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DDQ cathodes for seawater cells

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A positive electrode containing 2,3-dichloro-5,6-dicyano-*p*-quinone (DDQ) as the cathode active material was discharged in a magnesium seawater cell at room temperature. Analysis of the dissolved species of DDQ in water and potential sweep voltammetry studies were also carried out. The open circuit voltage of the DDQ–Mg cell was as high as 2.2 V and the single cell could be discharged at current densities greater than 50 mA cm^{-2}. However, the current efficiencies for the DDQ cathodes in a three-cell immersion-type battery were not high enough for high drain applications, probably due to a high leak current through the common electrolyte.

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1. Introduction

Some of the results obtained using 2,3-dichloro–5,6-dicyano–*p*-quinone (DDQ) as the cathode active material in a seawater cell have already been reported as part of a study on developing new seawater batteries [1]. The test results showed that a DDQ electrode gave a high potential in seawater and could be discharged at high current densities with little polarization. The present work was undertaken to evaluate the capability of DDQ cathodes bonded with polystyrene and to study in more detail the cathodic behaviour of DDQ in seawater, with the intention of developing a high power seawater battery for high drain applications, such as for the propulsion of lifeboats.

2. Experimental procedure

2.1. *Test cell*

The cathodes tested were prepared from a blend of 72 wt% DDQ (Merck, > 98%), 7 wt% graphite, 7 wt% acetylene black and 14 wt% polystyrene. Polystyrene was added as a solution of toluene. After removing toluene by evaporation, 3 g of the mix was pressed onto a collector 20 mm x 30 mm in size at about 200 kg cm^{-2} with approximately half on each side of the collector. The cathodes were allowed to dry in air for at least one week before use in a cell. The average thickness of the cathodes was 3.5 mm after drying. The cathodes made this way were dropped from a height of 1 m with only minor damage at the point of impact and could be discharged with minor swelling at the corners. Silver screen and woven carbon fibre were tested as the current collector. The results obtained with the silver collector are described here.

The anodes were cut from 0.9 mm thick magnesium alloy AZ61 (Al ~ 6%, Zn ~ 1%, Mn ~ 0.2%) and were the same size as the cathode. A cell contained one DDQ cathode and two anodes of magnesium alloy with a separation of 1 mm using cubic spacers (Fig. 1).

A cell was activated in a 200 cm^3 beaker by adding 150 cm^3 of 3% NaCl solution saturated with $Mg(OH)_2$. The open circuit voltage was measured for 10 min before the discharge was begun. Cells were discharged at room temperature (20–25° C) using a constant current without the circulation of the electrolyte.

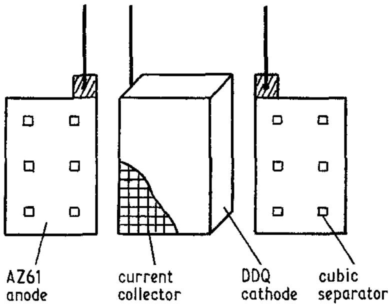

Fig. 1. Test cell.

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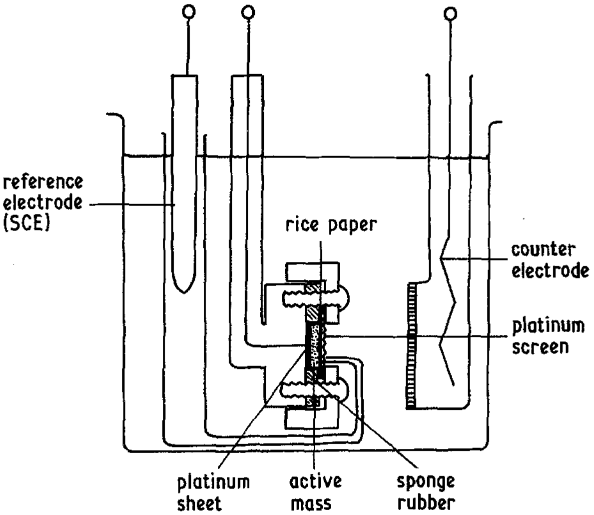


Fig. 2. Cell assembly for sweep voltammetric measurement.

