SECOND QUARTERLY REPORT

for

DEVELOPMENT OF PILE TYPE, HIGH DISCHARGE RATE
NICKEL-CADMIUM SQUIB BATTERIES

JUNE 5, 1966 - SEPTEMBER 4, 1966

CONTRACT NO.: NAS5-10160

Prepared By

GULTON INDUSTRIES, INC.
ALKALINE BATTERY DIVISION
212 Durham Avenue
Metuchen, N. J.

For

GODDARD SPACE FLIGHT CENTER

Greenbelt, Maryland

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Prepared By:

S. Charlip

S. Charlip
Section Head
Engineering Development

Approved By:

H. N. Seiger

H. N. Seiger
Director of Research

R. C. Shair

R. C. Shair
Vice President
Research & Development

DEVELOPMENT OF PILE TYPE, HIGH DISCHARGE RATE,
NICKEL-CADMIUM SQUIB BATTERIES

by

S. Charlip

ABSTRACT

The object of this report is to summarize the work and results accomplished during the past quarter in a program directed toward the design and development of a pile type, nickel cadmium, squib battery.

Cells with 2 square inches of active area were constructed and subjected to 10 ampere pulse discharges. The resultant voltage fell below 1.0 volts per cell. Previously cells with 4 square inches of active area gave 1 volt at 20 amperes.

Several intermediate sizes of cells with electrode areas of 2.40, 2.76, and 3.14 square inches were constructed and tested. It was found that there is no linear relationship between current density and voltage. The larger plates showed little improvement in voltage. The 2.76 square inch plate appears to be the minimal electrode required, based on cell data only. Cells were pulsed for 20 milliseconds to determine the presence and effects of concentration polarization and activation polarization on positive and negative electrodes respectively.

A five cell battery (of 2 square inch electrodes) was assembled and tested. Sealing problems were encountered during the battery assembly.

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INTRODUCTION

During the first quarter, efforts were directed to project organization, engineering analysis of design parameters, and the development of sintering and impregnation techniques for bipolar plates.

Sintering and impregnation problems, uniquely associated with bipolar plates, were overcome, and techniques for sintering and impregnating circular electrodes were developed. These differed considerably from the techniques employed in the manufacture of any conventional electrodes.

The objectives are: the development of a bipolar battery capable of yielding a pulse of 10 amperes for 1 second above 5 volts with a minimum capacity of 150 mAh, within a cylindrical envelope of 3 cubic inches (less terminal hardware).

Several cells with active sinter areas of 4 square inches (2¼ inch dia.) were constructed and tested in an open beaker for capacity and pulse discharge. The results indicated that the cells are capable of higher capacities than required. The test results were reported in the First Quarterly Report.

The 4 square inch plates, when manufactured into a bipolar battery, would have bordered on the limit of the allowable space and would have exceeded that limit after the module was encapsulated. Several intermediate plate sizes were constructed and tested for capacity and pulse discharge. Plates with 2 square inches of active area (1-5/8 inch dia.) were constructed first. This size was considered the smallest theoretically capable of meeting the discharge requirements. Several cells were built and tested, including a 5 cell module.

Intermediate size plates between 1-5/8 and 2-1/4 inches in diameter were also constructed and tested. The results of these tests and their meaning are discussed in this report.

TECHNICAL DISCUSSION

The data given in the First Quarterly Report, based on single cell discharges, indicated that a battery consisting of 5 cells with 4 in^2 active area was capable of sustaining a 20 ampere discharge while maintaining a voltage on or above 1.0 volt per cell. Since a battery with this area would have a volume greater than 3.00 in^3 when completely encapsulated, it was necessary to go to a smaller size.

It would seem logical that if the area and the current were reduced by half, the current density would remain constant and, therefore, the cell voltage would also remain constant. The first step was to reduce the area to 2 in^2 (a circular plate of 1-5/8 in. dia. of active area). The results obtained were not those anticipated. Therefore, three other sizes were prepared, increasing the diameter by 1/8 inch in each case.

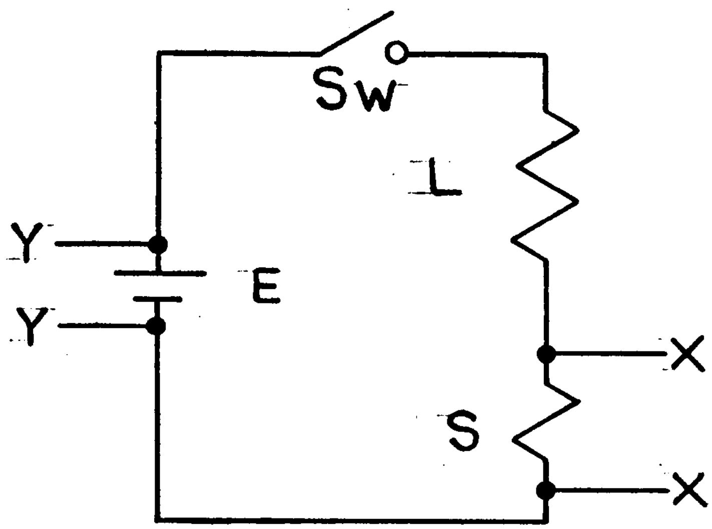
Test Procedure

Two types of test procedures were used to evaluate the current-voltage relationship. The first procedure used was described in the First Quarterly Report and consisted of the actual pulse discharge of 10 amperes for 1 second. In this case, the cell or battery under test was backed up by a high capacity (35 Ah) battery of 28 volts to sustain a constant current regardless of the voltage changes in the test cell.

The second type of test consists of a pulse discharge of 20 milliseconds duration through a fixed load. The advantage in this type of testing lies in the fact that the test cell is supplying the energy and not acting as a resistor during a forced discharge. In some cases there has been a discrepancy between the two methods. As a check of the first method, a series of pulse discharges were conducted using the second method. For a better understanding of the problems of current density and electrode area, reference electrodes were used with the fixed load pulses. The test cell was made up of two end plates (sintered on one side only) with nickel tabs spot-welded to the outside (bare) end of the cell. A 7 mil separator, of a nonwoven nylon, was placed between the plates, and the cell was clamped between two plastic blocks. The assembly was then immersed in a beaker containing a 34% solution of KOH. The nickel tabs protruded above the electrolyte and were connected to the test equipment.

Figure 1 shows a schematic diagram of a circuit for pulse discharges. The key element in the circuit is the switch (SW). In order to obtain a good contact for a short duration of time, a rotary switch was made. A diagram of this switch is shown in Figure 2. The switch is driven by a 27 RPM motor having adjustable contacts controlled by spring tension. The contact time can be set by adjusting the angle of the contact arm and the spring tension. The load bank ("L") is adjusted to vary the discharge conditions, and the shunt ("S") measures the current flowing in the circuit.

The instrumentation employed measures the current flowing through X-X. The terminal load was measured prior to discharge using a Mueller Bridge. From the above data, cell or battery voltage was calculated. Alternately, battery voltage may be measured across the terminals and the reading used to calculate current. To avoid the effects of distributed load and terminal resistance of the battery, voltage and current were not measured simultaneously.



