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Polyaniline: characterization as a cathode active material in rechargeable batteries in aqueous electrolytes

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An analytically pure form of chemically synthesized polyaniline having the emeraldine oxidation state has been used as a cathode active material together with a Zn anode in the fabrication of rechargeable cells in 1.0 M aqueous $ZnCl_2$ electrolyte (pH ~ 4). The experimental capacity and energy density based only on the weight of polymer employed in constructing the cell are 151.5 Ah kg^{-1} and 159.1 Wh kg^{-1} respectively at a constant discharge current of 0.75 mA cm^{-2} (average discharge voltage 1.05 V). The cell reactions in the charge and discharge processes have been determined. The modified capacity and energy density, when taking into account the calculated weights of Zn and HCl involved in the discharge reactions, are 109.3 Ah kg^{-1} and 114.8 Wh kg^{-1} respectively. The cell shows excellent recyclability and coulombic efficiency.

1. Introduction

There has recently been very considerable interest in the use of 'polyaniline' as a cathode active material in rechargeable batteries using aqueous [1–4] and non-aqueous electrolytes [5–7]. De Survile *et al.* [1] have shown, in extensive studies, that unspecified forms of polyaniline could be used both as the cathode and anode in a rechargeable battery in 6N aqueous H_2SO_4. More recently, both we [2] and Kitani *et al.* [3, 4] have described the use of polyaniline as a cathode material in rechargeable batteries in an aqueous $ZnCl_2$ or $ZnSO_4$ electrolyte in conjunction with a Zn anode. The composition of polyaniline used in constructing the cells in the above studies was not clearly defined and it was not possible to determine accurately the electrochemical reactions associated with the charge and discharge processes. In most cases the polyaniline was synthesized electrochemically.

In the present study we have constructed the cell from an analytically pure form of chemically synthesized polyaniline in the form of a powder. Elemental analysis and oxidation state studies show that the material synthesized is a polyaniline base in the emeraldine oxidation state, $[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-(C_6H_4)-N=(C_6H_4)=N-]_x$. This now permits what we believe is a realistic determination of the cell reaction and major electrochemical characteristics of this type of battery under the experimental conditions employed.

2. Experimental details

Emeraldine hydrochloride, i.e. the protonated form of emeraldine base was synthesized by the oxidative polymerization of aniline in 1.0 M aqueous HCl by $(NH_4)_2S_2O_8$ and converted to emeraldine base by treatment with 0.1 M aqueous NH_4OH as described elsewhere [8]. Elemental analysis for $C_{24}H_{18}N_4$: Calc. C, 79.53; H, 5.01; N, 15.46%. Found C, 78.79; H, 4.95; N, 15.83%; total %C + %H + %N = 99.57%.

The electrochemical cell consisted of a circular disc of Pt (1.5 cm^2) to one edge of which a Pt wire was spot welded. This electrode was placed on the flat inverted bottom of a plastic vial cap (2.2 cm diameter) with the Pt wire pointing upwards, perpendicular to the Pt disc. A Pyrex glass tube (3 cm long; 1.0 cm internal diameter; 0.8 cm^2) was placed on the Pt disc. The tube was then clamped and molten paraffin wax was poured into the outside hollow area between the tube and the wall of the vial cap until the wax level reached the top of the cap. The clamp was removed after 15 min at which time the Pt disc was attached firmly to the bottom of the glass tube by the paraffin wax with the Pt wire protruding vertically through the paraffin wax seal.

The apparatus was then transferred to an argon-filled glove bag which was purged three times to ensure that all air was removed. The remainder of the cell construction was carried out under argon. A mixture of 7.0 mg of emeraldine base and ~ 1.4 mg of carbon black was placed on a glazed weighing paper. The mixture was then poured down the glass tube so that it rested on the exposed Pt surface. Two circular glass filter papers, each ~ 0.8 cm^2, were then placed on top of the emeraldine base powder which was itself resting on the Pt disc.

