

MONO-CHLORO-SUBSTITUTED *m*-DINITROBENZENE COMPOUNDS AS CATHODE MATERIALS IN MAGNESIUM BATTERY

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The performance of mono-chloro-substituted *m*-dinitrobenzene compounds in magnesium battery is reported here. While the operating voltage is improved, the current efficiency is lowered by the chloro-substituents. The influence is explained taking into account inductive and mesomeric effects of the substituents.

Key words: Magnesium battery, chloro-substituted *m*-dinitrobenzene compounds, cathode material, watt hour per gram

INTRODUCTION

Among the organic compounds *m*-dinitrobenzene (*m*-DNB) has long been considered as possible cathode material for primary magnesium batteries [1-4]. The influence of substituted groups in *m*-DNB was studied [1-2] and showed that electron withdrawing groups increase the operating potential of *m*-DNB and electron donating substituents decrease the operating potential. However the influence of substituents of *m*-DNB at different possible positions have not been studied. There is also no detailed account of coulombic efficiency, when such groups are attached to the ring, at different current densities and at different temperatures. The present study involves the effect of mono-chloro-substitution on *m*-DNB at the three possible positions. Chloro-2,4-dinitrobenzene has been investigated [5] to some extent.

The following compounds are studied

- (i) *m*-Dinitrobenzene (*m*-DNB)
- (ii) 1-Chloro 2,4-dinitrobenzene (Cl-2,4 DNB)
- (iii) 1-Chloro 2,6-dinitrobenzene (Cl-2,6 DNB)
- (iv) 1-Chloro 3,5-dinitrobenzene (Cl-3,5 DNB)

EXPERIMENTAL

Fabrication of cell and discharge study

Magnesium alloy AZ31 of area 3 x 3 cm is used as anode. Circular type cathode of area 6.3 cm² has been used. The cathodes are prepared by pressing the cathode mix containing *m*-DNB or Chloro-substituted *m*-DNB (0.4 gm), acetylene black for conductance (0.2 gm), barium chromate for inhibition of magnesium corrosion (0.012 gm) and 3% carboxy methyl cellulose as binder (0.25 ml) on a 20 mesh copper grid at an optimised pressure. The cathode is closely packed between two anodes interposed by polyester cloth separator. Magnesium perchlorate (2 M) is used as electrolyte.

The cells are discharged at different current densities (0.8 to 8 mA cm⁻²) through a constant current discharge unit at 303K, 293K and 273K.

Polarographic study

Stock solution and supporting electrolyte

Saturated solutions ($< 10^{-3}$ M) of these compounds are prepared in water and magnesium perchlorate (10⁻¹ M) as supporting electrolyte, the pH being 7 ± 0.2 .

Polarograms are run by using Tacussel electronic polaroprocessor.

RESULTS AND DISCUSSION

Cell voltage

Room temperature studies (303K)

Fig (1) shows the discharge curves of these four compounds at 0.8mA cm⁻² current density. Here almost all the compounds show

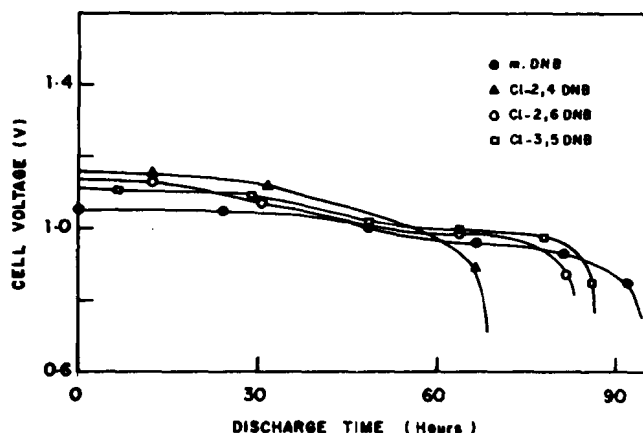


Fig.1: Discharge curves at 0.8mA.cm⁻² current density at 303K

twin discharge plateau. The chloro-substituted compounds show higher mean operating potential than *m*-DNB and the order of the operating potential is Cl-2, 4 DNB > Cl-2,6 DNB > Cl-3,5 DNB >

m-DNB. When current density increases the operating voltage of these compounds are slightly lowered as seen from Figs. (2) and (3).

