

PIC-BAT 209/11

SECONDARY CADMIUM-AIR BATTERIES

Otto C. Wagner

Power Sources Division, Electronic Components Laboratory
USAECOM, Fort Monmouth, N. J.

69-10285

In order to attain a maximum energy density from the cadmium-air system, sponge cadmium electrodes were developed in this program. The air-cathodes were supplied by two manufacturers who are presently fabricating state of the art electrodes. The separators were supplied by four manufacturers. No auxiliary charging electrodes were employed since the air-cathodes are bifunctional; i.e., they are charging and discharging electrodes.

The major failure modes of the cadmium-air system are: loss of capacity by the cadmium anode (fade-out), shorting by cadmium penetration, poisoning of the air-cathode and water loss.

Fade-Out Problem

When an alkaline cadmium electrode is continuously cycled on a deep discharge regime it loses capacity by a phenomenon referred to as fade-out. This phenomenon is often observed in nickel-cadmium and silver-cadmium batteries when the cells become cadmium limiting on discharge. The capacity loss is attributed to a loss in real surface area by the growth of cadmium crystals and by the subsequent blockage of the electrode pores^{1,2,3}.

The problem of fade-out was to a large extent overcome by the introduction of alpha ferric oxide into the active cadmium powder and by removal of CO₂ from the unit cell. As shown in figure 1 a control cadmium-air cell with a sponge negative containing no extender and exposed to CO₂ (black circles) lost 37 percent of its initial capacity in 12 cycles. A test cell (open squares) with a negative containing 5% ferric oxide and where CO₂ was removed from the unit cell was delivering 80% of theoretical capacity without any loss in capacity for 35 cycles. The combination of 5% ferric oxide extender and CO₂ exposure (black squares) resulted in the lost 30% capacity in 35 cycles, while the combination of no extender and no CO₂ exposure (open circles) resulted in a loss of 25% in capacity in 20 cycles. From these data it is seen that fade-out can be prevented by the addition of alpha ferric oxide extender to the active cadmium powder and by the removal of CO₂ from the unit cell.

The carbonate effect is again shown in figure 2. The figure shows the capacity of the sponge cadmium anode (containing 10% Fe₂O₃) as

PIC-BAT 209/11

percent of theoretical capacity versus cycle number. The prime variable was cycling in a carbonate free electrolyte (open circles) versus a carbonate saturated electrolyte (solid circles). From the figure it is seen that carbonate exposure decreased the capacity of the anode by 30 percent in 35 deep cycles, while the anode in a carbonate free electrolyte lost only 3 percent of its initial capacity in the same number of cycles.

Since carbonate increases the solubility of cadmium in 7 normal KOH by about one order of magnitude ⁴ it appears that carbonate accelerates the recrystallization process of the cadmium electrode ⁵, which at low current densities of charge and discharge results in a loss of real surface area and a subsequent blockage of the electrode pores ^{1,2}.

Cycling data of CO₂ scrubbed unit cadmium-air cells show that anodes containing 5 to 10 percent ferric oxide extender deliver 68 to 70 percent of theoretical capacity after 100 cycles at 100 percent depth of discharge (initial efficiency was 75%). These anode efficiencies result in energy densities of 40 to 45 watt-hours per pound for unit cadmium-air cells of 10 ampere-hour capacity.

Cadmium Penetration

In table I are shown the effects of overcharge, carbonate and separator system on shorting by cadmium penetration. Group A separator wraps were employed in a carbonate saturated cadmium-air cell containing a sponge anode. Group B separator wraps were with a carbonate saturated cell containing a sintered-nickel cadmium anode. Group C separator wraps were with a CO₂ scrubbed cell containing a sponge anode. After shorting the cells were rebuilt with new separator combinations, as shown in the table.

From the data it can be seen that cadmium penetration can be minimized or prevented by: (a) minimizing overcharge, (b) preventing carbonate buildup in the cell (compare group C with groups A and B) and (c) placing a layer of Pellon between the anode and main separator (compare A1 and A2). In addition, sintered-nickel cadmium anodes appear more resistant to shorting than sponge anodes (compare B with A).

