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CADMIUM-AIR CELL STUDIES

Otto C. Wagner

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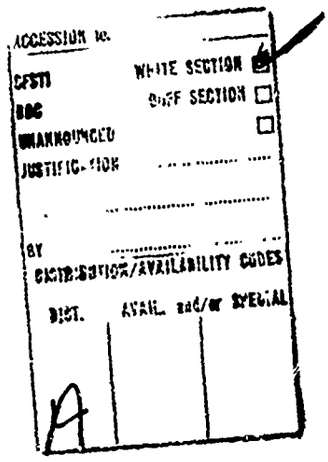

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a. 42 watthours/pound

b. 2.35 watthours/in^3

c. Price - about $500.00

d. $0.0017 per watthour per cycle (assuming 500 cycles).

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CADMIUM-AIR CELL STUDIES

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Electronics Technology and Devices Laboratory

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CADMIUM-AIR CELL STUDIES

INTRODUCTION

The cadmium-air battery was selected as the simplest system to develop as an electrically rechargeable metal-air battery. Zinc is a "hornets nest" of problem areas, such as shorting by zinc dendrites, "shape-change" loss of electrical capacity by zinc erosion and corrosion and redox capacity loss by soluble and/or colloidal platinum (oxygen catalyst of bifunctional air cathodes), iron, nickel, and other impurities which possess low hydrogen overvoltages. In the main, cadmium-air was selected as a stepping-stone toward the development of the more sophisticated, economically practical, and higher energy density zinc air system. However, it should be noted that cadmium-air or cadmium-oxygen batteries should establish a niche in the battery field for limited applications, such as space exploration, where cost is not critical, but where long life, as well as high energy density, is required.

In general, the cadmium-air battery is of interest to the battery technologist in that:

a. It has a theoretical energy density of 202 watthours per pound.

b. The stability and cycle life of the alkaline cadmium anode have been demonstrated in nickel-cadmium and silver-cadmium batteries.

c. The cadmium anode has a low self discharge rate.

d. The cost of the system should be comparable to that of nickel-cadmium batteries, assuming the platinum loading of the air-cathode is less than 6 mg/cm^2 and/or an inexpensive oxygen catalyst is employed.

Companies and Government Agencies reported to have been engaged in cadmium-air battery development are: (1) General Electric, (2) ESB, (3) Leesona Moos, (4) Union Carbide, (5) US Army Electronics Command, (6) Yardney Electric, (7) Astropower, (8) Energy Research, (9) Electro-Optical, and others.

The USAECOM program on cadmium-air batteries was initiated in the fall of 1967. The problem areas and their solutions were reported in earlier reports.[1,2,3,4] In summary, the problems and their solutions are as follows:

Problem	Solution
1. Shorting thru the membrane by cadmium penetration	1. Remove CO_2 from the in flowing air supply and charge at medium to high rates (about 10 mA/cm^2).

Problem	Solution
2. Capacity "fade out" and memory-type losses in capacity by the cadmium anode	2. CO_2 removal, employ 20-30% KOH electrolyte and occasional overcharge of the cell at medium to low rate of charge (trickle and/or pulse type charging).
3. Poisoning of the air cathode	3. Saturate the electrolyte with zincate or aluminate ions, CO_2 removal and, as reported in this report, the employment of washed dry-charged cadmium anodes.
4. Water Loss	4. Design a sump at the base, sides, and top of this unit cell. An electrolyte level indicator should be provided and the cell should be "topped" with distilled water when the cell level is low. Also, the use of 5-10 mil polyamide felt on the electrode faces provides sufficient "irrigation."
5. Instability of most state-of-the-art air or oxygen cathodes (of the bifunctional charging and discharging types).	5. At present the bifunctional platinum catalyzed Leesona cathode is regarded as state-of-the-art. The use of perovskites as air electrode catalysts should be investigated. In addition, air cathode weeping or flooding can be prevented by use of multi-layed wetproofed and optimumly catalyzed air cathodes. Each layer has a different degree of hydrophobicity - the most hydrophobic layer being on the electrode-air interface.

