

Short communication

Functionalized polythiophene-coated textile: A new anode material for a flexible battery

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Abstract

A new all-polymer battery system has been developed. Polypyrrole and styryl-substituted dialkoxyterthiophene (poly(OC₁₀DASTT)) are used as the cathode and anode material, respectively. The anode electrode is prepared by directly casting undoped neutral poly(OC₁₀DASTT) from chloroform solution on two different substrates (current-collectors), carbon-fibre mat or Ni/Cu-coated nonwoven polyester. Poly(OC₁₀DASTT) exhibits electroactivity on these two substrates, and batteries containing the polymers show different charge/discharge properties. All the batteries show a high discharge efficiency of over 94%, and a discharge capacity of 39.1 mAh g⁻¹ is obtained for the battery with an anode that consists of poly(OC₁₀DASTT) on Ni/Cu-coated nonwoven polyester.

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1. Introduction

Electronically conducting polymers exhibit a wide range of electrochemical properties that have been utilized in areas such as sensors [1], electrochromic devices [2], and charge-storage devices, i.e., supercapacitors [3] and batteries [4,5]. Conducting polymers possess several advantages as electrode materials in batteries. First, the electrochemical properties can be controlled at the molecular level by manipulating the monomer structure [6,7] or by doping [8,9]. Second, surface area can be controlled by the conditions used for polymerization and/or by the substrate on to which the polymer is coated.

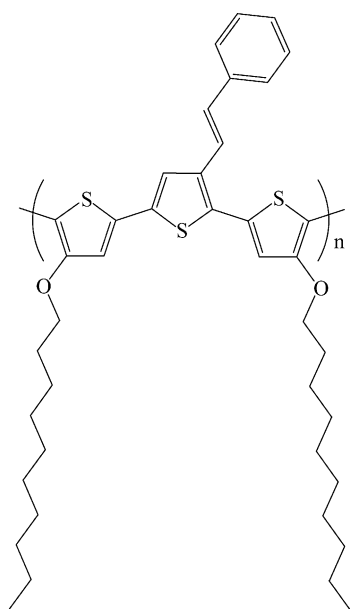
Killian et al. [10] reported a battery system based on the polymer polypyrrole, which exhibited a specific capacity of 22 mAh g⁻¹. The anode was polypyrrole containing polystyrenesulfonate (PSS) as dopant and the cath-

ode was polypyrrole containing perchlorate (ClO₄⁻) as dopant. A system based on polythiophenes was reported by Gofer et al. [11] where the cathode and anode materials were 3-(3,5-difluorophenyl)thiophene and 3-(3,4,5-trifluorophenyl)thiophene, respectively. This system produced a discharge capacity of 9.5–11.5 mAh g⁻¹. Another type of all-polymer battery reported by Rehan [12] with a poly(1-naphthol) cathode and a polyaniline anode gave a discharge capacity of 150 mAh g⁻¹. Polyaniline was also investigated as an anode material with a polyindole cathode by Cai et al. [13] and this cell exhibited a specific capacity of 79 mAh g⁻¹. An inorganic acid (perchloric acid or sulfuric acid) based electrolyte was used in these two systems. This requires the use of inert Pt or Pd substrates for the polymer coating.

In this paper a styryl-substituted dialkoxyterthiophene (OC₁₀DASTT) (**I**: shown below) in its undoped neutral state has been investigated for use as the anode material. The alkoxy substituents enhance the stability and processability [14] of the material. The cathode material is polypyrrole

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with hexafluorophosphate as a dopant, as described previously [15].



I

Structure of poly(OC₁₀DASTT)

Of particular interest is the ability to coat metallated textiles with this compound. This is considered to be the first step towards the development of a flexible textile battery, which is an area of great interest to those involved in the emerging field of electronic textiles.

2. Experimental

2.1. Preparation of electrodes

Polypyrrole films were electropolymerized galvanostatically at a current density of 1.0 mA cm^{-2} on stainless-steel mesh from propylene carbonate (PC) solution that contained 0.06 M monomer (pyrrole) and 0.05 M tetrabutylammonium hexafluorophosphate (TBAPF₆). This solution was de-oxygenated with nitrogen, and polypyrrole was electrodeposited to a charge density of 3.0 C cm^{-2} .

