Investigation of redox activity in the napthalenediimide-poly(3,4-ethylenedioxythiophene) cross-linked polymers

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ARTICLE INFO

ABSTRACT

Electroactive polymers, based on the concept of linking a redox-active core to a backbone with high electronic conductivity, are a class of interesting materials because of the possibility to independently control different properties like electrochromic contrast, conductivity, charge capacity and redox potential window by the proper choice of the two distinct components employed. In this regard, we recently developed a new napthalenediimide-poly(3,4-ethylenedioxythiophene) crosslinked polymer, which was applied in electrochromic and energy storage devices. In this paper the electrochemical characterization of the polymer by cyclic voltammetries and electrochemical quartz crystal microbalance investigations is described. The redox process of the polymer backbone shows the characteristic features of p-doping conducting polymers while the napthalenediimide redox units have a bi-electronic molecular like electrochemistry that strongly depends on the electrolyte cation. The polymer mass change during the voltammetric cycles reveals the role of the solvent in balancing the mass flux across the layer.

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1. Introduction

Electroactive Inherently Conductive Polymers (ICPs) are a wide class of materials that can be used in a variety of applications [1,2]. In fact, due to their peculiar property profile, ICPs are commonly employed in antistatic and electrostatic equipment, as solid-state capacitor electrodes, as substrate for metal deposition in printed circuit boards, as carrier conducting material in organic light emitting diodes (OLED), as hole conducting material in bulk heterojunction solar cells, and as electrode for inorganic electroluminescent lamps [3–6]. ICP films gain electrical conductivity by oxidation or reduction, usually accompanied by the insertion/desertion of anionic or cationic species to assure charge neutrality. The formed charge carriers (electrons or holes) are able to move along the π conjugated carbon double bonds of the polymer backbone, which imparts to the polymeric material intrinsic electronic conductivity [7]. Among other ICPs, the poly(3,4-ethylene dioxythiophene) (PEDOT) was developed during the second half of the 1980s in the Bayer AG research laboratory in Germany [8] and became one of the most interesting electroactive polymers for both fundamental investigations and practical applications. PEDOT is usually produced from the 3,4-ethylene dioxythiophene (EDOT) by chemical or electrochemical oxidative polymerization [5,9]. In its oxidized form it is an insoluble and infusible material. The chemical functionalization of the EDOT monomer, usually performed in one of both carbon atoms of the dioxanic ring, enables the insertion of specific functionalities, including higher solubility/processability, specific interactions for sensing applications and tuning of the electrochromic contrast. The functionalization of the dioxanic ring offers the possibility to tune the polymer properties without altering the features of the polymer backbone chain, i.e. the high electrical conductivity, as well as chemical and electrochemical robustness. Recently, this approach was used in our group to functionalize the EDOT monomer with a napthalenediimide (NTCI) redox center using a glutaric diester linkage to tether the NTCI core [10]. Indeed, we have also demonstrated that the polymer properties can be optimized using molecular design strategy of the starting monomers. Moreover, the EDOT-NCTI monomer with two polymerogenic units (see Scheme 1) enables the formation of the cross linked PEDOT-NCTI polymer with outstanding electrochemical stability. In these previous investigations, the PEDOT-NTCI system showed very interesting electrochromic [10] and charge storage properties [11] due to the simultaneous presence of the electroactive PEDOT backbone chain, which behaves as a p-dopable conducting polymer, and the side chain NTCI redox centers, which show molecular-like

Scheme 1. Chemical structure of the EDOT-NCTI monomer.

electrochemistry. In the present work, a deeper and more exhaustive electrochemical analysis was performed to understand the mechanism beyond the PEDOT-NTCI electrochemistry, in particular by using the electrochemical quartz crystal microbalance (EQCM).

2. Experimental

The EDOT-NTCI monomer was prepared according to the procedure previously described [10].

