Development of flat plate rechargeable alkaline manganese dioxide–zinc cells

Andreas Stani [a,*], Waltraud Taucher-Mautner [a], Karl Kordesch [a], Josef Daniel-Ivad [b]

[a] *Institute for Chemistry and Technology of Inorganic Materials, Graz University of Technology, Stremayrgasse 16, A-8010 Graz, Austria*
[b] *Pure Energy Visions Inc., 30 Pollard Street, Richmond Hill, Ont., Canada L4B 1C3*

Abstract

This paper was focused on the development of prototypes for flat plate RAM[TM] (rechargeable alkaline manganese dioxide) cells. In contrast to cathodes used in cylindrical RAM[TM] cells, the mechanical stability is a significant issue for the preparation of flat plate cathodes. Therefore, the choice of an appropriate binder, e.g. Oppanol, is very important. In this work, an improved preparation process of flat plate RAM[TM] cathodes was developed by investigating the single steps of the preparation method. It was further demonstrated that the most critical factor of zinc electrode performance was the electrolyte content of the anode gel. Best overall cell performance was achieved at 40% zinc amount and a Zn/ZnO ratio of 5.0, in combination with an electrolyte content of 50.5%. In order to stabilise the γ-structure of manganese dioxide and to enhance rechargeability, the addition of barium compounds was also studied. Cell cycling has shown that flat plate RAM[TM] cells with $BaSO_4$-modified cathodes outperformed control cells by 24%, mainly because of the minimised fade of discharge capacity. Moreover, the admixture of barium manganate to the cathode yielded more than 15% capacity improvement after 25 cycles, compared to the barium sulfate additive.
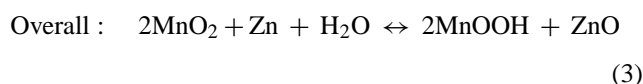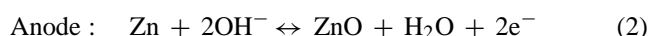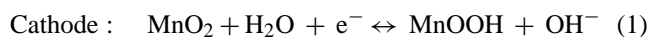© 2005 Elsevier B.V. All rights reserved.

Keywords: Rechargeable alkaline cells; Gelled zinc electrodes; Polymer bonded manganese dioxide cathodes; Flat plate design; Barium additives; Cycle life

1. Introduction

The RAM[TM] (rechargeable alkaline manganese) technology offers an environmentally responsible, low cost rechargeable battery system that can be utilised 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 [1–5]. The cylindrical RAM[TM] cell design is, in general, not different from a single-use primary alkaline cell. The basic construction allows to apply the same low-cost manufacturing process as for single-use primary alkaline cells. The production cost of RAM[TM]

cells is by far the lowest amongst all other rechargeable small format cells [6].

The simplified electrochemistry (discharge/charge) of RAM[TM] cells can be formulated as:

$$\text{Cathode}: \quad MnO_2 + H_2O + e^- \leftrightarrow MnOOH + OH^- \quad (1)$$

$$\text{Anode}: \quad Zn + 2OH^- \leftrightarrow ZnO + H_2O + 2e^- \quad (2)$$

$$\text{Overall}: \quad 2MnO_2 + Zn + H_2O \leftrightarrow 2MnOOH + ZnO \quad (3)$$

The first electron discharge step of manganese dioxide, according to Eq. (1), proceeds in a homogeneous reaction by the movement of protons and electrons into the lattice, resulting in a gradually decreasing value of x in MnO_x, from $x = 2$ to $x = 1.5$. This homogeneous reaction represents a conversion of one solid structure (MnO_2) into another ($MnOOH$) and is responsible for the typical sloping discharge curve [7].

* Corresponding author. Tel.: +43 3462 800 2676; fax: +43 3462 800 2847.
  E-mail address: andreas.stani@epcos.com (A. Stani).

RAM^{TM} cells are limited to the "one-electron" discharge of manganese dioxide that is realised through anode capacity limitation. The zinc anode is discharged through a dissolution process via formation of zincate ions. Once the electrolyte becomes oversaturated with zincate ions, solid zinc oxide starts to precipitate, as described in a simplified way in Eq. (2). After discharge, the above reactions are reversed during the voltage-controlled charging process.

