

## A novel cell: zinc/dichloroisocyanuric acid in aqueous chloride medium

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### Abstract

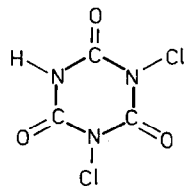
This paper reports the first results obtained from a dichloroisocyanuric acid-based zinc cell system in an aqueous medium of  $\text{NH}_4\text{Cl}$ - $\text{ZnCl}_2$  at different discharge rates ranging from 10 to 200 mA. The constant-current discharge method has been employed to evaluate cell parameters such as capacity, energy density and coulombic practical efficiency. The discharge data are in good agreement with those predicted from a standard model for primary cells. The novelty of the system lies in the fact that the organic material of the cathode possesses nontoxic properties and that the cell exhibits a high voltage of 2.0 V and a maximum current density of  $17 \text{ mA cm}^{-2}$  during discharge.

### Introduction

The development of metal-organic battery systems has received considerable attention in recent years because of the promise of high energy density, high operating voltage, and voltage stability. Conventional inorganic depolarizers, such as  $\text{MnO}_2$ ,  $\text{HgO}$ ,  $\text{CuO}$  and  $\text{AgCl}$ , have limited capacity output due to the transfer of only 1 or 2 electrons in their reduction processes. By contrast, certain organic depolarizers are capable of a 4- to 12-electron transfer in the electrochemical discharge reaction.

Among the various organic depolarizers, aromatic nitro compounds (e.g., *m*-dinitrobenzene) have dominated because of their high theoretical capacity [1, 2]. The main disadvantages of these cathode materials are: very low potential, low power density, high solubility and toxicity. In an effort to circumvent these problems, the investigations reported here examine the discharge behaviour of a cell using dichloroisocyanuric acid (DCIA) as a cathode depolarizer and a zinc anode in an electrolyte medium comprising a mixture of  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$  solutions.

It should be noted that DCIA belongs to the family of N-halogen cyclic ureide compounds that are known to possess nontoxic properties and, hence, are suitable for practical battery devices [3, 4]. The structure of DCIA is:



Based on a 4-electron transfer process, the coulombic capacity of DCIA is 419 A h (kg of DCIA)<sup>-1</sup>. The performance characteristics of Zn/NH<sub>4</sub>Cl–ZnCl<sub>2</sub>/dichloroisocyanuric acid have been studied by discharging the cells at different current drains, viz., 10, 25, 50, 75, 100, 125, 150 and 200 mA. Several battery parameters, such as internal resistance, capacity, energy density and coulombic efficiency, have been reported.

## Experimental

### *Cell fabrication and discharge study*

A zinc metal sheet of purity 99.97% (commercial grade) and dimensions 2×3×0.05 cm was used as the anode. A titanium expanded grid (6 mesh) of the same size as that of the zinc plate served as the current collector for the cathode. The cathode mix containing 1.0 g DCIA (Fluka), 0.3 g acetylene black (Travancore Electrochemical, India) and 0.8 ml of an aqueous solution of 2 wt.% carboxymethylcellulose (BDH) binder was spread over the titanium mesh at an optimized pressure. The cathode mix composition was optimized from capacity measurements as well as from measurements of the resistance of the compacted organic blend using the four-probe measurement technique (Digital Micro-ohm Meter, Agronic-54C, India). The latter measurements were conducted in the absence of a grid. The weight of the DCIA was kept constant. The only variable was the percentage of acetylene black; this ranged from 10 to 40 wt.%. The pressures employed during preparation of the compacted cathodes were 0.17, 0.33, 0.50, 0.67 and 0.83 tonnes cm<sup>-2</sup>.

DCIA cells were fabricated using two anodes and one cathode, separated by cellophane paper. The interelectrode distance was about 2 mm. The cells were assembled in a polypropylene container of size 3.5×2.5×1 cm. Before commencement of the discharge measurements, the cells were left idle in the electrolyte for 15 min so that the active material of the system could attain a constant open-circuit voltage. The voltage/potential versus time characteristics of the cells were measured for constant-current drains of 10, 25, 50, 75, 100, 125, 150 and 200 mA. A second set of experiments was performed in order to study the voltage/current relationship. The cutoff voltage of the cells was 1.0 V. Triplicate experiments were performed and a reproducibility of ±2% was obtained.