The purpose of this work was to integrate the above-listed improvements into cadmium-air cells which would be life cycled. In addition, it was of interest to determine the shelf life characteristics of the system.

EXPERIMENTAL PROCEDURE

The sponge cadmium anodes were prepared in the following manner: (a) Cadmium oxide (Fisher Certified, Cat. No. C-16) was homogeneously blended with 5% by weight of carbonyl nickel powder (International Nickel Company, Type 255) and 5% by weight of ferric oxide extender (Fisher Certified, Cat. No. T-315), and (b) 44 g of the cadmium oxide mix were mold pressed into an electrode containing an Aldex paper wrap (Aldine Corporation), a nickel Exmet grid (Exmet Corporation), and a .005" thick nickel tab. The electrode dimensions were: 0.095" in thickness, 3-1/2" in height, and 2-3/8" in width, and the electrode porosity (in the fully charged state) was 62.5%.

The unit cadmium-air cells were constructed as follows: The sponge cadmium anode was inserted into a heat-sealed polyamide Pellon bag of 5 mil thickness (2506 K, Pellon Corporation). Around this, one and a quarter layers of RAI 2991 membrane were laterally wrapped (Radiation Applications, Inc.). The wrapped negative was then inserted into an open "U"-type Pellon interseparator. This completed the separator system for the unit cell. The electrode pack was finally inserted into a bicell containing state-of-the-art bifunctional air-cathodes manufactured by Leesona Moos Corporation. Nylon mesh air spaces 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 instrumentation employed in this program is shown in Fig. 1. The unit cadmium-air cell was contained in a reaction kettle. An electrolyte reservoir provided electrolyte to the electrodes by means of the wicking action of the Pellon wraps. The cell was cycled using an automatic cycler with the voltage cutoff set to zero volts on discharge and 1.9 V on charge (C/5 rates of charge and discharge). Reference readings were taken with a potentiometer using a partially charged nickel-hydroxide reference electrode. Charge-discharge curves were automatically recorded by a Honeywell-Electronik voltage recorder. When desired, carbon dioxide was removed from the incoming flow of air by means of a scrubber which contained KOH solution. All tests on this program were run at room temperature ambient.

DISCUSSION AND RESULTS

E-I Curves of Cadmium-Air Cells

E-I curves of cadmium-air cells containing 20% KOH (CA-69-1) and 30% KOH (CA-69-2) are shown in Fig. 2. At current densities up to 250 mA/in^2 the cadmium anode sustains very little polarization or IR drop. However, the Leesona platinized cathode is subject to considerable polarization with 30% KOH electrolyte at current densities higher than 100 mA/in^2. In 20% KOH electrolyte the cathode suffers little polarization at current densities as high as 250 mA/in^2.

