AD

Research and Development Technical Report
ECOM-3558

AD 741342

SECONDARY ZINC-AIR CELL INVESTIGATIONS

Otto C. Wagner

April 1972

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NOTICES

Disclaimers

Disposition

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
US Army Electronics Command
Fort Monmouth, New Jersey 07703

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

3. REPORT TITLE
SECONDARY ZINC-AIR CELL INVESTIGATIONS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Technical Report

5. AUTHOR(S) (First name, middle initial, last name)
Otto C. Wagner

6. REPORT DATE
April 1972

7a. TOTAL NO. OF PAGES
28

7b. NO. OF REFS
9

8a. CONTRACT OR GRANT NO.

b. PROJECT NO. 1T6 62705 A 053

c. Task -02

d. Work Unit -042

9a. ORIGINATOR'S REPORT NUMBER(S)
ECOM-3558

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT
Approved for public release;
distribution unlimited

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
US Army Electronics Command
Attn: AMSEL-TL-PC
Fort Monmouth, New Jersey 07703

13. ABSTRACT

Zinc-air cells have been developed that are capable of delivering over 50 cycles. These cells were constructed with silver-amalgam air-cathodes, nickel screen charging electrodes, and teflonated zinc anodes. The major failure modes encountered in this study were: shorting by zinc penetration, loss of capacity by the zinc anode due to edge-corrosion and surface densification, platinum poisoning of the zinc anode when employing platinum-catalyzed air-cathodes, and passivation of the zinc anode by electrolyte starvation. It has been determined that shorting can be prevented by placing a layer of low hydrogen overpotential material, such as nickel felt, within the separator layers. The use of a nickel screen charging electrode, which is located between the separator-clad zinc anode and air-cathode, is also effective in preventing shorts between the anode and cathode, but not between itself and the anode. As a result of the intermediate shorts between the charging electrode and anode, the average capacity is lowered and becomes erratically variable from cycle to cycle. Capacity loss by the zinc anode due to edge corrosion (shape change) and surface densification can be significantly reduced by matrixing the anode with sintered silver foam of high porosity (94%) and by densifying the periphery of the anode. Poisoning of the zinc anode by platinum is prevented by employing air-cathodes which are catalyzed by materials that are electrochemically compatible with zinc, such as silver-amalgam. Passivation of the anode by electrolyte starvation is minimized by: (a) placing thin plastic spacers in the charging compartment, (b) locating an electrolyte reservoir above the electrodes, (c) providing narrow irrigation channels along the sides of the anode, (d) using a polyamide Pellon wick in the anode compartment, and (e) adding 0.5% mercuric oxide to the active zinc mix.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Metal-Air Cells						
Zinc-Air Cells						
Zinc Anodes						
Air-Cathodes						
Separators						
Storage Battery						
Electrochemical						

Reports Control Symbol OSD-1366

TECHNICAL REPORT ECOM-3558

SECONDARY ZINC-AIR CELL INVESTIGATIONS

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U.S. Army Electronics Technology
and Devices Laboratory (ECOM)

APRIL 72

DA Work Unit No. 1T6 62705 A 053 02 042

Distribution Statement

Approved for public release;
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US ARMY ELECTRONICS COMMAND
FORT MONMOUTH, NEW JERSEY

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SECONDARY ZINC-AIR CELL INVESTIGATIONS

INTRODUCTION

The electrically rechargeable version of the zinc-air system has attracted considerable attention because of its inherently favorable energy density and the abundance of zinc. Working models and prototypes of rechargeable zinc-air batteries have been constructed and evaluated by several investigators in the United States and abroad. Sufficient time has not yet elapsed to get answers to all the basic problems with the zinc-air system. Essentially, there are four basic problems; namely, shorting by zinc penetration, capacity loss by zinc corrosion (shape change), passivation of the zinc by electrolyte starvation, and carbon dioxide contamination of the alkaline electrolyte. The first two problems are extremely difficult to resolve and for that reason it is not possible to estimate a probable cycle life for the zinc-air system. Such a status is not unusual in the development of any new storage battery system. A probable satisfactory life of the system is based on the development of reliable electrodes and separators and the establishment of known characteristics of these components. It is, therefore, to the known limited rechargeability of the zinc anode that the main research and development emphasis must be placed, although such problems as cathode deterioration, because of catalyst degradation and changes in wetting behavior, should not be neglected.

A survey of research efforts by individual companies in the field of zinc-air and zinc-oxygen systems indicates that two basic approaches have been taken. One is the development of a dynamic system; that is, the employment of rotating electrodes and/or the use of pumped electrolyte. The other is the development of a static system; that is, the electrodes, separator, and electrolyte are stationary and the cells require no ancillary equipment.

Among the companies that have engaged in the development of the dynamic zinc-air systems are: Gulf General Atomics, Inc., Sony Corporation of Japan, Yardney Electric, Atomics International (Division of North American Rockwell Corporation), and Allis-Chalmers.

Among the companies that have developed static zinc-air systems are: Leesona Moos, Union Carbide, Astropower Laboratory (McDonnell Douglas), and Energy Research Corporation.

The Gulf General Atomics battery development[1] started in 1960. Their approach was the adoption of a circulating electrolyte to control deposition of zinc from a zincate-containing potassium hydroxide electrolyte at controlled current densities to produce a dense and active zinc layer during charge. During discharge, the zinc oxide that is formed is separated from the electrolyte in a storage reservoir and is the source of zinc for redeposition during charging. The circulating system also allows for control of temperature and water content of the battery, and for removal of carbon dioxide from the incoming air. The catalyzed porous nickel air-cathodes are operated by bubbling air through them. They can also serve as counter-electrodes during the charging. This battery was developed for vehicular power.

The Sony battery[2] was also developed for vehicular power and its operation is similar to that of the Gulf General Atomics' system. In this battery, pulverized zinc "fuel" is supplied into a fuel tank, the zinc being supplied with the KOH electrolyte into each cell during the feed period. The zinc is discharged on an anode substrate during an inactive feed period and the reaction products are removed during the next feed period. The reaction products are electrolyzed into zinc powder after the discharge process. The zinc powder then is used over again.

The Yardney battery[1] operated on the principle of rotating the anode substrate during charge, thereby preventing shape change and providing a uniform active zinc deposit for discharging. The battery requires no separators or circulating electrolytes. Charging was by means of a third electrode since the air-cathodes lost stability when charged.

The Atomics International[3] battery is similar in principle to the Yardney system, except that their system employs a rotating particle bed of zinc coated spheres instead of a rotating anode substrate. The spheres consist of small metal balls that freely cascade in a thin rotating cylindrical container during charge and are plated with an active zinc deposit. Best results were obtained with a silver-catalyzed air-cathode, where an expanded nickel screen was employed as a third charging electrode.

The Allis-Chalmers battery[4] uses a pumped electrolyte system whereby the electrodes are stationary and the electrolyte is circulated through the cell by a pump. This results in a dense crystalline zinc deposit which provides a more stable anode. Silver catalyzed air-cathodes were used, and the zinc anode was placed between two auxiliary charge electrodes and two air-cathodes.

In general, the energy densities of the dynamic systems are estimated and claimed to be between 25 to 60 Wh/lb, depending on the design and capacity of the battery. The cycle life is not always reported. In some cases over 100 cycles have been attained, mainly on shallow depths of discharge. The primary shortcomings of the dynamic systems are: (a) the loss in energy density that results from the ancillary equipment and large quantities of electrolyte, (b) mechanical difficulties in the transfer of zinc and zinc oxide, (c) parasitic currents from cell to cell that result in self-discharging, and (d) complexity of the many moving parts which often results in electrolyte leakages.

The static systems are limited primarily by the dendritic growth of zinc on charge, which causes internal shorting, and by the reshaping of the anode on cycling.

The Leesona Moos zinc-air system[5] could reach an energy density of 83 Wh/lb at the C/10 rate of discharge at 60% depth of discharge. These cells employed 200 mil thick zinc anodes and bifunctional platinum catalyzed air-cathodes (for charging and discharging). Not more than 20 cycles were reported.

Union Carbide investigated sealed zinc-oxygen cells[6] for space applications. The anodes were a zinc oxide type and of a zinc powder-carboxymethyl cellulose (CMC) gel structure. The cathodes were the "fixed-zone" electrodes, which consist of a layered structure of sintered nickel and carbon catalyst, and a platinum-catalyzed electrode. Cycle life was limited with the platinum electrodes because of the deposition of noble metal on the zinc electrode and the consequent formation of a hydrogen gassing couple. The best cells yielded several hundred cycles at 15% depth of discharge at a current density of 11-12 mA/cm^2. Deeper discharges decreased cycle life by zinc shape change and dendritic shorts. PERMION films were the preferred separators and electroosmotic transport of liquid was compensated by an interconnecting "liquid-leveling" channel between the electrolyte reservoirs above the positive and negative electrodes.

The Astropower effort[7] also was concentrated on sealed zinc-oxygen cells. The cells were designed to withstand pressures up to 500 psi. The best cells attained 200-300 cycles at 25% depth of discharge. The most promising separator system was an inorganic formulation containing magnesium and chromium (Type 4669-31) plus an electrolyte matrix based on potassium titinate in the anode compartment. The air-cathodes were platinum-catalyzed and the zinc anodes were conventional. Hydrogen evolution was a serious problem and several cells exploded during cycling. Cycle life was mainly limited by internal shorts and reshaping of the anode.

Energy Research is also developing a sealed zinc-oxygen system for ECOM under Contract DAAB07-71-C-0249. The unit cell is being designed to contain oxygen at a maximum pressure of 1000 psi. The pressure may be used as an indicator of state of charge of the battery. The more promising cells have exceeded 100 cycles at 33% depth of discharge.

Research and development effort at ECOM was directed towards a static zinc-air system. Not only is the energy density of this system greater than that of the dynamic system but its design and mode of operation are inherently simpler.

EXPERIMENTAL PROCEDURES

Zinc Penetration Test

The zinc penetration test equipment consists of a cell assembly which holds the separator under investigation between two zinc electrodes. One of these electrodes serves as an anode and provides for replenishment of zincate in the zincate-KOH electrolyte. The other electrode is the cathode upon which zinc is electrodeposited. Current is passed between the electrodes at a controlled current density until a zinc trail traverses the separator and is detected by shorting out on a platinum reference electrode which is located on the opposite face of the separator. The test separator is usually allowed to soak for 24 hours in 30% KOH saturated with zincate prior to assembling the test cell. The current is set at 10 mA/cm^2 and the platinum probe will show a voltage versus the cathode of 1.3 to 1.5 V. When metallic zinc reaches the probe, the voltage drops by 0.1 to 0.6 V. The control cell contained two layers of 1 mil thick cellophane and usually shorts in 50 to 80 minutes.

