

### Rechargeable Zinc Electrode with Calcium Hydroxide in Alkaline Manganese Dioxide - Zinc Cells

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#### ABSTRACT

The rechargeability performance of alkaline manganese dioxide - zinc cells has been studied by the addition and variation of the concentration of calcium hydroxide in the anode component of these cells. A remarkable improvement in the accumulated cyclic capacity of such cells is observed by adding calcium hydroxide to the anode in a molar ratio of Zn:Ca at 2:1. The improvement is explained due to the formation of an alkali insoluble complex, calcium zincate, in the anode from the interaction of calcium hydroxide and soluble zincate ions. This restricts the movement of the zinc ions within the anode cavity, and thus inhibits the formation of non-reversible haeterolite in the cathode.

#### INTRODUCTION

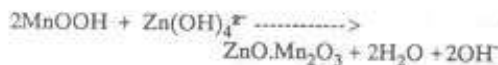
Efforts to recharge alkaline manganese dioxide zinc cells have been undertaken since the sixties [1]. Kordesch et al. carried out extensive studies to establish the detailed criteria for rechargeability of alkaline manganese dioxide - zinc cells [2]. It was established that a manganese dioxide electrode can only be discharged to one third of its original one electron capacity in order to remain rechargeable. Anodic Zinc limitation is considered the only practical way to prevent excessive deep discharge of the manganese dioxide cathode. This zinc anode is different from that used in AgO - Zn or Ni - Zn cells because cycling is usually carried out with

cathode limitation and an excess of zinc in latter cases.

Amalgamated zinc used in alkaline manganese dioxide-zinc cells undergoes the following oxidation reaction in an alkaline electrolyte during an electrochemical process:

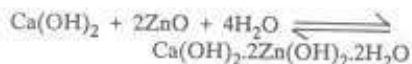


During charge/discharge cycles, the dissolved zincate ions continue to migrate to the manganese dioxide cathode through a separator where they become available to the manganite to form an insoluble haeterolite [3].



Once the haeterolite, ZnO.Mn<sub>2</sub>O<sub>3</sub>, is formed, it is impossible to oxidise it to its original manganese dioxide form on charging. This results in the net loss of both the cathode and anode capacities. This paper is devoted to the exploration of means of restricting the movement of zincate ions within the anode cavity in an insoluble but reversible complex form.

It is reported in the literature that calcium hydroxide readily reacts with zinc oxide in an alkaline medium to form a calcium zincate compound which is insoluble in strong alkali. Its reversibility in an electrochemical system is also well established [4]. It is expected that addition of calcium hydroxide to the zinc anode of rechargeable alkaline manganese dioxide - zinc cells may withhold the zincate ion within the anode without altering electrochemical behaviour of the cells.



This effect may lower the concentration of the discharged ZnO in the electrolyte, and thus restrict the movement of zincate ions into the cathode. Consequently, this study was carried out to observe the performance of the rechargeable zinc electrode in alkaline manganese dioxide - zinc cells in the presence of calcium hydroxide.