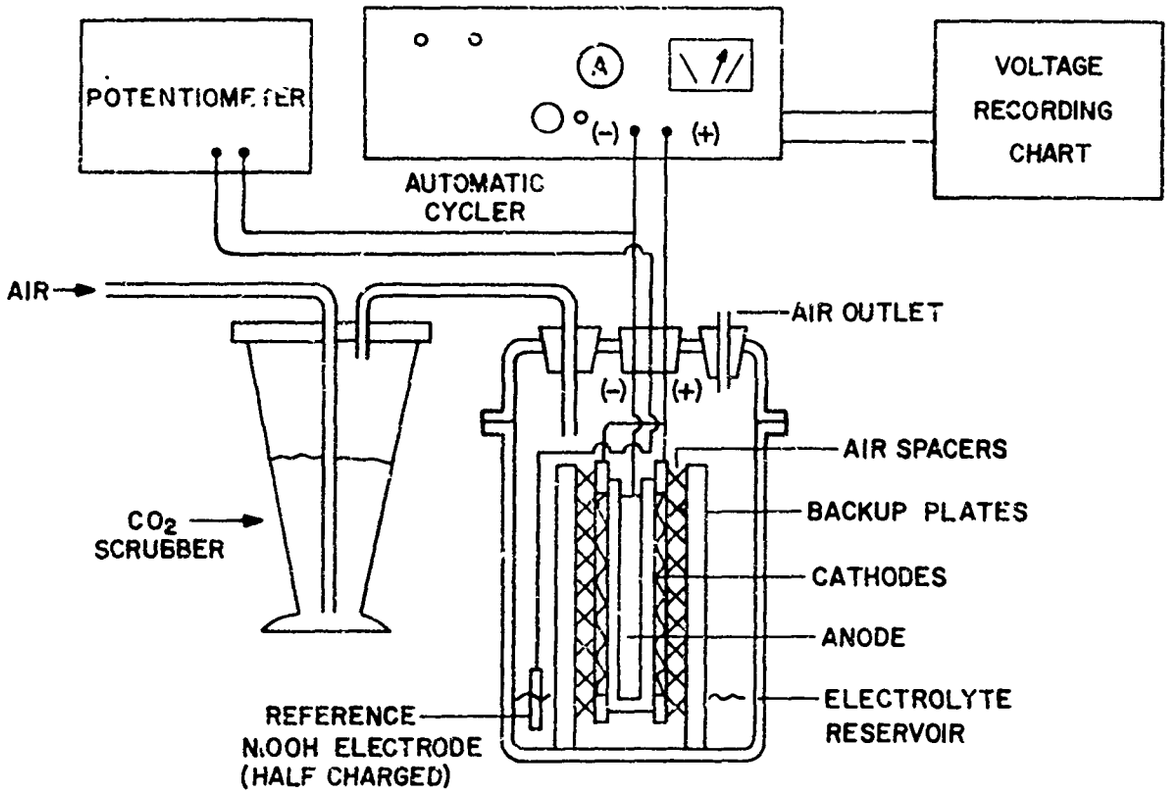
Air flow was at normal convection at current densities below 100 mA/in^2. At higher current densities, the air flow was pumped at a small pressure of several inches of water. Air was scrubbed in these tests. Pertinent design features are also shown in Fig. 2.

On the basis of these results, 20% KOH was selected as electrolyte for cadmium-air cell development and testing in this program.

