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PROGRAM TO DEVELOP AN INORGANIC SEPARATOR FOR A HIGH TEMPERATURE SILVER-ZINC BATTERY

PERIOD ENDING 29 APRIL 1966

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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QUARTERLY PROGRESS REPORT

PROGRAM TO DEVELOP AN INORGANIC SEPARATOR FOR A HIGH TEMPERATURE SILVER-ZINC BATTERY

by

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prepared for

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FOREWORD

The research, development and testing activities discussed in this report were sponsored by Lewis Research Center, National Aeronautics and Space Administration, Cleveland, Ohio. This report covers the period January 29 through April 29, 1966 and was prepared under Project Work Order Number 177091-01.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

1.0 INTRODUCTION AND SUMMARY

This report provides a complete summary of the work completed during the quarter ending April 29, 1966. Essentially all of the work planned for Tasks I and II has now been completed except for the work on cell cases which was not scheduled for completion until September 1966 and certain multiplate cell tests which have been rescheduled by the NASA Project Officer in accordance with Technical Direction No. 1, dated April 19, 1966. Because nearly all of the component testing and evaluation work is complete, the balance of the program will be devoted to multiple cell efforts and no additional partial cell testing is anticipated. It is likely, however, that some redesign of multiple plate cell components and assembly will be necessary during the second half of this program as test results on multiple plate cells are obtained. This may require limited single cell testing of innovations prior to full scale evaluation in multiple plate cells, but the amount of this work is expected to be limited.

Successful test cell operation at 30 ma/cm^2 at both 25° and 100°C has been obtained. While the cells have demonstrated the capability for operation at current densities of 50 ma/cm^2 and higher, recharge rates are excessive due to the 1/2 hr-1 hr test regimens. Cell 139 has completed 2129 cycles at 25°C at 10 ma/cm^2 confirming the long-life characteristics of this system.

Polysulfone case and frame parts appear to be superior to PPO due to the difficulty in injection molding PPO and warpage and distortion of PPO frame parts in service.

The terminal design developed for use in the 5 Ah cell has been improved.

Gassing tests have been completed at 25° and 100°C. It was found that no significant gassing occurs at room temperature regardless of the state of charge of the cell. At 100°C no gassings occur when the cell is at the argenteous state of charge. On cycling at current densities up to 20 ma/cm^2 little gassing occurs at 25°C on a 1/2 hr-1 hr regime. At 100°C, less cell gassing was observed during cycling than on stand, because the average state of charge during cycling is below full charge.

Experimental results show that KOH concentrations ranging from 30% to 45% can be used satisfactorily with this system.

Preliminary 5 Ah models of several designs are being tested prior to building the required multiplate test cells for evaluation.

An outline of the work planned for the next quarter is included in this report. This work will emphasize multiplate cell fabrication and testing and particular emphasis will be placed on component assembly, sealing and structural considerations.

2.0 TECHNICAL DISCUSSION

2.1 TASK I — Design of a Multiplate 5 Ah Cell

The grooved frame multiplate cell design which is being investigated in this program is fully described in SM-48461-Q2[1] and detailed component and assembly drawings are also included in this report. Initially the cell cases used were fabricated by cementing together polyphenylene oxide parts machined from molded PPO plates. When tested for KOH and gas leakage, it was found that these cases tended to develop leaks in the cemented joints, especially at elevated temperatures and pressures. It was also determined that the machined plastic components tended to warp upon ageing and that the resulting distortion also caused leakage around the frame assemblies and might also cause fracture of the separators if a substantial amount of warpage of the plastic components takes place. This distortion was believed to be due to inherent stresses in the molded plastic sheets. This problem was discussed with the supplier who suggested that the plastic sheet be annealed before and/or after machining. This was done and appeared to be helpful although annealing does not completely resolve the problem.

2.1.1 Molded Cases

The problem of providing a dimensionally stable case was also approached by obtaining injection molded cases. These cases were approximately the same size as the cemented case assemblies except for their height which could be cut down to the desired size. The first molded cases obtained had a wall thickness of only 0.062 in. This was found to be too thin for application in the 5 Ah multiplate cell as the side walls bulged appreciably at 20 psi internal pressure. They are suitable, however, for use in developing assembly technology and for electrical testing of unsealed configurations. Based on our studies of gassing rates and other tests, the wall thickness required for application in these cells will be established and thicker walled cell cases will be obtained for mechanical testing. This work is now in progress and is discussed in detail in Section 2.2.3 of this report.

2.1.2 Plastic Frames

Two types of separator holding frames have been investigated. These are identified as Type E and Type E'.

Type E frames have been grooved to provide for four positive and five negative electrodes. Type E' frames are grooved for five positive and four negative electrode plates.

Because the molded cases were slightly larger than those assembled by gluing together machined parts, the groove depth and frame thickness both could be increased slightly to increase the mechanical stability of the separator-frame assembly. Deepening the frame grooves allows the inorganic separator to be inserted more deeply into the frames which is also an advantage. This should improve the sealing of the separators to the frames and prevent leakage around the separator through the glued joints which can cause shorting with resulting depression of the OCV.

2.1.3 Terminals

The method of attaching the electrode connector tabs to the terminal bases has been modified to avoid the possibility of stressing the separators when the connectors are bent. The revised design allows the connectors to be brought straight up and connected to a long screw which passes through the holes in each of the tabs, spaces are provided, as shown in the drawings, in order to complete the assembly. Drawings and pictures of parts are shown in Figures 1 through 9.

2.2 TASK II – Fabrication, Testing and Evaluation of Components

2.2.1 Electrodes

2.2.1.1 Configuration

The test cell consists of one positive electrode and two negative electrodes, inserted in a frame holding two separators cemented in the grooves.

The frame is made out of PPO or polysulfone in three parts (bottom and two sides) cemented together.

PPO frames have been found to be generally less satisfactory than polysulfone frames because of the tendency of PPO parts to warp and distort in service. Polysulfone only exhibits this problem to a slight degree and appears to be the preferred material for frames. Distortion

