INVESTIGATIONS ON A NOVEL ZINC/DDH PRIMARY CELL SYSTEM

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SUMMARY

A novel zinc-N,N'-dichlorodimethylhydantoin (Zn/DDH) organic primary cell system has been studied under various current drains. The attractive feature of this system is its high open circuit (2.12 V) and closed circuit voltages (2.00 V) and non-toxicity in comparison with conventional aromatic nitro compounds (eg. Zn/m-ditrobenzene OCV: 1.10; CCV: 0.90 V). Several battery parameters viz. internal resistance, capacity, energy density and coulombic efficiency have been calculated.

KEY WORDS: Zn/DDH cell, internal resistance, capacity, energy density, coulombic efficiency.

INTRODUCTION

In recent years much attention has been focused on metal-organic battery systems because of their high specific capacity in comparison with the conventional systems based on inorganic depolarisers. Hitherto, a number of organic depolarisers have been coupled with Mg or Zn; among them, aromatic nitro compounds especially meta-dinitrobenzene (m-DNB), have dominated over others due to their multi-electron transfer property during electrochemical reduction [1]. But the disadvantages of these cells are: very low voltage, low power density, high solubility and toxicity. In an effort to circumvent these problems, halogen containing compounds (eg. N-halogen organic compounds) have been reported recently [2-4].

The present paper reports the experimental studies based on a novel cathode material such as N,N′-dichlorodimethylhydantoin (DDH) in conjunction with zinc anode using 30% KOH as the electrolyte. The studies have furnished information about the various battery parameters viz. internal resistance, capacity, energy density and coulombic efficiency.

EXPERIMENTAL DETAILS

Zn sheet (0.5 mm thickness) and Ti expanded grid (6 mesh) each having the dimensions of 3 X 2 cm^2 were used as anode and the cathode current collector, respectively. The cathode mix containing 1 g DDH, acetylene black in various quantities and 0.5-1.0 ml of an aqueous solution of carboxymethylcellulose binder was spread over the Ti mesh at an optimised pressure. Two anodes and one cathode were separted by a cellophane paper in the fabrication of the cells wherein the acetylene black content in the cathode mix has been varied from 10-40%. 30% KOH was used to activate the cell. After complete wetting of the electrodes in the electrolyte, the cells were discharged at constant current drains of 10, 25, 50, 75, 100, 125 and 150 mA at 30 ± 0.5°C. Half cell potentials of the DDH cathode were measured against Ag/AgCl reference electrode at regular intervals of time during discharge. Cut-off voltage of the cell was kept as 1.50 V. All the experiments were performed in tripilicate and a reproducibility of ± 2% was obtained.

RESULTS AND DISCUSSION

Voltage vs time measurements of Zn/DDH cells have been carried out at a constant current drain of 25 mA employing

different percentages of acetylene black in the cathode mix (Fig. 1). The cells show an open circuit voltage of 2.12 V. The capacity of the cells for 10, 20, 30 and 40% acetylene black are found to be 12.5, 62.5, 87.5 and 89.6 Ah(kg of DDH)$^{-1}$, respectively. The capacity of the cell is found to increase with increase in acetylene black quantities and reaches an optimum value at 30 - 40%. These results are further confirmed by voltage-current measurements (Fig. 2). The observed linearity is indicative of the ohmic-controlled polarisation. The internal resistance of the cell with respect to 10, 20, 30 and 40% composition of the cathode mix is found to be 13.00, 4.75, 3.57 and 3.54 milliohm, respectively. These data substantiate the capacity measurements confirming the fact that below 30% the internal resistance of the cell gradually increases leading to the poor conductivity of the cathode which in turn is responsible for the low capacity. The differences in capacities and internal resistances of the cells employing 30 and 40% acetylene black are negligible and hence 30% has been taken as the effective concentration.

