INVESTIGATIONS ON MAGNESIUM-META-DINITROBENZENE ORGANIC CELL AT DIFFERENT TEMPERATURES

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ABSTRACT

Magnesium-meta-dinitrobenzene, hereafter referred to as Mg/DNB, organic cells are considered as a high energy density primary power source, though lacking in a high power density capability. To improve the current drain characteristics of the DNB, electrolytic manganese dioxide is incorporated in the cathode. The cathode variables are optimised after selection of suitable grid. Fifteen percent of manganese dioxide additive to the cathode mix is found to deliver good reduction efficiency at moderate current drain. Performance results of Mg/DNB cell at moderate current drain at room temperature (30°C) and temperature down to −20°C are reported. High energy density per unit weight, voltage stability till 80% of its capacity, low cost and availability of DNB are the important and attractive features of this organic battery system.

Key Words: Magnesium, Organic battery

INTRODUCTION

Recent advances in science and technology leading to miniaturisation in circuitry and reduction in the volume of electronic equipments require new and sophisticated power sources having high energy density, high power density and long shelflife. The need for the high energy density batteries has become extremely pressing during the last two decades which thereby led to many investigations [1,2] to explore organic materials as attractive and useful cathode depolarisers.

Inorganic substances like oxides of Mn, Pb, Ag, Cu, Ni, Hg and halides of Ag, Cu, Pb are mainly used as cathode depolarisers in the electrochemical power generating systems, namely, primary and secondary batteries [3]. These inorganic depolarisers are capable of undergoing one or two electron-transfer. Therefore, a large quantity of these materials are required to deliver one unit ampere-hour capacity. On the other hand, organic compounds are capable of undergoing electron-transfer as large as 6 to 12 single or two steps. Obviously these materials exhibit very high energy density per unit weight of the material. Unlike inorganic substances, a very small quantity of the organic substance is required to offer a unit ampere-hour capacity. Data on the theoretical capacity of different cathode materials are compared in Table I.

Table-I: Energy density comparison of different cathode materials

Cathode materials	Electrons transferred	Theoretical ampere-hour per gram of the material
AgO	2	0.43
CuO	2	0.67
MnO_2	1	0.31
$PbCl_2$	2	0.19
AgCl	1	0.18
DNB	12	1.92

During the last two decades many investigations were carried out on a variety of organic substances for their suitability as cathode depolarisers. Some of them are high energy yielding, some are high voltage giving and some others are capable of high reversibility. A few are, however, capable of giving high energy density and high reversibility. The

organic nitrocompounds get reduced reversibly and hence operate well as cathodic materials and generate high energy in actual performance of the cells. On the basis of a survey of the existing literature, the DNB has been selected as the suitable cathode depolariser and the preliminary results were reported already [4]. This paper presents results of Mg/DNB cells with modified cathode at 30°C and down to −20°C. Many investigators have studied the reduction products of many organic compounds in magnesium perchlorate electrolyte which are analysed and identified also [5]. It is found that reduction depends upon three parameters: pH of the electrolyte, catalyst and rate of the reaction. The use of electrolytic manganese dioxide as the suitable addition is tried here for better reduction and to achieve higher current drain at different temperatures.

EXPERIMENTAL

Magnesium alloy (AZ 31) sheet of 0.8 mm thickness is used as the anode. The dimensions of the anodes are 6 × 4 cm. The top portion of this anode is soldered to copper wire which acts as the lead. To find out a suitable and well conducting grid for the cathode, a number of metallic meshes like copper, nickel and nickel-plated iron with different mesh sizes were investigated and 20 mesh of copper grid is found to give good results and hence chosen for this work. Cathodes of the same dimensions as that of the anode were prepared by pressing cathode mix containing 3 gm of DNB, 1.5 gm of acetylene black and 0.5-1.0 ml of 2% carboxymethyl cellulose solution, on the copper mesh at an optimised pressure. Magnesium perchlorate with certain addition agents for controlling corrosion is used as the electrolyte. Synthetic fibre, special paper or cotton pad are used as the separator material in different designs of the cells depending upon the nature of requirement. Fabrication and composition details of the battery elements are described in the Indian patent [6].

