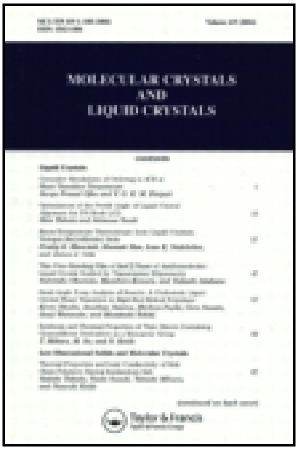

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Alan G. Macdiarmid [a], Shao-Lin Mu [a], Nanayakkara L.D. Somasiri [a] & Wanqun Wu [a]
[a] Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, 19104, U.S.A.

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ELECTROCHEMICAL CHARACTERISTICS OF "POLYANILINE" CATHODES AND ANODES IN AQUEOUS ELECTROLYTES

ALAN G. MACDIARMID, SHAO-LIN MU, NANAYAKKARA L.D. SOMASIRI, and WANQUN WU
Department of Chemistry, University of Pennsylvania,
Philadelphia, Pennsylvania, 19104, U.S.A.

Abstract - The quinoid-benzenoid-diimine form, $(=(C_6H_4)=N-(C_6H_4)-N=)_x$ of "polyaniline" shows excellent cathode characteristics including recyclability when used in conjunction with a zinc anode in an aqueous electrolyte of (1.0M $ZnCl_2$ + 0.5M NH_4Cl) having a pH of ~ 4. The reduced form of this material, $(-(C_6H_4)-N(H)-(C_6H_4)-N(H)-)_x$ can be used as an anode in conjunction with a PbO_2 cathode in an aqueous 0.5M $Pb(BF_4)_2$ electrolyte.

INTRODUCTION

The synthesis, chemistry, cyclic voltammetry and change in conductivity of certain forms of "polyaniline" in the presence of aqueous media have been described in our previous paper.[1] The nomenclature used for the various forms of polyaniline in this communication is identical to that employed in the above paper. The cyclic voltammetry studies showed that forms 1A and 2A of polyaniline could be interconverted with ~ 100% coulombic efficiency over at least 50 complete cycles in a (1.0M $ZnCl_2$ + 0.5M NH_4Cl; pH ~ 4) aqueous electrolyte when cycled between 0.50V and 1.40V (Zn^{+2}/Zn reference electrode).[1,2] This suggested that form 1A of polyaniline might act as an excellent cathode in rechargeable battery cells employing a zinc anode.[2]

The use of a water-based electrolyte in rechargeable batteries has certain obvious advantages--an important one being that the ionic conductivity of aqueous electrolytes is greater than that of non-aqueous electrolytes and hence, other factors being equal, cells employing aqueous electrolytes might be expected to deliver a higher output current. Studies by Jozefowicz[3] have shown that forms 1S and 2S may be used as the anode and cathode in a rechargeable battery cell in aqueous 1N H_2SO_4. These cells exhibited an open circuit voltage of ~ 0.40 volts. Few data were given concerning the recyclability of either the anode material or the cathode material in any aqueous electrolyte.

THE Zn/1.0M $ZnCl_2$ + 0.5M NH_4Cl + 0.1M $NaBF_4$/POLYANILINE (2A) CELL

Three types of cells were studied having the above configuration in which form 2A of polyaniline was used as the anode.

Cell Using Electrochemically Synthesized Polyaniline

Approximately 3.1 mg of form 2S were deposited electrochemically on both sides of a 3.2 cm^2 piece of Pt foil as described previously[1] and was used as the cathode together with a lightly amalgamated zinc anode in the above electrolyte (pH ~ 4-5). Subsequent studies showed that it was not necessary to have $NaBF_4$ in the electrolyte. As described previously[1], the 2S form will dissociate spontaneously and essentially completely to the 2A form in an aqueous solution of this pH. All experiments were performed in air unless stated to the contrary.

The cell was discharged at a constant current of 0.05mA/cm^2 to a cell potential of 0.85V at which time the very pale yellow color characteristic of the 1A form was clearly apparent on the Pt foil electrode. The discharge reaction is :

$$\underset{\text{(form 2A)}}{[=(C_6H_4)=N-(C_6H_4)-N=]_x} + xZn + 2xHCl \rightarrow \underset{\text{(form 1A)}}{[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-]_x} + xZnCl_2 \qquad (1)$$

The cell was then recharged at a constant current of 0.05mA/cm^2 to a potential of 1.40 volt at which time the dark green color of form 2A was visible on the electrode. A total of 46 complete cycles were performed. The coulombic efficiency for all cycles fell between 92-99% and the capacity at the end of the 46th cycle was 96% that of the first cycle. The charge and discharge currents were then increased to 0.1mA/cm^2. The coulombic efficiency for each complete cycle remained within the range 93-96% for the next 155 cycles and the capacity at the end of the 155th cycle, i.e. a total of 201 cycles was 92% that of the 47th cycle. The cell was then charged at 0.1mA/cm^2 from 0.70V to 1.35V. Six hours after termination of charging the cell potential had fallen to 1.29V but during the next 30 days it decreased only slightly to 1.20V. Upon discharging to 0.70V at 0.1mA/cm^2 a 98% coulombic recovery was obtained.

