

THE EFFECT OF THE AMOUNT OF ELECTROLYTE IN THE ANODE GEL ON THE RECHARGEABILITY OF ALKALINE MANGANESE DIOXIDE-ZINC CELLS

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Summary

The zinc-limited anode technology for rechargeable alkaline manganese dioxide-zinc cells is well known. Attempts have been made to relate the rechargeability of these cells with the amount of electrolyte available in the anode gel. The rechargeability of the cells is found to increase with the amount of electrolyte up to 35 - 40% of the dry weight of the anode mass. Further increases in the amount of electrolyte were found to be detrimental to the rechargeability of the cells. Analysis of cathodes after running several cycles shows higher amounts of zinc in those from cells with greater amounts of electrolyte. This could be due to haeterolite formation in the cathode which poisons it thus explaining the reduced rechargeability with excess electrolyte.

Introduction

Rechargeable alkaline manganese dioxide-zinc cells consist of a zinc-limited anode in order to limit the discharge of manganese dioxide to its first electron only, as it is known that Mn(II) is not rechargeable under battery conditions [1]. Failure of the zinc anode during cycling is usually observed because of the following two factors:

(a) decreased conductivity of the zinc metal particles in the anode gel as cycling proceeds due to the deposition of a passivating, non-conducting, zinc oxide layer;

(b) drying of the anode gel due to electrolyte losses.

Several remedies have been suggested for the first problem, including the addition of conductive metal powders in the anode gel [2]. For the second problem, one remedy has been to add more electrolyte to the anode

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gel. It is expected that an increased supply of hydroxyl ions will bring an improvement to the accumulated capacity of the anode.

Experimental

Two methods of adding a surplus of electrolyte to the anode gel are suggested:

(a) direct addition of a larger amount of electrolyte to the dry anode mixture;

(b) the creation of an electrolyte reservoir in the centre of the anode cavity of the cells.

Several D-size (LR-20) and C-size (LR-14) cells were produced in the laboratory, and studied at room temperature (22 ± 2 °C), in two ways:

(i) measuring the short circuit current of the cells immediately after production, and at weekly intervals for up to five weeks to observe the decline in current with time;

(ii) measuring each cycle and calculating the accumulated capacity up to 50 cycles. Discharge was continuous at 3.9 ohm load until the cell voltage reached 0.9 V, and charging was at a constant 1.72 V, using the taper charging method, until the cells were completely charged.

(a) Direct addition of electrolyte to the dry anode mixture

Several standard design D-size cells (shown in Fig. 1) were produced in the laboratory with the same cathodic composition, but with the anodic composition varying with regard to the amount of electrolyte. Each cell contained the same cathodic mass but the amount of anodic mass was varied to ensure that they all had the same theoretical zinc capacity. Four types of cells A, B, C, and D, were produced having, respectively, 25, 30, 35, and 50% of electrolyte by weight in the anode gel of the dry anode mixture. The electrode compositions of the cells were:

Cathodic composition. Electrolytic manganese dioxide (IBA 18) 80.00%; graphite (Lonza KS 44) 8.00%; acetylene black (IC Carbon 3) 0.50%; puzzolana cement 2.50%; distilled water 9.00%.

Anodic composition. Zinc powder 6% amalgamated (Varta) 65 - 40.00%; zinc oxide (Merck) 5.20%; magnesium oxide (Merck) 2.20%; carboxymethyl cellulose (Fluka AG) 2.60%; potassium hydroxide 9 N (Loba) 25 - 50.00%.