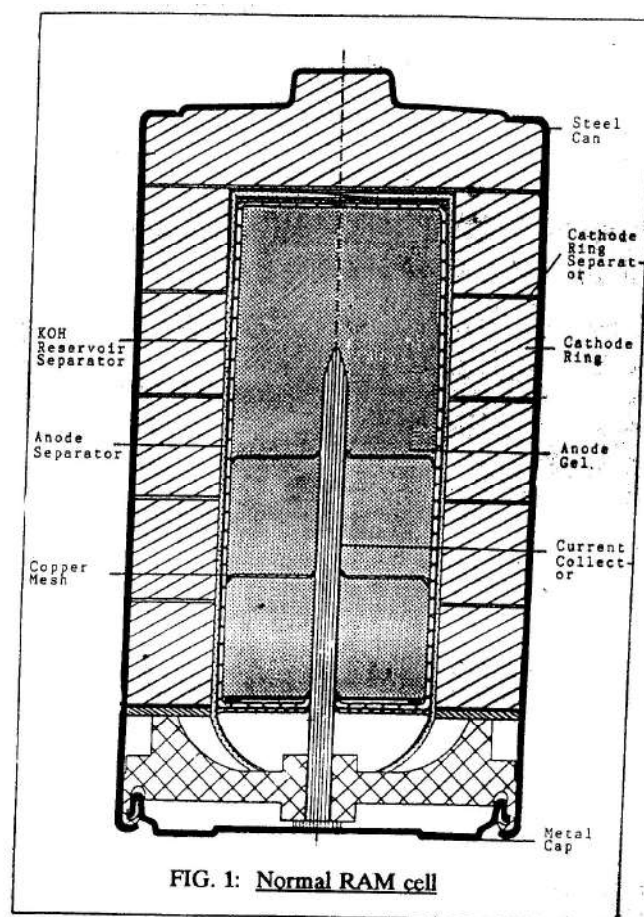


FIG. 1: Normal RAM cell

a cathode current collector (obtained from Varta AG, West Germany). The theoretical capacity of the cathode based on one electron discharge was kept constant at 14 Ampere hour (Ah). Anode sausage casing separator (obtained from Delfei Company, Austria), and electrolyte reservoir separator (obtained from Dexter Corporation, U.S.A.), were introduced into the hole in the centre of the cathode rings of each cell. This was followed by introducing a copper cage which also acts as an anode current collector. The anode paste was dispensed into the copper cage. Each cell has a theoretical zinc capacity of 5 Ah. To keep this capacity constant in all types of cells, the amount of anode paste was varied accordingly. The cells were then impregnated with excess electrolyte (9M KOH) under vacuum and sealed using a plastic grommet to prevent any short circuit. A provision was made to introduce electrolyte into each cell after intervals of 10 cycles (about 2ml) so that electrodes do not dry up. Fig 2 shows different steps in the production of D-size (LR 20) cells in the laboratory.

The cell testing was carried out in three standard ways. All the measurements were recorded at room temperature (25°C).

#### Open Circuit Voltage and Short Circuit Current Measurements

The open circuit voltage (U) and short circuit current (I) of the cells were measured immediately on production and later at weekly intervals up to five weeks to observe the decline in current with time. The results are shown in Tab 3.

#### Single Cycle and Accumulated Cycles Capacity

The single cycle capacities of each type of cell up to 50 cycles were measured on a computer-controlled electronic cell testing system as shown in Fig 3. The cells were discharged at a load of 2.2 ohm to a cut-off voltage 0.9V. After each discharge, the cells were charged at a constant 1.72V by a taper-charging method for 24 hours. The accumulated cyclic capacity is then calculated by the addition of each single cycle capacity. The results are shown in Fig 4 and 5 respectively for single cycle capacity and accumulated cyclic capacity for each type of cell.

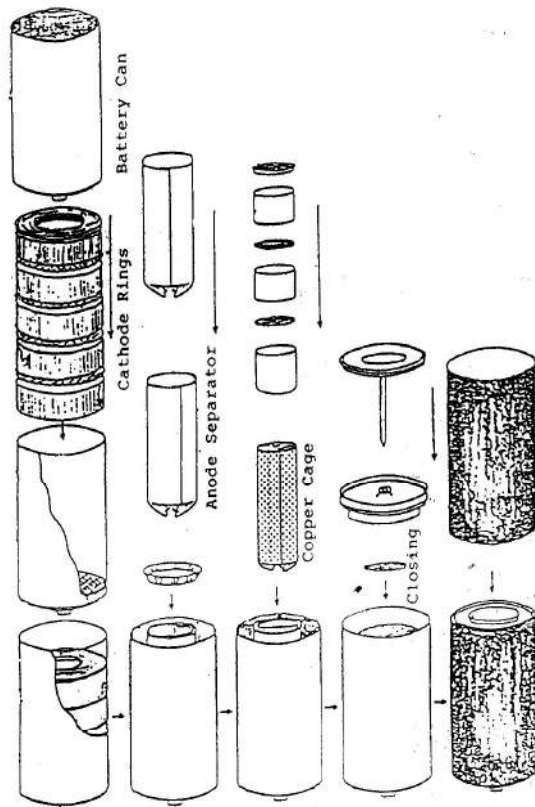


FIG. 2: Different steps in the production of D - size (LR20) cells in the laboratory.

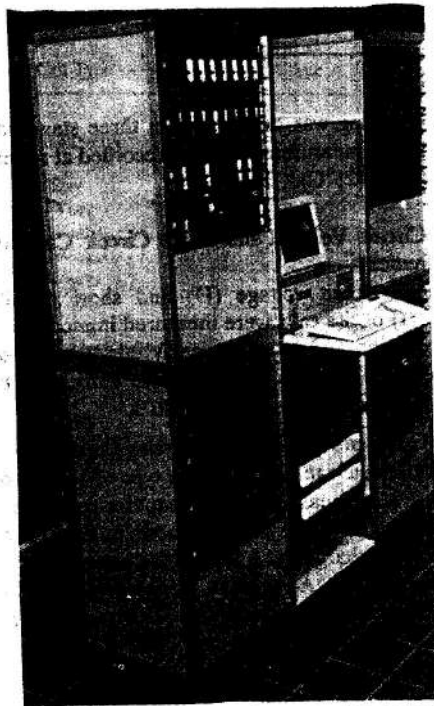


FIG. 3: Computer-controlled discharge-charging equipment.