Cell Using Chemically Synthesized Polyaniline

A 7% (by weight) solution of ethylene propylene terpolymer binder in cyclohexane was mixed with 2.5mg of carbon black and 25 mg of polyaniline form 2S (Cl^- anion) powder prepared chemically as previously described[1]. The fluid mixture was painted on to ~ 1.5cm^2 of a carbon rod current collector and was dried under dynamic vacuum. In a typical experiment the carbon rod/polyaniline electrode was placed 1 cm from an amalgamated zinc sheet electrode in 10ml of (1.0M $ZnCl_2$ + 0.5M NH_4Cl; pH ~ 4) electrolyte. The cell exhibited an open circuit voltage of 1.40V and a short circuit current of ~ 150mA. The cell was then cycled between 1.40V and 0.70V at 1mA for 19 cycles. Coulombic efficiencies of over 95% for each cycle and ~ 100% retention in capacity from the first to the 19th cycle were observed.

Cell Using a Flashlight Battery Configuration

In a preliminary experiment, 300mg of polyaniline powder (form 2S) (Cl^- anion) synthesized as described previously[1] were mixed with 10% by weight of carbon black and formed into a paste with 0.5 ml of (1.0M $ZnCl_2$ + 0.5M NH_4Cl) electrolyte. The cell was constructed from a commercial "AA" size flashlight battery by removing all electroactive materials and replacing them with the above paste which was separated from the lightly amalgamated Zn casing by a porous Celgard 3500 film. A carbon rod ($1.5cm^2$) was inserted as a current collector and the top of the cell was sealed with molten paraffin wax. The cell exhibited an open circuit voltage of 1.40V and a short circuit current of ~ 800mA. It was recycled at a constant current of ~ 5.0mA between 1.40V and 0.50V with a coulombic efficiency of > 90%. Each charge and discharge cycle took ~ 6 hours.

CELL CHARACTERISTICS

Based on the sum of the weights of all three compounds involved in the discharge reaction given by equation 1 and on a very slow average discharge voltage of 1.1V, the cell described in this study has a semi-theoretical energy density of 184 watt hr/kg (capacity = 167 amp hr/kg). This compares favorably with the theoretical energy density of 186 watt hr/kg for a lead-acid battery. The actual capacity realized from a cell of this type is critically dependent on the method of fabrication of the cathode. It should also be noted that the 1.40V used for termination of the charging cycle has been chosen arbitrarily as a voltage at which good recyclability in cyclic voltammetry experiments has been observed[1]. Ongoing 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.

THE POLYANILINE (FORM 1A)/0.5M $Pb(BF_4)_2/PbO_2$ CELL

Preliminary studies were carried out on a rechargeable cell using polyaniline (form 1A) as an anode and PbO_2 as a cathode in a supporting electrolyte of 0.5M $Pb(BF_4)_2$. The simplest overall discharge reaction is:

$$\underset{\text{(form 1A)}}{[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-]_x} + xPbO_2 \rightarrow \underset{\text{(form 2A)}}{[=(C_6H_4)=N-(C_6H_4)-N=]_x} + xPbO + xH_2O \qquad (2)$$

Since the potential of the PbO_2 electrode is very sensitive to the pH of the electrolyte the cell reaction and potential will depend on pH.

A polyaniline (form 1A) film was prepared electrochemically[1]. The PbO_2 powder was attached to a Pt grid current collector using the ethylene propylene terpolymer binder described previously. The cell exhibits an open circuit voltage of ~ 1.40V. Its coulombic efficiency and capacity on cycling between 1.25V and 0.80V at 0.05mA/cm^2 remained in excess of 95% during 40 cycles. Form 1A of polyaniline apparently acts as a reasonably good anode in a cell of this type.

CONCLUSION

The practical development of a rechargeable cell of the above type using a polyaniline cathode may well be limited by the less than ideal recycling properties of zinc anodes. However, these studies show conclusively that an organic polymer can serve in an aqueous electrolyte as a cathode active material exhibiting excellent recyclability and a good gravimetric energy density and that it also has potentiality as an anode in an aqueous electrolyte.

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