curves at 1 A
(Cell Specs as Indicated)

TABLE II

VOLTAGE AT END OF DISCHARGE PERIOD (1/2 HOUR)

Regime: 1/2 hr - 2.5 A discharge
1 hr - 1.4 A charge

Design Feature	Cell No.	Cycles									
		5	500	1000	1500	1930	2250	2500	2800	2900	3194
Standard Negative	ZL-11-1	1.40	1.30	1.28	1.28	1.34	1.29	1.29	1.29	—	—
	ZL-11-2	1.40	1.34	1.34	1.34	1.36	1.31	1.28	1.28	—	—
	ZL-11-3	1.40	1.31	1.30	1.30	1.32	—	—	—	—	—
	ZL-11-4	1.40	1.30	1.28	1.28	1.32	1.32	1.30	1.29	—	—
	ZL-11-5	1.40	1.28	1.28	1.28	1.32	—	—	—	—	—
PbO in Negative	Average	1.40	1.31	1.30	1.30	1.35	1.31	1.29	1.29	—	—
	ZL-11-6	1.40	1.30	1.28	1.26	1.30	1.26	1.30	1.26	—	—
	ZL-11-7	1.40	1.32	1.30	1.28	1.34	1.30	1.30	1.30	1.18	—
	ZL-11-8	1.40	1.31	1.28	1.27	1.30	1.30	1.30	—	—	—
	ZL-11-9	1.40	1.34	1.34	1.34	1.35	1.36	1.20	1.20	1.22	0.98
	ZL-11-10	1.40	1.30	1.27	1.26	1.24	1.20	1.20	1.20	—	—
Average	1.40	1.31	1.29	1.28	1.30	1.28	1.26	1.25	1.20	0.98	

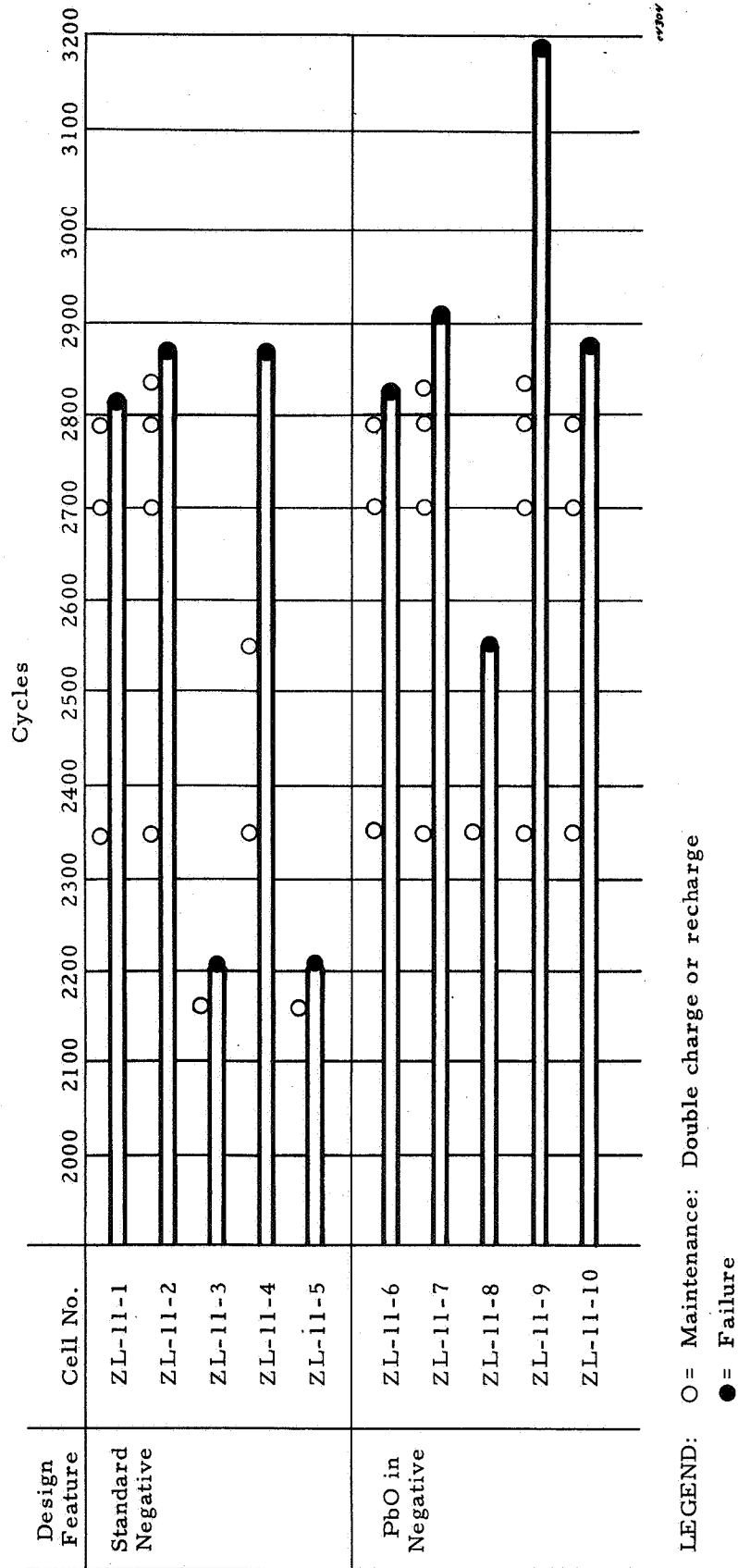


Figure 2. Cycling Performance of Cells on the 90 Minute Regime

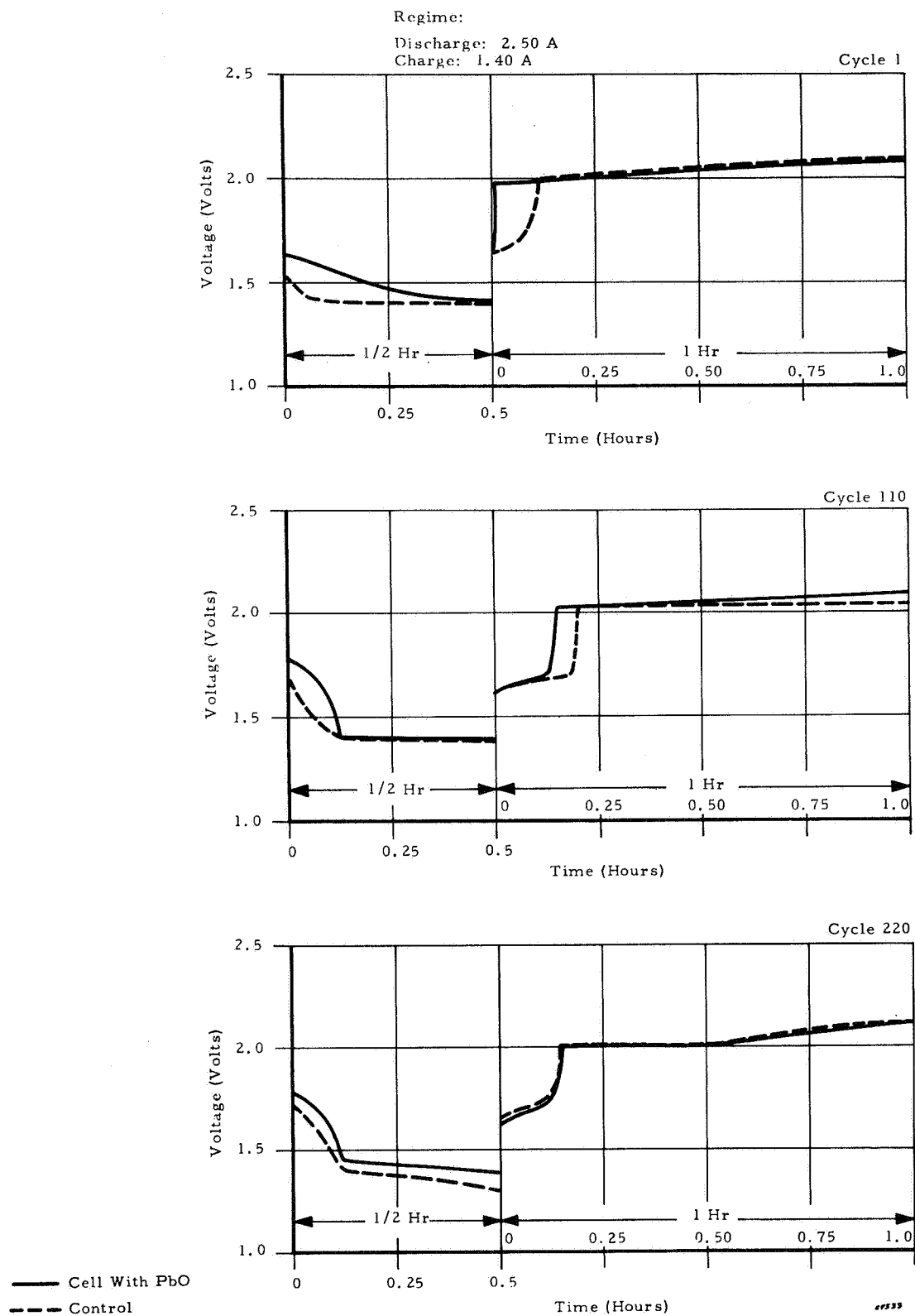


Figure 3. Cycling Curves of Cells With and Without PbO

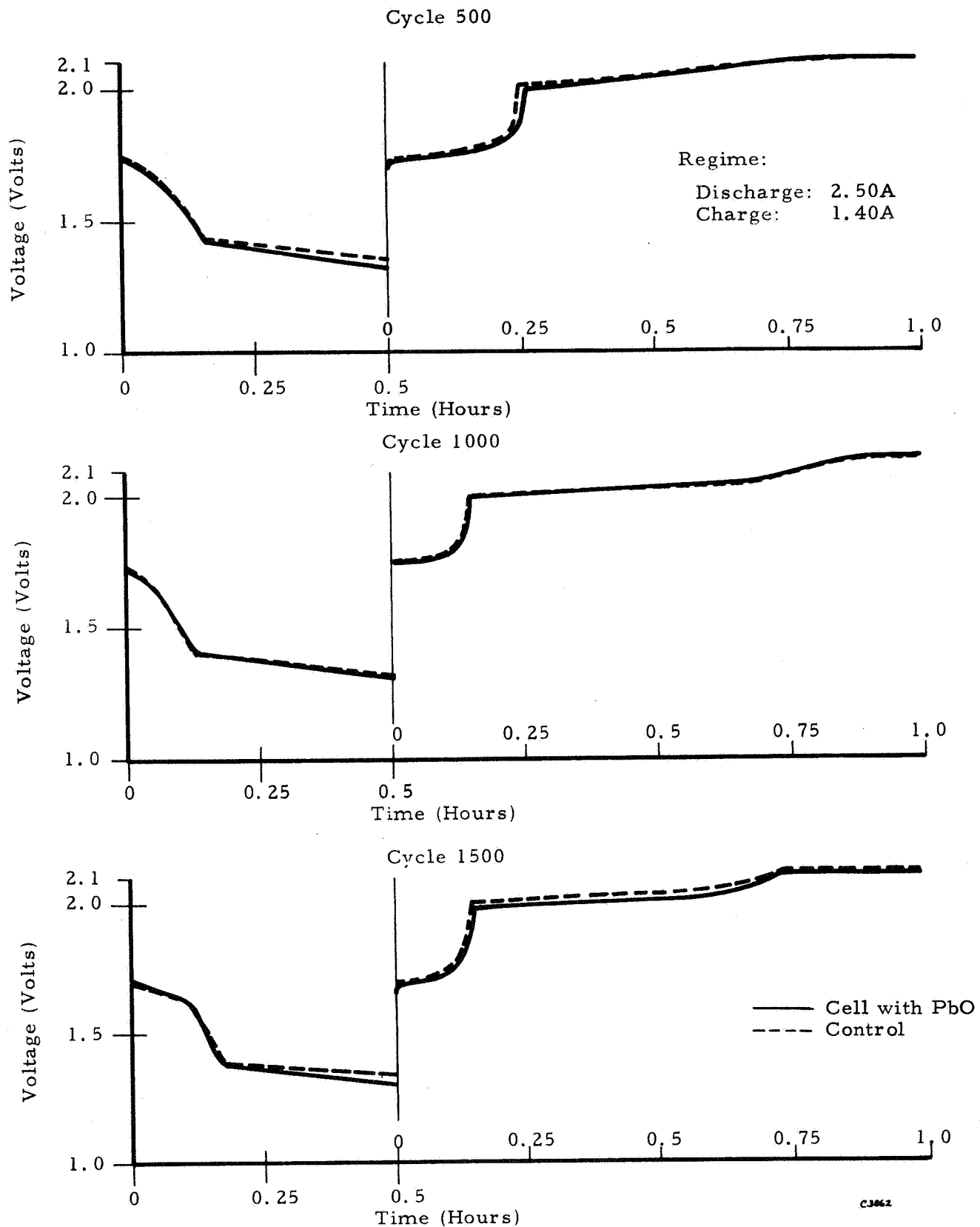


Figure 4. Cycling Curves of Cells With and Without PbO

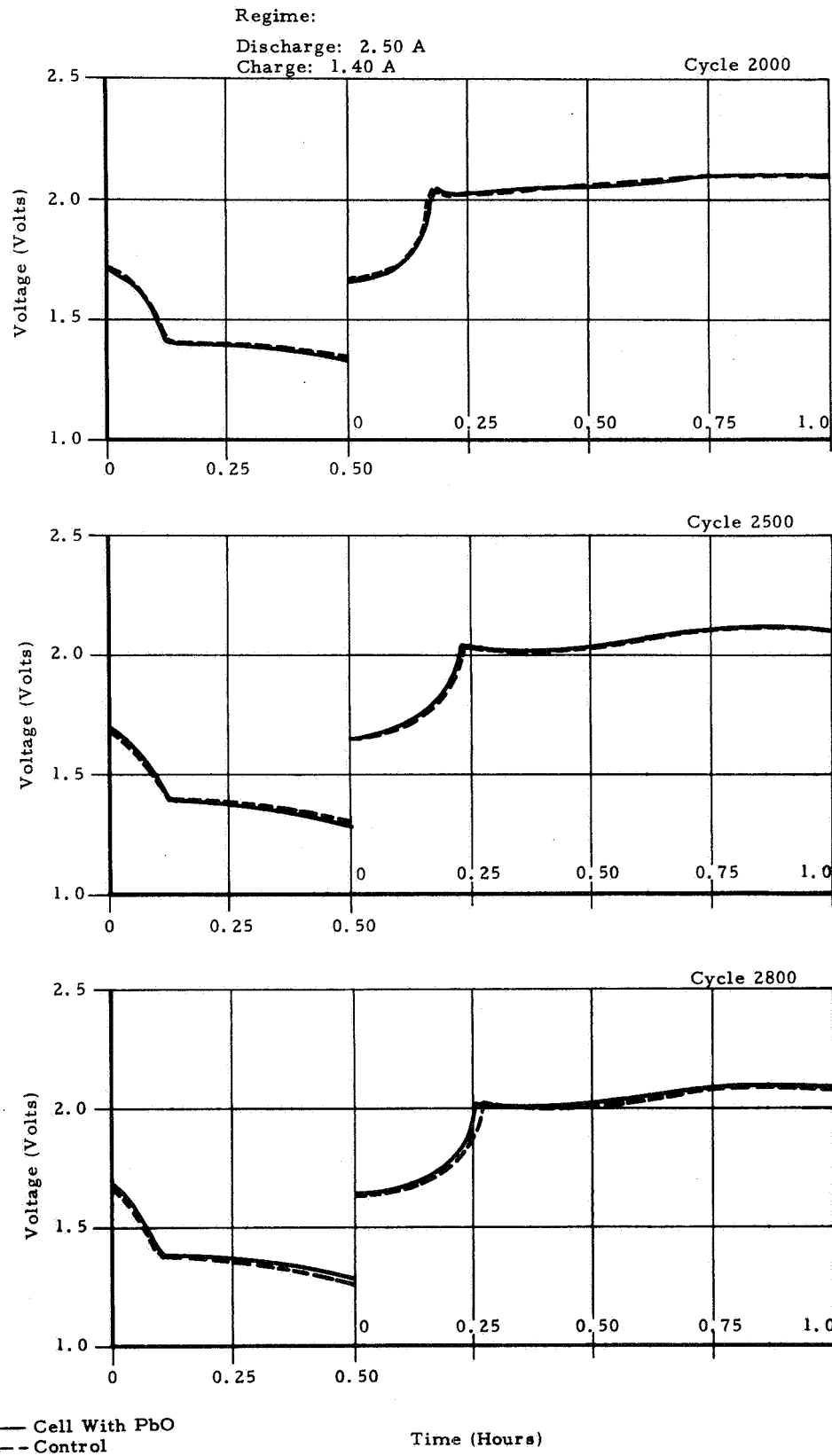


Figure 5. Cycling Curves of Cells With and Without PbO

TABLE III

FAILURE ANALYSIS OF ZL-11 SERIES

Cell No.		Failure Cycle	Capacity at			OCV Stand		Examination
Standard			2.5 A	Drain at 0.5A	Total	0 Hr	2 Hr	
ZL-11-1		2809	1.70 Ah	0.35 Ah	2.05 Ah	1.82 V	1.78 V	No cracks
ZL-11-2		2783	2.00 Ah	0.25 Ah	2.25 Ah	1.83 V	1.80 V	No cracks
ZL-11-3		2212	—	—	—	—	—	One slight
ZL-11-4		2873	0.8 Ah	0.25 Ah	1.05 Ah	1.82 V	1.80 V	One severe
ZL-11-5		2212	—	—	—	—	—	No cracks
Additive								
ZL-11-6		2848	1.25 Ah	0.35 Ah	1.60 Ah	1.82 V	1.76 V	No cracks
ZL-11-7		2905	1.90 Ah	0.15 Ah	2.05 Ah	1.84 V	1.81 V	No cracks
ZL-11-8		2554	—	—	—	—	—	One slight
ZL-11-9		3194	0.25 Ah	0.25 Ah	0.50 Ah	1.81 V	1.78 V	Four severe
ZL-11-10		2894	1.90 Ah	1.00 Ah	2.90 Ah	1.84 V	1.83 V	No cracks

The cost of the extra silver is negligible compared with the labor involved in building plastic frames around each electrode.

Five cells were built and compared with five controls. Table IV and Figure 6 show the differences between the two groups of cells in formation capacity and discharge voltage.

The cells were then placed on automatic cycling on the 90-minute period regime (2.5 A discharge for 1/2 hour, 1.4 A charge for 1 hour). The group of cells with large electrodes exhibited erratic behavior and were discontinued after 100, 145 and 300 cycles for rebalancing individual cells. After 432 cycles, they were finally discontinued, whereas the control reached 500 cycles to date without adjustment.

The excess silver may have created, among other factors, a zinc limiting condition faster than in the regular cells. It was decided to drop this approach and use another method for immobilizing the silver electrodes in the control cells.

Immobilized Cell Pack

It was found more expedient to pour a thin layer of epoxy (3 grams) in the bottom of the cell case before inserting the cell pack. After cure, the epoxy immobilizes the cell pack in all directions without getting into the electrodes or the separators because of its relatively high viscosity.

3.1.2 Separator System

3.1.2.1 Separators

Type 3420-09 is used exclusively. The specifications as established on previous contracts (NAS 3-7630 (Reference 1) and NAS 3-8513 (Reference 2)) were maintained throughout this program.

All separators were 100% inspected and segregated for exclusive use on this task. The detailed order was as follows:

TABLE IV
CAPACITY ON FORMATION

Positive	Cell No.	Output	Plateau Voltage
1.6" x 1.6" (Control)	ZL-24-1	7.85 Ah	1.46 V
	ZL-24-2	7.90 Ah	1.46 V
	ZL-24-3	7.75 Ah	1.45 V
	ZL-24-4	8.10 Ah	1.45 V
	ZL-24-5	8.10 Ah	1.45 V
	Average	7.90 Ah	1.45 V
1.88" x 1.95" (Large)	ZL-24-6	9.50 Ah	1.44 V
	ZL-24-7	9.60 Ah	1.44 V
	ZL-24-8	9.60 Ah	1.44 V
	ZL-24-9	9.60 Ah	1.43 V
	ZL-24-10	8.60 Ah	1.44 V
	Average	9.40 Ah	1.44 V

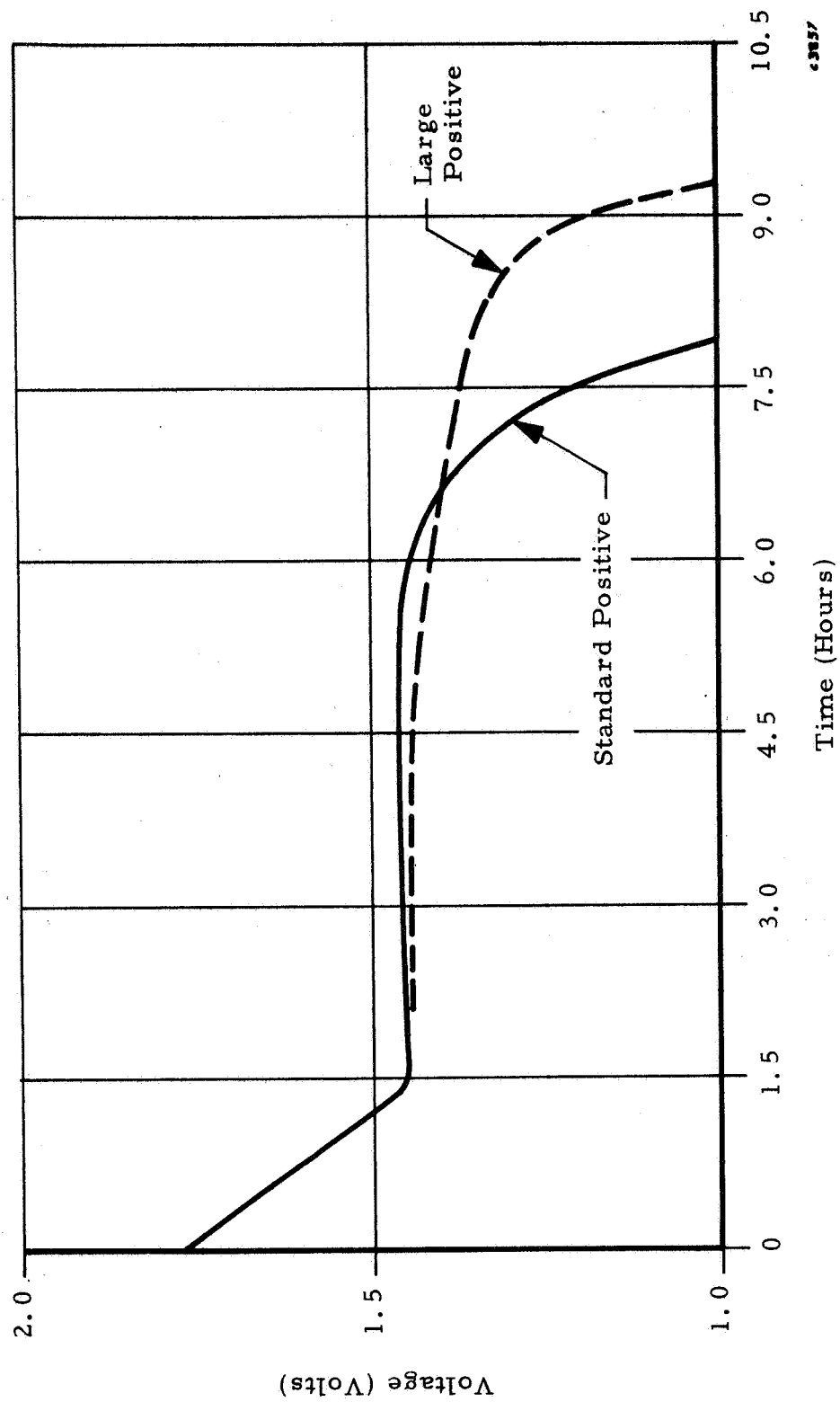


Figure 6. Discharge of Curves of Cells With Two Different Sizes of Positive Electrodes

1. Absorption: 9.5-10.5% (run absorption check on all pieces)
2. Thickness: $0.025'' \pm 0.001''$
3. Must be flat
4. Must be free of holes, chips, discolorations, cracks, pits, and other mechanical imperfections
5. All pieces must be examined under at least a 10X microscope to be certain there are no microfissures, cracks, etc.

For this work, a new batch of granulated pressing powder is made and its identity is kept separate throughout the manufacturing process.

3.1.2.2 KT Interseparators

Because of the discontinuance of the present KT paper by the supplier, a new KT made by another supplier was acquired and compared with the previous one in the presence of KOH at 25°C and at 100°C. Samples soaked in excess KOH, using two different concentrations (30 and 45%), were left on stand up to 75 days along with blanks (KOH without materials) to establish the variations of free KOH content and carbonation. The liquors were analyzed initially, after 20 and 75 days. For a given set of conditions, temperature and KOH concentration, the three liquors show no significant difference within the experimental errors (Table V).

3.1.3 Case

Cases made of polysulfone P-1700 and polyphenylene oxide 534-801 were used for case-to-cover seal investigation and ultimate material selection (see Paragraph 3.1.4). However, in the absence of any obvious disadvantage for either material, polysulfone was constantly used because of its transparency which permits easier quality control in the final assembly stage.

3.1.4 Case-to-Cover Seal

As a preliminary testing procedure for seal integrity, it was decided to pressure test each case with dry nitrogen at 100 psig for 5 minutes at 25°C. A test fixture was designed and built for this purpose. Figure 7 is a schematic of the set up and the detailed testing procedure. Two sealing methods were investigated.

TABLE V
EFFECT OF KOH ON KT INTERSEPARATOR MEASURED BY
VARIATION OF CONTENTS (g/l) OF FREE KOH AND CARBONATE

Material in KOH	Temperature	30% Solution						45% Solution					
		Free KOH			Carbonate			Free KOH			Carbonate		
		Initial	20 Days	75 Days	Initial	20 Days	75 Days	Initial	20 Days	75 Days	Initial	20 Days	75 Days
Blank	25°	382	387	379	21	12	38	647	666	607	17	23	35
KT-Original	25° C		378	360		19	41		657	599		21	45
KT-New			389	353		17	31		642	605		23	38
Blank	100° C	384	384	407	17	16	31	636	655	671	17	19	35
KT-Original			400	381		21	21		653	641		23	38
KT-New			404	393		19	21		652	609		21	31

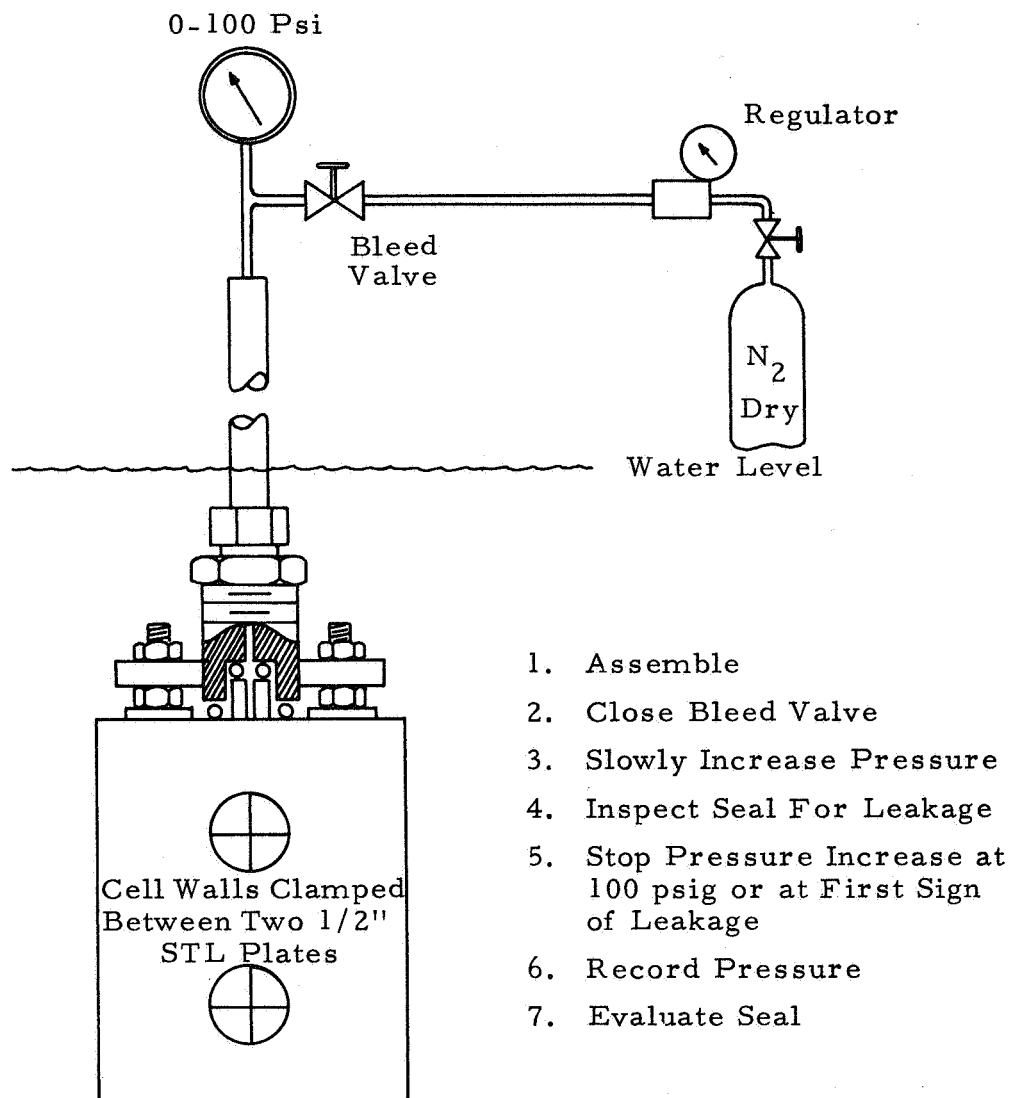


Figure 7. Text Fixture for Cast-to-Cover Seal

3.1.4.1 Hot-Gas Welding

This was done by using a "Corofac" Model EHGG-4000 welding gun and accessories. The welding is made with round filler rods of parent materials (1/8" diameter). Preliminary sealing experiments were started on polysulfone cases to get an idea of the variability inherent in the method and of the possible parameters, such as time, annealing, design configuration.

Using available 1/8" diameter polysulfone welding rods and keeping the gas pressure constant at 6 psi, the temperature was determined as a function of the distance from gun tip to weld area. Table VI is a quick evaluation on a few cases.

TABLE VI
HOT-GAS WELDING TEST

<u>Case</u>	<u>Distance</u>	<u>Temperature</u>	<u>Remarks</u>
ZL-7-1	1/8"	463°F	Scorched; bad
ZL-7-2	1/4"	387°F	Scorched; bad
ZL-7-3	1/2"	386°F	Scorched; bad
ZL-7-4	3/4"	320°F	No scorching; good
ZL-7-5	3/4"	324°F	No scorching; good
ZL-7-6	1"	332°F	Fair

During this test, the thin wall at the top of the case (1/16" thick) distorts and melts before the 1/8" rod does. Attempts to procure 1/16" rods were unsuccessful (either not available or too expensive to get them extruded). When the concurrent investigation of another welding method (ultrasonic welding) showed more promising results, no additional work was attempted on the hot gas welding.

3.1.4.2 Ultrasonic Welding

A Branson J-32 Ultrasonic Welding System was used with a specially designed titanium horn. Tests on PS (polysulfone) and PPO (polyphenylene oxide) cases

were started to establish the optimum values for proper sealing of the following parameters:

1. pressure of the horn
2. weld time
3. hold time, after weld
4. power

The object was to develop an operating procedure that will produce a seal capable of withstanding an internal pressure of 100 psig. As a start, it must meet the requirement of withstanding 100 psig with no drop in pressure or no bubbles under water for 5 minutes.

Annealing

PS and PPO cases were annealed before welding. The most suitable annealing procedure found is the following:

<u>Material</u>	<u>Medium</u>	<u>Temperature</u>	<u>Part</u>	<u>Time</u>
Polysulfone	Glycerine	330°F	Case	2 minutes
			Cover	4 minutes
PPO	Glycerine	295°F	Case	1 hour
			Cover	1 hour

After this procedure, all internal stresses were eliminated. When stresses are present, the parts craze or crack when in contact with acetone (5 seconds for PS material) and P-Dioxane (5 minutes for PPO material). After this procedure, the parts submitted to the same organic liquids for the same periods of time did not experience any failure (craze or crack).

Welding

The parameters involved were optimized and held to the following:

<u>Material</u>	<u>Pressure</u>	<u>Weld Time</u>	<u>Hold Time</u>
PS	92 psi	2.5 sec.	1.0 sec.
PPO	92 psi	2.75 sec.	1.5 sec.

Eight PS cases and five PPO cases consecutively welded passed the pressure test (100 psi for 5 minutes at room temperature) one after the other without leaking.

To go one step further, several welded cases were prepared for testing for 200 hours with a pressure differential of 50 psig at 25°, 100°, and 135°C.

