SHORT COMMUNICATION

Performance characteristics of zinc–N,N′-dichlorodimethyl hydantoin primary cell

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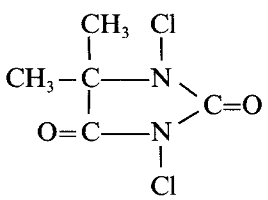
1. Introduction

Conventional inorganic depolarizers such as MnO_2, CuO, AgO, AgCl, $PbCl_2$ etc., have limited capacity output due to one or two electron transfer in their reduction processes, whereas organic compounds are capable of 4 to 12 electron transfer in their electrochemical reactions. Several organic compounds have been studied in conjunction with magnesium anodes [1, 2] and a few studies have been reported on the use of various N-halogen organic compounds in primary batteries [3–6]. The present work reports on the performance of a cell consisting of N,N′-dichlorodimethyl hydantoin (DDH) as cathode depolariser and zinc as anode, the cell being activated by a mixture of NH_4Cl and $ZnCl_2$ solutions.

The structure of DDH is,



Based on a four electron transfer process, the coulombic capacity of DDH is 32.65 A min g^{-1}. The performance characteristics of DDH were studied by discharging the cells at different current drains, *viz.* 10 to 300 mA.

2. Experimental details

2.1. *Fabrication and discharge study*

Zinc metal sheets of purity 99.97% (impurity contents; Fe 0.02%, Cu 0.002%, Sn 0.001%, Sb 0.001%, As 0.001% and Al 0.005) of dimensions 2 cm × 3 cm × 0.05 cm were used as anode and titanium expanded grid (6 mesh) of the same dimensions as that of the zinc plates was used as current collector for the cathode. The cathode was prepared using 1 g DDH (Aldrich), 0.3 g acetylene black and 0.8 ml of an aqueous solution of 2% carboxymethylcellulose binder on a titanium grid at an optimized pressure. Two anode plates were placed on either side of the cathode and separated by a cellophane separator. Different percentages of acetylene black, *viz.* 10, 20, 30 and 40%, were used in the fabrication of the Zn/2 M NH_4Cl (AR BDH grade)/DDH cell. A constant current drain of 100 mA was used. Following this, a combination electrolyte mixture of 2 M NH_4Cl and 8% $ZnCl_2$ by weight (AR Chemco grade) was used in the fabrication of further zinc based cells. After complete wetting of the electrodes, the cells were discharged at constant currents of 10 to 300 mA at 30 ± 1° C using a Colora thermostat (West Germany). All the experiments were repeated at least three times; a reproducibility of ±2% was obtained.

2.2. *Half cell potential*

The half cell potential of the DDH electrode was measured against an Ag/AgCl reference electrode at regular intervals during the discharge of the cell.

3. Results and discussion

3.1. *Capacity with different percentages of acetylene black*

Figure 1 demonstrates the voltage against time behaviour of the Zn/2 M NH_4Cl/DDH cell system for different amounts of acetylene black at a constant current discharge of 100 mA. From this it is clear that the capacity increases with increase in percentage of acetylene black up to a concentration of 40%. It is also seen that for the same current values the voltage increases with increase in acetylene black content. Capacities reached a maximum level between 30 and 40% acetylene black. Below 20%, the capacity fell sharply due to the increase in the internal resistance of the cell. The capacity difference is negligible between 30 and 40%, hence 30% is taken as the ideal concentration of acetylene black in the present investigations.

3.2. *Capacity at various percentage of $ZnCl_2$ in 2 M NH_4Cl solution*

To evaluate the effect of the addition of $ZnCl_2$ on the performance of the cell, the cells were discharged in different concentrations of $ZnCl_2$ (by weight) in 2 M NH_4Cl at 100 mA current drain and the capacity of the cell in each case was determined (Fig. 2). The cells only gave 6.5 A min g^{-1} without addition of $ZnCl_2$ whereas with the addition of 8% $ZnCl_2$ the cells gave 18.0 A min g^{-1} capacity. The capacity increased with increase in $ZnCl_2$ concentration and reached a maximum at a value of 8% $ZnCl_2$. The addition of $ZnCl_2$ to a solution of NH_4Cl prevents the formation of thick crusts of crystalline NH_4Cl above the liquid surface,