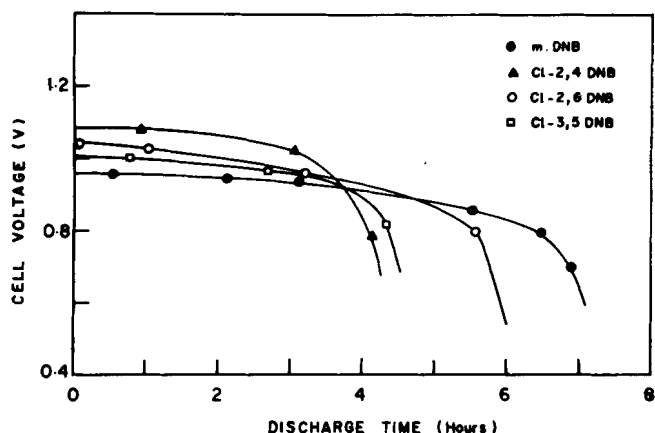


Fig.2: Discharge curves at 8mA.cm⁻² current density at 303K

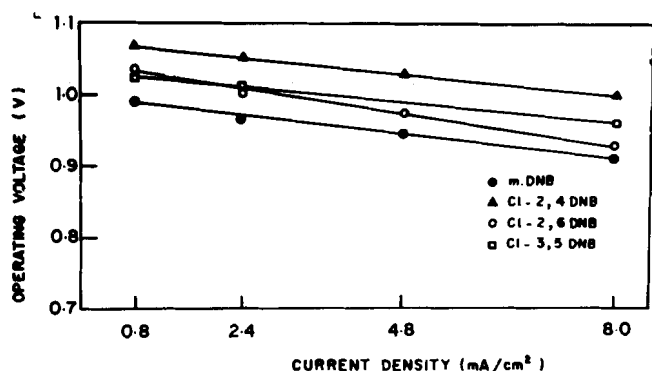


Fig.3: Current density vs operating voltage curves at 303K

It is also seen that there is a single discharge plateau at higher drain rates. From Fig (3), the internal resistance values computed indicated slightly higher value for the Cl-2,6 DNB (vide Table I).

TABLE-I: Internal resistance values of m-DNB and chloro-substituted m-DNB compounds

Compound	Internal resistance of cell (Ω)
m-DNB	1.81
Cl-2,4 DNB	1.47
Cl-2,6 DNB	2.27
Cl-3,5 DNB	1.48

This reduces its operating potential. Polarographic studies also confirm the two-stage reduction observed at low current drain (Table II).

TABLE-II: Half wave potentials ($E_{1/2}$) of m-DNB and chloro substituted m-DNB compounds

Compounds	$E_{1/2}$ values (V)	
	I Wave	II Wave
m-DNB	-0.460	-0.597
Cl-2,4 DNB	-0.379	-0.525
Cl-2,6 DNB	-0.413	-0.502
Cl-3,5 DNB	-0.437	-0.516

The $E_{1/2}$ values of these chloro-substituted compounds are more positive than m-DNB. This explains the higher operating voltage of these compounds. The nitro groups are reduced polarographically at more positive potential in the following order Cl-2,4 DNB > Cl-2,6 DNB > Cl-3,5 DNB > m-DNB as seen in the first wave. The order is different for the second wave.

In the performances of the cell, the same behaviour is observed.

Low temperature studies

Figs.(4) and (5) show the discharge curves of these compounds at 8 mA cm⁻² current density at 293K and 273K. At lower temperatures,

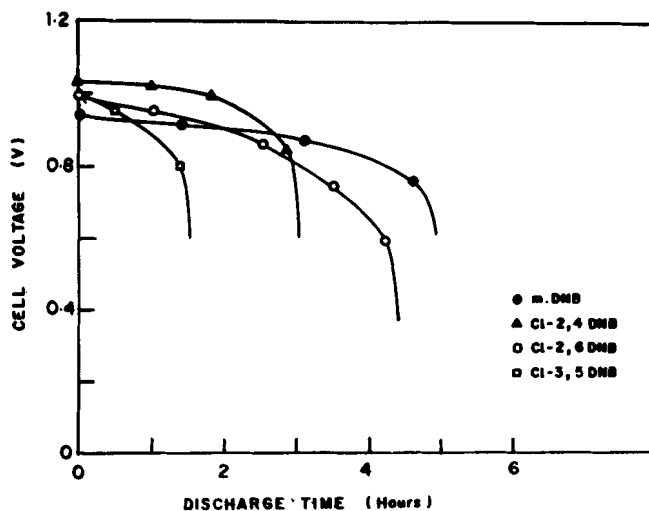


Fig.4: Discharge curves at 8mA.cm⁻² current density at 303K

when the cells are discharged at different current densities, the operating voltages of these compounds are lowered considerably.

AMPERE HOUR AND WATT HOUR EFFICIENCY

Ampere hour and watt hour per gram efficiency

Room temperature studies

Tables III and IV illustrate ampere hour per gram and watt hour per gram of these compounds at 303K.

