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ENGINEERING REPORT



DIVISION OF GENERAL MOTORS, ANDERSON, INDIANA

SILVER-ZINC SECONDARY BATTERY INVESTIGATION

Fourth Quarterly Technical Progress Report

Covering the Period

1 April 1963 to 1 July 1963

Dated

2 July 1963

Contract Nr. AF 33(657)-8943

Project Nr. 8173

Task Nr. 817304-1

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FOREWORD

This report was prepared by Delco-Remy Division of General Motors Corporation, Anderson, Indiana, on Air Force Contract Nr. AF 33(657)-8943, under Task Nr. 817304-1 of Project Nr. 8173, "Investigation of Silver-Zinc Battery". The work was administered under the direction of Flight Accessories Laboratory, Wright Air Development Division; Mr. J. E. Cooper was task engineer for the laboratory.

The assistance of Dr. T. P. Dirkse, Professor of Chemistry, Calvin College, Grand Rapids, Michigan, as consultant on this project is greatly appreciated.

This report is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

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ABSTRACT

Three sealed 25 a.h. cells constructed with positive plates to which 1% palladium was added by impregnation with a palladium salt have completed 2900 cycles of operation at 80°F. Cycling is continuing at 25% depth of discharge which is 50% of the monovalent capacity.

Six additional sealed 25 a.h. cells containing positive plates made with 1% palladium silver powder supplied by a vendor have reached 1400 cycles at 80°F. Cycling is continuing at 25% depth of discharge which is 50% of the monovalent capacity.

Hydrogen evolution studies at 75°F have been completed. The results indicate that 4% HgO addition to the negative plate in 45% KOH results in the least amount of gas production in a 30-day period.

Sealed 25 a.h. cells containing 2% and 4% HgO additions in the negative plate material have completed 833 and 620 cycles respectively during operation at 25% depth of discharge at 80°F. Two 25 a.h. cells, one containing regular silver plates and the other containing 1% palladium silver plates, were cycled at 15°F at 25% depth of discharge. The zinc negative plate is limiting cycle life at this temperature.

Four sealed 18 cell, 37 a.h. batteries have been constructed and placed on cycle life test.

I. Introduction

This report covers the last three month's work of the twelve month program. Specific items have been investigated throughout the twelve month period to provide design criteria for long life, light weight, sealed secondary batteries for aerospace applications. Most of these items have been completed and are recorded in the last three Quarterly Reports. The remaining items in the program are:

- A. Palladium additions to the silver plate
- B. H₂ evolution studies on the negative plate

The results of these investigations have been incorporated in four batteries which have been placed on cycle life test and which will be discussed in this report. All work has been directed at meeting the following specifications:

5000 continuous cycles at 27 ± 1.5 volts while operating in the temperature range of 0°F to 100°F in vacuum of 10^{-9} mm Hg and in a zero gravity environment. A cycle is defined as 35 minutes discharge at 20 amperes followed by 85 minutes recharge.

The two-hour cycle as defined above is used exclusively in this program, except for initial conditioning deep discharges.

II. Factual Data

A. Palladium Additions to the Silver Plate

Three sealed silver-zinc cells of 25 a.h. nominal capacity were constructed with silver plates impregnated with 1% palladium and partially formed dry - charged negatives by methods described in the First and Second Quarterly Reports of this contract.

These cells are still cycling and thus far have completed 2900 cycles at 80°F operating at 25% depth of discharge. Figure 1 shows the average end of charge, initial discharge and end of discharge voltages for three cells.

Six additional sealed cells of 25 a.h. nominal capacity were constructed with positives containing 1% palladium coated about the particles and activated in 40% KOH. These cells are cycling at 25% depth of discharge and to date have reached 1400 cycles.

Figure 2 shows the average end of charge, initial discharge and end of discharge voltages of three cells cycling at constant potential charge.

Figure 3 shows the average end of charge, initial discharge and end of discharge voltages of three cells cycling at constant current charge.

Two cells, one containing positives with 1% palladium coated particles and the other with regular positive plates, were cycled at 15°F at 25% depth of discharge. Third electrode voltages were recorded. The cell containing regular positives failed at 9 cycles, while the cell containing 1% palladium coated particles failed around 138 cycles. The cause of failure in the standard cell was the inability of the silver positive plate to accept charge in the 85 minute period before going into the gassing voltage levels, allowing the negative plate to limit the capacity. The cause of failure in the 1% palladium cell was due to the negative plate limiting the cell capacity.

Figure 4 shows the end of charge and discharge voltage of the cells and the respective electrode voltages.

B. Hydrogen Evolution Studies on the Negative Plate

Figure 5 shows the total amount of hydrogen evolved over a 30-day period

for the mercury additions in the indicated electrolytes at 75°F. The complete data for hydrogen evolution at 125°F, 100°F, and 75°F with various mercuric oxide percentages in the negative plate and in various electrolyte concentrations will be furnished in the Final Report. This study is now complete.

In line with some conclusions mentioned in the Second Quarterly Report concerning 2% and 4% mercuric oxide additions in the negative material, 25 a.h. sealed cells activated in 40% KOH have completed cycle life tests at 80°F and the results are shown in Figure 6. The 4% mercuric oxide addition gives the least amount of cycles.

The following 18 cell, 37 a.h. batteries have been constructed, activated in 45% KOH, and placed on cycle life test. A battery is considered a failure when three cells fail, but cycling is continued until a total of 9 cells fail. No failure analysis have been conducted as yet, but this information will be included in the Final Report of this contract.

Battery #1 containing 2% mercuric oxide in the negative active material failed after 440 cycles. Figure 7 shows the initial charge and discharge curves of the battery. Figure 8 shows the end of discharge voltages at indicated cycles and the failing cells. This battery was cycled at a 25% depth of discharge.

Battery #2 containing 4% mercuric oxide in the negative active material failed after 512 cycles. Figure 9 shows the initial charge and discharge curves of the battery. Figure 10 shows the end of discharge voltages at indicated cycles and the failing cells. This battery was cycled at 25% depth of discharge.

Battery #3 containing 1% palladium in the positive plate and 2% mercuric oxide in the negative active material has reached 500 cycles, with one cell that failed at 312 cycles. Figure 11 shows the initial charge and discharge curves of the battery. Figure 12 shows the end of discharge voltages at indicated cycles and the failing cell. This battery is cycling at 25% depth of discharge.

Battery #4 containing 1% palladium in the positive plate and 2% mercuric

oxide in the negative active material failed at 268 cycles. This battery was cycled at 40% depth of discharge. Figure 13 shows the initial charge and discharge curves of the battery. Figure 14 shows the end of discharge voltages at indicated cycles and the failing cells.

III. Summary

The use of palladium in the positive plate appears to increase the cycle life of silver zinc cells when cycled at 25% depth of discharge. The operation on the monovalent silver level during charge and discharge appears to be exhausted anywhere from 400 to 1000 cycles. Additional cells are under construction with 2% palladium in the positive plate to determine if operation on the monovalent voltage level can be extended in cycle life and if higher depths of discharges (40%) can be accomplished for at least 500 cycles.

