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Cathode modification in the Leclanché cell

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Abstract The application of porous conductive glassy carbon as the cathode and carrier of cathodic active mass in the Leclanché cell improved all of its operational parameters. All the tests required by international standards showed that this improvement made the modified cell competitive even for the better-classified batteries based on the zinc chloride electrolyte. The major benefits of this modification were improved voltage stability during discharge and a higher electrical capacity of the cathode.

Keywords Leclanché dry cell · Carbon · Manganese dioxide

Introduction

The zinc/manganese dioxide system, first used in the Leclanché cell, is still the base system in the construction of zinc-carbon dry cells, which are the most popular primary cells [1]. Leclanché cells, the basic type of zinc-carbon cells, consist of a zinc anode, a cathode in the form of manganese dioxide with a carbon black mixture with a carbon collector and a water-based electrolyte of ammonium chloride and zinc chloride.

The discharge mechanism of the Leclanché cell is complex and there are products of the electrode reactions such as ammonia complexes [e.g. $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ and oxychloride species [e.g. $\text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2$] which are insoluble [1, 2]. Precipitation of these compounds

increases the cell resistance. Insoluble complexes of zinc form a solid layer between the anode and cathode of the cell. This solid layer prevents ion transport between the electrodes, which generates great pH changes. This is also the reason for the rise in the concentration of electrode reaction products in the anode and cathode areas. It leads not only to the rise of the cell resistance but also to cell leakage due to unwanted starch hydrolysis.

In a series of papers [3, 4, 5] we have demonstrated that porous conductive glassy carbon can be used as the reactive mass carrier and the current collector in lead-acid batteries [3, 4] and secondary cells with a $\text{NiOOH}/\text{Ni}(\text{OH})_2$ cathode [5]. Using porous glassy carbon covered with a thin layer of metal, it is possible to prepare high-surface-area metallic electrodes with the minimum use of metals. Reticulated vitreous carbon (RVC) was found to be a good substrate in building cells.

In this paper we demonstrate the behavior of the Leclanché cell with a modified cathode (MCLC). The carbon (graphite) rod used normally in the cell for the cathodic current collector has been substituted 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 (mixture of MnO_2 with acetylene black). In this situation, each pore acts as a semi-separate cell. If an unwanted reaction takes place in this semi-cell, e.g. precipitation of insoluble compounds, only this small part of the cathode area is switched off. For this reason, the proposed modification of the cathode construction should lead to better parameters of operation.

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Experimental

Cell construction

Figure 1 shows the construction details of the modified Leclanché cell. Compared to the standard construction of a round cell, our battery contains a different type of the cathode [6]. We have used RVC (ERG Materials and Aerospace Corporation) for the cathode

current collector and the cathode active mass holder. A RVC of 20 ppi (pores per inch) porosity was used in the construction of the modified cell.

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 (+). The contact between the RVC and carbon rod was mechanical (by pressing) and it was reliable. All mounted batteries had good electrical contact before and after testing.

Owing to this modification, the amount of the cathodic active mass (MnO_2 + carbon black) has been increased by ca. 10% and, in consequence, also the electrical capacity has been raised.

The experimental batteries with 12 mm diameter size (AA size) were assembled from standard factory elements normally used in AA battery production (except for the RVC).

Chemicals and materials

All chemicals were high-quality grade. They were used without further purification. The electrolyte was prepared from de-ionized water (Millipore) and from ZnCl_2 , ZnO , and NH_4Cl (all from POCh, Poland). The electrolyte contained the substrates at concentrations given by the following weight ratio ($\text{NH}_4\text{Cl}/\text{ZnCl}_2/\text{ZnO}/\text{H}_2\text{O}$): 28/16/0.5/55.5.

The high-powered cell cathode contained the standard weight ratio of 10:1 of electrolytic manganese dioxide to acetylene black dioxide [both from the Central Laboratory of Batteries and Cells (CLAiO), Poznań, Poland]. The commercially available elements needed for battery construction, AA size zinc cups, separators saturated with electrolyte and gaskets, were supplied by CLAiO and Danish Polish Batteries (Poland).