Capacity Maintenance of Formed and Unformed Cells

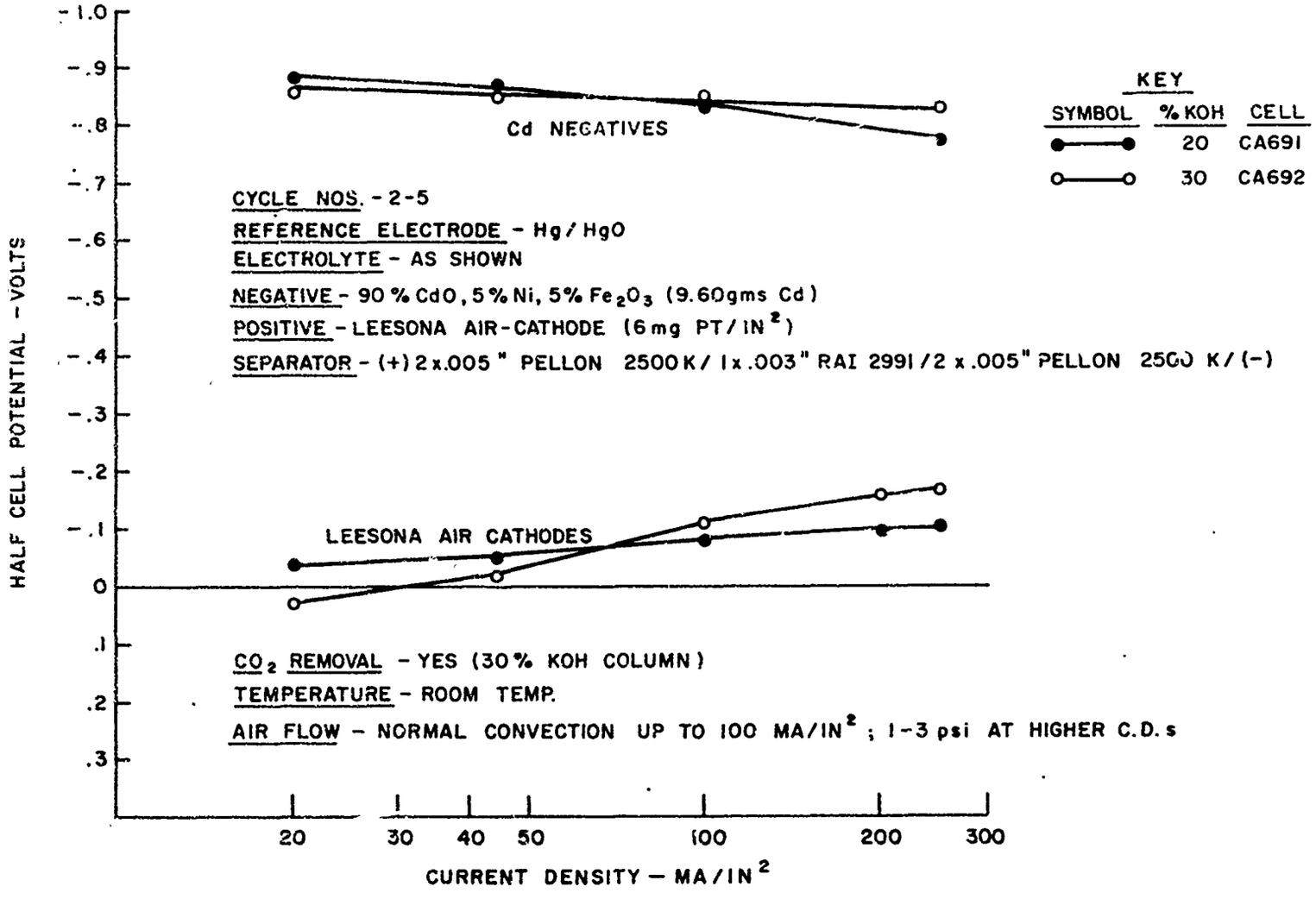
Two similarly designed and constructed cadmium-air cells were cycled at 100% depth of discharge. As shown in Fig. 3, the cell with an unformed cadmium anode lost about one third of its initial capacity in 40 cycles. By unformed, it is meant that the anode was initially in the oxide state and required in situ charging. The cell with a dry charged (formed) cadmium anode suffered no capacity loss in 50 cycles and was allowed to life cycle (to be discussed in the next section).