IV. Distribution List

Cys Activities at WPAFB

1 ASAPT
1 ASAPRL (Library)
1 ASEP
2 ASRMA
1 ASRMOO
5 ASRMFP-2

Other Dept of Defense Activities

Army

1 Dr. Adolf Fischback (Chairman)
Special Purpose Battery Branch
Power Sources Division
U.S. Army Signal R&D Laboratory
ATTN: SIGRA/SL-PSS
Fort Monmouth, New Jersey

1 OASD (R&E), Rm 3E-1065
The Pentagon
ATTN: Technical Library
Washington 25, D. C.

1 Commanding Officer
Diamond Ordnance Fuze Laboratory
ATTN: Library Rm 211, Bldg. 92
Washington 25, D. C.

1 U.S. Army Signal R&D Laboratory
ATTN: Mr. P. Rappaport
Fort Monmouth, New Jersey

1 Mr. E. F. Cogswell
Electrical Power Branch
Engineering R&D Laboratory
Fort Belvoir, Virginia

Navy

1 Mr. P. Cole
Naval Ordnance Laboratory
(Code WB)
Silver Spring, Maryland

Cys Navy

1 Mr. W. H. Fox
Office of Naval Research
(Code 425)
Department of the Navy
Washington 25, D. C.

Air Force

1 AFCRL (CRZK, Mr. Doherty)
L G Hanscom Fld
Bedford, Mass.

1 SSD (SSTRE, Maj. Iller)
AF Unit Post Office
Los Angeles 45, Calif.

10 ASTIA
Arlington Hall Stn
Arlington 12, Va.

National Aeronautics and Space

Administration

2 NASA
Lewis Research Center
ATTN: Dr. Louis Rosenblum
2100 Brookpark Road
Cleveland 35, Ohio

1 NASA
Marshall Space Flight Center
ATTN: M-G & C-EC,
Mr. E. H. Cagle
Bldg. 4487 - Guidance & Control
Huntsville, Alabama

Non Government

1 Calvin College
Department of Chemistry
ATTN: T. P. Dirkse
Grand Rapids, Michigan

1 Power Sources Division
Telecomputing Corporation
ATTN: J. Rhyne
3850 Olive Street
Denver, Colorado

IV. Distribution List (Continued)

Cys Non-Government (Contd)

- | | |
|---|--|
| 1 | Gulton Industries, Inc.
Alkaline Battery Division
ATTN: R. C. Shair
212 Durham Avenue
Metuchen, New Jersey |
| 1 | Dr. Arthur Fleischer, Consultant
466 South Center Street
Orange, New Jersey |
| 1 | P. R. Mallory & Company
ATTN: Mr. R. E. Ralston
3029 E. Washington Street
Indianapolis 6, Indiana |
| 1 | Lockheed Missiles & Space Company
ATTN: J. E. Chilton
Sunnyvale, California |