E	=	Bipolar Battery
SW	=	Rotating Switch
L	=	Load Back
S	=	Shunt
XX	=	To Oscilloscope for Current Measurement
YY	=	To Oscilloscope for Voltage Measurement

FIGURE 1. HIGH CURRENT - LOW VOLTAGE DISCHARGE APPARATUS

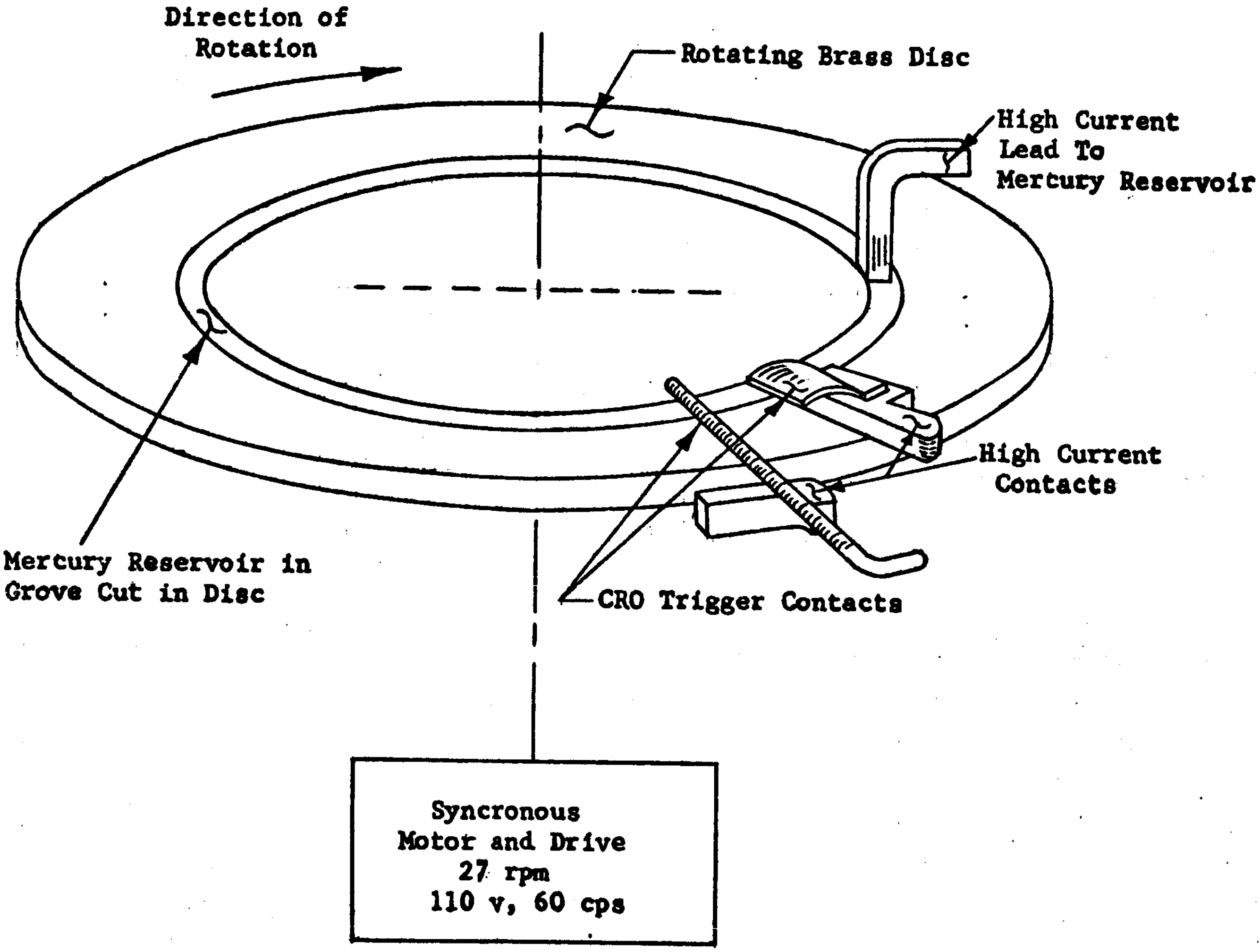


FIGURE 2. MOTOR DRIVEN SWITCH

SUMMARY OF TEST RESULTS AND CONCLUSIONS

Two end plates and four bipolar (middle) plates (1-5/8 inch dia.), 2 in^2 of sinter area, were impregnated according to the procedure set forth in the First Quarterly Report. The weight gain of the positive electrodes averaged 0.7 gram, equivalent to a theoretical capacity of 202 mAh. With a utilization coefficient of 80% at the C rate, this is equal to 162 mAh. The negative electrodes gained an average of 0.9 gram, and at a 50% utilization, this is equivalent to 169 mAh. The requirements call for 150 mAh.

After formation cycling and capacity determination, the end plates were assembled into a flooded cell. The cell was charged at 15 mA for 16 hours and pulsed at 10 amperes (forced discharge) with the voltage being recorded on a Brush Recorder Mark II. Figure 3A and Figure 3B show the results of the first and second pulses respectively. Subsequent tests gave the same results--the cell voltage fell just below 1.0 volts at the end of discharge. This is below the expected values based on the results obtained with the 4 in^2 electrodes.

The two end plate (2 in^2) electrodes were fully discharged and disassembled from the cell. They were washed to remove all KOH and dried. A nickel tab was spotwelded on each electrode and the cell reassembled. It was charged (in a beaker) at 15 mA for 16 hours and then pulsed at fixed loads using an oscilloscope and camera to record the current. The results are shown in Figure 4. Calculating the voltage drops at these currents, the resulting cell voltage was plotted on a graph, shown in Figure 5. A cell voltage of 1.28 volts is assumed at zero current, as this is the normal open circuit voltage of a nickel-cadmium cell. The results show that at 10 amperes a cell voltage of 0.98 volts can be expected. This agrees with the forced discharge results.

To gain some insight into the problem, a series of pulses were made using a Hg/HgO reference electrode. The traces are shown in Figure 6. The results show that the negative electrode is highly polarized ($\Delta V = 0.66$) at the beginning, but recovers about 0.1 volt during the first 8 milliseconds. The positive electrode only drops 0.25 volt after 1 millisecond, but continues to decrease with time at a rate greater than the negative increases, resulting in a steady decrease of voltage with time. During the same time period, shown in Figure 4b, there is very little change in current. It should be noted that these tests are at constant load, not necessarily constant current, as are the forced discharge tests. It is postulated that both electrodes suffer from activation polarization, the negative more than the positive. However, the positive electrode is greatly susceptable to concentration polarization as indicated by the increase with time. To rule out the possibility of a "state of charge" effect, three pulses were performed at 1 minute intervals without recharging. These traces are shown in Figure 6d and are almost superimposed one on another. There is no change in the rate of decay with state of charge.

