



Effect of polymerization potential on the actuation of free standing poly-3,4-ethylenedioxythiophene films in a propylene carbonate electrolyte

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ABSTRACT

The linear actuation of poly-3,4-ethylenedioxythiophene (PEDOT) films polymerized at different potentials (0.8–1.3 V) at -27°C in propylene carbonate (PC) solutions of TBACF₃SO₃ (tetrabutylammonium trifluoromethanesulfonate) was examined under isotonic (constant force) and isometric (constant length) conditions. The actuation properties were evaluated by electrochemomechanical deformation measurements (ECDM) during cyclic voltammetry, square wave potential steps and long term cycling. The ECDM response revealed mixed ion actuation behaviour for PEDOT films polymerized at the potential extremes of 0.8 and 1.3 V. At intermediate polymerization potentials from 0.9 to 1.2 V, cation-driven actuation was observed involving immobilized triflate anions (CF₃SO₃⁻). Long term experiments (50 cycles) showed that films prepared at polymerization potentials of 0.8 V exhibited mainly anion-driven actuation, during potential steps to and from 1.0 V; conversely PEDOT prepared at a polymerization potential of 1.1 V showed exclusively cation-driven actuation. PEDOT films prepared at a polymerization potential of 1.1 V showed the maximum cation-driven actuation during cyclic voltammetry experiments including long term cycling. SEM images showed an open porous structure in all of the PEDOT films.

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1. Introduction

The conducting polymer poly-3,4-ethylenedioxythiophene (PEDOT) has been applied in light emitting diodes [1], conductive fillers [2] and anti-static elements [3], but has seldom been considered for use in actuator devices [4]. Conducting polymer actuators in the form of free standing films have mainly been based upon polypyrrole (PPy) [5–7] and less research has been undertaken using PEDOT. One of the reasons for this can be found in the lower strain (1–4%) generated by PEDOT films, compared to over 10% strain with certain PPy films [5].

A disadvantage with PPy actuators is that the electronic conductivity decreases by two or three orders of magnitude as the polymer is reduced. This causes a decrease in performance; since only a small part of the polymer film will then be actively contributing to the actuation.

Better electrochemical stability for PEDOT films compared to PPy films has been found, partly because the β -site of the heterocyclic ring (dioxy-bridge) in EDOT is blocked, which prevents α – β and β – β couplings from occurring during electrochemical polymerization, yielding more ordered polymers with longer conjugation lengths [8]. Since PEDOT is more electrochemically stable

than PPy, it can be used at higher and lower potentials in actuators without the same degree of degradation.

In the case of PPy free standing films polymerized and cycled in propylene carbonate (PC) using tetrabutylammonium triflate (TBACF₃SO₃) as the electrolyte, cation-driven actuation was observed during film reduction, which depends upon the presence of immobilized triflate anions (CF₃SO₃⁻) [9], while under wider potential cycling the actuation can be described as involving mixed ion movement (cation- and anion-driven actuation) [10]. PEDOT films polymerized under similar conditions, using TBACF₃SO₃ in a PC electrolyte, showed mainly cation-driven actuation, again resulting from triflate anions immobilized during electropolymerization with practically no actuation observed upon oxidation [4,10], similar to the behaviour seen with PEDOT/PSS [11] or PPy/DBS [12] where the associated cations determined the actuation, while dual ion movement was observed with PEDOT/TBAPF₆ films in PC [13].

The actuation properties of conducting polymer films can be controlled through the choice of polymer [14] and polymerization conditions, such as temperature [15] and electrolyte concentration [16,17], which influence the structure of the conducting polymer network. Electrochemical polymerization in the case of galvanostatic (constant current), potentiodynamic (constant scan rate) or potentiostatic (constant potential) conditions leads to different conducting polymer structures, all of which influence actuation properties [18,19]. The rate of deposition of the polymer on the

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working electrode in particular affects the structural diversity of the resulting conducting polymer network. In the case of potentiostatic polymerization, studies of PEDOT-bilayers [10] showed a dependence of the deflection (actuation) upon the polymerization potential, in that a low polymerization potential led to a regular polymer network with open pores resulting in high conductivity and a high extent of actuation. With higher polymerization potentials the PEDOT-bilayer polymer network showed more closed pores with irregular chain formations resulting in a lower degree of actuation [10]. Consideration also needs to be given to the relative effects of ion and solvent movement and its effects on conducting polymer volume [20], with solvent transfer and polymer reconfiguration shown to be steps which can follow charge transfer in the case of PEDOT [21]. Osmotic effects induced from a build up of charge inside the conducting polymer can lead to a considerable movement of solvent, in excess of that associated directly with the solvation shells of anions and cations [22].

An investigation of the actuation properties of PEDOT free standing films (using electrochemomechanical deformation measurements (ECDM) analysis) polymerized at different potentials has not been reported to date. The dependence of the actuation properties on the polymerization potential should provide important information about which preparation conditions lead to solely cation-driven actuation or also to anion-driven actuation. If mixed ion effects during oxidation and reduction take place, the resulting strain values for the linear actuators are smaller compared with purely anion- or cation-driven actuation. Therefore it is of interest for the development of PEDOT films to control the actuation to create a uniform anion- or cation-driven actuation. Isometric and isotonic tests are necessary to measure the fundamental properties of actuators including stress and strain.

