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ENGINEERING REPORT

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Delco-Remy

DIVISION OF GENERAL MOTORS, ANDERSON, INDIANA

SILVER-ZINC SECONDARY BATTERY INVESTIGATION

Third Quarterly Technical Progress Report

Covering the Period

1 January 1963 to 1 April 1963

Dated

2 April 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.

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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 1900 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 supplied by a vendor have reached 500 cycles at 80°F. Cycling is continuing at 25% depth of discharge which is 50% of the monovalent capacity.

The silver particle size study is completed. A complete analysis of this work will be presented in the Final Report of this contract.

Current density and KOH concentration studies are completed. Operation of sealed 25 a.h. cells at low current density and 45% KOH yield the best average cycle life at 25% depth of discharge at 80°F.

Expander studies on the negative plate are complete, and the results indicate that 2% PVA extends the cycle life average more consistently at 25% depth of cell capacity at 80°F.

Hydrogen evolution studies at 125°F indicate that 4% HgO addition to the negative plate in 30% 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 in 40% KOH have completed 687 and 500 average cycles respectively during operation at 25% depth of cell capacity at 80°F.

I. Introduction

This report covers nine month's work with emphasis on the work of the last three months. Specific items have been investigated to provide design criteria for long life, light weight, sealed secondary batteries for military aerospace applications.

These items are:

A. Palladium additions to the silver plate
B. Silver particle size effects on capacity and cycle life
C. Effect of current density and KOH concentration on cycle life
D. Expander studies on the negative plate
E. H_2 evolution studies on the negative plate.

The final data obtained as a result of this work, as well as the data previously obtained from completed items of work, will be utilized in the construction of test cells and batteries which will best meet 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 charge.

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 1900 cycles at 80°F operating at 50% utilization of the monovalent charge capacity, realizing a 25% depth of discharge for the cells.

Figure 1 shows the average end of charge, initial discharge and end of discharge voltages. Considerable monitoring has been necessary to maintain the required a.h. input causing some cycle operation at the divalent voltage level during charge. The drop-off in discharge capacity beyond the 1000 cycle mark is due to the decreasing limits of negative plate capacity.

Three additional sealed cells of 25 a.h. nominal capacity were constructed with positive plates containing particles coated with palladium to the extent of 1%. Initially, 66 cycles were given at about 75% of the monovalent capacity and 40% depth of cell capacity after which time the cells lost capability of operation solely on the monovalent voltage level. The rate was reduced to 50% of the monovalent capacity and 25% depth of cell capacity. The cells continued to cycle to 500 cycles at which time failure occurred due to loss of negative plate capacity. Figure 2 shows the average end of charge, initial discharge, and end of charge voltages for these cells.

Six additional sealed cells were constructed with positives containing 1% palladium coated about the particles and activated in 40% KOH. These cells are cycling at 80°F at 50% depth of monovalent charge capacity and 25% depth of cell capacity. To date they have reached 400 cycles and are still cycling. Three of these cells are charged at constant current and three by constant potential charge.

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

Figure 4 shows the average end of charge, initial discharge, and end of discharge voltages of the three cells cycled at constant potential charge.

B. Silver Particle Size Effects on Capacity and Cycle Life

This work has been completed. Photomicrographs are being prepared of plates cycled 1000 times containing silver powders of five different particle sizes sintered at three different temperature ranges of 800°F, 1000°F, and 1200°F.

Chemical analysis is being made to determine the silver deposition in the separators that has occurred at 1000 cycles.

The entire data covering this study will be presented in the Final Report of the subject contract.

C. Effect of Current Density and KOH Concentrations on Cycle Life

Nine sealed cells of 25 a.h. capacity activated with 40% KOH were placed on cycle test at 80°F at 25% depth of discharge with three cells representing each of three different current density ranges from .035 amp/in^2 to .112 amp/in^2. These cells contained different numbers and thicknesses of plates to operate at the required current densities. These cells have completed cycle life. The failure analysis will be reported in the Final Report of the subject contract.

Figure 5 shows the number of cycles obtained at the various current densities employed. The 812 cycles obtained at a current density of .070 amp/in^2 is the standard design of all 25 a.h. cells used in this program during operation at 25% depth of discharge. Figure 6 shows the average end of discharge voltages obtained at the indicated cycles of each current density employed.

Fifteen 25 a.h. sealed cells were placed on cycle test at 80°F, operating at 25% depth of discharge, with three cells representing each KOH concentration of 5%, 15%, 30%, 40%, and 45%. These cells have completed cycle life and the maximum number of average cycles obtained was

962 cycles in 45% KOH. Figure 7 shows the number of cycles obtained in the indicated KOH concentrations.