As a sideline, an attempt was made to determine the water vapor permeability constant, P, for polysulfone and PPO at various temperatures by sealing a certain amount of 45% KOH in welded and top-potted cases. One case of each material was submitted for 120 hours to each of the following temperatures: 25°C, 50°C, 75°C and 135°C. A control case without KOH was also tested at 135°C. The cases were accurately weighed before and after the test and checked for alkali traces. No alkali trace could be detected after the test along the seals, even after inverting the cases for 64 hours so that KOH was in direct contact with the seals.

Table VII is a list of the data. When plotted on a semi-logarithmic graph, the data fit remarkably a straight line (Figure 8) which shows that the weight loss being an exponential function of the temperature may be due solely to the diffusion of gases through the case plastic. This offers further evidence that leakage through poor sealing can be ruled out.

TABLE VII
WATER WEIGHT LOSS THROUGH SEALED CASES AFTER 120 HOURS (GRAMS)

Material	Temperature	Original Weight	Final Weight	Difference	Remarks
Polysulfone P-1700	50°C (KOH)	76.795 g	76.721 g	0.074 g	Crazing
	75°C (KOH)	77.350	77.192	0.157	
	100°C (KOH)	77.030	76.747	0.283	
	135°C (KOH)	76.564	75.664	0.900	
	135°C (dry)	62.983	62.854	0.129	
PPO (534-801)	50°C (KOH)	69.033	68.982	0.051	Turned Darker Turned Darker
	75°C (KOH)	71.443	71.325	0.118	
	100°C (KOH)	69.914	69.654	0.260	
	135°C (KOH)	70.889	70.070	0.819	
	135°C (dry)	55.719	55.665	0.054	

Ultrasonically welded, fully sealed cases containing KOH appear therefore able to withstand sterilization without leaking alkali. The weight loss observed can be traceable to water vapor diffusion through the case plastic.

Evidence of the integrity of the ultrasonic weld of the cover to the case was more firmly established by repeated and varied testing at 135°C.

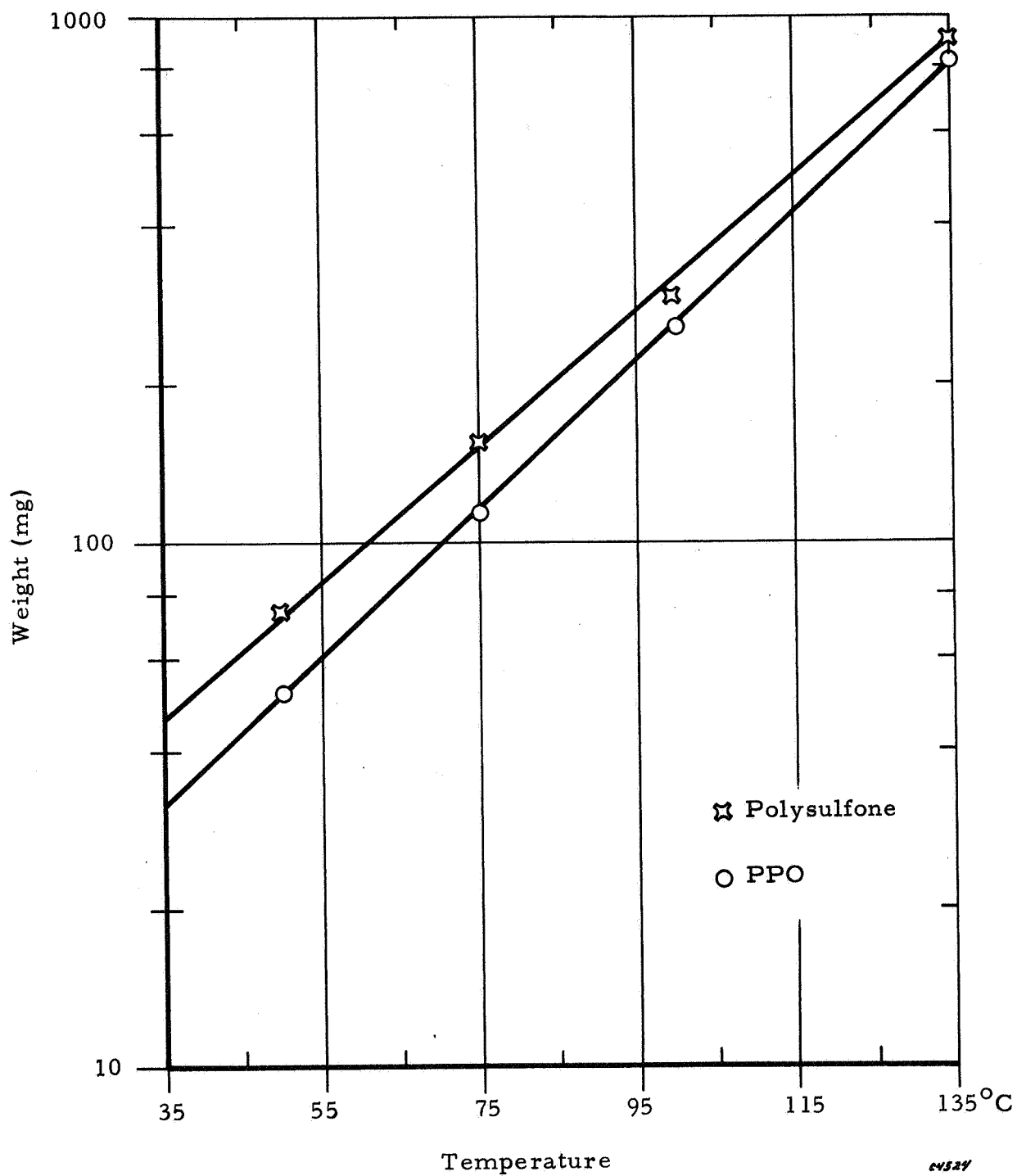


Figure 8. Water Weight Loss After 120 Hours Through Plastic 5 AH-Cell Case

Cases Partially Filled with KOH and Sealed — Five polysulfone cases and five PPO cases were filled with 10 cm^3 of 45% KOH and then sealed. Three of each group were left at 135°C for 120 hours, and two of each group for 200 hours. After determining that no trace of alkali could be detected at the welded seams immediately after test, nor after 60 hours in an inverted position, their weight loss was measured. The data presented in Table VIII show less weight loss with PPO than PS over 200 hours, but in both materials the water permeability is relatively low and will be certainly tolerable to a cell undergoing a loss of less than 5% water.

Cases Pressurized at 50 psig — Three PS cases were sealed and subjected to 50 psig continuously for 200 hours at 135°C . Two cases passed the test successfully. The third one presented a leak after 187 hours, only at the pressure fixture adapted on the top of the cover and not at the welded seams.

Ultrasonically welded PPO cases were also submitted to the same test. A pressure drop of about 8 psig was observed during this test period which may have been due to diffusion as no leakage under water could be detected before or after the high temperature 200-hour pressure test. From these data, the calculated diffusion rate is less than $5 \times 10^{-5} \text{ cm}^3/\text{second}$.

Figures 9 and 10 show the set-ups for ultrasonic welding and pressure testing of welded cases.

3.1.5 Terminals

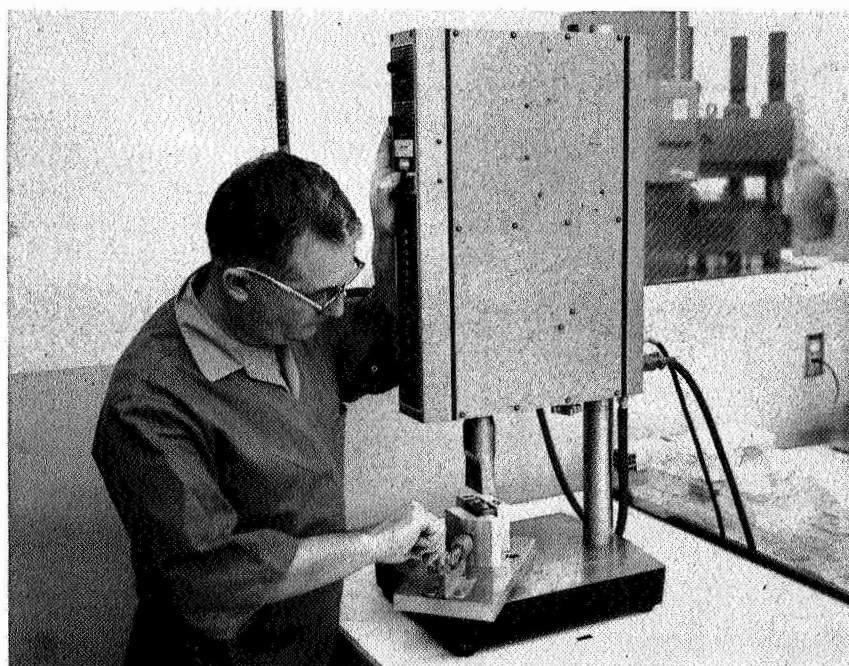
No work was contemplated on the terminal seal. The only modification introduced was to the attachment of leads to the terminal. Instead of a hollow terminal where the leads are fed through and soldered through the top, the terminal used was a blind terminal, with a hole through the bottom about half-way up. The leads were inserted and soldered through the bottom (Figure 11). This improvement prevents any possibility of leakage through the terminal hole caused by poor soldering or solder corrosion.

Another improvement was the use of indium solder which is more resistant to alkali attack and high temperature.

TABLE VIII

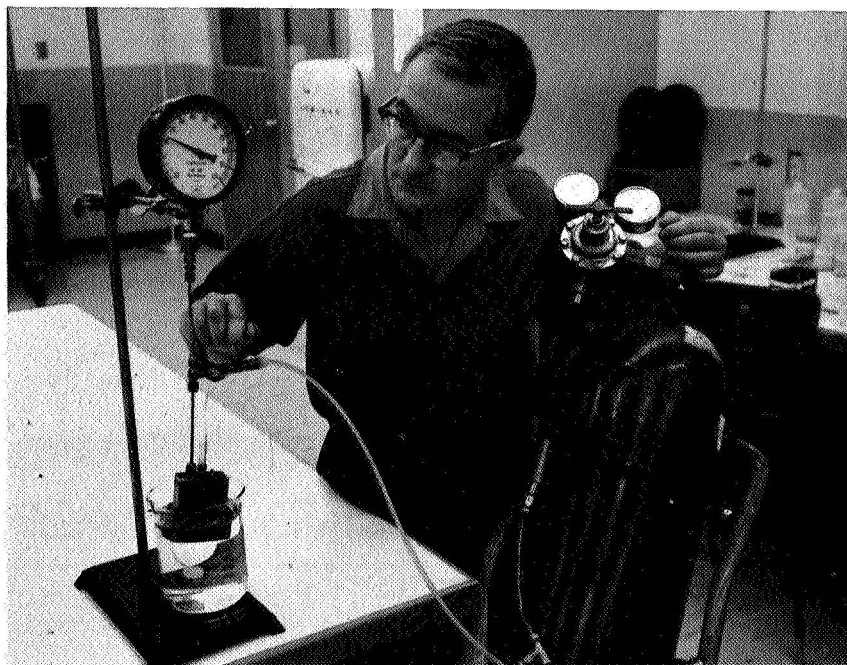
WEIGHT LOSS OF SEALED CASES PARTIALLY FILLED WITH
KOH AND SUBMITTED TO 135°C FOR INDICATED TIME

	120 Hours		200 Hours	
	Case	Loss	Case	Loss
Polysulfone	ZL-16-13	1.041 g	ZL-16-16	1.033 g
	ZL-16-14	0.542	ZL-16-17	1.581
	ZL-16-15	0.718		
	Average	0.800 g	Average	1.307 g
PPO	ZL-16-18	0.702 g	ZL-16-21	0.879
	ZL-16-19	0.738	ZL-16-22	0.889
	ZL-16-20	0.701		
	Average	0.740 g	Average	0.884 g



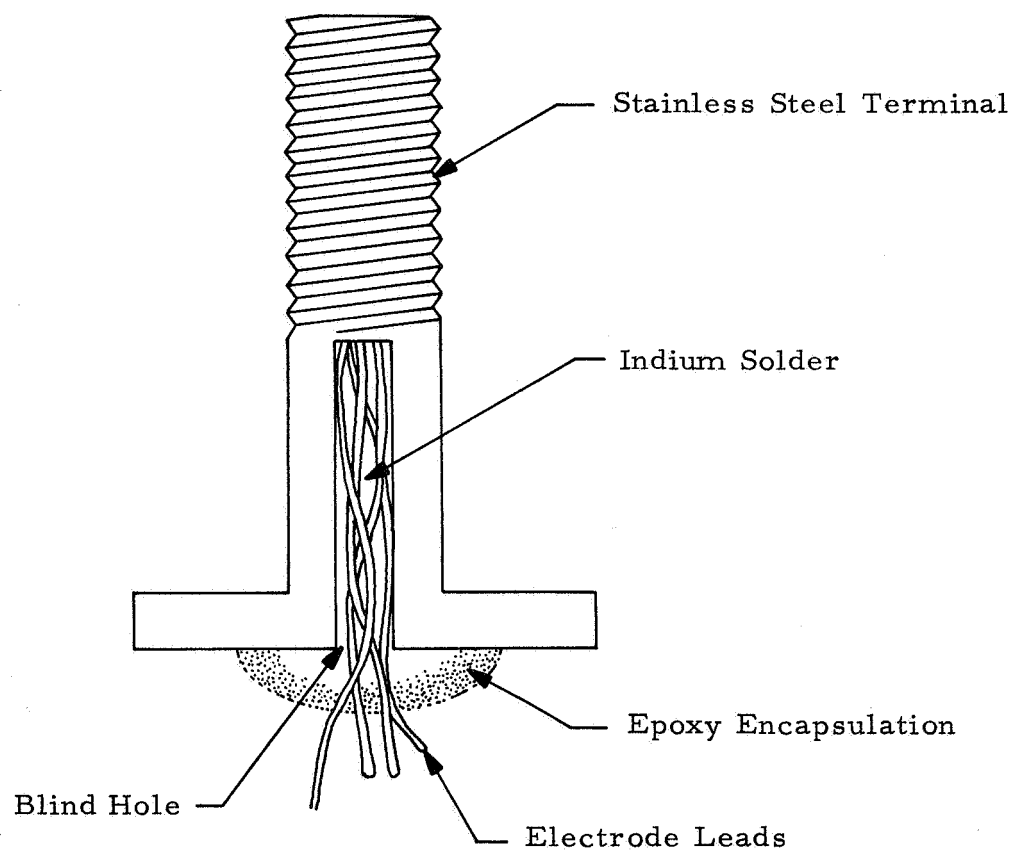
c3916

Figure 9. Ultrasonic Welding of Cover to Case



C4269

Figure 10. Pressure Testing of Cell After Welding



4538

Figure 11. Electrode Lead Attachment to Cell Terminal

As an added protection feature, the base of the terminal is encapsulated in epoxy to cover the exposed solder joint of the leads to the terminal.

3.1.6 Connection Methods and Collectors

Although keeping methods and components similar to those employed in Contract NAS 3-7639 (Reference 1), a small effort was devoted to reinforcing the silver grid to avoid corrosion observed under a continuous cycling at 100°C (Contract NAS 3-7639) which may have been a contributing factor in the cycle life of some cells.

The new grid material selected was a heavier silver exmet, 5 Ag-14-1/0, than the one originally used in the 5-Ah cell, 3 Ag-10-3/0.

3.1.6.1 Corrosion Test

Silver electrodes using the regular and new exmets were assembled in dummy cells, one between two solid nickel sheet counter electrodes, and tested at 100°C under continuous overcharge to determine their ability to stand corrosion.

After 200 hours, silver plates overcharged in free KOH at 100°C against solid nickel counterelectrodes were found extremely warped and corroded, regardless of the silver grid used. The test was repeated with separators and nickel counterelectrodes tightly sandwiching the silver plates as in a normal cell assembly.

It can be pointed out that in the cycling regime of 1/2-hour discharge, 1-hour charge there is no more than nearly 10 minutes of overcharge, which, over 600 cycles, is equivalent to 100 hours of real overcharge. The previous test was therefore considered to be excessively severe. In the repeat test, the progress of corrosion was checked every 48 hours.

It was found that the corrosion and degradation affected only the sintered silver powder, rather than the grid. Weights of grid devoid of silver powder were compared with original weights and were found unchanged for both Exmets.

To prevent the corrosion of the silver leads, ACORN rubber cement was applied around each wire lead filling a Teflon sleeve slipped tightly on the wire down to the base of the wire.

In order to remove all doubts about the effect of a heavier silver exmet grid on the electrical performance at room temperature, the next test was undertaken concurrently.

3.1.6.2 Cell Tests

Five cells were built using the heavier silver exmet, but otherwise of the same design as cells used in Contract NAS 3-7639 (Reference 1).

Three total discharge cycles were given to determine their capacity and voltage uniformity (Table IX). Table X gives their end of discharge voltages at various cycles and a capacity check after 300 cycles. Figures 12 and 13 show their cycling performance at various cycles. They failed at around 2100 cycles because of cracked separators. Upon disassembly, all other components appeared satisfactory. Table XI gives a summary of the cycling data.

3.1.7 Electrolyte

The 30% KOH concentration was used in most tests of Task I. However, a study of the effect of KOH concentration was deemed necessary because it was known from other tests (Reference 3) that the charged wet stand capacity retention is improved with higher electrolyte concentration.

Forty and forty-five percent KOH were used in a group of cells to be compared with the 30% KOH on the same 90-minute period regime. Unfortunately, the cells used had large size silver electrodes (refer to Paragraph 3.1.1.2). Table XII and Figure 14 show the differences caused by the change in electrolyte concentration.

On the 90-minute period regime, the same condition of imbalance prevailed through the automatic cycling (see Paragraph 3.1.1.2) after 432 cycles. The shifting of the positive electrodes was then corrected by immobilization of

TABLE IX

FIVE-AH CELL PERFORMANCE DATA (1 A DISCHARGE)
(HEAVY SILVER EXMET 5 Ag-14-1/0)

Cell No.	Cycle 1		Cycle 2		Cycle 3	
	Output	Voltage	Output	Voltage	Output	Voltage
ZL-1-1	7.5 Ah	1.45 V	7.5 Ah	1.45 V	7.1 Ah	1.45 V
ZL-1-2	7.5	1.46	7.5	1.45	7.0	1.45
ZL-1-3	7.8	1.45	7.2	1.45	6.9	1.45
ZL-1-4	7.7	1.46	7.6	1.45	7.4	1.45
ZL-1-5	7.4	1.45	7.5	1.45	7.1	1.45
	==	==	==	==	==	==
Avg.	7.6 Ah	1.45 V	7.45 Ah	1.45 V	7.1 Ah	1.45 V

TABLE X

(Exmet 5 Ag-14-1/0)

VOLTAGE AT END OF DISCHARGE PERIOD (1/2 HOUR)

Cell No.	Cycles				
	5	500	1000	1500	1950
ZL-1-1	1.50	1.46	1.46	1.45	1.45
ZL-1-2	1.50	1.45	1.45	1.44	1.44
ZL-1-3	1.50	1.45	1.44	1.43	—
ZL-1-4	1.50	1.47	1.47	1.46	1.46
ZL-1-5	1.50	1.45	1.45	1.44	1.44
Average	1.50	1.45	1.45	1.44	1.45

300 CYCLE CAPACITY CHECK

Cell No.	Capacity	Average Voltage
ZL-1-1	4.2 Ah	1.34 V
ZL-1-2	3.8	1.33
ZL-1-3	4.0	1.33
ZL-1-4	3.6	1.33
ZL-1-5	5.1	1.33
Average	4.1	1.33

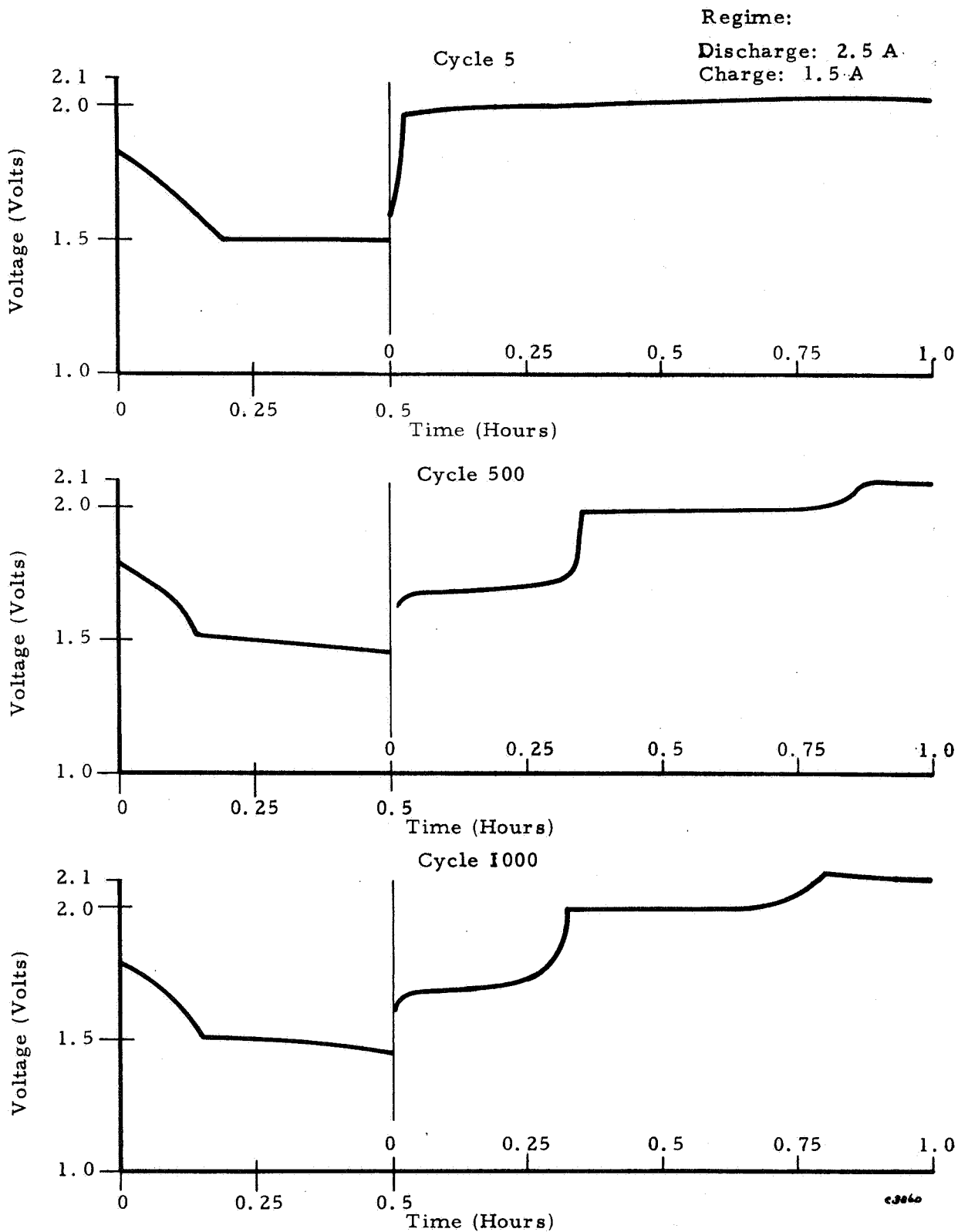


Figure 12. Cycling Curves of Cells With 5 Ag-14-1/0 Exmet

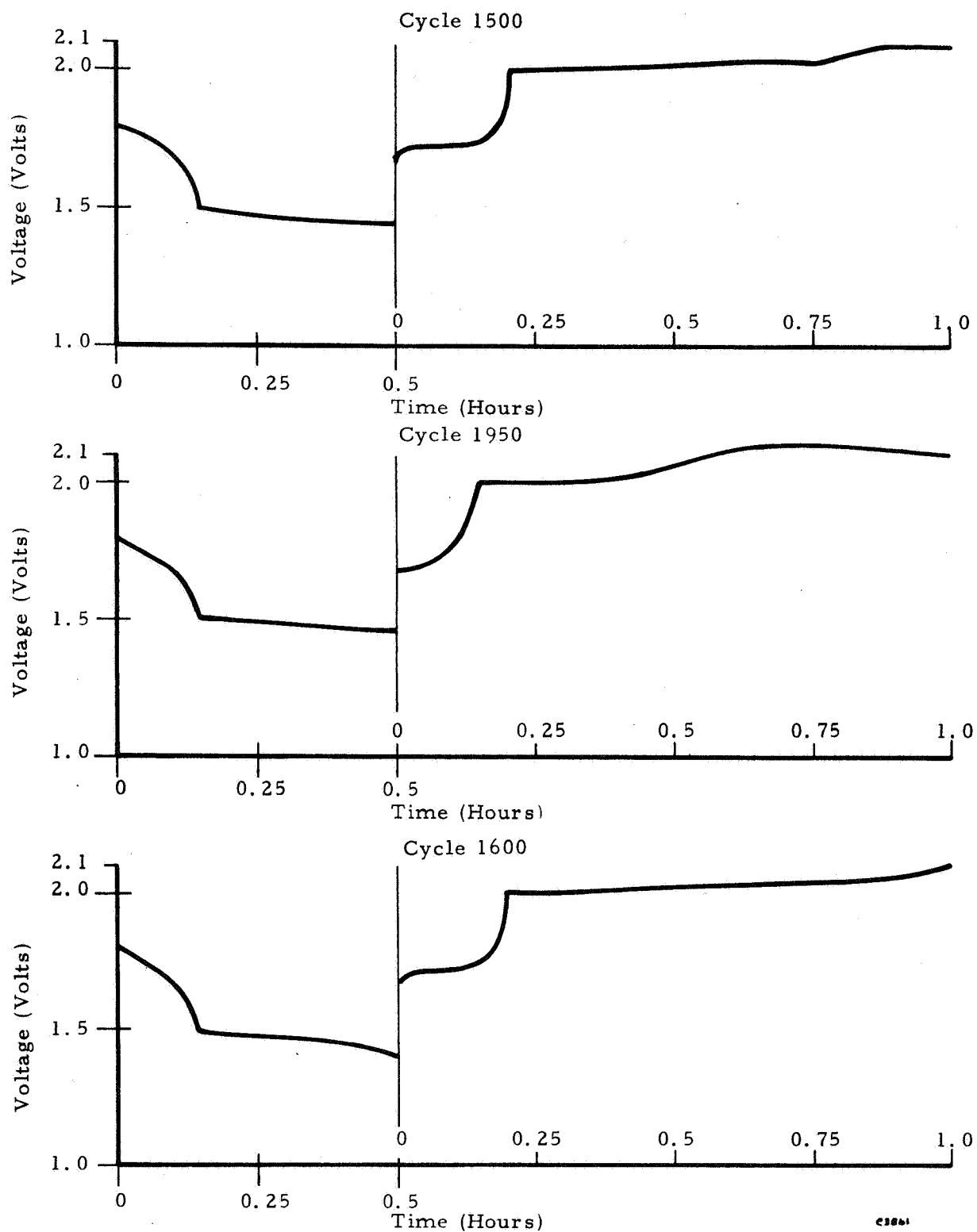


Figure 13. Cycling Curves of Cells With 5 Ag-14-1/0 Exmet

TABLE XI
GROUP ZL-1
CYCLING DATA SUMMARY

Cell No.	Cycles	Final Capacity
ZL-1-1	2300	---
ZL-1-2	2120	1.80 Ah
ZL-1-3	1650	---
ZL-1-4	2147	1.50 Ah
ZL-1-5	2183	---
Average	2080	
Mean Deviation	< 10%	

TABLE XII

FORMATION WITH DIFFERENT
KOH CONCENTRATIONS

Design Feature	Cell No.	Output	Plateau Voltage
30% KOH	ZL-25-1	9.66 Ah	1.44 V
	ZL-25-2	9.75 Ah	1.44 V
	Average	9.71 Ah	1.44 V
40% KOH	ZL-25-3	9.41 Ah	1.42 V
	ZL-25-4	9.58 Ah	1.42 V
	Average	9.50 Ah	1.42 V
45% KOH	ZL-25-5	9.00 Ah	1.39 V
	ZL-25-6	8.00 Ah	1.36 V
	Average	8.50 Ah	1.38 V

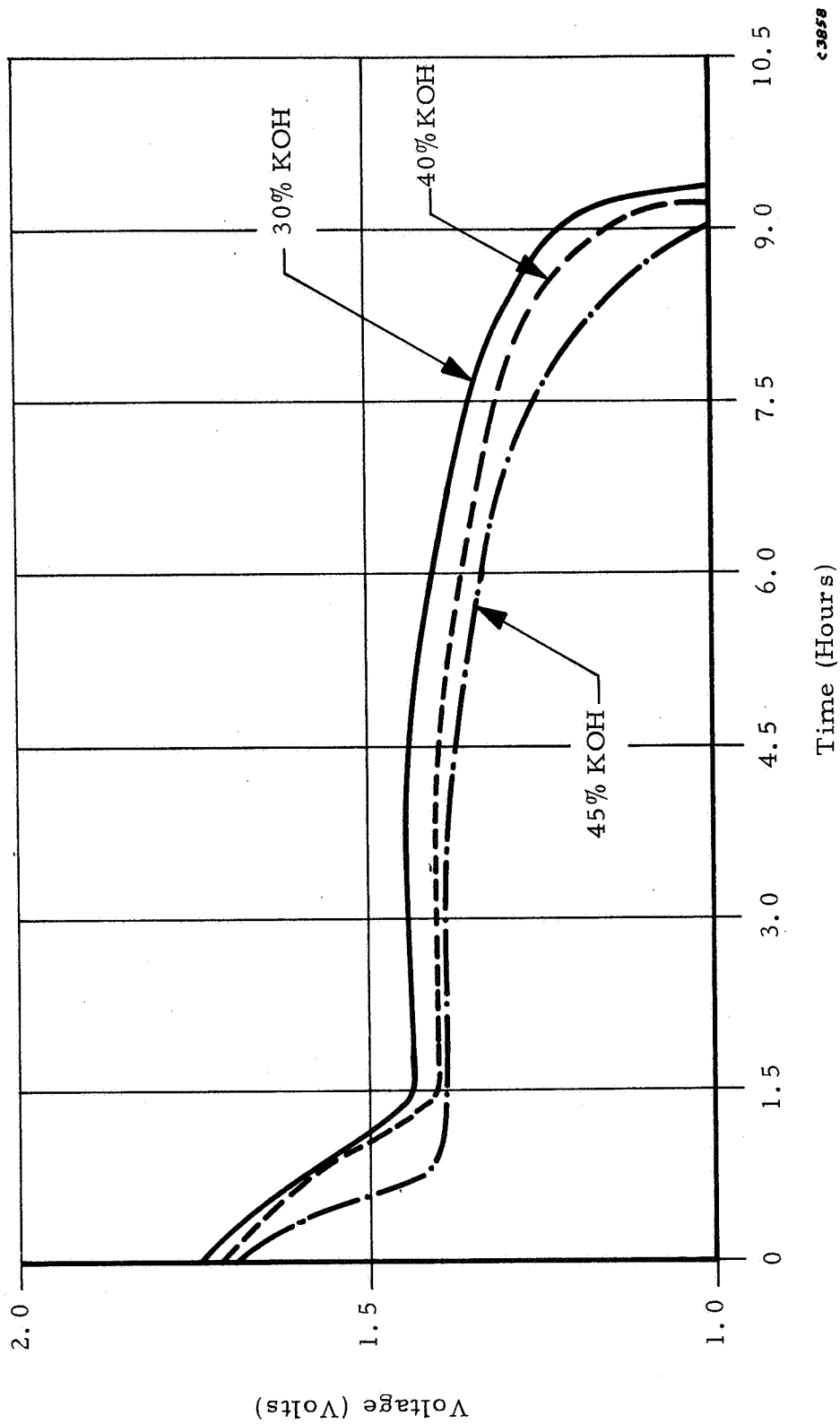


Figure 14. Discharge Curves of Cells With Various Concentrations of KOH

the cell pack with epoxy, thus reverting to the standard positive electrode size.

From the available data, it seems reasonable to use 40% KOH, considering that the capacity and plateau voltage are acceptable and that charged wet stand capacity retention will certainly be improved.

A group of five cells was therefore built integrating all the modifications (cell pack immobilization, 40% KOH electrolyte) and put on test. Table XIII gives their original performance. All data are presented at periodic cycles in the tables entitled "Uniformity Study" giving for each cell of each group:

1. the charge characteristics:

OC = overcharge percentage

m% = monoxide plateau percentage of total charge period

V_f = final voltage at the end of the charge period.

2. the discharge characteristics:

p% = peroxide plateau percentage of total discharge period

V_p = plateau voltage

V_e = end voltage at the end of the discharge period

3. the electrolyte addition in cumulative amounts from the beginning of the test.

Data are reported in Tables XIV, XV, XVI and Figures 15, 16 and 17. When the cells failed to meet the capacity cycling requirement (voltage dropping below 1.0 V before the end of the discharge period), the cells were given a capacity check. Table XVII shows that the capacities were still over 4 Ah, the limit set by the work statement for completion of the test, even after 1300 cycles.

The cells failed the capacity requirement beyond the 1500 cycle mark (Table XVIII). Upon dissection and examination, the separators were not cracked, the electrodes were found completely discharged but in good condition, and the zinc electrodes were not slumped (Figure 18). Some minute shorts may have caused the charge inefficiency. (Note that the cells of this group were not built with the new 3420-09 separator introduced in the last part of Task II.)

