

The mechanism of capacity fade of rechargeable alkaline manganese dioxide zinc cells

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Abstract

Recent experiments showed, that in contrast to traditional opinion, if the cathode was protected by anode limitation the capacity fade of Rechargeable Alkaline Manganese Dioxide Zinc (RAMTM) cells was not caused by the EMD cathode, but by the gelled zinc anode. The key is the electrolyte. The cathode competition for the electrolyte and the increasing requirement of chemically formed ZnO for more electrolyte caused an electrolyte deficiency at the front face of the anode and finally caused precipitation of zincate and passivation of zinc. The crust is a mixed material of precipitation and passivation products. The low solubility ZnO is formed by decomposition of electrochemically generated zincate ions $[\text{Zn}(\text{OH})_4]^{2-}$ and also by recombination of zinc with oxygen during overcharge. The progressively thickened “crust” at the front face of the anode increases the resistance, then finally causes the cell to fade. The crusting is a redistribution of active material and electrolyte between the front and rear of the cylindrical gelled zinc anode. More electrolyte and proper charging can delay such a “crusting” phenomenon. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: RAM batteries; Zinc; Manganese; Capacity; Electrolyte; Rechargeability

1. Introduction

Rechargeable Alkaline Manganese Dioxide Zinc (RAMTM) batteries have been studied by Kordesch et al. at the Technical University Graz since 1977 and then developed at Battery Technologies, in Canada after 1988. The capacities were improved more than double from 1989 to 1992. Rayovac (USA), Pure Energy Battery (Canada), Young Poong (South Korea) and Grand Battery Technology (Malaysia) have successfully produced RAM batteries under BTT's licence [1]. Panon Enterprises (Hong Kong) obtained the licence including the mainland of China in 1995. Due to their competitive performance and price, RAM batteries captured more than 50% of the small rechargeable cell market in North America within a span of only six months after Rayovac started to produce in 1993. Even so, the RAM batteries only occupied 1% share of the rechargeable battery market in the world [2]. The RAM system has huge potential in the worldwide market.

To further improve the rechargeability of RAM cells, the gradual capacity fade of RAM batteries has been studied extensively [3]; for example, it was shown that some destruction of the $\gamma\text{-MnO}_2$ structure occurs during the 2nd electron discharge and the formation of haeterolite ($\text{ZnO} \cdot \text{Mn}_2\text{O}_3$) or other phases. A lot of work has also been devoted to cathode additives, for example, Bi–manganese dioxide, Pb–manganese dioxide [4–10] and Ti–CMD [11–13]. However, there is no significant effect to be found on the improvement of any higher voltage (over 0.9 V) rechargeability by these additives. On the other hand, Kordesch pointed out that the improvements by adding recharging catalysts or structural modifiers are very spectacular in the absence of zinc [14]. Our recent experiments found that the anode mainly controlled the fade of RAM battery capacity, while rechargeability of the cathode kept very well after the first cycle.

2. Experiments and discussions

All AA cells are discharged at 3.9 Ω and cut off at 0.9 V then recharged at 1.72 V for 15 h except when noted specially.

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Table 1
OCV and SCC before opening and after rebuilding and charging

OCV (V)		SCC (A)	
Before opening	After charging	Before opening	After charging
~1.4 V	~1.7 V	~1.6 A	~3.6 A

Two standard cells were completely discharged and recharged for 60 cycles. They showed no leakage and their capacities had been down to 0.3–0.25 Ah. Removing the used cathodes, grinding them to a powder and then re-granulating the cathode powder with a small amount of fresh KOH produced cathodes for two cells (cell 2 and 3). The anode was made with new zinc powder and a ZnO content of 20% ZnO (for added rechargeable capacity). The anodes of the newly prepared cells are practically in a charged state. A new separator was used. The cell 1 is the standard. The open circuit voltages (OCV) and the short circuit currents (SCC) before opening and after rebuilding and recharging are listed in Table 1.

The first six cycles of cells 2 and 3 (except initial discharge) had almost the same capacity as the standard cell 1 (see Fig. 1)! These experiments show clearly that the rechargeability of electrolytic manganese dioxide (EMD) is still retained very well. However, this experiment alone cannot point out the reasons why the cells normally fade.