D. Expander Studies on the Negative Plate

Twelve additional 25 a.h. sealed cells activated in 40% KOH containing polyethylene oxide in the negative material have completed cycle life tests operating at 25% depth of discharge at 80°F. An average of 601 cycles was obtained. The cause of failure in all cells was shorting of the negative material through the separators to the positive plates.

The polyethylene oxide apparently resists mass migration of zinc, but in doing so it upsets the current density balance along the plate causing high current density points at the plate perimeter and dendrites are produced that otherwise would not occur. At any rate, the polyethylene oxide is not as good as PVA in its maximum concentration.

Figure 8 shows the average cycle life obtained by all cells in which various binders have been tested during this program.

E. Hydrogen Evolution Studies on the Negative Plate

In the Second Quarterly Report data was furnished covering hydrogen evolution at 100°F for various percentages of HgO content in the negative material, with and without amalgamated grids, in saturated and unsaturated zincate solutions of 30%, 40% and 45% KOH. These evolution studies have been continued at 125°F and 75°F on the following combinations of mercuric oxide in the negative material with zincate-free electrolyte concentrations.

1. 1% HgO in zinc plate tested in 30%, 40%, and 45% KOH
2. 2% HgO in zinc plate tested in 30%, 40%, and 45% KOH
3. 4% HgO in zinc plate tested in 30%, 40%, and 45% KOH

Figure 9 shows the total amount of hydrogen evolved over a 30-day period for the mercury additions in the indicated electrolytes at 125°F. The data for hydrogen evolution at 75°F is not yet completed, but they will be presented along with the complete study in the Final Report of the subject contract.

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. cells are now on cycle test to ascertain whether or not additional percentages of mercury additions in the negative plate would be detrimental, or otherwise, to life.

Figure 10 shows the average number of cycles thus far obtained by groups of twelve 25 a.h. cells containing 1% (control), 2% and 4% HgO additions to the negative plates. These cells were activated in 40% KOH, cycling at 25% depth of cell capacity at 80°F.

III. Summary

The palladium effect appears to hold up for the life of the positive plate at 25% depth of discharge on the 2-hour cycle; however, the recharge voltage had to be increased as cycling progressed because the negative plate would gradually lose capacity unless this measure was taken. The first group of cells with palladium treated positive plates achieved 900 cycles while operating in the voltage range 1.68 - 1.42 or 0.26 volts. A 28-volt battery would have 18 or 19 cells and could operate with a voltage spread of about $\pm$ 2.4 volts. While this spread is not as low as desired ($\pm$ 1.5 volts), it is less than half the spread for non-palladium cells.

An additional benefit which accrues from the use of the palladium treated positives is lack of the pressure build up which is characteristic of non-palladium cells. Measurement of internal pressure on two cells showed zero pressure rise on one and a slight negative pressure on the other, both over many hundreds of cycles. This result was expected from two standpoints: first, the charge voltage is well below the oxygen gas evolution point, and second, the rate of hydrogen gas take-up by palladium-treated positives is appreciably faster than non-palladium positives, as reported in the First Quarterly Report.

The silver particle size study through 1000 cycles of operation has been completed. The results show that large particles break down on cycling and small particles either grow or agglomerate. Thus the tendency is for particle size to become uniform on cycling regardless of the starting size. The morphology is irregular dendritic after cycling has progressed for a time. There was no evident effect of particle size, in the range studied, on efficiency of utilization of positive plate material.

There is a marked effect of current density on cycle life for equivalent depths of discharge. The use of more and thinner plates to reduce current density and yet achieve the same capacity rating more than doubled life in going from the highest current density used to the lowest. Thus increased cycle life can be obtained at the penalty of increased weight and bulk due to the increased number of separators involved. This result increases the importance of separator research programs aimed at reducing separator thickness.

The effect of KOH concentration on cycle life is also very great; life is doubled in going from 30% KOH to 45% KOH.

Expander studies on the negative plate show that polyethylene oxide is quite effective in preventing mass migration of zinc; however, it results in growth of zinc dendrites straight through the separator and consequent failure by shorting. It is less effective in extending life than polyvinyl alcohol. The use of 2% PVA is more effective in prolonging life than 1%. The maximum quantity of PVA that can be used is 2%.

Hydrogen evolution studies on the negative plate at 125°F have been completed. The reduction in hydrogen gassing is quite marked in going from 1% to 4% HgO; however, there was little effect of KOH concentration in the range 30 - 45%. It may be remembered that there was a very definite decrease in hydrogen gassing rates as KOH concentration was increased at 100°F. Gassing rate measurements are in progress at 75°F.

Cycle life tests of cells made with negative plates containing 2% and 4% HgO are under way. The purpose of these tests is to determine whether these amounts of HgO have any effect on cycle life; if there is no effect, it is planned to increase the amount of HgO in negative plates to secure the beneficial effects of reduced hydrogen gas evolution.