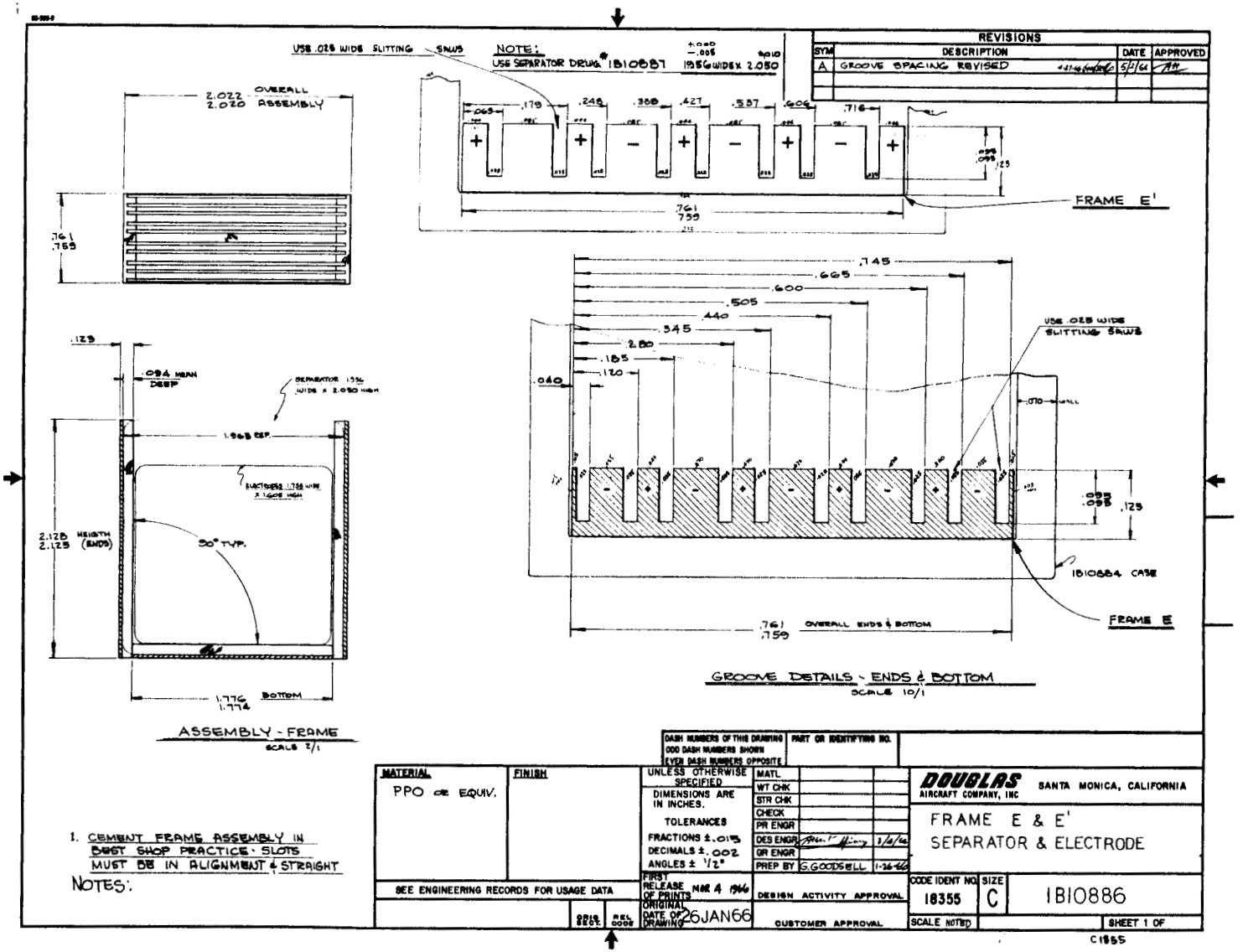

Figure 1. Frame E and E' Separator and Electrode

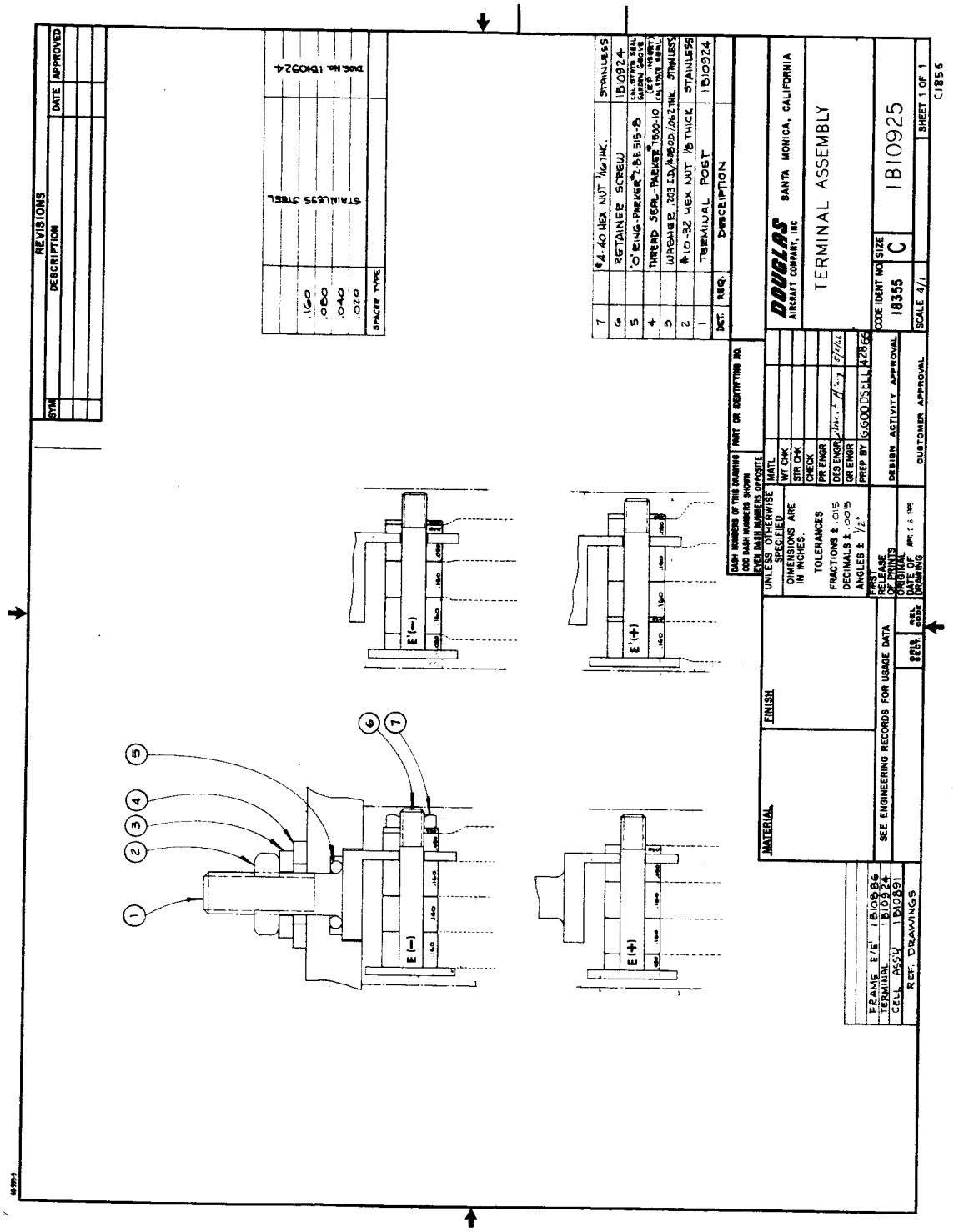

Figure 2. Terminal Assembly

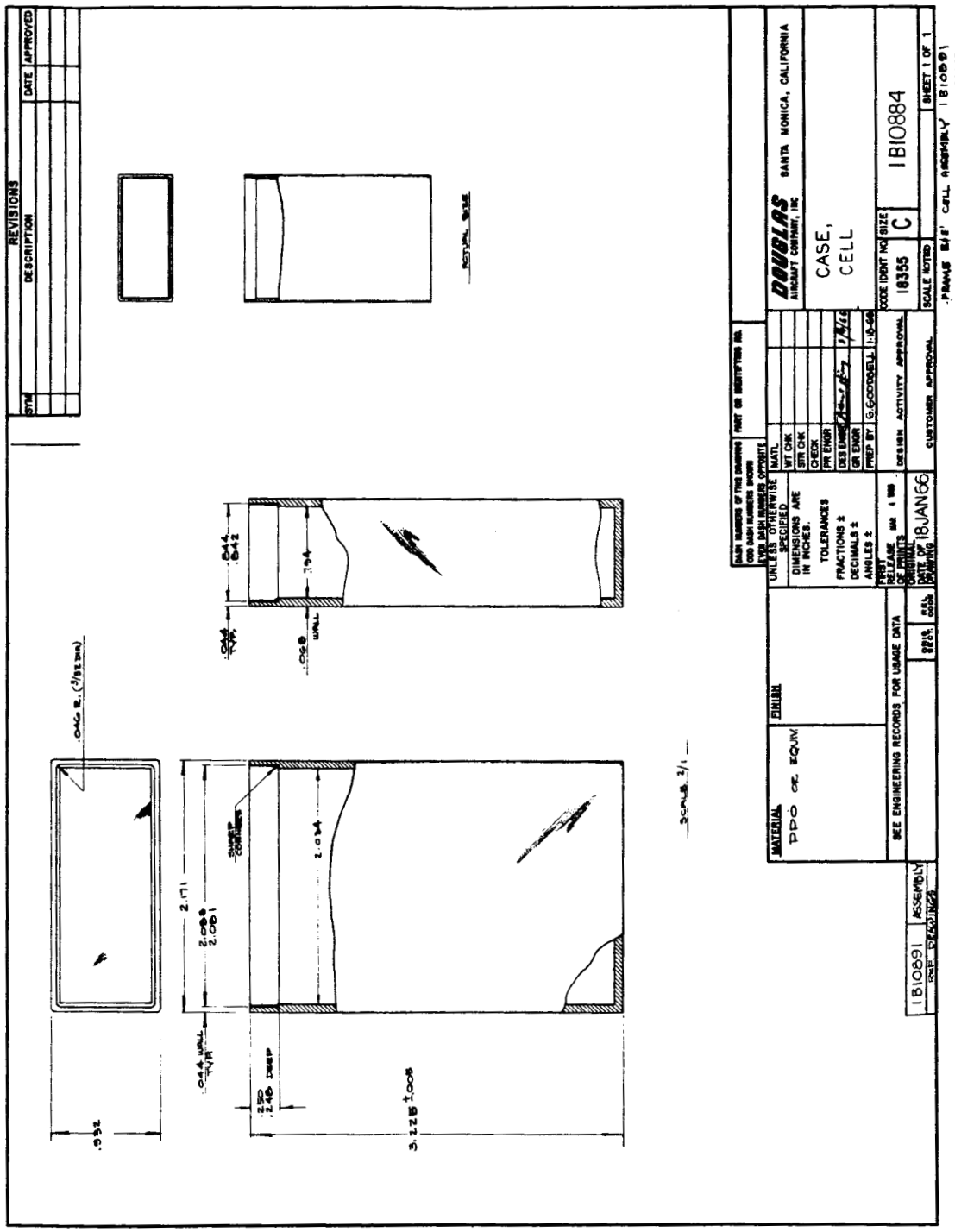

Figure 3. Case, Cell

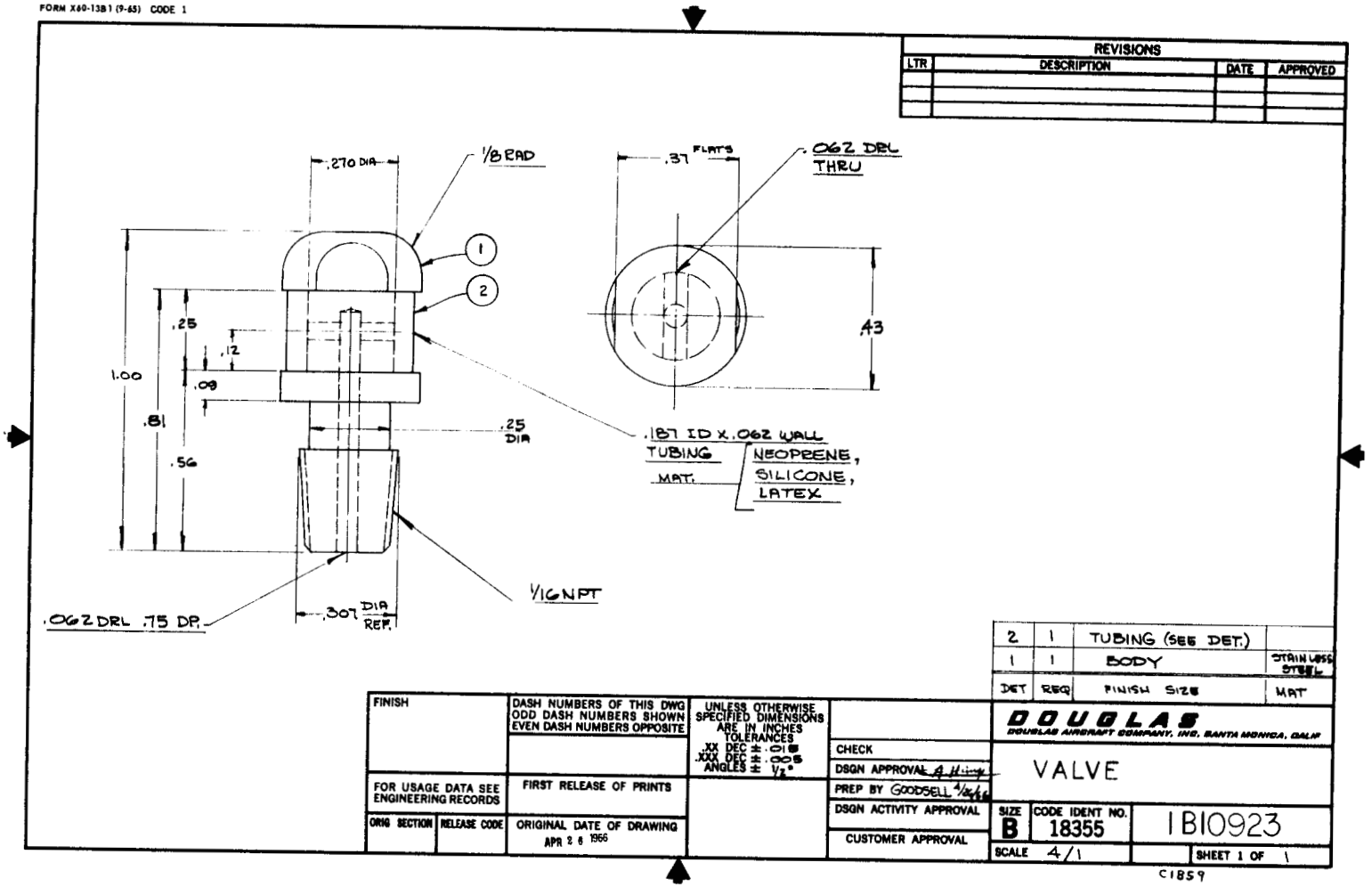

Figure 4. Valve

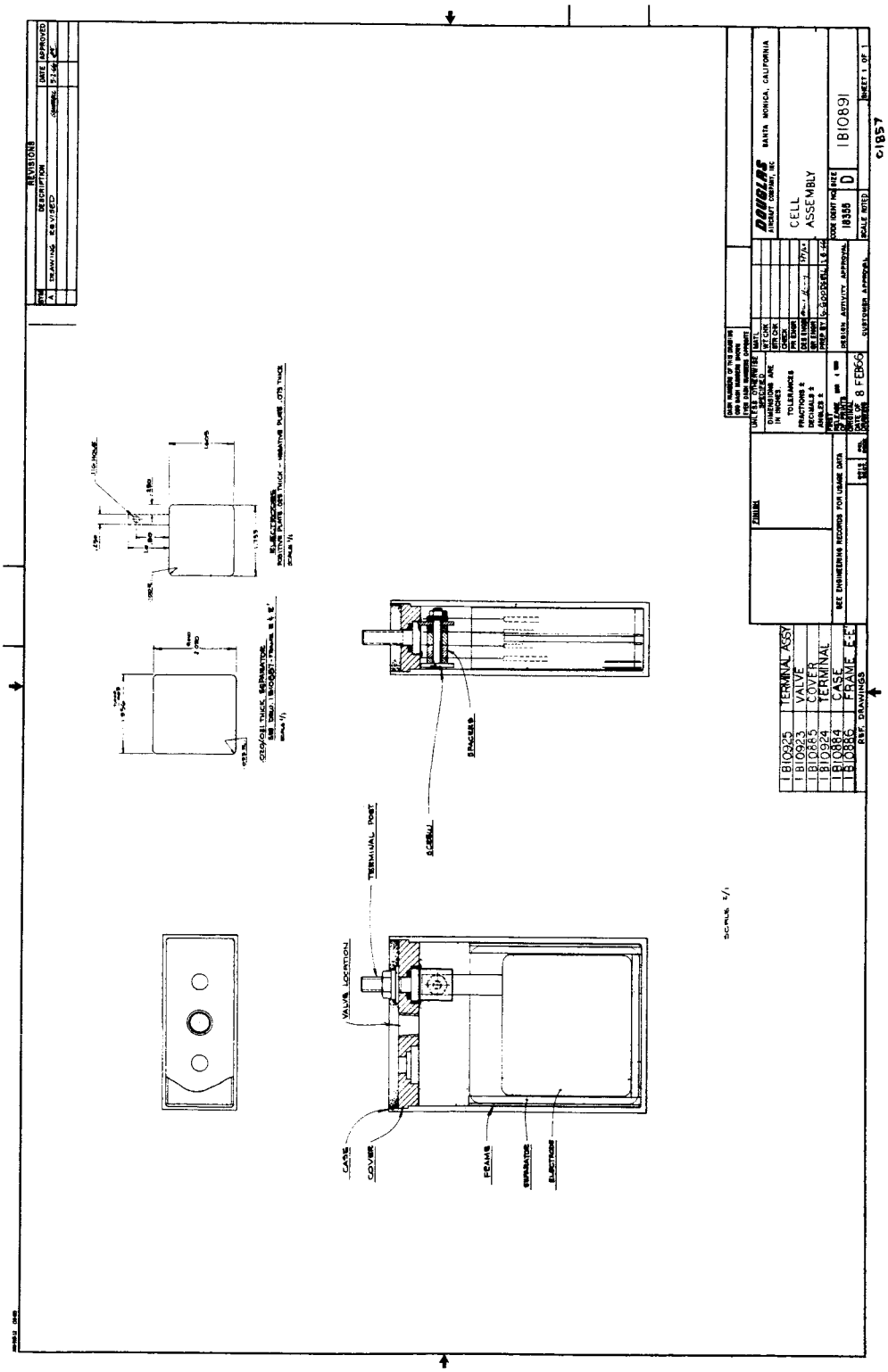

Figure 5. Cell Assembly

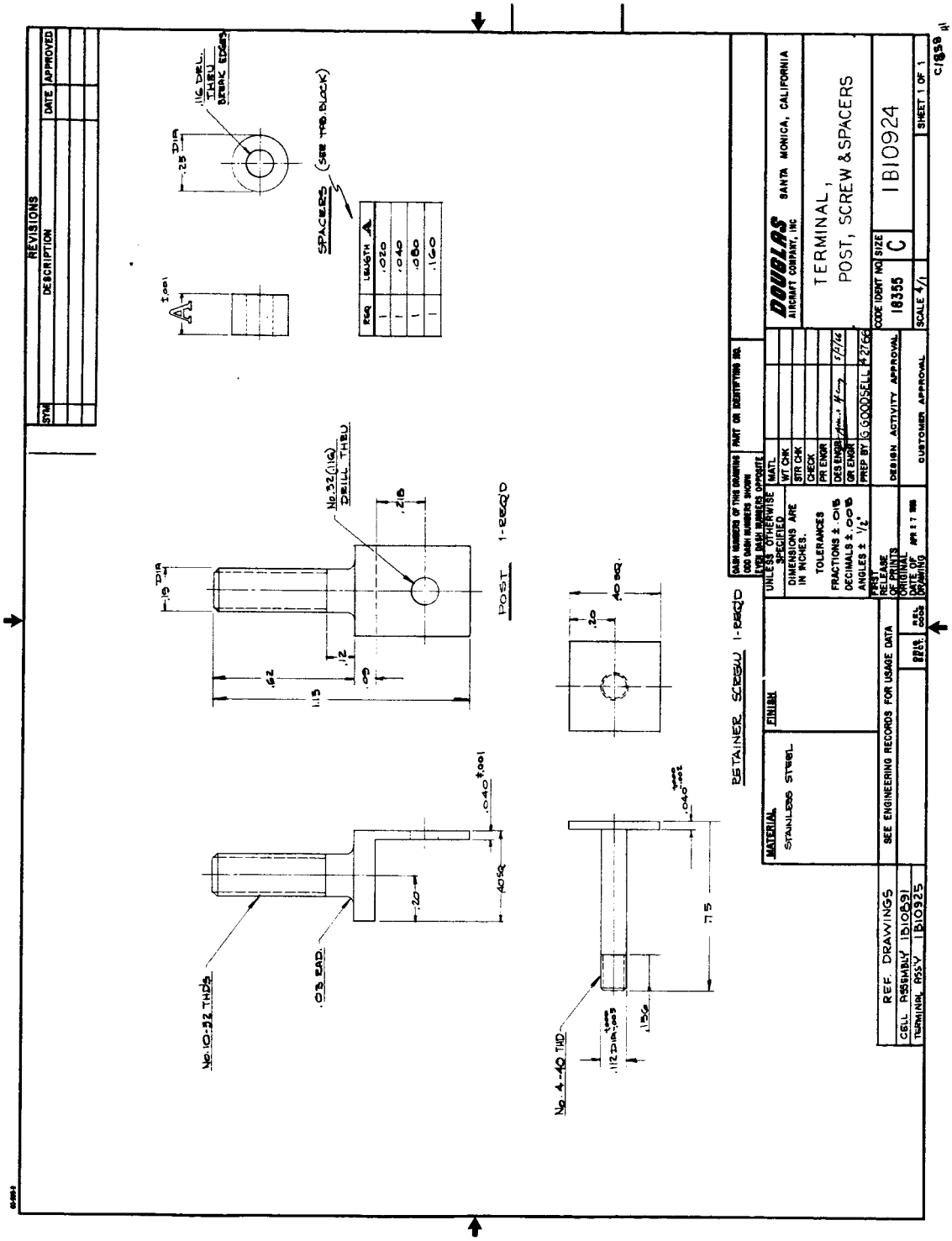

Figure 6. Terminal, Post, Screw and Spacers

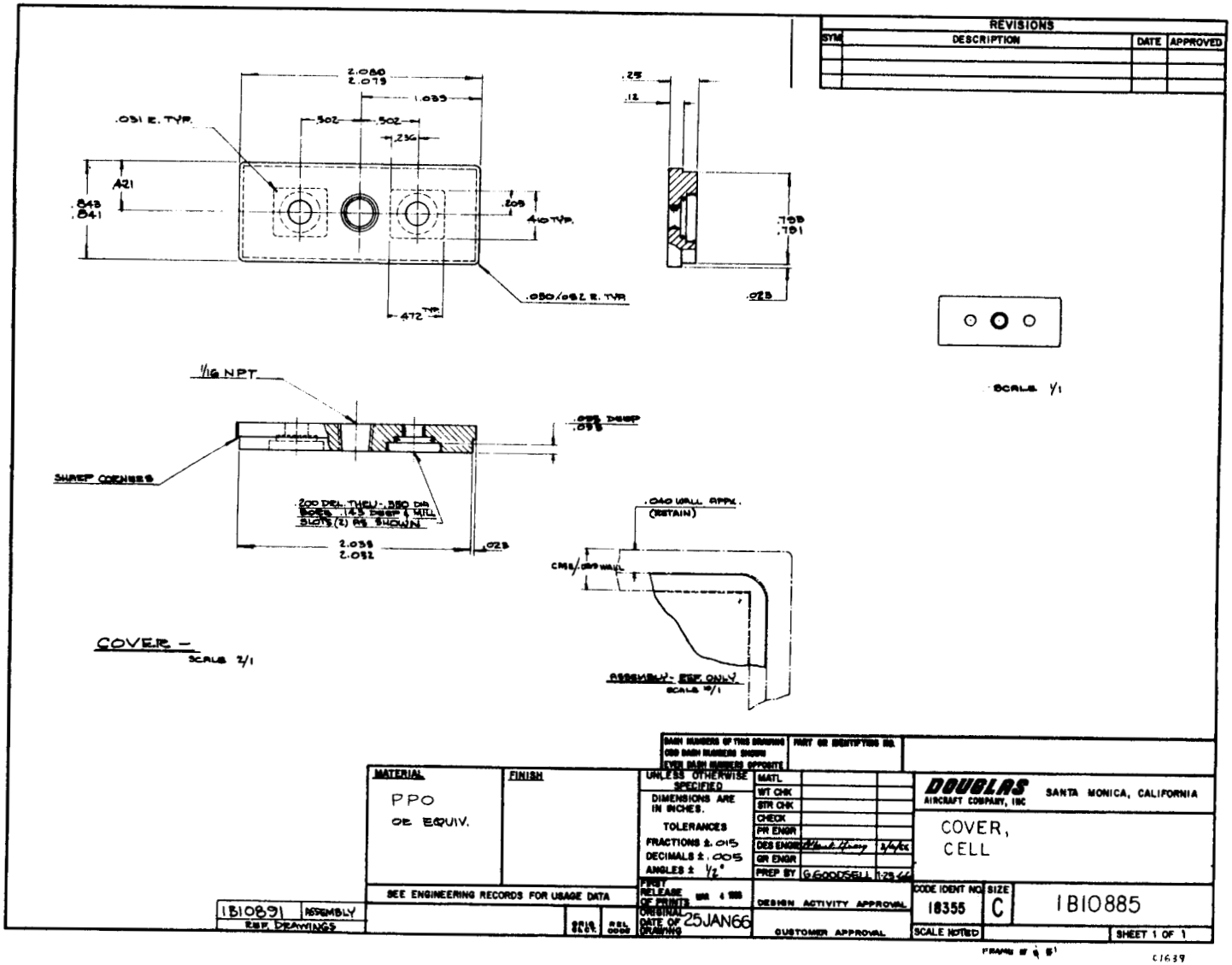

Figure 7. Cover, Cell

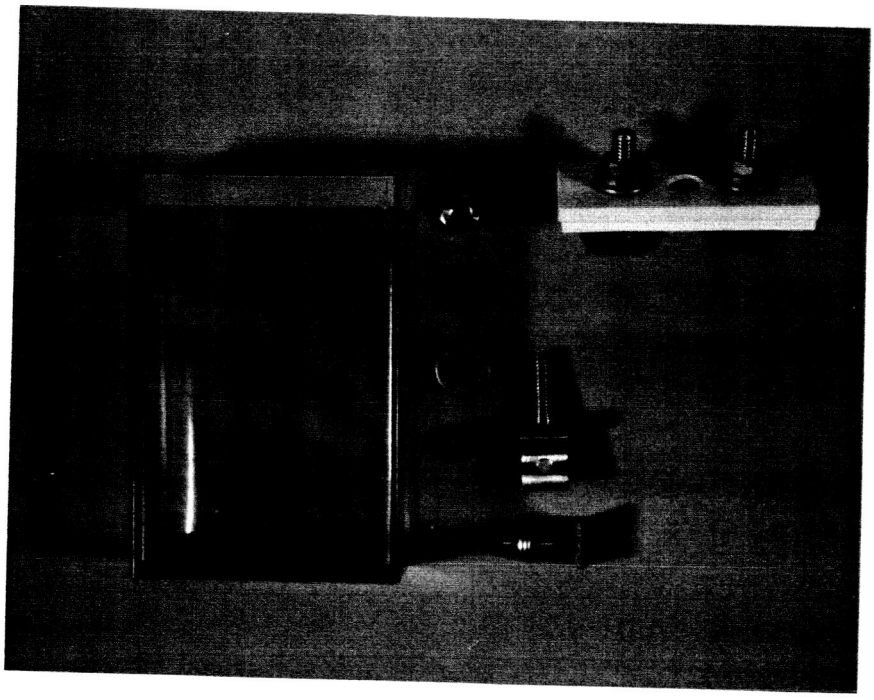

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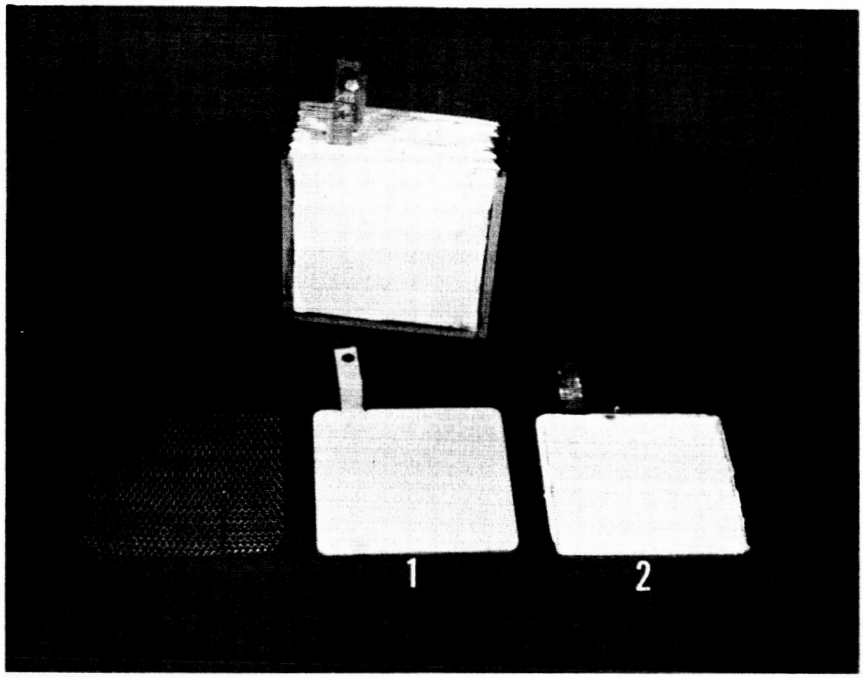
Figure 8. Multiplate Cell Case, Cover and Terminal Components



1. Positive
2. Negative

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Figure 9. Multiplate Electrode and Separator Assembly

of the plastic frame can cause leakage through the strong seal between the separator and the frame or even fracture of the separator if it is severe.

We are concentrating much effort on this problem and the related problem of cementing or sealing the separators to the frame in order to insure leak-tight seals that will avoid self-discharge and loss of OCV on stand and prevent separator fracture resulting from distortion of the frame assembly.

2.2.1.2 Cycling Tests

Tables I, II, and III show a complete survey of all tests run to date on the single electrode cell (ESC-designation) having one positive electrode, two negative electrodes and two separators.

The tables show the difficulty in reaching a large number of cycles at current densities higher than 30 ma/cm^2 on the 1/2-hour discharge, 1-hour charge cycling period because of the increasing depth of discharge.

Another difficulty stems from the fact that at $100^{o}C$ the electrolyte is consumed at a rapid rate, whether through evaporation or through electrolysis, due to high rate charge and overcharge. A change was made in the charging procedure whereby the current and the voltage are controlled during the entire charge hour. The charge is done essentially in two steps. The current is relatively high on the first portion where the cell voltage is still on the monovalent silver oxide plateau, then switched to a lower value when riding on the divalent silver oxide plateau. On both portions, the voltage is limited to a value low enough to minimize gassing at a given current and a given temperature.

