

## Performance characteristics of magnesium–*N,N'*-dichlorodimethylhydantoin primary cell

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(Received July 27, 1990)

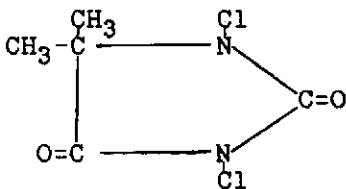
### Abstract

The electrochemical characteristics of cells using *N,N'*-dichlorodimethylhydantoin (DDH) as a cathode depolarizer and magnesium anodes are reported. The discharge behaviour of DDH gives high cathode potential and efficiency. The discharge data are fitted to a general equation to express the voltage/current features of the system. Cyclic voltammograms of DDH in neutral electrolytes substantiate the claimed reduction behaviour. Magnesium bromide solution provides higher capacities than  $\text{Mg}(\text{ClO}_4)_2$  but corrosion of the magnesium anode is more severe in the former electrolyte.

### Introduction

Magnesium batteries offer several advantages over conventional systems. They have high energy density, long shelf life, and good low-temperature performance. Inorganic depolarisers such as  $\text{MnO}_2$ ,  $\text{CuO}$ ,  $\text{HgO}$ ,  $\text{AgCl}$  and  $\text{PbCl}_2$  have an inherently limited coulombic capacity output by comparison with organic depolarisers. This is because the former materials undergo a 1- or 2-electron transfer, whereas organic compounds are capable of a 6- to 12-electron transfer, as in the case of nitro and nitroso compounds. In the, 1950s, Glicksman and Morehouse [1, 2] studied, extensively, a number of organic compounds as cathodic depolarisers in batteries. Among these, aromatic nitro compounds were later found [3] to be superior to other series of organic compounds because of their high coulombic capacity. Only a few investigations have been reported [4, 5] on the performance of various N-halogen organic compounds in primary reserve batteries. The present work reports experiments on a battery couple consisting of *N,N'*-dichlorodimethylhydantoin (DDH) as a cathode depolariser and magnesium alloy as anode material; activation is achieved with  $\text{Mg}(\text{ClO}_4)_2$  and  $\text{MgBr}_2$  electrolytes.

The structure of DDH is:



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DDH is a strong oxidising agent, as the reactive positive halogen ion attached to the nitrogen atom in the molecule is released as chlorine in an oxidation reaction. Based on a 4-electron transfer process, the coulombic capacity of DDH is  $32.6 \text{ A min g}^{-1}$ . The open-circuit voltage of  $\text{Mg}/\text{Mg}(\text{ClO}_4)_2/\text{DDH}$  is 2.50 V, which is 1.0 V higher than that of an  $\text{Mg}/\text{Mg}(\text{ClO}_4)_2/\text{meta-dinitrobenzene}$  system. The characteristics of DDH have been studied by discharging cells at different current drains, viz., 25–250 mA, with magnesium perchlorate and magnesium bromide electrolytes. Cyclic voltammetric studies of DDH in these electrolytes have also been carried out. The discharged magnesium anodes have been analysed by scanning electron microscopy (SEM).

## Experimental

### *Fabrication and discharge study*

In order to determine a suitable cathode current-collector (grid), plates were prepared using stainless steel, copper, nickel, or titanium expanded grids. The latter metal was found to be most suitable due to its superior resistance to corrosion. Hence, titanium expanded grids (6 mesh) were employed throughout this investigation.

$\text{Mg}/\text{DDH}$  cells were assembled in Perspex containers of size  $3.5 \times 2.5 \times 1.0$  cm. Magnesium alloy (AZ 31) sheets of dimensions  $2 \times 3 \times 0.5$  cm were used for the anodes. The cathode mix, containing 1 g DDH, 0.5 g acetylene black, and 0.8 ml of an aqueous solution of 2% carboxymethyl cellulose binder was pressed onto a titanium metal expanded grid at an optimised pressure. In each cell, the cathode was situated between two anodes and separated from them by a Cellophane paper. The cells were activated with electrolyte solutions of 2 M magnesium perchlorate and magnesium bromide. Sufficient time was allowed for the complete wetting of the electrodes before the discharge was commenced. The cells were discharged at constant currents in the range 25–250 mA. All experiments were carried out at room temperature ( $30 \pm 1$  °C). Duplicate experiments were also undertaken.

