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Performance of 2,4-dinitrophenol as a positive electrode in magnesium reserve batteries ☆

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Abstract

Magnesium is an interesting anode battery material with many advantages such as its high standard potential of (−2.37 V), low cost and good low-temperature performance due to an exothermic corrosion reaction during discharge. Organic aromatic nitro compounds undergo multi-electron transfers of up to 18 during discharge, and hence, give high specific energies (up to 2 A h/g) in comparison with conventional inorganic battery depolarizers such as MnO_2, HgO, CuO and AgO. Thus, it is worthwhile fabricating and studying the performance of a battery system combining magnesium and 2,4-dinitrophenol (DNP) using aqueous halide electrolytes like $MgCl_2$, $MgBr_2$ and $Mg(ClO_4)_2$.This paper describes the preparation of DNP cathodes after standardization of the cathode mixture. Mg/DNP cells (1 V, 1 A h) have been assembled using the above cathode in conjunction with magnesium alloy (AZ 31) anodes and discharged at different current densities (1.7, 3.3, 5, 6.6 mA/cm^2) in 2 M $MgCl_2$, $MgBr_2$ and $Mg(Cl0_4)_2$. Cyclic voltammograms of DNP have been recorded in 2 M $Mg(ClO_4)_2$ at various sweep rates and concentrations in order to understand the reduction behavior. The study suggests that DNP is a suitable organic compound for use as a positive electrode material in magnesium reserve batteries.

Keywords: Magnesium; Organic cathodes; 2,4-Dinitrophenol; Reserve batteries

1. Introduction

Magnesium-based batteries [1,2] are of immense technical interest for a variety of reasons. The metal is readily available, easily machinable and possesses a high negative thermodynamic potential. The components are eco-friendly and cheap. Further, the batteries operate over a wide temperature range (−40°C to +60°C) and are gaining importance due to the possible substitution for costly lithium-based batteries [3,4] in several applications. Several organic, as well as inorganic compounds, have been investigated as possible candidates for use as positive electrode (cathode) active materials in magnesium batteries [5–7]. Among these, organic compounds containing nitro groups exhibit multi-electron transfers, and hence, are particularly recommended for use in battery applications. A comprehensive study of different organic compounds for use in reserve batteries with high specific energies was carried out by Glicksman and Morehouse [8,9]. It was concluded that dinitro compounds are promising cathode materials for use in magnesium-based systems as they involve as much as a 12 electron transfer during reduction. A study on the utility of *meta*-dinitrobenzene as well as substituted dinitrobenzene was reported by Sivasamy et al. [10]. In view of the above, it is useful to study the effect of substituents on the performance of substituted *meta*-dinitrobenzene in conjunction with magnesium anodes in different aqueous magnesium halides/perhalates as electrolyte solutions. This paper reports the performance of DNP in magnesium reserve batteries at different current densities and with different electrolytes, viz., 2 M aqueous solutions of magnesium chloride, magnesium bromide and magnesium perchlorate. Cyclic voltammetric studies have

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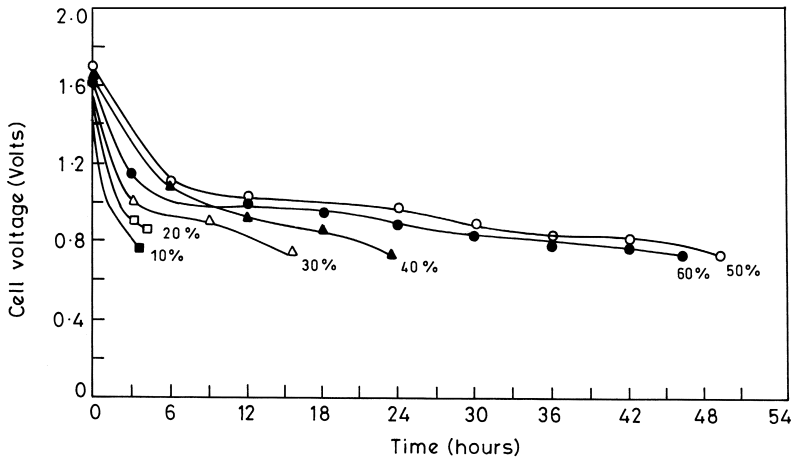

Fig. 1. Discharge curve of Mg/DNP cells: optimization of acetylene black.

been carried out on DNP to ascertain the nature of the reduction taking place in different aqueous magnesium electrolyte solutions.

