NASA CR-965

INORGANIC SEPARATOR FOR A HIGH TEMPERATURE SILVER-ZINC BATTERY

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FOREWORD

The work described herein was done at the Astropower Laboratory, Missile and Space Systems Division, Douglas Aircraft Company, under NASA Contract NAS 3-7639 with Mr. D. G. Soltis, Space Power Systems Division, NASA-Lewis Research Center, as Technical Manager. The report was originally issued as Douglas report SM-48461-F, June 1967.

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1.0 INTRODUCTION AND SUMMARY

1.1 Douglas Battery Research and Development

Since 1962, Astropower Laboratory, Missile & Space Systems Division, Douglas Aircraft Company, has conducted research and development programs related to high energy density batteries. The silver-zinc system has been given particular emphasis in this work because of its high energy density per unit weight and volume. Use of silver-zinc batteries in space, military and commercial applications has been limited, however, because of short cycle life, inability to withstand repeated deep discharges, and temperature sensitivity which limits their application to the normal ambient range (Reference 5). Because the shortcomings of presently available silver-zinc cells are basically related to the cellophane and other plastic separators used in their construction (Reference 6), our work has emphasized the development and evaluation of inorganic separators. The broad objectives of these programs include long cycle life at both ambient and elevated temperatures, capability for repeated deep discharge, capability for a large number of total discharges, long wet stand capability over a broad temperature range, and improved charge retention.

1.2 NASA-Lewis Program, NAS 3-6007

Based upon the promising preliminary results obtained in Douglas proprietary programs (References 2, 3, and 7), Contract NAS 3-6007, "Program to Develop an Inorganic Separator for a High Temperature Silver-Zinc Battery," was established by NASA-Lewis in 1965 (Reference 1). The purpose of this program was to evaluate the Astroset inorganic separators in the temperature range 25° to 100° C and to determine cell characteristics at 25°, 50°, 100° and 150° C. Test cells fabricated completed more than 2700 cycles at 25° C and 2280 cycles at 100° C at 20 mA/cm^2 current density and 20% depth of discharge.

1.3 NASA-Lewis Program NAS 3-7639

Having demonstrated the feasibility of using Astroset inorganic separators in silver-zinc test cells, Contract NAS 3-7639, "Program to Develop an Inorganic Separator for High Temperature Silver-Zinc Batteries," was initiated by Lewis Research Center on 29 July 1965. The objectives of this program were to design a multiplate 5-Ah cell based on the inorganic separators and electrodes given preliminary evaluation in NAS 3-6007, to fabricate, test and evaluate cell components and cycle test and characterize 5-Ah multiple plate cells built from these components. At the conclusion of the program, ten, 5-Ah cells were to be delivered to NASA-Lewis Research Center.

The objectives described in the work statement have been satisfactorily accomplished and thirty-five 5-Ah cells were constructed for cycle testing and characterization in Task III of this program. So far,

ten of the group of fifteen cells being tested at 25° C at 20 mA/cm^2 current density have completed 2300-2950 cycles. A second group of ten cells has completed 1100-2200 cycles at 30 mA/cm^2. A third group of ten cells completed 400-591 cycles at 30 mA/cm^2 at 100° C. It should be noted that the cycle life performance demonstrated by these 5-Ah cells at both room temperature and 100°C far exceeds that of any other silver-zinc cells presently available. Although not a direct objective of this program, the components used in fabricating these 5-Ah cells have also demonstrated the capability to survive thermal sterilization at 145°C. This capability is of significant value in extending the operating temperature of these cells beyond 100°C, and for use in batteries which must be heat sterilized for specific mission applications. The work done in this program has clearly demonstrated the value of this type of construction, and the effectiveness of practical, multiple plate cell designs employing Astroset inorganic separators. Additional work should now be done related to improving electrode compartment seals, electrodes, and cell sealing for long range operation at 25° and 100°C.

2.0 TECHNICAL DISCUSSION

2.1 Task I – Design of a Multiplate Five Ampere-Hour Cell

The work statement stipulated that Astropower Laboratory design a multiplate cell comparable to a conventional 5 ampere-hour cell on a weight, capacity, power and volume basis. It was understood, however, that the design principles used in conventional cells are based upon organic separator technology which is inadequate for cells using inorganic separators and capable of long cycle life at elevated temperatures. The multiplate cell design was based on electrodes and other components previously evaluated in NASA Contract NAS 3-6007 by Astropower Laboratory. The multiplate cell design had the following physical characteristics as ultimate design objectives:

Maximum weight filled	4.6 ounces $^{+0.4 \text{ ounces}}_{-0.0 \text{ ounces}}$
Volume	4.78 cubic inches
Height	2.91 inches
Width	2.08 inches
Depth	0.79 inch

These specific dimensions were for general guidance only and could be changed for design purposes because an optimized cell was not an objective of this program.

During the investigation, several multiplate 5 ampere-hour design concepts were studied. These designs were based on Astroset inorganic separators and novel methods of separator and electrode packaging as contrasted to conventional cell designs using plastic separators.

The basic multiplate cell designs were detailed and thoroughly analyzed for (1) ease and simplicity of fabrication and assembly, (2) provisions for adequate quality control, (3) adequate and positive sealing, (4) reproducibility, (5) capability of withstanding environmental requirements, (6) simple and effective means of activation, and (7) use of materials and processes which are presently available. Particular attention was placed on Item 7 because the availability of materials capable of withstanding operation at 100°C for extended periods of time and the extreme corrosive characteristics of hot potassium hydroxide is limited and little applicable testing data are available.

The analysis of multiplate cell designs indicated that the groove type design provided the best initial approach to the problems of cell assembly, fabrication, sealing, reproducibility, and material availability. Figure 1 is a perspective view of the grooved cell case. Astroset inorganic separators were individually inserted into the slots in the cell case and sealed in place. The silver and zinc electrodes were then placed into their

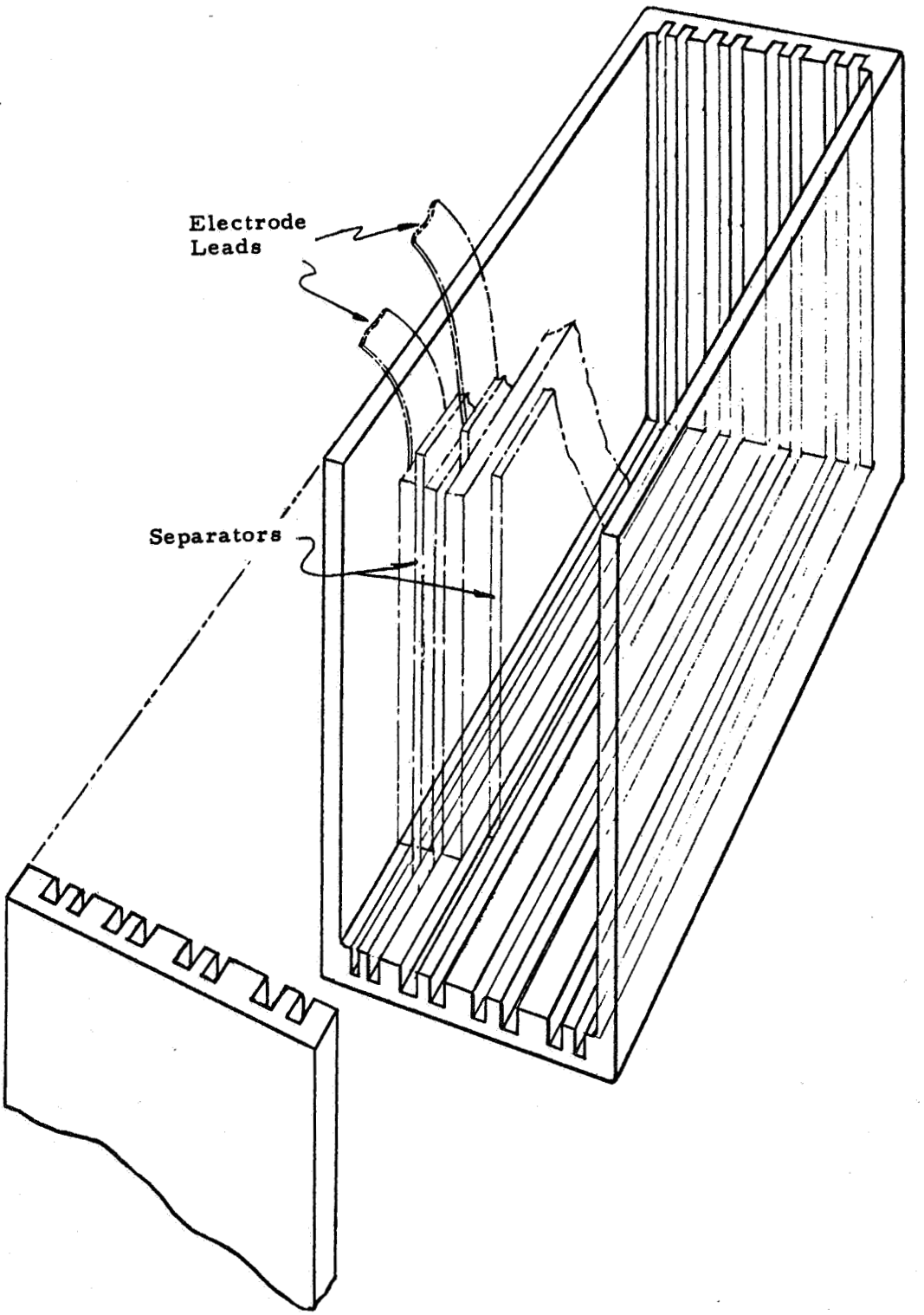


Figure 1. Groove Type Design.

compartments between the separators. The electrode tabs were fastened to the terminals in the cover assembly. A flexible, high temperature KOH absorbent organic material was then sealed over the top of each electrode to compartmentalize the electrodes. After sealing the cover to the case, the cell was activated through the port in the cover and the port is sealed with a cap or plug.

The advantages of the groove type design are –

1. that grooved case can be fabricated to close tolerances by means of accurate molds,
2. that the inorganic separators can be inserted into the grooves and sealed in place by an appropriate cement,
3. that quality control measures including inspection can be performed on each component prior to the assembly,
4. that positive electrode compartmentalization and separator sealing can be accomplished,
5. that reproducibility of the inorganic separators, electrodes, cases and terminal-cover assemblies can be assured,
6. that separators and electrodes are firmly positioned within the cell case thereby providing adequate protection against mechanical environments,
7. that the design permits simple and adequate activation procedures, and
8. that basically all materials used in this design are within the present state-of-the-art and are available from industry.

A modification of this design improving the assembly and inspection methods was proposed by the Project Officer. The modification provided a grooved frame consisting of two sides and a base into which the inorganic separators were inserted and sealed in place, thereby providing a positive means of quality control testing and inspection. The electrodes were then inserted between the separators followed by an additional inspection. The three-sided separator-electrode frame assembly was then inserted into the cell case and cemented to the inside mating surfaces of the cell case. The remaining assembly procedures are the same as described for the original groove type design. Figure 2 shows this design concept.

A model multiplate cell incorporating this design was fabricated for verification of the assembly advantages. After cementing the separators in the grooves of the bottom and side plastic pieces, the electrodes were inserted and the electrode pack assembly was inserted into a smooth-wall case and the cover was finally cemented to the case. There was no difficulty in the assembly of this design.

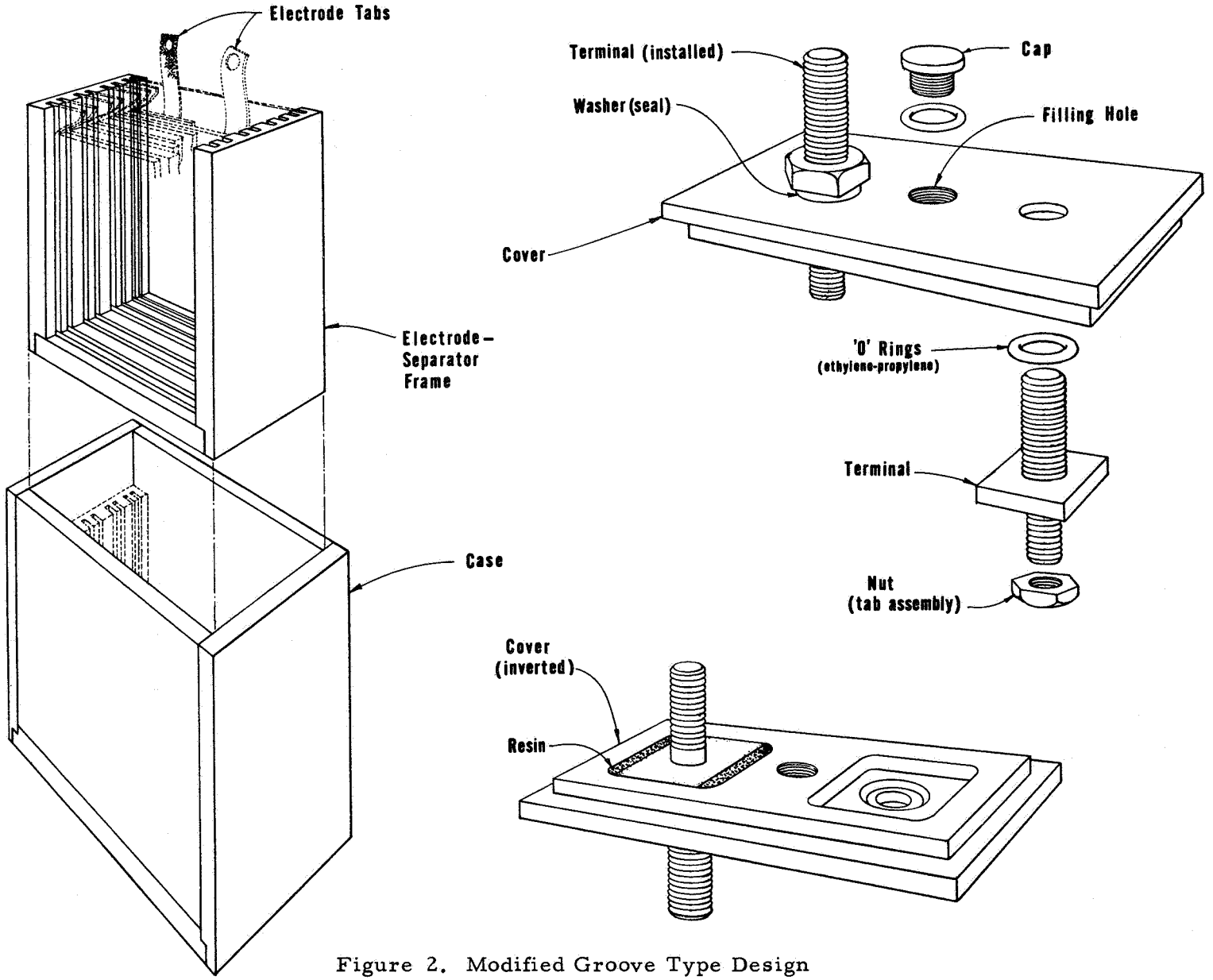


Figure 2. Modified Groove Type Design

The detailed assembly procedure was as follows:

1. Cell Case – The case walls and bottom are sealed together on a mandrel. The case material used is PPO. Chloroform or a 10 to 20% PPO solution in chloroform was used as the cement. The case assembly is dried at room temperature under light pressure. After air drying, the assembly is baked in an oven at 60 to 70°C to eliminate solvent traces. The assembled case is then tested for gas leakage at 5 psi pressure and for KOH leakage by filling the case with 45% KOH and letting it stand for 24 hours at 100°C. The case assembly is accepted for use if it passes these tests without leaking.

2. Frame – The frame consists of three parts – two sides and one bottom. The three parts have aligned grooves. The separators are assembled by cementing them into the frame grooves. The spacings between separators are then checked with feeler gages to insure ease of electrode insertion.

3. Cover – The terminals are assembled to the cover with Shell Resin 901/B-3 which has proven to be leak proof at temperatures ranging from -30°C to 150°C.

4. Plates – The electrode plates are fabricated with the connector tabs cut to length and punched at the proper location for attachment to the terminal base. Positive plates are prepared from Handy and Harmon Silpowder 130. Negative plates are prepared from a mixture of 98% ZnO and 2% HgO and are wrapped in KT paper approximately 20 mils thick.

5. Assembly – The plates are then slipped into their respective cavities. The positive plates are wrapped in a "U" of absorbent material that serves as an electrolyte retainer. The punched connector tabs are attached to the cell terminals. Finally, the entire assembly is inserted in the case and the cover is sealed in place.

6. Valve – A valve is used as a means of sealing the cell temporarily until more data are obtained on gassing characteristics and the magnitude of pressure build up encountered during operation at 25° and 100°C.

The modified groove design was used during the early preliminary multiplate cell design evaluation portion of the program (Section 2.2.1.5). However, due to dimensional instability of the frame materials during cycle testing a modified frame design was adapted. This design is discussed in Section 2.1.3.

2.1.1 Molded Cases

To expedite the work on this contract, a survey of existing molds which might be available from several battery manufacturers

was made. A case was selected that closely approximated the dimensions of the fabricated cases described above. One hundred of these cell cases molded from PPO were ordered.

These cases were approximately the same size as the cemented case assemblies, except for their height which was cut down to the desired size. The first molded cases obtained had a wall thickness of only 0.062 inch. This was found to be too thin for the 5 ampere-hour multi-plate cell, because the side walls bulged appreciably at 20 psi internal pressure. They were suitable, however, for use in developing the assembly technology and for electrical testing of unsealed cells. Based on studies of gassing rates and other tests, the wall thickness required for these cells was established and thicker-walled cell cases were then obtained for mechanical testing. This work is discussed in detail in Section 2.2.3 of this report.

2.1.2 Plastic Frames

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

Type E frames were 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 cementing together machined parts, the groove depth and frame thickness could both be increased slightly to increase the mechanical stability of the separator-frame assembly. Deepening the frame grooves allowed the inorganic separator to be inserted more deeply into the frames, which was also an advantage. This improved sealing the separators to the frames and prevented leakage around the separator through the grooves which could cause shorting.

2.1.3 Modified Frame Design

Although the rigid frame design proved to be satisfactory for use in Task II of this program for evaluating cell components, problems of dimensional instability of the frame materials were encountered at 100°C in contact with KOH. The resulting frame warpage caused leakage around the separators or separator cracking, depending on the nature of the sealant, resulting in interelectrode shorting. Accordingly, the original frame design was modified as shown in Figures 3 and 4.

This design is comprised of negative electrode compartment subassemblies assembled from two Astroset separators using epoxy cement and special Teflon tape frames. A Teflon tape collar is cemented to the top of each assembly to assure interelectrode separation and to prevent zinc bridging. Figures 5 and 6 are photographs of the final design adopted, and later used in the Task III cells in this program.

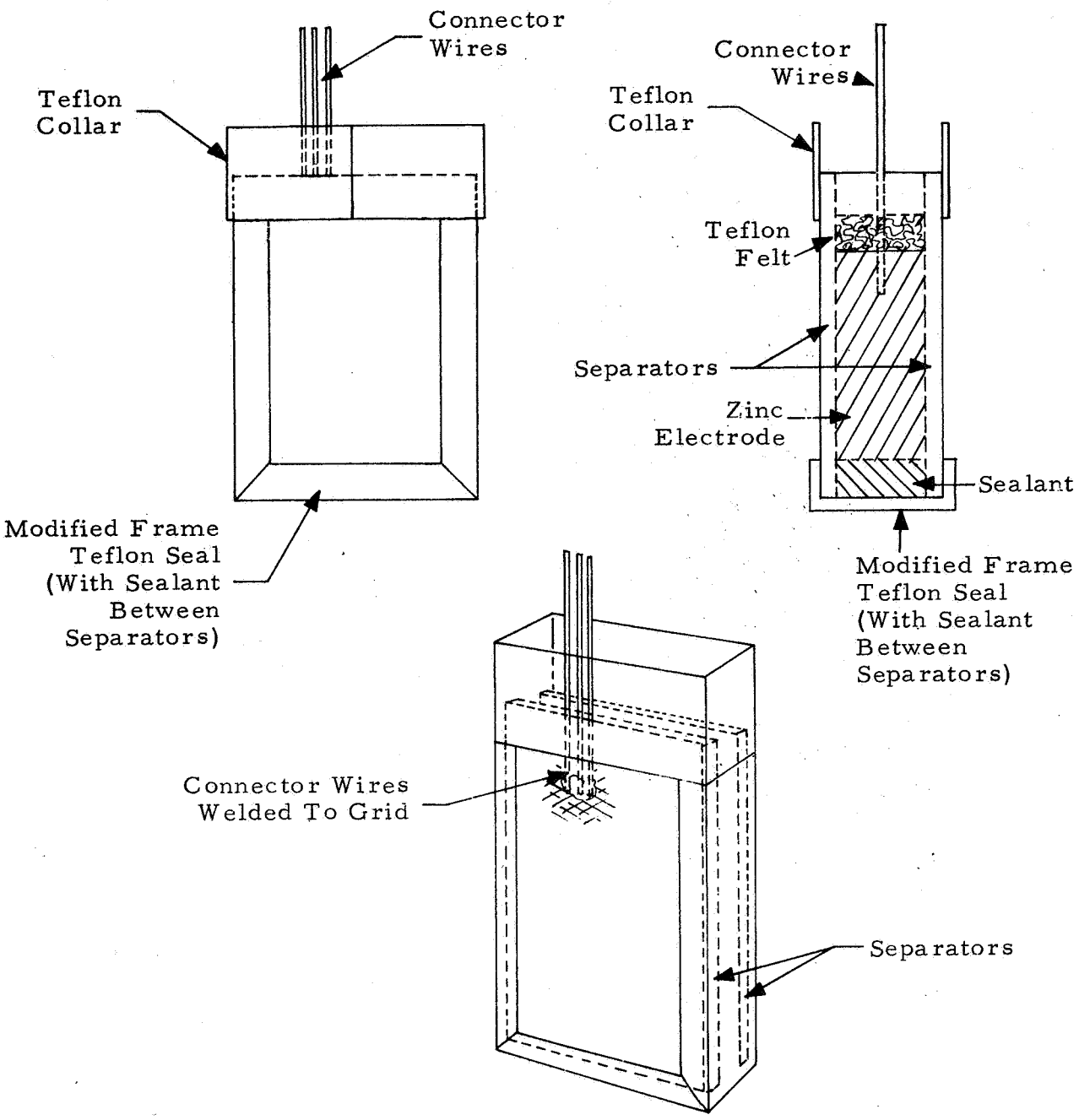


Figure 3. Negative Compartment

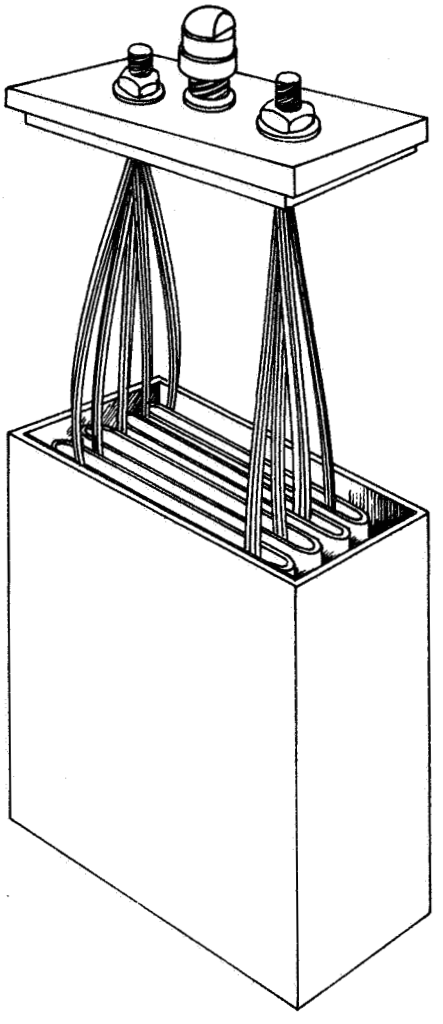


Figure 4. 5 Ah Multiplate Cell and Hardware

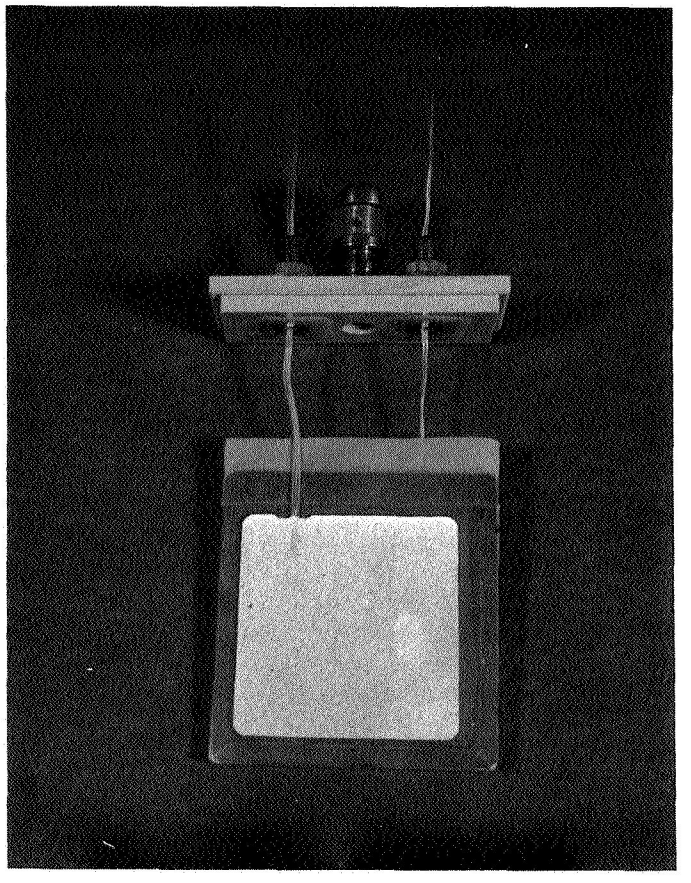


Figure 5. 5 Ah Cell Components Prior to Assembly

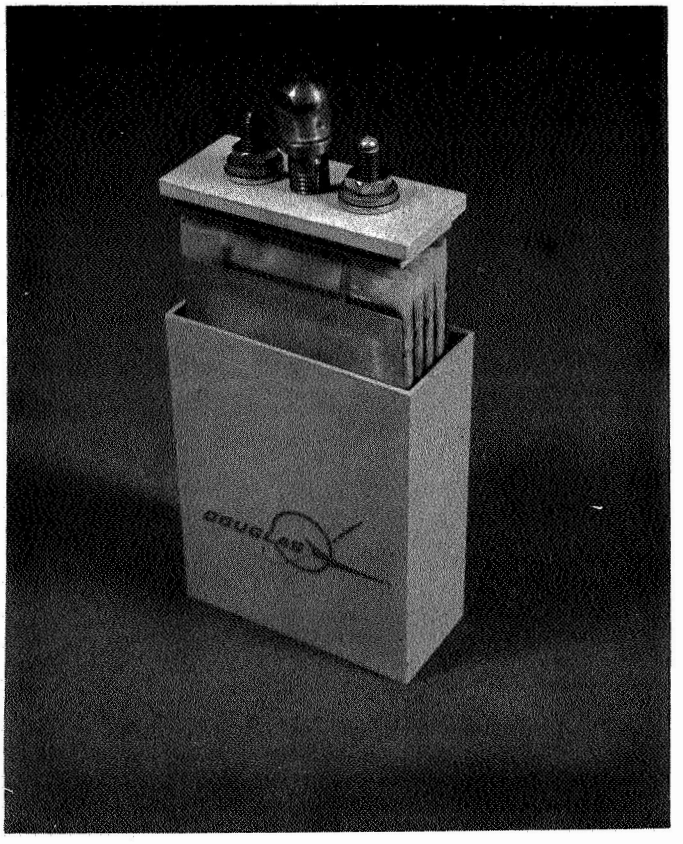


Figure 6. 5 Ah Multiplate Cell Assembly

Thirty-five 5 ampere-hour cells, fabricated in accordance with this modified frame design, were cycle tested as described in detail in Section 2.3 of this report. These cells are capable of 2458 cycles at 25°C at 20 mA/cm^2 on a 1/2-hour, 1-hour discharge-charge regime; 2036 cycles at 30 mA/cm^2 at 25°C on the same regime, and 591 cycles at 30 mA/cm^2 at 100°C. This performance is substantially better than that of any silver-zinc cells presently available.

Ten cells of the same design were also fabricated and delivered to NASA-Lewis as required by the contract.

2.2 Task II – Fabrication, Testing and Evaluation of Cell Components

The objective of Task II was to fabricate the various cell components in accordance with the cell design established in Task I and to test and evaluate them in accelerated screening tests. These tests were run in test cell fixtures similar to those used during the initial work on this battery under Contract NAS 3-6007. The tests were run in a secondary mode using 140 cycles as a cut-off on a 1/2-hr, 1-hr cycle regime at 100°C. The materials and components were also tested for use at 150°C in a caustic atmosphere. Each component was developed to the point where it could be incorporated into 5 ampere-hour cells.

2.2.1 Electrodes

The electrodes used in Task II were selected from those tested in the previous contract (Reference 1) which demonstrated satisfactory operation in test cells on a 1/2 x 1/2 hr cycle regime at 20 to 30 ma/cm^2 at 100°C. They were designed to insure intimate contact with the current collector and easy assembly into the cell.

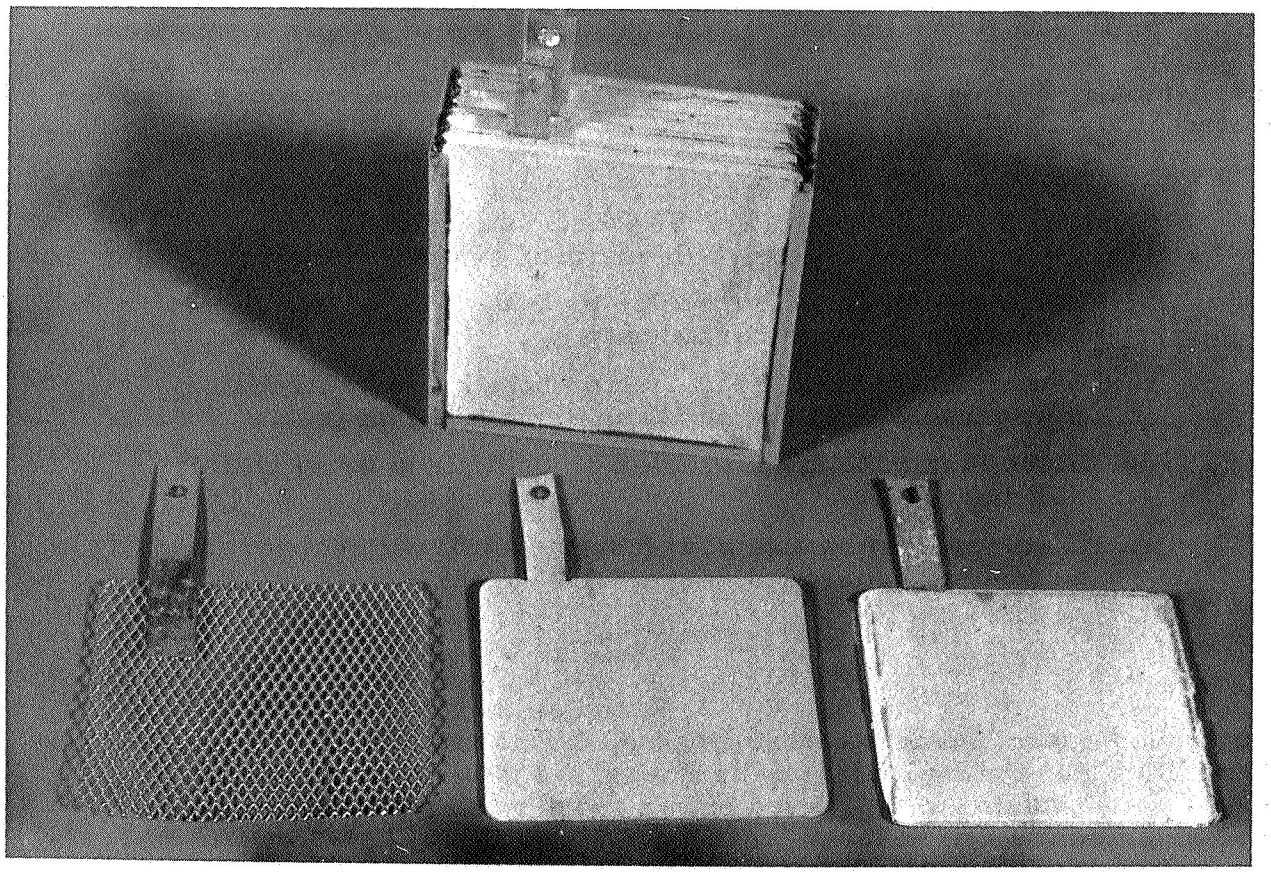
The electrodes selected for evaluation were submitted to screening tests which included cycle testing at room temperature and 100°C. Tests were also made to evaluate methods of attaching the terminal connector to the current collector followed by thermal degradation tests at 150°C for 100 hours to determine the stability of the electrodes in KOH. Optimization of the electrodes for 150°C operation was outside the scope of this contract.

Test electrodes were cycle tested at 25°C and 100°C on a 1/2-hour, 1-hour regime at various current densities using 140 cycles as the cut-off criterion.

After selecting the electrodes for the Task III cells, the fabrication techniques and assembly methods used were reviewed by the NASA Project Officer and approved.

2.2.1.1 Electrode Fabrication

Electrode fabrication was covered by process specifications requiring rigid quality control and insuring reproducibility. These electrodes were pressed in a die to the specified thickness and controlled to ±0.001 inch. Figure 7 shows typical electrodes used in these evaluations. The weight of these electrodes was controlled to ±2.5%. Early electrodes used in Task II were fabricated using expanded silver metal current collectors with a silver strip spot-welded to the grid. Dimensions of the grid location of the terminal connector are specified. Initially, the positive plates used 50% silver, 50% silver I oxide as the active material, and the negative plates incorporated polyvinyl alcohol as a binder. However, the final formulation of these electrodes was:



1. Positive
2. Negative

Figure 7. Multiplate Electrode and Separator Assembly

Positive: 100% silver powder, pressed and sintered.

Negative: 98% zinc oxide, 2% HgO with KT paper pressed into both sides of the electrode.

2.2.1.2 Tests

A. Thermal Degradation of Electrodes

Silver and zinc electrodes were submitted to 35% KOH for 100 hours at 100°C to determine their mechanical stability. See Figures 8, 9 and 10. Silver electrodes were unaffected mechanically by this test. The following types of zinc electrodes were tested:

a. Unsupported electrode: Standard formulation
98% ZnO and 2% HgO
More than 60% of the material disappeared

b. Same electrode (a) supported on both sides by KT paper.
Less than 15% was corroded.

c. Same electrode (a) supported on both sides by Asbestos.
More than 60% of the active material disappeared.

d. Same electrode (a) supported on both sides by nylon felt.
50% corroded.

e. Electroplated sponge zinc (commercial) with copper support.
Completely corroded, except for copper.

B. Cycling

Based on these findings, Type "b" electrodes described above were selected for use in test cell cycle tests in Task II and for the multiplate cells during the latter part of this program. Silver plates made from pressed silver powder followed by sintering were also selected for use in these tests.

A set of 30 cells were manufactured under strict specifications to determine their capability under six sets of conditions (five cells per variation):

At 25°C	20 ma/cm^2	35 ma/cm^2	50 ma/cm^2
At 100°C	20 ma/cm^2	35 ma/cm^2	50 ma/cm^2

A new case for single electrode testing was designed and fabricated (see Figure 11). This cell consists of a grooved, 3-sided frame which can hold one or two separators, so that cells could be tested having either one positive electrode and one negative electrode or one positive electrode and

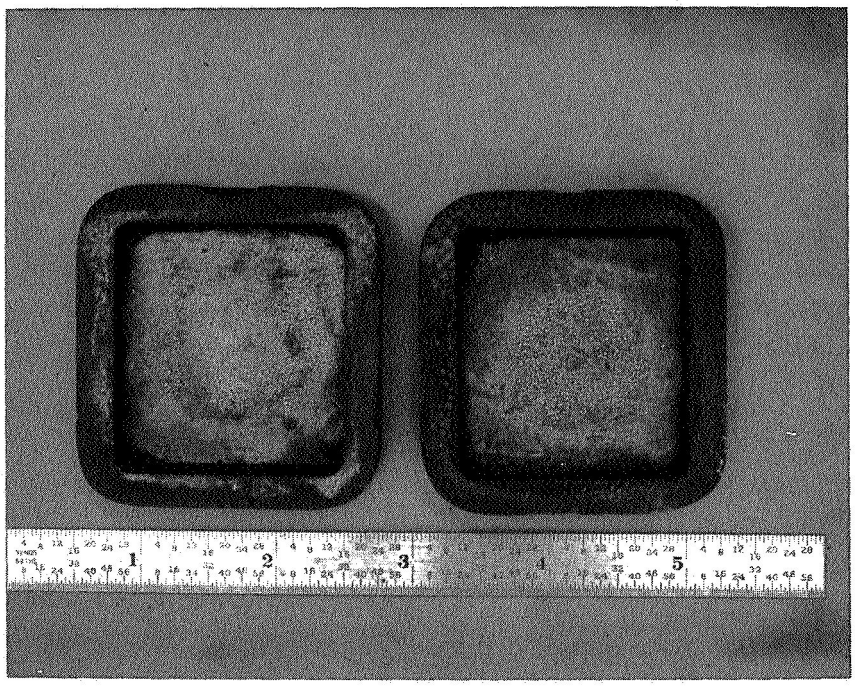
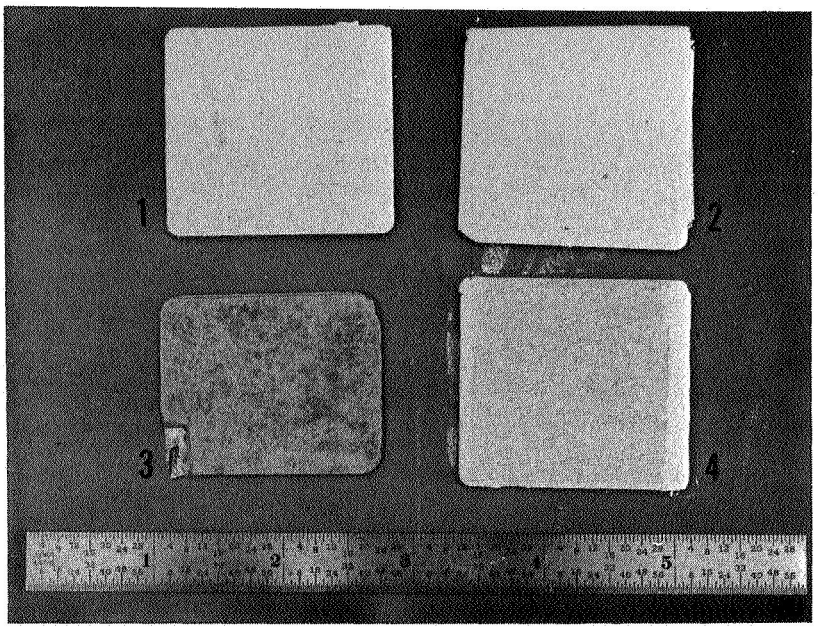
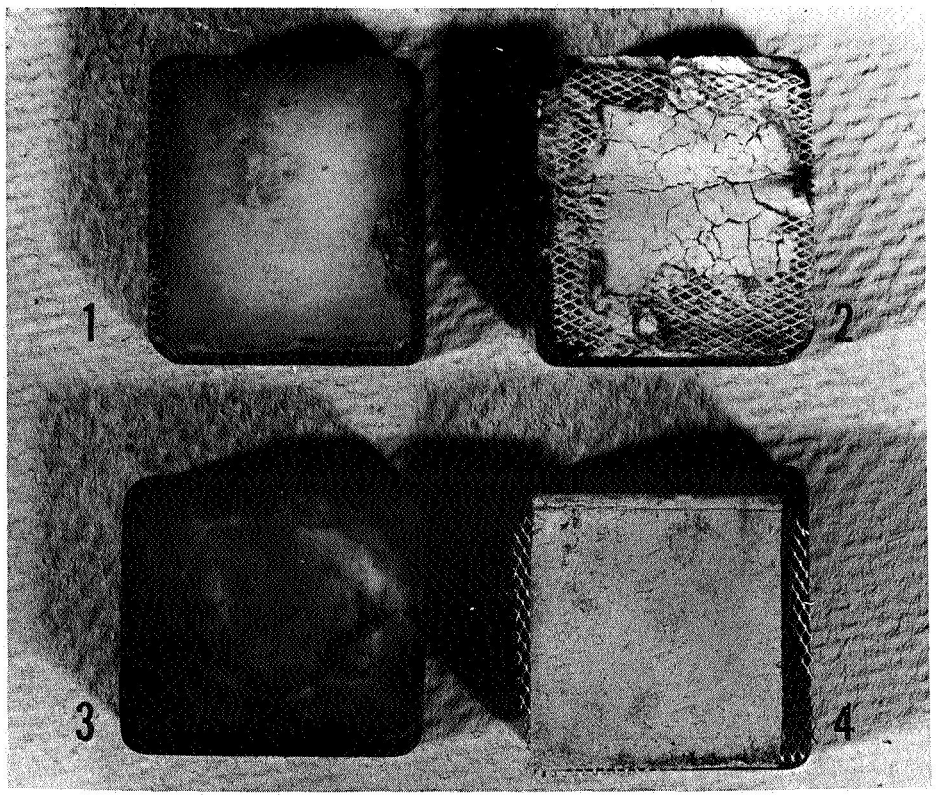


Figure 8. Silver Electrodes After Thermal Degradation Test



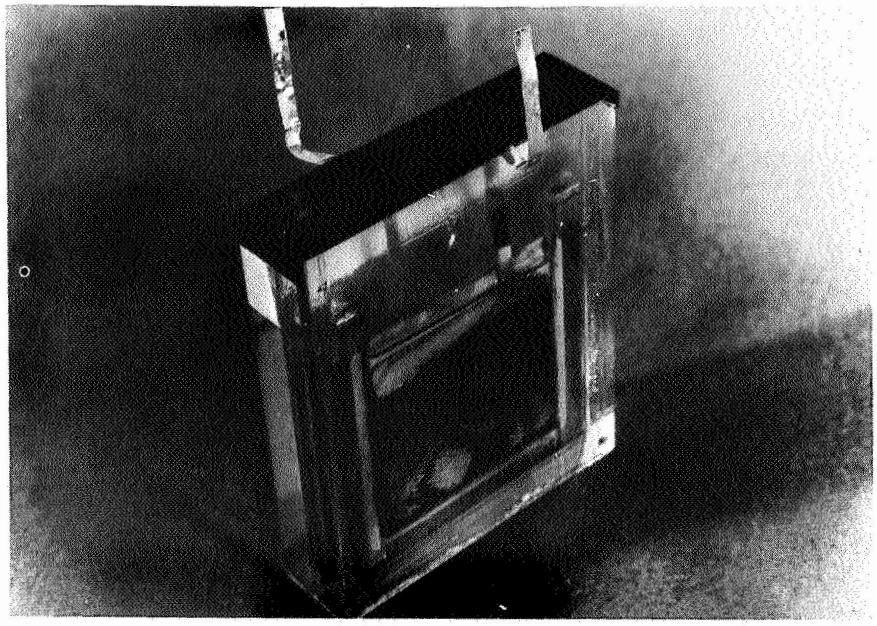
1. Zinc Electrode Potassium Titanate NSM
2. Zinc Electrode Pellon Support
3. Sintered Silver Electrode No NSM
4. Zinc Electrode Asbestos NSM

Figure 9. Electrodes Before Thermal Degradation Test (NSM = Network Support Material)



1. Zinc Electrode, Potassium Titanate NSM
2. Zinc Electrode, Pellon Support
3. Sintered Silver Electrode, No NSM
4. Zinc Electrode, Asbestos NSM

Figure 10. Electrodes After Thermal Degradation Test (NSM = Network Support Material)



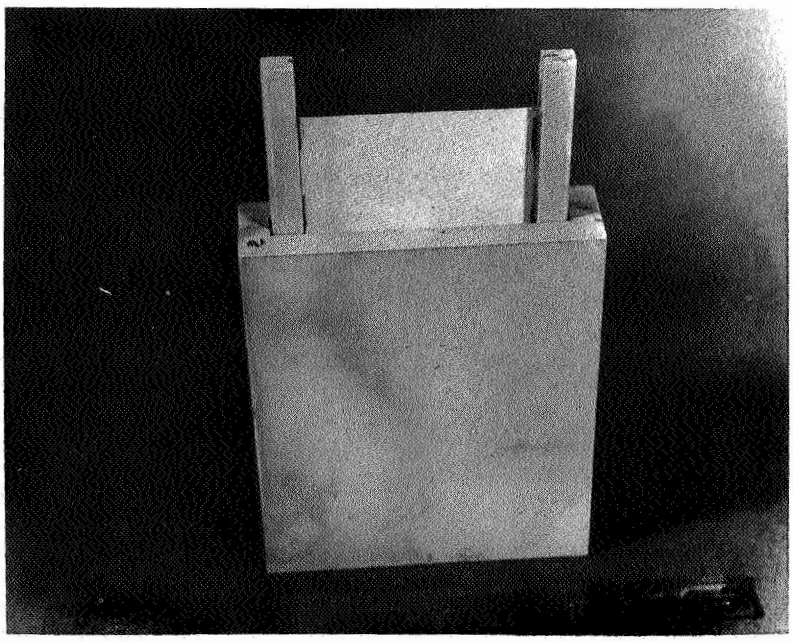


Figure 11. Single-Electrode Test Case

two negative electrodes. This approach guided the electrochemical development of the electrodes toward the multiplate configuration.

Typical test results obtained with the single compartment test cells are summarized in Table I. These results encompass 57 test cells, the majority of which successfully completed the required 140 cycles at both 25°C and 100°C.

Table II provides a description, including case material and electrode formulations, of single compartment test cells assembled for the various tests planned. Fourteen test cells were not placed on cycle test due to unsatisfactory performance during cell formation. These 14 test cells were assembled without Network Support Material (NSM) in the zinc electrode to determine the effect on cell performance in the new configuration. The results clearly demonstrate that the use of NSM is essential to satisfactory cell operation.

The electrode test cell results shown in Table I indicate that 19 cells completed the required 140 cycles at 25°C and 18 cells completed 140 cycles at 100°C. These cycle tests were run on Test Cell No. ESC-0077 completed 125 cycles at 100°C after which its capacity began to decline. Upon disassembly of the cell, it was found that the zinc electrode had expanded excessively within the electrode compartment and had broken the separator.

Test Cell No. ESC-0046, ESC-0069, ESC-0073 and ESC-0098 completed 140 cycles at 100°C on a 30-minute discharge at 35 ma/cm^2 current density and a 60-minute charge at 19 ma/cm^2 current density cycle. Figure 12 shows charge-discharge curves at 100°C for the 100th and 140th cycles on Test Cell No. ESC-0046. Four test cells also completed 140 cycles at room temperature on the same test schedule. Test Cell No. ESC-0091 completed 116 cycles at 100°C when it was removed from test for the reason given for Test Cell No. ESC-0077.

Test Cell No. ESC-0078 completed 129 cycles at 100°C. Figure 13 shows the voltage curves for the 25th and 100th cycles. This test cell was cycled at 50 ma/cm^2 discharge current density and 27 ma/cm^2 charging current density on a 1/2-hour discharge, one-hour charge test schedule. The first and 50th cycle charge-discharge curves for Test Cell No. ESC-0045 at 100°C are shown in Figure 14. The test schedule was the same as for Test Cell No. ESC-0078. After 56 cycles were completed at this current density, cell case leakage developed and the test was stopped. Two additional test cells which were cycled at 50 ma/cm^2 discharge current density at 100°C completed 70 and 83 cycles before the tests were discontinued; these were Test Cells Nos. ESC-0089 and ESC-0099.

TABLE I

ELECTRODE TEST CELL CYCLE TEST RESULTS,
REGIME: 1/2 HOUR DISCHARGE/1 HOUR CHARGE

Test Cell No.	Test Temp.	Current Density Discharge (ma/cm^2)	Current Density Charge (ma/cm^2)	Number of Cycles Completed	Remarks
ESC-0016	25°C	20	14	140	Completed Cycle Test
ESC-0018	25°C	20	14	140	Completed Cycle Test
ESC-0019	25°C	20	14	140	Completed Cycle Test
ESC-0020	25°C	20	14	140	Completed Cycle Test
ESC-0023	25°C	20	14	140	Completed Cycle Test
ESC-0027	25°C	20	14	140	Completed Cycle Test
ESC-0033	25°C	20	14	140	Completed Cycle Test
ESC-0037	25°C	20	14	140	Completed Cycle Test
ESC-0039	25°C	20	14	140	Completed Cycle Test
ESC-0043	25°C	20	14	140	Completed Cycle Test
ESC-0051	25°C	20	14	140	Completed Cycle Test
ESC-0056	25°C	20	14	140	Completed Cycle Test
ESC-0057	25°C	20	14	140	Completed Cycle Test
ESC-0064	25°C	20	14	140	Completed Cycle Test
ESC-0065	25°C	20	14	140	Completed Cycle Test
ESC-0071	25°C	20	14	140	Completed Cycle Test
ESC-0074	25°C	20	14	140	Completed Cycle Test
ESC-0075	25°C	20	14	140	Completed Cycle Test
ESC-0076	25°C	20	14	140	Completed Cycle Test
ESC-0026	100°C	20	14	140	Completed Cycle Test
ESC-0028	100°C	20	14	140	Completed Cycle Test
ESC-0030	100°C	20	14	140	Completed Cycle Test
ESC-0032	100°C	20	14	140	Completed Cycle Test
ESC-0034	100°C	20	14	140	Completed Cycle Test
ESC-0035	100°C	20	14	140	Completed Cycle Test
ESC-0038	100°C	20	14	140	Completed Cycle Test
ESC-0040	100°C	20	14	140	Completed Cycle Test
ESC-0042	100°C	20	14	140	Completed Cycle Test
ESC-0047	100°C	20	14	140	Completed Cycle Test

(Continued)

TABLE I (continued)

ELECTRODE TEST CELL CYCLE TEST RESULTS,
REGIME: 1/2 HOUR DISCHARGE/1 HOUR CHARGE

Test Cell No.	Test Temp.	Current Density Discharge (ma/cm^2)	Current Density Charge (ma/cm^2)	Number of Cycles Completed	Remarks
ESC-0049	100°C	20	14	140	Completed Cycle Test
ESC-0060	100°C	20	14	140	Completed Cycle Test
ESC-0062	100°C	20	14	140	Completed Cycle Test
ESC-0063	100°C	20	14	140	Completed Cycle Test
ESC-0066	100°C	20	14	140	Completed Cycle Test
ESC-0067	100°C	20	14	140	Completed Cycle Test
ESC-0068	100°C	20	14	140	Completed Cycle Test
ESC-0077	100°C	20	14	125	Zinc electrode expanded
ESC-0082	100°C	20	14	140	Completed Cycle Test
ESC-0081	25°C	35	19	140	Completed Cycle Test
ESC-0084	25°C	35	19	140	Completed Cycle Test
ESC-0092	25°C	35	19	140	Completed Cycle Test
ESC-0105	25°C	35	19	140	Completed Cycle Test
ESC-0046	100°C	35	19	140	Completed Cycle Test
ESC-0069	100°C	35	19	140	Completed Cycle Test
ESC-0073	100°C	35	19	140	Completed Cycle Test
ESC-0091	100°C	35	19	116	Zinc electrode expanded
ESC-0098	100°C	35	19	140	Completed Cycle Test
ESC-0083	25°C	50	27	140	Completed Cycle Test
ESC-0090	25°C	50	27	91	Zinc electrode expanded
ESC-0094	25°C	50	27	140	Completed Cycle Test
ESC-0097	25°C	50	27	140	Completed Cycle Test
ESC-0102	25°C	50	27	140	Completed Cycle Test
ESC-0045	100°C	50	27	56	Electrodes dried out due to case leakage. Zinc electrode passivated — dark blue color. Separator and silver electrodes appear satisfactory.

