3,3'-Dinitrobenzophenone as a cathode material in a magnesium/zinc based primary battery

R Renuka\(^1\), V John Fredrick\(^1\) S Saravanan\(^2\) & P C Srinivasan\(^2\)

\(^1\)Central Electrochemical Research Institute, Madras Unit, CSIR Madras Complex, Chennai 600 113, India
\(^2\)Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India

Received 11 February 2000; revised 27 September 2000

The efficiency of 3,3'-dinitrobenzophenone 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 14e reduction seems to be responsible for the electrochemical reaction causing the reduction of 3,3'-dinitrobenzophenone to the diamino derivative, including the reduction of carbonyl group.

Organic nitro compounds are promising candidates for battery cathodes because the reduction of a single nitro group to the amino group involves addition of six electrons thus making high ampere-hour capacity realizable. Several nitro compounds have been investigated for their performance as cathodes in primary batteries. They include \(m\)-dinitrobenzene\(^1\),\(^2\), alkyl substituted dinitrobenzenes\(^3\), \(p\)-nitrotoluene\(^4\),\(^5\), 1-nitronaphthalene\(^6\), \(p\)-nitrophenol\(^7\), \(p\)-nitroniline\(^8\), 2,2-dinitrostyrene\(^9\), 2-nitrophenylpyruvic acid\(^10\), picric acid and trinitrostilbene\(^11\). In the present study, the performance of 3,3'-dinitrobenzophenone as a cathode material in a magnesium/zinc based primary cell is discussed. The importance of investigating this compound lies in understanding the effects of dispersion of two nitro groups on separate benzene rings and of the presence of the additional reducible group, viz., carbonyl functionality. Thus, nuances in battery discharge of novel nitro compounds as contrasted with that of the popular \(m\)-dinitrobenzene could be discerned.

Materials and Methods

Unless otherwise specified, all chemicals were E Merck extra pure products.

Preparation of 3,3'-dinitrobenzophenone

5 g of benzophenone was dissolved in 25 ml of conc. sulphuric acid and then nitrating mixture containing 280 ml of conc. sulphuric acid and 140 ml of fuming nitric acid was added with constant stirring. The resulting clear solution was heated to 85°C over water bath for 4-5 h. Then the solution was allowed to attain room temperature; it was then poured over crushed ice. The resulting solid was filtered, dried and recrystallized from alcohol. Yield of 3,3'-dinitrobenzophenone (m.p. 152°C) was about 8 g.

Cell discharge studies

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

A magnesium alloy AZ31 sheet (0.0015 m thick) and a zinc sheet (99.9% purity; 0.002 m thick) were respectively used as the magnesium and zinc anodes. Zeolite modification of 3,3'-dinitrobenzophenone was made by continuously stirring a blend of 10:1 zeolite: 3,3'-dinitrobenzophenone 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 3,3'-dinitrobenzophenone and colloidal graphite on a nickel plated mild steel or copper mesh of dimensions 0.04 m x 0.025 m. The material was then compacted using a hydraulic press.

In the cell, a 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 comprised ZnCl\(_2\) (28 wt per cent) and NH\(_4\)Cl (23 wt per cent) in 100 ml water for zinc cells and \(2M\) MgCl\(_2\) or \(2M\) MgCl\(_2\) or \(2M\) MgBr\(_2\) or \(2M\) MgBr\(_2\) or \(2M\) MgBr\(_2\) or \(2M\) MgBr\(_2\) or \(2M\) MgBr\(_2\).
Mg(ClO₄)₂ for magnesium cells. Unless otherwise specified, the battery discharge was made at a constant current drain of 50 mA. Separation of the electrode reaction product from the zeolite matrix was done using chloroform (E Merck, GR).

Cyclic voltammetric measurements were recorded using a PAR instrument having a potentiostat/galvanostat model 163, a current-to-voltage converter model 176, a universal programmer model 175 and a model RE 008 xy recorder. A platinum foil of large area was used as the auxiliary electrode while saturated calomel electrode (SCE) was used as the reference. The solutions were deaerated by passing oxygen-free nitrogen through them. The cyclic voltammograms of the chloroform extract of the cathode mix were registered using HMDE (Metrohm) and Walpole acetate buffer, pH 3.6 containing 0.1M KNO₃. The number of electrons involved in the reduction process has been determined by quantification of discharge capacity versus theoretical capacity and supplemented by coulometry using an assembled coulometric set up.

