

Zinc contamination in the cathodic material of exhausted alkaline manganese dioxide batteries

Nikos Vatistas^{*}, Mauro Bartolozzi

Chemical Engineering Department, University of Pisa, Via Diotisalvi 2, 56100 Pisa, Italy

Received 16 July 1998; accepted 8 January 1999

Abstract

The cathodic compartment of the alkaline manganese batteries is contaminated by zinc ions from the anodic compartment during discharging: in this work we consider how discharging conditions affect the zinc concentration in the cathodic compartment. Various conditions of discharging have been tested and the mean and local concentration of zinc in the cathodic compartment has been determined. Experimental results show that the cathodic compartment of discharged batteries contains a small concentration of zinc, and that the discharge conditions and the discharging level affect the concentration of the zinc in this compartment. A deeper knowledge of the chemical composition of spent batteries improves recycling processes and allows the cathodic and anodic materials to be recovered separately. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alkaline-batteries; Batteries; Discharge; Manganese; Migration; Zinc

1. Introduction

Alkaline zinc manganese batteries, due to their easy use and good discharge characteristics/price ratio, are widely used. The most significant improvement observed over the past ten years for this kind of battery has been the decline in the use of mercury and the introduction of ‘mercury free batteries’ [1]. Even so, the high concentrations of heavy metals in the exhausted batteries of this type impose either a proper landfill disposal to assure their safe disposal or a recycling process [2,3].

Various recycling processes have been proposed, and some of them are already operating, but usually they are not specific and recycle any type of spent dry batteries. Most of them operate in Switzerland: the Recytec process has been operating since 1994 [4]; the Batrec (battery recycling) plant operates with a capacity of 3000 tons per year [5,6]. The more recent Batenus process operates in Germany and has a capacity of 7500 tons/year [7]. A specific recovery process operates in USA to recover metal from the exhausted nickel–cadmium, nickel–iron and nickel–metal hydride batteries, with a capacity of 2300 tons/year [8].

Exhausted batteries of a specific type need an easier and consequently less expensive recovery process than a multi-purpose one. The specific process depends on some characteristics of the batteries such as their discharge state, whether their collection has been differential or not, their stocking conditions etc. The economical waste management plan will strongly depend on those characteristics [9,10].

We think that the knowledge of the chemical composition of the anodes and cathodes of the spent batteries will help to propose more specific and efficient recycling processes. For this reason, in this work we intend to establish the chemical composition variations of the cathodic and anodic compartments with the discharging conditions of the alkaline manganese dioxide batteries.

2. Discharge of the alkaline manganese dioxide batteries

2.1. Performance and discharge of the alkaline manganese dioxide batteries

The low cost and high reliability of Alkaline Manganese Dioxide Batteries induce a large use of them in

^{*} Corresponding author. Fax: +39-050-511266; E-mail: vatistas@ing.unipi.it

industrial and military applications. Manufacturing, technical and performance characteristics of this kind of battery are easily available. The open circuit voltage ranges from 1.5 to 1.6 V, depending on the manganese dioxide formulation, while the typical operating voltage ranges from 1.1 to 1.3 V under moderate discharge conditions. The discharge curve has a moderate slope with an energy density of 165 Wh/kg. The operating temperature ranges from -20 to 54°C , while up to an 85% charge capacity is still present after 4 years storage at 21°C .

The chemically active components are high purity zinc powder for the anode, electrolytically produced manganese dioxide (EMD) for the cathode and concentrated potassium hydroxide solution for the electrolyte. During cell discharge, the manganese dioxide is reduced and the zinc is oxidised, while ions are transported through the conductive alkaline electrolyte. The simplified cell reaction is: $\text{Zn} + 2\text{MnO} \rightarrow 2\text{ZnO} + \text{Mn}_2\text{O}_3$.