(Continued)

TABLE I (continued)

ELECTRODE TEST CELL CYCLE TEST RESULTS,
REGIME: 1/2 HOUR DISCHARGE/1 HOUR CHARGE

Test Cell No.	Test Temp.	Current Density Discharge (ma/cm^2)	Current Density Charge (ma/cm^2)	Number of Cycles Completed	Remarks
ESC-0078	100°C	50	27	129	Zinc electrode expanded
ESC-0079	100°C	50	27	29	Zinc electrode expanded
ESC-0089	100°C	50	27	70	Zinc electrode terminal wire became loose
ESC-0099	100°C	50	27	83	Zinc electrode expanded

TABLE II

ELECTRODE TEST CELL CONSTRUCTION

Cell Number	Case Material	Terminal	Electrode Formulation (Neg)					Grid Location (Neg)			KT Paper			Pressing	Comments
			PVA %	Dextrose %	None	ZnO %	HgO %	Center	In Back	Type Exmet	Yes	No	Other	Load (tons)	
ESC-0001	Celcon	Exmet	4.5			90.3	5.2	X		3/0		X		15	Note: All silver electrodes were standard, i.e. 50/50 Ag/Ag_2O 3/0 Exmet-2 sided EXCEPT where noted in this "comments" column
ESC-0002	Penton	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0003	Celcon	Exmet		4.5		90.3	5.2	X		3/0		X		15	
ESC-0004	Penton	Exmet		4.5		90.3	5.2	X		3/0		X		15	
ESC-0005	Penton	Exmet		4.5		90.3	5.2	X		3/0		X		15	
ESC-0006	Celcon	Exmet		4.5		90.3	5.2	X		3/0		X		15	
ESC-0007	Alphalux 400	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0008	Alphalux 400	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0009	Alphalux 400	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0010	Alphalux 400	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0011	Alphalux 400	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0012	Alphalux 400	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0013	Alphalux 400	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0014	Penton	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0015	Penton	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0016	Penton	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0017	Penton	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0018	Celcon	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0019	Penton	Exmet	4.5			90.3	5.2	X		3/0		X		(-32+80)15	
ESC-0020	Celcon	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0021	Alphalux 400	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0022	Alphalux 400	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0023	Alphalux 400	Exmet	4.5			90.3	5.2	X		3/0		X		15	

(Continued)

TABLE II (continued)

ELECTRODE TEST CELL CONSTRUCTION

Cell Number	Case Material	Terminal	Electrode Formulation (Neg)					Grid Location (Neg)			KT Paper			Pressing Load (tons)	Comments
			PVA %	Dextrose %	None	ZnO %	HgO %	Center	In Back	Type Exmet	Yes	No	Other		
ESC-0024	Celcon	Exmet	4.5			90.3	5.2	X		3/0		X		-32+80(15)	
ESC-0025	Penton	Exmet	4.5			90.3	5.2		X	6/0		X		15	
ESC-0026	Penton	Exmet	4.5			90.3	5.2		X	6/0		X		15	
ESC-0027	Penton	Exmet	4.5			90.3	5.2		X	6/0		X		15	
ESC-0028	Penton	Exmet	4.5			90.3	5.2		X	6/0		X		15	
ESC-0029	Penton	Exmet	4.5			90.3	5.2		X	6/0		X		15	
ESC-0030	Penton	Exmet	4.5			90.3	5.2		X	6/0		X		15	
ESC-0031	Penton	Exmet	4.5			90.3	5.2		X	6/0	X		On top	15	
ESC-0032	Penton	Exmet	4.5			90.3	5.2		X	6/0	X		On top	15	
ESC-0033	Penton	Exmet	4.5			90.3	5.2		X	6/0	X		On top	15	
ESC-0034	Penton	Exmet	4.5			90.3	5.2		X	3/0	X		On top	15	
ESC-0035	Alphalux 400	Exmet	4.5			90.3	5.2		X	3/0	X		On top	15	
ESC-0036	Alphalux 400	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0037	Alphalux 400	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0038	Penton	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0039	Alphalux 400	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0040	Penton	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0041	Blue Teflon	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0042	Blue Teflon	Exmet	4.5			90.3	5.2	X		3/0		X		15(-32+80)	
ESC-0043	Celcon	Exmet	4.5			90.3	5.2	X		3/0		X		15	
ESC-0044	Alphalux 400	Exmet	4.5			90.3	5.2		X	3/0	X		On top not pressed	15(-32+80) 3	Silver electrode old style pressed on 3/0 Exmet Ag grid using Standard 50/50 mix Pressed at 3 tons
ESC-0045	Alphalux 400	Exmet	Same as ESC-0044												
ESC-0046	Alphalux 400	Exmet	"	"	"										
ESC-0047	Alphalux 400	Exmet	"	"	"										

(Continued)

TABLE II (continued)

ELECTRODE TEST CELL CONSTRUCTION

Cell Number	Case Material	Terminal	Electrode Formulation (Neg)					Grid Location (Neg)			KT Paper			Pressing Load (tons)	Comments
			PVA %	Dextrose %	None	ZnO %	HgO %	Center	In Back	Type Exmet	Yes	No	Other		
ESC-0048	Celcon	Exmet	Same as ESC-0044												
ESC-0049	Celcon	Exmet	"	"	"										
ESC-0050	Penton	Exmet	4.5			90.3	5.2	X		4/0		X		15	Std Ag electrode pressed @ 3 tons but 4/0 Exmet
ESC-0051	Penton	Exmet	4.5			90.3	5.2	X		4/0		X		15	
ESC-0052	Penton	Exmet	Same as Cell ESC-0044 except PVA was 52-22												Std Ag w/4/0 Exmet pressed @ 3 tons electrode
ESC-0053	Penton	Exmet	"	"	"	"	"	"	"						
ESC-0054	Alphalux 400	Exmet	"	"	"	"	"	"	"						
ESC-0055	Penton	Exmet	"	"	"	"	"	"	"						
ESC-0056	Alphalux 400	Exmet	"	"	"	"	"	"	"						
ESC-0057	Alphalux 400	Exmet	"	"	"	"	"	"	"						
ESC-0058	Penton	Exmet	4.5			90.3	5.2	X		4/0		X		3	Std Ag elec. but pressed @ 3 T
ESC-0059	Inorganic Filled Teflon	Exmet	4.5			90.3	5.2	X		3/0		X		15	Std Ag pressed @ 3 T using 4/0 Exmet
ESC-0060	Penton	Exmet	4.5			90.3	5.2	X		3/0		X		15	3 T pressed Ag elec. to 4/0 Exmet
ESC-0061	Inorganic Filled Teflon	Exmet	4.5			90.3	5.2	X		6/0	X		Placed on both sides	15	Std Ag elec. but with 6/0 Exmet
ESC-0062	Inorganic Filled Teflon	Exmet w/ v-shaped tab	4.5			90.3	5.2		X	6/0	X		Both sides	15	6/0 Exmet on Std Ag electrodes
ESC-0063	Inorganic Filled Teflon	Exmet w/ v-shaped tab	4.5			90.3	5.2		X	3/0	X		Top	3	6/0 Exmet on Std Ag electrodes
ESC-0064	Inorganic Filled Teflon	Exmet w/ v-shaped tab	4.5			90.3	5.2		X	3/0	X		Both sides	15	6/0 Exmet on Std Ag electrode
ESC-0065	Inorganic Filled Teflon	Exmet	4.5			90.3	5.2		X	3/0	X		Both sides	15	Std Ag electrode to 6/0 Exmet
ESC-0066	Inorganic Filled Teflon	Exmet w/ v-shaped tab	4.5			90.3	5.2		X	3/0	X		Both sides	15	6/0 Exmet in Std Ag electrode
ESC-0067	Inorganic Filled Teflon	Exmet w/ v-shaped tab	4.5			90.3	5.2		X	3/0	X		Placed on both sides	15	Std Ag electrode to 6/0 Exmet

(Continued)

TABLE II (continued)

ELECTRODE TEST CELL CONSTRUCTION

Cell Number	Case Material	Terminal	Electrode Formulation (Neg)					Grid Location (Neg)			KT Paper			Pressing Load (tons)	Comments
			PVA %	Dextrose %	None	ZnO %	HgO %	Center	In Back	Type Exmet	Yes	No	Other		
ESC-0068	Celcon	Exmet	4.5			90.3	5.2		X	6/0	X		Both sides	15	6/0 Exmet on Std Ag electrode
ESC-0069	Inorganic Filled Teflon	Exmet w/ v-shaped tab	--	--	X	98	2	Neg elec pressed on Ag Exmet screen which was placed over a Zn perforated sheet		6/0		X	Top	3	6/0 Exmet on Std Ag electrode
ESC-0070	Inorganic Filled Teflon	Exmet w/ v-shaped tab	Same as ESC-0071												
ESC-0071	Inorganic Filled Teflon	Exmet w/ v-shaped tab	--	--	X	98	2	Neg elec pressed in cavity	X	3/0	X		Top	3	Ag elec pressed in cavity @ 3 T 3/0 Exmet
ESC-0072	Inorganic Filled Teflon	Exmet w/ v-shaped tab	Same as ESC-0071												
ESC-0073	Zytel	Exmet w/ v-shaped tab	4.5			90.3	5.2		X	3/0	X		Both sides	15	Std Ag elec grid on one side
ESC-0074	Inorganic Filled Teflon	Zn not welded Exmet w/ v-shaped tab	--	--	X	98	2		X	3/0	X	2 on top elec 1 on bottom elec		3	4/0 Exmet on Std Ag electrode
ESC-0075	Zytel	Exmet w/ v-shaped tab	4.5			90.3	5.2	X		6/0	X		Both sides	15	6/0 Exmet on Std Ag electrode
ESC-0076	Zytel	Exmet w/ v-shaped tab	4.5			90.3	5.2	X		6/0	X		Both sides	15	Std Ag electrode 6/0 Exmet
ESC-0077	Zytel	Exmet w/ v-shaped tab	4.5			90.3	5.2		X	3/0	X		Both sides	15	Std Ag electrode grid on bottom
ESC-0078	Alphalux 400	Exmet tab w Ag spot-welded	--		X	98.0	2.0		pos. & neg.	3/0	X		Both sides	3	All silver electrodes were standard 50/50 Ag/AgO
ESC-0079	Alphalux 400	Exmet tab w Ag spot-welded			X	98.0	2.0		pos. & neg.	3/0	X		Both sides	3	3/0 Ag exmet 1-sided except where noted in this column with silver strip spot welded to terminal tab
ESC-0080	Alphalux 400	Exmet tab w Ag spot-welded			X	98.0	2.0		pos. & neg.	3/0	X		Both sides	3	

(Continued)

TABLE II (continued)

ELECTRODE TEST CELL CONSTRUCTION

Cell Number	Case Material	Terminal	Electrode Formulation (Neg)					Grid Location (Neg)			KT Paper			Pressing Load (tons)	Comments
			PVA %	Dextrose %	None	ZnO %	HgO %	Center	In Back	Type Exmet	Yes	No	Other		
ESC-0081	Alphalux 400	Exmet tab w Ag spot-welded			X	98.0	2.0		pos. & neg.	3/0	X		Both sides	3	All silver electrodes were standard Le. 50/50 Ag/AgO 3/0 Ag exmet 1-sided except where noted in this column with silver strip spot-welded to terminal tab
ESC-0082	Alphalux 400	Exmet tab w Ag spot-welded			X	98.0	2.0		pos. & neg.	3/0	X		Both sides	3	
ESC-0083	Alphalux 400	Exmet tab w Ag spot-welded			X	98.0	2.0		pos. & neg.	3/0	X		Both sides	3	
ESC-0084	Alphalux 400	Exmet tab w Ag spot-welded			X	98.0	2.0		pos. & neg.	3/0	X		Both sides	15	
ESC-0085	Alphalux 400	Exmet tab w Ag spot-welded			X	98.0	2.0		pos. & neg.	3/0	X		Both	15	
ESC-0086	Alphalux 400	--	--	--	--	--	--		--	--	--	--	--	--	
ESC-0087	Alphalux 400	Exmet tab w Ag spot-welded	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	
ESC-0088	Alphalux 400	Exmet tab w Ag spot-welded	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	
ESC-0089	Alphalux 400	Exmet tab w Ag spot-welded	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	
ESC-0090	Alphalux 400	Exmet tab w Ag spot-welded over tab	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	
ESC-0091	Alphalux 400	Exmet tab w Ag spot-welded over tab	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	
ESC-0092	Alphalux 400	Exmet tab w Ag spot-welded over tab	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	

(Continued)

TABLE II (continued)

ELECTRODE TEST CELL CONSTRUCTION

Cell Number	Case Material	Terminal	Electrode Formulation (Neg)					Grid Location (Neg)			KT Paper			Pressing Load (tons)	Comments
			PVA %	Dextrose %	None	ZnO %	HgO %	Center	In Back	Type Exmet	Yes	No	Other		
ESC-0093	Alphalux 400	Exmet tab w Ag spot-welded over tab	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	All silver electrodes were standard Le. 50/50 Ag/AgO 3/0 Ag exmet 1-sided except where noted in this column with silver strip spot-welded to terminal tab
ESC-0094	Alphalux 400	Exmet tab w Ag spot-welded over tab	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	
ESC-0095	Alphalux 400	--	--	--	--	--	--	--	--	--	--	--	--	--	
ESC-0096	Penton	Exmet tab with Ag strip spot-welded to tab	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	
ESC-0097	Penton	Exmet tab with Ag strip spot-welded to tab	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	
ESC-0098	Penton	Exmet tab with Ag strip spot-welded to tab	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	
ESC-0099	Penton	Exmet tab with Ag strip spot-welded to tab	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	
ESC-0100	Penton	Exmet tab with Ag strip spot-welded to tab	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	
ESC-0101	Penton	Exmet tab with Ag strip spot-welded to tab	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	

(Continued)

TABLE II (continued)

ELECTRODE TEST CELL CONSTRUCTION

Cell Number	Case Material	Terminal	Electrode Formulation (Neg)					Grid Location (Neg)			KT Paper			Pressing Load (tons)	Comments
			PVA %	Dextrose %	None	ZnO %	HgO %	Center	In Back	Type Exmet	Yes	No	Other		
ESC-0102	Alphalux 400	Exmet tab with Ag strip spot-welded to tab	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	All silver electrodes were standard Le. 50/50 Ag/AgO 3/0 Ag exmet 1-sided except where noted in this column with silver strip spot-welded to terminal tab
ESC-0103	Alphalux 400	Exmet tab with Ag strip spot-welded to tab	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	
ESC-0104	Alphalux 400	Exmet tab with Ag strip spot-welded to tab	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	
ESC-0105	Alphalux 400	Exmet tab with Ag strip spot-welded to tab	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	
ESC-0106	Alphalux 400	Ag strip spot-weled to Grid	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	
ESC-0107	Alphalux 400	Ag strip spot-welded to Grid	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	
ESC-0108	Alphalux 400	Ag strip spot-welded to Grid	4.5			90.3	5.2		pos. & neg.	3/0	X		Both sides	15	

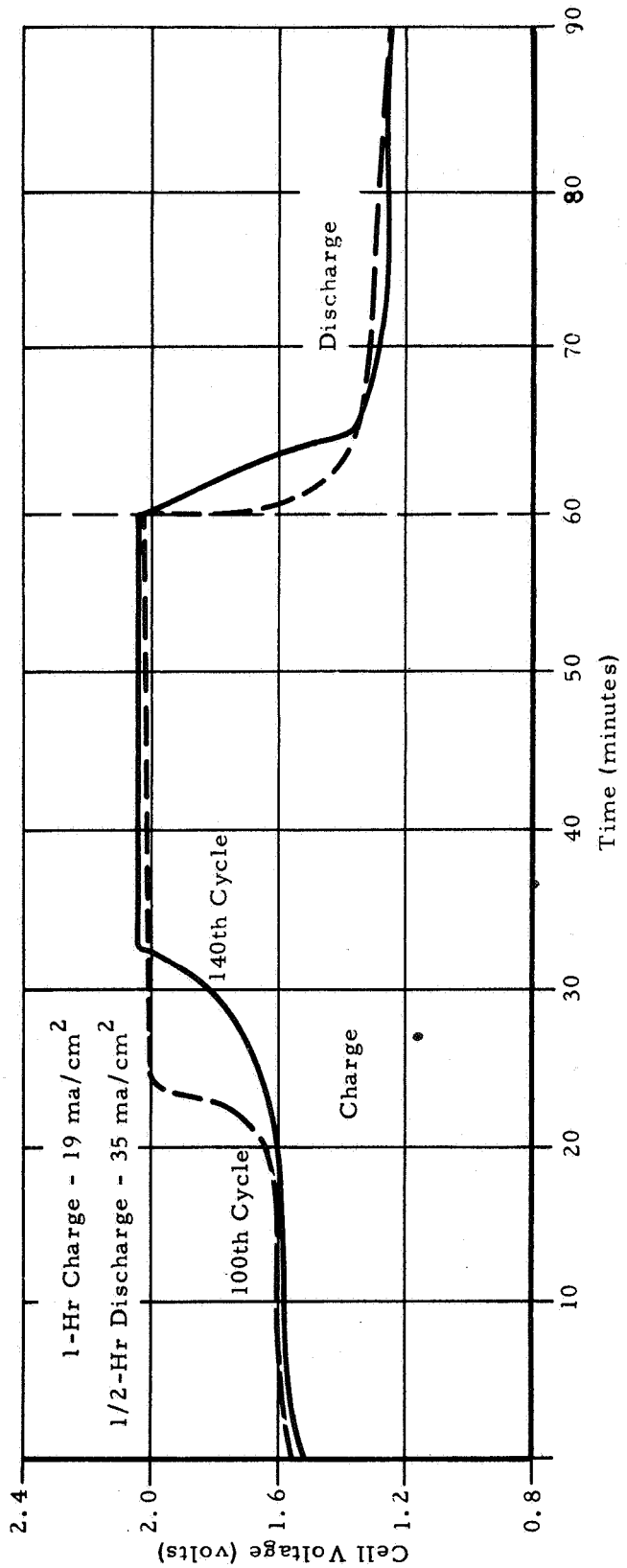


Figure 12. Charge-Discharge Curve Silver-Zinc Test Cell ESC-0046 Cycling at 100°C

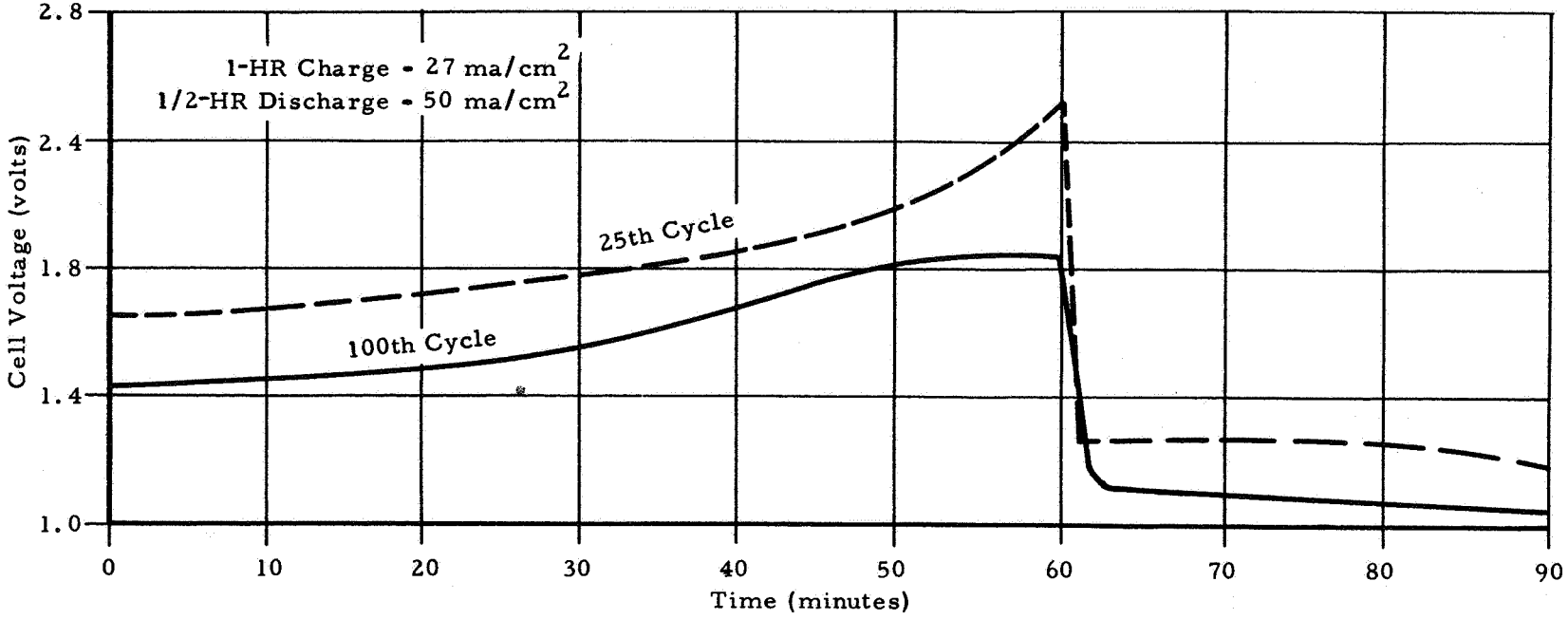


Figure 13. Charge-Discharge Curve Silver-Zinc Test Cell ESC-0078 Cycling at Room Temperature

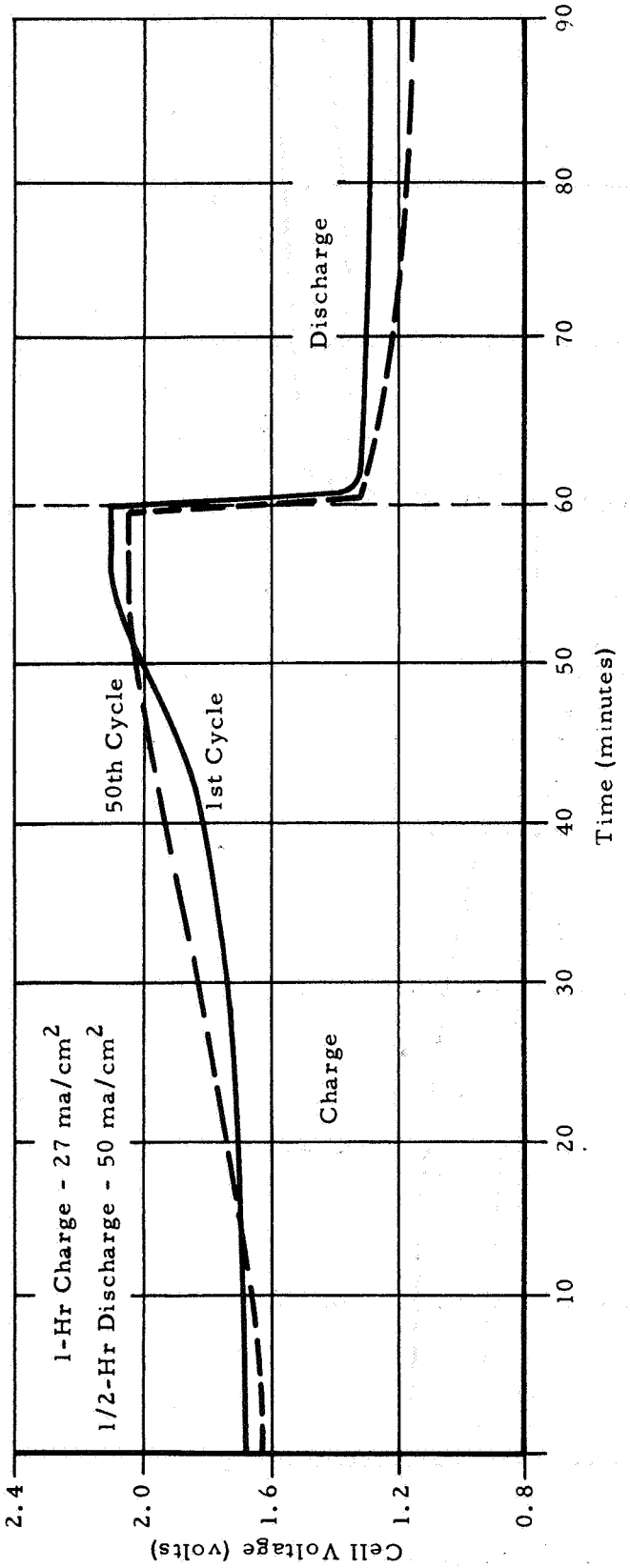


Figure 14. Charge-Discharge Curve Silver-Zinc Test Cell ESC-0045 Cycling at 100°C

Four test cells, ESC-0083, ESC-0094, ESC-0097 and ESC-0102, completed 140 cycles at 25°C at a discharge current density of 50 ma/cm^2 and a charge current density of 27 ma/cm^2 on a 30-minute discharge, 60-minute charge test schedule. Figure 15 shows the voltage curves for the 20th and 100th cycles for Test Cell No. ESC-0083 at 25°C and 50 ma/cm^2 discharge current density.

These cycle test data on single test cells indicated that the 140-cycle cutoff requirement specified in the work statement was readily obtained on cells at both 100°C and 25°C at a discharge current density of 20 ma/cm^2.

Table III summarizes the cycle test results for a number of two-plate test cells cycled at 100°C and 25°C at discharge current densities of 20 ma/cm^2 and 40 ma/cm^2. At room temperature, four cells completed the required 140 cycles on a 30-minute discharge and 60-minute charge cycle test schedule at 20 ma/cm^2. These were Test Cell Nos. ESC-0112, ESC-0013, ESC-0121, and ESC-0127. During assembly of Test Cell No. ESC-0114 the separator was apparently broken, as was evidenced when the cell was disassembled following the completion of 23 cycles. Test Cell Nos. ESC-0128 and ESC-0137 also completed 140 cycles on the same cycle test schedule at 100°C. Three additional test cells (ESC-0122, ESC-0126 and ESC-0135) had completed more than 100 cycles at 100°C and 20 ma/cm^2 discharge current density when they lost capacity due to the depletion of active material in the zinc electrode.

Several test cells (ESC-0018, ESC-0140 and ESC-0142), cycled at 25°C at a discharge current density of 40 ma/cm^2 on a 30-minute discharge and a 60-minute charge test schedule, completed the required 140 cycles. Test Cell No. ESC-0132 completed 134 cycles, Cell Nos. ESC-0135 and ESC-0138 completed 100 cycles at 100°C and 40 ma/cm^2 discharge current density.

A number of two-plate test cells cycled at 100°C and 25°C at discharge current densities of 40 ma/cm^2 and at 20 ma/cm^2 did not complete 140 cycles. Test Cell No. ESC-0132 completed 134 cycles and Test Cell Nos. ESC-0134 and ESC-0138 completed 100 cycles at 100°C and 40 ma/cm^2 discharge current density.

These cells were tested in half-case assemblies in which electrode cavities were deeper than the thickness of the positive and negative plates. Because of the excessive space available around the zinc electrode, slumping and expansion of the electrode resulted during cycling. This expansion exerted pressure on the separator causing it to bow because of the space available behind it in the positive compartment. The problem was overcome in the new three-electrode test cases where the positive electrode is held firmly between the two separators with

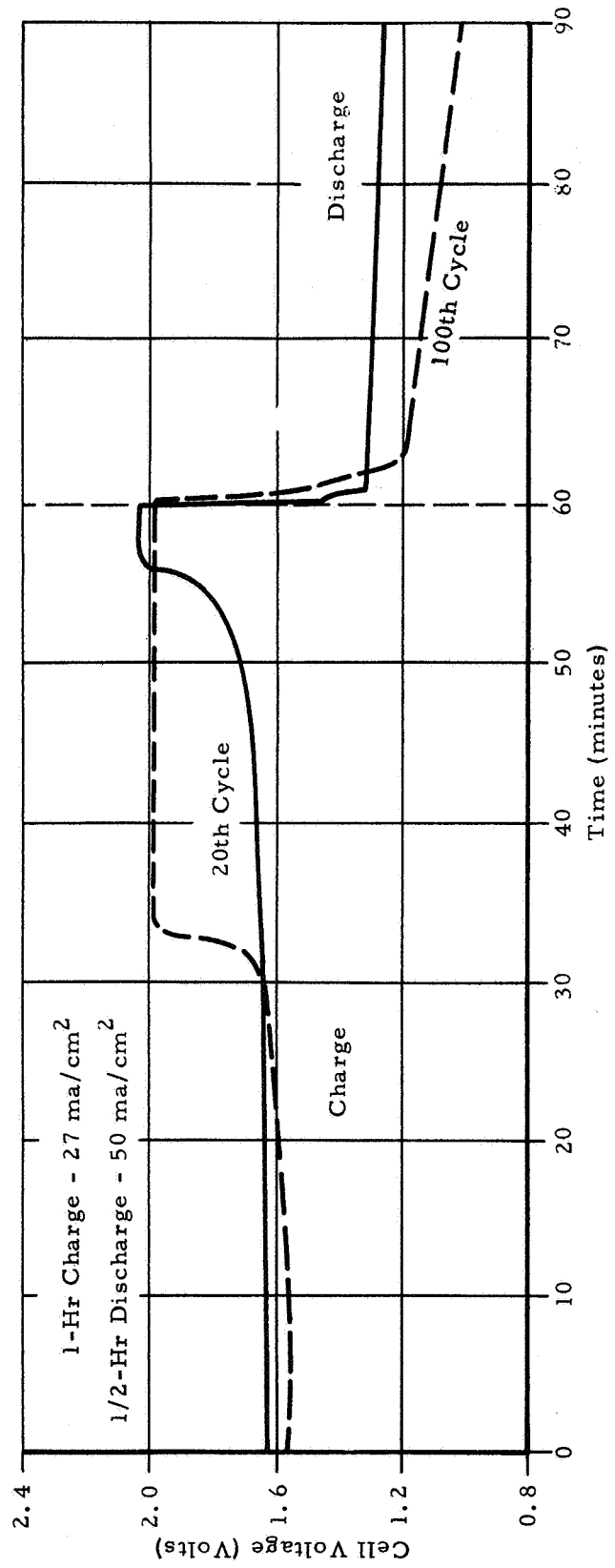


Figure 15. Charge-Discharge Curve Silver-Zinc Test Cell ESC-0083 Cycling at RT

TABLE III

CYCLE TEST RESULTS
ELECTRODE TEST CELL CONFIGURATION - ONE POSITIVE AND ONE NEGATIVE

NOTE: Cycle Test Regime: 30-Minute Discharge and 60-Minute Charge

Test Cell No.	Cycle Test Temp.	Current Density Discharge (ma/cm^2)	Current Density Charge (ma/cm^2)	Number of Cycles Successfully Completed	Remarks
ESC-0122	100°C	20	11	114	Zinc Electrode
ESC-0123	↓	↓	↓	54	↓
ESC-0124				78	
ESC-0126				120	
ESC-0128				140	Note 1
ESC-0135				101	Zinc Electrode
ESC-0137				140	Note 1
ESC-0130	100°C	40	22	88	Zinc Electrode
ESC-0131	↓	↓	↓	93	↓
ESC-0132				134	
ESC-0133				60	
ESC-0134				100	
ESC-0136				96	
ESC-0138				100	
ESC-0141				66	
ESC-0112	25°C	20	11	140	Note 1
ESC-0113	↓	↓	↓	140	↓
ESC-0114				23	Separator Broken during Assembly
ESC-0121				140	Note 1
ESC-0127				140	↓
ESC-0116	25°C	40	22	46	Zinc Electrode
ESC-0117	↓	↓	↓	21	Cause of Failure Unknown
ESC-0118				140	Note 1
ESC-0119				72	Zinc Electrode

TABLE III (Continued)

CYCLE TEST RESULTS
ELECTRODE TEST CELL CONFIGURATION - ONE POSITIVE AND ONE NEGATIVE

Test Cell No.	Cycle Test Temp.	Current Density Discharge (ma/cm^2)	Current Density Charge (ma/cm^2)	Number of Cycles Successfully Completed	Remarks
ESC-0120	25°C	40	22	45	Zinc Electrode
ESC-0140	↓	↓	↓	140	Note 1
ESC-0142	↓	↓	↓	140	Note 1
ESC-0143	↓	↓	↓	79	Zinc Electrode

Note 1. Cell completed the cycling requirement of the contract, however, the cell is capable of continued cycling.

one zinc electrode on either side. Because all components fit together in a tight pack, lateral movement was precluded and zinc electrode changes were minimized.

Experimental results showed that the cycle performance of the new three-plate cell design was considerably better than that of the two-plate cell design. The cell identification number for the three-plate test cell was "B", i.e., ESC-B-000.

Table IV is a summary of the three-plate test cells cycled at 100°C and 25°C on a 1/2-hour discharge and a 1-hour charge schedule at discharge current densities of 20 ma/cm^2 and 40 ma/cm^2. Ten of these test cells completed the required 140 cycles at 25°C and 20 ma/cm^2 discharge current density. Several of these new test cells were permitted to continue cycling and exceeded 400 cycles. Test Cell No. ESC-B-139 completed more than 700 cycles under the same test conditions. These cells were assembled in molded C-11 polystyrene cell cases. A Lucite shim was used in these cell assemblies to provide electrode cavities of the same dimensions as used in the Lucite and PPO cell cases fabricated in the machine shop.

Test Cell Nos. ESC-B-157, ESC-B-158, ESC-B-159, and ESC-B-160 completed the required 140 cycles at 100°C and 20 ma/cm^2 discharge current density indicating that the three-plate test cell design can meet the 140 cycle requirement at both 100°C and 25°C at a discharge current of 20 ma/cm^2 and a charge current density of 12 ma/cm^2.

Based upon the attainment of 140 cycles at both 100°C and 25°C at 20 ma/cm^2 discharge current density, another group of test cells was placed on cycle test at 25° and 100°C at 30 ma/cm^2 discharge current density. These test results are shown in Table IV.

Table V shows electrode construction and formulation for all test cells of the new configuration (one positive and two negative electrodes and two inorganic separators). The positive electrode formulation was identical for all cells but several different methods were used in applying the network support material in the negative electrode. The electrode current collectors and tabs were of the same design in all cells.

2.2.1.3 Cycle Tests

Tables VI, VII and VIII 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

TABLE IV

CYCLE TEST RESULTS
ELECTRODE TEST CELL CONFIGURATION - ONE POSITIVE AND TWO NEGATIVES

NOTE: Cycle Test Regime: 30-Minute Discharge and 60-Minute Charge

Test Cell No.	Cycle Test Temp.	Current Density Discharge (ma/cm^2)	Current Density Charge (ma/cm^2)	Number of Cycles Successfully Completed	Remarks
ESB-B-157	100°C	20	12	140	Note 1 (Table III)
ESC-B-158				140	
ESC-B-159				140	
ESC-B-160				140	
ESC-B-166				28	Silver Electrode Swelled and cracked separator
ESC-B-167				30	Loose Electrode/Separator frame
ESC-B-168	100°C	30	20	50	
ESC-B-169				43	
ESC-B-170				37	
ESC-B-171				21	
ESC-B-175				18	
ESC-B-176				18	
ESC-B-177				12	Cell Case Bulged Due to accidental overheating
ESC-B-181				28	
ESC-B-184				35	
ESC-B-185				34	
ESC-B-186				69	
ESC-B-187				34	
ESC-B-139	25°C	20	12	140	Note 1 (Table III)
ESC-B-144					
ESC-B-145					
ESC-B-146					
ESC-B-147					
ESC-B-148					
ESC-B-149					
ESC-B-150					
ESC-B-151					
ESC-B-152					
ESC-B-165	25°C	30	20		
ESC-B-172				22	Cell Dried Out
ESC-B-173				5i	Possible Short
ESC-B-174				52	Loose Electrode/Separator
ESC-B-178				70	Frame Possible Short
ESC-B-179				79	Frame Possible Short
ESC-B-180				67	Loose Electrode/Separator frame
ESC-B-153	25°C	40	28	24	Cell reversed*
ESC-B-154				69	Broken lead to zinc electrode
ESC-B-155				121	Cell Dried Out
ESC-B-156				83	Cell reversed*
ESC-B-161				66	Cell Dried Out
ESC-B-163				34	Cell Reversed*

*Cycle test timer failure

TABLE V

ELECTRODE TEST CELL CONSTRUCTION - ONE POSITIVE AND TWO NEGATIVES

Test Cell Number	Case Material	Positive Formulation		Negative Formulation					
						KT Paper			
		100% Ag	50-50 Ag/Ag_2O	ZnO %	HgO %	U-Wrap	10% Fibres	Other	Comments
ESC-B-144	Lucite	x		98	2	x			Collector (All Cells): Ag EXMET 3Ag-10-3/0 Lead (All Cells): Ag tab 1/4" x .006" Tab spot welded to grid for all electrodes
ESC-B-145	↑	x		98	2			Pellon U-Wrap	
ESC-B-146		x		98	2	x			
ESC-B-147		x		98	2	x			
ESC-B-148		x		98	2	x			
ESC-B-149		x		98	2	x			
ESC-B-150		x		98	2	x			
ESC-B-151		x		98	2	x			
ESC-B-152		x		98	2	x			
ESC-B-153	↓	x		98	2	x			
ESC-B-154	Lucite	x		98	2	x			
ESC-B-155	PPO	x		98	2	x			
ESC-B-156	↑	x		98	2	x			
ESC-B-157		x		98	2	x			
ESC-B-158		x		98	2	x			
ESC-B-159		x		98	2	x			
ESC-B-160		x		98	2	x			
ESC-B-161		x		98	2	x			
ESC-B-162		x		98	2	x			
ESC-B-163		x		98	2	x			
ESC-B-164		x		98	2	x			
ESC-B-165		x		98	2			Asbestos U-Wrap	
ESC-B-166		x		98	2	x			
ESC-B-167		x		98	2	x			
ESC-B-168		x		98	2	x			
ESC-B-169		x		98	2	x			
ESC-B-170	↓	x		98	2	x			
ESC-B-171	PPO	x		98	2	x			
ESC-B-172	Lucite	x		98	2		x		
ESC-B-173	↕	x		98	2		x		
ESC-B-174	Lucite	x		98	2		x		
ESC-B-175	PPO	x		98	2		x		
ESC-B-176	↕	x		98	2		x		
ESC-B-177	PPO	x		98	2		x		
ESC-B-178	Lucite	x		98	2		x		
ESC-B-179	Lucite	x		98	2		x		
ESC-B-180	PPO	x		98	2		x		
ESC-B-181	↑	x		98	2		x		
ESC-B-182		x		98	2		x		
ESC-B-183		x		98	2		x		
ESC-B-184		x		98	2	x			
ESC-B-185		x		98	2	x			
ESC-B-186		x		98	2	x			
ESC-B-187	PPO	x		98	2	x			

TABLE VI

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

TABLE VII

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

Cell No.	Original Capacity Q_o (Ah)	Discharge: Rate (mA)	Discharge: Current Density (mA/cm^2)	Discharge: Depth of Discharge (% of Q_o)	Number of Cycles	Testing Continued	Testing Stopped	Dissection Comments
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	
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 VIII)
a = cell dried out
b = case leakage
c = broken lead
d = loose frame

TABLE VIII

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

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°C the electrolyte is consumed at a rapid rate, whether through evaporation or through electrolysis, due to high rate charge and overcharge at current densities of 30 ma/cm^2 or greater.

Typical charge-discharge curves for cells at current densities ranging from 10 ma/cm^2 to 50 ma/cm^2 at 25°C and 100°C can be seen in Figures 16 through 20.

Depth of discharge is based on 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 VIII.

The test cells were capable of supplying a reasonable output over 1-Ah at current densities of 30 ma/cm^2. The limitation on cycle-life can be attributed to the high recharge rate.

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.

Three of the single-electrode cells which were continued on cycle test until failure completed as many as 3123 cycles. Test Cell ESC-B-139 was removed from cycle testing after 3123 straight cumulative cycles. Analysis of the cell showed that failure was due to separator breakage caused by warpage of the plastic frames. The cell was cycled for 622 cycles at 19% depth of discharge based on the original capacity Q_o (20 ma/cm^2) followed by 2501 cycles at 8% Q_o (10 ma/cm^2).

Test Cell ESC-B-202 completed 1620 cycles; 212 of these were cycles at 54% Q_o (40 ma/cm^2) and the other 1408 cycles were at 11% Q_o. Failure was due to capacity loss of the zinc electrode.

Test Cell ESC-b-205 completed 2110 cycles (42 cycles at 60% Q_o (50 ma/cm^2 followed by 2068) cycles at 11%

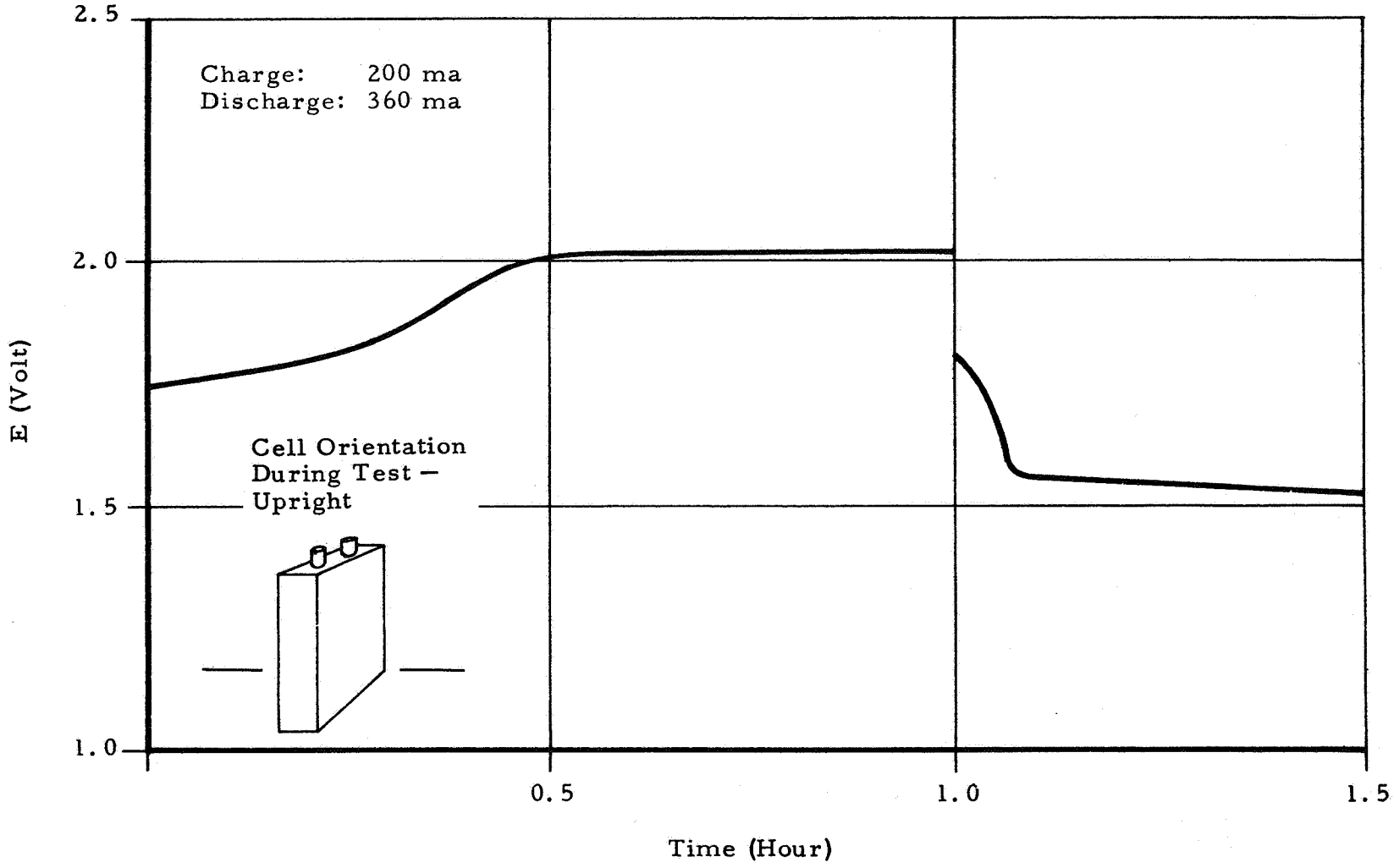


Figure 16. Test Cell No. 139 After 1000 Cycles at 10 ma/cm^2 at 25°C

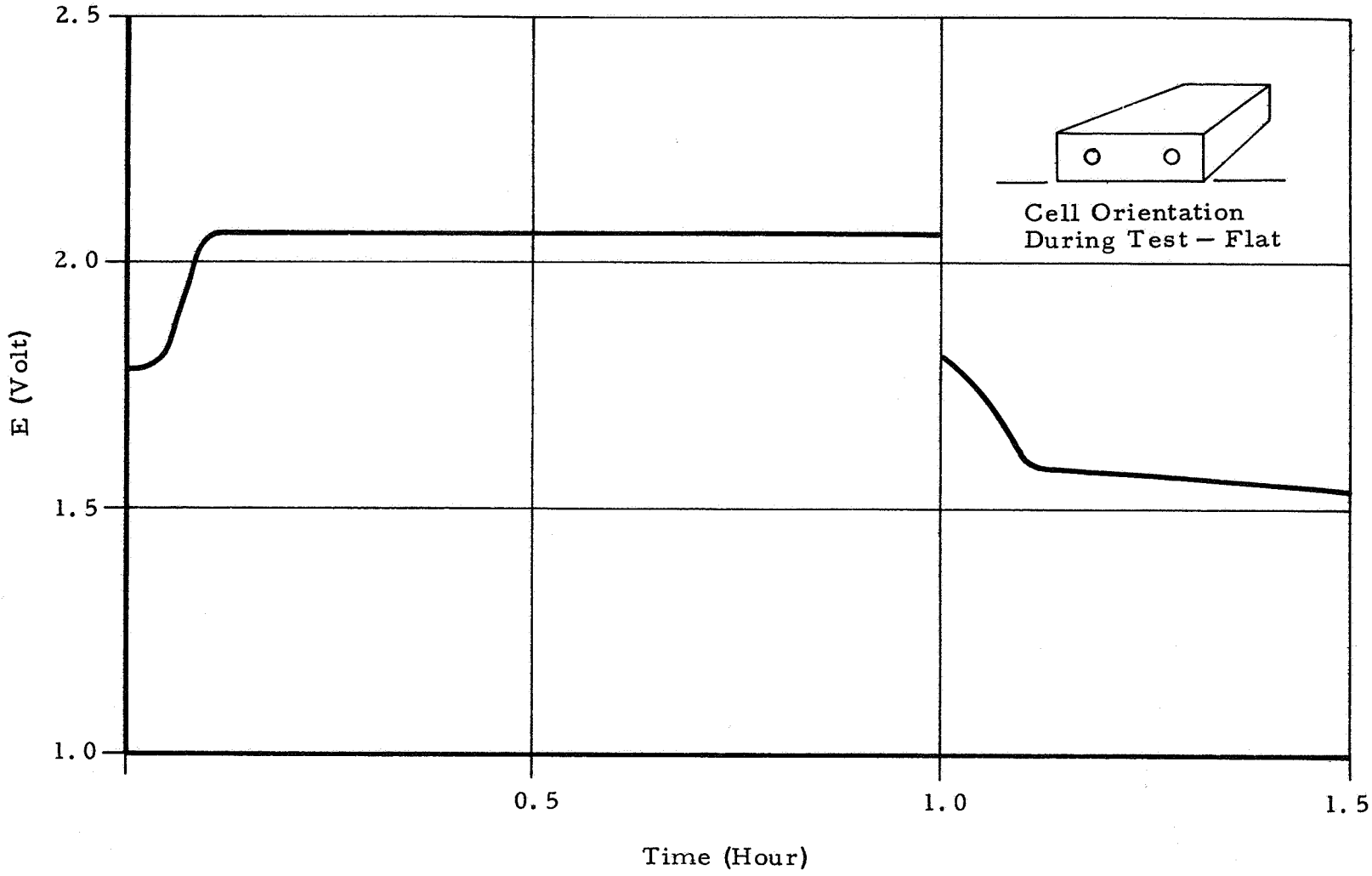


Figure 17. Test Cell No. ESC-B-208 After 300 Cycles at 10 ma/cm^2 at 25°C (Cell cycled for 163 cycles at 30 ma/cm^2 at 25°C prior to this cycle test)

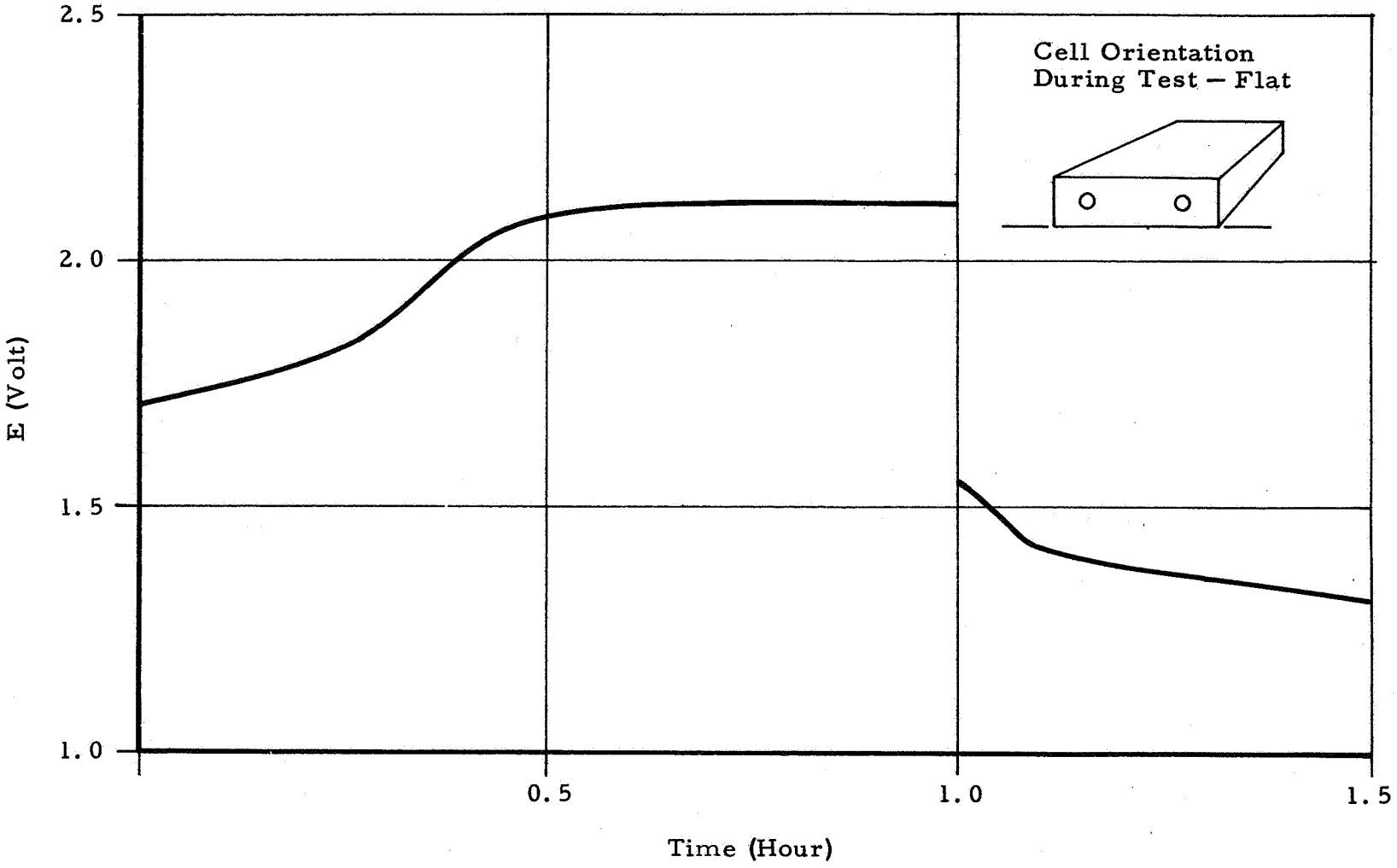


Figure 18. Test Cell No. 215 After 75 Cycles at 30 ma/cm^2 at 100°C

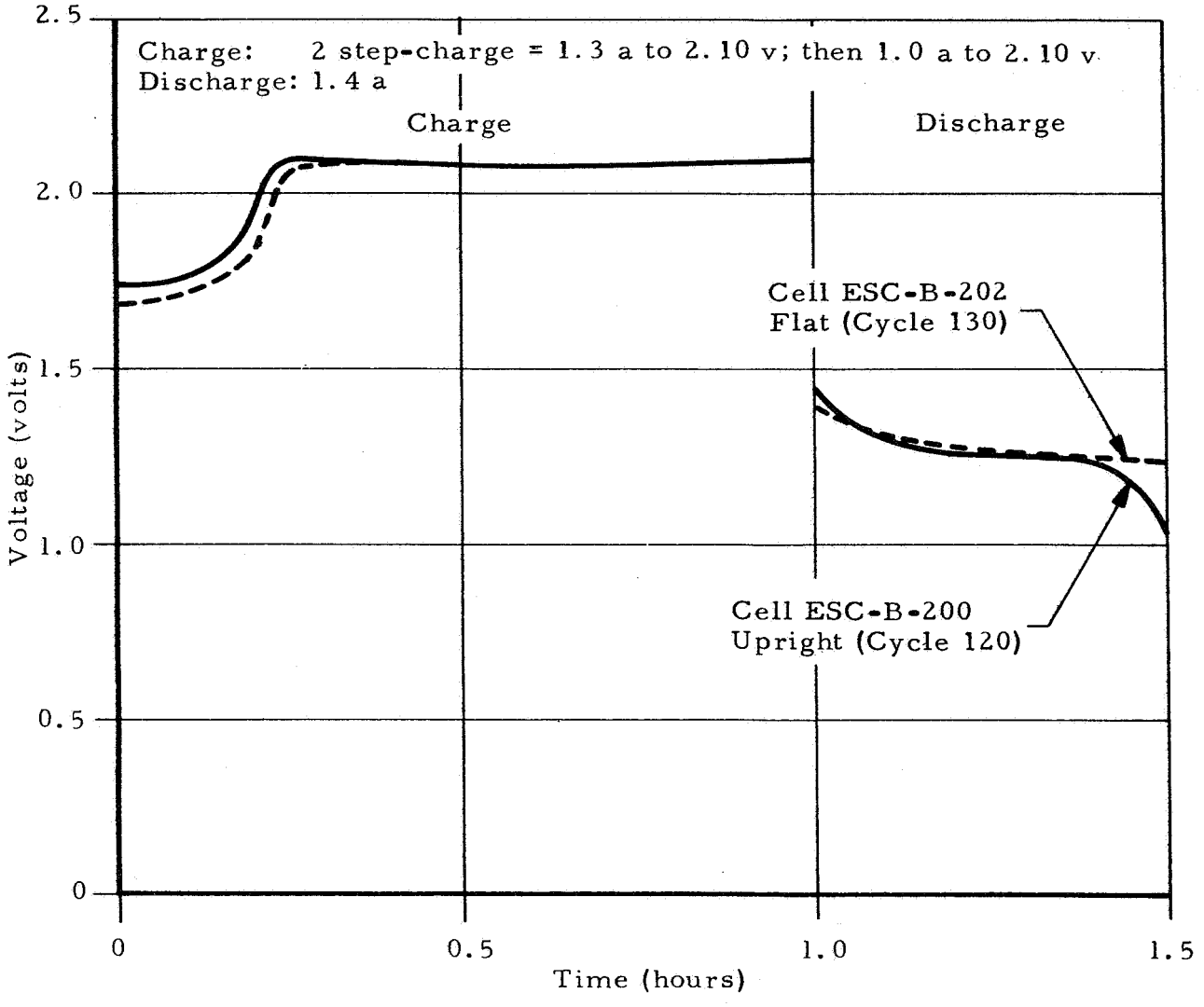


Figure 19. Complete Cycle. 40 ma/cm^2 at 25°C

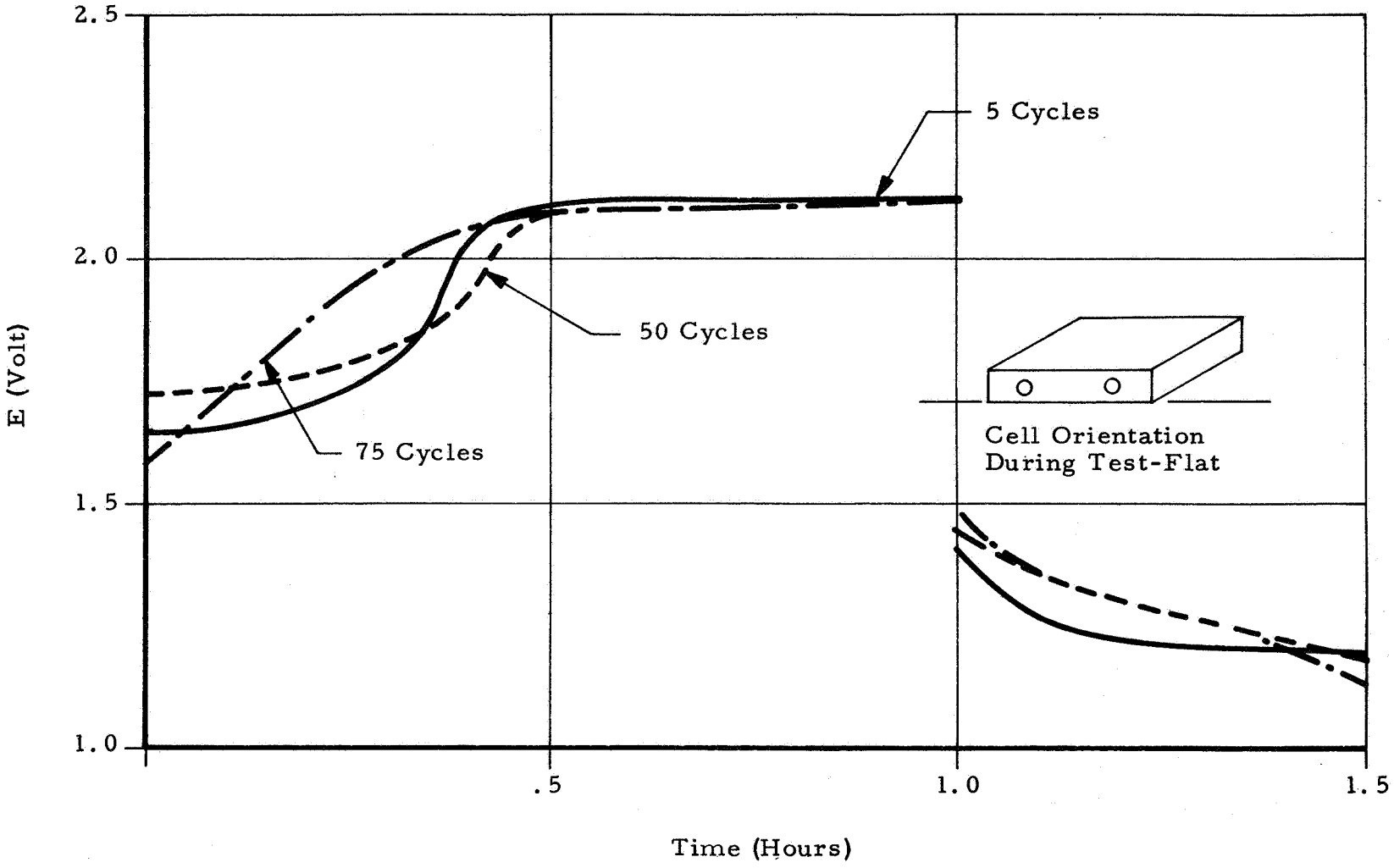


Figure 20. Test Cell ESC-B-212 Cycle Test at 50 ma/cm^2 at 25°C

Q_o). Cell failure was caused by leakage through the separator-frame sealant resulting in internal shorting.

