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TECHNICAL REPORT ECOM-0257-1

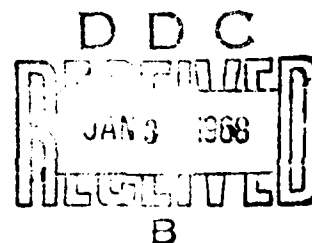
RECHARGEABLE METAL-AIR CELL

FIRST QUARTERLY REPORT

By

C. E. Kent and E. G. Siwek

DECEMBER 1967



ECOM

UNITED STATES ARMY ELECTRONICS COMMAND • FORT MONMOUTH, N.J.

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GENERAL ELECTRIC COMPANY
Schenectady, New York

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1 May 1967 to 31 July 1967

CONTRACT NO. DAAB 07-67-C0257
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Prepared By

C. E. Kent and E. G. Siwek
Electrochemical Systems Branch
Chemical Systems and Processes Laboratory
Research and Development Center
General Electric Company
Schenectady, New York

For

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ABSTRACT

Preliminary design calculations indicate potential energy densities of the following ranges for operating cells:

- Lead-Air 30 - 33 watthours/pound
- Cadmium-Air 35 - 45 watthours/pound
- Zinc-Air 30 - 60 watthours/pound

Principal technical problems associated with the battery systems under study are:

1. Obtaining maximum anode utilization in terms of ampere-hours per square foot of electrode geometric surface area during successive charge-discharge cycling.
- *2. Control of corrosion of the cathode (air electrode), particularly during the charge portion of the charge-discharge cycle.
3. Control of gases generated during the charge and discharge portions of the charge-discharge cycle.
4. Use of the air electrode (cathode), in alkaline electrolyte systems as a bifunctional electrode, i.e., as an electrode operable during both the charge and the discharge modes of the charge-discharge cycle.

In addition:

5. The Lead-Air system requires a low cost, non-platinum catalyst air electrode.
6. The Zinc-Air system requires the control of electrolyte migration during charge-discharge cycling.

* Lithiated nickel oxide coating of the nickel substrate of cathodes intended for use as bifunctional electrodes appears to be useful as a corrosion control device.

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Section 1

PROGRAM OBJECTIVES AND APPROACH

The objective of this program is to develop a rechargeable metal-air prototype battery that is an improvement over existing battery systems in terms of a combination of energy density, useful life, and cost. The metal-air battery will be directed toward use as a power source for portable military communications equipment.

The energy density design goals are 25 and 50 watthours per pound at -40°F and 80°F respectively when discharged at a C/5 rate. The cycle life capability goal is 500 continuous six-hour cycles at 80°F at a 60 percent depth of discharge using a C/4 discharge rate. End of life is defined as the point at which the cell capacity falls below 60 percent of its rated capacity.

The approach will center on zinc-air, cadmium-air, and lead-air cells. These three systems will be analyzed on a competitive basis with maximum emphasis placed on the limiting technical problems associated with each system. One of the three systems will be selected as most promising, optimized in terms of cell design, and tested. Prototype cells will be built and delivered.

Section 2

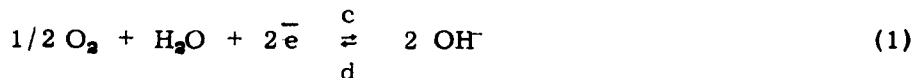
GENERAL BACKGROUND

CATHODE (AIR ELECTRODE) IN ALKALINE SYSTEMS

The high energy density capability of metal-air cells is primarily determined by the positive air electrode (cathode), which, unlike a conventional battery cathode does not store its oxidant internally, but converts the oxygen available from the ambient air and hydrogen from the electrolyte into the electrochemically active species, the hydroxyl ion. However, the weight of the air electrode is not negligible and must be considered in energy density calculations. In combination with an anode, which stores its active species internally and can be designed to yield a high specific capacity, the air electrode's weight contribution to cell weight becomes minimal. For this reason, the higher the specific capacity of the anode in a metal-air cell, the more favorable is the energy density of the cell.

Data obtained on a lightweight developmental single-sided* zinc-air cell illustrates the dependence of the energy density of the zinc-air cell on the energy density of the anode (Table 1). In all cases, the cathode weight assumed is identical. The volume and cost of the battery system can also be shown to depend primarily upon the specific capacity of the metal anode.

As stated previously, the capacity of the air electrode in an alkaline system is dependent upon its ability to manufacture hydroxyl ions during discharge. Its use as a bifunctional electrode in an alkaline system is also dependent upon its ability to convert hydroxyl ions to oxygen and water:



The water evolved during the charge portion of the cycle is returned to the electrolyte. The oxygen liberated from the air electrode during charging can oxidize the cathode substrate and the catalyst, particularly palladium and platinum. The oxidation of the substrate and catalysts alters the diameters of the discrete metal particles in the cathode, thus changing the cathode porosity and possibly damaging the wet proofing film.

As part of the evaluation program, nickel substrates will be tested as supporting cathode structures. Pre-oxidation of the nickel substrate prior to catalyst loading and waterproofing could avoid or minimize oxidation damage to the cathode during cell operation. Pre-oxidation of the catalysts,

* A single air electrode facing one side of the zinc anode.

Table 1

COMPARISON OF ZINC-AIR CELL ENERGY DENSITY
VERSUS ANODE SPECIFIC CAPACITY

Zinc Anode Specific Capacity		Watthours	Cell Energy Density Watthours/Pound
<u>Ampere-minutes/ Square Centimeter</u>	<u>Milliampere-hours/ Square Centimeter</u>		
1	17	0.67	18
3	50	2	40
6	100	4	60

such as platinum, which is the most stable catalyst oxide along with lithium doping to improve conductivity, is also suggested as a means for extending cathode life.

It is hoped that the above treatment of the cathode will result in a 500-cycle air electrode. If a 500-cycle air electrode cannot be achieved, it will be necessary to incorporate a separate charging electrode which will result in a weight penalty for the system. The charging electrode would be used to recharge the anode, thus sparing the cathode from possible oxidation damage because of oxygen evolution from the cathode during charging of the cell.

In order for an air electrode to be used successfully in an alkaline system, consideration must also be given to oxygen pressure developed within the cell particularly during charge.

Practical cell design indicates the advantage of a closed cell except for the air exposed gas diffusing cathode. During charge, this electrode (whether it is the cathode of a two electrode system operating as a bifunctional electrode or as a separate charging electrode) must allow oxygen to diffuse through it to the ambient without forcing electrolyte out of the cell. These considerations also emphasize the need for consistent hydraulic, catalytic, and electrical conductivity properties of the air electrode used either as a monofunctional or bifunctional electrode expected to function for 500 cycles.

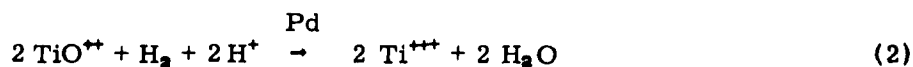
CATHODE (AIR ELECTRODE) IN ACID SYSTEMS

In addition to the parameters discussed in the previous subsection in an air (oxygen) electrode used in an acid electrolyte system, such as the lead-air cell, the following must be considered:

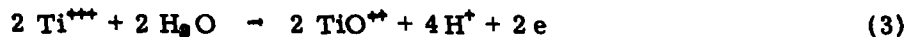
1. Platinum is required as a catalyst which precludes the use of a less expensive catalyst.
2. The acid electrolyte cannot, and this is an advantage, adsorb carbon dioxide from the air; hence, carbonate poisoning of the cathode is not probable.

CATHODE (REDOX TYPE) IN ACID SYSTEMS

To avoid the use of expensive platinum in the air electrode, consideration should also be given to the redox electrode. A redox electrode, in fuel cell terminology, is one which employs an intermediate couple to transfer the energy from the fuel or air reaction to the electrode. Thus, a titanium couple has been used to form a redox electrode for hydrogen. The hydrogen reduces titanous ion to titanous in the presence of a suitable catalyst such as palladium black:



The titanous ion is reoxidized to titanyl at the electrode:

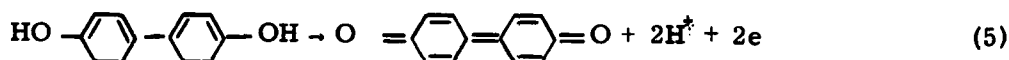


The net reaction is oxidation of the hydrogen:



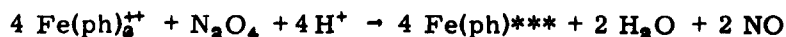
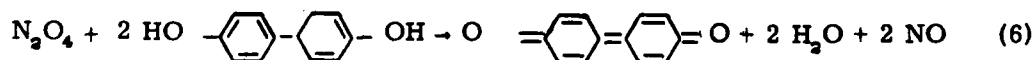
The advantages of the redox approach are twofold: the separation of electrode kinetics from fuel or air reaction kinetics; and the possibility of using lower weight and lower cost non-platinum catalysts. The disadvantage lies in the theoretical loss of cell voltage since the redox couple must operate at a lower voltage than the fuel couple. This loss in practice is not as severe as might be expected, since the direct electrodes show substantial polarization losses which partially offset the lower potentials for redox couples. As a result, the working potentials of both types of electrodes can be the same with the selection of suitable redox couples.

For air (oxygen) electrodes, the most suitable redox couples found have been bromine-bromide, Ferroin-Ferrin, and dihydroxybiphenyl-diquinobiphenyl. Bromine is too volatile for use in small cells, and will not be considered. Ferroin is both a specific and generic name for the ferrous complexes with 1, 10 phenanthroline. Ferroin itself is ferrous tris 1, 10 phenanthroline, and is used as the sulfate or perchlorate in analytical chemistry for a redox indicator and in analysis for traces of iron. Substituted phenanthrolines give other Ferroin type complexes, generally with shift or redox potential or depth of coloration of the complex. The hydroquinone 4, 4' dihydroxybiphenyl disulfonic acid, is readily oxidized in acid solution to the quinone:

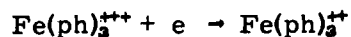
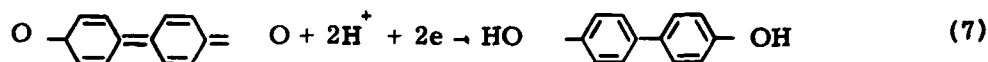


Unlike most quinone-hydroquinone couples, this has a high redox potential of over one volt.

Both Ferroin and 4, 4' dihydroxybiphenyl are readily oxidized by molecular oxygen using nitric oxide as catalyst:



The oxidized forms are reducible at inert electrodes:

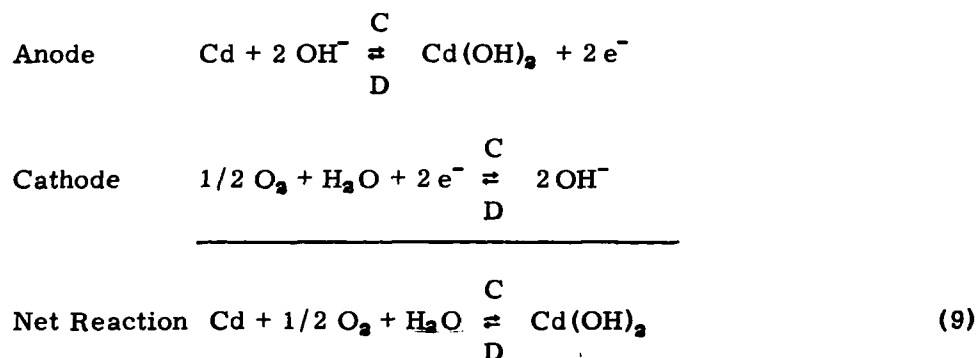


The net electrode reaction is the same as for the catalyzed air electrode:



CADMIUM-AIR CELLS

In the cadmium-air system, the reversible reactions occurring are:



Thus one water molecule is removed from the electrolyte during discharge for every reacting cadmium atom. This has the effect of increasing the KOH concentration, especially in the vicinity of the cathode. It also requires that sufficient electrolyte be present to furnish this water as well as the necessary amount of electrolyte to fill the cell structure between anode and cathode. This is the minimum amount of electrolyte required for operation, excluding any water loss due to evaporation of electrolyte through the cathode.