2. Experimental

2.1. Chemicals

2,4-DNP, magnesium perchlorate, (E. Merck, Germany), magnesium bromide, magnesium chloride (Loba Chemie, AR) were used.

2.2. Cell assembly and discharge studies

AZ 31 magnesium alloy sheets of 1.5 mm thickness and 6 cm^2 area were used as anodes. The cathode current-collector was a copper mesh and was of the same size as the anode. The cathode consists of a mixture of 2,4-DNP initially optimized with varying amounts of acetylene black and 2 wt.% of aqueous carboxymethylcellulose (CMC) binder. The cathode mixture was spread uniformly over the current-collector and compacted at an optimized pressure of 300 kg/cm^2. The electrodes were then wrapped with cellophane sheets that served as separators.

2.3. Cyclic voltammetric studies

The DNP test solution was placed in an electrochemical cell and bubbled with nitrogen gas to give an inert atmosphere. A BAS-100A electrochemical analyser (Bio Analytical Systems, USA) was used for cyclic voltammetric studies. The electrochemical cell consisted of a glassy-carbon working electrode (area = 0.7 cm^2) and an Ag/AgCl reference electrode. Voltammograms were recorded in the potential range from −200 to −500 mV using a scan rate of 5–200 mV/s. The experiments were repeated for concordancy.

The cells were assembled with one cathode placed between two anodes. The cells were activated at room

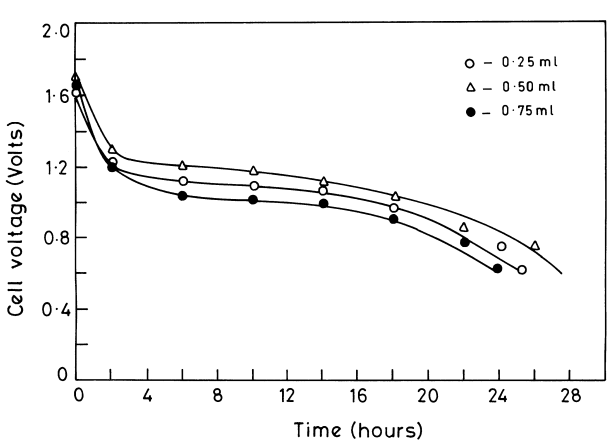

Fig. 2. Discharge curve of Mg/2,4-DNP cells: optimization of binder (CMC).

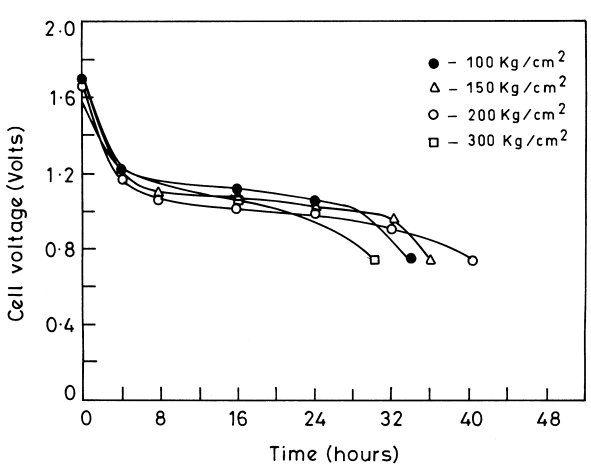

Fig. 3. Discharge curve of Mg/DNP cells: optimization of pressure.

