

SHORT COMMUNICATION

Para-nitroaniline as a depolarizer for magnesium batteries

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1. Introduction

Organic compounds containing nitro groups have been attractive and widely investigated in conjunction with magnesium anodes [1–5]. A number of such compounds like *p*-nitrotoluene (PNT), *m*-chloronitrobenzene etc., have been extensively studied in this laboratory as depolarizers for magnesium primary cells [6–8]. The present work concerns an experimental study on the discharge behaviour and reduction efficiency of *p*-nitroaniline (PNA) in Mg/PNA cells.

2. Experimental details**2.1. Chemicals**

PNA (E. Merck, Germany), MgCl₂, MgBr₂ [Loba/Chemie, AR] and Mg(ClO₄)₂ (E. Merck, AR) were used.

2.2. Cell assembly and discharge studies

Cathodes consisting of 1 g PNA, 50% by weight of acetylene black, 0.4–1 ml of carboxy methyl cellulose (CMC) binder were blended thoroughly and spread over both sides of a copper mesh grid current collector (3 cm × 2 cm area). The electrode was pressed at an optimized pressure of 680 kg cm⁻².

Magnesium alloy sheets [AZ 31] of 3 cm × 2 cm area were used as anodes. The cells were assembled by wrapping the prepared cathodes with multilayers of cellophane sheets and then sandwiched between two anodes.

The cells were activated at room temperature using various test electrolytes (2 M MgCl₂, 2 M MgBr₂ and 2 M Mg(ClO₄)₂) and discharged in PVC containers at different current densities of 1.1, 2.1, 4.2 and 8.3 mA cm⁻². Experiments were repeated to test reproducibility and were reproducible within ± 2%.

2.3. Cyclic voltammetry

PNA was dissolved in small amounts of pure acetonitrile and was then made up to the required concentration using the supporting electrolyte, i.e. 2 M Mg(ClO₄)₂. A sample of the test solution was used in an electrochemical cell containing glassy carbon of area 0.07 cm² as working, a platinum wire as counter and Ag/AgCl as reference electrode. The solution was bubbled with nitrogen gas so as to obtain an inert atmosphere.

A BAS-100A electrochemical analyser (Bio-analytical system, USA) along with a digital plotter (DMF-40 series, Houston Inst. Division) were used for the CV studies. The experiments were run in 5, 10, 15 and 20 mM concentrations [C] at 50, 100, 150, 200, 250 and 300 mV s⁻¹ sweep rates (γ). The potential scanning range was –200 to –700 mV.

3. Results and discussion

Discharge characteristics of Mg/PNA cells at different current densities and for electrolytes are presented in Figs 1–4 and the results are summarized in Table 1. The discharge curves show a flat profile. The cathodic efficiency and the number of electrons transferred during discharge is presented in Table 2.

It can be seen from the discharge curves (Figs 1–4) that the overall operating potential is higher in the case of MgCl₂ and is in the order MgCl₂ > MgBr₂ > Mg(ClO₄)₂. It is clear from Table 1 that almost the same capacity is obtained in all the electrolytes investigated at lower current drains (up to 25 mA). However, at higher current densities (above 2.1 mA cm⁻²), MgCl₂ exhibits superior performance. These facts may be attributed to the higher conductivity [9] and more acidic nature of MgCl₂.

The complete reduction of *p*-nitroaniline to *p*-phenylenediamine (Fig. 5) involves six electrons at 100% cathodic efficiency. The number of electrons

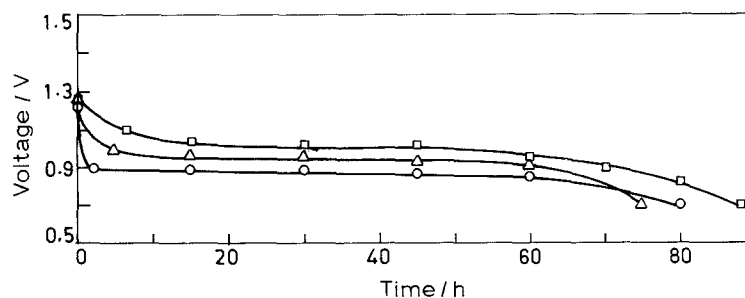


Fig. 1. Discharge curve of Mg/PNA cells at 1.1 mA cm⁻² in (□) MgCl₂, (○) Mg(ClO₄)₂, and (Δ) MgBr₂.

Table 1.

| Electrolyte | Capacity/Ah g ⁻¹ | | | |
|------------------------------------|-----------------------------|-------------------------|-------------------------|-------------------------|
| | 1.1 mA cm ⁻² | 2.1 mA cm ⁻² | 4.2 mA cm ⁻² | 8.3 mA cm ⁻² |
| MgCl ₂ | 1.10 | 1.07 | 0.85 | 0.45 |
| MgBr ₂ | 0.94 | 0.95 | 0.60 | 0.25 |
| Mg(ClO ₄) ₂ | 1.00 | 0.95 | 0.40 | 0.15 |