The main goal of this research work is focused on the development of flat plate electrodes for RAM^{TM} cells. This electrode design is expected to extend the capabilities of the MnO$_2$–Zn system into applications presently not suited for cylindrical cells, especially with regard to the progressive miniaturisation of electronic devices. A flat plate electrode design should result in higher current densities, better utilisation of the active material (especially of very thin electrodes) and improved rechargeability and therefore, a less prominent capacity fade during cycling [8,9]. Besides all that, the flat plate electrode design also offers the well-known advantages of cylindrical RAM^{TM} cells, e.g. excellent charge retention, no memory effect, environmental superiority and low costs.

This paper will concentrate on first prototypes of flat plate RAM^{TM} cells. The choice of the polymer binder, the mixing sequence of dry components, as well as the drying process and the applied pressure, are essential issues for sufficient stability of flat plate electrodes. These topics will be discussed in detail in this work. Concerning the anode of flat plate RAM^{TM} cells, parameters as the zinc amount, the Zn/ZnO ratio and the electrolyte content, have to be optimised. Furthermore, based on our experience made with the addition of BaSO$_4$ to the manganese dioxide cathode of cylindrical RAM^{TM} cells [10–12], the admixture of barium compounds will also be studied in order to improve the cycle life of flat plate RAM^{TM} cells.

2. Experimental

2.1. Preparation of gelled zinc electrode

Gelled zinc anodes, that can also be found in various applications where zinc is used as anodic depolariser, were used for the preparation of flat plate electrodes. The gelled mixture, consisting of zinc (Type 00F4, Umicore Zinc-Belgium), zinc oxide (Merck, Germany) and Carbopol (Type 934, The BFGoodrich Comp., USA), was pasted onto a copper screen (mesh or expanded metal) and wrapped into an envelope of a multi-component separator (Type CT0449, thickness: 0.178 mm, electrolyte absorption: 298 g m^{-2}, wet ionic resistance: 120 mΩ cm^2 in 30% KOH; Scimat Limited Techno Trading Estate, UK). The anode formulation was varied within a wide composition range, especially concerning the zinc/zinc oxide ratio and the electrolyte content. All flat plate RAM^{TM} cells were balanced at 150% of the one-electron capacity of manganese dioxide, because the influ-

ence of the zinc electrode on the cycle life of these cells should be minimised. Typical anode weight and capacity: 2.2 g/750 mAh.

2.2. Preparation of manganese dioxide electrode

In contrast to cathodes used in cylindrical cells, mechanical stability is very important for flat plate cathodes, as there is no can or sleeve which provides additional mechanical stability to the electrode. The only way of making flat plate electrodes mechanically stable, is to add some binder to the cathode mix. This can be achieved either using a "dry" or "wet" preparation method [13]. Both kinds of preparation use a solution of an appropriate polymer added to a mix of electrolytic manganese dioxide (EMD, Tosoh Corp., Japan), graphite (KS 44, TIMCAL Ltd., CH), carbon black (Acetylene Black, Denka Corp., Japan) and other additives to achieve a slurry-like cathode mass. If the solvent is evaporated before further processing of the cathode, the preparation method is called "dry". This method involves re-granulating of the dried slurry and pressing of the obtained powder. In the case of preparing the cathodes the "wet" way, the solvent is evaporated after the preparation sequence is finished and electrode geometry and thickness are finalised. All cathodes tested in this work were prepared using the "wet" method that is described in detail in Fig. 1. Besides the choice of the polymer binder, the current collector is another key factor for the mechanical stability and the performance of flat plate cathodes. Different types of nickel substrate, as expanded metal (3Ni4-4/0A and 4Ni10-5/1HX, Exmet Corp., USA) and foam (Z110, Exmet Corp., USA), were tested as current collector. The dry components of the cathode mix (EMD, graphite, carbon black and other additives) were homogenised using a ball mill. A paste-like cathode mass was achieved by adding a solution of the polymer binder in an organic solvent. This paste was applied to the current collector by rolling and pressing. The final thickness of the polymer bonded cathodes varied between 0.5 and 1.2 mm. The geometry of a typical cathode was 3.3 cm × 3.3 cm (approximately 11 cm^2) with a thickness of 1.2 mm. Typical cathode weight and 1e$^-$ capacity: 2.0 g/500 mAh.