Figure 21 is a photograph showing separator frames removed from test cells after many cycles.

The following results were obtained during these tests:

1. The practical cycle operating current density appeared to be 30 ma/cm^2 for these test cells because of the high charge rate required by the short cycle regime.
2. The zinc electrodes using KT paper pressed into both sides were capable of long cycle life even though some electrode changes were noted.
3. The zinc electrode must be supported by NSM to prevent excessive slumping and other changes that reduce its efficiency.
4. The silver-zinc test cells using Astroset inorganic separators were capable of long cycle life at relatively high current densities.

2.2.1.4 Gassing Tests

Gassing tests were run to determine the extent of gas evolution under different conditions of stand and cycling at 25° and 100°C. This, in turn, would establish the practical limits 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 22).

The tests were made on dummy cells and complete cells.

A. Dummy Cells

The dummy cells were 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%.

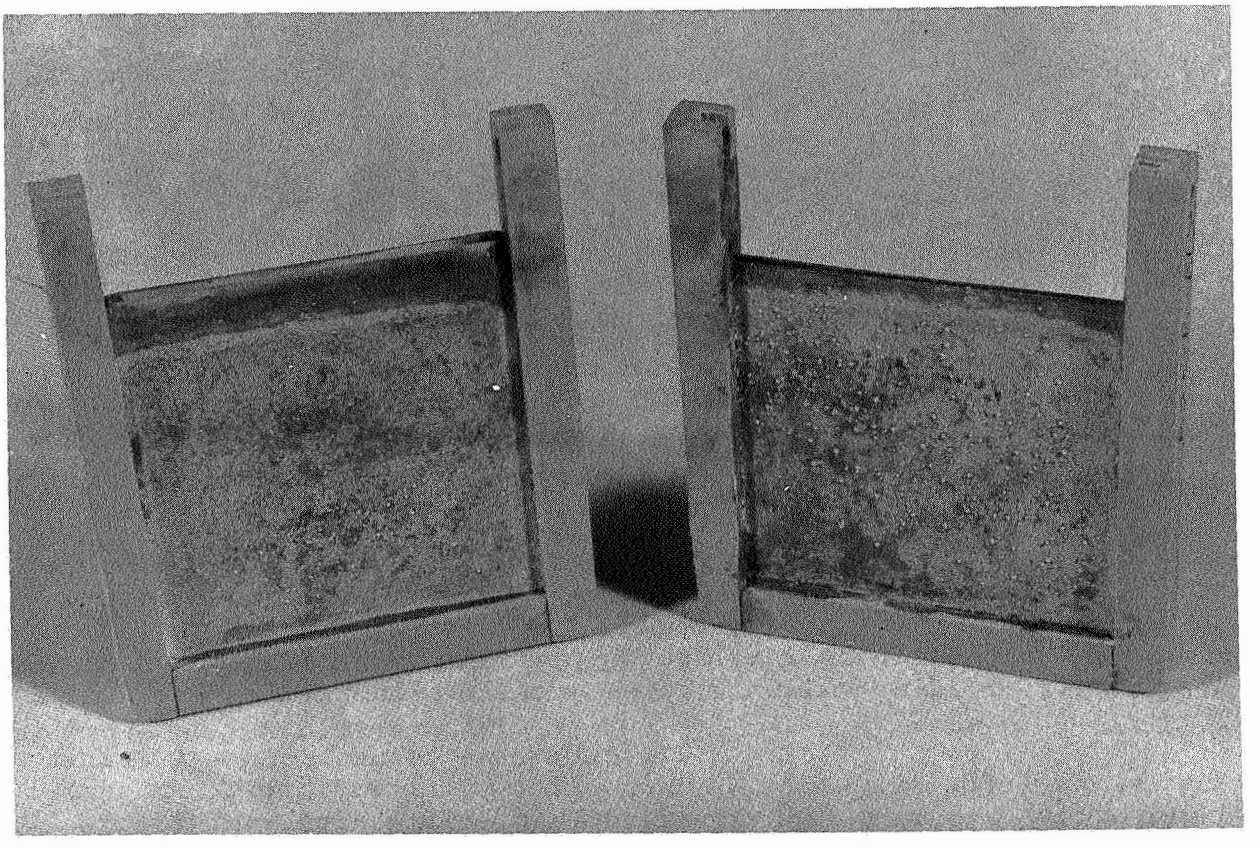


Figure 21. Inorganic Separators Removed From Test Cells No. ESC-B-149 After 495 Cycles (Left) and No. ESC-B-151 After 347 Cycles (Right)

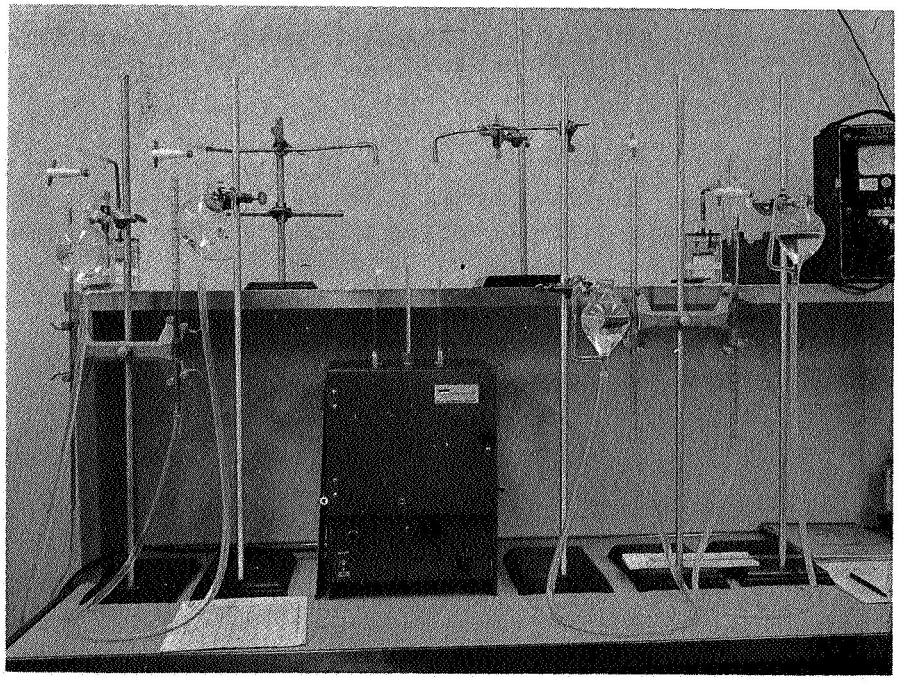


Figure 22. Cell Gassing Experimental Setup

Model #2: Separators mounted in frame and filled with 30% KOH also had approximately 20 cm^3. It could 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.

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 IX and Figure 23)

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 for the remainder of the 408 hours, indicating capacity retention and a no-short condition.

It can be concluded that the present electrode-separator system is adequate on stand at room temperature in a sealed condition.

TABLE IX

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

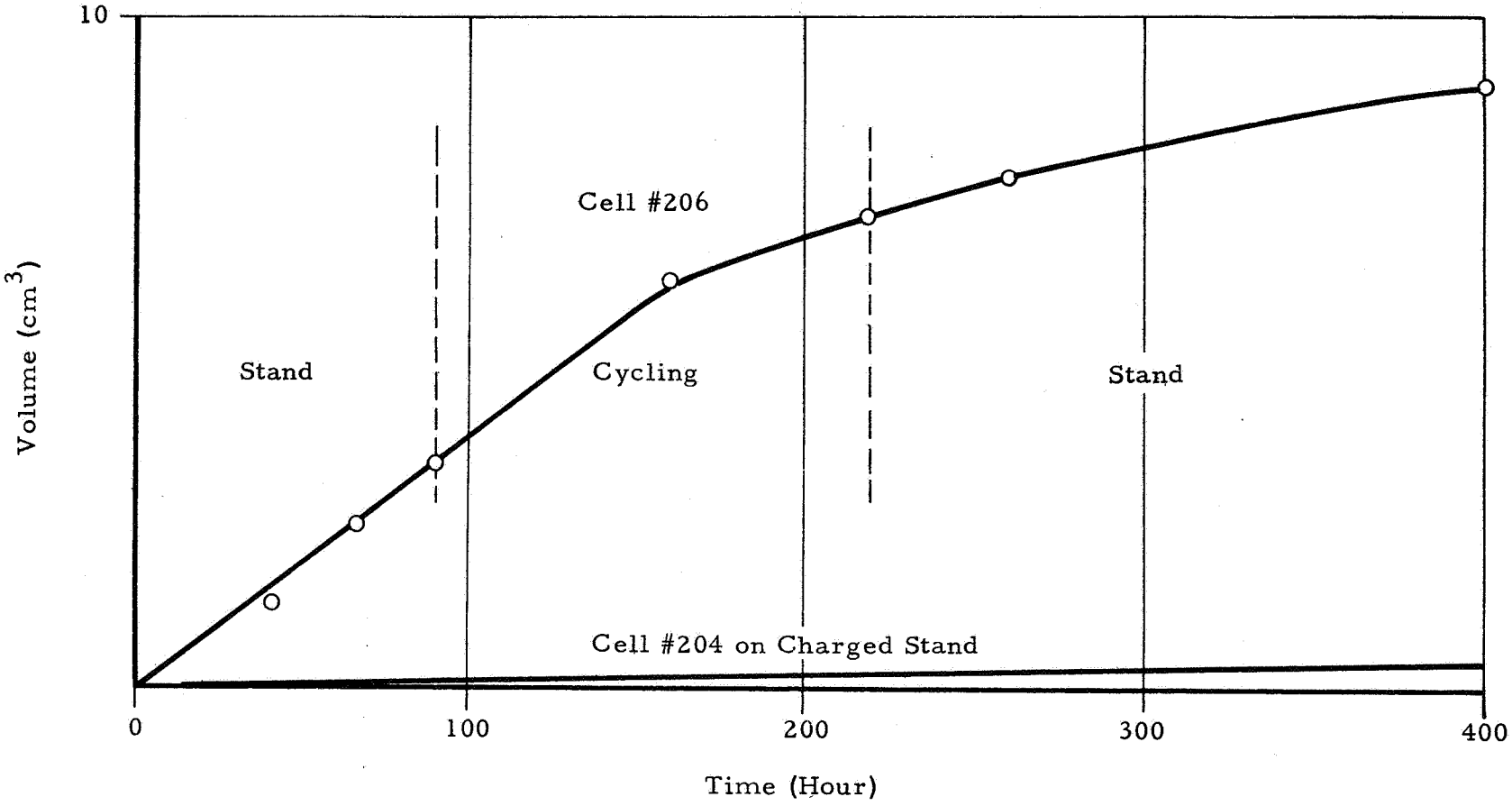


Figure 23. Total Volume of Gas Evolved at 25°C

Insignificant pressure build-up in the multiplate cell configuration is contemplated.

b. High Temperature (Table X and Figure 24)

(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 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 XI)

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.

TABLE X

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)

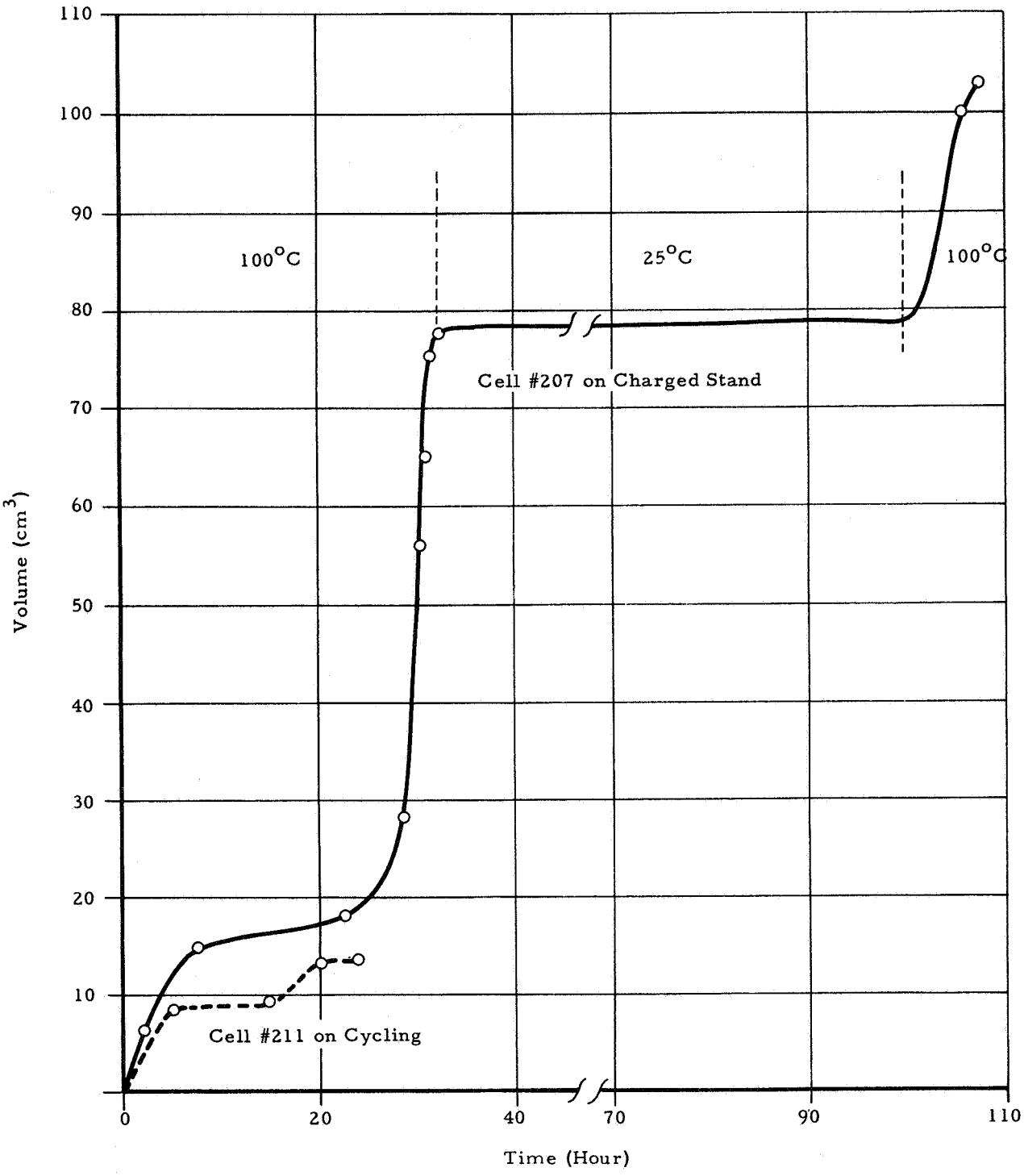


Figure 24. Total Volume of Gas Evolved at 100°C

TABLE XI

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

b. High Temperature (Table XII)

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.

2.2.1.5 Preliminary Multiplate Cell Tests

In order to preview the performance of the electrodes and other cell components in 5 Ah cells, a number of multiplate cells were fabricated and cycle tested at 25°C and 100°C at various current densities. These cells were built using machined frames with the modified groove design described in Section 2.1 and several different frame cements. Test results are shown in Table XIII.

The design is indicated by D-series (D-1, D-2, etc). The grooved frame type is referred to as E, E', E'', E''', each of which designates slight modifications of groove dimensions and spacing.

The frame sealants used are indicated by their trade names – RTV, Shell Epon, Ethylene-Propylene (uncured liquid EP), Epibond, Br-89 and Br-92, (Epoxies supplied by the American Cyanamid Company for cementing polysulfone) and All-Bond.

Table XIII shows that generally these cells were capable of long cycle life at room temperature. Cell failures were caused by sealant failures, frame warpage or low zinc electrode capacity. Frame warpage generally caused at least one separator in the assembly to crack resulting in a decline in cell capacity and termination of the test.

The best results, overall, were obtained with design D-10, using the E''' frame and All-Bond cement. However, the problem of frame warpage was apparent, especially at high temperature, where better results were obtained with a flexible cement such as RTV.

It is significant that as many as 1465 cycles were obtained at 25°C by multiplate cell MC-15 as shown in Table XIII. Cell performance remained essentially unchanged for over 1,000 cycles at which time a slight decline in cell performance was noted. After cell failure at 1465 cycles, the cell was disassembled and analyzed. Inspection clearly showed failure of the frame sealant (RTV). It was apparent that even longer cell life would have resulted if the frame sealant had not failed. These tests indicated the long cycle capability of the inorganic separators using a preliminary multiplate design.

TABLE XII

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

TABLE XIII

MULTIPLATE CELL (MC) CYCLING DATA

(25°C Except When Indicated By*)

Cell No.	Design				Discharge				No. of Cycles	Remarks
	Code	Frame	Cement	Original Capacity Q_o	Period (hrs)	Rate (A)	Current Density (mA/cm^2)	Depth of Discharge % Q_o		
13	D-1	E	RTV	4.9	A	1	7	10	205	L.C.
14	D-2A	E	Ep. 901	5.3	A	1	7	10	325	F.W.
15	D-3	E'	RTV	4.9	A	1	7	10	1465	S
16	D-2B	E	E.P	5.0	A	1	7	10	262	L.C.
17	D-2	E	RTV	4.5	C	1	7	100	19	F.W.
18	D-4	E'	RTV	5.8	A	1	7	9	167	L.C.
19	D-5	E'	Ep. 901	5.1	A	1	7	10	163	F.W.
20	D-4A	E'	Ep. 901	5.1	C	1	7	100	18	F.W.
22	D-7	E'	RTV	6.2	A	1	7	8	499	L.C.
23	D-7	E'	RTV	6.0	B	2	14	17	170	L.C.
24	D-5A	E'	RTV	4.8	A	1	7	10	326	F.W.
25	D-5A	E'	RTV	6.7	B	2	14	16	1054	S
26	D-7	E'	RTV	6.3	A	1	7	8	438	L.C.
27	D-7	E'	RTV	6.3	C	1	7	100	9	S
28	D-8	E''	RTV	6.0	B	2	14	17	78	F.W.
29	D-8	E''	RTV	5.8	B	2	14	17	82	S
30	D-7A	E'	BR-89	6.8	B	2	14	15	156	F.W.
31	D-8	E''	Epibond	7.1	A*	1	7	7	155	L.C.
32	D-8	E''	BR-89	6.9	A*	1	7	7	113	L.C.
33	D-8	E''	BR-92	6.6	A	1	7	8	154	F.W.
45	D-8	E''	All-Bond	5.2	A	1	7	10	265	F.W.
48	D-8	E''	All-Bond	6.4	A	1	7	8	512	F.W.
56	D-10	E'''	RTV	5.6	A*	1	7	9	163	F.W.
57	D-10	E'''	RTV	5.6	A*	1	7	9	167	F.W.

Key

*Run at 100°C

A = 1/2 x 1/2 hr (discharge-charge)

B = 1/2 x 1 hr (discharge-charge)

C = 24 hrs (discharge-charge)

FW = Frame Warpage

LC = Low Capacity

S = Sealant Failure

Four of the twelve multiplate cell cycle tests completed over 400 cycles, and two of these cells exceeded 1,000 cycles. Multiplate cell MC-25 completed 1,054 cycles before the frame sealant failed. The rest of the multiplate cells failed at different cycling intervals when frame warpage, sealant failure, or zinc electrode degradation resulted in terminating the cycle tests.

Four of these multiplate cells were cycled at 100°C. Again, frame warpage caused at least one separator to crack in the frame assembly, resulting in the termination of two of the four tests after completing over 160 cycles. Of special interest were cells MC-56 and MC-57 which completed 163 and 167 cycles as shown in Table XIII. These cells were heat soaked at 135°C for three hours before being placed on cycle test. Discharge curves for these cells display a high discharge plateau of about 1.5 V as shown in Figures 25-27. Two other cells (MC-31 and MC-32) tested at 1000°C continued to cycle before loss of zinc electrode capacity caused cell failure.

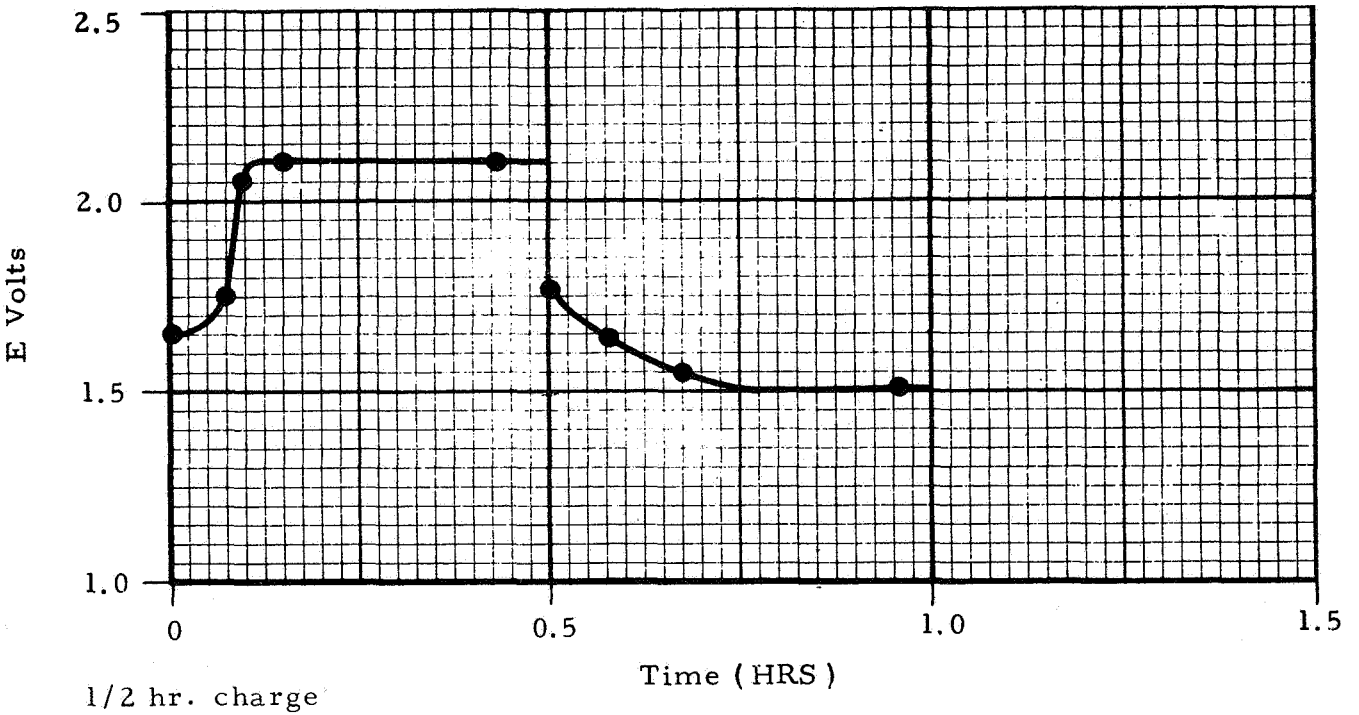
The results confirmed the capability of these cells to fulfill the contract requirements but also emphasized the need for design, sealant, and zinc electrode modifications.

2.2.1.6 Test Cells Operating in Various Orientations

One of the design objectives of this program was a cell usable in any operating position. In order to achieve this desired versatility, it was necessary to develop a technique for closing the tops of the separator-electrode pack so the electrodes would be retained in place when the cell was placed in any position. The materials that were evaluated as top closures included Armalon felt, All-Bond epoxy, Nylon felt, RTV, potassium titanate fibers and plastisols. Table XIV shows the results obtained on multiple plate cells tested in three different orientations — upright, flat and inverted.

The cycle test evaluations of top closure materials and techniques show that the multiplate test cells will cycle satisfactorily in any attitude without significant change in performance. As shown in Table XIV, cycle life surpassed the required 140 cycle cut-off in all tests, except for MC-42 and MC-49. Analysis of these cells showed fabrication errors to be the cause of poor performance. To illustrate the relative uniformity of the number of cycles completed in each attitude, the average number of cycles in each orientation was calculated and shown in Figure 28. The average number of cycles in the upright position was about 335, 395 in the flat position, and 315 in the inverted position. The change in attitude did not seem to affect the performance significantly.

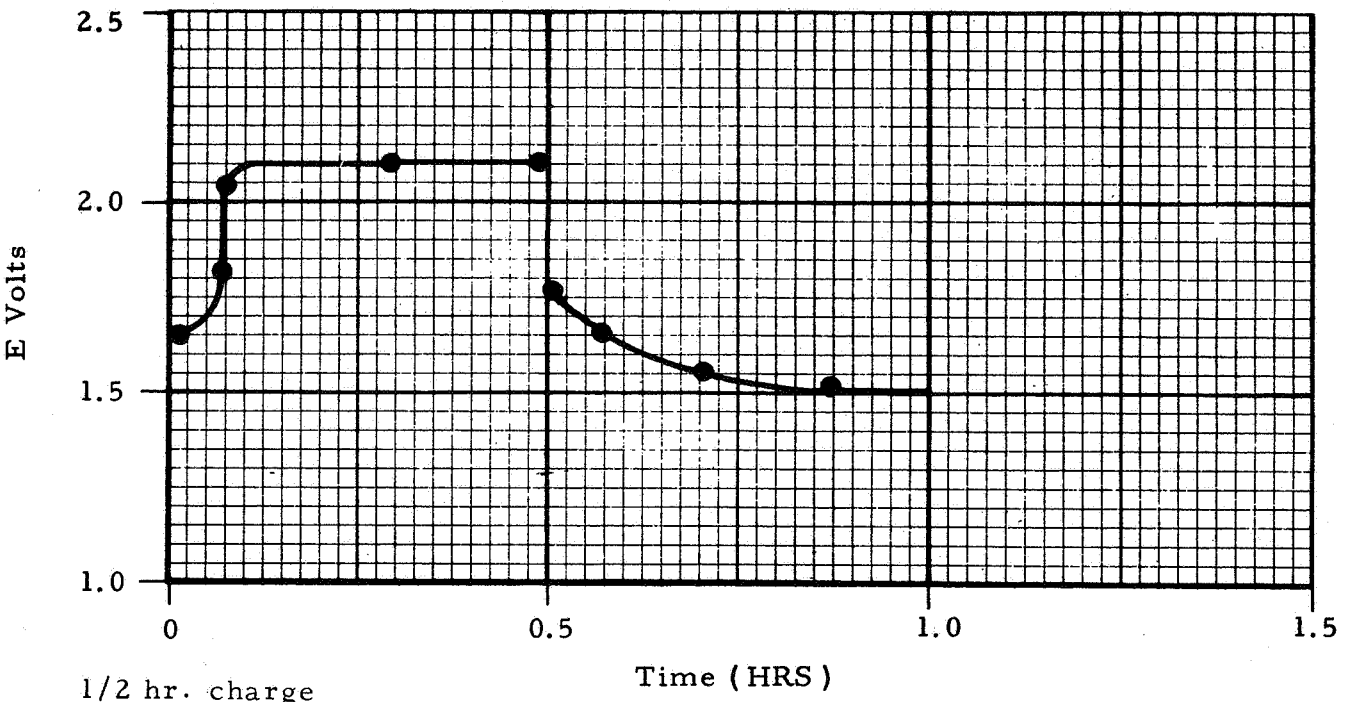
To further illustrate the lack of effect of different cell positions on performance, three charge-discharge curves were plotted showing cell characteristics during cycling. Figure 29 shows



1/2 hr. charge
1/2 hr. discharge $\frac{C}{5}$

t = 1

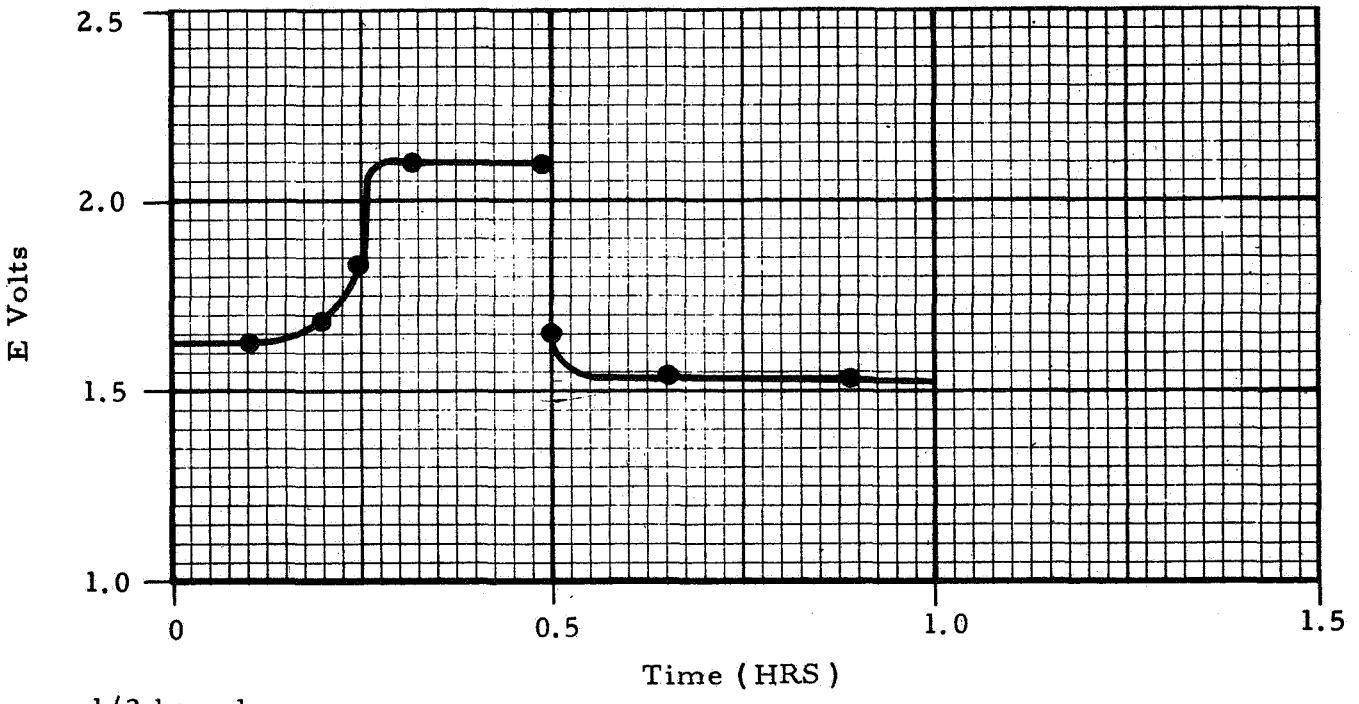
Figure 25. 5 Ah Cell MC-56 Fifth Cycle at 100 °C at $\frac{C}{5}$ After Heat Soak at 135 °C



1/2 hr. charge
1/2 hr. discharge $\frac{C}{5}$

t = 100 °C

Figure 26. 5 Ah Cell MC-57 Fifth Cycle at 100 °C at $\frac{C}{5}$ After Heat Soak at 135 °C



1/2 hr. charge
1/2 hr. discharge $\frac{C}{5}$

t = 100 °C

Figure 27. 5 Ah Cell MC-57 140 Cycles at 100 °C at $\frac{C}{5}$ After Heat Soak at 135 °C

TABLE XIV

MULTIPLATE CELL CYCLING DATA AT 25°C AT DIFFERENT ATTITUDES

Cell No.	Design					Discharge					No. of Cycles
	Code	Frame	Cement	Original Capacity Q_o	Negative Compartment Top-filler	Period (hrs)	Rate (A)	Current Density (mA/cm^2)	Depth of Discharge % of Q_o	Mode	
MC-42	D-8	E"	Allbond	1.4	Armalon Felt	1/2 x 1/2	1	7		Up	39
MC-43				5.2					10	Flat	276
MC-44				5.0					10	Upside Down	259
MC-45	D-8	E"	Allbond	5.0	Allbond	1/2 x 1/2	1	7	10	Up	265
MC-46				5.3					10	Flat	515
MC-47				5.1					10	Upside Down	339
MC-48	D-8	E"	Allbond	6.4	Epibond	1/2 x 1/2	1	7	8	Up	512
MC-49				5.5					9	Flat	76
MC-50				7.1					7	Upside Down	280
MC-59	D-10	E'''	Allbond	6.9	Nylon Fibers	1/2 x 1/2	1	7	7	Up	485
MC-60				7.4					7	Flat	589
MC-61				5.9					8	Upside Down	360
MC-62	D-10	E'''	Allbond	6.0	RTV	1/2 x 1/2	1	7	8	Up	361
MC-63				6.6					8	Flat	352
MC-64				4.4					11	Upside Down	296
MC-65	D-10	E'''	Allbond	5.7	U-218x	1/2 x 1/2	1	7	9	Up	249
MC-66				4.5					11	Flat	252
MC-67				5.1					10	Upside Down	337

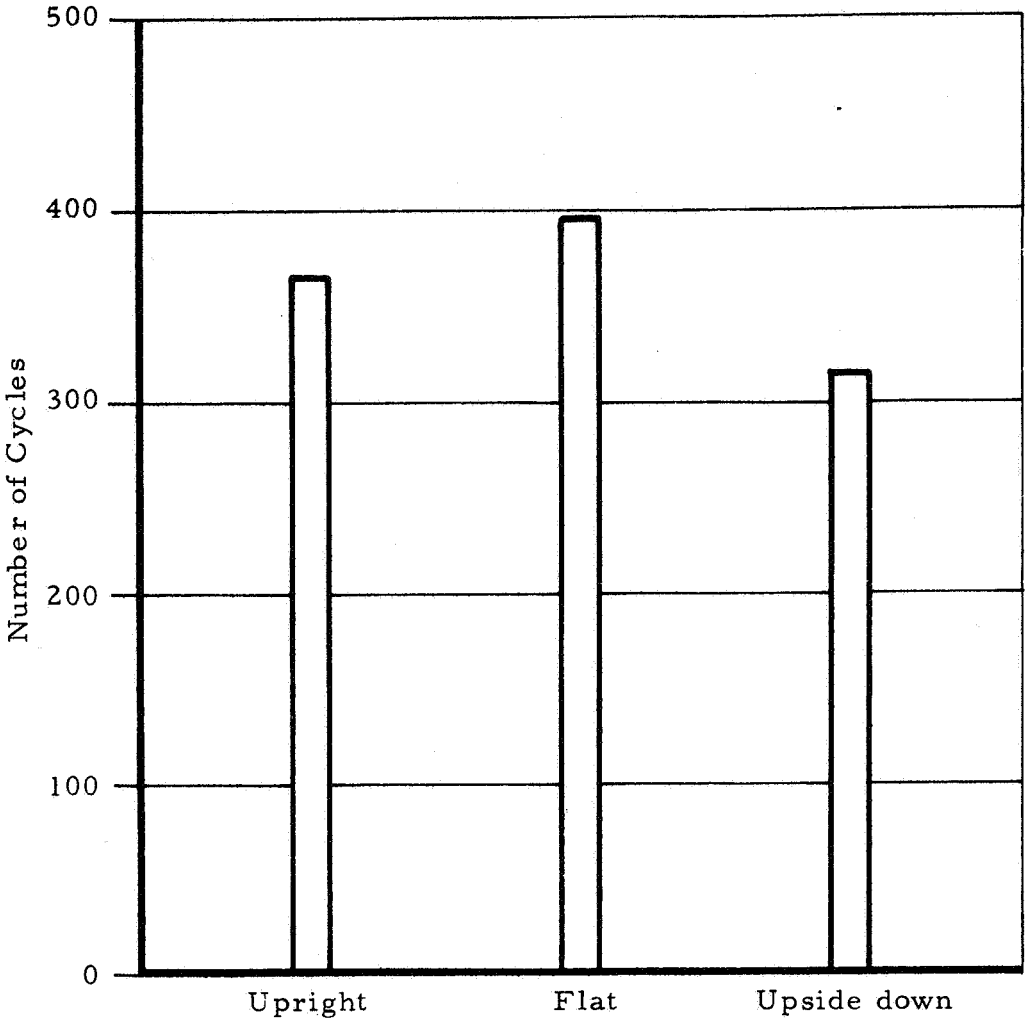


Figure 28. Comparison of Cycles Completed at Each Attitude

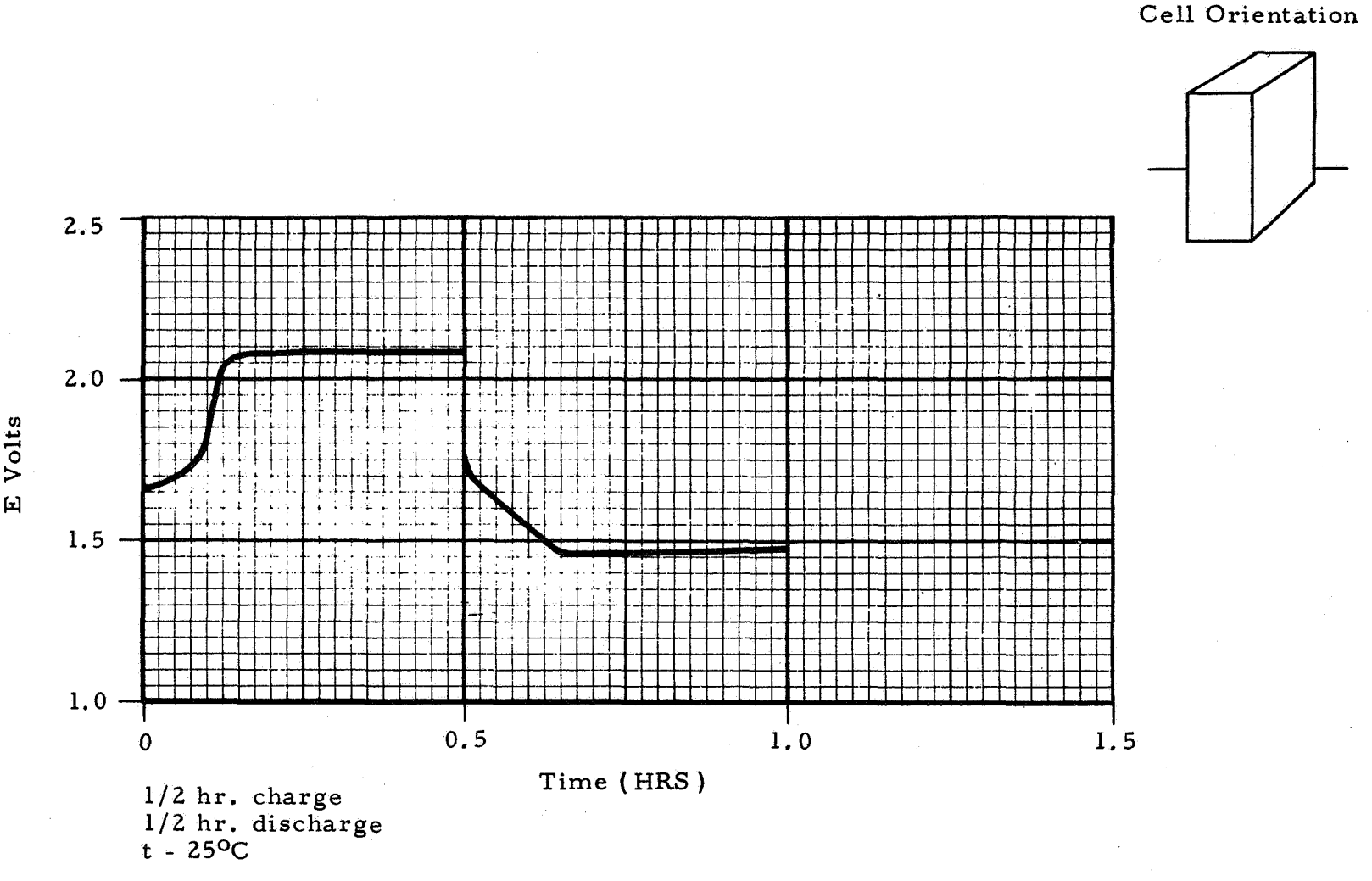


Figure 29. Test Cell MC-62 After 290 Cycles at C/5 at 25°C

multiplate cell MC-62 cycling in the upright position; discharge voltage plateau is about 1.45 volts. Figures 30 and 31 show multiplate cells MC-66 and MC-67 cycling in the flat and upside down positions; discharge plateaus for these cells are about 1.37 volts.

Examination of these multiplate cells cycling in different orientations showed that a combination of negative compartment top filler materials should be used. This is because the porous top fillers, such as the nylon fibers and Armalon felt, tend to dislodge somewhat in the inverted position. While the negative electrode material loss was very slight, elimination of any electrode material was realized when the porous top filler was held in place with an epoxy adhesive, such as Allbond cement. RTV silicone rubber used as a top filler was not effective because it loses its adhesion in the electrolyte with time. The rigid epoxies are excellent top fillers, except they allow some electrode material loss through a small hole left in the epoxy for adding electrolyte. The closure design shown in Figure 32 permits cell operation in any orientation without loss of performance.

2.2.1.7 Technical Directive No. 1

Technical Directive No. 1 was issued on April 19, 1966 to permit a preliminary evaluation of design configuration and components prior to fabricating the eight multiplate cells specified in the work statement (Task II, Paragraph 7). A copy of TD-1 is included in Appendix A of this report, along with our test procedures.

All of the tests specified in TD-1 have been completed and the results are shown in Table XV.

Six multiplate cells, MC-38, 39, 54, 55, 56, and 57, were fabricated and tested in accordance with the specification outlined in Technical Directive No. 1. All cells passed the required electrolyte leak tests. They were then given one formation cycle and then discharged at 3 A at 25°C (20 ma/cm^2). They were then discharged at 3 A at 100°C.

The internal resistance of each cell was measured three separate times while charging on the argentic plateau. All measurements were consistent and very close. The average values reported in Table III are accurate to within 0.005 ohm.

As can be seen from Table XV the cells fabricated with epoxy cements (MC-38, MC-39, MC-54, and MC-55) lost their normal open-circuit voltage and exhibited a decline in capacity after the high temperature test.

Analysis of these cells showed separator fractures caused by plastic frame warpage. However, cells MC-56, MC-57, in which a flexible sealant (RTV) was used continued to maintain normal

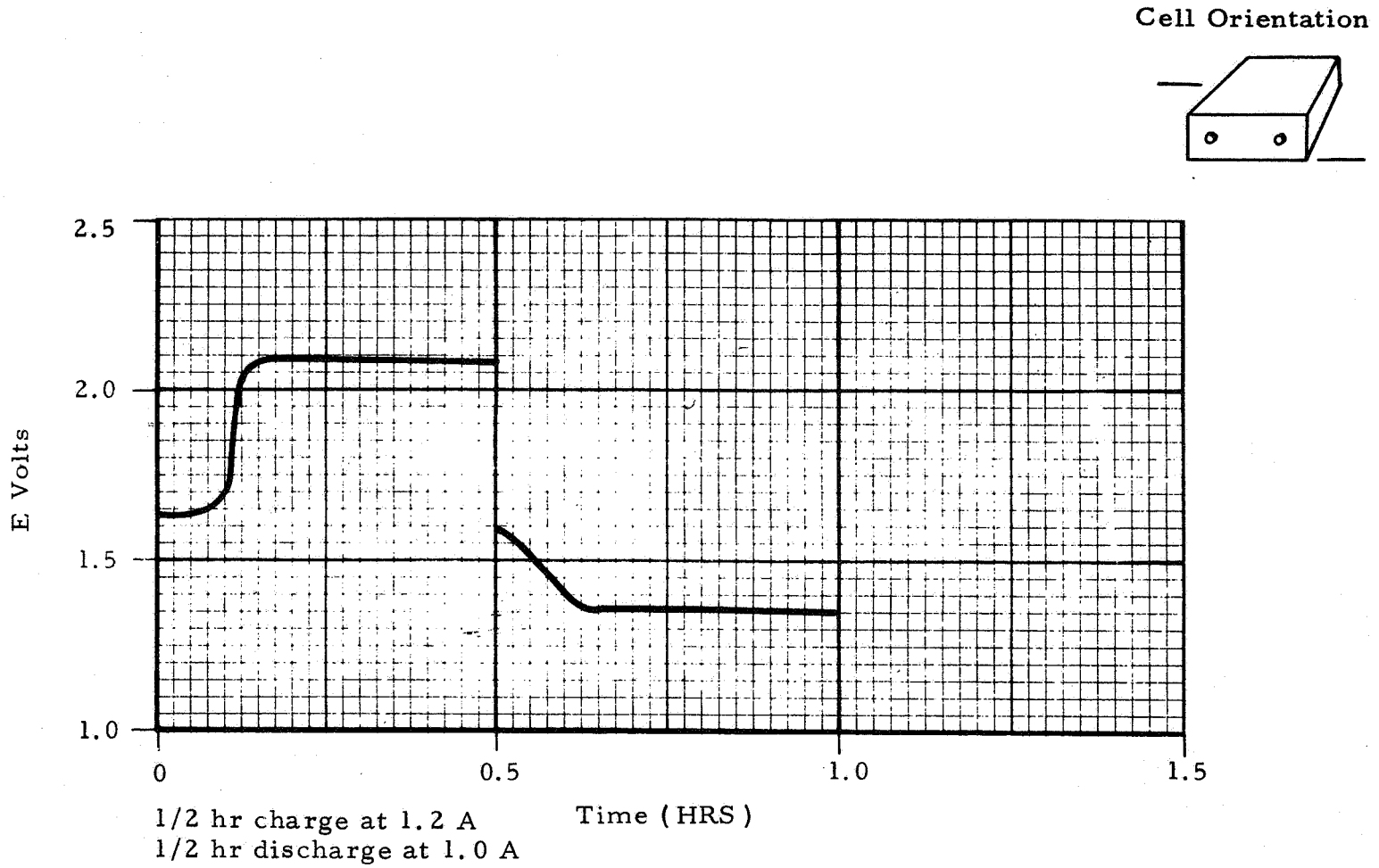


Figure 30. Test Cell MC-66 After 252 Cycles at $\frac{C}{5}$ at 25°C

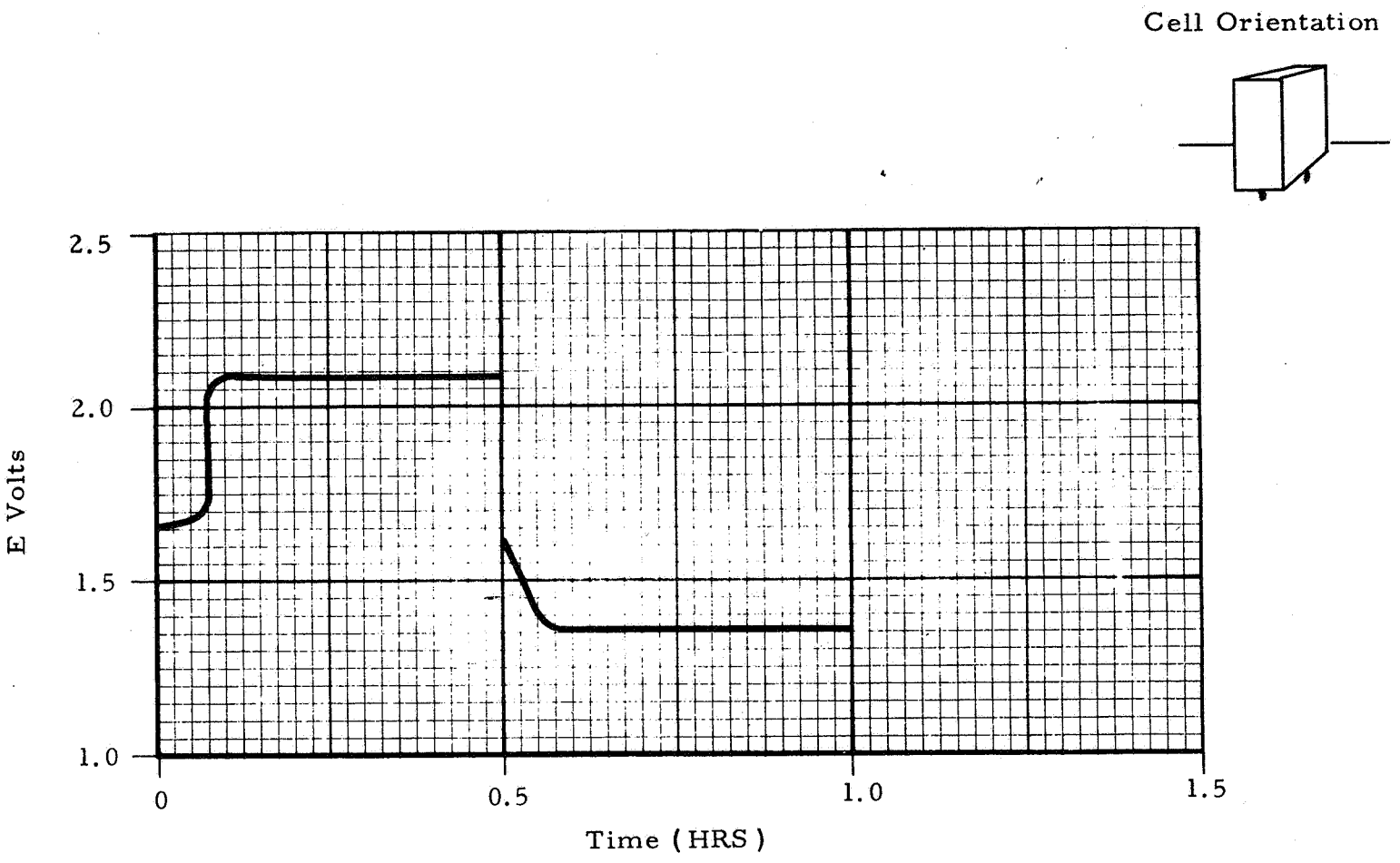


Figure 31. Test Cell MC-67 After 335 Cycles at C/5 at 25°C

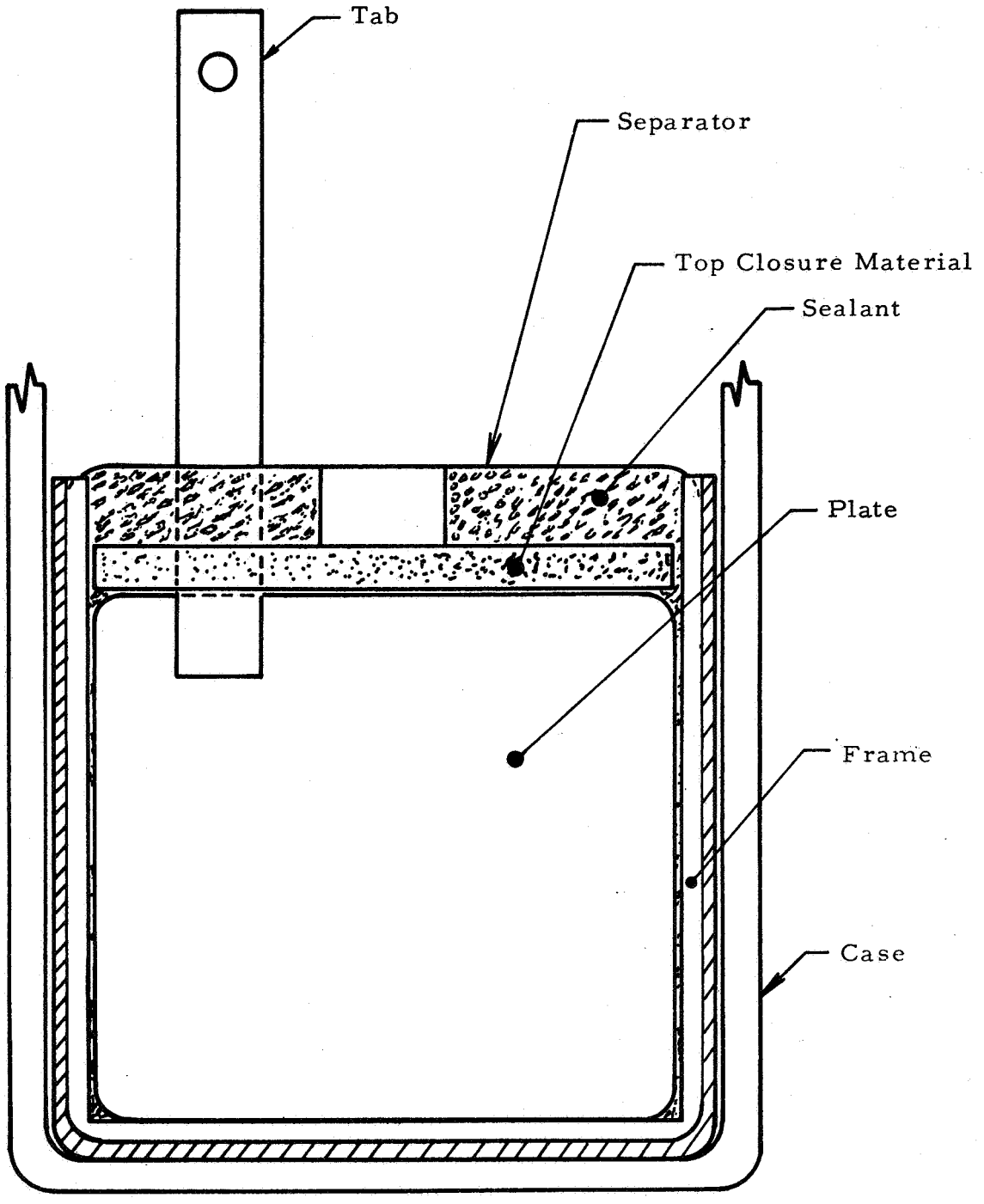


Figure 32. Top Closure for Negative Electrode Compartment

TABLE XV

SUMMARY OF TEST RESULTS – TECHNICAL DIRECTIVE NO. 1

Cell No. and Cement	Outputs (Ah) at Cycles # 1 1.5A 25 °C	# 2 3A 25 °C	# 3 3A 100 °C	Internal Resistance (ohm.)	After Heat Exposure 3 hrs/135 °C OCV	Capacity After Recharge
MC-38 All-Bond	5.5	4.8	4.2	0.057	1.58	1.2 Ah
MC-39 All-Bond	5.4	4.5	4.2	0.057	1.58	1.0
MC-54 All-Bond	5.1	5.4	6.0	0.063	1.76	1.2
MC-55 All-Bond	5.6	4.7	4.5	0.067	1.83	1.0
MC-56 RTV	5.6	5.7	6.3	0.06	1.86	2.0
MC-57 RTV	5.6	5.7	6.3	0.06	1.86	2.8

good open circuit voltage (1.86 V) and retained considerably greater capacity than the cells using the rigid cements.