Zinc-Air Cell Construction and Testing

The zinc anodes were prepared in the following manner: (1) zinc oxide (Fisher Certified, ACS, Z-52) was homogeneously blended with 0.5% by weight of mercuric oxide (Fisher Certified, ACS, M-174) and distilled water so that a thin paste was formed, (2) sufficient teflon emulsion (Dupont #30 TFE Emulsion) was blended into the paste to provide 2% by weight of teflon solids, (3) the mixture was dried at 110°C overnight, (4) the dry mix was ground into a powder and sifted through a 60 mesh screen, and (5) 12.50 g of dry powder were mold pressed into an electrode containing an Aldex paper wrap (Aldine Corporation) and a 5 Ag 15-2/0 silver grid (Exmet Corporation) with attached 5 mil thick silver tab. The electrode dimensions were: 0.115" in thickness, 2.0" in width, and 1-5/8" in height. The electrode porosity in the fully charged state was 78%.

The zinc-air cells were constructed as follows: (1) the zinc anode was inserted into an open U of polyamide Pellon felt (5-6 mil 2506K from Pellon Corporation) which was 2.0" wide and 2.5" high on each side of the anode, (2) the anode and Pellon wrap were inserted into an anode compartment (clearance: 2-1/4" x 0.125") consisting of a three-sided ABS frame, (2 sides plus base, each 1/8" x 1/8") onto which had been epoxy-sealed[#] the main separator layers (2.5" x 2.5"), such as a layer of 10 mil nickel felt (nickel Feltmetal #6-440 of 75% porosity by Huyck Metals, Inc.) sandwiched between two layers of 3 mil fibrous sausage casing (Consumer Products Division of Union Carbide Corporation), (3) onto both sides of the anode electrode pack and along the edges (1/8" wide) were epoxy-sealed[#] single layers of 5 mil Pellon 2506K onto which were attached (epoxy-bonded at the edges) expanded nickel charging screens (2-1/2" wide x 1-5/8" high, 5 Ni 10-2/0 from Exmet Corporation) which contained 5 mil nickel tabs and vertical 30 mil thick teflon spacers that were 1/16" wide and separated 1/2" apart, (4) on both sides of the electrode stack were attached (with epoxy on the teflon strips) Pellon clad (5 mil 2506K) silver-amalgam air-cathodes (2-1/2" wide x 2" high electrodes from Energy Research Corporation with attached 5 mil silver tabs) which had been cemented with epoxy onto lucite cell walls that provided the necessary air-space opening for said cathodes, and (5) cell construction was completed by epoxy-sealing lucite cell walls along the sides and base of the cell.

The test setup is shown in Figure 1. Nylon spacers of 100 mil thickness were placed on the air side of the air-cathodes and the complete unit cell was secured between lucite supports. The cell was contained in a reaction kettle. A nickel hydroxide reference electrode was placed in a

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[#] Conap, Inc. Epoxy is thinly spread on 1/8" wide surface which had been cleaned with acetone. Pieces are cured under pressure (back plates plus clamp) at 140°F for two hours.

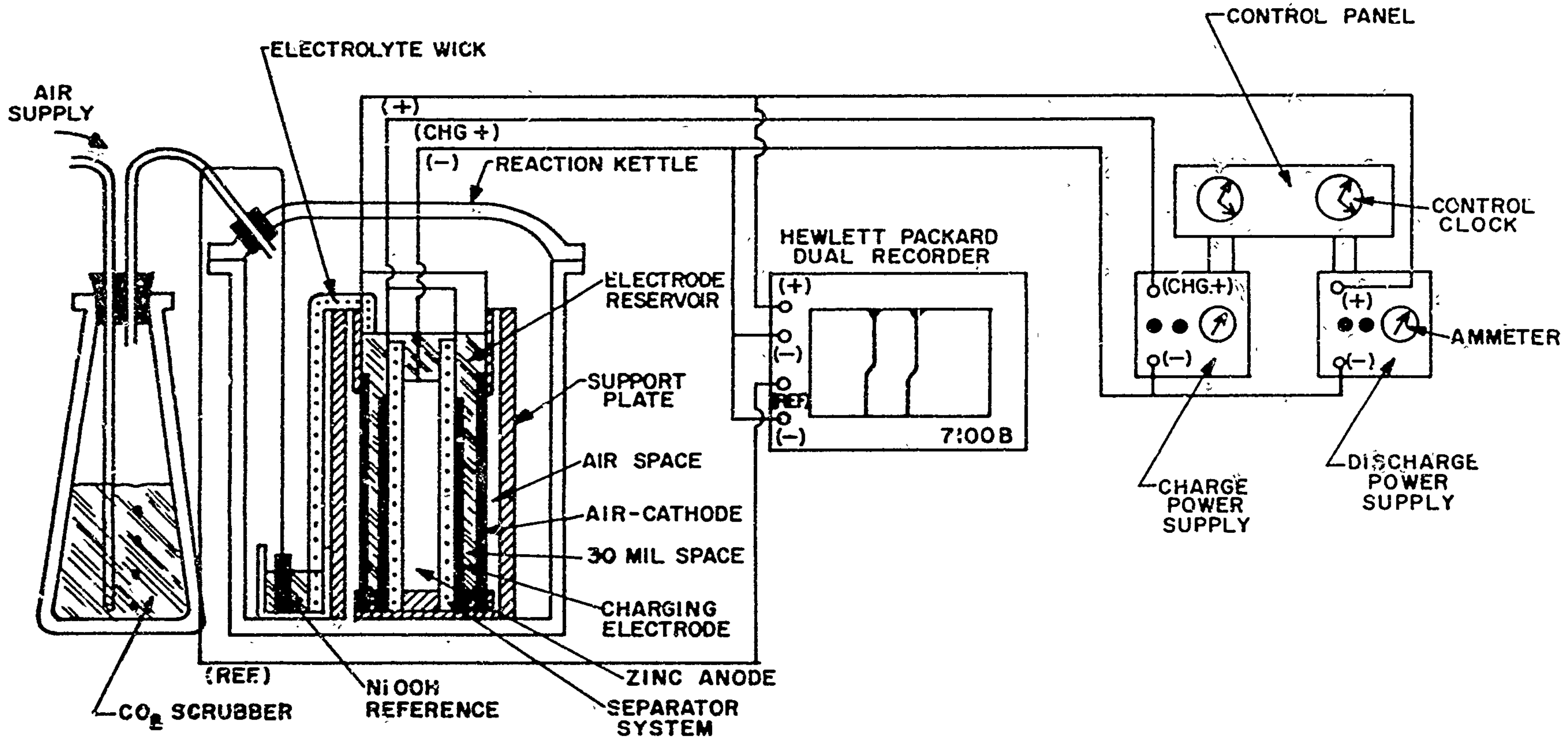


FIG. I INSTRUMENTATION

beaker of 30% KOH and a polyamide Pellon wick, soaked with electrolyte, formed an electrolyte bridge between beaker and cell reservoir which also contained 30% KOH. The incoming air was supplied at a partial pressure of 3-5" of water and was scrubbed free of carbon dioxide by means of a column of 20% KOH solution. The cell was cycled by means of automatic timers which controlled the charge power supply circuit and discharge circuit which also employed a power supply to maintain a constant current. Discharge cutoff was set to 0.5 V. After cutoff, the cell remained on open circuit until the clock control activated the charge circuit. Charging was strictly time controlled. Cell potential and reference readings were recorded on a Hewlett Packard 7100B dual point recorder. All tests were run at room temperature ambient.

Zinc Electrode Test

Two types of zinc anodes were constructed. The mold pressed zinc anodes were prepared, as described under the "Zinc-Air Cell Construction and Testing" Section, using the same zinc oxide mixes and molds (2.0" wide x 1-5/8" high). The matrixed electrodes were prepared by: (a) pasting a wet zinc oxide mix into the pores of a silver foam structure of 94% porosity (Metallurigical Division of General Electric Company), (b) drying, and (c) pressing to a porosity of 75% (as metal zinc) in the same mold as above. The single electrode nickel-zinc cells (one zinc anode versus two nickel hydroxide cathodes) were then fabricated as follows: (1) two nickel-hydroxide cathodes (40 mil thick, 1-7/8" wide, 1-1/2" high, manufactured by General Telephone and Electronics Company) were wrapped in 5 mil polyamide Pellon separators (2506K from Pellon Corporation), (2) the Pellon wrapped cathodes were placed inside an accordion wrap of 3 mil fibrous sausage casing (Union Carbide) and the two separator-clad cathodes were folded around the zinc-anode, and (3) the electrode pack was shimmed into a cell case to which were attached the cover and terminals. The cell also contained a partially charged nickel hydroxide reference electrode which was wrapped in a casing separator.

Cycling was similar to that of the zinc-air cells. The charging was at 500 mA for 1-1/4 hours and the cell was discharged at 500 mA to a 0.6 V cutoff. After cutoff, the cell was on open circuit until switched back on charge. Cell and reference potential readings were recorded on a multipoint Honeywell-Electronik voltage recorder.

DISCUSSION AND RESULTS

The most critical mode of failure for the zinc-air cell is shorting by the growth of dendritic zinc through the separator layers on charge and overcharge. The first cell, ZA-691, constructed and evaluated in this program, shorted in the first cycle. To resolve this problem, a study had to be made of zinc penetration.

Shorting by Zinc Penetration

In studying the problem of shorting by dendritic zinc, a convenient zinc penetration test cell was developed by Yardney Electric Corporation and is fully described in a publication released by the Air Force Aero Propulsion Laboratory.[8]

The results of various separator combinations are shown in Table I which indicates the time to short for each test.

Table I. Zinc Penetration Test Results

	Separator Combinations	Time to Short (Minutes)
1.	2 layers of PUDO 300, .001" thick cellophane (control cell)	50 - 80
2.	2 layers of .003" fibrous sausage casing	600
3.	2 layers of PUDO 300 Cellophane plus Igepal CO 730	280
4.	2 layers of PUDO 300 Cellophane plus Emulphogene BC 840	180
5.	1 layer of PUDO 300/1 layer of 0.010" thick sintered nickel plaque (80% porous)/1 layer of PUDO 300	Over 12,000 (No Short)
6.	1 layer of 0.0015" Astroset 3420-09/ 1 layer of 0.010" thick Huyck nickel felt (75% porous)/1 layer of 0.0015" Astroset 3420-09	Over 12,000 (No Short)

The first test, the control cell, lasted 50 to 80 minutes before failure. This time interval is much shorter than that reported by Yardney. This may be attributed to their using 44% KOH saturated with zincate compared to the zincate saturated 30% KOH. The second test shows that sausage casing is much more effective in resisting zinc penetration than cellophane, even after compensating for the greater thickness of casing. The third and fourth tests were to determine the effectiveness of certain additives which have been reported by several investigators to be effective in retarding zinc penetration. These additives were smeared between the two layers of cellophane. The results show that both the Igepal CO 730 and the Emulphogene BC 840 are slightly beneficial but are not effective zinc penetration stoppers. In the fifth test, a 10 mil sintered nickel plaque was sandwiched between two layers of cellophane. The rationale is that by placing a layer of material of low hydrogen overpotential in the separator wraps, then any zinc that penetrates the pores of this material will be oxidized by the following reaction:

Zinc in the Pores: $Zn + 2\ OH^- + 2\ e^- \longrightarrow Zn\ (OH)_2$

Nickel Surface: $2\ H_2O + 2\ e^- \longrightarrow H_2 + 2\ OH^-$

The test results show that this separator system prevented shorts. No shorts occurred, even after 12,000 minutes. The test was stopped because of the large accumulation of zinc on the cathode.