2.3. Assembling of flat plate RAM^{TM} cells

Due to the fact that all flat plate RAM^{TM} cells were intended to be prototypes, aspects of future mass production were neglected. Therefore, a simple, easy to use and reusable casing design was chosen. The cell casing consisted of acrylic glass plates and different types of rubber seals (Fig. 2). Depending on electrode thickness and cell type, u-shaped or rectangular rubber seals coated with silicon grease, were used to prevent leakage. A definite pressure was applied to the electrode stack by using a proper rubber seal and/or additional spacers. In certain cases, even hot melt was used for sealing the top part of the cell casing. The electrolyte of flat plate RAM^{TM} cells was 9 M KOH (typically 2.0 g for cells
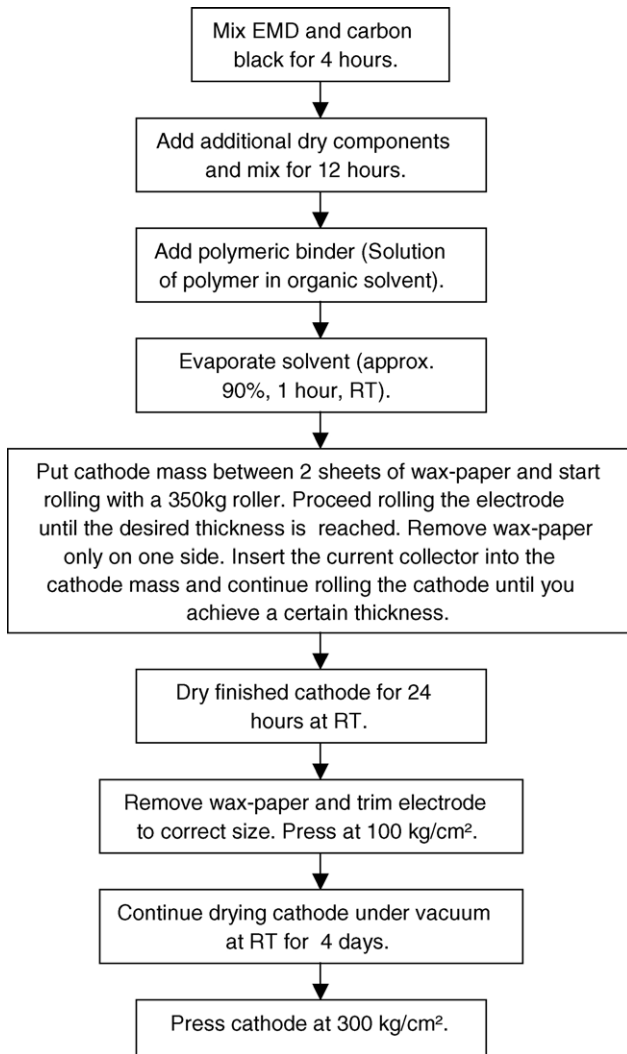
Fig. 1. Steps for wet preparation of flat plate cathodes for RAM[TM] cells.

with 11 cm² electrodes). The volume of the cell assembly was 3.3 cm × 4.0 cm × 0.2 cm (2.64 cm³). After assembly of casing, cells were filled with electrolyte and soaked overnight under vacuum.
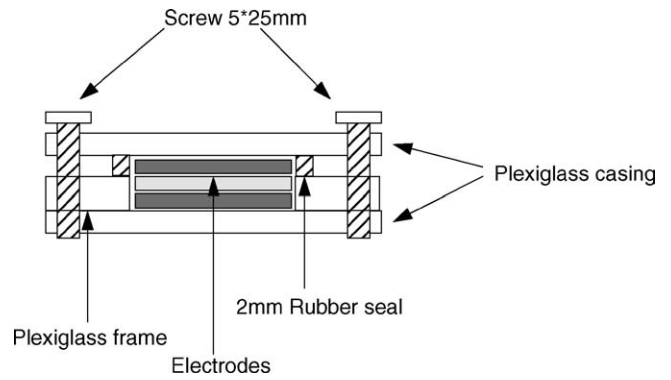

Fig. 2. Cross-sectional view of casing type used for sandwich-type cells.

2.4. Cell testing

The cycle life of flat plate RAM[TM] cells was recorded using a computer-controlled multi-channel testing system (designed and assembled at University of Technology Graz). Cells were discharged at a constant resistance to a cut-off voltage (COV) of 0.9 V and then taper-charged with constant voltage at 1.75 V, as demonstrated in Fig. 3. After 25 cycles, the prototype cells were post-mortem analysed focusing on mechanical stability and thickness of the electrodes. More than 500 cells were assembled during this study, the typical number of cells for one experiment was six (three cells for control group, three cells for test group).