Three more cells were discharged and recharged for 41 cycles, finally having capacities of about 0.4 Ah and no leakage. In one experiment, a hole was drilled into the top seal of the cell, and then the cell was soaked in KOH in a sealed bottle overnight. Then the hole was sealed with wax (Cell 4).

In the next step, the top seal of the second cell was cut away, thereby the cathode, anode, separator and nail were

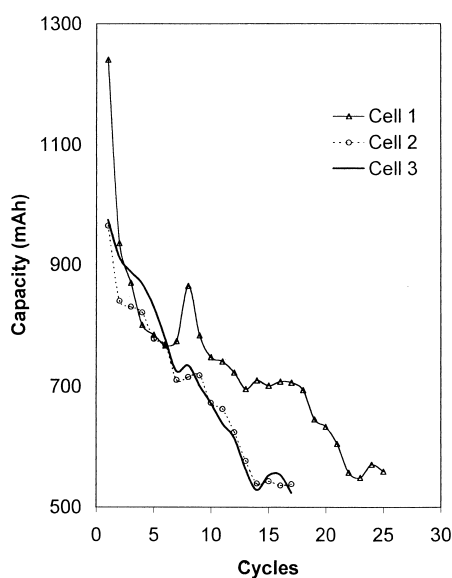


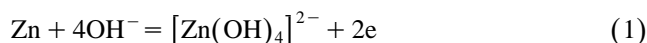
Fig. 1. Comparison of cycle performances between fresh EMD and used EMD shows that the original capacity of used EMD is still retained very well.

shortened by about 2 mm. The anode was stirred with the same nail carefully without damaging the separator. The cell was then sealed with a new top seal (Cell 5). The third cell was made with used, re-granulated EMD and a fresh anode, as in the previous experiment (Cell 6).

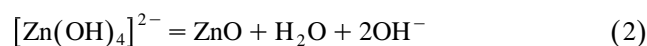
The Cells 4 and 5 were first charged at 1.65 V for 15 h. The SCC and OCV before opening and after charging are listed in Table 2. Cell 4 could not be restored to a good performance (Fig. 2). Considering the fact that 10% of the cathode and anode material of cell 5 had been removed for opening and repairing, cell 5 had nearly the same specific capacity as the completely rebuilt cell 6. The diagram of 40 more cycles of cell 5 shows that it has a similar behavior and specific capacity to that of standard cell 1 (Fig. 3).

It was found that the color of the anode surface layer (toward the separator) was black and hard, and the inside layer (toward the nail) was metallic gray and still soft after some ten cycles. After drying in air, the anode showed three different color layers, black (close to separator), yellow (middle layer) and white (close to the nail). Simply filling with KOH, without breaking the hard layer, could not repair the cell, because the hard layer was non-porous and possessed a high resistance (lack of OH⁻ ions). After stirring and filling with more KOH solution, the anode material dissolved again, at least the hard layer was destroyed, and the rechargeability of the anode recovered very well.

When discharging, the following reaction takes place [15]:



However, an independent chemical decomposition will occur simultaneously.



The discharge takes place preferentially at the front face of the zinc electrode, for example, about 0.1 cm [16]. The decomposition of zincate releases electrolyte (OH⁻ ions and water) near the cathode. Therefore, a re-distribution of electrolyte between cathode and anode happens. After Mn(OH)₂ formation during local deep discharge, there cannot be a release of the electrolyte due to its irreversibility. The formation of haeterolite (ZnO · Mn₂O₃) also uses up some KOH without release. The original hydrophobic

Table 2
SCC and OCV of cell 4 and 5 before opening and after filling with KOH and charging

Cells	OCV (V)		SCC (A)	
	Before charge	After charge	Before charge	After charge
Cell 4	1.41	1.62	1.7	3.9
Cell 5	1.40	1.62	1.6	3.3