Discharge measurements

Discharge measurements of the modified Leclanché battery were performed at CLAiO, using procedures required by the international norms for zinc-manganese primary cells (IEC 86-1 + A#) based on a zinc chloride electrolyte [heavy duty (HD) type]. For comparison, a number of commercial HD batteries have been tested with the same procedures. It should be noted that the

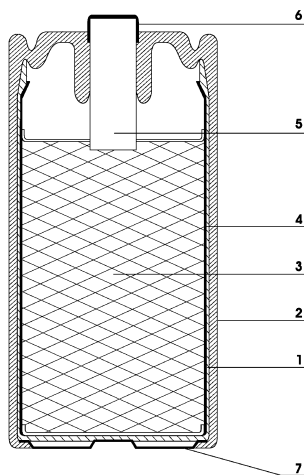


Fig. 1 Cross section of the Leclanché cell with a modified cathode: 1, zinc can; 2, plastic sleeve and closure; 3, porous conductive glassy carbon filled with MnO_2 , acetylene black and ammonium chloride electrolyte; 4, separator saturated with ammonium chloride electrolyte; 5, carbon electric contact; 6, electrode metal cup (+); 7, metal bottom (-)

modified Leclanché cell studied here is based on an ammonium chloride electrolyte and as such should be classified as a general purpose (GP) battery. The discharge modes comprised the following tests:

1. Open circuit voltage (OCV) measurements. IEC norm is max. 1.725 V.
2. A $43\ \Omega$ discharge simulated the work of portable radio receivers (4 h daily until 0.9 V). The IEC norm is 27 h.
3. A $10\ \Omega$ discharge simulated the work of portable tape recorders and players (1 h daily until 0.9 V). The IEC norm is 4 h.
4. A $3.9\ \Omega$ discharge simulated the work of electric toys (1 h daily until 0.8 V). The IEC norm is 1 h.
5. A $1.8\ \Omega$ discharge simulated the work of flashlights (15 s per minute impulses until 0.9 V). The IEC norm is 75 impulses.
6. Leakage test before and after full discharge.

The batteries were tested at CLAiO in two tests. For each, 100 batteries were tested, with 25 batteries in one mode of discharging. More than 70% of the batteries passed the first test. After changing some construction steps, 100% of the batteries passed the second test. The results demonstrated in this paper concern the 100 batteries that passed the second test in four modes (25 batteries per each mode of discharging).

Results

Figure 2 presents the results of the MCLC discharge in different test modes with comparison to the IEC norms.

Figure 3 shows the continuous discharge curve for the MCLC under the $10\ \Omega$ load. The obtained discharge curve is characterized by a well-shaped plateau and a longer discharge compared to normal batteries. It is attributable to the increased loading of the cathodic active mass presented in the cell container (see Cell construction section, above).

In Fig. 4a–d are the intermittent discharge curves obtained in different test modes according to the IEC norms.

Table 1 collects the results obtained for our MCLC in different modes of battery testing. Series of 25 units of AA cells constructed in our laboratory were used in each test. The table contains extreme and average results for

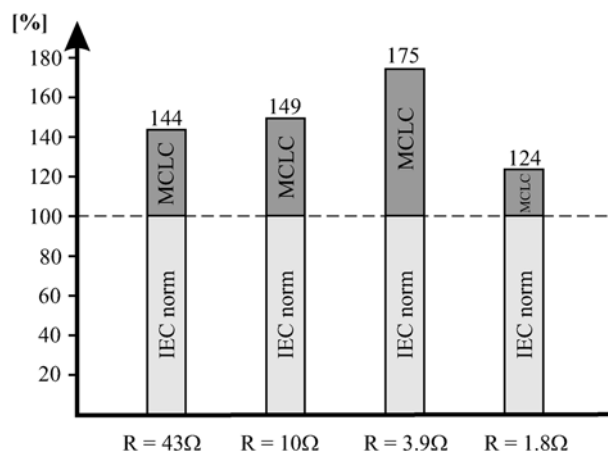


Fig. 2 The results of the MCLC discharging in different test modes in comparison to IEC standards