Cadmium Poisoning of the Air-Cathode

Both types of air-cathodes evaluated in this program became severely polarized towards the end of discharge in cells discharged at current densities greater than 10 MA/cm². On subsequent recharge the cathodes were reactivated and exhibited a normal E-I discharge response versus the fully charged cadmium anodes. However, versus nearly fully discharged cadmium anodes the air-cathodes become inactive. Even when a fresh uncycled air-cathode was discharged against a nearly fully discharged cadmium anode the cathode became inactive.

Chemical analysis indicates the presence of cadmium in the air-cathode after cycling-the concentration of cadmium in the cathode was 0.1 mg/cm^2 . It is believed that during the end of discharge the cadmium anode increases the concentration of soluble cadmate ion ($\text{Cd}(\text{OH})_2^-$) in the electrolyte to a quantity sufficient to poison the air-cathode. This is presently being explored by chemical analysis of the electrodes and electrolyte. This poisoning occurs when the electrolyte is free of carbonate ions or other impurities. Figure 3 shows that when the electrolyte is saturated with carbonate ions inactivation of the air-cathode will not occur. For comparison, the figure includes the polarization of the air-cathode and cadmium anodes in pure 7 normal KOH (open circles) and 7 normal KOH saturated with carbonate (solid circles).

It is reported that cadmium forms a soluble cadmium carbonate species $\text{Cd}(\text{CO}_3)_2^{-4}$, which is about ten times more soluble than the cadmate ion in 7 normal KOH^{4,6}. Apparently the cadmium carbonate species is beneficial to the air-cathode in that it prevents poisoning by the cadmate ion. However, as was shown in the Figure 2 carbonate severely decreases the capacity of the cadmium anode (after 20 cycles) and therefore is not desirable as an additive to the electrolyte. Consequently, a search was made for electrolyte additives which would: (a) prevent poisoning of the air-cathode by cadmium and (b) would be innocuous to the cadmium anode.

One such additive has been found. As shown in Figure 4, when the electrolyte is saturated with zincate ion the air-cathode will not inactivate at the end of discharge and the electrical efficiency of the anode is not impaired after 10 deep discharge cycles. Since overcharge did not show a zinc deposition step it is apparently safe to saturate the electrolyte with zincate in a rechargeable cadmium-air cell. I might add that aluminate has also been found to prevent cathode poisoning. At present cadmium-air cells with zincate electrolyte are being life cycled and other additives are being screened in an effort to understand and better control the poisoning effects of the air-cathode.

Water Loss and Unit Cadmium-Air Cell Design

The 10 ampere-hour unit cadmium-air cells lost about 0.5cc of water per cycle at the C/5 rate of charge and discharge. As shown in Figure 5, a prototype 10 ampere-hour unit cell design includes a sump at the base of the cell which contains 5cc of reserve electrolyte (as water). The excess water would prevent drying of the cell for about 10 cycles (the unit cells cycled in this program had a sump with 100cc of excess electrolyte). The battery could be watered every 10 cycles through a filling hole in the cover, after unscrewing the sealing plug. The required amount of water could be indicated by constructing the cell with a transparent or translucent plastic frame through which the electrolyte level can be seen and adjusted.

Electrolyte adsorbent polyamide Pellon is placed in both the anolyte and catholyte compartments to transport electrolyte from the sump to the electrodes. The main separator consists of two layers of a non-oxidizable and non-degradable membrane, such as Astroset 3420-09 or RAI, P-300. The anode is 100 mils thick, with an apparent porosity of 62%, and contains 5% ferric oxide extender and 5% carbonyl nickel conductor. The air-cathodes are bifunctional with a platinum loading not exceeding 6 mg/cm². The electrolyte is 30% KOH saturated with zincate. To prevent carbonate buildup in the cell replaceable ascarite air spacers can be attached to the air faces of the air-cathodes or barium hydroxide can be added to the base of the sump.