INSTRUMENTATION



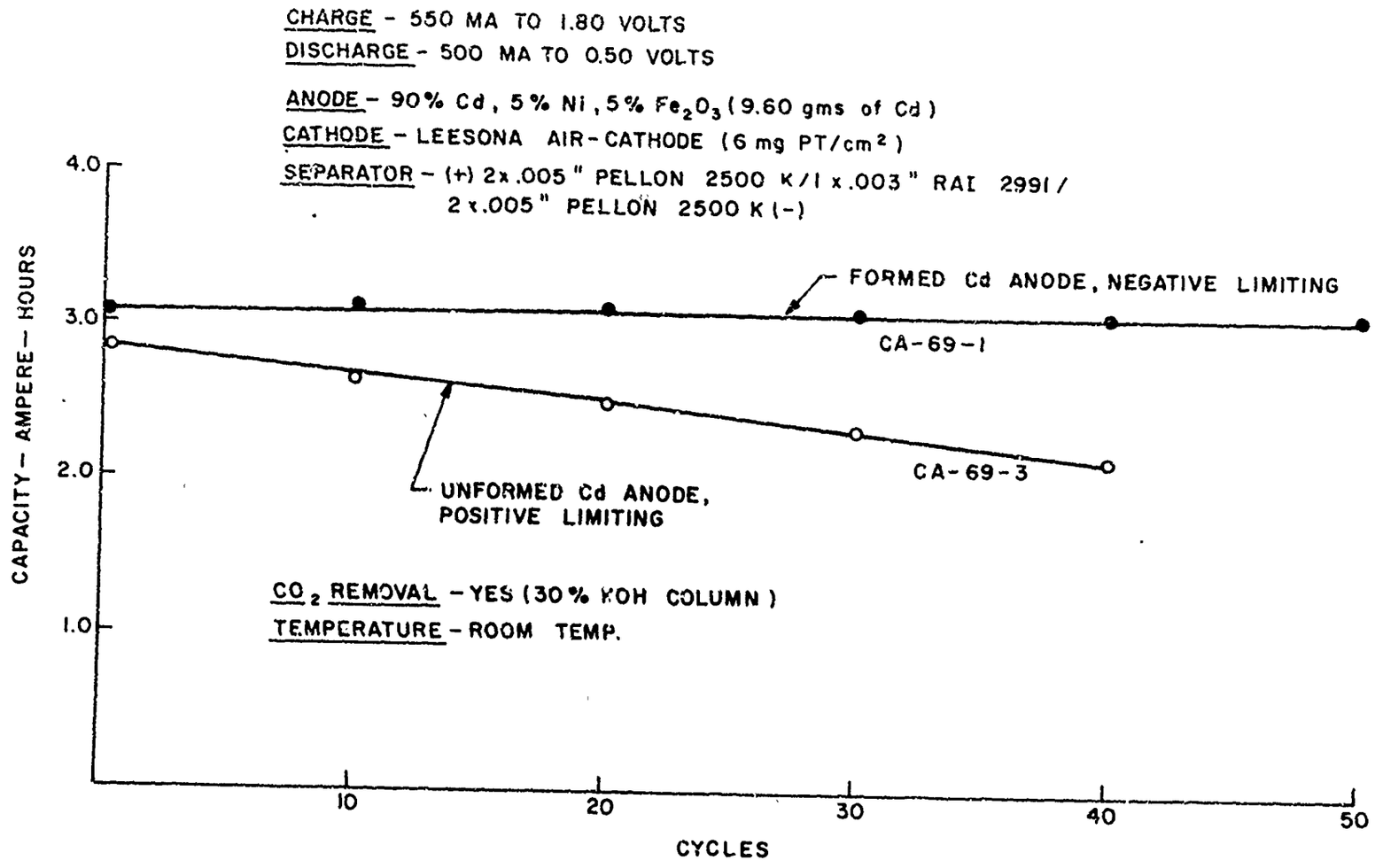
UNIT CELL WITHIN REACTION KETTLE

FIG. 1



E - I CURVES OF CADMIUM - AIR CELLS (CA-69-1 AND CA-69-2)

FIG. 2



CADMIUM AIR CELLS - UNFORMED VERSUS FORMED CADMIUM ANODES

FIG. 3

In the case of the unformed cell, it was noted that the electrolyte in the sump was brownish with suspended and colloidal oxides and/or hydroxides of cadmium. It appears that the unformed anode sheds sufficient amounts of oxide and hydroxide to contaminate the air cathode. By contamination it is meant that catalytic platinum sites were wetted and partially flooded as a result of cadmium oxide-hydroxide precipitation. In short, the unformed cadmium anode has a negative synergistic effect on its cathode mate. This results in the cell becoming positive limiting on discharge and the resulting capacity loss increases with each subsequent cycle.

Life Cycling of CA-69-1

The capacity maintenance curve of Cell CA-69-1 is shown in Fig. 4. It should be noted that the capacity loss was almost nil for 450 cycles. After 450 cycles, the cell was stored in the semi-charged state for one year. As shown in Table I and in Fig. 4, the cell was positive limiting after one year of storage. The resulting capacity loss was about 20% and the closed circuit voltage had dropped from 0.73 to 0.50 volts. Reference readings showed that these losses were caused by the air cathode. After about 30 cycles (Cycle 480), the net capacity loss was 12%. The closed circuit voltage, however, did not improve appreciably.