The sixth test was similar to the fifth. A 10 mil layer of nickel felt of 75% porosity, manufactured by Huyck Metals Company, was sandwiched between two layers of Astroset 3420-09 (a flexible inorganic membrane fabricated by Astropower Laboratories). As with the fifth test, no shorting occurred, even after 12,000 minutes of charge.

The significance of this work is that a separator system has been found that will prevent shorts in alkaline zinc batteries. A patent was granted on this finding and assigned to the US Government.[9]

Development of Rechargeable Zinc-Air Cells

Bifunctional Zinc-Air Cells

With a separator system that will prevent shorting by zinc penetration, it appeared at first that zinc-air cells could be designed, constructed, and cycled without encountering any serious failure modes. The first cell constructed with a nickel felt layer in the separator system was the ZA-692. The Huyck nickel felt was located between two layers of 1.5 mil Astroset 3420-09 (a flexible inorganic membrane developed by Astropower Laboratories). Polyamide Pellon 2506K was used as an electrolyte matrix, or wicking interseparator. The air-cathodes were bifunctional platinum-catalyzed electrodes from Leesona Moos (that is, they are charging and discharging electrodes). The zinc anode had 5% Teflon binder and no mercuric oxide. The cell was charged and discharged at 500 mA ($100\ mA/in^2$). As shown in Table II, the cell rapidly lost capacity in three cycles. No shorts were detected since the open circuit potential was a normal 1.41 V after an overnight charged stand. In addition, the charging curve was smooth on each cycle; shorting produces an erratic charge curve.

After five cycles, the cell was modified by epoxy-cementing a lucite electrolyte reservoir on top of the cell. After the epoxy had set (overnight), the cell was vacuumed at 28" of mercury for five minutes to remove the entrapped gases in the anode and cathode compartments. Five cm^3 of 30% KOH were added to the cell (the concentration of the original electrolyte) and cycling was resumed. As shown in the table, 85% of the original capacity was restored in Cycle 6. However, after 5 cycles (Cycle 10), the capacity was down to the original low level and cycling was stopped. Dissection of the cell showed that no zinc had penetrated the separator layers. It appeared that the cell failed by dryout due to overcharge and insufficient electrolyte transport through the separator system.

ZA-693 and ZA-694 were constructed with an extra layer of Pellon interseparator in the anode and cathode compartments and a 10 cm^3 reservoir above the electrodes. ZA-693 had the same main separator as ZA-692, while ZA-694 had the layer of 10 mil Huyck nickel felt sandwiched between two layers of 3 mil fibrous sausage casing (Union Carbide). The initial cycling data of both cells, as shown in Table II, indicate an improvement in capacity over ZA-692. However, both cells failed in eight cycles. Vacuuming the cells raised the capacity to some extent, which indicates that the cells were still electrolyte starved - possibly in the negative compartment during charge since the anode is the active electrode during charge.

Table II. Performance Data of Unit Zinc-Air Cells

CELL NUMBER	CYCLE NUMBER	Ah (in)	Ah (out)	COMMENTS
ZA-691	1	6.00	2.25	partial short
	2	6.00	0.00	dead short
ZA-692	1	6.00	2.70	none
	2	6.00	1.40	no shorts
	3	4.60	1.00	no shorts
	4	4.60	0.75	no shorts
	5	4.60	0.50	no shorts
	6	4.60	2.25	cell modified
	7	4.60	2.00	none
	8	4.60	1.75	none
	9	4.60	1.20	none
	10	4.60	0.70	none
ZA-693	1	4.60	2.75	none
	2	4.60	2.20	none
	3	3.50	1.90	cell vacuumed
	4	3.50	2.10	none
	5	3.50	1.85	none
	6	3.50	1.35	none
	7	3.50	1.05	none
	8	3.50	0.90	none
ZA-694	1	3.50	2.90	none
	2	3.50	2.50	none
	3	3.50	1.85	none
	4	3.50	1.55	none
	5	3.50	1.25	none
	6	3.50	1.95	cell vacuumed
	7	3.50	1.50	none
	8	3.50	1.10	none
ZA-695	1	7.00	5.50	none
	2	7.00	5.60	none
	3	7.00	5.50	none
	4	7.00	5.50	none
	5	7.00	5.50	5 cm^3 of water added
	6 → 9	7.00	5.50 → 4.50	none
	10	7.00	4.25	5 cm^3 of water added
	11 → 14	7.00	4.10 → 3.70	none
	15	7.00	3.45	5 cm^3 of water added
	16 → 19	7.00	3.00 → 1.90	none
	20	7.00	1.40	100 ppm of Pt found in zinc anode

Table II. Performance Data of Unit Zinc-Air Cells (Cont)

CELL NUMBER	CYCLE NUMBER	Ah (in)	Ah (out)	COMMENTS
ZA-711	1	8.50	5.90	none
	2	6.50	5.50	none
	3	6.50	2.80	none
	4	6.50	0.70	none
ZA-712	1	5.2	3.90	none
	2	4.2	4.00	none
	3→11	2.5	2.50	partial shorts to 3rd electrode
	12	4.2	3.65	cell vacuumed and 2 cm^3 of water added
	13	4.2	3.60	none
	14→24	2.5→2.3	2.50	none
	25	4.2	3.40	cell vacuumed and 2 cm^3 of water added
	26	4.2	3.45	none
	27→38	2.5	2.5→1.5	heavy shorts to 3rd electrode
	39	4.2	2.20	cell vacuumed and 5 cm^3 of water added
	40	4.2	2.75	none
	41→48	2.5	2.3→1.3	none
	49	4.2	2.10	cell vacuumed and 5 cm^3 of water added
	50	4.2	2.45	none
ZA-713	1	7.00	6.75	none
	2	7.00	6.70	none
	3→18	3.50	3.50	none
	19	7.00	5.10	5 cm^3 of water added
	20	7.00	5.70	none
	21→29	3.50	3.50	none
	30	7.00	4.85	2 cm^3 of water added
	31	7.00	5.00	none
	32→40	3.50	3.50	none
	41	7.00	4.70	5 cm^3 of water added
	42	7.00	4.75	none
	43→48	3.50	3.50	none
	49	7.00	4.00	3 cm^3 of water added
	50	7.00	3.90	none
ZA-714	1	7.00	6.00	none
	2	7.00	4.50	none
	3→10	3.50	3.3→0.8	none
	11	7.00	1.25	5 cm^3 of water added
	12	7.00	1.00	none
	13→18	3.50	0.9→0.4	none
	19	7.00	0.60	5 cm^3 of water added
	20	7.00	0.55	none

Table II. Performance Data of Unit Zinc-Air Cells (Cont)

CELL NUMBER	CYCLE NUMBER	Ah (in)	Ah (out)	COMMENTS
ZA-715	1	7.00	6.50	none
	2	7.00	6.75	none
	3→10	3.50	3.5→2.4	none
	11	7.00	2.50	5 cm^3 of water added
	12	7.00	2.40	none
	13→18	3.50	2.4→1.0	none
	19	7.00	1.10	5 cm^3 of water added
	20	7.00	1.10	none

NOTE: All cells listed in Table II were charged and discharged at 500 mA.

ZA-695 was constructed with the following design features:

(1) 1/8" wide channels were located on the bottom and sides of the anode.

(2) The zinc density was reduced from 2.0 to 1.7 g/cm^3.

(3) Two layers of Pellon in the anode and cathode compartments.

(4) A 10 cm^3 reservoir above the electrodes.

As shown in Table II, the capacity maintenance of the cell was good for about 15 cycles (all cycles were at 100% depth of discharge). This performance indicates an improvement in electrolyte transport and cell irrigation. Cross-sectional drawings of the cell are shown in Figure 2, which include top, side, and front views.

The E-I curves of ZA-695 are shown in Figure 3. Here the anode and cathode half-cell potentials are plotted versus a mercury-mercuric oxide reference electrode. The capacity maintenance curve and design data are shown in Figure 4. After 15 cycles, the capacity dropped very rapidly and cycling was stopped at 20 cycles. The cell was dissected and the anode was analyzed for platinum by X-ray spectrometry. Over 100 parts per million of platinum were detected in the zinc oxide. This large quantity of platinum is believed to be sufficient to induce rapid self-discharge by local action and should account for a major portion of the capacity fall-off of ZA-695. Platinum attack of the zinc anode has been reported by other investigators to be responsible for zinc-air cell failures.[6,7] It is apparent that an air-cathode must be employed in which the catalyst is electrochemically compatible with zinc. For that reason, the investigation proceeded towards the use of silver-amalgam air-cathodes.

NOTE:
NOT IN SCALE.