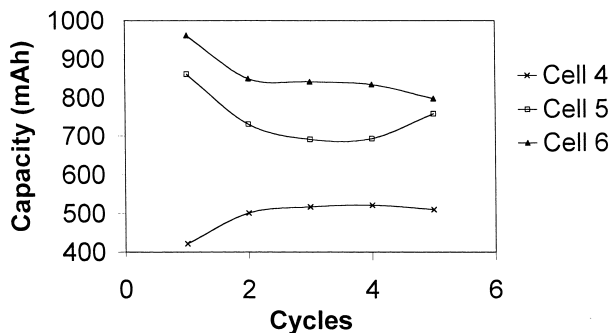


Fig. 2. Comparison of cycle performances of three used cell 4, 5 and 6 repaired three ways.

pores [17] of EMD may be wetted to a certain degree during cycling, but some of the initially open pores in the cathode are blocked due to the expansion of EMD during discharge. As a result, some free electrolyte is locked-up inside. That this may be true is shown by the fact that the cathodes of cells cycled for 60 or more cycles are much wetter than those of fresh cells.

All the factors mentioned above also build up an electrolyte gradient in the opposing anode cylinder, with lower KOH concentration at the separator side of the anode. The cathode, being richer in KOH also has limitations; if the KOH penetrates between the MnO_2 and graphite interfaces, or forms a film between the can and the cathode rings, the electronic conductivity is destroyed. This could be shown by the following experiment (cell 9); after some very small holes were drilled through the can into the cathode pellets, any added electrolyte did not help at all; subsequently the performance was poor because the skin and contact of the pellets was damaged and wet (Fig. 4).

The solubility of electrochemically generated zincate is as much as three times the equilibrium solubility [18–20]. The decomposition rate of zincate is unknown but, in Kordesch's opinion, such decomposition may be accelerated by some nucleation agent added to the cells. The precipitation of ZnO is not much evident in one cycle

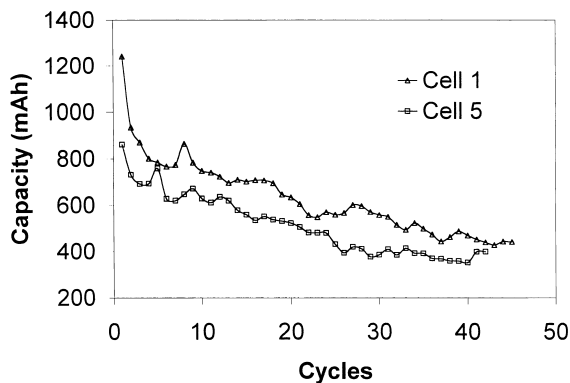


Fig. 3. Curves of 40 more cycles of the cell 5 with filled KOH and stirred shows that it almost has a similar behavior to the standard cell 1, and nearly the same specific capacity too, considering that its 10% active material was removed to provide enough space for good sealing.

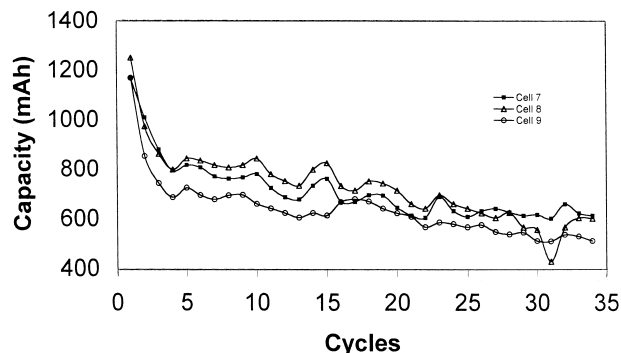


Fig. 4. Cyclic performance of three cells drawn by average data of each group. The Cell 7 contained 4.5 g anode gel and more KOH than others. The standard Cell 8 contained 5 g anode gel. Cell 9 has 4 holes with 1 mm diameter on the wall of each pellet.

because it is a slow process, but its accumulative action over many cycles may be noticeable.

The oxygen produced at the cathode during charging can be recombined by zinc [21]. The dissolution of chemically generated ZnO , formed by both, recombination and zincate decomposition, causes the deficiency of electrolyte. Hard ZnO precipitates near the separator interface, where the concentration of electrolyte is lowest, it certainly will block the transfer of ions.