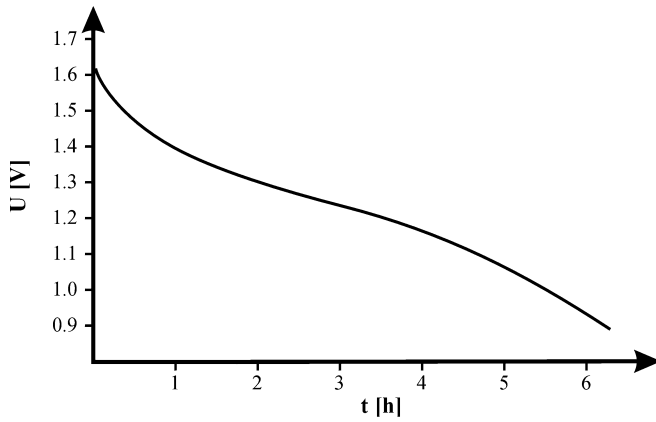


Fig. 3 The continuous discharge curve of MCLC under 10Ω load

the discharge time and cell capacity (Ah) obtained in different test modes. This table also contains average and extreme OCV values.

It has to be noted that the batteries were stored for 1 month after full discharge (below 0.2 V) and neither during nor after this time was any electrolyte leakage observed.

Fig. 4 **a** The intermittent discharge curves obtained in mode 43Ω load, 4 h daily. **b** The intermittent discharge curves obtained in mode 10Ω load, 1 h daily. **c** The intermittent discharge curves obtained in mode 3.9Ω load, 1 h daily. **d** The intermittent discharge curves obtained in mode 1.8Ω load, 15 s per min