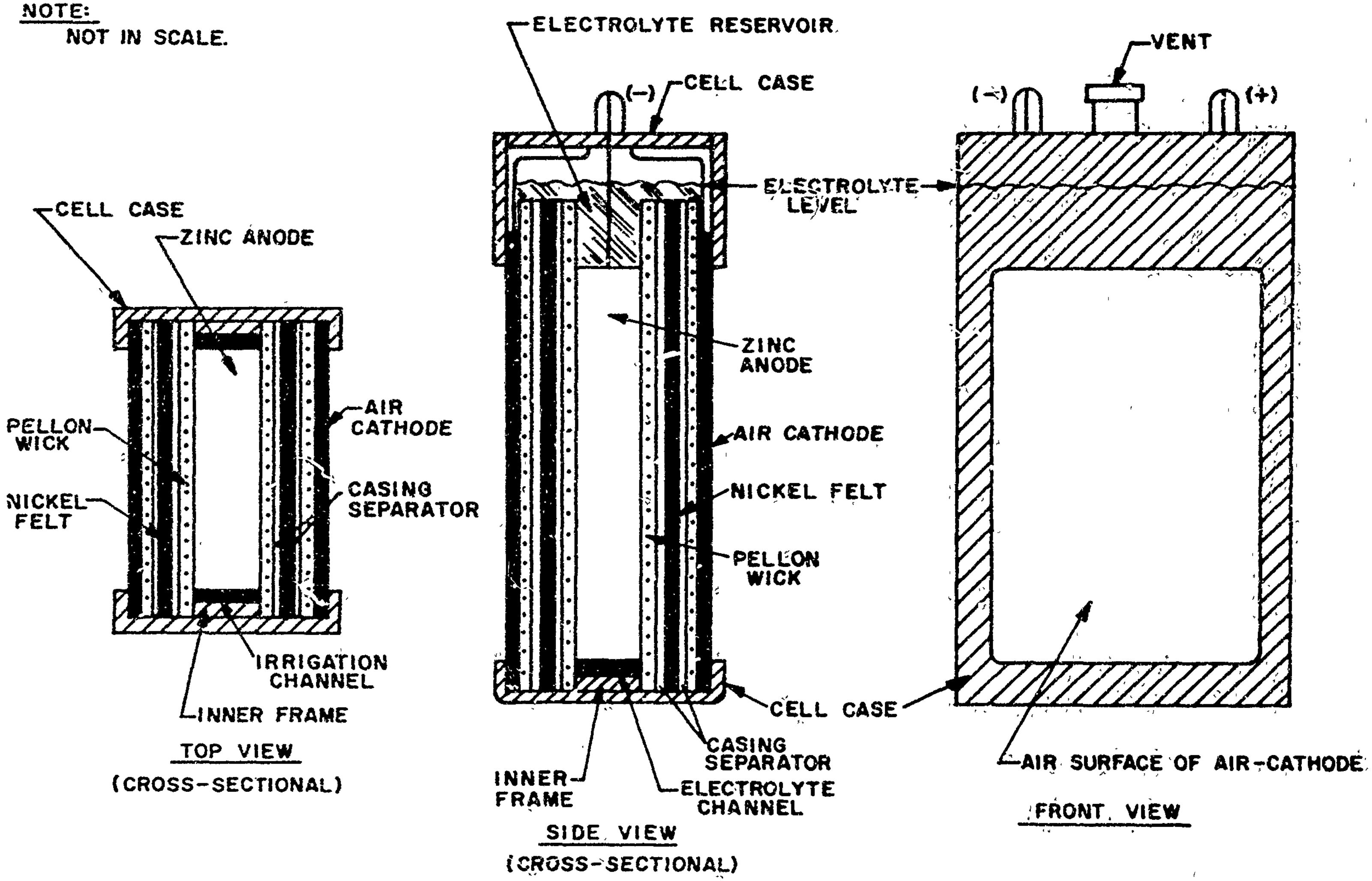


FIG.2 CROSS-SECTIONAL VIEWS OF ZA-695 A PLATINUM CATALYZED BIFUNCTIONAL ZINC-AIR CELL.

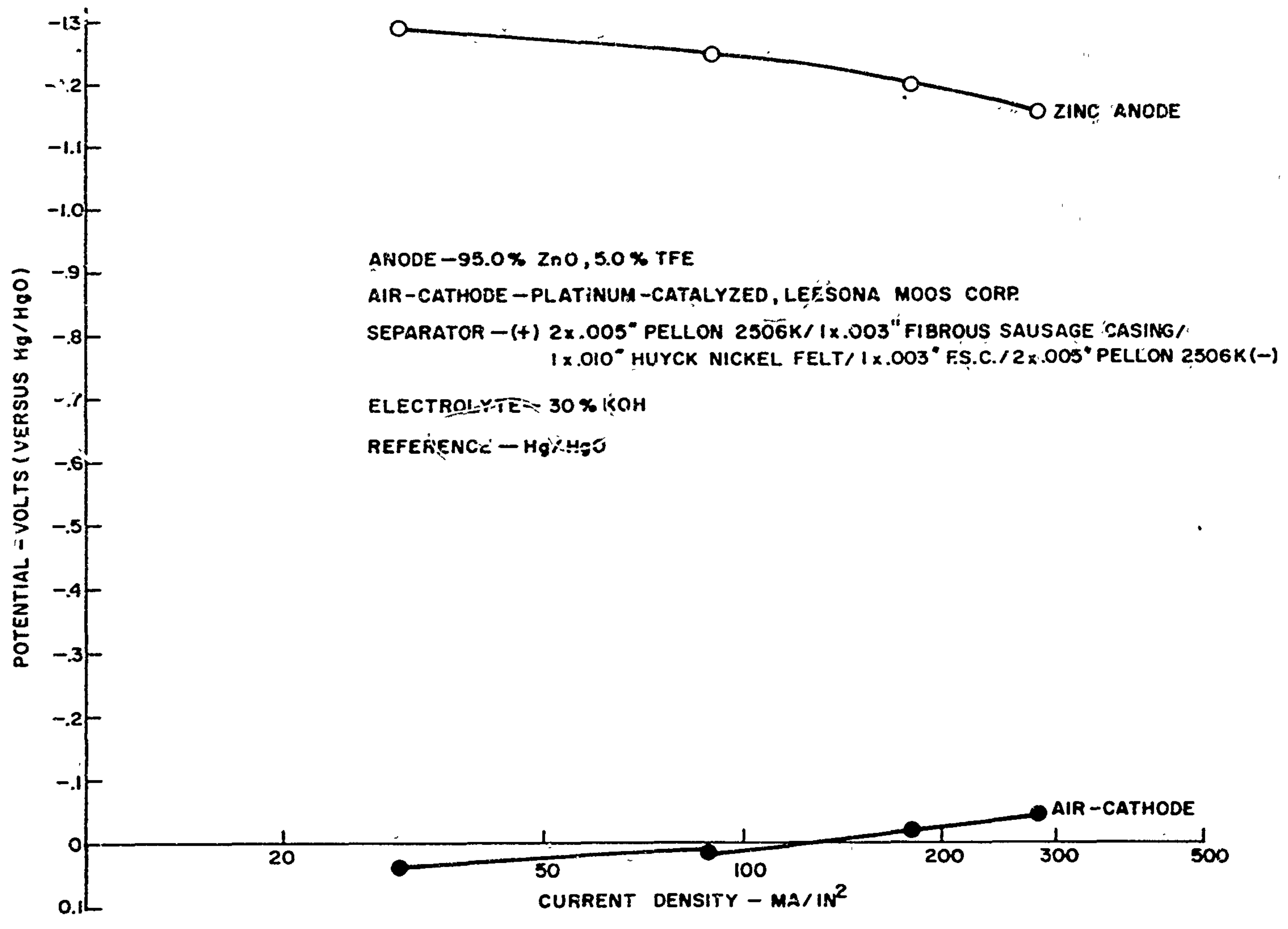


FIG. 3 E-I CURVES OF ZA-695

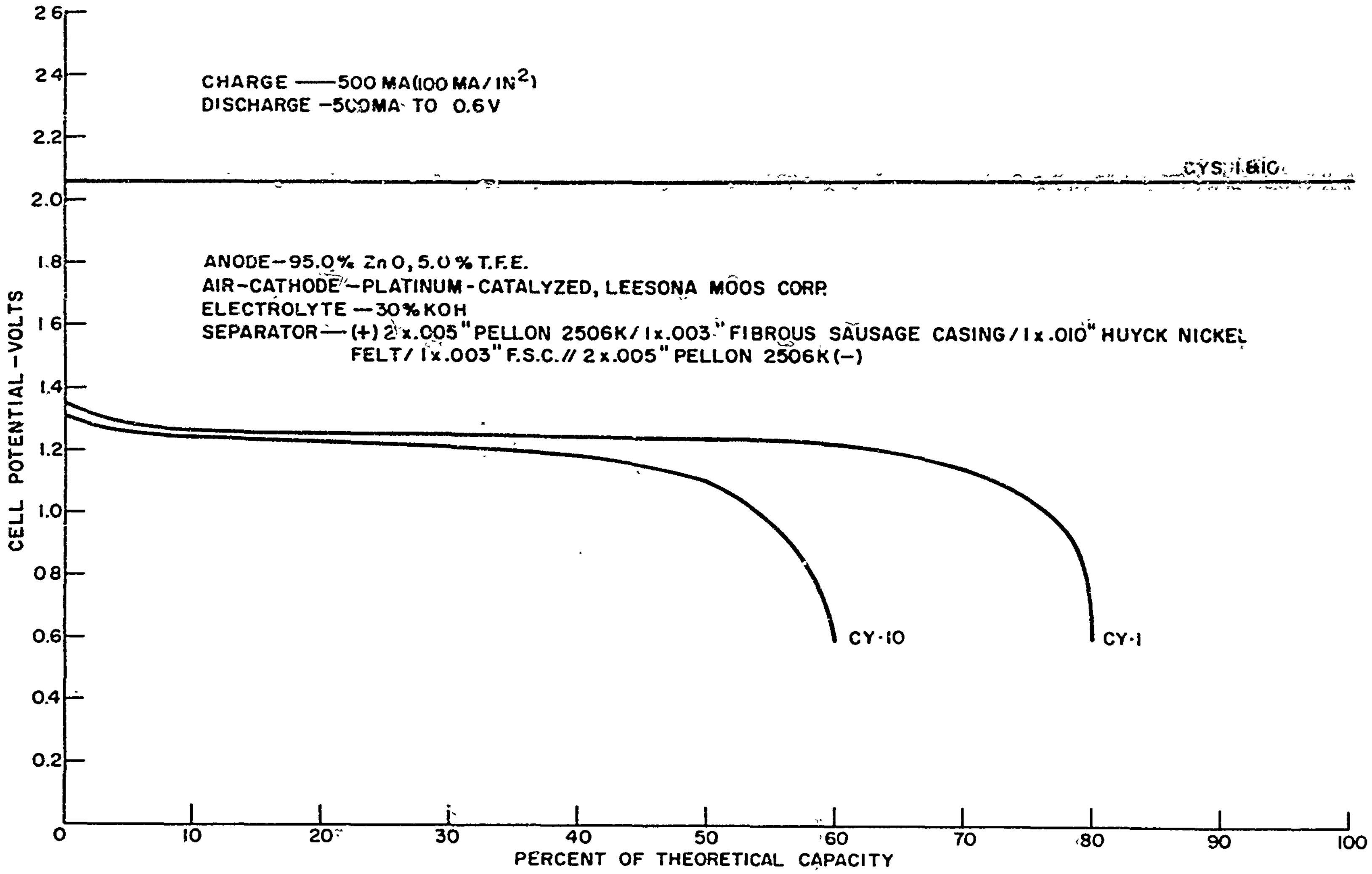


FIGURE 4 CHARGE AND DISCHARGE CURVES OF ZA-695 (CYCLES 1 AND 10)

Monofunctional Zinc-Air Cells

The silver-amalgam zinc-air cells are monofunctional; i.e., the silver-amalgam air-cathodes can only be used for discharging. Charging will destroy the catalytic action of the cathode. Therefore, an auxiliary or a third charging electrode is required in the cell, usually an expanded nickel screen. ZA-711 was constructed with an Allis-Chalmers silver-amalgam electrode opposite one face of the zinc anode and a 5 Ni 7-2/0 nickel Exmet charging screen (electrode) opposite the other anode face. The irrigation and reservoir arrangement was similar to that of ZA-695. The nickel felt-sausage casing separator combination was located between the anode and nickel Exmet screen, while only one layer of casing, sandwiched between two layers of Pellon 2506K, was located between the anode and air-cathode.

