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Short communication

New cathode mixture for the zinc–manganese dioxide cell

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Abstract

A modified zinc–manganese dioxide cell with a new cathodic active mass constitution was investigated. This modification improved all operational parameters of this cell, particularly voltage stability during discharge and increased electrical capacity of the cathode, making it competitive even with the better classified commercial ‘‘Heavy Duty’’ (HD) batteries based on zinc chloride electrolyte.

Major benefits of this modification were: an improved voltage stability during discharge and a higher electrical capacity of the cathode.

Keywords: Zinc–manganese dioxide cell; Cathodic active mass; Porous conductive glassy carbon (PCGC)

1. Introduction

The zinc–manganese dioxide system, first used in the Leclanché cell, is still considered as the basic system used in the construction of zinc–carbon dry cells, the most popular primary cells. Nowadays, the energy needed for the production of primary cells is more than 10 times larger than the energy obtainable from the cell. For this reason, the main aim in the construction of new types of the cells is the reduction of this energy waste.

Zinc–manganese dioxide cells consist of a zinc anode, a cathode in the form of manganese dioxide combined with carbon black mixture, a carbon collector, and water based electrolyte with zinc chloride (‘‘Heavy Duty’’ (HD) batteries) and ammonium chloride (Leclanché batteries). The conducting material, e.g. acetylene black, is added in the amount from about 3% to about 15% by weight, based on the total weight of the cathode material. For the amount of the conducting material lower than 3%, the electronic conductivity decreases, resulting in overpotential of electrode processes. For the amount higher than 15%, the energy density decreases and side reactions due to the conducting material become severe.

The discharge mechanism of the zinc–manganese dioxide cell is complex and there are products of the electrode reactions such as ammonia complexes and oxychloride species, which are insoluble. Precipitation of insoluble compounds increases cell resistance. These complexes of zinc form a solid layer between the anode and cathode of the cell. This layer prevents the ion transport between the electrodes, generating large pH changes and the increase in the concentration of electrode reaction products in the anode and the cathode areas. These changes lead not only to the increase of the cell resistance, but also unwanted self-discharging reactions. To avoid these problems the carbon (graphite) rod, usually used in the cell for the cathodic current collector has been substituted in demonstrated construction by porous conductive glassy carbon (PCGC) with open pores. In our cathode construction, PCGC is used as the current collector and the carrier for the cathodic active mass. This modification allowed to change the constitution of cathodic active mass (mixture of MnO_2 with acetylene black) towards to increasing of MnO_2 amount.

In a series of papers [1–3], we have demonstrated that porous conductive glassy carbon can be used as the reactive mass carrier and the current collector in lead–acid batteries [1,2] and secondary cells with $NiOOH/Ni(OH)_2$ cathode [3]. Reticulated vitreous carbon (RVC®) was found to be a good substrate for building cells. This material was used as the cathodic active mass carrier and current collector in a Leclanché cell [4].

In this work, we demonstrate the behavior of the modified zinc–manganese dioxide cell with a new cathodic mixture. This modifications improved all of the operational parameters of the modified cell.

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2. Experimental

2.1. Cell construction

Fig. 1 shows the comparison of the construction details of the standard and modified zinc–manganese dioxide cells. Compared to the standard construction of a round cell, our battery contains a different type of the cathode [4]. We have used reticulated vitreous carbon, RVC® (ERG-Materials and Aerospace Corporation), of 20 ppi (pores per inch) porosity for the cathode current collector and the cathode active mass holder.

The material is characterized by an open pore structure on random carbon struts, with a void volume as high as 97%. Additionally, the carbon rod was significantly shortened just to function as the electric contact between the porous current collector (RVC) and the outside battery pole (+). Due to this modification, the amount of the cathodic active mass (MnO_2 + carbon black) has been increased at least 10%, the amount of carbon additives has been decreased and, in consequence, also the electrical capacity has been raised. The experimental batteries with 12 mm diameter size (AA size) have been assembled from standard factory elements normally used in AA batteries production (except for RVC®).