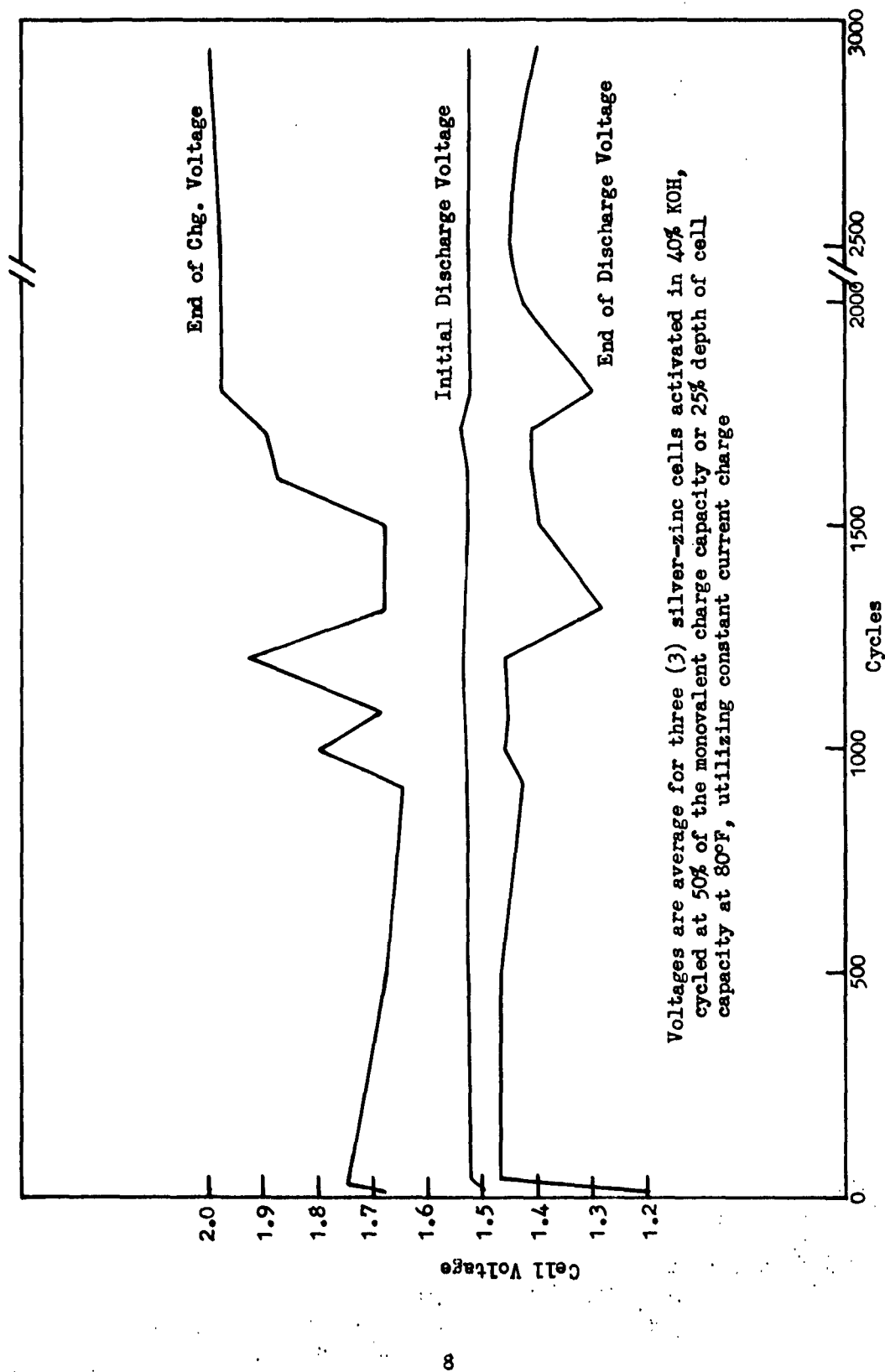


FIGURE 1 Cycle Voltage Data of 1% Palladium Impregnated Silver Plates

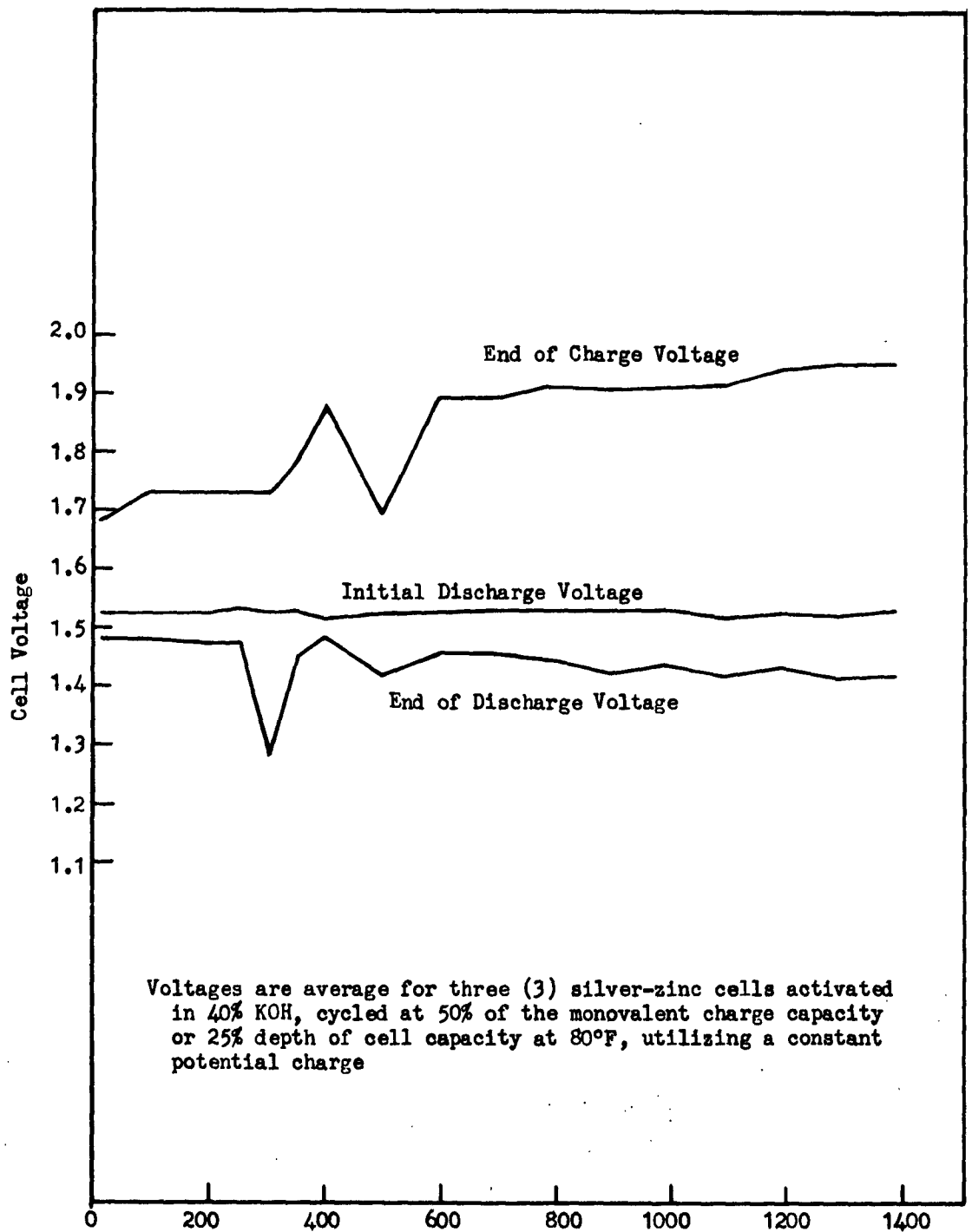


FIGURE 2 Cycle Voltage Data of 1% Palladium Coated Silver Particles