As shown in Table II, ZA-711 rapidly lost capacity after two cycles. It was noted that the third electrode promoted dryout of the cell, since the electrolyte level dropped from about 1/2" above the electrodes to the top edge of the electrodes after a vacuum treatment. The dryout was believed to be due to oxygen entrapment in the charging compartment which usually occurs when overcharging a secondary cell with a tightly packed separator system. An obstruction-free path is essential as oxygen evolves through the electrolyte in the charging compartment. Another shortcoming of the ZA-711 design was that the zinc anode contained a significant amount of uncharged zinc oxide on the face opposite the air-cathode. Therefore, it was necessary to charge the anode on both faces, as well as to provide bubble-free electrolyte paths for the charging electrodes.

ZA-712 was designed and built with the above mentioned modifications. The main design features were:

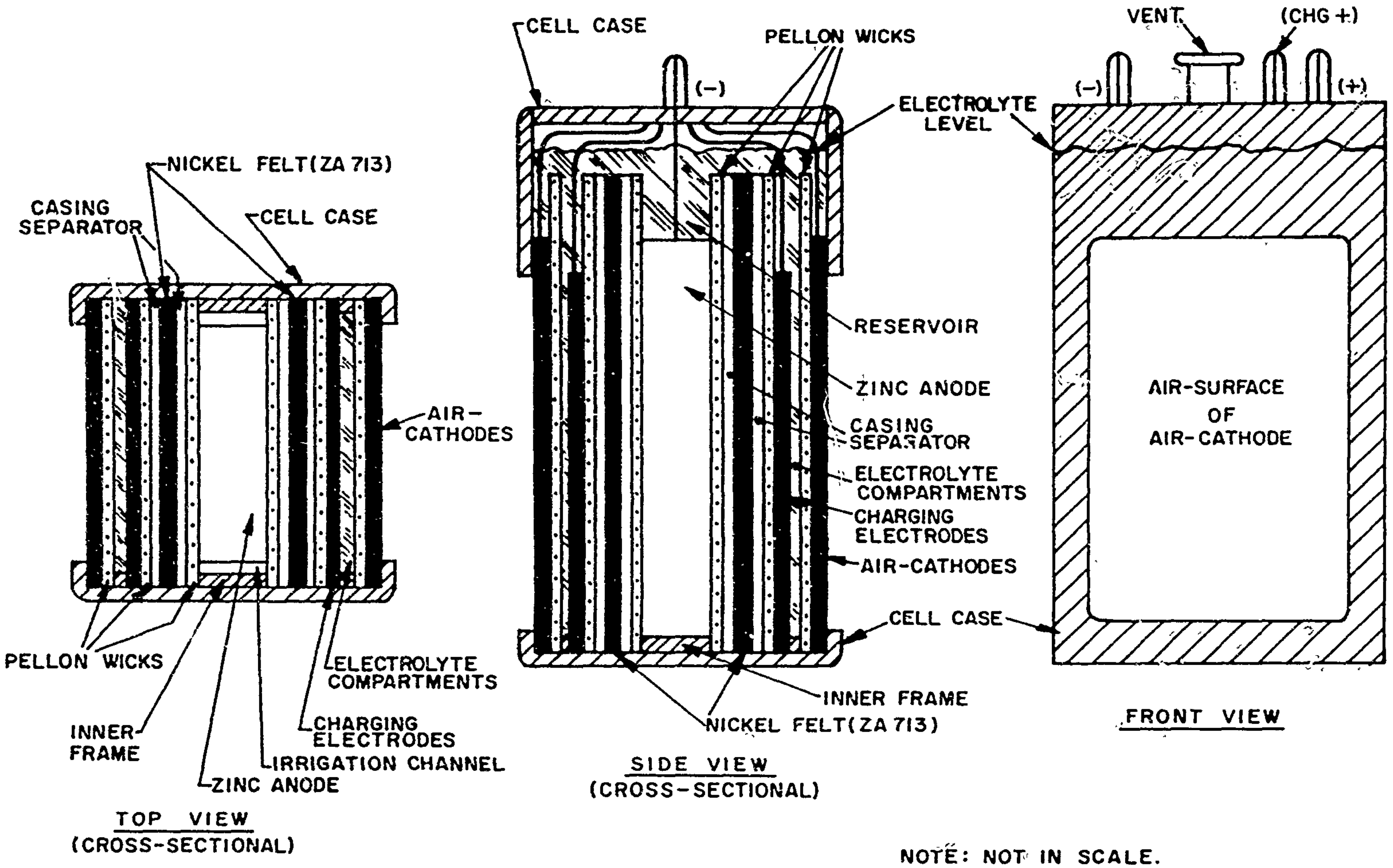
(1) 30 mil Teflon spacers, 1/16" wide, were located between the charging electrode and Pellon 2506K clad silver-amalgam electrodes. The spacers were situated 1/2" apart and were positioned in the vertical direction.

(2) The nickel Exmet (5 Ni 7-2/0) charging electrodes were located between the zinc anode and the two air-cathodes.

(3) The main separator consisted of two layers of fibrous sausage casing. The nickel felt was omitted to determine the effectiveness of the charging electrode in preventing zinc penetration shorts to the air-cathodes.

(4) 1/8" irrigation channels on the bottom and sides of the zinc anode and a 10 cm^3 reservoir above the electrodes.

Cross-sectional views of ZA-712 and ZA-713 are shown in Figure 5. E-I curves were obtained for ZA-712 and are plotted in Figure 6. The half-cell potentials are plotted versus an Hg/HgO reference electrode. Cycling was at 50% depth of theoretical capacity with two 100% deep discharges every 10 cycles. Capacity maintenance data are shown in Figure 7 in the form of discharge curves for Cycles 1, 25, and 50.



NOTE: NOT IN SCALE.