A circular Zn electrode (0.75 cm^2, 0.25 cm thick), having a vertical ~ 5 cm 'stem' was cut from a zinc sheet. The 'stem' served as the connecting lead to the electrode. It was lightly amalgamated by dipping into

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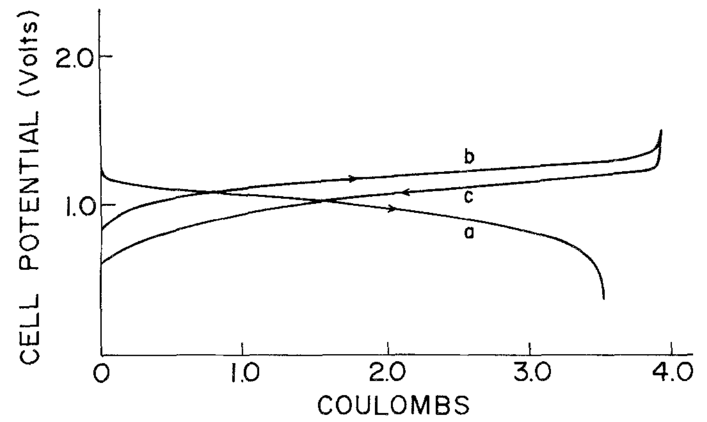

Fig. 1. Discharge/charge curves of emeraldine base/1.0 M $ZnCl_2$/Zn cell. (a) First discharge, (b) first charge, (c) second discharge.

1.0 M $HgCl_2$ solution for ~3 seconds and was rinsed in distilled water. It was then placed in the cell so that the circular flat Zn surface was in good contact with the glass filter paper. The electrode was then mechanically clamped firmly in place under downward pressure.

Approximately 2 ml of 1.0 M $ZnCl_2$ solution (pH ~ 4) degassed previously by passing argon for 1 h, was then poured down the glass tube. About 0.5 cm layer of molten paraffin wax was finally poured on to the top of the electrolyte. All experiments were carried out under argon inside a glove bag.

3. Results and discussion

3.1. *Electrochemical determination of the oxidation state of polyaniline base*

The cell described above exhibited an immediate pre-equilibrium initial open circuit voltage of 1.18 V against Zn i.e. +0.18 V (against SCE). The emeraldine base was then reduced to leucoemeraldine base during 97 min at a constant current of 0.75 mA cm^{-2}. The area referred to is the 0.8 cm^2 of Pt disc inside the circular glass tube. This reduction step was terminated when the final cell potential reached 0.50 V (against Zn) i.e. −0.50 V (against SCE). The relationship between the cell potential and the coulombs in the reductive reaction is shown in curve (a) Fig. 1. As can be seen, no significant reduction occurred after the cell potential reached 0.65 V (against Zn), i.e. −0.35 V (agaisnt SCE) when the cell potential began to drop sharply. The total charge liberated when the cell potential reached 0.65 V was 3.50 C. The calculated charge required for complete reduction of 7.0 mg of emeraldine base to leucoemeraldine base according to equation (1) is 3.73 C.

$$[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-(C_6H_4)-N{=}(C_6H_4){=}N-]_x + (2x)H^+ + (2x)e \qquad (1)$$
$$\downarrow$$
$$[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-(C_6H_4)-N(H)-(C_6H_4)-N(H)-]_x$$

If the error in weighing the 7.0 mg of emeraldine base is ±0.2 mg then the oxidation state of the analytically pure emeraldine base used in this study can be expressed by the formula:

$$[(-C_6H_4)-N(H)-(C_6H_4)-N(H)]_{\overline{0.531 \pm 0.014}}[(C_6H_4)-N{=}(C_6H_4){=}N-]_{0.469 \pm 0.014}$$

Hence the polyaniline appears to have an oxidation state close to that of emeraldine, $[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-(C_6H_4)-N=(C_6H_4)=N-]_x$.

