

2- β -Dinitrostyrene as a cathode material in a magnesium/zinc-based primary battery

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Abstract

The efficiency of 2- β -dinitrostyrene as a cathode material in a magnesium/zinc-based primary battery is examined. The discharge performance of the cell is investigated under different parametric variations such as temperature, nature of electrolyte, current drain and zeolite modification. A seven-electron reduction seems to be responsible for the discharge of the cell. The end-of-discharge product is anthranilic acid. Participation of oxygen in the reduction process is indicated. The chemical reaction responsible for discharge involves electroreductive cyclization of 2- β -dinitrostyrene to indole, which is further converted into anthranilic acid by oxygen. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: 2- β -Dinitrostyrene cathode; 2- β -Dinitrostyrene organic battery

1. Introduction

Organic nitro compounds are promising candidates for cathode materials in primary batteries. Various nitro compounds have been investigated for their cathode performance in zinc- and magnesium-based cells. Such nitro compounds include *m*-dinitrobenzene [1,2], alkyl-substituted dinitrobenzenes [3], *p*-nitrotoluene [4,5] 1-nitronaphthalene [6], *p*-nitrophenol [7], *p*-nitroaniline [8], picric acid and trinitrostilbene [9]. In the present study, the performance of 2- β -dinitrostyrene as a cathode material in a magnesium/zinc-based primary cell is examined.

2. Experimental

Unless otherwise specified, all chemicals were E. Merck extrapure products. 2- β -Dinitrostyrene (melting point, 104°C) was prepared by base-catalyzed condensation of 2-nitrobenzaldehyde with nitromethane [10].

Double-distilled water was used in preparing the electrolyte solutions. The zeolite used was a β -zeolite (Union Catalysts, India).

Magnesium alloy AZ31 (0.0015-m thick) and zinc (99.9% purity, 0.002-m thick) sheets were used as magnesium and zinc anodes, respectively. Zeolite modification of 2- β -dinitrostyrene was made by continuously stirring a blend of 10:1 zeolite:2- β -dinitrostyrene in benzene for 10 h. The solid was then filtered, washed and dried.

The cathode plate was made by mounting a uniform mixture of PTFE binder (0.2 ml), zeolite-modified or unmodified 2- β -dinitrostyrene and colloidal graphite on nickel-plated mild steel or copper mesh of dimensions 0.04 m \times 0.025 m \times 0.002 m. The material was then compacted using a hydraulic press.

In the cell (Fig. 1), the cathode was kept between two anodes. Direct contact of the cathode with anodes was prevented by pasting a pair of thin PVC wires on to the inner side of the zinc sheets.

The electrolyte was composed of ZnCl₂ (28%) and NH₄Cl (23%) in 100 ml water for zinc cells, and 2 M MgCl₂ or 2 M MgBr₂ or 2 M Mg(ClO₄)₂ for magnesium cells. Unless otherwise specified, battery discharge was conducted at a constant-current drain of 100 mA. Separation of the electrode reaction product from the zeolite matrix was achieved by using chloroform (E. Merck, GR).

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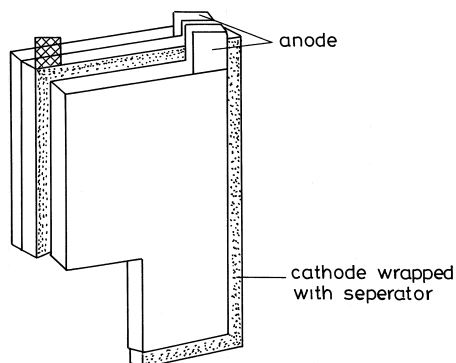


Fig. 1. Cell assembly of zinc (or magnesium)-2-β-dinitrostyrene cell.

Cyclic voltammograms were recorded by means of a PAR system which consisted of a potentiostat/galvanostat model 163, a current-to-voltage converter model 176, a universal programmer model 175, and an X–Y recorder, model RE 008. A platinum foil of large area was used as the auxiliary electrode while a saturated calomel electrode was used as the reference. The solutions were de-aerated by purging with oxygen-free nitrogen. The cyclic voltammograms of the chloroform extract of the cathode mix were recorded with a HMDE (Metrohm) and a Walpole acetate buffer (pH 3.6, 0.1 M KNO_3).

3. Results and discussion

3.1. General discharge performance

The discharge curves of 2-β-dinitrostyrene battery in magnesium- and zinc-based cells are shown in Figs. 2–4.