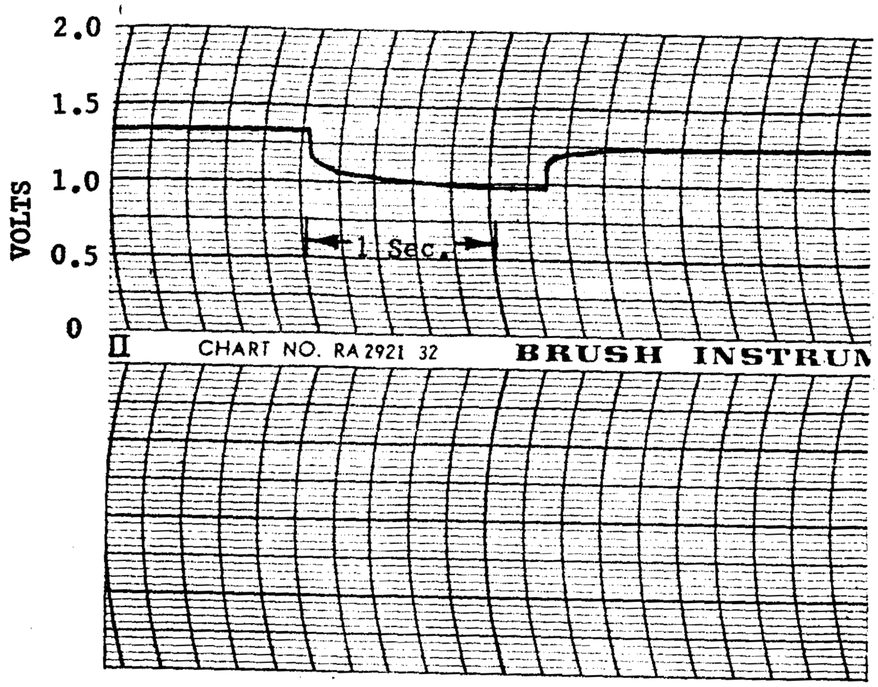


FIGURE 3a. PULSE NO. 1 10 AMPERES
PULSE DISCHARGE FOR A SINGLE BIPOLAR CELL
WITH 2.07 IN^2 ACTIVE PLATE AREA

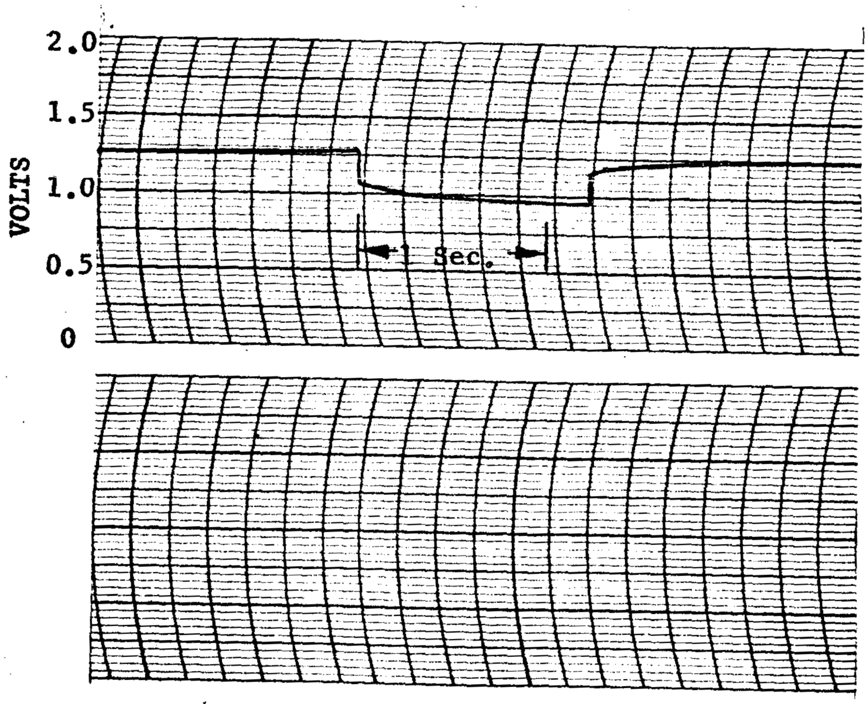


FIGURE 3b. PULSE NO. 2 10 AMPERES
PULSE DISCHARGE FOR A SINGLE BIPOLAR CELL
WITH 2.07 IN^2 ACTIVE PLATE AREA

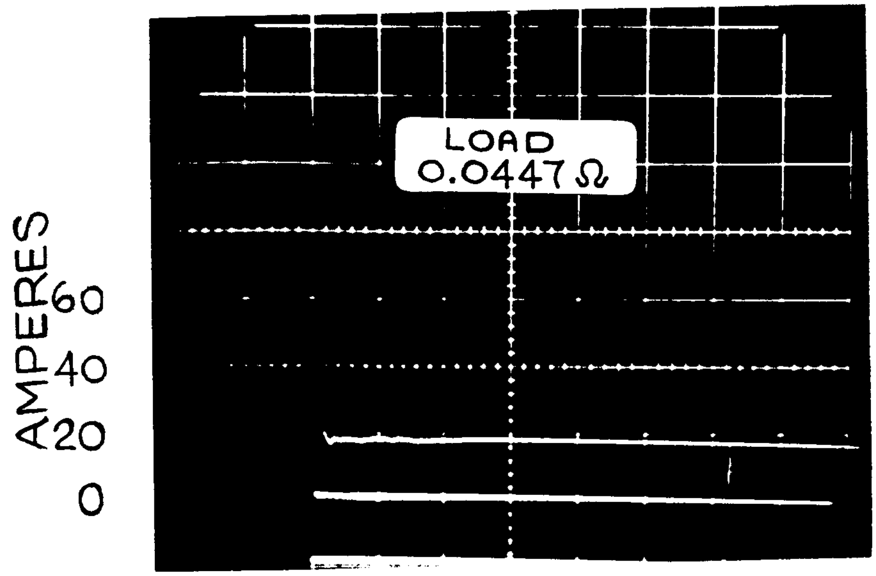


FIG. 4a

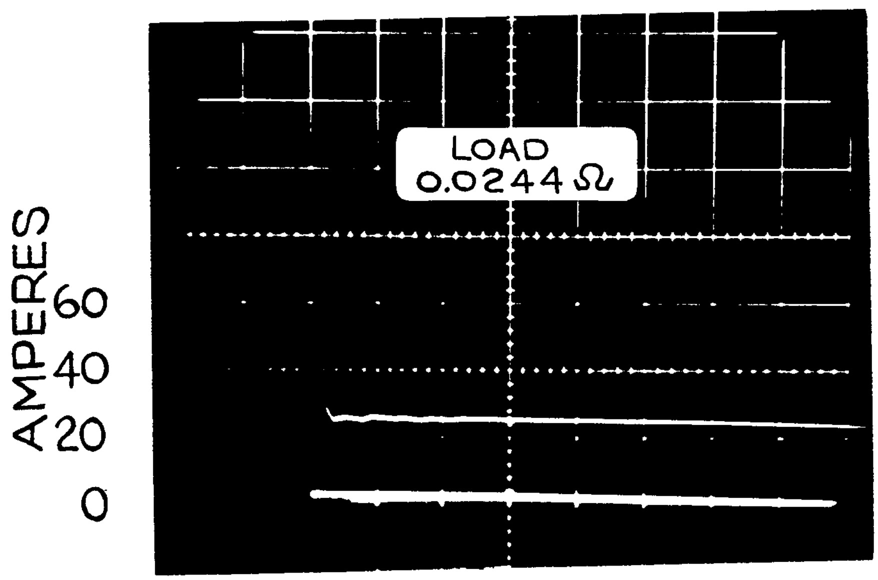


FIG. 4b

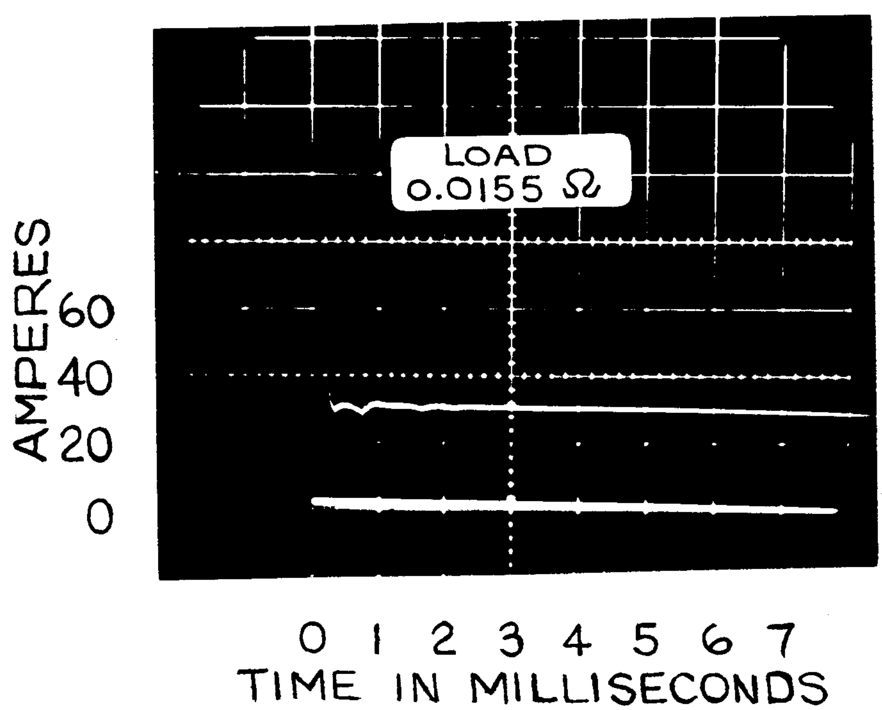


FIG. 4c

OSCILLOSCOPE TRACES of
4 SQUARE INCH BIPOLAR ELECTRODES

8-1006

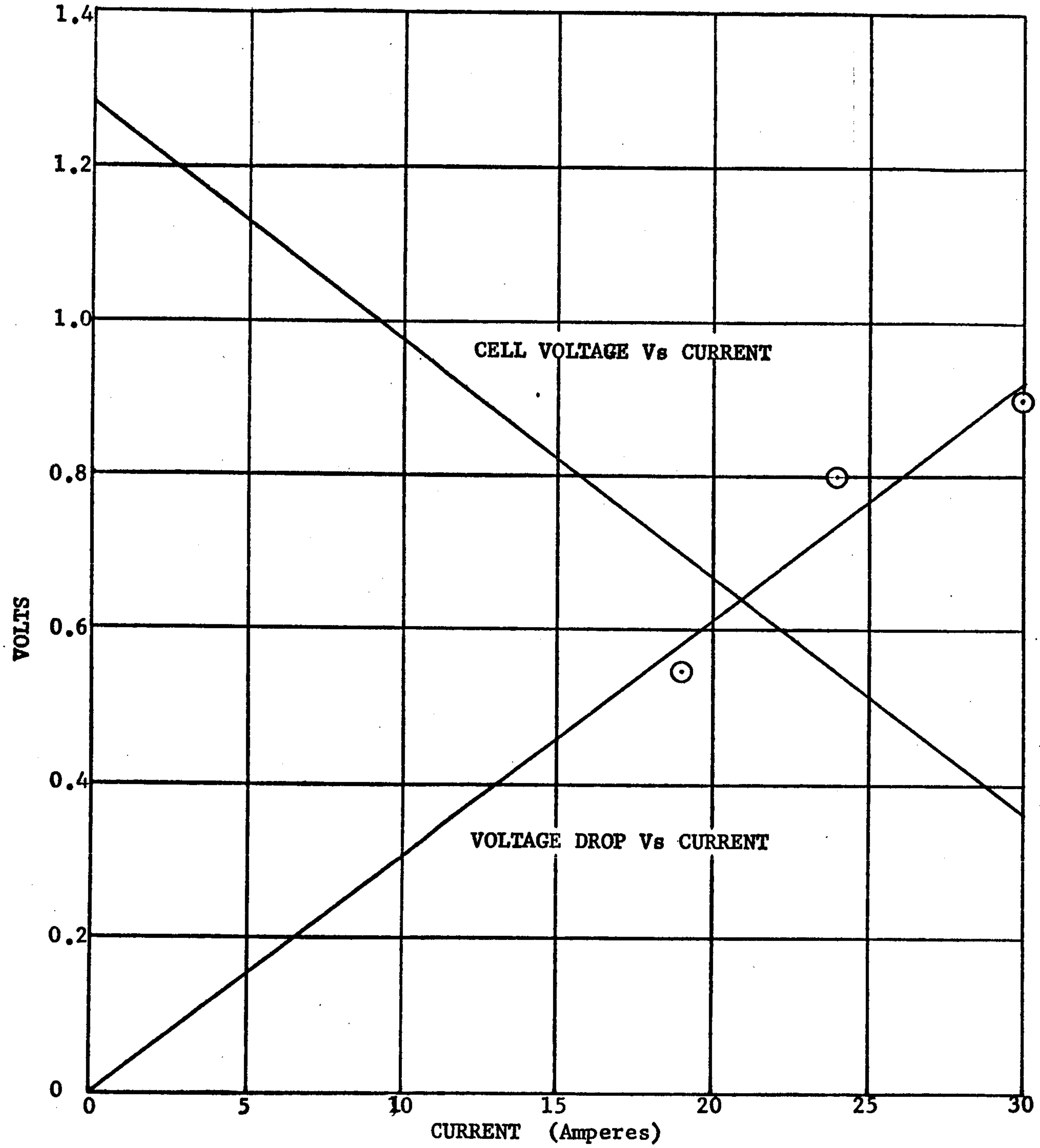


FIGURE 5. VOLTAGE-CURRENT RELATIONSHIP
SINGLE BIPOLAR CELL, FOUR IN^2 ACTIVE AREA
(From Oscilloscope Pictures)

4-1007

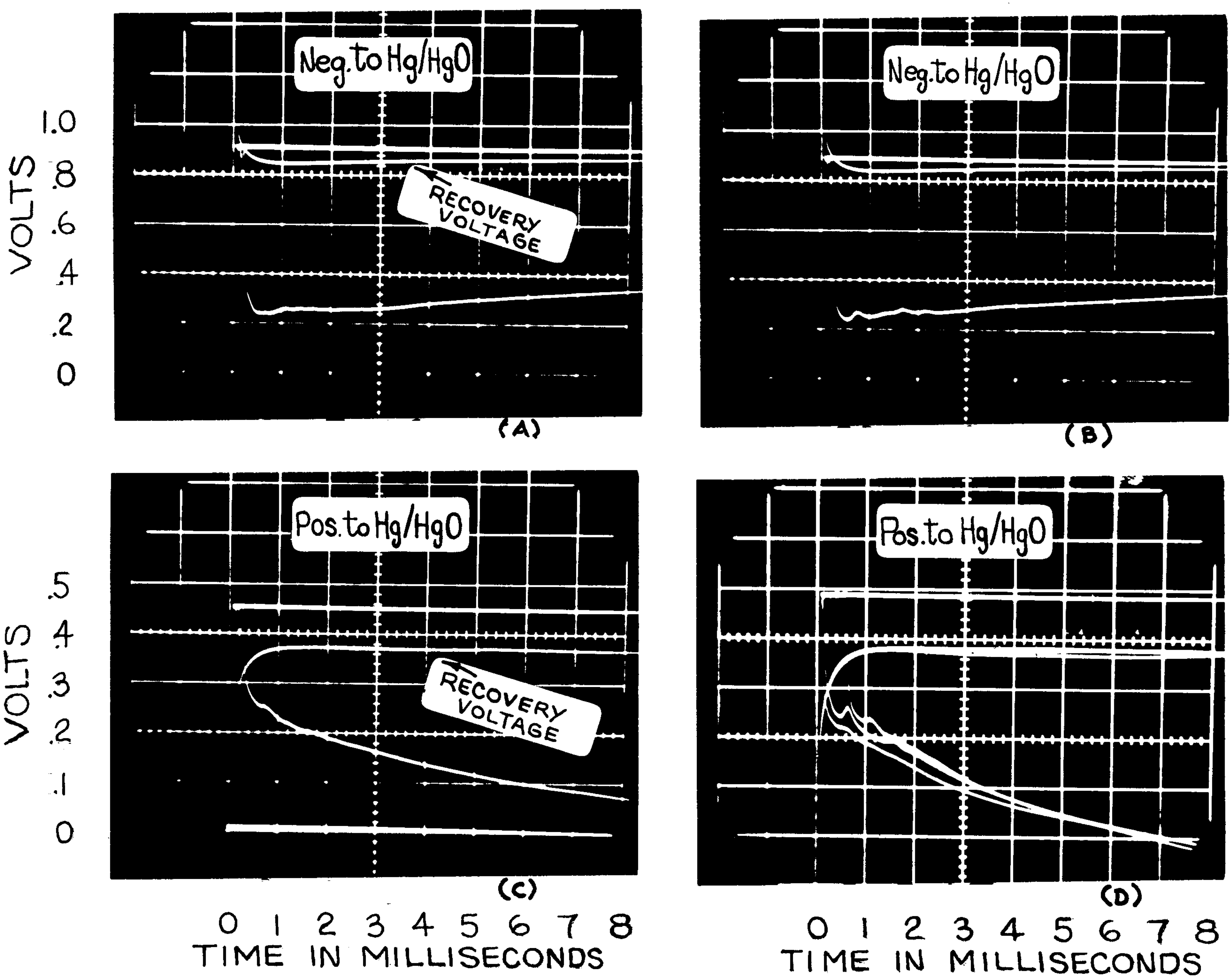


FIG. 6 ELECTRODE TO REFERENCE PULSES
ALL LOAD AT 0.0244 Ω, I ~ 24 AMPERES

8-1093

The next three larger cell sizes were tested using only the forced discharge method at constant current. The results are shown in Figures 7, 8, and 9. These indicate that the 2.76 in^2 (1-7/8 dia.) area electrodes are minimal for one pulse. There is some increase in voltage as the area is increased from 2.07 to 2.40, and again to 2.76. However, there is a larger jump in performance data for the 3.14 in^2 area electrodes shown in Figure 9. There appears to be a discontinuity since the area increase in each case is approximately the same ratio of 1.15:1. The capacities to area of electrode in each case were kept approximately equal for all 4 sizes.