An actual 24 volt, 25 ampere-hour cadmium-air battery is being constructed by General Electric for the US Army Electronics Command. The battery is being built according to the design parameters that were derived from this program. It is estimated that the unit cells will have an energy density of 45 watt-hours per pound at the C/5 rate and the battery plus case hardware will have an energy density of 35 watt-hours per pound. At present, a test cell has exceeded 300 deep discharge cycles⁷. Therefore, the goal of 500 cycles for the battery can be anticipated.

Conclusions

1. Loss of capacity by the cadmium anode can be prevented by use of ferric oxide extender and removal of CO₂ from the cell.
2. Cadmium penetration can be prevented by removal of CO₂ from the cell, minimizing overcharge and placing an inert electrolyte adsorbent inter-separator between the cadmium anode and main separator.
3. Poisoning of the air-cathode can be prevented by using KOH electrolyte saturated with zincate.
4. Water loss can be compensated by providing the unit cell with an electrolyte sump.
5. Unit cadmium-air cells have been built with a cycle life greater than 300 cycles and an energy density in the range of 40 to 45 watt-hours per pound.

References

1. Investigation on the Negative Electrode of Nickel-Cadmium Cells with Sintered Plates, J. P. Harivel, B. Morignat and J. Migeon, SAFT, Fourth International Symposium on Batteries, Brighton, England, Oct. 64.

2. Charge Acceptance of Cadmium Hydroxide Electrodes at Low Temperatures, Y. Okinaka, Bell Telephone Laboratories, Extended Abstracts of the Chicago Meeting of the E. C. S. Oct. 65.
3. Rechargeable Metal-Air Cell, Technical Report ECOM-0257-3 H. H. Hirsch, W. J. Vander Grinten, W. N. Carson, P. J. Moran, General Electric, Contract No. DAAB07-67-C-0257, April 68.
4. Solubility of CdO in KOH, K_2CO_3 and Their Mixtures, G. M. Jost, Texas Instruments, Inc., Extended Abstracts of the Philadelphia Meeting of the E. C. S., Oct 66.
5. Effect of Carbonate on the Rate Oxygen Recombination in Sealed Nickel-Cadmium Batteries, Y. Okinaka, and D. Turner, BTL, Extended Abstracts of the Buffalo Meeting of the E. C. S., Oct 65.
6. The Nature of Cadmium Ions in Hydroxide and Carbonate Solutions, P. G. Lake, J. M. Goodings, Can. J. Chem., 7, 1089-96(1958)
7. Secondary Cadmium-Air Cells, O. C. Wagner, USAECOM, 22nd Annual Power Sources Conference, May 68.