### *Half-cell potential*

The half-cell potential of the DDH electrode was measured against an  $\text{Ag}/\text{AgCl}$  reference electrode at regular intervals during cell discharge. All potentials are reported with regard to this electrode.

### *Cyclic voltammetric studies*

Stock solutions of 0.1 M  $\text{Mg}(\text{ClO}_4)_2$  anhydrous (Baker Analyzed Reagent) and 0.1 M  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  (Riedel–De Haen AG, Seelze–Hannover) were prepared in double-distilled water. A 0.1 M DDH solution (Aldrich Chemical Company, Inc.) was prepared in 100% ethanol immediately prior to experimentation.

All studies were conducted with a BAS 100A Electrochemical Analyser (Bio Analytical System, U.S.A.) in conjunction with a DMF-40 series (Houston Instrument Division) digital plotter. A platinum electrode (2 mm dia. embedded

in Teflon) and an Ag/AgCl electrode were used as the working and reference electrodes, respectively. A platinum wire of large area served as a counter electrode. The cyclic voltammograms were recorded in the potential range between  $-200$  and  $-600$  mV versus Ag/AgCl.

### SEM analysis of magnesium alloy

When the cut-off voltage of the cell was reached, the magnesium plates were immediately removed and cleaned in a boiling solution of 20%  $H_2CrO_4$ , containing 0.02%  $AgNO_3$ , for 2 min. The plates were then washed with double-distilled water.

## Results and discussion

### Effect of acetylene black content on capacity

Cells ( $Mg/Mg(ClO_4)_2/DDH$ ) were fabricated using percentages of acetylene black varying between 10 and 60%. The actual capacities of the cells were determined for constant-current discharge at 25 mA; the results are plotted in Fig. 1. It can be seen that both the voltage and the capacity of the cell increase with increasing acetylene black content. The voltage-current relationship for differing percentages of acetylene black is given in Fig. 2. Slope values are higher in lower concentrations of acetylene black due to an increase in the internal resistance, and therefore to a reduction in the conductivity of the cathode.

### Half-cell potential

The half-cell potential of the DDH cathode was measured as a function of time at various constant-current drains in both  $Mg(ClO_4)_2$  and  $MgBr_2$

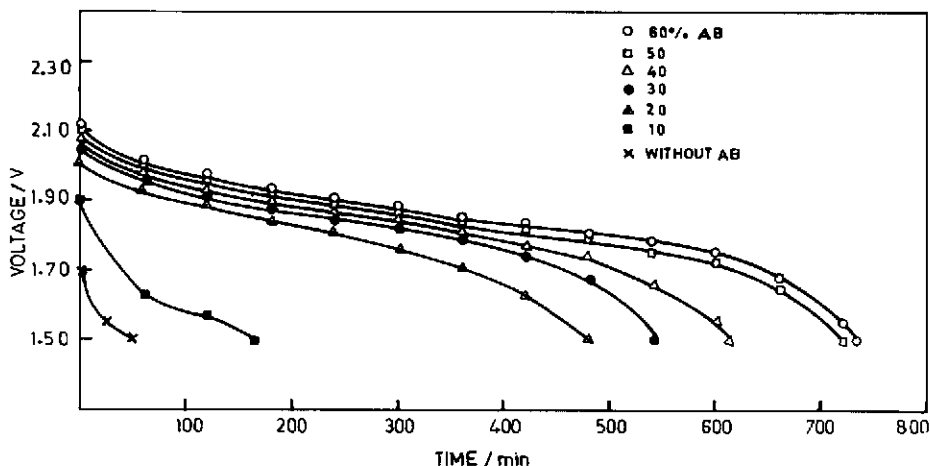


Fig. 1. Effect of acetylene black content on the performance of an  $Mg/Mg(ClO_4)_2/DDH$  cell at 25 mA current drain.