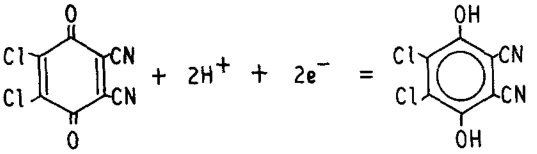
2.2. *Potential sweep voltammetry*

Potential sweep voltammetry was used to study the behaviour of the DDQ electrode in seawater. The cell assembly is shown in Fig. 2. The active mass used was a mixture of DDQ : graphite : acetylene black in the ratio 70 : 15 : 15. The sweep rate used was 0.12 mV s^{-1}. More details of the experimental procedures can be found elsewhere [2].

3. Results and discussion

3.1. *Single-cell discharges*

Some typical discharges of the DDQ cells are shown in Fig. 3 and a few of the results with single cells are listed in Table 1. The coulombic efficiencies were calculated from the dry mix composition and the known weights of cathodes, current collectors and binders, on the assumption that the following gross equation holds (236 Ah kg^{-1}):



(1)

The figures for specific energy in Wh kg^{-1} and specific power in W dm^{-3} in columns 4 and 5 of Table 1 are based on dry cell weight, excluding the weights of the cell casing, electrolyte and leads, and calculated for the average cell voltages to each end voltage listed in the table.

The open circuit voltage is about 2.2 V. The discharge voltage decreases to a low stable level from the initial high voltage at low discharge rates. The cathodes made without using any binder gave two clear potential plateaus during discharge [1]. When the binder is used to make the positive plates, the length of the upper plateau and the coulombic efficiency decline significantly at high discharge rates. The test results show that the cell can be discharged at a current density of 50 mA cm^{-2}. However, these results are still unsatisfactory for applications where high power is required since the current efficiencies at discharge rates higher than 50 mA cm^{-2} are unacceptably low. At least 40% utilization would be desired at 100 mA cm^{-2} discharge rate.

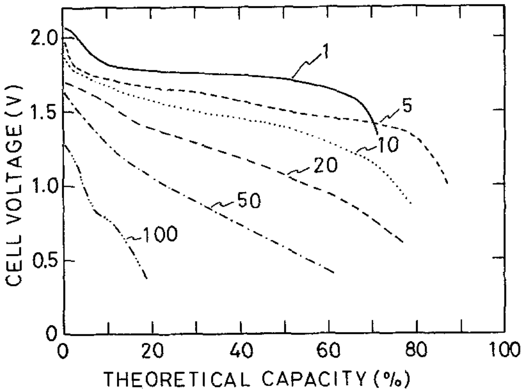


Fig. 3. Single-cell discharges for DDQ–Mg seawater cells. The numbers give discharge current densities in mA cm^{-2}.

Table 1. Single-cell discharges at room temperature

Current density (mA cm^{-2})	End voltage (V)	Current efficiency of DDQ (%)	Energy density (Wh Kg^{-1})*	Specific power (W dm^{-3})†
1	1.4	70	95	3
5	1.2	83	100	14
10	1.1	73	82	26
20	1.0	56	55	45
50	0.9	31	28	105
100	0.8	8	6	185

* Based on dry cell weight, excluding the weights of the cell casing, electrolyte and leads.
† At average voltage.

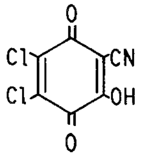
3.2. *Three-cell battery*

A three-cell battery was fabricated using the equal size cells described above. The battery case, which is shown in Fig. 4, consisted of three cell compartments. Ports, 1 cm wide by 0.5 cm long, were inserted into two diagonally opposite corners of each cell compartment to reduce internal short circuiting.