This procedure has been successful in reducing maintenance on cells tested on regimes as high as 40 ma/cm^2 and $100^{o}C$.

Some cells were tested lying flat on their wide side in an attempt to minimize zinc shape loss and therefore capacity loss. It appears that this procedure helped in prolonging the cycle-life of the cell with higher voltage plateau and higher end-of-discharge voltage.

TABLE I

CYCLING TESTS AT 25°C
(ESC-B CELLS, 1/2 x 1 HR REGIME)

Cell No.	Original Capacity Q_o (Ah)	Discharge			Number of Cycles	Testing Continued	Testing Stopped	Dissection Comments
		Rate (mA)	Current Density (mA/cm^2)	Depth of Discharge (% of Q_o)				
139	1.8	700	20	19	622	NR		
144	1.7	↓	↓	21	413		LC	
145	1.7			21	276		LC	
146	2.2			16	140		LC	
147	2.1			17	402		LC	a
148	2.1			17	227		LC	
149	2.1			17	483		LC	
150	2.1			17	340		LC	a
151	2.2			16	314		LC	
152	2.2	↓	↓	16	388	NR		
172	1.7	1000	30	29	23		LC	
173	1.8	↓	↓	28	50		LC	
174*	1.9			26	167		LC	
178	2.2			23	56		LC	
179	2.1			24	75		LC	
180*	1.7			29	91		LC	d
188	2.2			23	108	NR		
189	2.3			22	110	NR		
190	2.3			22	136	NR		
191	2.3			22	134	NR		
208	1.6	↓	↓	31	166	NR		

TABLE I (Continued)

CYCLING TESTS AT 25°C
(ESC-B CELLS, 1/2 x 1 HR REGIME)

Cell No.	Original Capacity Q_o (Ah)	Discharge			Number of Cycles	Testing Continued	Testing Stopped	Dissection Comments
		Rate (mA)	Current Density (mA/cm^2)	Depth of Discharge (% of Q_o)				
153	2.0	1400	40	35	24		LC	d
154	2.3	↓	↓	30	66		LC	c
155	2.2			32	87	NR		
156	2.3			30	81		LC	
162	1.9			37	4		LC	c
163	1.9			37	15	NR		
164	1.8			39	12		LC	
165	1.8			39	21	NR		
200	1.3			54	106	NR		
202	1.3	↓	↓	54	213	NR		
205	1.5	1800	50	60	42	NR		
212	1.3	↓	↓	69	95	NR		

LC = low capacity: test was stopped because capacity of cell was smaller than capacity required by regime
NC = test continuing on new regime because capacity of cell was smaller than capacity required by original regime (See Table III)
a = cell dried out
b = case leakage
c = broken lead
d = loose frame
* = cycling period = 1/2 / 2-1/2 hrs

TABLE II

CYCLING TESTS AT 100°C
(ESC-B CELLS, 1/2 x 1 HR REGIME)