PIC-BAT 209/11

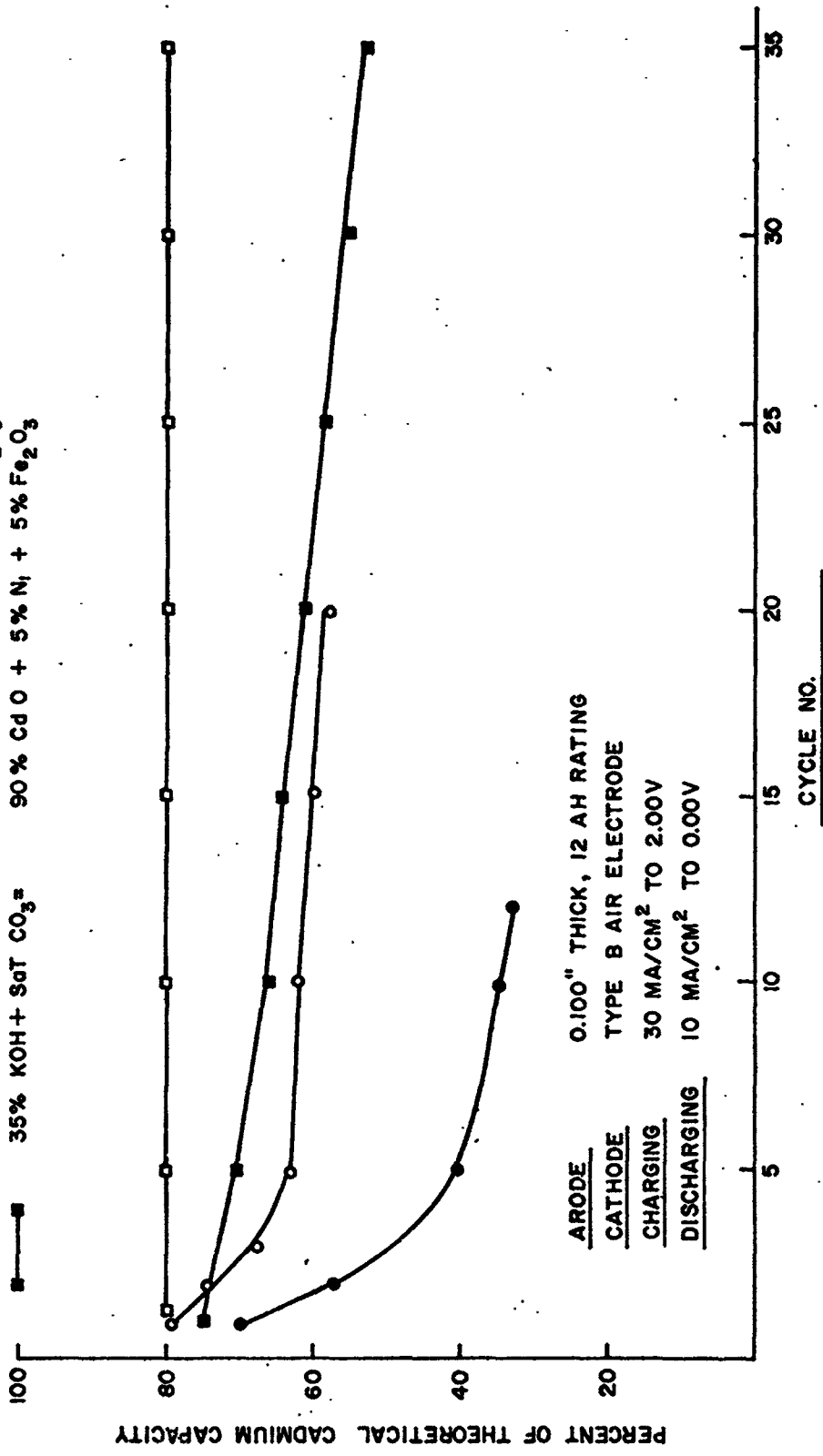
Table I - The Effect of Overcharge, Carbonate and Separator System on Cadmium Penetration.

	<u>Separator System</u>	<u>Cycles to Short</u>	<u>Total AH of Overcharge</u>
A	<u>Sponge Cadmium - Air Cell (CO₃⁼ Saturated)</u>		
A1	(+) 1 X .001" Cellophane/1 X .006" Pellon (-)	58	48
A2	(+) 1 X .006" Pellon/2 X .001" Cellophane (-)	9	5
A3	(+) 1 X .006" Pellon/2 X .002" Astroset /1 X .006" Pellon (-)	75	76
B	<u>Sintered Nickel Cadmium-Air Cell (CO₃⁼ Saturated)</u>		
B1	(+) 1 X .006" Pellon (-)	98	56
C	<u>Sponge Cadmium-Air Cell (No CO₃⁼ In Electrolyte)</u>		
C1	(+) 1 X .006" Pellon/2 X .002" Astroset /1 X .006" Pellon (-)	120 + (still cycling)	180 +
C2	(+) 1 X .006" Pellon/1 X .0015" RAI P300 /1 X .006" Pellon (-)	20 + (still cycling)	20 +

