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Performance characteristics of organic–inorganic composite electrodes in magnesium reserve batteries

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Abstract

Electrochemical characteristics of *m*-dinitrobenzene (*m*-DNB) based composite cathode materials involving compounds such as AgCl, TiO_2, HgO and CuCl have been investigated and (Mg AZ31 alloy anode) as an activated battery system using 2 M magnesium perchlorate aqueous electrolyte. The concentration of the composites has been optimized so as to obtain high electrochemical performance of Mg/*m*-DNB reserve batteries through constant current discharge studies. Mg/*m*-DNB cells containing 5-wt % of HgO when discharged at current density of 2.1 mA cm^{-2} delivered 5.3 Ah capacity corresponds to a columbic efficiency of 97% as compared to the cells without composite.

1. Introduction

Of late, organic nitro compounds of metal-organic cell systems have received attention as attractive cathodes owing to their flat discharge voltage and high theoretical energy density [1–4]. Further, these compounds undergo reduction involving 2–12 electron transfer reactions when compared to 1 or 2 electron transfers with inorganic cathode materials such as MnO_2, HgO, CuO, PbO_2, AgO, NiO_2, etc. Glicksman and Morehouse have investigated the electrochemical behaviour of several organic compounds [5–8]. Over the last decade, renewed interest has been shown on substituted organic compounds namely, *p*-nitro-benzoic acid, *p*-nitrophenol, *p*-nitrotoluene, monochloro nitrobenzene, etc., as attractive cathode materials [9–19] for magnesium reserve batteries. Although, these organic compounds exhibited flat discharge profile, the low current capability of the materials could be improved by using composites with suitable inorganic materials. In this paper, composites of *m*-DNB with materials such as AgCl, TiO_2, HgO and CuCl have been prepared in different concentrations viz., 2, 5, 10 and 20-wt % and studied individually with Mg AZ31 alloy anodes in a reserve battery configuration. Cells were assembled and subjected to constant discharge studies at different discharge rates. The reaction involved in this couple using neutral magnesium perchlorate electrolyte is given below [11].

$$6Mg + C_6H_4(NO_2) + 8H_2O \longrightarrow C_6H_4(NH_2)_2 + 6Mg(OH)_2 + H_2\uparrow$$

2. Experimental

2.1. *Chemicals*

m-DNB (Fluka AG, Switzerland), AgCl, TiO_2, HgO and CuCl (BDH), 2 M magnesium perchlorate, (Loba/Chemie, AR), acetylene black (AB) (Travancore chemicals) and magnesium AZ31 alloy sheets (Elecktron Co., UK) were used.

2.2. *Cell fabrication and discharge studies*

Mg alloy (AZ31) sheets of 0.5 mm thickness and dimensions of 6 cm × 4 cm were used as anode. Copper grids of the same size were used as current collector for the cathode. *m*-DNB was mixed with acetylene black in order to enhance the electronic conductivity and surface area for better electrochemical performance. The cathode mix consisted of either *m*-DNB or *m*-DNB composites as active material (3 g), 50-wt % of conducting material (acetylene black) and 2.5 ml of an aqueous solution of 2–3 wt % carboxymethyl cellulose as binder. The prepared mix was spread over a copper mesh current collector of

the same size as that of the anode and pressed at 420 kg cm^{-2} pressure. *m*-DNB composites were prepared by grinding *m*-DNB with different wt % of either CuCl or AgCl or HgO or TiO_2 in a hand mortar for 30 min. A typical cell contained a cathode plate wrapped with multi layers of cellophane separator and sandwiched between two magnesium alloy anodes. These cells were assembled in a polyvinyl chloride (PVC) container and activated with 2 M magnesium perchlorate electrolyte. Adequate time was allowed for complete wetting of the electrodes before commencing the discharge process. The cells were discharged at different current drains (100, 200, 300 and 400 mA) at constant temperature of 28 ± 2 °C.

2.3. *Particle size and surface area analyses*

Particle size measurements of CuCl, AgCl, HgO and TiO_2 were carried out using a Malvern Instrument (UK), Easy Particle Sizer – Type 3600E. Surface area measurements were performed by a Quanta chrome high-speed gas sorption analyzer, model Nova-1000.

3. Results and discussion

3.1. *Optimization of conducting material in the cathode mix*

Organic depolarizers are non-conducting in nature [20] and in order to enhance the electronic conductivity and to minimize the IR drop; conductivity material (acetylene black) with high surface area and low particle size was incorporated in the cathode mix. Further, it was ascertained [11, 21] that the AB possesses more surface area and high conductivity.

