

MONO METHYL SUBSTITUTED *m*-DINITROBENZENE COMPOUNDS AS CATHODE MATERIALS IN MAGNESIUM BATTERIES

K. SIVASAMY* and S. RAJESWARI

Department of Analytical Chemistry, University of Madras, Madras 600 025 (India)

K. DAKSHINAMURTHI

Central Electrochemical Research Institute — Madras Unit, CSIR Complex, Madras 600 113 (India)

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Summary

The three possible mono methyl substituted *m*-dinitrobenzenes have been compared with *m*-dinitrobenzene as cathode materials in magnesium batteries. The compounds with *ortho* or *para* substituted groups show better ampere hour efficiencies than those with *meta* substituted groups. Inductive effects contribute to higher degrees of electroreduction of the nitro groups, resulting in higher efficiency.

Introduction

Conventional inorganic depolarisers such as Ag₂O, MnO₂, AgCl, PbCl₂, etc., are limited in output capacity due to single or two electron transfer in the electrochemical reaction. Several classes of organic compounds [1 - 4] with multi-electron transfer per molecule offer promise for use in batteries. *m*-Dinitrobenzene (*m*-DNB) with as high as 12 electron transfers per molecule (1.91 A h g⁻¹) has been extensively studied as a cathode material in magnesium batteries.

The effect which substituents in the benzene nucleus have on the performance of dinitro compounds has been studied by Glicksman and Morehouse [5, 6]. Electron attracting substituents such as -NO₂, -CN, -CHO, -CONH₂ enhance the cell potential, while electron repelling groups such as -CH₃, -NH₂ reduce the cell potential.

In this paper the results of studies of the effect mono methyl substituents have on the performance of *m*-dinitrobenzene in magnesium batteries at different currents and temperatures are reported. The following compounds have been investigated:

*Author to whom correspondence should be addressed.

- (i) *m*-dinitrobenzene (*m*-DNB)
- (ii) 3,5-dinitrotoluene (3,5-DNT)
- (iii) 2,4-dinitrotoluene (2,4-DNT)
- (iv) 2,6-dinitrotoluene (2,6-DNT)

Experimental

Fabrication of cell and discharge study

Circular disc cathodes of 2 cm dia. were used with 20 mesh copper grid as current collector. They were prepared by pressing the cathode mix, containing 0.4 g *m*-DNB (or the substituted compounds), 0.2 g of acetylene black (for conductivity), 0.012 g of BaCrO₄ (for inhibition of magnesium corrosion), and 0.25 ml of 3% carboxymethyl cellulose solution binder, on to the copper mesh at an optimised pressure. Magnesium perchlorate (2 M) was used as the electrolyte. The 3 × 3 cm anodes were made from a 0.8 mm thick magnesium alloy (AZ31) sheet. In each cell the cathode was situated between two anodes and separated from them by a woven polyester cloth. The cells were discharged at constant currents of 0.8, 1.6, 2.4, 4.8 and 8 mA cm⁻² at room temperature (30 °C), 20 °C and 0 °C.

All the experiments were repeated at least three times and a reproducibility of ±2% was obtained.

Half cell potential. The open-circuit half cell potential of *m*-DNB and substituted *m*-DNB electrodes was measured with regard to a calomel electrode in 2 M Mg(ClO₄)₂ electrolyte.

Polarographic study

Stock solution and supporting electrolyte. The concentration of the reactive species was 10⁻⁴ M l⁻¹ in water while 10⁻¹ M l⁻¹ magnesium perchlorate was used as a supporting electrolyte.

GC mass spectra analysis

The discharge products of *m*-DNB and substituted compounds were extracted with various solvents and analysed by gas chromatography/mass spectra (GC/MS).

