TECHNICAL NOTE

Magnesium/zinc–N,N′-dichlorodimethylhydantoin novel dry cells: a preliminary study

R. UDHAYAN, D. P. BHATT

Laboratories of Batteries and Fuel Cells, Central Electrochemical Research Institute, Karaikudi 623 006, India

Received 5 February 1992; revised 27 June 1992

1. Introduction

In recent years, much attention has been focused on the development of metal–organic batteries in preference to conventional inorganic material based battery systems. A number of organic compounds have been coupled with magnesium or zinc; among these, aromatic nitro compounds (e.g. meta-dinitrobenzene, *m*-DNB) have dominated over others, particularly because of their high theoretical capacity [1]. The main disadvantages of these cells are: very low cell voltage, low power density and high toxicity. In order to circumvent these problems and also to change the existing scenario of the dry cells [2], we have recently investigated certain novel N-halogen organic compounds as cathodic depolarizers for reserve cells, primarily because of their high cell potential and non-toxicity [3–7]. This paper presents first results for N,N′-dichlorodimethylhydantoin (DDH) based magnesium and zinc dry cells which are fabricated in different standard sizes such as A and D. The electrolytes employed in the respective cells are aqueous salts of magnesium perchlorate and ammonium chloride. Several battery parameters such as internal resistance, specific capacity, specific energy and coulombic efficiency are also reported.

2. Experimental details

2.1. *Fabrication of extruded magnesium cans*

Magnesium alloy (AZ 31) sheets of 0.80 and 0.50 mm thicknesses were used for the fabrication of D and A-size cans, respectively. Since magnesium is a very light metal, and also flammable, much care was taken during the fabrication. Only wooden tools were used for the flattening of the sheets. The sheets were cut to the required dimensions to fabricate the D and A-size cans. The sheets were made into cylindrical form using a round wooden rod. Then the edges were riveted using aluminum rivets. The bottom sheet was joined using Araldite.

2.2. *Zinc cans*

D size zinc cans as received from Estrela Batteries (India) were used for the fabrication of Zn/DDH organic dry cells. D-size and A-size cells were discharged at various current drains. For capacity calculations, the cut-off voltage of the magnesium and zinc dry cells were 1.5 and 1.0 V, respectively.

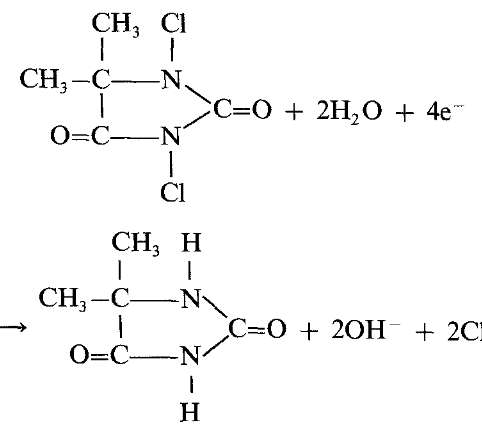
2.3. *Magnesium/zinc–DDH dry cell fabrication*

The bobbin mix formulations for constructing the dry cells were as shown in Table 1. A carbon rod was inserted in the middle of the bobbin blend and acted as the cathode current collector. The separator was prepared by soaking a synthetic paper with wax. Fig. 1 shows the cross-section of the metal–organic dry cell. The cells were discharged at various current drains between 20 and 500 mA at 30 ± 1° C. Triplicate experiments were performed and the results were reproducible within ±2%.

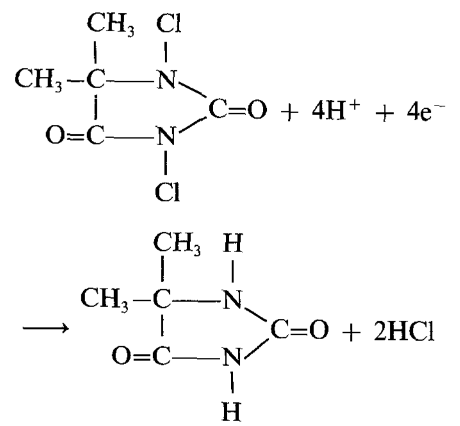
3. Results and discussion

The electrochemical reactions of DDH during its reduction can be represented as follows.