Neither high- nor low-compaction pressure was suitable for the performance of the cells. An optimum pressure of 340 kg cm^{-2} (Fig. 2) applied over the cathode area and 80 wt.% colloidal graphite (Fig. 3) was adequate for good performance in both zinc- and magnesium-based cells. For magnesium cells, magnesium perchlorate electrolyte was superior to magnesium chloride and bromide (Fig. 4). A small amount of (0.1 wt.%) V_2O_5 increased the ampere-hour capacity by about 7%. With respect to the current-collector, copper mesh was superior to nickel-plated mild steel (Table 1).

Comparison of the performance of a zinc-2-β-dinitrostyrene cell with that of conventional cells of manganese dioxide coupled with magnesium or zinc is presented in Fig. 5. Although the cell voltage of the 2-β-dinitrostyrene cell is not as high as that of cells based on manganese dioxide, the former gives almost a flat discharge.

The effect of temperature variation on discharge performance is shown in Fig. 6. As the temperature decreases, there is a decline in the capacity of the zinc-based cells together with a slight fall off in cell voltage. At 0°C , the total output of the cell is only 60% of that delivered at room temperature. By contrast, magnesium cells exhibit excellent low-temperature performance. This is due to the well-established heat-generating corrosion of the magnesium anode [11].

3.2. Zeolite modification of 2-β-dinitrostyrene

Zeolites are attractive materials for electrodes because they are ion-exchange materials, they have molecular sieving properties, and they are catalysts. Several examples of

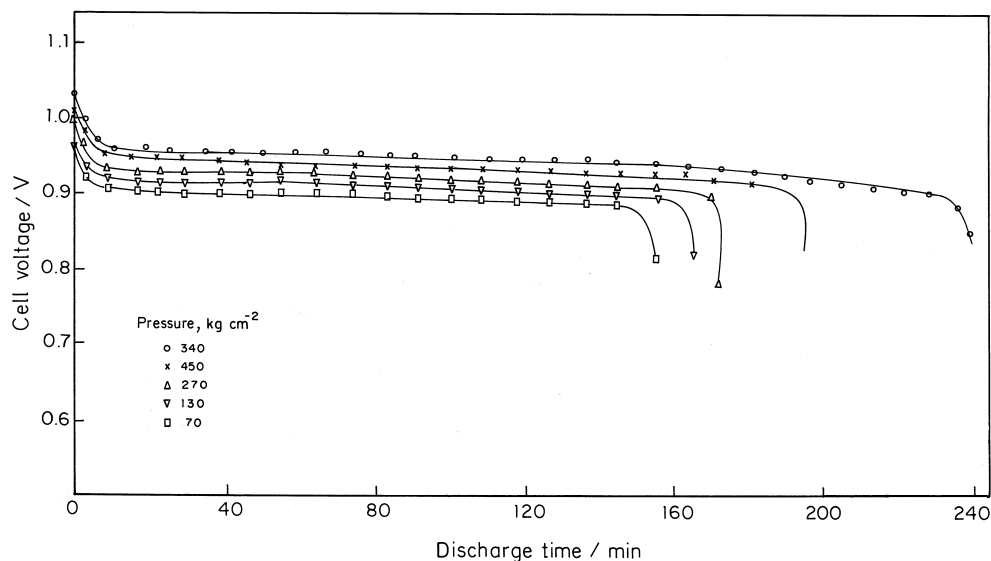


Fig. 2. Effect of compaction pressure on discharge performance of $\text{Mg}/\text{Mg}(\text{ClO}_4)_2$ -2-β-dinitrostyrene (1.66 g) cell. Colloidal graphite, 80 wt.%; constant-current drain = 100 mA.