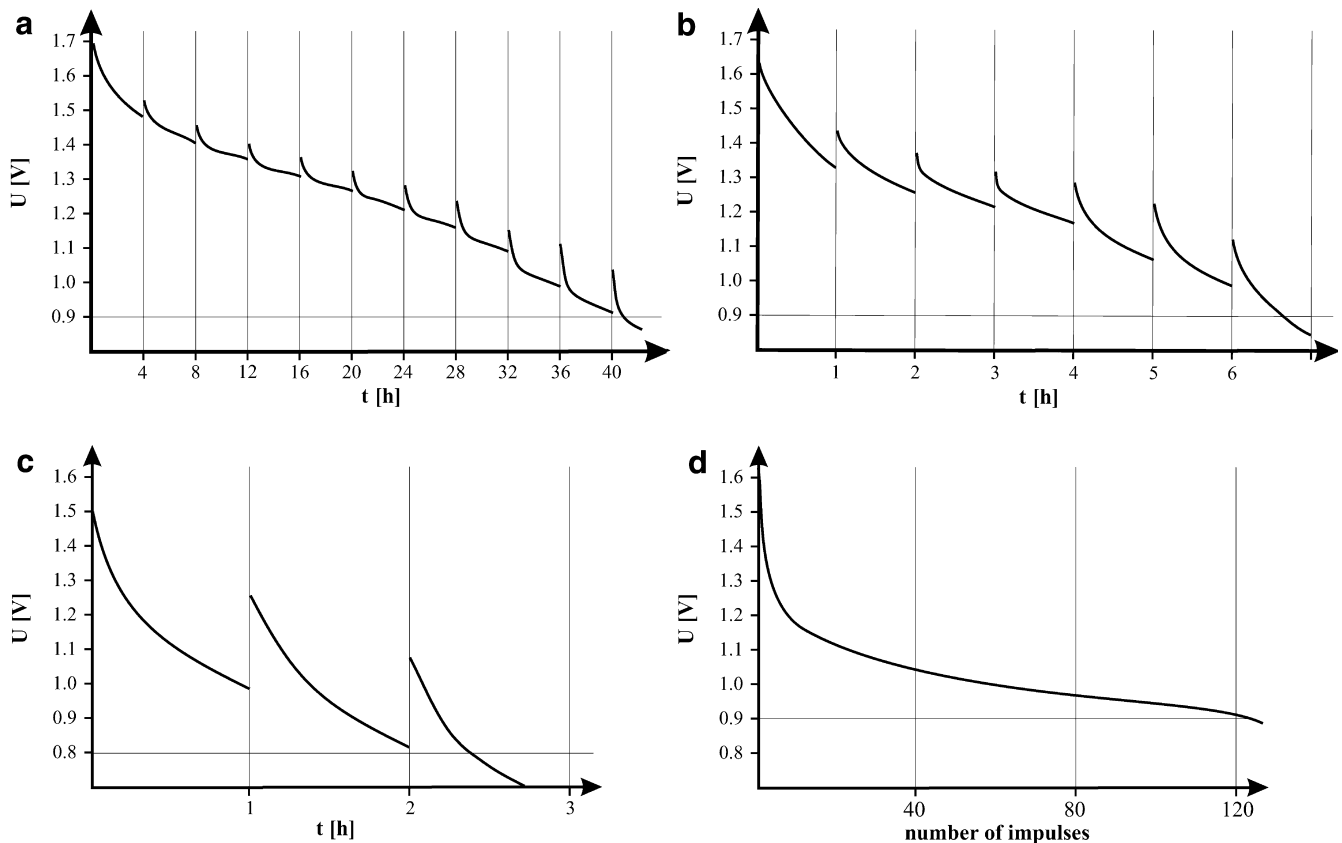


Table 2 collects the average results for discharge time obtained for our MCLC and the average results obtained for five types of commercial HD batteries. These results were compared to the IEC norms. The measurements were performed in the same test mode.

Discussion

The MCLC performed best in the test simulating the operation in portable radio receivers (43Ω load) and electric toys (3.9Ω load). Despite the fact that our battery is based on the ammonium chloride electrolyte [and as such should be classified in lower standard batteries (GP)], it has the same or better parameters of work as HD batteries based on the zinc chloride electrolyte. Only the results obtained in the test mode simulating flashlights were they significantly behind those for the HD batteries, but they still satisfied international norms. Also, the OCV for fresh batteries was exceeded by ca. 0.025 V, which is probably due to a low ZnO concentration in the electrolyte. Another reason for this could be the higher purity of the chemicals used herein in comparison to standard batteries. The OCV value did not change during 3 months storage.

From a rough economic calculation we found that the introduction of porous glassy carbon to zinc-manganese cells should rise the battery manufacturing cost by ca. \$0.005–0.01 per unit relative to classical GP Leclanché cells based on the ammonium chloride elec-

Table 1 Discharge parameters in different test modes for a Leclanché cell with the modified cathode

Extreme values (max–min) of OCV: 1.82 to 1.68 V; average OCV: 1.75 V				
Test mode	Extreme values (max–min) of discharge time or impulse number	Average discharge time or impulse number	Extreme values (max–min) of cell capacity (Ah)	Average capacity of studied cells (Ah)
43 Ω , 4 h daily	41.6–36.0 (h)	39.0 (h)	1.19–1.01	1.10
10 Ω , 1 h daily	6.74–5.62 (h)	6.09 (h)	0.78–0.60	0.69
3.9 Ω , 1 h daily	2.45–1.58 (h)	1.95 (h)	0.63–0.42	0.54
1.8 Ω , 15 s/min	121–71 impulses	97 impulses	0.29–0.18	0.23

Table 2 Comparison of average discharge parameters in different test modes for the MCLC and five types of commercial HD batteries with IEC norms

Test mode	IEC norm	Average discharge time for MCLC	Average discharge time for commercial HD batteries
43 Ω , 4 h daily	27 h	39.0 h	32.25 h
10 Ω , 1 h daily	4 h	6.09 h	6.1 h
3.9 Ω , 1 h daily	1 h	1.95 h	1.76 h
1.8 Ω , 15 s/min	75 impulses	97 impulses	139 impulses

trolyte (in comparison to a HD zinc-manganese cell based on ZnCl_2). Our calculations included the costs of materials and technological changes in the mounting process of the cells.

Conclusion

The use of conductive porous glassy carbon as the cathode and the carrier of cathodic active mass in the Leclanché cell improved all its operational parameters. This improvement made the modified cell competitive

for the better-classified batteries based on the zinc chloride electrolyte.

The modification mainly caused:

1. Improved voltage stability during discharge.
2. A rise of electrical capacity.
3. An increased discharge current.

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