TABLE XIII
FORMATION OF STANDARD CELLS
WITH 40% KOH ELECTROLYTE

Discharge Rate: 1.0 A to 1.0 V

Cell No.	Capacity	Plateau Voltage
ZL-32-1	7.30 Ah	1.42 V
ZL-32-2	7.80 Ah	1.42
ZL-32-3	7.40 Ah	1.42
ZL-33-4	7.60 Ah	1.42
ZL-34-5	7.80 Ah	1.42
Average	7.60 Ah	1.42 V

TABLE XIV
UNIFORMITY STUDY

Group: No. ZL-32

Regime: Discharge: 2.5 A for 1/2 hr

Charge: 1.3 A for 1 hr

Voltage Limit: 2.05 V/cell

Temperature: 25 °C

Cycle 10

Cell Number		1	2	3	4	5	Avg.
Charge (OC = 5.9 %)	m%	15	15	15	15	15	15
	V _f	2.05	2.05	2.05	2.05	2.05	2.05
Discharge	p%	32	32	32	32	32	32
	V _p	1.42	1.42	1.42	1.42	1.41	1.42
	V _e	1.40	1.40	1.40	1.40	1.40	1.40
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0

Cycle 300

Charge (OC = 4.0 %)	m%	29	29	29	29	40	31
	V _f	2.03	2.04	2.02	2.04	2.00	2.03
Discharge	p%	31	31	31	31	23	30
	V _p	1.31	1.35	1.36	1.35	1.32	1.34
	V _e	1.30	1.30	1.30	1.30	1.29	1.30
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0

TABLE XV
UNIFORMITY STUDY

Group: No. Z1-32

Regime: Discharge: 2.5 A for 1/2 hr

Charge: 1.3 A for 1 hr

Voltage Limit: 2.05 V/cell

Temperature: 25°C

Cycle 600

Cell Number		1	2	3	4	5	Avg.
Charge (OC = 9.6 %)	m%	19	19	19	19	19	19
	V _f	2.08	2.04	2.03	2.05	2.00	2.04
Discharge	p%	30	30	30	30	30	30
	V _p	1.30	1.32	1.33	1.31	1.33	1.32
	V _e	1.27	1.28	1.31	1.29	1.30	1.29
Electrolyte Addition	Cum. Amt (cc)	2.0	2.0	3.0	3.0	3.0	2.6

Cycle 900

Charge (OC = 9.0 %)	m%	18	18	18	18	18	18
	V _f	2.07	2.06	2.08	2.07	2.07	2.07
Discharge	p%	29	29	29	29	29	29
	V _p	1.30	1.33	1.33	1.31	1.34	1.32
	V _e	1.25	1.25	1.26	1.22	1.27	1.25
Electrolyte Addition	Cum. Amt (cc)	5.0	7.0	5.0	4.5	3.0	4.9

TABLE XVI

UNIFORMITY STUDY

Group: ZL-32

Regime: Discharge: 2.5 A for 0.5 hr

Charge: 1.3 A for 1.0 hr

Voltage Limit: 2.05 V/cell

Temperature: 25°C

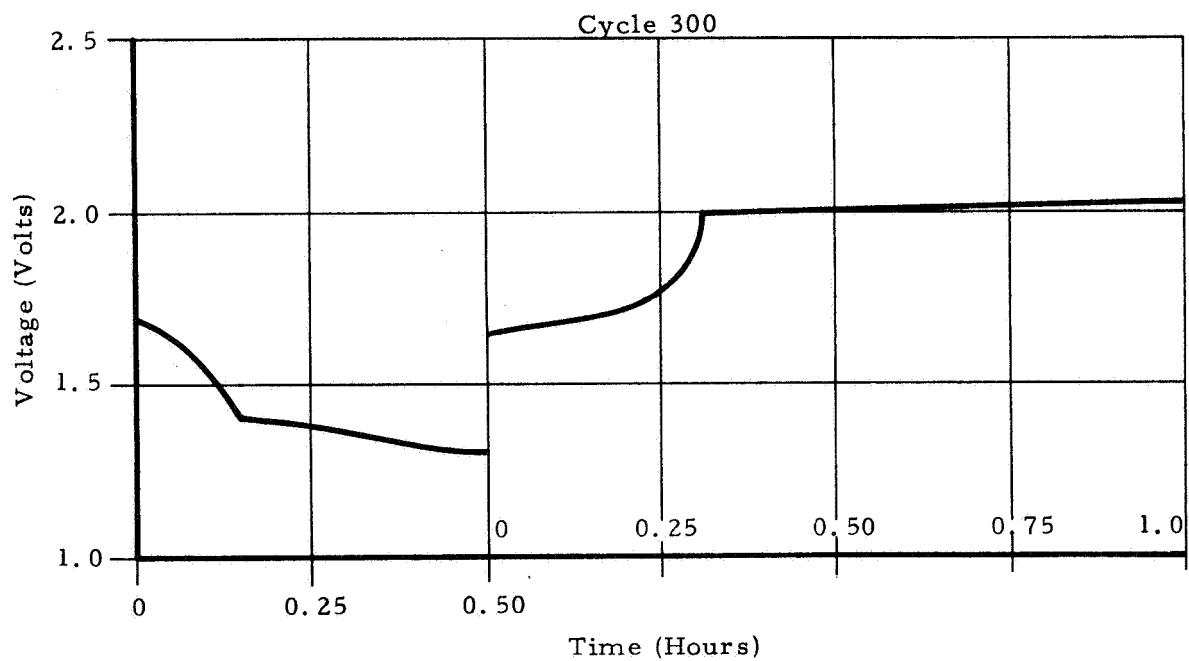
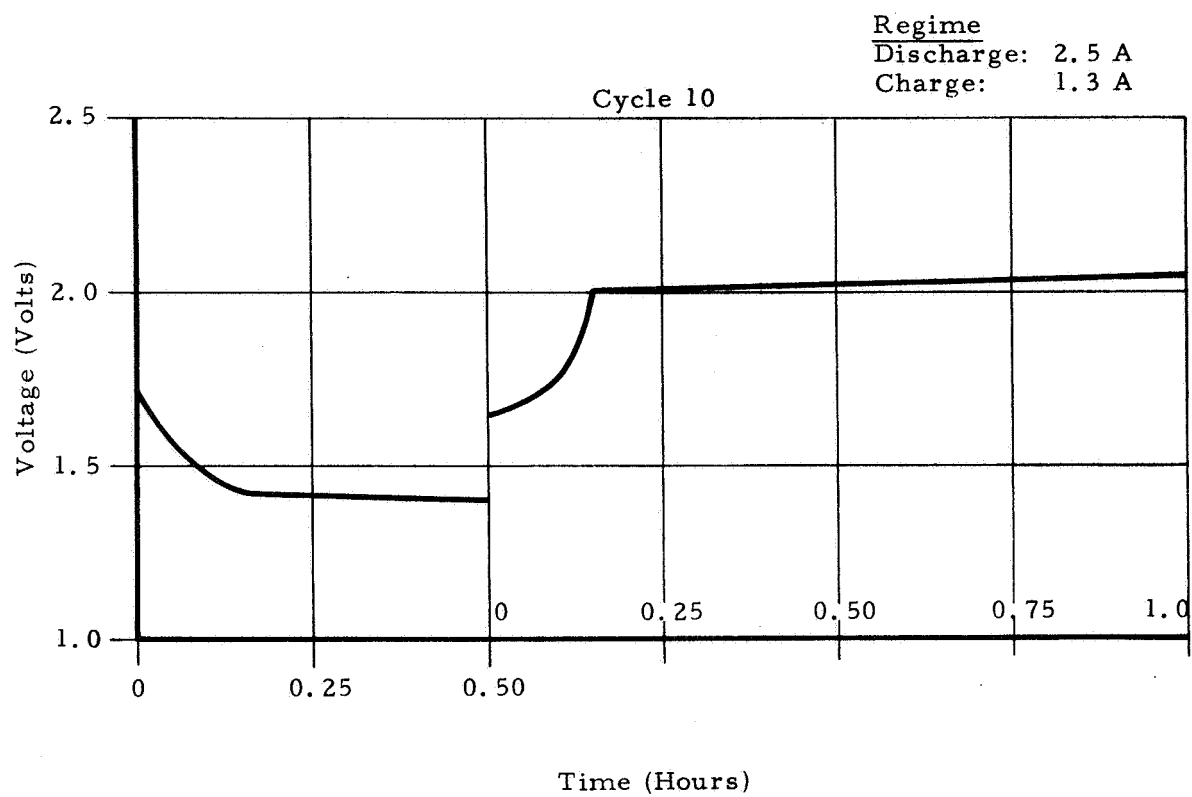
Cycle 1200

Cell Number		1	2	3	4	5	Avg.
Charge	m%	18	18	29	18	20	21
	(OC = 8.3%) V _f	2.03	2.09	1.98	2.06	2.01	2.03
Discharge	p%	34	37	26	34	37	34
	V _p	1.30	1.35	1.34	1.32	1.33	1.33
	V _e	1.28	1.32	1.31	1.30	1.32	1.31
Electrolyte Addition	Cum. Amt (cc)	7.5	10.5	9.5	10.0	5.5	8.6

Cycle 1500*

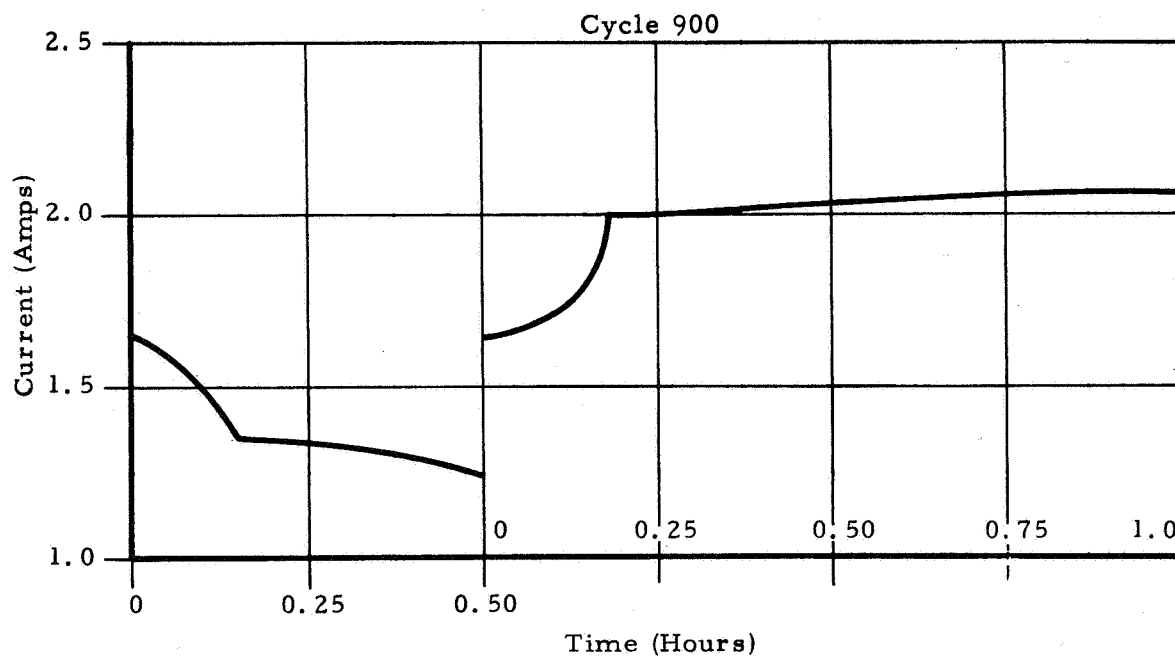
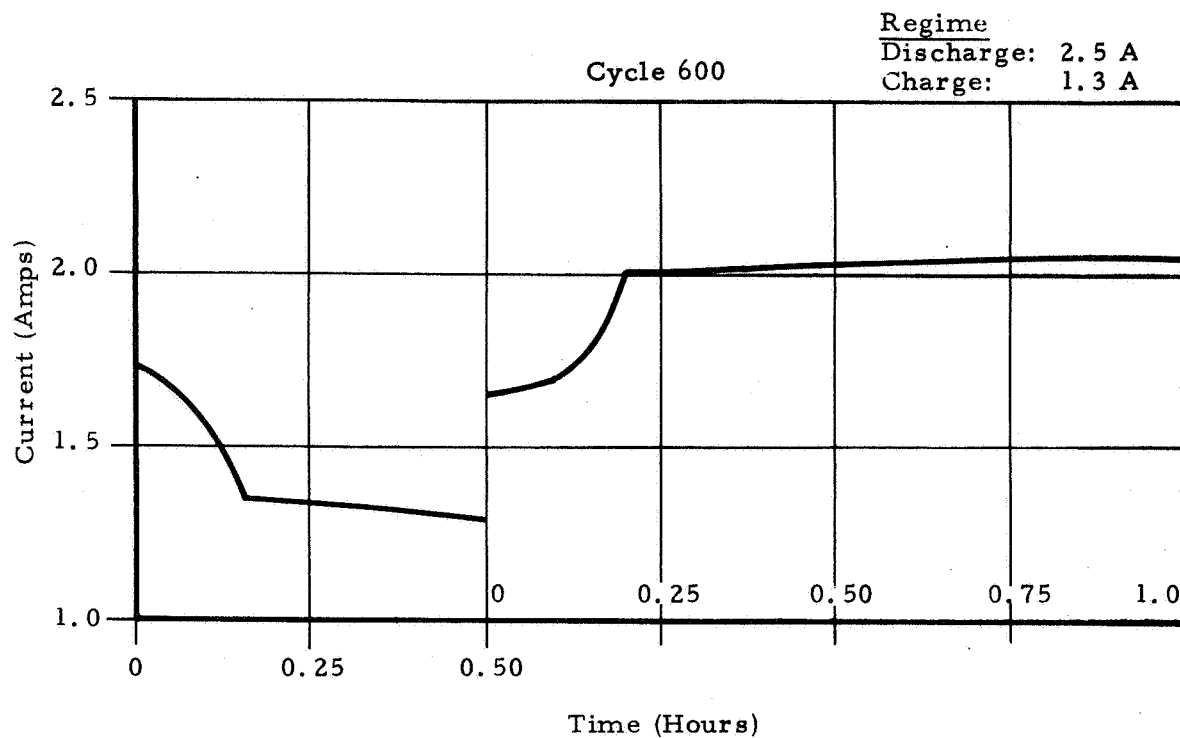
Charge	m%	14	17	18	17	20	17
	(OC = 5.2%) V _f	2.12	2.12	2.14	2.04	2.16	2.12
Discharge	p%	35	34	35	33	30	33
	V _p	1.26	1.24	1.30	1.24	1.30	1.27
	V _e	1.16	1.16	1.20	1.20	1.24	1.19
Electrolyte Addition	Cum. Amt (cc)	13.0	17.5	19.5	16.5	12.0	15.7

*At cycle 1330, current and voltage limits were increased to 1.5 A and 2.12 V/cell, respectively.



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Figure 15. Group ZL-32 Typical Cycling Curves



CY299

Figure 16. Group ZL-32 Typical Cycling Curves

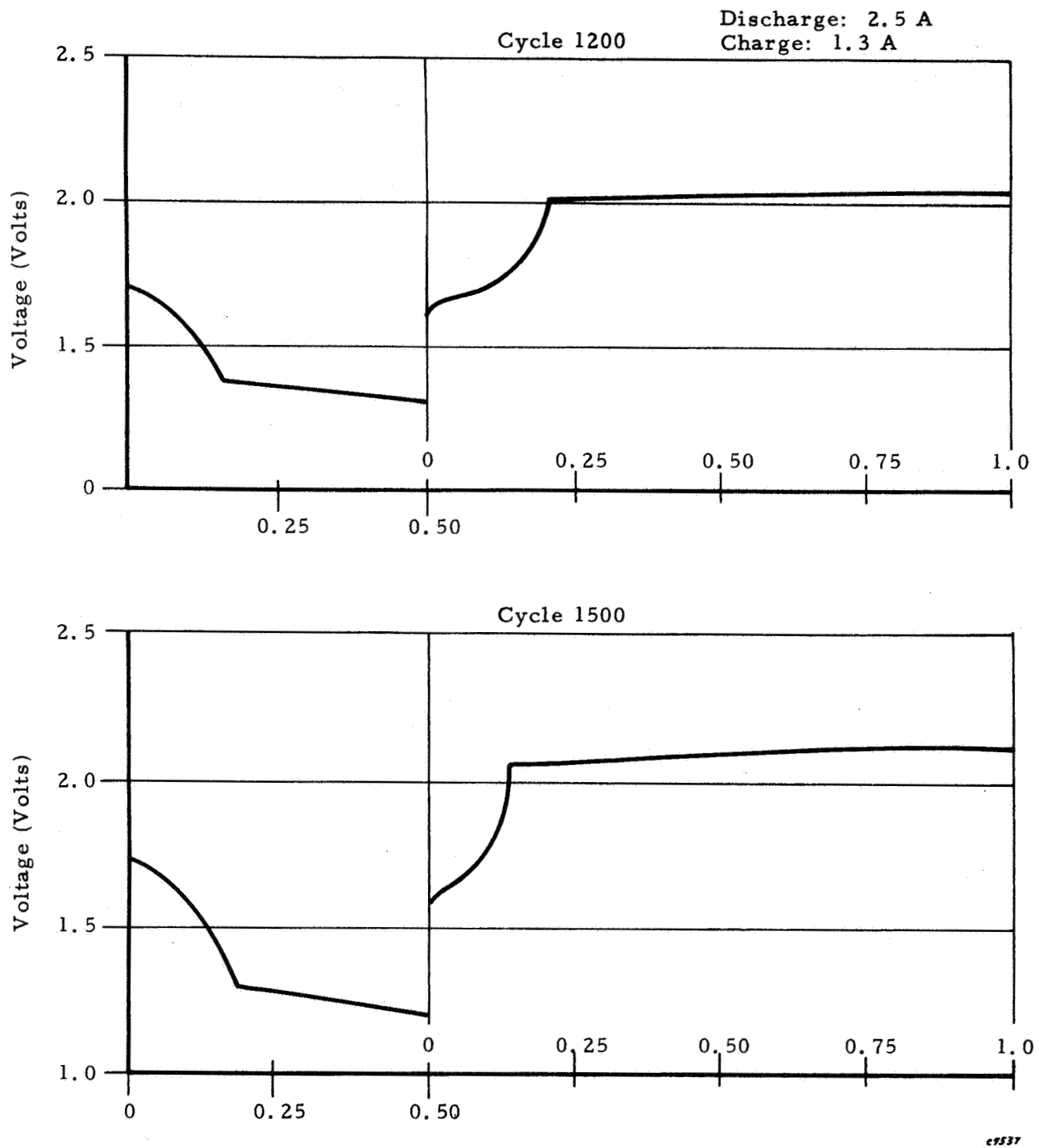


Figure 17. Group ZL-32 Typical Cycling Curves

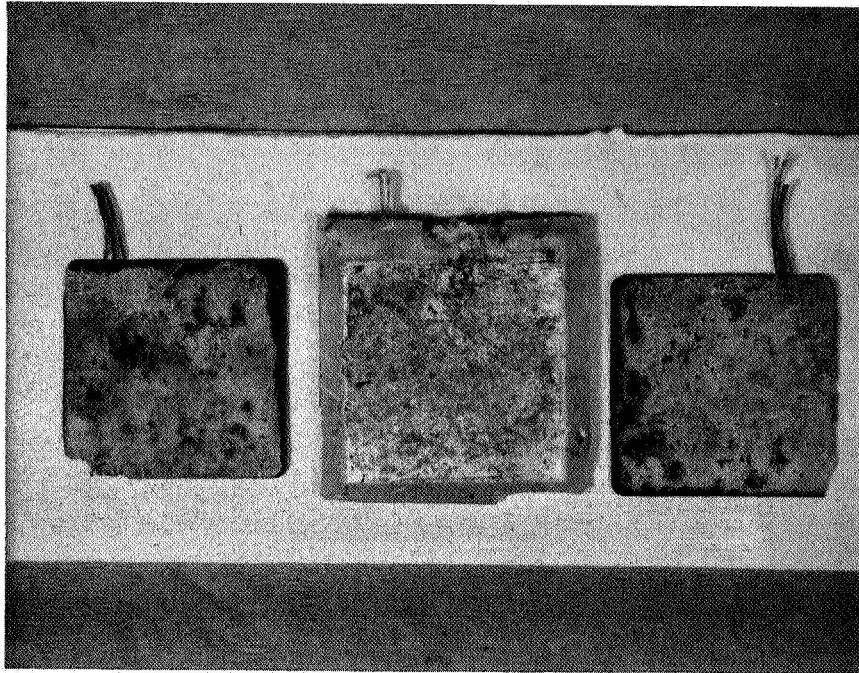
TABLE XVII

GROUP ZL-32 CAPACITY CHECK DURING
THE 90-MINUTE CYCLING

Cycle No.	Capacity				
	Cell #1	Cell #2	Cell #3	Cell #4	Cell #5
1152		4.0 Ah			
1160			4.5 Ah		5.0 Ah
1174	5.0 Ah			4.9 Ah	
1237	4.25 Ah				
1258					4.7 Ah
1326	4.50 Ah				
1336		4.15 Ah			
1341				4.8 Ah	
1342			4.6 Ah		
1377			5.3 Ah		
1492				4.7 Ah	
1504			3.75 Ah		
1571	2.7 Ah				
1583				2.5 Ah	
1628		1.6 Ah			
1632					3.8 Ah

TABLE XVIII
GROUP ZL-32 - TEST SUMMARY

Cell No.	Original Capacity (Ah)	Total Cycles	Final Capacity (Ah)
1	7.30	1571	2.70
2	7.80	1628	1.60
3	7.40	1504	3.75
4	7.60	1583	2.50
5	7.80	1632	3.75
Average	7.60	1583	2.80
Deviation	<3%	<4%	35%



CV519

Figure 18. ZL-32 Cell Electrode Set After 1632 Cycles.
Bottom corners were chipped during dis-
assembly.

TABLE XIX

MATERIAL TESTS

(Average of 2 samples tested for 200 hours at indicated temperatures)

Item	Material (Resin, Hardener Ratio)	Test Condition	Color	Surface	Hardness		% Weight Change
					Immediately After Test	After Washing and Drying	
1	Allbond w/filler (control) 50/50	Original 25°C	Grey NC	Smooth Smooth	— NC	— NC	0 -0.18
		100°C	sl. darker	sl. pitted	NC	NC	-0.23
		135°C	sl. darker	sl. pitted	NC	NC	-0.22
2	Allbond unfilled 64/86	Original 25°C	amber light brown	smooth smooth	— NC	— NC	— -0.11
		100°C	dark brown	sl. pitted	NC	NC	+0.07
		135°C	dark brown	sl. pitted	NC	NC	+0.43
3	Epon 815 94/6 A	Original 25°C	light yellow light yellow	smooth smooth	— NC	— NC	— -0.27
		100°C	dark yellow dark yellow	smooth rough	NC	NC	+0.32
		135°C	dark yellow	rough	NC	NC	+0.37
4	Epon 815 83/17 T-1	Original 25°C	light yellow light yellow	smooth smooth	— NC	— NC	— -0.02
		100°C	dark yellow dark yellow	gummy gummy	soft very soft	NC NC	+0.01 +0.47
		135°C	dark yellow	gummy	very soft	NC	
5	Epon 815 77/23 T-1	Original 25°C	light yellow light yellow	smooth smooth	— NC	— NC	— -0.00
		100°C	dark yellow dark yellow	gummy degraded	soft very soft	NC NC	-2.06 -4.19
		135°C	dark yellow	loose material			

NC = No Change
sl. = slightly

(Continued)

TABLE XIX (Concluded)

MATERIAL TESTS

(Average of 2 samples tested for 200 hours at indicated temperatures)

Item	Material (Resin, Hardener Ratio)	Test Condition	Color	Surface	Hardness		% Weight Change
					Immediately After Test	After Washing and Drying	
6	Epon 815 92/8 A	Original 25°C 100°C 135°C	light yellow light yellow yellow dark yellow	smooth smooth sl. pitted	— NC NC NC	— NC NC NC	— -0.5 +0.2 -2.4
7	Epon 815 90/10 A	Original 25°C 100°C 135°C	light yellow light yellow yellow dark yellow	smooth smooth smooth rough	— NC NC NC	— NC NC NC	— -0.4 -0.5 -5.8
8	Acorn #724 Rubber Cement	Original 25°C 100°C 135°C	orange dark red light yellow dark yellow	smooth, some bubbles smooth, some bubbles smooth, some bubbles smooth, some bubbles	— NC NC NC	— NC NC NC	— +0.9 -1.9 -4.8
9	Chloroprene Rubber	Original 25°C 100°C 135°C	black black black black	smooth sl. pitted sl. pitted smooth	— sl. harder sl. harder sl. harder	— NC NC NC	— -7.1 -9.9 -11.2
10	Silastic Rubber 35 (Dow Chemical)	Original 25°C 100°C 135°C	light tan light tan light tan tan	smooth smooth smooth rough dissolved	— NC NC NC	— NC NC NC	— -0.3 -6.7 -81.2
11	Silastic Rubber 55 (Dow Chemical)	Original 25°C 100°C 135°C	tan tan tan tan	smooth smooth smooth dissolved	— NC NC	— NC NC	— -0.3 -12.7

3.1.8 Separator Edge Seals

To select a material for the separator edge seal that may be capable of resisting chemical attack by KOH at elevated temperatures (as high as 135°C) for 200 hours, several formulations were considered. Material tests and bond tests were made.

3.1.8.1 Material Tests

Samples of each material (2" in diameter by 0.5" thickness) were made and, after measuring their physical characteristics (dimensions, volume, and weight), were submitted to 45% KOH for 200 hours at 25°, 100°, and 135°C.

The list of materials tested and the test results are reported in Table XIX.

The epoxy type Allbond originally used (control) and Epon 815 with hardener not higher than 8% appeared promising. Of the elastomeric types, ACORN #724 rubber cement is the only one that may offer a possibility (see Paragraph 3.1.8.3).

3.1.8.2 Bond Tests

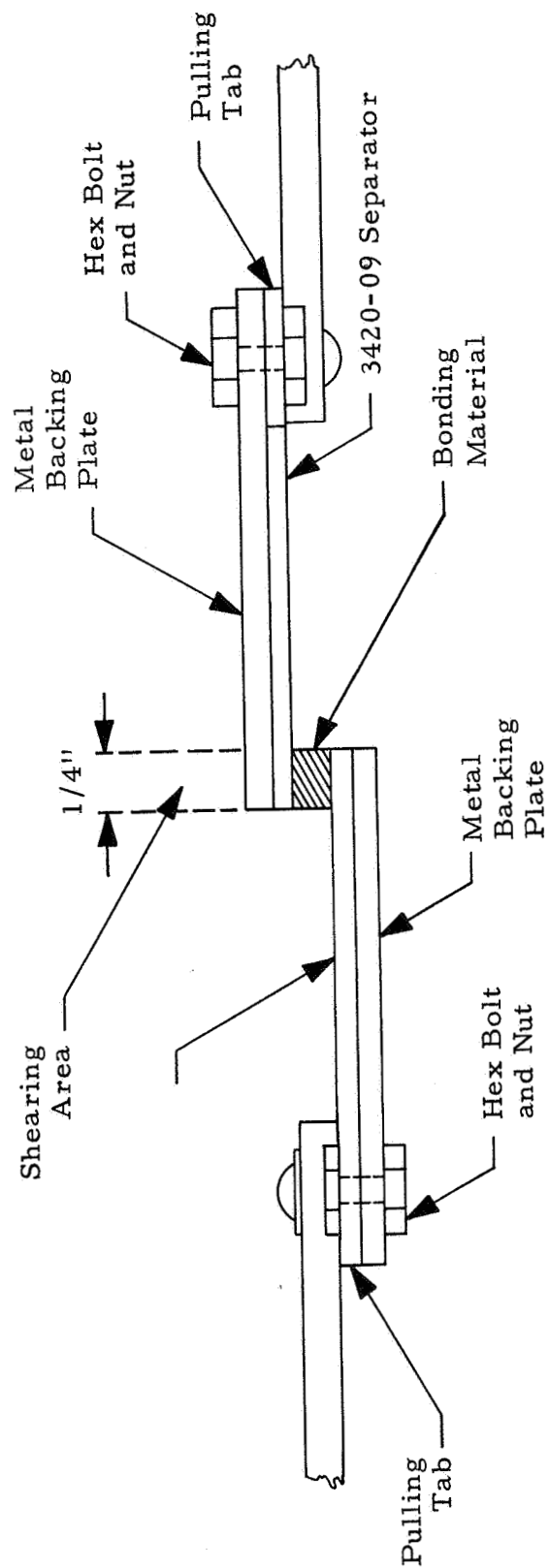
To determine the figure of merit of separator edge seals under dry and wet (KOH) conditions at temperatures as high as 135°C, attempts were made to measure the peel strength and shear strength of the epoxy-bonded separator over a bonded area of the same width as the edge seal area of the wafer construction (i. e., 1/4").

1. For comparative and correlative purposes, the 3420-09 inorganic separator was tested by itself to determine its modulus of rupture and its tensile strength. The results are shown in Table XX.
2. For the peel strength test, no satisfactory method was found suitable because the separator breaks transversally before the epoxy bond peels off.
3. For the shear strength test, a special shearing jig was set up as depicted in Figure 19. Each separator was cemented to a metal backing plate to avoid breaking the separator under tensile pull. Two samples of Allbond epoxy-bonded separators (control) were tried dry at 25°C. The separators broke under tensile pull, sliding away from the metal plates. The entire bonded separator areas remained intact. The values obtained (about 6000 psi) represent the tensile strength of the epoxy-filled separator.

TABLE XX

SEPATATOR 3420-09 PHYSICAL CHARACTERISTICS

Modulus of Rupture (psi)	Tensile Strength (psi)
9150	2040
9190	1850
9180	2020
9100	
8990	
9100	
9170	
9000	
8500	
<u> </u>	<u> </u>
Average: 9040	1970
Mean Deviation: ±135	±80



CS62

Figure 19. First Concept for Epoxy Separator Bond Shear Test

A new set-up was devised to determine the true value of the shear strength of the bond (Figure 20). The tests were run on bonded separator samples in the dry condition and in the wet condition (immersion in 45% KOH for 200 hours) at 25°C and 100°C (Table XXI). Generally, the oven cure and the separator edge impregnation before bonding improve the adhesiveness. On the basis of these data, the Epon 815 with 8% hardener A appeared to be a little superior to the control Allbond up to 100°C. However, the wide scatter of data does not support a firm conclusion.

Tests at 135°C were run on selected compositions only in conditions duplicating actual cell assembly where the bonded areas are under compression. Table XXII shows a better average for Epon, but here again the range of data for both epoxies is quite wide.

Because the cell is not intended for operation over 100°C, and based on the extensive experimental evidence of reliable usage in actual cells at temperatures up to 100°C, Allbond epoxy as used previously is therefore retained as the separator edge sealant.

3.1.8.3 Cells with Separator Edges Sealed with Rubber Cement

Recognizing that the bond tests were not too meaningful with an elastomeric seal, six cells were made for actual test purposes. They were built with chloroprene rubber gasket cemented with Acorn 724 to seal the separator edges.

For fast evaluation, five cells were tested at 100°C on the 1/2-hour, 1-hour cycling regime. After a few cycles, electrolyte spewage occurred, causing premature drying. After refilling, the cells kept cycling but with constant electrolyte spewage and foaming. The cells were stopped after 80 cycles for dissection and examination. The separators were not cracked, but delamination of the seals was common to all wafers. Greenish foam noted in the electrolyte and pinkish color on the positives led to the belief that the chloroprene was electrochemically attacked.