2.2. Ionic transport during the discharging process and chemical composition of the compartments

In this work we are interested to find out what kind of ions are transported between the two compartments of alkaline manganese dioxide batteries. Each specific ion that is transported during the discharging process has a different effect on the contamination that takes place in the anodic and cathodic compartments and then causes a different final chemical composition on the exhausted battery. To point out this effect, we consider two different transported ions, hydroxide ion and zinc ion. When the hydroxide ion is transported from the cathode towards the anode compartment, the first compartment becomes less basic and the second one more basic; when the transport of zinc ions occurs from the anode to the cathode, its effect is the decrease of zinc concentration in the anodic compartment and the contamination of the manganese oxide with zinc ions in the cathodic compartment. In the first case, we have a pH variation in the two compartments, while in the second case, a contamination of manganese oxide occurs in the cathodic compartment and the final chemical composition in the two cases are completely different.

2.3. The variation of the chemical composition of the electrodes and electrolyte during the discharging process

The battery anodes and cathodes are three-dimensional electrodes impregnated with the electrolyte. The graphite in the cathodic compartment acts as a three-dimensional feeder with respect to the non conductive manganese dioxide which is the active component of the cathode. The zinc powder in the anodic compartment is the anodic component and an anode current collector is present.

When discharging of the battery begins, the electrochemical reactions in the anodic and cathodic compart-

ments principally concern the regions of the two electrodes that are close to the separator and the transported ions only need to move to a small distance. As the discharging continues, the active components of these regions become exhausted and the electrochemical reactions progressively concern regions that are further away from the separator, so the transported ions need to move longer and consequently the internal resistance of the batteries also increases.

Discharging changes the chemical composition of the electrolyte in the two compartments and, during discharging, the hydroxide ions are probably transported from the cathodic compartment towards the anodic one. At the same time, zinc ions are produced in the anodic compartment and can be transported in the opposite direction, towards the cathodic compartment. The ions with higher mobilities migrate between the two compartments of the battery during discharging but, if their concentrations decrease, other ions with a lower mobility can move.

2.4. The performance characteristics curves and the chemical characteristics curves

The performance characteristics curves report the operating voltages vs. service time, normally at constant resistance. The availability of the performance characteristic curves, for any size of batteries at various values of resistance, allows a more suitable use of the batteries. The performance characteristics indicate the variation of voltage as the battery discharging proceeds. This variation is due to changes in the chemical composition of the anodic and cathodic compartments. We think that, since the characteristics performance curves allow a more suitable use of the batteries, in the same way, knowledge of the characteristics curves which show the chemical compositions of the cathodic and anodic compartment vs. discharge will be useful for proposing new and more suitable and efficient recovery processes.

A series of discharging processes at constant resistance was performed to obtain the chemical characteristics curves, using different values of constant resistance and various values of the cut-off voltage. At the end of discharging, the anodic and cathodic compartments were analysed separately.

3. Experimental details

The batteries used in this work were a common brand, size AA, (MN1500-LR6), with an expiry date of January 2002. The experiments were performed at the beginning of 1998. Constant resistance discharging conditions were adopted and the range of the resistance used was from 10 to 220 Ω . Other discharging processes were performed using the same constant resistance and varying the cut-off

voltage value. Normally, four batteries were discharged simultaneously using various resistance values and the operating voltage values obtained were measured and recorded every 2 min using a 14-channel analogue/digital 16-bit converter Cole Palmer MAC-14 and a PC. The measured voltage and the known values of the resistance used allowed the current and the electric charge vs. service time to be calculated for each discharged battery.

After discharging, each battery was first weighed, then cut and dismantled in several parts: a cathodic material (graphite and manganese oxides) that was in the form of dark brown chips, an anodic material (zinc) that had the form of a granular grey cylinder, an iron case and a polymeric membrane. The weight of the battery was about 23 g. Around 300 mg in weight was usually lost during dismantling.