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

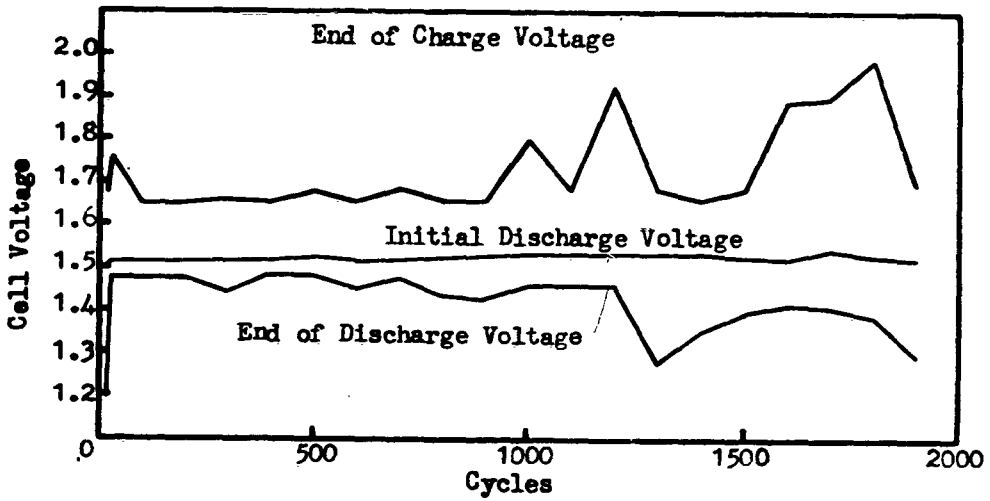
Non Government

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

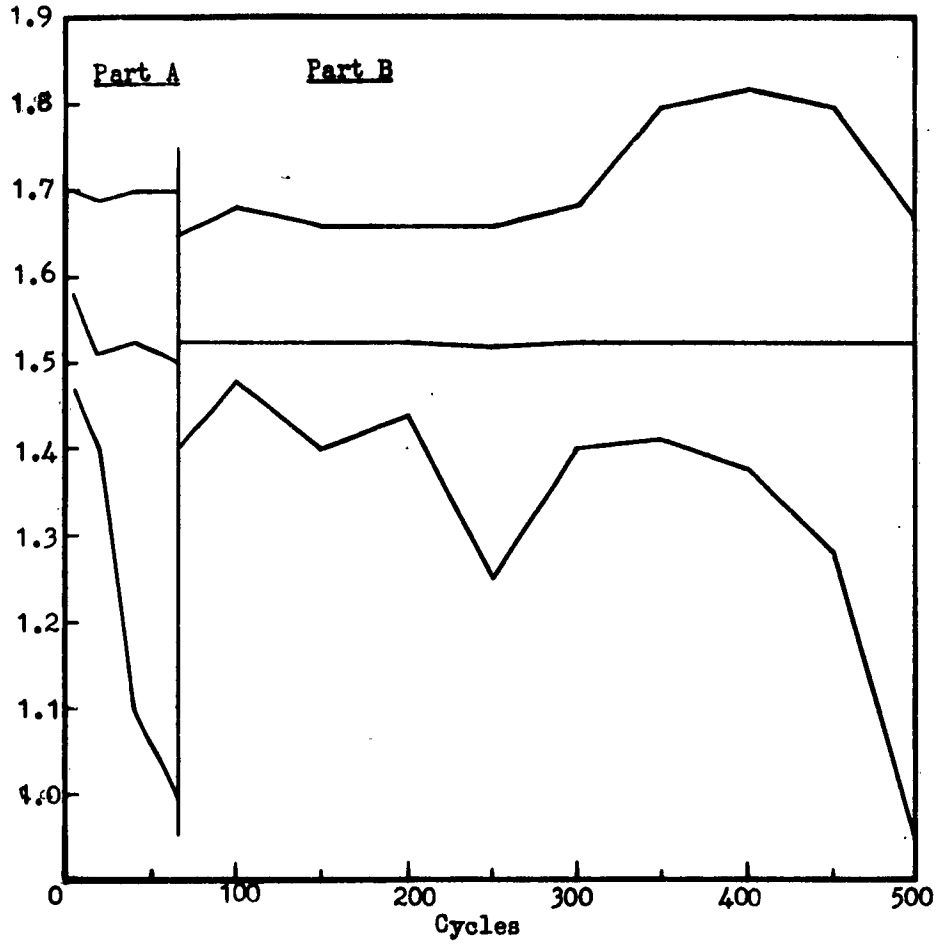
IV. Distribution List (Continued)

Cys	Non-Goverment (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



Voltages are average for three (3) silver-zinc cells activated in 40% KOH cycled at 50% of the monovalent charge capacity, or 25% depth of cell capacity at 80°F. utilizing a constant current charge.