Cell No.	Original Capacity Q_o (Ah)	Discharge			Number of Cycles	Testing Continued	Testing Stopped	Dissection Comments
		Rate (mA)	Current Density (mA/cm^2)	Depth of Discharge (% of Q_o)				
157	2.1	700	20	17	181		LC	
158	2.1	↓	↓	17	253		LC	a
159	2.1			17	222		LC	a
160	2.1			17	179		LC	
166	1.9			18	29		LC	d
167	1.9			18	35		LC	d
196	2.2			16	50	NR		
201	1.3	↓	↓	27	192		LC	
168	2.5	1000	30	20	43		LC	d
169	2.5	↓	↓	20	120		LC	d
170	2.5			20	38		LC	d
171	2.6			19	18		LC	
175	1.3			38	44		LC	d
176	1.9			26	19		LC	
181	2.2			23	28		LC	a
184	2.1			24	82		LC	
185	2.1			24	48		LC	c
186	1.7			29	74		LC	d
187	2.2			23	77		LC	
197	2.0	↓	↓	25	48		LC	

TABLE II (Continued)

CYCLING TESTS AT 100°C
(ESC-B CELLS, 1/2 x 1 HR REGIME)

Cell No.	Original Capacity Q_o (Ah)	Discharge			Number of Cycles	Testing Continued	Testing Stopped	Dissection Comments
		Rate (mA)	Current Density (mA/cm^2)	Depth of Discharge (% of Q_o)				
203	1.3	1000	30	38	63		LC	
209	1.6	↓	↓	31	14	NR		
215	1.3			38	78	NR		
216	1.7			29	30	NR		
226	1.6			31	70	NR		
228	1.5			33	100	NR		
198	2.1	1400	40	33	69		LC	
214	1.3	↓	↓	54	13	NR		
217	1.7			41	6	NR		
218	1.6			44	28	NR		
225	1.6			44	54		LC	b
227	1.6			44	32		LC	
219	1.6	1800	50	56	3	NR		

LC = low capacity: test was stopped because capacity of cell was smaller than capacity required by regime
NR = test continuing on new regime because capacity of cell was smaller than capacity required by original regime (See Table III)
a = cell dried out
b = case leakage
c = broken lead
d = loose frame

TABLE III

CYCLING ON NEW REGIME AT 25°C (1/2 / 1/2 HR)

Cell No.	Original Capacity Q_o (Ah)	Previous History		New Regime (NR)		Straight Cumulative Cycles
		Depth of Discharge (% of Q_o)	Number of Cycles	Depth of Discharge (% of Q_o)	Number of Cycles	
188	2.2	23	108	7	12	120
189	2.3	22	110	7	95	205
190	2.3	22	136	7	133	269
191	2.3	22	134	7	932	1066
139	1.8	19	622	8	1507	2129*
152	2.2	16	388	9	147	535
208	1.6	31	166	9	404	570
205	1.5	60	42	10	1104	1146*
200	1.3	54	106	12	83	189
202	1.3	54	213	12	895	1108*
155	2.2	32	87	23	21	108
163	1.9	37	15	26	9	24
165	1.8	39	21	28	108	129
212	1.3	69	95	38	68	163
	CYCLING ON NEW REGIME AT 100°C					
196	2.2	16	50	7	1	51
209	1.6	31	14	9	151	165
226	1.6	31	70	9	2	72
217	1.7	41	6	9	87	93
228	1.5	33	100	10	125	225
214	1.3	54	13	12	116	129
215	1.3	38	78	12	176	254
216	1.7	29	30	21	66	96
219	1.6	56	3	22	71	74
218	1.6	44	28	31	25	53

* Tests still continuing. (All others stopped because of low capacity.)

Typical charge-discharge curves for cells at various current densities and at 25°C and 100°C can be seen in Figures 11 through 15.

Figure 10 shows separator frames removed from test cells after many cycles.

Depth of discharge reflects actual cell capacity (defined as cell capacity on the first cycle at a discharge current density of 10 ma/cm^2 to a final cutoff voltage of 1.0 V out of the cell). This value is highest on the first cycle run at low rate, at 25°C, after a normal charging regime at 3 ma/cm^2. These conditions do not usually prevail during the course of a cycling test program, but they do give a common reference from which to gauge the actual effect of the depth of discharge on cycling.

Some cells that could not meet the cycling capacity requirement after a certain number of cycles were switched to a new regime, as shown in Table III.

The test cells are capable of supplying a reasonable output over 1 Ah at current densities of 30 ma/cm^2. The limitation on cycle-life comes exclusively from the recharge which is not as efficient when the charge current density is too high. The fact that the cycling period is 1/2-hour, 1-hour imposes a recharge current density of at least 75% of the discharge current density.

For this reason, the original capacity of the latest cells has been reduced by undercharging the cells on formation in an attempt to avoid repeated overcharging on automatic cycling at high current densities.

If the cells whose premature failure was obviously caused by poor mechanical assembly are discounted, the total number of cells tested up to 30 ma/cm^2 (which seems to be the practical limit of current density) is 23 cells at 25°C and 25 cells at 100°C.

2.2.1.3 Gassing Tests

Gassing tests were run to determine the extent of gas evolution under different conditons of stand and cycling at 25°C and 100°C.

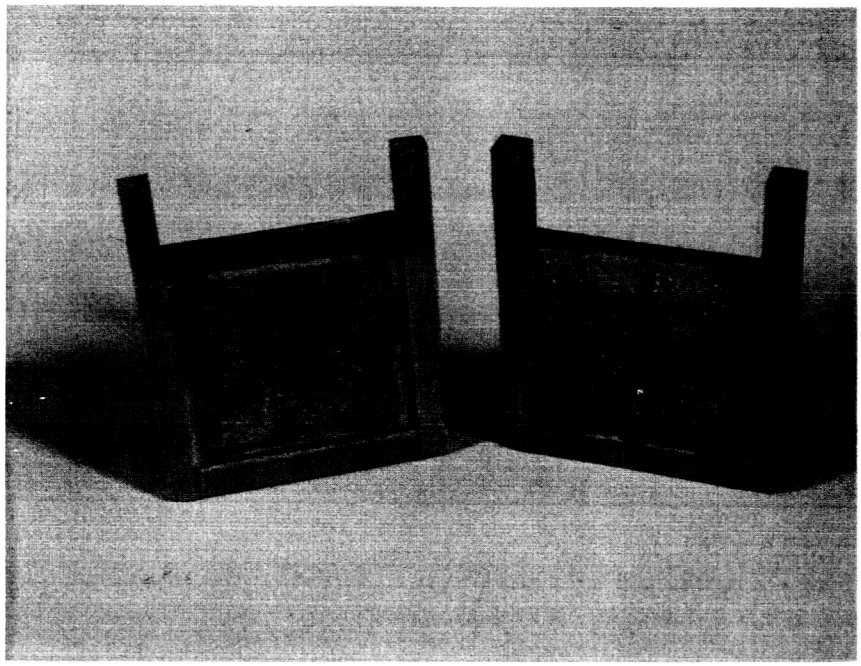

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Figure 10. Inorganic Separators Removed From Test Cells No. ESC-B-149 After 495 Cycles (Left) and No. ESC-B-151 After 347 Cycles (Right)