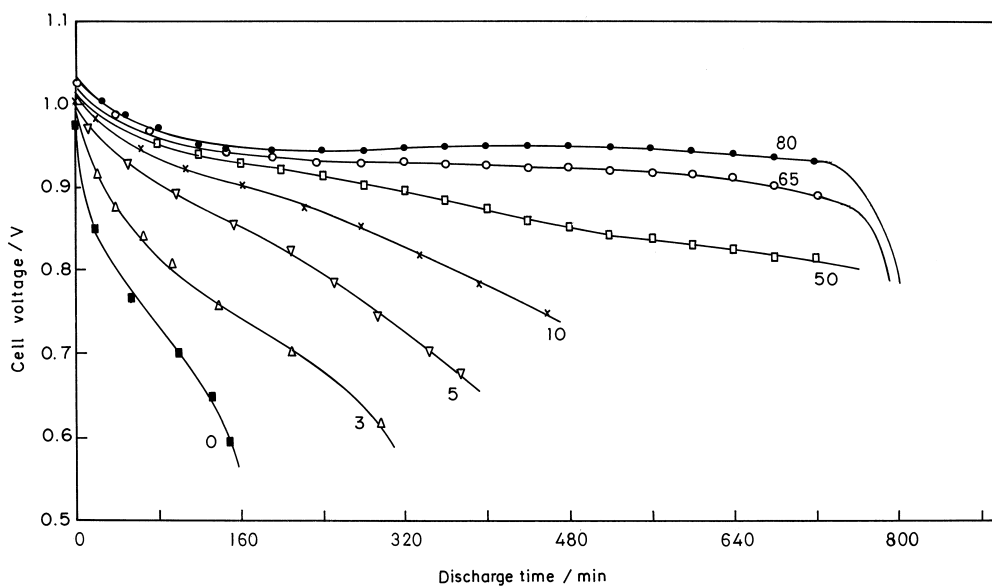


Fig. 3. Effect of colloidal graphite content on discharge performance of Mg/Mg(ClO₄)₂-2-β-dinitrostyrene (0.72 g) cell. Compaction pressure, 340 kg cm⁻²; constant-current drain = 100 mA.

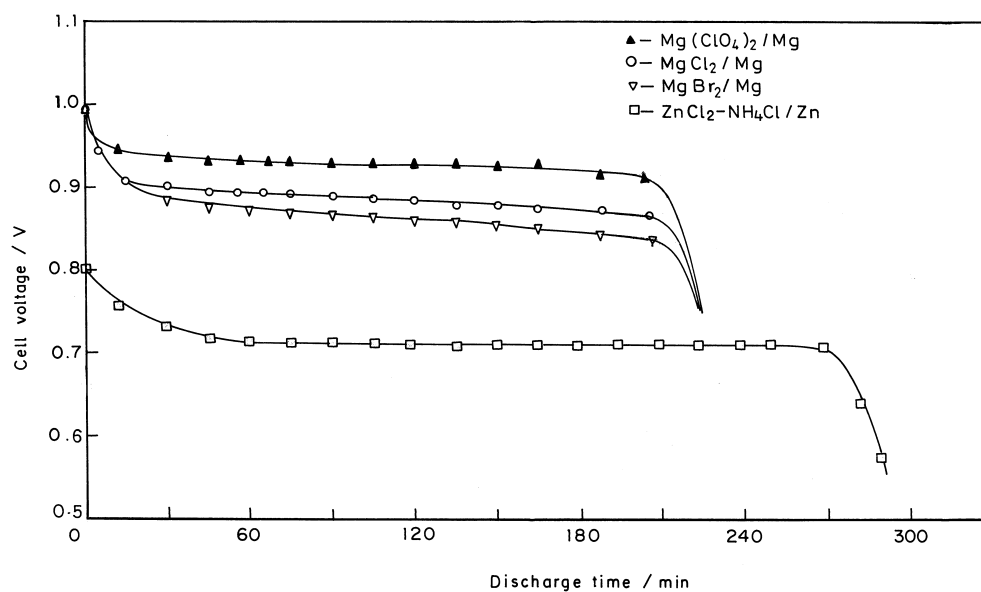


Fig. 4. Discharge curves of zinc (or magnesium)-2-β-dinitrostyrene (0.45 g) cell.

Table 1

Ampere-hour capacity of 2-β-dinitrostyrene cathode

| Anode | Cathode current-collector | Electrolyte | V ₂ O ₅ catalyst(wt.%) | Zeolite modification | Capacity (A h g ⁻¹) |
|-------|---------------------------|--|--|----------------------|---------------------------------|
| Mg | Cu mesh | 2 M Mg(ClO ₄) ₂ | – | – | 0.71 |
| Mg | Cu mesh | 2 M MgCl ₂ | – | – | 0.71 |
| Mg | Cu mesh | 2 M MgBr ₂ | – | – | 0.71 |
| Mg | Cu mesh | 2 M Mg(ClO ₄) ₂ | 0.1 | – | 0.75 |
| Mg | Cu mesh | 2 M Mg(ClO ₄) ₂ | – | Yes | 0.89 |
| Zn | Cu mesh | ZnCl ₂ /NH ₄ Cl | – | – | 0.83 |
| Zn | Cu mesh | ZnCl ₂ /NH ₄ Cl | 0.1 | Yes | 0.91 |
| Mg | Ni-plated mild steel | 2 M Mg(ClO ₄) ₂ | – | – | 0.57 |
| Zn | Ni-plated mild steel | ZnCl ₂ /NH ₄ Cl | – | – | 0.69 |