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

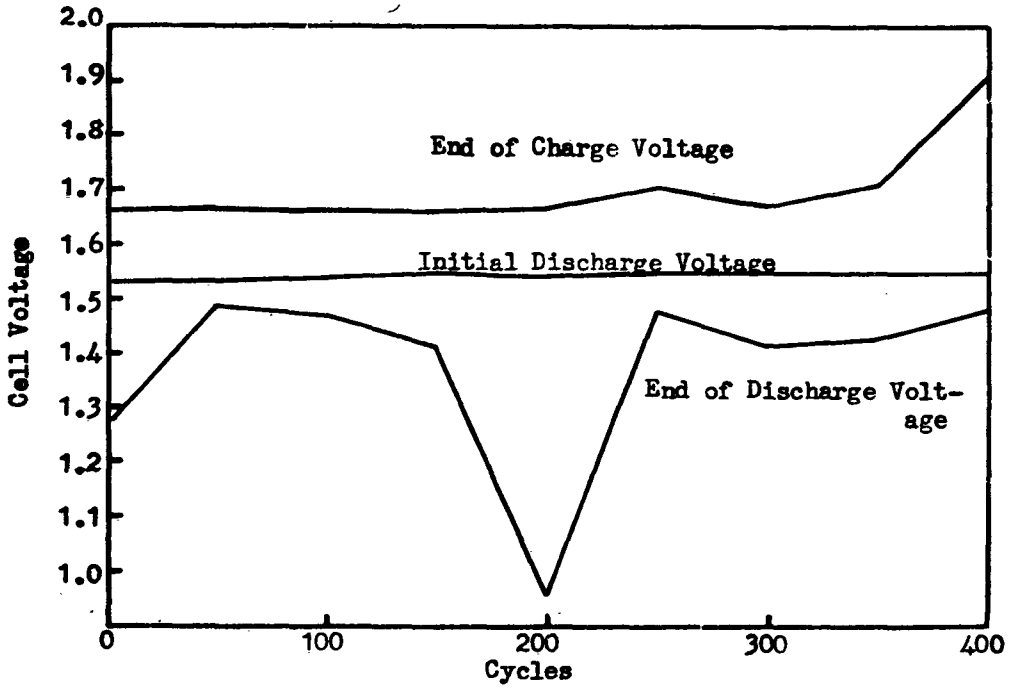


Voltages are average for three (3) silver-zinc cells activated in 40% KOH utilizing a constant current charge.

Part A - 66 cycles of operation at 75% of the monovalent charge capacity and 40% depth of cell discharge at 80°F.

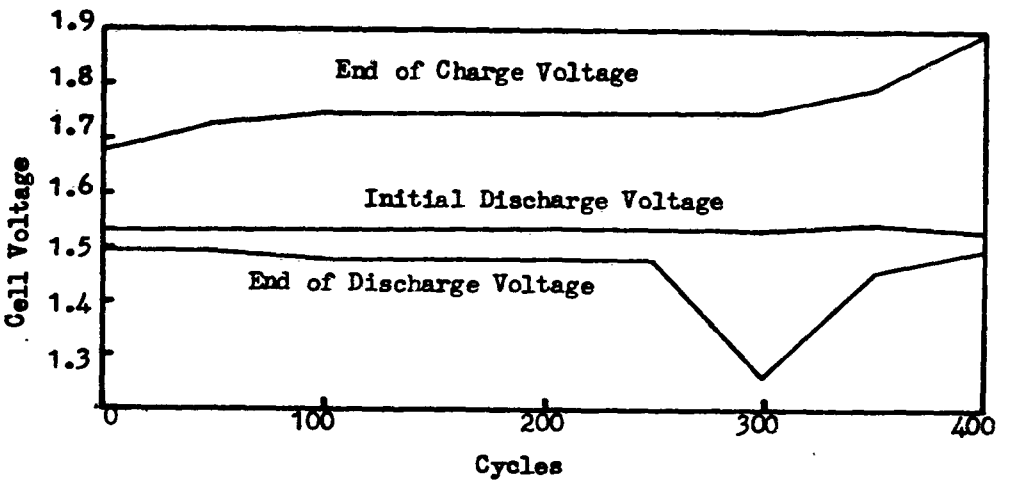
Part B - 434 cycles of operation at 50% of the monovalent charge capacity and 25% depth of cell discharge at 80°F.

FIGURE 2 Cycle Voltage Data of 1% Palladium Coated Silver Particles at Varying Discharge Depths



Voltages are average for three (3) silver-zinc cells cycled at 50% of the monovalent charge capacity, or 25% depth of cell capacity at 80°F utilizing a constant current charge.