Results

Cell voltage

Room temperature studies (30 °C)

Figure 1 shows the discharge curves of the four compounds at 0.8 mA cm⁻² current density. At such low currents there are two discharge plateaux in the case of *m*-DNB and 2,4-DNT. 3,5-DNT shows an initially high potential which rapidly falls to a constant voltage discharge plateau; the

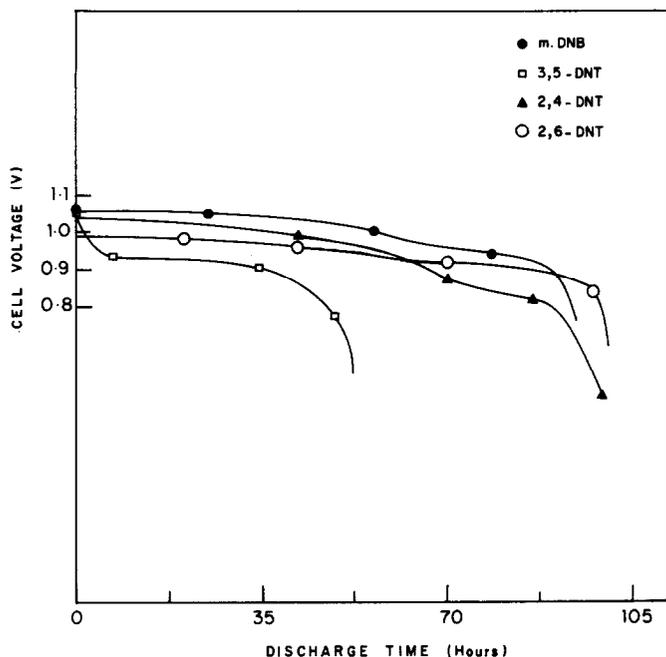


Fig. 1. Discharge curves at 0.8 mA cm^{-2} current density at 30°C .

discharge duration is only about half that exhibited by other compounds. 2,4-DNT exhibits a sloping 'S' shaped second discharge plateau. It is observed that at progressively higher currents there is only a single discharge plateau; see Fig. 2 at 8 mA cm^{-2} .

The average operating voltages of the cells using the four compounds at different currents are presented in Fig. 3. The computed internal resistances (Table 1) indicate that 3,5-DNT has the highest value of the four compounds tested. The average operating voltage at different currents is in the following order $m\text{-DNT} > 2,4\text{-DNT} > 2,6\text{-DNT} > 3,5\text{-DNT}$. As expected from refs. 5 and 6 3,5-DNT exhibits the highest initial voltage but polarisation and its high internal resistance reduce it to a low value soon after the start of the discharge.

Table 2 shows the open-circuit half cell potential of these compounds after 1 h and 24 h. Again, as expected, 3,5-DNT exhibits a higher potential than the other substituted compounds.

Polarographic studies of these compounds also indicate two waves. Table 3 shows that their half-wave potentials are in the following order: $m\text{-DNT} > 3,5\text{-DNT} > 2,4\text{-DNT} > 2,6\text{-DNT}$. This trend coincides with the half cell and operating voltages of the cells other than for 3,5-DNT.

Ampere hour per gram and watt hour per gram efficiency

Tables 4 and 5 show the effect which the substituent has on the ampere hour per gram (A h g^{-1}) and the watt hour per gram (W h g^{-1}) output.

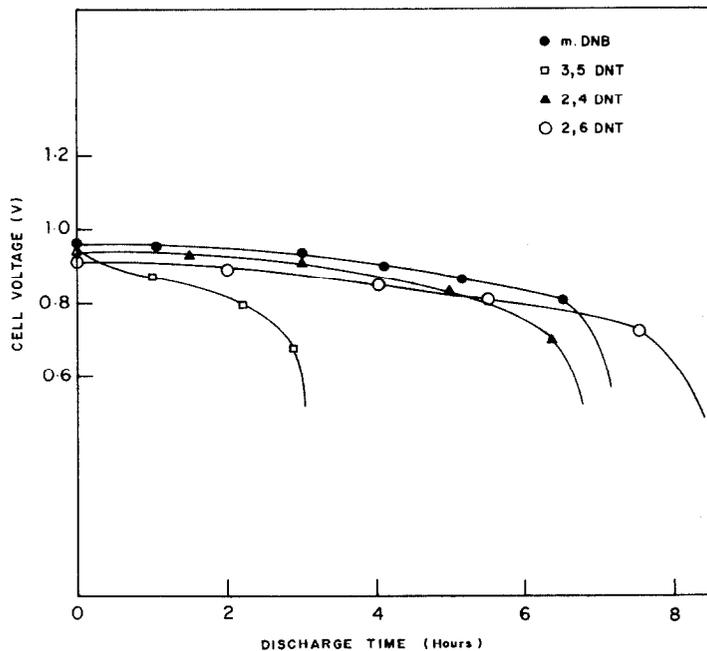


Fig. 2. Discharge curves at 8.0 mA cm^{-2} current density at 30°C .