Of the metal-air systems under consideration in this program, cadmium has the lowest theoretical voltage, 1.22 volt, and next to the lowest theoretical energy density, 0.48 ampere-hours/gram cadmium (metal only) (Table 2); nevertheless, the system deserves serious consideration. Cadmium anodes have been successfully used in combination with several types of cathodes, most notably nickel hydroxide and silver oxide. The stability and cycle life of cadmium electrodes in these systems have been demonstrated. These facts, plus its reasonably low self discharge rate, suggest the possibility of cadmium-air cells achieving energy densities of 40 watthours/pound. The success of cadmium as an anode in alkaline systems is due in large measure to:

Table 2

THEORETICAL ENERGY DENSITY OF
ANODE METALS FOR AIR CELLS

<u>Metal</u>	<u>Open Circuit Voltage</u>	<u>Ampere-hours/ Gram</u>	<u>Watthours/ Gram</u>
Zn	1.64	0.82	1.35
Fe	1.28	0.96	1.23
Cd	1.22	0.48	0.59
Pb	1.60	0.26	0.42

Note: Values based only on the mass of metal.

- Very low solubility of the cadmium hydroxide oxidation product, $\text{Cd}(\text{OH})_2$
- Minimum self discharge when conductive support materials are used
- The restriction of oxygen to the system

It is necessary to achieve maximum cadmium loading, yet maintain a large surface area and porosity favorable to internal access of electrolyte. The maximum cadmium loading, large surface area, and high porosity favor optimum anode performance. To accomplish optimum performance cadmium anodes are generally made by only two methods. The first method involves the deposition of cadmium-cadmium hydroxide in small pores of sintered nickel plate. Pore diameters used in this method are usually less than 10 microns diameter (Refs. 1, 2). The second method consists of cadmium-cadmium hydroxide mixed with a binder and pasted or pressed into plates with or without a screen or expanded metal substrate (Refs. 3, 4, 5). Other methods of preparing cadmium anodes have also been suggested.

The change in volume of the active species when cadmium is converted to cadmium hydroxide during discharge tends to close interconnecting pores within the anode, thus restricting the access of hydroxyl ions to the cadmium. For this reason, pore size control in cadmium anodes is critical.

In order to maintain optimum utilization of cadmium, it is also necessary that adequate electronic conductivity is present throughout the anode, particularly in the case of the relatively low conductivity cadmium hydroxide particles generated during discharge of an electrode. Cadmium impregnated sintered nickel plates generally yield excellent performance with respect to cadmium utilization (Ref. 6). This is attributed to the electronic conductivity and more closely controlled pore size of the nickel sinter. The weight penalty incurred by the use of the nickel sinter; however, partly offsets these advantages. For this reason, pasted plate anodes are slightly higher in overall energy density than sintered nickel substrate anodes.

In order to obtain the advantages of both anode types, it may be possible to use lightweight conducting fibers such as graphite or nickel plated magnesium incorporated into pasted electrodes. Such fibers would improve the mechanical strength and electronic conductivity of the electrode structure. Charkey (Ref. 7) used nylon fibers for strength.

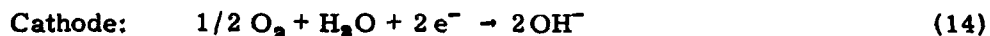
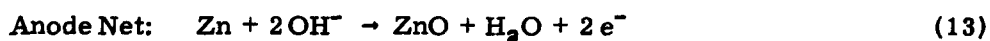
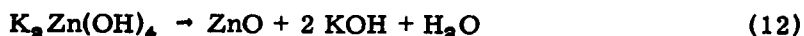
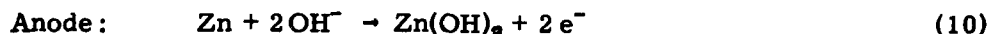
Another factor to be considered in the design of cadmium anodes is "fading," or the loss of useful capacity during successive charge-discharge cycles. Kroeger (Ref. 8) investigated "fading" of electrodes by employing two types of substrates: 1) fine pore nickel sinter plate and; 2) coarse pore plate prepared from cadmium impregnated sintered fibers. Kroeger found the nickel sinter plates to behave best with respect to "fading".

Other factors, such as the effect of electrolyte concentration, physical pressure on anodes, and anode thickness, need to be considered as they affect initial capacity and "fading" or loss of capacity during successive charge-discharge cycles.

ZINC-AIR CELLS

Of the systems to be studied for this program, zinc offers the highest theoretical open circuit voltage and energy density (see Table 2). While these numbers in Table 2 do not completely determine the merits of a specific system, they do indicate the potential merits of the zinc-air cell.

Although the following discharge reactions simplify the complex mechanisms known to occur at alkaline zinc-air electrodes, they are useful for discussing the main problem areas:



If only the overall reaction (15) is considered, one might infer that the electrolyte does not participate in the reaction; the KOH concentration remaining constant. If reaction (13) and (14) are considered, it is seen that the electrolyte tends to be diluted in the vicinity of the anode and concentrated in the vicinity of the cathode during discharge. The design of an alkaline zinc-air cell, which might include a membrane separator functioning as a diffusion barrier between the anode and cathode tends to isolate the anode from the cathode and accentuates the effects of reactions (13) and (14).

Dilution of the anolyte is also evident by the partial reaction of KOH via reaction (11), and because all of the potassium zincate in solution is not removed by reaction (12) at the end of discharge. Opposite effects occur during charge.

Excessive dilution of the anolyte near the end of discharge may impede reaction (11) because the solubility of the zincate is strongly KOH concentration dependent. This may lead to passivation of a low surface area zinc electrode.

While very high specific capacities have been used for primary zinc-air systems (e.g., 170 milliampere-hours/square centimeter single-sided), this is not the case for electrically rechargeable zinc-air systems. Cycling capacities as low as 25 milliampere-hours/square centimeter have been reported (Ref. 9). Rechargeable single-sided zinc-air experimental cells have been cycled 50 times at 80 milliampere-hours/square centimeter at the C rate, using anodes 1/16 inch thick and using 2.5-3 millimeters/ampere-hour of 30 percent KOH. Separate charging electrodes were used to protect the cathodes from chemical and mechanical deterioration during charge. The cathodes in this case were monofunctional rather than bifunctional. After 50 cycles the zinc anodes began to show a lateral redistribution of zinc in the electrode structure with an attendant loss of capacity in excess of ten percent of the original capacity. This phenomena of redistribution of zinc in the electrode structure is commonly referred to as shape change.

Another critical consideration in the design of a zinc electrode is the continuous exposure of such an electrode to dissolve gaseous oxygen and hydrogen producing contaminants released from the cathode.

LEAD-AIR CELLS

The theoretical energy density of the lead-air system is the lowest energy density of the air cells under study (Table 2). It is unlikely that a practical system with greater than 35 watthours/pound can be developed; a more likely energy density is 28 to 30 watthours/pound. This suggests that the utility of the lead-air system will depend largely upon reducing the cost of the air electrode. This can be done by changing from the platinum catalyzed air electrode to the redox type electrode.

The advantages of the lead-air system are: the lead anode is relatively low in cost per unit of stored energy and is likely to continue to be in the foreseeable future; the technology of the lead electrode is well advanced and can readily be adapted commercially to air cell needs; the lead anode gives excellent cycle life without severe limitations on charge-discharge rate, the form of electrode or electrolyte composition; the demands on cell construction materials are not severe; and the acid electrolyte cannot adsorb carbon dioxide from the air feed. Disadvantages are: anodes undergo sulfation in the discharged state; air (oxygen) electrodes for acid systems require use of platinum as a catalyst and are expensive; and the energy density is limited. These latter two disadvantages are serious limitations on the utility of lead-air cells, and interact unfavorably with each other. Thus, if the energy density could be increased, then the cost of the air electrode would not be as critical, since the cost per unit of energy would be decreased. The air electrode acts only as a converter and its cost is amortized over the capacity of the anode. Also, if the air electrode cost is reduced, the same benefit will accrue.

IRON-AIR CELLS

No work was performed on iron-air cells during this quarter. Any such work will await results in October 1967 or work under way at Fort Monmouth by ECOM personnel.

Section 3

TECHNICAL APPROACH

CATHODE (AIR ELECTRODE) IN ALKALINE SYSTEMS

Major effort will be directed toward the development of a bifunctional air electrode which results in a minimum of electrolyte contamination. Such contamination could result in self discharge of the various anodes under study.

Cathode support materials to be examined are:

- Polymer bonded nickel on nickel screen
- Porous nickel plaque

Waterproofing agents to be examined are:

- Tetrafluoroethylene
- Polyvinylidene fluoride

Catalysts to be examined are:

- Platinum
- Silver
- Spinel

The support materials were selected on the basis of prior experience with them, their stability, particularly in alkaline systems, and their dimensional controllability. Of the two waterproofing agents selected, tetrafluoroethylene (TFE) is widely used as a waterproofing agent. Polyvinylidene fluoride, however, offers advantages in terms of lower cost and ease of processing as compared with tetrafluoroethylene.

Platinum and silver were selected for the catalyst studies because of their established performance as monofunctional cathodes. Spinel was selected because of its potential use as a bifunctional cathode, its projected lower cost than platinum or silver, and its processing ease. In order to limit the number of variables under study during a single experiment, the following will be done:

- In the catalyst screening studies, a standard catalyst support structure and waterproofing agent will be maintained whenever possible; lithiated nickel screen plus bonded preoxidized lithiated nickel plus TFE from aqueous dispersion as a binder-waterproofing.
- Circular faced cells having a cross sectional area of 10 square centimeters, will be used in the component studies with cadmium anodes.

Because cathodes developed during this program must be compatible with the anodes under study, dissolved species peculiar to the various anodes will be introduced into the cells containing experimental cathodes. The component study phase of this program will consist of:

- Catalyst screening studies
- Structure optimization, including waterproofing agents
- Driven single-sided cell cycling tests

One or two cathode types will be selected on the basis of the results from the component study for cell optimization development. Should a satisfactory bifunctional electrode not result from the component study by January 1968, then the best materials for a two terminal, three electrode cell will be selected.

CADMIUM -AIR CELLS

In order to maximize the energy density of a cadmium-air battery to fit into a proposed battery case having internal dimensions of 11.5 by 7.0 by 3.0 inches, the following are necessary:

- A thick anode, up to 0.130 inch, of high cadmium utilization over successive charge-discharge cycles (Ref. Calculations in the Appendix)
- A thin, lightweight, long lived cathode
- Cell configuration designed for minimum electrolyte volume
- A stable, low impedance, highly absorbent separator
- A system capable of operation with air containing carbon dioxide

Screening Program for Cadmium-Air Cells

A screening program has been developed for determining the interactions and limits of the cell components. The components to be evaluated are listed in Tables 3 and 4 for the anode and cathode, respectively. The test schedule is outlined in Tables 5 and 6. These test cells will be power-supply driven using cadmium impregnated sintered nickel plaque counter electrodes. The counter electrodes will contain excess active cadmium so that they will not be overcharged or overdischarged during cycling.

At least three anode types will be evaluated. Impregnated sinter (A) is the porous nickel substrate anode used in nickel-cadmium batteries. An attempt will be made to locate sintered plaque whose support structure is nickel mesh rather than the perforated nickel plated steel strip now in hand. This more open structured support should allow freer access of the electrolyte in thicker anodes. Pasted or pressed oxide (B) will be of at least two types: B₁ containing conducting and strengthening fibers, and B₂ with less binder and no fibers. Two types of binder will be used; polyvinyl alcohol and a fluorocarbon.

Table 3

ITEMS FOR STUDY - CADMIUM ANODE EVALUATION

<u>Anode Type</u>	<u>Anode Thickness (inches)</u>	<u>KOH Concentration</u>
A. Impregnated nickel plaque	E. 0.070	H. 31%
B. Pasted cadmium oxide	F. 0.100	I. 36%
C. Electrolytic deposited (ED) Cd (OH) ₂ on nickel screen	G. 0.130	J. 45%
D. Impregnated nickel (sponge)		

Table 4

ITEMS FOR STUDY - AIR CATHODE EVALUATION

<u>Catalyst</u>	<u>Waterproofing Agent</u>	<u>Substrate</u>	<u>KDH Con- centration</u>	<u>Carbonate</u>
K. Platinum	M. TFE	O. Porous sin- tered nickel	H. 31%	Q. * Normal
L. Spinel	N. Polyethylene		I. 36%	R. None
		P. Porous bonded nickel catalyst	J. 45%	

* The term "normal" is used here to denote the estimated amount of carbonate that will exist in the electrolyte after 200 charge/discharge cycles in ambient air. The charge and discharge rates for these cycles will be C/5 based on the estimated capacity of the anode.

