# IMPROVEMENT OF THE CYCLE LIFE OF AA-RAM CELLS

(RECHARGEABLE ALKALINE MANGANESE DIOXIDE)

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## Introduction

The RAM™ Technology offers an environmentally responsible, low cost rechargeable battery system that can be utilized for practically all applications where single-use cells (alkaline-manganese, zinc-carbon) are currently being used. In addition, it can replace nickel-cadmium and nickel-metal hydride cells in a variety of applications with improved charge retention even at higher operating temperatures and in intermittent use and it works well with solar charging [1]. This abstract discusses the improvement of the cycle life of AA-RAM cells caused by changing the formulation of the zinc-gel-anode.

## Experimental

The main goal of this work is to improve the cycle life of AA-RAM cells, focusing the main interest on the zinc-gel-anode.

The standard formulation of the anode was modified by adding $Ca(OH)_2$ to the anode mass and EDTA to the ectrolyte of the zinc anode [2]. To study the effect of these additives, more than 100 AA-RAM cells were manufactured and tested under standard conditions with a special computerized testing-equipment. Each cycle started with discharging the cell at 3.9 Ω to a cut-off voltage of 0.9 V followed by charging at 1.72 V for 15 hours. To minimize the problem of slightly varying performance frequently observed with handmade cells a group of at least 3 modified cells was compared with a group of 3 reference cells.

For a better understanding of the obtained results, electroanalytical experiments were carried out in addition to standard testing procedures. More than 50 cells were manufactured in order to investigate the effect of EDTA at various concentrations on cycle life of these cells. Additionally, cyclovoltammetric studies were used to determine the optimum EDTA concentration range.

Another part of this work was dedicated to the investigation of the migration of zinc species from the anode to the manganese dioxide cathode during the cycle life. The migration is made possible due to the high solubility of $[Zn(OH)_4]^{2-}$ in 9N KOH, that is used as standard electrolyte in RAM cells. Precipitation of ZnO from oversaturated electrolyte followed by reaction (1) can cause an irreversible modification of the manganese dioxide structure and thereby a loss of active cathode material can be found [3].

$$2\ MnO_2 + H_2O + ZnO + 2e^- \rightarrow ZnMn_2O_4 + 2\ OH^- \qquad (1)$$

Therefore, an electroanalytical procedure was developed to determine the zinc-species in the cathode [4]. Different test cells, standard and modified cells with EDTA or $Ca(OH)_2$, were manufactured and the cathodes were removed every 10th discharge cycle and dissolved for the polarographic analysis. This procedure was continued up to the 50th cycle.

Along with the polarographic experiments, scanning electron microscopy (SEM) was used to investigate the effect of $Ca(OH)_2$ and EDTA on the structure of the anodes of the cells which had been taken apart after cycling.

## Results and Discussion

The results obtained from various test series showed a positive effect on the cycle life behaviour of cells with EDTA as an additive to the electrolyte. At EDTA concentrations between 1mM and 30mM a significant increase of the discharge capacity after 25 cycles could be found. The EDTA cells outperformed the reference cells by up to 20 % between the 30th and the 70th cycle. The cumulative capacity of these cells after 70 cycles could be improved by more than 10 %.

The addition of $Ca(OH)_2$ could not increase the cumulative capacity of these test cells, although the capacity fade was diminished. They have less capacity loss, but lower initial capacity due to an increase of electrochemically inactive material in the anode mass.

The results of the polarographic analysis of the manganese dioxide cathode showed that the zinc migration was especially limited by the addition of $Ca(OH)_2$ . The average zinc loss of the anode of reference cells was found to be 7.5 % after 50 cycles compared with only 4.8 % for $Ca(OH)_2$ cells.

The SEM pictures of zinc electrodes showed that the structure of $Ca(OH)_2$ anodes after 50 cycles was very similar to that of an uncycled anode gel and totally different from cycled reference anodes. No significant difference between EDTA and reference anodes could be observed. Both showed the same needle-like structure, although the structure of EDTA anodes seem to be more porous.

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## References

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