

Short communication

## Electrochemical behaviour of mono-chloronitrobenzene as cathode material for magnesium reserve batteries

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### Abstract

Mono-chloronitrobenzene (MCNB) is investigated as a cathode material for magnesium reserve batteries that use a magnesium anode and a 2 M magnesium perchlorate aqueous electrolyte. The composition of the conducting material (acetylene black) in the cathode mix is optimized to obtain better electrochemical performance. The reduction mechanism of mono-chloronitrobenzene is examined by means of cyclic voltammetry using a glassy carbon electrode. Discharge studies at different current drains indicate that Mg–MCNB cells exhibit the highest Coulombic efficiency (86%) at a current drain of 100 mA. The reduction of MCNB to mono-chloroaniline is irreversible and diffusion-controlled. © 2005 Elsevier B.V. All rights reserved.

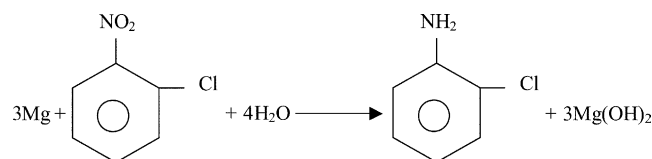
**Keywords:** Mono-chloronitrobenzene; Cathodes; Magnesium reserve batteries; Efficiency

### 1. Introduction

Organic nitro compounds have been used as cathode depolarizers [1–4] in electrochemical energy devices due to the fact that they are capable of undergoing reduction that involves 2–12 electron-transfer reactions compared with the 1 or 2 electron-transfer experienced with conventional inorganic cathode materials such as CuO, HgO, MnO<sub>2</sub>, etc.

Various organic compounds have been examined as cathode materials [5–15]. In addition, *p*-nitrotoluene, *p*-nitroaniline, *p*-nitrophenol, *p*-nitro-benzoic acid have been evaluated in terms of their performance as cathode depolarizers in magnesium reserve batteries [16–18]. The present communication describes the innovative use of mono-chloronitrobenzene (MCNB) as a cathode depolarizer in conjunction with magnesium AZ31 alloy as an anode in a reserve battery configuration with a 2 M magnesium perchlorate electrolyte. Cells are assembled and subjected to constant-current discharge at different discharge rates. The reduction mechanism of the material is investigated by means of cyclic voltam-

metry (CV) using glassy carbon electrode. The overall reaction of the cell may be written as:



### 2. Experimental

#### 2.1. Chemicals

Mono-chloronitrobenzene (Fluka AG, Switzerland), magnesium perchlorate (Loba/Chemie, AR), acetylene black (AB) (Travancore chemicals) and magnesium AZ31 alloy sheets (Elektron Co., UK) were used.

#### 2.2. Optimization of conducting material and discharge studies

A Mg (AZ31) alloy sheet (size: 3 cm × 2 cm × 0.15 cm) was used as anode. Organic compounds are non-conducting

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in nature [19]. Thus, in order to enhance the electronic conductivity and surface area of the electrodes for better electrochemical performance, mono-chloronitrobenzene was mixed with acetylene black. One gram of mono-chloronitrobenzene was mixed with varying proportions of AB (0–70%) and 0.5–1 ml of carboxy methylcellulose binder (2 wt.%). Each mixture was spread over a copper mesh current-collector of the same size as that of anode and pressed at  $200 \text{ kg cm}^{-2}$ . The pressed cathodes were wrapped with multilayers of cellophane separator. Particle size ( $20 \mu\text{m}$ ) and surface area ( $0.05 \text{ m}^2 \text{ g}^{-1}$ ) measurements of AB were undertaken. The cells were assembled by placing the cathode between a pair of Mg AZ31 anodes and then discharged at a constant-current of 100 mA in 2 M aqueous  $\text{Mg}(\text{ClO}_4)_2$  electrolyte. Duplicate experiments were performed and displayed a reproducibility of  $\pm 2\%$ . Some cells with the optimum quantity of conducting material were discharged at higher current drains (100, 200, 300 and 400 mA).