FIG. 5 CROSS−SECTIONAL VIEWS OF ZA−712 & ZA−713
SILVER−AMALGAM CATALYZED
MONOFUNCTIONAL ZINC−AIR CELLS

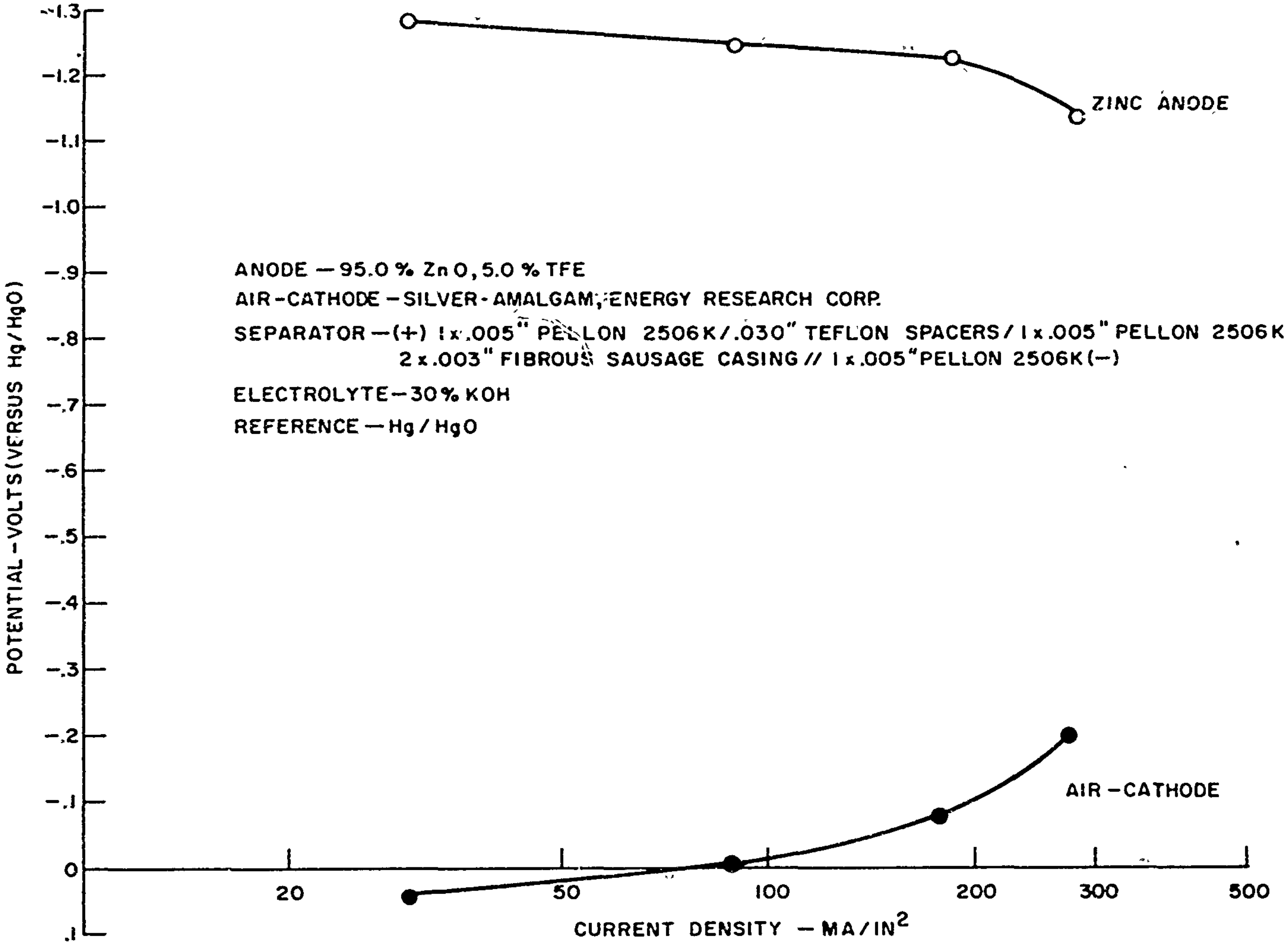


FIGURE 6 — E-I CURVES OF ZA-712

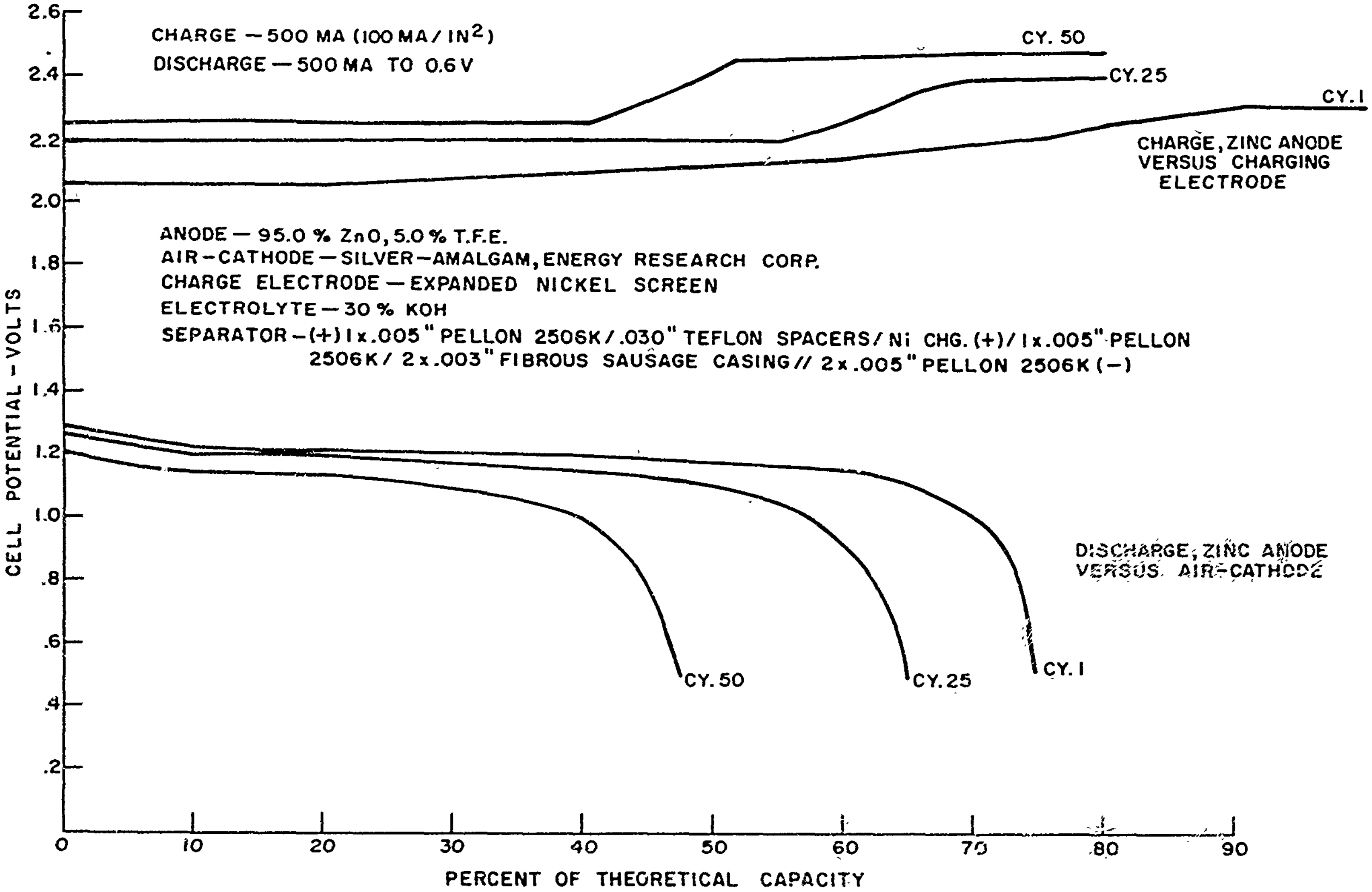


FIG. 7 CHARGE AND DISCHARGE CURVES OF ZA-712
(CYCLES 1, 25 AND 50)

Figure 7 also lists the pertinent design details. Partial shorts between the charging electrodes and zinc anode were noted after 7 cycles. These shorts became heavy after 25 cycles. However, there were no shorts between the anode and air-cathodes. This shows the effectiveness of the third electrode in preventing "dead shorts" between the anode and air-cathodes, although the capacity will be somewhat erratic from cycle to cycle.

Another problem with this cell was that the anode (readings versus a NiOOH reference electrode) was severely polarized during discharge after a 10 cycle shallow regime. This was corrected by a vacuum treatment prior to deep discharging. This polarization is attributed to hydrogen entrapment in the anode due to premature gassing on charge. This is usually corrected by amalgamation.

None of the anodes in the zinc-air cells up to ZA-712 were amalgamated since amalgamation promotes shape change. However, since mercury prevents hydrogen evolution on stand and during charge, amalgamation was employed in later designs. In the main, ZA-712 showed an excellent capacity maintenance curve and was the basis of a working model for later cell designs.

ZA-713 was constructed in a similar manner as Cell ZA-712, except that the anode contained 0.5% mercuric oxide to prevent premature hydrogen evolution, and a 10 mil layer of Huyck nickel felt was placed between the two layers of fibrous sausage casing. (See the drawings in Figure 5 for further details.) The cycling regime of ZA-713 was similar to that of ZA-712. E-I curves are plotted in Figure 8 and the capacity maintenance curves are shown in Figure 9 as charge and discharge curves for Cycles 1, 30, and 50. The figure also includes other pertinent design details. Although the closed circuit potentials of ZA-713 are slightly lower than that of ZA-712, its capacity maintenance is significantly better. In addition, no shorting was noted and polarization of the anode was minimal in that vacuuming was not required. Cycling was stopped after 50 cycles to examine the cell. There were no shorts and the anode had exhibited only a 10-15% change in shape along the top edge. With ZA-713, the limitations of ZA-712 had been overcome and a better working model had been established.

Monofunctional Versus Bifunctional Platinum-Catalyzed Zinc-Air Cells

It was of interest to compare the performance of platinum-catalyzed zinc-air cells which were cycled bifunctionally and monofunctionally, i.e., with a third charging electrode. All the earlier cells with platinum electrodes had been cycled bifunctionally and the platinum attack on the zinc anode was a serious problem. It was thought that perhaps on a monofunctional regime the platinum attack would be eliminated or reduced to a safe level, since platinate ions are usually formed during anodization. In addition, any loosely adherent particles of platinum are scrubbed off during anodization and then transported to the negative compartment over the top of the separator layers.