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



Voltages are average for three (3) silver-zinc cells activated in 40% KOH, cycled at 50% of the monovalent charge capacity, or 25% depth of cell capacity at 80°F, utilizing a constant potential charge.

FIGURE 4 Cycle Voltage Data of 1% Palladium Coated Silver Particles

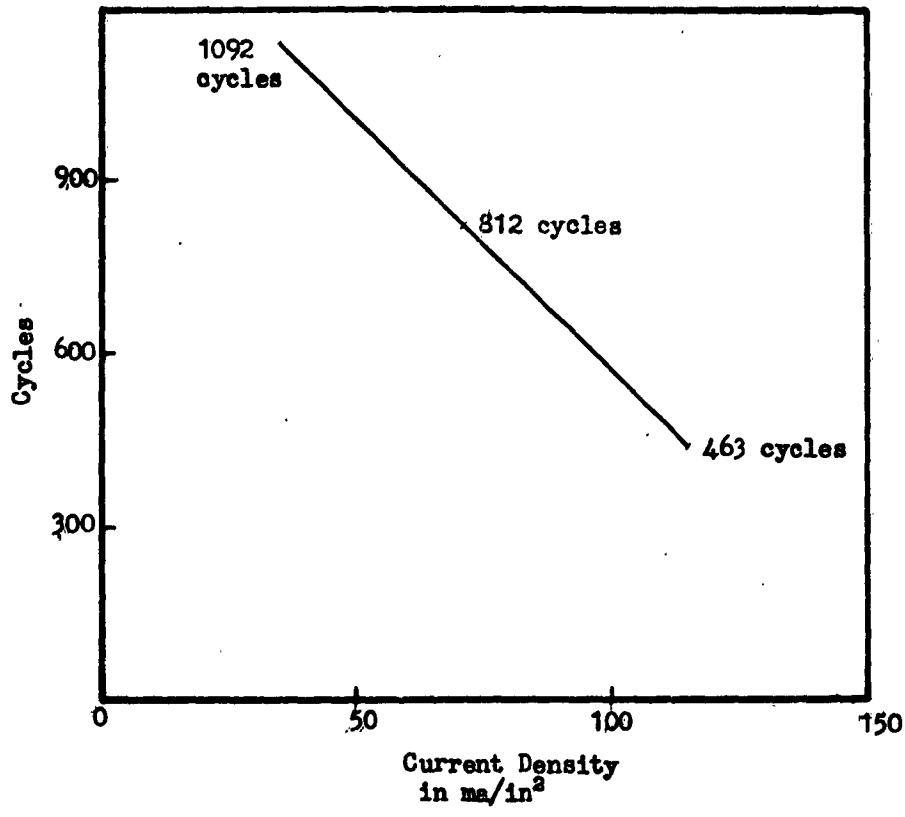
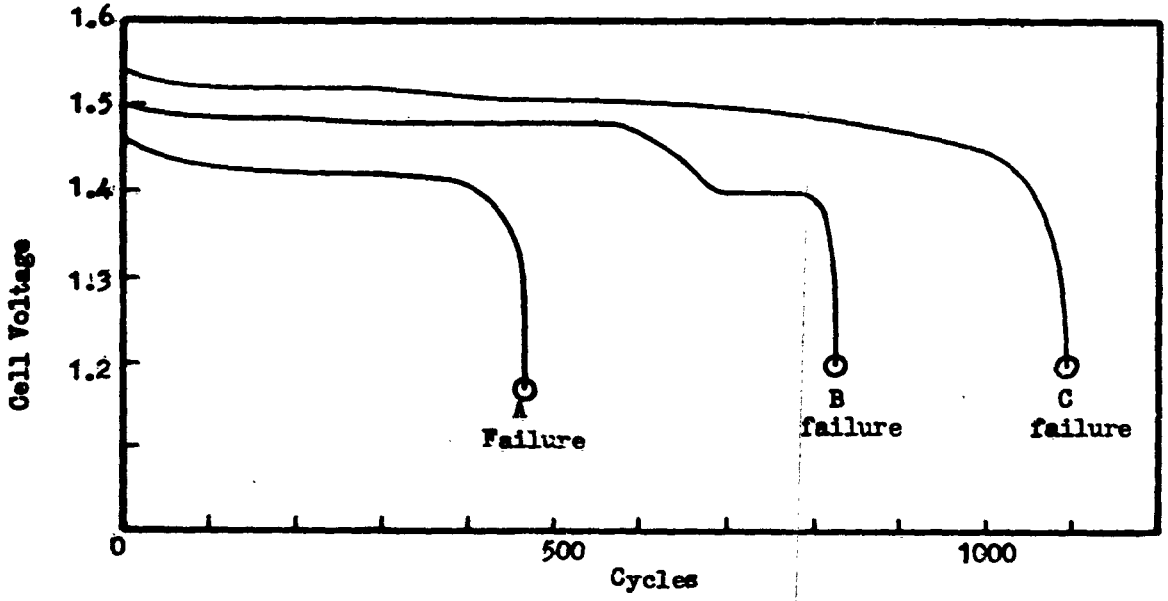


FIGURE 5 The Effect of Current Density on Cycle Life
at 25% Depth of Discharge
in 40% KOH
at 80°F.