### 2.3. Cyclic voltammetry studies

For cyclic voltammetry studies, MCNB was initially dissolved in small quantity of solvent and made up to different concentrations in a supporting electrolyte. Cyclic voltammograms were run at different concentrations and sweep rates between 0 and 500 mV, and were recorded with a low-current module electrochemical analyzer (model BAS 100A, Bio Analytical System Inc., West Lafayette, IN, USA) coupled to a digital plotter (DMF-40 Series Houston Instrument Division) and a dot-matrix printer (Panasonic KX-Plosi, NJ, USA).

The experimental cell was of a typical three-electrode glass design with provision for nitrogen purging. The studies were carried out at  $28 \pm 1^\circ\text{C}$ . A glassy carbon electrode embedded in Teflon and with an area of  $0.0707 \text{ cm}^2$  was used as the working electrode, together with an Ag/AgCl reference electrode and a platinum counter electrode. The reference electrode was connected through a salt bridge. The glassy carbon electrode was polished with alumina micro cloth for 2 min and then cleaned with distilled water. This treatment was followed by ultrasonic cleaning to remove any residual alumina particles from the surface. Finally, the electrode was washed with acetone.

The mono-chloronitrobenzene was dissolved in 10% ethanol solution and made up with 2 M  $\text{Mg}(\text{ClO}_4)_2$  supporting electrolyte to the desired concentration. The CV profiles were recorded over the potential range  $-400$  to  $-900 \text{ mV}$  at various scan rates (5, 10, 20, 40, 80, 160 and  $320 \text{ mV s}^{-1}$ ). The concentration of the mono-chloronitrobenzene solution was varied from 2.5 to 20 mM. The reproducibility of the cyclic voltammograms was  $\pm 2\%$ , which was verified periodically by recording the response under identical conditions. Purified nitrogen gas was bubbled into the cell before each experiment.

### 3. Results and discussion

The discharge behaviour of the Mg–MCNB cells at a constant-current drain of 100 mA with different concentrations of AB is shown in Fig. 1. The cells without AB exhibit a poor performance (0.1 Ah) due to the high internal resistance that arises from the non-conducting nature of the compound. Improved discharge characteristics are observed with increasing AB content. This behaviour is caused by an enhancement in the electronic conductivity of the cathode mix that, in turn, decreases the internal resistance of the cell. Further, the chain-like network of AB provides better water retention and hence an improvement in the electrochemical properties of the compound. Mg–MCNB cells with 50 wt.% AB exhibits the best performance ( $0.85 \text{ Ah g}^{-1}$ ). A reduction in the discharge characteristic is observed for cells with 60 and 70 wt.% AB. This decrease in the cell capacity is attributed to masking of the active material.

The voltage versus current relationships for different compositions of AB are presented in Fig. 2. The relationship is indicative of the internal cell resistance. It is evident that cells with 50 wt.% AB give a moderate slope even at higher current drain (400 mA), which indicates a low internal resistance. By contrast, the higher slopes for the cells with AB compositions of 10 and 30 wt.% suggests a higher or-

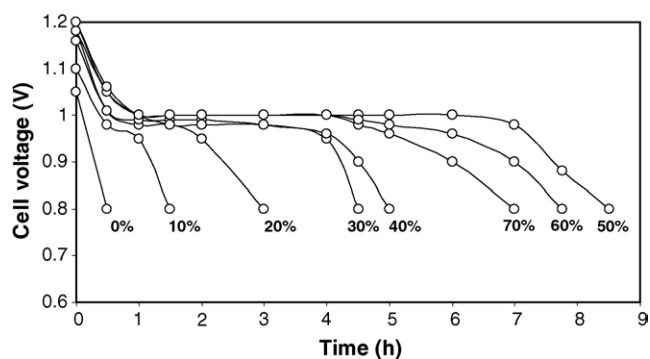


Fig. 1. Discharge behaviour of Mg–mono-chloronitrobenzene cells with different concentrations (wt.%) of acetylene black at a constant-current drain of 100 mA.