Table 5

ANODE EVALUATION TEST PROGRAM

<u>Test No.</u>	<u>Anode Type</u>	<u>Thickness</u>	<u>Electrolyte Concentration</u>	<u>Parameter in Focus</u>
1	A	F	H	Effect of KOH concentration
2	A	F	I	
3	A	F	J	
4	A	E	Best	Effect of anode thickness
5	A	G	Best	
6	B ₁	F	Best	Effect of anode type
7	B ₂	F	Best	
8	C	F	Best	
9	Best	E	Best	Check on thickness
10	Best	G	Best	
11	Best	Best	Next Best	Check on KOH concentration

Table 6

CATHODE EVALUATION TEST PROGRAM

<u>Test No.</u>	<u>Catalyst</u>	<u>Water-proofing</u>	<u>Substrate</u>	<u>KOH Concentration</u>	<u>CO₂</u>	<u>Parameter in Focus</u>
12	K	M	O	Best of H, I, J	None	Effect of type of waterproofing substrate
13	K	N	O	" " " " "	—	
14	K	Best	P	" " " " "	—	
15	K	Best	Best	2nd Best	None	Effect of KOH concentration and CO ₂
16	K	Best	Best	3rd Best	None	
17	K	Best	Best	H	Normal	
18	K	Best	Best	J	—	
19	L	Best	Best	H	None	Effect of KOH concentration on second catalyst
20	L	Best	Best	I	"	
21	L	Best	Best	J	"	

The electrolytically deposited (ED) plate represents potentially a high capacity electrode. As prepared, it is essentially porous cadmium hydroxide supported on a nickel screen or expanded metal. It can be made with variable porosity which should be an advantage as the electrode thickness is increased.

A fourth type of anode structure to be studied, if time permits, is impregnated nickel sponge. This utilizes a highly porous conducting substrate possessing larger pores than sintered nickel plaque. The possible advantages of using such a structure are: better internal access of the electrolyte, particularly with thick electrodes; and less weight penalty than with the sintered plaques.

The three thicknesses of anode to be studied may not disclose the optimum thickness, but should indicate the direction of thickness effect on energy density. The maximum thickness of 0.130 inch resulted from preliminary energy density calculations shown in the Appendix. The prescribed overall dimensions of the battery, plus valid assumptions on cathode air gap and separator thicknesses, determine this anode thickness. The KOH concentrations were chosen because 31 percent KOH possesses the highest conductivity, 36 percent KOH is a composition recommended by Harivel (Ref. 10), and 45 percent KOH is in an area that has received considerable attention by other investigators.

In the study program outlined in Table 5, the anode capacity and utilization will be evaluated by charging the anode to 1.04 volts cut-off (versus Hg/HgO reference electrode) and discharging it to a 0.7 cut-off voltage using a C/5 rate for discharge. A charging rate which is found to yield the highest discharge capacity upon discharge will be used. With this charging-discharging mode, the current density will be higher in the case of thicker anodes since the surface area of the anodes is constant. Each test will be continued long enough to establish a reasonably steady state performance or a definite trend. The anodes will be weighed before and after test to disclose any material loss. The problems of cadmium migration, fading, and charge retention will be more closely evaluated in double-sided* cadmium-air cell tests. Polarization curves will be taken during single-sided cell tests using a Hg/HgO reference electrode.

Eleven anode evaluation tests are shown on Table 5. Additional tests will be added if necessary. For example, it is not certain what pore volume and pore size is best for thick and thin electrodes prepared by the paste and the ED processes. Also, there is uncertainty as to the number of screens that should serve as substrates when electrode thickness is increased.

In the cathode single-sided** cell studies, it is assumed that the use of lithiated oxidized nickel substrate yields a bifunctional cathode (i. e., the

* Air electrodes on both sides of the cadmium electrode.

** A single air electrode facing one side of the counter electrode.

electrode will serve both for charging as well as discharging). At least two catalysts will be studied; platinum and a selected spinel. Other catalysts which hold promise of being stable during charging will be included in this study.

The effect of CO_2 in these cathode single-sided cells will be studied, although double-sided metal-air cells will provide more specific information relating to deterioration by CO_2 versus hours of exposure to cyclic charge and discharge. The KOH concentration that proves best in the anode study program will be used initially in the cathode study. A compromise KOH concentration may have to be selected for the full cell studies.

When the two series of anode and cathode cell studies are complete, the best conditions of each study will be combined into double-side metal-air cell tests. Beginning at this point, two general types of separators will be evaluated; felted nylon and modified cellophane. The loss rate of electrolyte will also be measured. Optimization of all parameters, investigation of additional charge-discharge regimes, cycle life, and charge retention studies will follow if the cadmium-air system is selected for the final phase of this program.

Equipment

Two automatic cycling equipments have been designed and are being assembled. One equipment is for testing anodes in double-sided anode counter electrode cells. It is arranged so that it can also cycle double-sided metal-air cells. Four cells can be cycled in series. The equipment is designed to discharge or charge the cells at predetermined fixed current densities to given cut-off voltages, or for preset times, whichever occurs first. The voltages, current densities, and times may be set to different values for charging and discharging. Voltages are measured and recorded against Hg/HgO reference electrodes and current is also simultaneously recorded. Polarization data can also be obtained with this equipment by manually varying current density.

A single cell automatic cycling equipment has also been built. One double-sided cadmium-air cell has been tested with this equipment. The data on this cell and an earlier manually operated cell are given in the Section dealing with Experimental Results.

ZINC-AIR CELLS

Although the goals of the zinc-air cell development of program are identical to the other systems under consideration, the technical approach used must consider problems peculiar to the zinc-air system. The major problem areas are:

1. Need for suitable membrane separator to isolate the zinc electrode from the air electrode. Such a membrane serving as a "seal"

minimizes the nonelectrochemical oxidation of the zincate and low hydrogen overvoltage contaminants generated by the cathode interacting with the zinc anode. The membrane "seal" also confines zinc dendrite growth to the zinc compartment, thereby preventing cell shorting, provided that the membrane pore size can be maintained throughout the useful life of the cell.

Other separators necessary for consideration are highly electrolyte absorbent. Among these is Pigmentary Potassium Titanate* PKT. Since its capillarity surpasses that of the common fibrous separators used in batteries by approximately two orders of magnitude, it will be tested. Recently R. G. Haldeman (Ref. 11) presented data on the bubble pressures which relate to capillary forces of some novel matrix materials such as PKT.

2. Need for maintenance of electrolyte balance during charge and discharge. The use of a membrane seal without osmotic pumping effects results on discharge in an increased electrolyte level in the zinc compartment and a decrease electrolyte level in the cathode compartment. This occurs because the discharge current carried additional mass to the zinc compartment in the form of OH^- ions increasing its total mass content in the form of ZnO , water, and some dissolved zincate. For purposes of qualitative discussion, potassium ion mobility has been ignored. A smaller mass is simultaneously removed from the air compartment during discharge. It will be seen in Section 4 that osmotic pumping effects are significant. The level charges are the opposite of those discussed above.
3. Need to minimize the electrolyte content in the zinc compartment.
4. Need to minimize shape change of the anode during successive charge-discharge cycles.
5. Need for operation of the cells at electrolyte concentrations in excess of 40 percent KOH because membrane separators and zinc electrodes promise to operate better at higher alkaline concentrations.
6. Need for a bifunctional air electrode compatible with the zinc-air cell built as a compartmented cell.

Screening Program

The screening program for zinc-air has been designed principally to result in stability of the zinc anodes and air cathodes.

Cell experiments will be conducted to evaluate the following:

* E. I. Dupont de Nemours, Inc.

- Electrolyte concentrations from 31 to 40 percent KOH
- Various types of air electrodes as they become available
- High capillarity separator tests, PKT, CeO₂
- Low capillary fibrous separators
- Membrane separators other than cellophane, i.e., Permium 2.2 XH, Series 2, from the ARI Research Corpt., and Films B₁ and C₁ from the Borden Chemical Co.
- Electrolyte volume stabilization in both zinc and air compartments
- Electrolyte volume optimization during cycling
- Specific capacity optimization during cycling

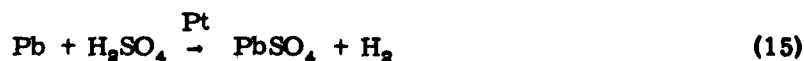
These test cell experiments will be evaluated, with few exceptions, in terms of degradation processes and mechanisms of the various cell components. Preliminary experimental work discussed in the Experimental Results Section indicates that electro-osmotic pumping of electrolyte through the membrane separator may be a problem with respect to maintaining the two compartment cell design. Therefore the distribution and flow of electrolyte as a function of the membrane type will also be measured. Capillary rise, bubble pressure, or both will be observed in cells assembled with initially charged and initially discharged zinc anodes.

LEAD-AIR CELLS

Emphasis in the study of lead-air cells will be placed on development of a suitable redox electrode, and performance studies. For lead-air cells, the redox electrode will consist of a porous carbon or graphite substrate which is impregnated with sulfuric acid solution and a trace of nitric acid (to supply the nitric oxide catalyst). The redox couple will be either insoluble or strongly adsorbed on the carbon to prevent migration away from the electrode. For this reason, the unsulfonated 4, 4' dihydroxybiphenyl will be used at first since it is insoluble.

Tests with Ferroin will be limited to determining behavior unless the biphenyl system is not satisfactory. The Ferroin system is very soluble, and may not be sufficiently absorbed to be useful without modification.

In addition to redox cells, lead-air cells with gas electrodes will be made and evaluated to serve as a comparison for the redox cells. A key problem in using platinum catalyzed electrodes is the migration of small amounts of platinum to the anode. This, if it occurs, will give catastrophic results since platinum in trace amounts catalyzes the self-discharge of lead anodes to very high rates:



In order to avoid the early loss of the cell, ion exchange membrane (IEM) will be used as a barrier. The electrode will be placed on the membrane.

This approach was dictated in part by the availability of IEM electrode assemblies used in fuel cells.

The preliminary cell design is based on fitting the system into a standard battery size delivering a nominal 24 volts. The available space is 11 1/2 inches long, 7 inches high, and 3 inches wide; these being the dimensions for the active components after furnishing an allowance for cell case and battery case. An operating voltage of 1.2 volts/cell has been assumed since the current density for the C/5 discharge will be relatively low. Assuming 50 percent utilization of the anode electrochemically (remainder is grid and support), that the anode is all lead, the charged cell electrolyte has a specific gravity of 1.280 (34.7 percent), and the discharged cell electrolyte has a specific gravity of 1.060 (9 percent).^{*} The results are:

- Weight of lead-ampere-hour = $\frac{207}{2} \times \frac{1}{26.8} \times 2 = 7.80$ grams
(50 percent utilization)
- Volume of lead/ampere-hour = $\frac{7.80}{11.3} = 0.684$ cubic centimeters
- Volume of initial (charged) acid = 125 cubic centimeters per equivalent
- Volume of acid/ampere-hour = $\frac{125}{26.8} = 4.67$
- Total volume, acid plus lead/ampere-hour = $4.67 + 0.68 = 5.35$ cubic centimeters
- Weight/ampere-hour = 5.98 (acid) + $7.80 = 13.78$ grams
- Weight/volume ratio = 2.58
- Number of cells = $\frac{24}{1.2} = 20$
- Thickness allowance = $\frac{11.5}{20} = 0.575$ inch per cell
- Area of cell = 7 inches $\times$ 3 inches = 21 square inches =
135 square centimeters $\times$ 2 = 270 square centimeters

This assumes a double-sided air electrode per cell. Table 7 gives the calculated battery parameters. The air gap is the only adjustable parameter, and the maximum capacity has been fitted in. Note that porosity of lead electrolyte volume per ampere-hour is minimum and changes in porosity are cancelled out. Also, the low heat rate will allow use of the 0.125 inch gap which is the basis of further design.

^{*} These acid gravities in the electrolyte are standard for the charged cell, but smaller for the discharged cell compared to current lead-acid battery practice. The lower value gives more capacity.

The test cells will use Lucite cases with commercial anodes. The principal change for air cells, which will be worked out later, from present designs will be greater capacity per unit of area and reduction in grid weight per unit of capacity. For the cathode development, present commercial anodes are satisfactory.

Both air electrode and redox electrode cells will be constructed and tested in the next quarter. Redox electrodes based on 4, 4' dihydroxybiphenyl will be used at loadings of a 0.01 gram to 0.03 gram per centimeter squared of 0.050 inch thick electrode. Cycling of the cells will be done using a controller now under construction using C/5 charge and C/5 discharge rates. Cell voltage will be monitored, and used to cut off the cell operation at fixed high and low levels. No work is planned on anode development.