The synthesis and characterization of the OC₁₀DASTT monomer is reported elsewhere [16]. Poly(OC₁₀DASTT) had an average molecular weight of approximately 8000 Da (MALDI-MS analysis), and exhibited a conductivity in the oxidized and neutral states of 1.1 and $1.2 \times 10^{-4} \text{ S cm}^{-1}$, respectively. The undoped neutral polymer was dissolved in chloroform and drop cast on to either carbon-fibre mat (Spectracarb 1010, Spectracorp, USA) or Ni/Cu-coated nonwoven polyester (Laird Technologies # 3027-217). Several coats were applied to give a polymer coating of $\sim 1 \text{ mg cm}^{-2}$.

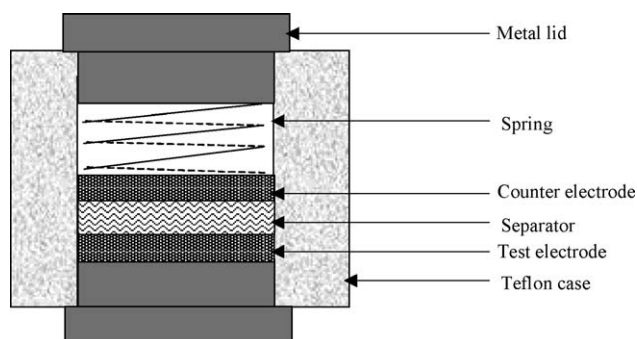


Fig. 1. Schematic diagram of Teflon test cell.

2.2. Fabrication of cell

The polymer–polymer battery system was tested in a Teflon test cell (Fig. 1). In this cell, PPy/PF₆ was coated on a stainless-steel mesh ($1 \times 1 \text{ cm}^2$), and acted as the cathode while poly(OC₁₀DASTT)/ClO₄ coated on the textile ($1 \times 1 \text{ cm}^2$) was used as the anode.

The electrolyte was 1.0 M LiPF_6 in 1:1 ethylene carbonate (EC):dimethylcarbonate (DMC) solution. The separator was Celgard 2500 (microporous polypropylene membrane). The cells were assembled in an argon-filled glove box (Unilab, Mbraun, USA).

2.3. Electrochemical properties

Cells were tested using a battery-testing device (Neware Electronic Co., China). The cells were charged galvanostatically at a certain current density to a cell voltage of 1.65 V , then discharged using the same current to a cut-off voltage of 0.2 V . For the cycle-life test, a charge/discharge current density of 0.05 mA cm^{-2} was applied. Cyclic voltammetry of the polymer was performed using an EG&G PAR 363 Potentiostat/Galvanostat, a MacLab 400, and EChem v 1.3.2 software (AD Instruments). The electrochemistry was performed using a standard one-compartment three-electrode cell with a stainless-steel mesh counter electrode, a Ag/Ag⁺ (CH₃CN) reference electrode, and a $0.05 \text{ M TBAPF}_6/\text{PC}$ electrolyte.

2.4. Surface morphology

The surface morphologies of the electrodes were investigated by means of a scanning electron microscope (SEM, Leica Model Stereoscan 440) with a secondary electron detector. All electrode materials were sputter-coated with gold in advance.

3. Results and discussions

3.1. Surface morphology

The surface morphology of the polymer, poly(OC₁₀DASTT), cast on different substrates is shown