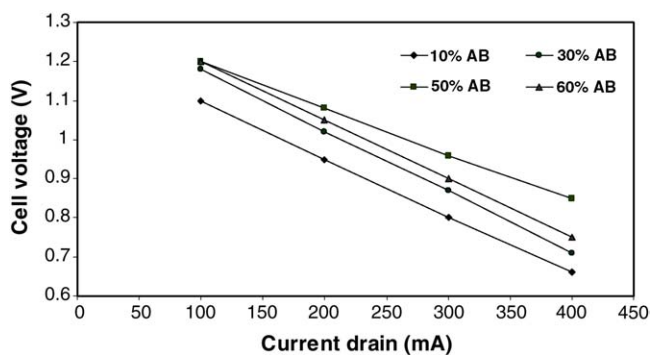


Fig. 2. Cell voltage vs. current relationship of Mg–mono-chloronitrobenzene cells with different concentrations of acetylene black.

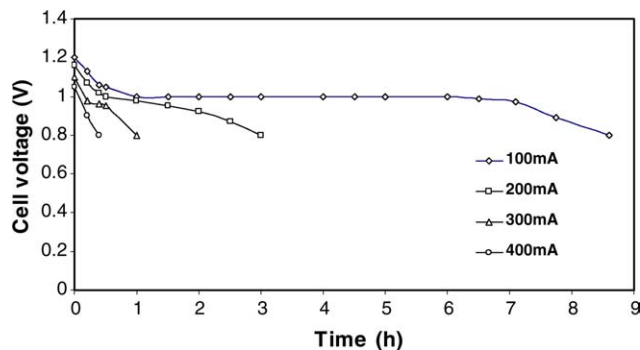


Fig. 3. Discharge behaviour of Mg–mono-chloronitrobenzene cells under different current drains.

der of ohmic polarization. The discharge behaviour of the cells under different current drains, viz., 100, 200, 300 and 400 mA, is shown in Fig. 3. The data reveal that the cathodic polarization increases with increase in the current density and results in a loss of cell capacity. The specific capacities (Ah), coulombic efficiencies (%) and number of electrons transferred ( $n$ ) for Mg–mono-chloronitrobenzene cells at different current drains are listed in Table 1. At a current drain of 100 mA, the cell delivers 0.86 Ah, which corresponds to 86% Coulombic efficiency and the transfer of the 5.16 electrons. On increasing the discharge rate, however, the coulombic efficiency drastically decreases to as low as 16% for a current drain of 400 mA, which is equivalent to a transfer of less than one electron. This severe decline in performance is attributed to increased polarization of the electrodes, as is evident from the results given in Fig. 3. Also, it is quite interesting to note the flat discharge profile around 1.0 V at a current drain of 100 mA.

Typical cyclic voltammograms for 10 mM mono-chloronitrobenzene in 2 M  $\text{Mg}(\text{ClO}_4)_2$  solution on a glassy carbon electrode at different sweep rates are presented in Fig. 4. A well-defined cathodic peak ( $i_p$ ) is observed at all the sweep rates. The peak potentials ( $E_p$ ) appear in the range  $-550$  to  $-650$  mV for the different concentrations and sweep rates. With increase in sweep rate and concentration, the peak potential shifts towards the cathodic direction (more negative values), which confirms the irreversible behaviour of the compound. Plots of  $i_p$  versus  $\gamma^{1/2}$  ( $\gamma$  = sweep rate) and  $i_p$  versus  $C$  ( $C$  = concentration) drawn from the cyclic voltammetry data are given in Figs. 5 and 6, respectively. The lin-

Table 1

Capacities (Ah), coulombic efficiencies (%) and number of electrons involved during reduction for Mg–mono-chloronitrobenzene cell at different current drains

Current drain (mA)	Capacity ( $\text{Ah g}^{-1}$ )	Coulombic efficiency (%)	Number of electrons
100	0.86	86	5.16
200	0.60	60	3.60
300	0.30	30	1.80
400	0.16	16	0.96