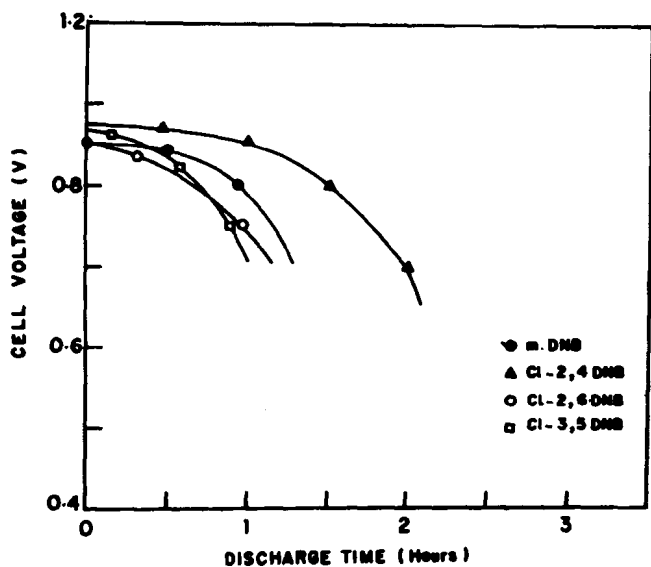


Fig.5: Discharge curves at 8mA.cm⁻² current density at 273K

TABLE-III: Ampere hour per gram at different current densities at 303K

Compounds	Ampere hour per gram			
	0.8 mA. cm ⁻²	2.4 mA. cm ⁻²	4.8 mA. cm ⁻²	8 mA. cm ⁻²
m-DNB	1.12 (0.9)	0.96 (0.9)	0.94 (0.85)	0.83 (0.8)
Cl-2,4 DNB	0.83 (0.9)	0.59 (0.9)	0.53 (0.85)	0.49 (0.85)
Cl-2,6 DNB	1.00 (0.9)	0.93 (0.9)	0.73 (0.85)	0.69 (0.8)
Cl-3,5 DNB	1.03 (0.9)	0.85 (0.9)	...	0.54 (0.8)

Parenthesis shows cut off voltage of the cell

TABLE-IV: Watt hour per gram at different current densities at 303K

Compounds	Watt hour per gram			
	0.8 mA. cm ⁻²	2.4 mA. cm ⁻²	4.8mA. cm ⁻²	8 mA. cm ⁻²
m-DNB	1.1	0.93	0.89	0.75
Cl-2,4 DNB	0.87	0.63	0.55	0.49
Cl-2,6 DNB	1.04	0.93	0.71	0.65
Cl-3,5 DNB	1.06	0.86	...	0.52

Even though chloro-substituted compounds have higher operating potential than m-DNB, the coulombic performance is lower than m-DNB. The order of ampere hour efficiency is as follows: m-DNB > Cl-2,6 DNB > Cl-3,5 DNB > Cl-2,4 DNB

The Cl-3,5 DNB is better than Cl-2,6 DNB at lower current

density only. There is no improvement in watt hour output per gram for the chloro- substituted compound as the ampere hour efficiency is low compared to m-DNB. The order of watt hour output is m-DNB > Cl-2,6 DNB > Cl-3,5 DNB > Cl-2,4 DNB, same as above.

Low temperature studies

Tables V and VI illustrate the ampere hour per gram and watt hour per gram at 303K, 273K temperatures. When temperature is lowered

TABLE-V: Ampere hour per gram at 293K and 273K at different current densities

Compound	Ampere hour per gram			
	293K temperature		273K temperature	
	2.4 mA. cm ⁻²	8 mA. cm ⁻²	2.4 mA. cm ⁻²	8 mA. cm ⁻²
m-DNB	0.73 (0.8)	0.63 (0.75)	0.30 (0.75)	0.15 (0.6)
Cl-2,4 DNB	0.46 (0.8)	0.38 (0.8)	0.42 (0.8)	0.24 (0.7)
Cl-2,6 DNB	0.65 (0.85)	0.41 (0.75)	0.29 (0.7)	0.13 (0.7)
Cl-3,5 DNB	0.38 (0.8)	0.17 (0.75)	0.21 (0.7)	0.08 (0.7)

Parenthesis shows cut off voltage of the cell

TABLE-VI: Watt hour per gram efficiency at different current densities at 292K and 273K temperatures

Compound	Watt hour per gram			
	293K temperature		273K temperature	
	2.4 mA. cm ⁻²	8.0 mA. cm ⁻²	2.4 mA. cm ⁻²	8.0 mA. cm ⁻²
m-DNB	0.66	0.54	0.26	0.13
Cl-2,4 DNB	0.45	0.36	0.39	0.20
Cl-2,6 DNB	0.64	0.36	0.25	0.10
Cl-3,5 DNB	0.36	0.16	0.18	0.07

there is a marked improvement in the performance of Cl-2,4 DNB. At 273K it is better than even m-DNB.