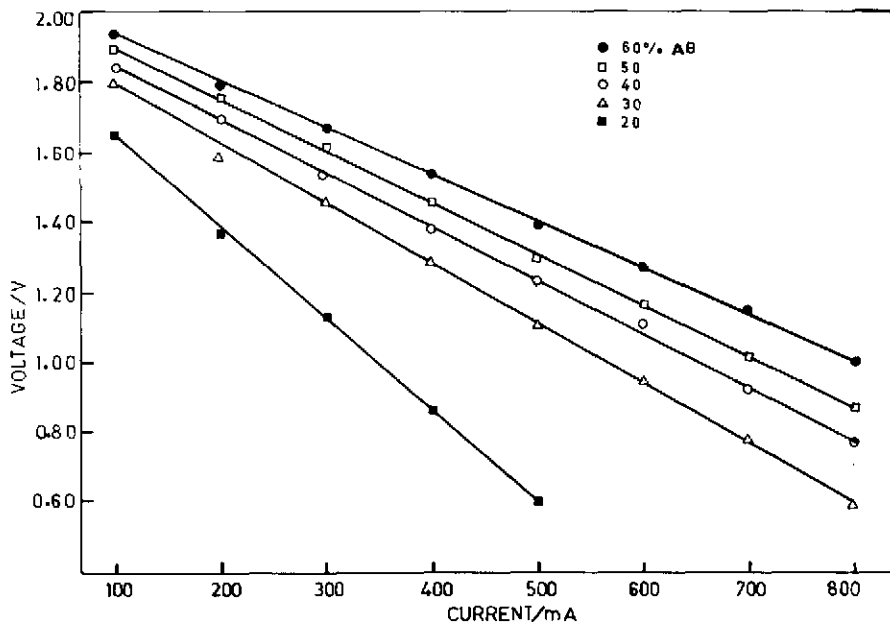


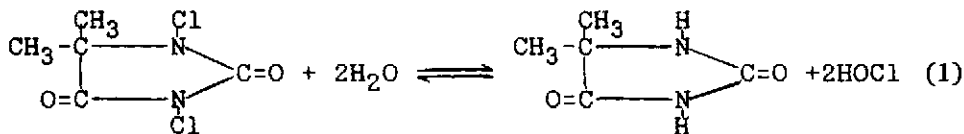
Fig. 2. Voltage/current characteristics of  $Mg/Mg(ClO_4)_2/DDH$  cells with differing acetylene black contents.

electrolytes, Fig. 3(a), (b). The potential is much higher than those for other organic compounds due to the presence of the halogen group (i.e., an electron attracting substituent) in DDH.  $Mg/MgBr_2/DDH$  cells exhibit a slightly higher potential and higher capacities than cells employing  $Mg(ClO_4)_2$ . This behaviour results from the lower pH. Chemical corrosion of the magnesium electrode is, however, greater in cells using  $MgBr_2$ .

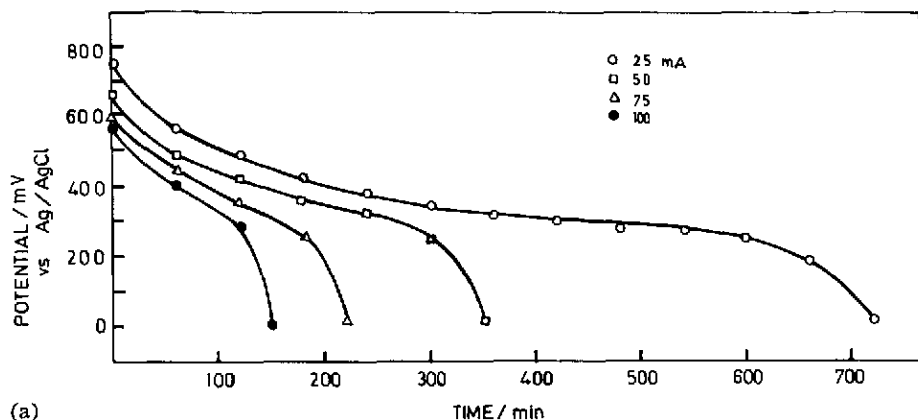
#### *Discharge characteristics of $Mg/Mg(ClO_4)_2/DDH$ and $Mg/MgBr_2/DDH$ cells*

The discharge characteristics of the cells under various constant-current drains are shown in Fig. 4(a), (b). The open-circuit voltage of the cells is 2.50 V and the closed-circuit voltage 2.1–2.0 V. As the current density increases, the cathode polarisation increases, resulting in a loss of cell capacity for a constant cut-off voltage.