2.2.2 Inorganic Separators

The inorganic battery separators used in the development of a 5 ampere-hour multiplate battery capable of long cycle life and operation at temperatures as high as 100°C were based on Astroset separator materials previously developed by Astropower Laboratory (Reference 1) and evaluated under NASA Contract NAS 3-6007, "Inorganic Separator for High Temperature Silver-Zinc Battery" (Reference 2). These separators are prepared from special formulations by high pressure compaction and sintering in order to develop the physical, chemical and electrical characteristics necessary for effective performance in high energy density batteries.

2.2.2.1 Separator Scale-Up

In order to scale-up the inorganic separators used in the previous work (Reference 1) to the size and shape required by this program, new compacting tooling was designed and fabricated for producing inorganic separators for the 5 Ah test cells and batteries. Figure 33 is a photograph of the die set used. Figure 34 is a drawing of this tooling, which shows the dimensions and tolerances for each of the die components.

2.2.2.2 Separator Evaluation

For quality control purposes, the transverse strength, percent absorption and resistance to KOH of the inorganic battery separators is regularly determined. As discussed previously, process improvements, mechanization, and the development of skilled personnel have resulted in a general improvement of separator quality. The transverse strength of Type 5-036-011 inorganic separator was increased substantially. Earlier tests showed a transverse strength of about 5000 psi for this material (Reference 1), whereas, current tests indicate a transverse strength of about 7000 psi as a result of improved processing methods and techniques. The level of uniformity of strength and absorption is also very high, indicating adequate process control.

2.2.2.3 Selection of Astroset Inorganic Separator for Task III Cells

During the component evaluations investigations carried out under Task II of this program, Astroset Type 5-036-011 inorganic separators were used in fabricating the test cells. These separators were selected based on long cycle life obtained at 25° and 100°C in the work done during the previous contract NAS 3-6007, they are characterized by good resistance to KOH at temperatures up to 150°C, high strength (7000 psi modulus of rupture) and low resistivity.

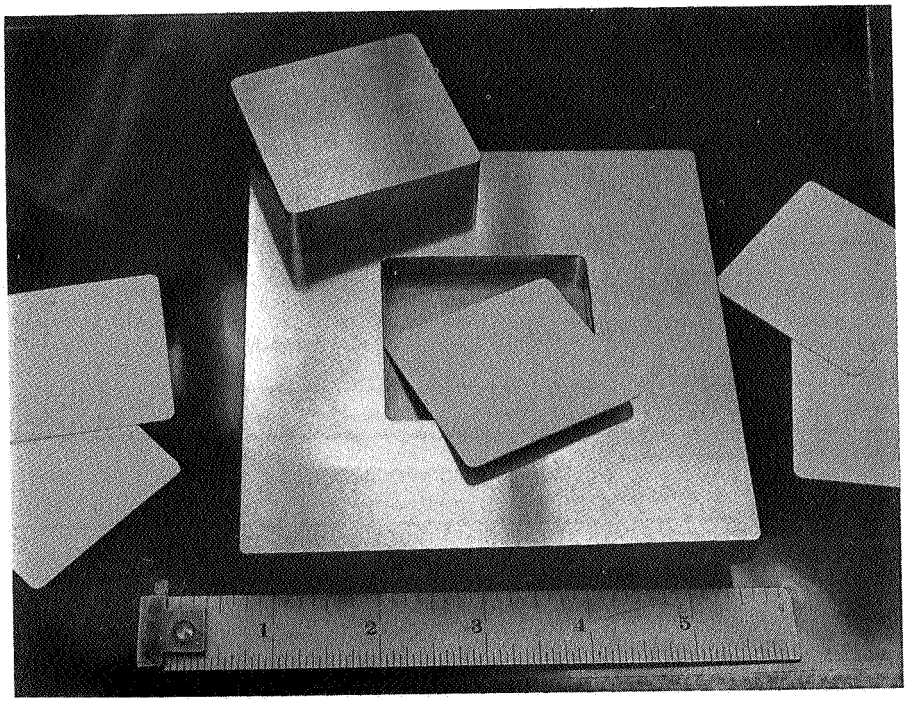
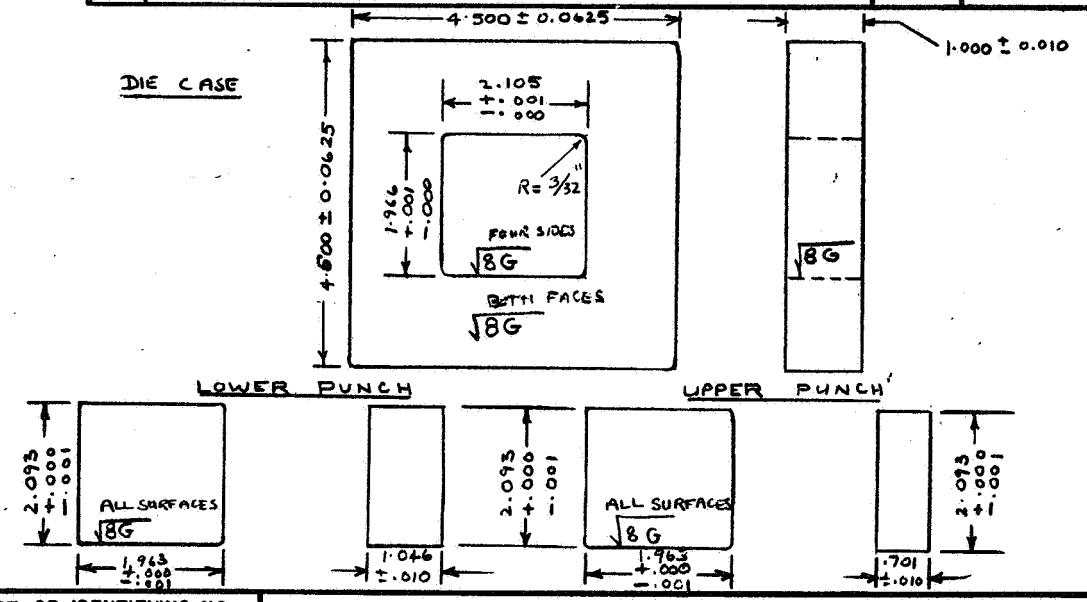


Figure 33. Die Set for Compacting 5 Ah Inorganic Separators

X 60-999 (REV 4-64)

REVISIONS			
SYM	DESCRIPTION	DATE	APPROVED



PART OR IDENTIFYING NO.	
DASH NUMBERS OF THIS DRAWING ODD DASH NUMBERS SHOWN EVEN DASH NUMBERS OPPOSITE UNLESS OTHERWISE SPECIFIED	MATERIAL OIL HARDENING TOOL STEEL
DIMENSIONS ARE IN INCHES TOLERANCES FRACTIONS ± DECIMALS ± ANGLES ±	FINISH GRIND AS NOTED

SEE ENGINEERING RECORDS FOR USAGE DATA

ORIG SECT.	REL CODE	FIRST REL OF PRINTS / ORIG DATE OF DWG
		9-7-65

MATL		
WT CHK		
STR CHK		
CHECK		
PR ENGR		
DES ENGR		
GR ENGR		
PREP BY	George Bolyn	9-7-65

DOUGLAS AIRCRAFT COMPANY, INC — SANTA MONICA, CALIFORNIA

Figure 34. Punch and Die for Battery Separators

9-7-65
DESIGN ACTIVITY APPROVAL

CUSTOMER APPROVAL

CODE IDENT NO.	SIZE	
18355	A	NAS 3-7639-02
SCALE - HALF		SHEET 1 OF

When the original cell design was changed from the rigid frame type to the modified frame, electrode compartment, it was found that Astroset Type 3420-09 separators had superior bonding characteristics with the electrode compartment sealants used. Because the other characteristics of 3420-09 separators were equal or superior to the 5-036-011 type, they were selected for application in the Task III 5 Ah cell. Table XVI compares the significant characteristics of the two separator materials.

TABLE XVI

CHARACTERISTICS OF ASTROSET INORGANIC SEPARATOR

Astroset Type	Resistivity (ohm-cm)	KOH Compatibility at 180°C	Transverse Strength (pso)	Bonding Characteristics
5-036-011	40	Good	7000	Fair
3420-09	18	Good	10,000	Good

2.2.2.4 Separator Fabrication

Complete processing, testing and inspection specifications have been prepared covering separator manufacture. These specifications include raw materials, material preparation, compaction, sintering, inspection standards and quality control procedures.

In order to improve separator quality and to maintain a high level of uniformity and reproducibility of separator characteristics, many operations formerly performed manually have been mechanized. Figure 35 is a photograph of a ceramic plate pulverizer used for granulating separator pressing materials. Mechanization of the granulation method has resulted in greatly increased yields of pressing material, improved uniformity and reduced contamination. Figure 36 is a photograph of a high intensity magnetic chute used for removing magnetic iron from both raw materials and processed separator materials. The introduction of this magnet has resulted in a substantial reduction in iron spots in the sintered separators and in improved quality.

Figure 37 is a photograph of a blending machine which has been modified for vacuum drying. Granulated pressing materials can be dried to the desired moisture content rapidly while being blended. Use of this machine has resulted in improved quality and uniformity and has also increased the yield of usable pressing materials.

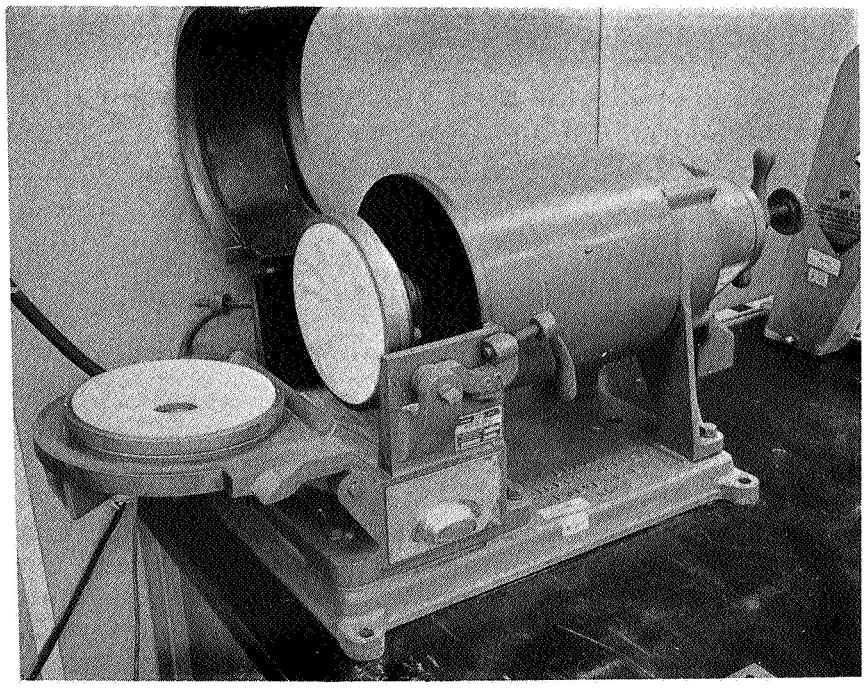


Figure 35. Ceramic Plate Pulverizer

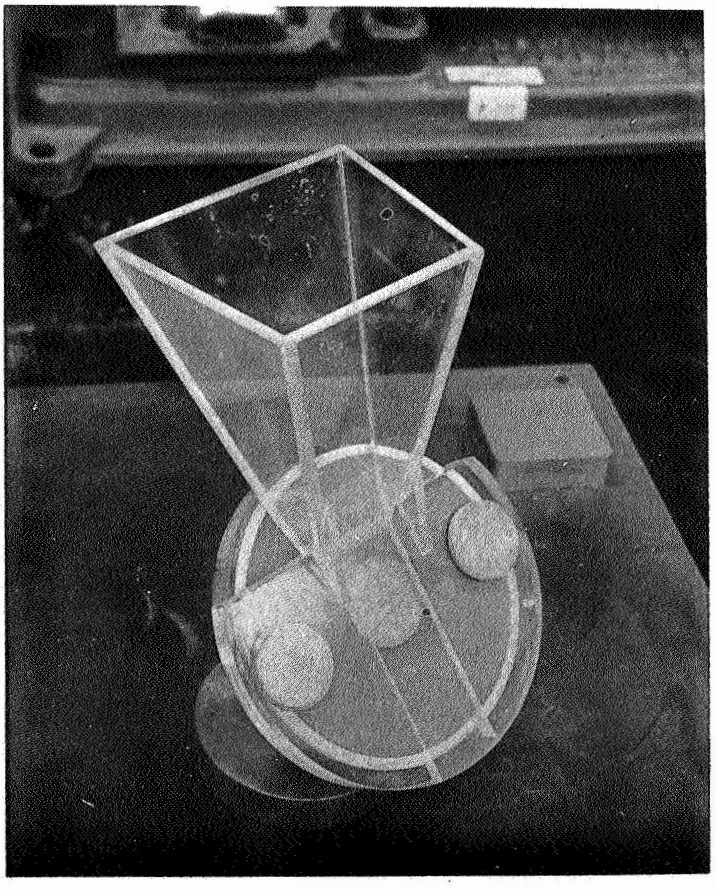


Figure 36. High Intensity Magnet for Removing Iron from Separator Materials

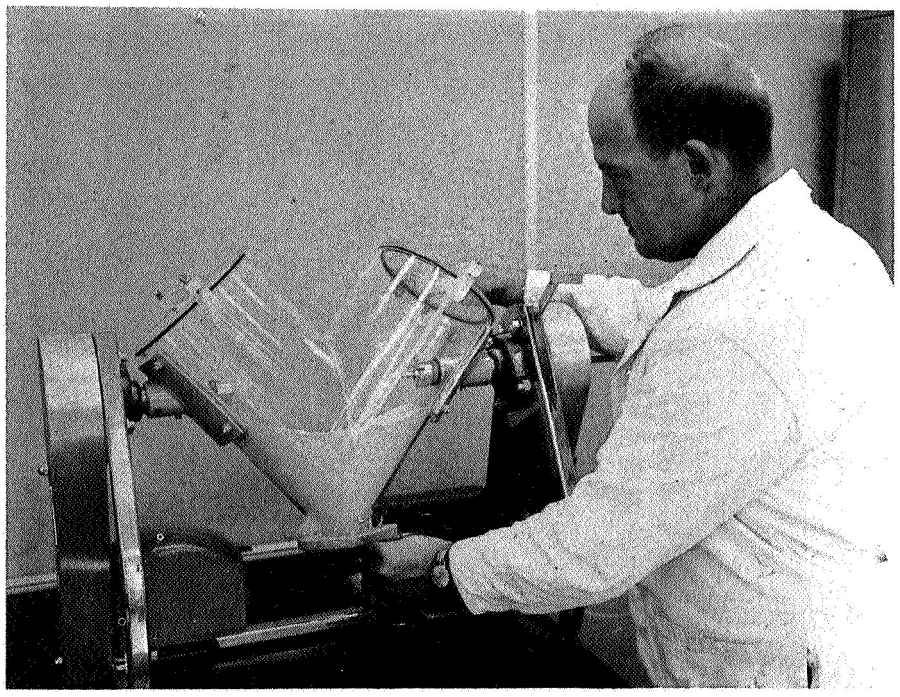


Figure 37. Mixer-Blender Arranged for Vacuum Drying Separator Materials

An automatic program controller and recorder has been installed on the high temperature gas-air sintering furnace shown in Figure 38. This instrumentation, Figure 39, consists of a cam-operated temperature controller and recorder and makes it possible to exactly duplicate sintering time temperature curves from one run to another. The use of this equipment has resulted in a substantial improvement in the uniformity of sintered separators and has increased the yield of separators that meet all of the inspection standards.

In addition to improving the quality and uniformity of the inorganic battery separators, this additional equipment also increases inorganic separator productivity capacity, making it possible to produce the substantially increased quantity of separators required by this program.

2.2.3 Cases

The work statement for Contract NAS 3-7639 provided for the evaluation of two candidate materials for use in fabricating the 5 ampere-hour cases for evaluation in Task III of the program. The basic criterion for selection was overall suitability for use in the multiplate cells which would be tested at temperatures as high as 145°C and are subject to long time exposure to 100°C during cycle life testing. Material evaluation tested for individual strength, modulus of elasticity, dimensional compatibility and resistance to thermal degradation in contact with concentrated KOH.

Initially, actual copolymer (Celcon) and polyphenylene oxide (PPO) were evaluated as described below. The results of this evaluation indicated that PPO was a satisfactory case material for use in this program. Subsequently, however, molding difficulties were encountered with PPO and polysulfone was substituted for it because of its superior molding characteristics and its excellent physical, electrical and chemical characteristics.

2.2.3.1 KOH Compatibility Tests

One-thousand hour KOH-high temperature compatibility tests on PPO and Celcon case materials were carried out by completely submerging PPO and Celcon test samples in 35% KOH in stainless steel pressure vessels. The sealed pressure vessels were heated to 100°C ± 2°C for 1000 hours. Figure 40 shows one of the pressure vessels used in these tests. At each 100-hour interval, the test samples were removed from the container, washed, dried, and inspected for evidence of degradation, and then returned to the pressure vessel to continue the test. The 100-hour inspections showed no visible degradation of either PPO or Celcon after a total of 1000 hours of exposure. Test samples were photographed prior to the start of the tests (Figure 41) and again after completion of the tests (Figure 42). The only visible change that occurred was a change

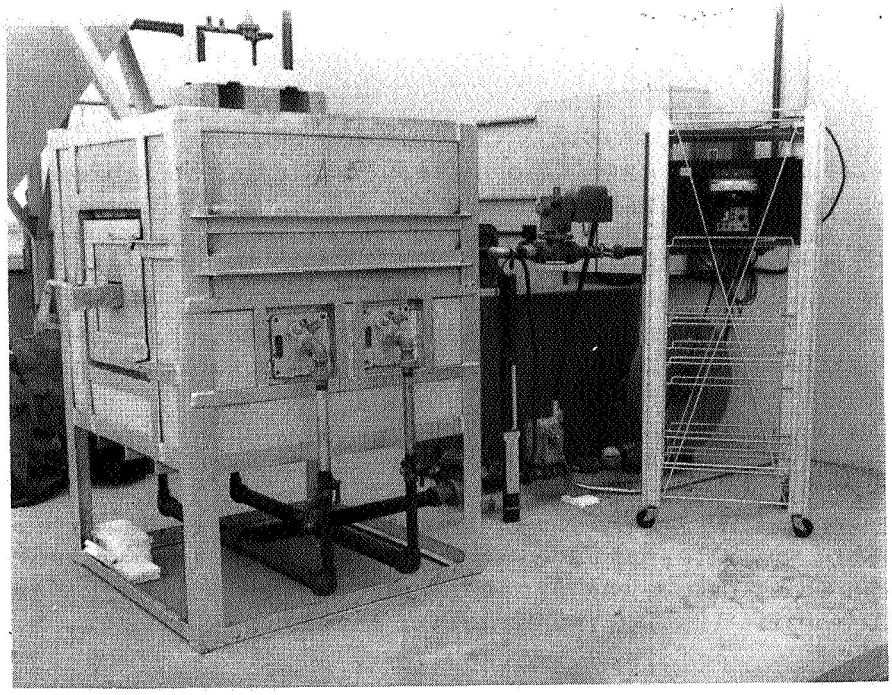


Figure 38. High Temperature Sintering Furnace

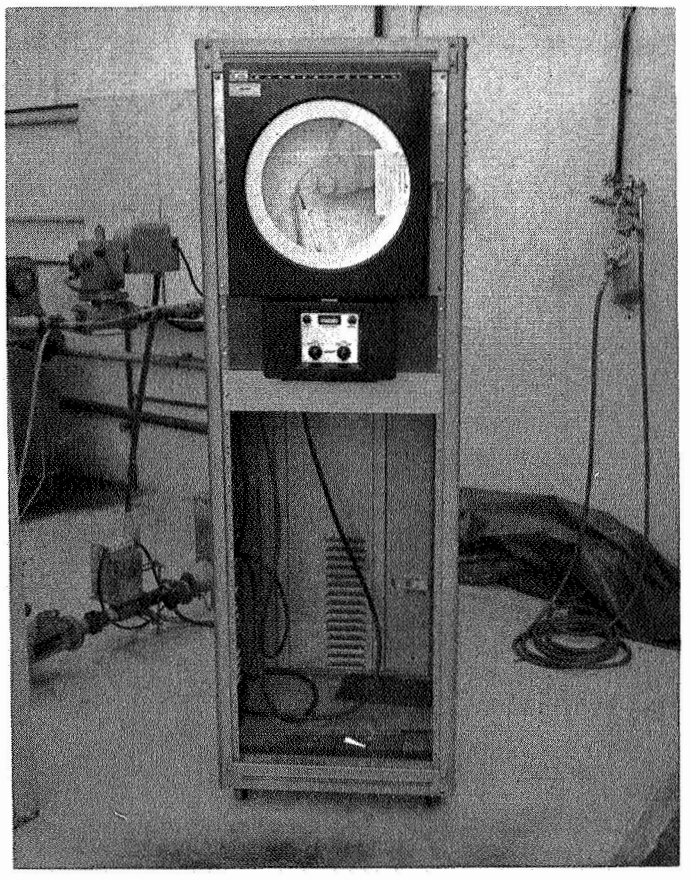


Figure 39. High Temperature Furnace Controller

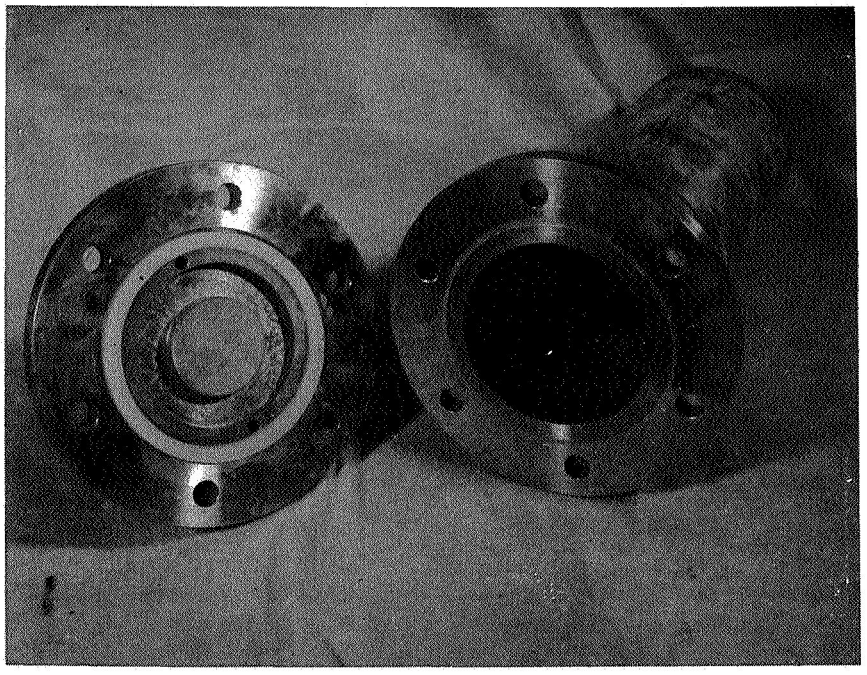


Figure 40. Stainless Steel Pressure Vessel

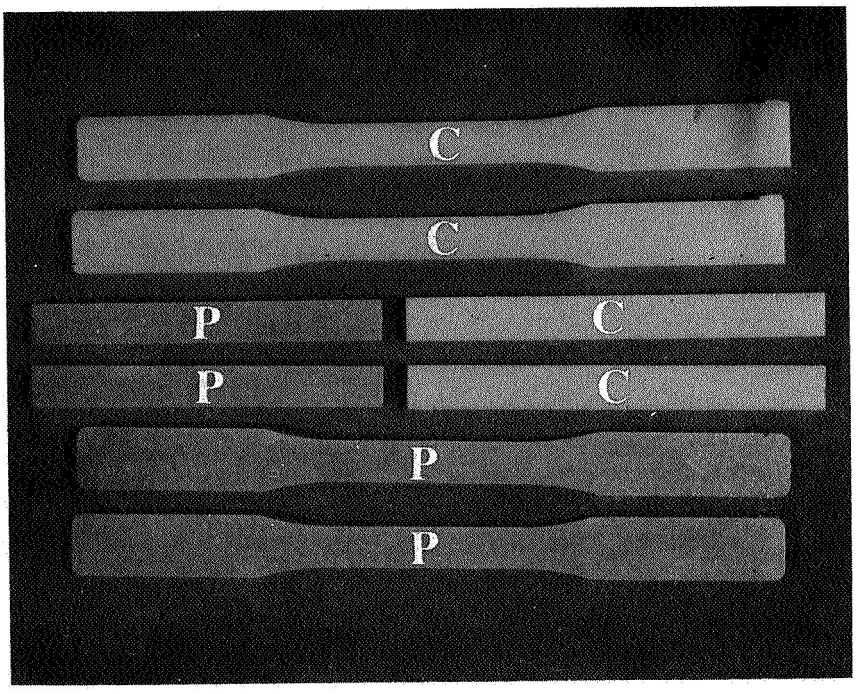


Figure 41. Test Samples of Celcon and PPO Prior to the 1000-hour KOH Compatibility Test

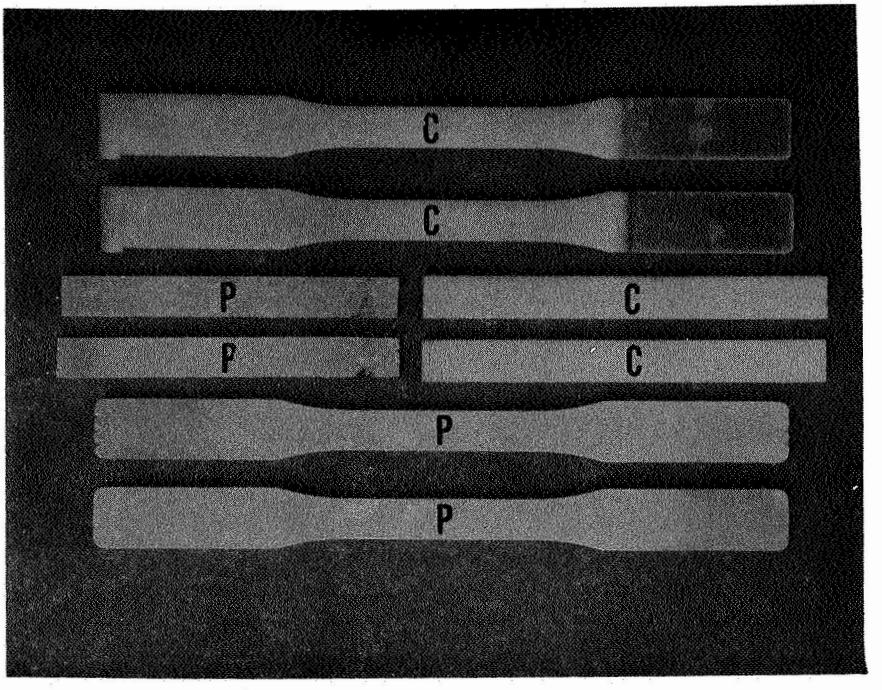


Figure 42. Test Samples of Celcon and PPO Following the 1000-hour KOH Compatibility Test

in color of the Celcon test specimens from white to beige where the test specimen protruded from the KOH solution. This discoloration can be noted in Figure 42 at the right ends of the two top Celcon test specimens. The PPO test specimens were unchanged in color.

Test results on the PPO and Celcon test specimens after 1000 hours exposure to KOH at 100°C are shown below:

1. Tensile strength and modulus of elasticity after exposure; tested and computed in accordance with ASTM D-638-64T.

Sample No.	Material	Ultimate Tensile (psi)	Average (psi)	Modulus of Elasticity	Average (psi)
1	Celcon	9,540		3.36×10^5	
2	Celcon	9,370		8.28×10^5	
3	Celcon	9,510	9430	5.17×10^5	5.17×10^5
4	Celcon	9,480		4.18×10^5	
5	Celcon	9,310		5.22×10^5	
6	Celcon	9,360		4.82×10^5	
7	PPO	10,600		5.05×10^5	
8	PPO	10,600		6.01×10^5	
9	PPO	10,600	10600	5.43×10^5	5.64×10^5
10	PPO	10,700		6.08×10^5	
11	PPO	10,700		6.02×10^5	
12	PPO	10,600		5.26×10^5	

2. Modulus of rupture after exposure; tested and computed per ASTM D-790-63.

Sample No.	Material	Modulus of Rupture (psi)	Average (psi)
1	Celcon	11,240	
2	Celcon	10,900	11,000
3	Celcon	10,900	
4	PPO	14,690	
5	PPO	15,210	15,000
6	PPO	15,100	

3. Dimensional stability and weight change after exposure. For this test the thickness and width were measured with a dial thickness gauge, to the nearest 0.001 inch, at several points along each sample before exposure. Following exposure, measurements were taken at identical points and compared with the initial values. In a like manner the length of each sample was measured between two specific points before and after exposure. For the weight change the samples were weighed on an analytical balance to four decimal places before and after exposure.

Material	Celcon	PPO
Average thickness change	0	0
Average width change	-0.16%	-0.05%
Average length change	-0.24%	0
Average weight change	-0.15%	-0.01%

4. Appearance after exposure: The samples after exposure were compared with unexposed samples for color. The Celcon had changed in color from a milk white to a light blue-gray in the area of total immersion in the solution. In the area where the tensile tabs were out of the solution in the vapor phase the color had changed to a dark beige. The color of both areas was the same in the interior of the sample as on the surface. After testing, the tensile bars turned blue in the areas of strain. The gloss of the Celcon resin was unchanged by exposure. The PPO was essentially unchanged in color and gloss after exposure.

5. Summary of test results:

Material	Test	Manufacturer's Data	Before KOH Exposure	After 1000 hr KOH Test
Celcon	Ultimate Tensile	8,800 psi	8,470 psi	9,430 psi
Celcon	Modulus of Elasticity	No value given	3.69×10^5 psi	5.17×10^5 psi
Celcon	Modulus of Rupture*	13,000 psi	12,000 psi	11,000 psi
PPO	Ultimate Tensile	9,000-10,000 psi	9,460 psi	10,600 psi
PPO	Modulus of Elasticity	$3.5\text{-}3.8 \times 10^5$ psi	3.4×10^5 psi	3.4×10^5 psi
PPO	Modulus of Rupture*	14,000-15,000 psi	13,000 psi	15,000 psi

*The modulus of rupture is a measurement of the load per unit area, placed in the center of a beam of test material, required to develop five (5) percent strain in the outer fiber.

Because one of the program requirements involves thermal cycling of activated multiplate cells at 145°C ± 2°C for three 36-hour soak periods, it was decided to submit test samples of PPO and Celcon to this test while they were submerged in 45% KOH during the evaluation of case materials; this was to select a case material that would also satisfactorily meet this requirement. Due to an error in calibration of the temperature recorder, a higher temperature was obtained for two and one-half of the 36 hour periods of test than planned. As a result, the test samples of PPO and Celcon were heated to 193°C for 93 hours plus 15 hours at 145°C. The PPO samples were unaffected by this test but the Celcon samples melted into a lump. An additional test on new Celcon test samples was conducted by heating the submerged samples in 45% KOH for 6 hours at 145°C ± 2°C. These samples also melted into a lump during this test. Based on these tests it was determined that PPO was a satisfactory case material and that Celcon was unsuitable for use in this program.

The test results on the PPO test specimens are shown below:

1. Tensile strength and modulus of elasticity after exposure to 45% KOH (tested in accordance with ASTM D-638-64T).

Sample No.	Material	Ultimate Tensile (psi)	Average (psi)	Modulus of Elasticity	Average (psi)
1	PPO	11,250		3.47×10^5	
2	PPO	11,250	11,260	3.58×10^5	3.49×10^5
3	PPO	11,340		3.51×10^5	
4	PPO	11,190		3.40×10^5	

2. Modulus of rupture, after exposure (tested in accordance with ASTM D-790-63).

Sample No.	Material	Modulus of Rupture (psi)	Average (psi)
1	PPO	14,590	
2	PPO	14,980	14,900
3	PPO	14,720	
4	PPO	15,330	

3. Dimensional Stability: For this test the thickness and width were measured with a dial thickness gauge in the nearest 0.001 inch, at several points along each sample, before

exposure. Following exposure, measurements were taken at identical points and compared with the initial values. In a like manner the length of each sample was measured between two specific points before and after exposure.

Average thickness change	+1.6%
Average width change	+0.3%
Average length change	-1.4%

4. Weight Change: The samples were weighed on an analytical balance to four decimal places before and after exposure.

Average weight change	-0.01%

2.2.3.2 Case Fabrication

The original 5 ampere-hour cell cases were assembled by cementing together components machined from flat stock. These PPO cases were satisfactory for the preliminary evaluation of the design concepts and for limited testing. They were expensive and difficult to fabricate because of the multiplicity of glued joints and the dimensional instability of the machined parts. Accordingly, an arrangement was made with a plastic molder to injection mold PPO and polysulfone cases using existing tooling.

The dimensions of these molded cases closely approximated the case design established in Task II, except for height, which could be machined to the desired dimension. Although the quality of these cases was not uniformly high, they were satisfactory for use in the component testing and evaluation work done in Task II of this program. These injection molding tools have been designed for molding Bakelite C-11 and the PPO cases produced with this testing were laminated and cracked due to inadequate gating and poor material flow. The polysulfone cover made with these tools were badly strained, but acceptable for component tests, although in a few instances, the cases cracked during cycle tests at 100°C and developed KOH leakage.

In order to have a satisfactory case for the cells fabricated in Task III of this program, Douglas provided injection molding tooling for molding PPO and polysulfone cases and covers. The dimensions of these cases approximated the 5 ampere-hour cell design parameters. Satisfactory polysulfone cases were obtained from these tools for use in fabricating the Task III cells. However, the molder was unable, even with extensive assistance from the material supplier, to produce PPO cases of acceptable quality due to molding material variations and other problems related to PPO. Figure 43 shows a typical PPO case showing molding defects.

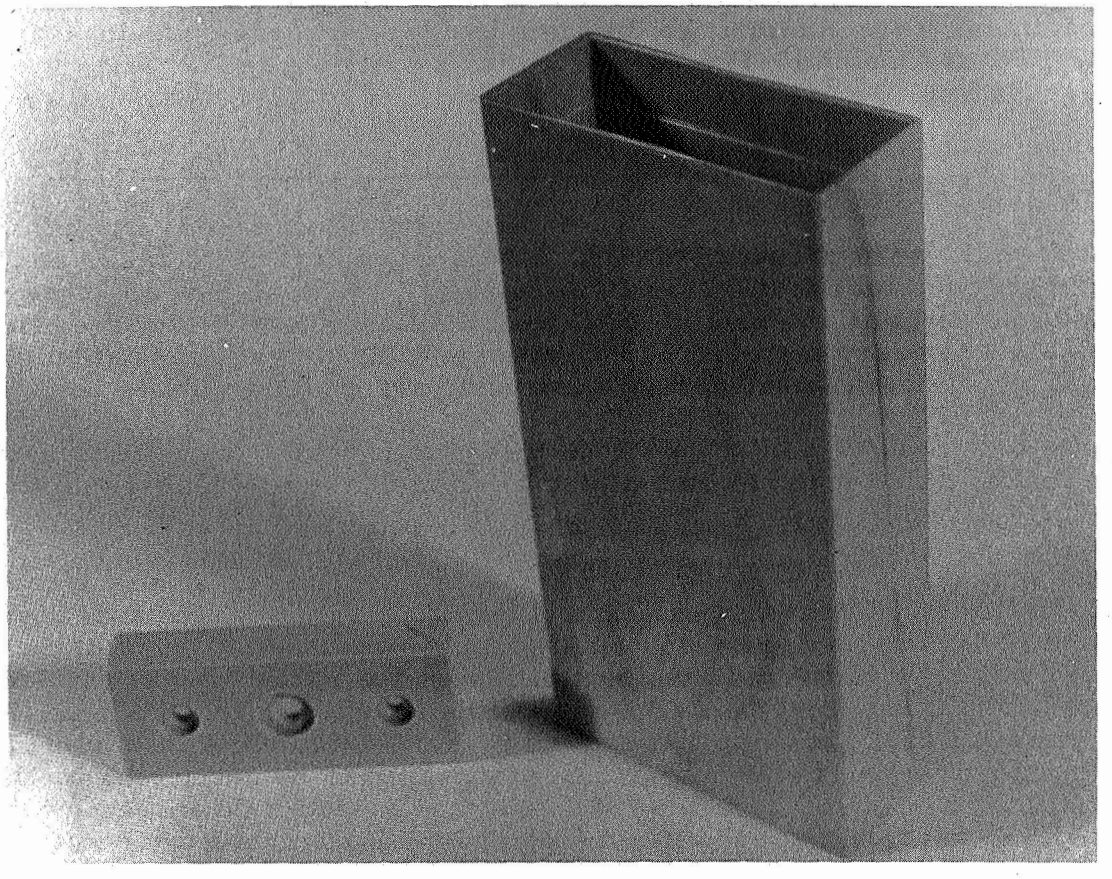


Figure 43. Molded PPO Case Showing Defective Structure Resulting from Improper Molding

The polysulfone cases produced with this tooling were uniformly of high quality and free from strains and functional defects. Typical 5 ampere-hour cases are shown in Figure 44.

Polysulfone was selected for use in the Task III 5-Ah cells based on these findings. Additionally, polysulfone test specimens were run through the complete test sequence previously described for PPO and Celcon. Polysulfone satisfactorily passed all tests without degradation.

2.2.3.3 Pressure Tests on Molded Cases

Molded polysulfone cases having 0.100 inch thick walls were pressure tested. It was found that these cases satisfactorily passed leak testing for 10 minutes at 30 psig at 125°C. They were also leak tight at 150 psig at 25°C but slight bulging was observed in all tests. The cases tested at 125°C retained a certain permanent bulge after cooling to room temperature. These data are shown in Table XVII.

In these same tests, the case to cover seals were also found to be satisfactory and showed no leakage up to 150 psig.

In one test a molded polysulfone case was subjected to 111 hours at 145°C in 30% KOH to simulate thermal sterilization. As shown in Figure 45, small cracks developed in the bottom of the case. These cracks radiated outward from the sprue marks. Molded cases that had not been heat treated were examined using polarized light. Stress areas were found but improved molding techniques relieved this problem. Other than these cracks, these cases appeared to be unaffected by the sterilization cycle. Figure 46 shows the polarized light inspection method used. Consequently, properly molded polysulfone cases were evaluated by this test and satisfactorily passed the thermal sterilization specifications at 145°C without any apparent effect.

2.2.4 Terminals

After a thorough review of existing plastic-to-metal and ceramic-to-metal terminal seal designs, it was decided that a plastic-to-metal seal could be used for the 5 ampere-hour cells in this program. As specified in the work statement, the terminal seal must be capable of sustaining 30 A pulses as well as operating at the one-hour rate.

Figure 47 shows the terminal design selected. It consists of a stainless steel screw and nut assembly and uses an ethylene-propylene thread seal and O-ring as primary seals. A secondary seal is provided by epoxy resin placed between the terminal components and the cell cover during assembly and then cured.

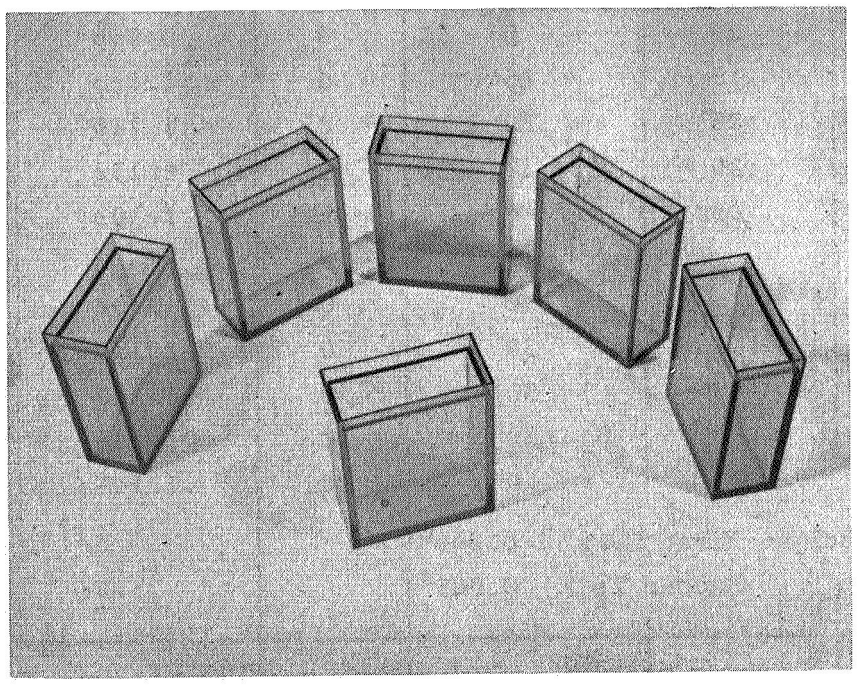


Figure 44. 5 Ah Polysulfone Cases from New Mold

TABLE XVII

CASE PRESSURE TEST RESULTS

Material	Temp., °C	Pressure, (psig)	Time, (min)	Thickness, (in)	Increase in Thickness, (in)
PPO	25	0	0	0.996	0
	115	15	0	1.065	0.069
	125	30	0	1.125	0.129
	125	30	5	1.132	0.136
	25	0	5	1.102	0.006
	25	0	0	1.102	0
	125	30	0	1.135	0.033
	125	30	5	1.140	0.038
	125	30	10	1.142	0.040
	25	0	10	1.111	0.009
Permanent Bulge: First Test: 0.006"					
Second Test: 0.009"					
Polysulfone (original)	25	0	0	1.000	0
	125	30	0	1.095	0.095
	125	30	5	1.101	0.101
	125	30	10	1.105	0.105
	125	30	15	1.110	0.110
(final)	25	0	15	1.002	0.002
Permanent Bulge: 0.002"					

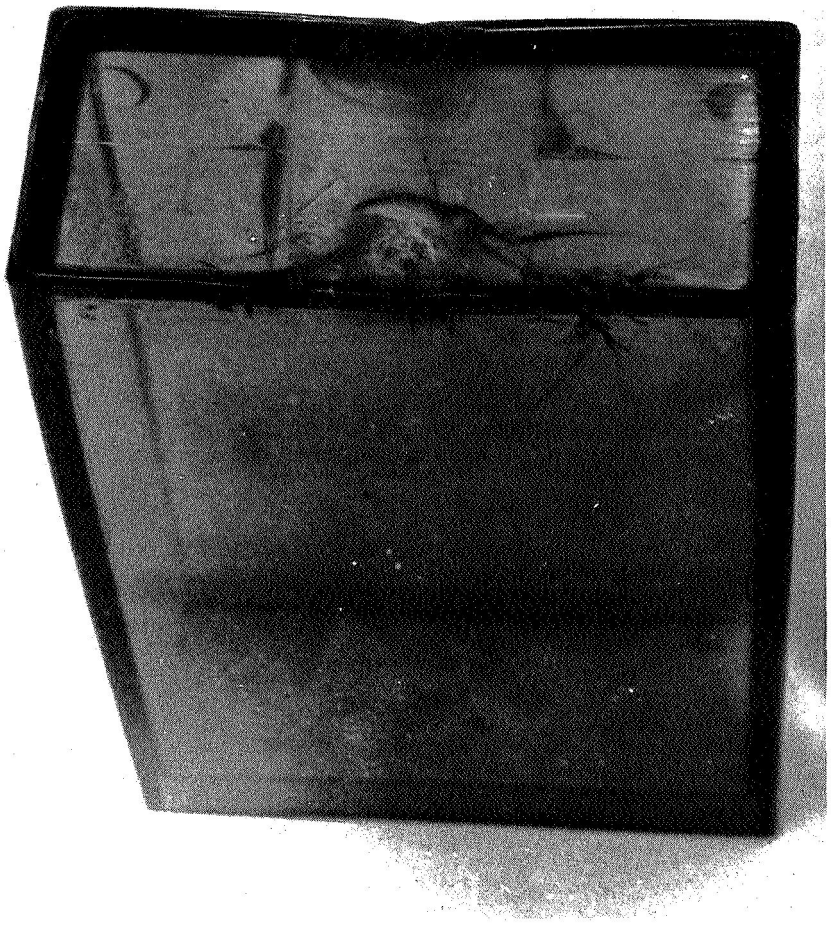


Figure 45. Cell Case Showing Cracks Radiating from Mold Marks as a Result of Improper Mold Design

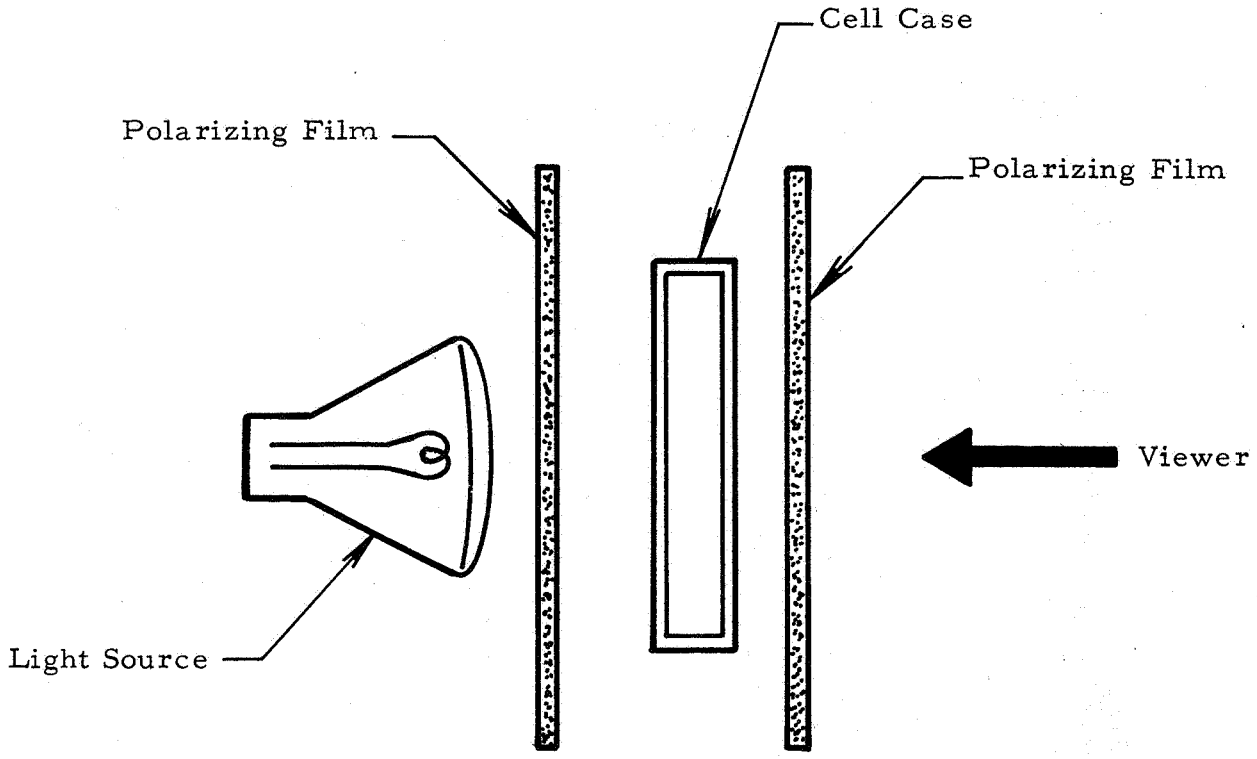


Figure 46. Polarized Light Inspection of Cell Cases

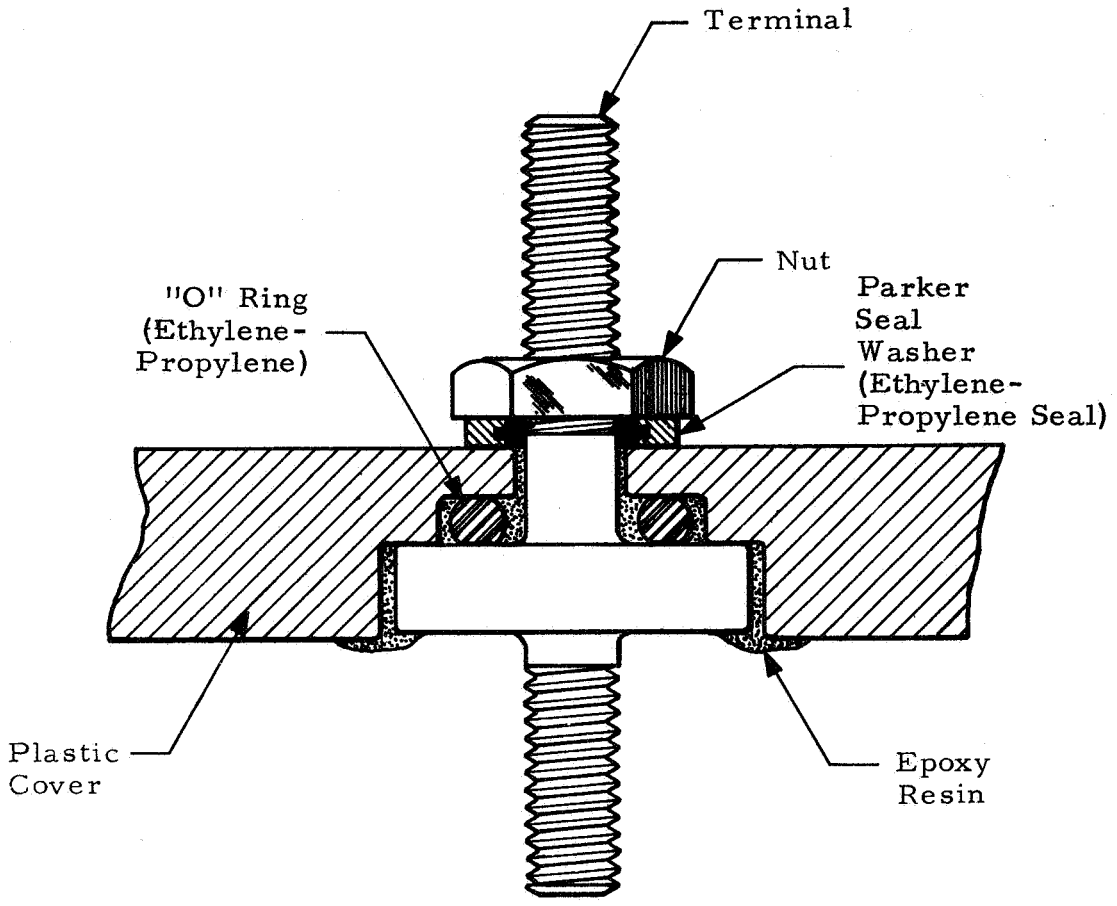


Figure 47. Terminal Seal Assembly

2.2.4.1 Test Fixture

A test fixture for testing terminal assemblies in KOH under thermal and pressure cycling was designed and fabricated.