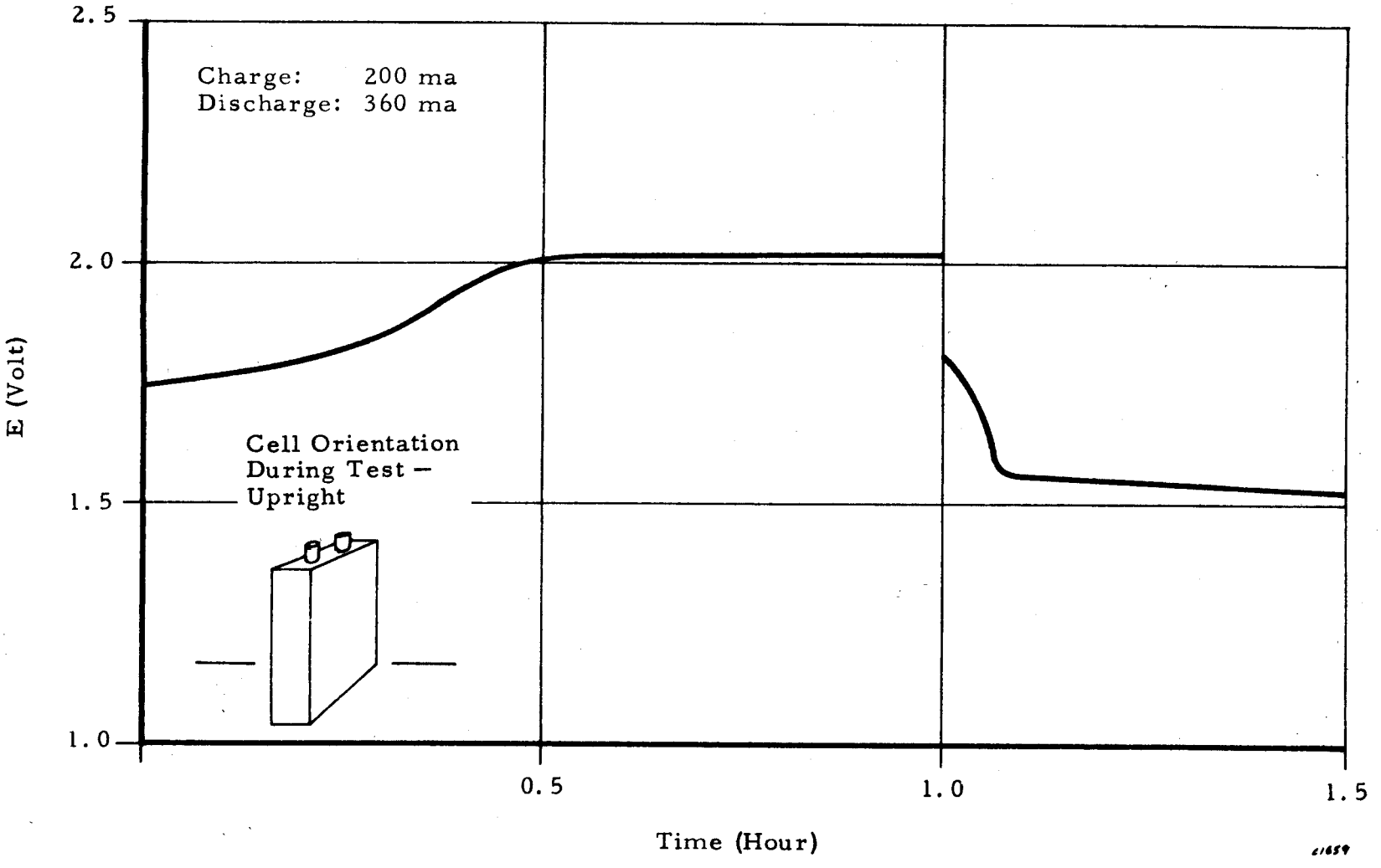

Figure 11. Test Cell No. 139 After 1000 Cycles at 10 ma/cm^2 at 25°C

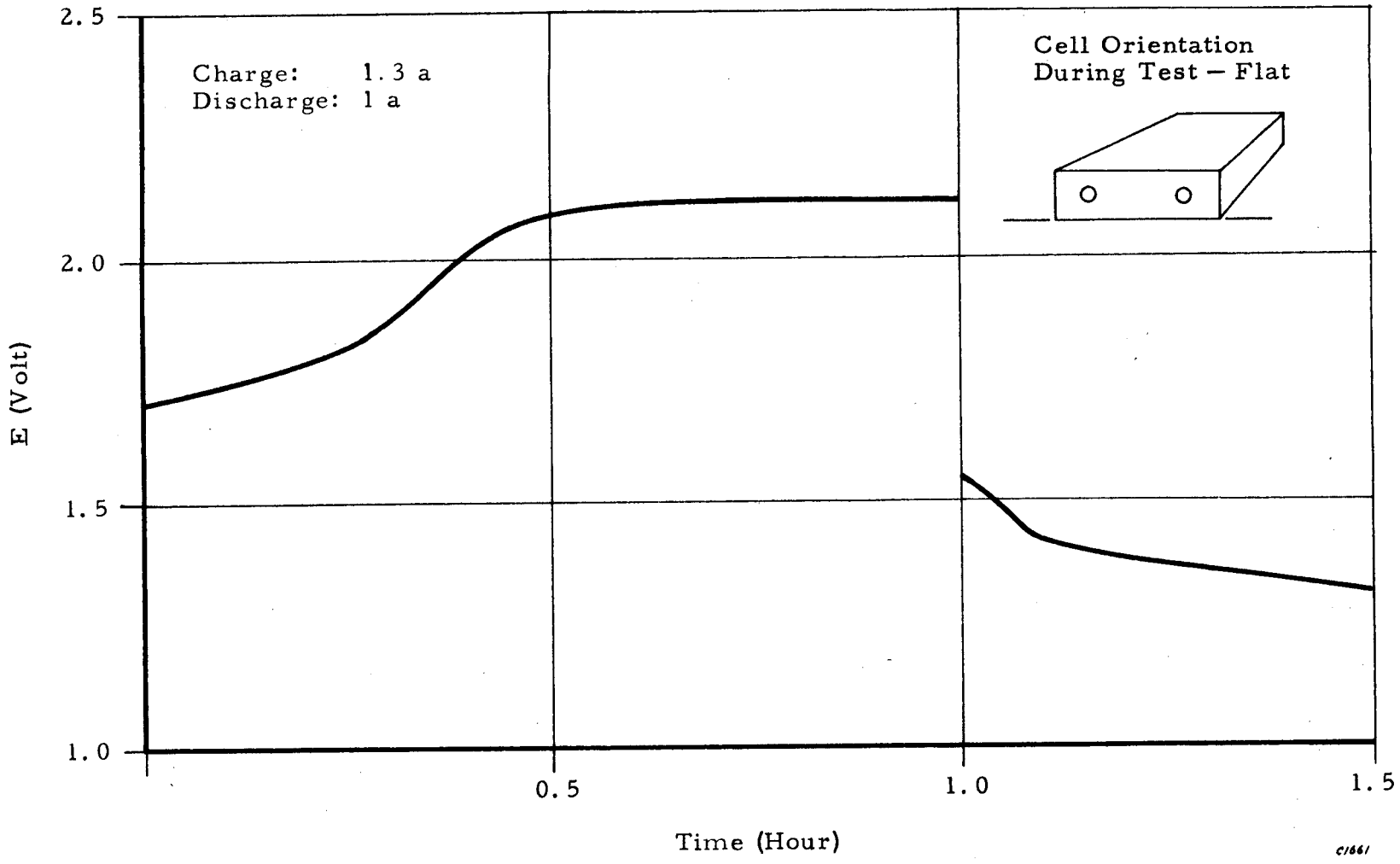

Figure 12. Test Cell No. 215 After 75 Cycles at 30 ma/cm^2 at 100°C

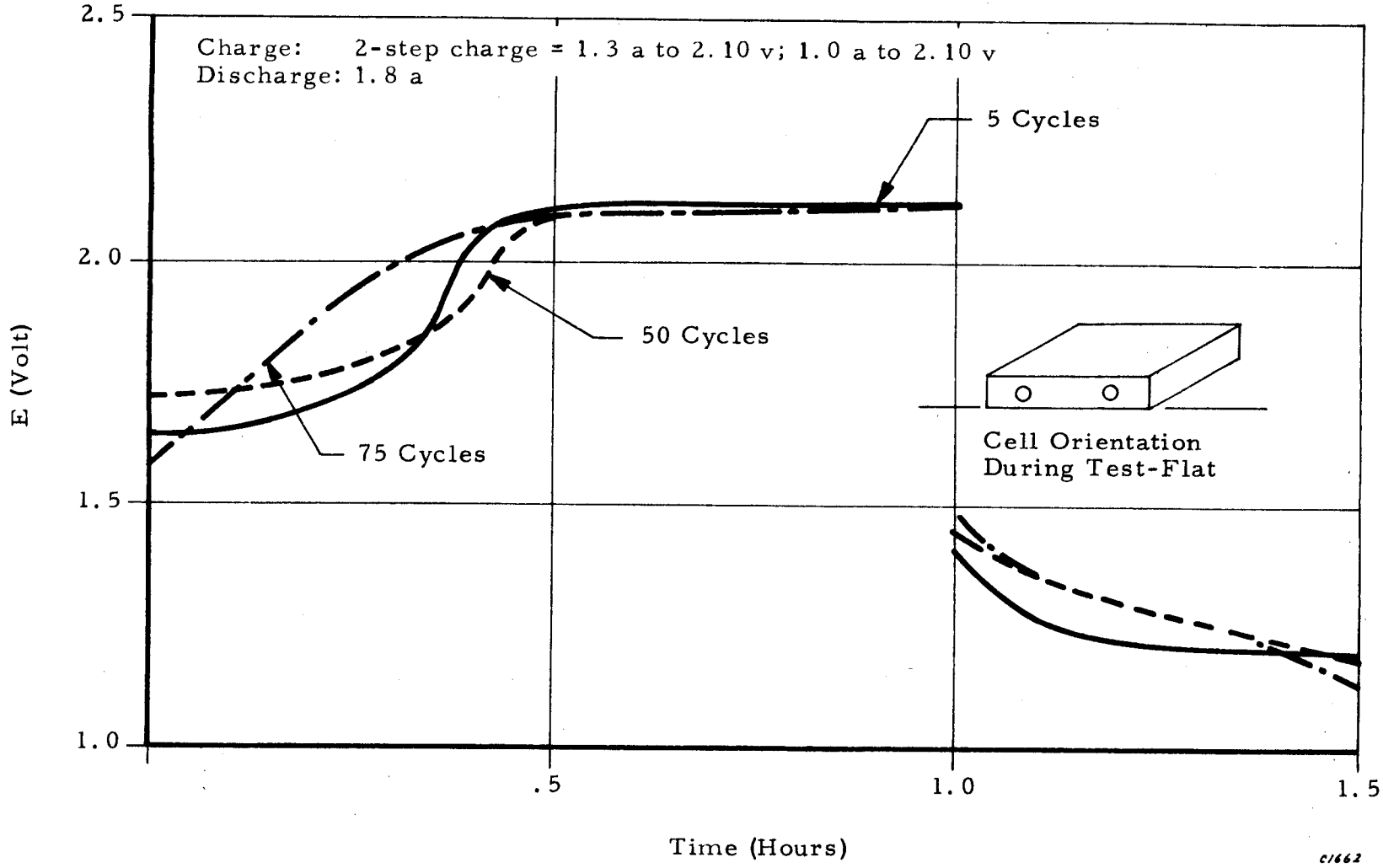

Figure 13. Test Cell ESC-B-212 Cycle Test at 50 ma/cm^2 at 25^{o}C

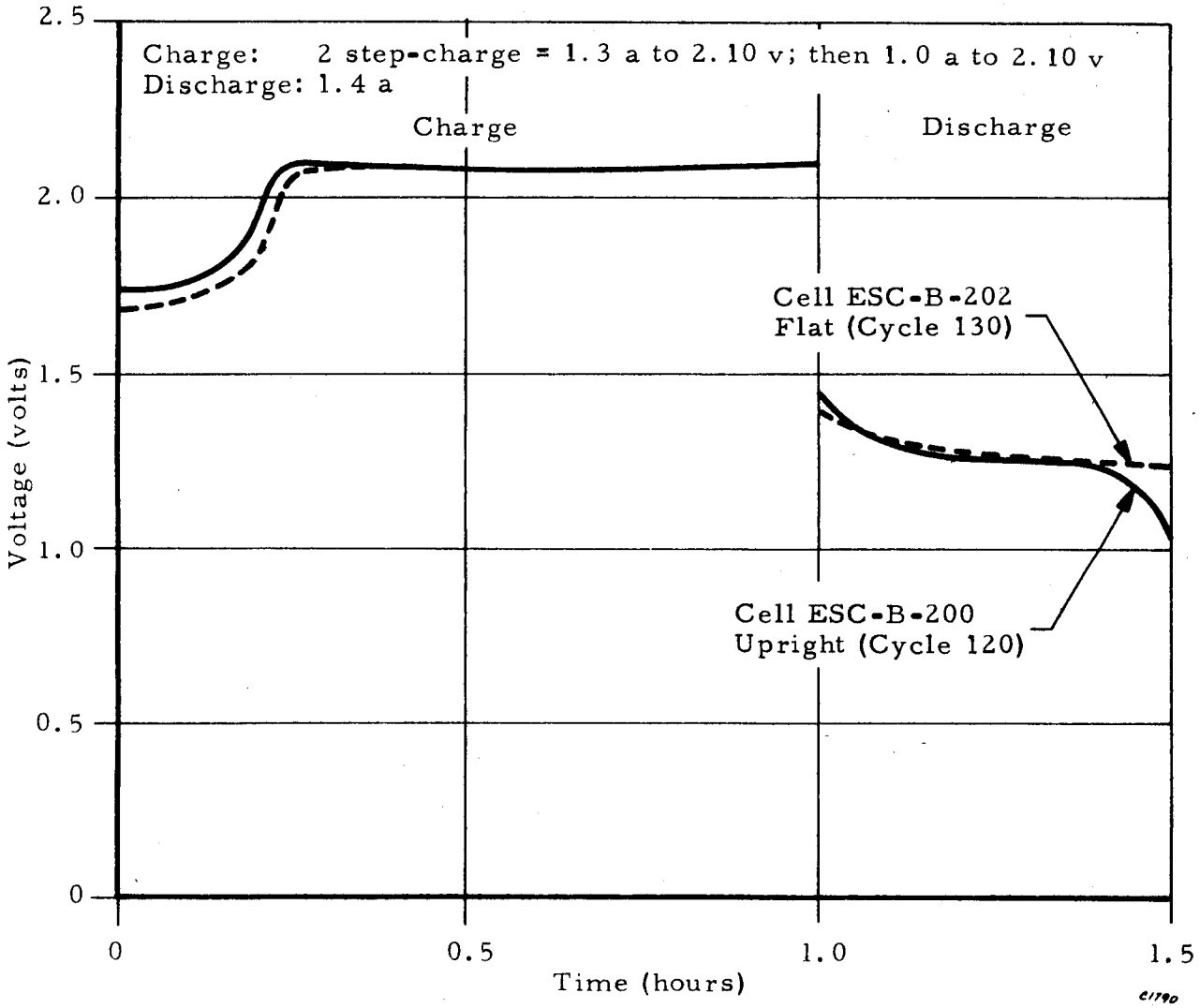

Figure 14. Complete Cycle. 40 ma/cm^2 at 25°C

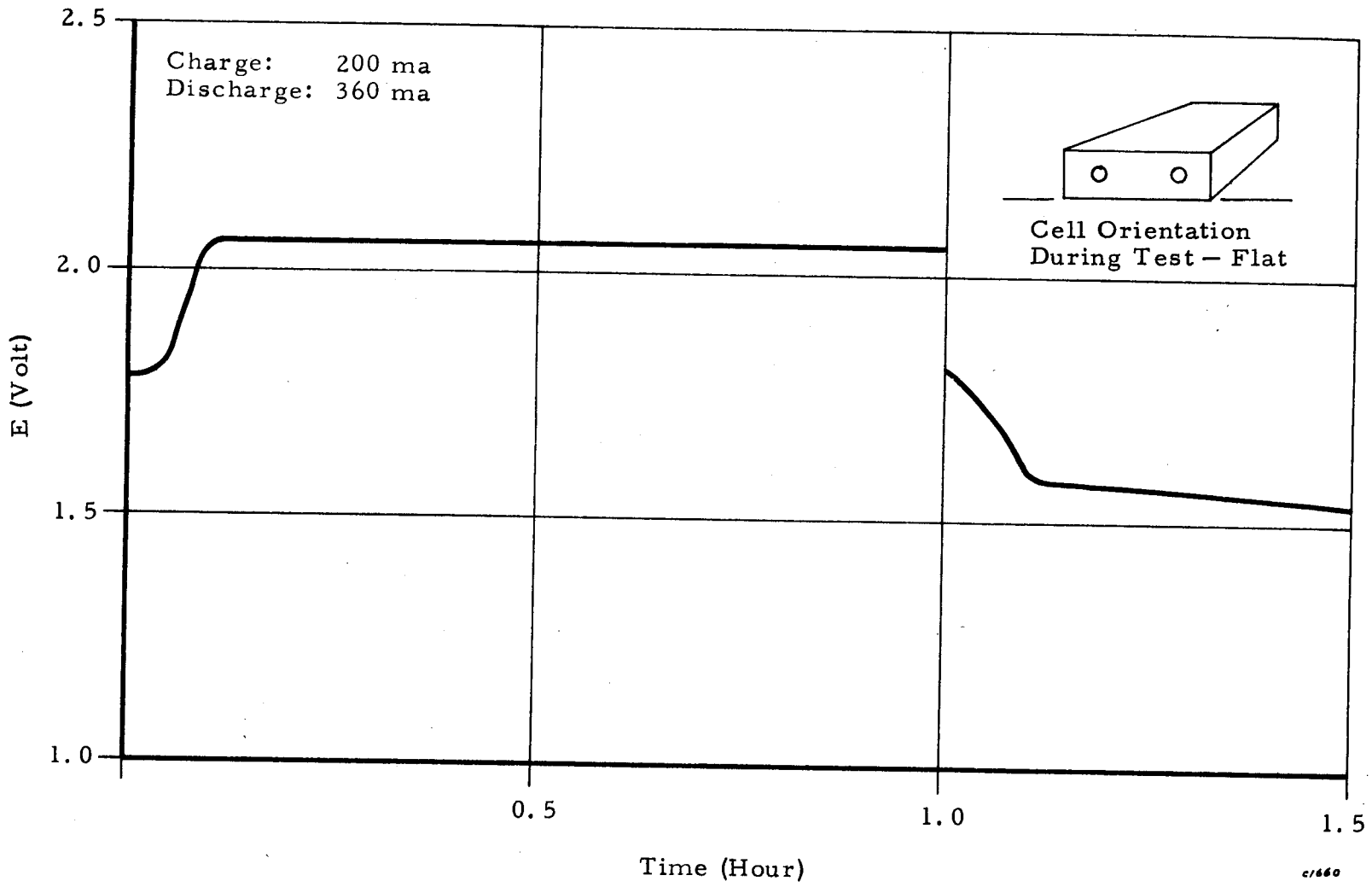

Figure 15. Test Cell No. ESC-B-208 After 300 Cycles at 10 ma/cm^2 at 25°C (Cell cycled for 163 cycles at 30 ma/cm^2 at 25°C prior to this cycle test)

This, in turn, will establish the practical limits of use of the cell in a sealed condition by computing (and later by actually measuring) the pressure build-up within the confines of the sealed cell.

The cells were connected to a gas eudiometer, each under a specific regime. The system was tested for leakage continuously, and the test discontinued when leakage developed (Figure 16).

The tests were made on dummy cells and complete cells.

A. Dummy Cells

The dummy cells are cases containing one or more components of the cell and tested at 100°C on stand in order to establish the contribution of each component to the gassing phenomenon. Models tested were the following:

Model #1: Blank cell containing 30% KOH alone. Three separate test runs at 100°C showed that the average stabilized figure of gas (evolved or expanded) after 5 to 8 hours was 20 cm^3 within 5%.