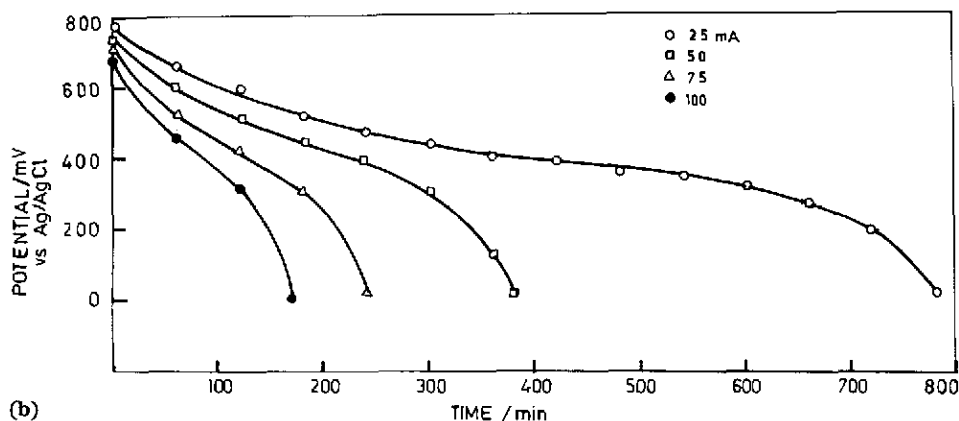
DDH hydrolyzes (during discharge) on coming into contact with water and hypochlorite is formed, i.e.,



On the basis of this reaction, the electrode mechanism during battery discharge is as follows [4],



(a)



(b)

Fig. 3. Effect of current drain on cathode potential of: (a)  $\text{Mg}/\text{Mg}(\text{ClO}_4)_2/\text{DDH}$ ; (b)  $\text{Mg}/\text{MgBr}_2/\text{DDH}$  cells.



#### Capacity and coulombic efficiency of DDH cells

The capacities of  $\text{Mg}/\text{Mg}(\text{ClO}_4)_2/\text{DDH}$  cells are  $18.0 (\text{A min g}^{-1})$  and  $32.4 (\text{W min g}^{-1})$  at a  $25 \text{ mA}$  current drain; the coulombic efficiency is  $55.1\%$  (Table 1). By contrast, cells with  $\text{MgBr}_2$  electrolyte give  $19.5 (\text{A min g}^{-1})$  and  $36.6 (\text{W min g}^{-1})$  with a coulombic efficiency of  $59.7\%$ . It is noted that the cathode material undergoes a reduction of up to  $60\%$ . It is also evident from the data in Table 1 that the cathode efficiency is better in  $\text{MgBr}_2$  than it is in  $\text{Mg}(\text{ClO}_4)_2$ . Furthermore, the cathode efficiency is higher at lower current drains.

Plots of cell voltage versus capacity for  $\text{Mg}/\text{Mg}(\text{ClO}_4)_2/\text{DDH}$  cells under current drains of  $25$  and  $125 \text{ mA}$  are given in Fig. 5. The following parameters

