



# Conducting Redox Polymer Based Anode Materials for High Power Electrical Energy Storage



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## ARTICLE INFO

### Article history:

Received 21 December 2015

Received in revised form 24 March 2016

Accepted 26 March 2016

Available online 7 April 2016

### Keywords:

conducting redox polymers

terephthalates

polythiophene

n-doping

## ABSTRACT

In this report we present the synthesis and characterization of two conducting redox polymers (CRPs) with polythiophene backbone and diethyl terephthalate pendant groups for the use as anode materials in secondary batteries. The materials show excellent rate capability allowing 30  $\mu\text{m}$  layers to be fully converted within seconds without the use of conductive additives. The high rate capability is traced to the open morphology of the materials that allows for fast ion transport, and to the mediation of electrons through the conducting polymer (CP) backbone. The requirements for the latter are i) that the redox chemistry of the pendant groups and the CP backbone overlaps and ii) that the CP conductivity is not compromised by the presence of the pendant groups. In the CRPs presented herein both these requirements are met and this is thus the first report on successful combination of the redox chemistry of organic redox molecules with the n-doping of conducting polymers.

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## 1. Introduction

Terephthalate derivatives have been extensively used as industrial precursor for polyesters. In the last few years, these electrochemically redox active organic molecules have also attracted significant attention for energy storage applications by virtue of their high reversible charge storage capacity and fast charge/discharge rates which make them competitive to conventional anode materials for lithium ion batteries [1–3]. Terephthalate analogues have two redox processes, resulting in a reversible capacity of 300  $\text{mAh g}^{-1}$  [4], which is comparable to that of graphite (372  $\text{mAh g}^{-1}$ ) [5]. In addition, the utilization of terephthalate-based anode materials also enables the use of cycling chemistries other than lithium-based. For instance, fast insertion/extraction of sodium, as well as of lithium ions in terephthalate crystals has been achieved experimentally [6].

Organic molecules are, however, often soluble in common liquid battery electrolytes, thus causing capacity decay during cycling. This problem has been effectively solved by anchoring the redox groups onto a polymer backbone. Using this strategy good cycling stability has been accomplished for nitroxide radical-based polymer materials [7]. For such materials, a charge hopping

process between redox centers has been proposed as the dominate electron transport mechanism and the rate capability is thus governed by the electron exchange rate which, in the case of nitroxide radicals, is relatively high [8,9]. For redox chemistries with less favorable kinetics such mode of charge transport must be supplemented by other conduction pathways and, even for the facile nitroxide radical redox reaction, this type of charge transport is expected to be effective only over relatively short distances as it relies on transport along a concentration gradient through the film. For large scale electrical energy storage, this shortcoming makes it necessary to use conducting additives, e.g. super P carbon, graphite or carbon nanotubes, that reduce the specific energy of the material [10,11]. In order to address both dissolution problems and conductivity problems, conducting polymers (CPs) have been utilized as backbone for high charge storage capacity redox groups, e.g. quinones onto a polypyrrole backbone [12] poly(3,4-ethylenedioxythiophene) substituted by naphthalene-bisimide [13] or N,N,N',N'-tetraalkylated-p-phenylenediamine [14]. The  $\pi$ -conjugated nature of CPs makes them electronically conducting upon n- and p-doping and the polymeric nature of the resulting materials also reduces problems with dissolution of the active materials due to the increased molecular size. Although most efforts have been devoted to the development of cathode electrode materials, this strategy has also been applied to anode materials based on CPs. Sen, et al. made a battery consisting of polypyrrole decorated with viologens as anode material coupled to a cathode material

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consisting of polypyrrole doped with 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid), yielding a polymer-based battery with a cell electromotive force (emf) of 1.0 V [15]. Otero, et al. prepared a naphthaleneamidinemonoimide-modified polythiophene which showed fast charge/discharge properties and a specific charge of 38 mAh g<sup>-1</sup> for the polymer reduction [16]. In these reports, redox molecules and CPs were combined and the materials were used as anode materials in batteries, but the redox reactions of pendant groups occurred in a potential region where the CP backbone is undoped and thus insulating.

In this report, we have prepared two diethyl terephthalate (DeT)-functionalized polythiophenes, poly(diethyl 2-(thiophen-3-ylmethyl)terephthalate) (PDeTmT) and poly(diethyl 2-(thiophen-3-ylethyl)terephthalate) (PDeTeT). Based on our previous matching studies of the two redox active moieties, the redox reactions of the DeT compound are expected to occur in the n-doping region of the polythiophenes [17]. The redox overlap between DeT electrochemistry and polythiophene n-doping was indeed confirmed in this investigation, e.g. reversible one electron reduction of the DeT group occurred at a redox potential of -2.2 V vs ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) which coincided with the n-doping region of the CP backbone in the conducting redox polymers (CRPs) presented here. Kinetic studies of the CRPs showed fast redox conversion rates of the pendant groups that we attribute to the conducting polymer assisted charge transport, resulting in that films with thickness up to several tenths of micrometers could be fully converted within the timescale of a few seconds with negligible resistive losses.