Model #2: Separators mounted in frame and filled with 30% KOH. It also had approximately 20 cm^3. It can be concluded that the effect of separators is nil.

Model #3: The positive plate was removed from a complete cell after formation and full charge. The case contained only frame, separators, two negative electrodes and KOH.

Gas evolution was linear at the rate of 60 cm^3 for 28 hours.

Model #4: The case contained only the frame, separators and one fully charged silver plate in KOH.

It was established that most of the gas came from the decomposition of divalent silver oxide into monovalent silver oxide and oxygen. The gas evolution is linear first until it reaches a certain equilibrium where little gassing occurs.

The plate was then removed and discharged at room temperature. The open circuit voltage against a freshly charged zinc plate and the remaining capacity showed that all the oxide then present was argenteous.

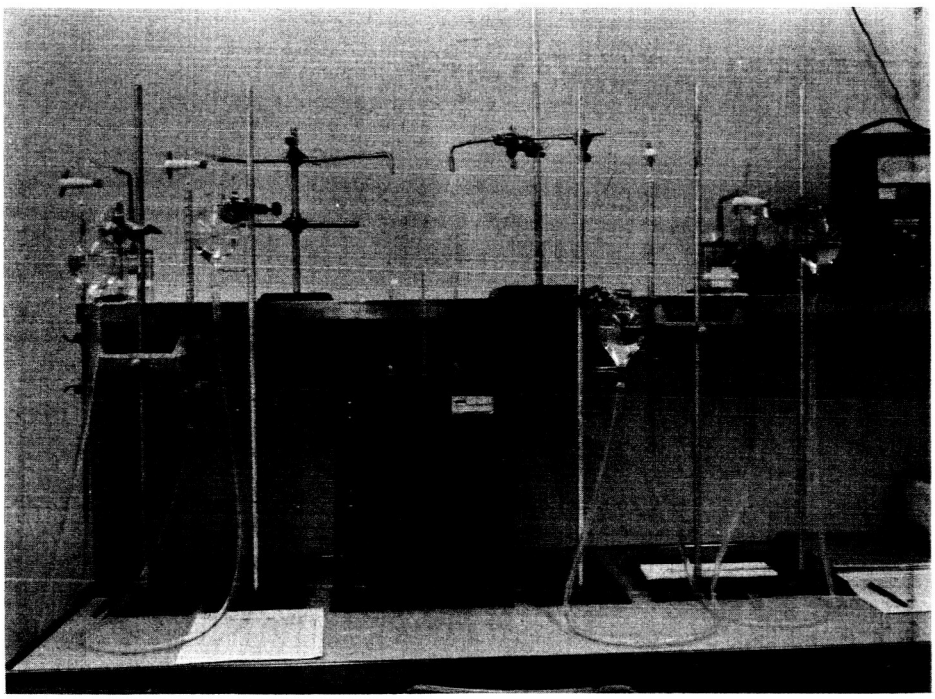

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Figure 16. Cell Gassing Experimental Setup

The total amount of gas recorded was 220 cm^3 after 22 hours. Excluding the 20 cm^3 due to KOH, most of the gas is oxygen.

B. Complete Cells

All cells were charged and discharged according to standard procedure:

Charge at 120 ma to 2.05 V
Discharge at 350 ma to 1.0 V

All cells were then recharged; after recharging, they were placed on stand for 24 hours to remove all accumulated gas, then connected to a gas eudiometer.

1. Stand Tests

a. Room Temperature (Table IV and Figure 17)

Cell #ESC-B-204 was left on stand in a relatively isothermic ambient environment fluctuating from 22 C to 25 C. The accumulated gas volume was approximately 0.25 cc after three days and did not exceed 0.30 cc. Volume then remained constant, indicating a capacity retention and no-short condition.

It can be concluded that the present electrode-separator system is adequate on stand at room temperature in a sealed condition. Insignificant pressure build-up in the multiplate cell configuration is contemplated.

b. High Temperature (Table V and Figure 18)

(1) Fully Charged Cell

Cell #ESC-B-207 was left on stand in an oven maintained at 100°C ± 2°C after it reached this temperature. The data show heavy gassing when the temperature reached 100°C. When the temperature was dropped to ambient, the gassing rate dropped to an insignificant value, but gassing resumed as soon as the temperature was increased. The test was discontinued when a leak developed in the system.

The test was repeated on cell #ESC-B-224. Left on stand in an oven maintained at 100°C ±2°C, after it reached this temperature. It produced 177 cc in 17 hours up to the point of equilibrium (where little gas is added), while the OCV dropped from 1.84 to 1.62. This figure is slightly

TABLE IV

GASSING DATA ON STAND AT 25°C

Cell #ESC-B-204

Elapsed Time (hrs)	Temperature °C	Accumulated Gas Volume (cm^3)	OCV
5	24	0.	1.84
8	22	0.	1.84
23	23	0.	1.84
31	23	0.	1.84
47	22	0.10	1.84
72	25	0.20	1.84
143	24.5	0.20	1.84
215	22	0.28	1.84
355	24	0.29	1.84
408	24	0.29	1.84

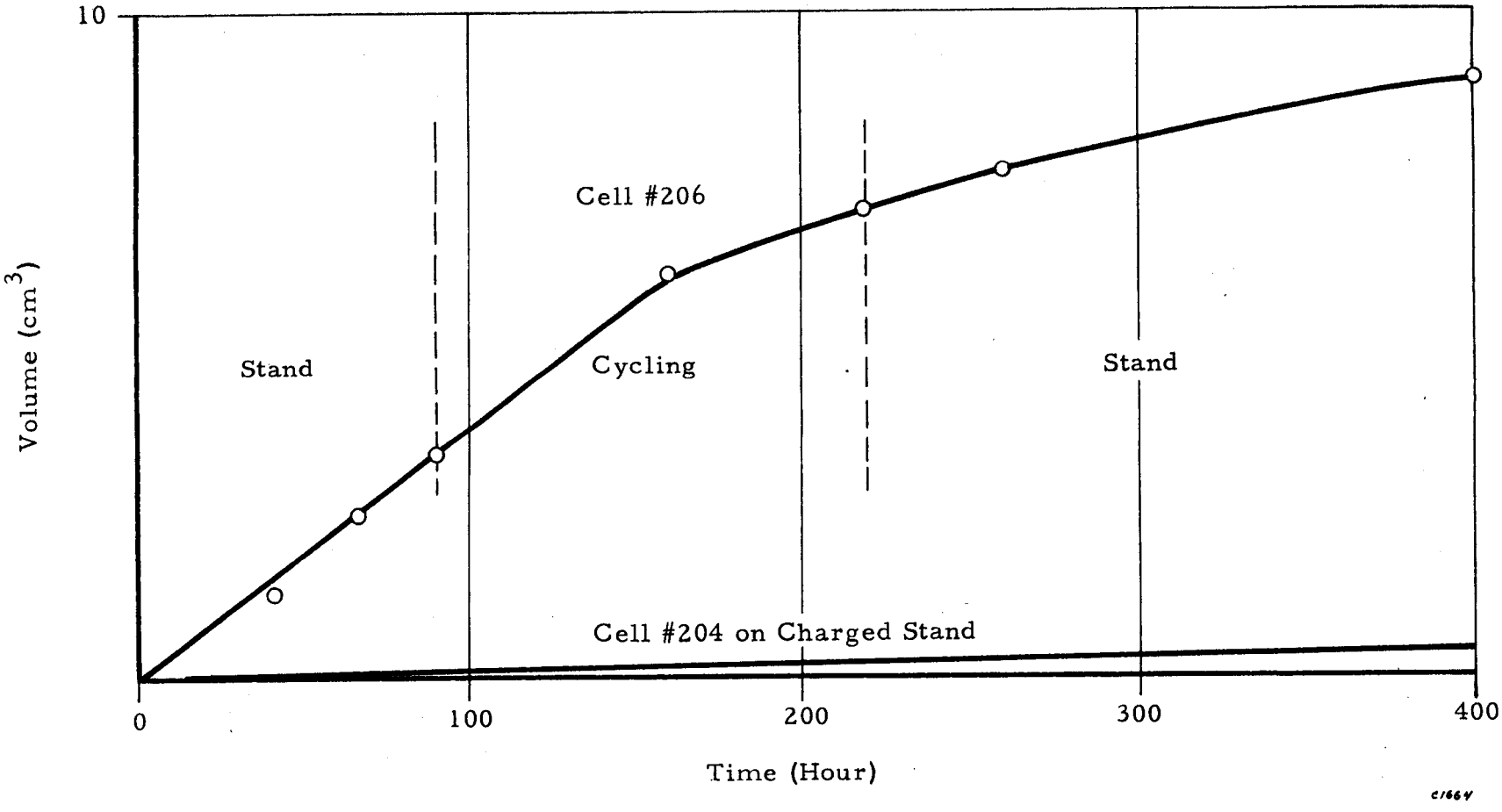

Figure 17. Total Volume of Gas Evolved at 25°C

TABLE V

GASSING DATA ON STAND AT 100°C

Cell #ESC-B-207

Elapsed Time (hours)	Temp. °C	Accumulated Gas Volume (cm^3)	Note
0.0	24	–	Oven on: Temperature Rising
0.5	55	0.5	
1.0	73	2.6	
1.25	84	4.1	
1.75	93	5.9	
2.50	102	8.7	Temperature Maintained
4.75	100	12.6	
7.50	100	14.8	
23.50	99	17.9	
29.25	102	28.5	
30.50	98	56.6	
31.0	98	65.3	Oven Off
31.75	55	75.9	Temperature Dropping and Maintained at 25°C
32.0	25	78.4	
103.0	25	78.4	
103.90	84	80.15	Oven on: Temperature Rising
105.0	100	88.60	
106.0	98	100.75	
107.5	98	108.20	Case leaking (Test Stopped)

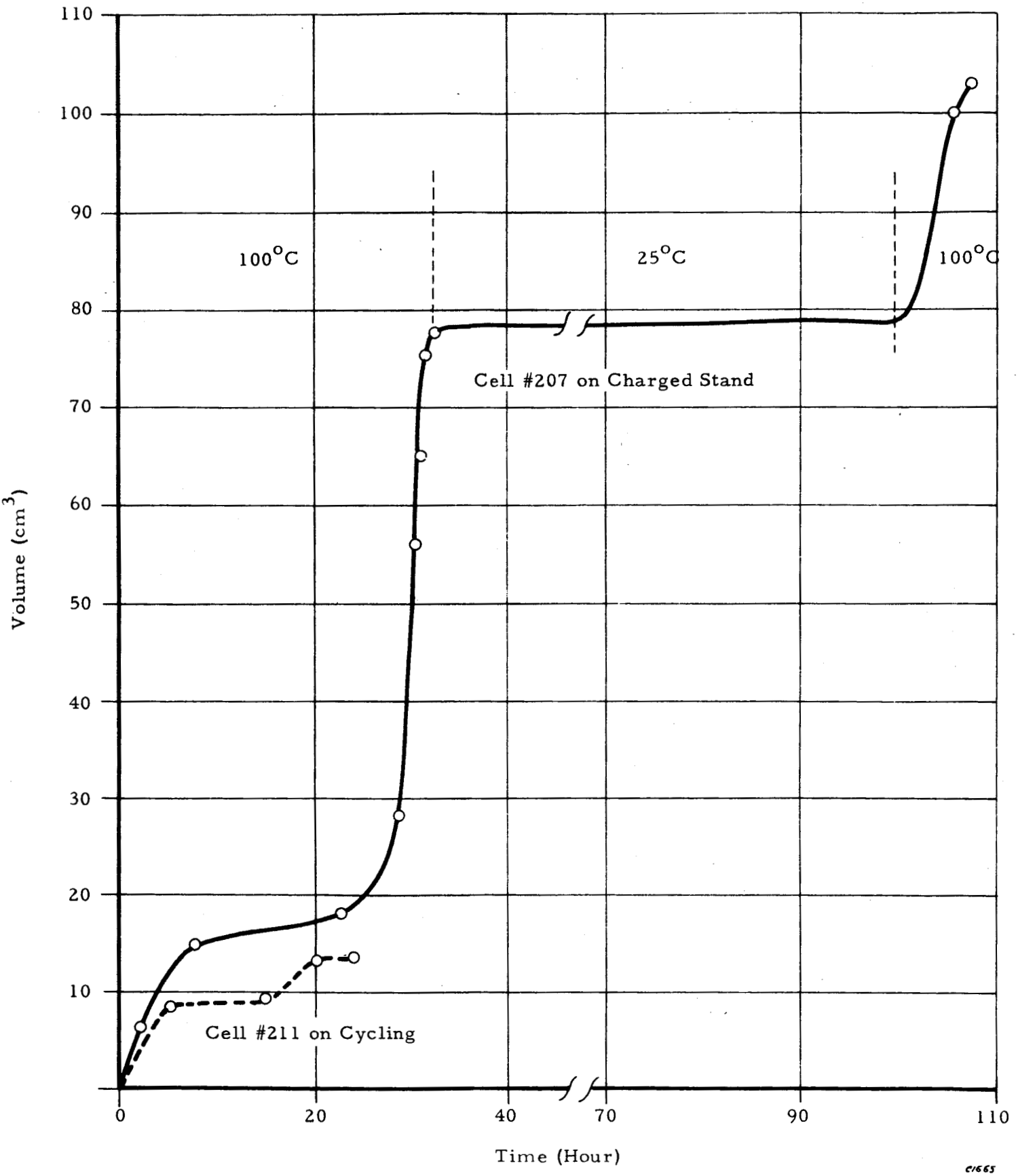

Figure 18. Total Volume of Gas Evolved at 100°C

lower than the figure given by the charged silver plate alone, probably because of some recombination of oxygen with the charged, zinc negative electrodes.