2.2. Chemicals and materials

All chemicals were high quality grade and were used without further purification. The electrolyte was prepared from de-ionized water (Millipore) and from $ZnCl_2$ (POCh, Poland), ZnO (POCh, Poland), and NH_4Cl (POCh, Poland). The electrolyte contained the substrates at concentrations given by the following weight ratios: 28/16/0.5/55.5 for ($NH_4Cl/ZnCl_2/ZnO/H_2O$) Leclanché cell and 0.5/40/0.5/59 for ($NH_4Cl/ZnCl_2/ZnO/H_2O$) "Heavy Duty" cell.

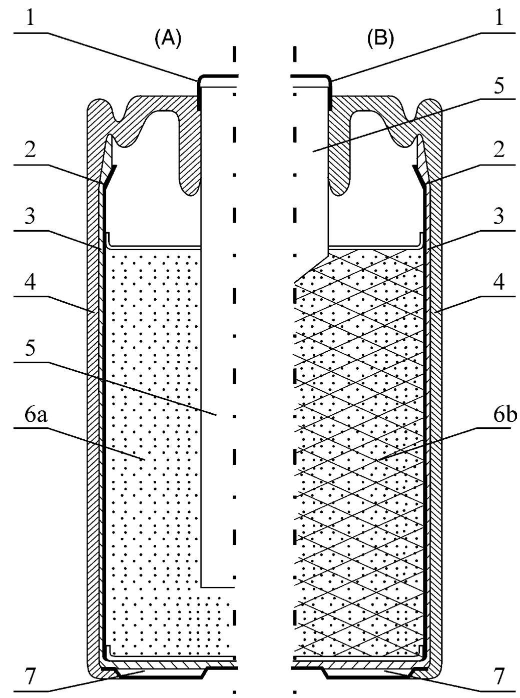

Fig. 1. Cross-section of the standard (A) and modified (B) zinc–manganese dioxide cells. (1) Electrode metal cup (+); (2) separator; (3) zinc can; (4) plastic sleeve and closure; (5) carbon electric contact; (6a) cathodic active mass; (6b) porous conductive glassy carbon filled with MnO_2, acetylene black and electrolyte; (7) metal bottom (–).

The high-powered cell cathode contained the standard weight ratio in the range from 10 to 1.5% by weight of acetylene black (supplied by the Central Laboratory of Batteries and Cells in Poznań, Poland), based on the total weight of the cathode material. The commercially available elements needed for batteries construction: AA size zinc

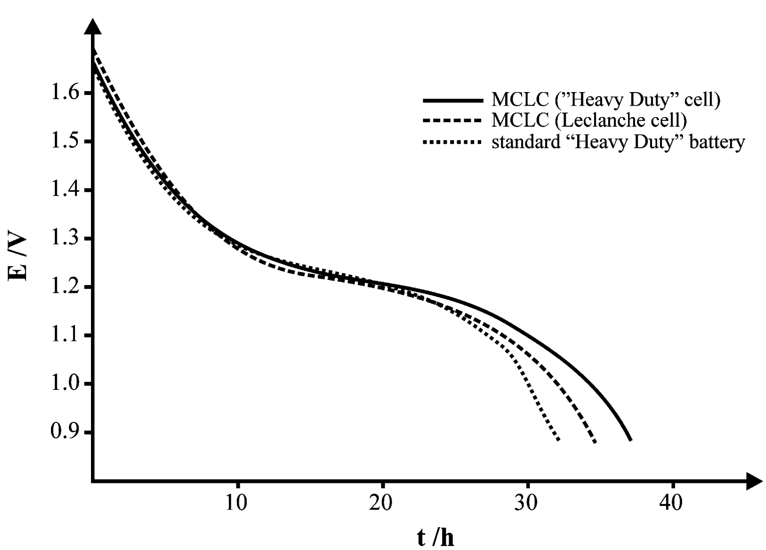

Fig. 2. Continuous discharge curves, under 43 Ω load of zinc–manganese dioxide cells with various electrolyte compositions given by the following weight ratios: 28/16/0.5/55.5 for ($NH_4Cl/ZnCl_2/ZnO/H_2O$) Leclanché cell and 0.5/40/0.5/59 for ($NH_4Cl/ZnCl_2/ZnO/H_2O$) "Heavy Duty" cell. Cathodic mass contain 2% acetylene black.