Zinc determination

One of each of the types of cell described above was opened in a beaker after running for 50 cycles. The cathode mass containing manganese dioxide, graphite, and haeterolite, was removed, weighed, and made into paste which was then oven dried, overnight, at 110 °C. One gramme of the dried mixture was digested in concentrated nitric acid for 4 - 5 h until the manganese dioxide and the haeterolite were dissolved. The solution was diluted with

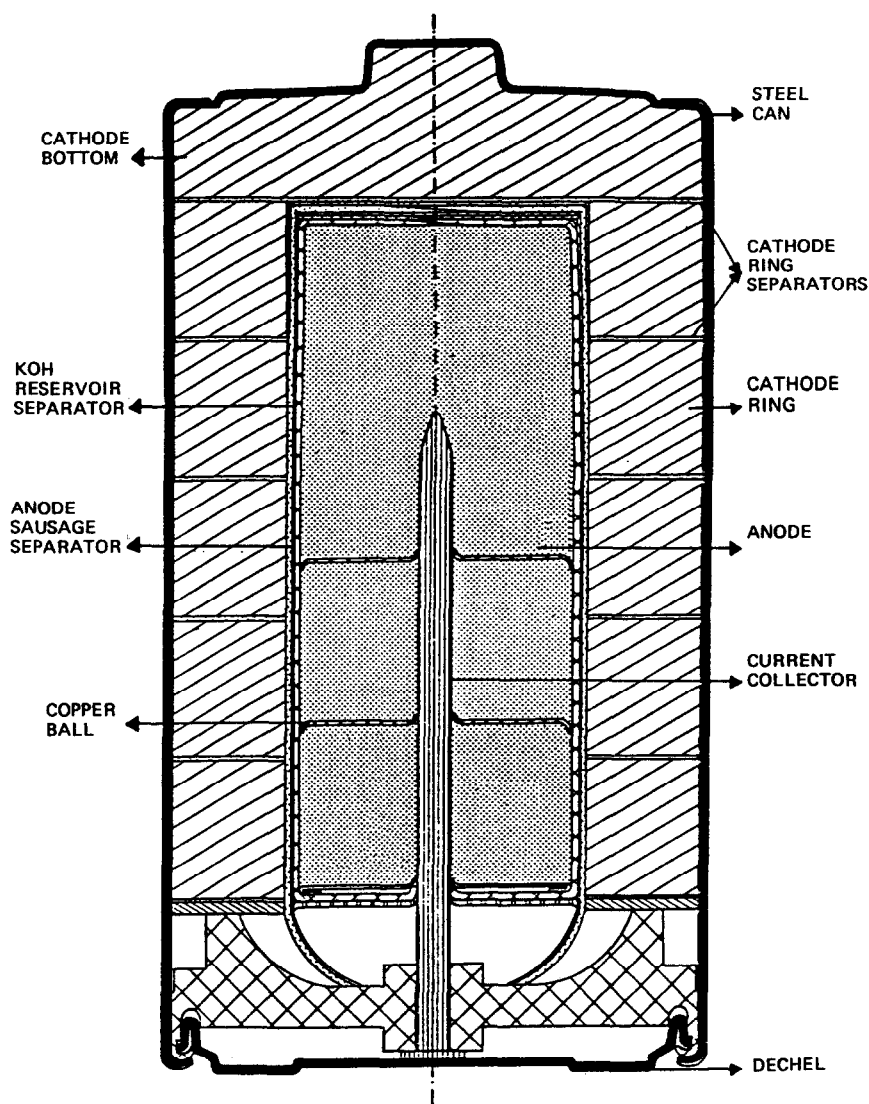


Fig. 1. Cross sectional view of a standard D-size (LR-20) rechargeable alkaline manganese dioxide-zinc cell.

distilled water to 1000 ml. The zinc content of the solution was determined by spectrophotometry using dithizone as a complexing agent.

Reagents. Dithizone: 0.002% solution in CCl_4 . Standard zinc solution: 1 mg/ml. 1 g of zinc metal was dissolved in 15 ml of HCl (1 + 1) and diluted to 1 l. Acetate buffer (pH 5): 50 g of anhydrous sodium acetate, dissolved in 30 g of glacial acetic acid, and diluted with water to 250 ml. Sodium thiosulphate: 10% solution. Wash solution: 10 ml of acetate buffer

+ 10 ml of sodium thiosulphate solution diluted with distilled water to 100 ml. Ammonia solution: Standard laboratory ammonia solution.