Although the cell was not designed for heat sterilization because of several features incorporated in the design (Pellon interseparator, inorganic separator

TABLE XXI
SHEAR STRENGTH OF BONDED SEPARATORS

Item	Material (resin, hardener)	After exposure to KOH for 200 hours					
		Dry		at 25°C		at 100°C	
		reading	average	reading	average	reading	average
1	Allbond with filler (edge impregnated) 50/50	2690 4150 2400 4100 2690 3090 4490 2240 3890 3060 4090 3300 2040 2210 2440	 3100	 370 510 410 310 800 410	 470	 420 390 400 830 125 125	 380
1A	Allbond with filler (edge not impregnated) 50/50	2600 3090 2610	2770				
2	Allbond unfilled (edge impregnated) 64/36	3480 3430 3850 3560 3620	 3790	1310 1470 540 560 320	 840	250 460 310	 340
2A	Allbond unfilled (edge not impregnated) 64/36	2830 2980 2240 2240 2400	 2540				
3	Epon 815 94/6A R. T. cure	2240 2240 2240 2560	 2320				
	Epon 815 94/6A oven cure	2640 2650 2690 2650 2690 2690 2850	 2700	650 790 750 370 490 620	 610	470 190 180 310	 290

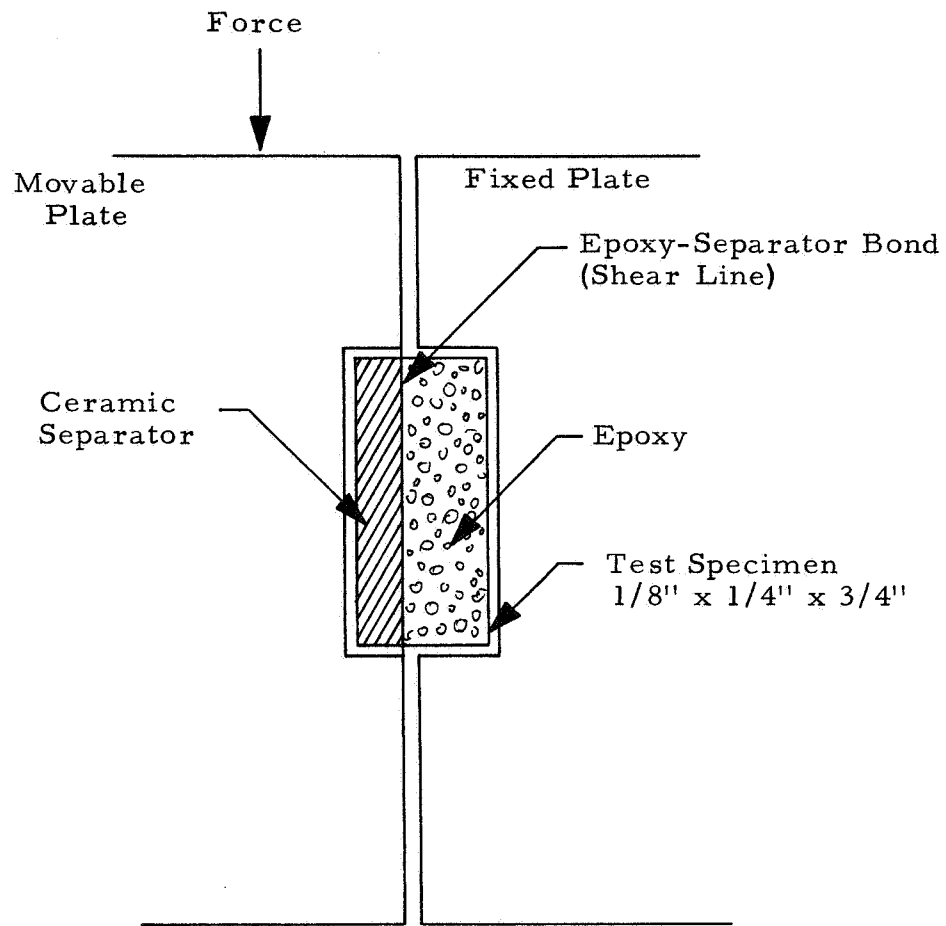
(Continued)

TABLE XXI (Concluded)

SHEAR STRENGTH OF BONDED SEPARATORS

Item	Material (resin, hardener)	After exposure to KOH for 200 hours					
		Dry		at 25°C		at 100°C	
		reading	average	reading	average	reading	average
6	Epon 815 94/8A R. T. cure	2560 2290 3070 1810	2430				
	Epon 815 94/8A oven cure (edge not impregnated)	2700 2850 3130 3600 4350 4390	3500	1270 310 670 1780 1100 620	790	210 610 110 1230 440	520
6A	Epon 815 94/8A oven cure (edge impregnated)	2560 2860 2800 2830 2180 3740	2830	790 840 440 1000 1330 980	900	260 420 1380 230 200 640	520
7	Epon 815 90/10A R. T. cure	1920 1230 2770 1890 1230 1390	1740				
	Epon 815 90/10A oven cure	3360 2270 2680 4220 3630 3040 3630	2860	760 580 640 550 750 580	640	440 460 190 540 330	390
8 and 9	Chloroprene rubber gasket cemented with ACORN 724	470 530 150 600 140 180	350	- - - - -	25*	- - - - -	25*

* estimated



CVS16

Figure 20. Second Concept for Epoxy-Separator Bond Shear Test

TABLE XXII
SHEAR STRENGTH OF BONDED SEPARATORS SUBMITTED
TO KOH AT 135°C FOR INDICATED HOURS (psi)

Item	Material	120 Hours			170 Hours		
		Readings	Range	Average	Readings	Range	Average
1	Allbond with filler (edge impregnated 50/50)	150 105		130	76 15 15 457 428 18		
						15-457	170
6 A	Epon 815 94/8A oven cure (edge impregnated)	555 210		380	204 148 506 41 477 161	41-506	260
							83%

not optimized for sterilization, cell not hermetically sealed), the remaining cell built with elastomeric edge sealant was heat sterilized at 135°C for 200 hours after being fitted with a 40 psig pressure relief valve and placed in a sealed chamber. Upon termination of the test, moisture was noted condensed on the internal walls of the chamber and was found to be neutral when tested with indicator paper.

The cell was then charged at 350 mA and was carried to 2.3 V cutoff voltage to get an input of 7 Ah. On discharge, the output at 1 A was 4.25 Ah with a plateau voltage of 1.18 V. During recharge, electrolyte spewage occurred with the green foam characteristics noted in the other five cells.

The cell was disassembled and the components examined.

1. The valve was checked: the first cracking pressure was 53 psi and the reseating 29 psi. The next four consecutive cracking pressures were 41 psi and reseating pressures 30 psi. The valve was disassembled. The rubber disk was intact and in good condition.
2. The wafers were in good condition — no delamination of the seals or collars, no cracks in the separators.
3. The electrodes were in good condition. The KT interseparator was intact, but the Pellon interseparator (nylon felt) was completely deteriorated.

In an overall evaluation, most of the components appear suitable for heat sterilization. As expected, the Pellon nylon felt is unsuitable, but can be replaced if need be. The separator edge seals appear capable of heat sterilization, but not suitable for cycling conditions. Although functional, the separator exhibited an increase in electrical resistance, translated by the decline in plateau voltage and capacity from the original unsterilized state. This was expected, as this separator 3420-09 was never recommended for heat sterilizable cells, because it lacks the requirement of low resistivity.

Since the present program is not concerned with heat sterilized cell development, further work along this line was discontinued as ordered by the NASA Program Manager (Reference 4).

3.1.9 Valves

In order to approximate the ambient conditions in actual cells, the valve evaluation was done in a KOH saturated atmosphere, with pressure up to 40 psig and temperatures up to 100°C. The testing procedure was set as follows:

1. The valve is adapted to the cover of a sealed and constrained plastic case capable of pressurization up to 50 psig. KOH is introduced into the empty case to approximately the same level as in a regular 5-Ah cell. The set-up has a pressure gauge and a fitting for introducing nitrogen under pressure.
2. The internal pressure is built up with nitrogen to cause the valve to open (the cracking pressure is noted) and to reclose upon loss of pressure (the reseating pressure is noted).
3. Ten consecutive observations are made 15 minutes apart every day over a period of 30 days.

Three different conditions were used:

- 25°C – upright position
- 25°C – occasional changes in attitude to cause KOH to come in contact with the valve
- 100°C – upright position

A few valves set at 40 psig cracking pressure were obtained from two suppliers, A and B, and our own shop (Douglas type C). Three valves of each model were tested. Because the valves are relatively expensive and are not considered an important factor in this program, the NASA Project Manager recommended another inexpensive valve, AA, to be tested. Average test results are presented in Tables XXIII, XXIV, XXV, and XXVI, respectively, for types A, B, C, and AA.

The valves appeared acceptable for room temperature operation on this program. The relatively inexpensive type AA were ordered for all cells required for the remainder of the program.

As this valve is a little too large for properly fitting in the present cover, being extremely close to the terminals, a new cover mold was ordered with terminal holes further apart so as to avoid the possibility of a short through the valve. At the same time, the new molded cover will be provided with a threaded center hole to accept the selected valve body.

TABLE XXIII
AVERAGE TEST DATA OVER 30 DAYS
VALVE A

Test Conditions		Cracking Pressure	Reseating Pressure
Temperature	Attitude		
25°C	Upright	39 psig	37 psig
25°C	Occasional Changes	failed after 16 days	
100°C	Upright	36 psig	29 psig

TABLE XXIV
AVERAGE TEST DATA OVER 30 DAYS
VALVE B

Test Conditions		Cracking Pressure	Reseating Pressure
Temperature	Attitude		
25°C	Upright	43 psig	33 psig
25°C	Occasional Changes	42 psig	31 psig
100°C	Upright	37 psig	31 psig

TABLE XXV
AVERAGE DATA FOR VALVE C

Test Conditions		Cracking Pressure (psig)	Reseating Pressure (psig)	Notes
Temperature	Attitude			
25°C	Upright	43	36	1
25°C	Occasional Changes	49	37	2
100°C	Upright	50	25	3

Notes:

1. Valve completed 30-day test.
2. Last reading before valve failed to crack after 9 days.
3. Last reading before valve failed to reseat after 9 days.

TABLE XXVI
AVERAGE TEST DATA OVER 30 DAYS
VALVE AA (INEXPENSIVE MODEL)

Test Conditions		Over 30-Day Test Period		After 30-Day Test Period	
Temperature	Attitude	Cracking Pressure (psig)	Reseating Pressure (psig)	Cracking Pressure (psig)	Reseating Pressure (psig)
25°C	Upright	41	36	41	36
25°C	Occasional Changes	39	0 ^(a)	39	0 ^(a)
100°C	Upright	40	41	41	27

^(a)Valve would not seat until pressure dropped to zero psig.

3.1.10 Gassing Study

The objective of this study was to determine the gassing characteristics of the cells under various cycling conditions:

- Group I: 25°C, 2-hour period regime
- Group II: 25°C, 24-hour period regime
- Group III: 40°C, 2-hour period regime

Each group consisted of 10 cells:

1. Five cells in a free-venting set up: gas was collected under inverted graduated cylinders.
2. Five cells in a pressurized condition: the cells were fitted with 40 psig relief valves and pressure gauges, with provision for gas venting and collection past the valve. One cell of this group was connected to a pressure transducer to record the pressure variations continuously.

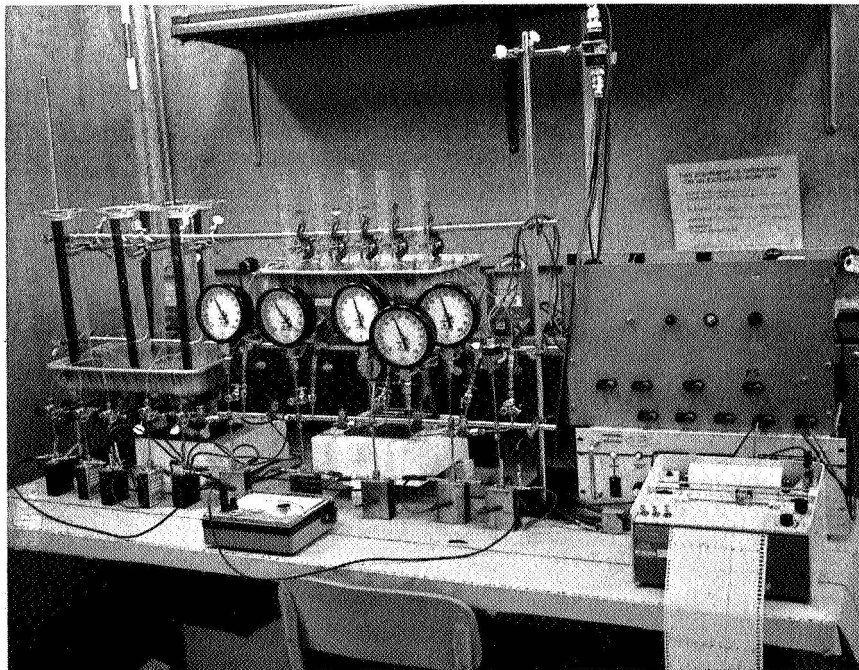
All cells had provision for sampling the collected gas to determine its composition. Figure 21 shows the set-up for one group.

3.1.10.1 Group I (25°C, 2-hour period)

The first 10 cell-group was tested at 25°C on the 2-hour period regime: 3 A discharge for 35 minutes, 1.4 A charge for 85 minutes.

The average gassing rate increased rapidly in the first 80 cycles to approximately 20 cc/hr and remained near this value for the remainder of the test (Tables XXVII and XXVIII). Average gassing rates and average cumulative gassing of pressurized cells were substantially lower than that of the free venting cells. The gassing rate also increased when the cell voltage limit was increased from 2.03 V to 2.10 V on Cycle No. 105 (Figure 22). This increase in the voltage limit of the charge cycle was necessary to replenish the energy removed on discharge. The gas collected during this test was almost entirely hydrogen.

After 207 cycles, the cells were all opened and the electrolyte readjusted. An average of 8 cc of electrolyte, equivalent to 9 liters of hydrogen gas, was required per cell. Average cumulative cell gassing, including that from formation and open circuit stand amounted to close to 9 liters within 5%.



C3724

Figure 21. Gassing Test Set-Up

TABLE XXVII

GASSING TESTS

Group I: Temperature: 25°C
 3 A discharge for 35 minutes
 1.4 A charge for 83 minutes
 Average voltage limit 2.1 V/cell

AVERAGE DATA AS A FUNCTION OF CYCLES

Time Elapsed (hrs)	Cycle No.	Free-Venting Cells					Pressurized Cells				
		Gas Composition			Gassing Rate (cc/hr)	Cumulative Gas Volume (cc)	Gas Composition			Pressure at end of Charge (psig)	Cumulative Vented Gas (cc)
		N ₂ (%)	O ₂ (%)	H ₂ (%)			N ₂ (%)	O ₂ (%)	H ₂ (%)		
0	0	23	57	20	—	—	14	76	10	—	—
6	3	25	44	31	0.0	0.0	14	72	14	0.0	0.0
24	12	15	25	60	0.6	5.8	12	47	41	1.5	0.0
46	23	8	6	86	0.8	25.0	15	85*	0	—	—
52	26	8	6	86	1.8	38.7	19	20	11	10.0	0.0
72	36	3	1	96	1.9	73.0	9	10	81	15.4	0.0
96	48	1	4	95	3.8	153.0	7	11	82	32.5	35.6
140	70	1	—	99	6.5	521.0	3	14	83	30.0	274.0
164	82	—	—	100	21.3	900.0	2	3	95	33.0	453.0
204	102	—	—	—	16.9	1702.0	—	—	—	33.8	760.0
392	196	—	—	—	20.5	5705.0	—	—	—	33.2	4076.0
460	230	1	8	91	22.3	7275.0	3	8	89	40.8	5623.0
520	260	—	—	—	20.0	8733.0	—	—	—	40.0	7603.0
600	300	—	—	—	20.5	10,123.0	—	—	—	40.0	8866.0
660	330	—	—	—	19.9	11,388.0	—	—	—	40.0	9769.0
720	360	—	—	—	13.4	12,546.0	—	—	—	40.0	11,225.0

* Pressurized cells were purged with oxygen.

- NOTES: 1. All cells were purged with oxygen at cycle 207 when electrolyte was added.
 2. Average charging voltage limit per cell was changed from 2.03 V to 2.10 V at cycle 101 to permit efficient charge to discharge ratio for continuous cycling.

TABLE XXVIII
GASSING TESTS

Group I = Temperature = 25°C
 3 A discharge for 35 minutes
 1.4 A charge for 85 minutes
 Voltage limit 2.03 V/Cell

STATUS OF INDIVIDUAL CELLS AT CYCLE 70

Test	Cell No.	Accumulated Gas Volume (cc)	Gas Composition			Pressure at end of Charge (psig)
			N ₂ (%)	O ₂ (%)	H ₂ (%)	
Free-Venting	ZL-22-1	270	—	—	100	—
	ZL-22-2	655	—	—	100	—
	ZL-22-3	490	4	1	95	—
	ZL-22-4	610	—	—	100	—
	ZL-22-5	700	—	—	100	—
Pressurized	ZL-22-6	263	4	20	76	30
	ZL-22-7	459	5	4	91	30
	ZL-22-8	111	2	7	91	20
	ZL-22-9	275	2	16	82	35
	ZL-22-10	264	2	21	77	35

Group I

Regime: 35 min. discharge = 3.0 A

85 min. charge = 1.4 A

Temp.: 25°C

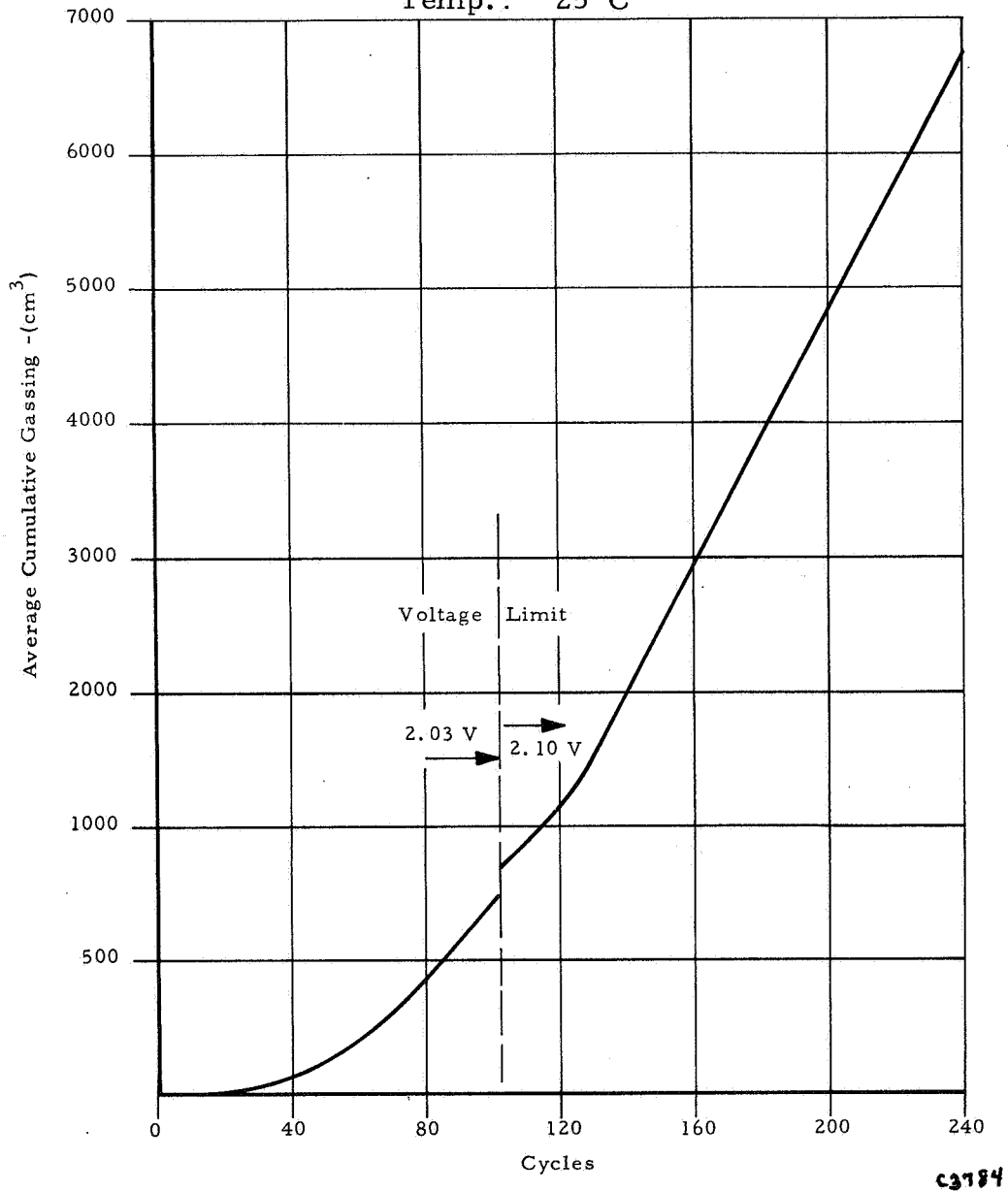


Figure 22. Gassing vs. Cycle (5 Ah Ag-Zn Cells)

This first group of 10 cells completed 360 cycles as scheduled on the 2-hour cycling regime. The data are presented in Table XXVII. Figure 23 shows the variation of the average gassing rate on cycling on this regime. Figure 24 shows the variation of the average gassing rate on charged stand at various times during the cycle life of the cells. Table XXIX gives a comparison of the amount of gas collected and measured versus the gas equivalent of electrolyte consumed during the entire testing period (including gas generated during stand). The total wet life of these cells was 80 days from formation to the last capacity checks. Barring possible leaks during the cycling, assembly and disassembly of the experimental set up, it appears that the gas collected was in all cases smaller than the gas equivalent of the water consumed. This coupled with the fact that the major percentage of gas composition was hydrogen in practically the entire life of the cells shows that some oxygen must have recombined with the zinc, more so in pressurized cells than in free-venting cells.

The cells after completing their cycling were checked for capacity and OCV. Immediately after 360 cycles, they were removed from cycling at the end of charge, then discharged to 1.0 V at the cycling rate 3 A, then drained to 1.0 V at 0.5 A for determining the total capacity.

The cell capacity was low to medium with a good OCV. A normal charge to 2.05V cut-off voltage could not restore all the available zinc capacity, because of the imbalance in the state-of-charge of the electrodes of opposite polarities. However, after charging and purposely overcharging the cells to let the zinc catch up with the silver, the capacity was restored in the range of 5 to 6 Ah (Table XXX).

Attempts were made to reduce the gassing which was deemed excessively abnormal. After purifying the same basic ingredients of the 3420-09 separator and establishing on our internal program that the new purified separator 3420-09 will cause less gassing, three cells were built and tested on the 2-hour period regime to quantitatively determine the amount of gassing reduction on the same regime.

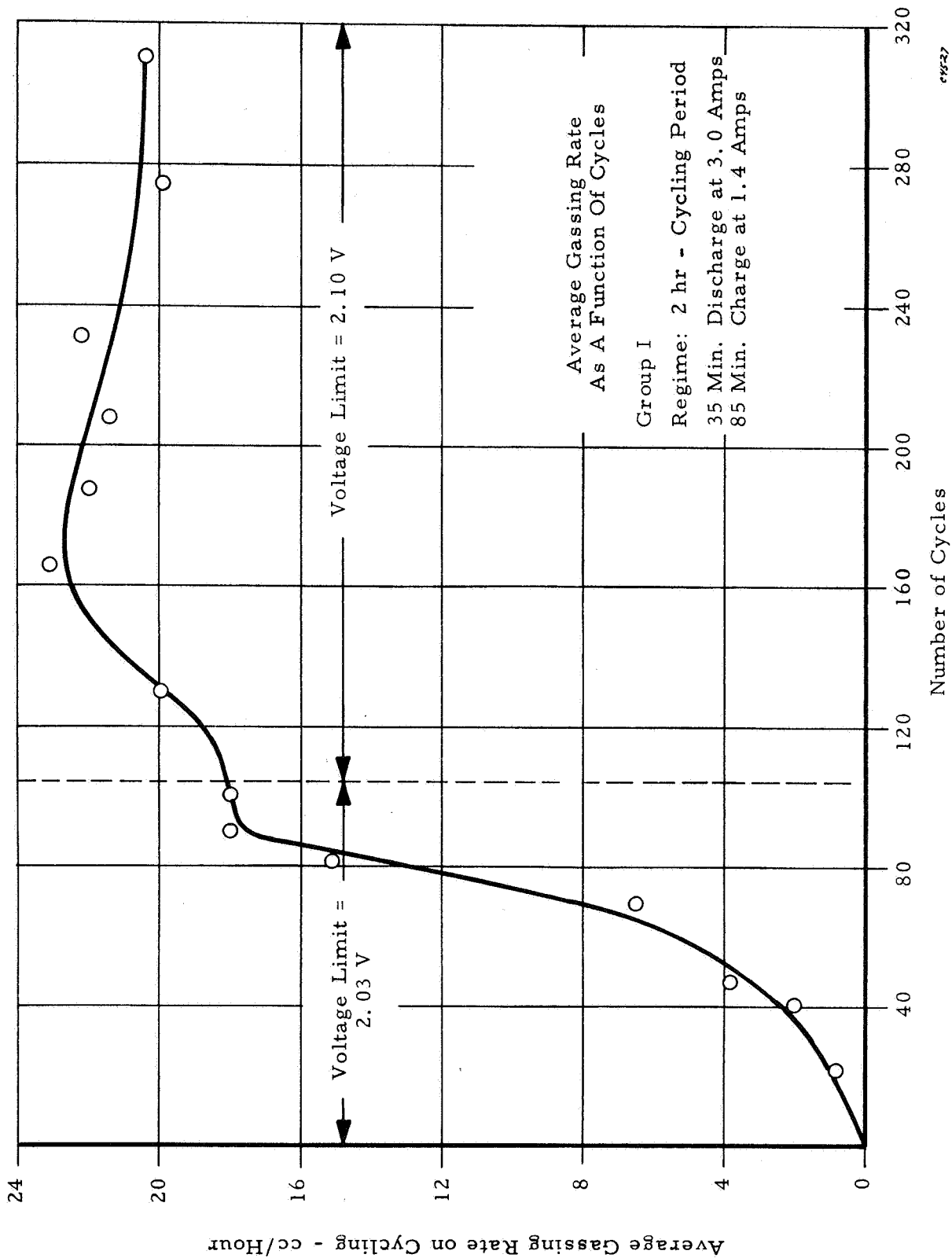
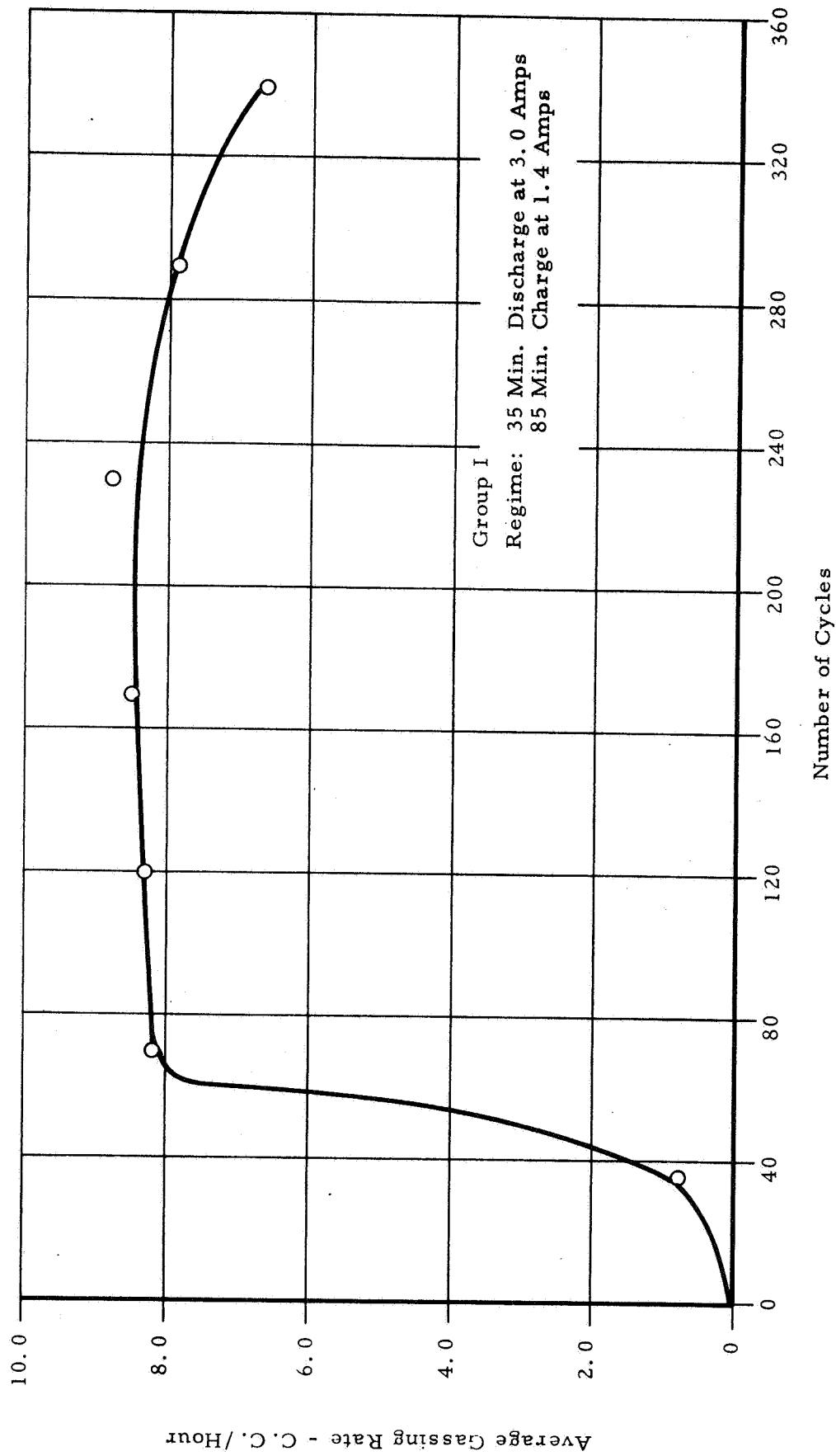


Figure 23. Average Gassing Rate of Free Venting Cells (DA-5) on Cycling at 25°C



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Figure 24. Average Open Circuit Gas Evolution of Free Venting Cells (DA-5) After End of Charge, on Stand at 25°C

TABLE XXIX

COMPARISON OF AMOUNTS OF GAS COLLECTED
AND GAS EQUIVALENT OF ELECTROLYTE CONSUMED
DURING THE ENTIRE TESTING PERIOD

Group I

Cycling Regime: 3 A discharge for 35 minutes,
1.4 A charge for 85 minutes.

Voltage Limit: 2.10 V per cell.

Temperature: 25°C

Total Cycles: 360

Total Wet Life: 80 days.

Set-Up	Cell No.	Water Weight Loss	Moles Water	Stoichiometric Gas Equivalent (l)	Gas Evolved (l) Measured
Free-Venting	1	13 g	0.712	24.0	19.4 [±] 5%
	2	14	0.777	26.1	21.2
	3	12	0.666	21.7	21.6
	4	13	0.712	24.0	21.3
	5	13	0.712	24.0	16.9
Average:		13	0.712	24.0	20.0
Pressurized	6	14	0.777	26.1	15.5 [±] 5%
	7	15	0.835	28.0	16.1
	8	15	0.835	28.0	(8.7*)
	9	14	0.777	26.1	18.7
	10	15	0.835	28.0	17.9
Average		14.5	0.806	27.0	17.0

*System leaked, value eliminated from average.

TABLE XXX

TESTS RUN AFTER COMPLETION OF
360 CYCLE GASSING TEST

Cell No.	Output After Cycling			Input to 2.15 V	20 Hours OCV > 1.85 V		
					Output		
	at 3 A	at 0.5 A	Total		3 A	0.5 A	Total
1	2.25	1.15	3.4 Ah	9.2 Ah	6.0	0	6.0
2	1.50	0	1.5	6.4	3.8	0	3.8
3	1.65	0	1.7	1.9	1.0	0	1.0
4	2.25	3.35	5.6	4.9	4.0	0	4.0
5	0.25	2.90	3.15	4.3	0.75	2.1	2.85
6	2.00	0.25	2.25	6.4	4.5	0	4.5
7	2.25	0.10	2.35	6.4	3.9	0	3.9
8	1.50	0.4	1.9	5.4	3.3	0	3.3
9	1.5	0	1.5	5.4	3.0	0	3.0
10	1.5	0	1.5	4.8	3.0	0	3.0

After charge to 2.10 V with a minimum input of 5 Ah regardless of voltage, and a maximum of 9 Ah.

Cell No.	Input (Ah)	End Voltage	OCV After 17 Hours	Output			Plateau Voltage at 3 A
				3 A	0.5 A	Total	
1	8.4	2.10	1.87	4.75	1.25	6.0	1.36
2	8.4	2.09	"	5.5	0.5	6.0	1.37
3	8.4	2.08	"	5.0	1.0	6.0	1.36
4	8.4	2.12	"	5.25	1.4	6.25	1.28
5	5.25	2.18	"	0.75	4.0	4.75	1.20
6	8.4	2.09	"	4.25	0.75	5.0	1.34
7	8.4	2.11	"	5.25	1.0	6.25	1.36
8	8.4	2.12	"	5.0	1.25	6.25	1.36
9	8.4	2.12	"	4.75	1.0	5.75	1.37
10	8.4	2.13	"	5.0	1.4	6.4	1.34

These cells have been removed from test after completing 241 cycles. Gas evolution was significantly lower (see Figure 25) when compared with the first 10 cell group run at 25°C over the same number of cycles. It shows a definite improvement and the present gassing may be more related to the high rate of charge of the 2-hour period regime. This is evidenced by the fact that after a few hours on stand the gassing rate is considerably reduced and tapers off, whereas the first 10 cell group exhibited constant gassing evolution in the same period (Figure 26).

The gas composition was almost entirely hydrogen as shown below.

Cell No.	Cycle No.	
	96	107
2	97% H ₂	90% H ₂
3	100% H ₂	95% H ₂

At that time, the cells were built with large size positive electrodes which, as noted in paragraph 3.1, led to premature zinc limiting conditions and may account for the predominant hydrogen composition of the gas evolved. In order to eliminate this factor, these cells were replaced by two new 3-cell groups with the regular (smaller) silver electrodes on the 2-hour regime to confirm cycling and gassing behavior compared to the original 10-cell group I. Formation data are given in Table XXXI.

