



In situ electrochemical characterization of poly-3,4-ethylenedioxythiophene/tetraalkylphenylene diamine films and their potential use in electrochemical energy storage devices



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ABSTRACT

There is currently a newfound interest in novel approaches towards the synthesis and design of new materials for electrical energy storage (EES). We present a new breed of materials, based on redox-active substituted (RAS) conducting polymers (CPs) that can provide high energy and power densities, high conductivity, long-term durability, and potentially lower costs. In the work presented, we investigate a model system to illustrate the approach's validity. We have modified PEDOT (3,4-polyethylenedioxythiophene) by covalently binding a small RAS, N1,N1,N4,N4-tetraalkylbenzene-1,4-diamine (TAPD). The addition of this pendant (RAS) gives rise to a dramatic increase in the energy density of the material compared to traditional CPs, due to the increased number of electrons transferred per monomer unit (from 0.6 e⁻ to 2.6 e⁻). In situ UV–Vis and Raman spectroelectrochemistry yielded important mechanistic information about the electrochemical reactions of RAS-CP, which directly affect device performance. Electrochemical quartz crystal microbalance (EQCM) studies provided important insights regarding the ion transport in the RAS-CP films during electrochemical cycling. Moreover, device level characterization has been done, and at high charge/discharge rates of 1C the capacity of our materials is ca. 65 mAh/g. Furthermore, the electropolymerized RAS-CP electrodes only contain active material, precluding the need for both binder and conducting additives.

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1. Introduction

The search for efficient, high energy density, high power density, inexpensive, safe, and electrochemically reversible electrochemical energy storage (EES) materials is one of the greatest challenges facing the academic and industrial communities [1]. It has been challenging for EES materials to concurrently meet all of these criteria. In the search for alternative materials, our group has determined that organic compounds could meet most of these challenges [2–6]. Organic materials are very promising electrode materials for EES applications due to the easy tuning of their energy levels (thus their formal potential, E^0) using organic synthesis, and because they lack heavy metals that generally compromise most of the metal oxides in traditional electrodes, they can also achieve higher capacity and lower costs while being more environmentally benign (this is especially true when considering metals such as cobalt) [1–7]. In addition, since the charge/discharge processes do not involve intercalation, they can sustain high C-rates and thus achieve high power densities.

Interest in the use of organic materials for electrochemical energy storage has increased recently within the scientific community, with most of the work concentrating on carbonyl functionalities [8–14]. For example, some research groups have synthesized, from plants, carbonyl based organic molecules and used them as electrode materials demonstrating promising performance [8], in terms of electrochemical reversibility and capacities. Moreover, these molecules are environmentally safe, and are derived from renewable feed-stocks. However, they generally suffer from low formal potentials (since carrying out reductions at positive potentials is a difficult task to accomplish), solubility issues, and poor conductivity leading to poor energy densities. Although, their gravimetric capacities and energy densities can be high, the volumetric capacity and energy density are generally low since organic materials typically have low densities.

Among organic materials, conducting polymers (CP) have also been studied as materials for positive electrodes in LIBs [15–22]. The main drawback of CPs is the low capacities (e.g. 20–30 mAh/g) due to the fact that only a fraction of an electron is transferred per monomer unit. However, they do offer high conductivity, no solubility into the electrolyte and high cycling ability. In our group, we have also employed them as electrocatalysts for organosulfur compounds for EES applications [23–26].

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In this manuscript we thoroughly investigate and elucidate the electrochemical mechanism of a test molecule serving as the prototype for a new class of materials that can preserve all of the attributes that make organic compounds attractive, while overcoming some of the drawbacks that typical organic electrode materials have such as low electronic conductivities and solubility into the electrolyte. We recently published on a promising material that combines a conducting polymer with a redox active substituent. The material uses a tetra-alkylated phenylenediamine (TAPD) redox active substituent (RAS) in combination with a poly-3,4-ethylenedioxythiophene (PEDOT) conducting polymer backbone (CP) [27].

The use of this approach (combining RAS with CPs) eliminates one of the main drawbacks of using traditional CP (low capacities and hence low energy densities), by increasing the number of electrons transferred per monomer unit from $0.6 e^-$ to $2.6 e^-$, while preserving their conductivity and insoluble properties (Scheme 1). Moreover, these redox processes take place at potentials exceeding 3 V vs Li/Li^+ . The CP (PEDOT) now serves as the conducting additive and binder (in addition to providing some modest capacity), while the RAS (TAPD) contributes a high number of electrons transferred at high formal potentials (E^0), resulting in high energy densities. We also previously discussed the design criteria employed for the selection of this material, the methodology for the synthesis and some electrochemical characterization.