After Cycle 480, the old cathode was replaced with an unused Leesona air-cathode. After two cycles, the cell capacity was back to 3.0 ampere-hours, which is the same as the initial cell capacity. This cell was left to life cycle without interruption.

From these tests, it is apparent that the USAECOM cadmium anode possesses many desired features, the main one being its stability on shelf and during life cycling. In addition, its energy density is more than twice that of the conventional sintered-nickel cadmium anode,[6] and it is inexpensive to fabricate (mold pressing, stokes pressing, and continuous roll pasting on a screen-grid).

Paper Design of a 24 Volt, 25 Ampere-Hour Cadmium-Air Battery

It is of interest to the battery technologist and design engineer to determine what a laboratory cell would look like as a finished product in the field. For this purpose, a paper design was worked up for a 24 volt, 25 ampere-hour cadmium-air battery. The pertinent design data are listed as follows:

a. Height of cell - 7.25"

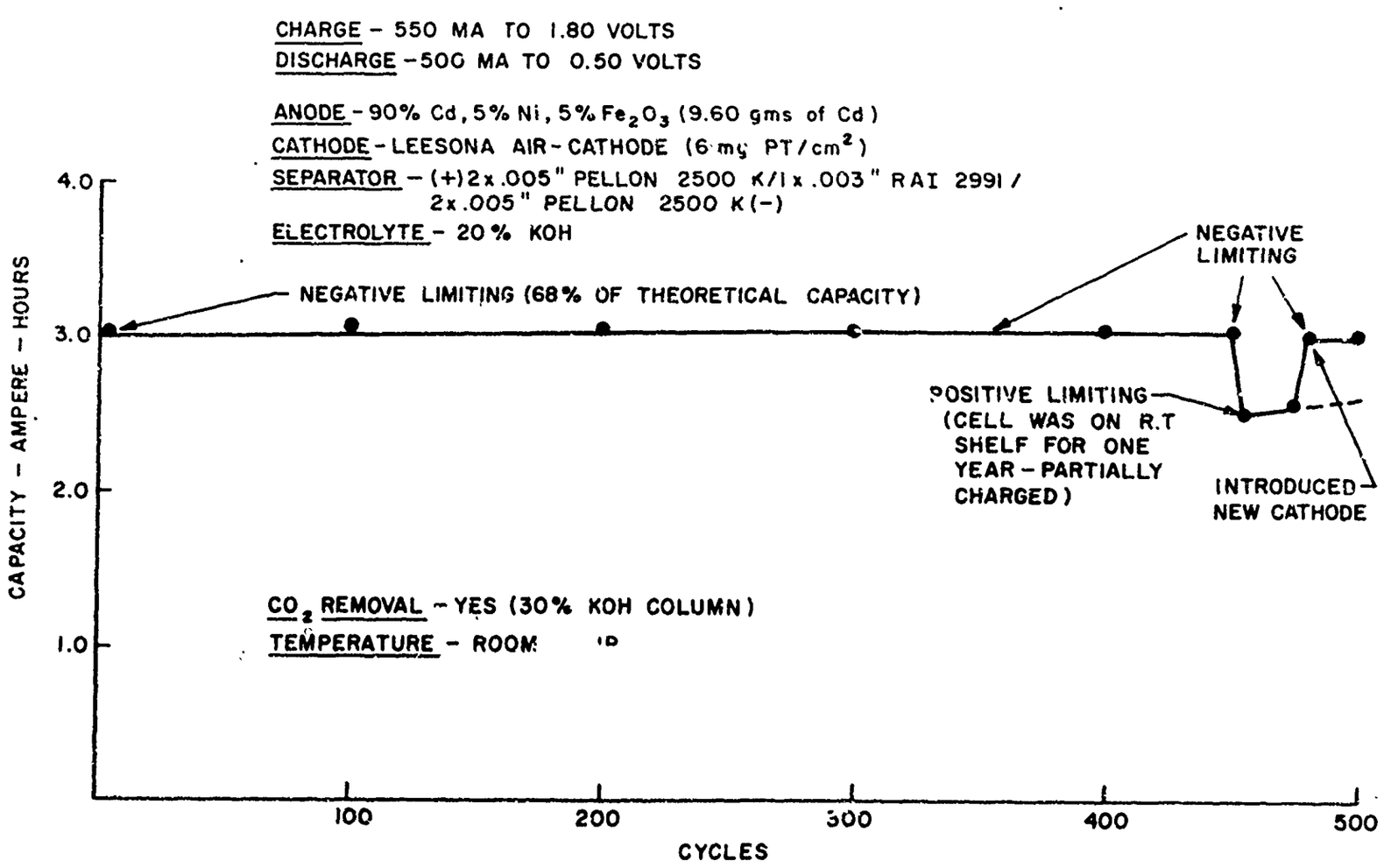
b. Thickness of cell - 0.394" (air spacers being 0.200" thick)