(2) Partially Charged Cell

Cell #ESC-B-223 was discharged until the upper OCV disappeared (approximately 40% of the capacity was taken out). The cell was then submitted to the gassing test at 100°C as above.

The total gas volume generated up to equilibrium was 18 cc after 6 hours, which is in the same range as the figure obtained with KOH alone (Model #1).

Based on these results it can be concluded that no significant gassing is expected on stand at room temperature, whatever the cell state-of-charge is. At 100°C, no gassing will occur as long as the cell has the argenteous oxide OCV.

2. Cycling

a. Room Temperature (Table VI and Figure 17)

Cell #ESC-B-206 was cycled on the 1/2-hour discharge, 1/2-hour charge regime (360 ma/450 ma) with intermittent stand periods. Up to 124 cycles were made with little gassing. The current density on discharge was 10 ma/cm^2, and the charge was voltage limited to avoid overcharge. This test was repeated at higher current density to determine the limits for practical operation without impairing the integrity of the seals. At 20 ma/cm^2 (cell #220), the total volume collected over 32 cycles was 0.75 cm^3.

b. High Temperature (Table VII and Figure 18)

Cell #ESC-B-211 was tested at 100°C ±2°C on the cycle regime described above. This test was discontinued after 24 hours because a leak developed in the system.

It is to be noted that the cell gassed less than the cell on stand at 100°C, and it can be conjectured that this is because the cell is in a medium charge state most of the time rather than in a fully charged state, as established by the test done on a partially charged cell on stand at 100°C.

TABLE VI

GASSING DATA ON CYCLING AT 25°C
(1/2 / 1/2 hr
360/450 mA)

Cell # ESC-B-206

Elapsed Time (hours)	Temp. °C	Accumulated Gas Volume (cm^3)	OCV	Note
15	25	0.4 c	1.84	Stand
40	23	1.40	1.84	
70	24	2.60	1.82	
90	25	3.40	1.82	
91	25	3.60		Cycling
160	24	6.10		60 Cycles
168	25	6.50		72 Cycles
187	24	6.60		96 Cycles
215	23	6.80		124 Cycles
217	24	7.10	1.63	Stand
260	24	7.60		
332	24	8.20		
380	24	8.80		
428	23	9.30		Test Discontinued Because of Leak in System

TABLE VII

GASSING DATA ON CYCLING AT 100°C
(1/2 / 1/2 hr
360/450 mA)

Cell #ESC-B-211

Elapsed Time (hours)	Temp. °C	Accumulated Gas Volume (cm^3)	OCV	Note
(7 days)	25	0.	1.84	Stand for one week
1 hr	93	6.2		Cycling
4	97	7.5		
5	98	8.4		
6	98	8.8		6 Cycles
6.5	25			Stand at R.T.
15.	25	9.0	1.62	
15.5	31	9.0		Cycling – Oven turned on
16	81	11.8		
17	98	12.8		
18	98	13.10		
20	98	13.20		
24	98	13.20		24 Cycles
				Test discontinued because of leak

On cycling, little gassing occurs at 25°C at current densities up to 20 ma/cm^2 on a 1/2-hour discharge, 1-hour charge regime, voltage limited on charge.

2.2.2 Inorganic Separators

Because satisfactory results have been obtained during the first half of this program using separators based on Astroset Type 5-036-011 and evaluated under NASA Contract NAS 3-6007,[2] no additional separator work has been done. The work performed in this program devoted to separator scale-up, fabrication, quality control and uniformity is reported in detail in SM-48461-Q1.[3]

2.2.3 Cases

As previously reported,[4] the case molder has had considerable difficulty in molding PPO and the first cases received were striated and appeared to be laminated. The dark brown striations extended from one case surface to the other and appeared to be laminations caused by overheated or burned molding material. Samples were broken apart and it could be seen that the striations were laminations and that the cases were not mechanically sound. Figure 19 is a photograph showing typical cases of this type.

Sample cases were also heated in an oil bath at 135°C. These cases cracked along the striations confirming our previous observations that these cases were not suitable for use in the program.

The problem was taken up with both the molder and the General Electric Company, manufacturer of the PPO molding compound. The General Electric representatives advised us that the problem was a molding problem and that these striations were caused by overheating the plastic in the molding machine. The overheated material, which was burned, caused the dark striations in the molded cases and the resultant unacceptable quality. The General Electric Company offered to consult with the molder and help him resolve the molding problem by showing him how to handle PPO on his machines. They also offered to provide molding material to the molder for use in this work at no charge to this program. They further offered to mold the required cases at their plastics laboratory if the present molder was unable to make the cases

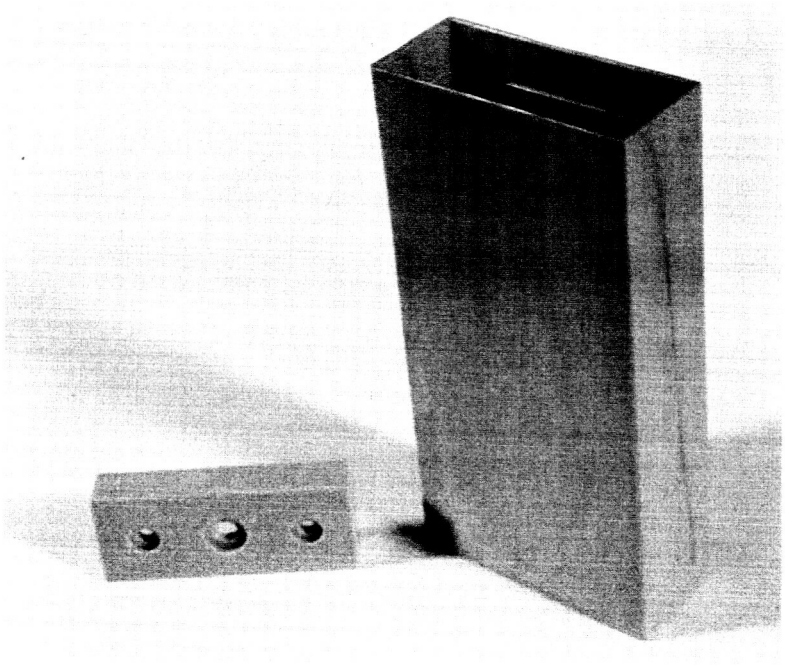

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Figure 19. Molded PPO Case Showing Defective Structure Resulting From Improper Molding

to an acceptable quality level, providing the tooling could be transferred to their factory.

The molder was then contacted by both Astropower Laboratory and the General Electric Company. As a result of these discussions the molder agreed to rerun the PPO material provided by General Electric. He agreed that the original run was defective due to burning of the material and that he would modify his processing techniques to avoid over-heating in accordance with General Electric's suggestions. Three different lots of PPO were provided by General Electric and molded under their supervision. These lots were identified as follows:

1. PPO-PX-0145
2. PPO-PX-0045
3. PPO-532-801

None of the PPO lots could be molded without striations but the PPO-PX-0045 material appeared to be the best of the three types tried. Sample cases of each type were tested by heating in oil at 135° and 145°C. All types failed by cracking as described above at 145°C. Samples of PPO-PX-0145 and PPO-532-801 appeared to be all right after heating at 135°C but otherwise appeared to be defective and quite similar to the cases originally received.

As a result of these extensive tests, it is indicated that it may not be possible at this time to obtain molded PPO cases of satisfactory quality for use in this program. This matter is being explored further with both General Electric and the molder.

As a result, cases molded from polysulfone have been ordered in both 0.062 and 0.100 in wall thicknesses. These cases appear to be free from molding striations but may present greater sealing problems than PPO. For the present, both materials will be investigated in order to insure selection of the best material for application in the multiplate 5 Ah cell in this program.

2.2.3.1 Pressure Tests on Molded Cases

In order to make a preliminary evaluation of the bursting strength of molded cases, samples were cut down to the proper

height and machined to accommodate the covers in accordance with the case drawing. These sample cases were then subjected to hydraulic pressure until bursting occurred. Both PPO and polysulfone cases were tested in order to make a preliminary comparison of the two materials.

The PPO cases burst at 70 psi and the polysulfone cases burst at 90 psi. The wall thickness of both cases was 0.065 inch. As noted above, the PPO cases are known to be structurally defective due to improper molding.

These results are quite promising, especially for the PPO material, and indicate that a properly molded PPO case of adequate wall thickness should be capable of withstanding the pressures anticipated in sealed silver-zinc multiplate cells operating at 100°C and room temperature. It is also indicated that polysulfone may also be satisfactory for this application as its bursting pressure was also slightly higher (20 psi) than PPO. These preliminary tests are not conclusive, however, and accurate bursting strength will be determined when the new polysulfone cases with 0.100 inch thick walls are received from the molder.

2.2.4 Terminals

No modifications of the terminal and seal assembly were made, except for the attachment of the tabs to the base, as described in paragraph 2.2.5.

However, to provide greater reliability and to overcome possible eventual leakage during the life of the cell, a search is still going on for better epoxies for use in encapsulation of the terminal base and for potting the top of the cover.

2.2.5 Connections

As described previously in paragraph 2.1, the attachment of the electrode tabs to the terminal base has been modified to facilitate production and assembly. The distance between the top of the electrodes (positive and negative) and the center of the hole punched in the tab is now the same for all electrodes. As a result the tabs now extend straight up out of the frame pack and a long screw and washers are used to complete the assembly.

Figure 20 is a sketch of the present assembly.

2.2.6 Electrolyte

The effect of KOH concentration on discharge rates was determined in test cells as specified in the work statement.

Eight ESC-B type cells were constructed for this test. Four used standard negative electrodes with the KT paper wrapped as a "U" around each negative electrode and four used negative electrodes with KT fibers blended into the negative mix material before pressing.

One cell of each group was activated with different KOH concentrations ranging from 30% to 45%. See Tables VIII and IX for details. All cells were given identical tests — complete discharge for three cycles at discharge drain levels ranging from 10 ma/cm^2 to 50 ma/cm^2. After 10 complete discharge-charge cycles, the cells were put on automatic cycling at the one-hour rate of discharge (30 ma/cm^2). As seen in the tables, the cells using the KT wrap around the negative electrodes were uniform and consistent. There was no significant difference between results at various KOH concentrations. Figure 21 shows capacity and plateau voltage evaluation versus current density for this type construction.

2.2.7 Preliminary Testing of Multiplate Cells

Several multiplate cells of different designs were built to learn more about assembly difficulties and shortcomings and the areas of potential operating trouble.

The models were made successively in a large case, then in a fabricated case as originally designed, then in a purchased molded case which approximates the dimensions of the fabricated case. The drawings in this report refer exclusively to the latter design. The molded case will be used for the improvement of the cell pack design (electrode pack configuration).

Based on the results of these preliminary tests, a design will be selected and pre-tested according to "NASA Technical Directive No. 1," dated April 19, 1966.

The different models tested are listed below along with their individual characteristics. Table X gives a summary of electrical test results.