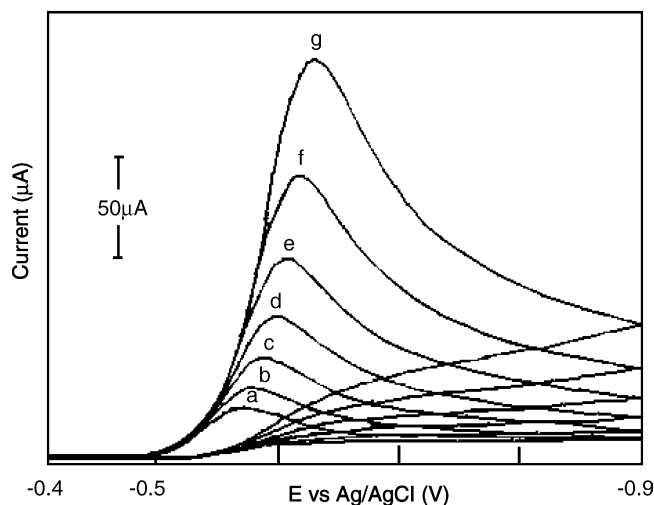


Fig. 4. Cyclic voltammograms of 10 mM mono-chloronitrobenzene in 2 M  $\text{Mg}(\text{ClO}_4)_2$  at various sweep rates: (a)  $5 \text{ mV s}^{-1}$ , (b)  $10 \text{ mV s}^{-1}$ , (c)  $20 \text{ mV s}^{-1}$ , (d)  $40 \text{ mV s}^{-1}$ , (e)  $80 \text{ mV s}^{-1}$ , (f)  $160 \text{ mV s}^{-1}$  and (g)  $320 \text{ mV s}^{-1}$ .

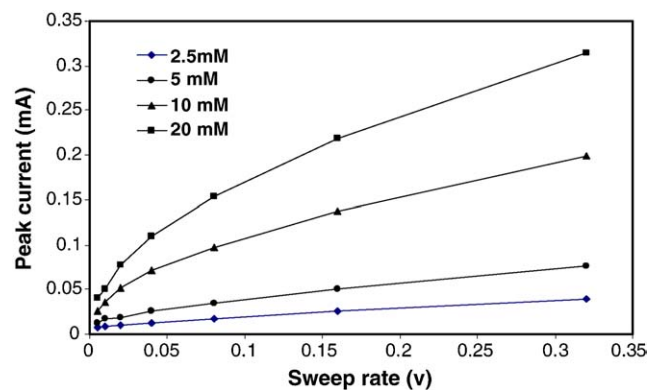


Fig. 5. Plot of  $i_p$  vs.  $\gamma^{1/2}$  for mono-chloronitrobenzene in 2 M  $\text{Mg}(\text{ClO}_4)_2$  at various concentrations.

ear behaviour of these plots suggests that the reduction of mono-chloronitrobenzene is a diffusion-controlled process. Mono-chloronitrobenzene is reduced to mono-chloroaniline, as illustrated in Fig. 7.

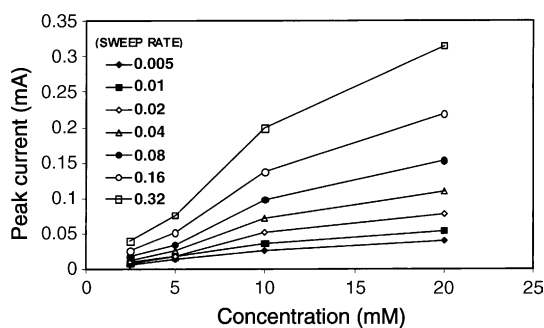


Fig. 6. Plot of  $i_p$  vs.  $C$  for mono-chloronitrobenzene in 2 M  $\text{Mg}(\text{ClO}_4)_2$  at different sweep rates.