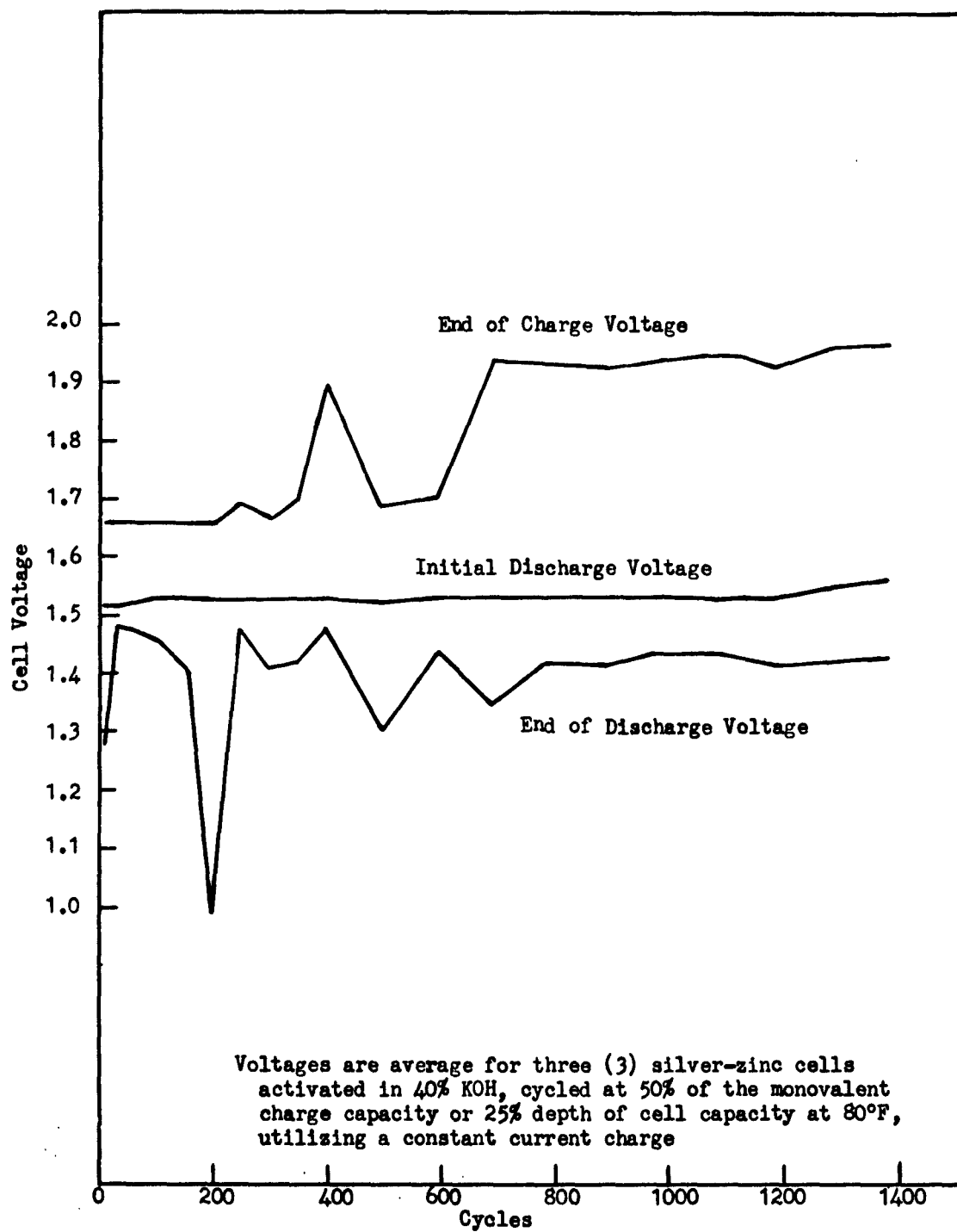


FIGURE 3 Cycle Voltage Data of 1% Palladium Coated Silver Particles

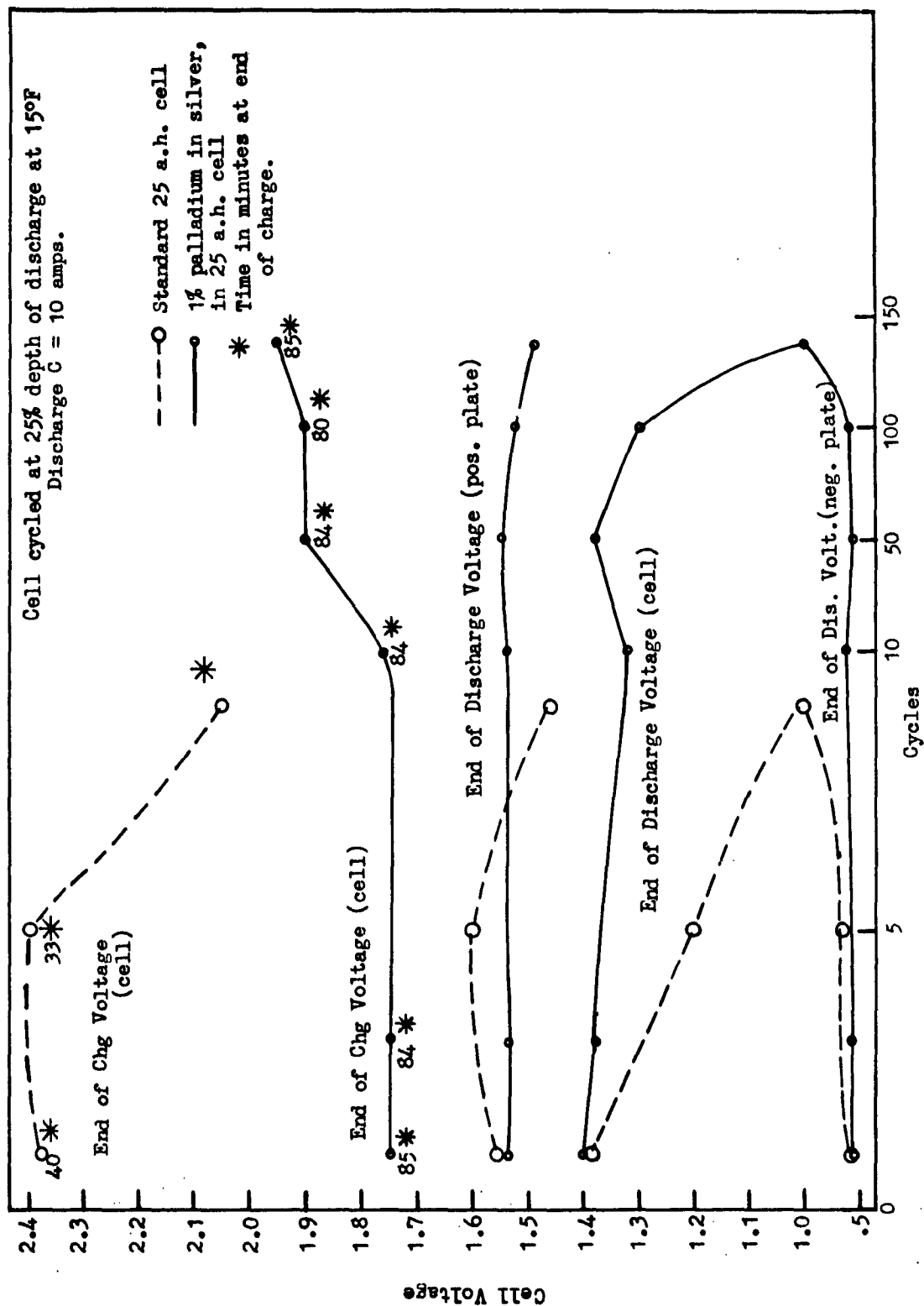


FIGURE 4 Cold Temperature Cycle Voltage Data

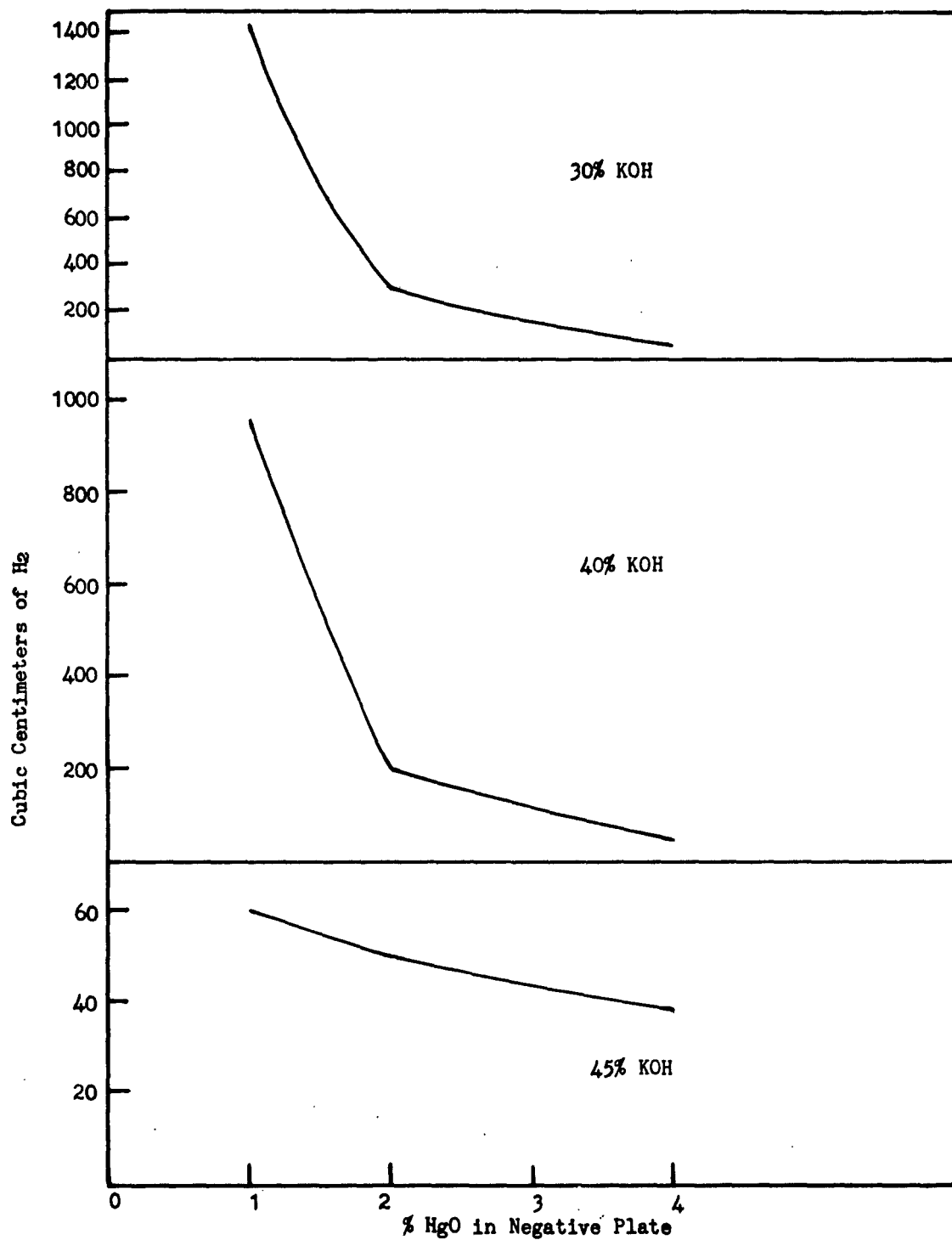