The coulombic efficiency for DDQ at 10 mA cm^{-2} was only 40–50% to an end voltage of 3 V in the immersion-type seawater battery (Fig. 5) and the energy density was calculated to be 25 Wh kg^{-1}, excluding the weight of the electrolyte. Compared to the results with single-cells, the coulombic efficiency appeared much lower in this battery, probably due to a high leak current through the common electrolyte.

3.3. *Reaction of DDQ with water*

During discharge of the DDQ–Mg cell the electrolyte became red-brown in colour due to dissolution of DDQ. It is reported that DDQ decomposes in water liberating HCN [3]. Analysis of the dissolved species was carried out to determine how it decomposes in water. DDQ dissolves in water to give initially a yellowish brown solution which soon turns wine-red. Its solubility was 2.97 g dm^{-3} at 20° C. The aqueous solution of DDQ was evaporated using a rotary vacuum evaporator and the substance obtained was recrystallized from chloroform twice. This substance changed from yellow to red when it absorbed moisture. The results of elemental analysis and molecular weight data obtained by mass spectroscopy are as follows: C: 37.68%, H: 0.77%; N: 6.3%; Parent peak: 217. This substance may be identified as:



(2)

The calculated values for C, H, N and the molecular weight are: C: 38.5%; H: 0.5%; N: 6.42%; mol. wt

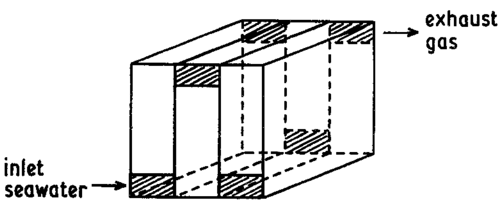


Fig. 4. Battery case for immersion-type battery.

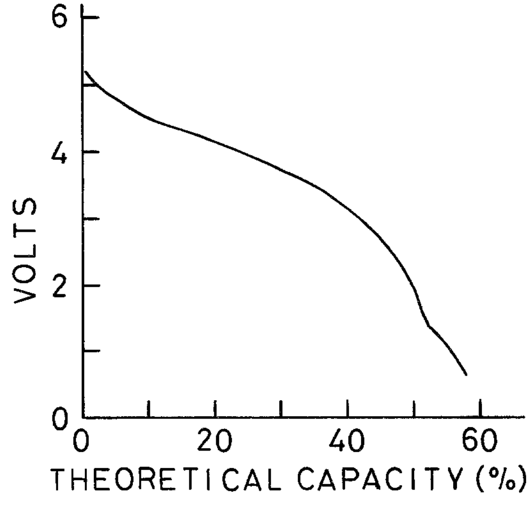
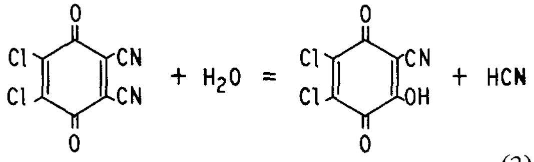


Fig. 5. Discharge of three-cell battery at 10 mA cm^{-2}.

218.0. The sample provided for the elemental analysis must have contained a small amount of water (about 0.3 mol water/mol DDQ). The reaction of DDQ with water therefore can be written as:



(3)

3.4. *Potential sweep voltammetry*

Voltammograms of DDQ in 3% NaCl saturated with $Mg(OH)_2$, different buffer solutions and 6 N HCl are shown in Fig. 6. The shape and position of the cathodic current peaks depend on the concentration and pH value of the electrolyte used. The DDQ electrode gives two main peaks in 3% NaCl solution and solutions having pH values greater than 2. The two peaks may be thought to correspond to the two electron transfers. However, since the peaks are broad, it is possible that an additional electrode reaction is included in what appears to be one peak. In aqueous mineral acids, the DDQ electrode gives one peak. The cyclic voltammetric curve can be reproduced periodically, indicating that DDQ is stable in aqueous mineral acids [4] and has potential as a cathode active material in a rechargable cell.