### *Half-cell potential measurements*

The half-cell potential of the DCIA electrode was measured, using a Ag/AgCl reference electrode ( $E=0.210$  V versus normal hydrogen electrode (NHE)), at regular time intervals during discharge of the cell. All experiments were performed at 30±1 °C.

## Results and discussion

### *Effect of acetylene black content on cell capacity*

Figure 1 represents the voltage versus time behaviour of the Zn/2 M NH<sub>4</sub>Cl/DCIA cell for different amounts of acetylene black at a constant-current drain of 25 mA. Clearly, the working voltage of the cell increases gradually with increase in the acetylene black concentration. The working-voltage plateau of the cells using 10, 20, 30 and 40 wt.% acetylene black is 1.46, 1.54, 1.59 and 1.60 V, respectively. Similarly, the capacity of the cell increases with increase in the percentage of acetylene black and reaches an optimum value at 30 to 40 wt.% (Fig. 2). These results are further

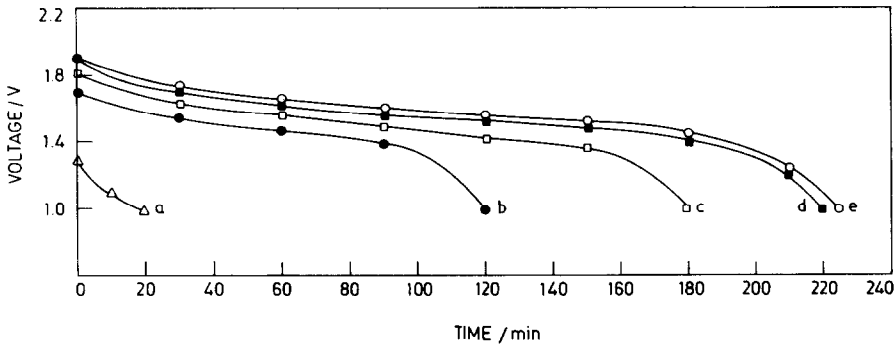


Fig. 1. Effect of acetylene black content on performance of Zn/NH<sub>4</sub>Cl/DCIA cell (current drain=25 mA); (a) blank; (b) 10, (c) 20, (d) 30, (e) 40% acetylene black.

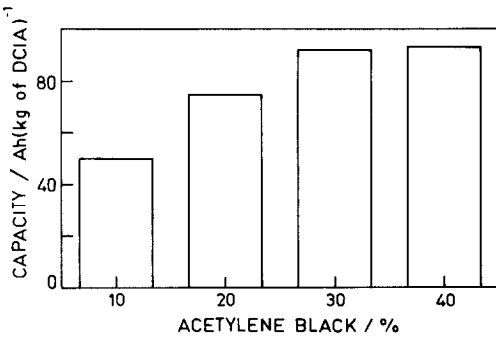


Fig. 2. Histogram showing the dependence of the capacity of a Zn/NH<sub>4</sub>Cl/DCIA cell on acetylene-black content (current drain=25 mA).

confirmed by voltage/current measurements and resistance studies using the four-probe technique. Linear behaviour is observed at each concentration of acetylene black. This demonstrates that the polarization is ohmic controlled (Fig. 3). The internal resistance of the cell is 9.09, 6.07, 4.06 and 3.92 mΩ for 10, 20, 30 and 40 wt.% acetylene black, respectively. It may be included, therefore, that below 30 wt.% acetylene black, the internal resistance of the cell has increased due to the decrease in the conductivity of the cathode.

The surface resistance parameters have been obtained for various compacted DCIA cathode blends in the absence of a grid and using 10, 20, 30 or 40 wt.% acetylene black in the cathode mix. The respective values are 7.06, 4.47, 3.02 and 2.94 mΩ. These results confirm that the presence of 30 to 40 wt.% acetylene black in the cathode mix gives rise to maximum conductivity. Similarly, a successive increase in the pressure, namely, 0.17, 0.33, 0.50, 0.67 to 0.83 tonnes cm<sup>-2</sup>, using 30 wt.% acetylene black results in a considerable decrease in resistance; the corresponding values are 10.08, 7.72, 3.94, 3.36 and 3.00 mΩ. These results demonstrate that the cell system behaves best with a 30 to 40 wt.% acetylene black content and a pressure of 0.83 tonnes cm<sup>-2</sup>.