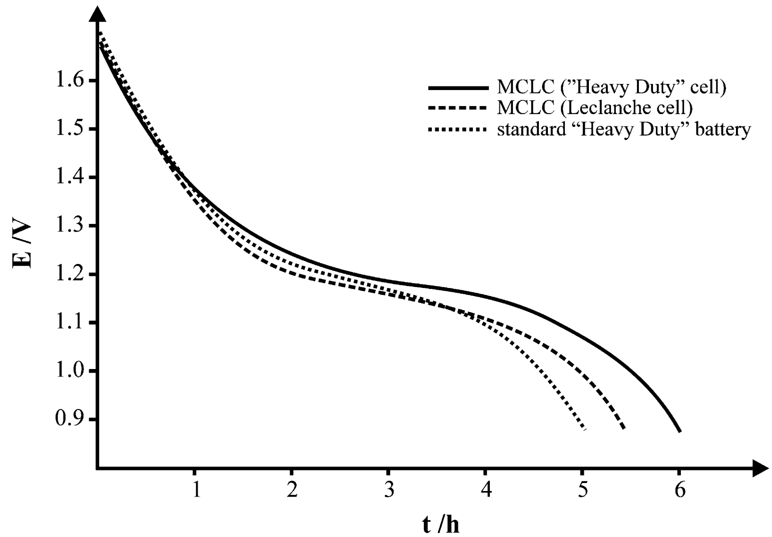

Fig. 3. Continuous discharge curves, under 10 Ω load of zinc–manganese dioxide cells with various electrolyte compositions given by the following weight ratios: 28/16/0.5/55.5 for ($NH_4Cl/ZnCl_2/ZnO/H_2O$) Leclanché cell and 0.5/40/0.5/59 for ($NH_4Cl/ZnCl_2/ZnO/H_2O$) "Heavy Duty" cell. Cathodic mass contain 2% acetylene black.

cups, separators saturated with electrolyte, and gaskets have been supplied by CLAiO and Danish Polish Batteries (DPB), Polish companies.

3. Discharge measurements

Discharge measurements of the modified zinc–manganese dioxide battery were performed in the 10 and 43 Ω continuous load tests mode at 20 °C. For comparison, a number of commercial HD batteries have been tested using the same procedures. These tests were performed with VoltaLab 40 (Radiometer Copenhagen) electrochemical analyzer.

4. Results and discussion

Figs. 2 and 3 show the comparison of typical discharge curves for the modified zinc–manganese dioxide batteries containing the electrolyte based either on NH_4Cl (previously described [4]), or $ZnCl_2$. The average results are presented for five known commercial brands of HD batteries in the 43 Ω (Fig. 2) and 10 Ω (Fig. 3) tests modes. For both modified cells, the amount of the acetylene black in cathodic active mass was 2%, based on the total weight of the cathode material.

By changing the electrolyte, the continuous discharge time is increased by 10% for 10 Ω, and by 20% for 43 Ω tests mode, in comparison to the standard HD batteries. Moreover, the electrical capacity is also increased with the

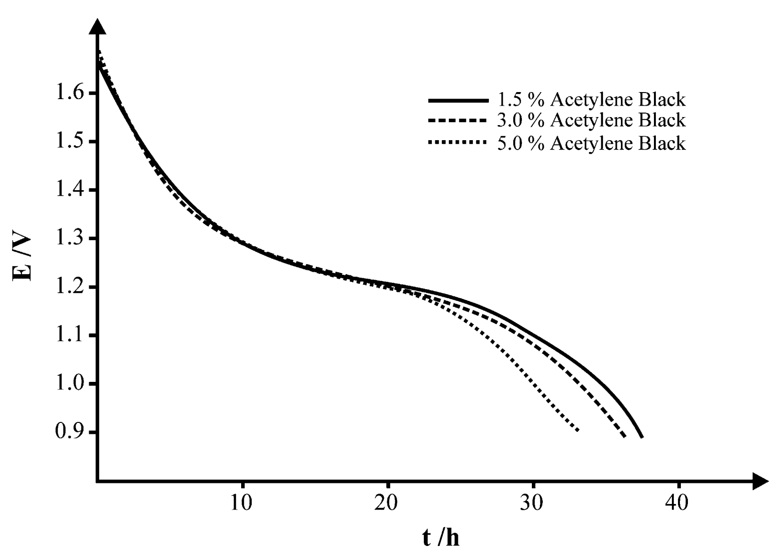

Fig. 4. Continuous discharge curves, under 43 Ω load of zinc–manganese dioxide cells with various amounts of acetylene black in the cathodic mixture: (solid line) 1.5% of acetylene black; (dashed line) 3% of acetylene black, (dotted line) 5% of acetylene black. The electrolyte composition ($NH_4Cl/ZnCl_2/ZnO/H_2O$) is given by the following weight ratios 0.5/40/0.5/59.