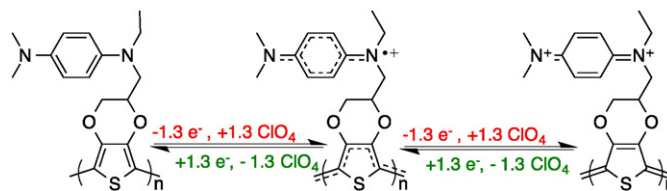
In this manuscript we significantly expand on our previous work by investigating, in detail, the electrochemical processes involved in PEDOT-TAPD redox reactions, their dependence on the electrolyte system, elucidating the mechanisms of the electrochemical reactions using in-situ spectroelectrochemical techniques, understanding the capacity fade phenomena, and controlling material morphology. Most importantly, we have designed a methodology to incorporate RAS-CPs into traditional coin cell electrodes, while demonstrating that PEDOT-TAPD by itself (without conducting additives or binders) can yield high capacity at high C-rates. A scheme for the electrochemical reactions of PEDOT-TAPD is presented in Scheme 2.

In the mechanistic investigations, we employed in situ Raman and ultra-violet visible (UV-Vis) spectroelectrochemical methods. To further investigate transport in the RAS-CP films, we performed electrochemical quartz crystal microbalance (EQCM) measurements. In order to assess the morphology dependence on the electropolymerization conditions, we used scanning electron microscopy (SEM) images, and finally we incorporated PEDOT-TAPD in common device tests (i.e. coin cell testing).

2. Materials and Methods

2.1. Materials

The synthesis of PEDOT-TAPD was done as reported in Ref. [27]. All other chemicals, unless otherwise noted, were purchased from Sigma-Aldrich and used as received. The glassy carbon electrodes were purchased from CH instruments. ITO glass slides were from NANOCS (the resistance of the ITO electrodes was 10 Ohms).



Scheme 2. Electrochemical reaction mechanism of a PEDOT-TAPD film.

2.2. Electrochemical and In Situ Measurements

Cyclic voltammograms were taken using a 3-electrode configuration employing a Hokuto Denko (HSV-100), Hokuto Denko (HABF 1580 m), or a Bio-Analytical Systems (BAS) CV-27 potentiostat. Electrochemical impedance spectroscopy was done using a Solartron potentiostat. The reference electrode used for the CVs and EIS experiments was a home-built Ag/Ag^+ using a silver wire, a fritted tube and a 50 mM $\text{AgClO}_4/0.1 \text{ M LiClO}_4/\text{AN}$ inner solution and was kept in a 0.1 M LiClO_4 storing solution. The working electrodes were GCE electrodes.

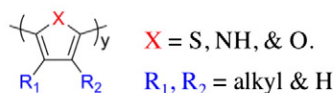
AT-cut quartz crystals (5 MHz) of 24.5 mm diameter with Au electrodes deposited over a Ti adhesion layer (Maxtek) were used for EQCM measurements. An asymmetric keyhole electrode arrangement was used, in which the circular electrodes' geometrical areas were 1.370 cm^2 (front side) and 0.317 cm^2 (back side), respectively. The electrode surfaces were overtone polished. The quartz crystal resonator was set in a probe (TPS-550, Maxtek) made of Teflon, in which the oscillator circuit was included, and the quartz crystal was held vertically. The probe was connected to a conventional three-chamber electrochemical cell by a home-made Teflon joint. One of the electrodes of the quartz crystal resonator, in contact with the solution, was also used as the working electrode. The frequency response, measured with a plating monitor (PM-740, Maxtek), and the current, measured with the potentiostat, were simultaneously recorded by a personal computer which was interfaced to the above instruments using LabVIEW (National Instruments). The admittance of the quartz crystal resonator was measured near its resonant frequency by an impedance analyzer (HP4194A, Hewlett-Packard) equipped with a test lead (HP16048A). A probe similar to the one used in the EQCM measurements, but which did not include an oscillator circuit inside, was used to accomplish a direct connection between the quartz crystal resonator and the impedance analyzer.

A diagram of the electrochemical cells used for Raman spectroelectrochemistry experiments is shown in the supporting information Fig. S.I.1. The UV-Vis experiment was done in a quartz cuvette, using a silver quasi reference electrode, a Pt coil as the counter electrode and a PEDOT-TAPD film-modified ITO electrode. Spectra were taken both while cycling the potential at 10 mV/s taking spectra every 10 s, and at specific potentials in the voltammetric profile. The UV-Vis spectroelectrochemistry experiments were carried out using a Hewlett Packard spectrophotometer (model 8453).

Raman measurements were done using a 3 electrode setup using a PEDOT-TAPD film modified GCE as the working electrode, a Pt coil counter electrode and a Ag wire quasi reference electrode. An inVia

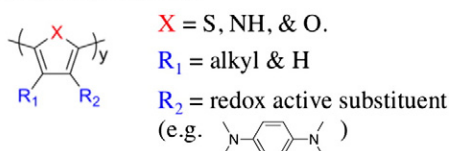
Traditional CPs:

e^- per monomer unit = 0.3 - 0.6



RAS-CPs:

e^- per monomer unit = 2.0 - 2.6



Scheme 1. Redox active substituted – conducting polymer (RAS-CP) concept.

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