Figure 1 shows the discharge behaviour of Mg/*m*-DNB cells at a constant current drain of 100 mA with different wt % of AB. An increase in the open circuit voltage (OCV) is observed with increase of AB content. Further, the cells containing 50 wt % of AB was found to give better performance (capacity 2.8 Ah corresponding to a specific capacity of 0.93 Ah g^{-1}). This is due to an increase in electronic conductivity of the cathode resulting in a decrease in the internal resistance of the cell. Moreover, the chain like network of AB provides better water retention characteristics and improves the electrochemical properties of the organic compound as the reduction process involves $8H_2O$ per mole of *m*-DNB. Below 50-wt % of AB, the electrochemical performance decreases indicating that the AB content is insufficient. In contrast, a reduction in discharge capacity is observed for the cells with 60 and 70-wt % of AB. The lowering in the cell capacity is ascribed to the masking of cathode active material. Therefore, 50% AB was used in the cathode mix for further investigations.

3.2. *Performance of Mg/m-DNB composites cells*

Figures 2–5 depict the discharge behaviour of *m*-DNB composite electrodes with different percentages (2, 5, 10 and 20 wt %) of AgCl, TiO_2, HgO and CuCl at 100 mA current drain, respectively. The discharge behaviour of Mg/*m*-DNB (Blank) cells is also presented for comparison. Table 1 presents the discharge capacities obtained for different *m*-DNB composites of varying compositions. The discharge capacities obtained for the composites are in the order: $HgO > TiO_2 \approx AgCl > CuCl$.

Figure 6 comparatively shows the discharge capacities obtained for different composite materials with varying compositions. An increase in the discharge capacity is observed with the addition of composite materials. In the case of electrodes with AgCl a uniform increase in capacity is observed with increase in AgCl content. However, it is interesting to note that the capacity obtained with other composite materials (TiO_2, HgO and CuCl) shows a negative trend beyond 10-wt %. The excessive addition (20-wt %) of composite materials dilutes the energy content of the cathode mix resulting in the reduction of discharge capacities. Nevertheless, the presence of the composite materials enhances the reduction efficiency of *m*-DNB. Among the investigated composite materials, 5% of HgO stands out to be high

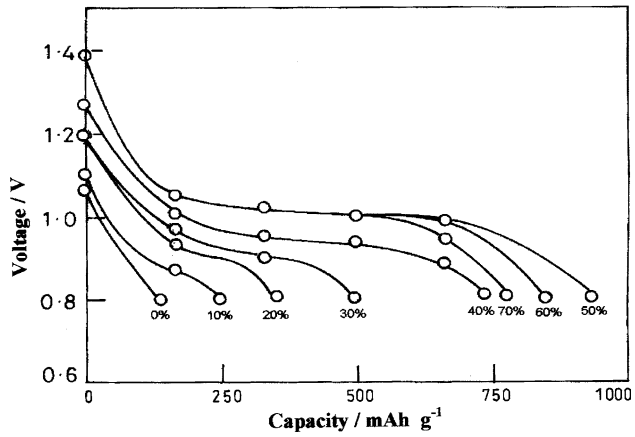

Fig. 1. Discharge behaviour of Mg/*m*-DNB cells at a constant current drain of 100 mA with different wt % of AB.

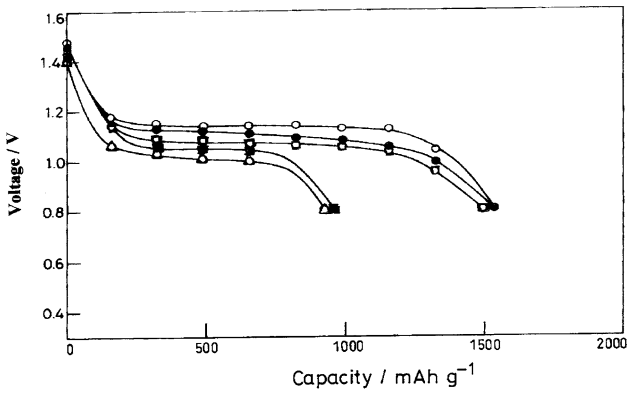

Fig. 2. Voltage vs. time curves of Mg/*m*-DNB composite cells with different wt % of AgCl. △: Blank; ■: 2 wt %; □: 5 wt %; ●: 10 wt %; ○: 20 wt %.

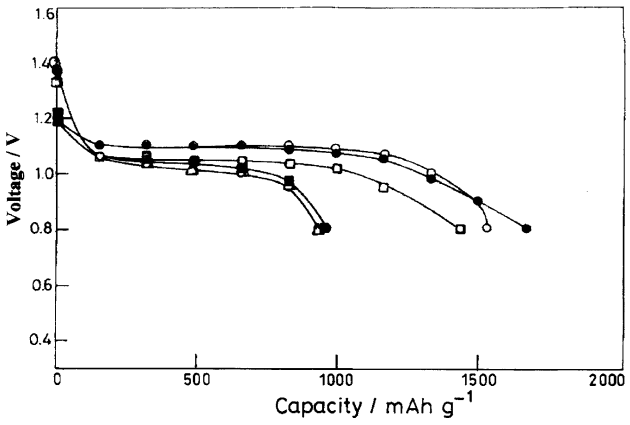

Fig. 3. Voltage vs. time curves of Mg/*m*-DNB composite cells with different wt % of TiO_2. △: Blank; ■: 2 wt %; □: 5 wt %; ●: 10 wt %; ○: 20 wt %.