RESULTS AND DISCUSSION

Mg/DNB cell of 3 AH is fabricated by putting one cathode having required quantity of the cathode mix between two anodes. The cells exhibit 1.5-1.6 V as the open circuit potential. Fig. 1-A shows this

behaviour of Mg/DNB cell at 100mA current drain. The performance characteristics of this cell at higher current drains viz.200 mA, 300 mA and 400 mA, are shown in Fig. 1.B. It can be noted from the figures that as the current drain increases, the capacity of cells falls sharply indicating higher polarisation at high rates of discharge. At the highest current drain corresponding to 400 mA, the capacity of the cells falls to negligibly small value.
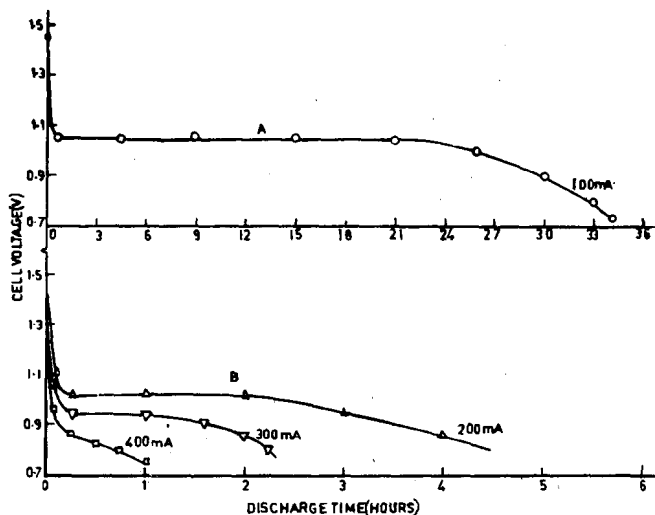

Fig. 1: Voltage vs time discharge curve of Mg/DNB cell at 30°C

To use this high energy system in modern applications, the current drain capability is to be improved. The addition of electrolytic MnO_2 to the organic cathode mix is therefore considered. Fig. 2 shows the effect of various percentages of MnO_2 in the DNB cathode mix. It is noted that as the percentage of MnO_2 increases, the capacity, i.e. the reduction efficiency of the cell, increases. However, addition beyond 15% starts bringing down the capacity instead of increasing it, as may be noted from Fig. 3. Fifteen percent of MnO_2 is, therefore, selected as the optimum concentration.
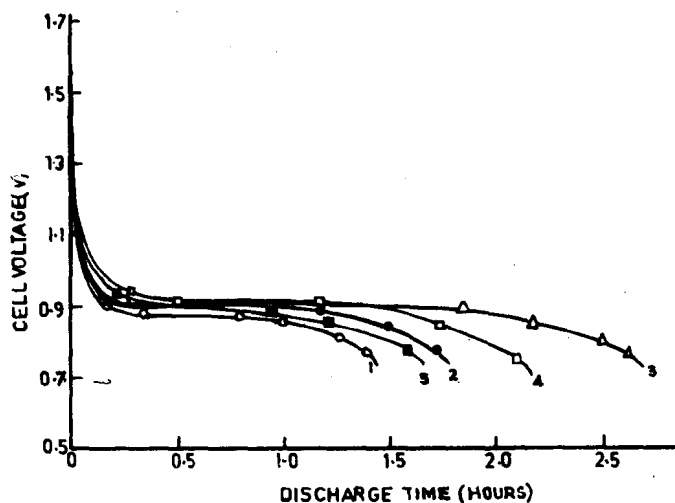

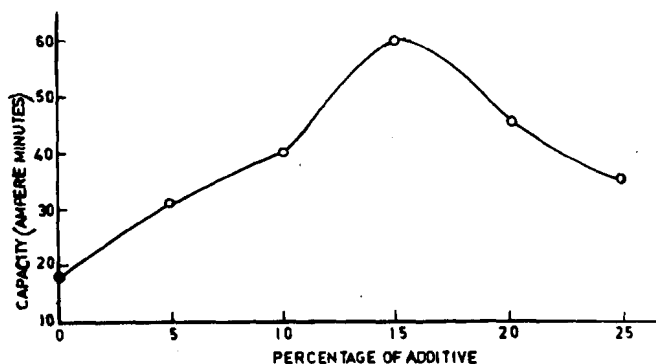Fig. 2: Effect of MnO_2 concentration in Mg/DNB cell at 30°C (current drain: 400mA)