An additional experiment was performed in order to demonstrate that the as-synthesized polyaniline base used in constructing the cell employed in the above study was slightly less oxidized than that expected for the emeraldine oxidation state. On oxidizing the leucoemeraldine base, i.e. $[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-(C_6H_4)-N(H)-(C_6H_4)-N(H)-]_x$ obtained at the conclusion of the above experiment, at a constant current of 0.75 mA cm^{-2} the cell potential began to increase rapidly at 1.40 V as shown by curve (b) Fig. 1 indicating the termination of a discrete oxidation step believed to be the attainment of the emeraldine oxidation state of polyaniline. A total charge of 3.82 C was involved in this step. Immediate reduction to a cell voltage of 0.65 V at 0.75 mA cm^{-2} as shown in curve (c) Fig. 1 resulted in the passage of 3.82 C representing 100% coulombic efficiency. This value can be compared with the corresponding value of 3.50 C obtained by a similar reduction of the as-synthesized polyaniline in the previous experiment to 0.65 V. The value of 3.82 ± 0.11 C is in agreement with the calculated value of 3.73 C for the reduction of 7.0 ± 0.2 mg of emeraldine base to leucoemeraldine base as given by equation 1. This serves as confirmatory evidence that the as-synthesized polyaniline was slightly less oxidized than that expected for the emeraldine oxidation state of polyaniline.

3.2. *Constant current discharge characteristics*

The maximum capacity of the cell calculated from equation (1) is 148.1 Ah kg^{-1} if only the weight of the emeraldine base is used. If the calculated weights of Zn and HCl involved in the discharge reaction are used this figure is reduced to 107.2 Ah kg^{-1}. The experimentally observed 3.82 C involved in the 0.75 mA cm^{-2} discharge reaction given in section 3.1

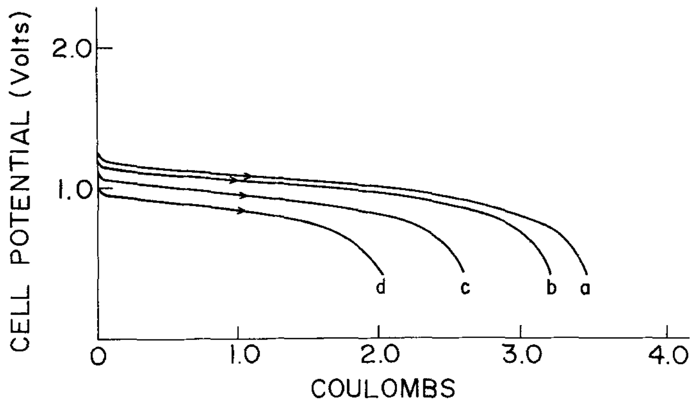

Fig. 2. Constant current discharge characteristics of emeraldine base/ 1.0 M $ZnCl_2/Zn$ cell at (a) 0.75, (b) 3.00, (c) 6.00, (d) 12.00 mA cm^{-2}.

corresponds to a capacity of 151.5 ± 4.3 Ah kg^{-1} based only on the weight of polyaniline (7.0 ± 0.2 mg) employed, corresponding within experimental error to the calculated value of 148.1 Ah kg^{-1}. When the weights of Zn and HCl consumed during the discharge reaction are taken into account this experimental capacity value is reduced to 109.3 ± 2.2 Ah kg^{-1}. The corresponding energy density values for the average discharge voltage of 1.05 V (see curve C, Fig. 1) are 159.1 ± 4.5 Wh kg^{-1} (based on the weight of emeraldine base employed) and 114.8 ± 2.3 Wh kg^{-1} (based on the weight of emeraldine base, together with Zn and HCl consumed during the discharge reaction). The energy density value of 159.1 Wh kg^{-1} is somewhat higher than the corresponding value of 139 Wh kg^{-1} reported by Kitani *et al.* [4] for electrochemically synthesized polyaniline.