FIGURE 5 Amount of H₂ Evolved in 30 Days at 25°C
in Indicated Electrolyte

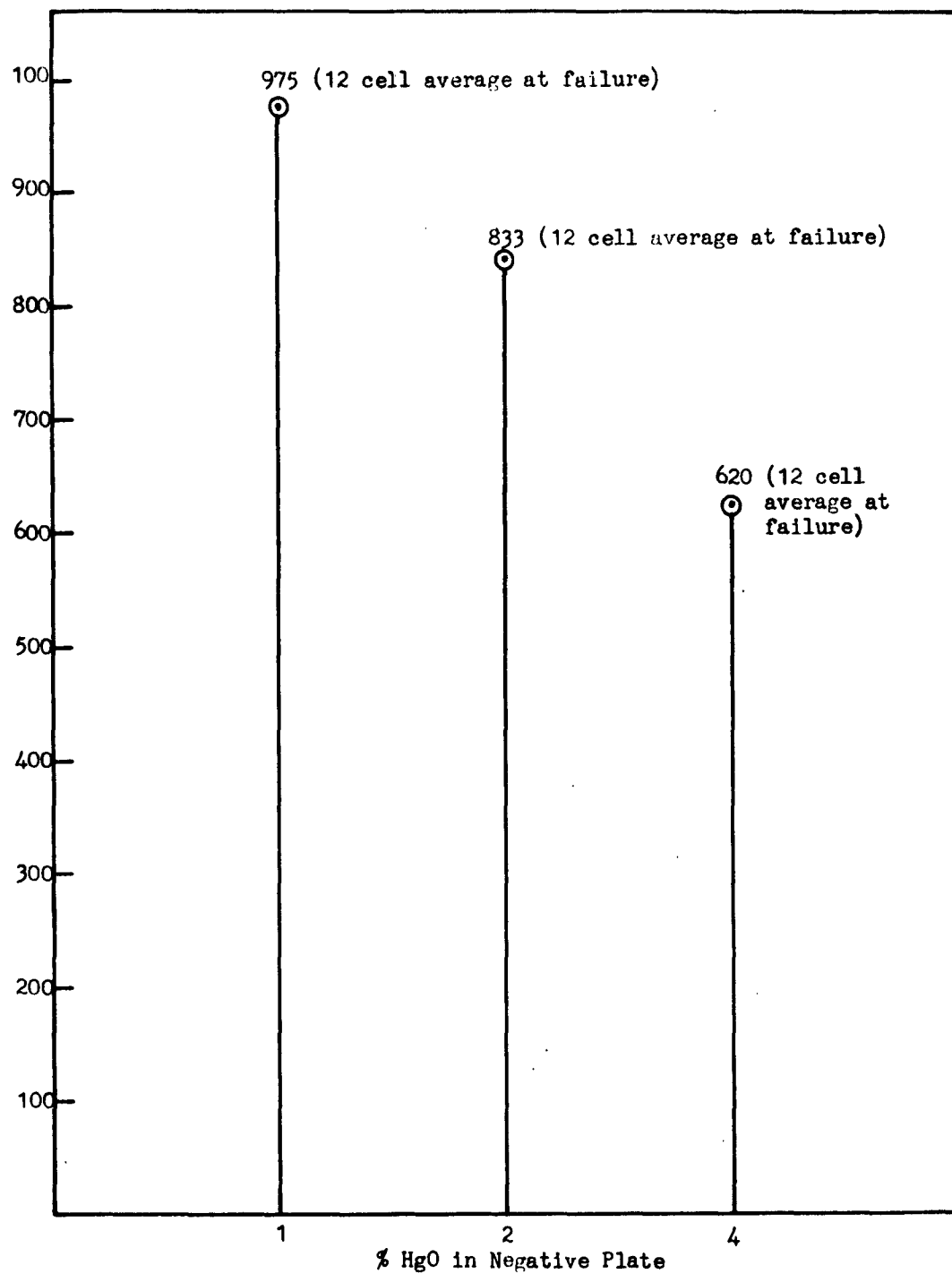


FIGURE 6 Average Number of 2-hour Cycles Obtained Versus Percent HgO in Negative Plate