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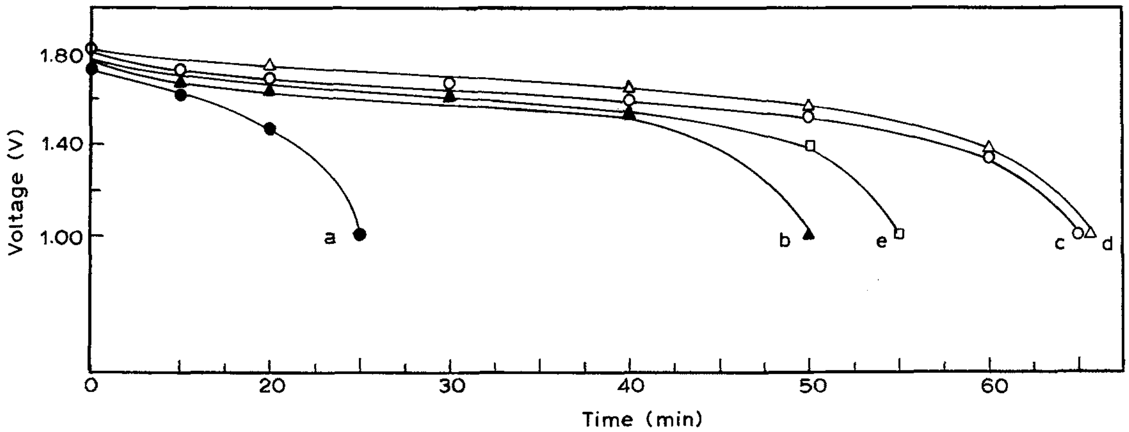


Fig. 1. Effect of acetylene black on Zn/NH_4Cl/DDH cell discharge behaviour at 100 mA current drain. (a) DDH alone, (b) 10%, (c) 20%, (d) 30% and (e) 40% acetylene black.

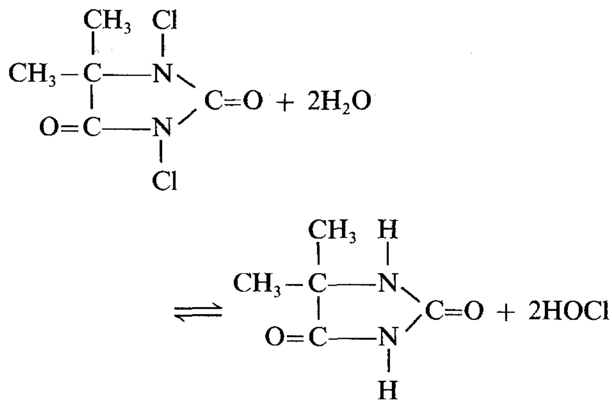
typical of the pure solution. Hence the capacity is enhanced by the addition of $ZnCl_2$ in NH_4Cl solution [7].

3.3. *Discharge characteristics*

The variation of cell voltage with current drain for a time interval of 30 s is shown in Fig. 3. The linearity of the curve indicates that the polarization is ohmic in nature and the internal resistance of the cell is 1.8 Ω.

The half cell potential of the DDH cathode was measured against an Ag/AgCl reference electrode at constant current drains of 25 to 100 mA (Fig. 4). The open circuit potential of the DDH cathode is ~ 1.0 V with respect to the Ag/AgCl, which is much higher than that for the nitro or nitroso organic compound, due to the presence of the halogen (electron attracting group) present in this compound.

The discharge characteristics of the cells at constant current drain are shown in Fig. 5. The open circuit voltage of the cell was 2.05 V and the closed circuit voltage 2.02 V at lower current drains. As the current increased the cathode polarization increased resulting in the loss of cell capacity against a constant cut-off voltage. DDH forms hypochlorite during discharge according to the following reaction:



The specific capacities (A min g^{-1} and W min g^{-1}) and the corresponding coulombic efficiencies of DDH were calculated (Table 1). From the reduction efficiencies of the cathode, it is noted that the utilisation of the cathode is around 70%. It may also be noted that the efficiency of the cathode falls with increase in current drain.

4. Conclusion

Zn/DDH cells operate at high voltage with high coulombic efficiency in an electrolyte consisting of 2 M NH_4Cl and 8% $ZnCl_2$. The cells show an operating