Table 3: Open circuit voltage (U) and short circuit current (I) measurements

Cell Type	% Ca(OH) <sub>2</sub> in anode	Weeks after Production	U	I
Type A	35%	0	1.59	16.70
		1	1.58	15.20
		2	1.58	15.90
		3	1.58	15.30
		4	1.58	15.60
Type B	45%	0	1.59	14.40
		1	1.58	14.10
		2	1.58	13.70
		3	1.58	13.40
		4	1.58	13.40
Type C	50%	0	1.59	13.70
		1	1.58	12.90
		2	1.58	12.30
		3	1.58	11.80
		4	1.58	11.70
Type D	55%	0	1.59	12.40
		1	1.58	11.80
		2	1.58	11.30
		3	1.58	11.50
		4	1.58	11.20
Type E	60%	0	1.59	11.20
		1	1.58	10.80
		2	1.58	10.30
		3	1.58	10.50
		4	1.58	10.20
		5	1.58	10.00

### Complexed Zinc Determination in the Cathode and Anode

A few samples of each type of discharged cell as described above were opened in a beaker after running for 50 cycles. The cathode mass containing discharged manganese dioxide, graphite, haeterolite, free zinc oxide, and anode mass containing calcium zincate, and free zinc oxide, were removed and separated in different beakers. The cathode masses, as well as anode masses were washed several times with KOH solution to wash off all free zinc oxide, and then oven-dried at 110°C overnight. The dried mixture was digested in concentrated nitric acid for 4 to 5 hours, and the paste was diluted with distilled water and filtered. The zinc content of the solution was determined by standard spectrophotometric method using dithizone as the complexing agent. The results are shown in Tab 4.

Table 4: Complexed zinc in anode paste and cathode after running 50 cycles

Cell Type	Type A	Type B	Type C	Type D	Type E
Anode (g)	2.15	3.88	4.90	5.50	5.55
Cathode (g)	2.70	1.05	0.25	0.20	0.18