Figure 1
Capacity Maintenance As A
Function Of Cadmium Mix
and CO₂ Exposure

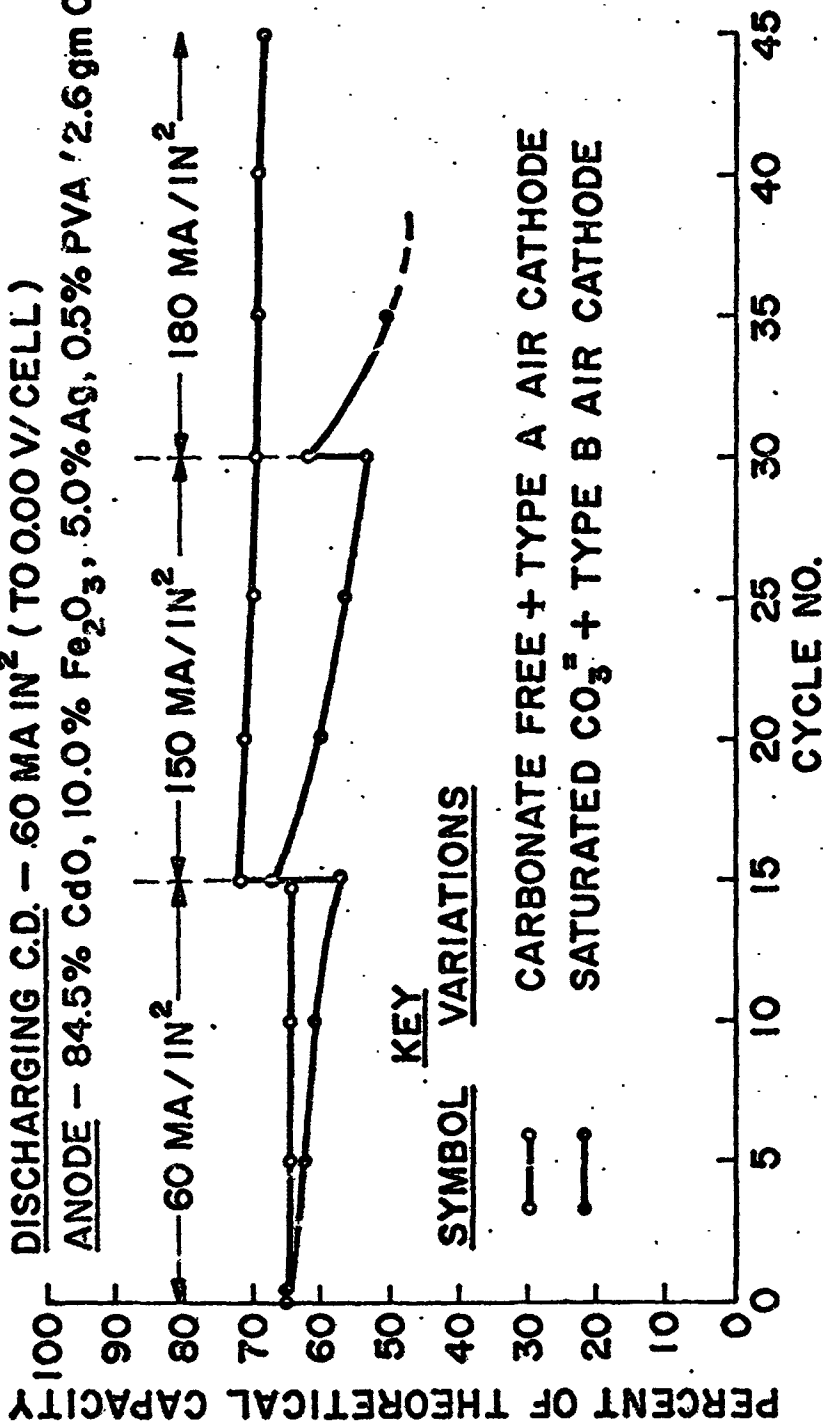
**CAPACITY MAINTENANCE OF A SPONGE CADMIUM ANODE
AS A FUNCTION OF CARBONATE EXPOSURE AND
PRESENCE OF Fe₂O₃ EXTENDER**

<u>SYMBOL</u>	<u>ELECTROLYTE</u>	<u>NEGATIVE FORMULATION</u>
○	35% KOH	94% Cd O + 5% Ni + 1% BINDER
●	35% KOH + Sat. CO ₃	94% Cd O + 5% Ni + 1% BINDER
□	35% KOH	90% Cd O + 5% Ni + 5% Fe ₂ O ₃
■	35% KOH + Sat CO ₃	90% Cd O + 5% Ni + 5% Fe ₂ O ₃