About 25 ml of slightly acid cathodic solution were added to a separating funnel followed by 5 ml of acetate buffer and 5 ml of thiosulphate solutions. This solution was shaken vigorously with 10 ml of the dithizone solution in CCl_4 until the green CCl_4 layer no longer changed color. The extract was shaken with 10 ml of wash solution. Free dithizone was washed from the CCl_4 layer with ammonia solution. The absorbance of the clear pink solution of zinc dithizonate was measured at 538 nm, using the solvent as reference.

(b) A novel cell design in which there is an electrolyte reservoir in the centre of the anode

A C-size (LR-14) cell was modified to accommodate additional electrolyte in the anode as gelled solution. Figures 2 and 3 show, respectively, the standard cell design and the new design. Accumulated cycle capacity on discharge and recharge was monitored as described earlier.

Results and discussion

The short circuit current measurements of the D-size cells, produced by direct addition of different quantities of electrolyte to the anode gel, are shown in Table 1. Table 2 indicates the decline in current with time. Figures 4 and 5 show, respectively, each cycle capacity, and accumulated cycle capacity up to 50 cycles, for each type of cell.

Determination of the zinc content of the cathodes of D-size cells after running for 50 cycles gave the following results:

Type	Amount of zinc found in cathode (g)
A	5.48
B	5.58
C	6.05
D	6.70

The accumulated capacity of the new C-size cell having an electrolyte reservoir in the centre of the anode is compared with that of the standard cell in Fig. 6. Figure 7 shows the discharge capacities of the above types of cell as a percentage of the anode's theoretical capacity.

Table 1 shows that the short circuit current of the cells increases with increased electrolyte in the anodes *i.e.*, the internal resistance of the cell reduces. The decline in current with time, as shown in Table 2, is almost the same for each of the four types of cell.

The accumulated cycle capacity of the cell types increases with increase in electrolyte up to 35 - 40% by weight of dry anode mixture. Thereafter, a negative effect on accumulated cycle capacity is observed. Similar

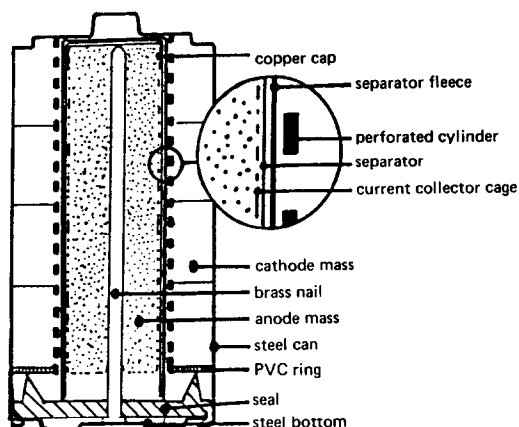


Fig. 2. Cross sectional view of a standard C-size (LR-14) rechargeable alkaline manganese dioxide-zinc cell.

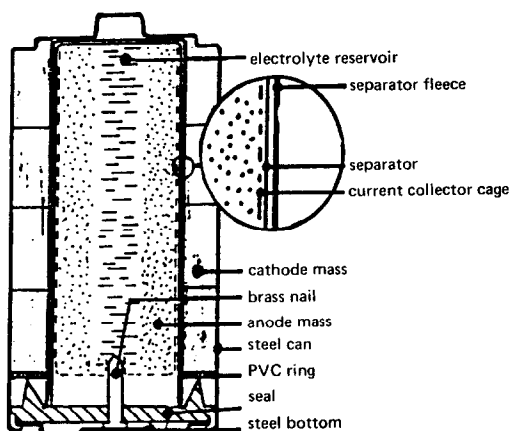
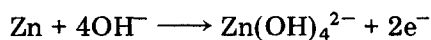


Fig. 3. Cross sectional view of a novel design of a C-size (LR-14) cell with an electrolyte reservoir in the centre of the anode cavity.

conclusions may be drawn from Fig. 6. The accumulated cycle capacity increases with increase in the amount of electrolyte in the reservoir. The anode paste does not usually contain more than 35 - 40% by weight of electrolyte in the dry anode mixture.