Table 7

LEAD-AIR BATTERY CALCULATIONS

	<u>Condition 1</u>	<u>Condition 2</u>	<u>Condition 3</u>
Air gap	0.250"	0.185"	0.125"
Allowed thickness/cell	0.575"		
Net cell thickness	0.325"	0.390"	0.450"
Cathode thickness	0.050"	0.050"	0.050"
Pb-H ₂ SO ₄ thickness	0.225"	0.290"	0.350"
Volume Pb-H ₂ SO ₄ /cell	77.5 cm ³	100 cm ³	120 cm ³
Ampere-hours/cell	12.8	16.6	20.0
Watt-hours/battery	308	398	480
Weight/cell			
Pb-H ₂ SO ₄	178g	229g	214g
Cathode	15g		
Case	<u>30g</u>		
Total	223g	279g	329g
Battery weight	9.84 lbs	12.3 lbs	14.5 lbs
Watt-hours/pound	31.4	32.4	33.1
Current, C/5 rate	2.56 amp	3.32 amp	4.00 amp
Current density	9.5 ma/cm ²	12.3 ma/cm ²	14.3 ma/cm ²
Heat evolved/cell	21 kcal	27 kcal	32.6 kcal
(1) Cal/min/cel (C/5 rate)	70 cal	90 cal	109 cal
(1) Cal/min/battery (C/5 rate)	1400 cal	1800 cal	2100 cal

(1) This includes I²r loss since calculated for operating voltage of 1.2 volts/cell. The $\Delta H - nV = T\Delta S$ where $T\Delta S$ = heat evolved.

Section 4

EXPERIMENTAL RESULTS AND DISCUSSION

CATHODE

Oxygen Evolution Polarization Measurements

Prior work in zinc-air has shown that the alkaline electrolyte is contaminated with nickel, and possibly with platinum when these two materials are used for a charging electrode in a zinc-air cell. The contamination of the zinc subsequently leads to self-discharge via local cell action on the zinc. Pre-oxidation of the nickel tends to minimize this contamination but to produce an insulating oxide film. Conductivity of this oxide film can be improved by lithiation.

For better understanding, oxygen overvoltage measurements were made on the following materials:

- Nickel plaque NT-40*
- Nickel plaque NT-40 after oxidation and lithium treatment
- Nickel plaque 4A**
- Nickel plaque 4A after oxidation and lithium treatment
- A TFE-bonded platinum black electrode

The oxidation-lithium treatment consisted generally of decomposition of lithium hydroxide in an atmosphere of mixed carbon dioxide and argon (Ref. 12). X-ray diffraction analysis of the resultant plaque indicated the presence (in descending order) of Ni, NiO Li₂O solid solution, and Li₂CO₃.

The oxygen evolution polarization measurements were generally after the method of Hickling and Hill (Ref. 13). The electrolyte was fresh 31 percent KOH. Results are shown in Figure 1. The data indicates:

- Little difference in polarization among types of nickel plaques
- Little effect of lithium treatment on polarization of nickel plaques
- The TFE electrode, below 10 milliampere per square centimeter, shows a lower polarization than the nickel plaque electrodes, and above 10 milliampere per square centimeter shows a higher polarization than the nickel plaque electrodes.

*Union Carbide Corporation - NT-40.007 inch thick; 3.8 microns mean pore diameter; 0.40 void fraction

**General Electric Company - 4A-0.016 inch thick; 0.88 void fraction, mean pore diameter unknown

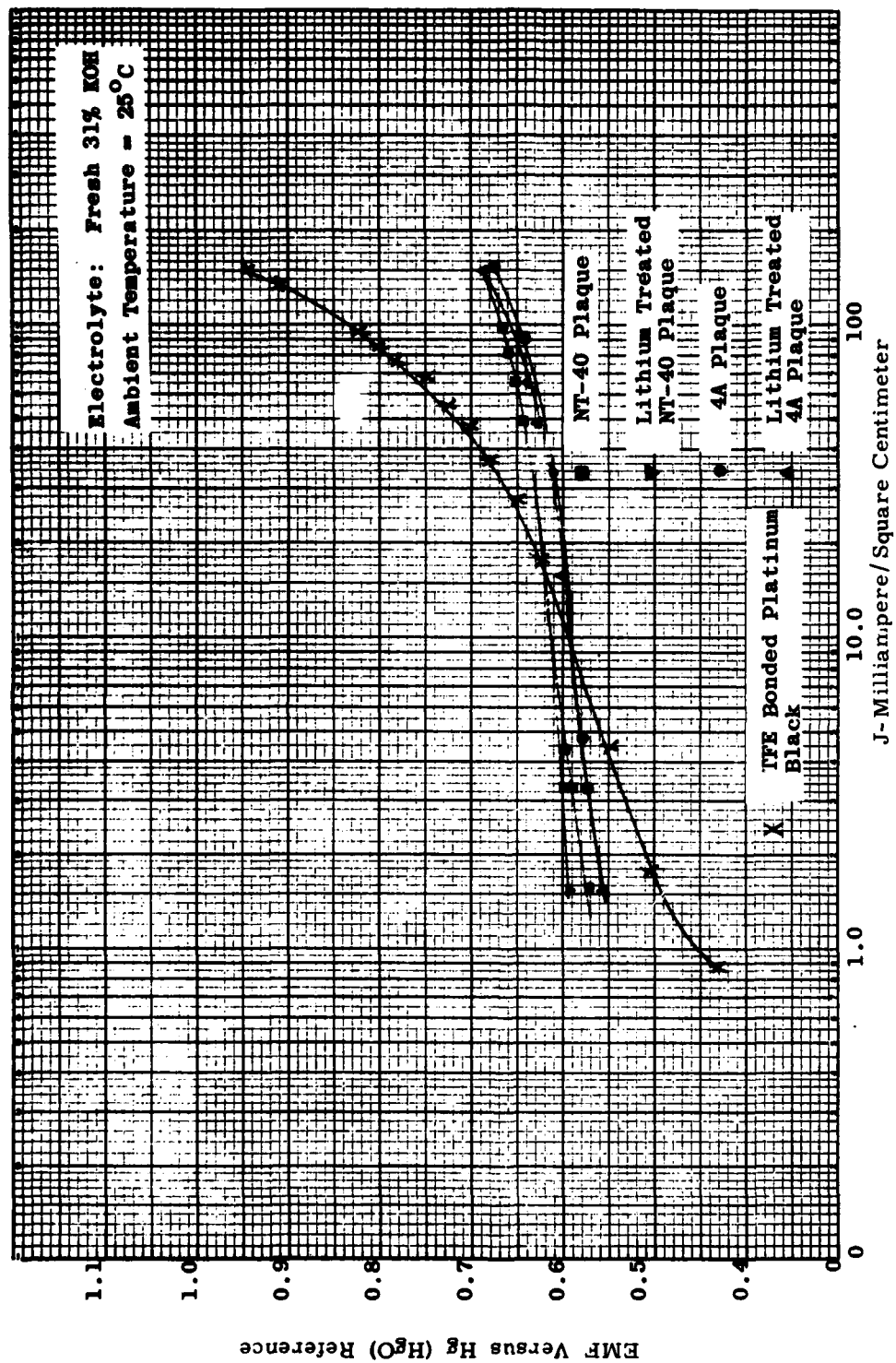


Figure 1. Oxygen Evolution Polarization Measurements

- A higher slope for the TFE electrode than for nickel plaque electrodes

It appears that the penalty of using an oxidized nickel surface, instead of platinum for charging is not great, and it is actually preferred above 10 milliamperes per square centimeter.

Lithium Treated Nickel

Three different nickel base materials were lithium treated: wire mesh, plaque, and powder. Two processes were investigated. One described above, the other is the method of Hyashi (Ref. 14). The former method gave some lithium carbonate contamination and showed a diffuse x-ray diffraction pattern for either NiO or NiO Li₂O solid solution. The latter method gave about equal amounts of Ni, and either NiO or NiO Li₂O solid solution. For this sample, a precision lattice parameter of $4.1772\text{\AA} + 0.002\text{\AA}$ was determined. This latter method will be used for future work.

Plaque Electrodes

Lithiated nickel plaques were platinum impregnated to a loading of 1 - 2 milligram platinum per square centimeter for use in cadmium and zinc cells reported elsewhere. The stability of the oxide film remains to be proven in this system.

Spinel Catalysts

Spinel catalysts were prepared for screening tests by Carson's method (Ref. 15).

For the compound CoO (Al₂O₃), stoichiometric amounts of cobalt nitrate hexahydrate and aluminum nitrate nanohydrate were dissolved in distilled water and evaporated to dryness followed by firing at 400°C for one hour. The resultant briquette was ball-milled for three days and screened through 270 mesh.

Conclusions and Future Plans

Material preparation is complete for catalyst screening tests. Catalyst screening and electrode structure optimization will be the major focus for the second quarter.

Cadmium-Air Cells

A double-sided cadmium-air cell, designated A-1, was assembled as shown in Figure 2. The anode was a Cd(OH)₂ impregnated sintered nickel plaque prepared on perforated nickel plated steel strip. It measured 33 mils thick with a sinter area of 4.05 square inches and had a theoretical capacity

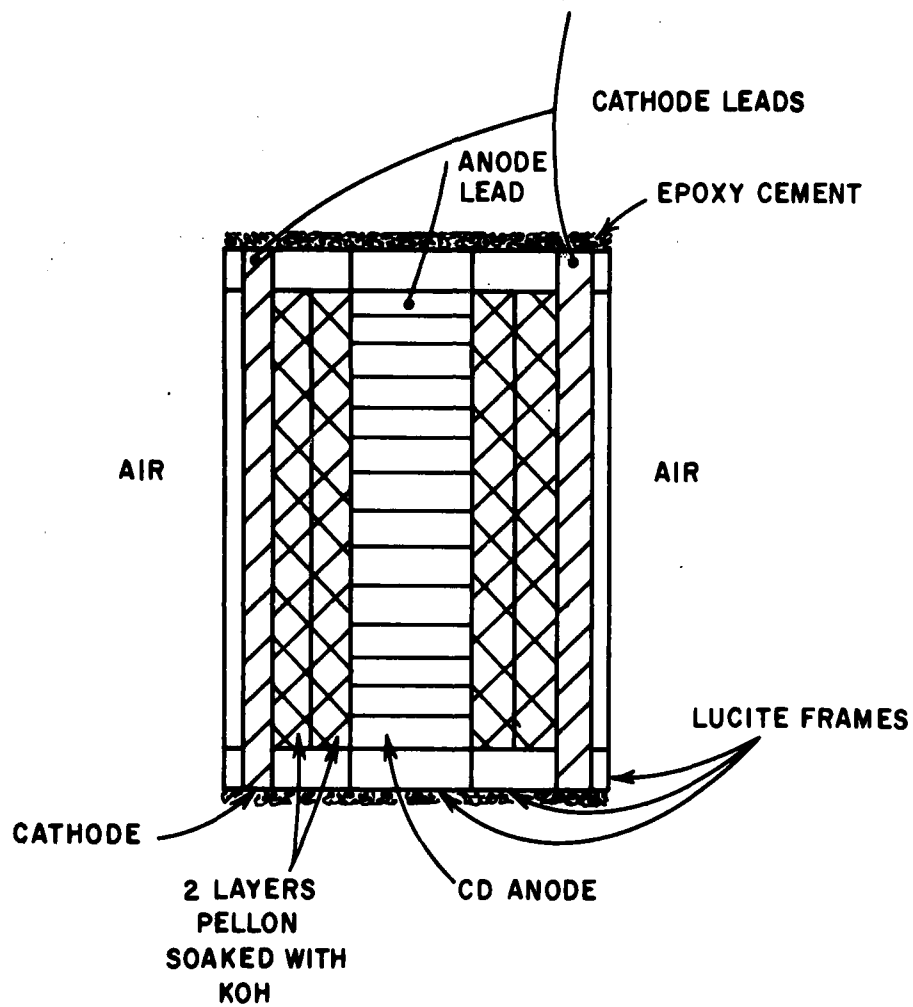


Figure 2. Schematic of Assembled Cadmium-Air Cell Using a Double-sided Air Electrode

of 1.15 ampere-hours based upon cadmium content. Four thicknesses of 0.008 inch felted nonwoven nylon were used as separators. The cathode was made by impregnating oxidized and lithiated sintered nickel plaques with a TFE + platinum black suspension. The 31 percent KOH was used for the electrolyte. All these components were mounted in a Lucite frame using epoxy to hold the assembly together.