On the basis of the above results, it is suggested that the differences in the capacity and the internal resistance of the cell are negligible between 30 and 40 wt.%

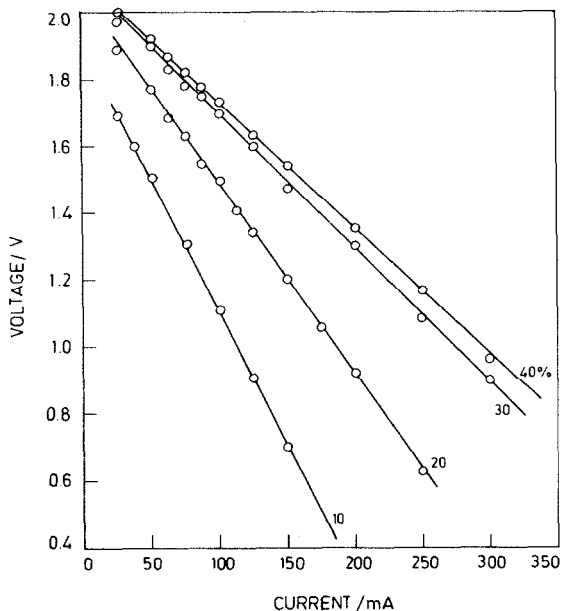


Fig. 3. Influence of acetylene-black content on voltage/current relationship of a Zn/NH<sub>4</sub>Cl/DCIA cell.

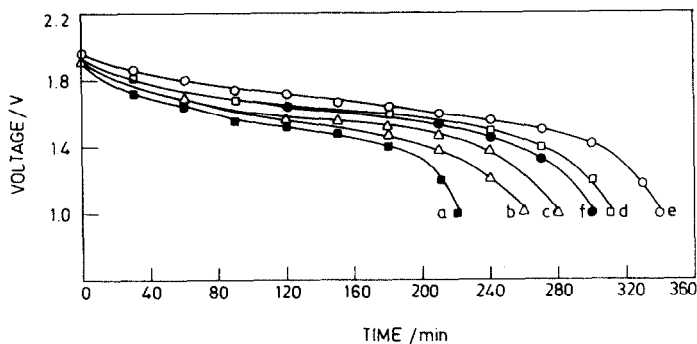


Fig. 4. Effect of different percentages of ZnCl<sub>2</sub> in NH<sub>4</sub>Cl (current drain=25 mA); (a) NH<sub>4</sub>Cl alone; (b) +2 wt.% ZnCl<sub>2</sub>; (c) +4 wt.% ZnCl<sub>2</sub>; (d) +6 wt.% ZnCl<sub>2</sub>; (e) +8 wt.% ZnCl<sub>2</sub>; (f) +10 wt.% ZnCl<sub>2</sub>.

and, hence, 30 wt.% can be taken as the effective concentration of acetylene black under the conditions of the present investigations.

#### *Influence of ZnCl<sub>2</sub> content on the performance of Zn/2 M NH<sub>4</sub>Cl/DCIA cell*

Different concentrations of ZnCl<sub>2</sub> (by weight) have been added to 2 M NH<sub>4</sub>Cl in different sets of experiments and the respective cells have been discharged at a constant-current drain of 25 mA (Fig. 4). The capacities of the cells have been further evaluated and the results are given in Fig. 5. It is found that the cells with NH<sub>4</sub>Cl electrolyte alone yield a capacity of 92 A h (kg of DCIA)<sup>-1</sup> whereas the addition of

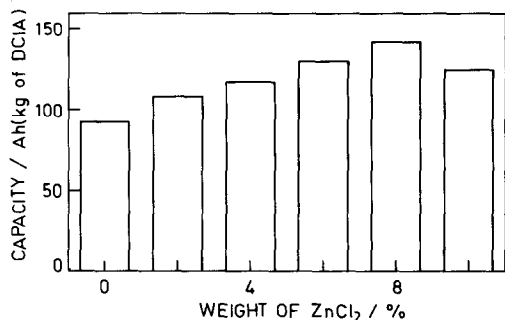


Fig. 5. Histogram showing the dependence of the capacity of a Zn/NH<sub>4</sub>Cl-ZnCl<sub>2</sub>/DCIA cell vs. ZnCl<sub>2</sub> concentration (wt.%) (current drain=25 mA).