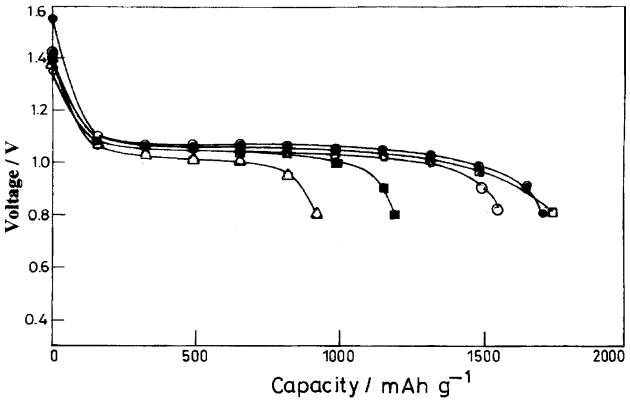

Fig. 4. Voltage vs. time curves of Mg/*m*-DNB composite cells with different wt % of HgO. △: Blank; ■: 2 wt %; □: 5 wt %; ●: 10 wt %; ○: 20 wt %.

performing delivering 5.3 Ah, which corresponds to 97% of cathodic efficiency. This superior performance may be ascribed to the higher hydrogen over voltage, a uniform increase in conductivity of the cathode due to the presence of mercury formed during the reduction of HgO and amalgamation of the magnesium anode by dissolved mercuric ions.

From the above investigations it is clear that *m*-DNB composite electrodes with 5-wt % of composite materials deliver higher discharge capacities than the bare *m*-DNB electrodes. In order to assess the performance of

Table 1. Effect of different percentages of the composite materials on the performance of Mg/*m*-DNB cells

Composite materials	Capacity (mAh g^{-1})			
	2 wt %	5 wt %	10 wt %	20 wt %
AgCl	966(51)	1500(83)	1533(63)	1533(87)
TiO_2	966(51)	1433(79)	1666(96)	1533(96)
HgO	1200(63)	1766(97)	1733(100)	1566(100)
CuCl	933(49)	1100(61)	1233(71)	1133(72)

Blank = 2.8 Ah → 49%; values in parenthesis indicate coulombic efficiency in percent.

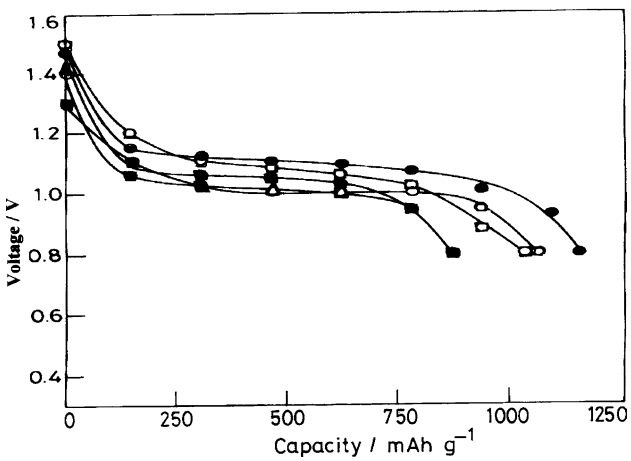

Fig. 5. Voltage vs. time curves of Mg/*m*-DNB composite cells with different wt % of CuCl. △: Blank; ■: 2 wt %; □: 5 wt %; ●: 10 wt %; ○: 20 wt %.

these electrodes at higher current drains *m*-DNB 5 wt % composite electrodes were subjected to constant current discharge studies at different current drains viz., 200, 300, 400 mA corresponding to current densities of 2.1, 4.2, 6.3 and 8.3 mA cm^{-2}.

It is clear that particle size and surface area are very important physical parameters in determining the electrochemical properties of the compound. Particle size measurements for HgO and TiO_2 were taken using methanol as dispersion medium, while iso-propylalcohol and benzene were used for CuCl and AgCl, respectively. It is evident that the particle size of HgO is minimum (Table 2) as compared to the other materials. Further, the high surface area measured for HgO (Table 2) may also contribute to the superior performance derived from *m*-DNB–HgO composites.