The cell was charged at a C/5 rate (4.5 milliamperes/square centimeters), then the discharge polarization curve shown in Figure 3 was obtained. After recharging at C/5, the cell was discharged at a C/5 rate to a cell voltage of 0.55 volt. These data are plotted in Figure 4. Based on theoretical capacity of 1.15 AH, the cadmium utilization is 66 percent at a cut-off voltage of 0.7 volt, and 80 percent at the 0.55 volt point. The cell was further cycled, but little useful data were obtained.

The cell was subsequently dismantled and the air electrode was tested against a zinc sheet using 31 percent KOH as the electrolyte. The pronounced polarization is shown in Curve A of Figure 5. The air electrode was then washed with a fresh KOH solution and rerun as shown in Curve B of Figure 5. The improvement noted in Curve B of Figure 5 suggests that carbonate had been present as indicated in Curve B of Figure 5. This conclusion is a tentative one based on past experience. This will be confirmed by additional experiments.

The following arrangement was used for Cell A-2: the automatic cycling equipment was used; the cell was tested in a bell jar to minimize CO_2 adsorption. A photo of the cell components is shown in Figure 6.

The test cell assembly is shown in Figure 7. A graduated tube is attached to the left side of the cell. This tube serves the dual function of providing a reservoir of electrolyte to measure electrolyte loss and a location for the mercury-mercuric oxide reference electrode, which is shown attached to the narrow portion of the reservoir tube. Another small tube is shown on the top of the cell. This tube serves as an oxygen vent during charging. It is not clear that this does an adequate job, therefore further modifications may be made above the tops of the electrodes. Cell A-1 included no vent and the polarization data suggest that residual oxygen gas may have been blanking off some of the electrodes.

The cadmium anode of Cell A-2 was made by tack welding together two of the 33 mil plates such as used in Cell A-1, resulting in a theoretical capacity of 2.30 ampere-hours. The plates were pretreated with KOH to remove any carbonate that might have been present as a result of exposure to air. Two, 0.005 inch thick nonwoven nylon sheets were used as separators. The cathode was of the same type used in Cell A-1. During the course of the run, the cover of the bell jar was removed fairly often, therefore the effects of CO_2 adsorption, if any, were not completely eliminated.