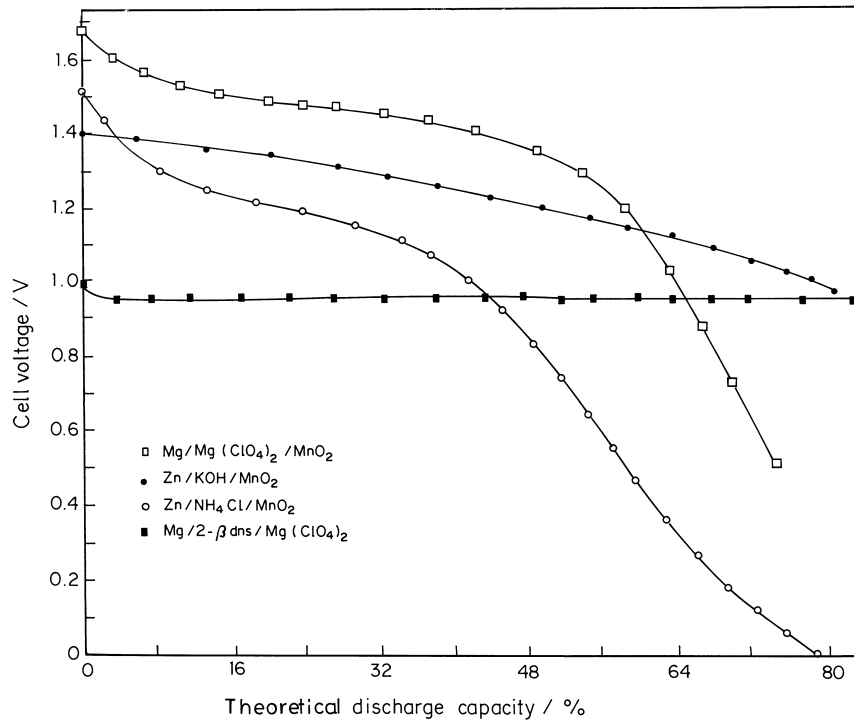


Fig. 5. Comparison of performance of 2- β -dinitrostyrene cell with that of conventional cells using magnesium or zinc.

the application of zeolites and their analogues in electrochemical phenomena can be quoted [12–34]. Recently, we have reported zeolite modification of chloranil and embelin battery cathodes [33,34]. The discharge curves of a

battery with and without zeolite modification are, respectively, shown in Fig. 7. Zeolite modification brings about a remarkable improvement in the ampere–hour capacity of the zinc-2- β -dinitrostyrene cell. The mechanism of partici-

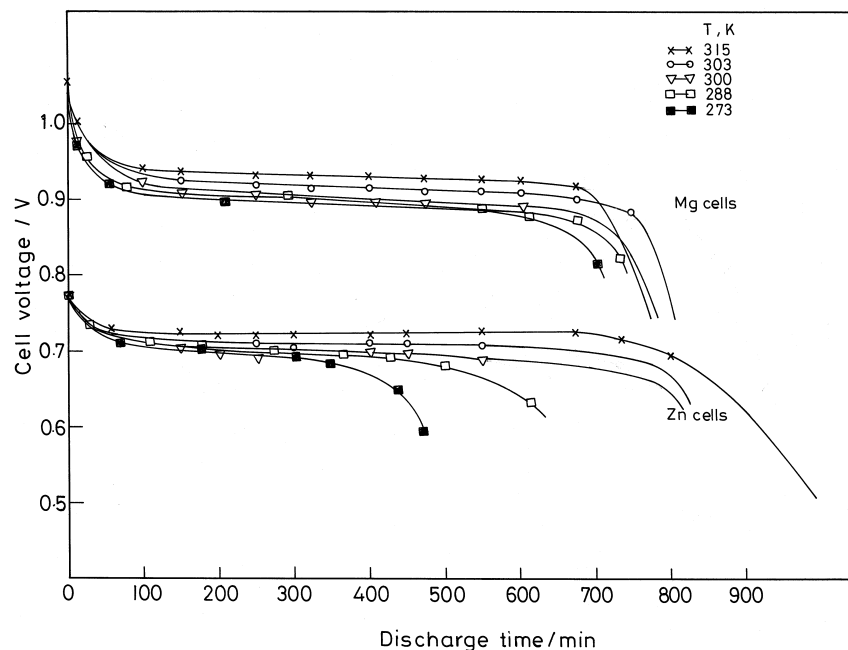


Fig. 6. Effect of temperature on discharge performance of zinc (or magnesium)-2- β -dinitrostyrene (1.5 g) cell.