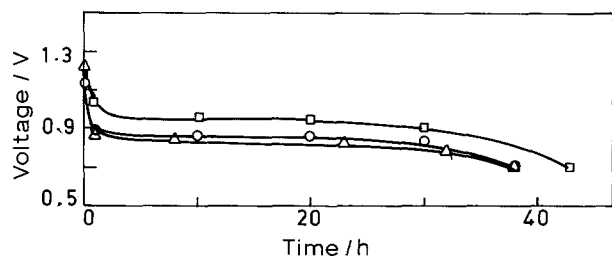
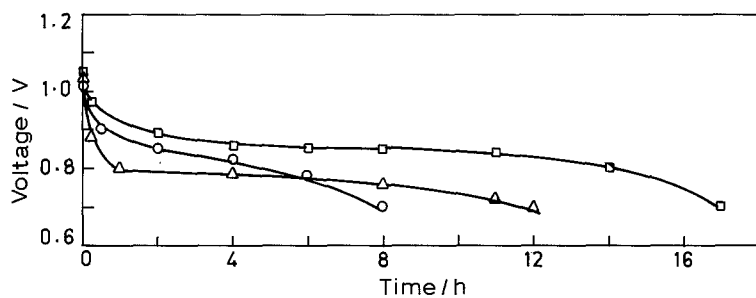
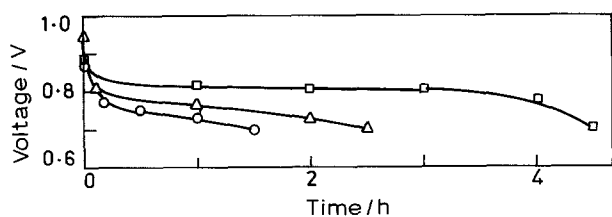
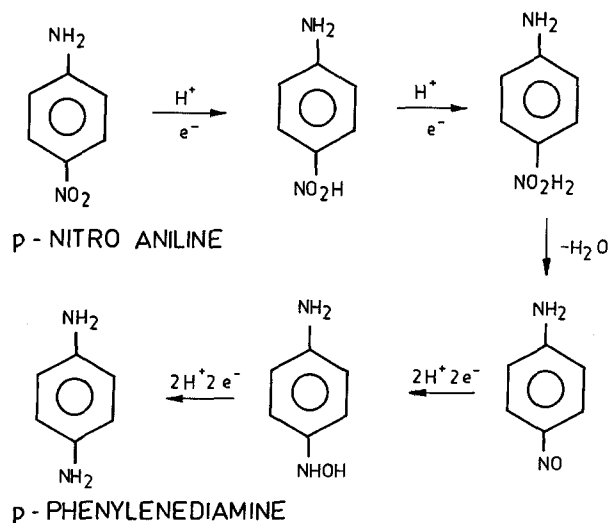
Fig. 2. Discharge curve of Mg/PNA cells at 2.1 mA cm⁻² in (□) MgCl₂, (○) Mg(ClO₄)₂, and (Δ) MgBr₂.

Table 2.

| Electrolyte | Current density/mA cm ⁻² | | | | | | | |
|------------------------------------|-------------------------------------|----|----------|----|----------|----|----------|----|
| | 1.1 | | 2.1 | | 4.2 | | 8.3 | |
| | <i>n</i> | % | <i>n</i> | % | <i>n</i> | % | <i>n</i> | % |
| MgCl ₂ | 5.7 | 95 | 5.5 | 92 | 4.3 | 73 | 2.7 | 38 |
| MgBr ₂ | 4.9 | 81 | 4.9 | 82 | 3.1 | 52 | 1.3 | 22 |
| Mg(ClO ₄) ₂ | 5.2 | 86 | 4.9 | 82 | 2.1 | 35 | 0.7 | 13 |

Fig. 3. Discharge curve of Mg/PNA cells at 4.2 mA cm⁻² in (□) MgCl₂, (○) Mg(ClO₄)₂, and (Δ) MgBr₂.Fig. 4. Discharge curve of Mg/PNA cells at 8.3 mA cm⁻² in (□) MgCl₂, (○) Mg(ClO₄)₂, and (Δ) MgBr₂.Fig. 5. Reduction mechanism of PNA to *p*-phenylenediamine.

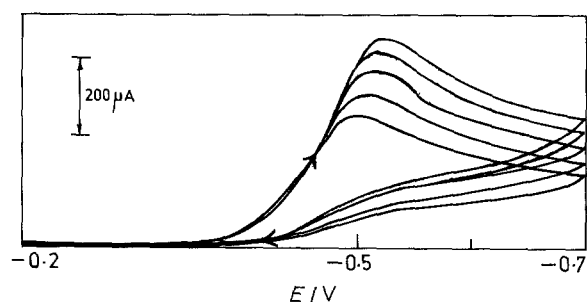


Fig. 6. Cyclic voltammogram of 5 mM PNA in 2 M magnesium perchlorate at various sweep rates.

transferred (n) and cathodic efficiency (%) are presented in Table 2. It can be seen that maximum efficiency, implying maximum number of electrons transferred, is for lower and medium current drains in all the electrolytes. However, maximum practical cell capacity is realized in the case of MgCl_2 , which may be due to the ease of reduction in slightly acidic medium.

Cyclic voltammetry studies were carried out to obtain information on the reduction of PNA. A typical voltammogram is presented in Fig. 6. A single well defined cathodic peak was obtained indicating that the reduction is irreversible and the potential (E_p) was in the range from -493 to -541 mV for different concentrations and sweep rates. The peak potential shifts in the cathodic direction with increasing sweep rate and concentration confirming the irreversibility of the compound.

A plot of i_p against $\gamma^{1/2}$ and i_p against C shows a linear relationship. A constant value is observed for $i_p/AC\gamma^{1/2}$ (where A is the area of the working electrode). These factors suggest that the reduction of PNA is diffusion-controlled.

4. Conclusions

(i) PNA depolarizer gives steady voltage at moderate current drains (up to 4.2 mA cm^{-2}).

(ii) The cathodic efficiency of PNA is 38% at 8.3 mA cm^{-2} in slightly acidic MgCl_2 as compared to 13% in $\text{Mg}(\text{ClO}_4)_2$ medium.

(iii) The irreversible and diffusion controlled nature of PNA has been confirmed by cyclic voltammetry.

References

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