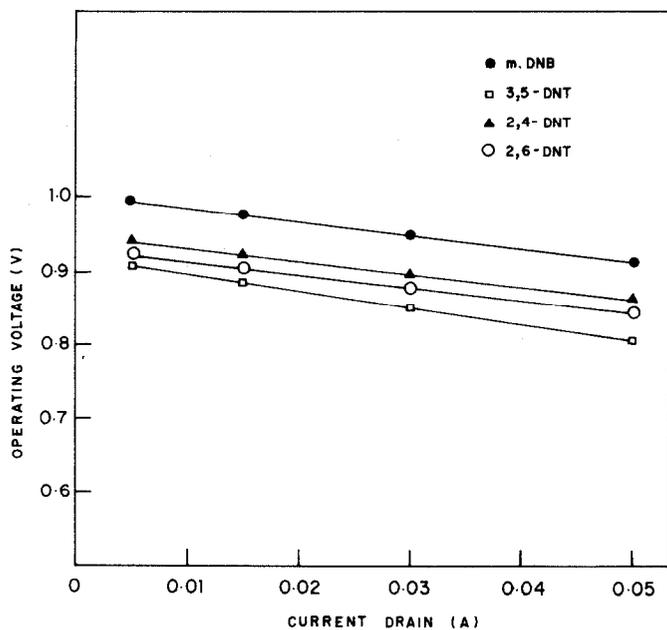


Fig. 3. Operating voltage vs. current drain at 30°C .

TABLE 1

Internal resistance values of cells using *m*-DNB and methyl substituted *m*-DNB

Compound	Internal resistance of cell (Ω)
<i>m</i> -DNB	1.81
3,5-DNT	2.53
2,4-DNT	1.67
2,6-DNT	1.74

TABLE 2

Half cell potential of *m*-DNB and methyl substituted *m*-DNB compounds

Compound	After 1 h	After 24 h
<i>m</i> -DNB	+0.142	+0.149
3,5-DNT	+0.022	+0.146
2,4-DNT	+0.086	+0.138
2,6-DNT	+0.052	+0.134

TABLE 3

Half wave potentials ($E_{1/2}$) of *m*-DNB and methyl substituted *m*-DNB compounds

Compound	$E_{1/2}$ values (V)	
	First wave	Second wave
<i>m</i> -DNB	-0.425	-0.575
3,5-DNT	-0.467	-0.527
2,4-DNT	-0.486	-0.588
2,6-DNT	-0.518	-0.605

TABLE 4

Ampere hour efficiency at different current densities at 30 °C

Compound	Ampere hour per gram				
	0.8 mA cm ⁻²	1.6 mA cm ⁻²	2.4 mA cm ⁻²	4.8 mA cm ⁻²	8.0 mA cm ⁻²
<i>m</i> -DNB	1.12 (0.9)	0.99 (0.9)	0.96 (0.9)	0.94 (0.85)	0.83 (0.8)
3,5-DNT	0.59 (0.8)	—	0.54 (0.7)	0.48 (0.7)	0.38 (0.6)
2,4-DNT	1.14 (0.8)	1.04 (0.8)	0.99 (0.8)	0.97 (0.75)	0.82 (0.7)
2,6-DNT	1.25 (0.85)	1.20 (0.85)	1.15 (0.8)	1.05 (0.75)	0.94 (0.75)

Parentheses show cut-off voltage of the cell.

TABLE 5

Watt hour efficiency at different current densities at 30 °C

Compound	Watt hours per gram				
	0.8 mA cm ⁻²	1.6 mA cm ⁻²	2.4 mA cm ⁻²	4.8 mA cm ⁻²	8.0 mA cm ⁻²
<i>m</i> -DNB	1.1	0.96	0.93	0.89	0.75
3,5-DNT	0.53	—	0.47	0.42	0.30
2,4-DNT	1.07	0.96	0.91	0.85	0.71
2,6-DNT	1.16	1.09	1.02	0.90	0.79

2,6-DNT exhibits the highest capacity in terms of both current and energy. 2,4-DNT shows higher $A\ h\ g^{-1}$ than *m*-DNB except at high currents. The *meta* substituted 3,5-DNT has poor performance at all currents yielding only half the output of the other compounds. The measured ampere hour efficiency is in the order: 2,6-DNT > 2,4-DNT > *m*-DNB \gg 3,5-DNT at all current densities. The energy density of *m*-DNB is slightly better than 2,4-DNT but otherwise the results shown in Table 5 are similar.