The cathodic material showed a mean humidity of 7.6%. This value was obtained by weighing the sample as such and after drying it for 5 h in a oven at 105°C. The chips were then powdered, dried again under the same conditions and about 300 mg of this powder were suspended in a solution of 10 ml of distilled water, 2 ml of concentrated sulphuric acid and 2 ml of 40% hydrogen peroxide. The slurry was heated for 10 min without boiling, then filtered in order to separate the graphite. The zinc and manganese were determined in the resulting solution using a Perkin Elmer Plasma 400 emission spectrometer. The anodic material sample was dried (8.4% humidity), then about 200 mg of dry powder was suspended in 10 ml of concentrated sulphuric acid and heated until it began to boil. It was necessary to add 1 ml of concentrated nitric acid in order to completely dissolve the granules. The zinc content in the resulting solution was determined by an emission spectrometer [11].

In some exhausted batteries, a fraction of the compact cathodic material was subjected to a mechanical surface treatment to reduce its roughness and the resulting smooth surface was used to determine the local zinc concentration, at various distances from the compartment separator. The local zinc concentration was obtained using dispersive X-ray spectrometry.

The alkalinity of the cathodic compartment changed during discharging, due to the migration of hydroxide ions towards the anodic compartment. In order to measure this variation, about 2 g of the dried and powdered cathodic material was suspended in 50 ml of distilled water. The slurry was heated for 10 min at 50°C, then filtered, in order to separate the solution from the solid, and the solution was titrated using 0.1 M hydrochloric acid. It was decided to titrate the solution instead of the slurry, owing to the complexity of performing the latter operation. In fact, during the titration of the slurry, when the pH reaches 8.6, the titration shows an irregular behaviour: after the introduction of more hydrochloric acid, the pH initially decreases and then increases very slowly. This was probably due to hydrolysis reactions.

4. Experimental results and discussion

Two series of discharging runs were performed. The first ones were explorative, to determine the most important effects of discharging conditions on the transfer of the major chemical species between the two battery compartments, while the second ones were concerned with the effect of discharge resistance at a constant cut-off voltage.

The analysis of new batteries was performed to determine the initial concentrations of zinc and manganese in the anodic and cathodic compartments. The cathodic compartment was found to have a manganese concentration of 54% and a zinc concentration of 0.34%, while the anodic compartment had a zinc concentration of 67%.

4.1. Discharging at various values of cut-off voltage and resistance

Discharging of the batteries was performed using the same resistance 10 Ω with different cut-off voltages of 1.02, 0.16 and 0.01 V. The first value is closest to the average conditions of exhausted batteries, while the second and third values represent an extremely high degree of discharging, performed to establish the maximum contamination of the compartments due to the transfer of species between them.

Fig. 1. shows a graph of voltage vs. service time. The first run has a service time of about 16 h, the second one of about 44 h and the third one of about 116 h. Various different discharging steps can be observed: (1) an initial decrease of voltage, during the first 2 h, (2) a slow decrease of voltage, during 2–18 h service time, (3) a sharp decrease of voltage, during a service time of 18–20 h, (4) a small voltage recovery, during a 20–25 h service time, (5) a plateau, during a 25–75 h service time and (6) a smooth decrease of voltage, during a 75–116 h service time.

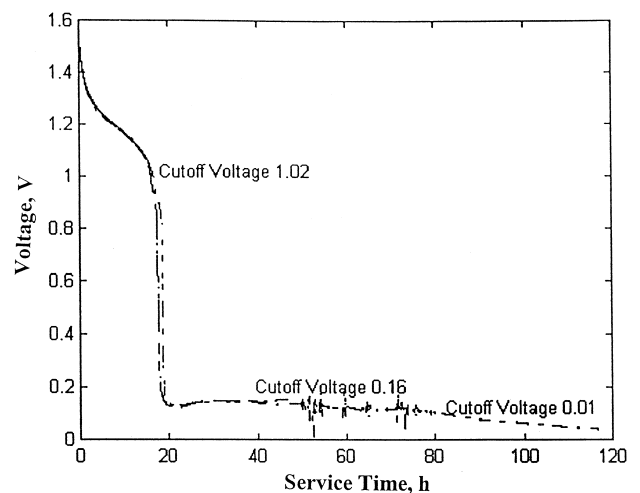


Fig. 1. Voltage vs. service time, using the same discharging resistance (10 Ω) and different cut-off voltages.