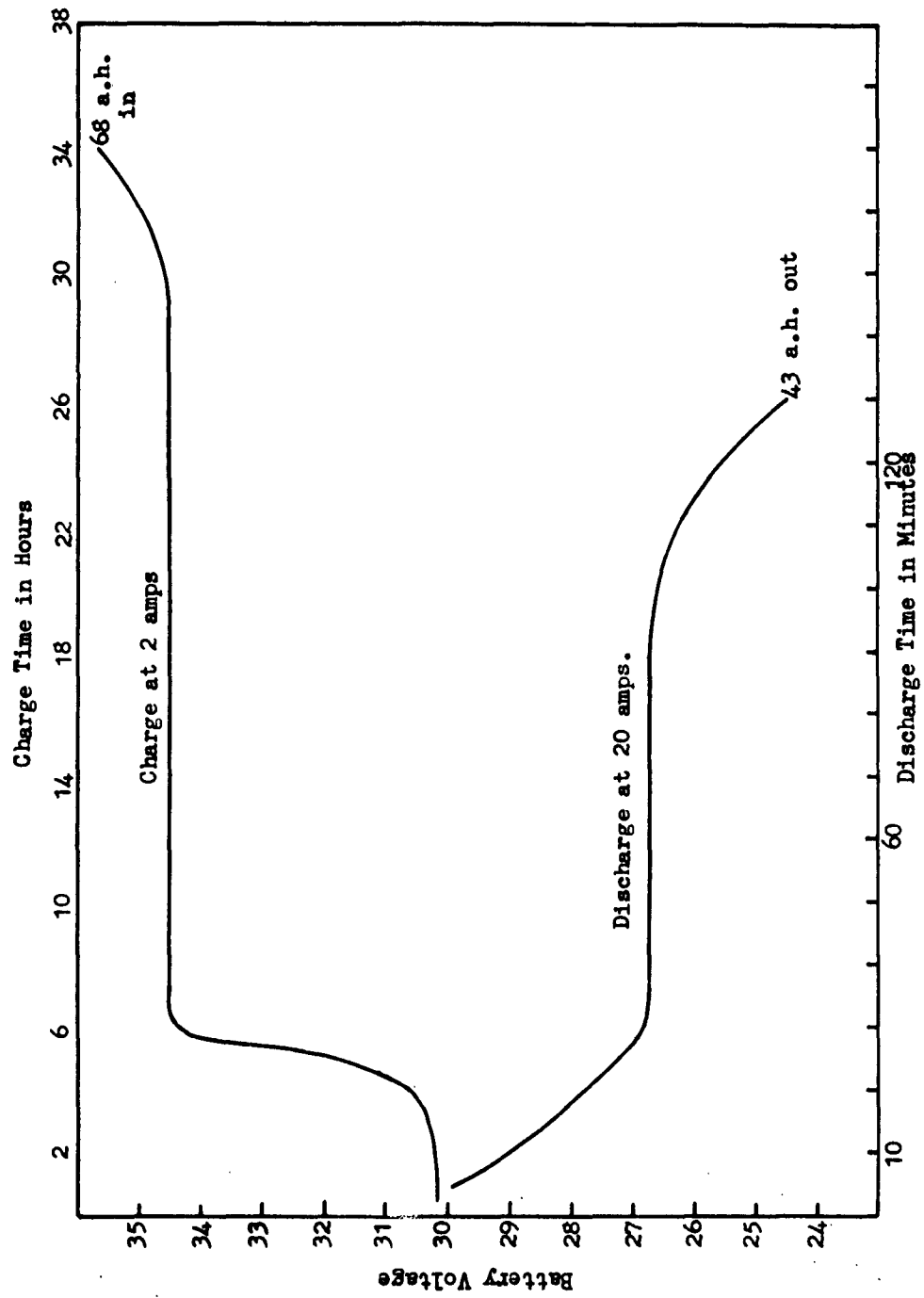


FIGURE 7 Battery #1 - Initial Charge and Discharge Curves

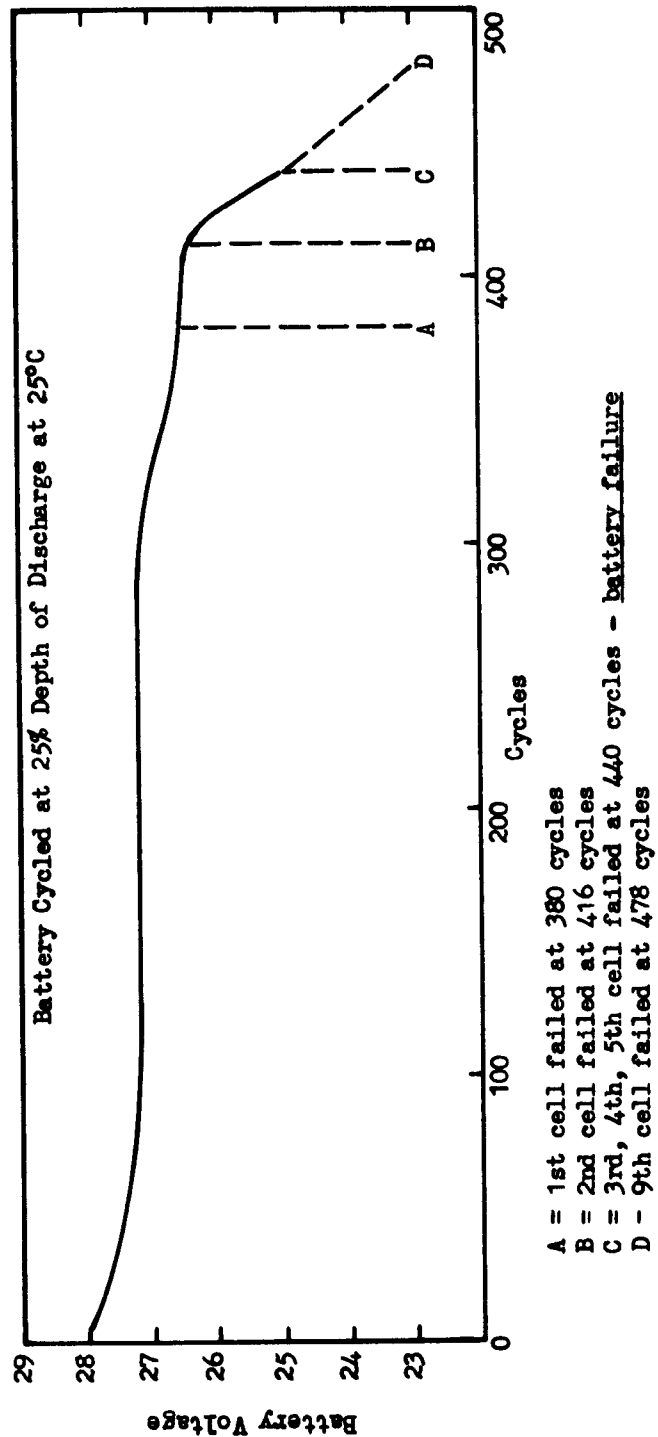