Performance at low temperatures

Table 6 shows $A\ h\ g^{-1}$ and $W\ h\ g^{-1}$ at 20 °C and 0 °C, when the following order of performance at different drain rates was observed: 2,4-DNT > *m*-DNB > 2,6-DNT > 3,5-DNT.

As expected, the performance at lower temperature was less than that observed at ambient temperature (30 °C).

Discussion

It can be seen from the experimental data that, of these substituted compounds, 2,6-DNT and 2,4-DNT have a somewhat better performance than *m*-DNB, while 3,5-DNT has a relatively poor performance.

The better ampere hour efficiency of 2,6-DNT and 2,4-DNT compared to *m*-DNB or 3,5-DNT is due to the inductive electron repelling effect of the methyl groups. In 2,6-DNT the proximity of the methyl group to both of the NO_2 groups (dual *ortho* position) results in superior performance. In 2,4-DNT, the methyl group is in the *ortho* or *para* position with respect to the two NO_2 groups, which results in a performance slightly inferior to that of 2,6-DNT. In 3,5-DNT, the methyl group is in the *meta* position in respect of both nitro groups and, hence, the positive effect of the methyl group on the NO_2 groups is not observed. Also, as expected from the theory of alternating polarities, the $-C-NO_2$ groups become electron deficient [7, 8]. This probably explains the low (almost half) efficiency displayed by 3,5-DNT. High internal resistance polarisation also contributes to the lower efficiency.

The reduction mechanism [9] illustrated in Fig. 4 indicates that protonation is a pre-requisite for electroreduction. The strong electric field of the double layer will influence the dipole moment or the polarisability of the reacting molecules. The methyl substituents in *ortho/para* position increase the electron density on the $-C-NO_2$ groups and facilitate the initial protonation reaction at the NO_2 groups and subsequent electron transfer. This is supported by the fact that the NH_2 groups in *ortho* or *para* positions aid the six electron transfer reaction; *i.e.*, reduction of NO_2 to NH_2 while, in the case of *p*-nitroacetanilide and *p*-dimethylaminonitrobenzene [10 - 12], the nitro group undergoes only a four electron transfer reaction. This is due to the reduced intensity of the inductive effect of the methyl groups as compared with the $-NH_2$ groups. Further, when the methyl groups are in the

TABLE 6
Ampere hour and watt hour efficiencies at different current densities at 20 °C and 0 °C

	20 °C				0 °C			
	2.4 mA cm ⁻²	4.8 mA cm ⁻²	8.0 mA cm ⁻²	8.0 mA cm ⁻²	2.4 mA cm ⁻²	4.8 mA cm ⁻²	8.0 mA cm ⁻²	8.0 mA cm ⁻²
Ampere hour per gram								
<i>m</i> -DNB	0.73 (6.8)	0.71 (0.8)	0.63 (0.75)	0.63 (0.75)	0.30 (0.75)	0.20 (0.7)	0.15 (0.6)	0.15 (0.6)
3,5-DNT	0.37 (0.8)	—	0.16 (0.8)	0.16 (0.8)	0.17 (0.6)	—	0.13 (0.6)	0.13 (0.6)
2,4-DNT	0.94 (0.7)	0.76 (0.7)	0.52 (0.7)	0.52 (0.7)	0.35 (0.7)	0.30 (0.6)	0.16 (0.6)	0.16 (0.6)
2,6-DNT	0.85 (0.7)	0.75 (0.7)	0.52 (0.7)	0.52 (0.7)	0.26 (0.7)	0.20 (0.6)	0.15 (0.6)	0.15 (0.6)
Watt hour per gram								
<i>m</i> -DNB	0.67	0.64	0.54	0.54	0.26	0.18	0.13	0.13
3,5-DNT	0.28	—	0.14	0.14	0.12	—	0.09	0.09
2,4-DNT	0.82	0.65	0.41	0.41	0.29	0.25	0.13	0.13
2,6-DNT	0.70	0.60	0.39	0.39	0.21	0.16	0.11	0.11

Parentheses show cut-off voltage of the cell.