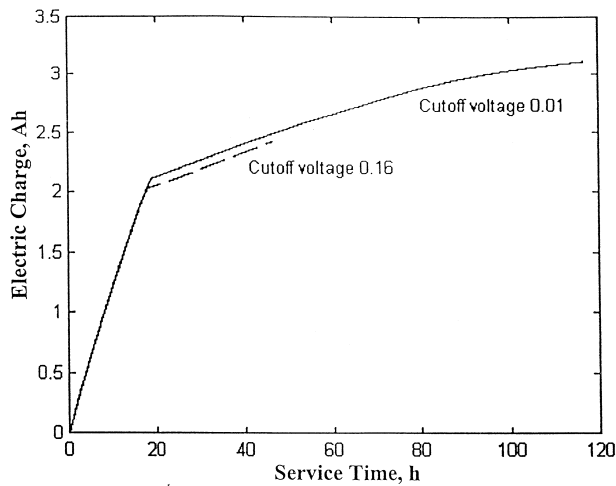


Fig. 2. Electric charge vs. service time, using the same discharging resistance (10Ω) and two different cut-off voltages.

Comparison of the three runs using the same resistance 10Ω points out that initial discharging is very similar in all runs, while a small delay is observed between the second and third runs for the step which presents the sharp decrease of the voltage. In any case, after this step, both the second and third runs show the same voltage recovery. Fig. 2, which shows the supplied electric charge vs. service time, also shows the effect of this delay for the second and third runs.

Similar discharging runs were performed using a higher resistance (20Ω) and cut-off voltages of 1.00 and 0.002 V respectively, and an even higher resistance value (110Ω). Fig. 3 shows the voltage behaviour of each run during its service time. The use of higher resistance makes the various steps that occur during the discharging smoother. For example, the sharp reduction of the potential observed in the previous case is reduced: (1) with a resistance of 10Ω , only 40 min are needed to reduce the voltage from 1 to

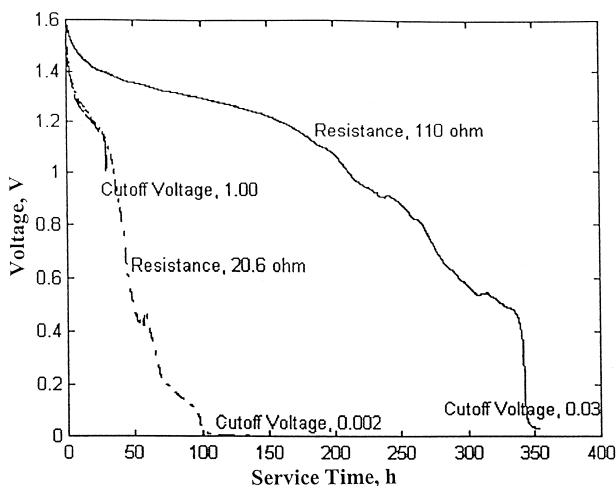


Fig. 3. Voltage vs. service time, using two different discharging resistances.

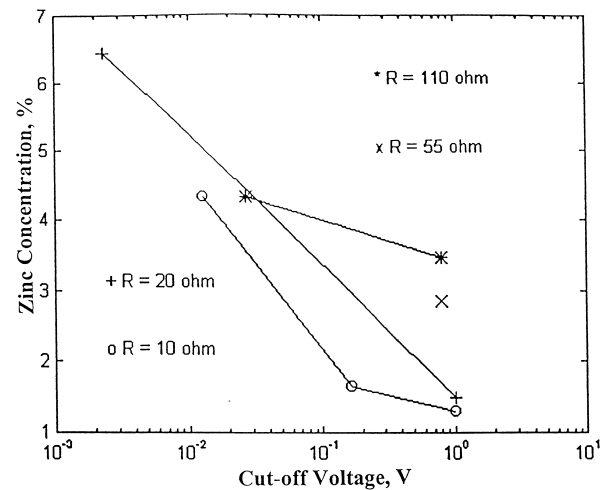


Fig. 4. Mean zinc concentration in the cathodic compartment vs. cut-off voltages, using different discharging resistances.