Table 1
Optimization of acetylene black in cathode mix

Cell parameter	Acetylene black (wt.%)						
	0	10	20	30	40	50	60
Open-circuit voltage (V)	1.60	1.63	1.61	1.65	1.68	1.69	1.67
Capacity (A h/g)	–	0.07	0.08	0.31	0.48	0.98	0.91

Table 2
Optimization of binder in cathode mix

Cell parameter	CMC binder (ml)		
	0.25	0.50	0.75
Capacity (A h/g)	0.50	0.55	0.48

Table 3
Optimization of pressure in cathode mix

Cell parameter	Pressure (kg/cm^2)			
	100	150	200	300
Capacity (A h/g)	0.68	0.72	0.82	0.60

temperature using the required volume of a 2-M aqueous solution of $MgCl_2$, $MgBr_2$ or $Mg(ClO_4)_2$ as the electrolyte and the performance characteristics were evaluated.

3. Results and discussion

Figs. 1–3 present the discharge behavior of Mg/DNP for optimization of acetylene black, binder and pressure, respectively, in the cathode mixtures at 20 mA in 2 M aqueous $Mg(ClO_4)_2$ solutions at 30°C. It is evident from Fig. 1 and Table 1, that the open-circuit voltage remains constant (1.43–1.45 V) with varying composition of acetylene black. This observation is in agreement with the findings of Tye [11]. Moreover, the capacity output increases with increase in acetylene black content up to 50 wt.%, and thereafter marginally decreases. This may be due to the reduction of electroactive species and hence to a decrease in the reaction sites. Accordingly, 50 wt.% AB was taken as an optimized quantity for further investigation. The binder composition of 0.5 cm^3 is found to be the optimum, as can be seen from Fig. 2 and Table 2. This fact could be due to the fall in resistance of the electrode with decrease in binder content. It is observed however, that a minimum of 0.4–0.5 cm^3 is necessary for the mechanical strength of the cathodes. Table 3 and Fig. 3 show that the maximum capacity obtained at 200 kg/cm^2 pressure can be assigned to maximum porosity of the cathode. Beyond this pressure, the capacity of the cell declines, which may be due to a decrease in porosity.

The discharge behavior of Mg/DNP cells follows a flat discharge plateau with an initial decay in voltage. The average operating voltage is in the order $Mg(ClO_4)_2 > MgCl_2 > MgBr_2$ (Figs. 4–7). The internal resistance

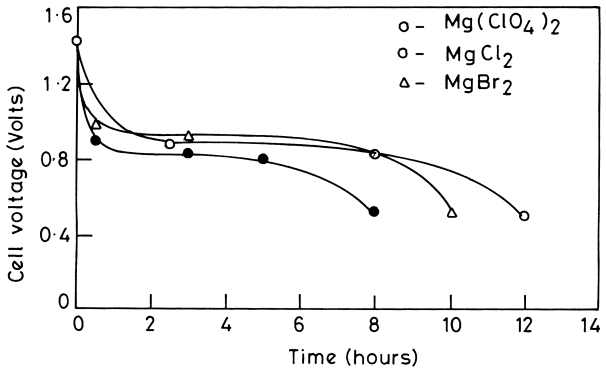

Fig. 5. Discharge curve of Mg/DNP cells in different electrolytes at 3.33 mA/cm^2.

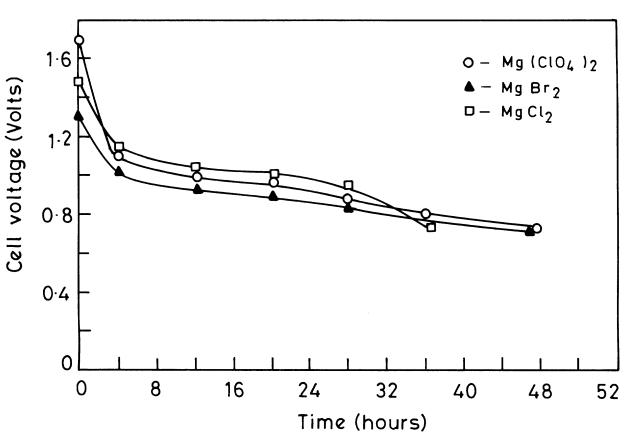

Fig. 4. Discharge curve of Mg/DNP cells in different electrolytes at 1.67 mA/cm^2.