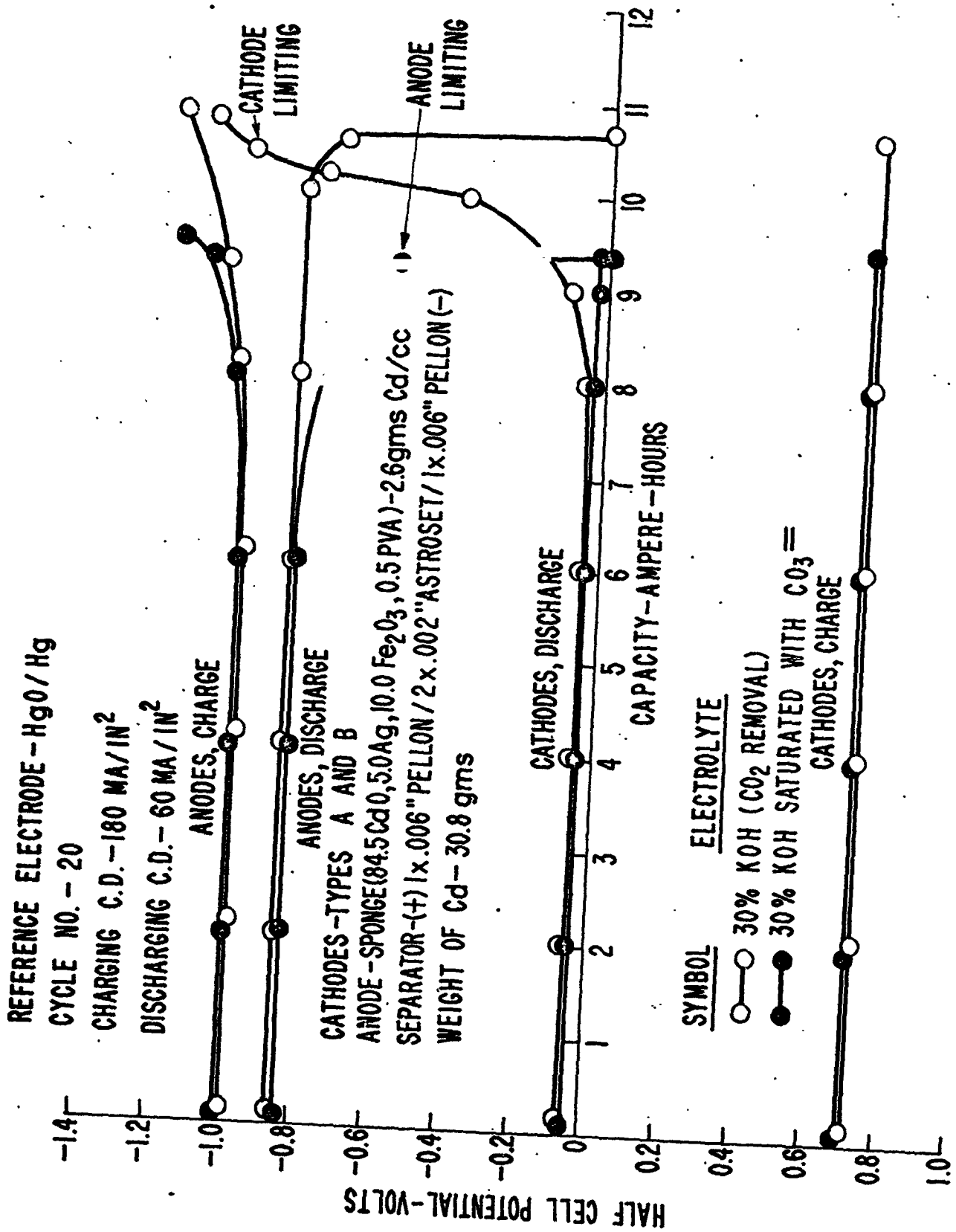
AV-4321-68

CHARGING C.D. - AS SHOWN (TO 1.9 V/CELL)
DISCHARGING C.D. - 60 MA IN² (TO 0.00 V/CELL)
ANODE - 84.5% CdO, 10.0% Fe₂O₃, 5.0% Ag, 0.5% PVA / 2.6 gm Cd/CC)

