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PERFORMANCE OF META-NITROANILINE IN MAGNESIUM RESERVE BATTERIES

S REKHA, R THIRUNAKARAN, A SIVASHANMUGAM, S GOPUKUMAR AND R GANGADHARAN

Central Electrochemical Research Institute, Karaikudi 630 006, Tamilnadu, INDIA

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IV/-1Ah Magnesium (Mg)/m-nitro aniline (MNA) cells have been constructed using Mg anode and MNA cathode. The cells were investigated for their performance behaviour at different current densities and with various aqueous magnesium electrolytes viz: magnesium chloride [$MgCl_2$], Magnesium perchlorate [$Mg(ClO_4)_2$] and magnesium bromide [$MgBr_2$], after initial standardization of the cathode mix. The discharge behaviour of the above magnesium cells are discussed in terms of cathodic efficiency of MNA. Cyclic voltammetric studies of MNA cells were carried out which indicates the irreversible nature of the depolarizer.

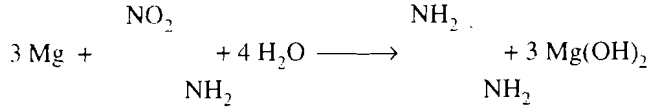
Keywords: m-Nitroaniline, Cathodes, Magnesium, Reserve batteries

INTRODUCTION

It is evident that the interest on the development of newer power sources, especially in primary battery system, using magnesium as anode is renovating and enterprising as an alternative to sophisticated and costlier lithium technology [1,2]. Further magnesium offers high energy, low cost, wide temperature range of operation and comfortable handling in conjunction with organic nitro-compounds.

Organic depolarizers especially dinitro aromatic compounds have been suggested as battery depolarizers in view of their reduction behaviours involving a transfer of 12 electrons. However, recent studies reveal that substituted mono nitro-aromatic compounds like p-nitrotoluene, p-nitroaniline etc., offer better reduction efficiency than dinitrocompounds. Organic aromatic nitro compounds have been attractive cathode depolarizers in conjunction with the magnesium anode as they offer high energy densities similar to conventional inorganic battery depolarizer like MnO_2, AgO, CuO etc.

In view of the above, it is of interest to carry out a comprehensive investigation on the performance of meta nitroaniline (MNA) as a cathodic depolarizer in magnesium reserve cells. The basic reaction involved is



$$3\,Mg + \underset{NH_2}{\overset{NO_2}{\text{C}_6\text{H}_3}} + 4\,H_2O \longrightarrow \underset{NH_2}{\overset{NH_2}{\text{C}_6\text{H}_3}} + 3\,Mg(OH)_2$$

In the present communication, we report the discharge characteristics of Mg/MNA cells using different aqueous magnesium electrolytes like 2 *M* aqueous $MgCl_2$, $MgBr_2$ and $Mg(ClO_4)_2$ at various current densities viz 1.7, 3.3, 5, 6.7 mA/cm^2

EXPERIMENTAL

Chemicals

MNA (E.Merk, Germany), $MgCl_2$, $MgBr_2$ [Loba/Chemie, AR] and $Mg(ClO_4)_2$ [E.Merk, AR] were used.

Anode and Cathode

Mg(AZ31) alloy, sheets of size 3 cm x 2 cm x 1.5 mm were used as the anode and the cathode was fabricated by the following method from a mix containing acetylene black (AB), carboxymethyl cellulose (CMC) binder optimised for pressure and composition.

Optimization of acetylene black (AB)

Organic nitrocompounds are well known for their low conducting nature [3,4] and hence MNA was mixed with AB to increase the conductivity and surface area of the electrodes. One gram of MNA was taken as cathode material and was mixed in varying proportions of AB (upto 60%) and 0.5 ml CMC binder. The prepared mix were spread over a copper mesh (current collector) and wrapped with multilayers of cellophane sheets and pressed at a pressure of 200 Kg/cm^2. The cells were assembled by placing the cathode in between a couple of Mg AZ31 anodes of above dimensions and discharged at a current density of 1.7 mA/cm^2 in 2 *M* aqueous $Mg(ClO_4)_2$ electrolyte.