Two new series of three cells each were started on the 2-hour period cycling regime for gassing rate determination. A definite improvement in the reduction of the gassing rate was observed. This was obtained as the result of several factors — purification of the basic ingredients of the inorganic separator, maintenance of the limiting voltage on charge at a low level (2.03 V/cell average) and change of the electrolyte concentration which was raised to 40% in anticipation of the wet stand tests. The gassing test data are depicted in Figures 27 and 28 and compiled in Table XXXII.

Over 360 cycles (30 days cycling on the 2-hour regime), the gassing rate averaged about 1 cc/hour, whereas the total gas volume evolved is equivalent to less than 0.5 cc of electrolyte. No replenishment of the cells was done

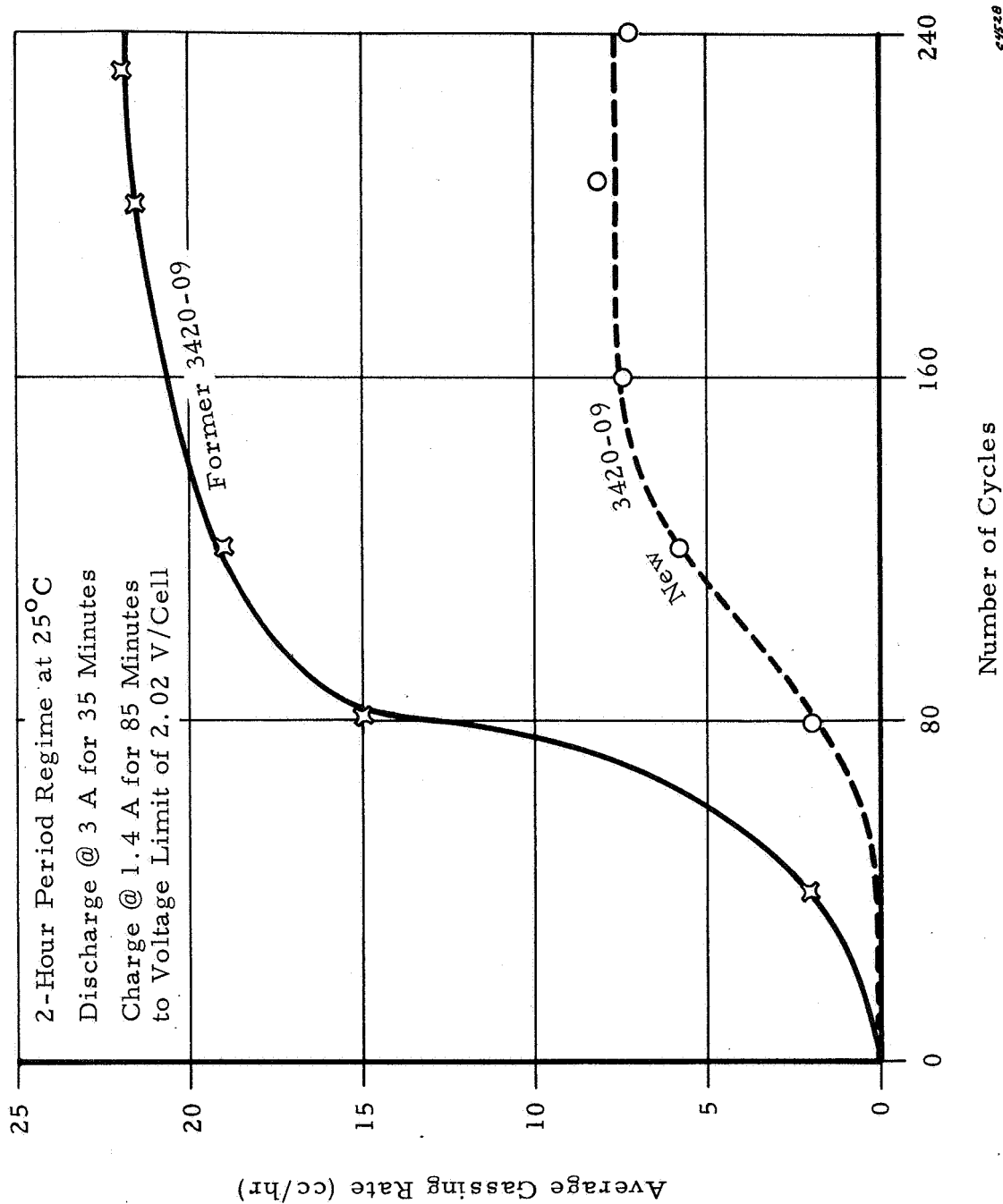


Figure 25. Gassing Rate of Cells on Cycling

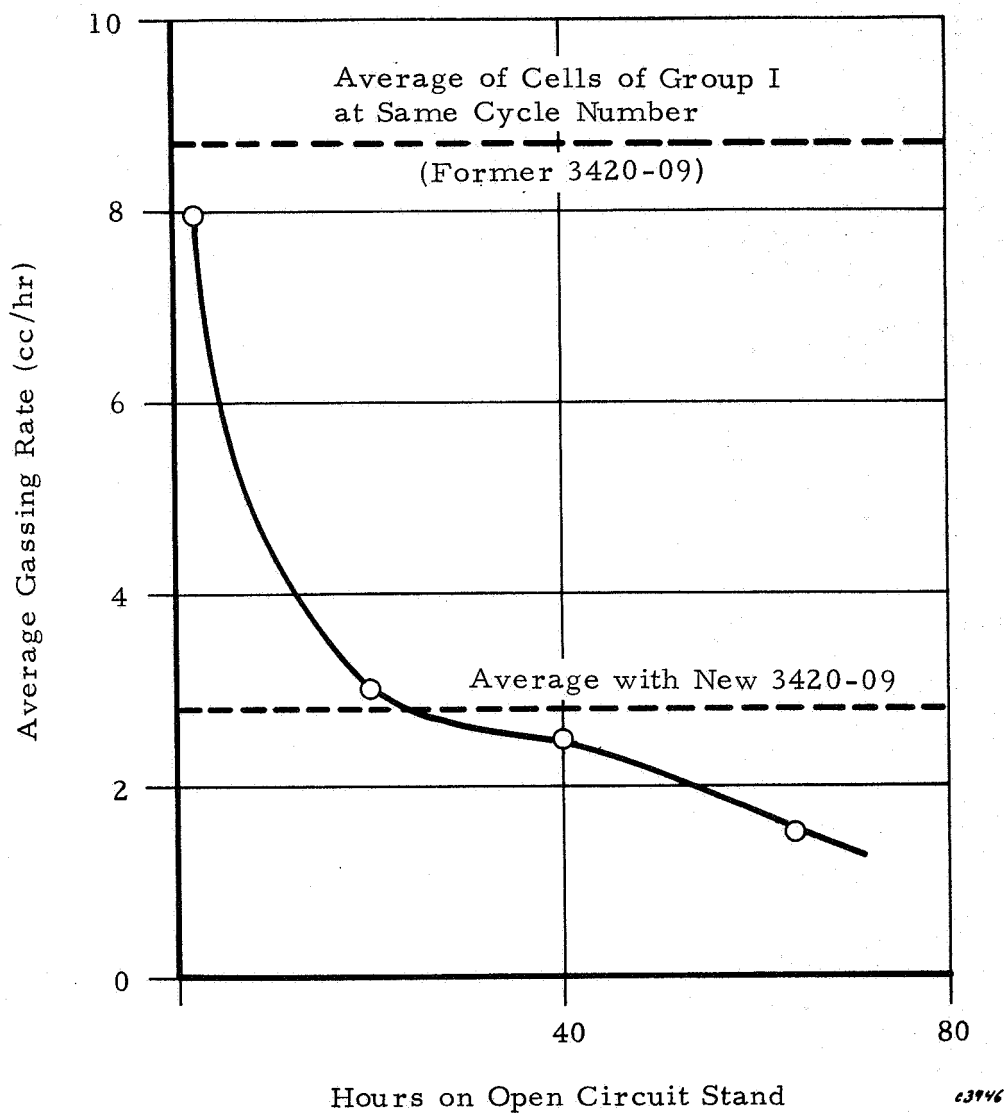


Figure 26. Gassing Rate of Cells on Open Circuit Stand at 25°C (after 215 cycles on 2-hour regime)

TABLE XXXI

FORMATION OF CELLS WITH NEW 3420-09

(Discharge at 1.0 A to 1.0 V)

Group	Cell No.	Capacity A	Voltage
ZL-33	ZL-33-1	8.0 Ah	1.44 V
	ZL-33-2	8.2 Ah	1.44 V
	<u>ZL-33-3</u>	<u>7.7 Ah</u>	<u>1.44 V</u>
	Average	8.0 Ah	1.44 V
ZL-34	ZL-34-1	7.8 Ah	1.45 V
	ZL-34-2	7.7 Ah	1.45 V
	<u>ZL-34-3</u>	<u>7.7 Ah</u>	<u>1.45 V</u>
	Average	7.7 Ah	1.45 V

2-Hour Period Regime at 25°C
 Discharge @ 3 A for 35 Minutes
 Charge @ 1.4 A for 85 Minutes
 to Voltage Limit of 2.02 V/Cell

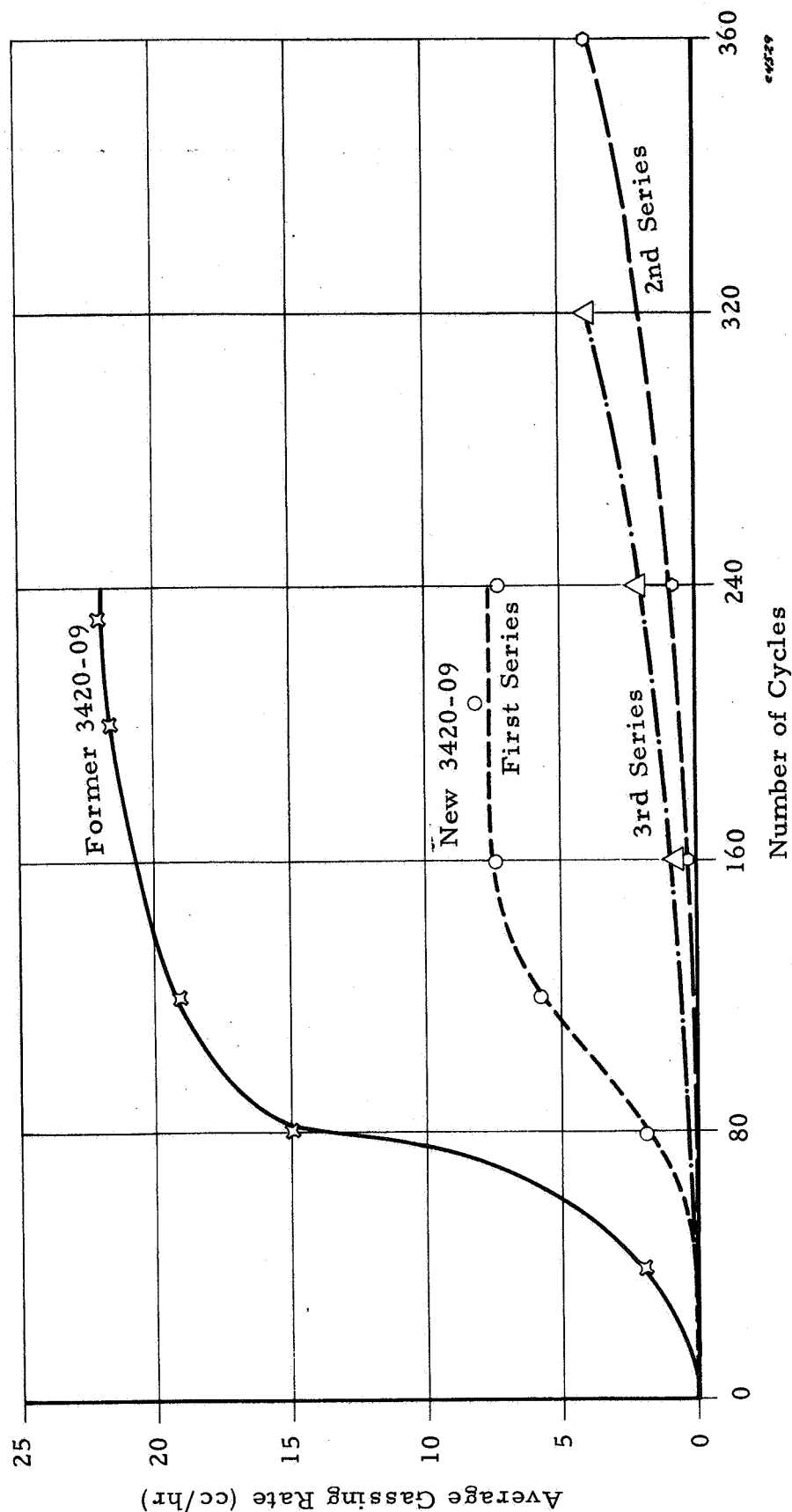


Figure 27. Gassing Rate of Cells on Cycling

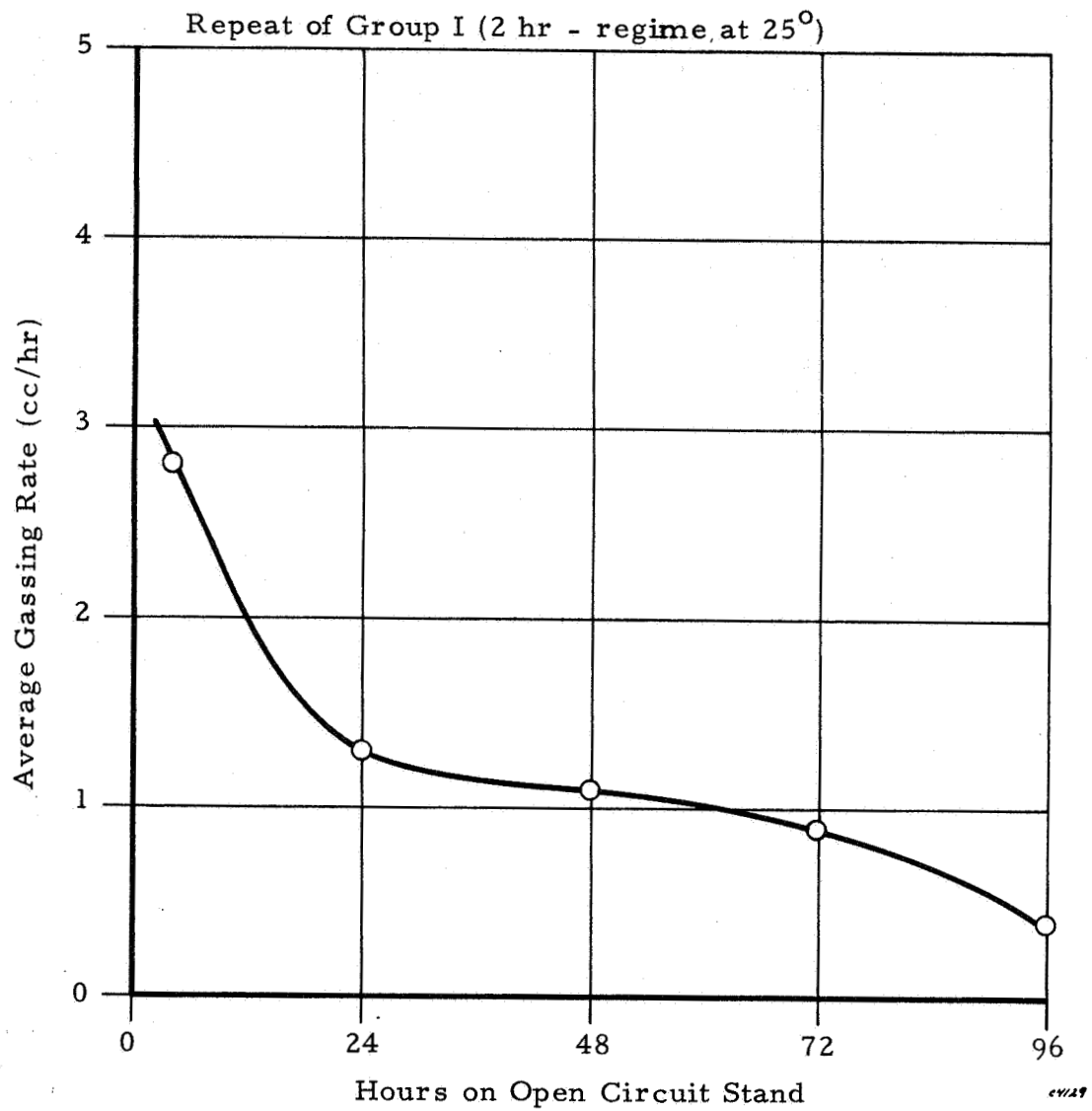


Figure 28. Gassing Rate of Cells on Open Circuit Stand at 25°C
(After 326 Cycles)

GASSING TESTS

Group I-A:
(Repeat of Group 1
with new 3420-09)

Temperature: 25°C
Cycling Period: 2 hours
Discharge: 3 A for 35 minutes
Charge: 1.6 A for 85 minutes
(voltage limited to 2.04 V/cell)

Average Data as a Function of Cycles

Time Elapsed (hrs)	Cycle No.	Free Venting Cells				
		Gas Composition			Gassing Rate (cc/hr)	Cumulative Gas Volume (cc)
		H ₂ (%)	O ₂ (%)	N ₂ (%)		
0	0	0	82	18	—	—
24	12				0.07	2
48	24				0.18	
72	36				0.18	
96	48				0.10	
120	60				0.19	17
144	72				0.10	
168	84				0.10	
	96				0.10	
	108				0.13	
	120	14.7	70	15.3	0.11	28
	132				0.11	
	144				0.13	
	156				0.14	
336	168				0.33	44
	180				0.41	
	192				0.82	79
	216	24.4	63	12.6	0.34	
	228				0.30	131
	240				0.31	
504	252				0.42	
	276				0.76	
	288				0.88	191
	300				1.67	
	312	52	34	14	1.88	
	324				2.50	446
672	336				3.01	
	348				3.27	
720	360				4.00	695

during the entire test. However, at one point of the test, it was necessary to raise the limiting voltage to 2.05 V/cell average in order to store enough capacity in the cells so as to keep them cycling continuously.

3.1.10.2 Group II (25°C, 24-hour period)

The second group of ten cells completed one month testing on the 24-hour cycle regime. Data are presented in Table XXXIII, Figure 29 shows the variation in average gassing rate with the number of cycles. Again, the amount of gas collected from the pressurized cells was less than from the free venting cells. The hydrogen component in the gas gradually increased during the test. A period of overcharge on cycle No. 7 caused generation of oxygen which could be readily detected in the gas analysis on the 8th cycle. The gas composition during a charge-discharge cycle is given in Table XXXIV. It would appear that the oxygen content reaches a maximum value near the end of charge. Gassing rates and composition of each free venting cell are given in Table XXXV for a typical cycle.

The average gassing rate during two cycles (Nos. 30 and 31) is shown in Figure 30. Gas composition during the cycle is also indicated. The gas composition represents an average of the gas being evolved. The gassing rate rises near the end of the charge cycle and then drops to the value observed at the end of the discharge cycle. Cycling curves of free venting and pressurized cells on the third and 30th cycle are presented in Figures 31 and 32. No electrolyte was added during these tests.

At the end of 30 cycles, all cells were charged and placed on open circuit stand and the gassing rate and voltage recorded. Gas evolution on open circuit stand decreased abruptly during the first two days from 9 cc/hour to 2.8 cc/hour, then decreased to 2 cc/hour over the next 12 days (Figure 33).

The gassing rate on cycling and on OCV after cycling depends on the duration of the test and on the number of cycles, i. e., on the cycling period selected. Because of the possibility of maintaining a low voltage limit at the end of the charge, the longer cycling period is favored.

GASSING TESTS

AVERAGE DATA AS FUNCTION OF CYCLES

* Average cell voltage rose to 2.08 V/cell on previous cycle by accident.

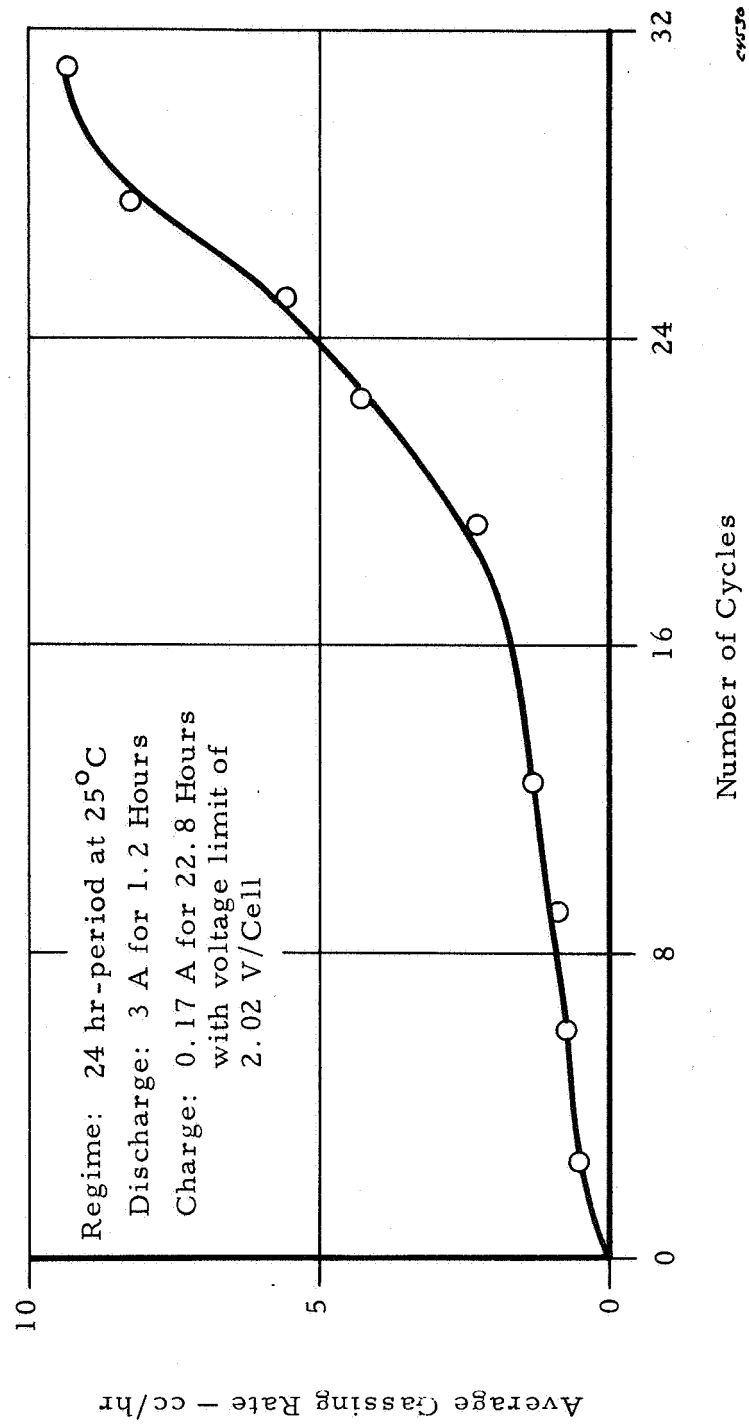


Figure 29. Average Gassing Rate of Free Venting Cells (DA-5) on Cycling

TABLE XXXIV
OXYGEN EVOLUTION DURING THE COURSE OF A CYCLE

(Group II - 24 Hour - Regime at 25°C)
(Remainder = Hydrogen)

Cell Condition	Cycle 21		Cycle 28	
	Free Venting	Pressurized	Free Venting	Pressurized
<u>Discharge</u>				
After 1/2 Hour	43%	43%	—	—
After 1 Hour	42%	50%	17%	19%
<u>Charge</u>				
After 5 Hours	17%	38%	5%	9%
After 21 Hours	38%	30%	23%	16%

TABLE XXXV
GAS COMPOSITION AND GASSING RATE OF
FREE VENTING CELLS ON 27th CYCLE
(Group II - 24 Hour - Regime at 25°C)

Cell No.	Gas Composition			Gassing Rate cc/hr	Cumulative Gas Volume cc
	N ₂ %	O ₂ %	H ₂ %		
1	26	20	54	2.1	1030
2	24	12	64	10.8	1715
3	—	—	—	3.5	1085
4	11	21	68	13.3	2285
5	<u>30</u>	<u>28</u>	<u>42</u>	<u>10.0</u>	<u>2010</u>
Avg.	23	20	57	7.7	1630

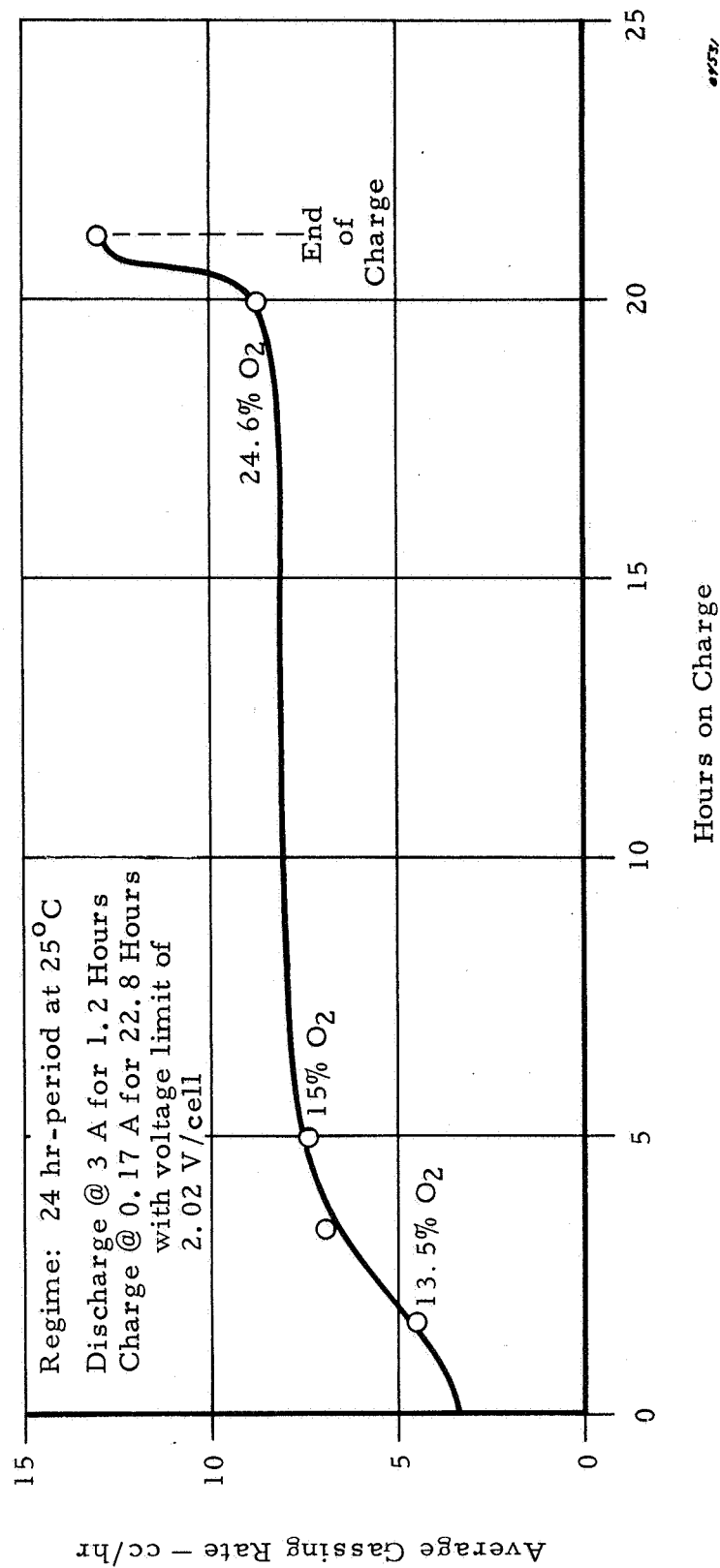


Figure 30. Average Gassing Rate and Gas Composition of Free Venting Cells on a 24-Hour Cycle (Cycle No. 30 & 31)