3. Results and discussion

3.1. Anode experiments

Results obtained from numerous experiments clearly indicate that the formulation of flat plate anodes can be modified in a wide composition range without lowering the overall cell performance, as long as the electrolyte content is kept above a certain level. A zinc amount of 36% still proved to be sufficient, which can be attributed to the high electrolyte level.
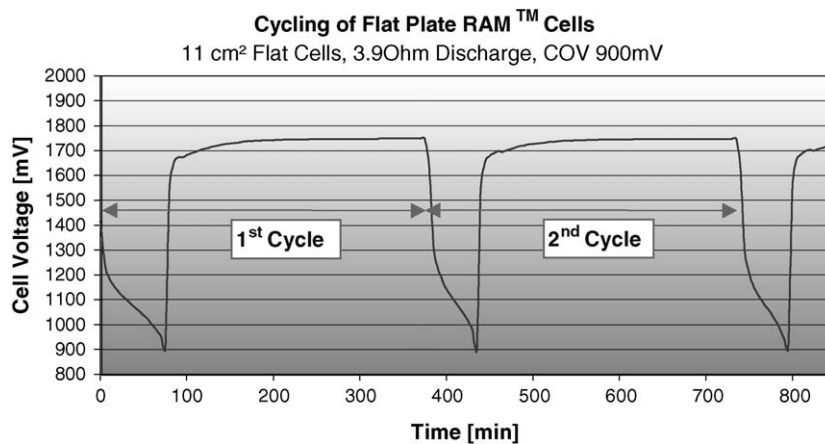

Fig. 3. Cell voltage during cycling of flat plate RAM[TM] cells.

Anode Testing
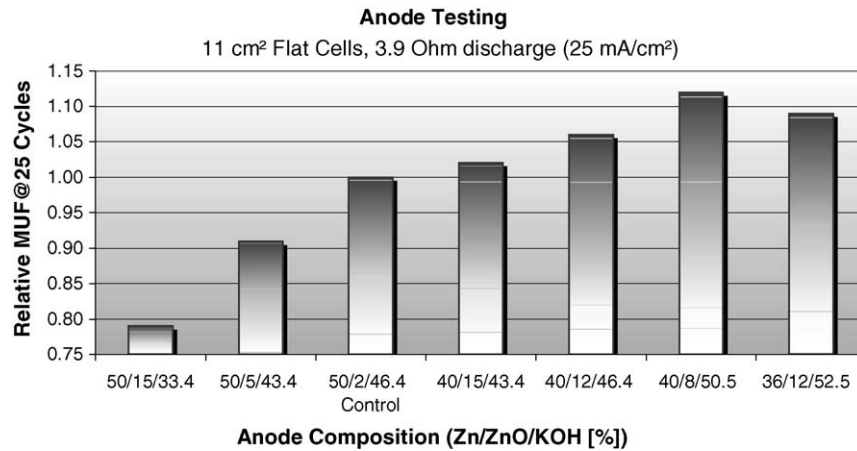11 cm² Flat Cells, 3.9 Ohm discharge (25 mA/cm²)

Fig. 4. Overall cell performance of flat plate RAM™ cells compared to control group.

Increasing the zinc oxide content, seems to be effective only at lower zinc levels, since the addition of zinc oxide simultaneously lowers the electrolyte amount. The electrolyte content of all cells performing better than control cells, was well above 40%, containing 40% zinc or even less. Fig. 4 presents the relative multiples utilisation factor (MUF) of anode testing as a function of anode composition (MUF = one-electron-capacity of MnO_2 × 25/cumulative capacity of test cells after 25 cycles). This figure clearly shows that the most critical factor for anode performance was found to be the electrolyte content of the anode gel. A relatively low zinc content together with a high Zn/ZnO ratio at a certain zinc level appeared to be very beneficial for overall cell performance. The best result was achieved at 40% zinc loading and a Zn/ZnO ratio of 5.0, in combination with an electrolyte content of 50.5% (Fig. 4).