0.16 V; (2) with a resistance of 20Ω , about 20 h are needed to reduce the voltage from 1.10 to 0.42 V and (3) using 110Ω , about 80 h are needed to reduce the voltage from 1.20 to 0.93 V.

The variety of voltages observed during service times with different resistance values indicates different controlling mechanisms during the discharging. Those mechanisms probably have different effects on the contamination of the two compartments.

4.2. Contamination of the anodic and cathodic compartments at various values of cut-off voltage and resistance

The anodic compartment contains zinc and chemical analysis performed on new and exhausted batteries showed that it does not contain any trace of manganese. Variable quantities of zinc were found in the cathodic compartment and its quantity vs. discharge is reported.

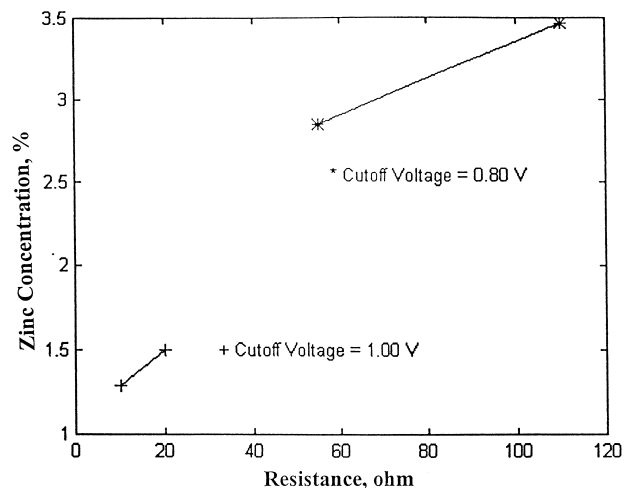


Fig. 5. Mean zinc concentration in the cathodic compartment vs. discharging resistance at two different cut-off voltages.

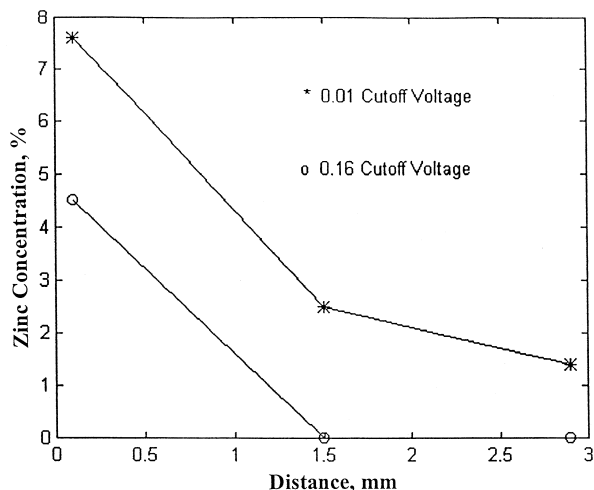


Fig. 6. Local zinc concentration in the cathodic compartment using the same discharging resistance (10 Ω) and two different cut-off voltages.

A zinc concentration of 0.35% was found in the cathodic compartment of new batteries, while higher concentration values were observed in exhausted batteries. The values of zinc concentration in the cathodic compartment using various cut-off voltage and resistance are reported in Fig. 4. The results show that as the cut-off voltage decreases, the concentration of zinc in this compartment increases. The same figure shows that as the value of the resistance used increases, the zinc concentration increases also. This last effect is highlighted in Fig. 5, where the zinc concentration vs. resistance value at two different cut-off voltages is reported.

A battery that was partially discharged in 1994 and then conserved was analysed after four years and the mean zinc contamination of the cathodic compartment was found to be 1.32%, a value very close to that of recently discharged batteries. This result points out that the transfer of zinc towards the cathodic compartment occurs during discharging and not during storage; in other words, this transfer is due to migration and not to diffusion of the zinc in the battery.