Battery Discharge

A five cell battery was assembled from the 1-5/8 diameter electrodes (2 in^2), with a separator of 7 mil non-woven nylon. Sealing the cells was found to be difficult. For this test, therefore, the battery was assembled in a different manner. The electrode flanges were coated with a sealant (of liquid neoprene) and "O" rings placed between each bipolar plate. The battery was assembled by stacking the plates on top of each other as follows. The electrolyte was added to the sinter, then the separator was placed over the sinter and more electrolyte added. The next bipolar plate was placed on top and the procedure repeated until the end plate was assembled. The battery was clamped between blocks of 1/2 inch thick lucite and fastened with machine screws around the periphery. A photograph of the battery is shown in Figure 10.

The battery was charged at 10 mA for 27-1/2 hours, with individual cells being monitored. Figure 11 shows the average cell voltage and the spread in cell voltages during the charge. The battery was placed on open circuit with all cell voltages monitored at 1.38 volts. It was then discharged at 100 mA as shown in the right hand side of Figure 11. This figure gives average cell voltages including voltage spread of each cell (battery voltage is five times the average cell voltage). The center cell fell to 0.18 volt after 55 minutes of discharge, although all other cells were at 1.20 volts. After the discharge, the battery was disassembled, the electrodes washed and dried, and reassembled changing the position of the bipolar electrodes. The resultant voltage readings were the same. The center electrode failed first, as before.

A careful study of the situation revealed that the center cell was not sealing and, therefore, losing electrolyte during overcharge; due to the compression method used, the gas pressure during overcharge was forcing electrolyte out. The cell was reassembled using Kel-F grease on the "O" rings. The cell was placed on charge and discharged at the 100 mA rate. All cell voltages were uniform with no visible leaks from the cells. The battery was pulsed at 10 amperes and the voltage recorded on the Brush Recorder Mark II. The results obtained (Fig. 12) are almost identical with those shown in Figure 3. The correlation between the 5 cell battery and the single cell of Figure 3 was made by dividing the battery voltage by 5.