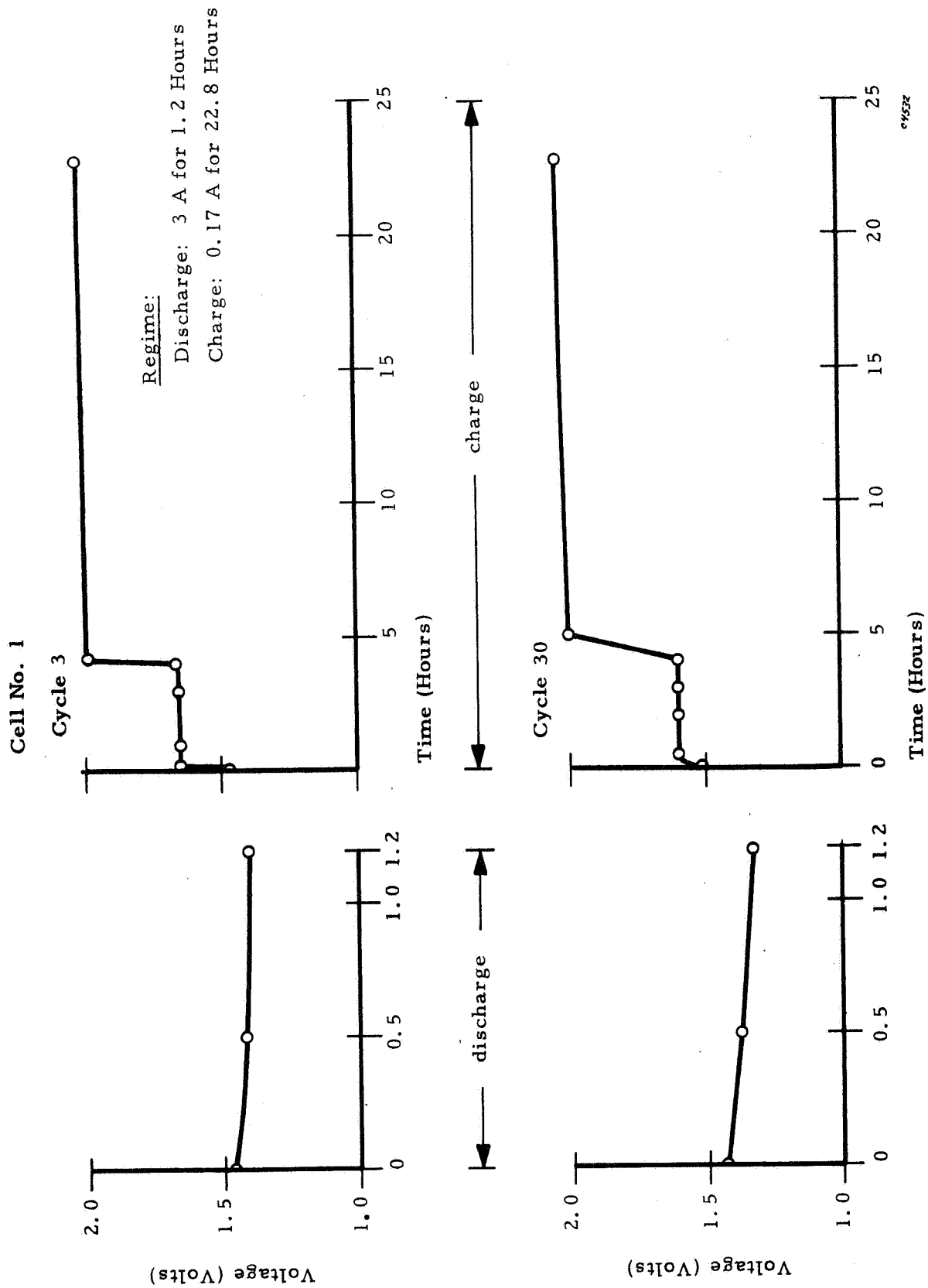


Figure 31. Cycling Curve of Free Venting DA-5 Cell
on 24-Hour Regime

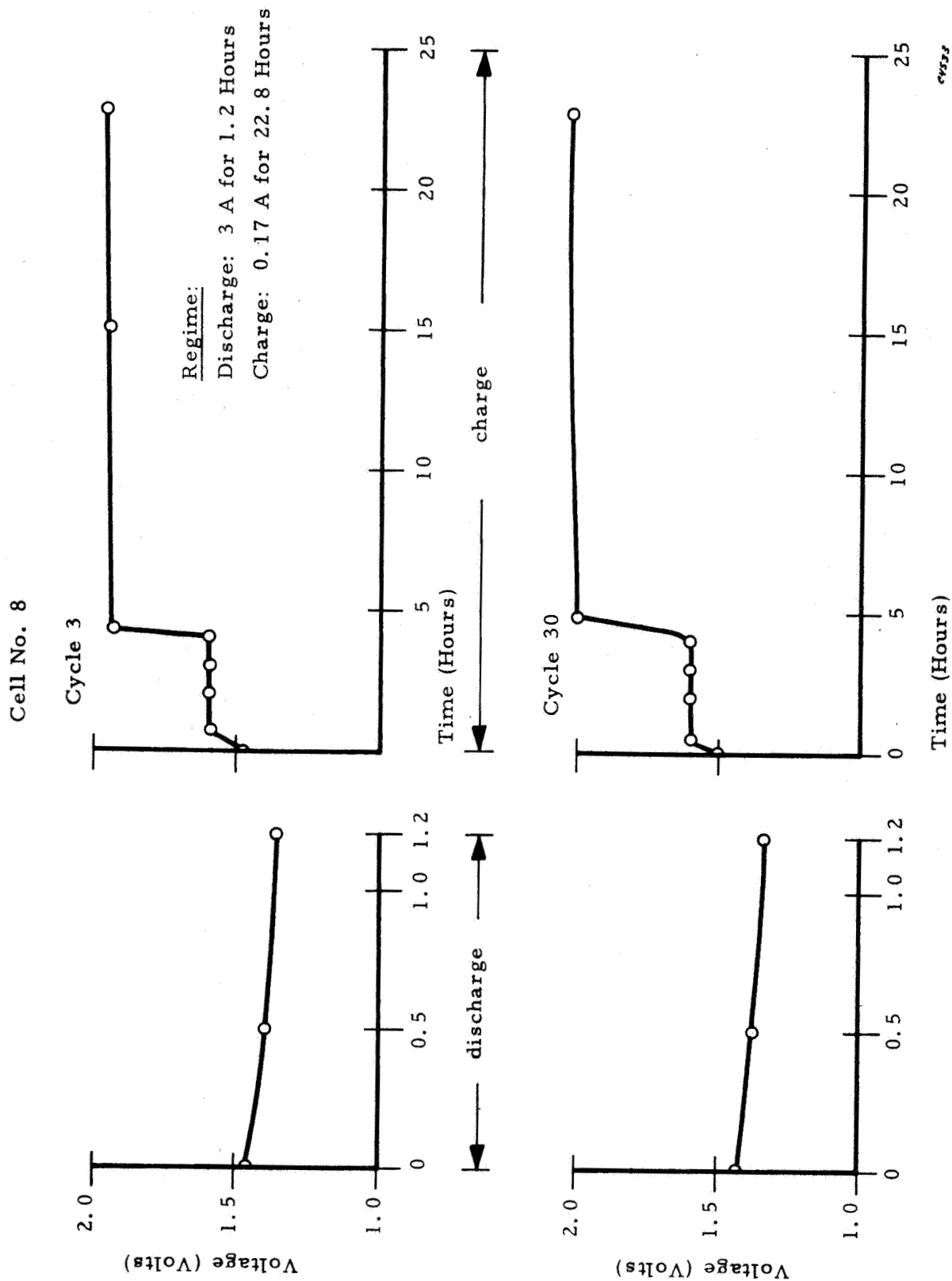


Figure 32. Cycling Curve of Pressurized DA-5 Cells
on 24-Hour Regime

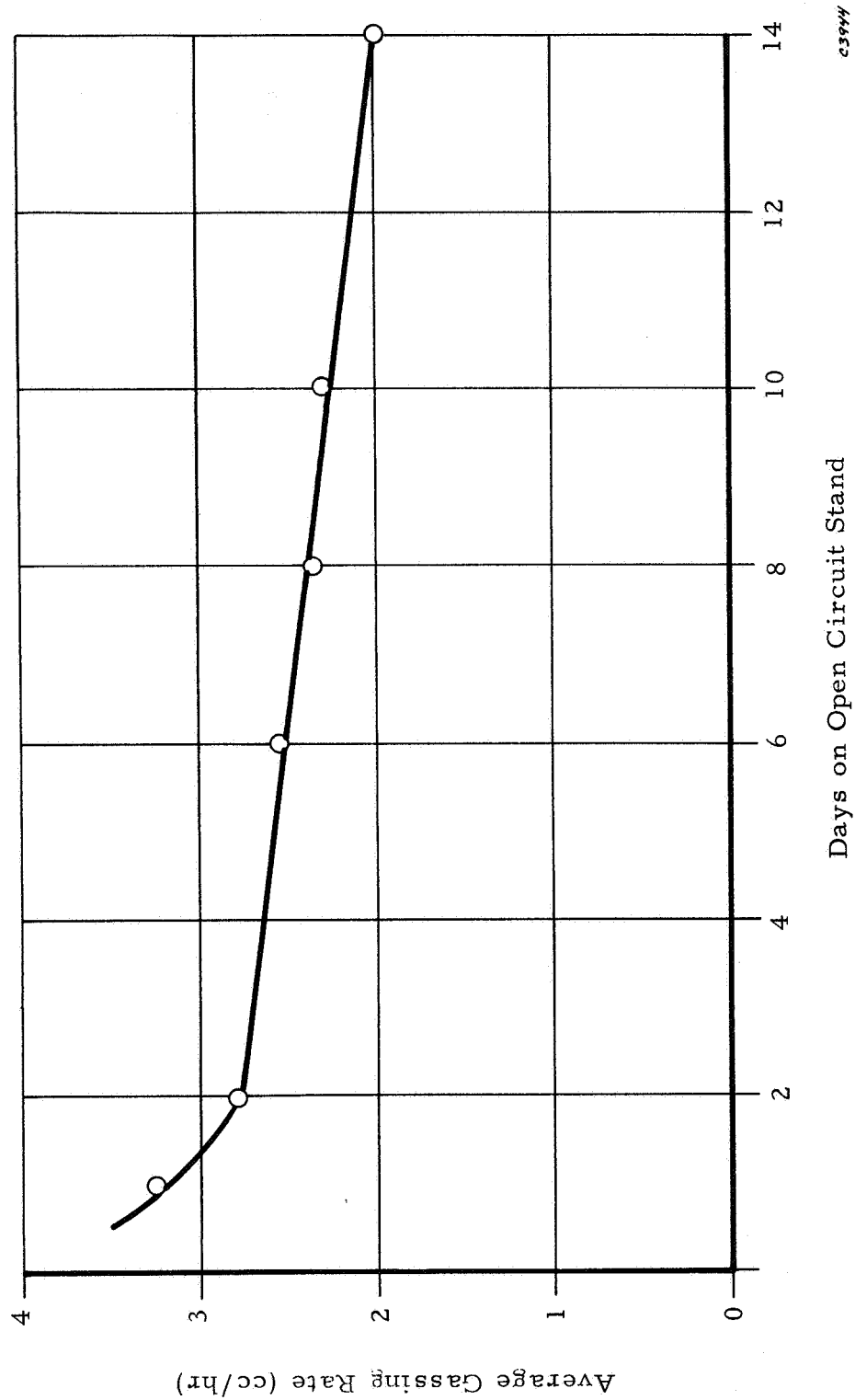


Figure 33. Average Gassing Rate of Cells on Open Circuit Stand (After 30 Cycles on a 24-Hour Regime)

3.1.10.3 Group III (40°C, 2-hour period)

The last test of the gassing study, cycling on the 2-hour period regime at 40°C was started on the following regime: 3 A discharge for 35 minutes, 1.6 A charge for 85 minutes with a voltage limit of 2.01 V/cell average.

Table XXXVI gives the complete test results at 40°C. Figure 34 gives a graphic comparison between the 25°C and 40°C tests on the same cycling regime (2-hour period), as a function of cycles over the 30-day period.

There is slightly more gassing at 40°C than at 25°C, and the difference should be considered as negligible and within normal limits of variations.

More significant is the fact that pressurized cells performed generally better than the free-venting cells; they vented less gas (831 cm³ compared with 971 cm³ for the free-venting cells) and their residual capacities at the end of charge after 360 cycles of 2-hour period regime were higher by an average of 40% (see Table XXXVII). However, all cells, after a normal recharge, yielded approximately 5 Ah.

3.2 TASK II: FINALIZED DESIGN, PRELIMINARY CELL TESTING

The objective of Task II is to fabricate a certain number of cells of the proposed final design for testing — charged wet stand at 25°C and 100°C, environmental tests, and electrical tests.

3.2.1 Wet Stand

Sixteen cells were scheduled for the wet stand tests as follows:

<u>Stand Time</u>	<u>25°C</u>	<u>100°C</u>
1 month	2 cells	2 cells
2 months	2 cells	2 cells
3 months	4 cells	4 cells
Constraint: OCV lower limit:	1.80 V	1.62 V

TABLE XXXVI

GASSING TESTS

Group III: Temperature: 40°C

Cycling Period: 2 hours

Discharge: 3.0 A for 35 minutes

Charge: 1.6 A for 85 minutes (voltage limited to 2.01 V/cell)

AVERAGE DATA AS A FUNCTION OF CYCLES

Time Elapsed (hrs)	Cycle No.	Free Venting Cells					Pressurized Cells				
		Gas Composition			Gassing Rate (cc/hr)	Cumulative Gas Volume (cc)	Gas Composition			Pressure at End of Charge (psig)	Cumulative Vented Gas (cc)
		H ₂ (%)	O ₂ (%)	N ₂ (%)			H ₂ (%)	O ₂ (%)	N ₂ (%)		
0	0	0	81.8	18.2	0	0	—	—	—	-4	0
24	12	8.4	51.8	39.8	0.59	14.2	11.6	75.0	—	7	0
48	24	—	—	—	0.56	27.6	—	—	—	15	0
72	36	32.0	48.5	19.5	0.47	39.0	28.2	63.4	8.4	24	0
96	48	—	—	—	0.45	49.8	—	—	—	28	0
120	60	—	—	—	0.44	60.4	—	—	—	35	15
144	72	33.0	45.5	21.4	0.54	74.0	34.1	54.9	7.7	30	19
168	84	—	—	—	0.62	88.8	—	—	—	31	24
	96	—	—	—	0.57	103.0	—	—	—	30	35
	108	—	—	—	0.58	117.0	—	—	—	29	48
	120	32.1	46.7	21.1	0.63	132.0	45.3	49.8	5.0	29	62
	132	—	—	—	0.63	147.0	—	—	—	30	74
	144	—	—	—	0.68	163.0	—	—	—	30	88
	156	37.1	42.3	2.05	0.66	180.0	49.0	47.5	3.5	30	104
336	168	—	—	—	0.68	196.0	—	—	—	30	116
	180	—	—	—	0.67	212.0	—	—	—	30	129
	192	44.9	35.2	19.9	0.73	230.0	55.0	41.8	3.2	30	144
	204	—	—	—	0.91	252.0	—	—	—	30	159
	216	—	—	—	0.89	273.0	—	—	—	30	177
	228	—	—	—	0.96	296.0	—	—	—	30	198
	240	61.8	22.1	16.1	0.93	318.0	68.8	26.8	4.4	30	219
504	252	—	—	—	1.29	349.0	—	—	—	30	255
	264	—	—	—	1.36	382.0	—	—	—	30	277
	276	64.7	16.3	18.9	1.70	423.0	78.0	16.6	5.4	29	318
	288	—	—	—	1.98	470.0	—	—	—	30	361
	300	—	—	—	2.39	528.0	—	—	—	30	415
	312	—	—	—	2.97	599.0	—	—	—	30	477
	324	—	—	—	—	700.0	81.8	14.1	4.1	30	548
672	336	—	—	—	3.25	802.0	—	—	—	31	631
	348	—	—	—	3.49	886.0	—	—	—	31	736
720	360	70.3	6.0	19.7	3.80	971.0	88.2	8.0	3.8	31	831

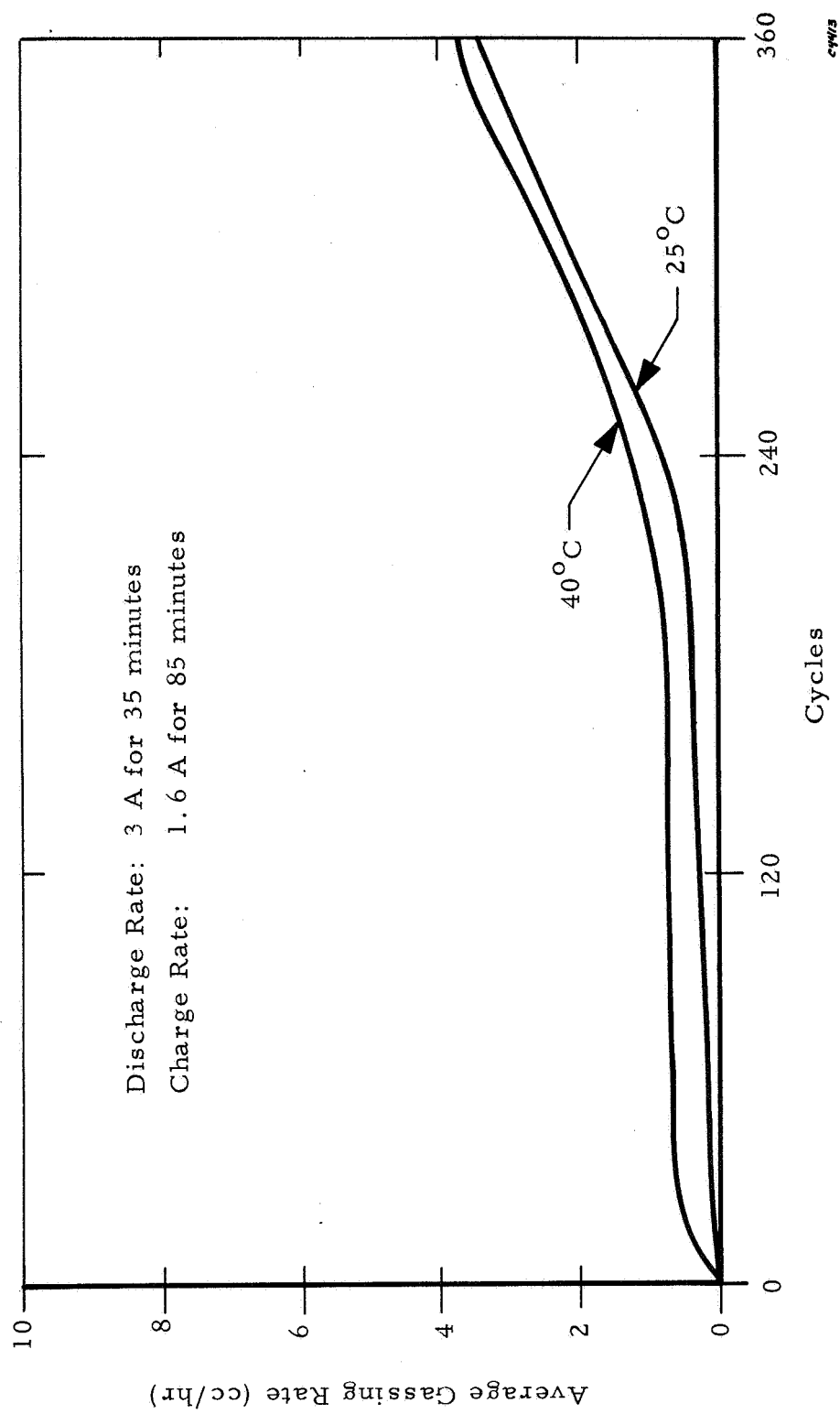


Figure 34. Gassing Rates at 25°C and 40°C on the 2 Hour-Period Regime

TABLE XXXVII

STATUS OF CELLS AFTER
GASSING TEST AT 40°C

(2-Hour Period Regime)
Group III

Set-Up	Cell No.	Output After End of Charge After 360 Cycles	Output After Recharge
Free Venting Cells	ZL-43-1	3.25 Ah	5.30 Ah
	-2	2.50	5.20
	-3	2.50	5.00
	-4	2.50	5.10
	-5	<u>2.65</u>	<u>4.90</u>
	Average	2.70 Ah	5.1 Ah
Pressurized Cells	ZL-43-6	4.0 Ah	4.9 Ah
	-7	2.7	4.6
	-8	3.0	4.9
	-9	4.6	5.0
	-10	<u>4.6</u>	<u>5.1</u>
	Average	3.8 Ah	4.9 Ah

If the OCV is reached before the requisite time, the cell is to be removed from stand and discharged to determine its capacity retention (or residual capacity). The cell is then given another charge and discharge to determine the actual capacity at the time of the test.

3.2.1.1 Wet Stand at 100°C

The results reported in Tables XXXVIII and XXXIX show that the capacity loss (about 23%) is contributed by the thermal decomposition of the argentic silver oxide, when comparing residual capacity with actual capacity at the time of the test.

Comparing this with the original capacity (formation), there is a greater loss, which is due partly to the argentic silver oxide thermal decomposition and partly to the zinc degradation resulting in hydrogen evolution (faster at high temperature). The relative loss percentages are respectively 23% caused by the silver and 21% caused by the zinc. Part of this zinc loss is recovered when the cell is overcharged beyond the normal cut-off voltage of 2.05 V. This is evidenced by the two cells (#9 and #10) which were purposely charged to 2.10 V and gave an output of 6.8 Ah instead of 6.0 Ah yielded by the other cells. This reduces the capacity loss due to zinc to only 13%.

The OCV decay at 100°C (given in graphical form for all cells in Figure 35) exhibits the same pattern as the voltage decline under electrochemical conversion at a light discharge rate.

3.2.1.2 Wet Stand at 25°C

The results are reported in Table XL. Figure 36 summarizes the capacity variation with time over the 3-month period.

3.2.2 Environmental Tests

A group of five cells was formed, charged and submitted to the environmental tests (shock, acceleration and vibration) as defined in Task II. (See Appendix A.) The cells maintained an OCV of 1.86 V throughout the tests. No physical damage was noticed. The test report submitted by the Ogden Technology Laboratories was sent to the NASA Project Manager.

TABLE XXXVIII
100°C WET STAND TEST DATA
(ZL-35 Series)

Cell Number →	9	10	11	12	13	14	15	16	
<u>1st Discharge</u> (Formation)(Ah)	7.85	7.95	8.00	7.80	8.00	8.00	7.85	7.85	Q ₁
First Run									
OCV at start (V)	1.86	1.86	1.86	1.86	1.86	1.86	1.86	1.86	
OCV after:									
21 hrs 100°C	1.58	1.56	1.59	1.59	1.59	1.56	1.58	1.58	
42 hrs 100°C	1.57	1.56	1.58	1.58	1.58	1.56	1.58	1.58	
<u>2nd Discharge (Ah)</u>	4.05	4.10	4.65	4.50	4.25	4.00	4.50	4.70	Q ₂
Recharge: Input to 2.05 V	5.5	5.5	6.1	5.5	5.5	6.3	6.3	6.3	
<u>3rd Discharge (Ah)</u>	5.1	5.0	6.0	5.25	5.30	6.25	6.25	6.25	Q ₃
Recharge	—	—	—	—	—	—	—	—	
Second Run									
OCV at start	1.86	1.86	1.86	1.86	1.86	1.86	1.86	1.86	
OCV after periods of:									
9 hrs 100°C	1.85	1.85	1.85	1.85	1.84	1.83	1.83	1.84	
9 hrs 100°C	1.85	1.84	1.81	1.81	1.70	1.64	1.69	1.73	
9 hrs 100°C	1.78	1.70	1.59	—	—	—	—	—	
9 hrs 100°C	1.60	1.58	—	—	—	—	—	—	
15 hrs 25°C	1.58	1.58	1.57	1.57	1.58	1.55	1.57	1.43	
16 hrs 25°C	1.56	1.56	—	—	—	—	—	—	
Hrs at 100°C above 1.58 V	36	36	27	27	18	18	18	18	
<u>4th Discharge (Ah)</u>	4.9	4.9	4.6	4.6	4.4	4.5	4.6	4.75	Q ₄
Recharge: Input (Ah) to 2.05 V	5.7	5.6	6.75	6.75	6.1	6.1	6.1	6.1	
to 2.10 V	6.9	6.9							
<u>5th Discharge (Ah)</u>	(6.8)*	(6.8)*	6.30	6.25	6.0	5.9	5.95	5.95	Q ₅

* discounted from average

TABLE XXXIX

100°C WET STAND TEST
AVERAGES OF 8 CELLS

(ZL-35 Series: Cells 9 through 16)

Tests	Consecutive actions as defined by Table II		Average Outputs (Ah)
	Formation	Q_1	7.75 Ah
First Run	Discharge after 42 hours at 100°C.	Q_2	4.35 Ah
	Normal recharge, then discharge.	Q_3	5.65 Ah
Second Run	Normal recharge, then submitted to average of 24 hours at 100°C.		
	Discharge.	Q_4	4.65 Ah
	Normal recharge, then discharge.	Q_5	6.05 Ah
Capacity retention with respect:			
First Run	To formation.	Q_2/Q_1	56%
	To actual capacity after test.	Q_2/Q_3	77%
Second Run	To actual capacity before test.	Q_4/Q_3	82%
	To actual capacity after test.	Q_4/Q_5	77%

Weight Loss (Electrolyte): 0.14 g/hr at 100°C for all cells over their entire exposure to 100°C.

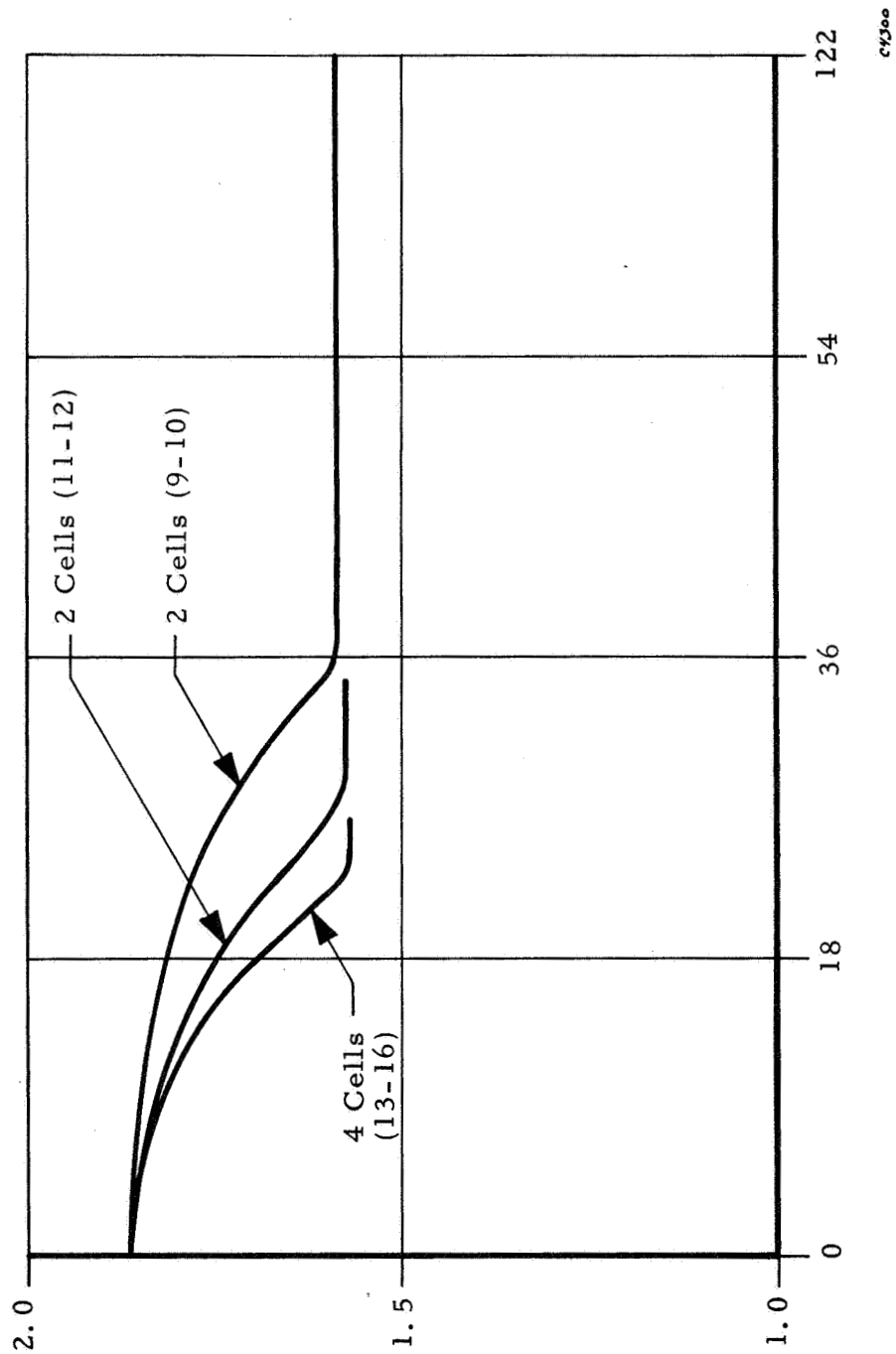


Figure 35. OCV Drop at 100°C of Charged 5 Ah-Cells
(Model DA-5-1-N) (2nd run)

TABLE XL
25°C WET STAND TEST
(ZL-35 Series)

Group	I		II		III				
Cell Number	1	2	3	4	5	6	7	8	
<u>1st Discharge (Ah)</u> (Formation)	7.90	7.80	7.95	7.80	7.95	7.50	7.95	7.95	Q ₁
OCV at Start (Volts)	1.86	1.86	1.86	1.86	1.86	1.86	1.86	1.86	
Recharge	—	—	—	—	—	—	—	—	
OCV After:									
1 month (Volts)	1.85	1.85	1.85	1.85	1.85	1.85	1.85	1.85	
2 months	—	—	1.85	1.85	1.85	1.85	1.85	1.85	
3 months	—	—	—	—	1.85	1.85	1.85	1.85	
<u>2nd Discharge (Ah)</u>									
1 month group	6.85	6.85	—	—	—	—	—	—	Q ₂₁
2 month group	—	—	6.6	6.5	—	—	—	—	Q ₂₂
3 month group	—	—	—	—	6.55	6.70	6.50	6.60	Q ₂₃
Recharge	—	—	—	—	—	—	—	—	
<u>3rd Discharge (Ah)</u>	8.0	7.60	7.60	7.40	7.45	7.45	7.45	7.55	Q ₃
<u>Average</u>	<u>1 Month</u>		<u>2 Months</u>		<u>3 Months</u>				
Capacity Retention with respect to:									
Original	88%		83%		84%				$\frac{Q_2}{Q_1}$
Actual After Test	88%		88%		88%				$\frac{Q_2}{Q_3}$

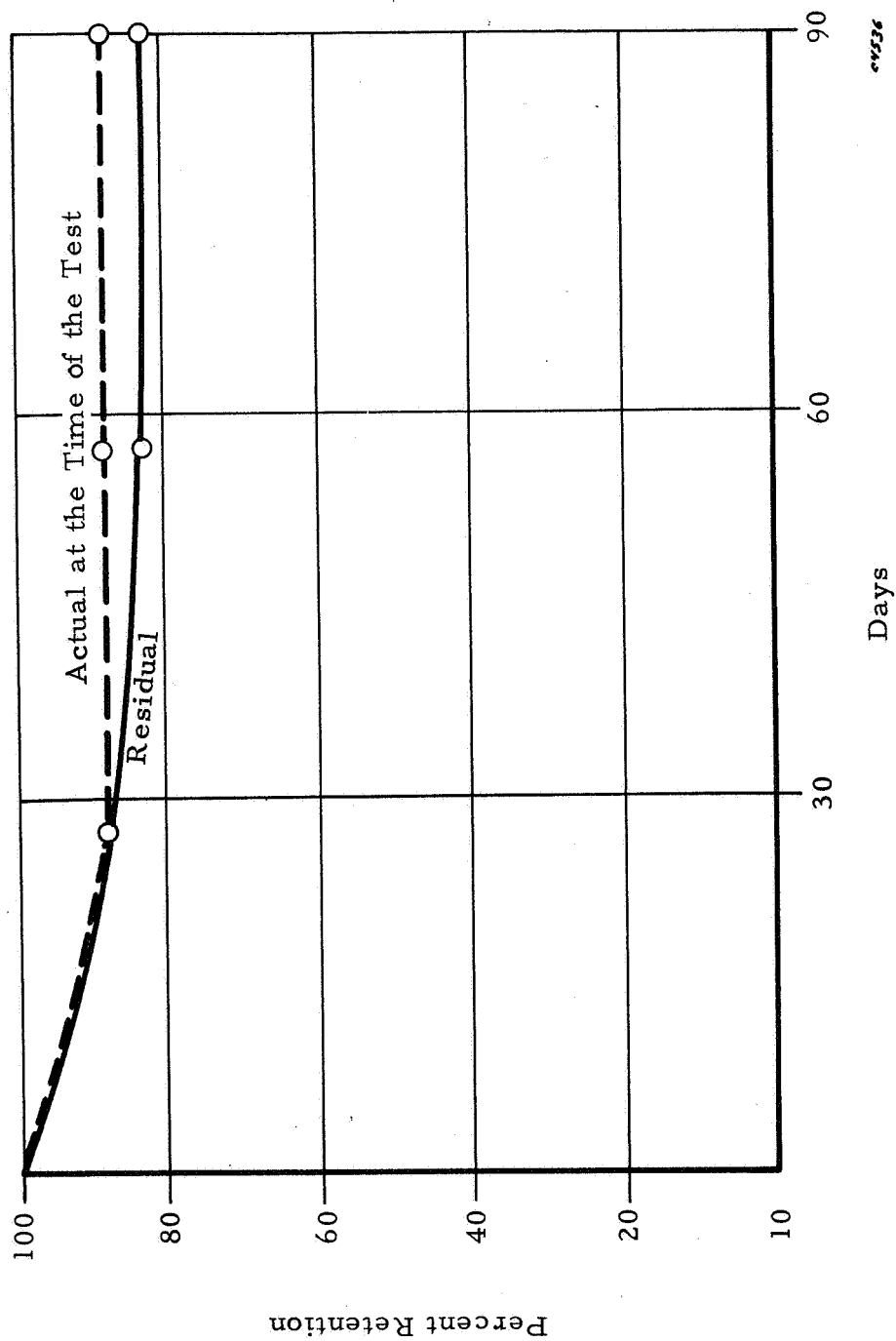


Figure 36. Capacity Retention on Charged Stand Over a 3-Month Period at 25°C

The cells were then submitted to electrical testing along with cells not environmentally tested, as described in the next paragraph.

3.2.3 Electrical Tests

Fifteen cells were scheduled for this test: five cells previously submitted to environmental testing; (as described in the previous paragraph, designated group A) and five cells used as controls (designated group B) and five cells provided with pressure gauges (designated group C).

The regime used on the cells of this group was intended to be severe in order to bring about any major deficiency on a fast preliminary evaluation in the range of 500 cycles.

The work statement calls for a regime of 1.5 hour-cycling period, 1/2-hour discharge, 1-hour charge, at 30% depth of discharge based on actual capacity. Taking 7.5 Ah as the average original actual capacity, the discharge and charge currents must therefore be 4.5 A and 2.5 A respectively.

This regime is extremely severe for this cell in three respects:

1. The depth of discharge of 30% of actual capacity is really 45% of rated capacity, since the cell is designed for a 5 Ah nominal capacity.
2. On the other hand, the cell is intended for a low rate operation and the 4.5 A discharge current is relatively too high for efficient performance since the plateau voltage will be low.
3. The cycling period imposes a recharge in one hour at a very high rate (20 mA/cm^2 instead of the normal 3 mA/cm^2) so that the coulombic efficiency is impaired and overcharges up to 25% may be needed. This has two side effects on the cell performance: heavy gassing which causes cutdown electrode surface area with subsequent higher current density and, more important, promotion of zinc penetration and zinc slumping.

The voltage limit set originally at 2.05 V/cell was found inadequate because of the high rate of charge after 170 cycles of this regime. A frequent verification of the output and input capacities show that the input was constantly lower than the output, because the high charging rate polarizes the cells very fast and raises their voltage prematurely to a point where the current tapers

off to a low value. A typical voltage-current cycling curve is shown in Figure 37. The standard 2.05 V limit is therefore insufficient to maintain a reasonable current over the 1-hour charge. At cycle 170, a few cells started showing signs of coming close to the 1.0 V limit before the end of the requisite discharge time. It was decided to raise the voltage to a point where the input was higher than the output. It is a fact that the voltage limit and the coulombic efficiency are a function of the charging rate and of the temperature. The limit was raised in small increments until the cells could cycle without frequent recharges.

An extra group of five cells (group D) was put on cycling with the high voltage limit (2.15 V/cell) set at the beginning.

Data up to 500 cycles were sent to the NASA Program Manager for review and approval to start Task III.

Cycling curves of groups A, B, and C show that the cells were at the beginning constantly undercharged.

All data are presented at periodic cycles in the tables entitled "Uniformity Study" giving for each cell of each group:

1. the charge characteristics:

OC = overcharge percentage

m% = monoxide plateau percentage of total charge period

V_f = final voltage at the end of the charge period.