8 wt.% ZnCl<sub>2</sub> results in a capacity improvement, i.e. 142 A h (kg of DCIA)<sup>-1</sup>. The capacity increases gradually with increase in ZnCl<sub>2</sub> concentration and exhibits a maximum value at 8 wt.% ZnCl<sub>2</sub>. The addition of ZnCl<sub>2</sub> to a solution of NH<sub>4</sub>Cl prevents the formation of thick crusts of crystalline NH<sub>4</sub>Cl above the liquid surface, typical of pure solution [5].

#### Discharge measurements

The discharge process of the Zn/DCIA cell in a medium of NH<sub>4</sub>Cl and ZnCl<sub>2</sub> is governed by the following electrochemical reactions:

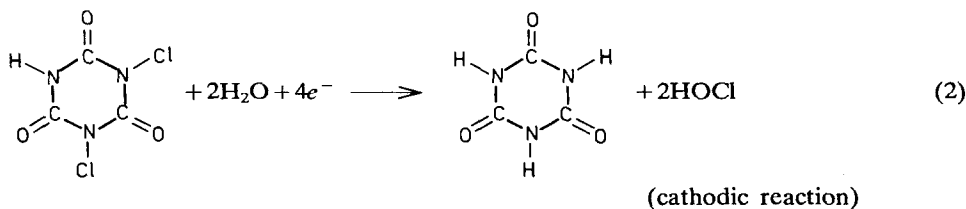
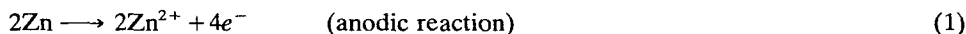
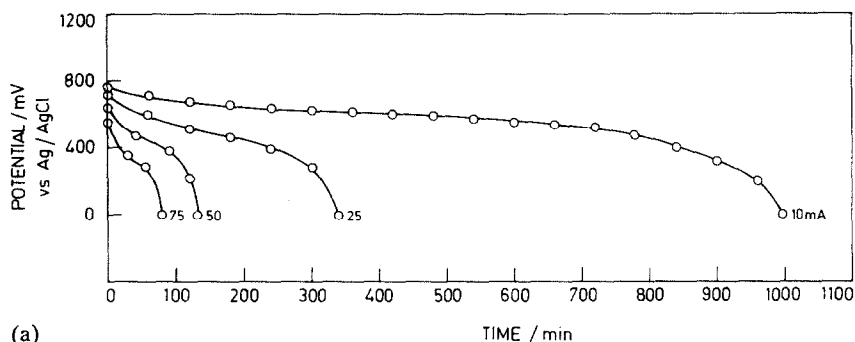
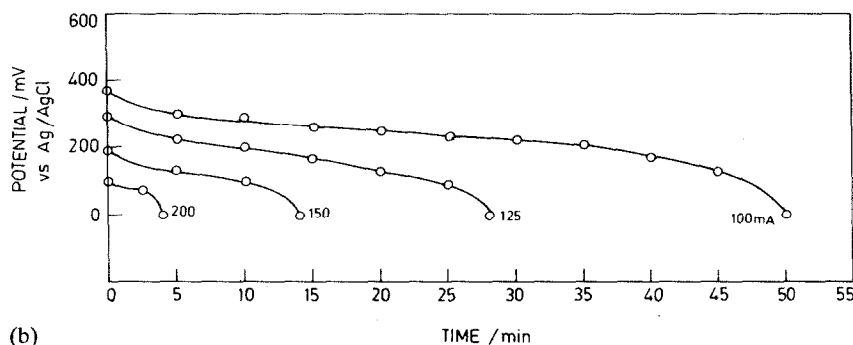