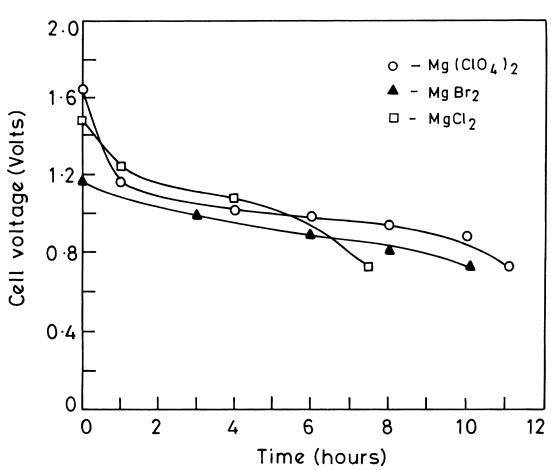

Fig. 6. Discharge curve of Mg/DNP cells in different electrolytes at 5 mA/cm^2.

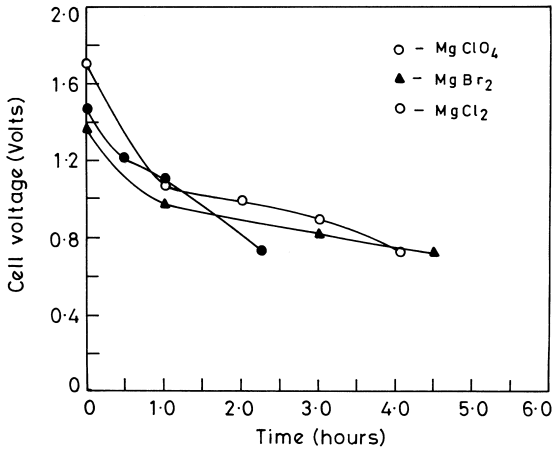

Fig. 7. Discharge curve of Mg/DNP cells in different electrolytes at 6.67 mA/cm^2.

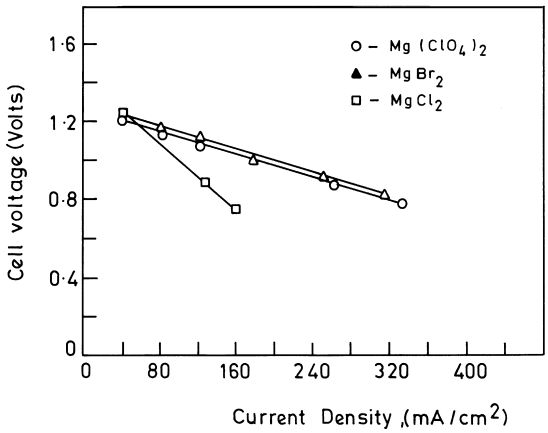

Fig. 8. Operating potential of Mg/DNP cells at various current densities and electrolytes.

(Table 4) of the cells in different electrolytes indicated that the lower value is obtained in the case of $Mg(ClO_4)_2$ and hence enhances the operating voltage. The average voltage of the cells at various current densities and in different electrolytes is presented in Fig. 8. Table 5 presents the capacity of Mg/DNP cells obtained at different current densities and electrolytes. It is seen that $Mg(ClO_4)_2$ exhibits superior behavior up to the highest current density investigated. It is observed that the performance in different electrolytes, viz., $Mg(ClO_4)_2$, $MgBr_2$, and $MgCl_2$, shows almost the same capacity up to the highest current density, even though the corrosion of Mg anode is different in each electrolyte [12].

Comparison of the present results with our earlier studies on 3,5-DNT (Table 6) shows that the capacity obtained in the case of DNP is higher throughout the investigated range of current density. This can be attributed to the ease of electron acceptance by the nitro group. Further, the higher efficiency of DNP can also be due to a greater degree of electrode reduction of the nitro groups due to an inductive effect. The number of electrons transferred is maximum in the case of $Mg(ClO_4)_2$ at all current densities investigated (Table 7). At higher current densities, however, the electron reduction is less due to increased polarization.