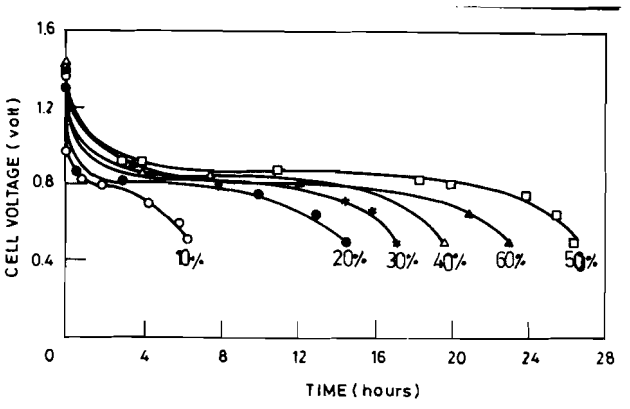


Fig. 1: Discharge curve of Mg/MNA cells: Optimisation of acetylene black

Optimization of binder composition

Cathodes were fabricated as described above using the optimized AB and different volume of 2% aqueous CMC binder ie., 0.25, 0.50, 0.75 ml. The cells were discharged at a current density of 1.7 mA/cm^2 in 2M aqueous $Mg(ClO_4)_2$ electrolyte.

Standardization of pressure

Cathodes containing optimized AB and CMC binder were pressed at various pressure viz., 100, 150, 200, and 300 Kg/cm^2. The discharge characteristics of the cells were studied at a current density of 1.7 mA/cm^2 and in 2 *M* aqueous $Mg(ClO_4)_2$ medium.

Discharge study

Mg/MNA cells containing two magnesium AZ31 anodes enveloping the cathodes fabricated with the optimized AB, binder composition and pressure were placed in a PVC container and activated with different electrolytes viz., 2M aqueous $Mg(ClO_4)_2$, $MgCl_2$ and $MgBr_2$. [5]. Their performance characteristics were evaluated at different current densities (1.7, 3.3, 5.0 and 6.7 mA/cm^2).

Cyclic voltammetry

Experimental solution was prepared by dissolving MNA in small amount of acetonitrile and made up to the desired concentration with 2M aqueous $Mg(ClO_4)_2$ electrolyte. The test sample was taken in an electrochemical cell and investigated at various concentration of MNA and sweep rates (50 to 250 mVs^{-1}) in the potential range 0.000 to -0.700 V.

All measurements were carried out with respect to Ag/AgCl reference electrode.

RESULTS AND DISCUSSION

Discharge characteristics of Mg/2 *M* aqueous $Mg(ClO_4)_2$/MNA cells for optimization of AB, CMC binder and pressure are presented in Figs. 1-3 respectively. From Fig. 1, it is inferred that the open circuit voltage remains constant for varying proportions of AB. This is in agreement with the observation of Tye [6]. The capacity output increases with increase in concentration of AB upto 50%. Further increase of AB decreases the capacity marginally which may be due to the masking of active materials and subsequent reduction in active reaction sites. Thus, 50% is taken as optimized composition for further discharge studies.

It is observed from Fig. 2. that 0.5 ml is the optimum binder composition. This fact may be accounted for the decrease in resistance of the electrodes.

Fig. 3. indicates that 200 Kg/cm^2 pressure gives higher capacity. Further, increase in pressure leads to capacity fall due to loss of porosity of the electrode and hence the standardised pressure is 200 Kg/cm^2 which also ensures adequate mechanical strength of the electrodes.