FIGURE 8 Battery #1 - End of Discharge Voltages and Failing Cells

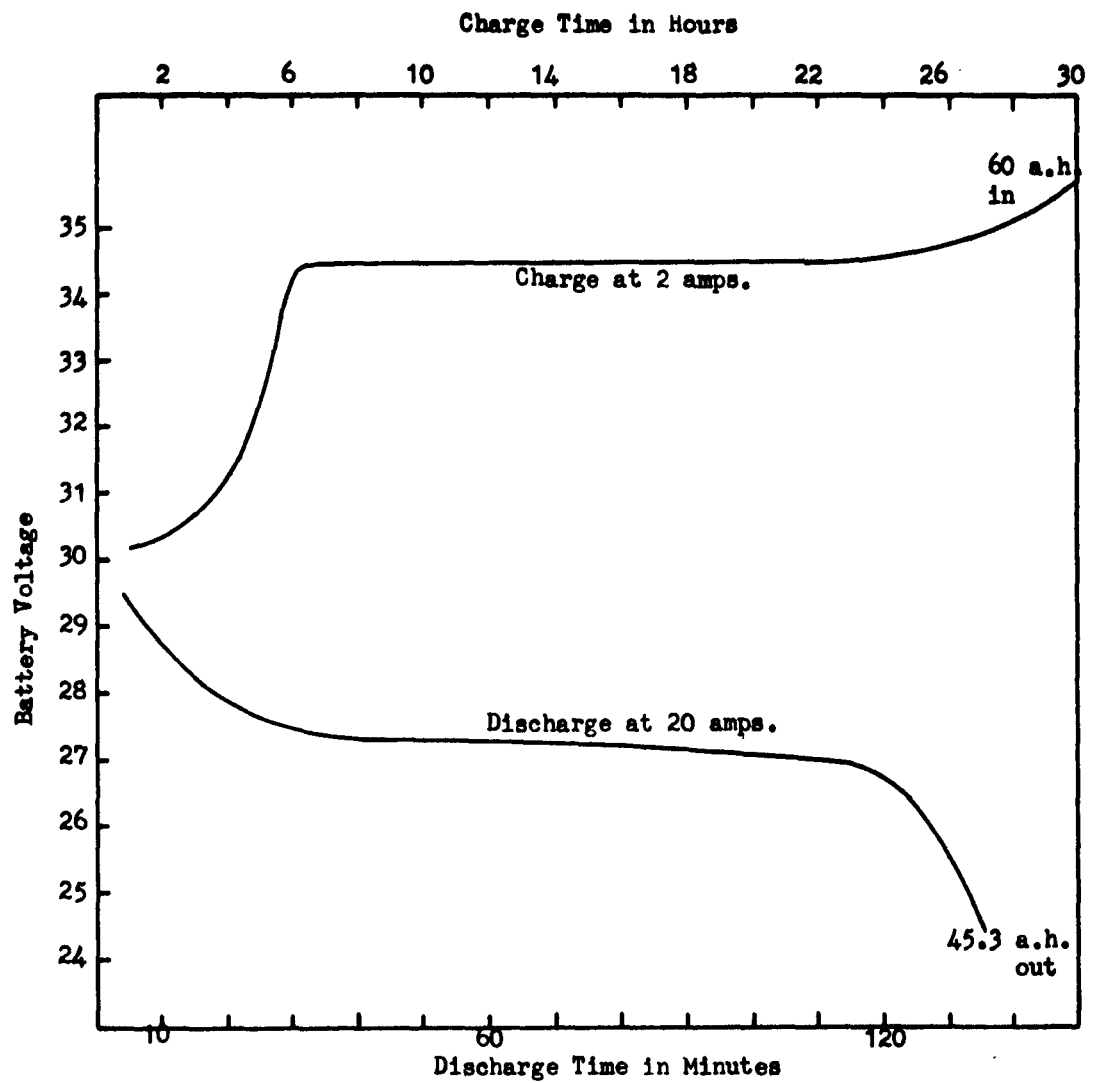
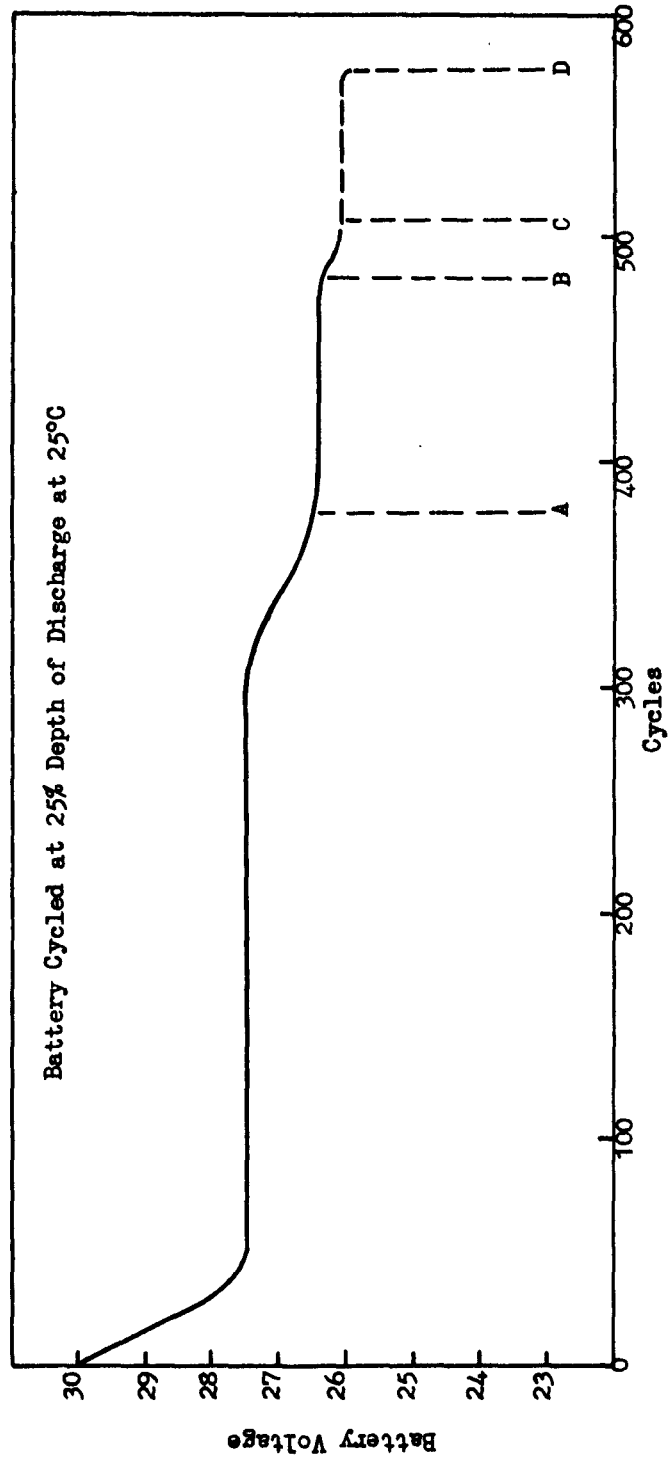