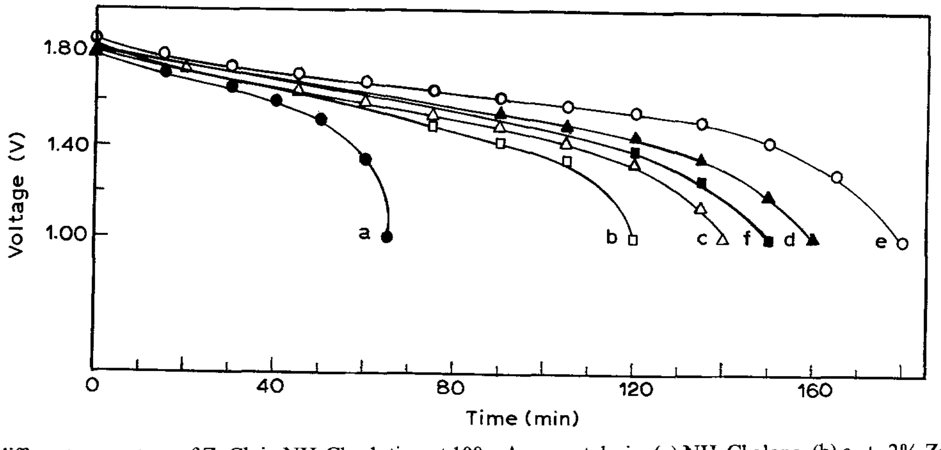


Fig. 2. Effect of different percentage of $ZnCl_2$ in NH_4Cl solution at 100 mA current drain. (a) NH_4Cl alone, (b) a + 2% $ZnCl_2$, (c) a + 4% $ZnCl_2$, (d) a + 6% $ZnCl_2$, (e) a + 8% $ZnCl_2$ and (f) a + 10% $ZnCl_2$ (wt %).

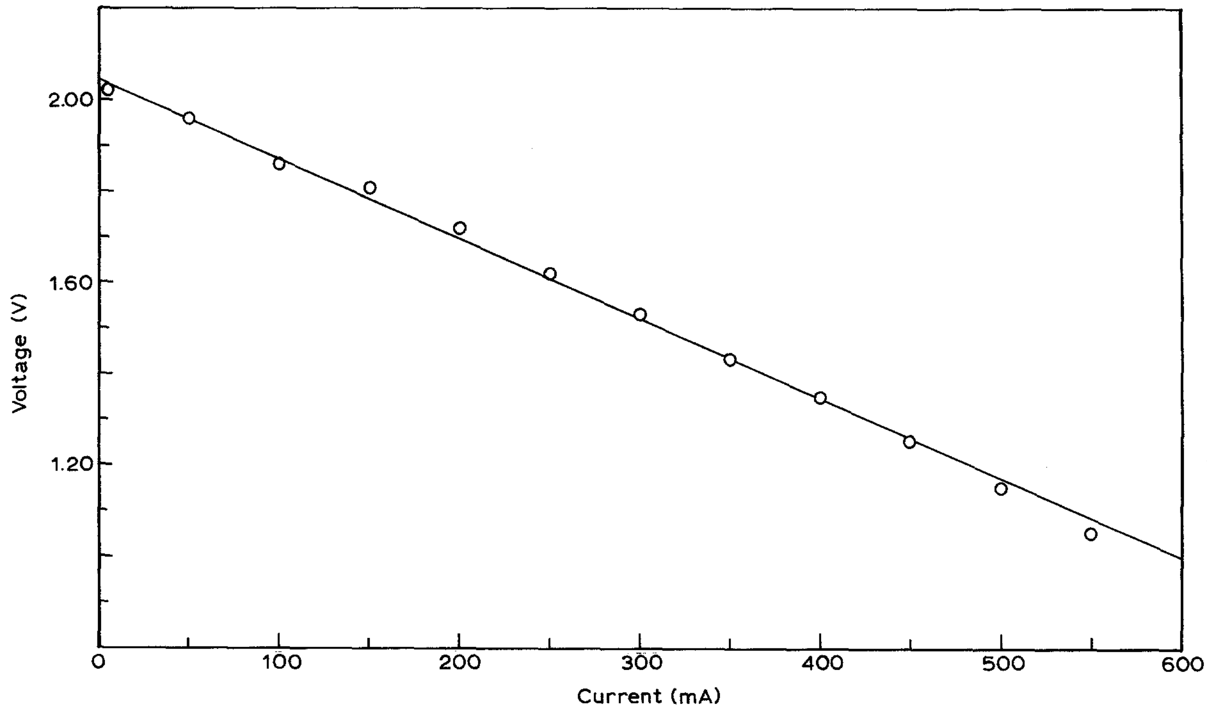


Fig. 3. Variation of voltage with current drain for Zn/DDH cell.