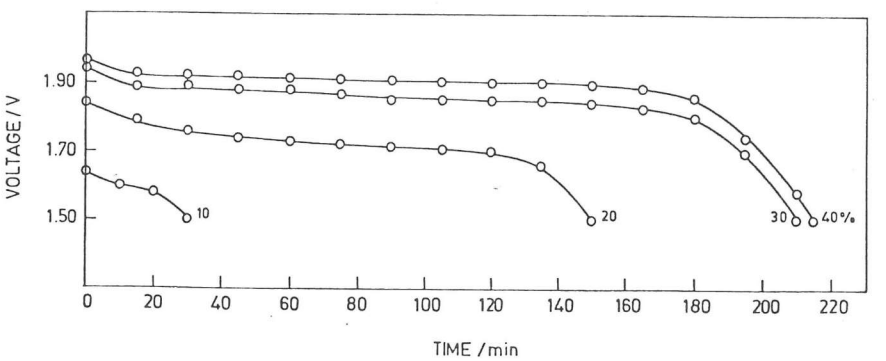


Fig. 1 Effect of acetylene black (Current drain: 25 mA).

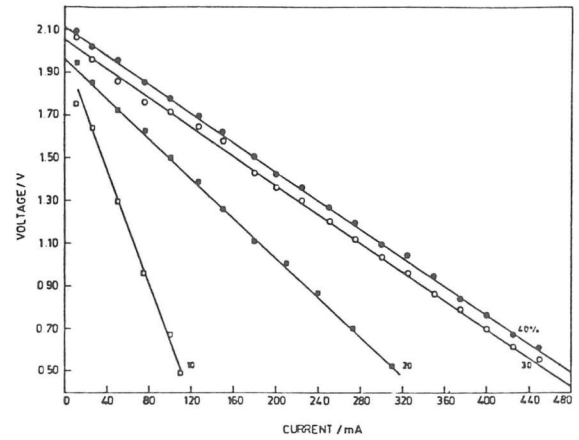


Fig. 2 I/E curves for different percentages of acetylene black.

The half cell potential of the DDH cathode has been measured at various current drains (Fig. 3). The open circuit potential (OCP) of the cathode is 654 mV and the closed circuit potential (CCP) is observed to be in the range of 480 and 120 mV when the current drain is varied from 25 to 150 mA. The observed OCP and CCP are much higher than those of other well-known organic depolarisers, eg. OCP of m-DNB is -100 mV and the CCP is -250 mV [5]. The observed higher potential of the DDH cathode could be attributed to the presence of loosely attached chlorine in the ring of the orgnic compound.

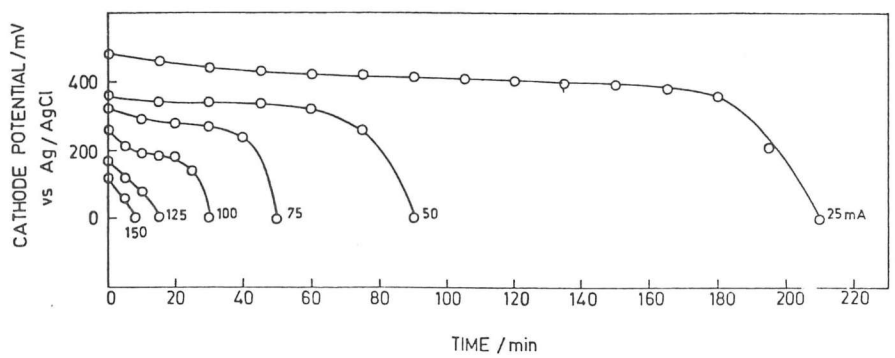
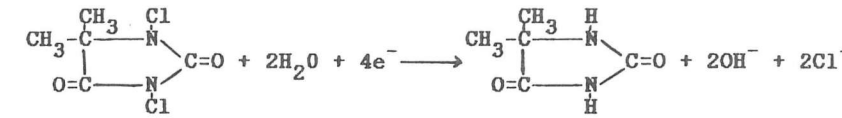


Fig. 3. Effect of current drain on cathode potential.