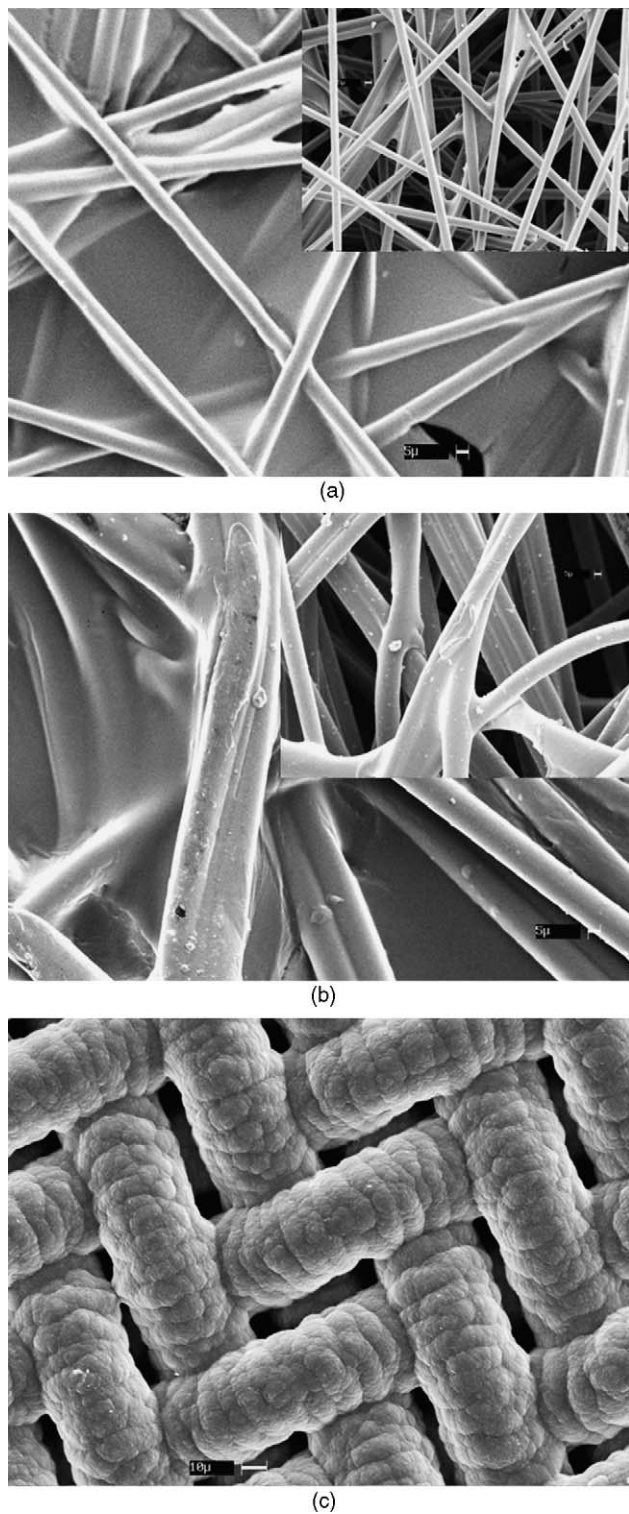


Fig. 2. Scanning electron micrographs of (a) poly(OC₁₀DASTT) on carbon-fibre mat; (b) poly(OC₁₀DASTT) on Ni/Cu-coated nonwoven polyester (with insets of blank substrates displayed); (c) polypyrrole on stainless-steel mesh.

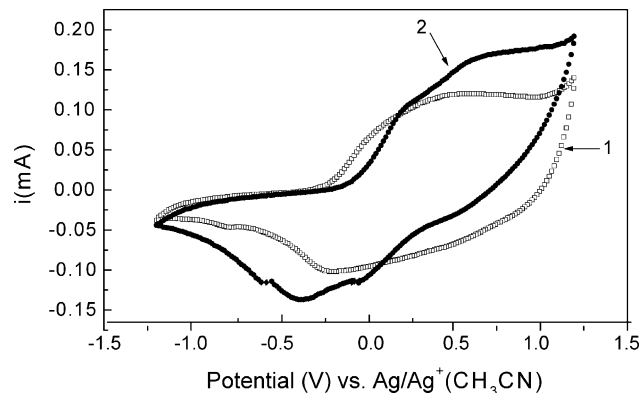


Fig. 3. Cyclic voltammograms for poly(OC₁₀DASTT) cast on different substrates. (Electrolyte is 0.05 M TBAPF₆ in propylene carbonate, scan rate = 10 mV s⁻¹, geometric area = 1 cm².) Curves: (1) poly(OC₁₀DASTT) on carbon-fibre mat; (2) poly(OC₁₀DASTT) on Ni/Cu-coated nonwoven polyester.

in Fig. 2. The images of coated substrates of carbon-fibre mat and Ni/Cu-coated nonwoven polyester, are presented in Fig. 2(a) and (b), respectively, with insets of the blank substrates displayed in the upper right corner for comparison. It can be seen that the poly(OC₁₀DASTT) completely covers the fibres with a smooth film.

The polymer has a propensity to form a web between the textile fibres. An image of the cathode material, polypyrrole, electropolymerized on stainless-steel mesh is presented in Fig. 2(c) and shows that the polymer grows uniformly on the mesh, with a typical cauliflower morphology.