This fixture consists of a base plate with a terminal seat as it will appear in the cell cover. The terminal configuration intended to be used in the cell is assembled to this dummy plate, which is screwed to a stainless steel chamber and sealed by an "O" ring. The chamber has three openings — one for supplying nitrogen pressure at the desired level, one for monitoring the pressure and one for the introducing of KOH in the chamber to cover the terminal (see Figures 48 and 49).

2.2.4.2 Terminal Testing

The terminal test performed was as follows:

a. The sample terminal was assembled on the base plate made of PPO.

b. The chamber was filled with 35% KOH.

c. The chamber was pressurized to 30 psig and the pressure maintained for 4 hours.

d. The assembly was cooled to -30° and held for 16 hours, then heated slowly to 150°C and held for 4 hours.

e. The assembly was maintained at 100°C and cycled as follows: 5 minutes at 30 psig, 5 minutes at atmospheric pressure, for a total of 8 hours.

No trace of alkalinity was detected at the external end of the terminal during the entire test and 24 hours later. The terminal was disassembled for examination. No attack could be detected on any material used or on the entire configuration. This design was incorporated into the multiplate 5 ampere-hour cells built and tested in Task III of this program.

2.2.5 Connections and Current Collectors

The electrode tab (current collector) connection to the cell terminal consisted of two basic designs — (1) silver tabs spot-welded or hot-forged to silver expanded metal grids cut to size, and (2) silver expanded metal grid in which a solid silver tab is an integral part of the grid. A KOH soak test was performed, in compliance with the statement of work. Two electrode current collector grids of the first design described above were completely submerged in 35% KOH in a stainless steel vessel, and maintained at 150°C ± 2°C for 168 hours. At the completion of the 168-hour soak test, the current collector grids were removed from the sealed vessel, washed, dried, and inspected under a microscope for corrosion. No evidence of corrosion was noted. Figure 50 is a photograph of the current collector grids taken after the 168-hour soak test. A 30 ampere current (dc) was then passed through each grid for a period of one minute with one current lead connected to the end of the silver tab and the other

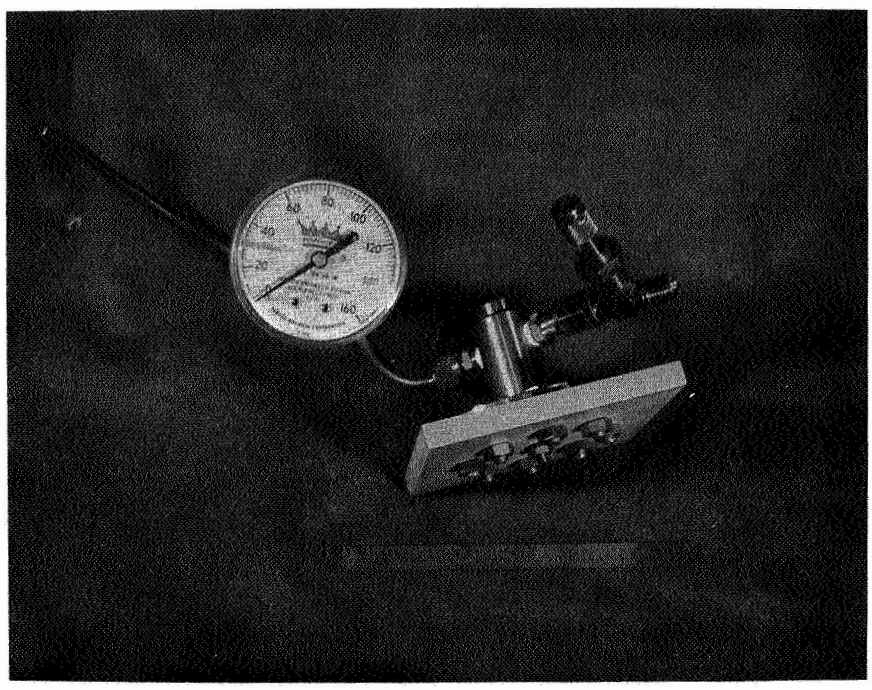


Figure 48. Battery Terminal Test Fixture

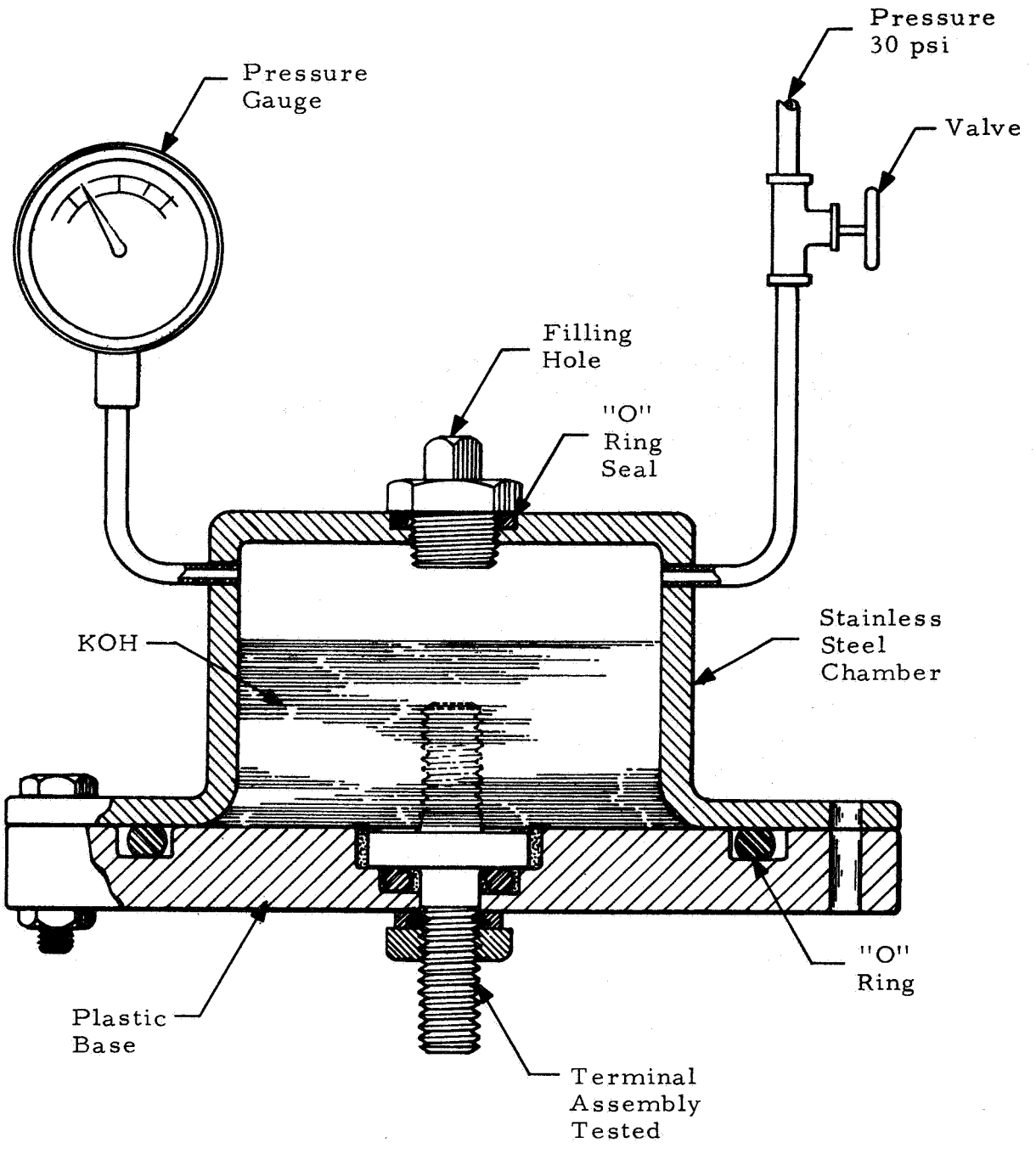


Figure 49. Test Fixture for Terminal Seal

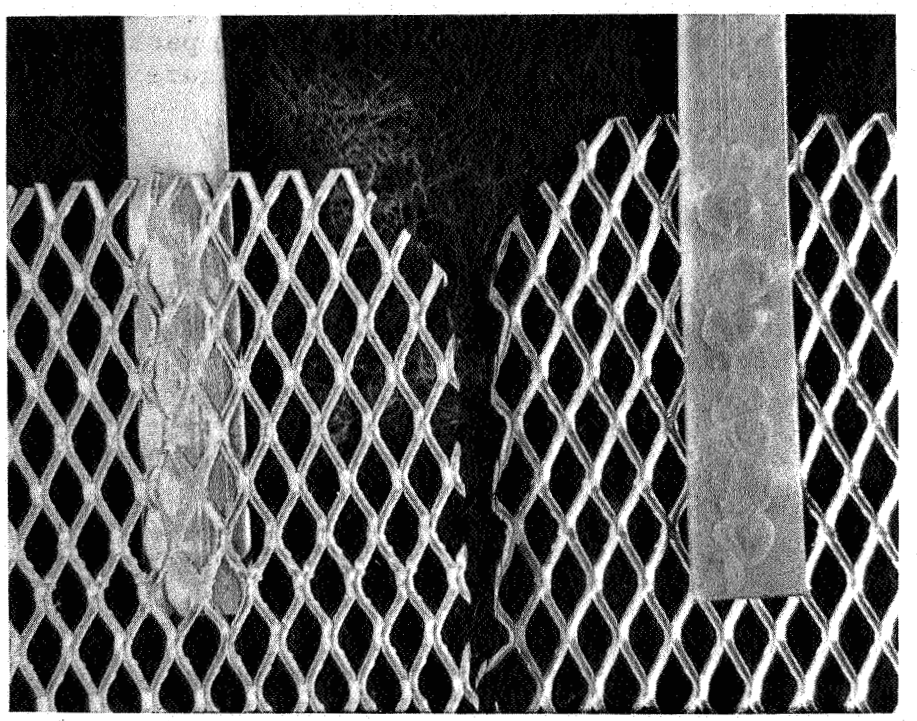


Figure 50. Silver Electrode Current Collector Grids Following Exposure to 150°C for 168 Hours in 35% KOH

current lead attached to the bottom of the silver grid. No evidence of resistance, corrosion or discoloration was detected. Finally, an attempt was made to mechanically pull the tab away from the grid at the welded joint by holding the grid in a vise and manually pulling the tab. It was dedetermined that when 10 pounds of force was applied, the Exmet grid pulled apart but the welded joint between tab and grid was unaffected.

2.2.5.1 Connection to Cell Terminals

The method of attaching the electrode tabs to the terminal base was designed to facilitate fabrication and assembly. The distance between the top of the electrodes (positive and negative) and the center of the hole punched in the tab is the same for all electrodes. As a result, the tabs extend straight up out of the frame pack and a long screw and washers are used to complete the assembly. Figure 51 is a sketch of the terminal-connector assembly.

2.2.5.2 Final Design of Collector-Connector-Terminal Assembly

To reduce the weight of the hardware components, such as the terminal screws, and to simplify cell assembly, the collector tabs were replaced with a multiple strand silver wire welded directly to the collector grids. This construction is shown in Figure 52. The use of flexible wire connector also made it possible to use terminals having through holes rather than the original nut and bolt assembly. The assembly of the connector to the terminals is shown in Figure 53. After threading the connector wires through the terminal screw holes, the wires were cut off flush with the top of the terminals and the space between the wires and the terminal body was filled with indium solder.

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%. Tables XVIII and XIX show the test results. 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 shown in these 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 54 shows capacity and plateau voltage evaluation versus current density for this construction.

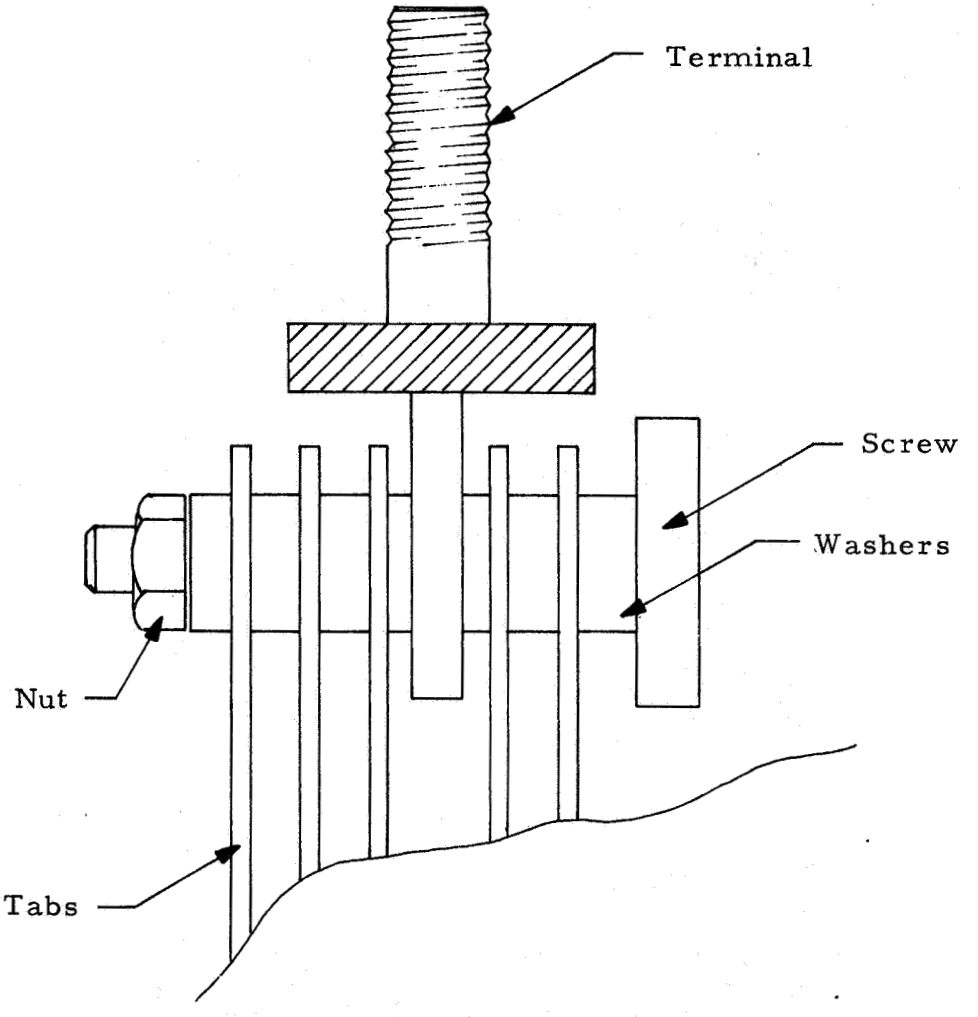


Figure 51. Vertical Tab Attachment to Terminal Base

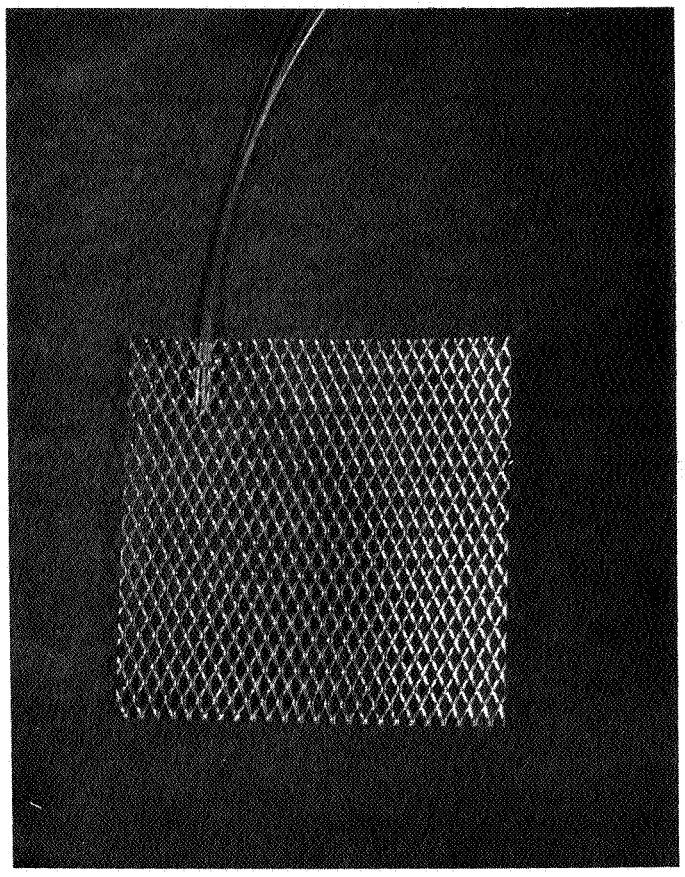


Figure 52. Connector Wires Welded to Electrode Grid

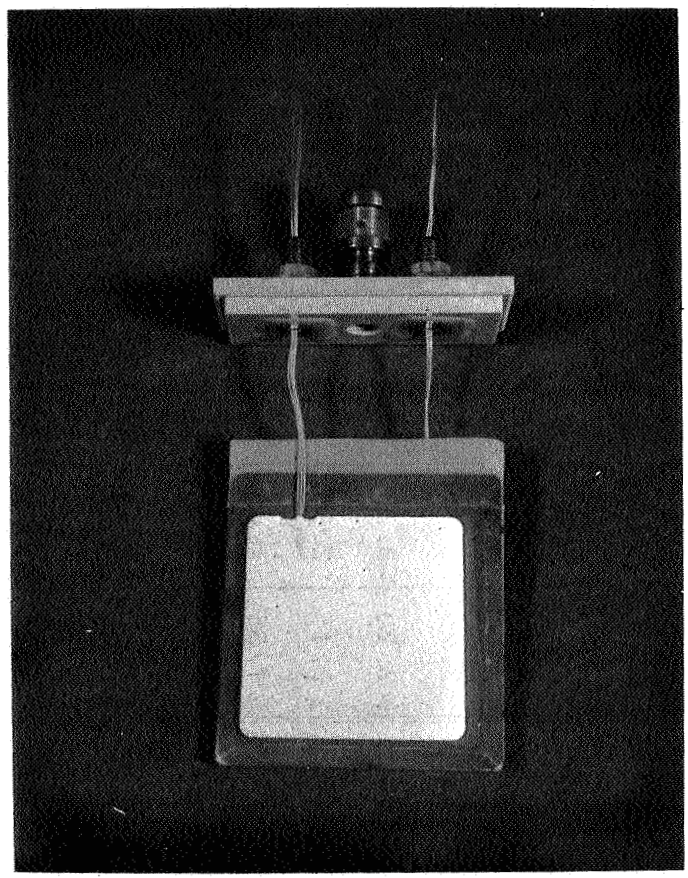


Figure 53. 5 Ah Cell Components to Assembly

TABLE XVIII

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 XIX

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%

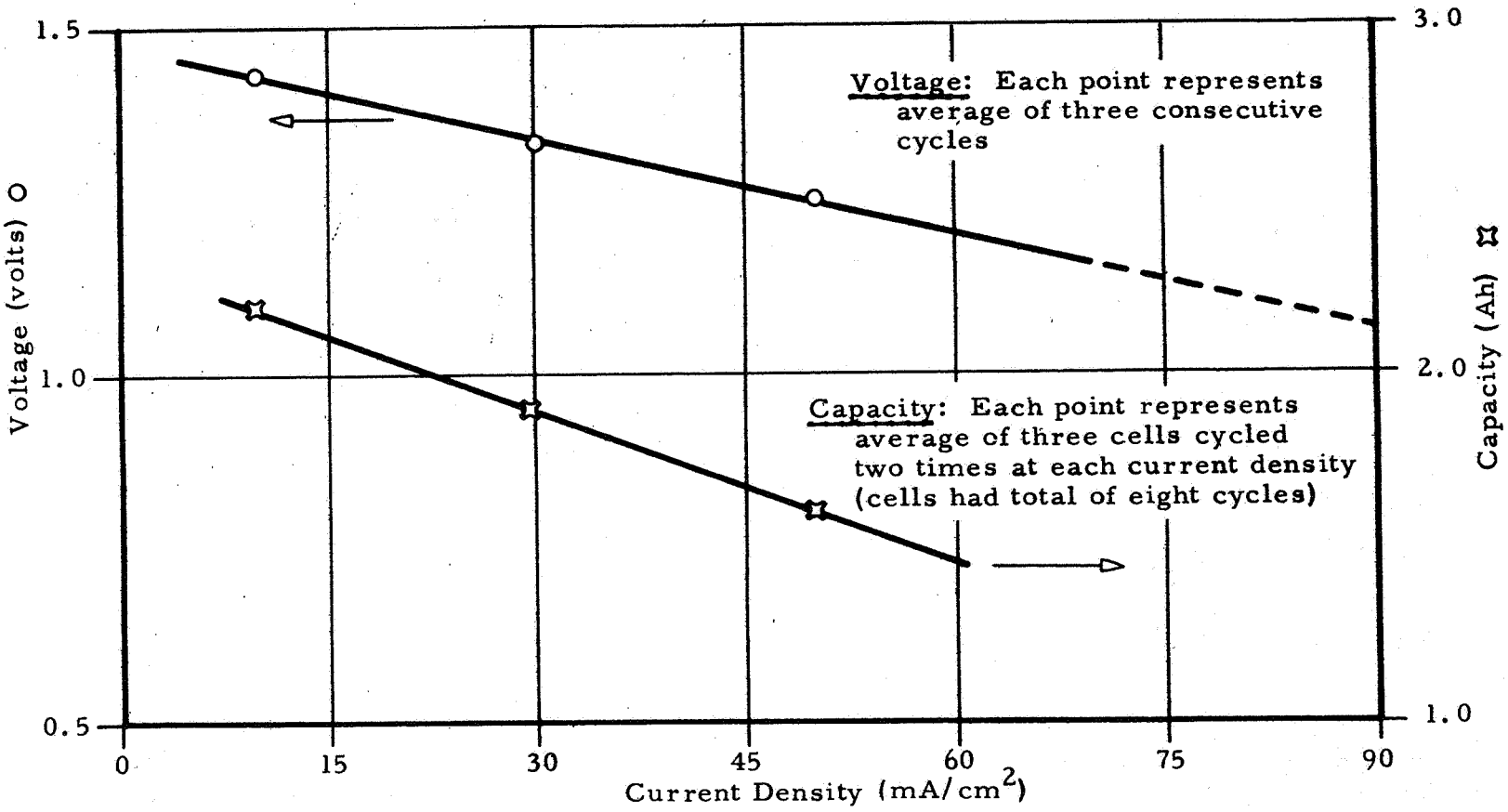


Figure 54. Average Plateau Voltage and Capacity vs. Current Density at 25°C

2.3 Task III — Evaluation and Characterization of Cell Construction

The objectives of Task III were to evaluate multiplate cell design effectiveness, weak points and areas requiring concentrated development prior to prototype cell fabrication. Accordingly, these evaluations provide the necessary information to determine the value of this cell construction.

Based on the data obtained in Tasks I and II and discussions with the Project Officer, thirty-five 5-Ah cells were fabricated. These cells presented the first group of cells built using the best components selected from the design and component studies carried out in the previous tasks and subjected to extensive evaluation.

These cells were assembled using eight Astroset Type 3420-09 inorganic separators. Each of the negative electrodes was assembled between two separators using modified Allbond epoxy as the electrode compartment sealant. Teflon tape seals were used around the two sides and bottom of this assembly and Teflon tape collars were cemented to the top of each assembly to preclude interelectrode shorting if zinc loss was experienced during prolonged cycling. The electrodes used in these cells were sintered silver positives and pressed zinc oxide (98%)-mercuric oxide (2%) negatives. The positive electrodes and negative subassemblies were assembled in polysulfone cases along with the terminals, valve and cell covers. A 20 psi relief valve was used in the construction of these cells.

These cells were tested in accordance with instructions from the Project Monitor as shown in Table XX. The cells were divided into four groups (Groups A, B, C and D). Group A (10 cells) was tested at 25°C at 20 ma/cm^2 with 5% overcharge; Group B at 30 ma/cm^2 at 25°C with 5% overcharge; Group C at 30 ma/cm^2 at 100°C with 10% overcharge. Group D was tested the same as Group A, except that the charge rates were to be adjusted as required. Groups A, B, and C were to have no charge rate adjustments. All cells were cycled on a 1/2-hour discharge, 1-hour charge regime using a 2.10 V maximum charging voltage. The cells were allowed to cycle continuously until they discharged below one volt, at which time they were recharged at 350 ma at ambient temperature to full charge and discharged at the cycle discharge rate, plus a drain at one ampere to one volt. If the total capacity delivered was equal to or greater than 4.0 Ah (80% of rated capacity), the cell was returned to its cycle regime. Loss of greater than 20% of rated capacity was defined as cell failure.

2.3.1 Cell Formation

After filling with 30% KOH, the 35, 5-Ah cells were formed by charging at 350 ma to 2.10 volts and discharged at 1 A to 1.0 V. The cells were then recharged at 350 ma to 2.05 volts. Cell capacities are given in Table XXI. The capacities of the 35, 5-Ah cells tested were remarkable for their uniformity. Twenty-three of the cells had an initial capacity of 7.4 Ah. Five cells had a capacity of 8.0 Ah and the overall range of capacity on first discharge was 7.3 to 8.2 Ah. Because the cells

TABLE XX

TEST VARIATIONS FOR FINAL DESIGN
5 AH – CELLS OF TASK III

Group	No. of Cells	Current Density mA/cm^2	Depth of Discharge (% of Actual)	Temperature °C	Overcharge	Charge Method Voltage Limited to 2.10 V
A	10	20	25%	25°C	5%	No charge rate adjustment
B	10	30	36%	25°C	5%	No charge rate adjustment
C	10	30	36%	100°C	10%	No charge rate adjustment
D	5	20	25%	25°C	as required	Charge rate adjusment as required

TABLE XXI

ORIGINAL CAPACITY OF TASK III 5-AH CELLS

Group A		Group B		Group C		Group D	
Cell No.	Capacity (Ah)	Cell No.	Capacity (Ah)	Cell No.	Capacity (Ah)	Cell No.	Capacity (Ah)
MC-136	7.4	MC-151	7.4	MC-161	8.0	MC-146	7.4
MC-137	7.4	MC-152	7.4	MC-162	8.0	MC-147	7.4
MC-138	7.4	MC-153	7.4	MC-163	8.2	MC-148	7.4
MC-139	7.4	MC-154	7.4	MC-164	8.0	MC-149	7.4
MC-140	7.4	MC-155	7.4	MC-165	7.9	MC-150	7.4
MC-141	7.4	MC-156	7.3	MC-166	8.0		
MC-142	7.4	MC-157	7.4	MC-167	7.8		
MC-143	7.4	MC-158	7.4	MC-168	7.8		
MC-144	7.4	MC-159	7.4	MC-169	8.0		
MC-145	7.4	MC-160	7.6	MC-170	8.2		

were charged at constant current to a voltage cut-off of 2.1 V in groups connected in series, the actual cell to cell uniformity is probably even better than these data indicate.

Typical formation discharge curves for one cell from each test group are shown in Figures 55, 56, 57 and 58.

2.3.2 Cycle Testing

After formation, the cells were placed on automatic cycling test consoles. After the Group A and D cells had accumulated about 1000 cycles at 20 ma/cm^2 at 25°C, the Project Officer, in agreement with Douglas Astropower, established that the first two cells from each group that ran down during automatic cycling and did not deliver the 4.0-Ah minimum capacity after a low rate charge would be disassembled for evaluation. However, subsequent cells that did not have a 4.0-Ah capacity after a low rate charge, but gave a sufficient capacity to meet the automatic discharge cycle, would be allowed to continue cycling, but with increased charge rates and maximum charge voltage. Cells which delivered 4.0 Ah or more would be returned to their original regimes. This would provide data to establish the cycle life capability with 80% capacity retainment as well as total cycle life capability at a given current density. Tables showing cell cycle life will show two columns: One column will show cycle life with 80% capacity retainment and no charge adjustments, and one column will show total cycles accumulated including charge adjustments.

2.3.2.1 Groups A and D, 20 ma/cm^2, 25°C

Fifteen 5-Ah multiplate cells were cycled automatically at 20 ma/cm^2 at 25°C. Charge rates were set at 1.3 A with a 2.10 volt maximum circuit (5% overcharge), while the discharge rate was 2.5 amperes using a fixed load. These cells were equipped with a 20 psi bunsen valve. No electrolyte additions were made during the initial 800 cycles. Thereafter, small amounts of water were added to each cell. Water additions averaged about 2 to 3 cc per cell per week.

It was noted that some carbonate build-up occurred from opening the cells during water additions.

All cells in Groups A and D displayed uniform discharge voltage plateaus of about 1.45 volts during the first 1300 cycles. Typical performance curves for each of these fifteen cells are shown in Figures 59-73. Thirteen of 15 cells continue cycle tests as of the end of this program. As many as 1455 cycles were completed at this rate without any cell failures, as shown in Table XXII. Cell MC-136 delivered 2.7 Ah after 1455 cycles, Cell MC-142 delivered 3.2 Ah after 1832 cycles, Cell MC-143 gave 3.4 Ah after 1588 cycles, while Cell MC-148 delivered 2.8 Ah at the end of 1912 cycles. These delivered capacities were after a 24-hour maximum charge period at 350 ma at ambient temperature and a 2.5 ampere discharge to 1.0 volt, plus a drain of one ampere to 1.0 volt.

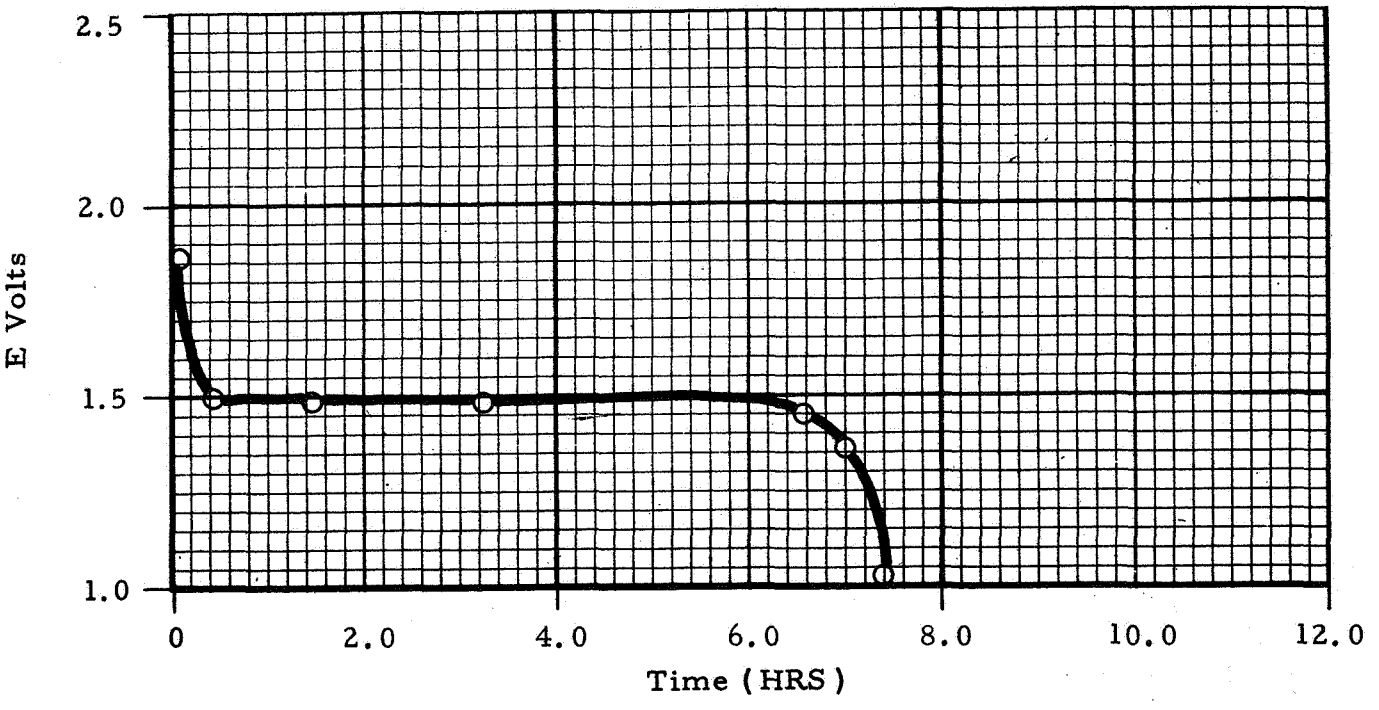


Figure 55. Formation Discharge of MC-137 at One Ampere at 25°C Group A

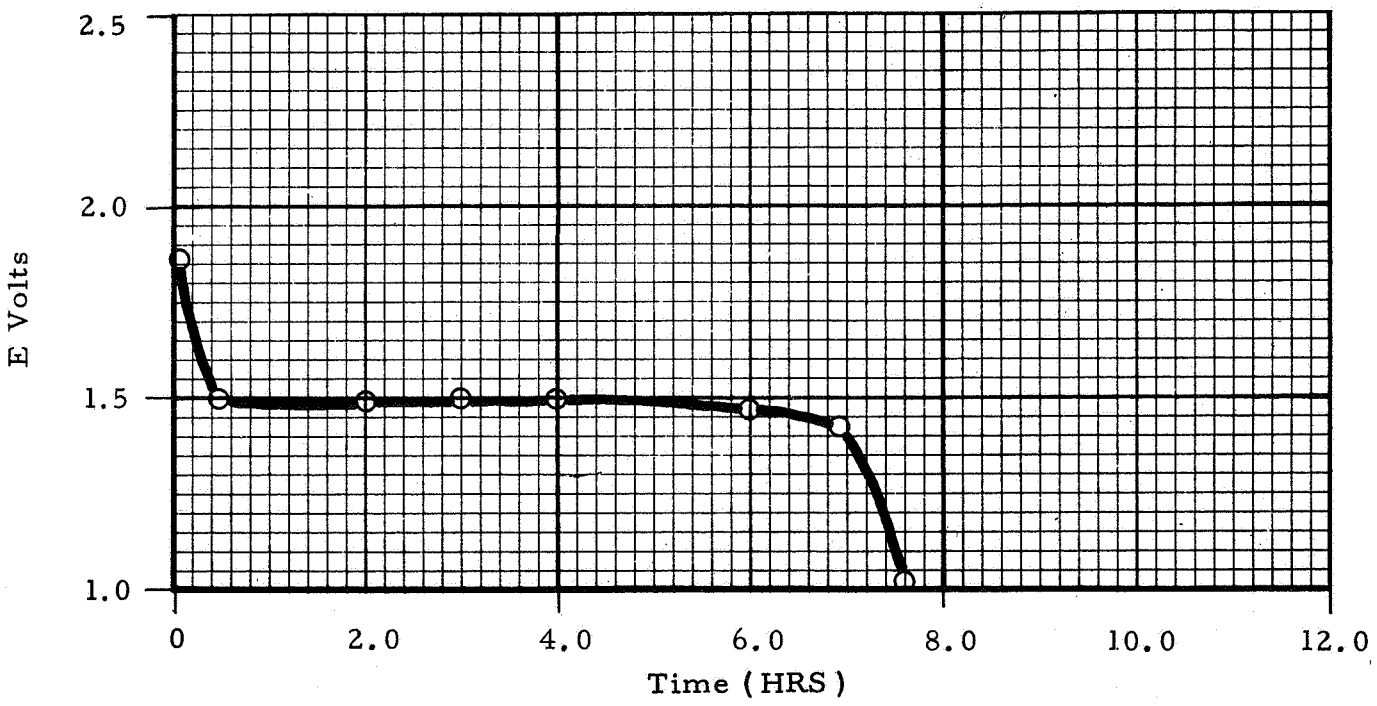


Figure 56. Typical Formation Discharge of MC-160 at One Ampere at 25°C Group B

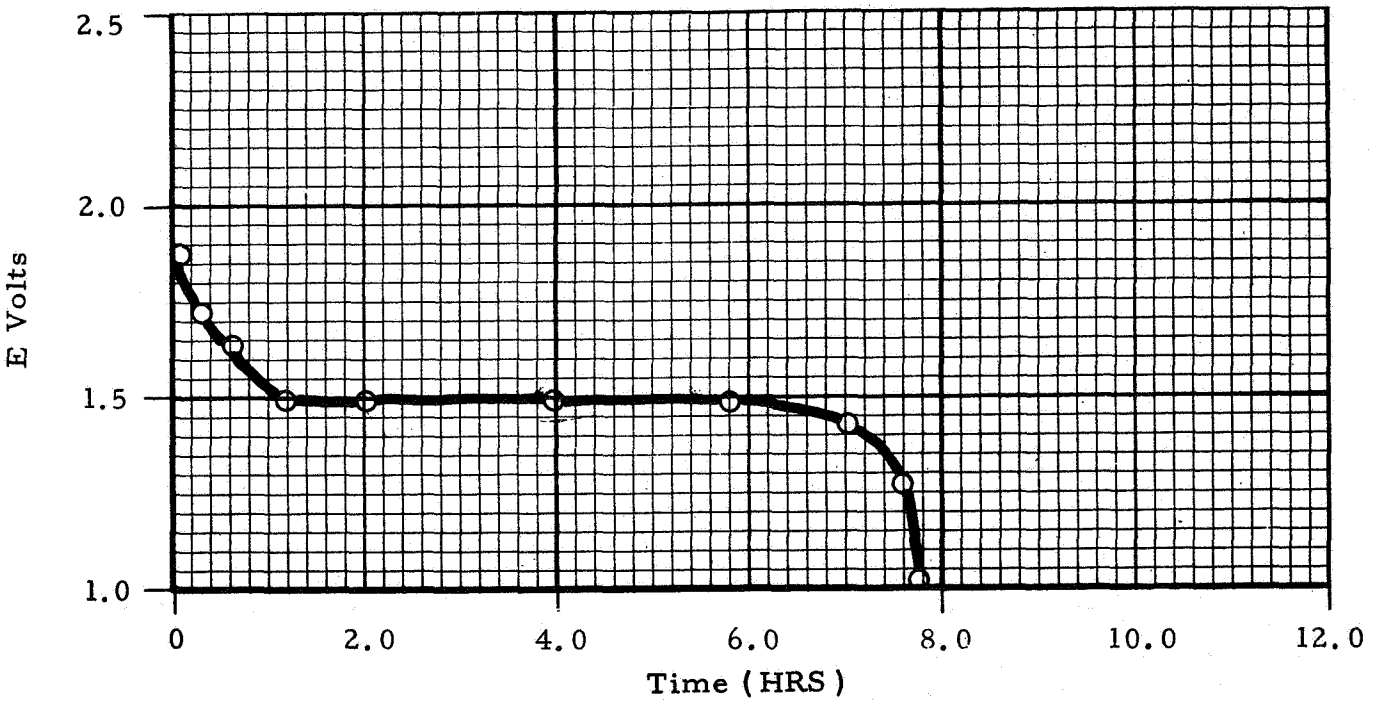


Figure 57. Typical Formation Discharge of MC-167 at One Ampere at 25°C Group C

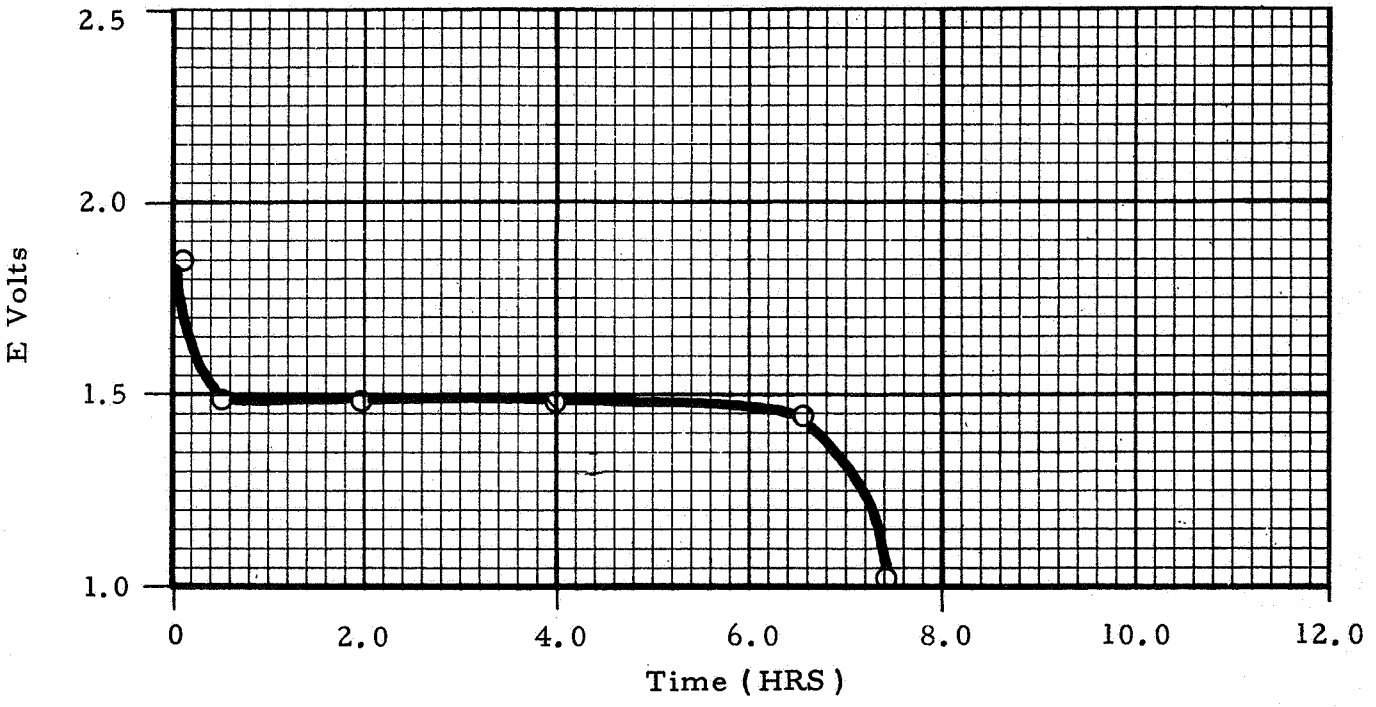


Figure 58. Formation Discharge of MC-148 at One Ampere at 25°C Group D

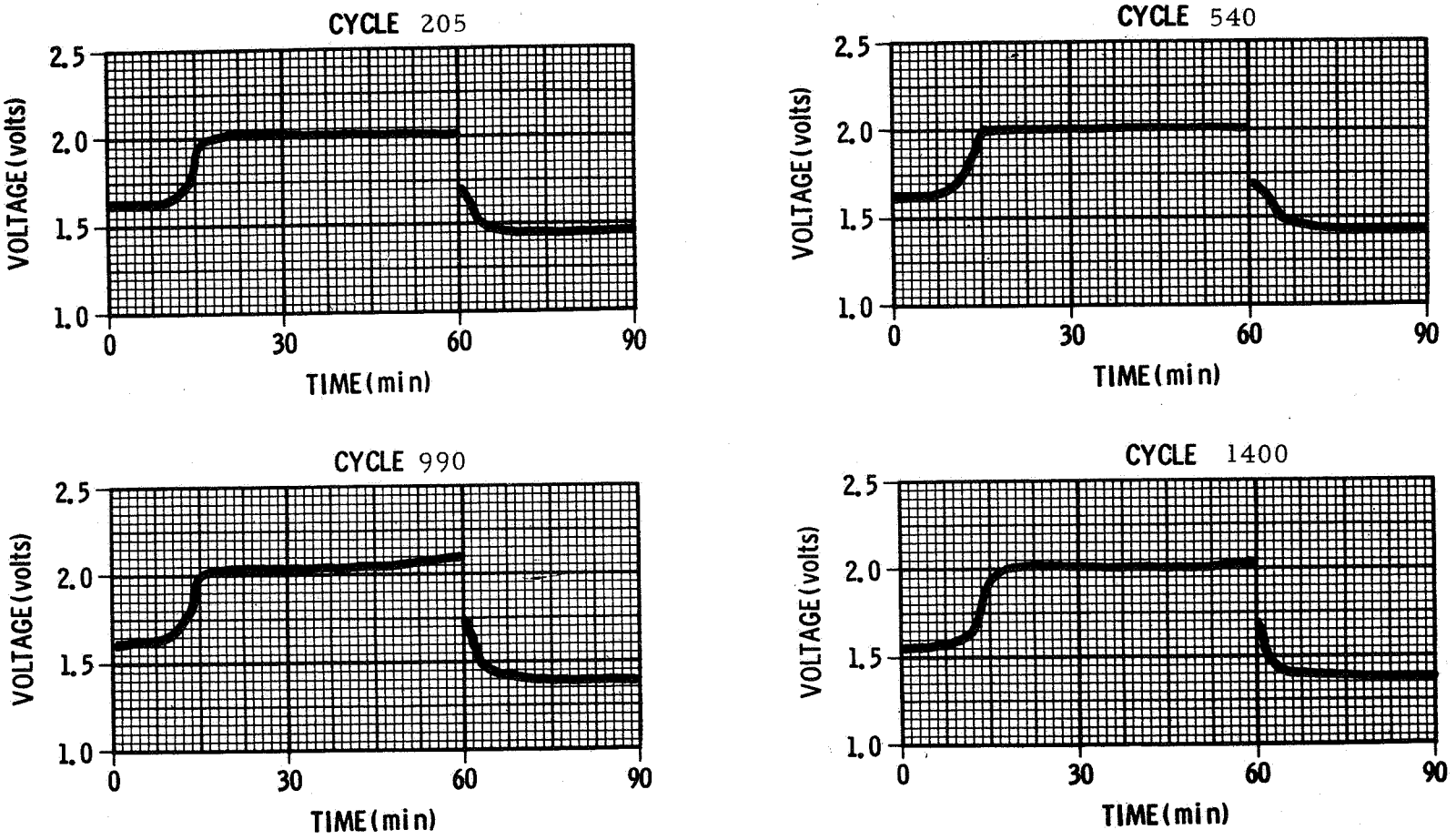


Figure 59. Cycle Characteristics of MC-136 at 20 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 2.5A
1 hour charge 1.3A

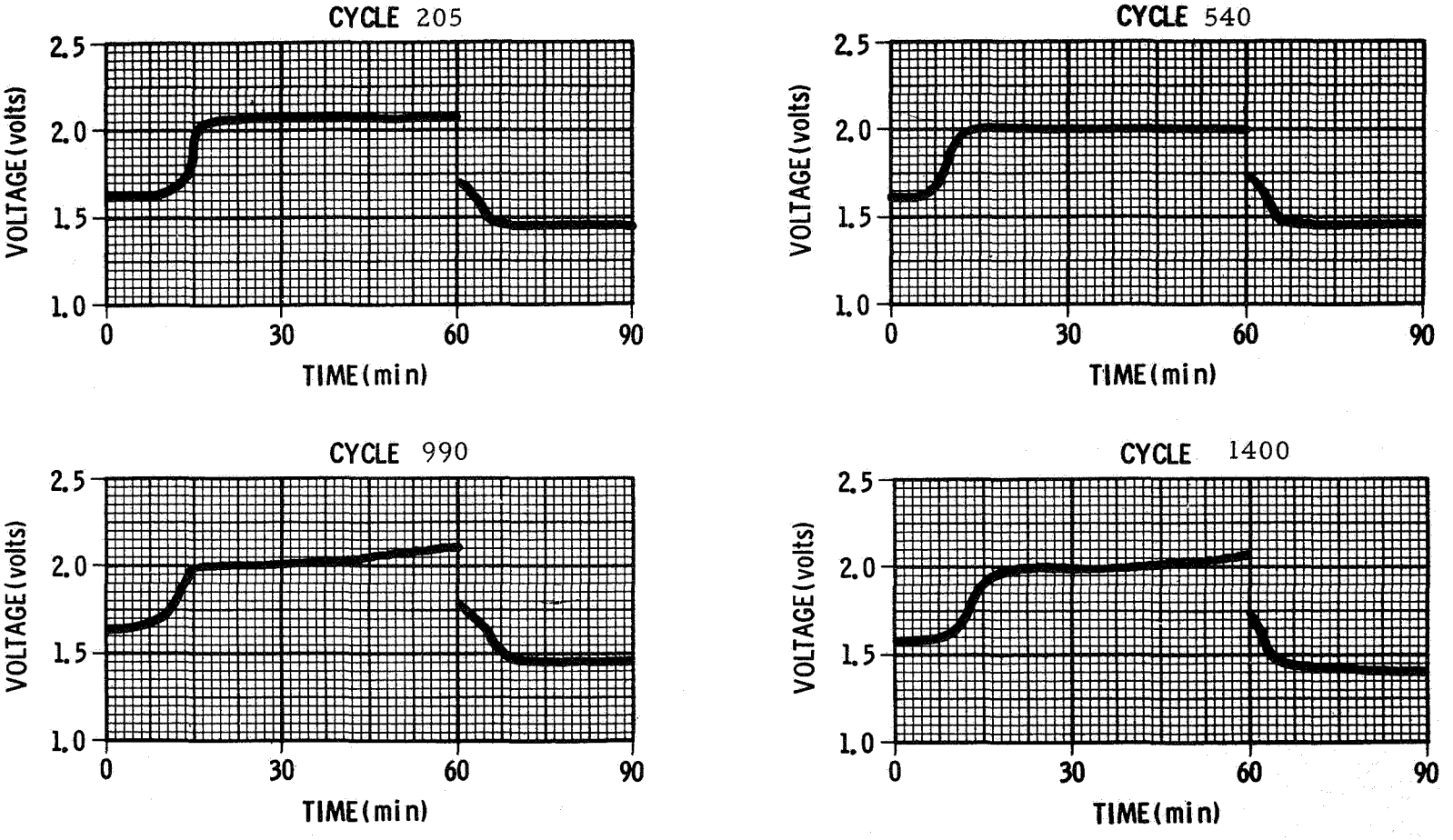


Figure 60. Cycle Characteristics of MC-137 at 20 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 2.5A
1 hour charge 1.3A