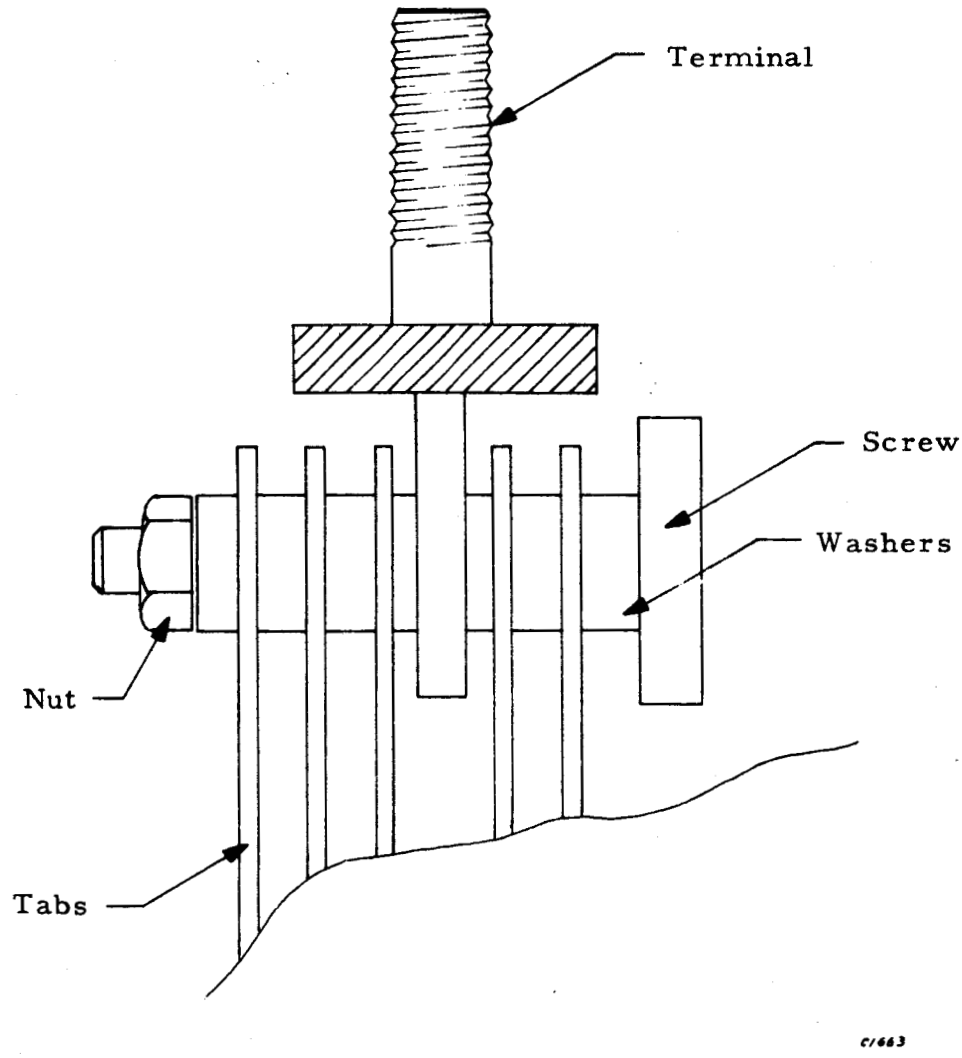

Figure 20. Vertical Tab Attachment to Terminal Base

TABLE VIII

CAPACITY (Ah) vs. KOH PERCENTAGE

Cycle	Cell No.		188	189	190	191	192	193	194	195
	Negative Design		KT Wrap				KT Fiber Mix			
	Current Density	Dschg Rate	30%	35%	40%	45%	30%	35%	40%	45%
1	10 mA/cm^2	0.350	2.25	2.30	2.30	2.30	2.40	1.60	1.85	2.20
2	10 mA/cm^2	0.350	2.20	2.20	2.15	1.80	1.85	1.60	1.50	1.80
3	10 mA/cm^2	0.350	2.15	2.30	2.30	2.50	1.60	1.40	1.65	1.65
4	50 mA/cm^2	1.8 A	1.55	1.45	1.45	1.30	1.50	1.00	1.20	1.30
5	50 mA/cm^2	1.8 A	1.60	1.80	1.80	1.80	1.45	1.10	1.10	1.25
6	50 mA/cm^2	1.8 A	1.60	1.45	1.75	1.60	0.95	0.70	1.35	1.35
7	30 mA/cm^2	1.0 A	1.95	1.80	2.0	1.60	1.30	0.90	1.40	1.70
8	30 mA/cm^2	1.0 A	1.85	1.80	1.8	1.75	1.25	0.90	1.55	1.60
9	30 mA/cm^2	1.0 A	1.25	1.40	1.2	1.90	1.10	0.90	1.50	1.40
KOH Concentration			30%	35%	40%	45%	30%	35%	40%	45%

TABLE IX

PLATEAU VOLTAGE (V) vs. KOH PERCENTAGE

Cycle	Cell No.		188	189	190	191	192	193	194	195
	Negative Design		KT Wrap				KT Fiber Mix			
	Current Density	Dischrg Rate	30%	35%	40%	45%	30%	35%	40%	45%
1	10 mA/cm^2	0.350 A	1.45	1.45	1.44	1.43	1.44	1.42	1.43	1.42
2	10 mA/cm^2	0.350 A	1.43	1.41	1.39	1.39	1.42	1.40	1.37	1.41
3	10 mA/cm^2	0.350 A	1.43	1.40	1.42	1.40	1.44	1.44	1.43	1.42
4	50 mA/cm^2	1.8 A	1.25	1.23	1.19	1.15	1.26	1.24	1.20	1.15
5	50 mA/cm^2	1.8 A	1.28	1.25	1.21	1.21	1.28	1.27	1.22	1.20
6	50 mA/cm^2	1.8 A	1.23	1.20	1.23	1.21	1.24	1.23	1.20	1.20
7	30 mA/cm^2	1.0 A	1.30	1.33	1.31	1.33	1.34	1.32	1.29	1.29
8	30 mA/cm^2	1.0 A	1.33	1.31	1.32	1.30	1.33	1.30	1.30	1.29
9	30 mA/cm^2	1.0 A	1.32	1.31	1.31	1.30	1.32	1.30	1.30	1.29
KOH Concentration			30%	35%	40%	45%	30%	35%	40%	45%

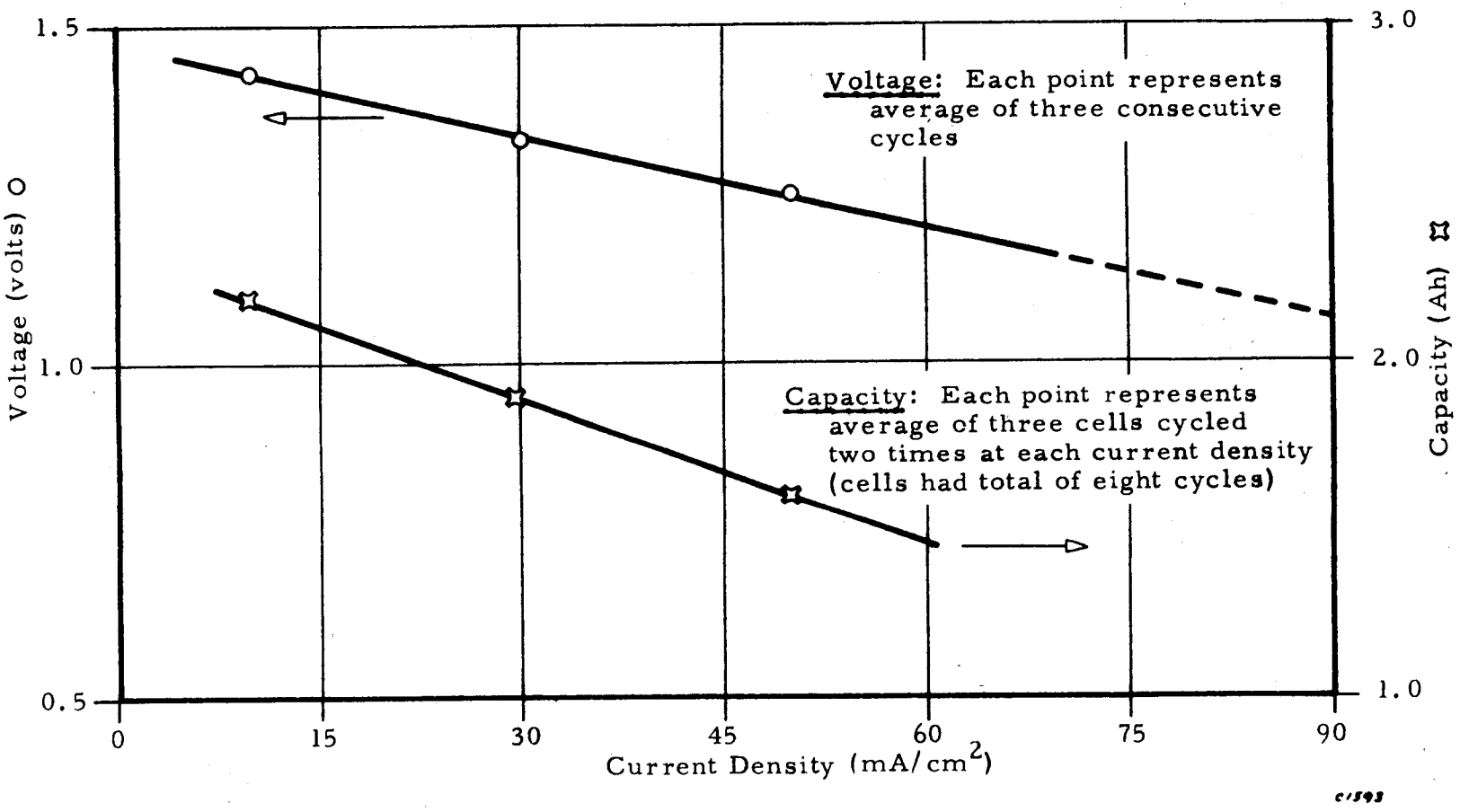

Figure 21. Average Plateau Voltage and Capacity vs. Current Density at 25°C

TABLE X

MULTIPLATE CELL TEST RESULTS

Type	Cell No.	Original Capacity Q_o (Ah)	Discharge				Temp °C	Number of Cycles
			Period (Hrs)	Rate (A)	Current Density (mA/cm^2)	Depth of Discharge (% of Q_o)		
Grooved Walls	MC-1	10.5	1 day	1.0	7	100	25	2
Grooved Frame in Big Case	MC-2	13.0	1/2|1/2	1.0	7	4	25	1165
	MC-3	9.3	1/2|1/2	2.0	20	8	25	427
Grooved Frame in Fabricated Case	MC-4	7.8	1/2|1/2	1.0	7	6.5	25	178
	MC-5	7.0	1 day	2.0	14	100	25	21
	MC-6	6.0	1/2|1/2	2.8	20	23	100	18
	MC-8	4.8	↓	1.0	7	10	25	97
	MC-9	5.0	↓	↓	↓	↓	25	102
	MC-10	5.1	↓	↓	↓	↓	25	435
	MC-11	4.5	↓	↓	↓	↓	100	60
	MC-12	4.7	↓	↓	↓	↓	100	67
Grooved Frame in Molded Case*	MC-13	4.9	1/2|1/2	1.0	7	10	25	178
	MC-14	5.3	↓	↓	↓	↓	↓	239
	MC-15	4.9	↓	↓	↓	↓	↓	239
	MC-16	5.0	↓	↓	↓	↓	↓	223
	MC-17	4.9	1 day	↓	↓	100	↓	8

*Tests in Progress

2.2.7.1 First Design

The case walls were grooved and the separators were cemented in place (MC-1 cell). This model was abandoned because of unreliability of the assembly.

2.2.7.2 Second Design

The case was made larger to permit use of a grooved frame to hold the separators and electrodes and the entire assembly was slipped into a smooth walled case (MC-2 and MC-3 cells). Because the capacity of these cells was greater than 10 Ah, it was decided to cut down the size of the cell to the normal dimensions of a 5 Ah package.

2.2.7.3 Third Design

In this design the fabricated cases and grooved frames were made smaller. The resulting cell capacity was in the order of 6 to 7 Ah (MC-4 through MC-12).

2.2.7.4 Fourth Design

Molded cases were used in these cells. This mechanical design and assembly will be maintained through the next phase and only internal cell pack designs will be varied, i.e., electrode pack configuration, in order to develop the best electrical performance. These tests have just been started and cells are now being cycled (MC-13 through MC-18).

In order to minimize growth of zinc vertically in the negative compartment, Teflon strips were inserted in the zinc cavity in the form of felt or microporous sheets. These concepts will be investigated further and the results reported as they are obtained.

After selection of the best design, five cells will be built and tested in accordance with "NASA Technical Directive No. 1," dated April 19, 1966.

2.3 Results and Conclusions

Test cells built using inorganic separators and the electrodes developed and evaluated in this program have been operated successfully at 30 ma/cm^2 current density at both 25° and $100^{\circ}C$. In these tests, 23 cells

were operated at 30 ma/cm^2 at 25°C and 25 cells at 100°C. This level of current density appears to be the upper limit at this stage of development of the cell configuration when operated on a fast (1/2-hour, 1-hour) cycle because of the problem related to recharging a cell in one hour at high rates. The electrodes and separators have demonstrated the capability for discharge at rates higher than 30 ma/cm^2, but partial recharge is the limiting factor.

Cell 139 has been operated for 2129 cycles at 10 ma/cm^2, confirming results previously reported as well as the long life capability of this system.

Difficulty has been encountered in using PPO for cases and frame components. Polysulfone appears to be a better material for these applications; satisfactory molded cases have been obtained and less distortion and warpage of frame parts has been observed. Much effort is being concentrated on the problem related to cases, frames and sealants in order to provide a stable assembly of cell components and to avoid leakage around separators due to frame warpage or sealant inadequacies.

The terminal design has been improved to allow the tabs to connect to the terminal without bending.

It has been found that no significant gassing occurs at room temperature on stand regardless of the state of charge of the cell. At 100°C, no gassing occurs as long as the cell is at the argenteous state of charge. On cycling, little gassing occurs at 25°C at current densities up to 20 ma/cm^2 on a 1/2-hour discharge, 1-hour charge regime. Less gassing occurs at 100°C on cycling than on stand at 100°C, because the cell is partially charged rather than fully charged most of the time.

It has been determined that KOH concentrations ranging from 30% to 45% can be used with this system. No significant difference in cell characteristics or performance were noted at the various concentrations listed.

Preliminary test models of several designs of multiplate cells have been fabricated and are being tested prior to fabricating multiplate test cells for evaluation.

The results obtained so far in this program show that the inorganic separators and electrodes used are capable of meeting the program requirements. Our efforts are now being largely devoted to resolution of case material, separator sealing and cell sealing problems and to finalizing multiplate cell design. Emphasis is also being placed on cell structural components such as the frames and techniques for sealing separators to frames in order to produce component assemblies that will prevent leakage from one electrode compartment to another or separator breakage due to warpage and distortion of the plastic frame.

3.0 WORK PLANNED

In the next quarter, it is anticipated that work will be concentrated on the construction and testing of multiplate 5 Ah cells.

After preliminary electrical tests to establish the internal cell pack design, the five cells of the selected electrochemical design will be constructed and tested as per NASA Technical Directive No. 1, dated April 19, 1966, calling for screening tests, for leakage, pressure, capacity, heat soak, internal resistance and stand.

After review of the data, eight cells will be built and tested as described in Task II, paragraph 7, for environmental performance (shock, vibration, acoustic noise, acceleration), temperature cycling and electrical testing.

Work during the period will emphasize assembly and structural considerations and sealing techniques.

4.0 PERSONNEL

A total of 8394 engineering hours have been expended on this project as of April 24, 1966. The personnel who have worked on this project and the approximate percentage of their time devoted to this program are as follows:

Dr. C. Berger	No direct charge
F. C. Arrance	100%
A. Himy	50%
A. Rosa	100%
Q. McKenna	100%
R. Sheridan	50%
H. Smith	100%

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