The oxidation reaction of the zinc electrode may be written as:



As the supersaturation of the zincate ions occurs, ZnO precipitates from zincate. It appears that by adding greater amounts of electrolyte in the anode, it is possible to keep more zincate ions in solution, thereby reducing the possibility of zinc passivation. An excess of electrolyte, however, has

TABLE 1
Short circuit current measurements

Cell type	Electrolyte in anode gel (%)	Weeks after production of the cell	Voltage (V)	Current (A)
A	25	0	1.59	23.40
		1	1.58	20.00
		2	1.58	20.80
		3	1.58	20.80
		4	1.58	20.60
		5	1.58	20.40
B	30	0	1.59	24.50
		1	1.58	22.10
		2	1.58	21.80
		3	1.59	21.70
		4	1.58	22.10
		5	1.58	21.70
C	35	0	1.59	26.20
		1	1.59	24.50
		2	1.59	23.10
		3	1.58	21.90
		4	1.58	22.20
		5	1.58	22.80
D	50	0	1.59	29.80
		1	1.59	28.30
		2	1.59	26.70
		3	1.58	26.30
		4	1.58	26.70
		5	1.58	26.80

TABLE 2
Percent. decline in short circuit current with time

Type	Electrolyte in anode gel (%)	Weeks				
		1	2	3	4	5
A	25	14.53	11.11	11.11	11.96	12.82
B	30	09.79	11.02	11.42	11.02	11.42
C	35	06.50	11.83	16.22	15.27	12.98
D	50	05.03	10.47	11.75	10.40	10.07

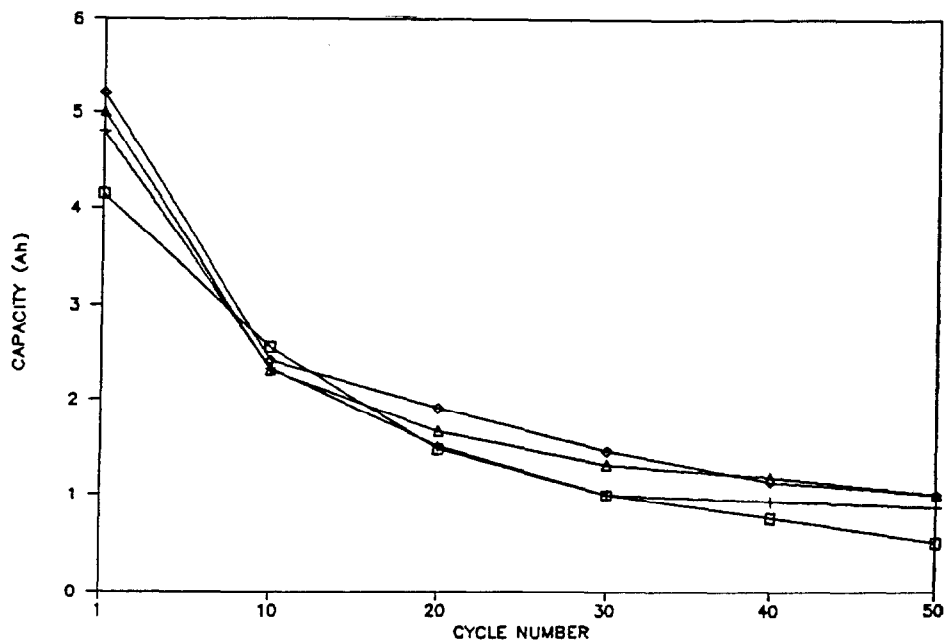


Fig. 4. Comparison of each cycle capacity in A h, of D-size cells discharged at 3.9Ω resistance until the cell voltage reached 0.9 V, and recharged at 1.72 V by the taper charging method each time before discharge. Type A (\square), 25%; type B (+), 30%; type C (\diamond), 35%; type D (\triangle), 50% electrolyte in the anode gel.