Fig. 3: Capacity vs percentage of MnO_2 additive

Fig. 4 presents the comparative performance of Mg/DNB cells with 15% MnO_2 and without MnO_2; the difference in capacity of the two at 100 mA discharge is negligibly small. But as the current drain increases, there is a gradual increase in the capacity delivered. At 400 mA current drain, the capacity of the cell with additive gives three times that of the one without additive. This figure ultimately reveals that 15% addition of MnO_2 to the cathode mix makes it capable of medium current drain discharge corresponding to about 8 mA/sq.cm.
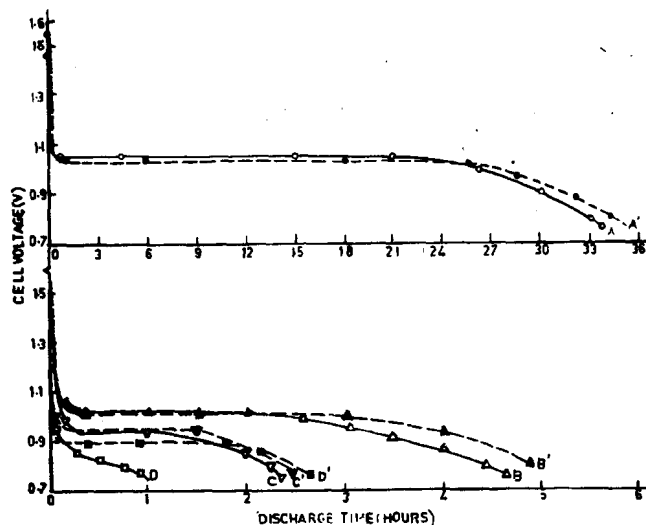

Fig. 4: Comparison of Mg/DNB cells with or without MnO_2 additive at 30°C. Curves A, B and C represent cathode mix without MnO_2 additive and curves A', B' and C' represent cathode mix with MnO_2 additive.

Fig. 5 demonstrates the discharge behaviour of Mg/DNB cell with additive at different current drains at 20°C. First curve corresponding to 100 mA discharge shows a flat voltage of 1 V till 85% of its capacity. But total capacity is reduced to 50% of its capacity at 30°C. At 200 mA discharge rate, the capacity is reduced, but the flat discharge of 0.9 V is obtained up to 80% of its capacity. At this rate the capacity corresponds to 50% of its capacity at 30°C. At higher current drains of 300 mA and 400 mA, however, no steady voltage is observed. Moreover, the capacity is reduced to one third of its capacity at 30°C.
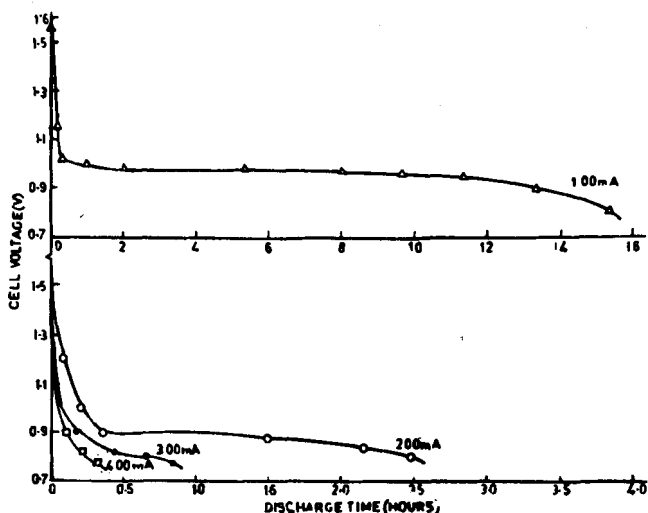
Fig. 5: Voltage vs time curves for Mg/DNB cells with MnO$_2$ additive at 20°C

The effect of temperature on the discharge voltage and capacity of the cells at 100 mA current drain is represented in Fig. 6.
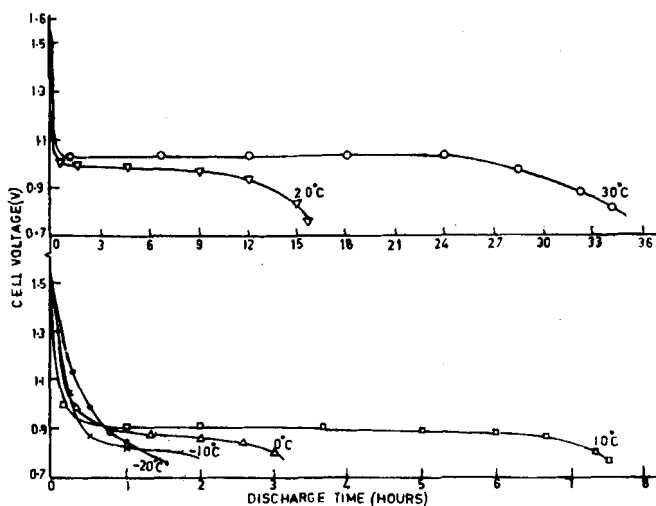