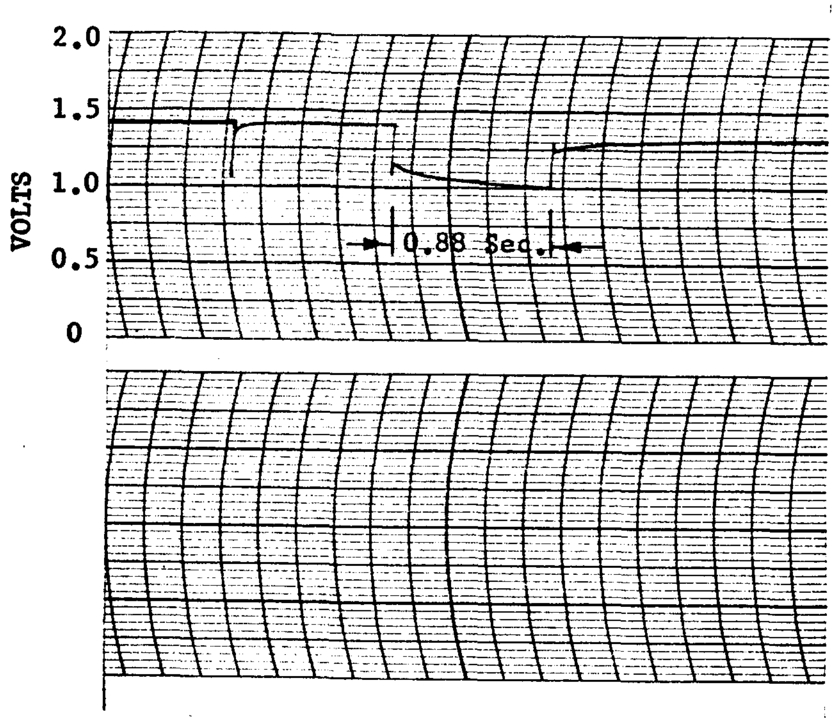


FIGURE 7a. PULSE #1 CURRENT 11.0 AMPERES
PULSE DISCHARGE OF A SINGLE BIPOLAR CELL
WITH 2.40 IN^2 ACTIVE PLATE AREA

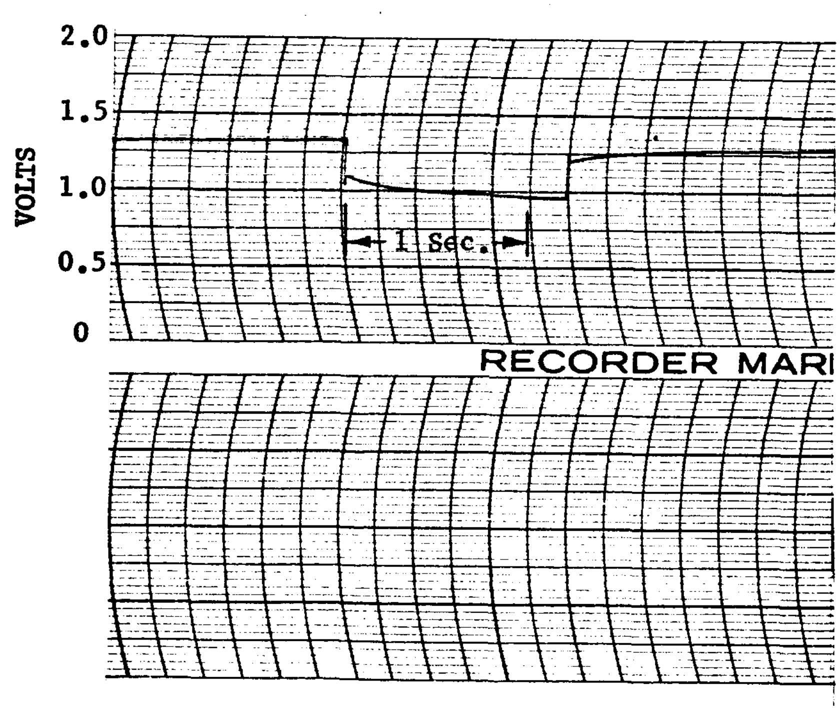


FIGURE 7b. PULSE #2 CURRENT 11.0 AMPERES
PULSE DISCHARGE OF A SINGLE BIPOLAR CELL
WITH 2.40 IN^2 ACTIVE PLATE AREA

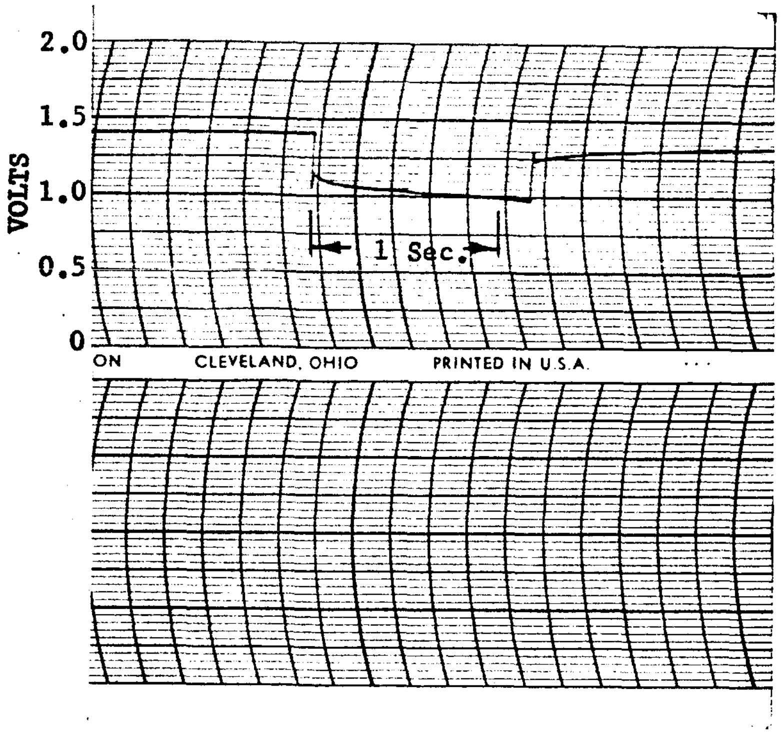


FIGURE 8a. PULSE #1 CURRENT 10.5 AMPERES
PULSE DISCHARGE OF A SINGLE BIPOLAR CELL
WITH 2.76 IN^2 ACTIVE PLATE AREA

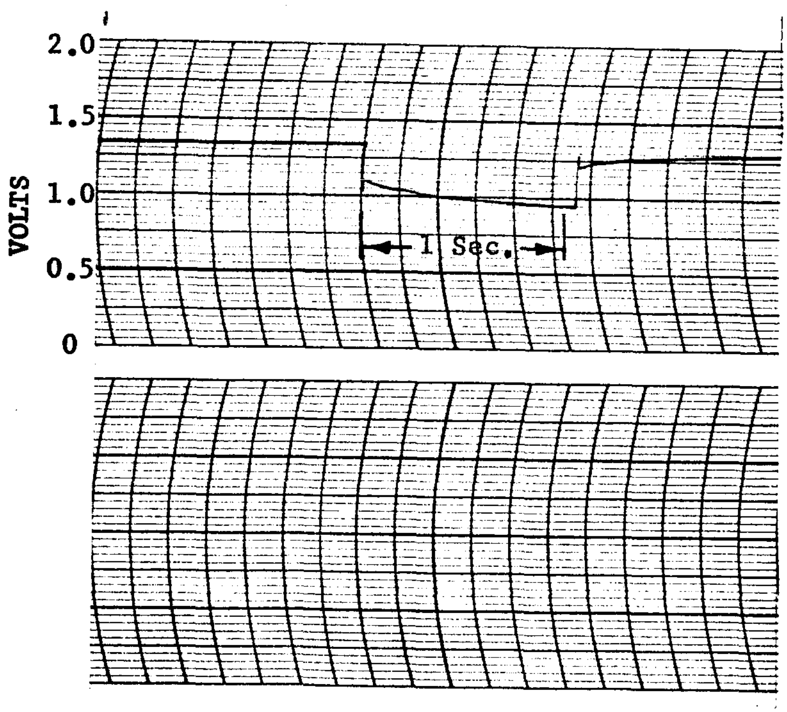


FIGURE 8b. PULSE #2 CURRENT 10.5 AMPERES
PULSE DISCHARGE OF A SINGLE BIPOLAR CELL
WITH 2.76 IN^2 ACTIVE PLATE AREA

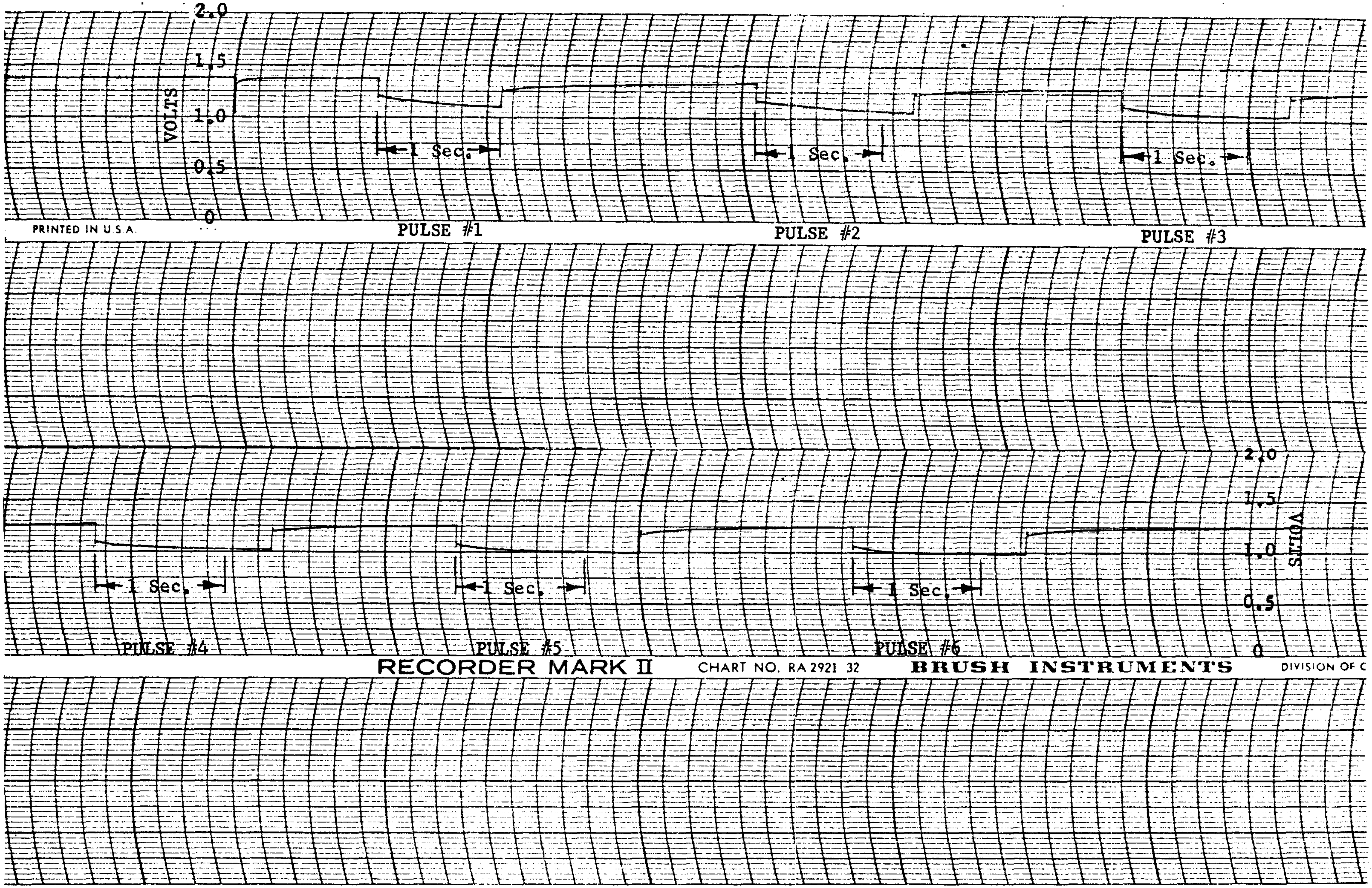


FIGURE 9. PULSE DISCHARGE FOR A SINGLE BIPOLAR CELL WITH 3.14 IN^2 ACTIVE PLATE AREA
CURRENT 10.5 AMPERES

4-1096