The cell described in the previous section was charged (leucoemeraldine base oxidized to emeraldine base) at a constant current of 0.75 mA cm^{-2}. This charging step involved only 3.50 C, i.e. the polyaniline base electrode was oxidized to only 94% of its maximum capacity based on equation (1). The slight decrease in capacity was apparently caused by the loosening of the upper wax seal which was visually observable. It is believed that this decreased the efficiency of the contact between the polyaniline powder and the Pt current collector. The overall charge/discharge reaction is given by equation (2).

$$[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-(C_6H_4)-N{=}(C_6H_4){=}N-]_x + (2x)HCl + (x)Zn$$
$$\text{charge}\uparrow \; \downarrow\text{discharge} \qquad (2)$$
$$[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-(C_6H_4)-N(H)-(C_6H_4)-N(H)-]_x + (x)ZnCl_2$$

The HCl required for equation (2) is provided by the partial hydrolysis of the $ZnCl_2$ in the electrolyte (pH ~ 4) *viz.*

$$ZnCl_2 + H_2O \rightleftharpoons Zn(OH)(Cl) + HCl \qquad (3)$$

At this pH it was shown previously [9] that the emeraldine base is electrochemically active presumably because of slight protonation.

At the end of the charging step, the cell was immediately discharged at a constant current of 0.75 mA cm^{-2}. The cell potential was then held at 0.65 V for 12 h before the next charging step was undertaken. This procedure was repeated for discharge currents of 3.00, 6.00 and 12.00 mA cm^{-2}. The relationship between the cell potential and the charge involved in each of these discharges is shown in Fig. 2. The corresponding average discharge voltage, energy density and power density values are given in Table 1.

3.3. *Cell recyclability studies*

Another cell was constructed as described in section 3.1 and was charged at 0.75 mA cm^{-2} from 0.65 V to 1.40 V and then immediately discharged to 0.65 V at 0.75 mA cm^{-2}. This deep charge/discharge process was carried out for 30 cycles. The coulombic efficiency and capacity values for selected cycles are given in Table 2. The coulombic efficiency of the cell remained over 97% after the second cycle and the capacity remained over 95% of that of the second cycle at the end of 30 cycles. It is believed that the slight decrease in cell capacity might have been related to the slow formation of gas, presumably H_2 formed on the Zn electrode which loosened the upper wax seal through which the Zn stem protruded, thus slowly decreasing the efficiency of the polyaniline/Pt contact. This study indicates that chemically synthesized emeraldine base exhibits very promising characteristics as a reversible cathode-active material under the experimental conditions employed.

It should also be noted that the 1.40 V used for termination of the charging cycle was chosen arbi-

Table 1. Average discharge voltage, energy density and power density values at different constant current discharge rates

Discharge current (mA cm^{-1})	*Average discharge voltage* (V)	*Energy density** (Wh kg^{-1})	*Power density** (W kg^{-1})
0.75	1.02	104.4	64.5
3.00	0.97	96.1	250.3
6.00	0.87	72.0	469.7
12.00	0.80	51.7	916.4

* Energy density and power density values are calculated based on the weight of polyaniline base used in cell construction together with the weights of Zn and HCl consumed during discharge.

trarily as a voltage at which good recyclability in cyclic voltammetry experiments was observed. On-going studies suggest that higher charging voltages with resulting increase in both capacity and energy density *may* be obtainable at the expense of some loss in recyclability where optimum pH and electrolyte composition have been determined precisely.

Table 2. Coulombic efficiency and normalized capacity for selected deep charge/discharge cycles

Cycle number (n)	*Coulombic efficiency** %	*Normalized capacity*† %
2	95.7	100
5	97.0	98.5
10	97.0	98.5
14	97.0	98.5
20	97.0	97.0
25	98.4	97.0
30	98.4	95.5

* [(Coulombs out)/(Coulombs in)].

† [(Coulombs out at end of nth cycle)/(Coulombs out at end of second cycle)].

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