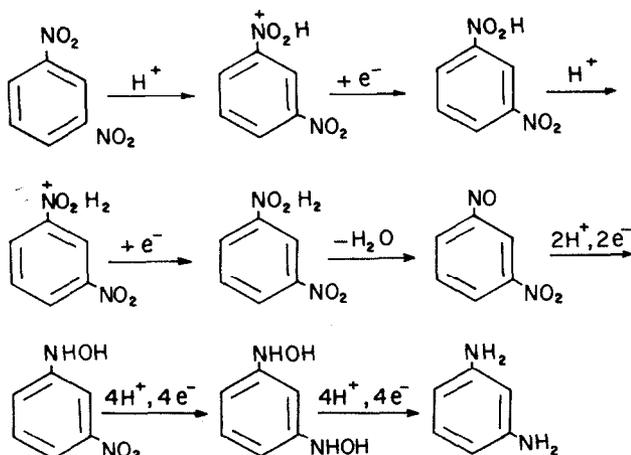


Fig. 4. Mechanism of electrochemical reaction of *m*-DNB.

m-position relative to the NO_2 group [13], the respective nitroso and hydroxylamine derivatives react chemically in an alkaline solution to form azoxy compounds. When the methyl groups are in the *ortho* or *para* positions, the hydroxylamine and nitroso derivatives do not react readily, and, as a result, the reduction proceeds to the amine stage. The impossibility of the formation of a quinonoid intermediate in the case of *meta* substituent may also be responsible for the lower reduction levels [14].

The introduction of a CH_3 group into the *ortho* or *para* positions, especially the dual *ortho* position as in the case of 2,6-DNT, aids the reduction of the NO_2 group, thereby improving the ampere hour output per gram.

Table 7 shows the ampere hour efficiency of the various compounds at different discharge rates. Since for two nitro groups the uptake of 12 electrons represents 100% efficiency, the experimental efficiency is proportional to the number of electrons transferred, as in Table 7. 2,6-DNT shows superior performance at all currents with 8 electrons ($8e$) being transferred

TABLE 7

Ampere hour efficiency and number of electrons transferred

Com- pound	0.8 mA cm ⁻²		1.6 mA cm ⁻²		2.4 mA cm ⁻²		4.8 mA cm ⁻²		8.0 mA cm ⁻²	
	A	B	A	B	A	B	A	B	A	B
<i>m</i> -DNB	59	7.1	52	6.2	50	6.0	49	6.0	44	5.3
3,5-DNT	33	4.0	—	—	31	3.7	27	3.2	22	2.6
2,4-DNT	65	7.8	59	7.1	56	6.7	55	6.6	46	5.5
2,6-DNT	71	8.5	68	8.2	65	7.8	59	7.1	53	6.4

A: Ampere hour efficiency (%).

B: Number of electrons transferred per mole.

followed by 2,4-DNT (7e) and *m*-DNB (6e). 3,5-DNT (4e), as explained earlier, does not undergo complete reduction due to side reactions. The more efficient reduction of 2,6-DNT and 2,4-DNT is essentially due to the inductive effect of the methyl group.

This is further confirmed by gas chromatographic mass spectrographic analysis. All the reactants form a mixture of azo, azoxy, nitroaniline, compounds after reduction: *i.e.*, complete reduction (12e) to diamine does not occur. The relative proportions of these products, however, vary between the different reactants.

Conclusions

(i) The ampere hour capacity of *m*-DNB reduction is enhanced by the presence of a methyl group due to an inductive effect.

(ii) There are two stages in electroreduction of the reactants, especially at low current drain.

(iii) There are two competing reactions, *viz.*, electrochemical reduction of the $-\text{NO}_2$ groups and chemical "condensation" of $-\text{NO}$ and $-\text{NHOH}$ to form azoxy compounds. Because of this 3,5-DNT shows poor efficiency during electrochemical reduction.

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