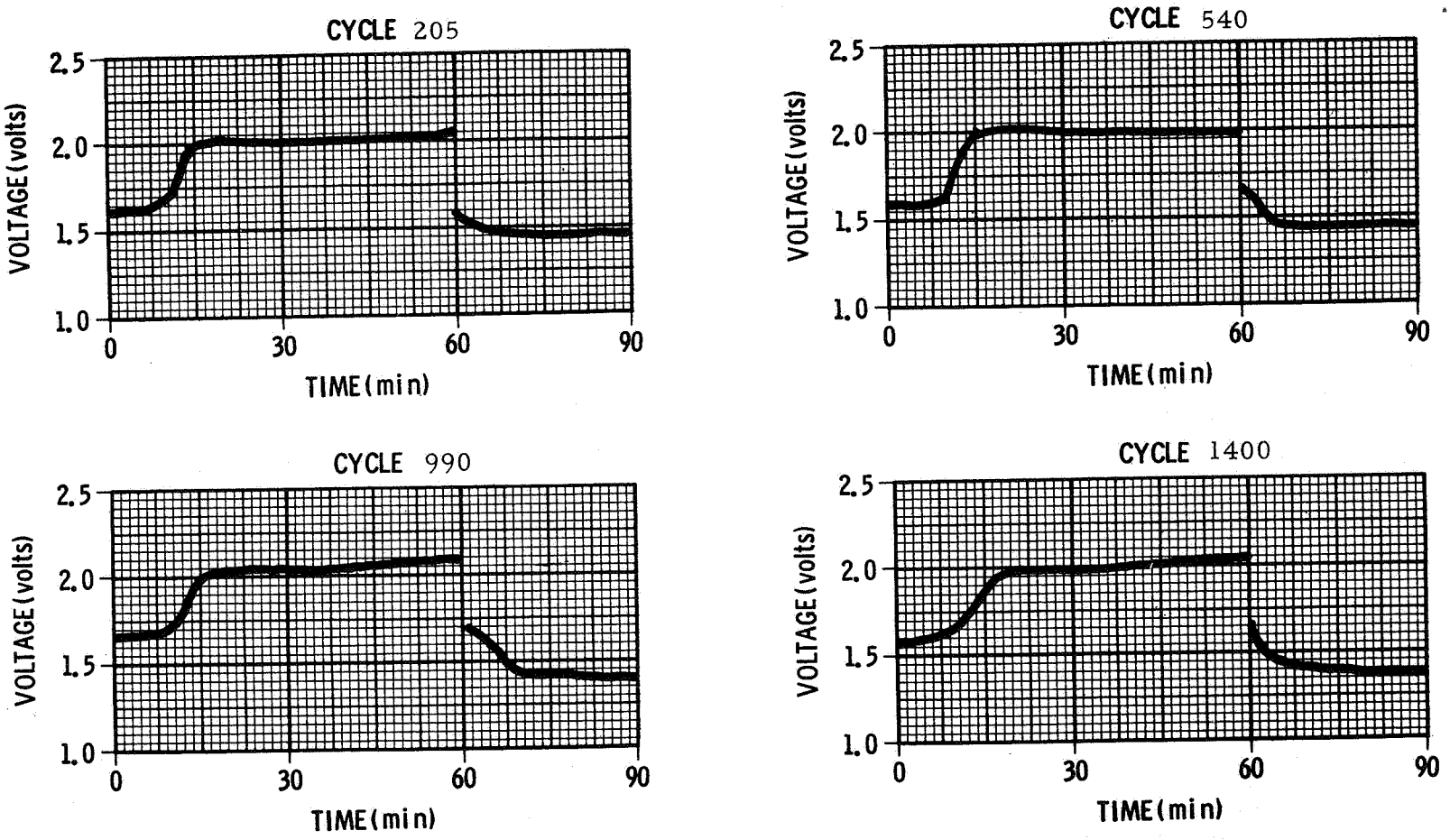


Figure 61. Cycle Characteristics of MC-138 at 20 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 2.5A
1 hour charge 1.3A

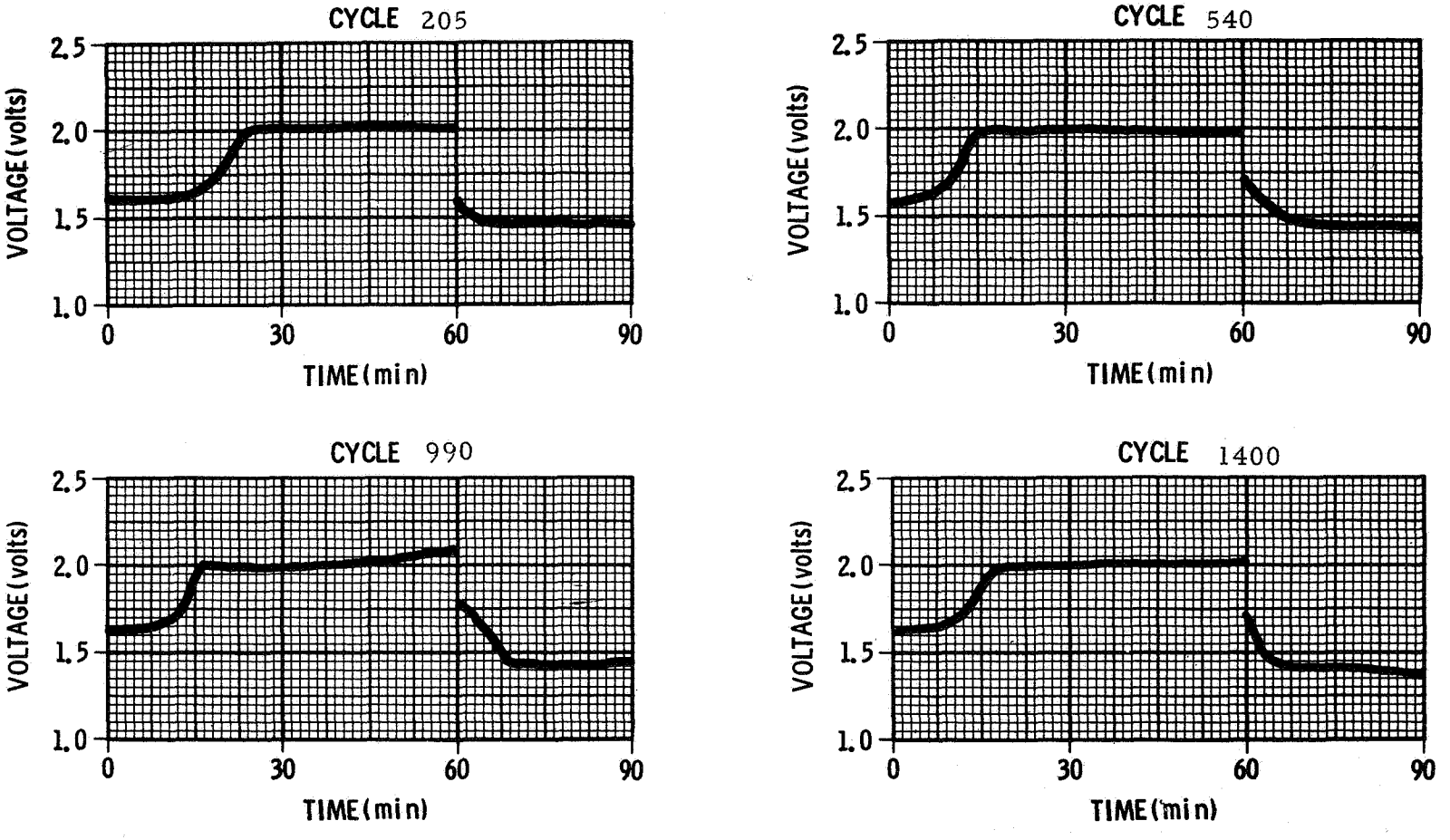


Figure 62. Cycle Characteristics of MC-139 at 20 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 2.5A
1 hour charge 1.3A

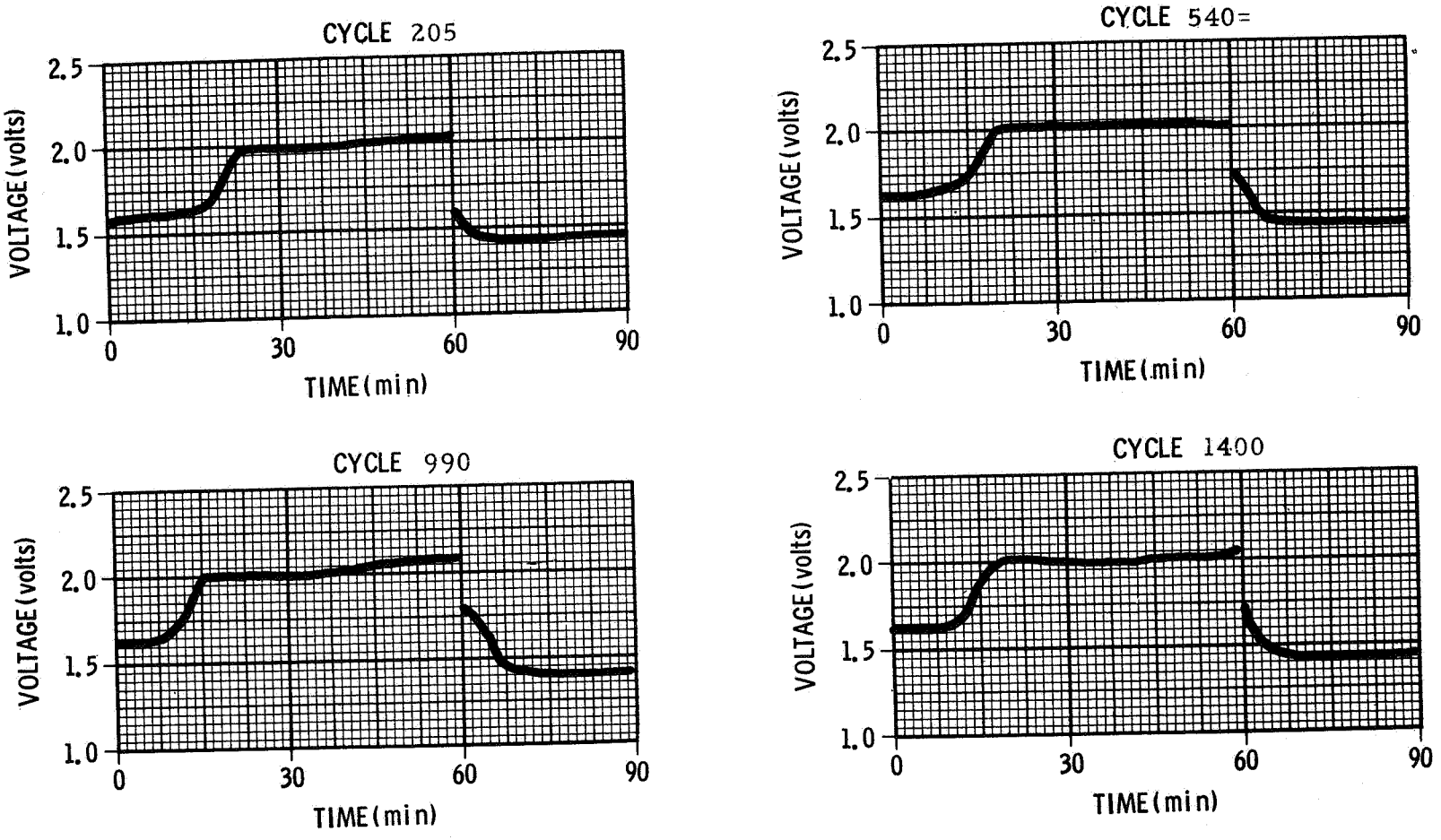


Figure 63. Cycle Characteristics of MC-140 at 20 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 2.5A
1 hour charge 1.3A

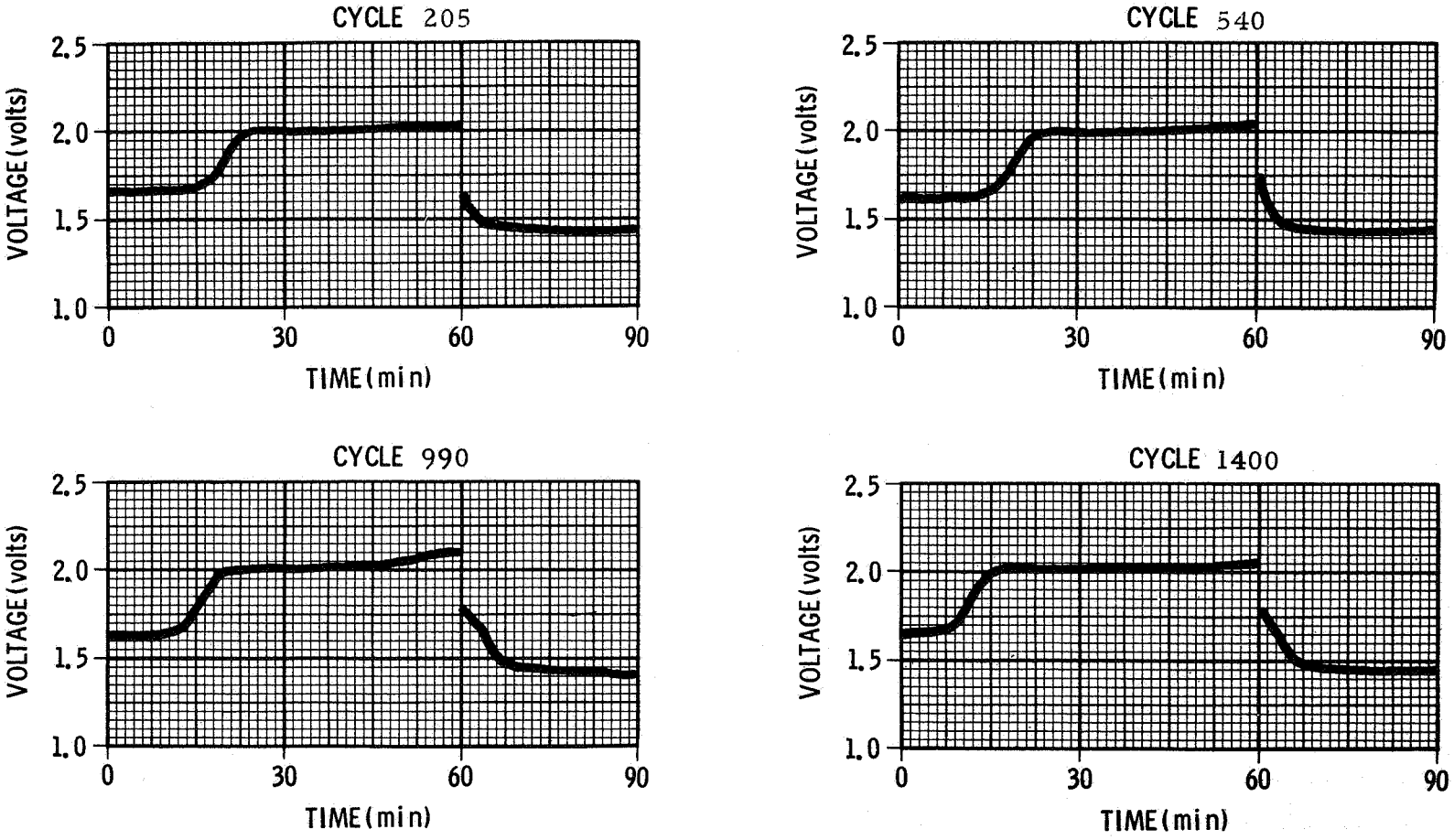


Figure 64. Cycle Characteristics of MC-141 at 20 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 2.5A
1 hour charge 1.3A

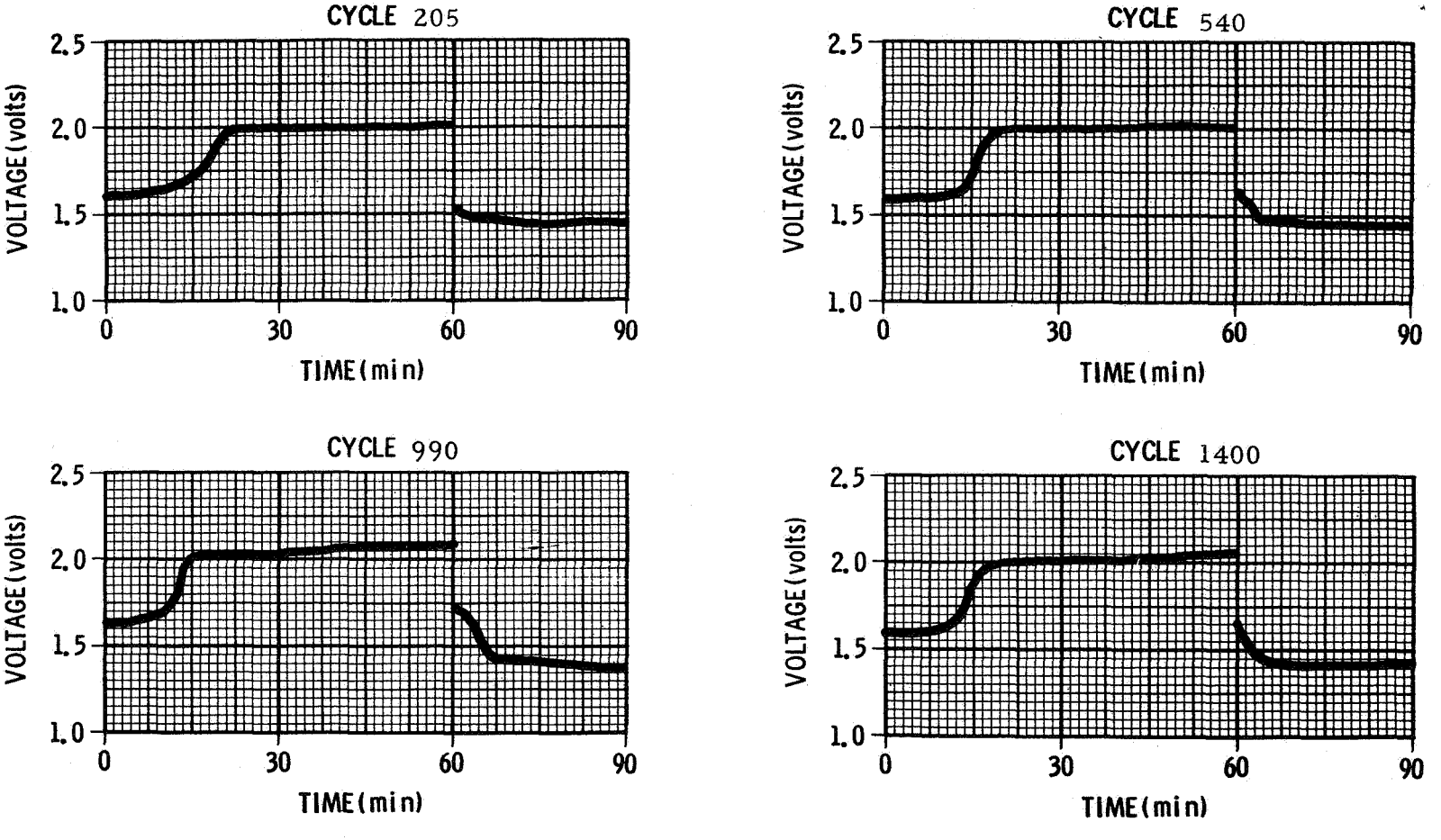


Figure 65. Cycle Characteristics of MC-142 at 20 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 2.5A
1 hour charge 1.3A

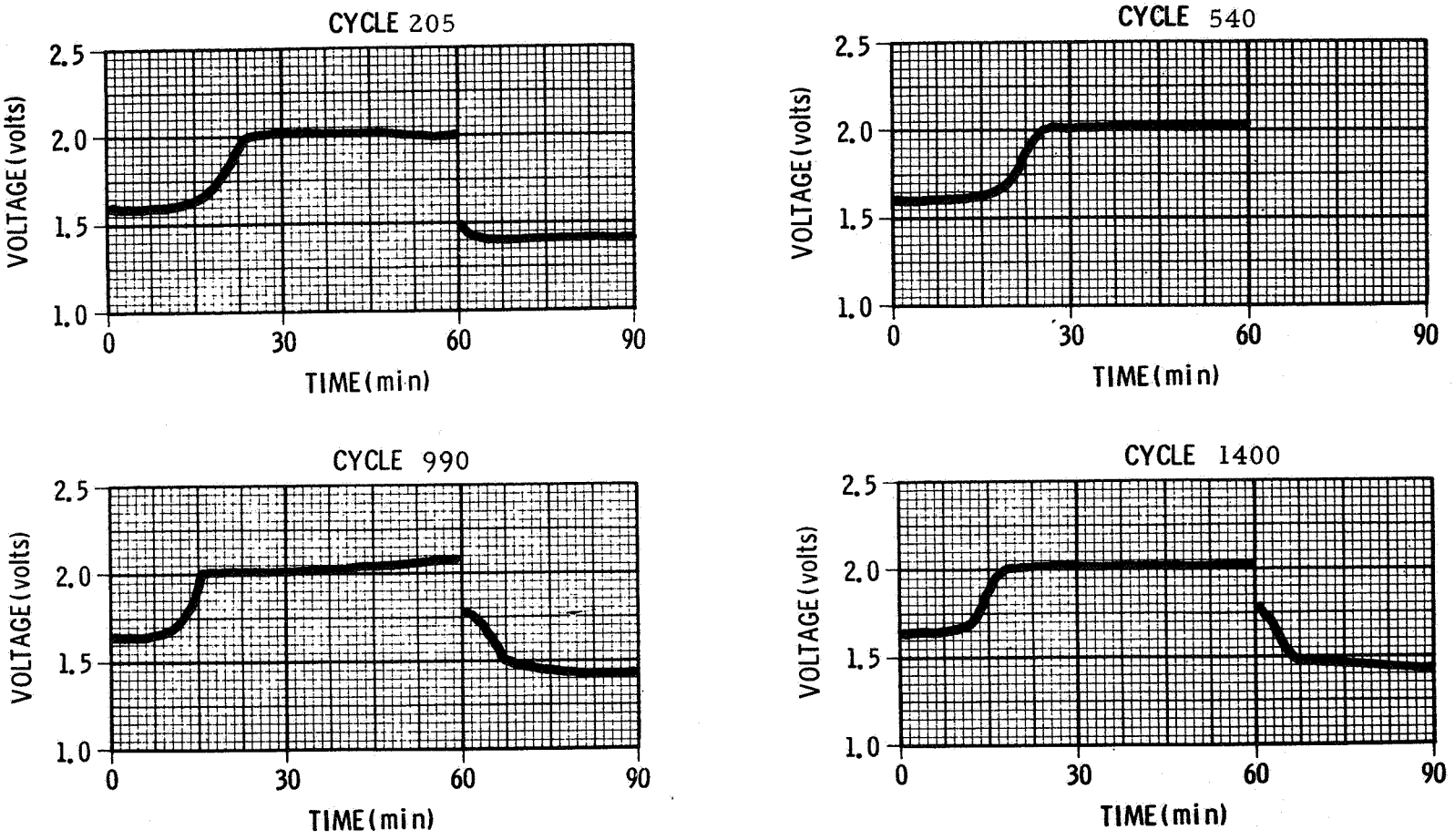


Figure 66. Cycle Characteristics of MC-143 at 20 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 2.5A
1 hour charge 1.3A

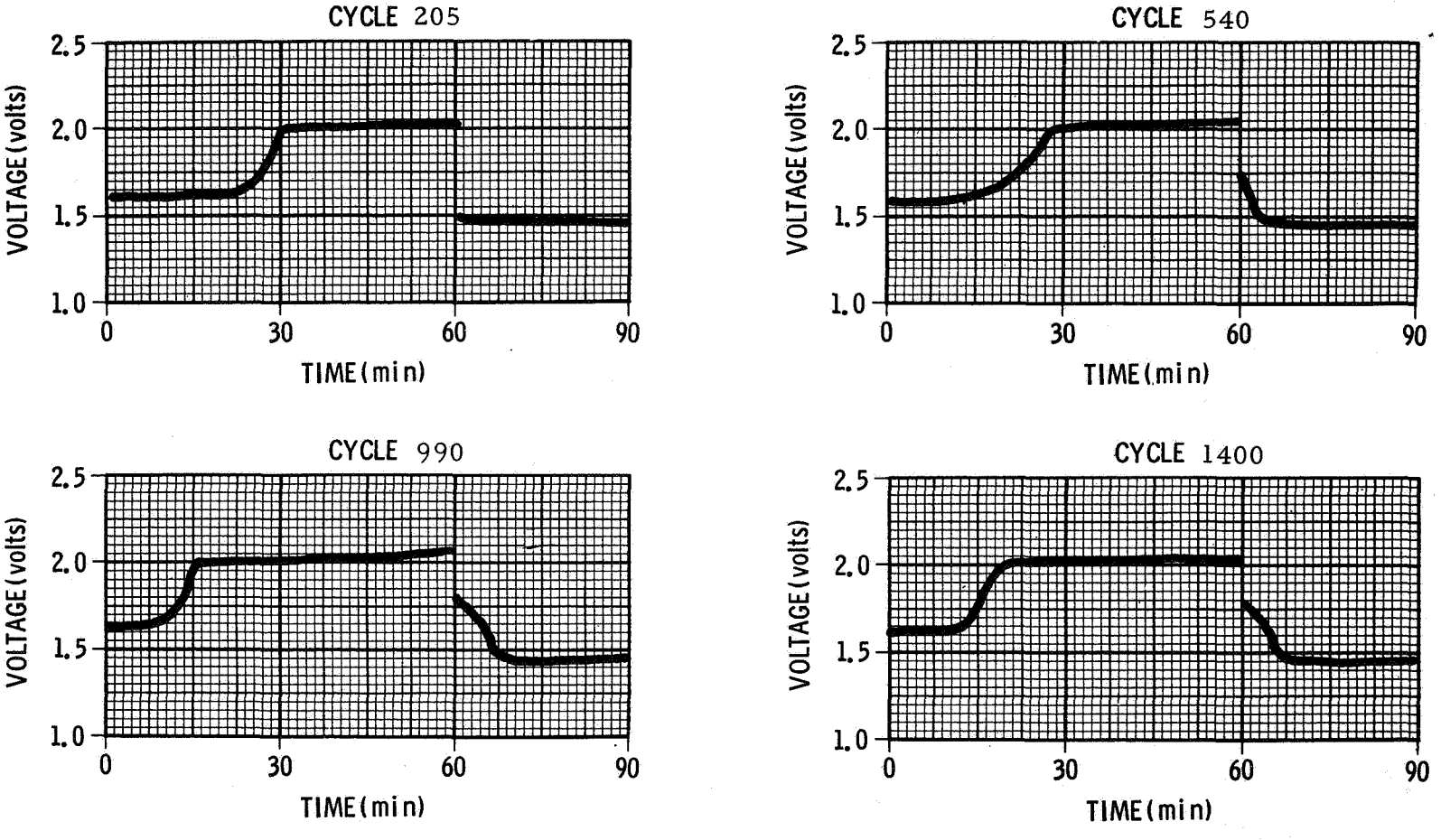


Figure 67. Cycle Characteristics of MC-144 at 20 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 2.5A
1 hour charge 1.3A

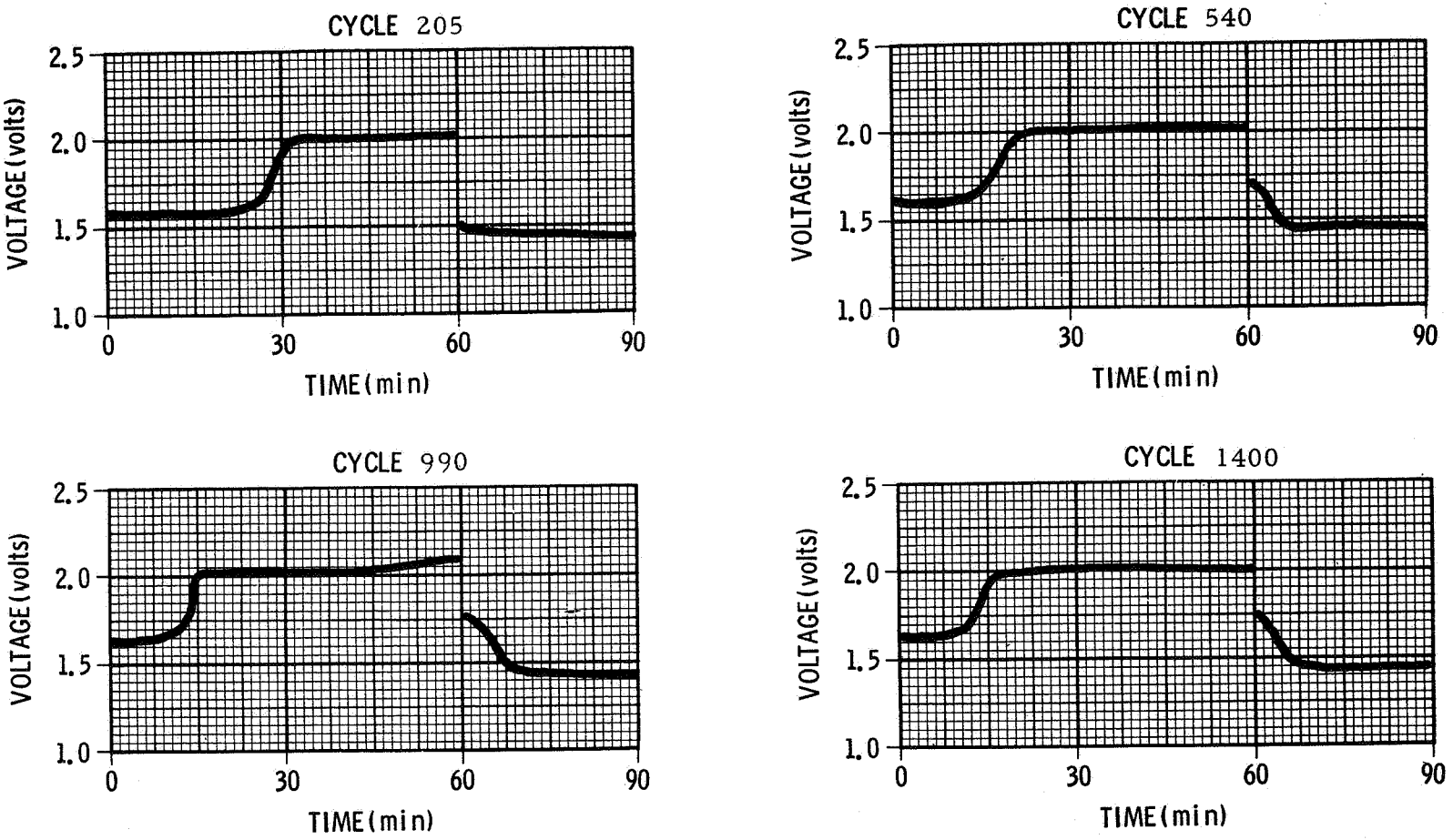


Figure 68. Cycle Characteristics of MC-145 at 20 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 2.5A
1 hour charge 1.3A

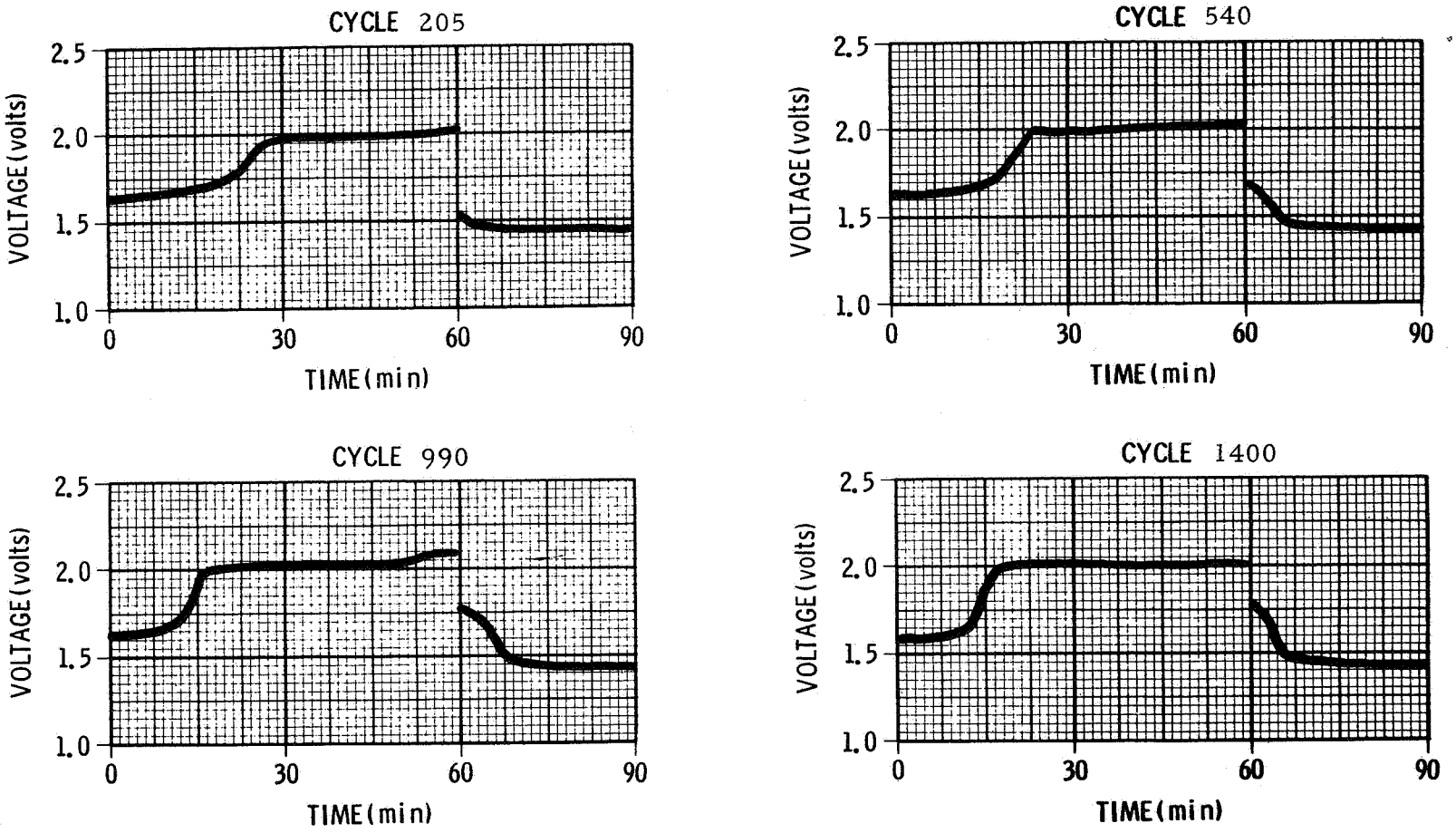


Figure 69. Cycle Characteristics of MC-146 at 20 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 2.5A
1 hour charge 1.3A

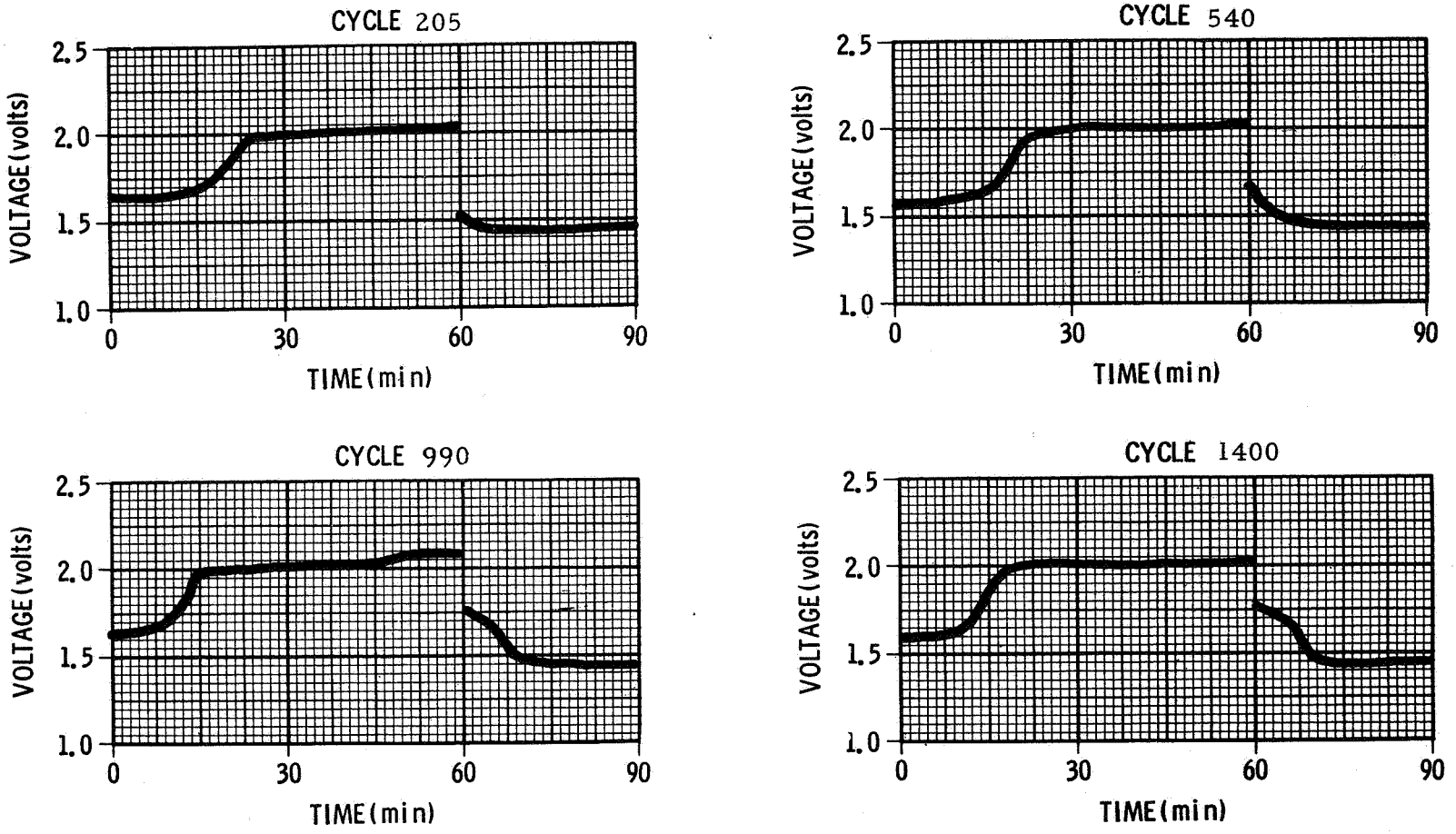


Figure 70. Cycle Characteristics of MC-147 at 20 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 2.5A
1 hour charge 1.3A

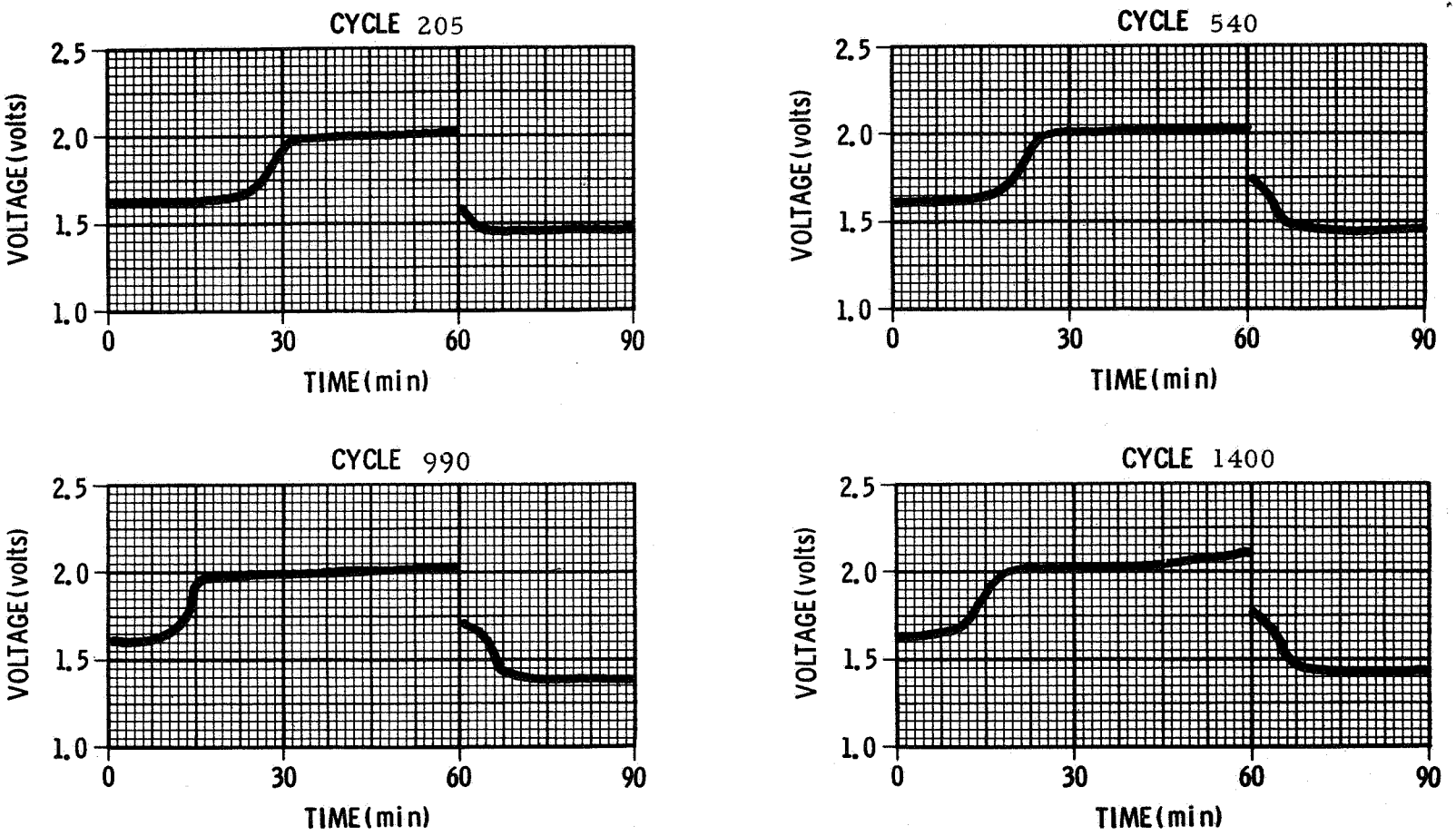


Figure 71. Cycle Characteristics of MC-148 at 20 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 2.5A
1 hour charge 1.3A

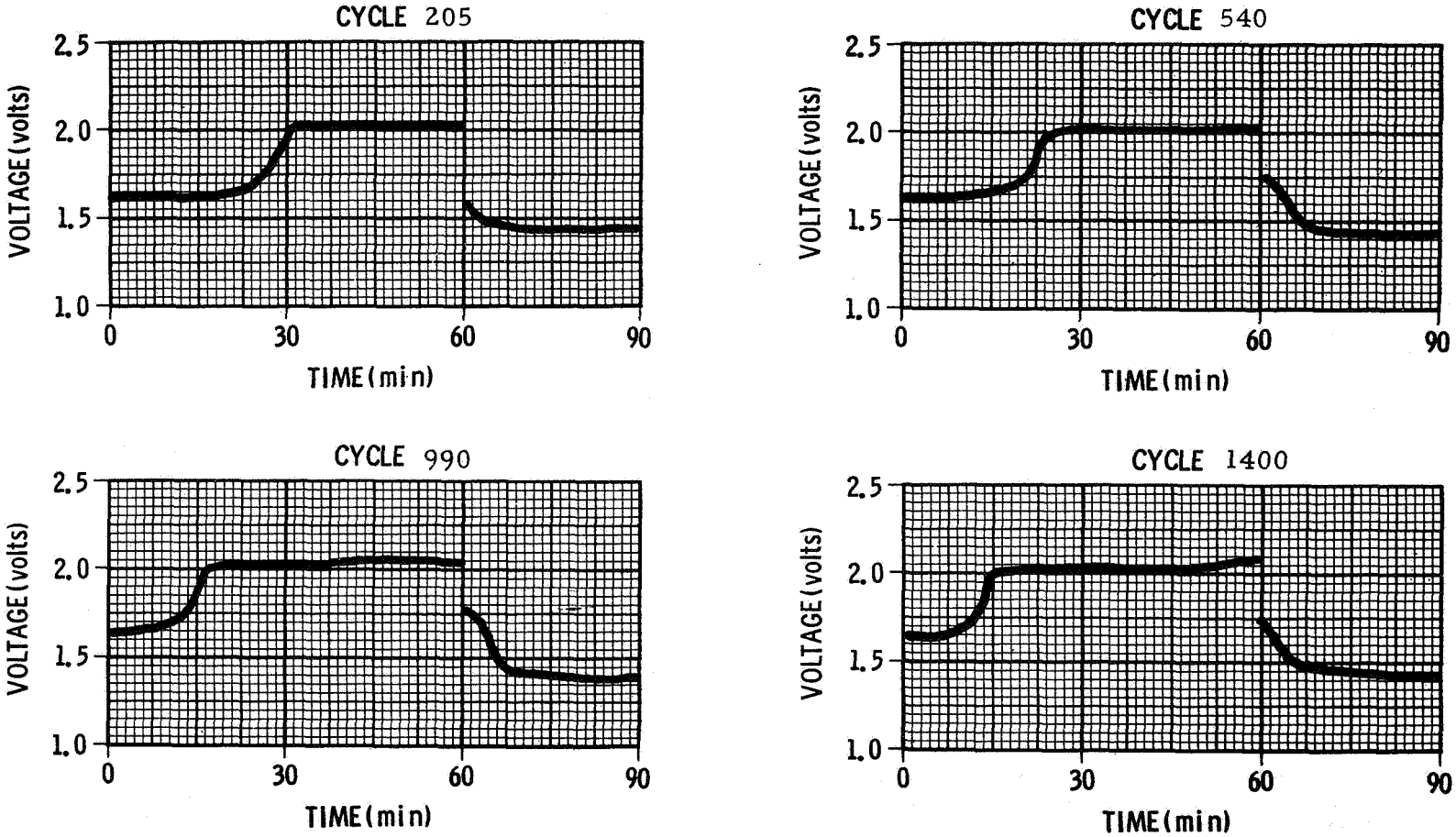


Figure 72. Cycle Characteristics of MC-149 at 20 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 2.5A
1 hour charge 1.3A

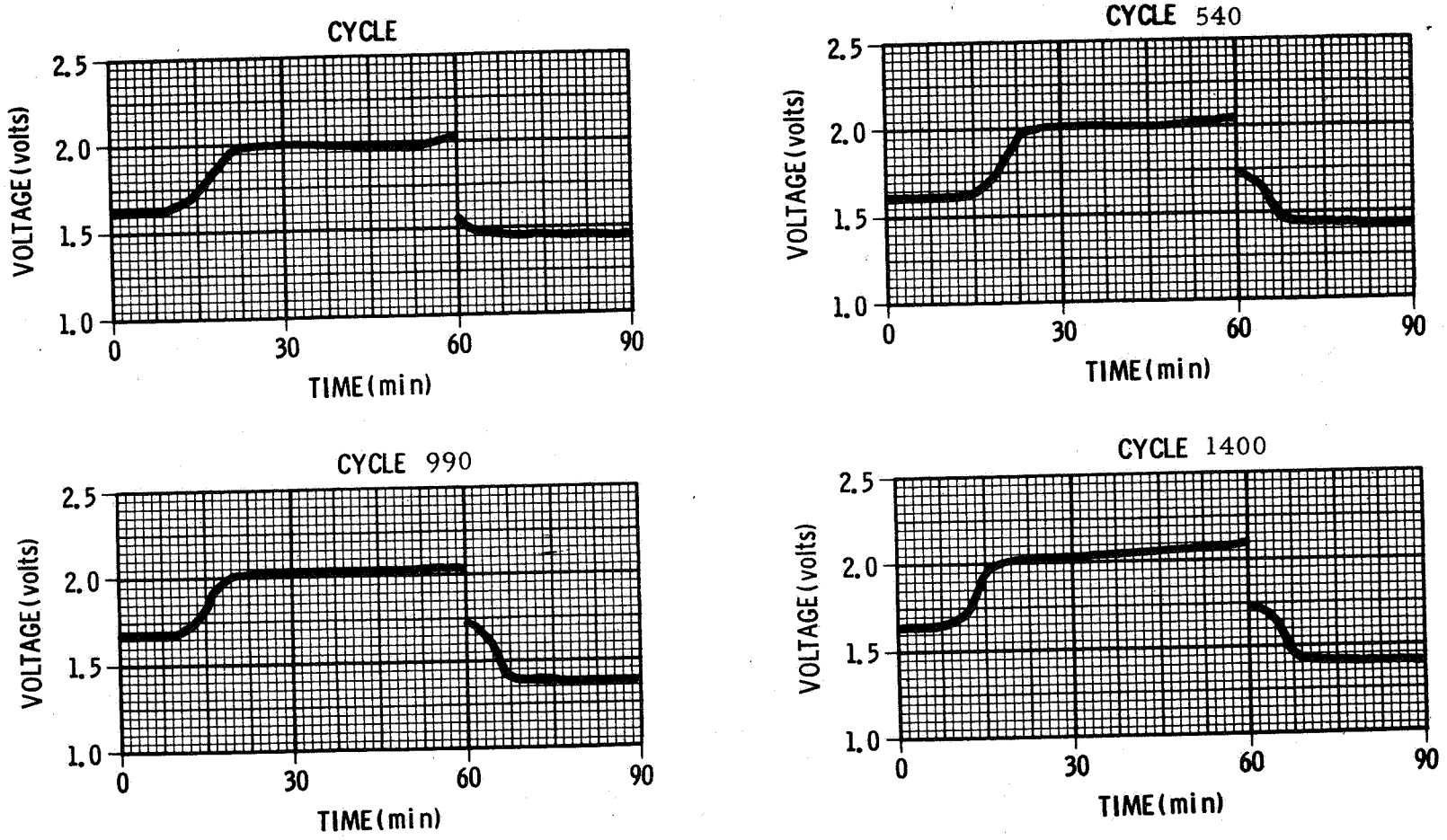


Figure 73. Cycle Characteristics of MC-150 at 20 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 2.5A
1 hour charge 1.3A

TABLE XXII

CYCLE TEST DATA FOR GROUPS A AND D, TASK III, CELLS

Temperature: 25°C
Regime: Period 1/2 hour/1 hour
Discharge: Rate 2.5 amperes; 1/2 hour; 18% depth of discharge based on minimum original capacity, 7.0 Ah.
Charge: Rate 1.3 A; 1 hour; overcharge 5% based on original set up; voltage limit: 2.10 V, maximum

Cell No.	1st Capacity Check		2nd Capacity Check		3rd Capacity Check		4th Capacity Check		Cycles Without Charge Adjustment	Total Cycles Accumulated (Including Charge Adjustments)
	Cycle	Output	Cycle	Output	Cycle	Output	Cycle	Output		
MC-136	1234	5.3	1371	4.1	1455	2.7	—	—	1455	1455
MC-137	1500	4.4	—	—	—	—	—	—	2395	2395
MC-138	975	4.7	1580	3.4*	1800	4.3	1945	3.4	1580	1945
MC-139	1500	5.3	1962	4.8	—	—	—	—	2264	2264
MC-140	1450	5.5	1593	5.3	1900	5.7	—	—	2250	2250
MC-141	CELL HAS CYCLED CONTINUOUSLY					—	—	—	2435	2458
MC-142	1755	6.8	1832	3.2*	2025	3.7	—	—	1832	2025
MC-143	1588	6.8	—	—	—	—	—	—	1588	1588
MC-144	1759	4.6	1982	6.0	—	—	—	—	2383	2383
MC-145	1735	4.5	1900	4.8	—	—	—	—	2384	2384
MC-146	CELL HAS CYCLED CONTINUOUSLY					—	—	—	2458	2458
MC-147	1737	5.5	—	—	—	—	—	—	2398	2398
MC-148	1391	4.8	1658	4.6	1739	4.0	1912	2.8*	1912	2101
MC-149	1296	4.1	1825	4.9	—	—	—	—	2329	2329
MC-150	1307	4.0	1500	4.0	1613	4.1	1941	4.1	2007	2007

*Charge adjusted to 1.4 amperes; voltage limit raised to 2.15 volts.

The cycle discharge rate was used to establish the capability of the cell to meet the cycle requirements. From Table XXII we can see that failure of the first four cells failing to date occurred after an average of about 1700 cycles at 20 ma/cm^2 at 25°C.

The average number of cycles at 20 ma/cm^2 at 25°C without any charge rate adjustments is 2111, based on an average of 15 cells. However, 12 of the 15 cells have had no charge adjustments. The charge adjustments were made after the cells gave less than 4.0 Ah during a capacity check. The rates were increased from 1.3 amperes to 1.4 amperes, and the charge voltage limit raised from 2.10 to 2.15 volts. The average number of cycles accumulated at the time of the rate adjustment was 1775 (Cells MC-138, MC-142 and MC-148).

