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Short communication

A study of a high-power, ammonium chloride zinc / manganese dioxide dry battery

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Abstract

A high-power, ammonium chloride zinc / manganese dioxide dry cell is prepared by modification to the components of the electrolyte and the cathode. Detailed studies are carried out on the effect of some factors which include the electrolyte, the moisture content, and the ratio of acetylene black to graphite. The cathode product is analyzed by X-ray diffraction. Specifications are given for the high-power cell. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: High-power; Ammonium chloride; Manganese dioxide dry battery; Electrolyte; Cathode; Moisture content

1. Introduction

Although the zinc / manganese dioxide dry cell has a history of more than 130 years, it is still the most produced portable source of electricity. Accordingly, there have been continuous studies [1–5] of its technology. In terms of the electrolyte employed, paper-lined zinc / manganese dioxide dry cells can be divided into ammonium chloride and zinc chloride types. In general, the $ZnCl_2$ cell displays better capacity at both high current drains and on continuous discharge. For this reason, $ZnCl_2$ cells are referred as high-power batteries. The superior performance of $ZnCl_2$ cells is offset, however, by more complex fabrication due to the requirement for more reliable seals [6]. Consequently, the NH_4Cl cell still commands a rather large proportion of the market for zinc / manganese dioxide dry cells. Thus, it is important to improve the heavy discharge performance of NH_4Cl cells.

In this paper, the heavy discharge time of NH_4Cl cells is increased to the high-power cell level by changing the components of the electrolyte and the cathode. The electrolyte, the moisture content and the ratio of acetylene black to graphite, all factors which effect cell performance, are examined in detail. The optimum cathode product is analyzed by X-ray diffraction.

2. Experimental

2.1. Electrolyte

The general NH_4Cl cell electrolyte (Eg) was obtained by the following process: (i) 90 g of $ZnCl_2$ was dissolved in 150 ml distilled water; (ii) zinc plates were increased in the $ZnCl_2$ solution which was then heated at 100°C for 1 h; (iii) after cooling, the solution was diluted to 20°Be with distilled water; (iv) 165 g of NH_4Cl was dissolved in the solution and the sediment was removed by filtration; (v) the final electrolyte was diluted to 21°Be.

High-power NH_4Cl cell electrolyte (Eh) was obtained by the following process: (i) 9 g $ZnCl_2$ was dissolved in 150 ml distilled water; (ii) zinc plates were immersed in the solution which was then heated at 100°C for 1 h; (iii) the solution was diluted with 150 ml distilled water; (iv) 45 g of NH_4Cl was dissolved in the solution and the sediment was removed by filtration; (v) the final electrolyte was diluted to 15°Be.

2.2. Cathode

The high-power NH_4Cl cell cathode (Ch) was as follows: (i) the electrolyte manganese weight ratio of electrolyte manganese oxide to carbon was 5.5:1; (ii) the

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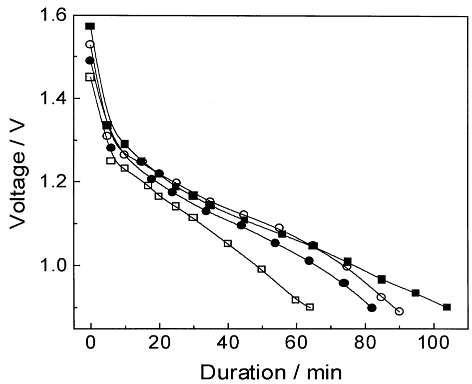

Fig. 1. Continuous discharge curves of R6 cells for a 3.9 Ω load: (■) Eh + Ch; (○) Eh + Cg; (●) Eg + Ch; (□) Eg + Cg.

weight ratio of acetylene black to graphite was in the range 3.4 to 10.0:1; (iii) 10 to 13 wt.% of solid NH_4Cl and 3 to 10 wt.% of solid $ZnCl_2$ were added to the cathode mixture; (iv) the moisture of bobbin was 26 to 32%.

The general NH_4Cl cell cathode (Cg) was as follows: electrolyte MnO_2:acetylene black:NH_4Cl = 86:14:16.

3. Results and discussion

3.1. Effect of electrolyte on performance of cells

The discharge characteristics of R6 cells using different electrolyte and cathode components are shown in Fig. 1. Through changing the cathode, the continuous discharge time for a 3.9 Ω load is increased by 28%. Through changing the electrolyte, the continuous discharge time for a 3.9 Ω load is increased by 39%. The continuous discharge time of the high-power cell is increased by 60% over that of the general cell. This illustrates that both the electrolyte and the cathode play important roles in changing the general cell to a high-power cell. It is commonly thought [6] that if the NH_4Cl concentration is lower than 7 to 10%, the anode product of the discharge reaction is $ZnCl_2 \cdot 4Zn(OH)_2$ rather than $ZnCl_2 \cdot 2NH_3$. The former product is an amorphous, porous sediment. As it cannot form a hard layer around the bobbin, it cannot hinder discharge even if present in a large amount. By contrast, $ZnCl_2 \cdot 2NH_3$ has a strong tendency to form a hard layer, which can hinder discharge. For this reason, the $ZnCl_2$ cell has better continuous discharge characteristics at high current drains than the NH_4Cl cell. In our high-power electrolyte, the NH_4Cl concentration is lower than 10 wt.%, although some solid NH_4Cl is added to the cathode mixture. It can be predicted that the anode discharge products would consist principally of $ZnCl_2 \cdot 4Zn(OH)_2$. Its tendency to form a hard layer is not strong, so the continuous discharge characteristics at high current drains will be improved. The above inferences are confirmed by the data given in Fig. 1 and by autopsy of the high-power cell after discharge (the bobbin is soft). The anode product has been analyzed by X-ray diffraction. All the following tests have been performed with high-power electrolyte.