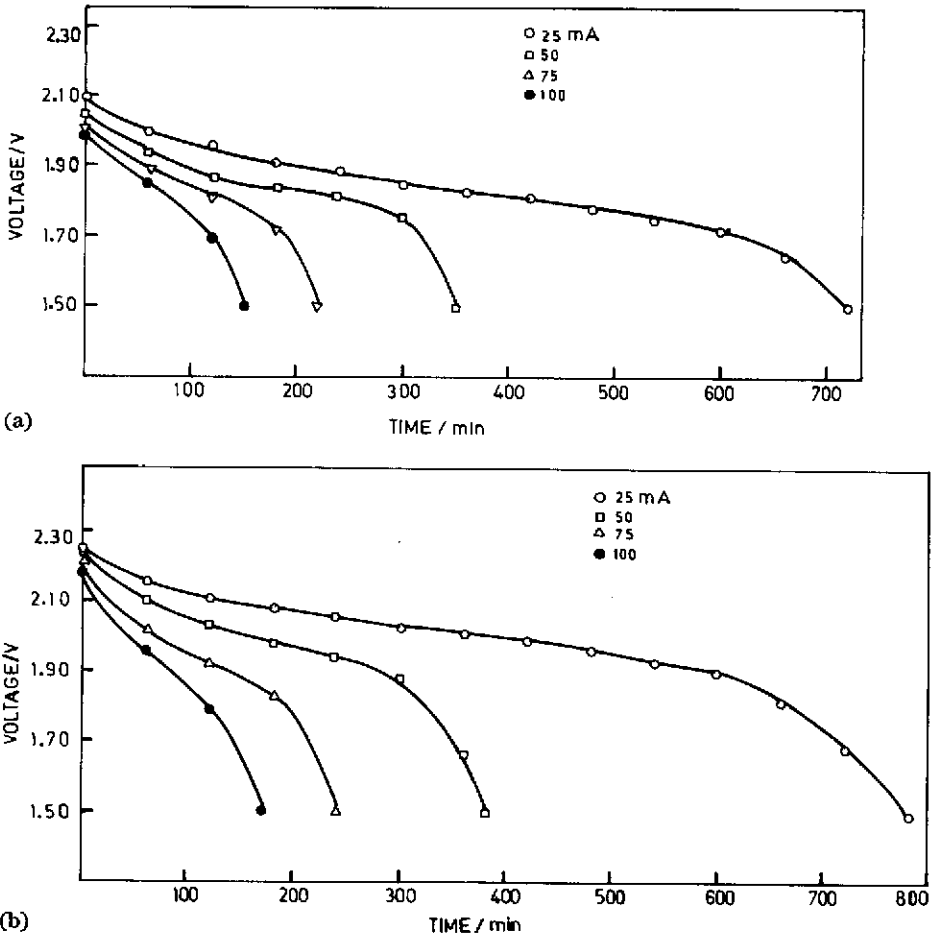


Fig. 4. Effect of current drain on voltage of: (a)  $\text{Mg}/\text{Mg}(\text{ClO}_4)_2/\text{DDH}$ ; (b)  $\text{Mg}/\text{MgBr}_2/\text{DDH}$  cells.

have been calculated using Shepherd's method [7]:

- (i) mean available active material,  $Q, = 16.9 \text{ A min cell}^{-1}$
- (ii) coefficient of polarization,  $K, = 0.26 \Omega \text{ cell}^{-1}$
- (iii) internal resistance of the cell,  $N, = 1.4 \Omega \text{ cell}^{-1}$
- (iv) constant closed-circuit voltage,  $E_s = 1.9 \text{ V}$ .

These values have been fitted into a general discharge equation for the  $\text{Mg}/\text{Mg}(\text{ClO}_4)_2/\text{DDH}$  system, i.e.,

$$E = E_s - K[Q/(Q - It)]I - NI \quad (4)$$

where  $E$  is the cell voltage during discharge at time,  $t$ . The calculated values of  $E$  from eqn. (4) are contrasted with the observed discharge voltages for a set of  $It$  values in Table 2. The observed good agreement, indicates that

TABLE 1

Cell capacity and coulombic efficiency  
Cut-off voltage, 1-5 V

Current drain (mA)	Mg/Mg(ClO <sub>4</sub> ) <sub>2</sub> /DDH			Mg/MgBr <sub>2</sub> /DDH		
	A	B	C	A	B	C
25	18.0	32.4	55.1	19.5	36.6	59.7
50	17.5	31.0	53.6	19.0	35.4	58.2
75	16.5	28.9	50.5	18.0	33.3	55.1
100	15.0	26.2	45.9	16.5	30.4	50.5
125	13.7	23.9	42.1	15.6	28.5	47.8
150	12.8	21.8	39.1	15.0	27.2	46.0
200	10.0	16.5	30.5	14.0	24.6	42.9
250	7.5	12.0	23.0	11.3	19.5	34.5

A, A min g<sup>-1</sup>.

B, W min g<sup>-1</sup>.

C, Coulombic efficiency (%).