FIGURE 9 Battery #2 - Initial Charge and Discharge Curves



A = 1st cell failed at 380 cycles
 B = 2nd cell failed at 488 cycles
 C = 3rd cell failed at 512 cycles, battery failure.
 D = 9th cell failed at 572 cycles

FIGURE 10 Battery #2 - End of Discharge Voltages and Failing Cells

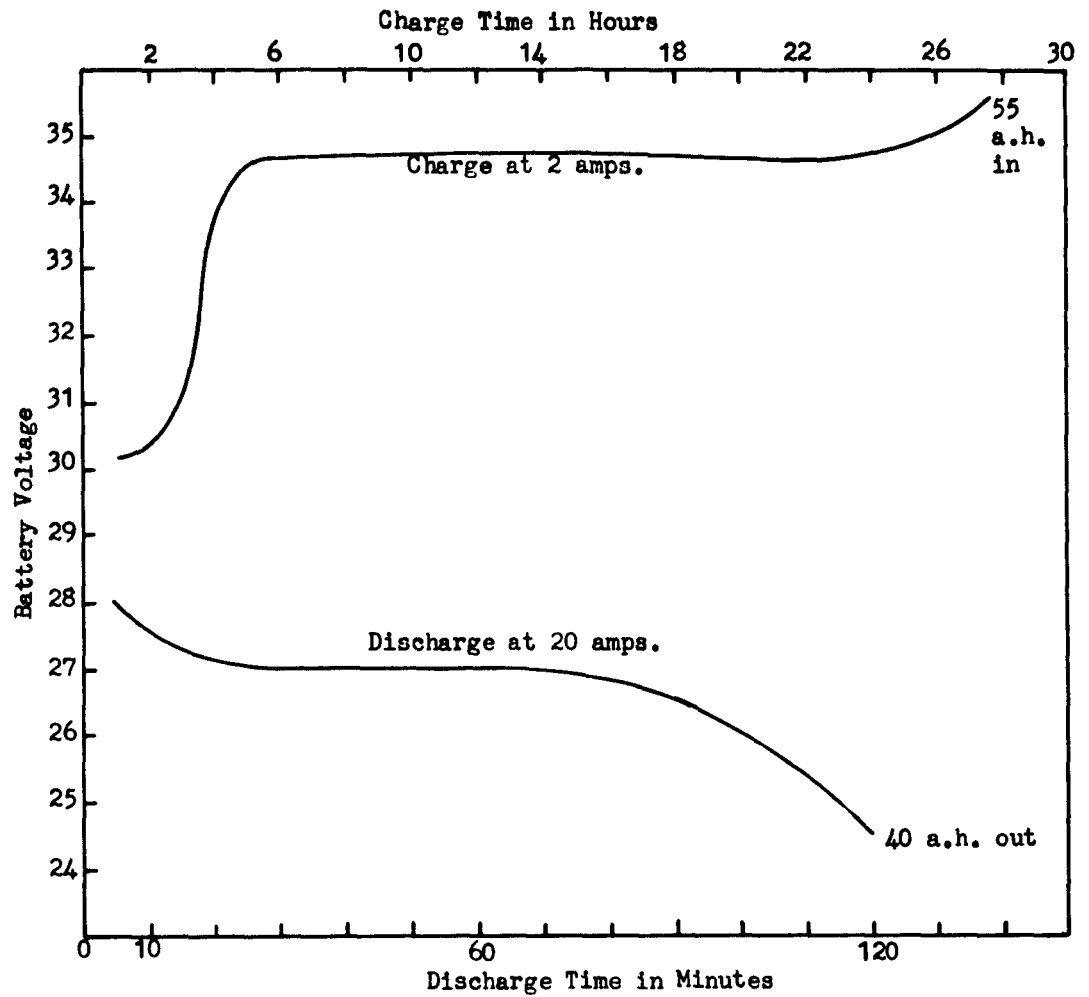


FIGURE 11 Battery #3 - Initial Charge and Discharge Curves

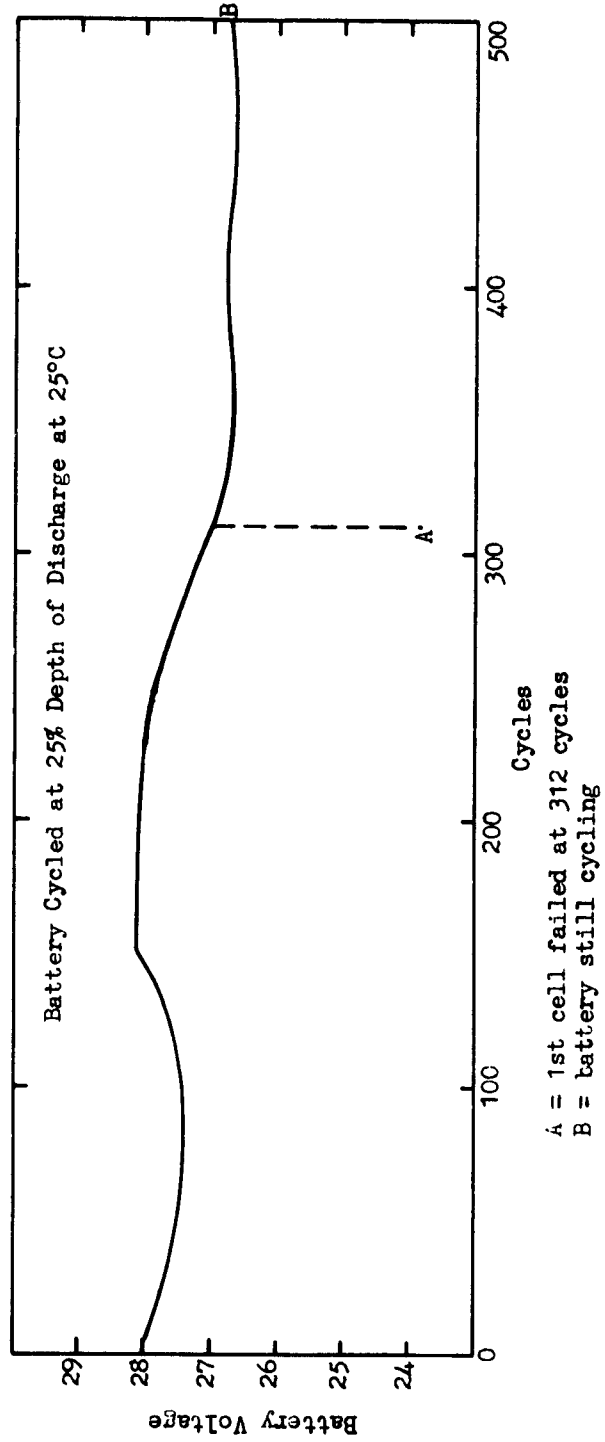


FIGURE 12 Battery #3 - End of Discharge Voltages and Failing Cells

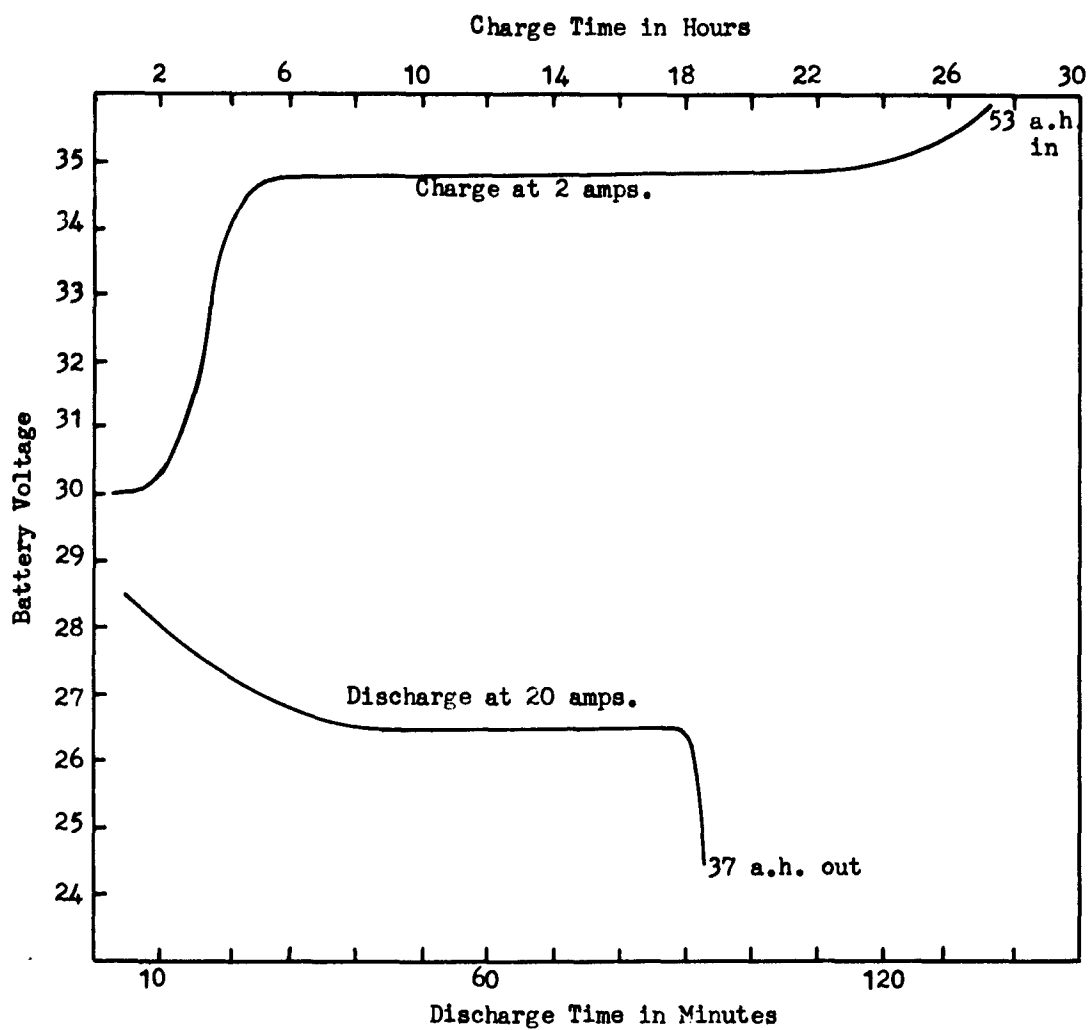
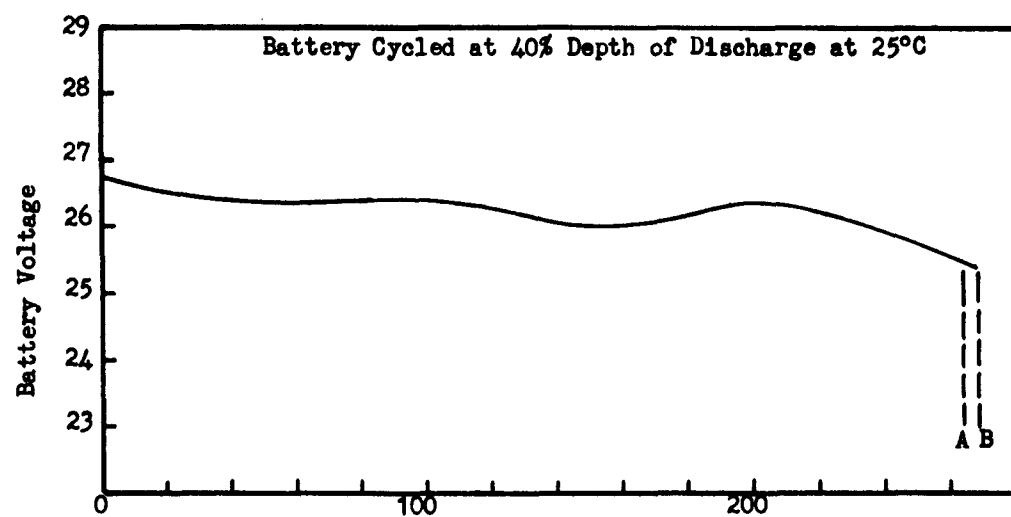


FIGURE 13 Battery #4 - Initial Charge and Discharge Curves



A = 1st cell failed at 264 cycles

B = Over 9 cells failed at 268 cycles, battery failed

FIGURE 14 Battery #4 - End of Discharge Voltages and Failing Cells