Cyclic voltammetric studies of DNP reveal only a well-defined cathodic peak the reduction process has an irreversible nature, as depicted in Fig. 9. The studies were carried out in the potential range 0.200–0.500 V for various concentrations and sweep rates. Further, with increasing sweep rate (ν) and concentration (C), the peak potential (E_p) shifts to a more negative value, thereby confirming the irreversible nature. All the studies were carried out in 2 M $Mg(ClO_4)_2$ electrolyte (Fig. 10). A plot of i_p vs. $\sqrt{\nu}$ gives a linear relationship (Fig. 11). These

Table 4
Internal resistance of Mg/DNP cells in different electrolytes

Electrolyte	Internal resistance (Ω)
$Mg(ClO_4)_2$	1.25
$MgBr_2$	1.36
$MgCl_2$	1.45

Table 5
Capacity (A h/g) at various current densities for different electrolytes

Electrolyte	Capacity (A h/g)			
	1.7[a]	3.3[a]	5.0[a]	6.7[a]
$Mg(ClO_4)_2$	0.96	0.80	0.67	0.33
$MgBr_2$	0.95	0.72	0.60	0.36
$MgCl_2$	0.74	0.52	0.45	0.18

[a]Current density (mA cm^{-2}).

Table 6
Comparison of 2,4-DNP with 3,5-DNT

Organic cathode	Capacity (A h/g)	
	1.6[a]	4.8[a]
3,5-DNT	–	0.48
2,4-DNP	0.96	0.67

[a]Current density (mA cm^{-2}).

Table 7
Capacity efficiency (%) and number of electrons transferred (n) in Mg/DNP cells

Electrolytes	Current density (mA/cm^2)							
	1.7		3.3		5.0		6.7	
	n	%	n	%	n	%	n	%
$Mg(ClO_4)_2$	6.6	55	5.5	46	4.6	38	2.3	19
$MgBr_2$	6.5	54	4.9	41	4.1	34	2.4	20
$MgCl_2$	5.1	42	3.5	29	3.1	25	1.2	10

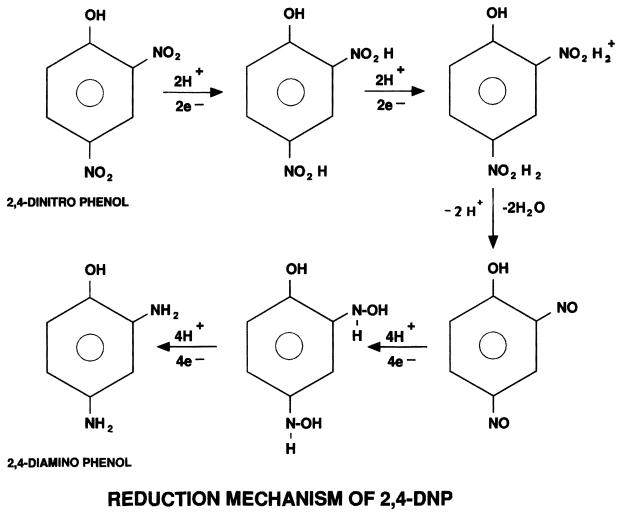

Fig. 9. Reduction mechanism of 2,4-DNP.

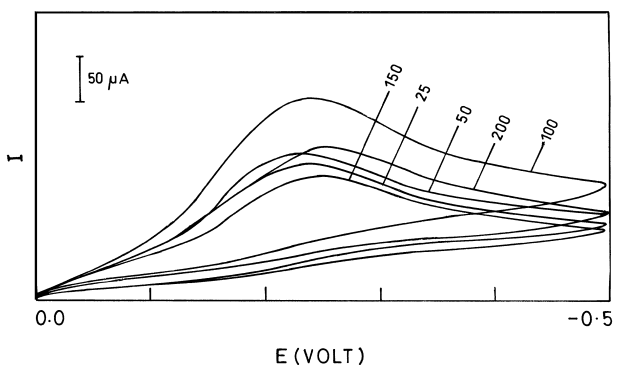

Fig. 10. Cyclic voltammogram of 7.5 mM 2,4-DNP in 2 M $Mg(ClO_4)_2$ at various sweep rates.

results suggest that reduction of DNP is diffusion-controlled.