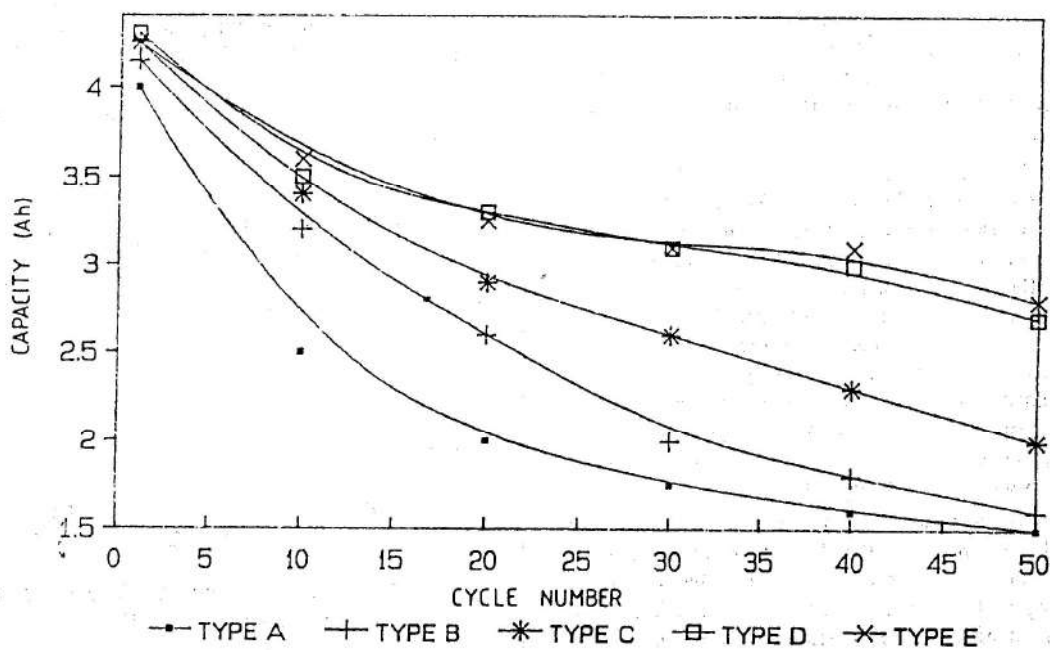


FIG. 4: Single Cycle Capacity of Cells

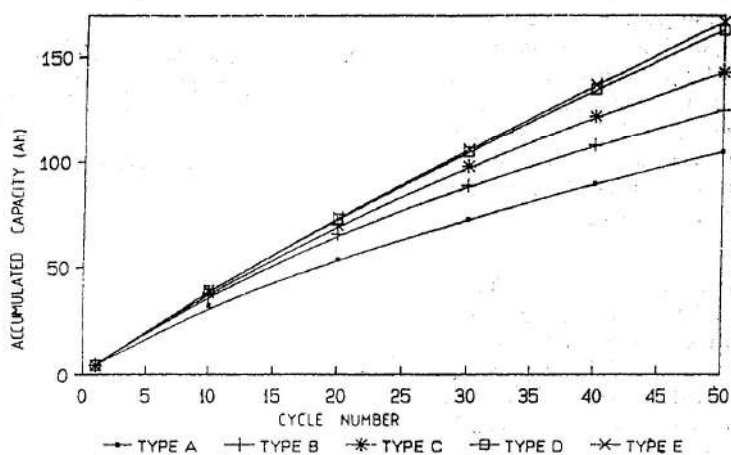


FIG. 5: Accumulated Cycle Capacity of Cells.

## RESULTS AND DISCUSSION

The results of gassing test performed on the anode paste containing calcium hydroxide as depicted in table 2 do not show any significant increase in volume at the set temperatures. The expansion and gassing of the anode paste is within the tolerance limit prescribed for rechargeable alkaline manganese dioxide - zinc cells [3].

The open circuit voltage (U) of all the five types of cell is quite comparable; however, the short circuit current (I) decreases with an increase in calcium hydroxide concentration in the anode. This could be attributed to the decrease in conductivity of the anode paste with an increase in calcium hydroxide content.

The first cycle capacity of each of the five types of cell is practically the same as is shown in fig 4. This demonstrates that an increase in calcium hydroxide concentration in the anode has practically no effect on the zinc utilization. However, as cycling continues, cells with a high content of calcium hydroxide in the anode continue to prove to be better performers. Type D and Type E cells behave similarly in spite of increasing the calcium hydroxide content in the anode of type E to 160%, suggesting that the limitation is now coming from the available zinc in the anode.

The zinc analysis of the discharged anodes after 50 cycles, as shown in Tab 4, confirms an increase in the withholding power of the zinc by the anode cavity with an increase in the calcium hydroxide content of the anode paste up to the type D cells. This is due to an increase in calcium zincate formation in the anode with an increase in the calcium hydroxide content. The zinc content in the anode of type D and Type E cells is the same, which represent about 87% of the total zinc available in the cell. This suggests that no more zinc is available in cell type E for available excess calcium hydroxide to form further complex as compared to cell type D. It confirms that studies of Jain et al., who have provided a compound stoichiometry of calcium zincate to a molar Zn:Ca of 2:1, suggesting that any calcium hydroxide in excess to that ratio of zinc may not form higher valence compounds [5].

The zinc content of the cathode decreases with an increase in the calcium hydroxide content of the anode. The zinc concentration in the cathode is due to haeterolite formation from interaction of manganite with zincate ions during charge/discharge cycles [3]. Since the movement of zincate ions is restricted within the anode by increasing the calcium hydroxide content in the anode by forming a calcium complex as said above, no excess zincate

ions are now available to the manganite to form haeterolite and thus, this is an expected trend.

## CONCLUSION

Addition of calcium hydroxide to the zinc anode of the rechargeable alkaline manganese dioxide - zinc cells improves the performance of these cells. The best performance is obtained on the addition of calcium hydroxide to the anode in the molar ratio of Zn:Ca, 2:1. This is attributed to the formation of a complex namely calcium zincate in the anode from the interaction of calcium hydroxide and zincate ions. This effectively restricts the movement of zinc ions within the anode cavity. No zincate ions are thus available for manganite in the cathode to form irreversible haeterolite, and destroy the cathode and anode capacities.

## ACKNOWLEDGEMENTS

One of the authors (YS) gratefully acknowledges the financial assistance from the Austrian Government, and permission by the University of Science and Technology, Kumasi, to carry out this research at the University of Technology, Graz, Austria.

## REFERENCES

1. Kang, H.Y., and Liang, C.C., *Journal of Electrochemical Society*, 6, 1968, 115.
2. Kordesch, K., and Gsellmenn, *Power Sources*, Academic Press, 1979.
3. Sharma, Y., *DSc Tech thesis*, University of Technology, Graz, Austria, (1989).
4. Sharma, R.A., *Journal of Electrochemical Society*, 8, 1988, p 1875.
5. Jain, R., McLarnon, F.R., and Cairns, E.J., *168th Meeting of the Electrochemical Society*, Las Vegas, NV, Paper No. 84, 1985.