As many as 2458 total cycles have been completed as of the end of the program. The average number of total cycles completed is 2259, discounting the two cells (MC-136 and MC-143) which were stopped as directed by the Project Officer. This represents 3400 hours of cycle operation at 25°C.

Figures 74 and 75 show the open circuit voltages obtained for periods ranging from 1 to 24 hours during the capacity ohecks shown in Table XXIV, as well as capacity degradation as a function of cycle life. In general, the open circuit voltage remained a nominal 1.86 ± 0.02 V with the capacity retained at about 5 Ah after cycling 1800 times.

Analysis of cells MC-136 (1455 cycles) and MC-143 (1588 cycles) showed no component failures. That is, all Teflon tape and collar seals had adhered to the separators and had maintained the compartmental seals. No loose negative electrode material was found outside the negative compartment. The polysulfone case and cover as well as the terminal assemblies were not effected by the 30% KOH. However, analysis of the electrolyte showed 26% carbonates. It should be noted that carbonation of the electrolyte increases cell resistance which results in greater difficulty in charging the negative electrodes.

Cell failure could not readily be attributed to any single factor. Apparently, the imbalance of charge between the zinc and silver plates resulting from normal changes in the zinc electrodes, and electrolyte carbonation both contributed significantly to cell failure.

Based on the results obtained in these tests, it is reasonable to project a minimum life of 3000-4000 cycles for the cells in this group. Even longer cycle life may be expected when the cells are sealed because electrolyte carbonation clearly limits the useful life of the present design. Improvement of the electrode will also contribute substantially to even longer cycle life.

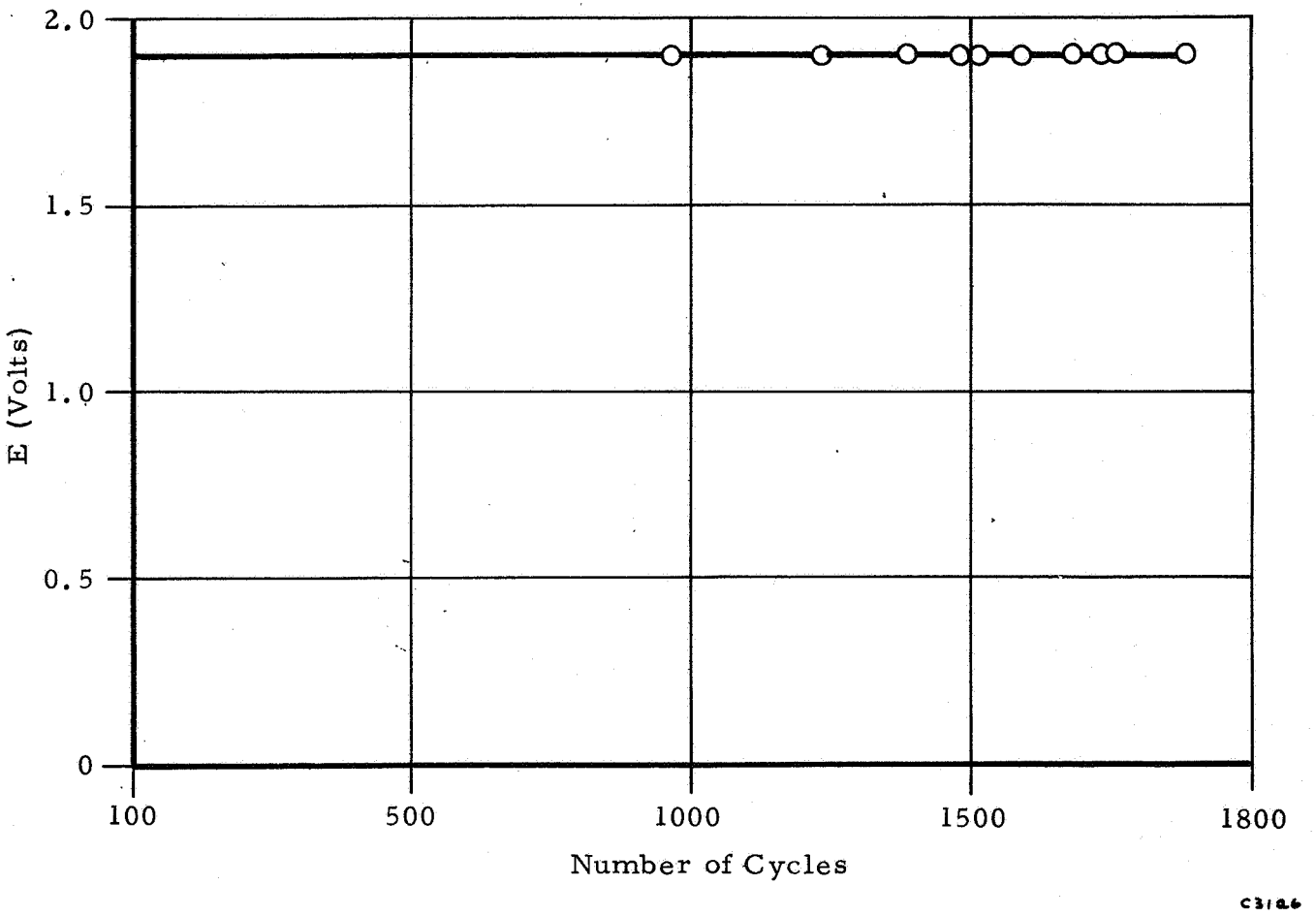


Figure 74. Open Circuit Voltage Group A Cells

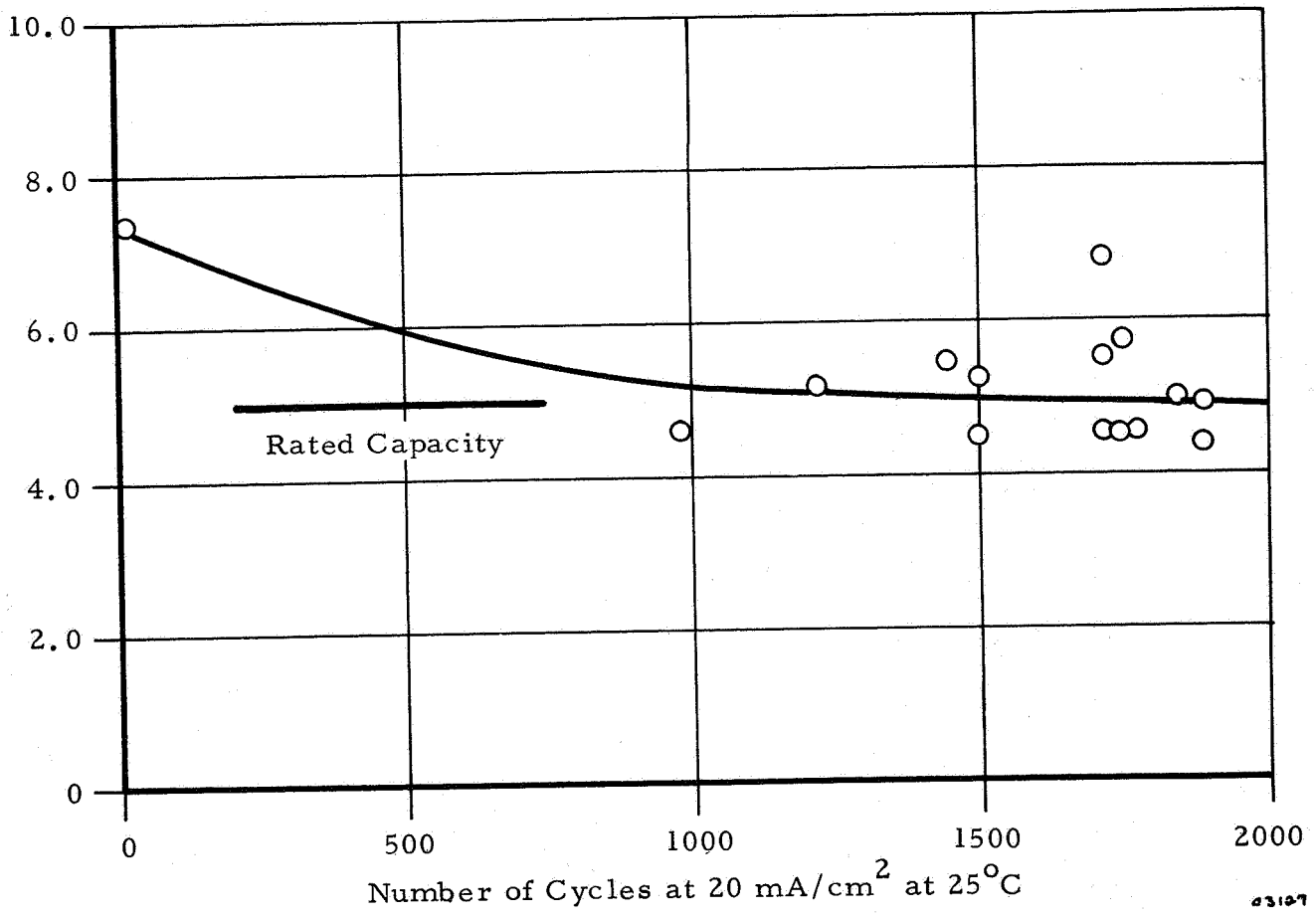


Figure 75. Capacity Retention of Groups A and D

2.3.2.2 Group B, 30 ma/cm^2, 25°C

Ten cells were automatically cycle tested at 30 ma/cm^2 at 25°C as described in Section 2.3. The charge rate was 2.0 amperes for one hour while the discharge rate was set at 3.75 amperes for 1/2 hour using a 5% overcharge.

Table XXIII shows the status of these cells at the end of this program. Four of ten did not fail after as many as 2088 cycles. This represents about 3100 hours of continuous cell operation. The average number of cycles completed at this regime by the six cells failing to date (less than 4.0 Ah) is 1245 cycles. The charge rate was raised from 2.10 to 2.15 volts to compensate for the inefficiency of the zinc electrode due to carbonation. Earliest cell failure occurred after 937 cycles. Three cells that have not failed have cycled without any charge rate adjustments and have completed an average of 2005 cycles as of this writing. Typical performance curves for each of these ten cells are shown in Figures 76 to 85 with the average discharge voltage plateau at about 1.43 V.

No electrolyte additions were required during the first 500 cycles. At this point, the average electrolyte addition (water) was about 3 cc per cell per week.

It is interesting to note that these cells generally maintained rated capacity for over 1000 cycles as shown in Table XXIII and illustrated in Figures 86 and 87, and had nominal OCV of 1.86 ± 0.02 volts confirming the integrity of the inorganic separator, component seals, and cell pack in general. The average number of cycles at the first recharge was 1201 cycles based on the ten cells tested.

Four cells in this group have been disassembled so far, including cells MC-156, MC-158, MC-159 and MC-160. Evaluation of the cell components of MC-158 (999 cycles) and MC-160 (1091 cycles) confirmed the integrity of the Teflon tape and collar seals after long cycle life. No adhesive losses were observed in either cell. The polysulfone case and cover and terminal assembly were not affected by the 30% KOH. Carbonate content in the electrolyte analyzed from these cells was 27%. Again, no single mode of failure was noted. Rather, it is felt that a compounding of factors, such as zinc electrode changes and electrolyte carbonation, led to cell failure. Cells MC-156 (1139 cycles) and MC-159 (1024 cycles) did show expansion of the zinc electrodes at the bottom of the zinc plate, resulting in a major crack in the separator at the bottom of the zinc electrode compartment causing failure. Inspection of other cell components from these two cells showed the case, cover, tape seals and terminal assemblies not effected by the 30% KOH during the cycle tests.

These tests confirm the data indicating the long cycle life capability reported for Groups A and D in Section 2.3.2.1. As was the case of the previous groups of test cells, carbonation and loss of

TABLE XXIII

CYCLE TEST DATA FOR GROUP B, TASK III, CELLS

Temperature: 25°C
Regime: Period 1/2 hour/1 hour
Discharge: Rate 3.75 amperes; 1/2 hour; 27% depth of discharge based on original minimum capacity 7.0 Ah
Charge: Rate 2.0 amperes; 1 hour; overcharge 5% based on original set up; voltage limit: 2.10 V maximum

Cell No.	1st Capacity Check		2nd Capacity Check		3rd Capacity Check		4th Capacity Check		Cycles Without Charge Adjustment	Total Cycles Accumulated (Including Charge Adjustments)
	Cycle	Output	Cycle	Output	Cycle	Output	Cycle	Output		
MC-151	1340*	4.0	1532	4.8	1614	4.6	—	—	1340	1854
MC-152	CELL HAS CYCLED CONTINUOUSLY					—	—	—	2036	2036
MC-153	1652	4.9	—	—	—	—	—	—	1970	1970
MC-154	1433	5.4	1637	3.0*	1671	3.7	1699	3.2	1637	1699
MC-155	1190	4.6	1674	3.8	—	—	—	—	1674	1674
MC-156	1138	2.5	—	—	—	—	—	—	1138	1138
MC-157	1176	6.3	—	—	—	—	—	—	2011	2011
MC-158	670	6.1	744	6.1	975	4.3	994	1.6	994	994
MC-159	670	6.2	871	5.0	937*	3.0	1024	2.4	1024	1024
MC-160	890*	5.0	974	4.1	1090	2.9	—	—	890	1090

*Charge adjusted to 2.1 amperes, voltage limit raised to 2.10 volts, maximum.

TABLE XXIV

CYCLE TEST DATA FOR GROUP C TASK III CELLS

Temperature: 100°C

Regime: Period 1/2 hour/1 hour

Discharge: 3.75 amperes; 27% depth of discharge based on original minimum capacity of 7.0 ampere-hours

Charge: 2.1 amperes; overcharge: 10% based on original set up; voltage limit: 2.1 v maximum

Cell No.	Cycles without Charge Adjustment	Total Cycles Including Charge Adjustments	Status of Tests	Remarks
MC-161	414	414	All tests completed	All cells cycled continuously until failure.
MC-162	494	494		
MC-163	455	455		
MC-164	523	523		
MC-165	591	591		
MC-166	586	586		
MC-167	524	524		
MC-168	530	530		
MC-169	496	496		
MC-170	398	398		

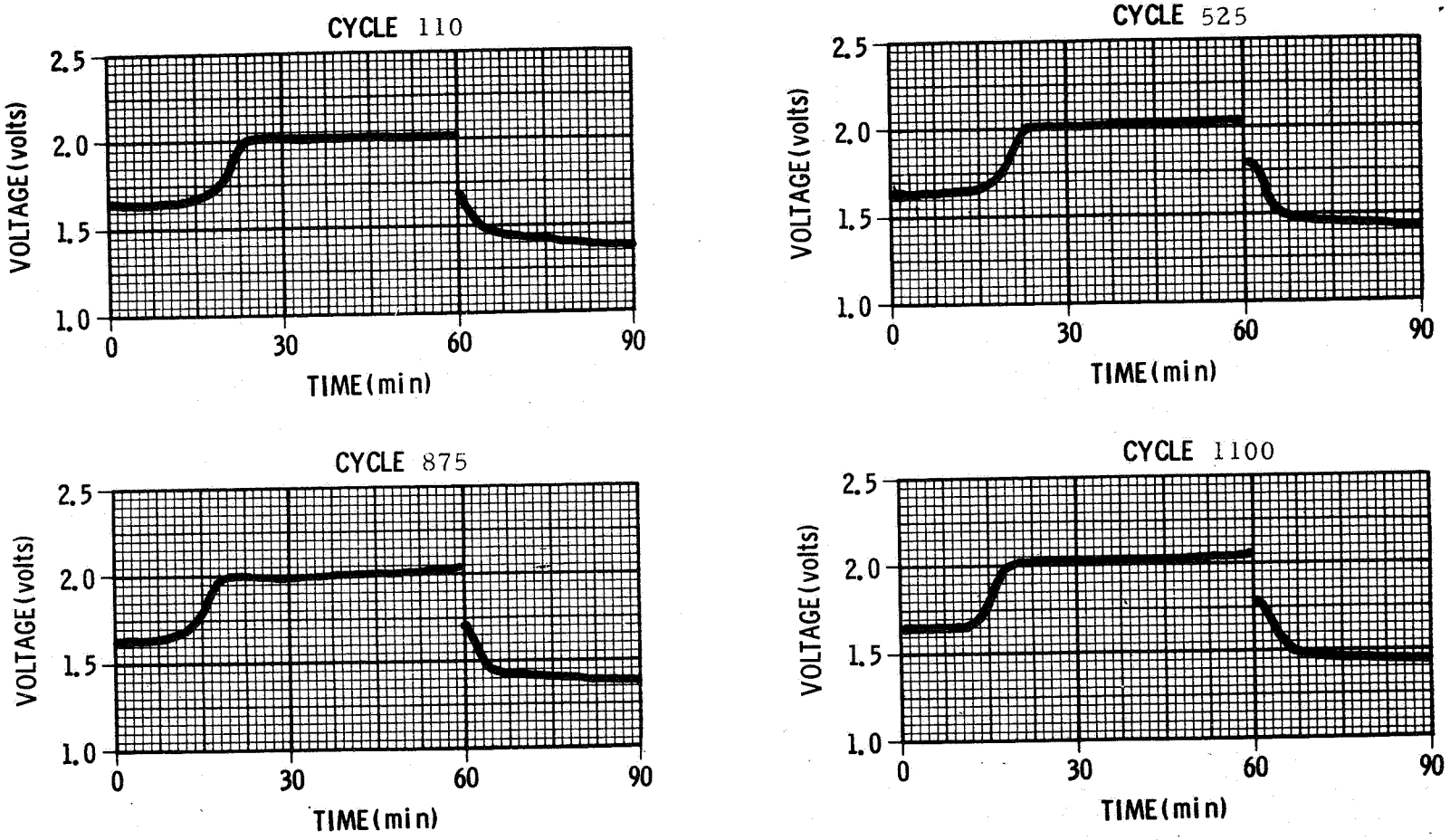


Figure 76. Cycle Characteristics of MC-151 at 30 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.00A

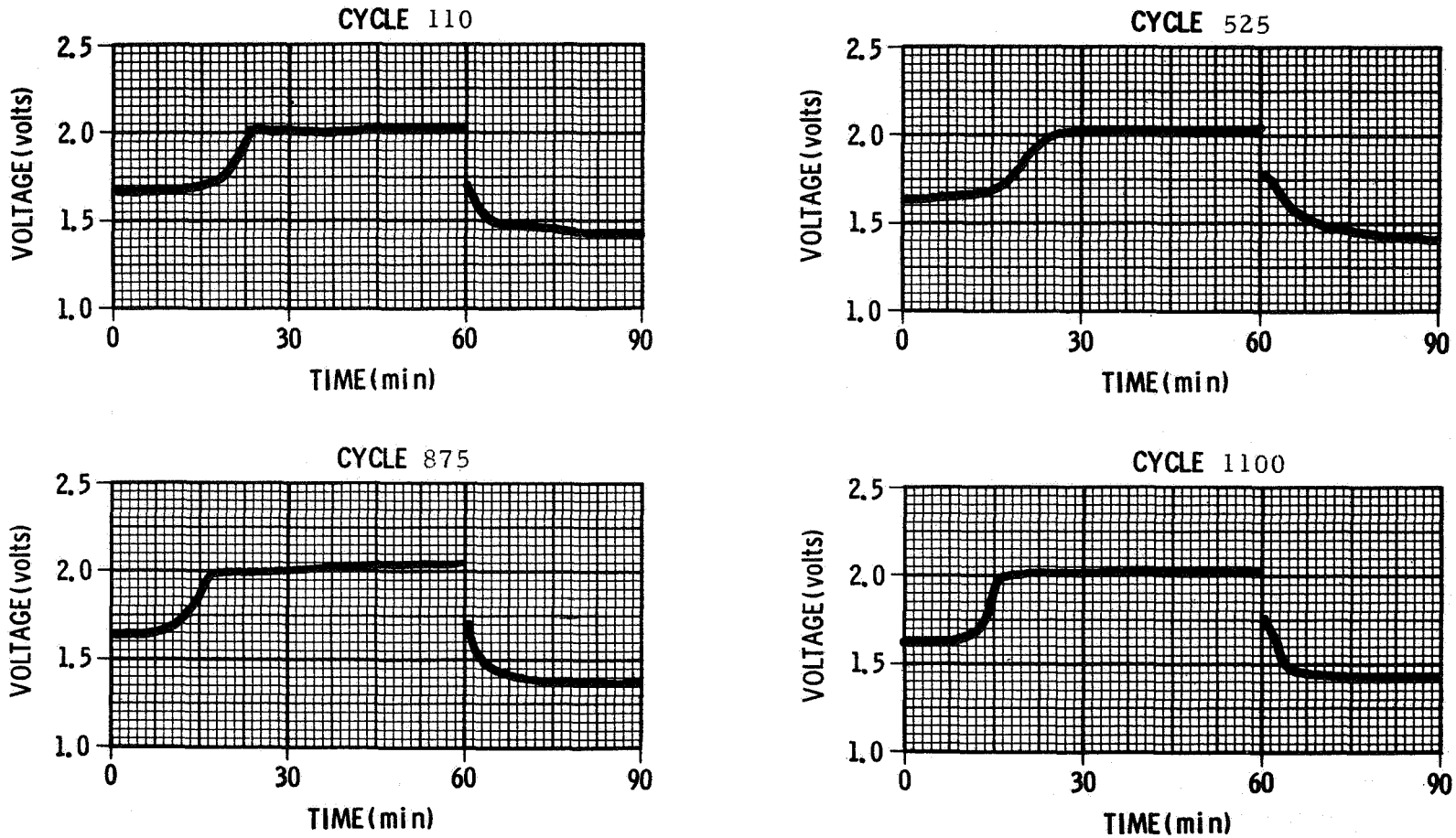


Figure 77. Cycle Characteristics of MC-152 at 30 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.00A

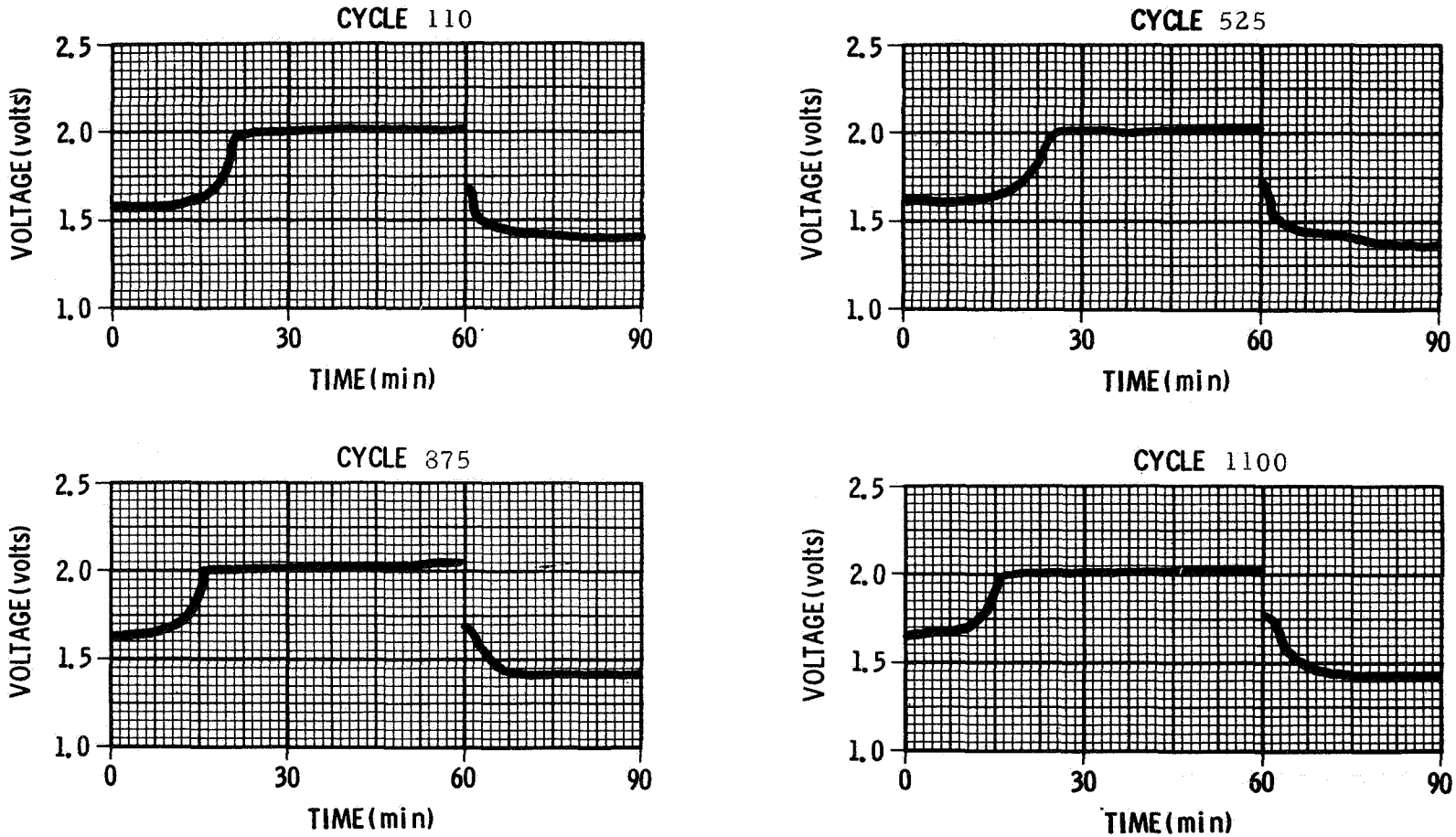


Figure 78. Cycle Characteristics of MC-153 at 30 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.00A

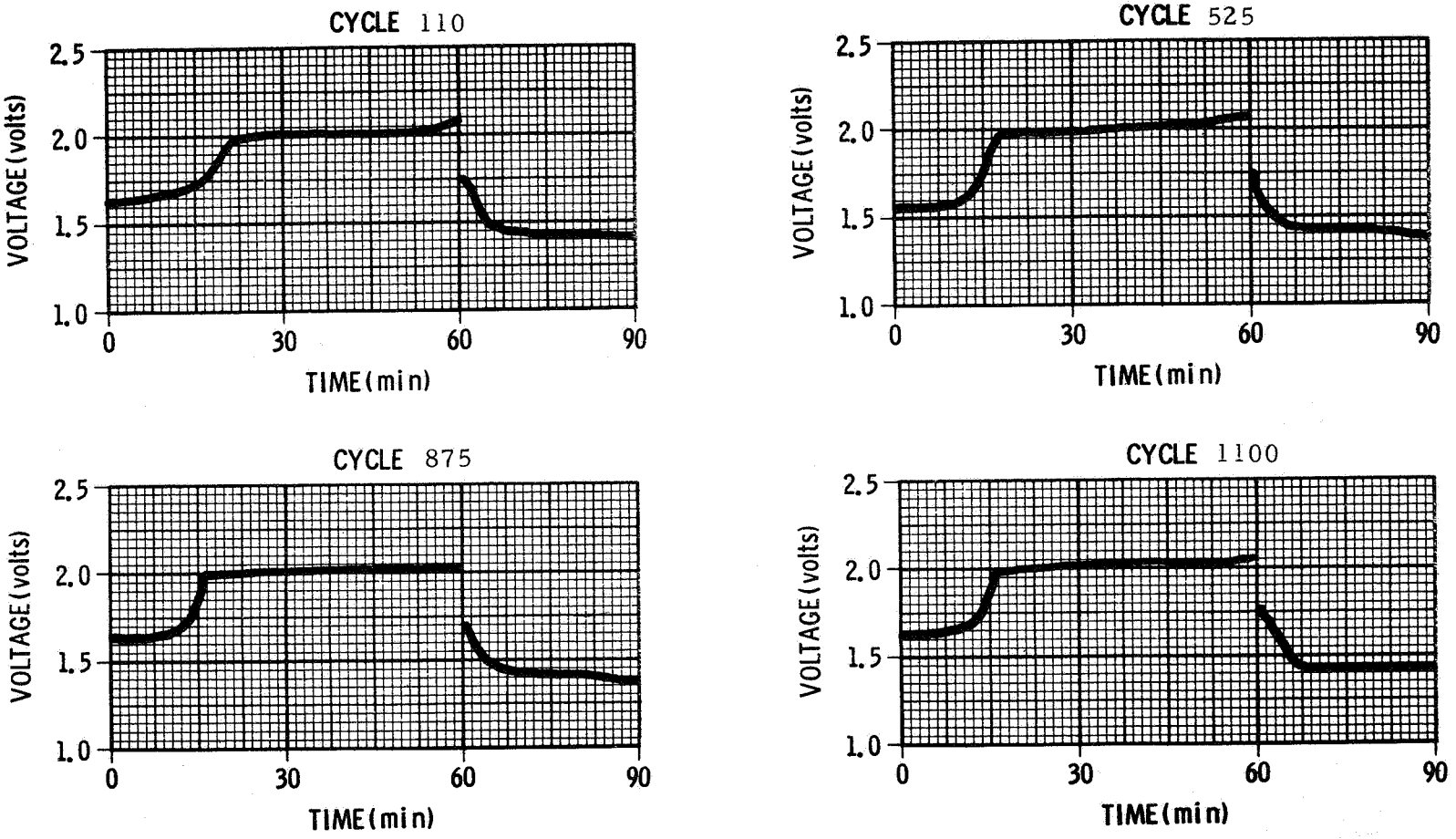


Figure 79. Cycle Characteristics of MC-154 at 30 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.00A

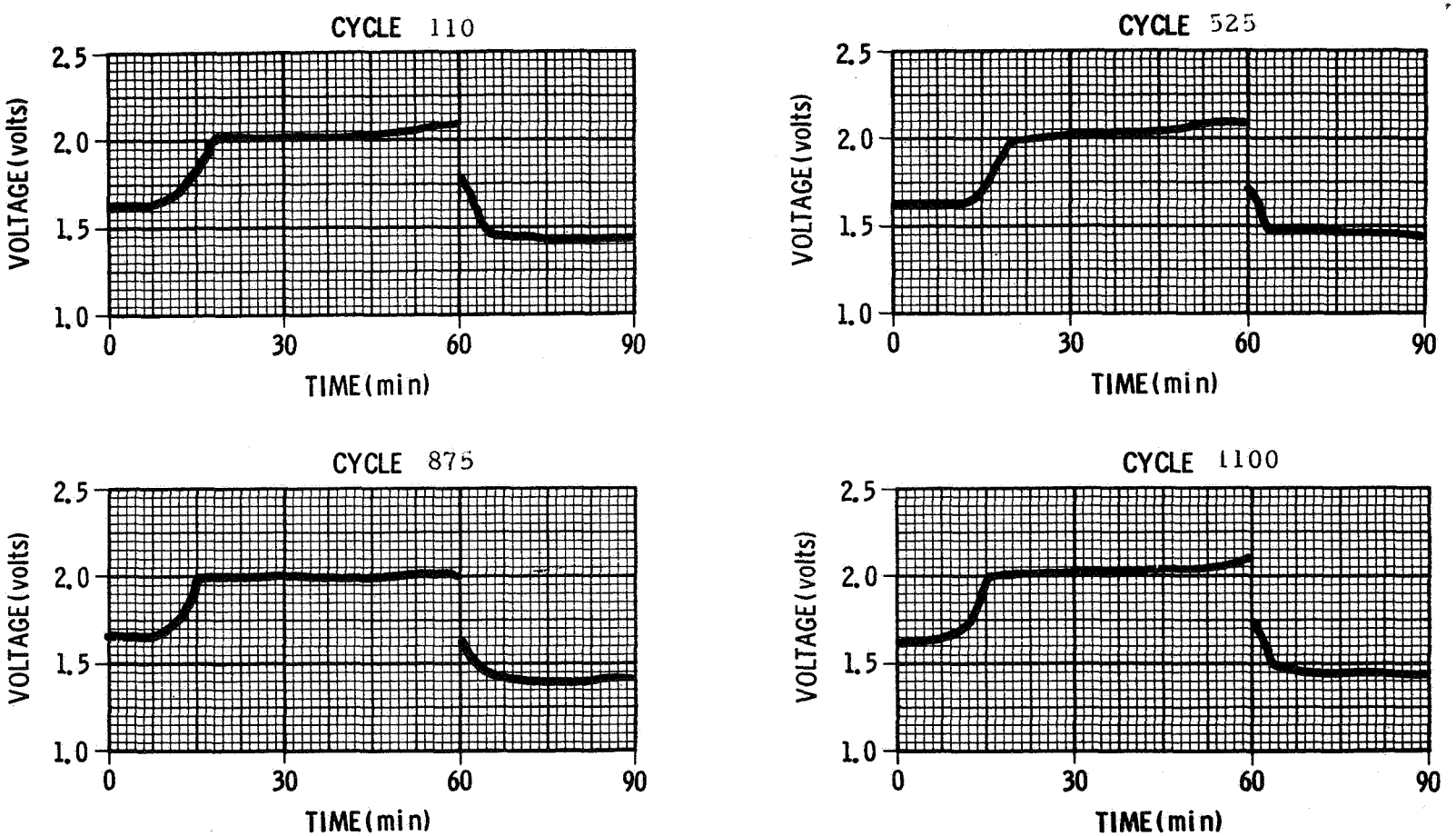


Figure 80. Cycle Characteristics of MC-155 at 30 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.00A

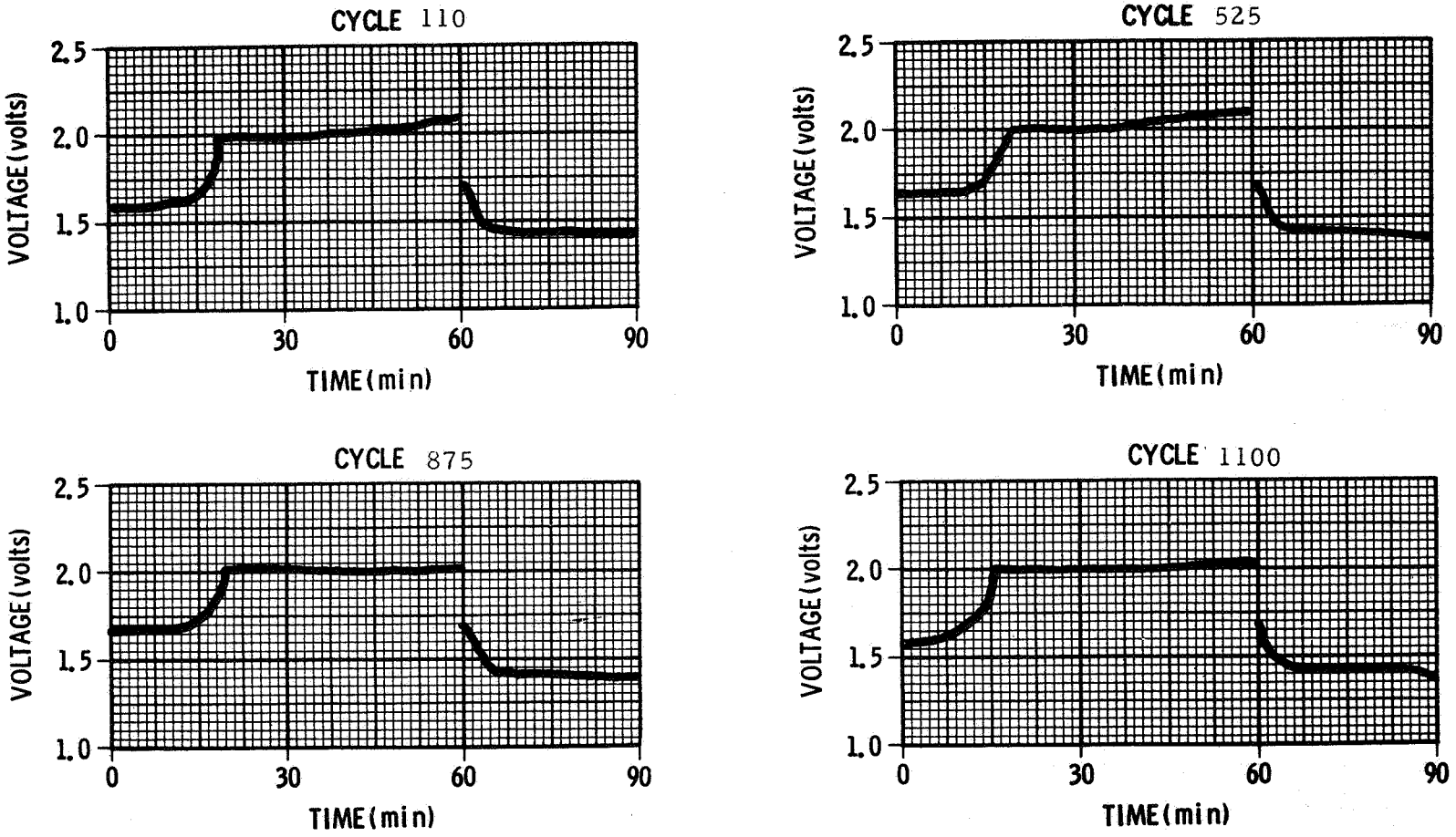


Figure 81. Cycle Characteristics of MC-156 at 30 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.00A

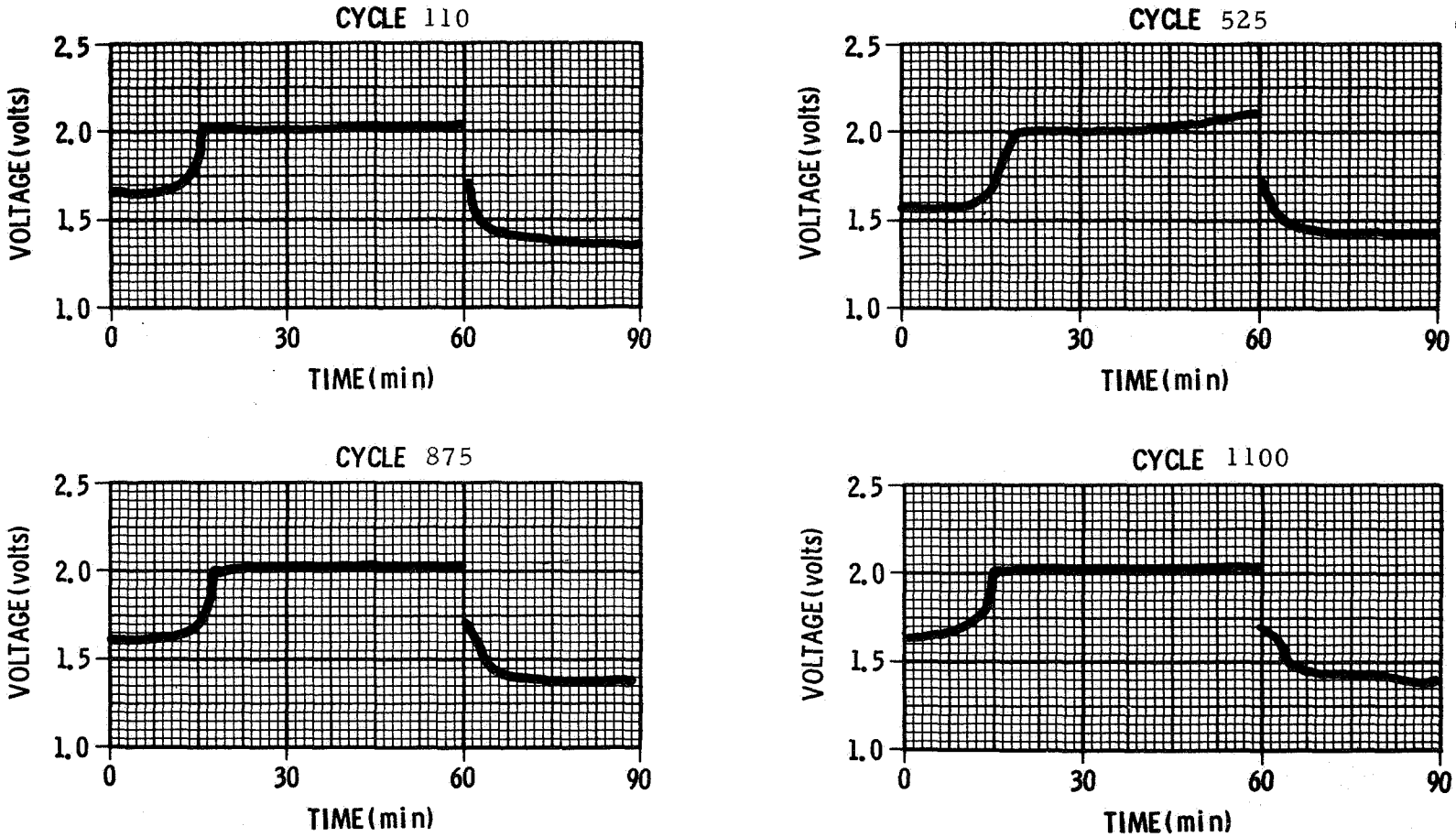


Figure 82. Cycle Characteristics of MC-157 at 30 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.00A

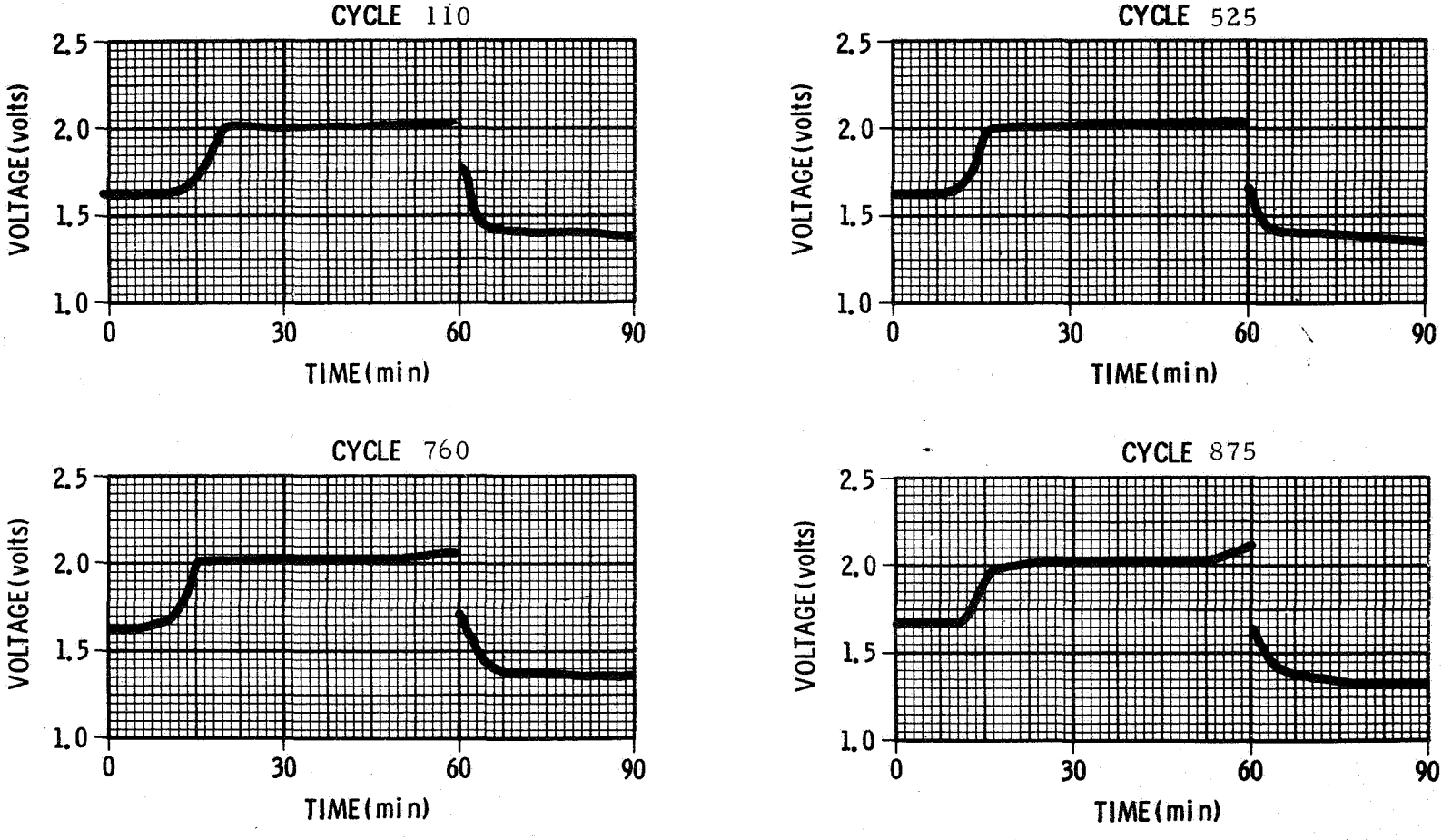


Figure 83. Cycle Characteristics of MC-158 at 30 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.00A

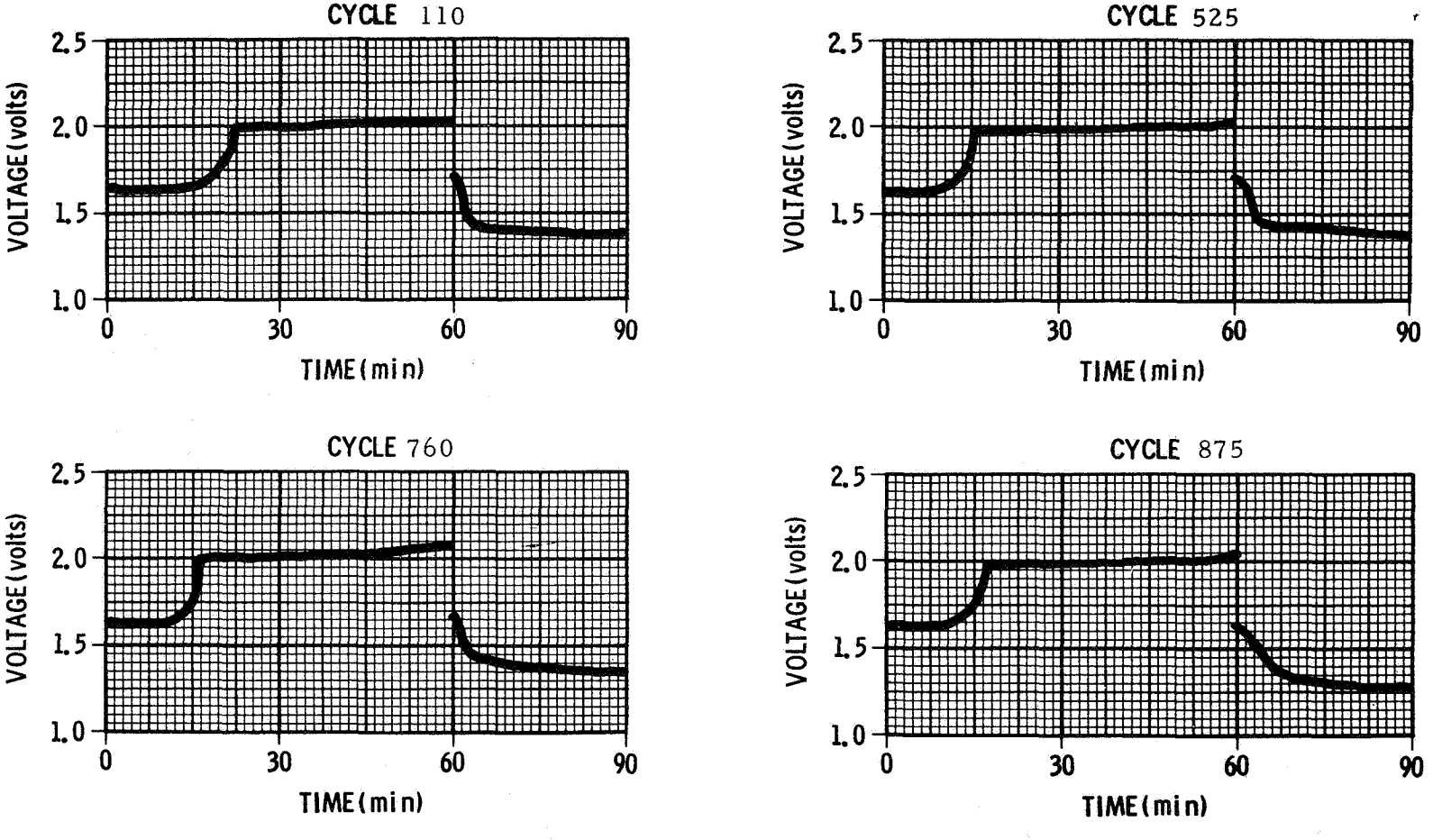


Figure 84. Cycle Characteristics of MC-159 at 30 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.00A

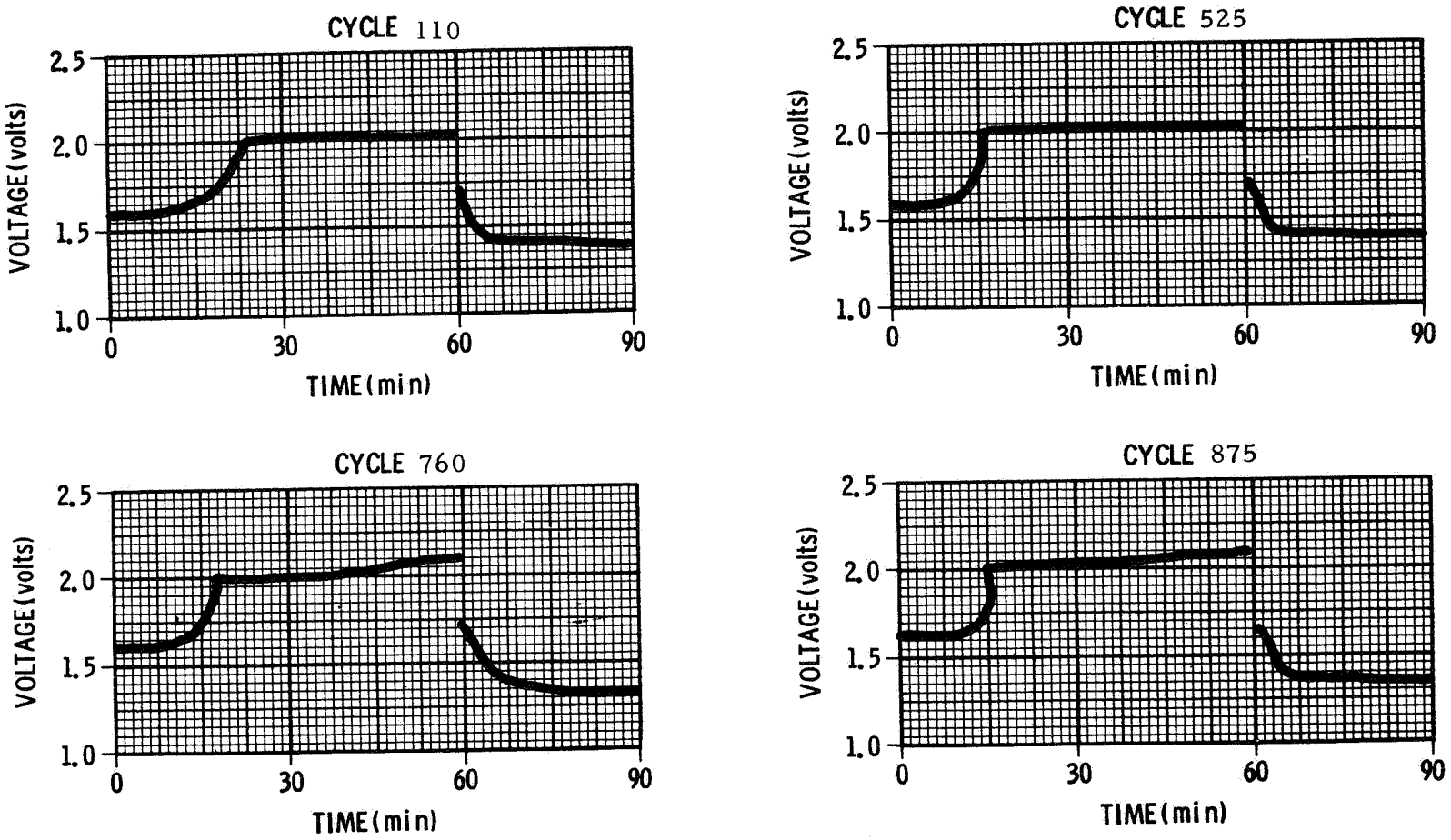


Figure 85. Cycle Characteristics of MC-160 at 30 mA/cm^2 at 25°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.00A

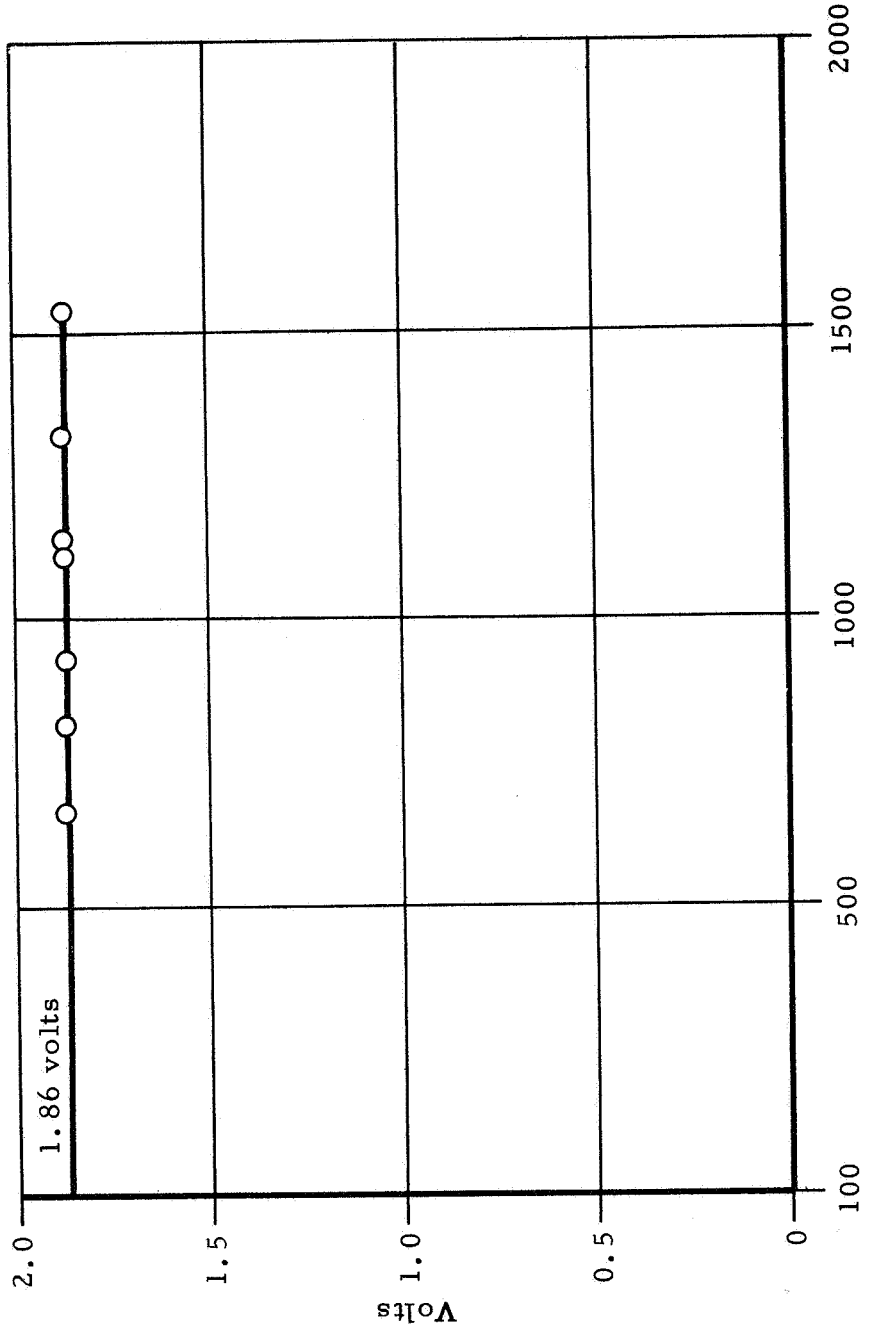


Figure 86. Open Circuit Voltage Group B Cells

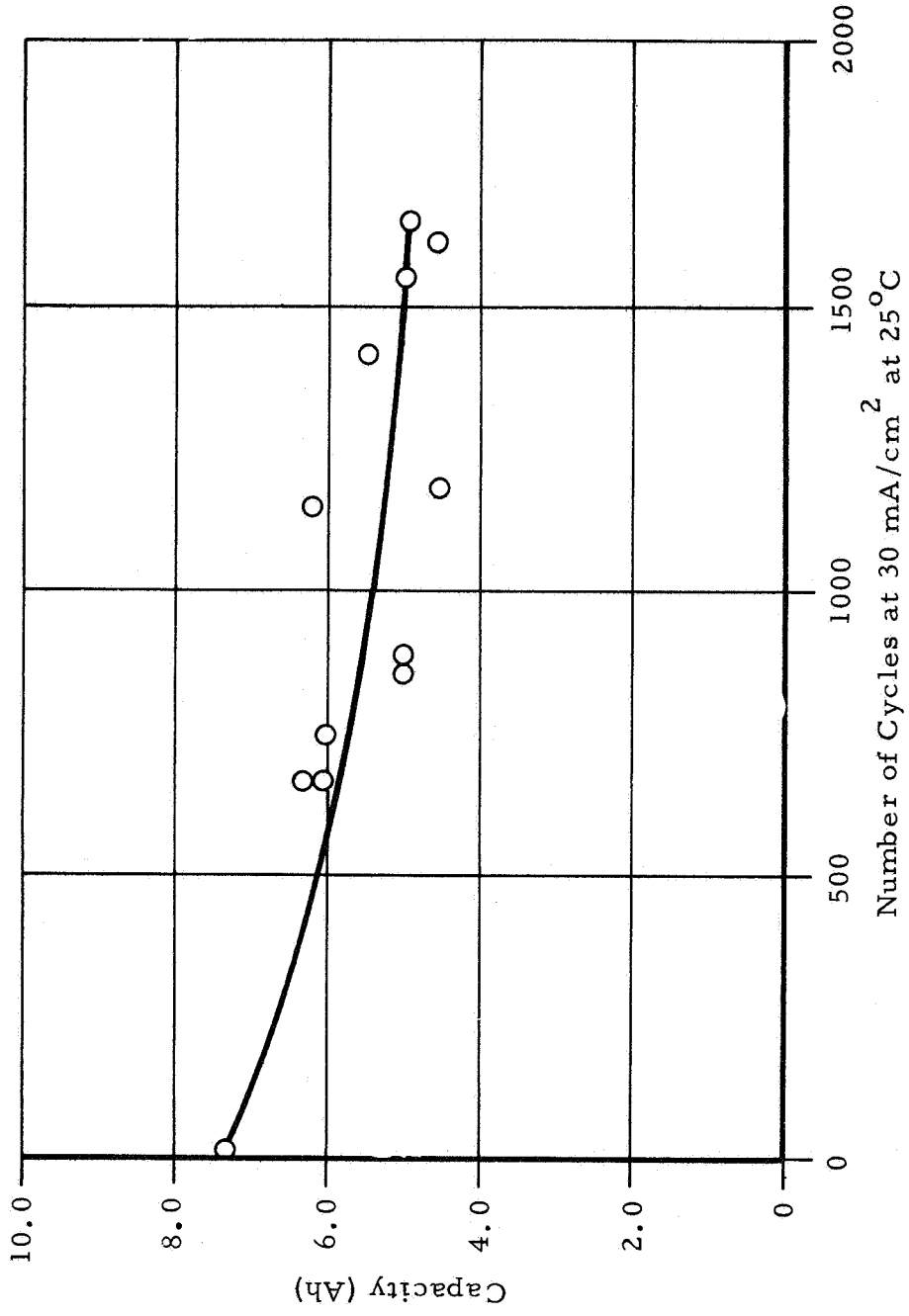


Figure 87. Capacity Retention of Group B Cells

electrolyte is a significant factor in dictating cycle life. These problems will be resolved by sealing the cells. Based on the test results obtained to date, the minimum cycle life projected for this group of cells is 2000 - 3000 cycles.