Figure 6(a) and (b) shows the half-cell potential of a DCIA cathode with respect to time at various current drains. The open-circuit potential (OCP) of the DCIA cathode is 840 mV. This is significantly higher than that exhibited by other organic depolarizers, e.g., the OCP of *m*-dinitrobenzene is 210 mV. The closed-circuit potential (CCP) of the DCIA cathode at current drains of 10, 25, 50, 75, 100, 125, 150 and 200 mA is 760, 720, 640, 530, 380, 290, 190 and 100 mV, respectively. The observed higher potential of the DCIA cathode can be attributed to the presence of a loosely attached Cl (i.e., an electron-attracting group) in the ring of the organic material.

The discharge characteristics of Zn/NH<sub>4</sub>Cl-ZnCl<sub>2</sub>/DCIA cells have been observed galvanostatically under continuous discharge at various current drains (see Fig. 7(a) and (b)). The open-circuit voltage (OCV) of the cell is 2.04 V while the closed-circuit voltage (CCV) is in the range 2.0 to 1.3 V when the current drain is varied from 10 to 200 mA. The plateau of the cell working voltage at 10, 25, 50, 75, 100, 125, 150 and 200 mA is 1.76, 1.65, 1.58, 1.50, 1.42, 1.38, 1.22 and 1.10 V, respectively. The observed values are much higher than those found for Zn/NH<sub>4</sub>Cl-ZnCl<sub>2</sub>/*m*-dinitrobenzene cells (OCV=1.21 V) [6]. It is noted that a decrease in the current drain



(a)



(b)

Fig. 6. Effect of current drain on cathode potential of Zn/DCIA cell.

results in a gradual rise in the cell capacity as well as an increase in the cell voltage.

As mentioned earlier, the theoretical capacity of DCIA is  $419 \text{ A h (kg of DCIA)}^{-1}$ . This is not realized in practice, as is evident from the above observations. There are valid reasons for these deviations. Generally, when chemical energy is converted into electrical energy, energy losses arise mainly due to three sources, viz., (i) activation losses; (ii) ohmic losses; (iii) concentration losses. The cell polarization due to these three factors is responsible for the delivery of only a fraction of the total available energy in a battery.

#### *Activation losses*

These occur when electrode reactions proceed at a slower rate than that at which the current is withdrawn. The losses are associated with the kinetic factors of the energy-producing reactions in the battery and are usually small except at high-rate discharge.

#### *Ohmic losses*

These are considered as the main source of energy loss in practical batteries and are mainly due to film formation on the electrode surface and resistance to the flow of ions in the electrolyte phase.

#### *Concentration losses*

This phenomenon arises from changes in the effective concentration of the active material and from problems with the transport of reactants/products from the elec-

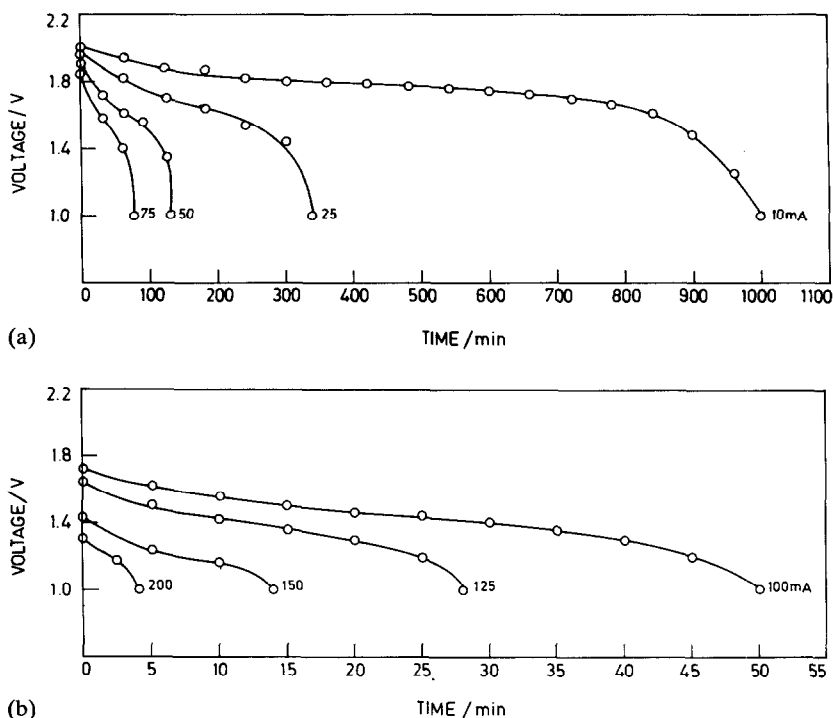


Fig. 7. Effect of current drain on cell voltage of Zn/DCIA cell.