In magnesium perchlorate electrolyte:



In ammonium chloride electrolyte [1]:



Figures 2–4 represent the discharge curves for magnesium and zinc based D and A-size cells at various current drains. The open circuit voltage (o.c.v.) of the Mg/DDH and Zn/DDH cells are 2.55 and 2.06 V,

0021-891X

Table 1. Bobbin mix formulations

Mg/DDH D-size cell	
Active material	8.00 g
Acetylene black	4.00 g
2.0 M $Mg(ClO_4)_2$	12.00 ml
2% starch	2.00 ml
Barium chromate	0.24 g
Mg/DDH A-size cell	
Active material	2.50 g
Acetylene black	1.25 g
2.0 M $Mg(ClO_4)_2$	4.00 ml
2% starch	0.50 ml
Barium chromate	0.08 g
Zn/DDH D-size cell	
Active material	8.0 g
Acetylene black	4.0 g
2.0 M NH_4Cl + 8% $ZnCl_2$ by weight	10.0 ml
2% starch	2.0 ml

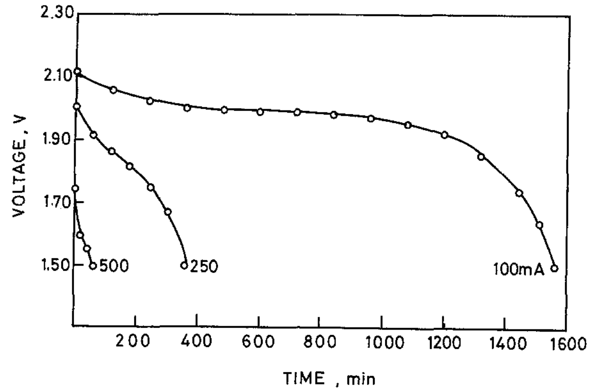


Fig. 2. Effect of current drain on the cell voltage of Mg/DDH D-size dry cell.

respectively. The observed voltages are much higher than those obtained with well known organic depolarizers such as in the *m*-DNB based cell systems [8, 9] (o.c.v. of Mg/*m*-DNB: 1.50; Zn/*m*-DNB: 1.00 V). The observed higher voltage of DDH may be attributed to the presence of loosely attached chlorine (electron attracting group) in the ring of the material. The internal resistances of the cells were calculated from the voltage against current profiles (Fig. 5). The values for different cells such as Mg/DDH D-size, Zn/DDH D-size and Mg/DDH A-size were found to be 1.00, 1.27 and 3.72 mΩ, respectively. The internal resistances were found to be significantly lower than previously reported values for the conventional D-size zinc–carbon–NH_4Cl cells (0.27 Ω) and zinc–carbon–$ZnCl_2$ dry cells (0.18 Ω) [10]. The cut-off voltage of the zinc–carbon–MnO_2 system ranges from 0.65 to 1.00 V per 1.50 V cell, depending upon the application. For the present magnesium and zinc based dry cells, the cut-off voltages were taken as 1.5 and 1.0 V, respectively. In terms of operating voltage, DDH based dry cells showed approximately 1.00 V higher voltage in comparison with conventional zinc–carbon–MnO_2 cells. This infers that cathode polarization is low in the case of DDH based dry cells. Higher internal resistance, as observed for the Mg/DDH A-size cell in comparison with the corresponding D-size module, may be attributed to the less active surface area in the former design. Table 2 gives the data for various battery parameters.

At low current drains (100 mA in the present work), the Mg/DDH dry cells gave an operating voltage of about 2.0 V. By lowering the discharge rate to the microampère level (the specifications as required for most dry cell utility applications), the service life, and the voltage, is increased. Although these data give rise to higher cell voltage and lower internal resistance and a material efficiency of around 60% at low discharge rate, other battery parameters such as specific capacity and specific energy need to be further improved by proper cell design and improved fabrication techniques. Forthcoming publications will deal with this problem.

4. Conclusions

On the basis of the present data, it is concluded that the DDH shows potential for use as a cathode depolarizer in dry cells and the most attractive features of this compound, in association with either zinc or magnesium, are its higher voltage in aqueous medium (Mg/DDH: 2.55 V; Zn/DDH: 2.06 V) and its non-toxicity. Other well known nitro or nitroso based organic dry cells (for example *m*-DNB) give voltages of less than 1.5 V. The coulombic efficiency of DDH

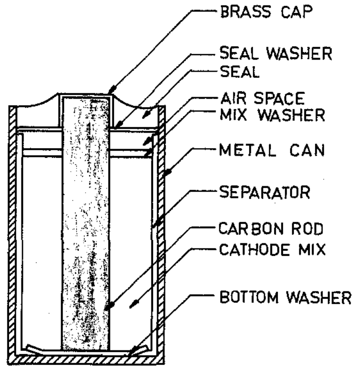


Fig. 1. Cross-section of metal–organic dry cell.

