Studies of Zn/ZnX₂/polyaniline batteries. 1. X = Cl and Br

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The cycling behaviour of polyaniline in chloride and bromide media is discussed. In both media some charge, equivalent to a charge storage capacity of 100 A h kg⁻¹, may be stored in the first oxidation step of polyaniline. Further evidence is presented that the oxidation product is emeraldine rather than the fully oxidized imine. In chloride media, attempts to store more charge led to rapid irreversible changes in the polymer and degradation in battery characteristics. In bromide media, further charge may be stored via the Br⁻/Br₅ couple and, although the Br₂ attacks the polymer slowly, the polymer retains the ability to cycle charge efficiently and gives a stable open-circuit voltage. The nature of the changes caused by Br₂ attack on the polyaniline is discussed. It is concluded that bromide is the better electrolyte, but self discharge by slow exchange of Br₅ in the polymer with Br⁻ in the surrounding electrolyte remains an unsolved problem.

1. Introduction

The last few years have seen intense activity towards the development of a ‘polymer battery’ [1] where the electroactive materials are conducting polymers. A favoured polymer has been polyacetylene [2] because it may be both p-doped by the intercalation of anions and n-doped by the intercalation of alkali metal cations. Both doping reactions are highly reversible and the combination of p- and n-doped materials leads to a rechargeable battery with a large voltage and high energy density. Unfortunately, however, the characteristics of the cell are limited by the poor chemical stability of polyacetylene particularly when positively charged [3, 4]. Hence the charge storage characteristics of other organic conductors are receiving attention.

Polyaniline was first prepared in the 19th century [5]; Moreover, its high conductivity and the possibility for utilizing its redox properties for electrical energy storage have been recognized for some time [6, 7]. Recent studies have concentrated on understanding the multistep oxidation processes of the neutral polymer [8–11]. Reversible charge–discharge cycling is likely to be limited to the first oxidation step; in acid solution it has recently been concluded by two different groups that the first oxidation product is the emeraldine salt, II [12] or the imine salt, III [9–11]
In both cases it can be seen that the doping process involves both protons and electrons and it was concluded by both groups that further oxidation leads to irreversible changes to the polymer. Whether the couple is in fact I/II or I/III, the potential for the redox change in the polymer is 0.2–0.3 V versus SCE, rather low for a battery electrode, but the absence of degradation processes and the ability of polyaniline to store considerable charge through this redox process have led to proposals for both aqueous [13] and non-aqueous batteries [14].

In the present study the charge–discharge characteristics of Zn–polyaniline batteries with both ZnCl₂ and ZnBr₂ electrolytes have been examined. Particularly with the ZnBr₂ cell, attention has been paid to the behaviour of the polyaniline when oxidized beyond the first oxidation step. The aim of the study was to assess whether the charge-storage capability of the polymer could be increased by oxidation of the Br⁻ in the polymer to Br₅⁻ and to investigate the structural changes resulting from attack by bromine. In an earlier paper it was shown that the Br⁻/Br₅⁻ couple could be cycled within polypyrrole, but the stability of the oxidized polymer was insufficient for battery application [15].

2. Experimental details

The polyaniline electrodes were prepared and the model battery assembled by the following procedure. The support for the polyaniline was a high-porosity, reticulated vitreous carbon (RVC) disc (radius, 2.5 cm; height, 0.5 cm) fixed to a graphite disc as a current collector. This structure was mounted inside a cylindrical, polyethylene cell and was separated from the zinc disc electrode by a cellulose membrane. A hole in the zinc electrode allowed the introduction of a probe to control the potential of the RVC electrode versus SCE. To enhance the uniformity of deposition, the solution was pumped through the cell. The weight of the deposit was determined from the charge using a calibration graph. After this preparation the polyaniline was conditioned to the chosen electrolyte by repeated soaking of the cell with new aliquots of this electrolyte for 24 h.

Charge–discharge cycles were obtained at constant current, and the voltage between the zinc and polyaniline electrodes was monitored as a function of time.

Some experiments used a 0.06 cm² polished, vitreous carbon disc electrode as the support for the polyaniline. In these cases the film was formed by cycling the potential between −0.3 V and +0.8 V versus SCE in a solution of 1.5% aniline in 0.5 mol dm⁻³ H₂SO₄ and then conditioned with the medium of choice. Experiments with these electrodes employed a standard, three-electrode cell.

The compositions of both the chemically and electrochemically prepared samples of polyaniline were determined by elemental analysis. The composition of films after exposure to Br₂ was also investigated by mass spectroscopy (Hitachi–Perkin Elmer RMV spectrometer). Conductivities were measured on pressed (3 tons cm⁻²) polyaniline discs; a Kulike and Sofia four-probe head (linearly arranged) was used in conjunction with a digital voltmeter and ammeter (Keithley).

All chemicals were commercially available grades and were used as supplied. The RVC was from Fluorocarbon Co. and had a porosity of 100 pores per inch.

3. Results and discussion

3.1. Chemical composition of the polyaniline samples

Before constructing the model battery, some tests were performed to determine the yield of polyaniline (mg C⁻¹) and its chemical composition. The polymer was deposited from a solution of 1.5% aniline in 0.5 mol dm⁻³ H₂SO₄ onto platinum and gold anodes (each of area 10 cm²) and used a potential of +0.8 V. Ten experiments were carried out and charges between 1 and 10 C cm⁻² were used in the polymerizations. After each deposition the electrode was