2. the discharge characteristics:

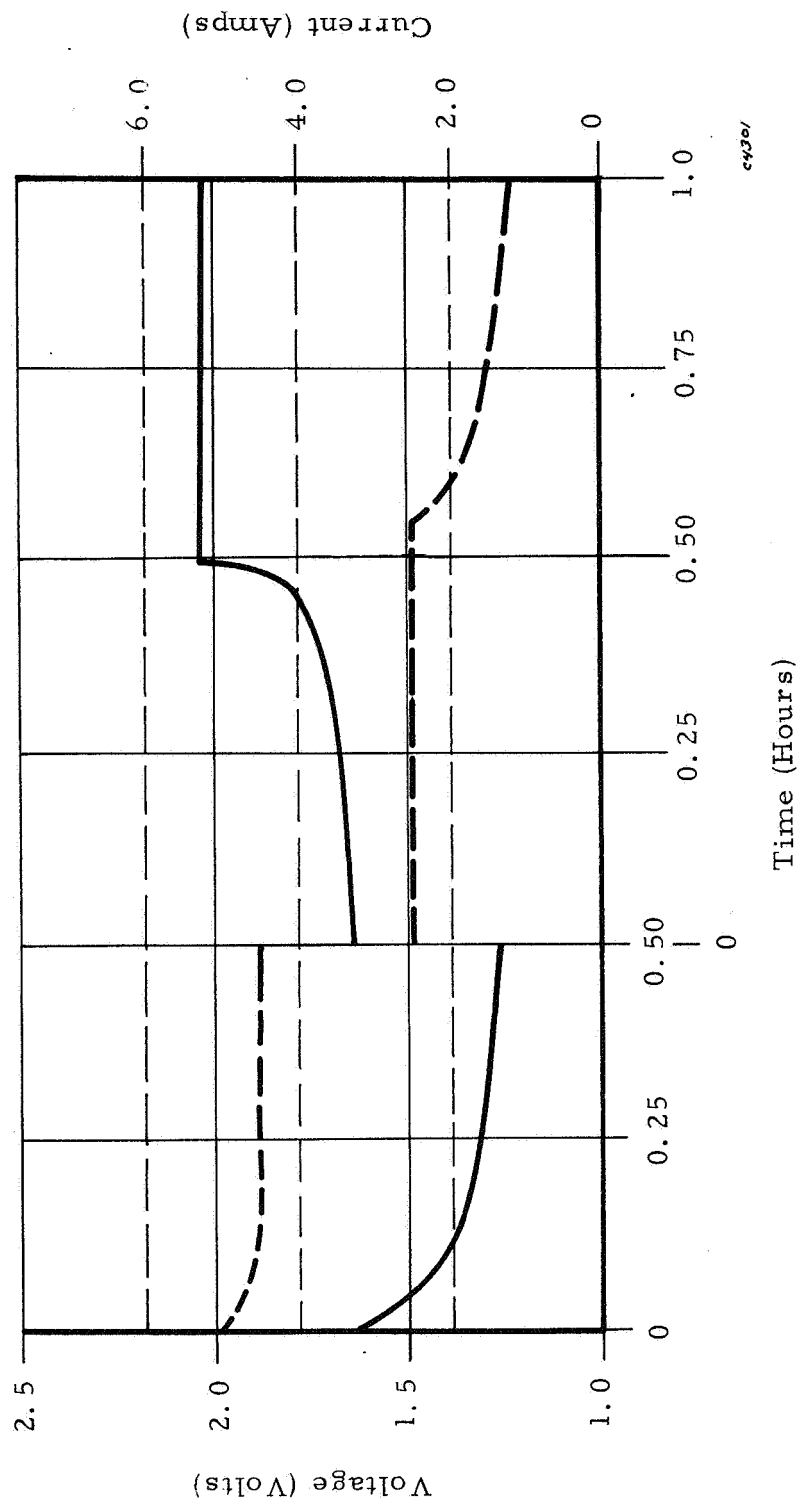
p% = peroxide plateau percentage of total discharge period

V_p = plateau voltage

V_e = end voltage at the end of the discharge period

3. the electrolyte addition in cumulative amounts from the beginning of the test.

The referenced tables and figures are:



Solid Line: Voltage
Dotted Line: Current

Figure 37. Typical Voltage-Current Relationship During Cycling

for Group A	Tables XLI, XLII, XLIII	Figures 38, 39
Group B	Tables XLIV, XLV, XLVI	Figures 40, 41
Group C	Tables XLVII, XLVIII, IL	Figures 42, 43
Group D	Tables L, LI, LII	Figures 44, 45

Table LIII is a compilation of the total cycles to failure on all cells of the four groups with their final capacity check.

The post-failure examination of the cell components showed common traits of failure for all cells of the four groups:

- A few cracked separators
- Evidence of zinc penetration
- Severe zinc electrode erosion and slumping (50 to 60%).

The wafer edge sealant was intact and the positive electrodes in good condition, although half-way discharged because of the missing zinc eroded area (see Figure 46).

3.3 TASK III: FABRICATION, TEST AND DELIVERY OF CELLS

The objective of Task III is the fabrication of 210, 5-Ah cells for testing. The cells will be fabricated in six lots of 35 cells each according to the finalized design, approved at the end of Task II.

Twenty-five cells from each lot will be delivered to the Naval Ammunition Depot, at Crane, Indiana, Battery Testing Laboratory, for tests as directed by NASA.

Ten cells will be retained in our laboratory for various tests as summarized in Table LIV.

For the sake of convenience and easy reference, each set of test conditions is coded A through F. Each lot is numbered 1 through 6. Tests A, B, and C will apply to odd-numbered lots (1, 3, 5) and tests D, E, and F will apply to even-numbered lots (2, 4, 6).

TABLE XLI

UNIFORMITY STUDY

Group: No. A (Environmentally Tested)

Regime: Discharge: 4.5 A for 0.5 hr

Charge: 2.5 A for 1.0 hr

Voltage Limit: 2.05 V/cell

Temperature: 25°C

Cycle 1-10

Cell Number		1	2	3	4	5	Avg.
Charge (OC = -8%)	m%	38	38	38	38	38	38
	V _f	2.06	2.05	2.07	2.07	2.06	2.06
Discharge	p%	19	19	19	19	19	19
	V _p	1.32	1.33	1.33	1.34	1.31	1.33
	V _e	1.28	1.28	1.29	1.29	1.28	1.28
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0

Cycle 100

Charge (OC = -5%)	m%	34	34	34	34	34	34
	V _f	2.08	2.05	2.07	2.06	2.09	2.07
Discharge	p%	19	19	19	19	19	19
	V _p	1.28	1.32	1.30	1.30	1.29	1.30
	V _e	1.25	1.29	1.28	1.27	1.25	1.27
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0

TABLE XLII
UNIFORMITY STUDY

Group: No. A (Environmentally Tested)

Regime: Discharge: 4.5 A for 0.5 hr

Charge: 2.5 A for 1.0 hr

Voltage Limit: 2.05 V/cell

Temperature: 25°C

Cycle 170

Cell Number		1	2	3	4	5	Avg.
Charge (OC = -2%)	m%	31	41	31	31	62	39
	V _f	2.03	2.02	2.10	2.05	1.98	2.04
Discharge	p%	25	25	25	25	25	25
	V _p	1.23	1.20	1.25	1.15	1.22	1.21
	V _e	1.20	1.15	1.22	1.10	1.18	1.17
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0

Cycle 310*

Charge (OC = +16%)	m%	26	26	26	26	26	26
	V _f	2.07	2.19	2.33	2.09	2.03	2.14
Discharge	p%	25	25	25	25	25	25
	V _p	1.24	1.24	1.19	1.26	1.26	1.24
	V _e	1.10	1.19	1.13	1.24	1.20	1.19
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0

* After Cycle 200, voltage limit raised to 2.15 V/cell, and current to 2.75 A.

TABLE XLIII

UNIFORMITY STUDY

Group: No. A (Environmentally Tested)

Regime: Discharge: 4.5 A for 0.5 hr

Charge: 2.75 A for 1.0 hr

Voltage Limit: 2.15 V/cell

Temperature: 25°C

Cycle 500

Cell Number		1	2*	3*	4	5	Avg.
Charge (OC = 18%)	m%	35	—	—	32	15	—
	V _f	2.12	—	—	2.12	2.10	—
Discharge	p%	25	—	—	25	25	—
	V _p	1.14	—	—	1.24	1.24	—
	V _e	1.06	—	—	1.20	1.20	—
Electrolyte Addition	Cum. Amt (cc)	7.00	—	—	5.00	5.00	—

Note: #2 and #3 failed at cycles 477 and 462, respectively.

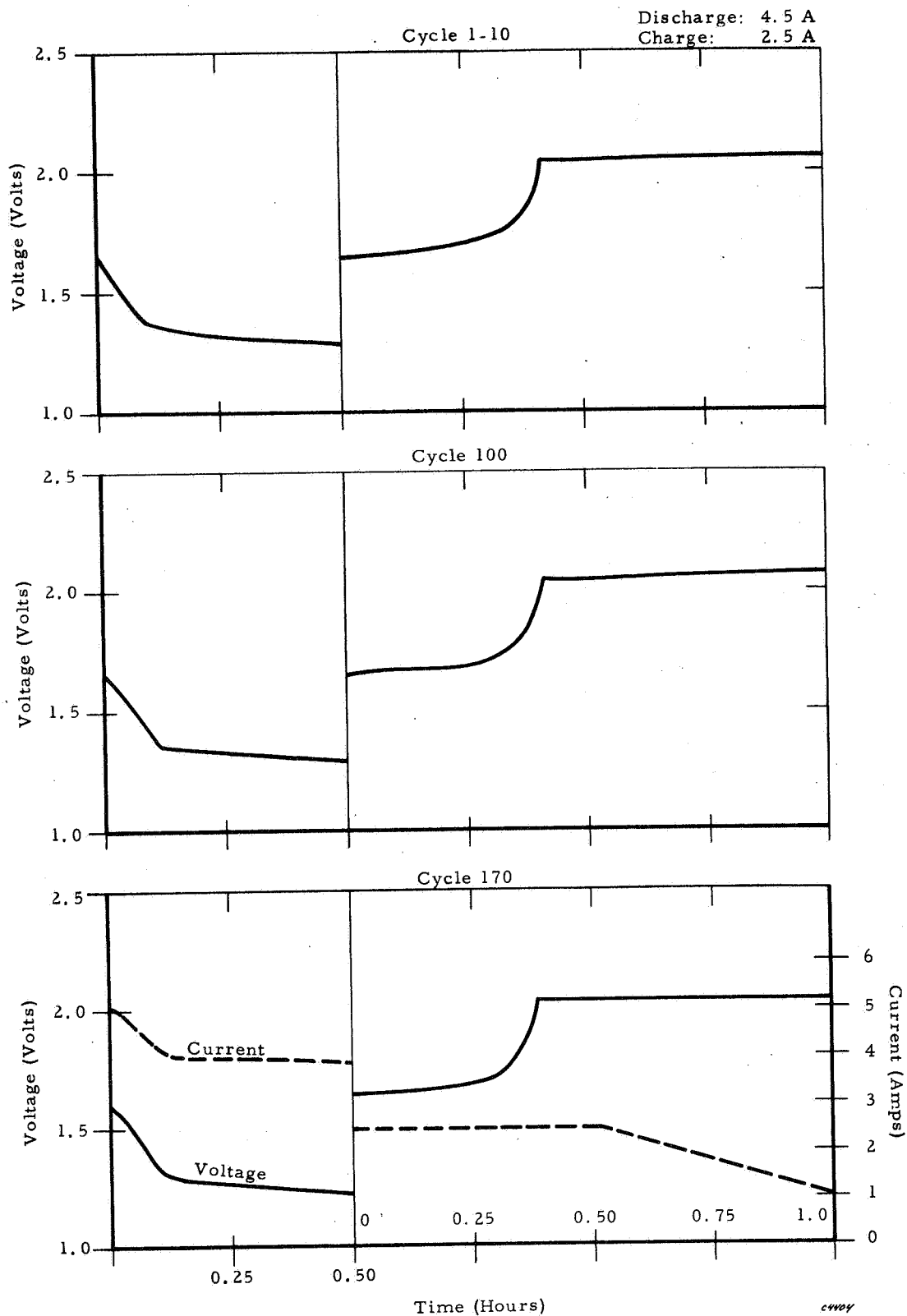


Figure 38. Group A (Environmental Test) Typical Cell

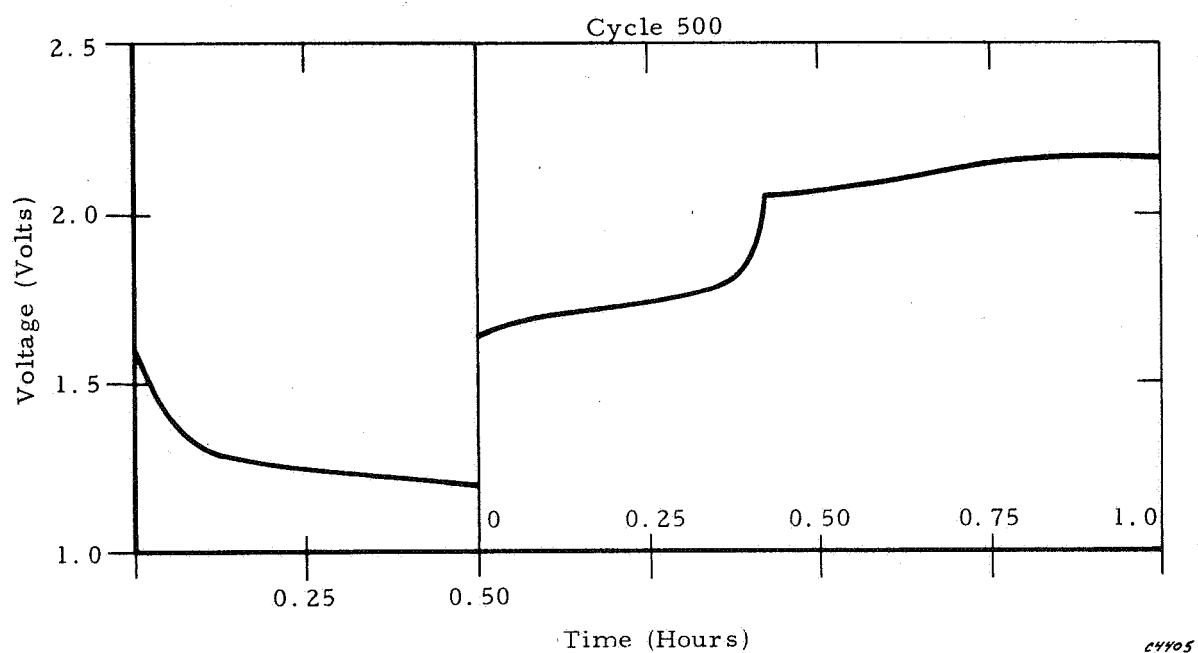
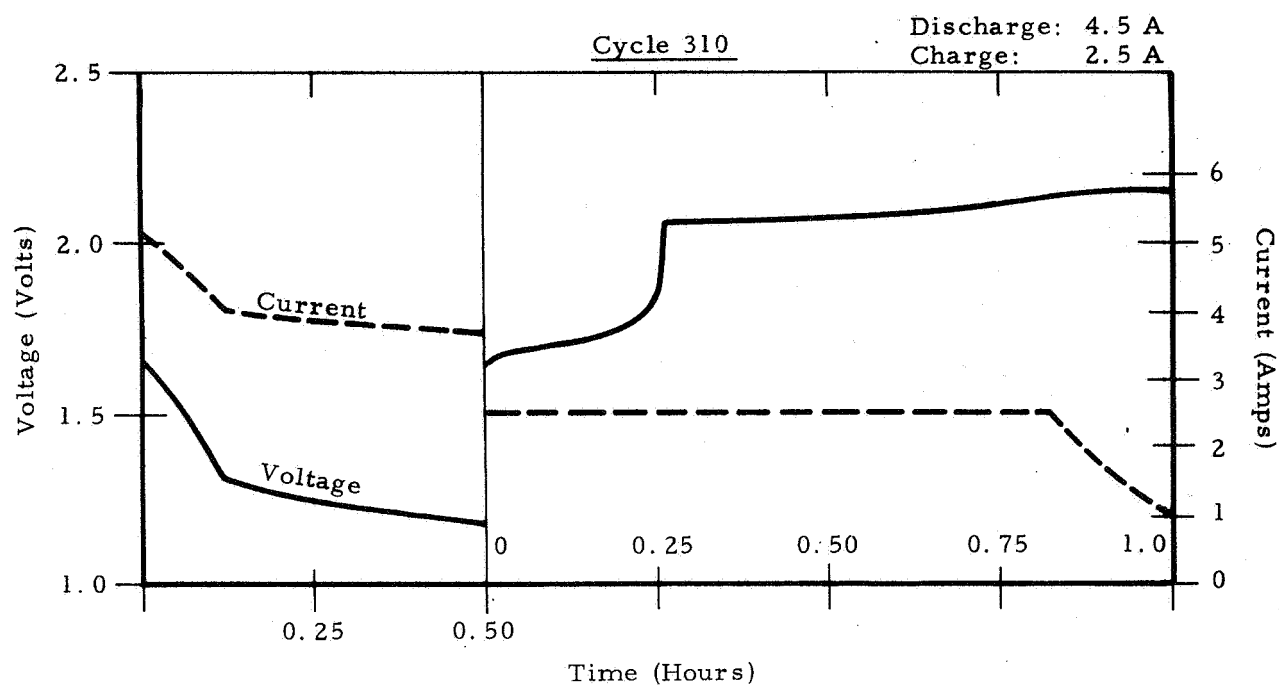


Figure 39. Group A (Environmental Test) Typical Cell

TABLE XLIV
UNIFORMITY STUDY

Group: No. B (Control)

Regime: Discharge: 4.5 A for 0.5 hr

Charge: 2.5 A for 1.0 hr

Voltage Limit: 2.05 V/cell

Temperature: 25°C

Cycle 1-10

Cell Number		6	7	8	9	10	Avg.
Charge (OC = -7%)	m%	44	44	44	44	44	44
	V _f	2.05	2.05	2.04	2.05	2.06	2.05
Discharge	p%	22	22	22	22	22	22
	V _p	1.31	1.33	1.32	1.32	1.31	1.32
	V _e	1.28	1.29	1.30	1.30	1.29	1.29
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0

Cycle 100

Charge (OC = -3%)	m%	38	38	38	38	38	38
	V _f	2.08	2.09	2.06	2.09	2.09	2.08
Discharge	p%	19	19	19	19	19	19
	V _p	1.29	1.32	1.31	1.33	1.29	1.31
	V _e	1.24	1.27	1.28	1.30	1.25	1.27
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0

TABLE XLV

UNIFORMITY STUDY

Group: No. B (Control)

Regime: Discharge: 4.5 A for 0.5 hr

Charge: 2.5 A for 1.0 hr

Voltage Limit: 2.05 V/cell

Temperature: 25°C

Cycle 170

Cell Number		6	7	8	9	10	Avg.
Charge (OC = -2%)	m%	31	62	31	38	31	39
	V _f	2.09	1.97	2.05	2.01	2.10	2.04
Discharge	p%	25	25	25	25	25	25
	V _p	1.29	1.29	1.29	1.30	1.27	1.29
	V _e	1.26	1.14	1.26	1.26	1.24	1.23
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0

Cycle 310*

Charge (OC = +25%)	m%	22	22	22	22	22	22
	V _f	2.14	2.12	2.15	2.17	2.13	2.14
Discharge	p%	31	31	31	31	31	31
	V _p	1.25	1.29	1.26	1.25	1.28	1.27
	V _e	1.21	1.26	1.23	1.21	1.25	1.23
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0

*After 200 cycles, voltage limit raised to 2.15 V/cell, and current to 2.75A.

TABLE XLVI

UNIFORMITY STUDY

Group: No. B (Control)

Regime: Discharge: 4.5 A for 0.5 hr

Charge: A for 1.0 hr

Voltage Limit: 2.15 V/cell

Temperature: 25°C

Cycle 500

Cell Number		6	7	8	9	10	Avg.
Charge (OC = 20%)	m%	20	20	20	20	20	20
	V _f	2.18	2.12	2.14	2.20	2.18	2.16
Discharge	p%	30	30	30	30	25	29
	V _p	1.32	1.32	1.32	1.15	1.34	1.29
	V _e	1.28	1.28	1.28	1.05	1.30	1.28
Electrolyte Addition	Cum. Amt (cc)	4.0	5.0	9.0	9.5	3.0	6.0

Cycle 700

Charge (OC = 15%)	m%	17	15	15	17	15	16
	V _f	2.20	2.09	2.19	2.10	2.18	2.15
Discharge	p%	30	30	30	30	30	30
	V _p	1.24	1.22	1.32	1.20	1.30	1.26
	V _e	1.16	1.16	1.26	1.04	1.28	1.18
Electrolyte Addition	Cum. Amt (cc)	11.5	12.0	16.0	16.5	13.0	13.8

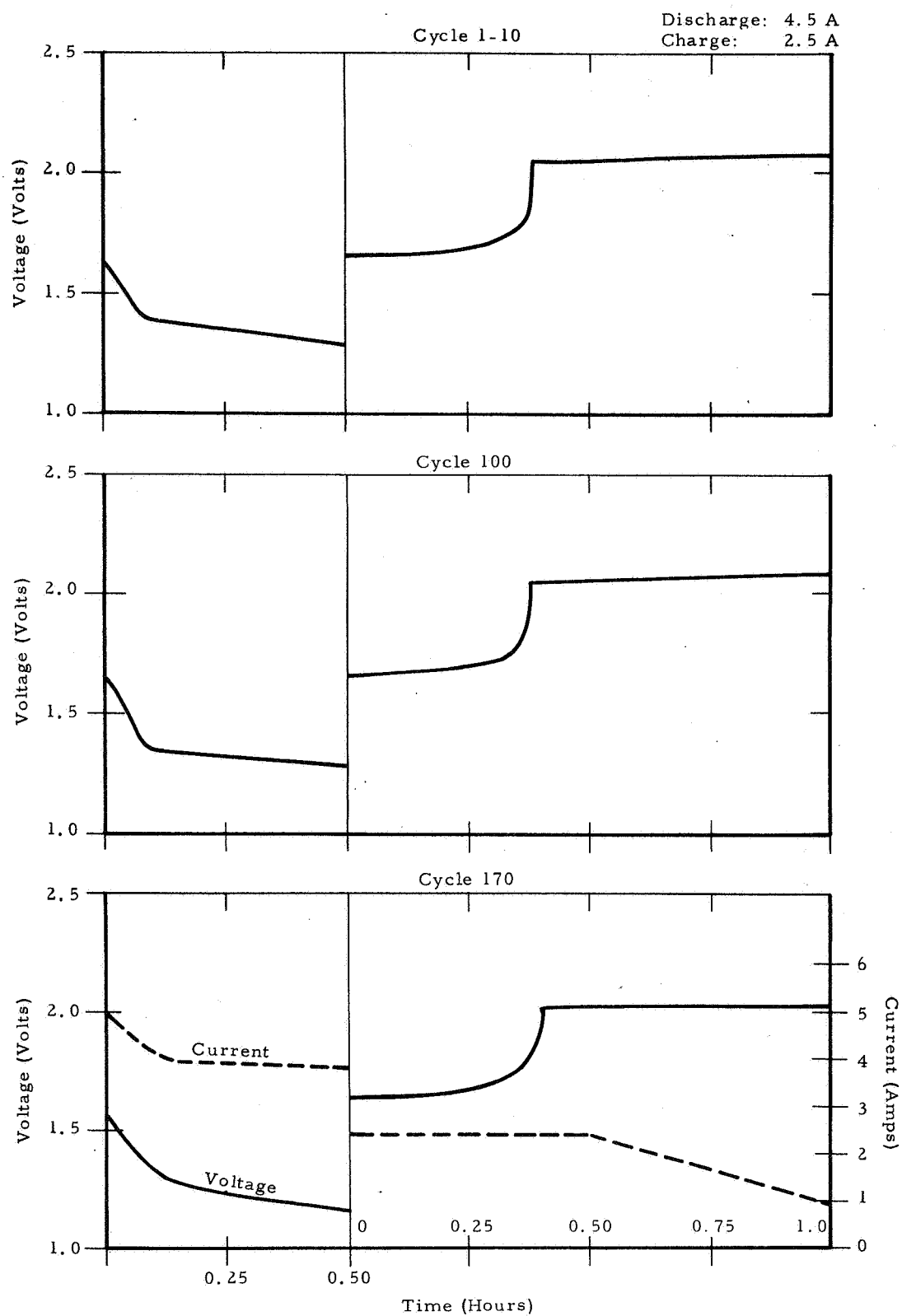
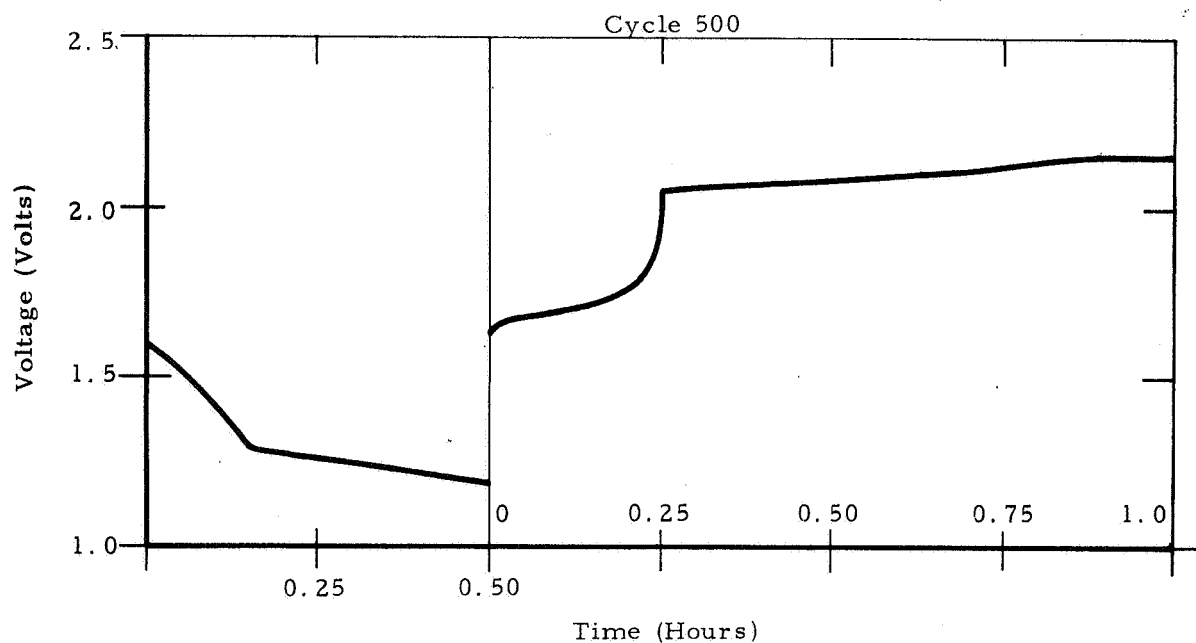
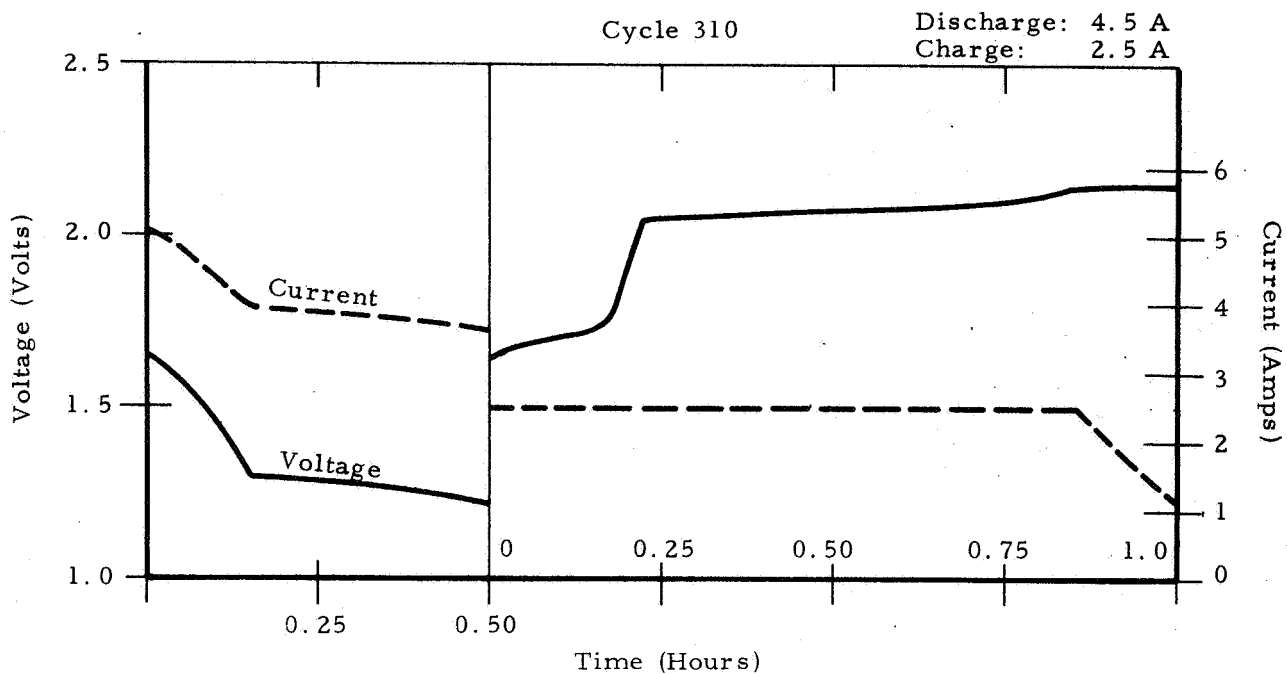


Figure 40. Group B (Control) Typical Cell



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Figure 41. Group B (Control) Typical Cell

TABLE XLVII

UNIFORMITY STUDY

Group: No. C (Pressure Gauge)

Regime: Discharge: 4.5 A for 0.5 hr

Charge: 2.5 A for 1.0 hr

Voltage Limit: 2.05 V/cell

Temperature: 25°C

Cycle 1-10

Cell Number		11	12	13	14	15	Avg.
Charge (OC = -4%)	m%	50	50	50	50	50	50
	V _f	2.06	2.06	2.06	2.06	2.06	2.06
Discharge	p%	16	16	16	16	16	16
	V _p	1.27	1.26	1.26	1.26	1.26	1.26
	V _e	1.24	1.23	1.23	1.23	1.23	1.23
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0
Pressure	psig	6.0	6.0	5.0	5.0	6.0	5.6

Cycle 100

Charge (OC = -1%)	m%	42	42	42	42	42	42
	V _f	2.09	2.08	2.08	2.08	2.07	2.08
Discharge	p%	19	19	19	19	19	19
	V _p	1.28	1.26	1.28	1.28	1.28	1.28
	V _e	1.23	1.21	1.23	1.23	1.23	1.23
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0
Pressure	psig	33	22	30	29	21	27

TABLE XLVIII
UNIFORMITY STUDY

Group: No. C (Pressure Gauge)

Regime: Discharge: 4.5 A for 0.5 hr

Charge: 2.5 A for 1.0 hr

Voltage Limit: 2.05 V/cell

Temperature: 25°C

Cycle 170

Cell Number		11	12	13	14	15	Avg.
Charge (OC = +1%)	m%	31	31	31	31	34	31
	V _f	2.04	2.05	2.08	2.02	2.03	2.04
Discharge	p%	25	25	25	25	25	25
	V _p	1.22	1.18	1.19	1.18	1.23	1.20
	V _e	1.20	1.13	1.15	1.14	1.19	1.16
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0
Pressure	psig	33	26	29	30	24	28

Cycle 310*

Charge (OC = +16%)	m%	26	26	26	26	26	26
	V _f	2.16	2.16	2.09	2.15	2.10	2.13
Discharge	p%	25	25	25	25	25	25
	V _p	1.24	1.19	1.23	1.22	1.24	1.22
	V _e	1.17	1.12	1.20	1.17	1.20	1.17
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0
Pressure	psig	30	28	30	31	25	29

*After 200 cycles, voltage limit raised to 2.13 V/cell, and current to 2.75 A.