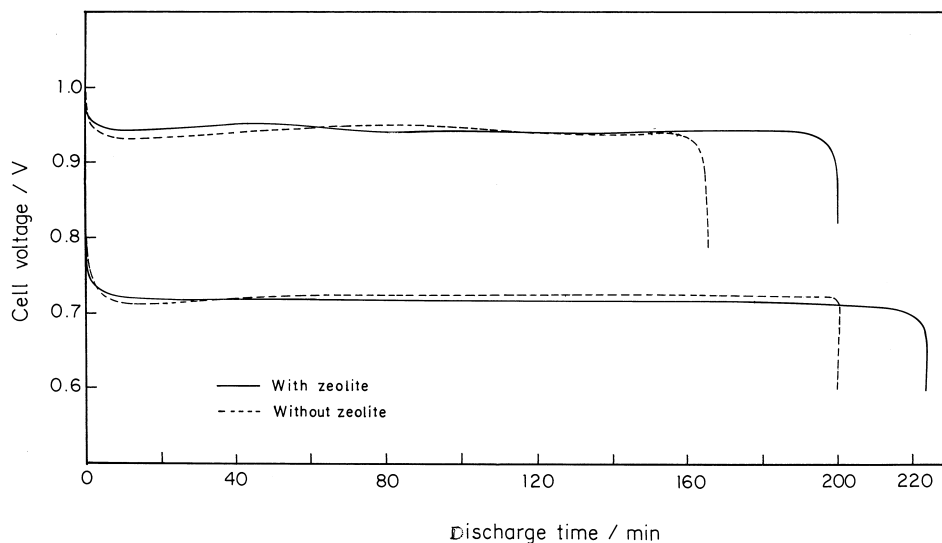


Fig. 7. Effect of zeolite modification on discharge performance of Zn/ZnCl₂-NH₄Cl or Mg/Mg(ClO₄)₂-2-β-dinitrostyrene (0.34 g) cell. Colloidal graphite, 80 wt.%; compaction pressure, 340 kg cm⁻²; constant-current drain = 100 mA.

pation of zeolites in organic reactions is now well-understood. It occurs through: (i) stabilization of short-lived radicals, (ii) Bronsted acidity and (iii) product selectivity. The mode of assistance depends on the Si:Al ratio.

The variation of cell voltage with current density is shown in Fig. 8. The slope of the plot can be taken as a measure of the gross internal resistance of the cell. A comparison of the internal resistance for a cell with zeolite and without zeolite shows that introduction of zeolite increases the internal resistance. This is, however, com-

pensated by the increased ampere-hour capacity which emanates from the large pore size of the β-zeolite, enabling a more uniform distribution of colloidal graphite, facile access of the electrolyte and prevention of gas entrapment in the cathode.

3.3. Cyclic voltammetry

Cyclic voltammograms of the cathode active material on a mercury electrode (only the organic component,

