

## Short Communication

# 1-Nitronaphthalene as a cathode material for magnesium reserve batteries

R. Thirunakaran, S. Vasudevan, A. Sivashanmugam, Gopu Kumar, N. Muniyandi

Central Electrochemical Research Institute, Karaikudi 630 006, Tamil Nadu, India

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### Abstract

1-Nitronaphthalene has been investigated for use as a battery depolarizer in conjunction with a high-energy magnesium anode. Acetylene black is added to improve the conductivity of the non-conducting organic compound and its concentration in the mix is optimized for better performance of the cathode. To assess its suitability and its characteristics as a cathode active material, magnesium/1-nitronaphthalene cells are fabricated and discharged in different electrolytes (magnesium chloride, magnesium bromide and magnesium perchlorate) at various current densities. The capacity delivered by the cell system shows better reduction efficiency of the 1-nitronaphthalene depolarizer. Cyclic voltammetric studies are carried out on a glassy-carbon electrode to understand the reduction behaviour of 1-nitronaphthalene.

**Keywords:** Nitronaphthalene; Cathodes; Magnesium reserve batteries

## 1. Introduction

Organic compounds have high theoretical coulombic capacities because they involve up to a twelve-electron transfer [1–3]. Several organic compounds, e.g. *p*-nitrotoluene, *p*-chloronitrobenzene, *p*-nitroaniline, *p*-nitrophenol, *p*-nitrobenzoic acid [4–8], have recently been investigated in terms of their performance as cathode depolarizers in magnesium primary reserve cells. 1-Nitronaphthalene has not been investigated previously as a battery cathode material. Accordingly, a study is reported here of the cyclic voltammetry of this compound in neutral magnesium electrolyte solution. Mg/1-nitronaphthalene cells have been fabricated and discharged under different conditions to understand the suitability of the organic material for battery applications. In this communication, we report the performance characteristics of 1-nitronaphthalene as a cathode material in magnesium primary reserve cells that employ various 2 M magnesium electrolytes at different discharge rates (25 to 100 mA).

## 2. Experimental

### 2.1. Chemicals

1-Nitronaphthalene (E. Merck, Germany), magnesium bromide, magnesium chloride, (Loba/Chemie, AR) and magnesium perchlorate (E. Merck, AR) were used.

### 2.2. Cell assembly and discharge studies

Magnesium alloy (AZ31) sheets (3 cm × 2 cm × 0.15 cm) were used as the anodes. The cathode current-collector was a copper grid and was of the same size as the anode. The cathode mix comprised 1 g of 1-nitronaphthalene with varying amounts of acetylene black; 0.3 ml of 2 wt.% aqueous carboxymethyl cellulose (CMC) was used as a binder. The cathode mix was spread uniformly over the copper grid and pressed at an optimized pressure of 680 kg cm<sup>-2</sup>. Excess moisture was removed with filter paper. The electrodes were wrapped with cellophane sheets which acted as the separators.

The cells were assembled with one cathode placed between two anodes. The cells were activated at room temperature using the required volume of a aqueous solution of 2 M MgCl<sub>2</sub>, MgBr<sub>2</sub> or Mg(ClO<sub>4</sub>)<sub>2</sub> as the electrolyte. All cells were discharged at 25, 50, 75 and 100 mA at 27 ± 1 °C to an end voltage of 0.5 V. Duplicate experiments were performed and these displayed a reproducibility of ± 2%.

### 2.3. Cyclic voltammetric studies

The required amount of 1-nitronaphthalene was dissolved in a small quantity of pure ethanol and made up with the required electrolyte solution. The test solution was placed in the electrochemical cell and bubbled with nitrogen gas to give an inert atmosphere.

BAS-100A Electrochemical Analyser, a low current module (Bio Analytical Systems Inc. USA), were used for cyclic

voltammetric studies. The electrochemical cell consisted of a glassy-carbon working electrode (area = 0.07 cm<sup>2</sup>) embedded in Teflon, an Ag/AgCl reference electrode, and a platinum foil auxiliary electrode. The glassy-carbon electrode was polished using alumina or microcloth for 3 min and then washed with double-distilled water. The experiments were performed in 5, 10, 15 and 20 mM concentrations at sweep rates of 50, 100, 150 and 200 mV s<sup>-1</sup>. Cyclic voltammograms were recorded in the potential range -300 to -700 mV. The experiments were repeated to provide consistency.

### 3. Results and discussion

The effect of different concentrations of acetylene black on the discharge behaviour of Mg/1-nitronaphthalene cells at a 25 mA current drain in 2 M Mg(ClO<sub>4</sub>)<sub>2</sub> electrolyte is shown in Fig. 1. It is evident that, in the absence of acetylene black, the capacity delivered by the cathode is less due to the non-conducting nature of the organic compound which, thereby, possesses a high internal resistance. The capacity increases with increasing concentration of acetylene black up to 70% due to an increase in conductivity at higher concentrations. The increase in capacity at 60 and 70 wt.% acetylene black was marginal. Hence, an acetylene black concentration of 60 wt.% was taken for further investigations.

The discharge behaviour of Mg/1-nitronaphthalene cells in different magnesium electrolytes at a current drain of 25, 50, 75 and 100 mA is given in Figs. 2–5, respectively. The capacity obtained at all current drains and in all electrolytes is almost the same with, as expected, a slightly superior performance in the MgCl<sub>2</sub> electrolyte. This may be attributed to the slightly low pH (pH: 5–6) of the electrolyte which enhances the conductivity and, in turn, decreases the internal

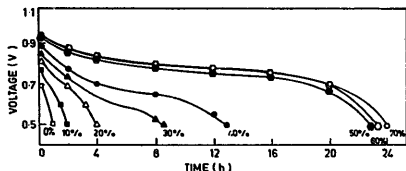


Fig. 1. Effect of acetylene black (wt.%) on the discharge behaviour of Mg/Mg(ClO<sub>4</sub>)<sub>2</sub>/1-nitronaphthalene cells at 25 mA current drain.