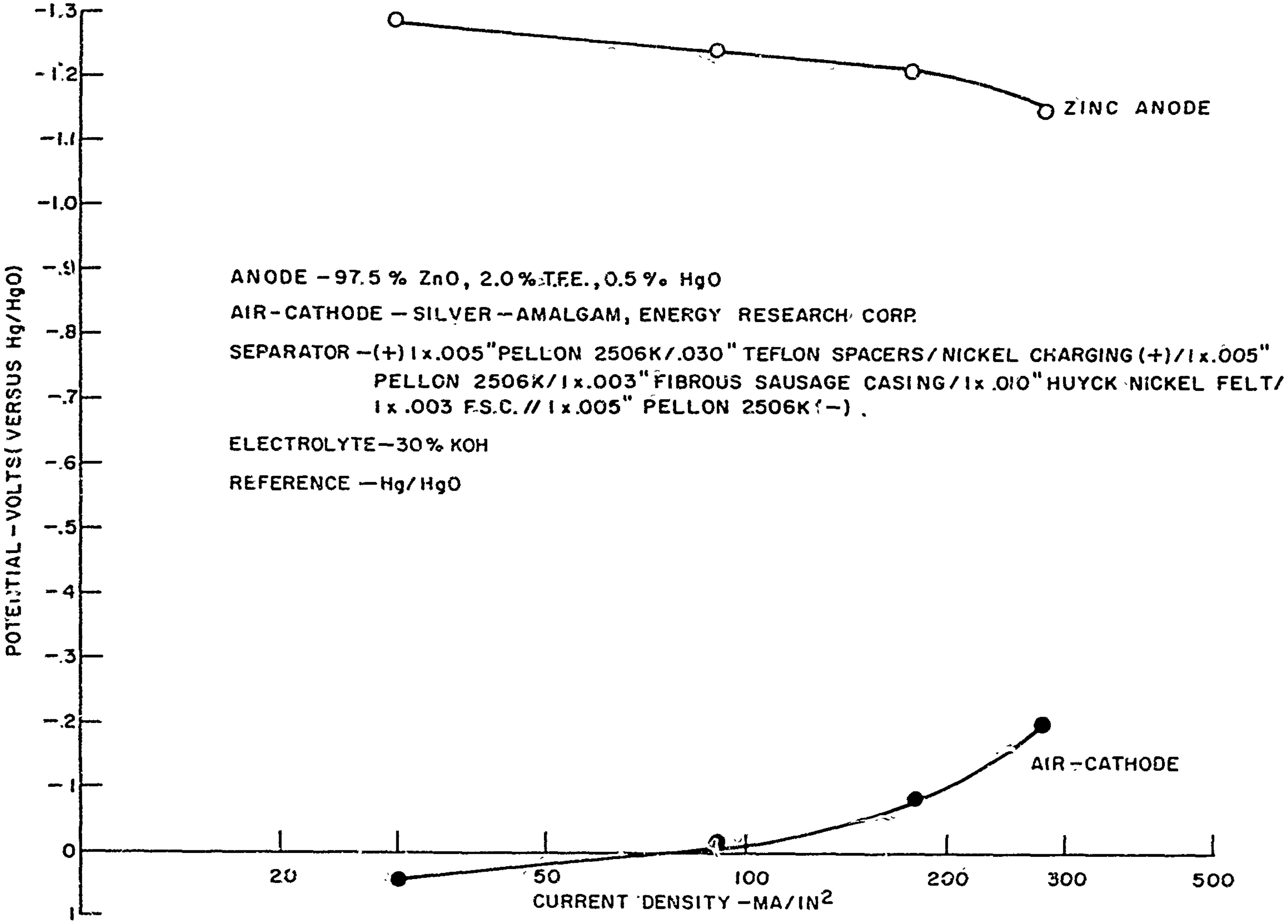


FIGURE 8 E-I CURVES OF ZA-[illegible]13

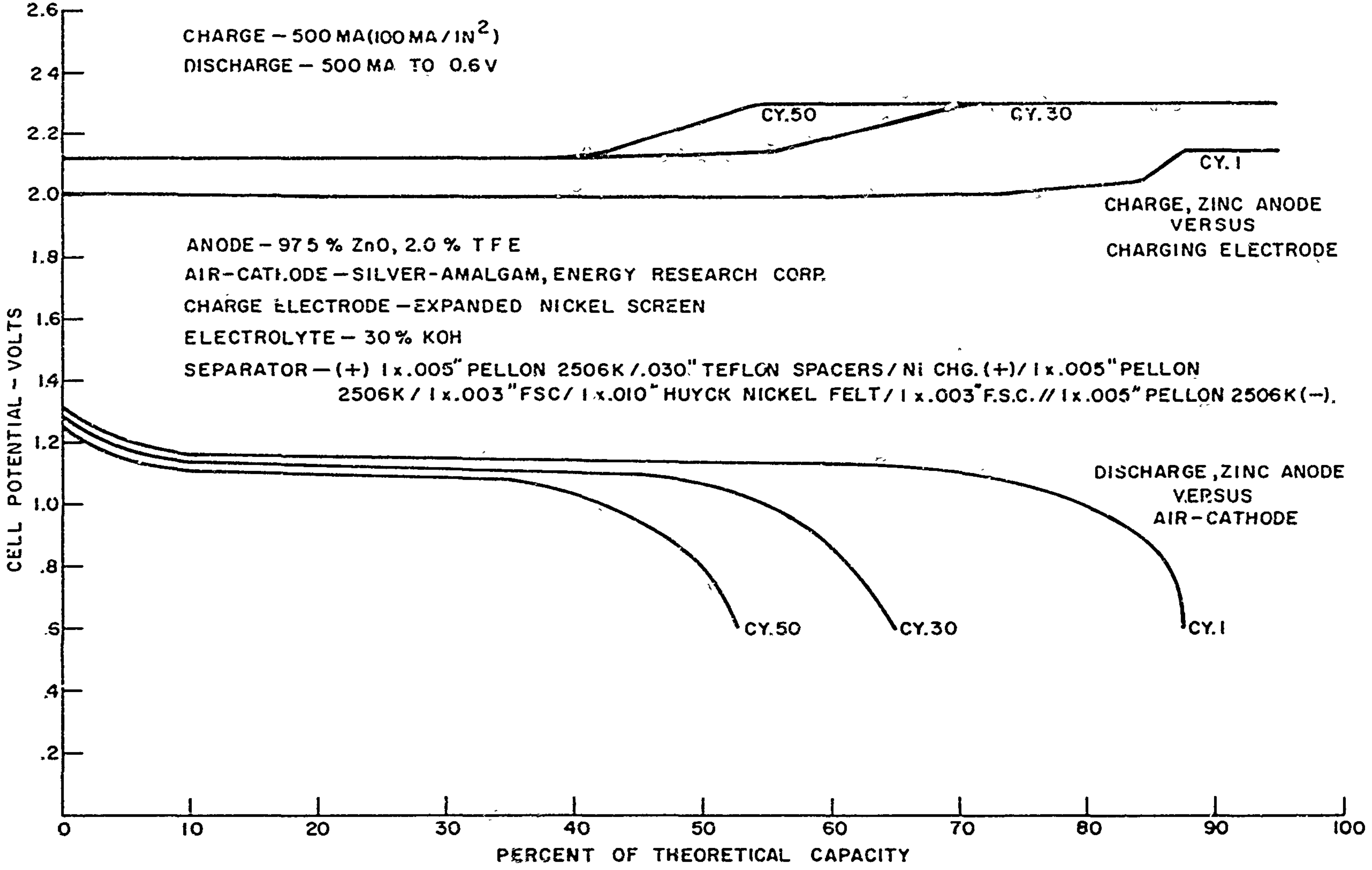


FIGURE 9 CHARGE AND DISCHARGE CURVES OF ZA-713
(CYCLES 1, 30 AND 50)

ZA-714, the bifunctional cell, was constructed with two Leesona Moos platinum air-cathodes (no third electrode), a main separator consisting of a 10 mil layer of Huyck nickel felt sandwiched between two layers of Energy Research ER 1001 (a ceric-oxy-hydroxide type inorganic membrane), and an anode similar to that of ZA-713. The Energy Research inorganic separator, as well as the Astropower inorganic membranes of earlier designs, were introduced for the purpose of evaluating materials that resist oxidative attack, since the cellulosics are very susceptible to degradative attack by oxygen, peroxyl ions, and KOH.

ZA-715, the monofunctional cell, was constructed with two Leesona Moos platinum air-cathodes, two nickel Exmet charging electrodes, a main separator of two layers of fibrous sausage casing sandwiching a 10 mil layer of Huyck nickel felt, and an anode as per ZA-713 and ZA-714.

The closed circuit potentials of ZA-714 and ZA-715 were similar. However, as shown in Table II, the drop in capacity of both cells was rapid - the decrease in capacity being much greater for ZA-714, the bifunctional cell. A comparison of the capacity maintenance curves of ZA-712 - 715 is shown in Figure 10. The detrimental effect of platinum is best illustrated by comparing the curves of ZA-713 and ZA-715, which are designed alike, except for the air-cathodes; the former being silver-amalgam and the latter, platinum. Even on a monofunctional regime, the platinum-catalyzed zinc-air cell (ZA-714) was very poor in performance. This is mainly attributed to platinum attack of the zinc anode which is accelerated by the flooded conditions of these cells.

Zinc Shape Change Studies

This problem, although not catastrophic, is very serious. Even the best cells evaluated (ZA-712 and ZA-713) exhibited about 10-15% change in shape, mainly on the top edge of the anode. In addition, the anode thickness in the center region increased about 25%.

To study the shape change problem in a more simplified electrochemical system, single electrode nickel-zinc cells were constructed with one test zinc anode situated between two nickel-hydroxide cathodes. The separator wrap consisted of one layer of polyamide Pellon 2506K on the positive electrodes and one layer of fibrous sausage casing on the negative electrode in the form of an accordion wrap. Construction and testing details may be found in the Experimental Procedures Section. Cycling was rapid, i.e., charging at 500 mA for 1-1/4 hours followed by a 500 mA discharge to a 0.6 V cutoff.

Five cells were evaluated. The design variables and cycling data are shown in Table III. The first cell, NZ-691, was a control for NZ-692. The anodes were pressed to a contour of about 30%, i.e., the center was 22 mil thick and the edges were 32 mil thick. The test electrode (NZ-692) was flattened to 22 mil throughout after contouring so that the periphery was densified. Therefore, while the NZ-691 anode was contoured and possessed an average porosity of 72%, the porosity of the NZ-692 anode was 60% at the periphery and 72% at the center. The cycling data of the two cells are shown in Figure 11, as well as in Table III.

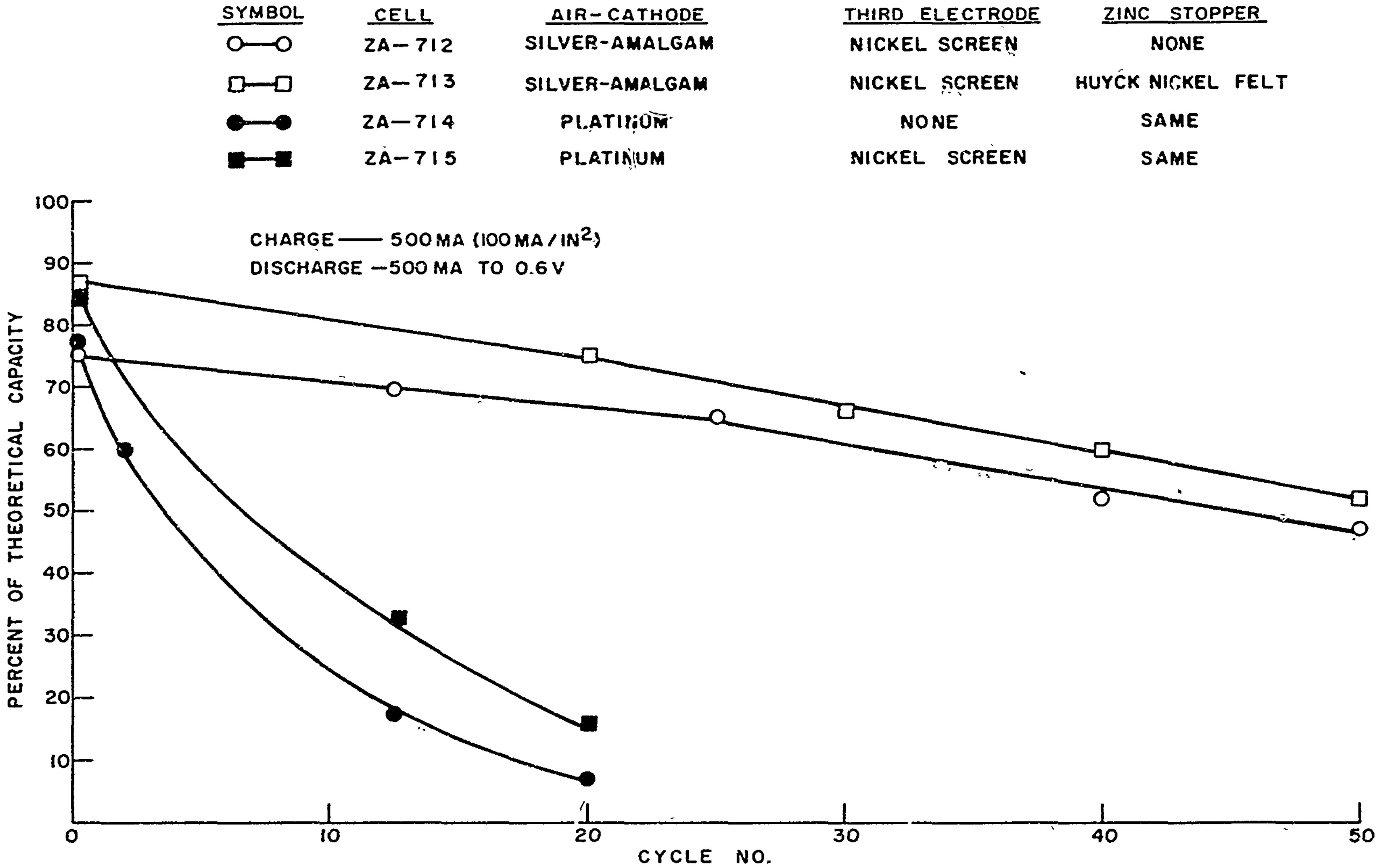
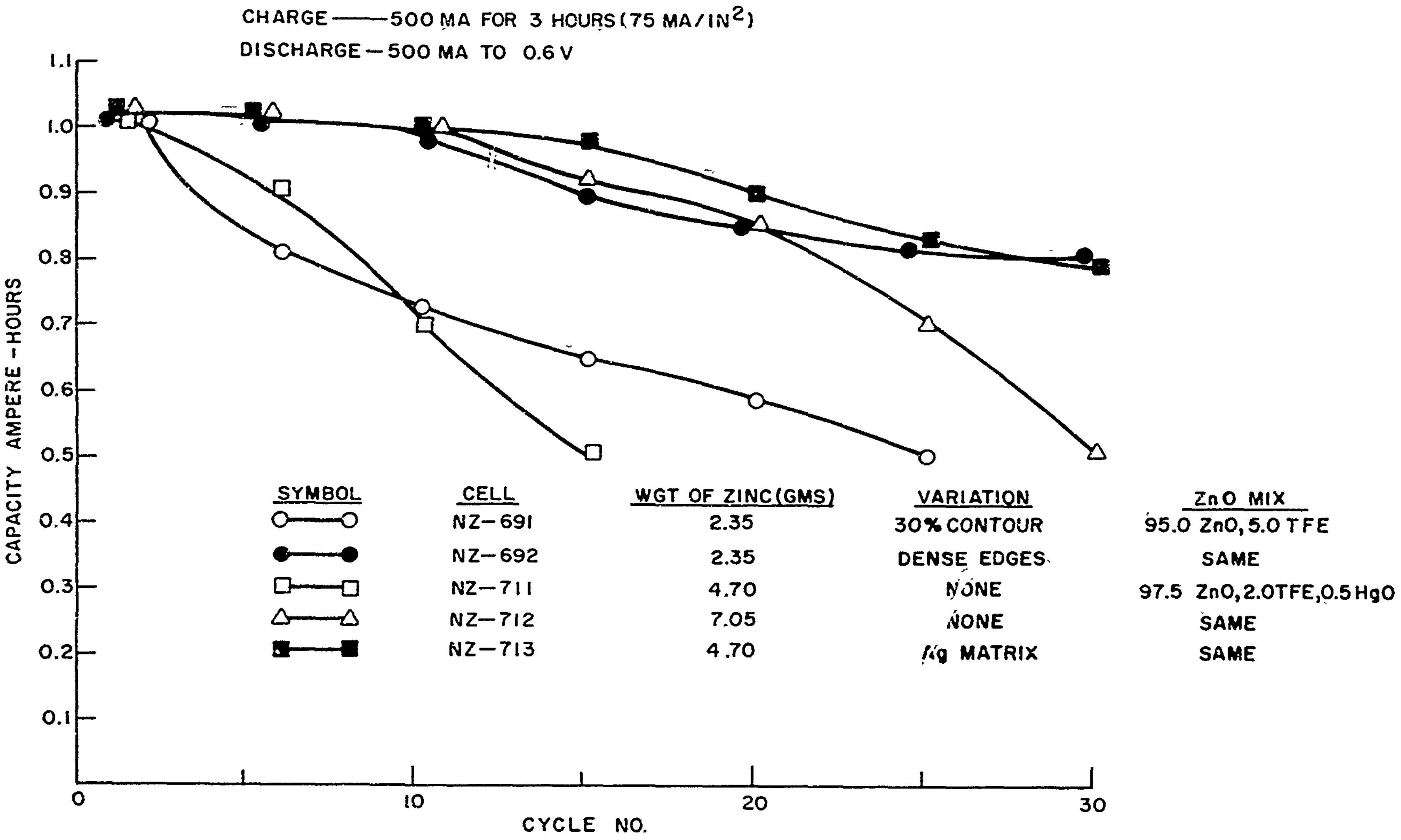