Average end of discharge voltages of sealed cells activated in 40% KOH operating at 25% depth of discharge at three different current densities at 80°F.

A cells operating at .112 amp/in^2

B cells operating at .070 amp/in^2

C cells operating at .040 amp/in^2

FIGURE 6 Average End of Discharge Voltages in Current Density Study

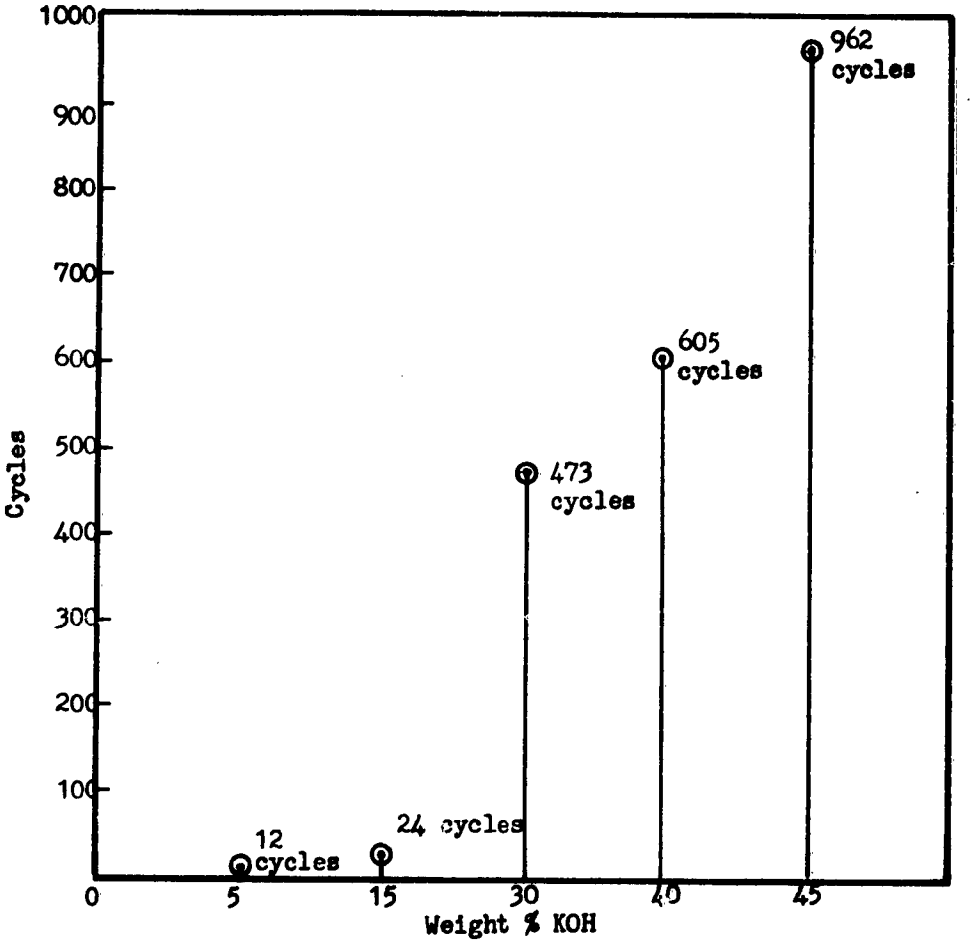
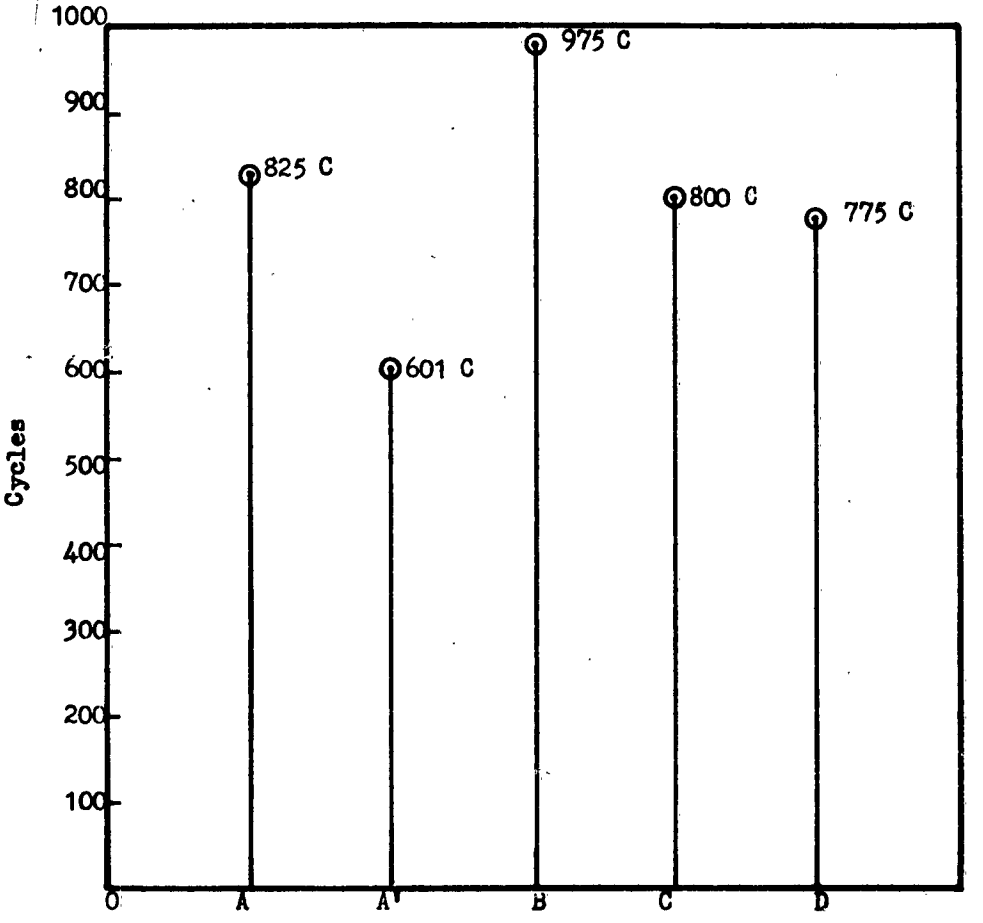