2. Experimental

2.1. Materials

EDOT (3,4-ethylenedioxythiophene) (Aldrich) was distilled and stored in the dark under nitrogen. The electrolyte tetrabutylammonium trifluoromethanesulfonate (TBACF₃SO₃) (Aldrich) and the solvent PC were used as supplied.

2.2. Film deposition

PEDOT was deposited potentiostatically in a three electrode cell at polymerization potentials of 0.8–1.3 V (vs. Ag wire) from a propylene carbonate solution containing 0.1 M EDOT and 0.1 M TBACF₃SO₃ on a stainless steel working electrode using a CH Instruments electrochemical workstation (model 440). The counter electrode was a Pt-grid and the reference electrode was an Ag wire. Before electropolymerization the electrolyte solution was purged with nitrogen to remove oxygen. The temperature of the polymerization cell was held constant at –27 °C. The electropolymerization of PEDOT/PC/TBACF₃SO₃ was stopped when a total charge of 16.7 C was passed (the stainless steel working electrode surface area was 4.16 cm²), which corresponds to a film thickness [23] of 20 μm for PEDOT/PC/TBACF₃SO₃.

2.3. Electrochemical measurements of free standing PEDOT films

The PEDOT films were peeled off the stainless steel electrode and cut into 1.2 × 0.3 cm strips. For linear actuation of the free standing PEDOT films a Dynamical Muscle Analyzer (Scientific Inc.) was used. One side of the PEDOT films was fixed to a polyvinyl chloride holder with a Pt wire as the contact at the base, and the other side was connected to the servo actuator arm—the length between the clamps was 4 mm. For linear length change a constant

force of 61 mN (1.35 MPa) was applied and each film was preloaded overnight before the ECDM measurements were commenced. For force measurements a constant length was maintained. The free standing PEDOT films were connected to the working electrode in a three electrode cell containing a reference electrode Ag/AgCl (3 M KCl, +0.207 V vs. SHE) and a Pt sheet counter electrode. The films were cycled in 0.1 M TBACF₃SO₃ propylene carbonate solution at a scan rate of 2 mV s⁻¹ between +1.0 and –1.0 V (first cycle started at 0.0 V and scanned to –1.0 V, then to 1.0 V) using a BAS 100B/W (Bioanalytical Systems Inc.) Electrochemical Analyser. Electrochemical potential step experiments were performed between 1.0 and 0.0 V, and between 1.0 and –1.0 V, with either 32 or 30 s per step.

2.4. Conductivity measurements

The conductivity of dry, free standing polymer films was measured using a Jandel four-probe conductivity meter (Model RM2, Jandel 4-Point Probe Head). The conductivity was measured before and after ECDM measurements on several different areas on the front side of the polymer films and mean values with standard deviations were obtained.

2.5. SEM images

For scanning electron microscopy (SEM) experiments a Phillips XL30-FEG instrument was used.

3. Results and discussion

3.1. ECDM measurements with cyclic voltammetry

Free standing PEDOT films were used for isotonic measurements (1.35 MPa) to analyse the strain during cyclic voltammetry experiments. The PEDOT films were prepared potentiostatically (at 0.8–1.3 V) in TBACF₃SO₃ (0.1 M) at a low temperature (–27 °C), and were subsequently cycled in a propylene carbonate TBACF₃SO₃ electrolyte (Fig. 1a–f).

The major actuation mode observed with the PEDOT films was cation-driven actuation, seen by the lengthening of the films during the reduction process (Fig. 1a–f; the arrows indicate the direction of the strain curves, all of which are for the second CV cycle that these films were exposed to). As the positive charges on the conducting polymer were neutralised on the cathodic sweep, TBA⁺ cations (and solvent) moved into the films to balance the charge of the immobilized triflate anions. For the first film (Fig. 1a) a maximum strain of 1.3% (calculated from the deepest point of the curve at 0.1 V) was produced as the potential reached –1.0 V, while the largest film lengthening (3.9%) was seen for the PEDOT film prepared at 1.0 V (Fig. 1c). Conversely, when the films were oxidized on the anodic sweep, the positive charges created on the PEDOT led to cation expulsion and film contraction. In each case the relative contributions of ion movement and solvent flux to the actuation cannot be determined from these experiments, and the additional influence of solvent needs to be kept in mind as a further contributing factor [21].

In the case of the PEDOT films formed at the potential extremes of 0.8 and 1.3 V (Fig. 1a and f), a subsequent film expansion was observed during the anodic scan in the potential range from 0.3 to 1.0 V by up to 0.5%, which can be ascribed to a certain degree of anion-driven actuation during the later stages of the oxidation process. A slight contraction in strain of 0.2% was also observed during the cathodic sweep beginning at 1.0 V for the film prepared at 0.8 V (Fig. 1a) up until the first reduction peak at 0.05 V, before the film lengthened upon further reduction. It is assumed that mixed ion movement affected the actuation properties right across the redox cycle [13]. At polymerization potentials of 0.9–1.2 V (Fig. 1b–e) only

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