3.2. Cyclic voltammetry

Cyclic voltammograms were obtained for poly(OC₁₀DASTT) coated on to different substrates (Fig. 3). For both coated substrates, the oxidation/reduction of the

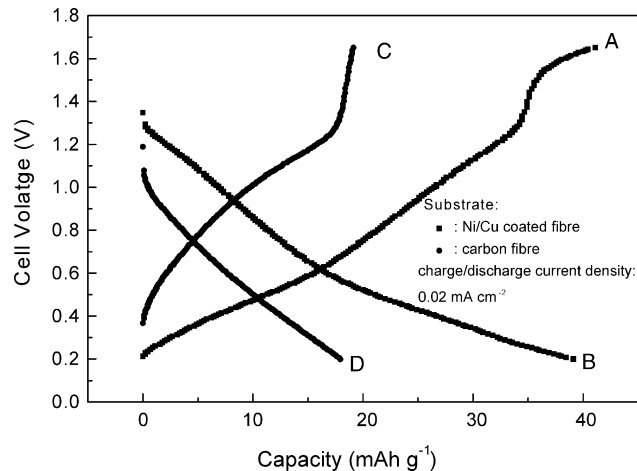


Fig. 4. (A, C) charge and (B, D) discharge curves for cells at the charge/discharge current density of 0.02 mA cm⁻² (poly(OC₁₀DASTT) on substrates of (A, B) Ni/Cu-coated nonwoven polyester and (C, D) carbon-fibre mat.

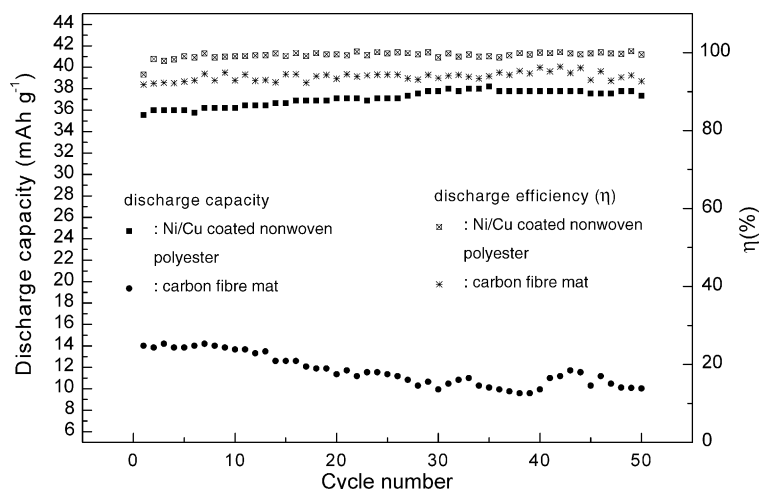


Fig. 5. Cycle-life of cells composed of poly(OC₁₀DASTT)/LiPF₆/PPy (anode substrates are Ni/Cu-coated nonwoven polyester or carbon-fibre mat).

conducting polymer coating is obvious and is similar to that observed for the polymer coated on a more conventional electrode substrate [16].

3.3. Charge/discharge characteristics

Galvanostatic charging and discharging were used to evaluate the capacity. In this work, the cells were designed to be anode-limited. The charge/discharge capacity was calculated based on the amount of the active material (poly(OC₁₀DASTT)) in the anode (Fig. 4). The cell voltage decreases/increases as the depth of the discharging/charging is increased, which is characteristic of rechargeable batteries. Charge and discharge capacities of 41.1 and 39.1 mAh g⁻¹, respectively, are obtained for the cell with poly(OC₁₀DASTT) on a Ni/Cu-coated nonwoven polyester. This is much higher than the 22 mAh g⁻¹ that has been reported for polypyrrole systems [10] or the 9.5–11.5 mAh g⁻¹ for polythiophenes [11]. It is however, still lower than the discharge capacity reported in Refs. [12,13], but it should be noted that an inorganic acid was used in these latter two systems. By comparison, the cell that employed poly(OC₁₀DASTT) on the carbon-fibre mat substrate as an anode exhibits much lower charge and discharge capacities of 19.1 and 18.0 mAh g⁻¹. It can also be observed that the cell with poly(OC₁₀DASTT) on Ni/Cu-coated nonwoven polyester displays a higher discharge voltage and a lower charge voltage. These results indicate that the cell with an anode of poly(OC₁₀DASTT) on Ni/Cu-coated nonwoven polyester substrate possesses better charge/discharge properties as a rechargeable battery.