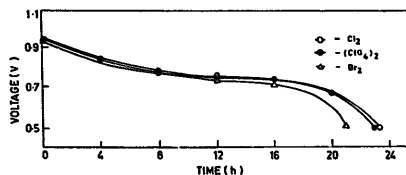


Fig. 2. Discharge behaviour of Mg/1-nitronaphthalene cells at a 25 mA current drain in 2 M aqueous solutions of MgCl<sub>2</sub>, Mg(ClO<sub>4</sub>)<sub>2</sub> and MgBr<sub>2</sub>.

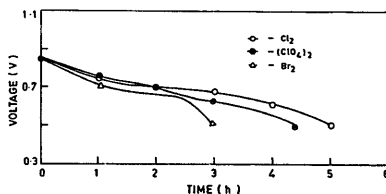


Fig. 3. Discharge behaviour of Mg/1-nitronaphthalene cells at 50 mA current drain in 2 M aqueous solutions of MgCl<sub>2</sub>, Mg(ClO<sub>4</sub>)<sub>2</sub> and MgBr<sub>2</sub>.

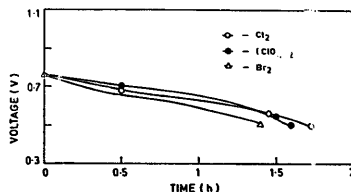


Fig. 4. Discharge behaviour of Mg/1-nitronaphthalene cells at 75 mA current drain in 2 M aqueous solutions of MgCl<sub>2</sub>, Mg(ClO<sub>4</sub>)<sub>2</sub> and MgBr<sub>2</sub>.

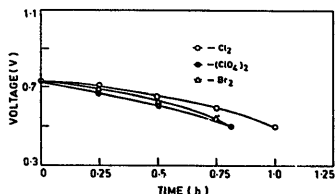


Fig. 5. Discharge behaviour of Mg/1-nitronaphthalene cells at 100 mA current drain in 2 M aqueous solutions of MgCl<sub>2</sub>, Mg(ClO<sub>4</sub>)<sub>2</sub> and MgBr<sub>2</sub>.

Table 1  
Capacity (Ah) and reduction efficiency (%) of 1-nitronaphthalene in different electrolytes

Electrolyte	Current density (mA cm <sup>-2</sup> )							
	2.1		4.2		6.3		8.3	
	Ah	%	Ah	%	Ah	%	Ah	%
MgCl <sub>2</sub>	0.58	62	0.25	27	0.13	14	0.10	11
Mg(ClO <sub>4</sub> ) <sub>2</sub>	0.57	61	0.22	24	0.12	13	0.08	9
MgBr <sub>2</sub>	0.52	56	0.15	16	0.11	12	0.08	9

resistance and, hence, offers a higher operating voltage. The lower performance in MgBr<sub>2</sub> electrolyte may be explained in terms of concentration polarization at the cathode–electrolyte interface. This obviously disturbs the solvation of the discharge product and leads to a famine of fresh surface for reduction.

Figs. 2–5 show that the discharge curves of Mg/1-nitronaphthalene cells in various electrolytes (MgCl<sub>2</sub>, MgBr<sub>2</sub> and

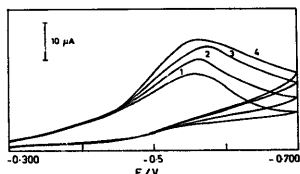


Fig. 6. Cyclic voltammogram of 5 mM 1-nitronaphthalene in 2 M  $\text{Mg}(\text{ClO}_4)_2$  at various sweep rates: (1) 50; (2) 100; (3) 150, and (4) 200  $\text{mV s}^{-1}$ .

$\text{Mg}(\text{ClO}_4)_2$  display steady operating voltages in the order:  $\text{MgBr}_2 < \text{Mg}(\text{ClO}_4)_2 < \text{MgCl}_2$ .

Almost the same capacity is obtained in all the electrolytes at 25 mA, see Table 1. On the other hand,  $\text{MgCl}_2$  gives superior performance at higher current drains (above 50 mA) due to the low pH of the electrolyte.

The reduction of 1-nitronaphthalene involves six electrons at 100% cathodic efficiency. The cyclic voltammograms of 2.5 mM 1-nitronaphthalene in 2 M  $\text{Mg}(\text{ClO}_4)_2$  at various sweep rates (50, 100, 150 and 200  $\text{mV s}^{-1}$ ) are presented in Fig. 6. These studies were performed in order to obtain information on the reduction of 1-nitronaphthalene. A well-defined single cathodic peak is observed and this indicates that the reduced compound is irreversible. The peak potential ( $E_p$ ) is in the range  $-550$  to  $-600$  mV for different concentrations and sweep rates. An increase in sweep rate shifts the potential to more negative values. This again confirms

that the reduced compound is irreversible. The plots of  $i_p$  versus  $\sqrt{\nu}$  ( $\nu$  = sweep rate) and  $i_p$  versus  $C$  (concentration) and thus suggest that the reduction of 1-nitronaphthalene is a diffusion-controlled process.

#### 4. Conclusions

It is concluded from the above discharge study that the capacity of  $\text{Mg}/1$ -nitronaphthalene cells is maximum in 2 M  $\text{MgCl}_2$ , even at a high current density. Cyclic voltammetric studies indicate that the reduction behaviour of 1-nitronaphthalene is irreversible and diffusion-controlled.

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