FIGURE 10 CAPACITY MAINTENANCE CURVES OF ZA'S 712, 713, 714 AND 715



SYMBOL	CELL	WGT OF ZINC (GMS)	VARIATION	ZnO MIX
○—○	NZ-691	2.35	30% CONTOUR	95.0 ZnO, 5.0 TFE
●—●	NZ-692	2.35	DENSE EDGES	SAME
□—□	NZ-711	4.70	NONE	97.5 ZnO, 2.0 TFE, 0.5 HgO
△—△	NZ-712	7.05	NONE	SAME
■—■	NZ-713	4.70	Ag MATRIX	SAME

FIGURE 11 CAPACITY MAINTENANCE CURVES OF VARIOUS TYPES OF ZINC ANODES

Table III. Zinc Electrode Studies

	NZ-691 (Control #1)	NZ-692 (Dense Edges)	NZ-711 (Control #2)	NZ-712 (Control #3)	NZ-713 (Ag Matrix)
Weight of Zinc (g)	2.35	2.35	4.70	7.05	4.70
Zinc Mixture	95 Zn + 5 TFE	95 Zn + 5 TFE	97.5 Zn + 0.5 HgO + 2.0 TFE	97.5 Zn + 0.5 HgO + 2.0 TFE	97.5 Zn + 0.5 HgO + 2.0 TFE

CYCLE NUMBER	NZ-691 (Ah)	NZ-692 (Ah)	NZ-711 (Ah)	NZ-712 (Ah)	NZ-713 (Ah)
1	1.02	1.03	1.01	1.03	1.03
5	0.81	1.03	0.90	1.03	1.03
10	0.70	1.00	0.70	1.00	1.00
15	0.65	0.90	0.50	0.92	0.98
20	0.59	0.85	----	0.85	0.90
25	0.50	0.83	----	0.70	0.83
30	----	0.82	----	0.50	0.79

It is apparent that densifying the anode edges significantly improves the capacity maintenance of the nickel-zinc cell. Reference readings (NiOOH reference) showed that both cells were positive limiting on discharge for every cycle. Examination of the anodes after cycling showed that shape change was about 50% for the control and 35% for the test electrode. These results show that edge corrosion can be significantly reduced by edge densification of the anode, which results in a significant increase in cell capacity.

Cells NZ-711, NZ-712, and NZ-713 were designed to determine the effect of a silver foam as an anode matrix on cell performance. NZ-711 and NZ-712, the controls, had no matrix. The former contained 4.70 g of zinc and the latter contained 7.05 g. The test cell, NZ-713, also contained 4.70 g of zinc and a silver foam matrix of 94% porosity (unfilled) manufactured by the General Electric Metallurgical Division in Detroit, Michigan. None of the anodes in these cells were contoured and the average anode porosity was 75%. These cells were cycled as per NZ-691 and NZ-692. The cycling data are shown in Table III and Figure 11. The control cell (NZ-711) with the same weight of zinc as the NZ-713, lost 50% of its initial capacity in 15 cycles. The control with 50% more zinc (NZ-712) lost 50% of its capacity in 30 cycles. The test cell (NZ-713) lost only 23% of its capacity in the same 30 cycles. In all cases, the cells were positive limiting on discharge. Dissection of the cells showed that the shape change was about 40% for NZ-711, 30% for NZ-712, and 35% for NZ-713. All electrodes had expanded about 15% in thickness.

It was noted that both controls had a surface layer of dense metallized zinc (all electrodes were in the discharged state). The surface of the test electrode was in the oxide state and appeared very spongy. It seems that while the silver matrix does not prevent shape change, it overcomes the surface densification effect that results from edge corrosion. By allowing the surface to remain porous, electrolyte transport is not blocked to the active material underneath the surface layers. Therefore, a greater utilization of active material is attainable in a zinc anode matrixed with silver.

Paper Design of a 25 Ah Zinc-Air Cell

The zinc-air cells employed in this program were only test vehicles used for the purpose of arriving at an optimum design. The energy densities of these cells were rather low, that is, in a range of 30 to 40 Wh/lb. These values can be doubled by: (1) using the design parameters of the best cell, ZA-713, (2) increasing the nominal capacity from 5 to 25 Ah, (3) reducing the internal free space for electrolyte, and (4) employing a lightweight cell case.

Assuming a zinc utilization of 0.50 Ah/g (60% of theoretical capacity), an anode thickness of 125 mil, a width of 3", and a zinc porosity of 78%, the anode will have a weight of 54 g in the charged state which includes a 5 Ag 15-2/0 silver Exmet grid plus a 5 mil silver tab. The anode height will be 5-1/4". From this configuration, the following weight and dimensional data of the 25 Ah zinc-air cell are derived:

(1)	Height of cell (with terminals)	7-1/4"
(2)	Width of cell	3-3/4"
(3)	Thickness of cell (with two 200 mil nylon Vexar air spacers	.500"
(4)	Weight of anode (charged)	54.0 g
(5)	Weight of two silver-amalgam air-cathodes plus 5 mil silver tabs (.020" x 5-1/4" H x 3" W)	23.0 g
(6)	Weight of two nickel charging screens plus 5 mil nickel tabs (.010" x 4-3/4" H x 3" W)	6.0 g
(7)	Two Huyck nickel felt layers (.010" x 5-1/2" H x 3-1/2" W)	12.0 g
(8)	Four layers of sausage casing (.003" x 5-3/4" H x 3-1/2" W)	4.5 g
(9)	Six layers of polyamide Pellon 2506K (.005" x 5-3/4" H x 3-1/2" W)	3.0 g
(10)	Fifteen Teflon spacers (.020" x 1/16" W x 5" H)	2.1 g
(11)	Cell case plus cover	30.0 g
(12)	Air spacers	10.0 g
(13)	40 cm^3 of 30% KOH electrolyte	52.0 g
(14)	Other (epoxy, terminals, etc.)	10.0 g
	TOTAL (wet cell weight)	206.6 g
		(0.405 lb)

(15)	Volume of cell	13.6 in^3
(16)	C/10 Capacity	25 Ah (60% of theoretical)
(17)	C/10 Closed Circuit Voltage	1.20 V
(18)	Energy	30 Wh
(19)	Weight Energy Density	75 Wh/lb
(20)	Volumetric Energy Density	2.2 Wh/in^3

The weight and volumetric energy densities are reasonable estimates for a zinc-air cell of nominal 25 Ah capacity. Actually on Cycle 1, the capacity will be about 33 Ah. By Cycle 25, it should be 27 Ah and at Cycle 50, 22 Ah.

CONCLUSIONS

Shorting of zinc-air cells by zinc penetration can be prevented by placing a layer of porous low hydrogen overpotential material, such as nickel felt, in the layers of separator material.

Passivation of the zinc anode by electrolyte starvation is minimized by: (a) placing 30 mil spacers in the charging compartment, (b) locating an electrolyte reservoir above the electrodes, (c) providing narrow irrigation channels along the sides of the anode, and (d) using a polyamide Pellon wick in the anode compartment.

The use of platinum-catalyzed air-cathodes in a static, flooded zinc-air system is detrimental in that platinum is transported to the zinc anode and promotes rapid self-discharge by local action.

The use of silver-amalgam air-cathodes along with auxiliary charging electrodes is compatible with the alkaline zinc anode. By these means, good capacity maintenance was attained for at least 50 cycles.

The addition of 0.5% mercuric oxide into the active zinc prevents premature hydrogen evolution on charge and thereby minimizes polarization of the anode during discharge caused by dryout of the anode on charge.

Capacity lost by the zinc anode due to edge corrosion (shape change) and surface densification can be significantly reduced by using a sintered silver matrix of very high porosity, and densifying the periphery of the anode.

A paper design of a 25 Ah zinc-air cell indicates an energy density capability of 75 Wh/lb.

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