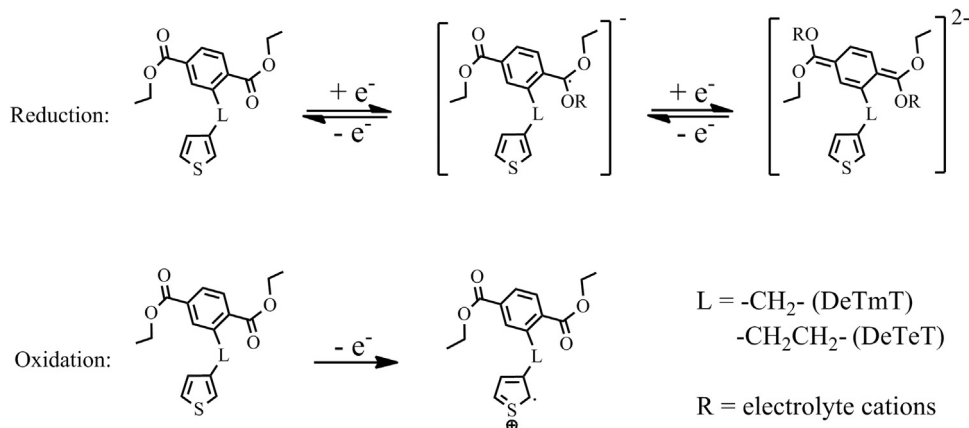
## 2. Experimental

All solvents and chemicals in this investigation were purchased from Sigma-Aldrich, and were used without further purification unless otherwise specified. The solvents in all electrochemical measurements were dried using molecular sieves, 3 Å. Monomers were synthesized as previously reported [18] and the monomers were dried in vacuum at 30 °C for 2 h before use. The polymerization was carried out at ambient temperature by cyclic voltammetry (Autolab PGSTAT302N potentiostat, Ecochemie, Utrecht, The Netherlands) in a three-electrode cell with a glassy carbon (GC, 0.3 mm in diameter) working electrode and a platinum wire counter electrode. The GC electrode was polished using 0.3 μm Alumina (micropolish II, BUEHLER, USA) and subsequently rinsed by ethanol and acetone. An Ag/Ag<sup>+</sup>(AgNO<sub>3</sub>) electrode was used as reference in which a silver wire immersed in the electrolyte solution containing AgNO<sub>3</sub> was placed in a separate compartment. The potential of the reference electrode was calibrated against the

Fc/Fc<sup>+</sup> redox couple in organic solvents and, if not stated otherwise, potentials are reported against Fc/Fc<sup>+</sup> throughout the report. CRPs were grown from an acetonitrile (MeCN) solution with 0.05 mol dm<sup>-3</sup> monomer and a 0.1 mol dm<sup>-3</sup> tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) supporting electrolyte. Polymer samples for scanning electron microscopy (SEM) were electropolymerized onto an indium tin oxide (ITO) glass at a constant potential of 1.3 V vs Fc/Fc<sup>+</sup> for 20s and then equilibrated at -0.5 V vs Fc/Fc<sup>+</sup>. The CRPs were rinsed using ethanol and acetone to remove monomers, oligomers or other possible byproducts formed during the polymerization. Polymer films with different thickness were prepared by varying the numbers of voltammetric sweeps during polymerization. Electrochemical characterization of CRPs was carried out in a three-electrode system as described above in a monomer free electrolyte solution. The solution was degassed by solvent saturated N<sub>2</sub>(g) for 10 minutes prior to polymerization and electrochemical characterization and an N<sub>2</sub>(g) atmosphere was maintained throughout all electrochemical processes. The as-prepared polymers were directly used for capacity fading studies while the polymer samples for kinetic studies were pre-cycled to a stable state. Morphologies of CRPs were characterized by a LEO1550 field emission instrument (Zeiss, Germany). The polymer samples were dried and Au-coated before SEM analysis. For comparison, SEM images of unsubstituted polythiophene were also obtained in the same way. Fourier transform infrared (FTIR) spectra of CRPs (pure sample) were recorded on a BRUKER Tensor 27 with a single reflection diamond ATR crystal and a DTGS detector. Ultraviolet-visible (UV-vis) spectra were acquired using an Agilent 8453 UV-visible Spectrometer.

## 3. Results and Discussion

Terephthalate-functionalized thiophene monomers show two redox processes at low potentials, with redox potentials at -2.2 and -2.6 V vs Fc/Fc<sup>+</sup>, respectively, and one oxidation process with a peak potential at 1.6 V vs Fc/Fc<sup>+</sup> (E<sub>Fc/Fc<sup>+</sup></sub> = 3.25 vs E<sub>Li/Li<sup>+</sup></sub> [19]). The low-potential reactions correspond to sequential one electron reductions of the DeT groups while the high-potential reaction stems from oxidation of the thiophene ring (see Scheme 1, DeTmT and DeTeT is diethyl 2-(thiophen-3-ylmethyl)terephthalate and diethyl 2-(thiophen-3-ylethyl)terephthalate, respectively) [18]. Electrochemical polymerization of the monomers involves oxidation of the thiophene unit, forming a radical cation which couples with another radical cation, giving a dication dimer that is subject to deprotonation and further oxidative dimerization, eventually resulting in polymers precipitated onto the electrode surface. The polymerization was followed by the build-up of current in the



**Scheme 1.** Reduction and oxidation mechanisms of terephthalate-functionalized thiophene monomers.

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