Especially during the later cycles, the increased electrolyte content was very important for keeping the discharge capacity from fading. A very good example of possible electrolyte depletion is displayed in Fig. 5. The low electrolyte amount together with a high active material utilisation due to Ba-manganate modified cathodes (Section 3.2.3), caused a steadily decreasing discharge capacity that is well pronounced within the first 15 cycles, while the fade of the control group was far less prominent.
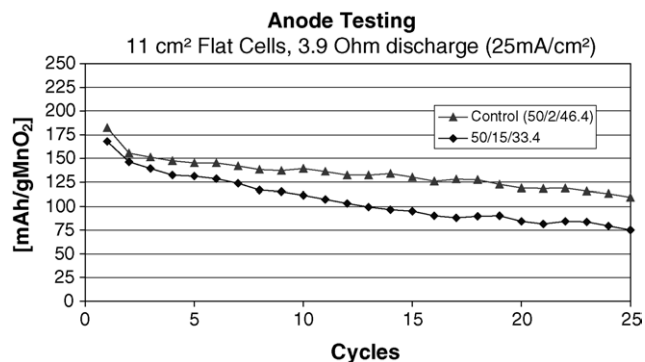
3.2. Cathode experiments

3.2.1. Cathode preparation

Three steps within the preparation process turned out to be very important for cathode performance: (i) the mixing sequence of dry components, (ii) the final drying of the electrode and (iii) the applied pressure.

The main modification in the mixing sequence of dry cathode components, as described in Section 2.2, was the separate treatment of EMD/carbon black and other additives. EMD and carbon black were ball milled separately for 4 h before graphite and other additives were added and ball milled for another 12 h (Fig. 1). Cathodes for control cells were prepared according to the standard procedure, meaning that EMD, carbon black, graphite and other additives were ball milled simultaneously for 12–16 h. Fig. 6 compares the cycle life of flat plate RAM™ cells that were prepared by the new, modified mixing sequence, to a control group. This figure indicates that cells with the improved mixing sequence outperformed the control group up to 15 cycles.

The kind of the final cathode drying method exemplified the great influence on cell performance of flat plate RAM™ cells. Vacuum drying of cathodes resulted in a large improve-

Anode Testing
11 cm² Flat Cells, 3.9 Ohm discharge (25mA/cm²)

Fig. 5. Cycle life of flat plate RAM™ cells with 50% Zn/15% ZnO/33.4% 9 M KOH anodes compared to control group.

Different Mixing Sequence
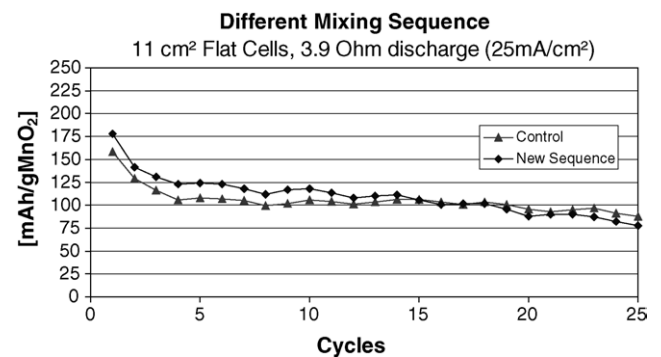11 cm² Flat Cells, 3.9 Ohm discharge (25mA/cm²)

Fig. 6. Cycle life of flat plate RAM™ cells with cathodes prepared according to the improved mixing sequence compared to control group.
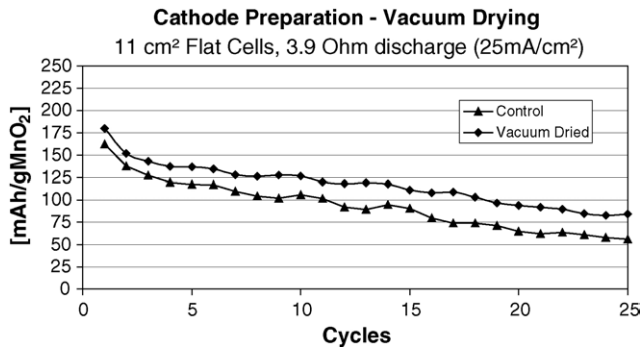
Fig. 7. Cycle life of flat plate RAM[TM] cells with vacuum dried cathodes compared to control group.

ment in overall cell performance. Fig. 7 displays the cycle life of vacuum dried cathodes up to 25 cycles. Test cells exceed the control group at every stage during cell cycling. There are at least two possible explanations for this result. First of all, the evaporating solvent increases the porosity of the electrode, which provides better electrolyte transport within the cathode. Secondly, manganese dioxide particles or bigger aggregates, covered with organic solvent, cannot participate in the reduction/oxidation process since they will not be reached by the electrolyte. Toluene, that was almost exclusively used as organic solvent, is a molecule with low polarity and therefore hydrophobic characteristics. In general, both effects are essential for good electrode performance.