Figure 7 shows capacity versus current density curves of Mg/*m*-DNB composite cells containing 5-wt % composite material. HgO composite exhibits uniformly higher capacities at all current drains (100–400 mA) as compared to other composites. The superior performance of HgO may be attributed to an increase in the electrical conductivity among the particles in the cathode mix due to the generated mercury, which contributes to the complete reduction of organic material. Furthermore, HgO can also modify the adsorption and charge transfer properties of the nitro compound. Thus, HgO improves the cathode efficiency of the Mg/*m*-DNB composite couple. Formation of an amalgamated Mg surface resulting from the reduced Hg^{2+} ions dispersed into the magnesium perchlorate electrolyte medium is not ruled out. This facilitates a reduction in the competitive H_2 evolution reaction at the magnesium surface.

4. Conclusions

Different *m*-DNB composites involving AgCl, TiO_2, HgO and CuCl in varying proportions (2–20 wt %) have been investigated as a cathode material in 2 M

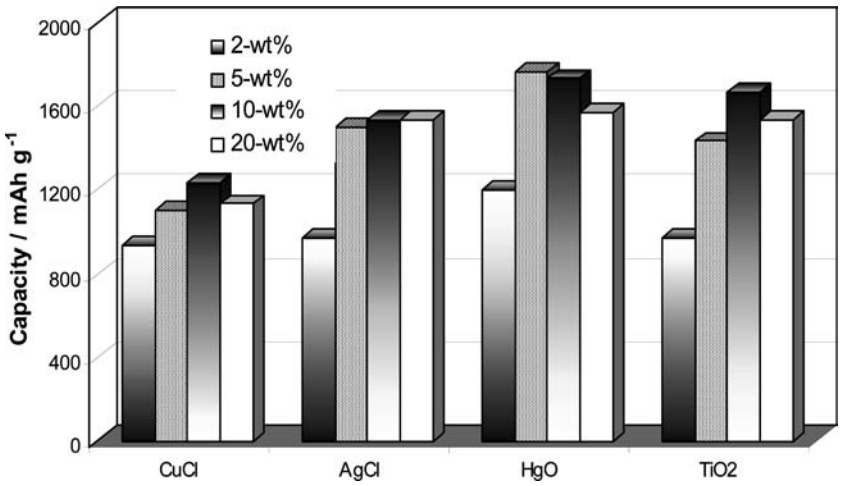

Fig. 6. Specific capacities obtained for different composite materials with varying compositions.

Table 2. Particle size and surface area data of the composite materials

Composite materials	Average particle size (μm)	Surface area (m^2 cm^{-3})
AgCl	14.3	0.08
TiO_2	16.6	0.11
HgO	12.9	0.46
CuCl	25.2	0.08

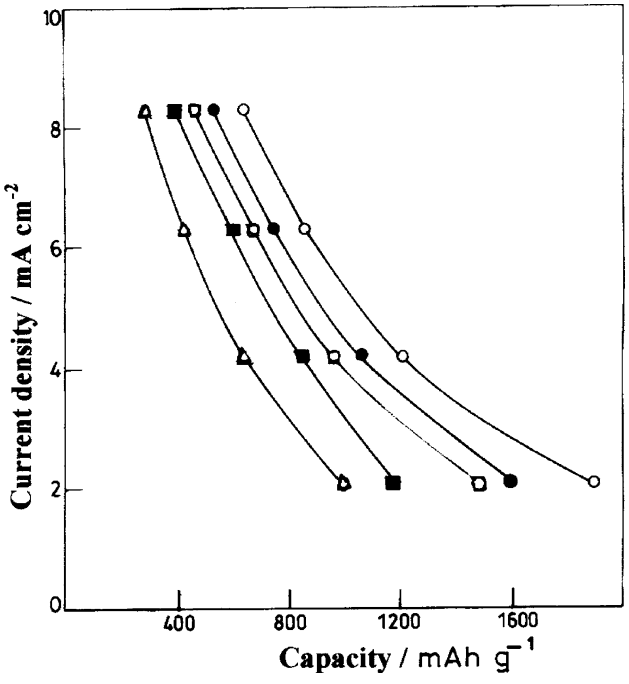

Fig. 7. Capacity vs. current density curves of Mg/*m*-DNB composite cells △: Blank; ■: 2 wt %; □: 5 wt %; ●: 10 wt %; ○: 20 wt %.

$Mg(ClO_4)_2$ aqueous electrolyte in conjunction with Mg AZ31 alloy anode at different current densities (2.1, 4.2, 6.3 and 8.3 mA cm^{-2}) after optimizing the AB content in the cathode mix. The optimum conducting material (AB) in the cathode mix was found to be 50 wt % to enhance the electrochemical performance of the *m*-DNB cathode. It was found that *m*-DNB containing 5 wt % of HgO composites out performed the other composites and delivered capacities of 5.3 and 1.9 Ah at current densities of 2.1 and 8.3 mA cm^{-2}, respectively.

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