The general mechanism for electro-reduction in aromatic nitro group is given in Fig. (6).

Increased availability of electrons at the -C-NO₂ (carbon atom carrying the nitro group) assists the initial protonation step thereby improving the overall current density. In the case of chloro-substituted m-DNB, increased electron availability at the -C-NO₂ is possible only in the case of Cl-2,4 DNB due to -I (by the theory of alternating polarity [6] and +T effect. This in effect means that the current efficiency should be greater for these compounds than

m-DNB. However it is seen that it is lower than m-DNB. The high electron availability probably renders the compounds active, thereby facilitating side reaction. This has in fact been observed in the case of chloro-substituted compounds. The condensation

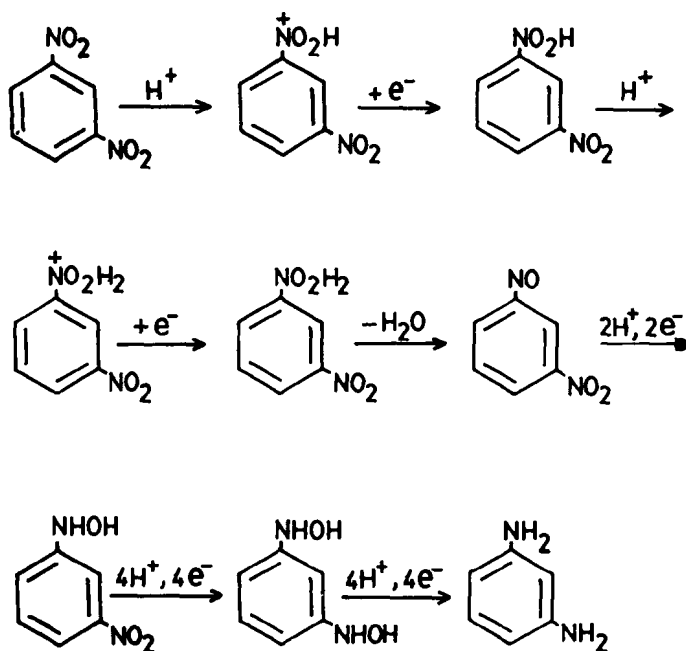


Fig.6: Mechanism of electrochemical reaction of m-DNB

between nitroso-and hydroxylamine is sufficiently rapid to permit the formation of considerable quantities of azoxy compounds. Thus there is a competition between electro-reduction of nitroso intermediate and its chemical condensation with already formed hydroxylamine derivative to form azoxy compound. This in effect reduces the current efficiency of Cl-2,6 DNB and Cl-2,4 DNB.

In the case of chloro-2,4 DNB, the chloro group is ortho to one nitro group and para to other nitro group. The presence of p-nitro group influences the formation of azoxy compounds more readily. This effect was observed in p-chloro nitrobenzene [7] when p-chloro nitrobenzene undergoes reduction; the speed of the condensation between p-chloro nitrosobenzene and p-chloro phenyl hydroxylamine even in acid solution is sufficiently rapid to permit the formation of considerable quantity of p-chloro azoxy benzene. This explains the lower efficiency observed for the ortho/para substituent. In the case of Cl-3,5 DNB, both -I and +T effect render the -C-NO₂ position more electron deficient comparatively than the ortho/para or dual ortho (Cl-2,6 DNB) substituents. This decreases the tendency for azoxy compound formation and improves the efficiency compared to 1-Cl-2,4 DNB. It is to be noted that the efficiency is still lower than that of m-DNB due to electron deficiency at -C-NO₂ position. That the variation in the

activity of the -C-NO₂ position is responsible for the alteration in current efficiency is borne by the fact that at lower temperatures, there is a change in the trend. At 273K Cl-2,4 DNB shows the best performance and is better than m-DNB. Due to lowering of temperature, moderation in the activity of the -C-NO₂ position reduces the side reaction (nitroso hydroxylamine condensation) thereby improving ampere hour per gram efficiency.

CONCLUSION

1. The operating voltage is increased by chloro substituents in m-DNB in all three positions.
2. There are two stages in electro-reduction of the compounds especially at low current drain.
3. There are two competing reactions viz. electro-reduction of -NO₂ group and chemical condensation of -NO and -NHOH to azoxy compound. Because of this, the current efficiency of the mono-chloro-substituted m-DNB is reduced especially for ortho/para and dual ortho substituents.
4. -I and +T effect of the substituents reinforce to affect the course of the reaction.

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