The pressure applied to the cathode during preparation, is another key factor for electrode performance. A certain level of pressure is necessary in order to provide enough mechanical stability. Besides that, there are two major properties which are strongly influenced by the applied pressure: electrical conductivity and porosity. The optimum pressure also highly depends on cathode formulation, especially on the type of polymeric binder and on its content. For example, cathodes used in AA-size RAM[TM] cells containing no additional binder, are pressed at approximately $2000\,kg\,cm^{-2}$,

whereas the pressure for flat plate electrodes is significantly lower. The influence of pressure applied to the cathode, is displayed in Fig. 8. The overall cell performance and the relative short circuit current (SCC) of flat plate RAM[TM] cells in comparison to a control group, are shown in this figure. The level of SCC of test cells steadily enhances with increasing pressure, while the highest overall cell performance after 25 cycles was found at $850\,kg\,cm^{-2}$. Further increasing of the applied pressure does not improve cell performance, that might be attributed to problems with the electrolyte transport caused by a lower level of porosity.

3.2.2. Polymer binder

The use of a non-conductive, organic material as cathode binder cannot be done without facing certain problems. Most of them are related to higher internal resistance and troubles with electrolyte soaking related to the hydrophobic nature of the majority of polymers. To overcome these difficulties, especially the lower electrical conductivity, various kinds of conductive materials, e.g. graphite, were added to the polymeric binder solution.

Different types of polymer binder were tested, and finally, Oppanol (Polyisobutene B10-150, BASF, Germany) turned out to be appropriate for this purpose [14]. After numerous experiments with different grades and levels of Oppanol and the incorporation of electrically conductive additives, the highest overall cell performance could be obtained with 3% Oppanol B80 admixture and 1% KS 2.5 graphite (TIMCAL Ltd., CH) addition to the polymeric binder solution. The best result of polymeric binder testing, that is displayed in Fig. 9, is compared to a control group without graphite. The performance improvement of cells with KS 2.5 addition is clearly evident, especially within the first cycles. After 10 cycles, these cells surpass the control cells by more than 20%. Although a slightly fading discharge capacity of test cells was observed, the overall improvement after 25 cycles is still 15%. Furthermore, a utilisation factor (UF, % of theoretical one-electron capacity of MnO_2) of 61% is quite satisfactory, as shown in Fig. 10.
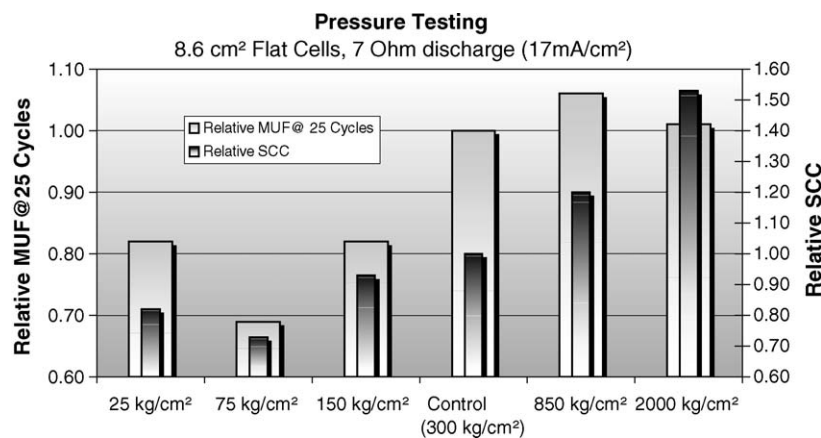

Fig. 8. Overall cell performance and relative SCC of flat plate RAM[TM] cells as a function of pressure applied to the cathode.
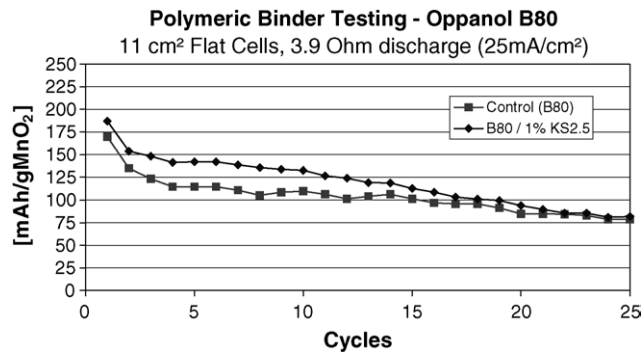
Fig. 9. Cycle life of flat plate RAM[TM] cells with cathodes prepared using an optimised polymer binder and graphite additive compared to control group.
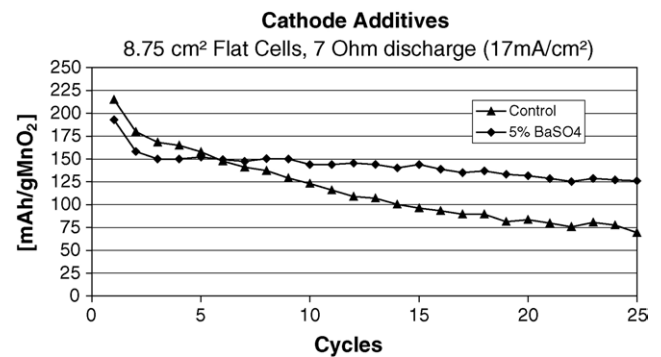