The cells were also investigated using a range of charge/discharge current densities. The discharge capacities are observed to decrease with increasing current density. Using poly(OC₁₀DASTT) on Ni/Cu-coated nonwoven polyester, discharge capacities of 35.4, 31.6, 31.1 and 20.9 mAh g⁻¹ are obtained at 0.05, 0.1, 0.2 and 0.5 mA cm⁻², respectively. The cell containing an anode of poly(OC₁₀DASTT) on carbon-fibre mat displays much lower discharge capacities of 13.7 and 6.2 mAh g⁻¹ at 0.05 and 0.1 mA cm⁻². This cell was not investigated at higher discharge current because of its low discharge capability even at 0.1 mA cm⁻².

The rate capability (ϕ) is an important parameter for estimating the fast-discharge properties of a cell:

$$(\phi) = \text{Capacity}_{\text{higher current}} / \text{Capacity}_{0.02 \text{ mA cm}^{-2}} \quad (1)$$

The observed rate capabilities are shown in Table 1. The data show that cells with a poly(OC₁₀DASTT) anode material on Ni/Cu-coated nonwoven polyester have a promising fast-discharge ability. The rate capability decreases slowly with increasing current, and it is 53.4% at 0.5 mA cm⁻². The cell using carbon-fibre mat as the anode substrate shows a poor rate capability, that declines significantly with increasing discharge current. It shows a rate capability of 34.4% at 0.1 mA cm⁻². The findings indicate that the cell with poly(OC₁₀DASTT) on a Ni/Cu-coated nonwoven polyester has a higher rate capability than one with carbon-fibre mat for a poly(OC₁₀DASTT)/LiPF₆/PPyPF₆ system. Thus, the former possesses better fast-discharge properties.

Table 1
Rate capability (ϕ) of cells containing poly(OC₁₀DASTT) cast on two different substrates as anode

Discharge current density (mA cm ⁻²)	0.02	0.05	0.1	0.2	0.5
ϕ Ni/Cu-coated nonwoven polyester (%)	100	88.07	80.68	79.54	53.40
ϕ Carbon-fibre mat (%)	100	76.07	34.72	Not investigated	Not investigated

3.4. Cycle-life

Discharge capacity as a function of the cycle-number is shown in Fig. 5. The cells with poly(OC₁₀DASTT) on Ni/Cu-coated nonwoven polyester as anode demonstrate a promising cycle-life, i.e., the discharge capacity does not deteriorate after 50 cycles. This cycle-life is similar to that of the polypyrrole system reported in Ref. [10], whereas only about 86% of the initial discharge capacity was retained after 50 cycles for polyaniline and polynaphthol systems [12]. No direct data exhibiting the dependence of discharge capacity on cycle-number was reported in Refs. [11,13]. By contrast, the discharge capacity of the cells with poly(OC₁₀DASTT) on carbon-fibre mat as anode dropped to 71.5% of the initial capacity after 50 cycles. The discharge efficiency (η), defined as the ratio of discharge capacity to charge capacity was also investigated and is reported in Fig. 5. Both types of cell show a high discharge efficiency of over 94%, although a slightly higher discharge efficiency is obtained for the cell with anode material on Ni/Cu-coated nonwoven polyester.

4. Conclusions

A styryl-substituted dialkoxyterthiophene polymer, (poly(OC₁₀DASTT)), has been successfully cast on two different substrates, namely carbon-fibre mat and Ni/Cu-coated nonwoven polyester, from a chloroform solution. The materials have been examined as anodes in the new battery system of poly(OC₁₀DASTT)/LiPF₆/PPyPF₆. Electron micrographs show that the cast polymer poly(OC₁₀DASTT) forms a smooth film on the substrates. Cyclic voltammograms indicate typical oxidation/reduction processes for poly(OC₁₀DASTT) on these two substrates. Batteries with these materials functioning as anodes are rechargeable but exhibit different electrochemical properties. The battery with the anode material on Ni/Cu-coated nonwoven polyester displays higher charge/discharge capacities, higher rate capability, superior discharge efficiency and a promising cycle-life. These observations demonstrate that the sub-

strate plays a very important role in the electrochemical performance of the polymer.

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