When DDH cathode comes in contact with water in presence of electrolyte, the discharge takes place as per the reaction:



Voltage vs time characteristics of Zn/DDH cells have been measured at various current drains (Fig. 4). The open circuit voltage (OCV) of the cell is 2.12 V and the closed circuit voltage (CCV) is found to be in the range of 1.94 to 1.60 V when the current drain is varied from 25 to 150 mA. The observed voltages are much higher than those obtained from Zn/m-DNB cell (OCV: 1.10; CCV: 0.90 V) [6]. The coulombic efficiency for 10, 25, 50, 75, 100, 125, 150 and 175 mA current drains is observed to be 20.2, 16.1, 13.8, 11.5, 99.2, 5.8 and 3.7%, respectively. The cell capacity and energy density of Zn/DDH cells are shown in Fig. 5. It is evident from the Fig. 5 that the increase of current drain results in the gradual loss of the cell capacity and energy density due to the increase in the cathode polarisation. The trend of energy density is similar to capacity values. This is in contrast to the other well-known organic systems (eg. m-DNB and its substituted compounds) wherein the energy density is lower than the corrosponding capacity [6]. The present system exhibits higher energy density due to its higher operating voltages.

In KOH solution, DDH cathode gives rise to very low efficiency and low capacity in comparison with $MgBr_2$, $Mg(ClO_4)_2$ and NH_4Cl electrolytes [7,8]. The low efficiency may be due to the poor stability and rapid polarisation of the cathode in alkaline solutions [9].

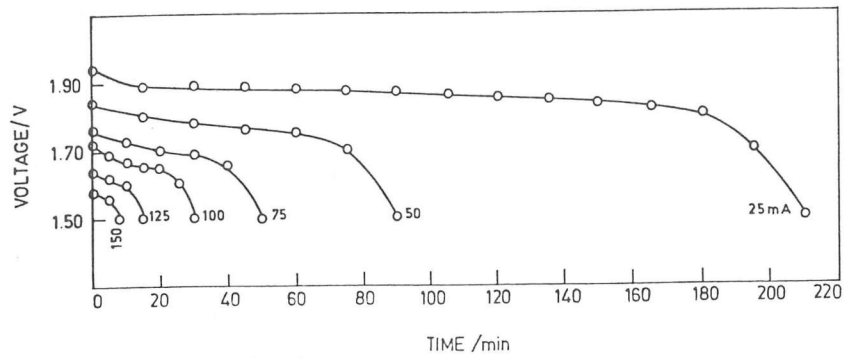


Fig. 4 Effect of current drain on cell voltage.

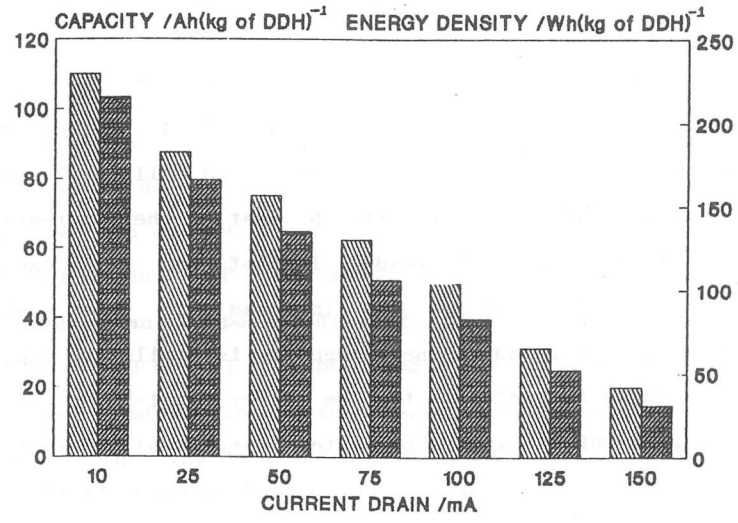


Fig. 5 Dependence of battery parametres with current drain.

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