The local zinc concentration in three different points of the cathodic compartment was measured for two batteries that had been discharged to different degrees with a resistance 10 Ω . The first one was discharged to a 0.16 V cut-off voltage, while the second one was discharged to a 0.016 V cut-off voltage. The local concentration of zinc vs. distance from the separator is reported in Fig. 6. It can be observed that the zinc in the less discharged battery is concentrated only close to the separator, while the completely exhausted battery shows a contamination of the whole cathodic compartment. The local zinc concentration obtained in the cathodic region points out that the contamination of the cathodic compartment only concerns a small region close to the separator, while this contamination is extended to the whole cathodic region for batteries discharged to very low cut-off voltages.

The γ - MnO_2 structure of the electrolytic manganese dioxide (EMD) contains a domain of intergrown β - MnO_2 (rutile) and ramsdellite MnO_2 . In the first structure, the interstitial space is constituted of narrow (1×1) channels; in the second structure, it is constituted of larger (2×1) channels [12]. The larger interstitial space of the ramsdellite or, more simply, the voids between particles of γ - MnO_2 and graphite probably allows a limited migration of zinc into the cathodic compartment.

The cathodic solution has a pH of 11.07, while an exhausted battery with 4.34% of zinc in the same compartment has a pH of 9.50. The titration of the solution, performed as described previously, showed that the exhausted battery only required 48% of the hydroxide acid compared to the new one.

5. Conclusions

Knowledge of the chemical composition of exhausted batteries is very important to establish the most suitable recycling process, consequently, several discharging tests on the alkaline manganese dioxide batteries were performed in order to understand the effect of discharging conditions on the migration of the more important chemical species between the cathodic and anodic compartments.

Some migration of zinc towards the cathodic compartment was observed and, at the same time, a decrease of the alkalinity in the same compartment was noted. No contamination of the anodic compartment by the manganese was observed. The mean and local zinc contamination in the cathodic compartment was obtained for various cut-off voltages and for different discharging resistance values.

The migration of zinc increases as the cut-off voltage decreases and as the discharging resistance increases. The maximum zinc concentration of the cathodic compartment obtained in this work was less than 7%, while at normal values of cut-off voltage the mean zinc contamination in the cathodic compartment was found to be less than 4% when high discharging resistances were used (55–110 Ω) and less than 2% when lower ones were used (10–20 Ω).

Acknowledgements

Financial support from University of Pisa is gratefully acknowledged.

References

- [1] M. Randall, Environ. Prog. 14 (1995) 232–239.
- [2] W.P. Hagan, R.G. Linford, J. Power Sources 15 (1995) 399–405.
- [3] S. Panero, C. Romoli, M. Achilli, E. Cardarelli, B. Scrosati, J. Power Sources 57 (1995) 9–12.
- [4] P.J. Ammann, Power Sources 57 (1995) 41–44.

- [5] A. Weber, A. Antenen, *Recycl. Met. Eng. Mater., Int. Symp.* 3rd, 957, in: P.B. Queneau, R. D. Peterson (Ed.), *Minerals, Metals and Materials Society*, Warrendale, PA, 1995.
- [6] R. Burri, A. Weber, *J. Power Sources* 57 (1995) 31–35.
- [7] S. Froehlich, D. Sewing, *J. Power Sources* 57 (1995) 27–30.
- [8] R. H. Hanewald, M. E. Schweers, J. J. Liotta, *Annu. Battery Conf. Appl. Adv.*, 11th, 207, Institute of Electrical and Electronics Engineers, New York, NY, 1996.
- [9] J.P. Wiaux, J.P. Waefer, *J. Power Sources* 57 (1995) 61–65.
- [10] J.L. Gascoigne, S.M. Ogilvie, *Issues Environ, Sci. Technol.* 3 (1995) 91.
- [11] M. Bartolozzi, G. Braccini, P.F. Marconi, S. Bonvini, *J. Power Sources* 48 (1994) 389–392.
- [12] M.M. Thackeray, M.H. Rossouw, A. de Kock, A.P. de la Harpe, R.J. Gummow, K. Pearce, D.C. Liles, *J. Power Sources* 43 (1993) 289–300.