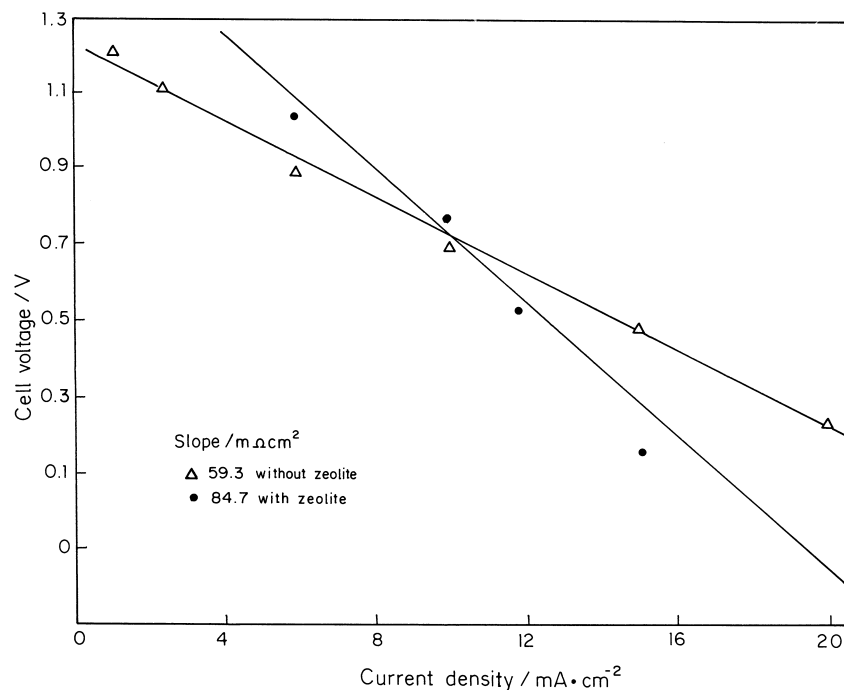


Fig. 8. Dependence of cell voltage on current density for Mg/2 M Mg(ClO₄)₂-2-β-dinitrostyrene cell, with and without zeolite modification.

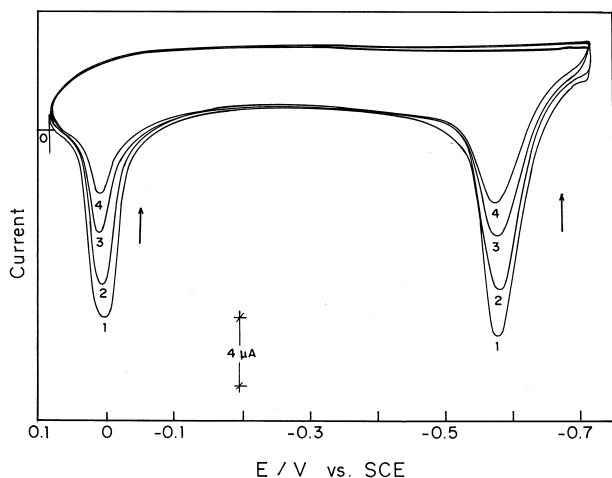


Fig. 9. Cyclic voltammograms of 2- β -dinitrostyrene at regular intervals during discharge. Curves (1)–(4) represent 10–40% discharge, respectively. Chloroform extract of cathode material was concentrated to 100 ml — 1 cm³ of this extract was made up to 250 cm³ in Walpole acetate buffer (pH 3.6, 0.1 M KNO₃).

removed from a battery at different stages during discharge) are shown in Fig. 9. The irreversible couple corresponds to the reduction of the nitro group [35]. In general, the polarographic reduction of a polynitro aromatic compound proceeds in a stepwise manner, and the first step corresponds to a four-electron change. This has been interpreted as corresponding to the reduction of one of the nitro groups to a hydroxylamino group. As the discharge of 2- β -dinitrostyrene progresses, one observes a reduction in the peak current of the cyclic voltammogram. This obser-

vation indicates a reduction in the quantity of the starting material, viz., 2- β -dinitrostyrene. A detailed study of polarographic reduction of 2- β -dinitrostyrene is being separately carried out and will be published later.

3.4. Spectral analysis

The infrared (IR) spectrum of the organic compound isolated from the end-of-discharge product (copper mesh as the current-collector and zinc as the anode) is shown as curve (b) in Fig. 10. The spectral pattern is completely different from that of 2- β -dinitrostyrene (curve a, Fig. 10). The absorption characteristics [36] of the nitro group (1550, 1420, 880 cm⁻¹) are absent in the spectrum of the product. On the other hand, frequencies characteristic of COOH (1760, 1440, 1320 cm⁻¹) and NH₂ (3300, 1580, 1250 cm⁻¹) functionalities are present.

The UV spectral analysis of the discharge product at different stages during cell discharge is given in Fig. 11. As discharge proceeds, the intensity of the absorption due to 2- β -dinitrostyrene ($\lambda_{\text{max}} = 320 \text{ nm}$, 392 nm) decreases and a new spectrum develops with three peaks at 288, 279 and 272 nm UV. The literature points out that a spectrum with three distinct peaks at 286, 278 and 270 nm is characteristic of indole chromophore. The UV spectrum of an authentic sample of indole is also included in Fig. 11 for comparison. The formation of indole from 2- β -dinitrostyrene can be accounted for by the electroreductive cyclization shown in Scheme 1. This involves a six-electron transfer from the negative (anode) to the positive (cathode) electrode.