**Results and Discussion**

**General discharge performance**

The discharge curves of 3,3'-dinitrobenzophenone cell in magnesium and zinc based cells are shown in Figs 1 and 2. Neither high nor low compaction pressure was suitable for the performance of the cells. A pressure of 3.4×10⁶ kg/m² (Fig. 1) applied over the cathode area and 80 wt. percent colloidal graphite (Fig. 2) were adequate for good performance in both zinc and magnesium based cells. For magnesium cells, magnesium perchlorate electrolyte was superior to magnesium chloride and bromide. A small amount of (0.1 wt. percent) V₂O₅ increased the discharge capacity by about 7 percent. V₂O₅ is a known catalyst for organic battery cathodes. Further, being a cation insertion material, V₂O₅ would intercalate Mg²⁺ or Zn²⁺ ions thus improving the battery capacity. For the current collector, copper was found to be superior to nickel-plated mild steel (Table I). This is owing to the superior electrocatalytic properties of copper compared to those of nickel.

The effect of temperature variation on discharge performance is shown in Fig. 3. As temperature decreases, there is a decrease in the capacity of the zinc based cells together with a slight decrease in the cell voltage. On the contrary, magnesium cells exhibit excellent low temperature performance because of the heat generating corrosion of magnesium anode. The

<table>
<thead>
<tr>
<th>Anode</th>
<th>Cathode</th>
<th>Electrolyte</th>
<th>V₂O₅ catalyst wt percent</th>
<th>Coulombic efficiency, Ah/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>Cu</td>
<td>2M Mg(ClO₄)₂</td>
<td>0.1</td>
<td>1.203</td>
</tr>
<tr>
<td>Mg</td>
<td>Cu</td>
<td>2M MgCl₂</td>
<td>—</td>
<td>1.158</td>
</tr>
<tr>
<td>Mg</td>
<td>Cu</td>
<td>2M MgCl₂</td>
<td>—</td>
<td>1.143</td>
</tr>
<tr>
<td>Mg</td>
<td>Cu</td>
<td>2M Mg(ClO₄)₂</td>
<td>0.1</td>
<td>1.203</td>
</tr>
<tr>
<td>Zn</td>
<td>Cu</td>
<td>ZnCl₂/NaCl</td>
<td>—</td>
<td>1.181</td>
</tr>
<tr>
<td>Zn</td>
<td>Cu</td>
<td>ZnCl₂/NaCl</td>
<td>—</td>
<td>1.304*</td>
</tr>
<tr>
<td>Mg</td>
<td>*Ni plated</td>
<td>2M Mg(ClO₄)₂</td>
<td>—</td>
<td>0.949</td>
</tr>
<tr>
<td>Zn</td>
<td>*Ni plated</td>
<td>ZnCl₂/NaCl</td>
<td>ms</td>
<td>1.003</td>
</tr>
</tbody>
</table>

*ms = mild steel
*with zeolite modification
discharge performance of 3-nitrobenzophenone (Table 2) reveals that under identical conditions, the capacity of a 3,3'-dinitrobenzophenone cathode is slightly more than twice that of 3-nitrobenzophenone cathode. It is of interest to note that benzophenone does not function as a depolarizer (Fig. 4) implying that the carbonyl group of benzophenone does not undergo reduction under conditions of battery discharge.

Zeolite modification of 3,3'-dinitrobenzophenone

Modified electrodes have received considerable attention in the recent past. Zeolites are attractive materials for electrode modification because they are ion-exchange materials, they have molecular sieving properties and they are potential catalysts. Several examples of the application of zeolites and their analogues in electrochemical phenomena can be quoted. Recently, we reported the zeolite modified chloranil, embelin, 2,13-dinitrostyrene, and 2-nitrophenylpyruvic acid battery cathodes. The discharge curves of the battery with and without zeolite modification are shown in Fig. 5. Zeolite modification brings about a remarkable improvement in the capacity of the dinitrobenzophenone cell (Table 1). The mechanism of participation of zeolites in organic reactions is now well understood. The participation is through (a) stabilization of short-lived radicals, (b) Bronsted acidity and (c) product selectivity, the mode of assistance being dependent on the Si/Al ratio. The variation of cell voltage with current density is shown in Fig. 6. The slope of such a plot can be taken as a measure of the gross internal resistance of the cell. A comparison of the internal resistance value for a cell with zeolite and without zeolite shows that introduction of zeolite increases the internal resistance of the cell. This is, however, compensated by the increased capacity. As discussed earlier, the improved

![Figure 3](image-url)  
Fig. 3—Effect of temperature variation on discharge performance of zinc (A) and (B) magnesium-3,3'-dinitrobenzophenone (0.285g) cell. Constant current drain = 50mA.

