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Short communication

Triethanolamine as an additive to the anode to improve the rechargeability of alkaline manganese dioxide batteries

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Abstract

Rechargeable alkaline manganese dioxide batteries use a zinc paste anode which undergoes shape change during charging, effecting its activity. A study on triethanolamine (TEA) as an additive to the zinc anode to control its shape change and retain activity is made. Voltammetric studies showed the potential of TEA in controlling shape change. Rechargeable alkaline manganese dioxide batteries are made in the laboratory and their cycle life characteristics are compared with and without TEA in the anode. An improvement is noticed in the cycle life capacity of the rechargeable alkaline manganese dioxide batteries with TEA especially after 12th cycle. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Rechargeable alkaline manganese dioxide batteries; Zinc anode; Triethanolamine

1. Introduction

Karl Kordesch et al. have made intensive research and development efforts to commercialize rechargeable alkaline manganese dioxide batteries [1] and these batteries have been available commercially since 1993 [2]. The cells contain no cadmium or mercury and exhibit the same good shelf life as the primary alkaline manganese dioxide cells. The positive electrode of rechargeable alkaline manganese dioxide cells consists of multiple cathode pellets formulated from electrolytic manganese dioxide, graphite and some additives to improve the cycle life capacity. The negative electrode of rechargeable alkaline manganese dioxide batteries is made of zinc powder paste. It is specially processed with certain additives to achieve low gassing properties [3].

However, there is a significant drop in the cycle life capacity of current rechargeable alkaline manganese dioxide batteries as the cycling continues. This is attributed partly due to the shape change of the electrodeposited zinc anode during charging of the batteries. A possible solution to the shape change problem may be a suitable substance which reduces the solubility of ZnO in the electrolyte by making a weak complex with zincate ions. Efforts are made to control the shape change of the zinc anode of rechargeable alkaline manganese dioxide batteries by adding triethanolamine (TEA) to the zinc anode. TEA is a well-known chelating agent and reduces the solubility of zincate ions in the electrolyte by forming a weak complex with it.

2. Experimental data

2.1. Voltammetric studies

An alkaline solution of 100 mM TEA in 7 M KOH was prepared. And 10 ml of the above TEA solution was used in the voltammetric studies. A three electrode system was chosen where zinc strip $(1 \text{ cm} \times 0.4 \text{ cm} \times 0.038 \text{ cm})$ was the working electrode, Ag/AgCl, the reference electrode and Pt as the auxiliary electrode. An EG&G Princeton potentiostat model 273 was employed and a scan rate of 20 mV/s was used.

The voltammograms of the blank (7 M KOH only) and KOH with TEA in the above concentration are shown below (Fig. 1).

The voltammograms showed two oxidation peaks and one reduction peak. Peak A is due to the dissolution of Zn and peak A' represents the complexation of ZnO after its formation on the zinc surface. Peak C is the reduction process

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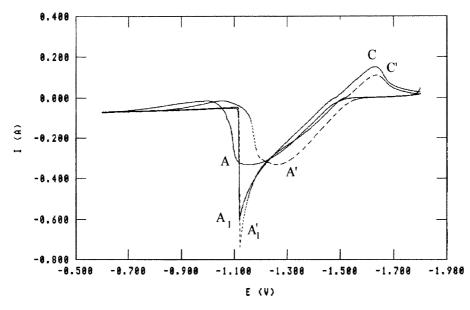


Fig. 1. Voltammogram of 7 M KOH in the presence of TEA at a concentration of 100 mM (- - -) compared to the voltammogram for the blank (---).

of ZnO producing Zn and regeneration of hydroxyl ions. The marked difference between the two voltammograms is the position of peak A which shifted towards the negative direction after the addition of TEA, A'. The difference between the reduction and the oxidation peak has been used to indicate the degree of reversibility of the process under study. The smaller the difference, the higher is the degree of reversibility. In the present study, the presence of TEA helps to increase the reversibility of the process at the anode and thus helps to resolve the problem of zinc passivation and to increase the capacity of the battery.

2.2. Practical testing

Several AA size rechargeable alkaline manganese dioxide cells were assembled in the research and development laboratory with and without addition of TEA in the anode. The standard cathode formulation of the existing rechargeable alkaline manganese dioxide batteries was used in producing these cells. The cells were tested by discharging them continuously at 300 mA drain to 0.8 V cut off and then charging them by standard rechargeable alkaline manganese dioxide charging method for the recommended time before subsequent discharge [4]. The performance of these AA size rechargeable alkaline manganese dioxide cells was compared to the existing Grandcell RAMTM batteries of the same configuration which were used as control.

These rechargeable alkaline manganese dioxide cells with TEA in the anode have the following cathode and anode formulation.

Cathode formulation: EMD, Graphite KS 44, Ag₂O, BaSO₄, KOH 9 M; anode formulation: zinc powder, PEG, In₂(SO₄)₃ Soln, Carbopol, KOH 9 M (with 5% ZnO and 0.2 M TEA); cell components: cathode, anode, and electrolyte KOH 9 M.



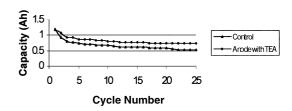


Fig. 2. Each cycle capacity of RAM with TEA as compared to the current grandcell AA cell (control).

Accumulative Capacity of AA (RAM LR6) Cells Discharge Rate: 300 mA Continuous Cut Off 0.8 V

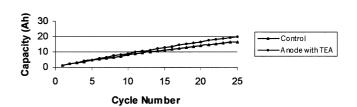


Fig. 3. Accumulative cycles capacity of RAM with TEA as compared to the current grandcell AA cell (control).

Figs. 2 and 3 show the results of testing of these rechargeable alkaline manganese dioxide batteries for 25 cycles.

3. Conclusion

Voltammetric studies showed the potential of TEA in controlling shape change. In the practical testing, a marked improvement is noticed in the cycle life capacity of the rechargeable alkaline manganese dioxide batteries with TEA especially after 12th cycle.

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