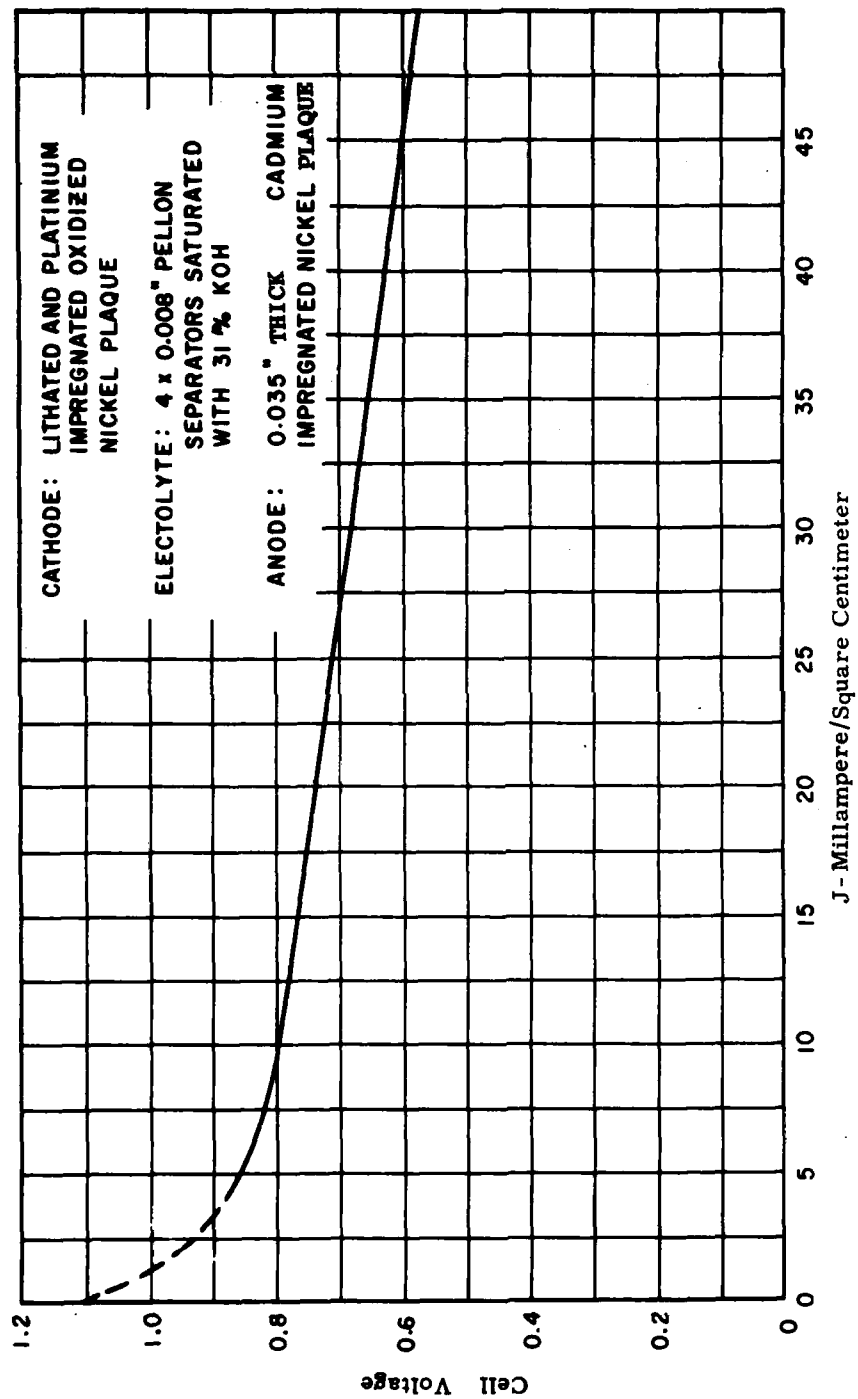


Figure 3. Polarization Curve for Cadmium-air Cell A-1

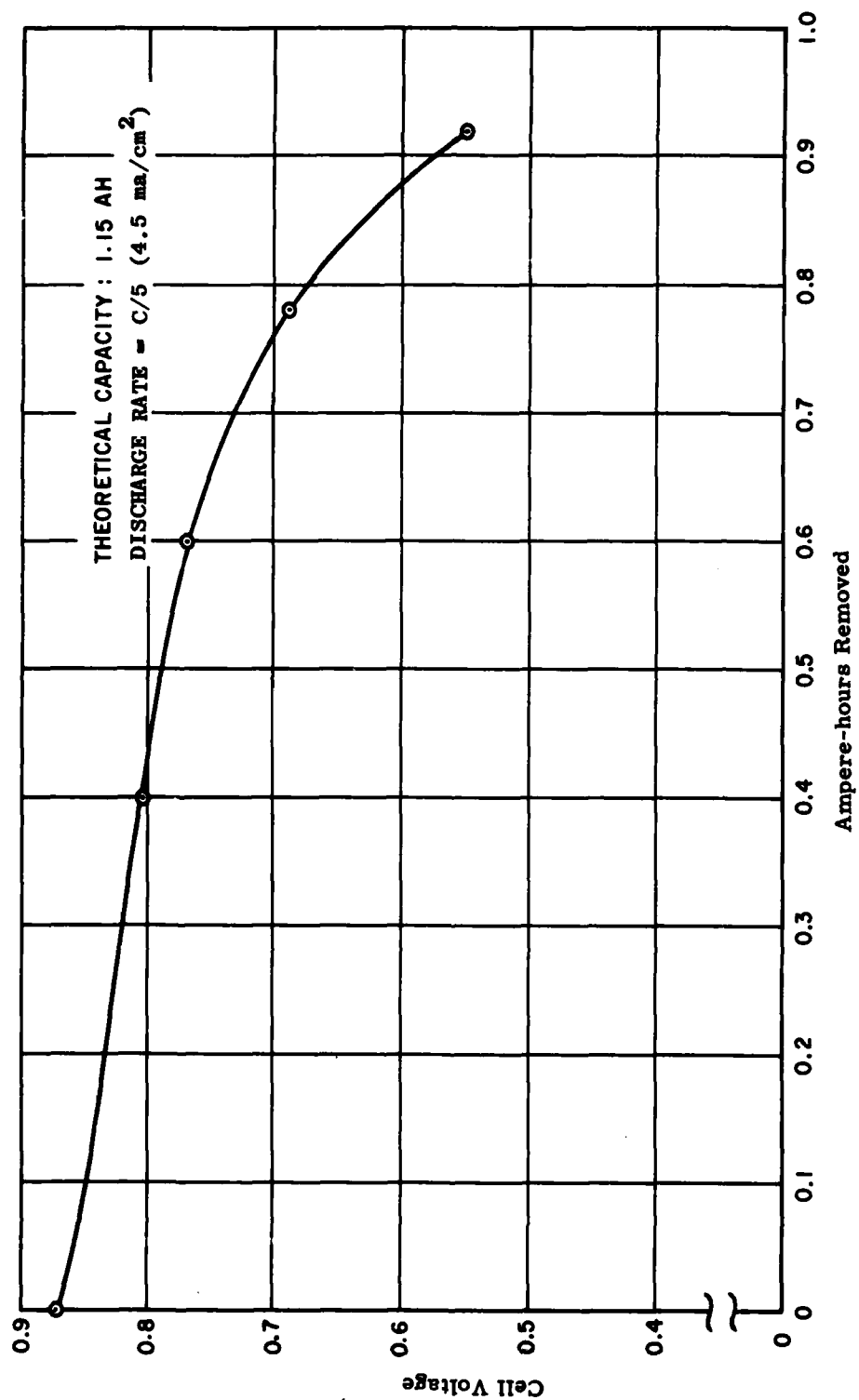


Figure 4. Cell Voltage Versus Ampere-hours Discharged for Cell A-1

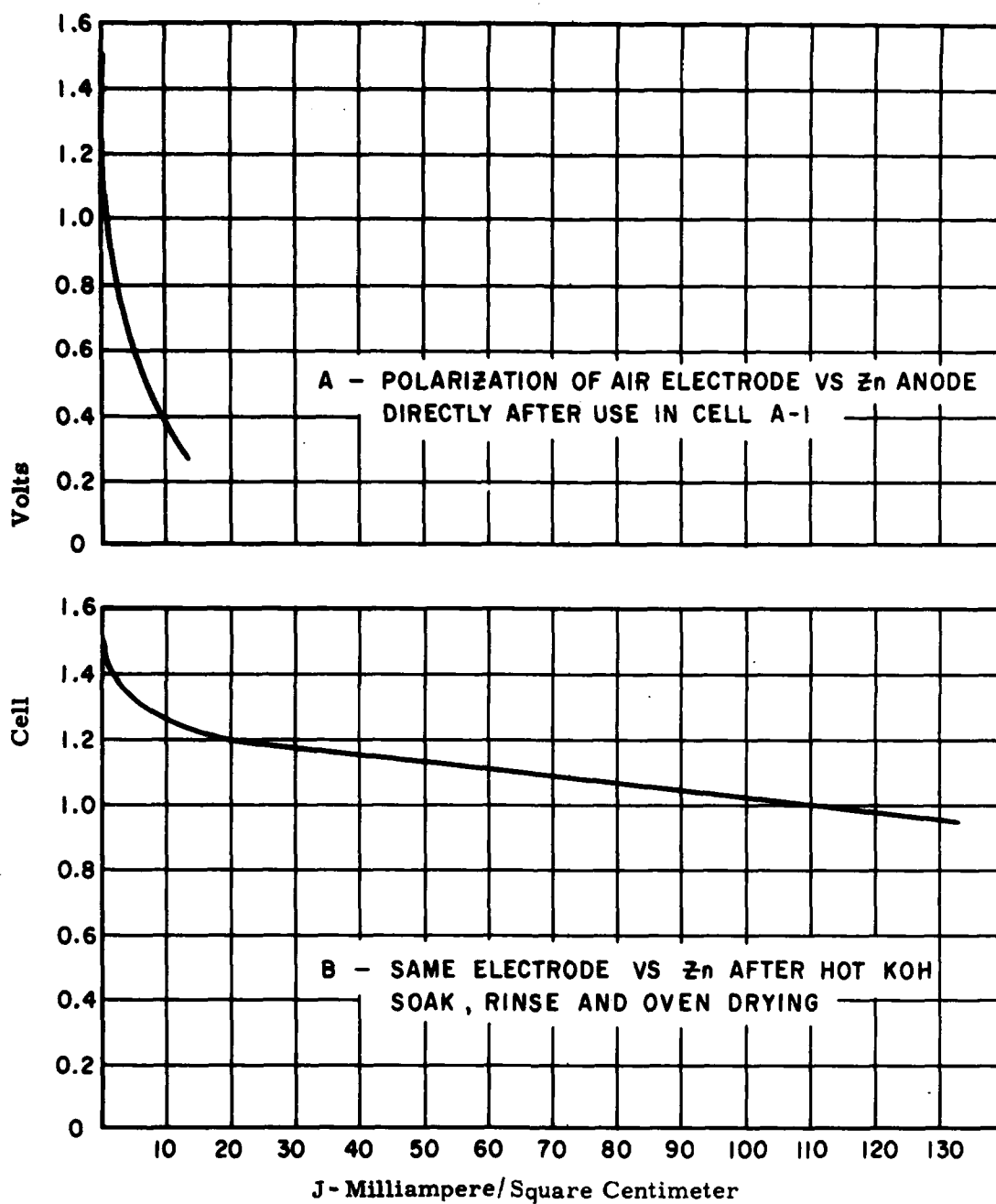


Figure 5. Apparent Carbonate Effect on Air Electrode

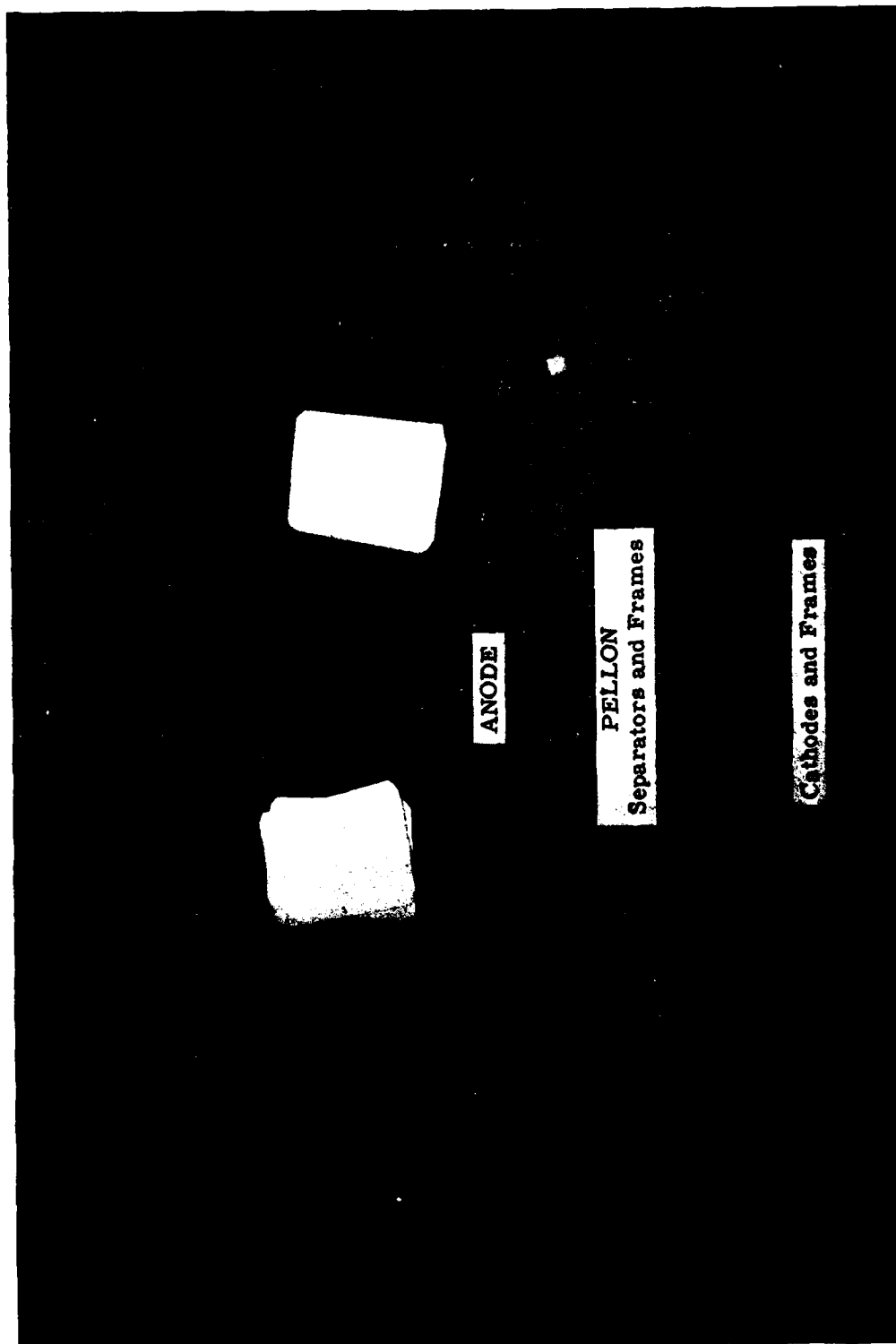


Figure 6. Components of Cadmium - Air Cell A-2

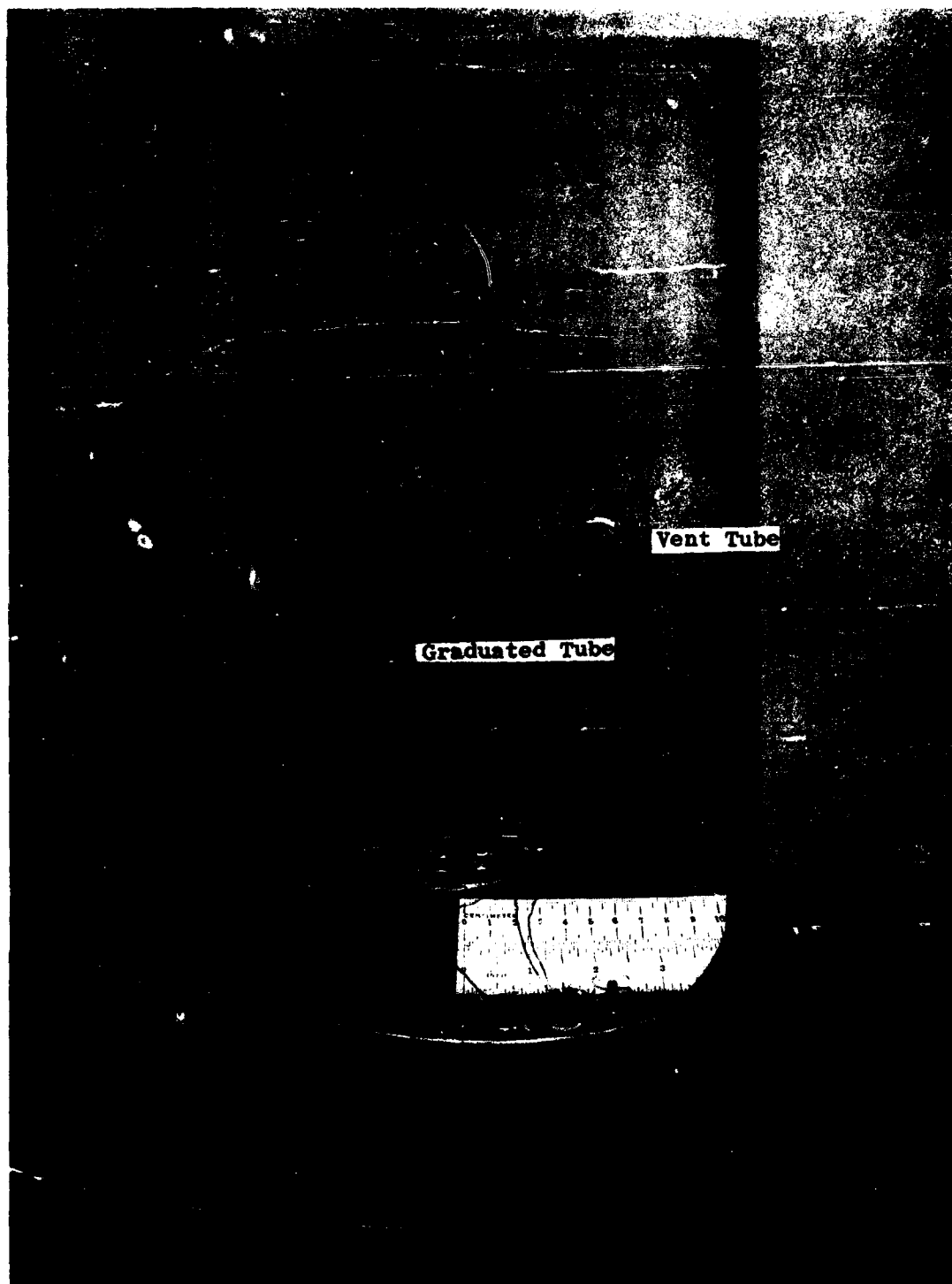


Figure 7. Test Cell Assembly

The Cell A-2 was charged and discharged at a C/5 rate which for this anode represented a current density of 8 milliamperes/square centimeter. As previously explained in the subsection, "Test Equipment," charging was stopped when the cell voltage reached 0.662 volts. At no time did the discharging time amount to 5 hours. This cell was cycled for a total of 35 complete charge-discharges. The recorder plots of cell voltage versus time for the 13th and 28th cycles are reproduced in Figure 8. The discharge voltage dropped slightly, (0.02 volt), from the 13th to the 28th cycle. The decrease in capacity versus cycling data are plotted in Figure 9. The slope of the curve declines and from an extrapolation of the curve it is estimated to have leveled off at 50 to 60 percent. The factors contributing to the loss in capacity are not known in detail. It is possible for the cadmium in the anode to be isolated by formation of $\text{Cd}(\text{OH})_2$, and also to migrate and become less accessible to electrolyte.

Will (Ref. 16) observed that frequently a heavy overcharge can partially restore the capacity of cadmium anodes if cadmium isolation is the reason for loss of capacity. The charging efficiency (utilization of charging current) was originally 92 to 94 percent and remained in the 90 percent range until after the 30th cycle. Then it dropped to 83 to 88 percent. A typical polarization curve for this cell is shown in Figure 10. The factors contributing to the observed resistance have not been determined. It is speculated that the cathode may have been partially blocked by gas evolved and trapped in the cell during the charge portion of the cycle.

A third cell, A-3 has now been assembled. It contains three, 0.033 inch anodes and a nylon mesh separator (1/8 inch square opening) to aid oxygen removal during the charging cycle. No significant data has yet been obtained.

ZINC-AIR CELLS

Vertically oriented rectangular cells 1 1/2 inches by 2 5/8 inches have been built. These cells are used with the 2 5/8-inch sides of the zinc electrode in the vertical position. The cells are strictly exploratory in design. The following describes one of the test cells:

Anode: 5 grams ZnO + 3 grams PKT + 2 percent HgO + 31 percent KOH having a theoretical capacity of approximately 140 milliamperes-hours/square centimeter was pasted to an etched expanded battery grade zinc mesh.

Separator: Standard cellophane sealed between rubber gaskets

Cathode: Platinum impregnated and wetproof nickel plaque type air electrode

Charging Electrode: Expanded nickel mesh, embedded in PKT - KOH paste positioned between the cellophane layer and air electrode.