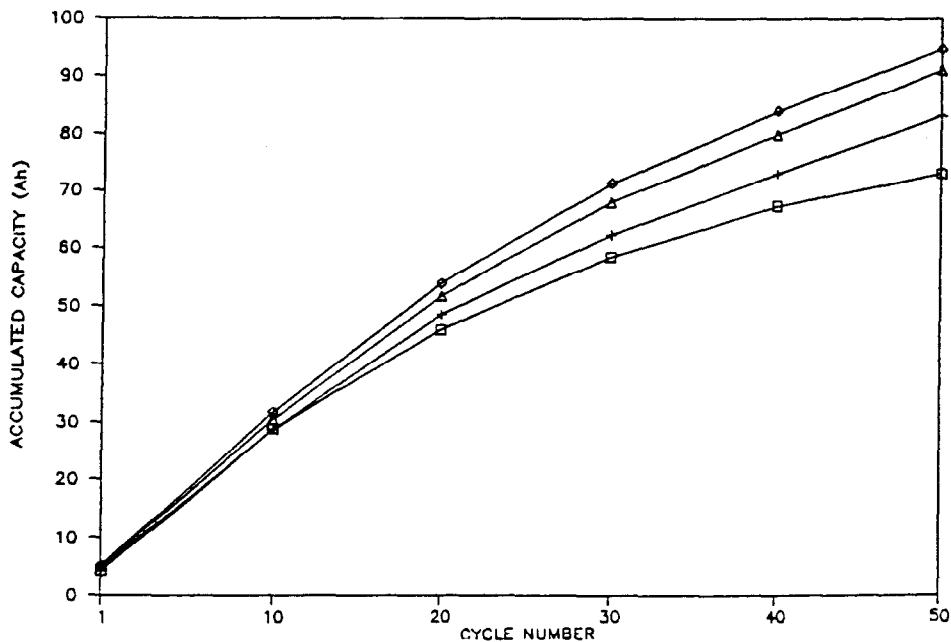


Fig. 5. Comparison of accumulated cycle capacities up to 50 cycles of D-size cells. Type A (\square), 25%; type B (+), 30%; type C (\diamond), 35%; type D (\triangle), 50% electrolyte in the anode gel.

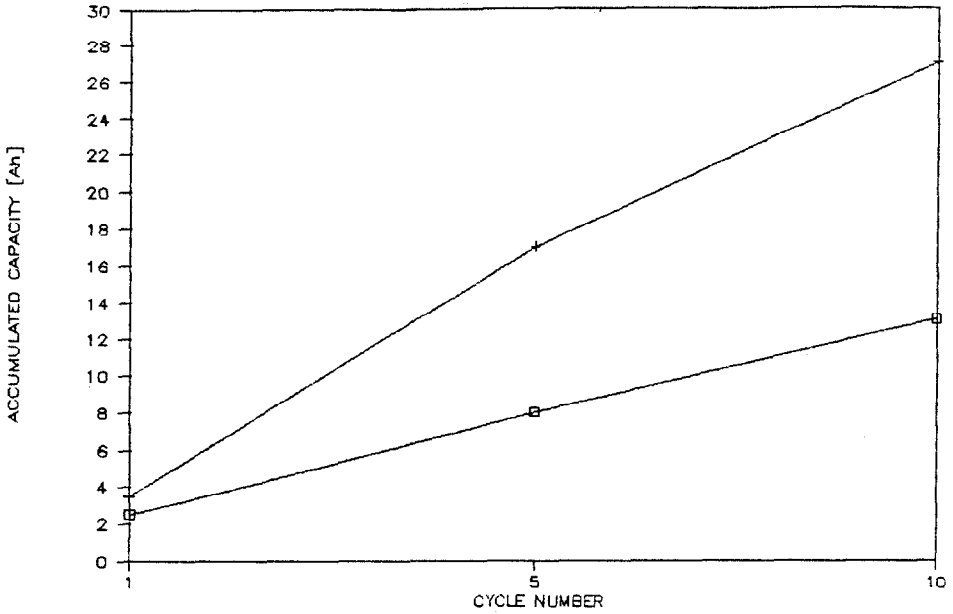


Fig. 6. Comparison of accumulated cycle capacities, in A h, of C-size (LR-14) cells. Standard design (□), a normal cell without electrolyte reservoir; Novel design (+), a new design cell with electrolyte reservoir in the centre of the anode cavity.