Fig. 11. Cycle life of flat plate RAM[TM] cells with BaSO$_4$-modified cathodes compared to control group.

3.2.3. Barium sulfate and barium manganate additives

For the rechargeability of manganese dioxide it is essential to maintain the tunnel structure of γ-MnO$_2$ during cycling of RAM[TM] cells. Various additives have been reported to be able to stabilise this structure by insertion of large cations, e.g. Ba^{2+} and Bi^{3+}, into the tunnels of the manganese dioxide lattice [15–17]. More recently, it was found that the incorporation of bismuth or barium into the cathodes improves cycle life, which is partly due to the suppression of electrochemically inactive phases such as birnessite (δ-MnO$_2$) and hausmannite (Mn$_3$O$_4$) during the one-electron process [18]. In our study, EMD samples were physically modified by simply ball milling of the cathode mix containing barium additives. The intention is to reduce the loss of electrochemically active material during cycling and hence to increase the cell capacity effectively.

Based on the experience made with the addition of BaSO$_4$ in cylindrical RAM[TM] cells, flat plate cathodes with different amount of additive were prepared and tested in comparison to control cells without additive. Flat plate RAM[TM] cells with BaSO$_4$-modified cathodes clearly exceeded control cells, mainly because of the minimised fade of discharge capacity (Fig. 11). Although the initial utilisation of control cells was significantly higher compared to test cells, they were

only better for the first five cycles, with a constantly fading discharge capacity up to 20 cycles. This fade could not be observed on BaSO$_4$-modified cells. In fact, discharge capacity almost remained constant after the first three cycles. Best overall cell performance could be obtained with 5% BaSO$_4$ admixture that yielded an enormous improvement of 24% after 25 discharge cycles, as shown in Fig. 12.

The main idea behind the introduction of manganate as cathode additive was developed by considering the impact of barium sulfate on manganese dioxide. The sulfate ion is a "necessary evil" for incorporating the barium ion into the manganese dioxide cathode, but since it is electrochemically inactive, it neither harms nor it is useful. When replaced by barium manganate, the barium ion can be incorporated into the cathode together with a manganese oxide ion, which might be able to contribute to the discharge capacity as well. Especially manganate (V) was regarded to be very promising, since it is unstable in 9 M KOH and disproportionates into manganate (VI) and manganese dioxide, which most certainly contributes to the discharge capacity [17].

Among several barium manganates (V), which had been reported to enhance cycle life of cylindrical RAM[TM] cells, the one with the most significant effect on cell performance, that is a mixture of Ba$_3$(MnO$_4$)$_2$/Ba$_5$(MnO$_4$)$_3$OH, was chosen.
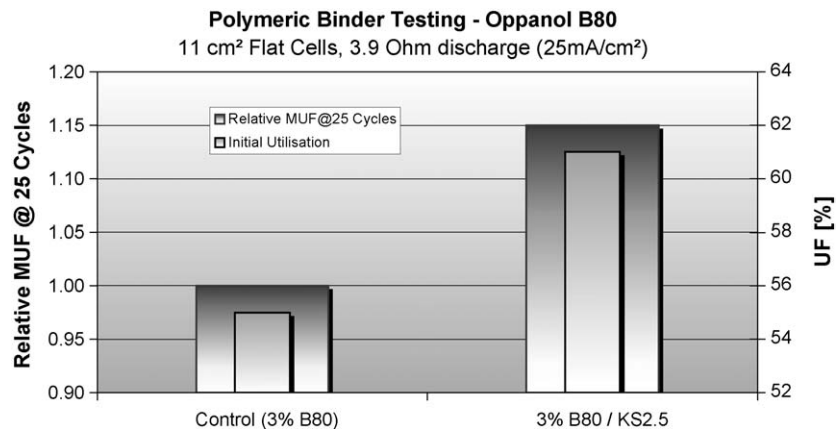