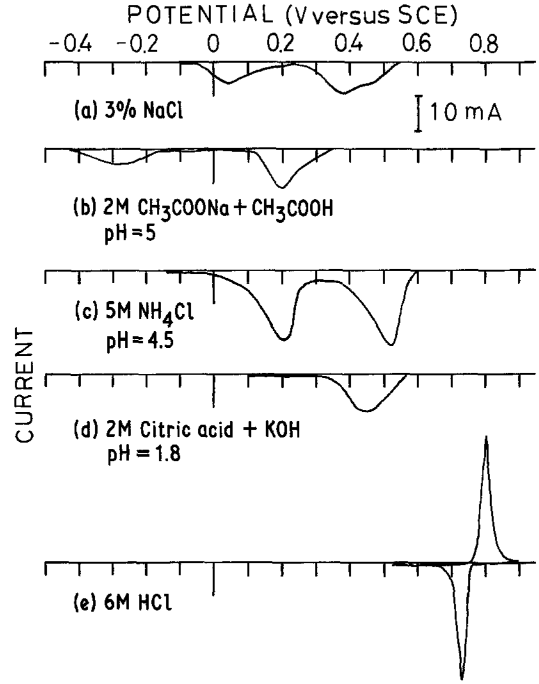


Fig. 6. Voltammograms of a DDQ electrode in various electrolytes.

The peak potentials observed in 3% NaCl solution saturated with $Mg(OH)_2$ were higher than values predicted from the pH dependence. This can be explained by the change in pH due to the formation of HCN according to Equation 3. Actually, 3% NaCl solution saturated with DDQ showed a pH value of 4.5, even if it was saturated with $Mg(OH)_2$ beforehand.

The mechanism of the electrochemical reaction of the dissolved quinones has been studied by Vetter [5, 6] and Dohrmann and Vetter [7]. If the same mechanism occurs for solid DDQ also, the reaction sequence in acid solutions can be written as follows:

$$\mathrm{DDQ} + \mathrm{H}^+ = (\mathrm{HDDQ})^+ \tag{4}$$

$$(\mathrm{HDDQ})^+ + \mathrm{e}^- = \mathrm{HDDQ} \tag{5}$$

$$\mathrm{HDDQ} + \mathrm{H}^+ = (\mathrm{HDDQH})^+ \tag{6}$$

$$(\mathrm{HDDQH})^+ + \mathrm{e}^- = \mathrm{HDDQH}. \tag{7}$$

According to the results of the voltammetry studies, when $7 > \mathrm{pH} > \sim 2$, the two charge-transfer reactions take place at different potentials but when $\mathrm{pH} < \sim 2$, they occur at roughly the same potential.

Since the electrode containing Substance 2 gave no current peak in the voltammogram at the same sensitivity and sweep rate, it can be concluded that the dissolved DDQ contributes very little to the cell capacity.

4. Summary

DDQ cathodes bonded with polystyrene were tested with the intention of developing a high power seawater battery. Although DDQ is very active as a cathode material, it was difficult to make suitable positive plates. The discharge characteristics of the cells and batteries, hand-made and unoptimized, were unsatisfactory for high power seawater batteries because of low coulombic efficiencies at high discharge rates. In addition to this, the formation of HCN due to decomposition of DDQ in water may prevent the use of DDQ as a cathode active material. However, the DDQ–Mg battery is still believed to be a candidate for a high power seawater battery because of its high voltage.

References

[1] M. Hiroi and N. Ichikawa, *Denki Kagaku (J. Electrochem. Soc., Japan)* **44** (1976) 423.
[2] M. Hiroi, *J. Appl. Electrochem.* **11** (1981) 589.
[3] J. Thiele and F. Günther, *Ann.* **349** (1906) 45.
[4] D. Walker and T. D. Waugh, *J. Org. Chem.* **30** (1965) 3240.
[5] K. J. Vetter, *Z. Naturforschung* **7a** (1952) 328.
[6] *Idem, ibid.* **8a** (1953) 823.
[7] J. K. Dohrmann and K. J. Vetter, *Ber. Bunsenges. Phys. Chem.* **73** (1969) 1068.