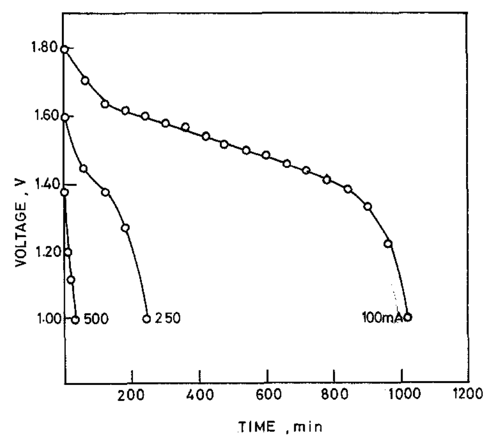


Fig. 3. Effect of current drain on the cell voltage of Zn/DDH D-size dry cell.

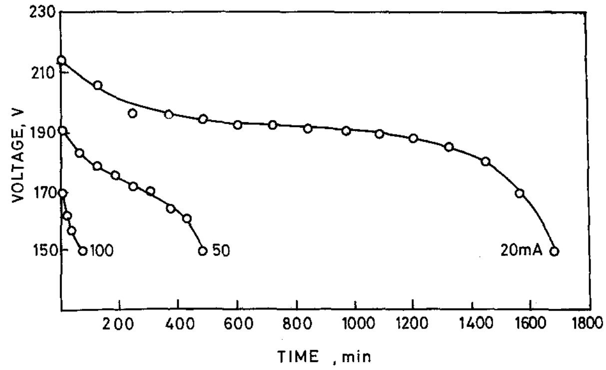


Fig. 4. Effect of current drain on the cell voltage of Mg/DDH A-size dry cell.

has been found to be around 60% at low discharge rates.

Acknowledgements

The authors thank M. Raghavan, Head, Engineering and Technical Services Division of this Institute for providing advice for the anode can fabrication. They also acknowledge the Council of Scientific and Industrial Research, New Delhi, for the award of a Senior Research Fellowship to RU.

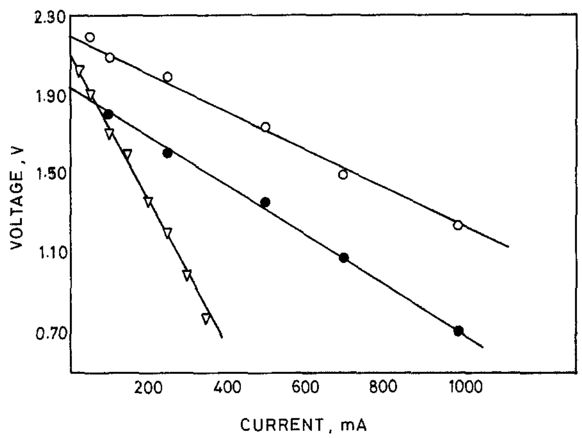


Fig. 5. Voltage–current profiles of metal–organic dry cells: (○) Mg/DDH D-size; (●) Zn/DDH D-size; and (▿) Mg/DDH A-size.

Table 2. Performance characteristics of Mg/Zn–DDH dry cells at different current drains

Current drain /mA	*Specific capacity* /A min g^{-1}	*Specific energy* /W min g^{-1}	*Coulombic efficiency* /%
Mg/DDH D-size: (*o.c.v. = 2.55 V*)			
100	19.5	39.0	59.7
250	11.3	20.3	34.6
500	3.8	6.1	11.6
Zn/DDH D-size: (*o.c.v.: 2.05 V*)			
100	12.8	19.8	39.2
250	7.5	9.8	23.0
500	1.9	2.2	5.8
Mg/DDH A-size: (*o.c.v.: 2.56 V*)			
20	13.6	26.0	41.7
50	9.6	16.8	29.4
100	3.2	5.1	9.8

References

[1] N. C. Cahoon, 'Primary Batteries', Vol. 2, John Wiley and Sons, New York (1976) p. 187.

[2] D. P. Bhatt, 'Leclanche dry cells – Indian Scene', Proceedings of the Workshop on Dry Cell Batteries, Acetylene black and other Battery materials', Madras (1988) p. 2.1.

[3] D. P. Bhatt and R. Udhayan, *Indian Patent 749/DEL/91.*

[4] R. Udhayan, D. P. Bhatt and P. B. Mathur, *J. Appl. Electrochem.* **22** (1992) 285.

[5] R. Udhayan, Ph.D. Thesis, Madurai Kamaraj University, Madurai, India (1991).

[6] R. Udhayan and D. P. Bhatt, *Electrochim. Acta* **37** (1992) 1971.

[7] L. R. Becon, A. L. Sotier and A. A. Roth, *J. Milk Food Technol.* **16** (1953) 61.

[8] C. K. Morehouse and R. Glicksman, *J. Electrochem. Soc.* **105** (1958) 306; **105** (1958) 619.

[9] C. K. Morehouse and R. Glicksman, *US Patent 2 874 079* (1959).

[10] T. R. Crompton, 'Small Batteries', Vol. 2, 'Primary cells', John Wiley & Sons, New York (1983) p.21.