![Figure 4](image-url)  
Fig. 4—Discharge curves of Zn/ZnCl₂-NH₄Cl based cells. dnp: 3,3'-dinitrobenzophenone; mnp:3-nitrobenzophenone; bhp:benzophenone 0.15 g of the cathode material + 80 wt. percent colloidal graphite. Cu mesh current collector, Compaction pressure: 3.4x10⁶ kg/m²

![Figure 5](image-url)  
Fig. 5—Effect of zeolite modification in the discharge performance of Zn/ZnCl₂-NH₄Cl-3,3'-dinitrobenzophenone (0.36g) cell.Colloidal graphite : 80 wt.percent Compaction pressure: 3.4x10⁶ kg/m². Constant current drain = 100 mA.

---

**Table 2—Ah capacity of 3-nitrobenzophenone cathode**

<table>
<thead>
<tr>
<th>Anode</th>
<th>Cathode</th>
<th>Electrolyte</th>
<th>V₂O₅ catalyst wt percent</th>
<th>Coulombic efficiency Ah/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>Cu</td>
<td>ZnCl₂/NH₄Cl</td>
<td>-</td>
<td>0.5284</td>
</tr>
<tr>
<td>Zn</td>
<td>Cu</td>
<td>ZnCl₂/NH₄Cl</td>
<td>0.1</td>
<td>0.5334</td>
</tr>
<tr>
<td>Zn</td>
<td>Cu</td>
<td>ZnCl₂/NH₄Cl</td>
<td>0.6015</td>
<td></td>
</tr>
</tbody>
</table>

* with zeolite modification
coulombic efficiency emanates from the assistance of large pore size B-zeolite which ensures a more uniform distribution of colloidal graphite, facile access of the electrolyte and prevention of gas locking in the cathode.

Since the highest capacity was obtained with a zeolite modified cathode, the influence of varied current drain on the cell performance was studied with a zeolite modified cathode and the number of electrons was deduced (Table 3). In the range 1 to 5 mA cm\(^{-2}\) a 14e reduction is realized whereas higher current drains result only in a 10e reaction. This was supplemented further by the coulometric analysis.

### Table 3—Influence of current drain on the capacity of the Zn/zeolite modified 3,3’-dinitrobenzophenone cell with and without zeolite modification.

<table>
<thead>
<tr>
<th>Current drain, mA/cm(^2)</th>
<th>Coulombic efficiency, Ah/g</th>
<th>No. of electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.302</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>1.299</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>1.304</td>
<td>14</td>
</tr>
<tr>
<td>7</td>
<td>1.138</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>1.141</td>
<td>10</td>
</tr>
<tr>
<td>15</td>
<td>1.131</td>
<td>10</td>
</tr>
<tr>
<td>25</td>
<td>1.127</td>
<td>10</td>
</tr>
</tbody>
</table>

### Cyclic voltammetry

The cyclic voltammograms of the cathode active material on mercury electrode (only the organic component removed from a battery at different stages during discharge) are shown in Fig. 7. The irreversible couples (a and b) correspond to the reduction of nitro group. In general, the polarographic reduction of a nitro aromatic compound proceeds in a stepwise manner, and the first step corresponds to a four electron change. This has been interpreted as corresponding to

![Fig. 6—Dependence of cell voltage on current density in Mg/2M Mg(ClO\(_4\))\(_2\)-3,3’-dinitrobenzophenone cell with and without zeolite modification.](image)

![Fig. 7—Cyclic voltammograms of 3,3’-dinitrobenzophenone at regular intervals during discharge, 1-4 represent respectively 10-40 percent discharge. Chloroform extract of the cathode material was concentrated to 100 ml. 1 ml of this extract was made up to 250 ml in Walpole acetate buffer pH 3.6 containing 0.1M KNO\(_3\).](image)