trochemical reaction site during the discharge operation. The later also give rise to pH variations [7]. The sudden fall in voltage at the end of discharge is indicative of concentration polarization.

#### *Theoretical calculation of battery parameters and correlation with experimental data*

In order to interpret the observed discharge data, experiments using low- and high-current drains of 10 and 100 mA have been chosen for analysis. Plots of cell voltage versus capacity for Zn/DCIA cells are given in Fig. 8. From this data, various cell parameters (e.g., internal resistance, polarization coefficient and mean available active material) have been calculated as according to the Shepherd model [8] for primary cells. The results are as follows:

- (i) mean available active material,  $Q=175 \text{ A h (kg of DCIA)}^{-1}$ ;
- (ii) coefficient of polarization,  $K=5.25 \text{ m}\Omega \text{ cell}^{-1}$ ;
- (iii) internal resistance of the cell,  $N=3.00 \text{ m}\Omega \text{ cell}^{-1}$ ;
- (iv) constant closed-circuit voltage,  $E_s=1.88 \text{ V}$ .

The values have been fitted into a general discharge equation for Zn/DCIA cell system, i.e.:

$$E = E_s - K[Q/(Q - It)]I - NI \quad (3)$$

where  $E$  is the cell voltage at any time  $t$  during discharge. The resulting calculated values of  $E$  are correlated with the observed discharge voltage for a set of  $It$  values in Table 1. Clearly, the general Shepherd equation for primary cells provides a good representation of the discharge data for Zn/DCIA cells.

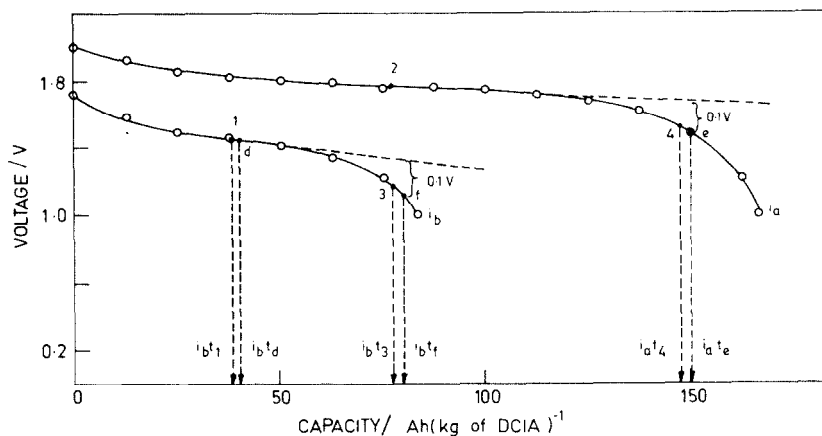


Fig. 8. Cell voltage vs. capacity for Zn/DCIA cell ( $i_a = 10$  mA;  $i_b = 100$  mA).

TABLE 1

Comparison of calculated and observed voltages of Zn/DCIA cell

Capacity (A h (kg of DCIA) <sup>-1</sup> )	Voltage (V) for $I = 10$ mA	
	calculated	observed
70	1.767	1.762
75	1.762	1.760
80	1.757	1.751
85	1.752	1.749
90	1.746	1.741
95	1.739	1.733
100	1.732	1.730
105	1.723	1.720
110	1.713	1.710
115	1.701	1.700
120	1.687	1.681
125	1.670	1.662
130	1.650	1.648
135	1.624	1.619