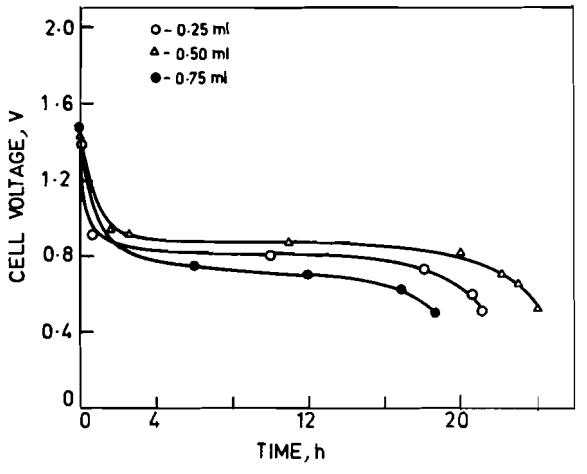


Fig.2. Discharge curve of Mg/MNa cells: Optimisation of binder (CMC)

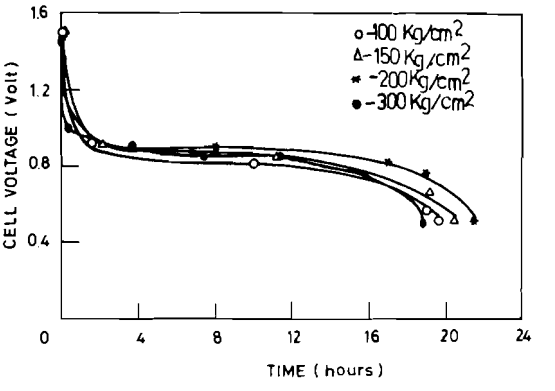


Fig.3. Discharge curve of Mg/MNA cells: Optimisation of pressure

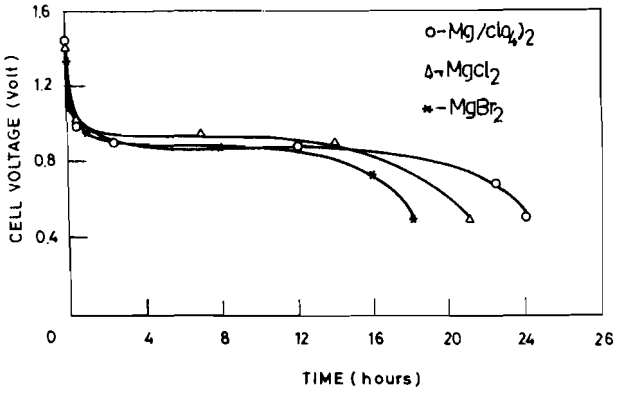


Fig. 4: Discharge curve of Mg/MNA cells in different electrolytes at 1.67 mA/cm²

Discharge characteristics of Mg/MNA at different current densities and in various electrolytes are shown in Figs. 4-7 and the results are tabulated in Table I. The discharge curves show a flat profile with initial decay of voltage and the average operating voltage is in the order $Mg(ClO_4)_2$ > $MgCl_2$ > $MgBr_2$

The internal resistance (Fig. 8 and Table II) of the cells in different electrolytes indicates the lower value for $Mg(ClO_4)_2$ which thereby enhances the operating voltage.

Table I indicates that at lower current densities (upto 3.3 mA/cm²) the performance of cells employing 2 *M* aqueous $Mg(ClO_4)_2$ shows marginally higher capacity but in the case of other two aqueous electrolytes ($MgCl_2$ and $MgBr_2$) similar performance is observed indicating that the reduction of nitro group in the meta-position is influenced in neutral aqueous $Mg(ClO_4)_2$ medium (*p*H = 6.8) rather than slightly acidic $MgCl_2$ (*p*H = 5.8) solution. However, at higher current densities all the three electrolytes show similar performance. This fact may be explained in terms of concentration polarisation of the electrodes which arises due