During recharging, at low over-potentials, a mossy Zn deposit may form, which is nonadherent, black and actually nonporous [22–25]. The formation of irregular zinc deposits is controlled by ion diffusion through a porous semi-blocking layer, a part of the crust composition, made of defective ZnO . Such a layer is slowly formed and progressively blocks the electrode surface, thus maintaining the current density at a low level.

In later cycles, the capacity is less sensitive to the load resistance. The explanation of “plateau cycle performance”, as it is called by Kordesch, may be that the ionic resistance of certain layers is becoming dominant and the ohmic load resistance seems less important.

Layer formation means slow diffusion processes, asking for relaxation and recovery periods. This is why pulse charging, with corrected frequency and “true” resistance-free charge voltages, overcharge protectors (oxygen gas elimination) can save and strongly improve the rechargeability [26].

Cell 7 had 0.7 to 0.8 g more KOH than the standard cell 8, but it had only 4.5 g anode gel (the standard cell had 5 g anode). Certainly, the capacities of early cycles are lower than that of standard cells because of less active anode material, but the capacity of the cycles is better after 25 cycles. This has some relation with the depth of discharge of the initial cycles, but more KOH in the anode can delay the thickening of crust and will also improve the anode cycling.

The progressive failure of plate-type zinc electrode can be attributed to shape change, zinc dendrites, and passiva-

tion. The cylinder type of the gelled zinc electrode is different from the situation with the plate zinc electrode. The term “shape change” describes the active material redistribution between edges and center of the plate zinc electrode [27–29]. The long-term cycling life of the planar zinc electrode is definitely limited by the shape change [30]. Fortunately the cylinder electrode has vertical symmetry without any right and left edge (neglecting the top and bottom). The problem of dendrites has been solved with proper separators for RAM batteries. Tight at the bottom, and with a long path at the top, spirally wound RAM cells experimentally made like Ni–Cd cells, suffered short circuits from the long top edge and the short distance between anode and cathode tape electrodes.

In the flooded electrolyte, the passivation occurs when a compact film forms directly on the surface of zinc. However, in the actual RAM cells, with a gelled zinc anode, the gradual loss of electrolyte during cycling (discussed above) reduces the pH at the front region of the zinc electrode to less than that required to prevent passivation [31]. This fact seems to be confirmed because there was no such crust layer found during some first cycles. Different to the plate zinc electrodes, the passive layer does not make the electrode fail but only fade, because the gaps and voids between the powder zinc moves the discharge to the inner regions of the zinc anode, which is still rich in electrolyte.

The gel agent plays a important role for the gelled zinc electrode. It exerts a great influence on electrolyte dispersion, hydrogen evolution and over-potential of powdered zinc. After 60 cycles no gel type materials were found in the zinc anode (starch was used as gel agent in the experiments listed). The damage to the gelling agent aggravates the poor distribution of free electrolyte.

3. Conclusions

In contrast to traditional opinions, the capacity fade of RAM cells (excepting the first cycle) is not mainly caused by a deep discharge of the cathode, but to a large extent by the anode. The critical point is the deficiency of KOH electrolyte. With the design requirement of anode limitation, the cathode is protected well and at least 100 good cycles are available. The gradually formed and thickened “crust” at the front of the anode, which is hard and nonporous, does increase the resistance of the anode and lead to a pronounced anodic capacity fade. The electrolyte deficiency is caused by the cathode binding some of the available electrolyte, and by chemically formed ZnO with a much lower solubility resulting from the decomposition of zincate and as a result of the recombination of zinc with oxygen gas appearing during charging, even with properly set charger voltages (under 1.7 V). The reason is that the Zn-potential is changed and the references are wrong. Such sources for oxygen gassing are the disproportionation of

Mn(VI) species and/or peroxide decomposition processes. This is not the oxygen overflow cycle, which starts above 2.0 V.

The anode “crust” is a mixed material of precipitated ZnO and of a passivation product, as well as mossy deposits formed during recharge. The effect of hydrogen on passivation was reported [32], but it is not yet proved in our present experiments. Modifying the gel zinc anode and the study of detailed charge models are giving RAM cells a huge potential for improvements.

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