Thin films of poly-MS525 were grown on Fluorine Tin Oxide (FTO, 15 Ω/square) sheets (10×20 mm^2) by electrochemical polymerization using cyclic voltammetry (CV), linear sweep voltammetry (LSV), potentiostatic (PS), galvanostatic (GS), pulsed-potentiostatic (PPS), and pulsed galvanostatic (PGS) techniques starting from 5 mM monomer solution in the supporting electrolyte (0.1 M electrochemical grade tetrabutylammonium perchlorate in a mixture of acetonitrile/dichloromethane 2:1 by volume). Electrodepositions were performed in a two compartment three-electrode cell with FTO (deposition area 1 cm^2), Ag/AgCl wire, and Pt foil (1.5×1.5 cm), as working, pseudoreference, and counter electrode, respectively. The solution was unstirred during all the deposition experiments. Fresh polymers were rinsed with acetonitrile before further characterizations. A single compartment three electrode cell was used for the electrochemical characterization of the prepared polymers using the deposed layer as working electrode. Cyclic voltammetry analysis was performed in two different electrolytes made by 0.1 M solution of tetrabutylammonium perchlorate (TBAClO$_4$) or lithium perchlorate (LiClO$_4$) in acetonitrile. The Ag/AgCl pseudo-reference electrode was calibrated before each measurement using 1 mM ferrocene solution in the supporting electrolyte. All the potentials are reported vs. Fc$^+$/Fc couple [12]. Correction by un-compensated IR drop was applied. Both electropolymerizations and the electrochemical measurements were performed in Ar filled glove box ([O$_2$] < 1 ppm).

Electrochemical quartz crystal microbalance (EQCM) analysis was performed on layers electropolymerized on gold disc working electrodes (active area 0.198 cm^2) deposited onto the quartz resonant element in a one compartment three electrode electrochemical cell under nitrogen purging. The resonance frequency of the quartz crystal was 9×10^6 Hz; the mass change for unit area (ΔM, μg/cm^2) was calculated from the change in the resonance frequency (Δf) using the Sauerbrey equation $\Delta f = -C_{SB} \Delta M$ where C_{SB} (Sauerbrey constant) is 183 Hz cm^2 μg^{-1} in our case.

Scanning Electron Microscopy (SEM) was performed at different magnifications using a TESCAN VEGA TS5136XM Scanning Electron Microscope. Samples for morphological analysis were produced on FTO substrate according to the procedure below described and sputtered with gold prior to the SEM analysis.

3. Results and discussion

3.1. Film morphology.

The surface morphology of two polymeric layers obtained at different charge densities is shown in Fig. 1. In particular, in

Fig. 1a and 1b the surfaces of samples polymerized by CV (charge density > 30 mC/cm^2) and PGS (charge density = 15 mC/cm^2) techniques are reported. Both layers show globular sub-micrometric particles whose size depends on the charge density: the higher the charge, the larger the particles. In fact, the average particle size of the CV sample is around 200 nm, which decreases to 50 nm (or less) for the layer obtained by PGS (Fig. 1c). Most of the electrochemical characterizations discussed hereafter refer to the sample obtained by PGS at 15 mC/cm^2, so its thickness was determined by SEM. Fig. 1d was taken on the border of a mechanically damaged sample and compares the morphology of the PEDOT-NTCI film (right top part) with the FTO substrate (left bottom part). The layer thickness is estimated to be in the range of 200/300 nm. This thickness is particularly attractive because it determines the EQMC regime [13] (see discussion hereafter).

3.2. Electropolymerization

The electrochemical polymerizations of EDOT-NTCI performed by the different techniques are reported in Fig. 2. The potentiodynamic CV technique at 50 mV/s (Fig. 2a, black curve) was first used to measure the oxidation potential and the characteristic i/V

Fig. 1. Morphological characterization of PEDOT-NCTI polymers: a) SEM image of layer obtained by CV; b) SEM image of layer obtained by PGS; c) particle-size distribution evaluated by measuring the about 200 particles; d) Section of the polymer obtained by PGS.