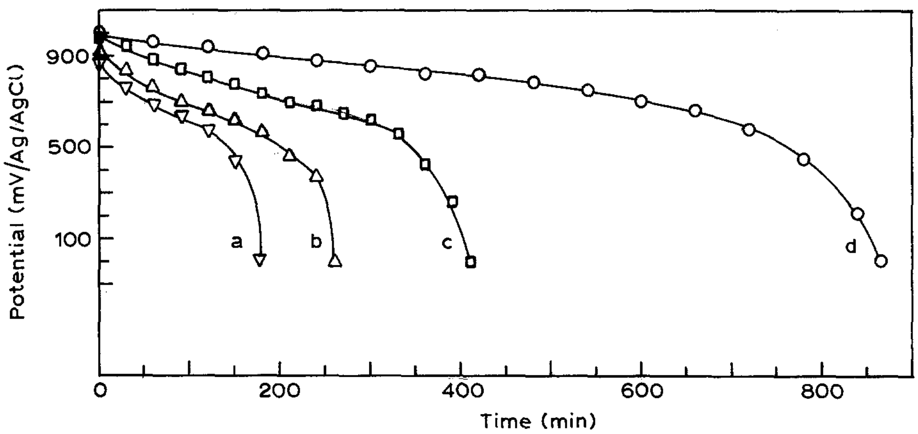


Fig. 4. Effect of current drain on cathode potential. (a) 100, (b) 75, (c) 50 and (d) 25 mA.

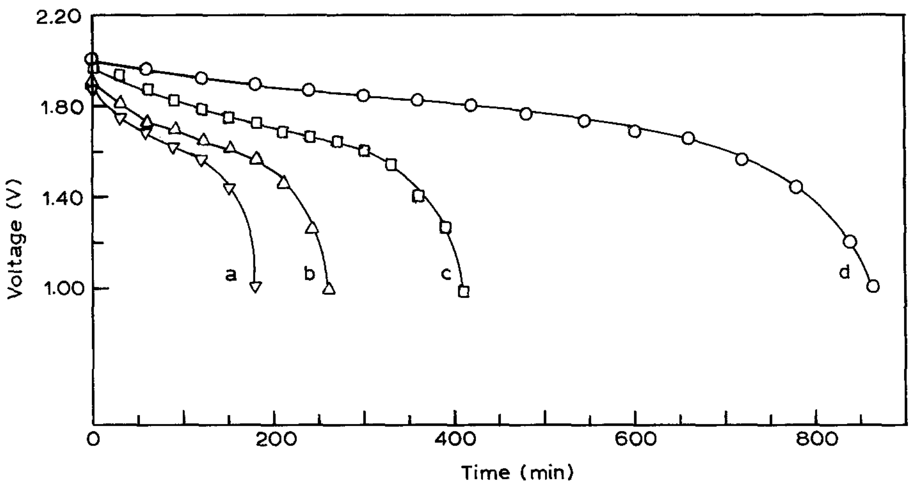


Fig. 5. Effect of current drain on cell voltage. (a) 100, (b) 75, (c) 50 and (d) 25 mA.

Table 1. Specific capacities and coulombic efficiencies of cells

Current drain (*mA*)	*Capacities*		*Coulombic efficiency* (%)
	($A\,min\,g^{-1}$)	($W\,min\,g^{-1}$)	
10	22.2	33.5	68.0
25	21.6	32.4	66.2
50	20.5	30.4	62.8
75	19.5	28.4	59.7
100	18.0	25.8	55.1
125	16.9	24.0	51.8
150	16.5	23.3	50.5
175	15.8	21.9	48.4
200	15.0	20.4	45.9
225	13.5	18.1	41.3
250	12.5	16.4	38.3
275	10.2	13.1	31.2
300	7.5	9.5	23.0

voltage of 2.0 to 1.8 V and the cathode efficiency is found to be 25 to 70% when the current drain is varied from 300 to 10 mA. These characteristics indicate that this cell may find applications where high energy density and voltage are the basic requirements.

Acknowledgements

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References

[1] N. Muniyandi, R. Udhayan, R. Balasubramanian and K. I. Vasu, *J. Electrochem.* **6** (1990) 405.

[2] K. Sivasamy, S. Rajeswary and K. Dakshinamurthi, *J. Power Sources* **25** (1989) 295.

[3] R. Udhayan, N. Muniyandi and P. B. Mathur, submitted to *J. Power Sources.*

[4] C. K. Morehouse, Proc. 10th Annual Battery Research and Development Conference, New Jersey (1956) 32.

[5] C. Lozier, Proc. 11th Annual Battery Research and Development Conference, New Jersey (1957) 8.

[6] N. C. Cahoon (ed.), 'The Primary Batteries', Vol. II, John Wiley and Sons, New York (1976) 187.

[7] K. V. Kordesch, 'Batteries', Vol. I, 'Manganese Dioxide', Marcel Dekker, New York (1974) 49.