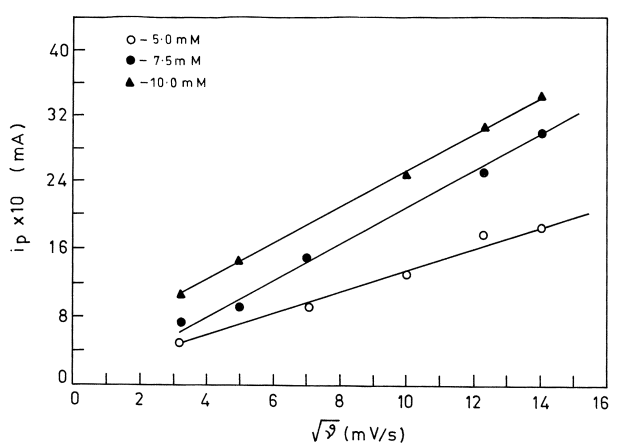

Fig. 11. Variation of peak current (i_p) with sweep rate (ν).

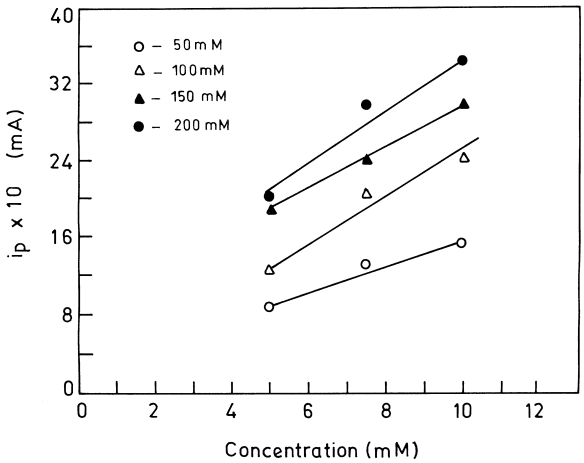

Fig. 12. Variation of peak current (i_p) with concentration (C) of DNP.

A plot of i_p vs. C also indicates a linear relationship (Fig. 12). A constant value is observed for $i_p/Ac\sqrt{\nu}$ (A = area of the working electrode) from Table 8. These factors further confirm that the reduction of DNP proceeds via a diffusion-controlled process. Qualitative analysis was carried out on the end product obtained after the discharge of the cells. The following procedure was performed to test for the presence of amine. The material was dissolved in dilute HCl and sodium nitrate solution was added. A clear solution was obtained. This was treated with β-napthol in NaOH solution and placed in ice-cold water for 5 min. A scarlet red dye was obtained, which thereby confirmed the presence of amine.

Table 8
Effect of concentration (C) and sweep rate (ν) on the reduction of DNP in $Mg(ClO_4)_2$ solution

Concentration (mM)	Sweep rate, ν (mV/s)	$i_p \times 10^5$ (mA)	$-E_p$ (mV)	$i_p/\sqrt{\nu} \times 10^{-5}$	$i_p/AC\sqrt{\nu}$
5	5	9.5891	269	4.288	12.25
	10	4.7823	260	1.512	4.32
	50	8.5247	275	1.206	3.46
	100	12.315	283	1.231	3.52
	150	19.809	305	1.617	4.62
	200	19.092	334	1.350	3.86
7.5	10	8.0275	223	2.538	4.83
	25	8.2136	241	1.643	3.13
	50	13.785	235	1.949	3.71
	100	20.755	224	2.075	3.95
	150	24.229	252	1.978	3.77
	200	29.990	261	2.121	4.04
10	10	10.357	250	3.275	4.68
	25	14.478	282	2.895	4.14
	50	15.771	297	2.230	3.19
	100	24.451	312	2.445	3.49
	150	30.451	325	2.486	3.55
	200	34.516	334	2.440	3.49

4. Conclusion

1. A steady operating voltage is observed for DNP in comparison to 3,5-DNT.
2. The cathode efficiency of DNP is 55% at low current densities (1.7 mA/cm^2) and is 19% even when the current density is increased to 6.7 mA/cm^2.
3. The electrochemical reduction of DNP is irreversible and diffusion-controlled.

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