c. Width of cell - 3.75"

d. Weight of negative cell - 92.50 g

e. Weight of cathode/cell - 32.0 g

f. Weight of cell - 202.70 g (0.45 lb)



CAPACITY MAINTENANCE OF CADMIUM - AIR CELL CA-69-1

FIG. 4

Table I. Performance of Cadmium-Air Cells

CA-69-1: Negative - fully formed, 90% Cd, 5% Ni, and 5% Fe_2O_3;
Cathode - Leesona Air-Cathode at 6 mg/cm^2;
Separator - (+) 2 x .005" Pellon/1 x .003" RA 1-2991, 2 x .005" Pellon (-);
Electrolyte - 20% KOH; CO_2 Removal - Yes.

Cycle No.	Charge Rate (mA)	Input (Ah)	Discharge Rate (mA)	Capacity (Ah)	CCV (V)	Negative Half Cell Potential
1	550	3.30	500	3.05	0.77	0.80
10	550	3.30	500	3.05	0.78	0.80
20	550	3.30	500	3.05	0.78	0.80
30	550	3.30	500	3.05	0.78	0.80
40	550	3.30	500	3.05	0.78	0.80
50	550	3.30	500	3.05	0.78	0.80
100	550	3.30	500	3.05	0.77	0.80
200	550	3.30	500	3.00	0.76	0.79
300	550	3.30	500	3.00	0.75	0.79
400	550	3.30	500	3.00	0.74	0.79
450	550	3.30	500	3.00	0.73	0.78
	Cell on stand, partially charged for 1 year.					
451	550	3.30	500	2.40*(+)	0.50	0.78
460	550	3.30	500	2.40*(+)	0.50	0.78
480	550	3.30	500	2.60	0.50	0.78
	Charge air cathodes with unused Leesona Electrodes.					
481	550	3.30	500	3.00	0.75	0.78
500	550	3.30	500	2.95	0.75	0.78
	*Positive limiting on discharge					
CA-69-2:	Same as CA-69-1 except electrolyte is 30% KOH					
1	550	3.30	500	3.05	0.76	0.80
5	550	3.30	500	3.05	0.76	0.80
10	550	3.30	500	3.05	0.76	0.80
CA-69-3:	Same as CA-69-1 except negative is unformed.					
1	550	3.30	500	2.90	0.75	0.80
10	550	3.30	500	2.63	0.73	0.80
20	550	3.30	500	2.46	0.71	0.80
30	550	3.30	500	2.32	0.68	0.80
40	550	3.30	500	2.12	0.65	0.80

g. Volume of cell - 10.4 in^3

h. Number of cells/battery - 32

i. Volume of battery - 256 in^3

j. Weight of battery - 14.4 lb

k. Watthours at C/5 rate - 600

l. Watthours/pound - 41.5

m. Watthours/in^3 - 2.35

Of additional interest to a battery engineer and technologist is what will the battery cost? The pertinent cost estimates are as follows:

a.	Price of platinum at 6 mg/cm^2 and at \$5.00/g	\$304.
b.	Other cathode parts	\$ 53.
c.	Price of cadmium anodes	\$ 25.
d.	Price of separators	\$ 23.
e.	Price of electrolyte	\$ 1.
f.	Price of frames, covers, etc.	\$ 8.
	TOTAL MATERIAL COST	\$414.
g.	Labor at \$3.00/hr	\$ 25.
h.	Overhead at 110% (very conservative)	\$ 27.
i.	Profit (10%)	\$ 50.
	TOTAL PRICE	\$516.
j.	Price per watthour	\$ 0.86
k.	Price per watthour per cycle	\$ 0.0017

From the above data it is seen that the cadmium-air battery could be a very popular system if the price of the platinum catalyzed air cathodes could be reduced by a factor of 5-10. For this reason, considerable effort is presently towards the development of a stable inexpensive bifunctional air cathode. The employment of spinels appears very promising,[5] so are the platinum doped tungsten bronzes. In addition, monofunctional cathodes are available which are relatively inexpensive, such as the Union Carbide fixed zone cathode and the American Cyanamid's silver amalgam air cathode. It is believed that the spinel type, the "fixed zone" type and the silver amalgam type will be the leading candidates in the USAECOM zinc-air program, with the latter because of its detrimental effect on the

CONCLUSIONS

A cadmium-air cell has been developed that: (a) will deliver at least 500 cycles at 100% depth of discharge for each cycle, (b) has an energy density of about 50 watthours per pound at the five hour rate of discharge, and (c) has a cadmium anode that does not lose capacity or significantly change its voltage characteristics after 500 deep cycles.

After one year of storage in the partially charged state, the cadmium anode did not suffer any losses in electrical capacity or voltage characteristics. However, the platinum-catalyzed, bifunctional Leesona air-cathode did suffer about a 15% drop in capacity after one year on shelf (room temperature). In addition, the air-cathode exhibits a large drop in closed circuit potential after the one year storage. Washing the cell and changing the electrolyte did not revive the cathode to any appreciable extent. Only changing the "aged" cathode with an unused Leesona electrode could revive the cell to its initial performance.

In situ formation of the cadmium anode promotes poisoning of the air-cathode. This is believed to be due to the precipitation and settling out of soluble cadmiate ions, as well as colloidal and suspended cadmium oxide and/or hydroxide on the active catalytic sites of the air-cathode. This poisoning results in large losses in electrical capacity, the losses increasing with increased cycling of the cell. This situation can be avoided by constructing the cadmium-air cell with washed dry charged cadmium anodes (charging the anode in a tank of 20-30% KOH under an electrode pack pressure of about 1-3 psi).

A paper design of the cadmium-air battery of nominal 25 Ah capacity and of 24 volts, and constructed with unit cells of the CA-69-1 design, possesses the following characteristics:

a. 42 watthours/pound

b. 2.35 watthours/in^3

c. Price of battery - about $500.00 at $0.86/watthour (cost of air cathodes being $360.00)

From these parameters it is seen that a cheaper air-cathode, as well as a more stable one, is required to make the USAECOM cadmium-air system more practicable.

FUTURE WORK

On the basis of the successful R&D efforts on the cadmium-air system at USAECOM, the following work appears to be warranted:

a. Development of air electrodes that are more stable on shelf than the state-of-the-art Leesona cathodes employed in the USAECOM cadmium-air models. Also, to select and/or develop less expensive bifunctional air electrodes than the platinum-catalyzed Leesona air cathodes.

b. Test actual cadmium-air battery cells at various temperatures and rates of discharge. Also, to determine the stability of the cadmium-air system on shelf in the charged and discharged states at various temperatures.

c. To attain cycle life data at various temperatures of optimumly designed and constructed cadmium-air batteries.

d. To develop a closed cadmium-oxygen system for space applications.

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