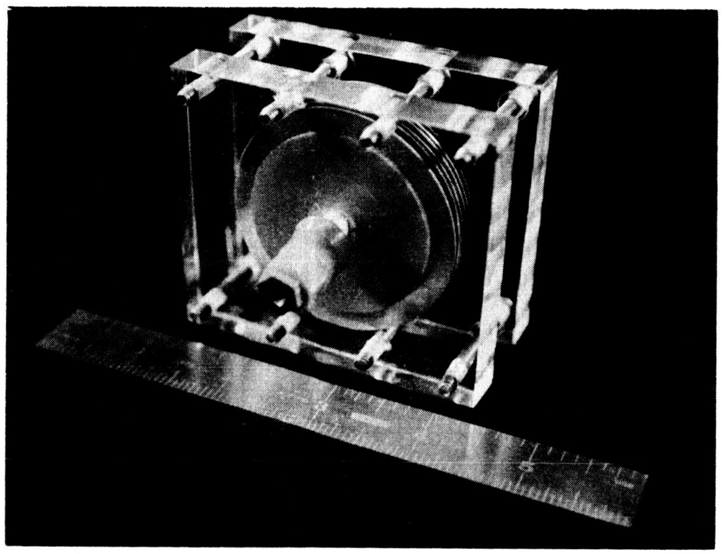


FIGURE 10. FIVE CELL BATTERY WITH 2 IN^2 OF SINTER AREA

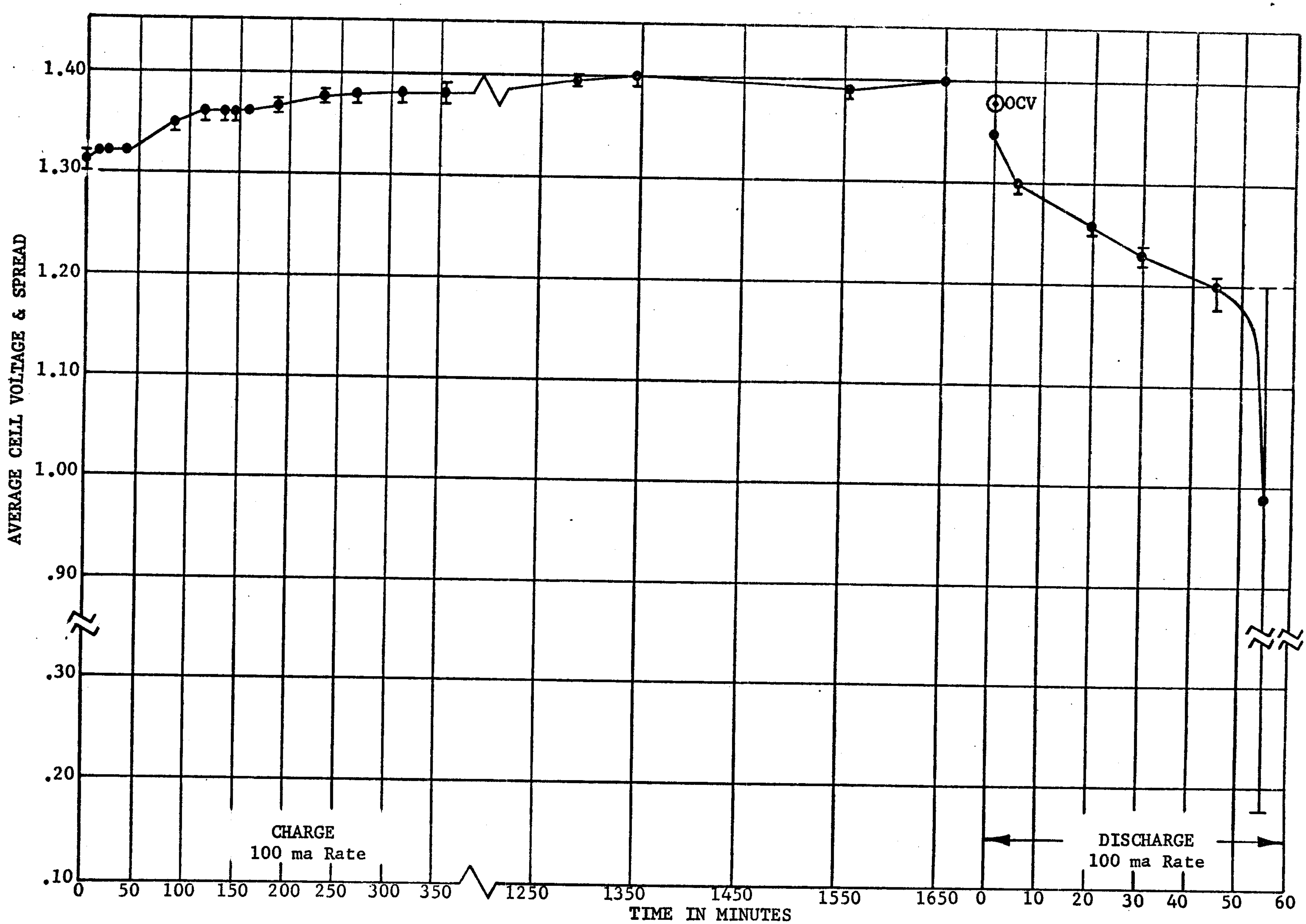


FIGURE 11. CHARGE & DISCHARGE OF A 5 CELL BATTERY SHOWING AVERAGE CELL VOLTAGE & SPREAD

4-1098

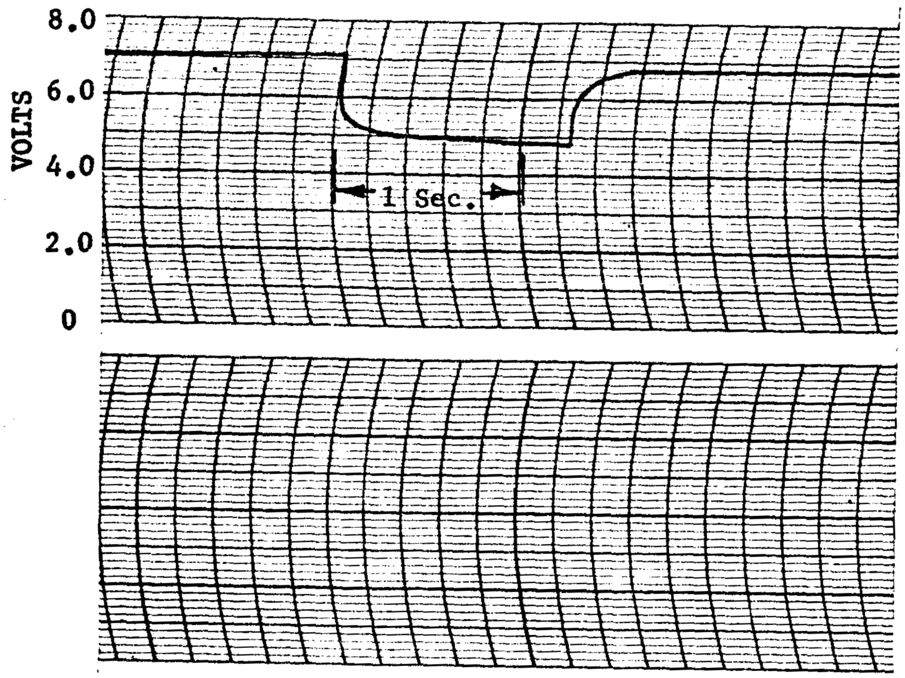


FIGURE 12a. PULSE NO. 1 CURRENT 10 AMPERES
PULSE DISCHARGE FOR A 5 CELL BIPOLAR BATTERY
WITH ACTIVE PLATE AREA OF 2.07 IN^2/ PLATE

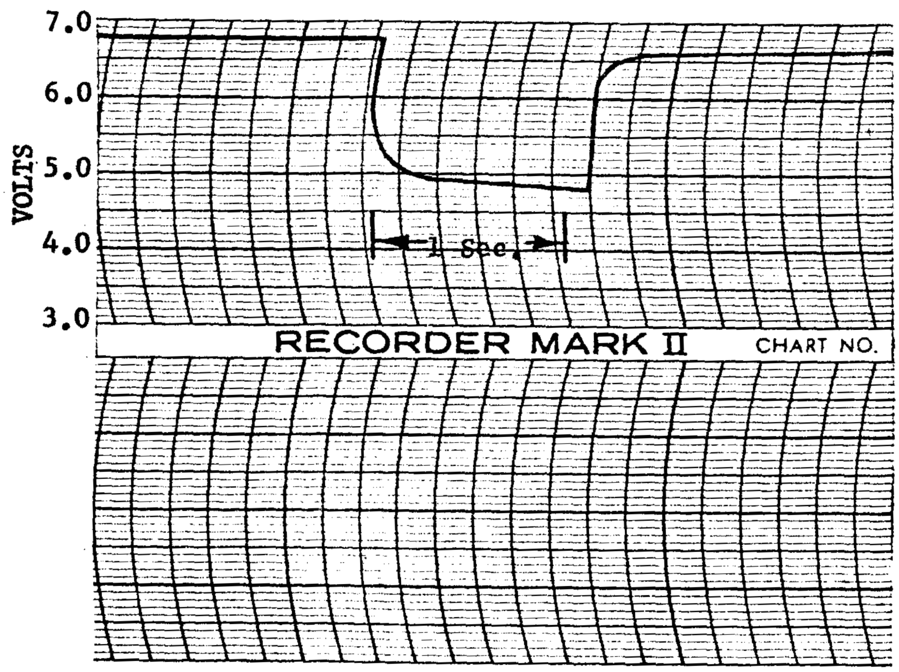


FIGURE 12b. PULSE NO. 2 CURRENT 10 AMPERES
PULSE DISCHARGE FOR A 5 CELL BIPOLAR BATTERY
WITH ACTIVE PLATE AREA OF 2.07 IN^2 /PLATE

4-1099

DISCUSSION OF RESULTS AND CONCLUSIONS

From the data obtained to date, it appears that the minimal plate size most likely to meet the discharge requirements has the 1-7/8" diameter sinter (2.76 in^2).