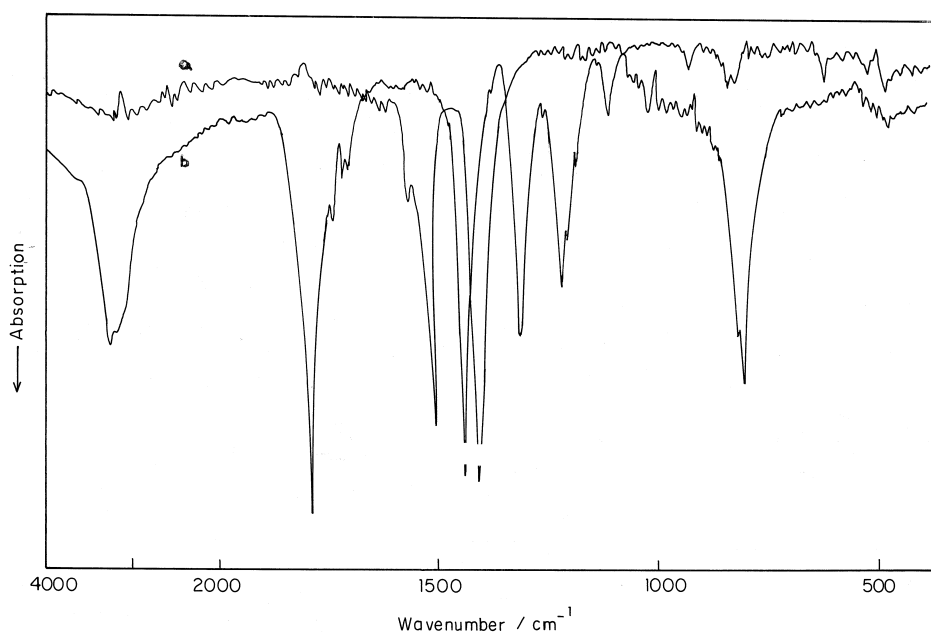


Fig. 10. IR spectrum of (a) 2- β -dinitrostyrene; (b) end-of-discharge product.

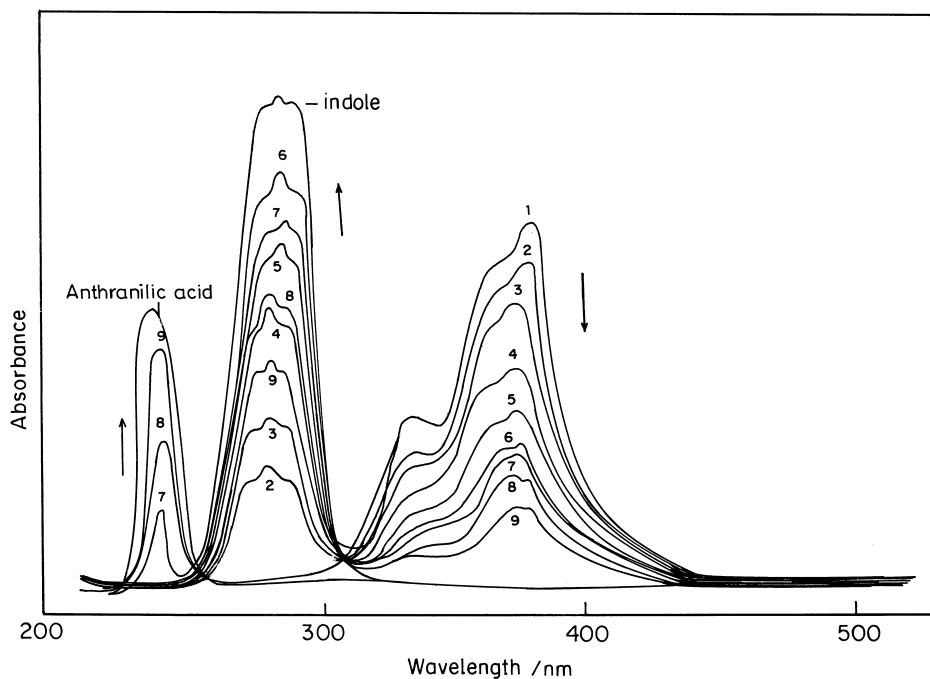
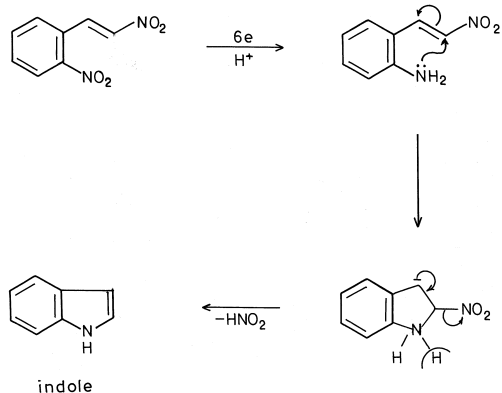