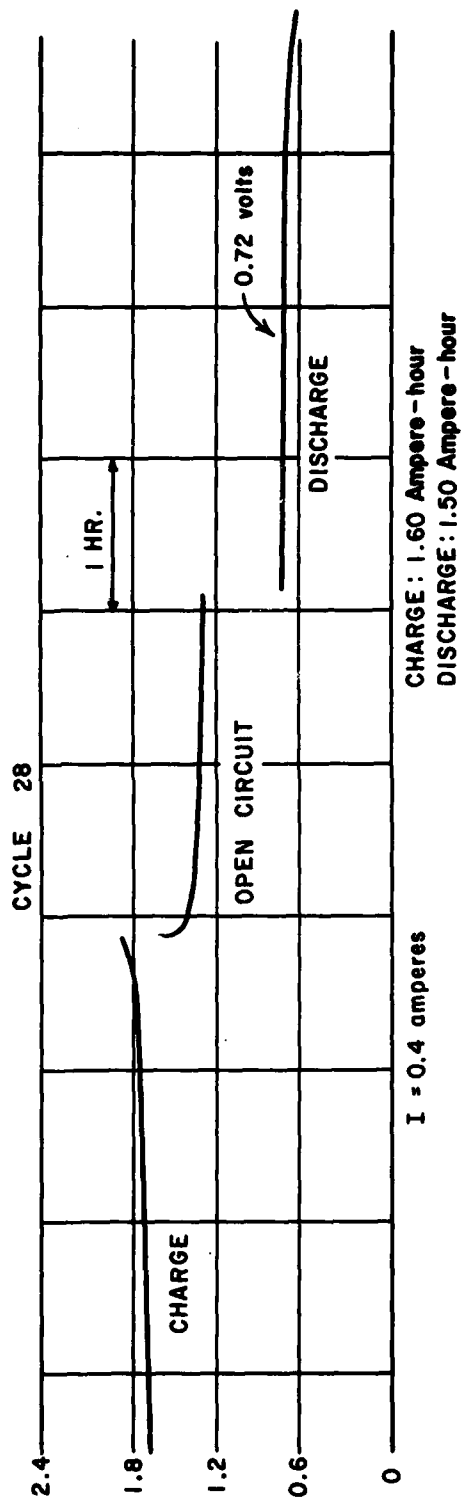
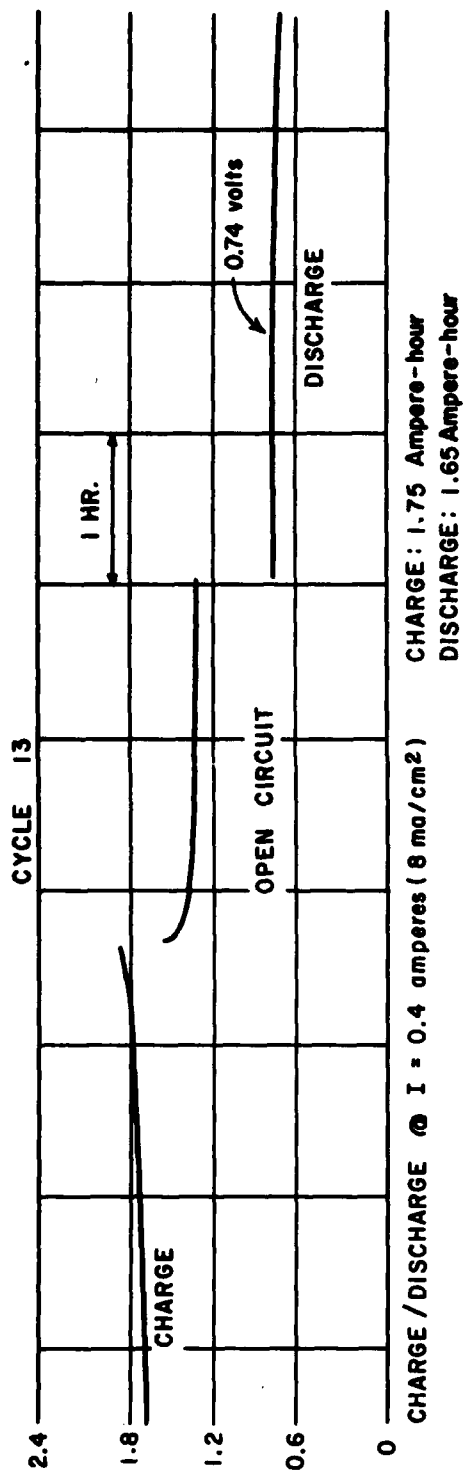


Figure 8. Voltage-time Traces for Cadmium-Air Cell A-2

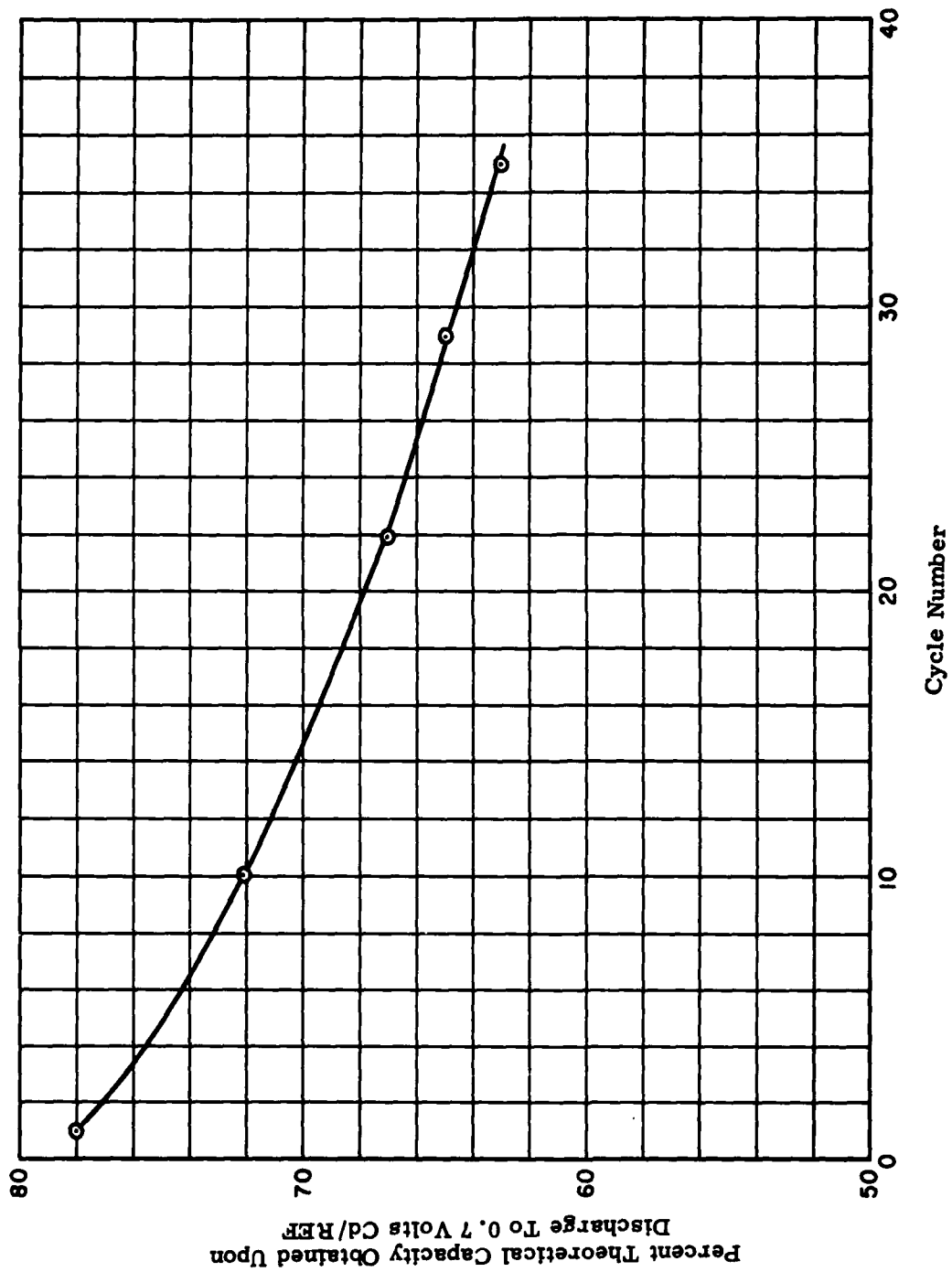


Figure 9. Change in Discharge Capacity on Cycling Cadmium-Air Cell A-2

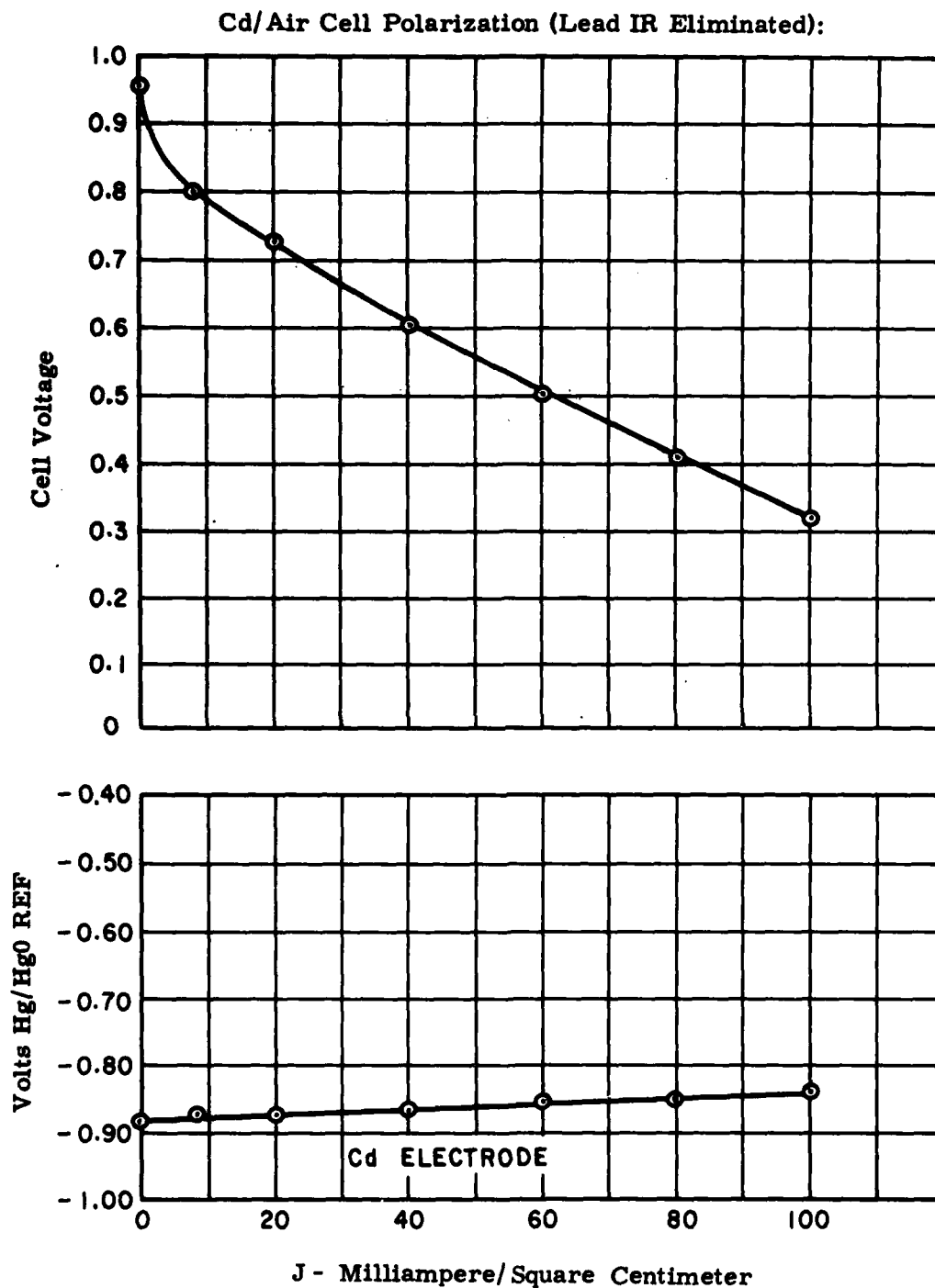


Figure 10. Cadmium-Air Cell A-2 Polarization

The charging electrode was wired to the air electrode so that it operated partly as a charging electrode. A Hg/HgO reference electrode was used to measure the polarization of the two electrodes separately.

After a C/15 rate initial charge the cells were cycled automatically in a sealed bell-jar filled with air at one atmosphere. Constant resistance discharges were timed at the two hour rate and constant voltage charges at the eight hour rate.

Hydrogen formation at the zinc electrodes was high based on visual observations and discharge capacities diminished substantially after five cycles. Degradation of air electrode performance was equally rapid. Speculation for the poor performance of this cell is:

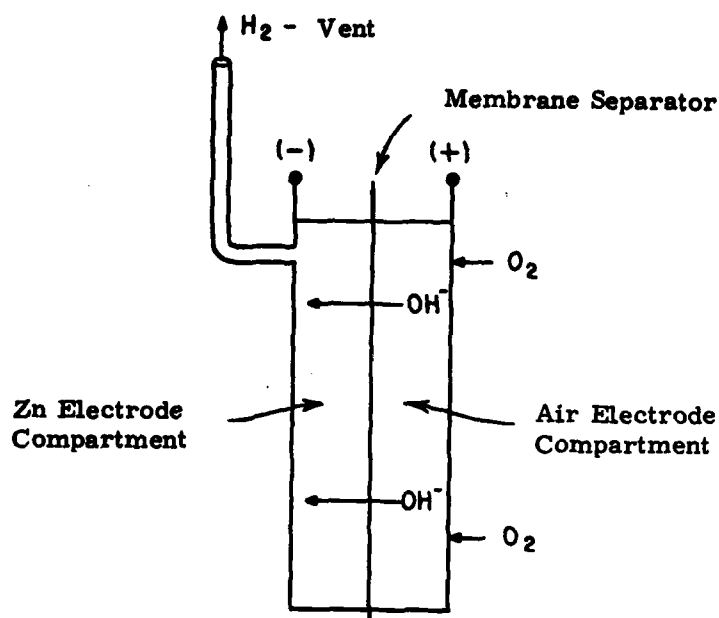
- Poor electrolyte control in the two compartment cell
- Contamination of the zinc
- Formation of an excessively large zinc surface during charge caused by the mixing of ZnO and PKT

Additional tests with other high capillarity materials such as CeO_2 will be conducted. Parallel tests using more conventional separator materials are also planned.