The plate has a capacity of approximately 200 mAh, at the 10 hour rate. The reduced voltage at the 10 ampere pulse discharge is primarily due to concentration polarization at the positive electrode, as evidenced by the oscilloscope traces.

Additional discharges will be conducted to determine the behavior of the 1-7/8 inch diameter electrodes in a five cell battery. Should the voltage fail to meet the 5 volts minimum, the plate with the 2 inch diameter will be used.

From the tests conducted with the 5 cell batteries, it appears that sealing will be a major problem in battery construction. It is presently contemplated to seal the individual cells using neoprene gaskets or "O" rings, then enveloping the 5 cell stack in an encapsulating compound.

Threaded terminals will be metallurgically bonded to the center of each end plate, with sufficient length protruding beyond the compound.

The progress of this work and the test results will be discussed in the next report.

WORK PLANNED

TASK II

1. Evaluate the effects of concentration and activation polarization and determine minimum plate area for a five cell squib battery.

2. Test and evaluate various separators.

3. Determine the amount of electrolyte and required compression on the wet separator.

4. Establish method for introducing electrolyte into the cell.

5. Test materials and techniques for sealing cells.

6. Evaluate potting compounds and methods for encapsulating five cell batteries.

TASK III

1. Fabricate, test, and evaluate performance of 5 cell battery.

2. Determine charging rates and overcharge capabilities.

3. Build 10 batteries.

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Department of the Army

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Attn: Dr. P. Joyner

American University
Mass. & Nebraska Avenues, N.W.
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Attn: Dr. R. T. Foley,
Chemistry Department

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Raleigh, North Carolina 27604
Attn: A. Chreitzberg

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19 West College Avenue
Yardley, Pennsylvania 19068
Attn: Dr. R. A. Schaefer/W. S. Herbert

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Menlo Park, California 94025
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Pasadena, California 91107
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Hartford, Connecticut 06101
Attn: Dr. W. P. Cadogan

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Newark, New Jersey 07105
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Dr. Arthur Fleischer
466 South Center Street
Orange, New Jersey 07050

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Schenectady, New York, 12301
Attn: Dr. R. C. Osthoff/Dr. W. Carson
Advanced Technology Lab.

General Electric Company
Missile & Space Division
Spacecraft Department
P. O. Box 8555
Philadelphia, Pennsylvania 19101
Attn: E. W. Kipp, Room T-2513

General Electric Company
Battery Products Section
P. O. Box 114
Gainsville, Florida 32601

General Electric Company
Research Laboratories
Schenectady, New York 12301
Attn: Dr. H. Liebhafsky

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6767 Hollister Street
Santa Barbara, California 93105
Attn: Dr. J.S. Smatko/Dr. C. R. Russell

Globe-Union, Incorporated
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Milwaukee, Wisconsin 53201

Gould-National Batteries, Inc.
Engineering and Research Center
2630 University Avenue, S.E.
Minneapolis, Minnesota 55418
Attn: J. F. Donahue

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Alkaline Battery Division
212 Durham Avenue
Metuchen, New Jersey 08840
Attn: Dr. Robert Shair

Hughes Aircraft Corporation
Centinda Ave. & Teale St.
Culver City, California 90230
Attn: T. V. Carvey

Hughes Aircraft Corporation
Bldg. 366, M.S. 524
El Segundo, California 90245
Attn: R. B. Robinson

Hughes Research Laboratories Corp.
3011 Malibu Canyon Rd.
Malibu, California 90265

IIT Research Institute
10 West 35th Street
Chicago, Illinois 60616
Attn: Dr. H. T. Francis

Institute for Defense Analyses
R&E Support Division
400 Army-Navy Drive
Arlington, Virginia 22202
Attn: Mr. R. Hamilton/Dr. Szego

Idaho State University
Department of Chemistry
Pocatello, Idaho 83201
Attn: Dr. G. Myron Arcand

Institute of Gas Technology
State and 34th Street
Chicago, Illinois 60616
Attn: B. S. Baker

Johns Hopkins University
Applied Physics Laboratory
8621 Georgia Avenue
Silver Spring, Maryland 20910
Attn: Richard Cole

Johns-Manville R&E Center
P.O. Box 159
Manville, New Jersey 08835
Attn: J. S. Parkinson

Leesona Moos Laboratories
Lake Success Park, Community Drive
Great Neck, New York 11021
Attn: Dr. H. Oswin

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Attn: Dr. E. M. Jost

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425 Volker Boulevard
Kansas City, Missouri 64110
Attn: Dr. B. W. Beadle

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Everett, Massachusetts 02149
Attn: Dr. J. O. Smith

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Rocketdyne Division
6633 Canoga Avenue
Canoga Park, California 91303
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12214 Lakewood Boulevard
Downey, California 90241
Attn: Burton M. Otzinger

Dr. John Owen
P. O. Box 87
Bloomfield, New Jersey 07003

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University of Pennsylvania
Moore School Building
200 South 33rd Street
Philadelphia, Pennsylvania 19104

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Chatsworth, California 91311
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Long Island City, New York 11101

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Astro Division
Hightstown, New Jersey 08520
Attn: Seymour Winkler

Radio Corporation of American
P. O. Box 800
Princeton, New Jersey 08540
Attn: I. Schulman

Radio Corporation of America
Somerville, New Jersey 08873
Attn: Dr. H. S. Lozier

Southwest Research Institute
8500 Culebra Road
San Antonio, Texas 78206
Attn: Dr. Jan Al

Sonotone Corporation
Saw Mill River Road
Elmsford, New York 10523
Attn: A. Mundel

Texas Instruments, Inc.
13500 North Central Expressway
Dallas, Texas 75222
Attn: Dr. Isaac Trachtenberg

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McGraw Edison Company
Watchung Avenue
West Orange, New Jersey 07052
Attn: Dr. P. F. Grieger

TRW Systems, Inc.
One Space Park
Redondo Beach, California 90278
Attn: Dr. A. Krausz, Bldg. 60, Rm 929

TRW Systems Inc.
One Space Park
Redondo Beach, California 90278
Attn: Dr. Herbert P. Silverman

TRW, Inc.
23555 Euclid Avenue
Cleveland, Ohio 44117
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Berkeley, California 94720
Attn: Dr. C. W. Tobias

University of Pennsylvania
Electrochemistry Laboratory
Philadelphia, Pennsylvania 19104

Western Electric Company
Suite 802, RCA Bldg.
Washington, D.C. 20006
Attn: R. T. Fiske

Westinghouse Electric Corporation
Research & Development Center
Churchill Borough
Pittsburgh, Pennsylvania 15235

Whittaker Corporation
P. O. Box 337
Newbury Park, California 91320
Attn: Mr. John Rhyne

Whittaker Corporation
3850 Olive Street
Denver, Colorado 80237
Attn: Borch Wendir

Yardney Electric Corporation
40-50 Leonard Street
New York, New York 10013
Attn: Dr. Geo. Dalin