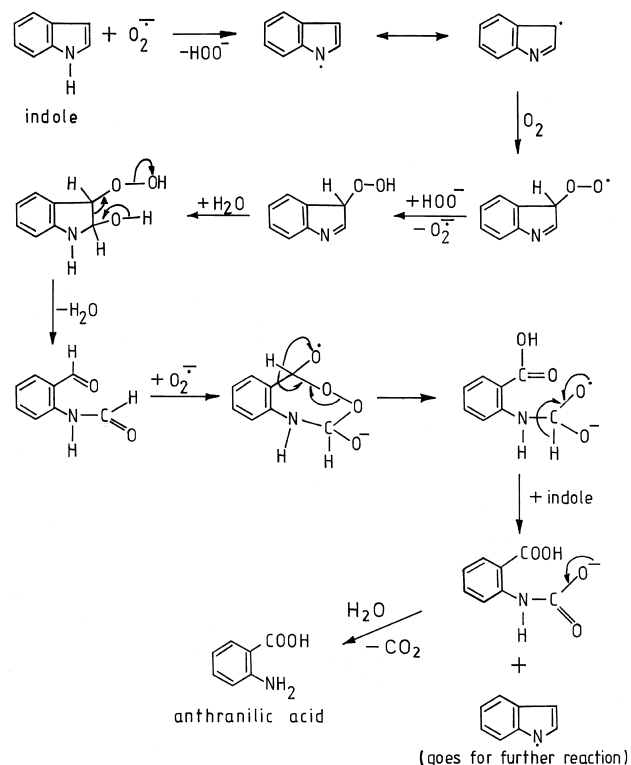
Fig. 11. UV spectra of 2-β-dinitrostyrene at regular intervals during discharge. Curves (1)–(4) represent 10–40% discharge, respectively. Chloroform extract of the cathode material was concentrated to 100 cm^3 — 1 cm^3 of this extract was made up to 250 cm^3 in chloroform (reference cell contained chloroform).

As discharge proceeds beyond 50%, the absorptions due to indole chromophore decrease while a new absorption emerges at 244 nm (Fig. 11). In the light of the IR data, the new absorption can be attributed to anthranilic acid. The ampere-hour capacity of a zinc-based cell with a copper mesh current-collector is 0.83 A h g^{-1} of cathode material, which amounts to about 100% conversion of the active material for a six-electron reduction of the nitro group. By comparison, the ampere-hour capacity of a magnesium-based cell with $\text{Mg}(\text{ClO}_4)_2$ electrolyte is 0.71 A h (i.e., 89.6% conversion). With a zeolite-modified cathode, the capacity of zinc- and magnesium-based cells is 0.913 and 0.89 A h g^{-1} , respectively. A six-electron transfer does not, however, account for the formation of anthranilic acid.



Scheme 1.

In the search for other possible reaction modes, it is considered that the participation of atmospheric oxygen may be involved. This proposition is strengthened by the



Scheme 2.

fact that indole derivatives react with oxygen and oxygen species and result in the cleavage of the pyrrole moiety [37–39]. Under such conditions, the parent indole is converted into anthranilic acid. Further, superoxide anion, O_2^- , is frequently invoked in the oxidation of indoles in electrochemical [37], biochemical [38] and photochemical [39] reactions. With this background, a one-electron reduction of molecular oxygen can be assumed to take place at the cathode to generate O_2^- which supplements the discharge and extends the current output (Scheme 2). By incorporating oxygen reduction, the ampere-hour capacity is now accounted for. Thus, an overall seven-electron reaction seems to be responsible for the discharge of 2- β -dinitrostyrene.

4. Conclusions

2- β -Dinitrostyrene is found to be an efficient cathode material for primary batteries. The discharge is flat and the reduction (seven electrons) proceeds through electroreductive cyclization to indole which is acted upon by oxygen to form anthranilic acid. The participation oxygen in the electrode discharge is a remarkable phenomenon which can be ascribed to defining 2- β -dinitrostyrene as an ‘air-breathing’ electrode.

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