The two compartment test cell utilizing a membrane separator continues to create a unique problem. In recent qualitative observations made on a compartmented zinc-air cell, the anticipated volume changes in the two compartments were not observed. An effect opposite to the one postulated in subsection "Zinc-air Cells," was observed.

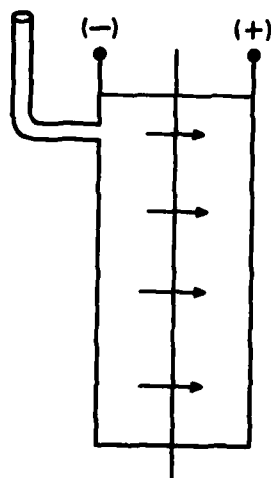
Part A of Figure 11 shows the anticipated electrolyte flow during discharge, namely from the air electrode compartment to the zinc anode compartment. Part B of Figure 11 represents an actual observation in a test cell. This behavior is tentatively attributed to electro-osmotic pumping through the membrane separator. As expected, reversed pumping occurred during charge.

Most of the tests in which the pumping action was observed were made using Union Carbide regenerated cellulose tubing, deglycerinated and desulfured, 0.0026 inch thick as the separator. Essentially, the same results were obtained using other membranes in the same type of cell.



Anticipated Electrolyte Transport

A. Without Electro-osmosis



Observed Electrolyte Transport

B. Presumably by Electro-osmosis

Figure 11. Mass Transport Inside Zinc-Air Cell with Membrane Separator During Discharge

Section 5

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- (19) Pfluger, H. L. , and Hoyt, H. H. , "Improved Separators for Silver Oxide-Zinc and Silver Oxide-Cadmium Cells for Spacecraft Application," Final Report on Contract NAS 5-3467, Goddard Space Flight Center, November 1964.
- (20) Pfluger, H. L. , and Hoyt, H. H. , "Improved Separators for Silver Oxide-Zinc and Silver Oxide-Cadmiun Cells for Spacecraft Application," Final Report on Contract NAS 5-9107, Goddard Space Flight Center, November 1965.

Appendix

PRELIMINARY ENERGY DENSITY CALCULATIONS ON THE CADMIUM AIR BATTERY

To explore the possible energy densities of the cadmium-air battery, three anode thicknesses were selected and analyzed.

Anode A, impregnated sintered nickel plaque, 0.070 inch thick, was selected because of the energy density requirements of the battery.

Anode B, pasted cadmium oxide, 0.130 inch thick, was selected because it represents the maximum anode thickness that can be contained in a battery box 11 inches long, after consideration is given to space requirements of cathodes, separators, and all component spacing.

Given:	Voltage	24 volts
	Discharge rate	C/5
	Plate dimensions	3 inches by 7 inches
	Battery length excluding case	11 inches
	Electrolyte	42 percent KOH Specific gravity 1.42
Assumed:	Operating voltage	0.78 volt/cell
	Number of cells	31 cells
	Separator thickness	0.008 inch thick
	Cathode thickness	0.012 inch thick
	Cathode	0.1 grams/square centimeter Two-sided cathode
	Cathode spacing	0.20 inch

Battery A Impregnated sintered nickel plaque, 45 weight percent $\text{Cd}(\text{OH})_2$, 67 percent void when charged.

A_1 0.070 inch thick, 65 percent utilization, (estimated).

A_2 0.130 inch thick, 60 percent utilization, (estimated).

Battery B Pasted cadmium oxide anode on nickel screen, 2.5 weight percent polyvinyl alcohol binder in solution, 67 percent void when charged.

- B₁ 0.070 inch thick, 62 percent utilization, (estimated),
- B₂ 0.130 inch thick, 57 percent utilization, (estimated),
- Battery C Electrodeposited anode on nickel screen, 4.5 weight percent nickel screen, 68 percent void when charged.
- C₁ 0.070 inch thick, 65 percent utilization, (estimated),
- C₂ 0.130 inch thick, 60 percent utilization, (estimated),

The cadmium loadings and void volumes are based on measured values for batteries A and C, and based on preliminary data in the case of battery B.

Void volume and pore opening percentages may have to be increased for thick anodes in order to obtain adequate cadmium utilization.

As shown in Table 8, the void volumes of each of the three batteries are approximately the same in the charged state, but the cadmium densities are not. For this reason, the void volumes of the three batteries are not the same in the discharged states. For example:

<u>Battery</u>	<u>*Percent Void Volume on Discharge</u>
A	54
B	42
C	39

These data include only the material within the battery compartment. When the weight of auxiliary equipment, battery box, and additional electrolyte to compensate for electrolyte lost through evaporation is added to the system, it is possible that the energy density may be reduced by one-third. If a CO₂ scrubber is necessary, a further weight penalty will be incurred.

Since the weights of the cathode and electrolyte are fairly well established, improvements in energy density depend upon improvement in cadmium utilization over the estimated values indicated on the Table 9 "Estimated Performance."

*Assuming 65 percent utilization

Table 8

WEIGHT ANALYSIS

	A ₁			B ₁			C ₁			A ₂			B ₂			C ₂		
	% of Total	Lbs		% of Total	Lbs		% of Total	Lbs		% of Total	Lbs		% of Total	Lbs		% of Total	Lbs	
Cathode	23.2	1.90		21.8	1.90		21.8	1.90		15.3	1.90		13.9	1.90		13.0	1.90	
Separator	6.9	0.56		6.5	0.56		6.4	0.56		4.5	0.56		4.1	0.56		3.7	0.56	
Anode																		
Total	58.3	4.76		56.9	4.93		57.1	4.97		69.0	8.62		67.3	9.25		68.9	10.23	
Cd	24.1	1.97		44.9	3.89		47.8	4.16		29.8	3.72		54.0	7.35		57.8	8.59	
Electrolyte																		
In Cathode & Separator	5.4	0.44		5.1	0.44		5.1	0.44		3.5	0.44		3.2	0.44		2.9	0.44	
In Anode	2.0	0.16		2.0	0.17		1.5	0.13		2.7	0.34		2.3	0.32		1.6	0.24	
For Anode Discharge	4.2	0.34		7.7	0.67		8.1	0.71		5.0	0.63		9.2	1.26		9.9	1.48	
100	8.16	100		8.67	100		8.71	100		12.49	100		13.73	100		14.85	100	

Table 9

ESTIMATED PERFORMANCE

	A ₁	B ₁	C ₁	A ₂	B ₂	C ₂
Cadmium (Pounds Total)	1.97	3.89	4.16	3.72	7.35	8.59
Cadmium (Pounds/Cell)	0.0635	0.125	0.134	0.120	0.237	0.277
Cadmium (Grams/Cell)	28.8	56.8	60.8	54.5	107.6	125.8
Ampere-hours/Cell (100% Utilization)	13.7	27.1	29.0	26.0	51.3	60.0
Estimated Utilization	0.65	0.62	0.65	0.60	0.57	0.60
Ampere-hours/Cell	8.9	16.8	18.9	15.6	29.2	36.0
Ampere-hours/Pound of Battery Weight	1.08	1.94	2.23	1.26	2.15	2.42
Watt-hours/Pound	25.9	46.6	53.5	30.2	51.6	58.1

Table 10

CONTRACT DAAB 07-67-C-0257
DISTRIBUTION OF TIME
MAY 1, 1967 THROUGH JULY 30, 1967

<u>Personnel</u>	<u>Man-Hours</u>
Dr. W. N. Carson, Jr., Electrochemist	8
Dr. W. J. Van der Grinten, Chemical Physicist	32
H. H. Hirsch, Metallurgist	225
C. E. Kent, Program Manager	66
G. Hahn, Mathematician	6
P. J. Moran, Specialist, Electrochemical	
Sub Total, Scientists and Engineers	<u>337</u>
Engineering Technicians	770.3
Shop and Services	<u>103.5</u>
TOTAL HOURS	<u>1,210.8</u>

Table 11

CONTRACT DAAB 07-67-C-0257
MEETINGS AND CONFERENCES
May 1, 1967 through July 30, 1967

<u>DATE</u>	<u>PLACE</u>	<u>PERSONS</u>	<u>SUBJECT</u>	<u>ACTION</u>
1967				
8 May	Schenectady, N.Y.	USA ECOM M. Sulkes G. Freisinger GE CO. C. E. Kent R. C. Osthoff A. Glenn W. N. Carson W. J. van der Grinten H. H. Hirsch P. J. Moran	Work Program for New Contract	Iron-air work by GE deferred for completion of ECOM in-house experiments in October. GE to emphasize the system most likely of successful development during the year.
17 May	Atlantic City, N.J.	USA ECOM M. Sulkes GE CO. W. J. van der Grinten C. E. Kent H. H. Hirsch	Standard Test Cells Reference Literature	Bibliography of Government reports provided. Use of vertical orientation on test cell agreed upon.
17 May	Atlantic City, N.J.	GE CO. W. N. Carson C&D Battery Co. E. Willihnganz	Anodes for Lead-air Cells	C&D Battery Co. will supply samples of porous lead.
26 May	Lynn, Mass.	GE CO. W. N. Carson RADC A. Ficket, DECO	Air electrodes for Lead-air Cells	Samples obtained of current style Ion Exchange Membrane electrodes for Acid Systems.
1 June	Pt. Monmouth N.J.	USA ECOM M. Sulkes H. Mandell G. Freisinger GE CO. H. H. Hirsch C. E. Kent	General Technical Discussion	Emphasis on Cadmium-air System.
5 June	National Lead Co.	GE CO. W. N. Carson National Lead J. Mees W. Bundy A. Fleischer, Consultant	Lead anodes	Samples of high porosity anodes to be supplied.
18 July	Schenectady, N.Y.	USA ECOM M. Sulkes GE CO. C. E. Kent W. N. Carson W. J. van der Grinten H. H. Hirsch	Experimental Planning	Progress Report.

F-200.1473 DD Form 1473: Document Control Data—R&D

Security Classification								
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(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)								
1. ORIGINATING ACTIVITY (Corporate author) Research and Development Center General Electric Company Schenectady, New York 12305		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED						
		2b. GROUP						
3. REPORT TITLE Rechargeable Metal-Air Cell								
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) First Quarterly Report (From 1 May 1967 to 31 July 1967)								
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6. REPORT DATE December 1967	7a. TOTAL NO. OF PAGES 55	7b. NO. OF REFS 20						
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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY US Army Electronics Command Fort Monmouth, New Jersey 07703 AMSEL-KL-PC							
13. ABSTRACT → Preliminary design calculations indicate potential energy densities of the following ranges for operating cells: <table border="0"> <tr> <td>Lead-Air,</td> <td>30-33 watthours/pound ;</td> </tr> <tr> <td>Cadmium-Air</td> <td>35-45 watthours/pound ;</td> </tr> <tr> <td>Zinc-Air</td> <td>30-60 watthours/pound .</td> </tr> </table> Principal technical problems associated with the battery systems under study are: 1. Obtaining maximum anode utilization in terms of ampere-hours per square foot of electrode geometric surface area during successive charge-discharge cycling; 2. Control of corrosion of the cathode (air electrode), particularly during the charge portion of the charge-discharge cycle; 3. Control of gases generated during the charge and discharge portions of the charge-discharge cycle. *Lithiated nickel oxide coating of the nickel substrate of cathodes intended for use as bifunctional electrodes appears to be useful as a corrosion control device.			Lead-Air,	30-33 watthours/pound ;	Cadmium-Air	35-45 watthours/pound ;	Zinc-Air	30-60 watthours/pound .
Lead-Air,	30-33 watthours/pound ;							
Cadmium-Air	35-45 watthours/pound ;							
Zinc-Air	30-60 watthours/pound .							

F-200.1473 DD Form 1473: Document Control Data—R&D—Continued

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		ROLE	WT	ROLE	WT	ROLE	WT
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