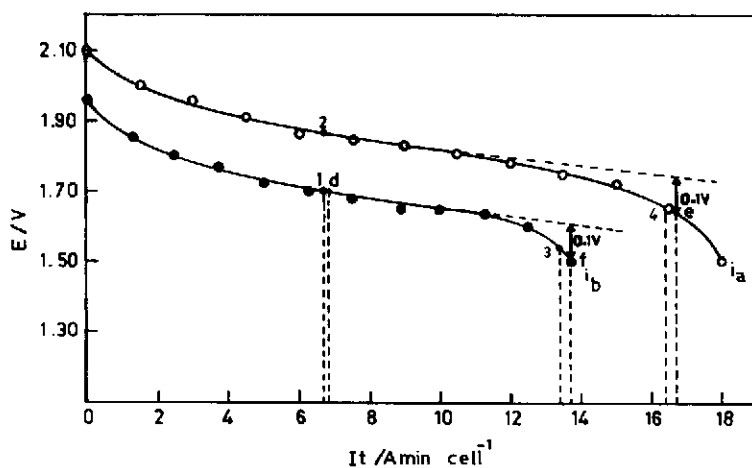


Fig. 5. Cell voltage vs. capacity for Mg/Mg(ClO<sub>4</sub>)<sub>2</sub>/DDH cell:  $i_a = 25$  mA,  $i_b = 125$  mA.

the discharge data fit well into the general equation proposed by Shepherd for primary cells.

#### Cyclic voltammetric behaviour

Cyclic voltammograms obtained on platinum in solutions of DDH in 0.1 M Mg(ClO<sub>4</sub>)<sub>2</sub> are given in Figs. 6 and 7. As shown in eqns. (2) and (3), DDH undergoes a 4-electron transfer. The redox behaviour is due to the substitution of two chlorine atoms by protons. As a consequence, the voltammograms exhibit redox peaks at -422 mV ( $E_{pc}$ ) and -357 mV ( $E_{pa}$ ) at a DDH concentration of 1.9608 mM. Analysis of these peaks using the criteria given by Nicholson [7] reveals a linear increase of  $I_p$  with  $\nu^{1/2}$  and

TABLE 2

Comparison of calculated and observed voltages of  $\text{Mg}/\text{Mg}(\text{ClO}_4)_2/\text{DDH}$  cell

Capacity ( $\text{A min g}^{-1}$ )	Voltage for $I=25 \text{ mA}$	
	Calculated (V)	Observed (V)
6.0	1.855	1.850
7.5	1.853	1.845
9.0	1.850	1.835
10.5	1.848	1.825

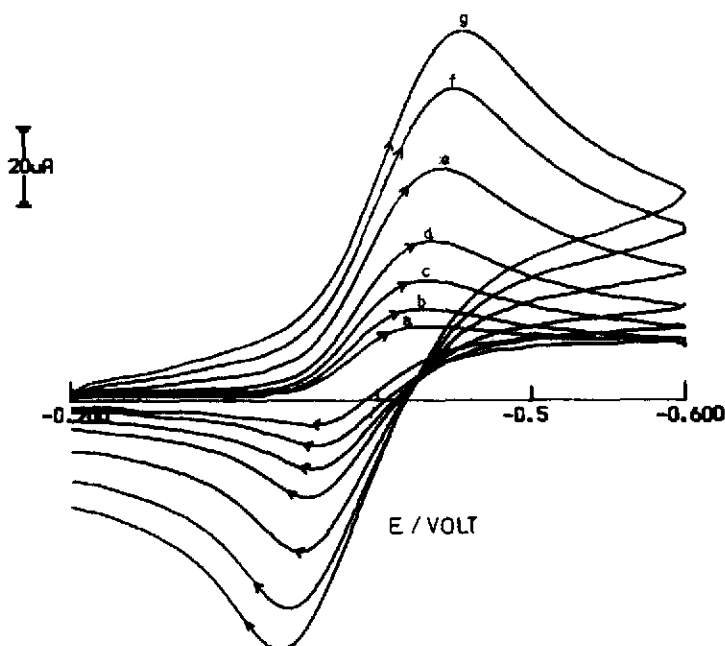


Fig. 6. Cyclic voltammograms on platinum in  $1.9608 \text{ mM DDH} + 0.1 \text{ M Mg}(\text{ClO}_4)_2/100\% \text{ C}_2\text{H}_5\text{OH}$  at (a) 5, (b) 10, (c) 20, (d) 40, (e) 100, (f) 200, (g)  $300 \text{ mV s}^{-1}$ .

an anodic shift in the peak potential with increase in sweep rate ( $\nu$ ). Values of  $\Delta E_p$  vary from 65 to 121 mV when the sweep rate is increased from 5 to  $300 \text{ mV s}^{-1}$ . This shift is higher than that expected for a 4-electron transfer (viz., 15 mV). These observations suggest that the system is quasi-reversible. In general,  $\text{Mg}(\text{ClO}_4)_2$  and  $\text{MgBr}_2$  electrolytes exhibit similar behaviours with regard to  $E_p$ ,  $I_p$  and  $\Delta E_p$  values.