2.3.2.3 Group C, 30 ma/cm^2, 100°C

Ten 5-Ah multiplate cells were formed as previously described in Section 2.3.1. After formation, the cells were automatically cycled using a 1/2-hour discharge, 1-hour charge cycle regime at 30 ma/cm^2 at 100°C with a 10% overcharge. The charge rate was 2.1 amperes while the discharge rate was 3.75 amperes using a fixed load.

During the initial 100 cycles, the cells required about 1.5 cc electrolyte per cell per day. At that time, the rubber bunsen valve sleeve decomposed as a result of continuous contact with the 30% KOH at 100°C. Since the sleeves were not replaced, all Group C cells completed the cycle tests as open cells. As a result, electrolyte additions averaged 2.1 cc per cell per day for the remainder of the test.

At the beginning, 20% KOH was added as make-up electrolyte. This was reduced to 10% after about 300 cycles, and water was added for the remainder of the test to prevent extreme electrolyte concentrations.

As many as 591 cycles were completed at this regime with five of ten cells from the group accumulating from 523-591 cycles, with a total group average of 501 cycles, as shown in Table XXIV. Discharge voltage plateaus for all cells were consistent at 1.50 volts during the first 200 cycles. Thereafter, the discharge voltage plateaus exhibited a gradual decline to about 1.45 volts just prior to failure. This was apparently related to the pick-up of carbonate contaminants in the electrolyte as a function of time. Typical charge-discharge performance curves for each Group C cell are illustrated in Figures 88 to 97.

After failure, each cell was disassembled for evaluation. Analysis of the cell components showed oxidation of the positive plates and their attached wires to the point where partial contact losses had occurred.

The polysulfone case and cover as well as the negative terminal assemblies were not effected by the long wet life of 100°C. The Teflon tape seals and collars showed a partial adhesive loss. However, the Astroset 3420-09 inorganic separator had no signs of pitting or erosion as a result of continuous cycling at 30 ma/cm^2 at 100°C.

These tests demonstrate the capability of the NASA 5-Ah inorganic separator cell to cycle at least 591 times at 30 ma/cm^2 at 100°C. Subsequent decline in performance is related to electrolyte loss and carbonation. Considerably longer cycle life at 100°C can be

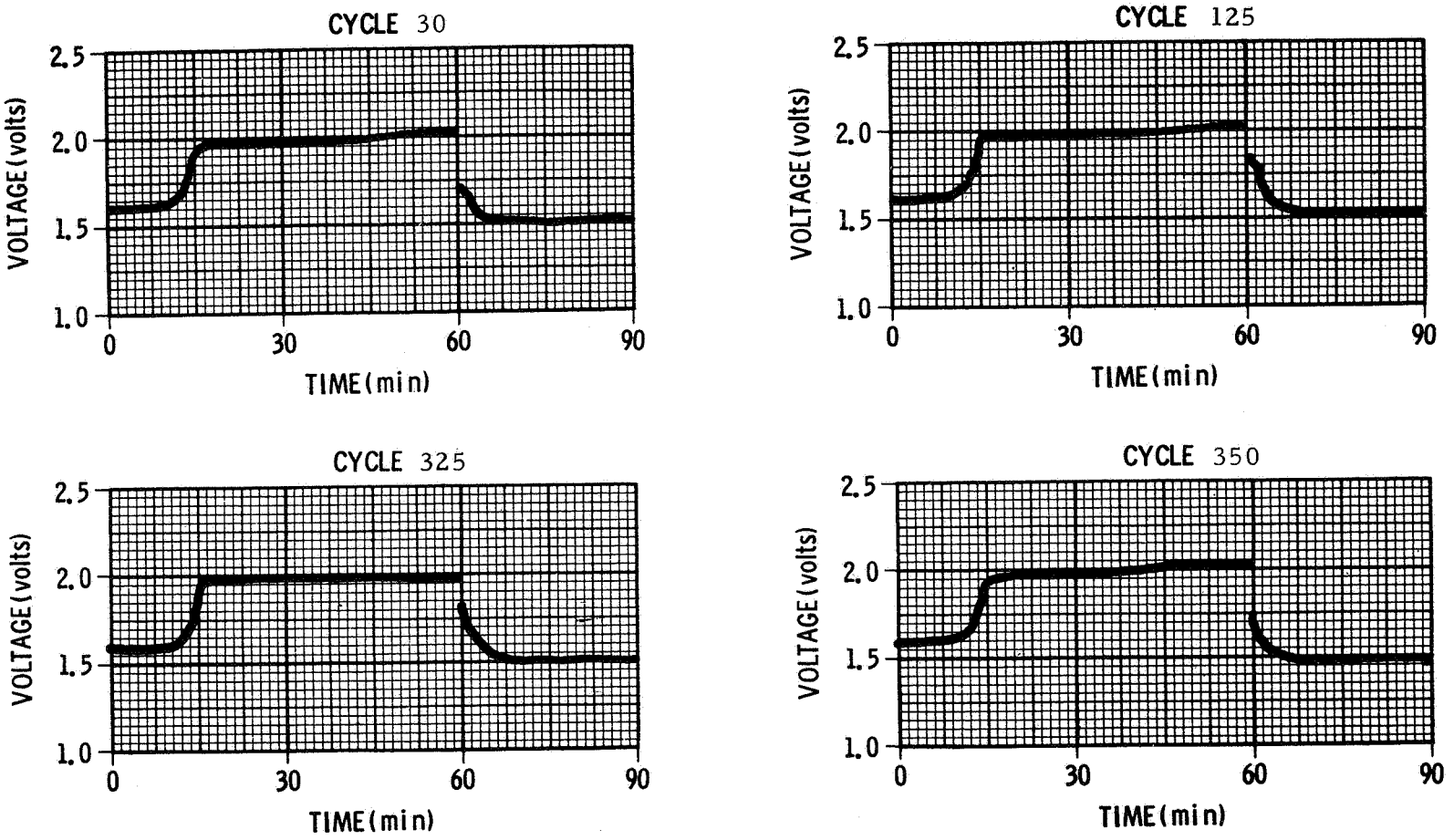


Figure 88. Cycle Characteristics of MC-161 at 30 mA/cm^2 at 100°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.10A

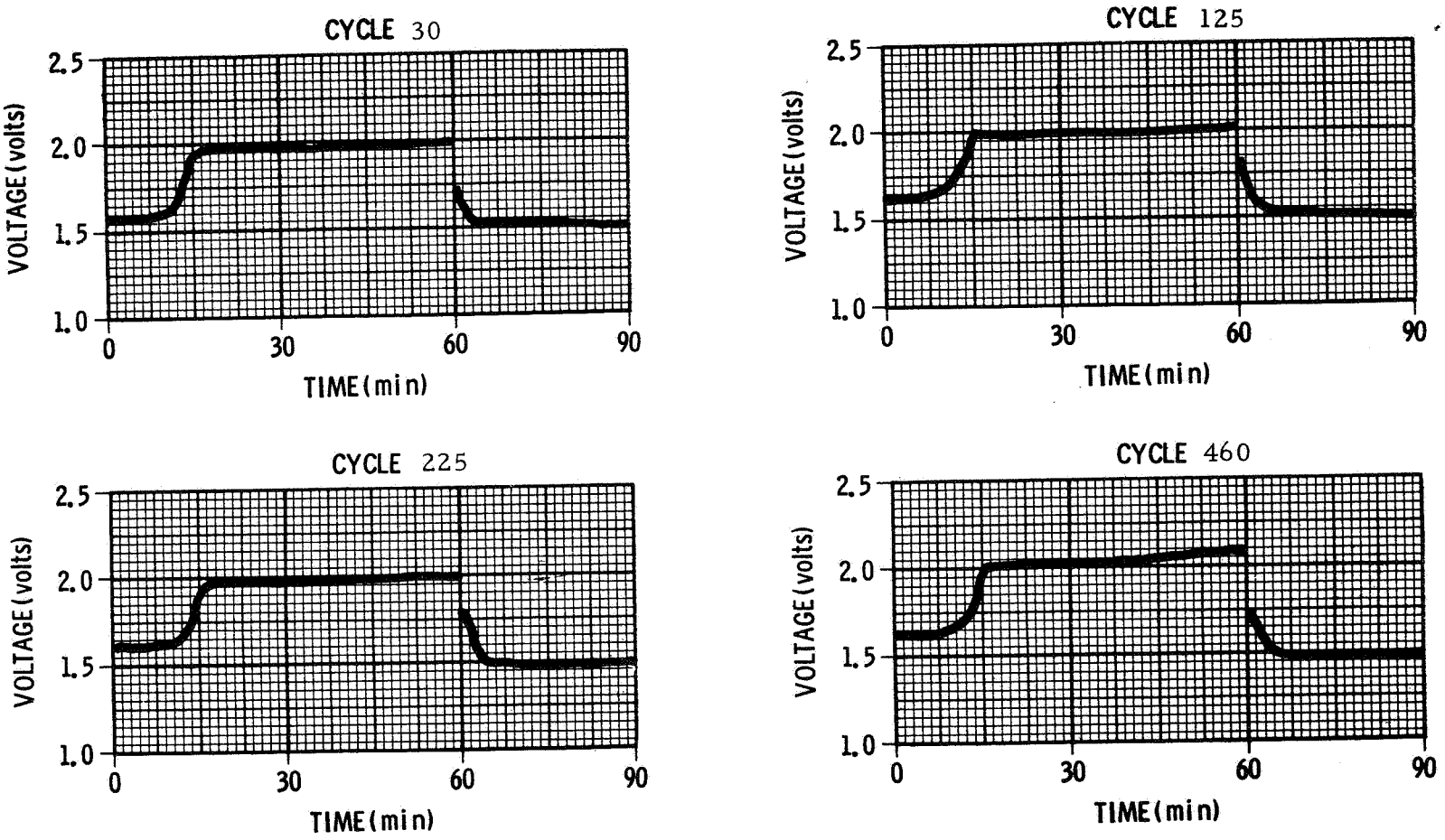


Figure 89. Cycle Characteristics of MC-162 at 30 mA/cm^2 at 100°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.10A

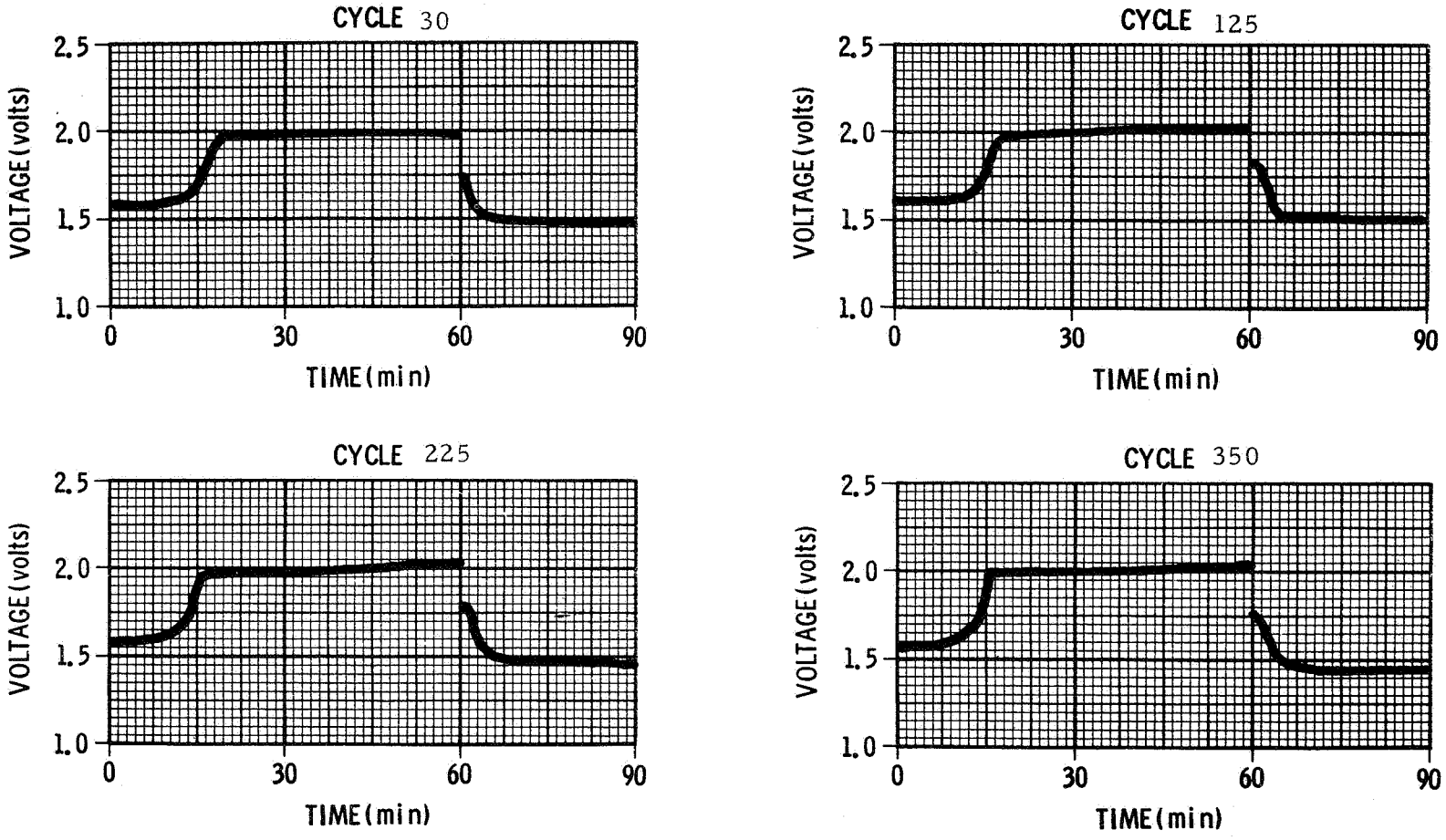


Figure 90. Cycle Characteristics of MC-163 at 30 mA/cm^2 at 100°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.10A

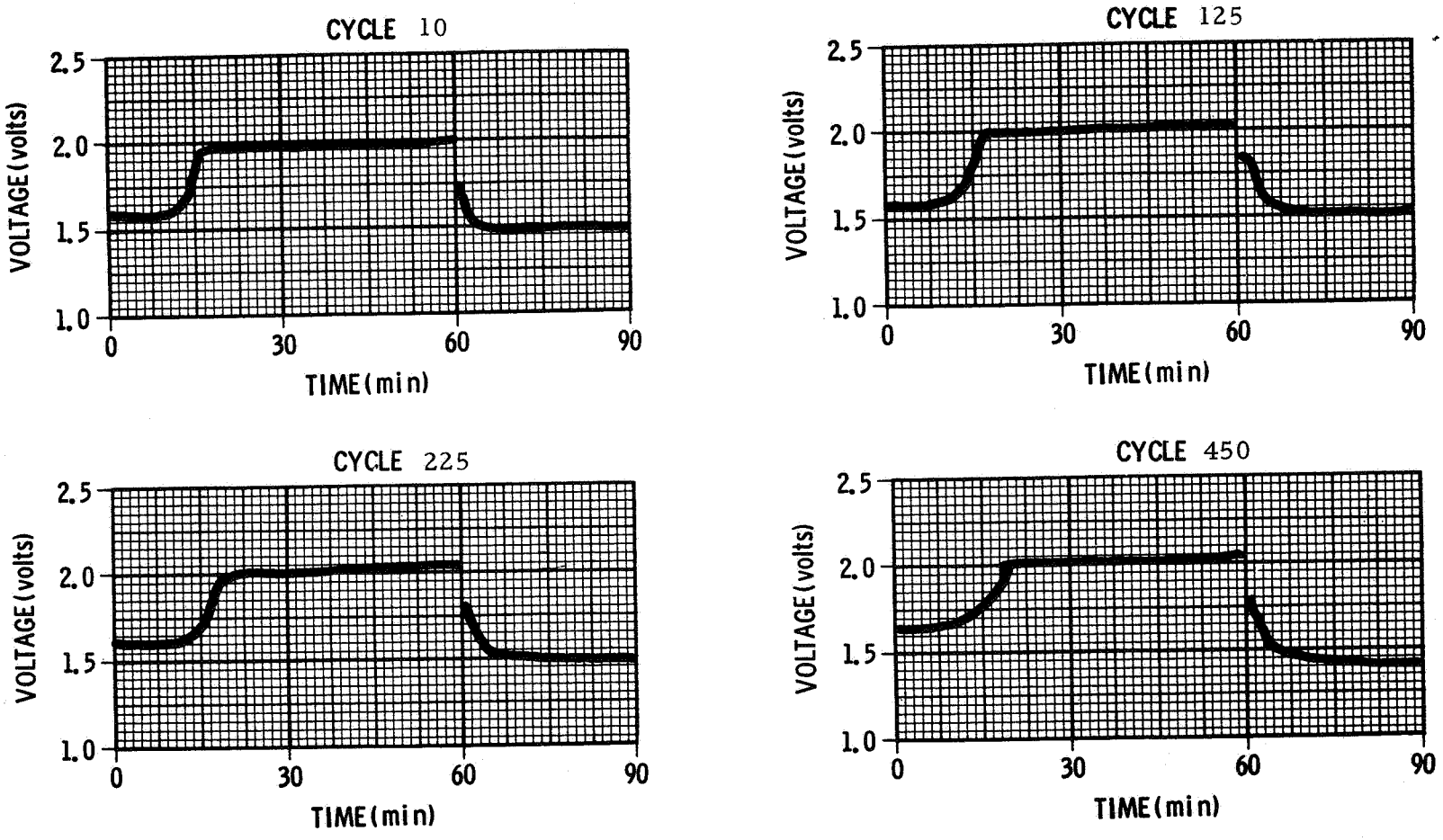


Figure 91. Cycle Characteristics of MC-164 at 30 mA/cm^2 at 100°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.10A

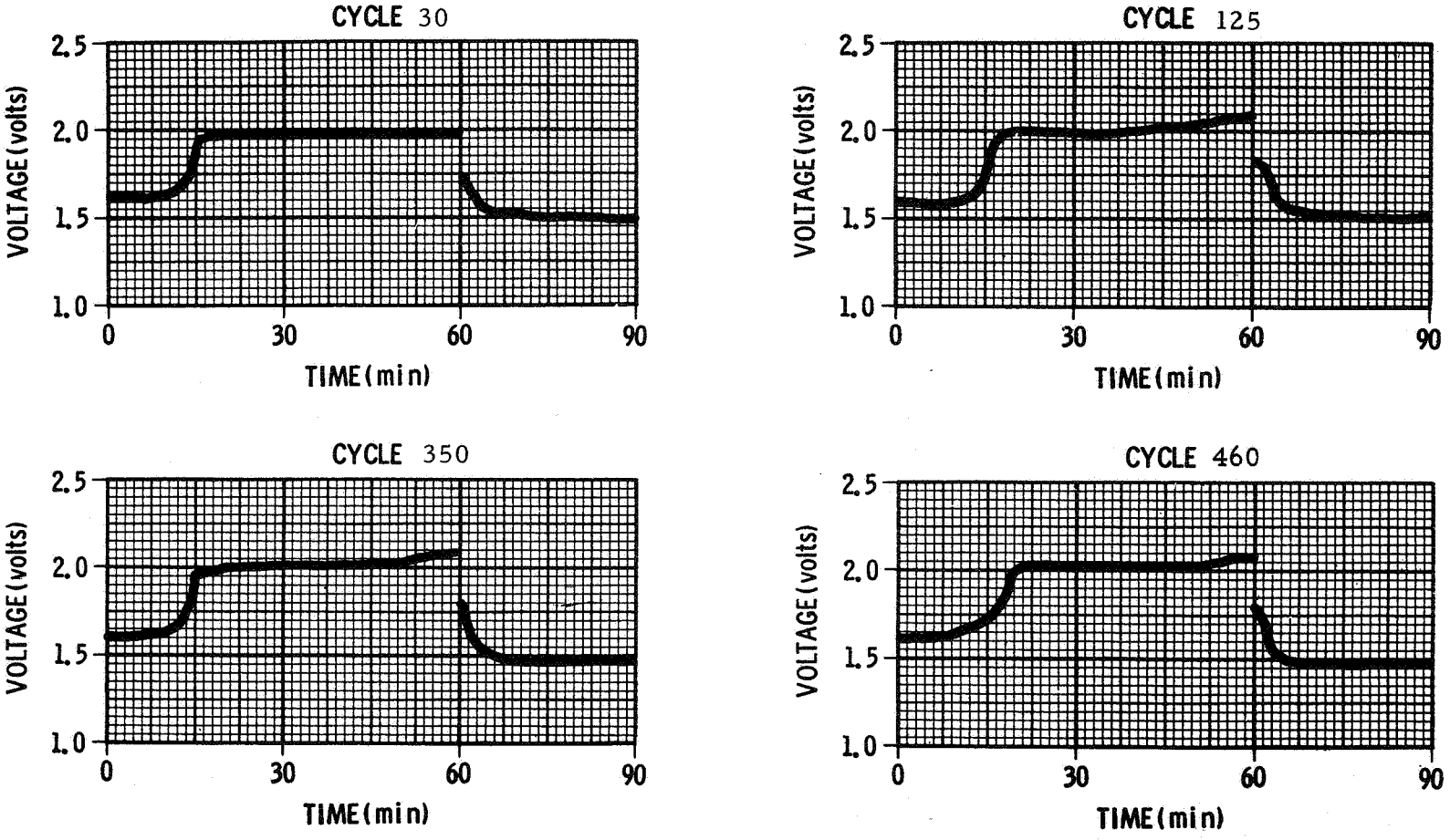


Figure 92. Cycle Characteristics of MC-165 at 30 mA/cm^2 at 100°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.10A

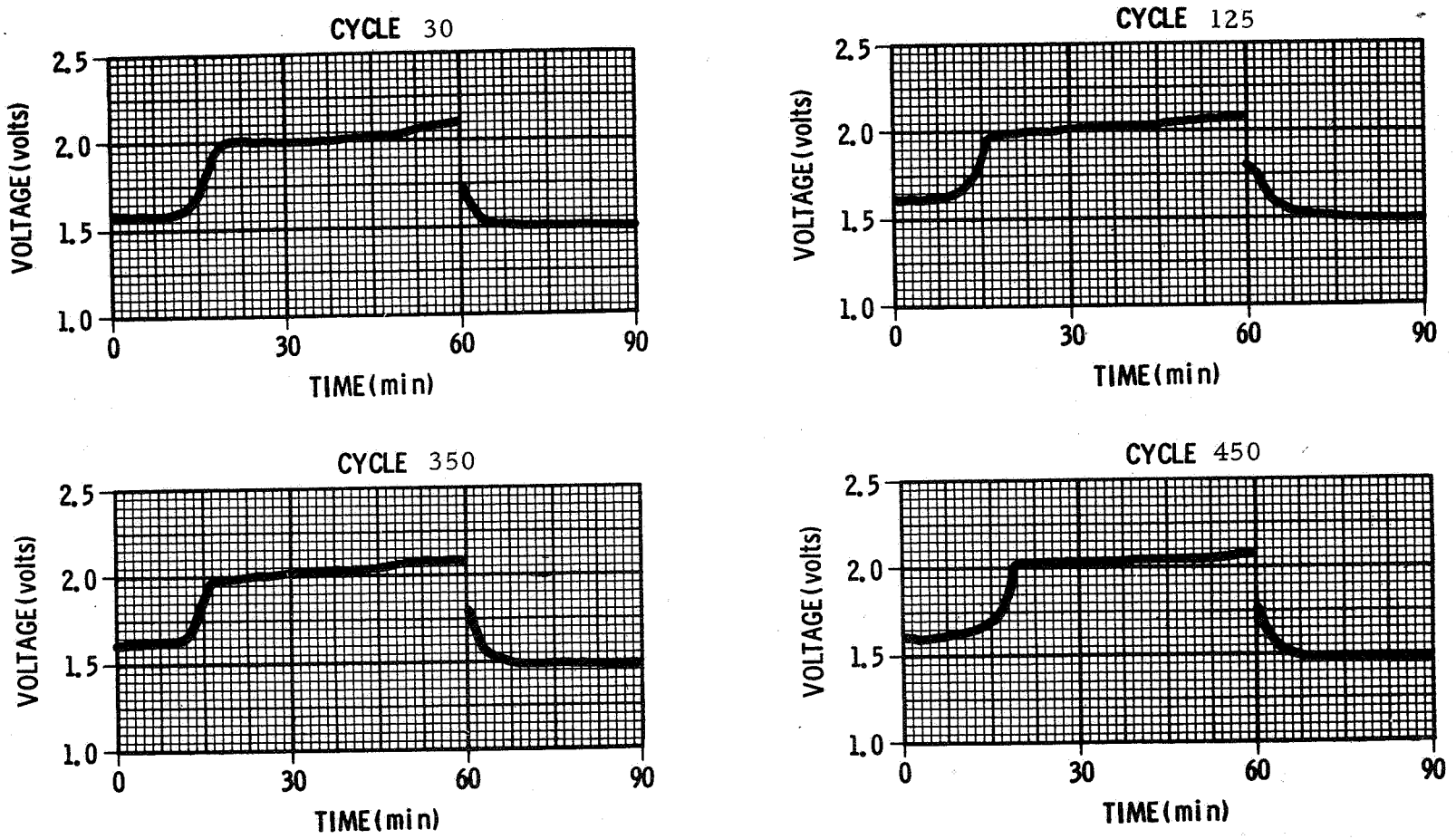


Figure 93. Cycle Characteristics of MC-166 at 30 mA/cm^2 at 100°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.10A

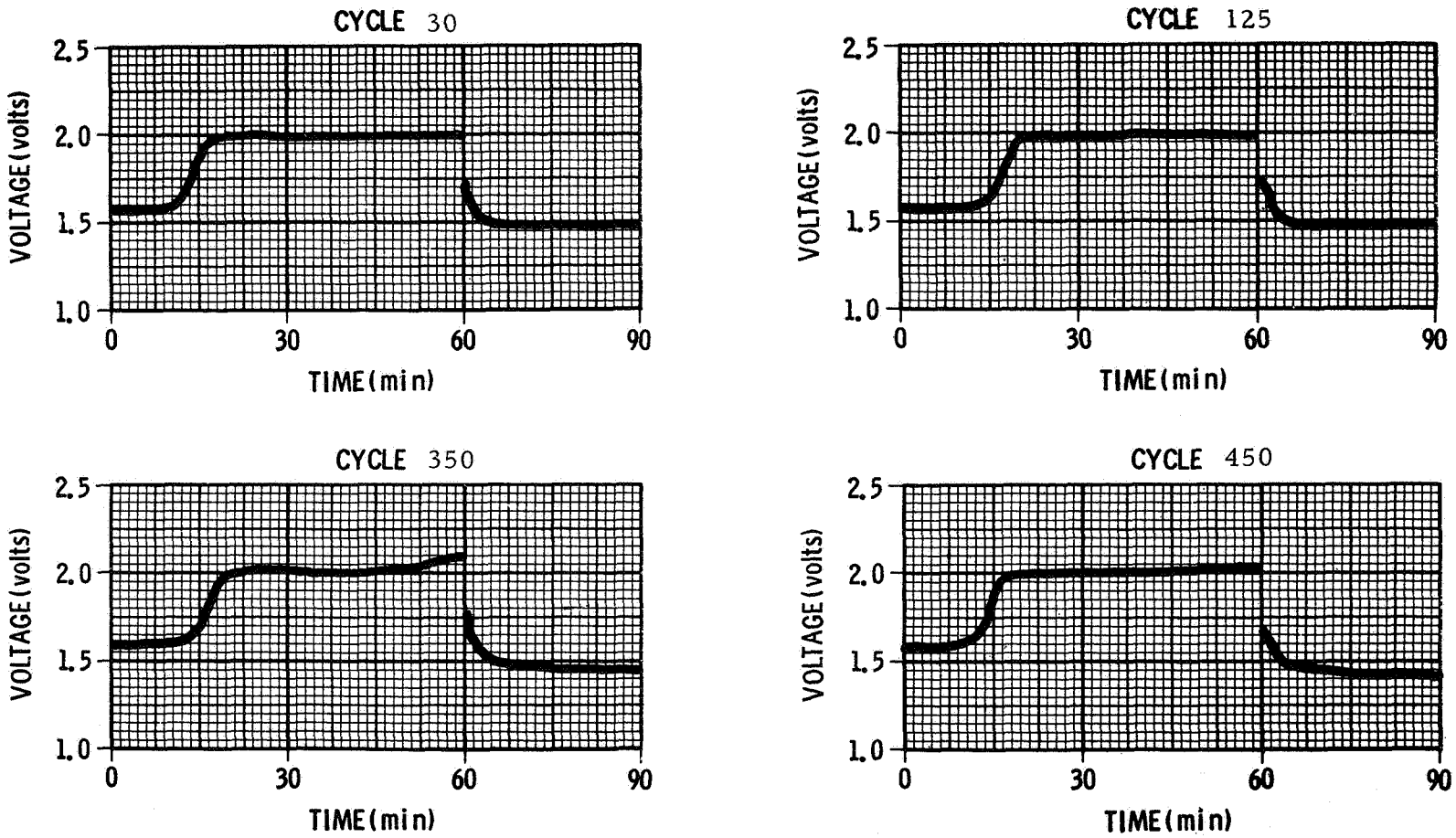


Figure 94. Cycle Characteristics of MC-167 at 30 mA/cm^2 at 100°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.10A

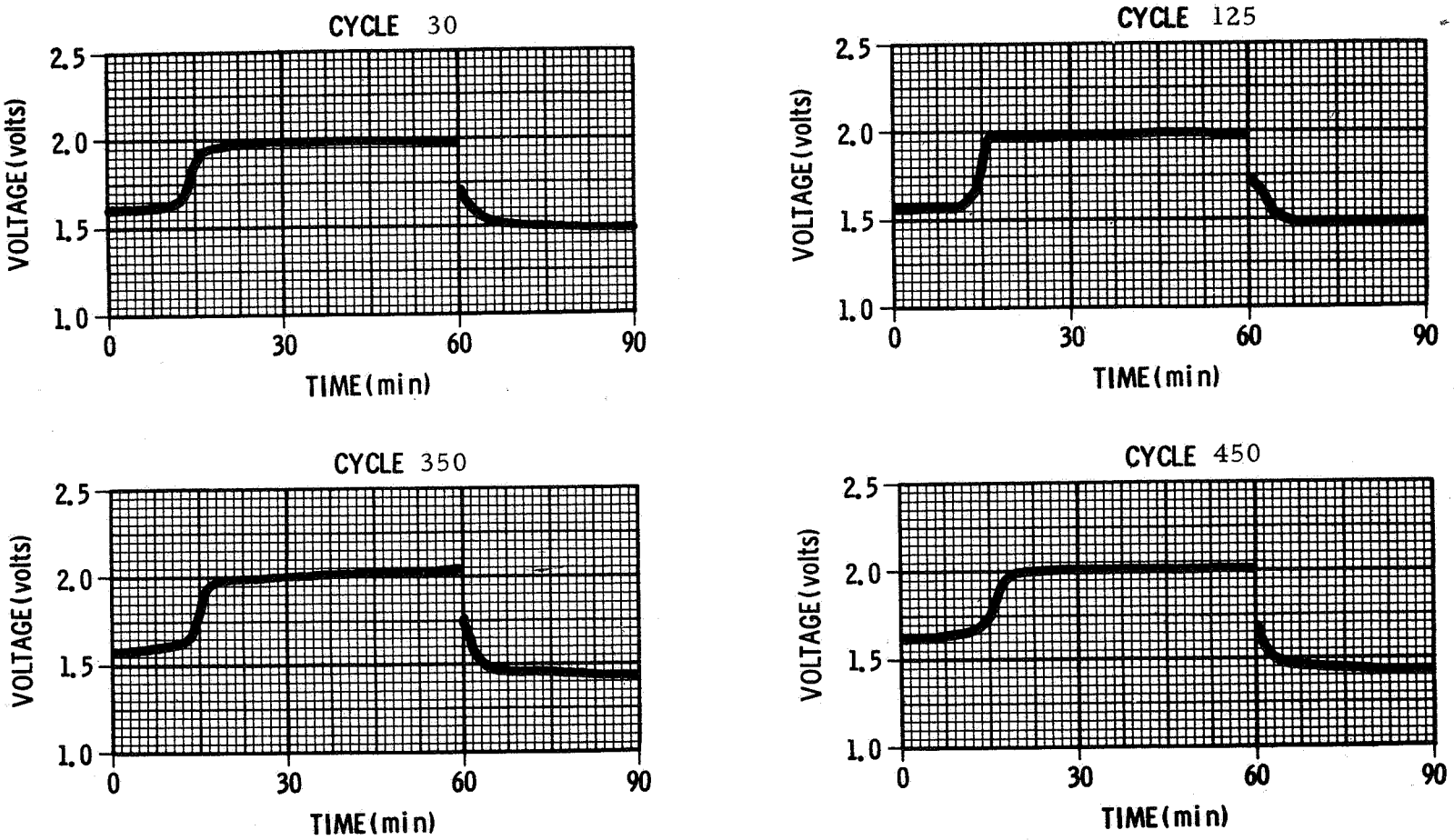


Figure 95. Cycle Characteristics of MC-168 at 30 mA/cm^2 at 100°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.10A

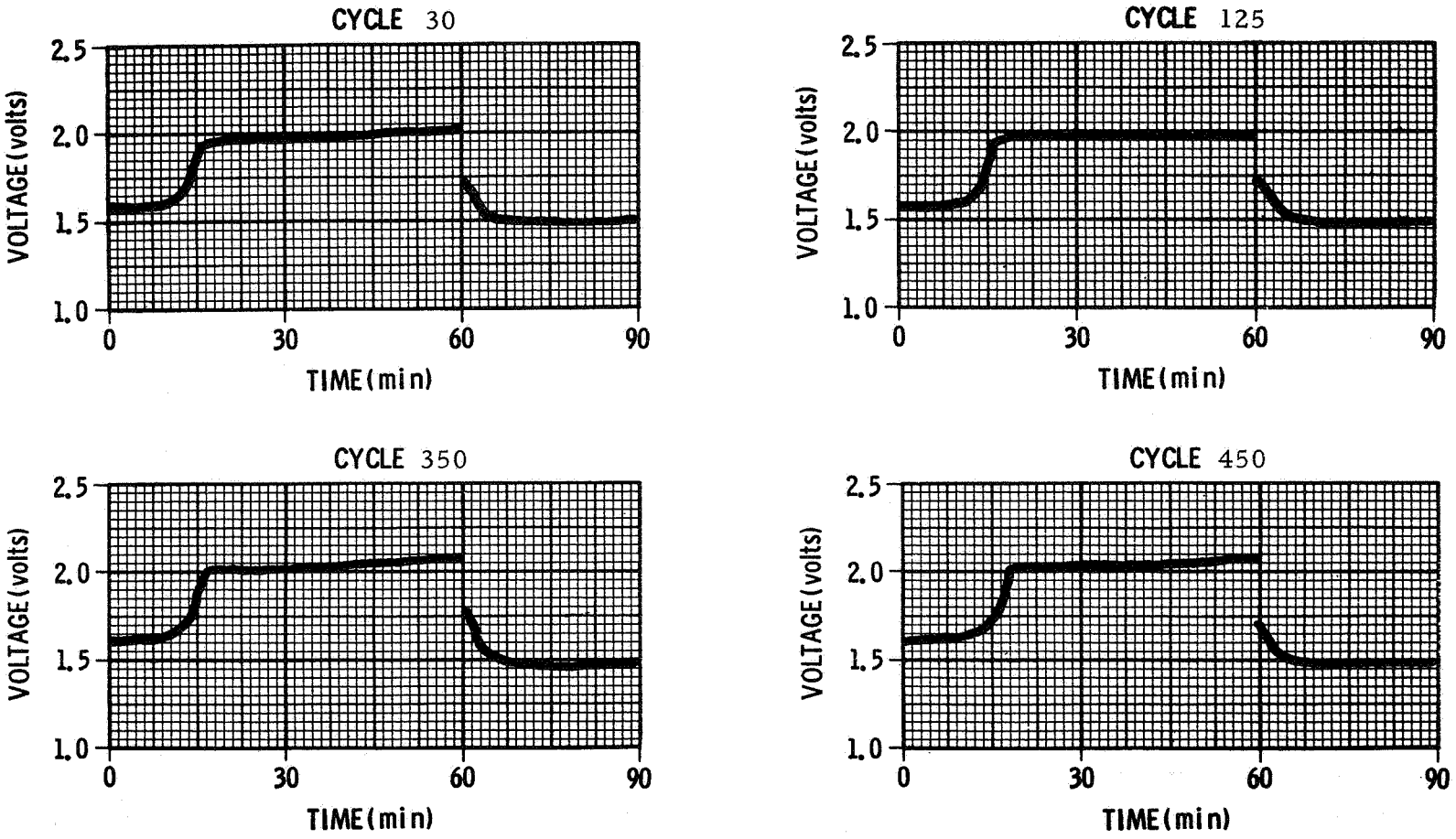


Figure 96. Cycle Characteristics of MC-169 at 30 mA/cm^2 at 100°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.10A

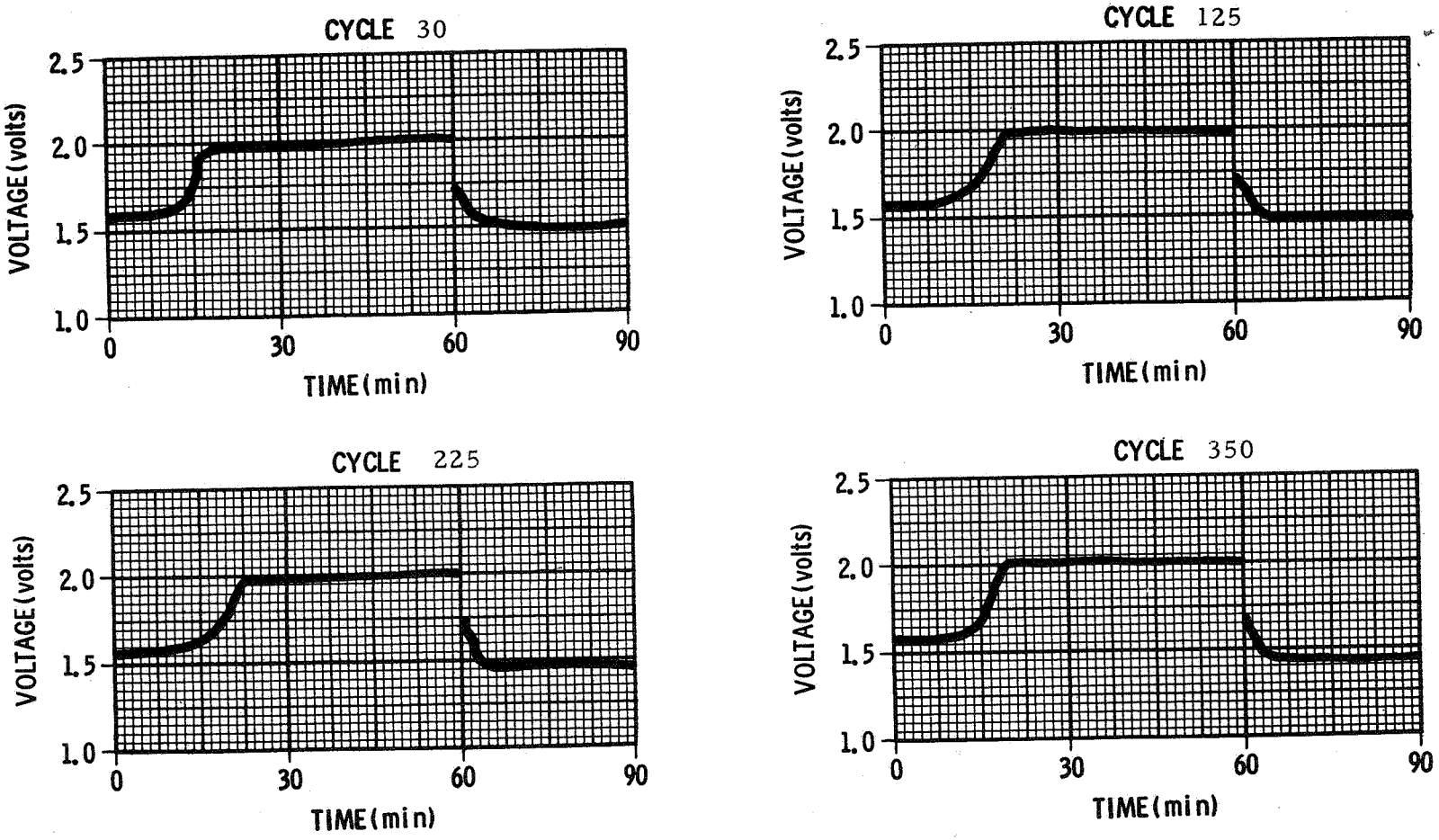


Figure 97. Cycle Characteristics of MC-170 at 30 mA/cm^2 at 100°C
Rates: 1/2 hour discharge 3.75A
1 hour charge 2.10A

expected with terminal connector redesign, insulation of the terminal connectors, cell sealing and improvements in the electrodes.

Based on this laboratory data, a minimum of 1500 to 2000 cycles at 100°C can be anticipated.

2.3.2.4 Task III – Summary of Cycle Test Results

The broad objectives of Task III were to obtain data that would enable the evaluation and characterization of the final 5-Ah multiplate design as well as establish the weak points and areas that would require further work prior to prototype cell fabrication.

Thirty-five cells were fabricated and tested. Fifteen cells were cycled at 20 ma/cm^2 at 25°C, ten cells were cycled at 30 ma/cm^2 at 25°C, and ten cells were cycled at 30 ma/cm^2 at 100°C. Thirteen of 15 cells at 20 ma/cm^2 at 25°C accumulated as many as 2458 total cycles. This represents over 3400 hours of operation. Five of ten cells cycling at 30 ma/cm^2 have achieved as many as 2036 total cycles, representing about 3100 hours of cycle life. The ten cells at 30 ma/cm^2 at 100°C averaged 501 cycles, with five of ten cells accumulating 523-591 cycles, or 885 hours of continuous cycling at 100°C.

In general, the rated capacity level was maintained after 1900 cycles at 20 ma/cm^2 at 25°C and 1000 cycles at 30 ma/cm^2 at 25°C with nominal open circuit voltages.

It should be noted that the level of cell to cell uniformity was exceptional for the 35 cells in this test group. This is apparent in the individual 5-Ah cell capacities on formation, as well as cycle life performance.

Discharge voltage plateaus were also uniform in each group ranging from 1.40 - 1.50 volts.

Analysis of the 25°C cells disassembled showed no component failures except in the case of MC-156 and MC-159. In these cells zinc electrode slumping had occurred resulting in loss of capacity and separator failure. Analysis of the electrolyte after testing showed carbonate contamination averaging 26%. Failure apparently resulted from changes in the zinc electrode as well as carbonate contamination of the electrolyte. The Group C cells at 100°C failed as a result of electrode changes, as well as carbonate build-up in the electrolyte.

From the data obtained thus far, it is reasonable to forecast longer cycles of 3000-4000 cycles at 20 ma/cm^2 at 25°C, 2000-3000 cycles at 30 ma/cm^2 at 25°C, and 1500 cycles at 30 ma/cm^2 at 100°C with improvements of the electrodes, protection of the terminal leads, and sealing the cell.

3.0 CONCLUSIONS

The experimental work done under Contract NAS 3-7639 resulted in the design, development and fabrication of 5-Ah multiplate silver-zinc cells using Astroset inorganic separators and electrode configurations which met or exceeded all work statement requirements and goals. This work has clearly demonstrated the value of this type of construction and the superior operating characteristics of NASA silver-zinc cells constructed with Astroset inorganic separators, both at 25°C and 100°C. It has been shown that:

1. 5-Ah silver-zinc cells of this type are capable of long cycle life at both 25° and 100°C. These cells have run for more than 2458 cycles at 20 ma/cm^2 and 2036 cycles at 30 ma/cm^2 on a 1/2 hour x 1 hour test regime as of this date and these tests are continuing. At 100°C, these cells were run for as many as 591 cycles at 30 ma/cm^2 before losing 20% capacity due to carbonation of the electrolyte and electrode changes.

2. The 5-Ah cells designed and evaluated in this program satisfactorily passed the shock, vibration, acceleration and acoustic noise tests specified in the work statement without apparent physical or electrical impairment.

3. The silver and zinc electrodes used satisfactorily met the component evaluation requirements specified in Task II of the program. These electrodes proved to be satisfactory in the 35, 5-Ah cells fabricated and evaluated in Task III of the program and for use in the 10, 5-Ah cells which were delivered to NASA/Lewis as required by the program. The test results obtained in Task III indicate that even longer cycle life and improved performance can be expected with further electrode improvement.

4. Astroset No. 3420-09 inorganic separators, which were selected for use in the Task III cells, are capable of at least 2458 cycles at practical drain rates. Their inertness to KOH over the concentration range of 30% - 45% at temperatures up to 150°C has been confirmed.

   These tests also establish their effectiveness in preventing electrode species migration, inertness to reaction with the silver electrode, prevention of zinc dendrite growth and applicability to practical high energy density cell designs.

5. Polysulfone molded with properly designed tools is a satisfactory case material for silver-zinc cells for operation over the temperature range of 25° to 100°C. The potential of this material for application in silver-zinc cells capable of thermal sterilization was also clearly established. Sealing techniques have been developed for the cell case and cover which permit internal pressures of 40 psi at temperatures of 20° to 150°C. Polysulfone cases of our design have been operated continuously

for more than 885 hours at 100°C without any evidence of attack, crazing or deterioration of any type.

6. A terminal design has been developed capable of operation at 40 psi over the temperature range 25°C to 150°C without electrolyte or gas leakage.

7. Current collectors and connectors designed and evaluated in this program are capable of operation at drains up to 30 amperes over the temperature range 25° to 150°C. An extension of the long cycle life performance obtained with the 5-Ah cells in Task III of this program can be expected as a result of further improvement of these components.

8. The cells designed and evaluated in this program can be operated using KOH concentrations ranging from 30% to 45% without substantially effecting operating characteristics or cell life. This flexibility, which is not available in conventional cells using plastic separators, is basically due to the inertness of the Astroset inorganic separator and is of considerable value in designing silver-zinc cells to meet specific space application requirements.

9. Successful completion of this program has established the value of this type of construction and the effectiveness of Astroset inorganic separators in practical multiple plate silver-zinc cells. These data form the basis for the continuation of this work and construction of prototype 5-Ah cells for extensive testing and evaluation by NASA. It is also desirable that some additional work be done to improve the case to cover seal for fully sealed operations and to further optimize the electrodes for even longer cycle life and improvement of overall operating parameters.

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NASA-Langley, 1967 —— 3