FIGURE 7 The Effect of KOH Concentration on Cycle Life



25 a.h. cells activated in 40% KOH cycled at 25% depth of discharge at 80°F

A = Polyethylene oxide binder (average for 6 cells)

A'= Repeat test on polyethylene oxide binder (average for 12 cells)

B = 2% PVA (average for 12 cells)

C = 1½% PVA (average for 12 cells)

D = 1% PVA (average for 12 cells, control)

FIGURE 8 Average Cycle Life of Various Negative Binders

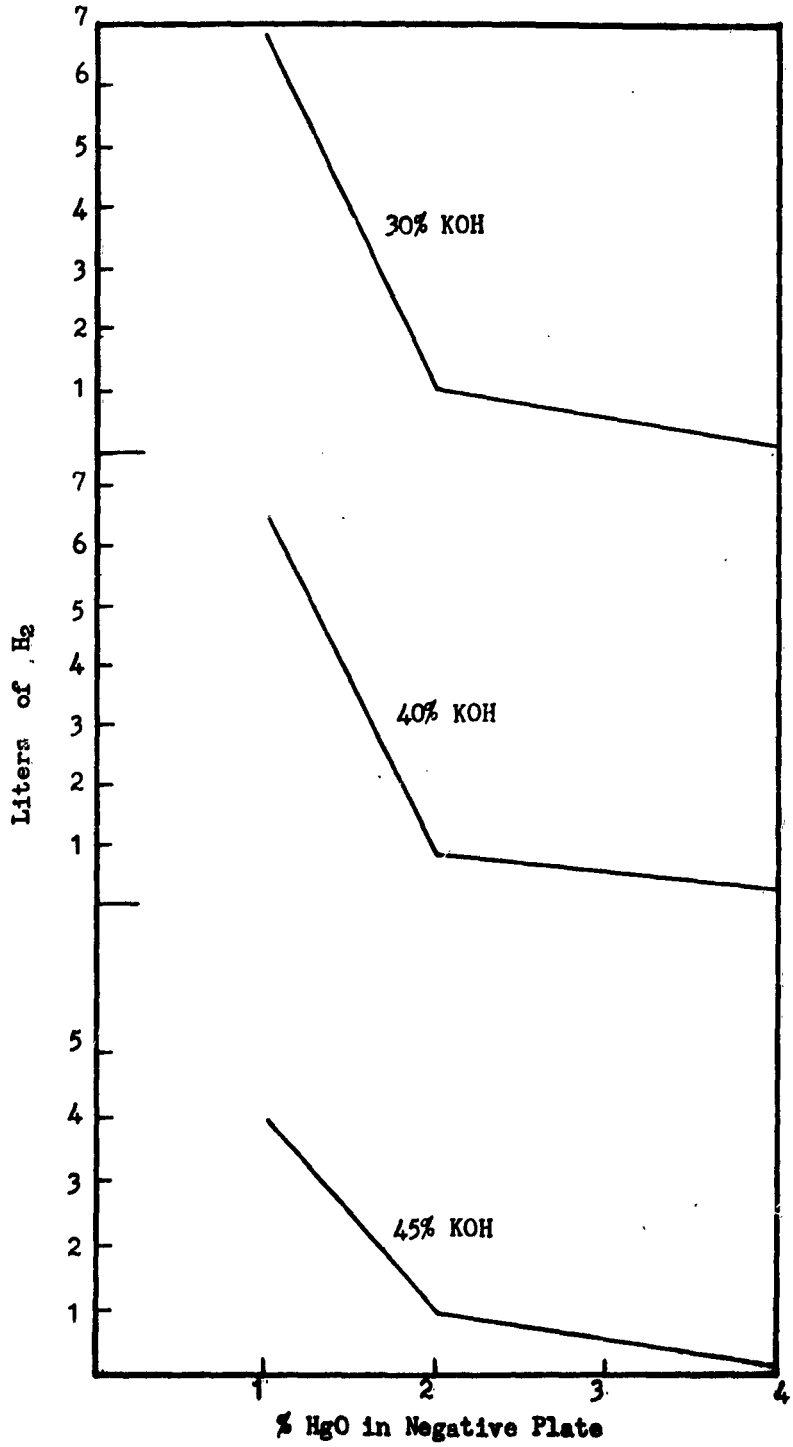
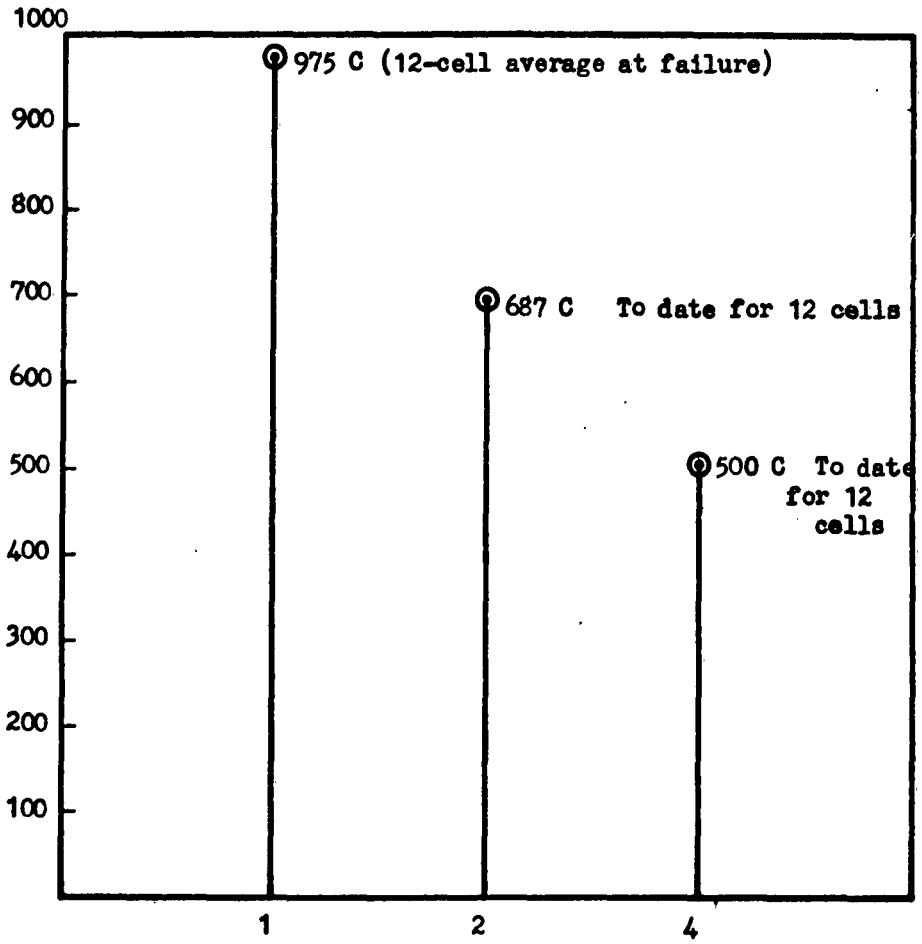


FIGURE 9 Amount of H_2 Evolved in 30 Days at 125°F in Indicated Electrolyte



25 a.h. sealed cells cycling at 25% depth of discharge at 80°F, containing 1%, 2% and 4% HgO in the negative plate in 40% KOH.

FIGURE 10 Average Number of Cycles Obtained Versus Percent HgO in Negative Plate