#### SEM analysis

Magnesium alloy (AZ31) has a uniform distribution of  $\text{MgAl}_2\text{Zn}_7$  precipitate at the grain boundaries, Fig. 8(a). After discharge, dissolution (corrosion)



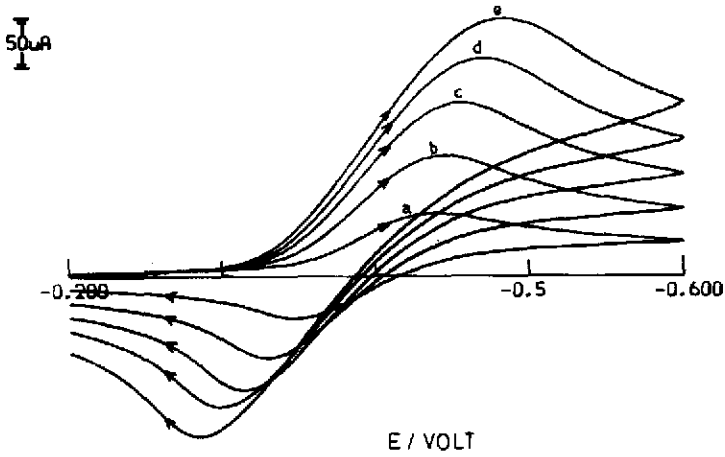
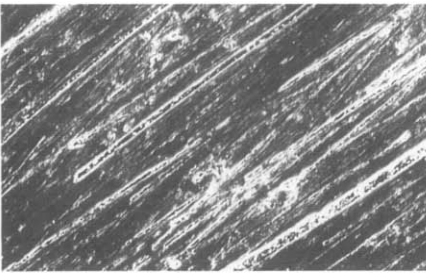
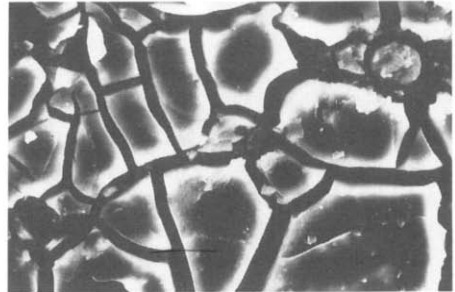


Fig. 7. Cyclic voltammograms on platinum in 0.1 M  $\text{Mg}(\text{ClO}_4)_2/100\% \text{C}_2\text{H}_5\text{OH}$  and (a) 1.9608, (b) 3.8462, (c) 5.6604, (d) 7.4074, (e) 9.0909 mM DDH, at  $100 \text{ mV s}^{-1}$ .



(a)



(b)



(c)

Fig. 8. Electron micrographs of: (a) magnesium alloy, AZ 31, ( $\times 435$ ); (b) alloy discharged in  $\text{Mg}(\text{ClO}_4)_2$  ( $\times 870$ ); (c) alloy discharged in  $\text{MgBr}_2$  ( $\times 870$ ).

of the magnesium anode is greater in  $\text{MgBr}_2$  than it is in  $\text{Mg}(\text{ClO}_4)_2$ , cf. (b) and (c), Fig. 8. In the former electrolyte, the pores are highly irregular in shape and the pore volume is very much larger.

## Conclusions

Cyclic voltammetric studies of DDH confirm that the compound is easily reducible in neutral electrolytes such as  $\text{Mg}(\text{ClO}_4)_2$  and  $\text{MgBr}_2$ .

Titanium expanded grid (6 mesh) is shown to be the best material for the cathode current-collector in  $\text{Mg}/\text{DDH}$  cells. The optimum content of conducting material (acetylene black) is 50%.

The capacity of the  $\text{Mg}/\text{MgBr}_2/\text{DDH}$  system is slightly higher than that of  $\text{Mg}/\text{Mg}(\text{ClO}_4)_2/\text{DDH}$ , but the magnesium anode is less stable in the former electrolyte.

## Acknowledgement

The authors are grateful to Professor S. K. Rangarajan, Director, Central Electrochemical Research Institute, Karaikudi, for his encouragement and permission to publish this paper.

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