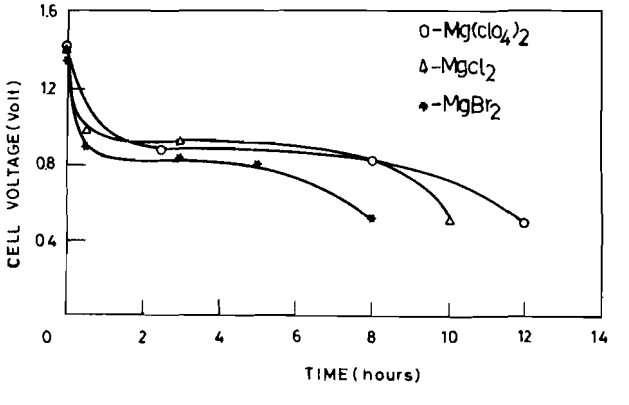


Fig. 5: Discharge curve of Mg/MNA cells in different electrolytes at 3.33 mA/cm²

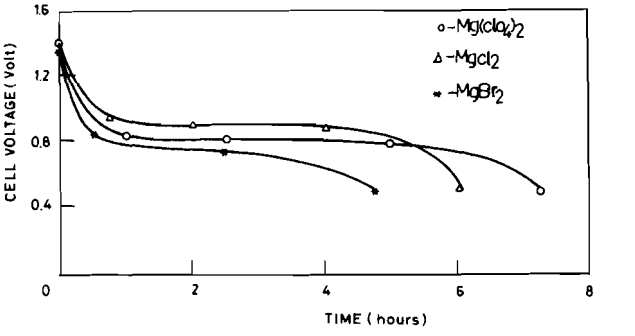


Fig. 6: Discharge curve of Mg/MNA cells in different electrolytes at 5.00 mA/cm²

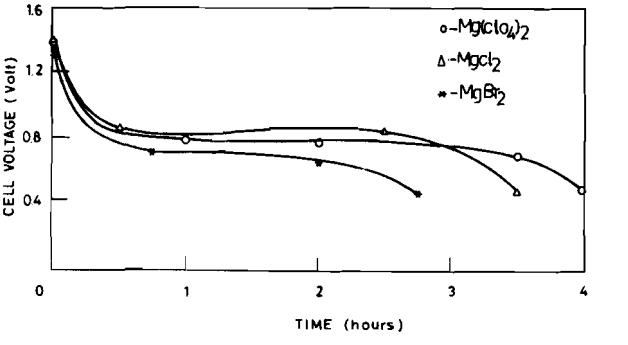


Fig. 7: Discharge curve of Mg/MNA cells in different electrolytes at 6.67 mA/cm²

to the formation of amines, a soluble reduction product of MNA which enables the attainment of saturation of $MgCl_2$ and $MgBr_2$ electrolytes and thereby offsets further reduction of MNA in $MgCl_2$ and $MgBr_2$ medium due to the slow stripping of the discharge product and so at low current densities a slight reduction of capacity is observed in $Mg(ClO_4)_2$ medium. Furthermore, the salvation of amines in $MgCl_2$ and $MgBr_2$ solutions marginally shifts their slight acidic *p*H towards neutral side thereby altering the corrosion rate of Mg anode.

TABLE I: Capacity (Ah/g) at various current densities for different 2 *M* aqueous magnesium electrolytes

Electrolyte	Ah/g Capacity Current densities at (mA/cm²)			
	1.7	3.3	5.0	6.7
$Mg(ClO_4)_2$	1.06	0.96	0.87	0.64
$MgCl_2$	0.84	0.80	0.72	0.56
$MgBr_2$	0.72	0.64	0.58	0.45

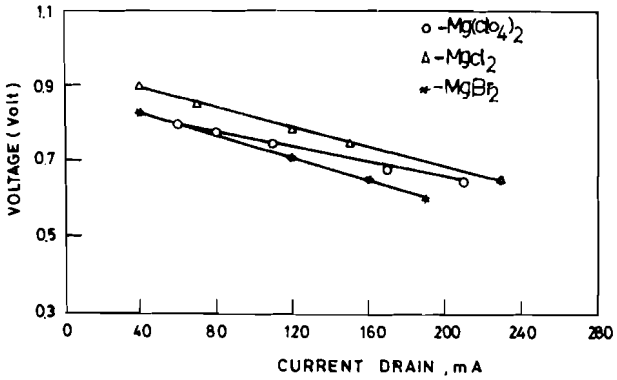


Fig. 8: Operating potentials of Mg/MNA cells at various current densities and electrolytes