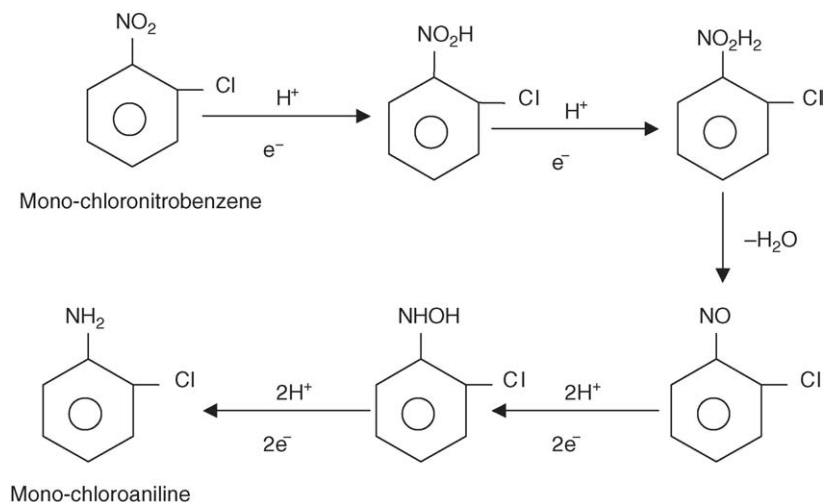


Fig. 7. Reduction mechanism of mono-chloronitrobenzene.

#### 4. Conclusions

Mono-chloronitrobenzene has been investigated as a cathode material for magnesium reserve batteries with a magnesium anode and a 2 M magnesium perchlorate aqueous electrolyte. The organic material is mixed with acetylene black to provide electronic conductivity. The optimum amount of acetylene black is 50 wt.%. At this concentration, the Mg/2 M Mg(ClO<sub>4</sub>)<sub>2</sub>/MCNB cell delivers superior performance. Discharge studies at different current drains indicate that higher Coulombic efficiencies (86%) are obtained at lower current drain. Cyclic voltammetric studies suggest that the reduction behaviour of MCNB is irreversible and the reaction is diffusion-controlled.

#### References

- [1] E. Uhler, Final Report, Contract No. DA 36-039-78048 (1960) (AD 403933).
- [2] R. Glicksman, C.K. Morehouse, *J. Electrochem. Soc.* 105 (1958) 299.
- [3] B. Gruber, Final Report, Contract No. DA 36-039-SC-87336 (1964) (AD 454913).
- [4] D. Linden (Ed.), *Handbook of Batteries and Fuel Cells*, McGraw-Hill, New York, USA, 1984.
- [5] R. Glicksman, C.K. Morehouse, U.S. Patent 2,855,452 (1958).
- [6] C.K. Morehouse, R. Glicksman, *J. Electrochem. Soc.* 106 (1959) 288.
- [7] C.K. Morehouse, R. Glicksman, U.S. Patent 2,836,644 (1958).
- [8] C.K. Morehouse, R. Glicksman, *J. Electrochem. Soc.* 105 (1958) 299.
- [9] D.P. Bhatt, N. Muniyandi, P.B. Mathur, *Trans. SAEST* 22 (1987) 13.
- [10] D.P. Bhatt, N. Muniyandi, P.B. Mathur, *Bull. Electrochem.* 4 (1988) 645.
- [11] N. Muniyandi, S. Vasudevan, S. Pitchumani, *J. Power Sources* 45 (1993) 119.
- [12] G. Kumar, S. Vasudevan, N. Muniyandi, *J. Power Sources* 39 (1992) 155.
- [13] R. Thirunakaran, S. Vasudevan, A. Sivashanmugam, Gopukumar, N. Muniyandi, *J. Power Sources* 58 (1996) 213.
- [14] R. Jasinski (Ed.), *High Energy Batteries*, Plenum Press, New York, USA, 1967.
- [15] G. Kumar, A. Sivashanmugam, N. Muniyandi, *J. Power Sources* 39 (1992) 121.
- [16] G. Kumar, A. Sivashanmugam, N. Muniyandi, *J. Appl. Electrochem.* 23 (1993) 265–267.
- [17] G. Kumar, A. Sivashanmugam, R. Sridharan, *J. Electrochem. Soc.* 140 (1993) 265–267.
- [18] A. Sivashanmugam, G. Kumar, N. Muniyandi, Extended Abstract, The Electrochemical Society Meeting, Honolulu, HI, USA, 16–21 May 1993, Abstract No. 101, 1993, p. 151.
- [19] N.C. Cahoon, *Primary Battery*, vol. II, Wiley, New York, USA, 1967.