Fig. 10. Overall cell performance and initial utilisation of flat plate RAM[TM] cells with cathodes prepared using an optimised polymer binder and graphite additive compared to control group.
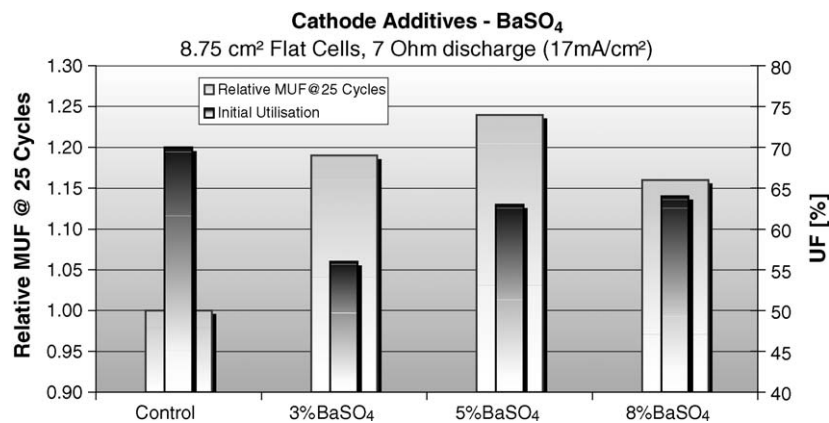
Fig. 12. Overall cell performance and initial utilisation of flat plate RAM^{TM} cells with BaSO$_4$-modified cathodes compared to control group.
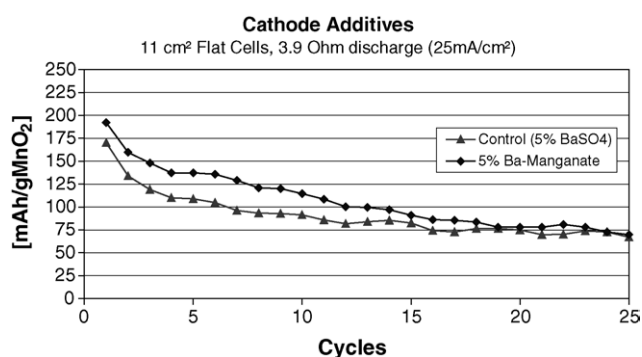

Fig. 13. Cycle life of flat plate RAM^{TM} cells with Ba-manganate-modified cathodes compared to control group.

The preparation of this manganate was carried out by a precipitation process, in the same way as described in [17]. Fig. 13 clearly shows the great improvement caused by the replacement of barium sulfate with barium manganate. Control cells are outperformed during cycle life by more than 15%. These results indicate that barium manganate probably acts in two different ways: (i) stabilisation of the γ-structure of manganese dioxide due to the barium ion and (ii) contribution of the manganate to the discharge capacity of the manganese dioxide. Further research work will be necessary to explain the fact that the achieved capacity enhancement even exceeds the possible, theoretical contribution of the manganate ion.

4. Conclusions

The results obtained during a period of more than 2 years of flat plate RAM^{TM} cell development clearly indicated the very promising potential of this new cell design. In this work, an optimised preparation technique of polymer bonded cathodes was developed. By means of studying the mixing sequence of dry components as well as the final drying process and the influence of applied pressure, an improved cell performance could be achieved. The addition of KS 2.5 graphite to Oppanol B80, exceeded control cells by 15%, after

25 cycles. It also turned out that the most critical factor of zinc anode behaviour is the electrolyte content in combination with a relatively low zinc amount and a high Zn/ZnO ratio.

This paper further clearly demonstrates that flat plate RAM^{TM} cells with BaSO$_4$-modified cathodes extremely outperformed control cells by 24%, mainly because of the minimised fade of discharge capacity during cycling. The admixture of barium manganate (V) to the cathode showed a large improvement of more than 15% during cycle life compared to barium sulfate. Barium manganate probably acts in two different ways: (i) stabilising of the γ-MnO$_2$ structure and (ii) additional contribution to the discharge capacity of MnO$_2$, that is probably due to a disproportionation reaction of the manganate ion. Finally, further studies are needed to elucidate the excellent behaviour of barium manganate in flat plate RAM^{TM} cells.

Acknowledgment

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