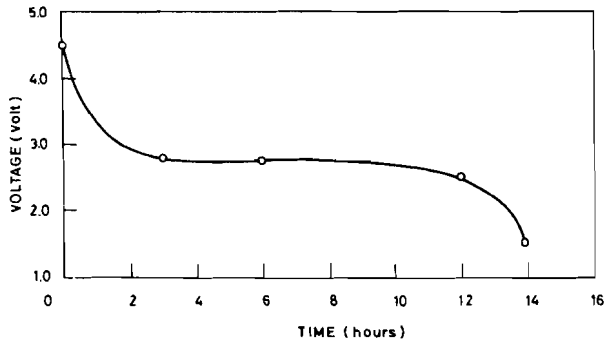


Fig. 9: Discharge curve of 3V/1Ah Mg/MNA battery in $Mg(ClO_4)_2$ electrolyte

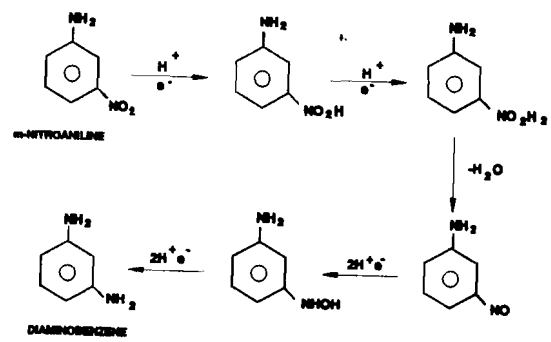


Fig. 10: Reduction Mechanism of MNA

It is interesting to observe that the performance of 3 V/1 Ah (Fig. 9) Mg/2 *M* aqueous $Mg(ClO_4)_2$/MNA battery discharge at current density of 4.16 mA/cm^2 is similar to that of its single cell i.e., same cathodic efficiency. The complete reduction of m-nitroniline to m-aminoaniline (Fig. 10) involves six electrons transfer at 100% cathodic efficiency. The number of electrons transferred (n) and cathodic efficiency are tabulated in Table III. It is seen that the efficiency and number of electron transfer decreases with increase in current density in all electrolytes. The maximum efficiency is found in 2 *M* aqueous $Mg(ClO_4)_2$ medium for all current densities.

The present work was compared with our earlier studies on PNA (p- nitro aniline) [6] and it is interesting to see that the capacity obtained is higher throughout the investigated current densities in MNA cells. This fact could be accounted as the ease of electron acceptance by nitro group in meta position and the higher degree of reduction of nitro group is due its inductive effect.

Cyclic voltammetry studies were carried out using a BAS-100A (electrochemical analyzer) to obtain information on the reduction behaviour on MNA. The voltammogram (Fig. 11) shows a well defined cathodic peak alone indicating the reduction process is irreversible and the reduction potential (E_p) was in the range of 0.000 to -0.500 V. For various concentration and sweep rates the peak potential shift to the cathodic direction confirming the irreversibility of the compound.

A plot of i_p *vs.* C (Fig. 12) and i_p *vs.* $\gamma^{1/2}$ (Fig. 13) shows a linear relationship and a constant value is observed for $i_p/AC\gamma^{1/2}$ (A = Area of working electrode) as presented Table IV. Thus, reduction of MNA is a irreversible and diffusion controlled process.

TABLE II: Internal registance of Mg/MNA cells in different 2 *M* aqueous magnesium electrolytes

Electrolyte	Internal resistance (Ω)
$Mg(ClO_4)_2$	1.00
$MgCl_2$	1.25
$MgBr_2$	1.70

TABLE III: Cathode efficiency (%) and number of electron(s) transferred in Mg/MNA cells in different 2 *M* aqueous magnesium electrolytes

Electro lyte	Current density (mA/cm^2)							
	1.7		3.3		5.0		6.7	
	n	%	n	%	n	%	n	%
X	5.4	91	4.9	82	4.5	74	3.3	55
Y	4.1	72	3.9	68	3.7	62	2.9	49
Z	3.7	62	3.3	55	3.0	50	2.3	38

X = $Mg(ClO_4)_2$; Y = $MgCl_2$ and Z = $MgBr_2$