TABLE 1L

UNIFORMITY STUDY

Group: No. C (Pressure Gauge)

Regime: Discharge: 4.5 A for 0.5 hr

Charge: 2.75 A for 1.0 hr

Voltage Limit: 2.15V/cell

Temperature: 25°C

Cycle 500

Cell Number		11	12	13	14	15	Avg.
Charge (OC = 17%)	m%	15	18	27	15	15	18
	V _f	2.12	2.20	2.12	2.16	2.16	2.15
Discharge	p%	30	30	30	30	30	30
	V _p	1.18	1.30	1.24	1.24	1.30	1.25
	V _e	1.12	1.20	1.16	1.16	1.26	1.18
Electrolyte Addition	Cum. Amt (cc)	4.0	6.0	4.0	5.0	5.0	5.0
Pressure	psig	29	28	30	28	26	28

Cycle 700

Charge (OC =	m%	17	20	20	24	20	20
	V _f	2.24	2.26	2.12	2.13	2.24	2.20
Discharge	p%	30	30	30	25	30	30
	V _p	1.20	1.20	1.18	1.20	1.22	1.20
	V _e	1.15	1.10	1.00	1.04	1.18	1.09
Electrolyte Addition	Cum. Amt (cc)	8.0	11.0	9.0	10.0	11.0	10.0
Pressure	psig	32	30	29	28	25	29

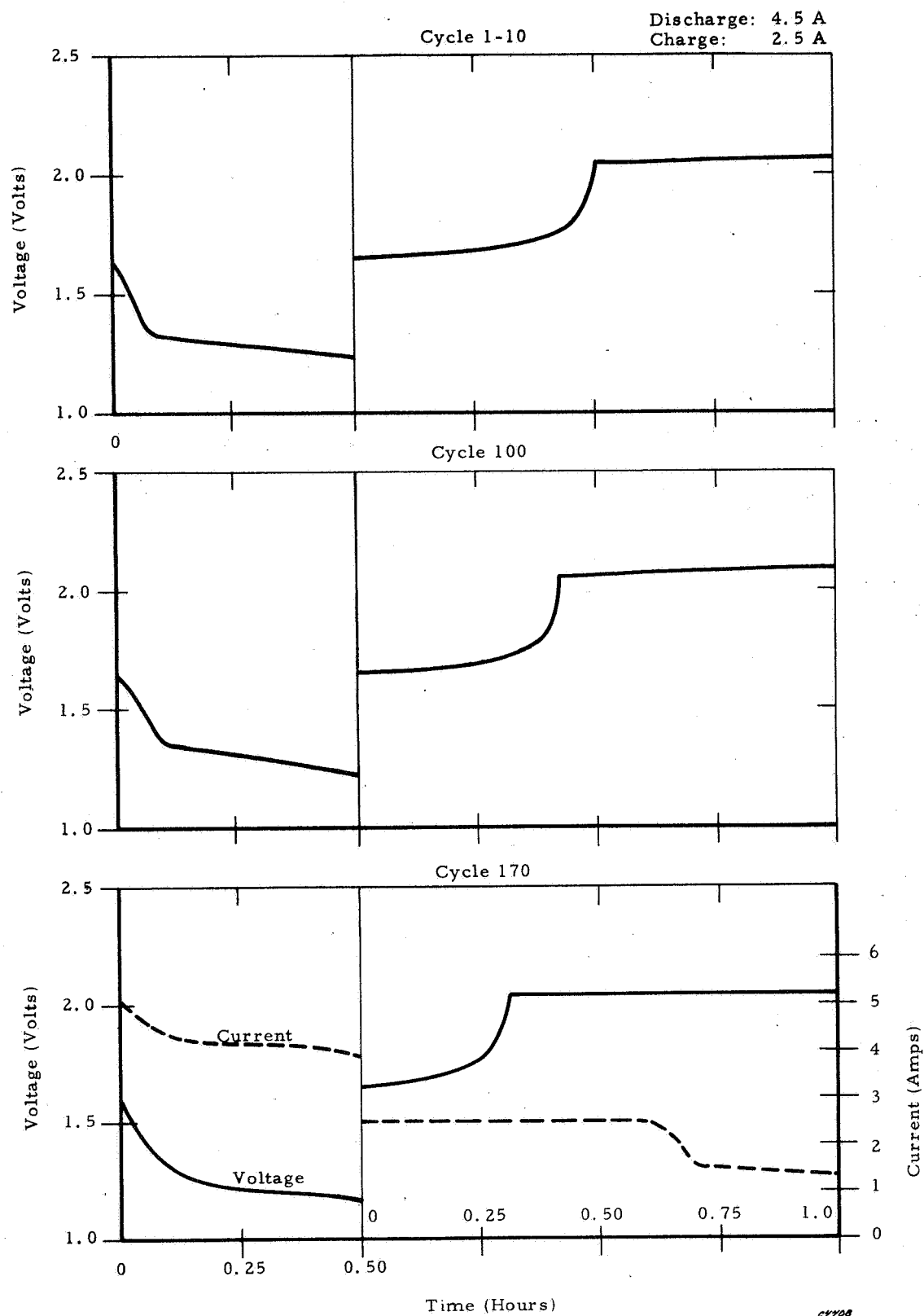


Figure 42. Group C (Pressure Gauge) Typical Cell

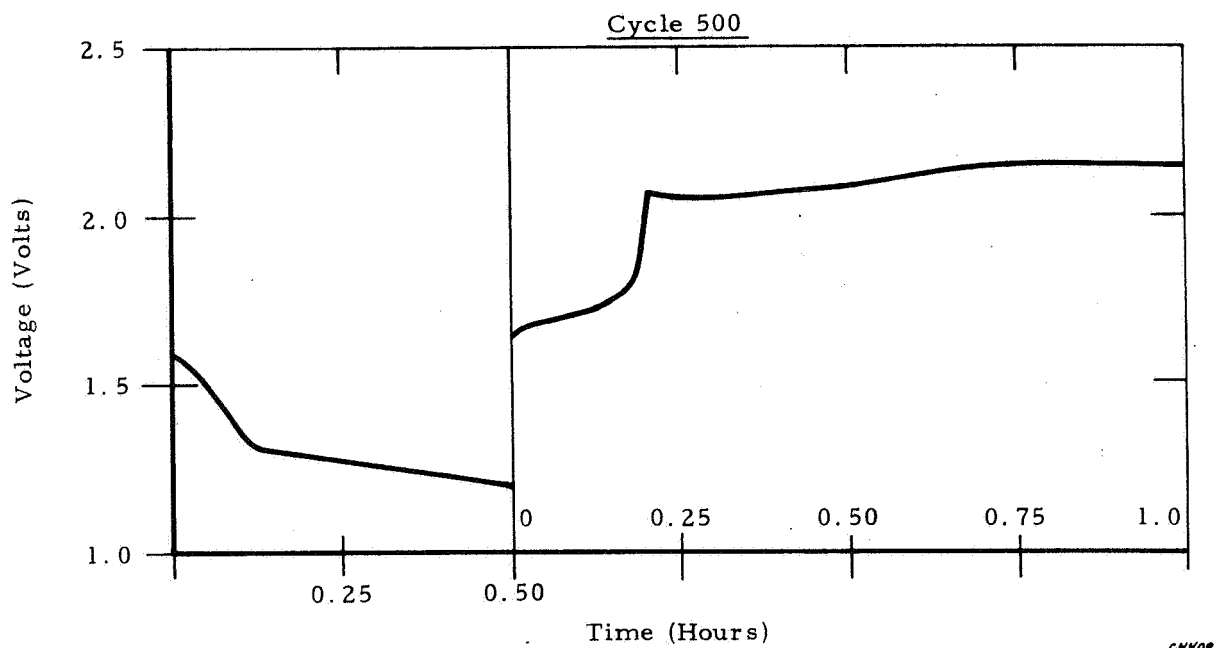
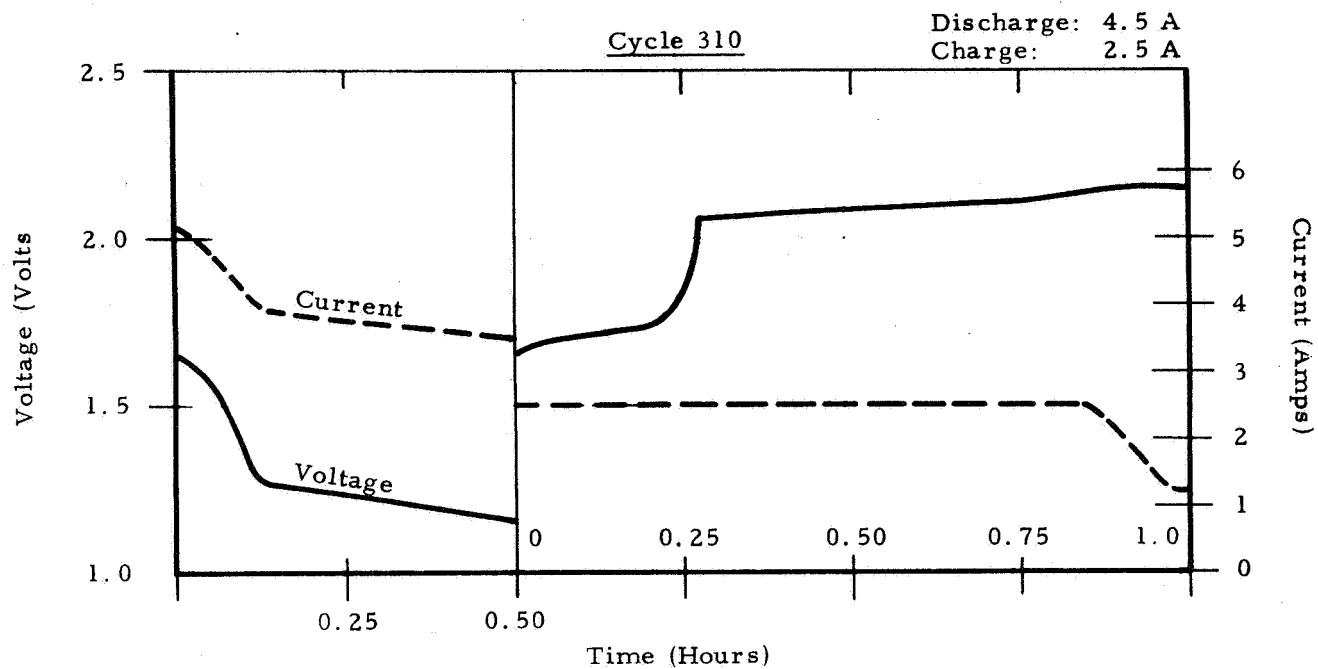


Figure 43. Group C (Pressure Gauge) Typical Cell

TABLE L

UNIFORMITY STUDY

Group: No. D (Repeat) (Cell 16 with pressure gauge)

Regime: Discharge: 4.5 A for 0.5 hr

Charge: 2.5 A for 1.0 hr

Voltage Limit: 2.15 V/cell

Temperature: 25°C

Cycle 1-10

Cell Number		16 *	22	23	24	25	Avg.
Charge (OC = 0%)	m%	43	43	43	43	43	43
	V _f	2.16	2.13	2.10	2.11	2.11	2.12
Discharge	p%	20	20	20	20	20	20
	V _p	1.23	1.26	1.29	1.28	1.27	1.27
	V _e	1.19	1.23	1.27	1.25	1.25	1.24
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0
Pressure	psig	18	—	—	—	—	—

Cycle 100

Charge (OC = 5%)	m%	33	33	33	33	33	33
	V _f	2.14	2.12	2.10	2.10	2.11	2.11
Discharge	p%	25	25	25	25	25	25
	V _p	1.18	1.27	1.32	1.30	1.30	1.27
	V _e	1.14	1.23	1.28	1.26	1.26	1.23
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0
Pressure	psig	29	—	—	—	—	—

*with pressure gauge.

TABLE LI
UNIFORMITY STUDY

Group: No. D (Repeat)

Regime: Discharge: 4.5 A for 0.5 hr

Charge: 2.5 A for 1.0 hr

Voltage Limit: 2.15 V/cell

Temperature: 25°C

Cycle 200

Cell Number		16 *	22	23	24	25	Avg.
Charge (OC = 8%)	m%	18	18	18	18	18	18
	V _f	2.20	2.15	2.16	2.06	2.21	2.16
Discharge	p%	33	33	33	33	33	33
	V _p	1.22	1.25	1.25	1.26	1.31	1.26
	V _e	1.18	1.22	1.21	1.22	1.27	1.22
Electrolyte Addition	Cum. Amt (cc)	0	0	0	0	0	0
Pressure	psig	34	—	—	—	—	—

Cycle 300

Charge (OC = 7%)	m%	25	25	25	25	25	25
	V _f	2.16	2.16	2.16	2.16	2.04	2.14
Discharge	p%	30	25	25	25	20	25
	V _p	1.20	1.20	1.28	1.32	1.24	1.25
	V _e	1.16	1.18	1.24	1.28	1.10	1.19
Electrolyte Addition	Cum. Amt (cc)	2	2	2	2	2	2
Pressure	psig	25	—	—	—	—	—

* with pressure gauge.

TABLE LII

UNIFORMITY STUDY

Group: D (Repeat)

Regime: Discharge: 4.5 A for 0.5 hr

Charge: 2.5 A for 1.0 hr

Voltage Limit: 2.15 V/cell

Temperature: 25°C

Cycle 450

Cell Number		16*	17	18	19	20	Avg.
Charge (OC =	m%	30	20	25	30	25	26
	V _f	2.10	2.16	2.15	2.12	2.12	2.18
Discharge	p%	20	30	25	25	25	25
	V _p	1.22	1.22	1.22	1.24	1.26	1.24
	V _e	1.17	1.19	1.19	1.16	1.20	1.18
Electrolyte Addition	Cum. Amt (cc)	6	8	8	9	8	8
Pressure	psig	27	--	--	--	--	--

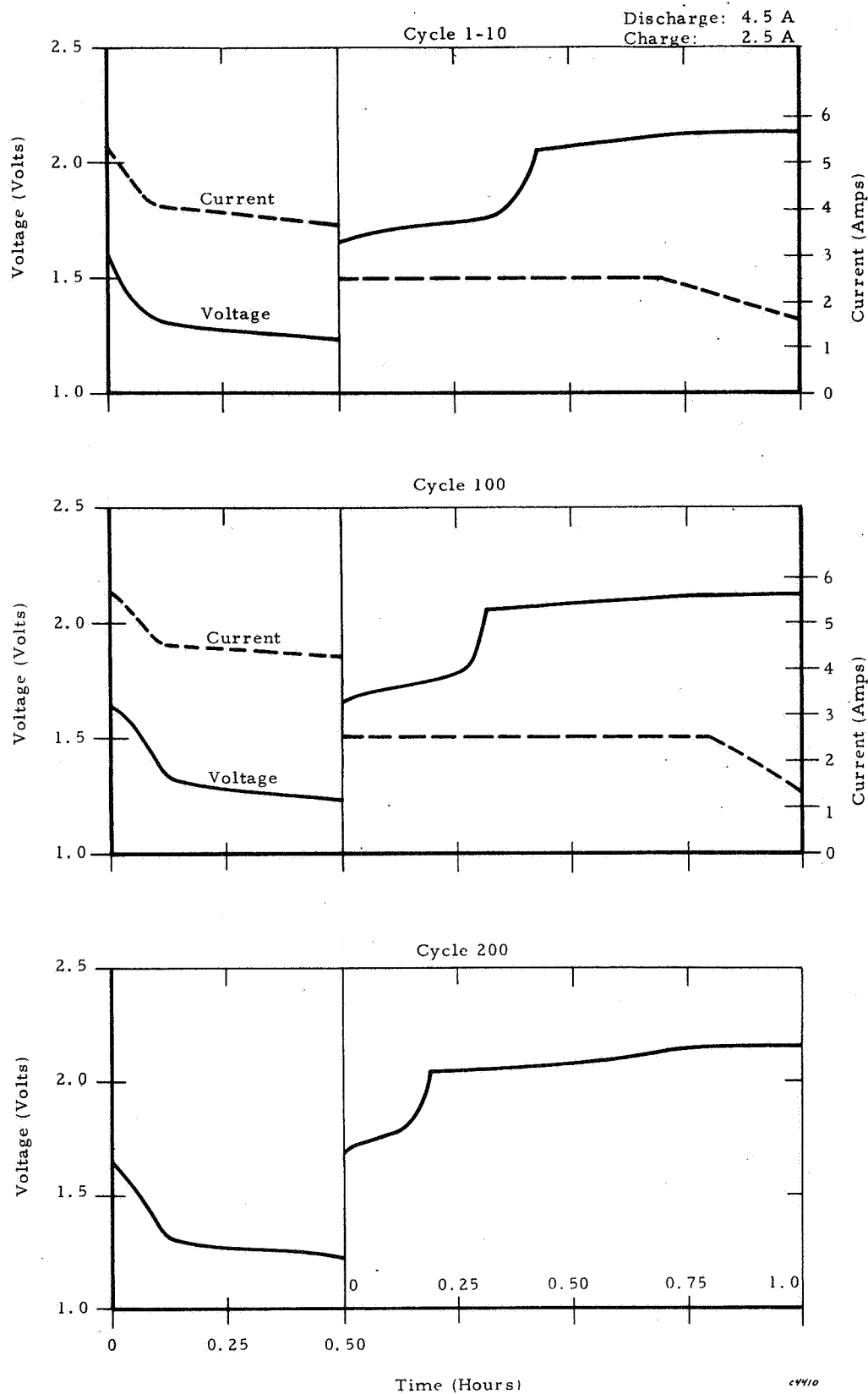


Figure 44. Group D: Repeat of Controls With Higher Voltage Limit

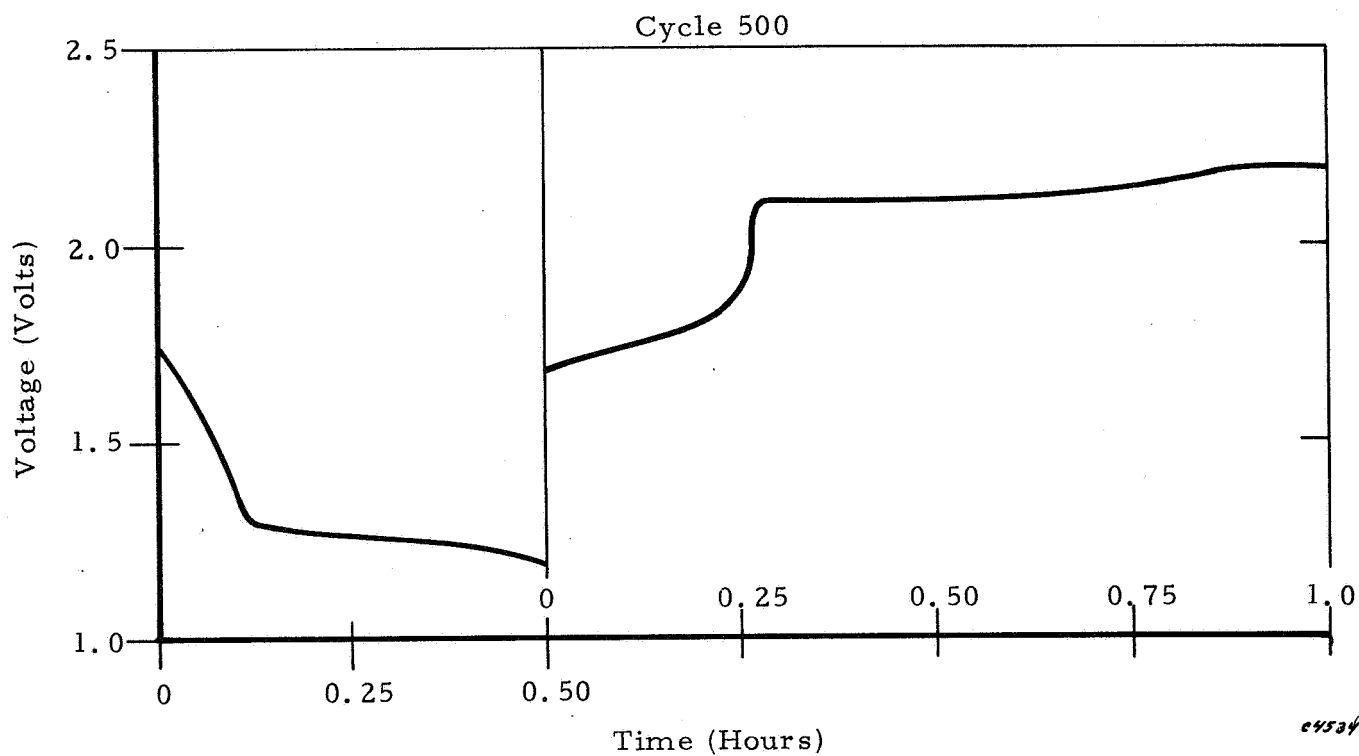
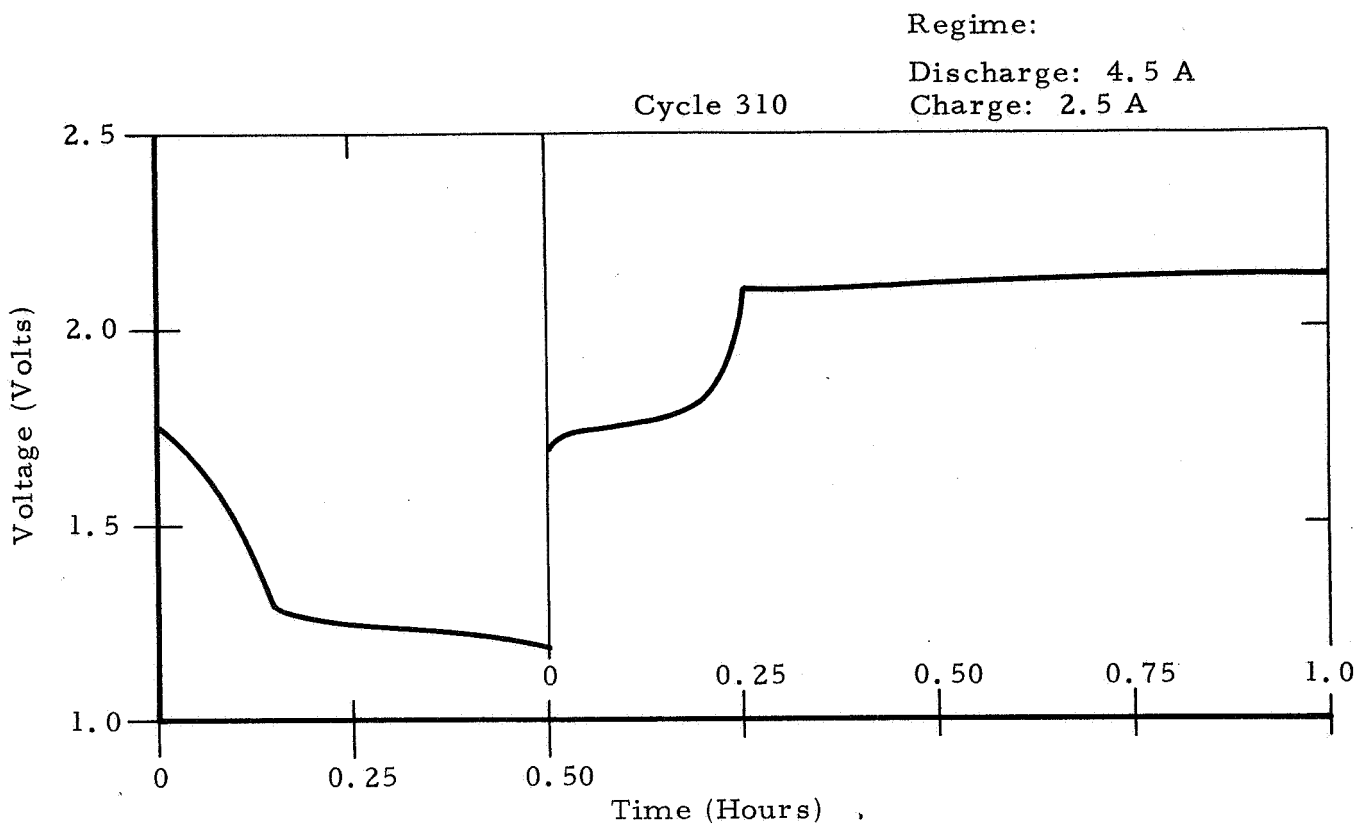
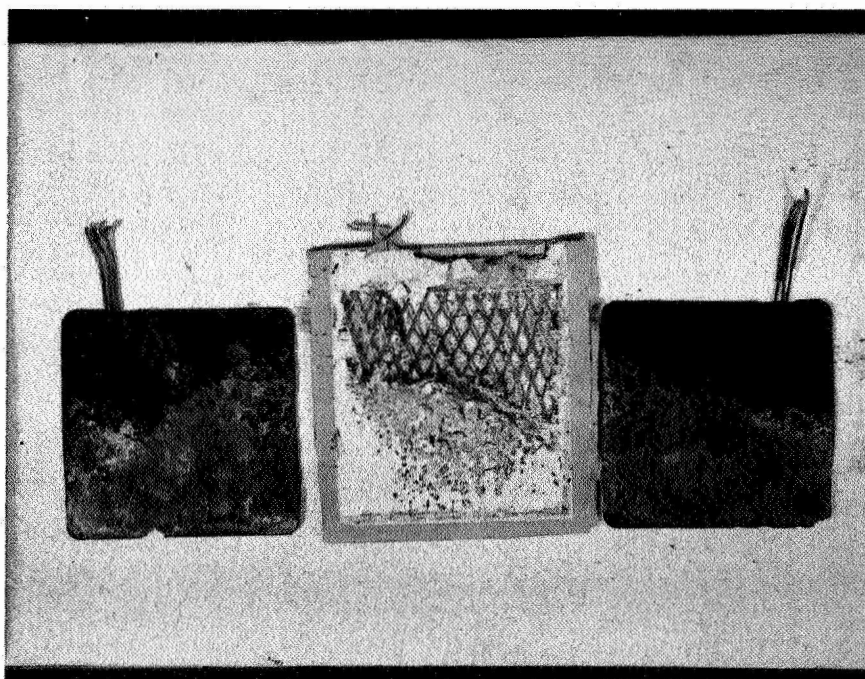


Figure 45. Group D: Repeat of Controls With Higher Voltage Limit

TABLE LIII
GROUP ZL-40 -- TEST SUMMARY

Group	Description	Cell No.	Total Cycles	Final Capacity (Ah)
A	Environmentally Tested	1	557	2.9 Ah
		2	477	2.4
		3	462	2.5
		4	590	3.2
		5	527	3.1
		Average	523	2.8 Ah
B	Controls	6	961	0.1 Ah
		7	960	2.6
		8	760	0.8
		9	730	2.0
		10	843	2.0
		Average	851	1.5 Ah
C	Pressure Gauges	11	789	2.7 Ah
		12	729	3.6
		13	880	2.6
		14	729	2.5
		15	866	2.6
		Average	787	2.8 Ah
D	Repeat of Controls	16*	531	1.6 Ah
		17	550	1.3
		18	464	1.2
		19	464	1.2
		20	457	2.4
		Average	487	1.5 Ah
Grand Average			662	

* with pressure gauge



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Figure 46. ZL-40-1 Cell: Condition of Electrodes After 557 Cycles at 45% Depth of Discharge of Rated Capacity

TABLE LIV
TASK III
CELL TEST DISTRIBUTION

Test Conditions	Test Groups					
	A	B	C	D	E	F
Orbit Period	1.5 hr	1.5 hr	24 hrs	2 hrs	2 hrs	Stand
Discharge/Charge	0.5/1 hr	0.5/1 hr	1.2/22.8 hr	0.58/1.42 hr	0.58/1.42 hr	
Current	3 A	3 A	3 A	3 A	5.4 A	
Temperature	25°C	100°C	25°C	25°C	25°C	25°C
Number of Cells per Lot	4	4	2	4	4	2
Lot Numbers	#1, #3, #5			#2, #4, #6		

The remainder of the program will cover specifically such tests and their correlation. Three independent variables are being considered:

- Current density or current, I
- Temperature, T
- Cycling period or depth of discharge, D

While two are maintained constants, the other variable is varied on 2 or 3 levels.

An overall view of the interrelationship of variables and test groups to be compared is given in Table LV. Each cell has a bi-numeral code: the first number refers to the lot (1 through 6) and the second number refers to the cell (1 through 25). For example, 1-24 means Cell #24 of Lot #1. Figure 47 is a photograph of completed cells built for this task.

TABLE LV

TASK III

CORRELATION OF VARIABLES

Independent Constants	Related Variables	Levels				Test Groups
		Period Time	Discharge Time	Depth (%) of actual (7.5 Ah)	Depth (%) of rated (5 Ah)	
Current: 3 A Temperature: 25°C	Period Depth	1.5 hr	0.5 hr	20%	30%	A
		2 hrs	0.582 hr	23%	35%	D
		24 hrs	1.2 hrs	48%	72%	C
Temperature: 25°C Period: 2 hrs	Current Density Current Depth	Current Density	Current	Depth (%) of actual (7.5 Ah)	Depth (%) of rated (5 Ah)	
		25 mA/cm ²	3 A	23%	35%	D
		45 mA/cm ²	5.4 A	42%	63%	E
Period and Depth (1.5 hr; 20%) Current: 3 A	Temperature			Temperature		
				25°C 100°C		A B



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Figure 47. Silver-Zinc Cells of Final Design for Task III

Section 4

COMMENTS AND CONCLUSIONS

The first year of this program was devoted to refining the cell design by investigation of the critical components of the 5-Ah cells. The silver electrode used a reinforced grid; the zinc electrode deemed acceptable was not modified, although a few tests showed the beneficial effect of PbO additive. The separator used was the same inorganic 3420-09, with stress on the quality control aspect. The case material selected was polysulfone over PPO, only on the basis of transparency. The cast-to-cover ultrasonic weld was successful for both materials. The terminal used remained unchanged.

The electrolyte concentration was changed to 40% on the basis of improved wet stand and lower gassing characteristics. However, the 30% should not be completely ruled out, since very good cycle life was consistently obtained with this concentration which minimizes zinc shape erosion.

The study on separator edge seals led to the conclusion of retaining the same material and method as previously developed.

A 40-psig valve was adapted to the cell cover to minimize electrolyte loss and promote gas recombination as shown in gassing studies conducted at three regimes and temperature combinations. Pressurized cells evolved less gas than free-venting cells.

All of these features were incorporated in the final cell design which was submitted to selected tests for final approval. Wet stand tests were satisfactory over three months. The environmental tests (shock, acceleration, vibration) showed no detrimental effect on the charged cells. The electrical tests run on a severe regime gave remarkably good results considering the

high rates imposed on charge and discharge on a cell intended for a low rate application.

Approval was granted by NASA for the fabrication of 210 cells in six lots to determine reproducibility of manufacture by repeated testing. Tests run on 60 cells in our laboratory and on 150 cells to be delivered to NASA will certainly make a good statistical survey of the performance capability of the 5-Ah cell.

REFERENCES

1. Arrance, F. C., "Program to Develop an Inorganic Separator for a High Temperature Silver-Zinc Battery, " NASA/Lewis Contract No. NAS 3-7639, Final Report No. SM-48461-F, dated June 1967.
2. Himy, A., "Improved Zinc Electrode, " NASA/Lewis Contract No. NAS 3-8513, Final Report No. SM-49142-F, dated May 1967.
3. Douglas Internal Program S.O. #81362-003, "Design Confirmation Program - Thermally Resistant Silver-Zinc Battery. "
4. NASA Technical Directive No. 1, by Mr. D. G. Soltis, dated January 12, 1968, Reference 9270.

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APPENDIX A
ENVIRONMENTAL TESTS

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Appendix A

ENVIRONMENTAL TESTS

Each of ten multiple-plate cells shall be subjected to shock, vibration, and acceleration tests as defined below.

At the conclusion of the environmental tests, the cells shall be examined for defects.

The environmental tests shall be performed in accordance with the following specifications:

SHOCK

The fully charged test cell shall be securely mounted in a test fixture specifically designed to support the cell in each of three perpendicular axes for shock testing. A Hyge 3001 hydraulic impulse shock stand shall be used to perform these tests.

Three shock impulses of 18G's shall be applied to the test cell along each of the three perpendicular axes making a total of 18 shock impulses per cell. Each input pulse waveshape shall be a half-size pulse for a time duration of eight milliseconds. The accelerometer pickups shall be placed directly on the cell case and on the test fixture at the cell mounting interface.

At the conclusion of each shock impulse, the cell shall be examined for cracks, dents or other damage. If there are no evidences of mechanical damage, the cell is acceptable for performing the next shock impulse. If there is evidence of damage, the test shall be terminated and an analysis shall be made to determine the reason for failure. If necessary, design corrections shall be made and additional multiple-plate cells shall be fabricated and tested as specified.

VIBRATION

The test cell shall be securely mounted in a test fixture specifically designed to support the cell in any of the three mutually perpendicular axes for vibration tests. A 6-100 shaker system shall be used to perform these tests. The test cell shall remain electrically inoperative throughout the vibration tests.

A resonant survey test shall be performed to determine the resonant modes of the test fixture and cell. A frequency sweep shall be made from 5 to 16 cps with a displacement amplitude of 0.368 inch and from 16 to 2000 cps at 5 G peak. This frequency sweep shall be performed once along each of the three mutually perpendicular axes. The accelerometer pickup shall be placed at the mounting interface between the vibration fixture and the test cell. During each frequency sweep in each direction, all resonant frequency points shall be recorded. The duration of each frequency sweep in each axis shall be one minute from 5 to 16 cps and ten minutes from 16 to 2000 cps. A resonant frequency test at one-half of each resonant frequency resulting from the resonant frequency sweep noted above, shall be performed for a period of 30 minutes for each resonant frequency.

At the conclusion of each vibration test in each of the three mutually perpendicular axes, the cell shall be examined for cracks, dents or other damage. If there are no evidences of damage, the cell is acceptable for performing the next vibration test. If there is evidence of damage, the procedures as described under Shock tests shall then be followed.

ACCELERATION

The cell shall be securely mounted in a test fixture specifically designed to support the cell in any of the three mutually perpendicular axes for the acceleration tests. A relatively small accelerator shall be used for these tests. The test cell shall remain electrically inoperative throughout the acceleration tests.

Acceleration tests shall be performed in accordance with the following procedure:

1. A sustained acceleration force of 7 G's shall be applied for five minutes along the longitudinal axis chosen in a direction simulating the lift-off of the transporting space vehicle.
2. A sustained acceleration force of 3 g's shall be applied for five minutes along the longitudinal axis in the opposite direction to that in Item 1 above.
3. A sustained acceleration force of 4.5 G's shall be applied for five minutes in both directions along each of the remaining two mutually perpendicular axes to the longitudinal axis of Items 1 and 2 above.

At the conclusion of each acceleration test specified in Items 1 through 3 above, the cell shall be examined for cracks, dents, or other damage. If there are no evidences of damage, the cell is acceptable for performing the next acceleration test. If there is evidence of damage, the procedures as described for shock tests shall be followed.