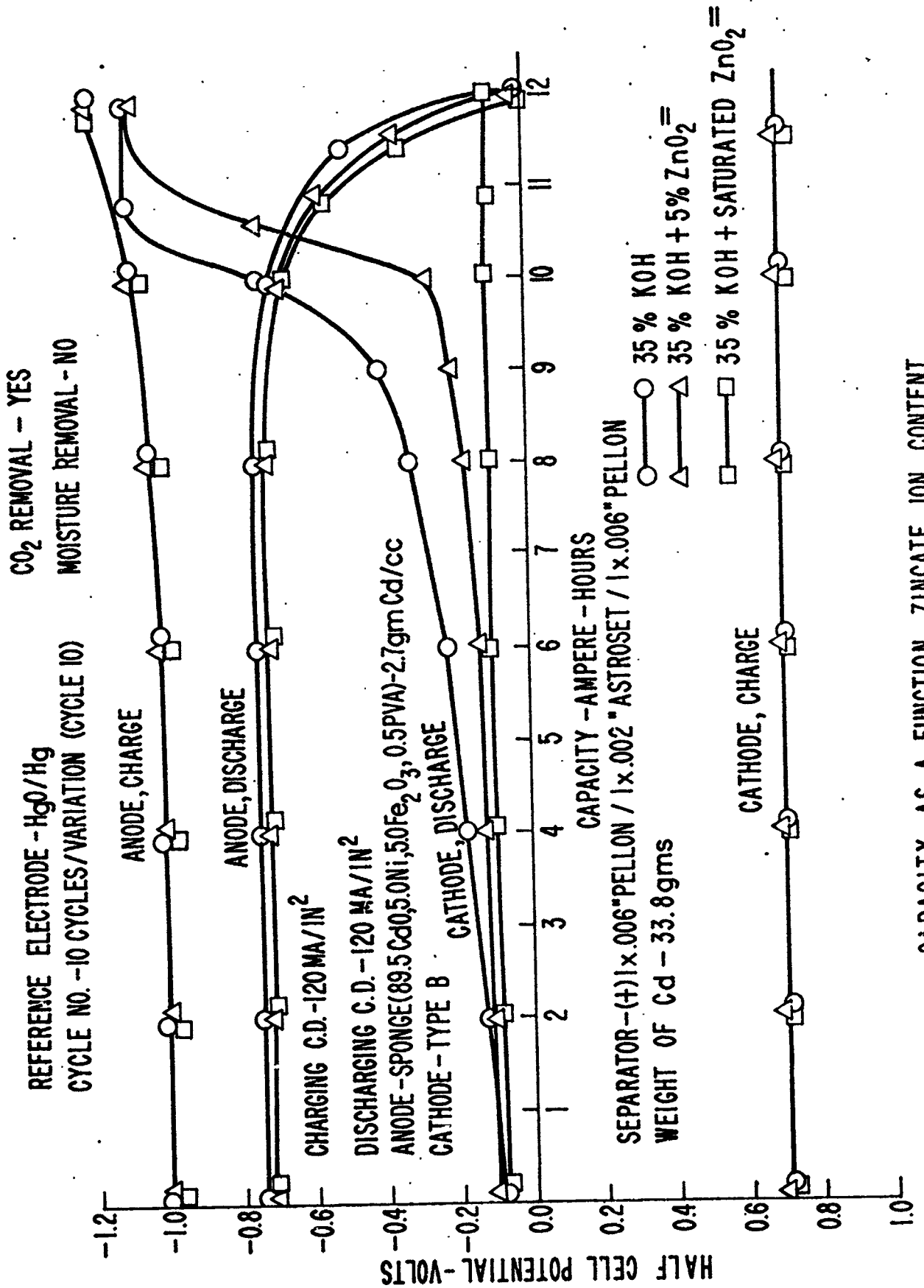


CAPACITY MAINTENANCE AS A FUNCTION OF CARBONATE EXPOSURE AND CHARGING CURRENT DENSITY



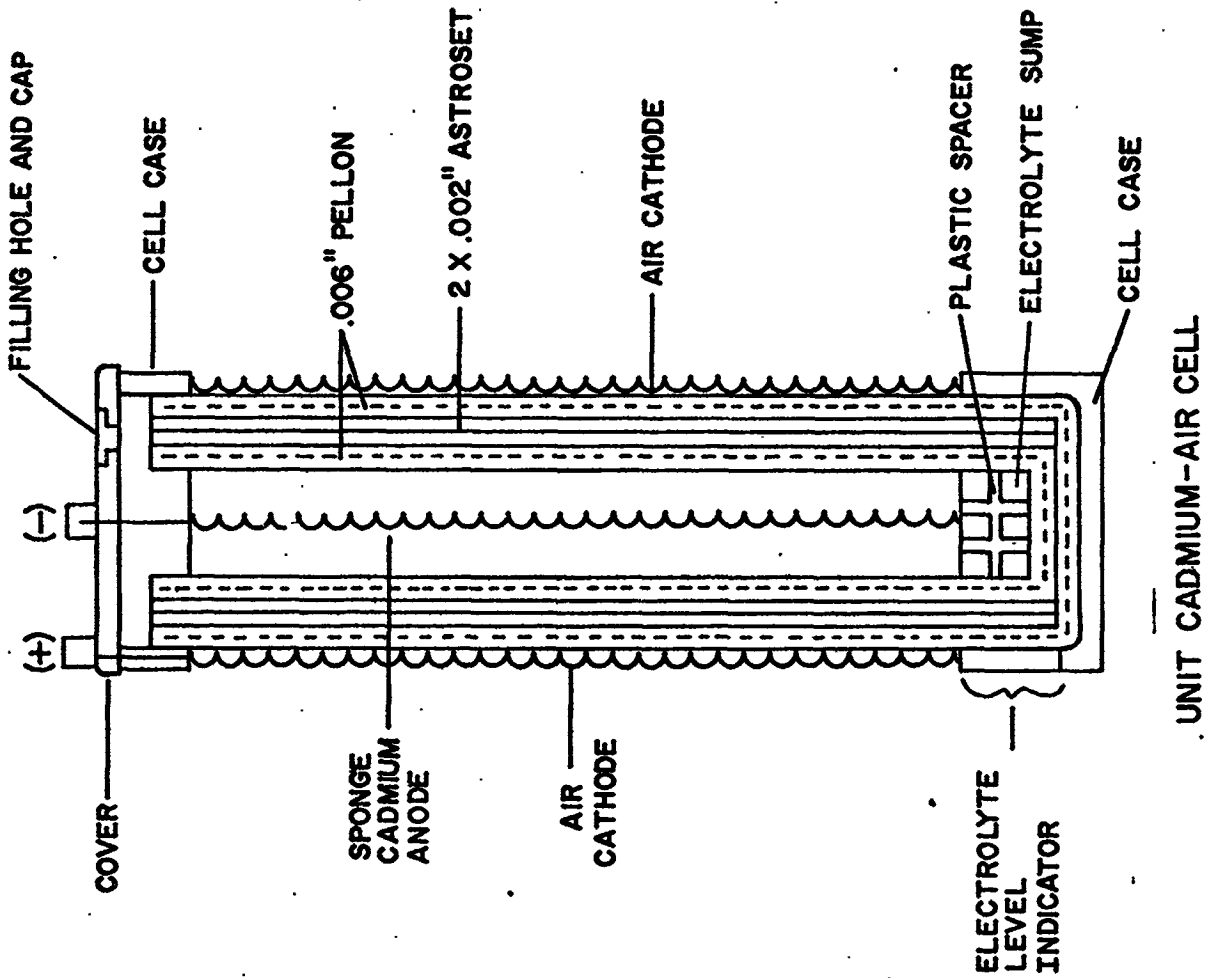


CAPACITY AS AFFECTED BY CARBONATE IN THE ELECTROLYTE



CAPACITY AS A FUNCTION ZINCATE ION CONTENT

AV-246B-68



UNIT CADMIUM-AIR CELL