3.2. Effect of moisture

The existence of water in the bobbin is essential. This is because water is not only an active material of cell reaction, but must also be sufficient to dissolve NH_4Cl and $ZnCl_2$ so as to form a passage for the ions. If the moisture is low, however, the internal resistance will be increased, and the utilization ratio of the cathode will fall. Table 1 shows the discharge characteristics of cells with different moistures. Clearly, the discharge time is reduced with decrease in moisture. Although the cell with 32.3% moisture has the longest discharge time, this value of moisture is a little high. The possibility of reducing the moisture is sought through changing the radio of acetylene black to graphite.

Table 1
Performance of high-power R6 cells with different moisture contents

Number	Moisture (%)	Continuous discharge time (min)	
		3.9 Ω load	5.0 Ω load
1	32.3	102	142
2	30.1	70	115
3	29.1	66	104
4	28.7	61	81
5	26.6	62	76

Table 2
Performance of high-power R6 cells with different ratios of acetylene black to graphite

Number	Acetylene black: graphite	Moisture (%)	Continuous discharge time (min)	
			3.9 Ω load	5.0 Ω load
1	3.5:1	27.1	87	131
2	4.0:1	28.0	88	158
3	4.8:1	28.8	89	152
4	5.9:1	29.6	90	150
5	7.4:1	29.8	91	145
6	9.7:1	31.2	97	142

Table 3
Performance of high-power R20 cells

Continuous discharge time (min)		Intermittent discharge time (min)
2.0 Ω load	4.0 Ω load[a]	5.0 Ω load (30 min day^{-1})
324	1170	1680

[a] $V_{cut\text{-}off} = 0.85$ V.

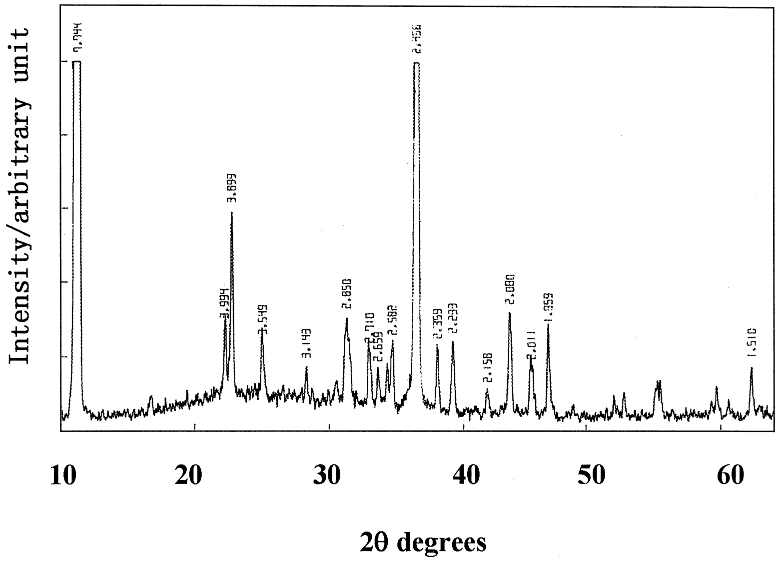

Fig. 2. X-ray diffraction pattern of anode product.

3.3. Effect of ratio of acetylene black to graphite

The carbon in the cathode mixture consists basically of acetylene black and graphite. Graphite has a much smaller specific volume and much poorer hygroscopicity than acetylene black. Thus, under the condition of no change in the ratio of MnO_2 to C, if the proportion of graphite in carbon is raised, the moisture of the bobbin will decrease and the internal resistance will increase; this situation is unfavorable for discharge. On the other hand, the amount of MnO_2 in the bobbin will be increased. This helps to increase the discharge time. Therefore, there should be an optimum ratio of acetylene black to graphite in carbon. The discharge characteristics of the six types of cells with different ratios of acetylene black to graphite are shown in Table 2. The optimum ratio is 4.0 to 4.8:1; the corresponding moisture is 28.0 to 28.8 wt.%.

3.4. High-power NH_4Cl cell

The high-power NH_4Cl R20 cells were fabricated with the above optimum specifications. The discharge characteristics are shown in Table 3. It is clear that the R20 cell also provides a level of high-power.

3.5. Analysis of cathode products

After continuous discharging with a 3.9 Ω load, the third kind cell in Table 2 was subjected to careful teardown analysis. The grey anode product on the zinc sheet was analyzed by X-ray diffraction; the pattern is shown in Fig. 2. In comparison with the standard data of the JCPDS, it is found that the phase of the anode product is $ZnCl_2 \cdot 4Zn(OH)_2$ (the peak at (2.456) is attributed to metal Zn substrate).

4. Conclusions

Lowering the NH_4Cl concentration in the electrolyte and changing the cathode components are key factors in producing high-power NH_4Cl cells. Increasing the moisture in the bobbin suitably is also necessary. There should be a suitable ratio of acetylene black to graphite. The details of the cell are as follows:

(i) 15°Be electrolyte of $ZnCl_2$ and NH_4Cl; $ZnCl_2$:NH_4Cl = 2:1 (wt.%);
(ii) moisture of the bobbin in the range 28 to 29 wt.%;
(iii) MnO_2:C = 5.5:1, acetylene black: graphite = 4.0 to 4.8:1;
(iv) 10 to 13 wt.% solid NH_4Cl and 3 to 10 wt.% of solid $ZnCl_2$ are added to the cathode mixture.

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