#### Determination of capacity, energy density and coulombic efficiency

Calculated values for the capacity, energy density and coulombic efficiency of DCIA at each current drain are presented in Table 2. The coulombic efficiency is determined on the basis of the Faraday equation (i.e. assuming a 4-electron transfer reaction). The data given in Fig. 9 reveal that an increase in current drain from 10 to 200 mA results in a subsequent decrease in cell capacity. For 10 mA, the capacity, energy density and coulombic efficiency are  $167 \text{ A h (kg of DCIA)}^{-1}$ ,  $293 \text{ W h (kg of DCIA)}^{-1}$  and 40%, respectively. It should be noted that DCIA-based zinc cells yield higher energy density than those employing other well-known organic compounds e.g., *m*-dinitrobenzene. This is obvious given the higher average voltage of the reported cell system. The coulombic efficiencies of the Zn/DCIA cell are presented in Fig. 10.



TABLE 2

Capacity, energy density and coulombic efficiency of Zn/DCIA cell

Current drain (mA)	Capacity (A h (kg of DCIA) <sup>-1</sup> )	Energy density (W h (kg of DCIA) <sup>-1</sup> )	Coulombic efficiency (%)
10	167	293	40
25	142	233	34
50	110	173	26
75	97	145	23
100	83	118	20
125	58	80	14
150	35	43	8
200	13	15	3

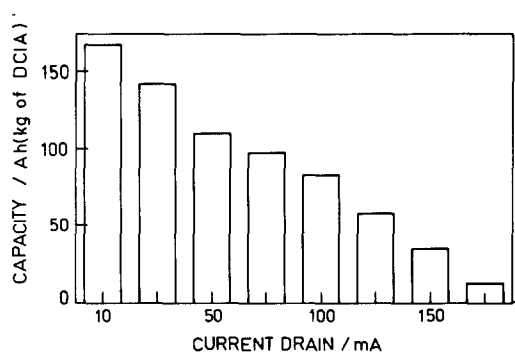


Fig. 9. Histogram showing the effect of current drain on the capacity of a Zn/DCIA cell.

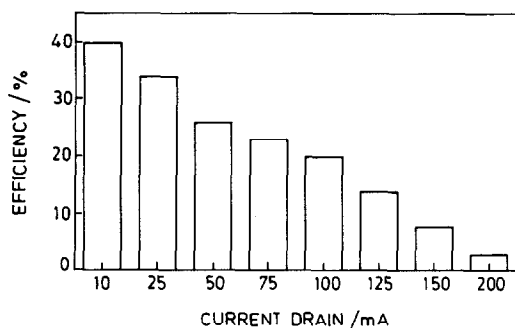


Fig. 10. Histogram showing the effect of current drain on the coulombic efficiency of a Zn/DCIA cell.

The percentage fall in the coulombic efficiency from 10 mA to higher current drains of 25, 50, 75, 100, 125, 150 and 200 mA is 85, 65, 58, 50, 35, 20 and 8%, respectively. Such characteristics indicate that the Zn/DCIA cell system possesses lower energy density and lower cell voltage compared with Mg/DCIA cells [9]. This is due to the

fact that magnesium has a higher electrode potential and a lower electrochemical equivalent than zinc.

## Conclusions

The above studies on Zn/DCIA cells have yielded the following results:

1. The optimum content of the conducting material (acetylene black) is 30 wt.%.
2. The addition of 8 wt.% ZnCl<sub>2</sub> to the base electrolyte produces maximum capacity.
3. The OCP of the DCIA organic cathode in the chloride medium is much higher (0.84 V) than that for other well-known manganese dioxide or aromatic nitro compounds.
4. The cell exhibits an OCV of 2.04 V and a CCV of more than 1.90 V at low current drains. This performance is superior to that for the Zn/*m*-dinitrobenzene system (i.e., OCV = 1.21; CCV: <1.00 V). Also, Zn/DCIA cells can be drained at rates up to 200 mA, i.e., 17 mA cm<sup>-2</sup>.
5. The capacity, energy density and coulombic efficiency are found to be maximum at a low discharge rate of 10 mA; the respective values are 167 A h (kg of DCIA)<sup>-1</sup>, 293 W h (kg of DCIA)<sup>-1</sup> and 40%.
6. The experimental data are in good agreement with those predicted by the Shepherd model for primary cells.

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