![Fig. 8—De polarograms for the reduction of 3,3’-dinitrobenzophenone (dnbp), 3-nitrobenzophenone (mnbp) and benzophenone (bp); dnbp’ is the 80 percent discharge product of dnbp. mnbp’ is the 80 percent discharge product of mnbp. Extraction and dilution same as that for cyclic voltammetry.](image)
the reduction of one of the nitro groups to hydroxylamino group. In the case of 3,3'-dinitrobenzophenone, two distinct processes, relating respectively to the formation of hydroxylamine (process a) and the amine (process b) are observed both in the cyclic voltammogram and in the polarogram (Figs. 7 and 8). In addition, the reduction mode of the carbonyl functionality is also seen, as a reversible couple at -1.08 V (Fig. 7, process c). As the discharge of 3,3'-dinitrobenzophenone progresses, there is a progressive reduction in the peak currents of the cyclic voltammogram and the polarogram. This observation indicates a reduction in the quantity of the starting material, viz., 3,3'-dinitrobenzophenone. It is of interest to note that in the discharge product, the wave due to the carbonyl group disappears even at a very early stage (~20 per cent) during the discharge (Fig. 7). It is, therefore, reasonable to propose that the carbonyl group (2e reaction) is also involved in the battery discharge.

Spectral analysis

The IR spectrum of the organic compound isolated from the end-of-discharge product (Cu mesh as the current collector and Zn as anode) is shown in Fig. 7, curve b. The spectral pattern is completely different from that of 3,3'-dinitrobenzophenone (Fig. 9, curve a). It can be seen that the absorptions characteristic of the nitro group (1536, 1461, 880/cm) are absent in the spectrum of the product, whereas absorptions characteristic of amino group are seen at 3480 (broad), 1630 (strong), 1314, 1280 (strong) cm\(^{-1}\). Further, the strong absorption at 1668 cm\(^{-1}\) characteristic of the carbonyl group in the dinitrobenzophenone is absent in the end-of-discharge product. This observation supports the possibility that the carbonyl group also undergoes electroreduction during the discharge.

The IR spectra of 3-nitrobenzophenone and its end-of-discharge product in a zinc-based cell are shown in Fig. 10 (curves a and b respectively). It can be seen that the carbonyl group remains unaffected in the spectrum. This observation also holds good for the end-of-discharge product of benzophenone (figure not shown). The implication of this is that the carbonyl group resists reduction both in benzophenone and in 3-nitrobenzophenone, whereas it gets reduced in
3,3'-dinitrobenzophenone only. Fig. 11 presents the UV spectral analysis of the end-of-discharge products of 3-nitrobenzophenone and 3,3'-dinitrobenzophenone. As can be seen, these spectra are distinct from the spectra of the respective reactants and of benzophenone. However, unlike IR spectra, the UV spectra are not helpful in segregating the carbonyl group participation in the cell discharge.

Conclusion
3,3'-Dinitrobenzophenone is found to be an efficient cathode material for primary batteries. The discharge though not very flat proceeds through a 14e reaction that includes the reduction of two nitro groups and of the single carbonyl group. The participation of carbonyl group in the cell discharge has been amply proved by cyclic voltammetry, polarography and spectral measurements. The reduction of the carbonyl group involves high $E^0$ value and occurs at high negative potentials. Therefore, the reduction of the carbonyl group is not generally feasible in a battery discharge as evidenced by the cell discharge performance of benzophenone and 3-nitrobenzophenone. The facile reduction of the carbonyl group in 3,3'-dinitrobenzophenone suggests that the group is rendered more electrophilic through extended conjugation of the two symmetrically located electron withdrawing nitro groups. Although the equivalent weight for theoretical Ah capacity is not comparable with that of the popular $m$-dinitrobenzene cathode, 3,3'-dinitrobenzophenone is superior to $m$-dinitrobenzophenone in other respects. For instance, partial reduction of nitro groups, coupling reactions of the azo and azoxy intermediate, etc., which are detrimental to the cathode performance of the $m$-dinitrobenzene are absent in 3,3'-dinitrobenzophenone.

Acknowledgement
The authors thank Union Catalysts, India, Prof. C.N. Pillai, Emeritus Scientist, CECRI Madras unit and Prof. B.Viswanathan, Chemistry Department, IIT Madras, for their help in the present work. Financial support to the work from the Council of Scientific and Industrial Research, New Delhi, India (vide EMR, II 80 (0027)/97) is gratefully acknowledged.

References