Fig 6: Voltage vs time curves for Mg/DNB cells with MnO$_2$ at different temperatures (current drain: 100mA)

As the temperature falls down from 30°C to −20°C, the polarisation in the cell increases gradually reducing the length of flat discharge plateau as well as its capacity. Fig. 7 shows the voltage vs current relationship of Mg/DNB cell with (A', B', C') and without (A,B,C) 15% MnO$_2$ at 30°C, 10°C and 0°C.

With additive added, the discharge potential (0.3-0.4V) is higher than without additive up to 100 mA current drain. The cells without additive are not capable of discharging at useful voltage above 100 mA current drain. This figure clearly establishes the capability of cells with additive to undergo discharge at higher current drains. Similar conclusion may be drawn from the comparison of cells with or without additive at −10°C and −20°C (Fig. 8).
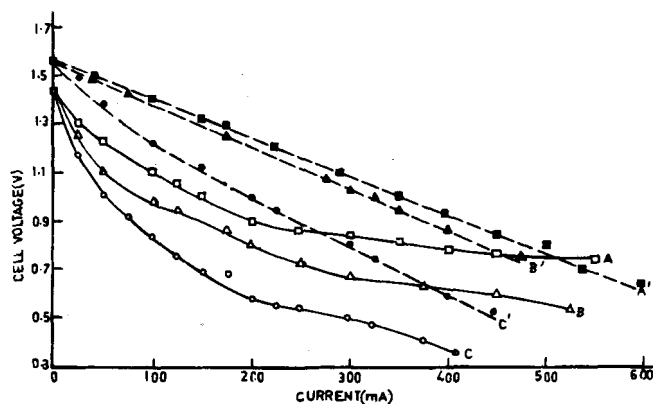

Fig. 7: Voltage vs current curves for Mg/DNB cells with or without MnO$_2$ additive at 0°C, 10°C and 30°C
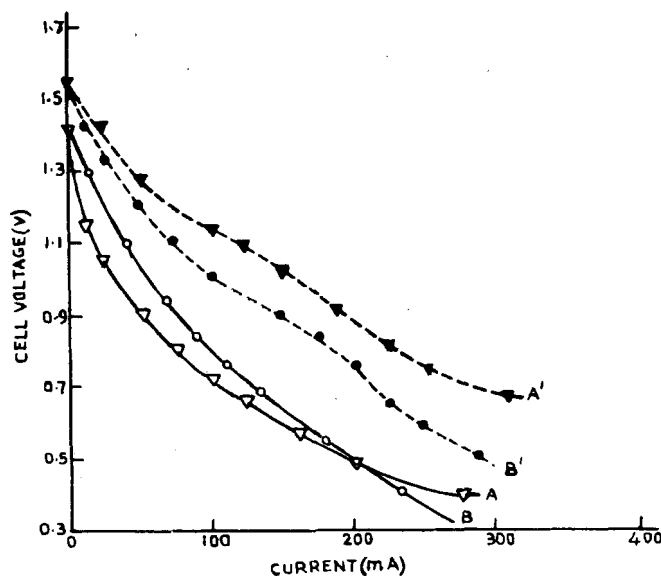

Fig. 8: Voltage vs current curves for Mg/DNB cells with or without MnO$_2$ additive at −10°C and −20°C.

From this, it can be inferred that at sub zero temperatures this cell is capable of discharging only at lower current drains like 100 mA, while at room temperature it can discharge at higher current drains i.e. up to 400 mA also.

CONCLUSIONS

Mg/DNB cell is found to deliver about 1 AH per g capacity of DNB active material at 100 mA current drain. Important characteristics of the system are: high energy density, and voltage stability till 80% of its discharge capacity at continuous current drain in contrast to the performance of conventional Leclanche system. The effect of different concentrations of electrolytic MnO$_2$ added to the organic cathode shows that 15% addition is suitable for the efficient reduction at comparatively higher current drains and stability of discharge voltage. This could possibly be explained as due to the catalytic nature of MnO$_2$ up to certain concentrations. The comparative data on these cells with or without additive indicate superior discharge capability of the cells with additive

at room temperature as well as at lower temperatures. Since the reported system works even at subzero temperatures with reduced efficiency, this may find immense use in several applications.

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