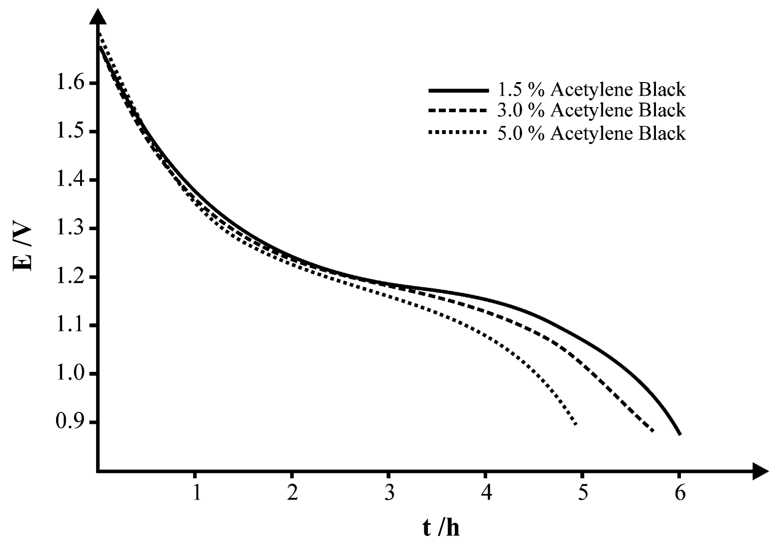

Fig. 5. Continuous discharge curves, under 10 Ω load of zinc–manganese dioxide cells with various amounts of acetylene black in the cathodic mixture: (solid line) 1.5% of acetylene black, (dashed line) 3% of acetylene black, (dotted line) 5% of acetylene black. The electrolyte composition ($NH_4Cl/ZnCl_2/ZnO/H_2O$) is given by the following weight ratios 0.5/40/0.5/59.

change of the electrolyte from NH_4Cl to $ZnCl_2$ by 5 and 10%, respectively.

The obtained discharge curves for modified batteries are characterized by a well-shaped plateau and a longer discharge as compared to normal batteries. This behavior is attributable to the increased loading of cathodic active mass presented in the cell container.

Figs. 4 and 5 show the discharge curves for the modified zinc–manganese dioxide batteries with the electrolyte based on $ZnCl_2$ with various concentrations of acetylene black in the cathodic mixture in the 43 Ω (Fig. 4) and 10 Ω (Fig. 5) tests modes.

By changing the cathode constitution (increasing the amount of MnO_2 and decreasing the amount of carbon additives), the continuous discharge time is increased by 15% for both 10 and 43 Ω tests modes in comparison to the standard HD batteries. The lowering of the amount of the acetylene black, the conductive and electrolyte holding material, below the 3% based on the total weight of the cathode material, has not increased cell resistance.

It is commonly thought known that the discharge mechanism of the zinc–manganese dioxide cell is complex and there are products of the electrode reactions such as ammonia complexes and oxychloride species, which are insoluble. Precipitation of insoluble compounds increases cell resistance. These complexes of zinc form a solid layer between the anode and cathode of the cell. Such layer prevents the ion transport between the electrodes. The application of PCGC and changing the cathodic active mass constitution decreases of the cell resistance. In other words, each pore of PCGC acts as a semiseparate cell. If unwanted reactions take place in this semi cell, e.g. precipitation of insoluble compounds, only this small part of the cathode area is switched off and the rest of the cell works properly.

The results presented earlier show that both the electrolyte type and the cathode constitution play an important role in changing the general Leclanché cell to a high-power ‘‘Heavy Duty’’ cell.

5. Conclusions

The application of porous conductive glassy carbon in the zinc–manganese dioxide cell allowed for lowering the amount of conductive carbon additives and has lead to an increase of the amount of the manganese dioxide It has caused rise of electrical capacity. The changes improved all operation parameters of the cell and they made the modified Leclanché cell competitive with the better-classified standard batteries based on the zinc chloride electrolyte.

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