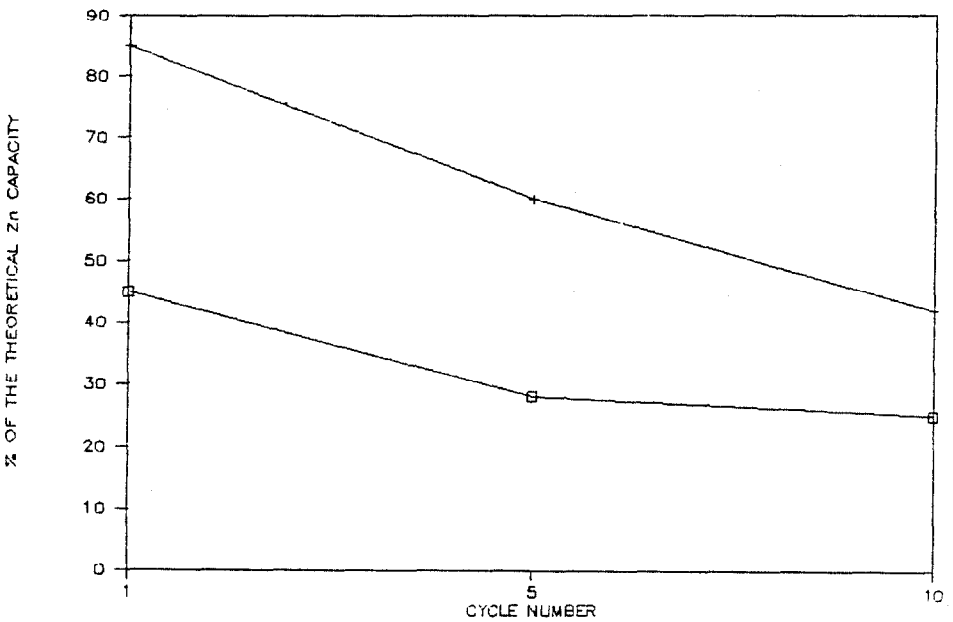
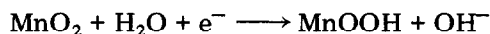
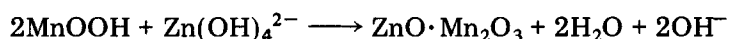


Fig. 7. Comparison of the percent. utilization of theoretical zinc capacity *vs.* cycles in C-size cells. Standard design (□), a normal cell; Novel design (+), a new design cell with electrolyte reservoir in the centre of the anode cavity.

a detrimental effect if it reduces the rechargeability of the cell's cathode. An excess of electrolyte carries more zincate ions into the cathode, forming haeterolite with MnOOH. The reaction can be written as:



As the MnOOH accumulates on the manganese dioxide particles, it is assumed to be immediately converted into haeterolite by interaction with zincate ions in the solution [3]. The reaction may be written as:



This is verified by the zinc content of the cathode. It was found to increase with increase in the amount of electrolyte, and is responsible for reducing the rechargeability of the cathode by producing haeterolite (Mn(II)).

Conclusion

It is possible to improve the zinc anodes of rechargeable alkaline manganese dioxide cells by optimizing the amount of electrolyte in the anode. Lesser amounts of electrolyte in the anode paste cause early cell failure during cycling. An excess amount of electrolyte, however, is detrimental to the rechargeability of the cathode for it transports zincate ions into the cathode very rapidly. 35 to 40% electrolyte by weight of the dry anode mixture is optimal. A novel design involves containment of the electrolyte as a gelled solution in the centre of the anode cavity. It is believed that this releases the electrolyte to the anode as required.

References

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