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Research paper

Enhancement of polypyrrole linear actuation with poly(ethylene oxide)

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ABSTRACT

In the present paper, we report the electro-chemo-mechanical deformation (ECMD) measurements of pristine polypyrrole (PPy) and polypyrrole/poly(ethylene oxide) composite films doped with dodecylbenzenesulfonate (DBS) under isotonic (constant force) conditions. The PPy/DBS and PPy-PEO/DBS films, the latter made from a polymerization solution containing 5 wt% PEO, were actuated potentiodynamically in an aqueous solution containing lithium bis-trifluoromethane-sulfonimide (LiTFSI). The obtained composite films were characterized with scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy and Fourier transform infrared spectroscopy (FTIR). The results confirmed the successful incorporation of PEO within the PPy film. The composite films showed a remarkable improvement in maximum strain achieved (of 7.7%), nearly double that of the pristine PPy/DBS film, had a higher conductivity, higher ion diffusion coefficient and faster strain rate. The ECMD measurements for both the pristine as well as the PEO-composite films showed cation driven actuation involving the migration of Li^+ cations in the aqueous electrolyte.

1. Introduction

Electroactive conducting polymers (ECPs) such as polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) have been extensively studied over the past decades in regard to their linear actuation properties [1–3]. ECPs have emerged as great candidates for soft artificial muscles or transducers due to being lightweight, flexible, and cost-effective actuators [4,5]. Studies on PPy and PEDOT films have demonstrated that expansion or contraction occurs due to the migration of solvated cations [6,7] and/or anions [8] during redox cycling [9]. For instance, cation driven actuation was observed in PEDOT films synthesized by potentiostatic electropolymerization in tetrabutylammonium trifluoromethanesulfonate ($TBACF_3SO_3$) electrolyte [10]. There have been several studies on the effect of solvent [11–13], electrolyte [14,15], polymerization conditions [7] on the actuation behavior of CPs. The electrochemically stimulated conformational relaxation (ESCR) mechanism is one of the models capable of explaining ECP actuation behavior, incorporating cation and anion roles [16] and the role of the solvent [17]. Nowadays, there is a particular interest in improving the strain of linear actuators by means of developing new polymer composite actuators for commercial applications [18–20].

Composites of polypyrrole (PPy) and poly ethylene oxide (PEO) have been demonstrated before for solid electrodes of lithium batteries [21]. It was found that improved charging/discharging cycle life was achieved with the suggestion that PEO supported higher diffusion coefficients of Li^+, found to be in range of $10^{-7}\,cm^2\,s^{-1}$ [22] in comparison to Li^+ ions in pure PPy particles, where diffusion coefficient was reported as only $10^{-12}\,cm^2\,s^{-1}$ [23]. Adapting the concept that PEO additives provide faster charging/discharging by facilitating ion diffusion, the group of Vidal [2,24] has carried out extensive studies on electro-active interpenetrated polymer networks (IPN), where PEDOT is deposited on both sides of solid polymer electrolyte (SPE) membranes based on PEO and nitrile butadiene rubber [25]. These bending IPN actuators can work in air and have shown a high cycle life and fast actuation up to 2 kHz [26]. The combination of PEO with CP in form of PEO fiber material [27], and modified with α-Methoxy ω-Na carboxylate PEO as the counterion in PPy electropolymerization to get anion exchange properties [28] have also been carried out. Increased ion permeability and/or diffusion have been reported in these investigations.

Our goal in this work was to investigate the effect of incorporating PEO in PPy on the linear actuation response of low-temperature-

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synthesized PPy. The novel linear actuators are designated as PPy-PEO/DBS. Electro-chemo-mechanical deformation (ECMD) studies under isotonic conditions, along with cyclic voltammetry and actuation under chronopotentiometric conditions were performed. The diffusion coefficients of the counterions in both films (PPy-DBS and PPy-PEO/DBS) were compared to evaluate the effect of PEO on the ionic mobility inside the films, and in turn, the strain rates. The films were also characterized by means of FTIR spectroscopy, SEM and EDX spectroscopy.

2. Material and methods

2.1. Materials

Sodium dodecylbenzenesulfonate (NaDBS, 99%), poly (ethylene oxide) (PEO, Average Mw ca. 100,000 g/mol), ethylene glycol (EG, 99.8%), bis(trifluoromethane) sulfonamide lithium salt (LiTFSI, 99%) were purchased from Sigma-Aldrich and used as received. Pyrrole (Py, ≥98%) from Sigma-Aldrich was distilled at reduced pressure prior use and stored at low temperature under Ar atmosphere. Deionized water (18.2 MΩ cm at 25 °C, Milli-Q+) was used for solutions.

2.2. Electropolymerization

The PPy-PEO/DBS (5 wt% PEO in polymerization solution) and PPy/DBS films were polymerized galvanostatically (0.1 mA cm^{-2}) on stainless steel working electrodes (surface area 6 cm^2) in a three-electrode cell (platinum woven mesh/gauze (25 × 25 mm) as counter electrode and Ag/AgCl wire as reference electrode, 0.52 V *vs*. SHE), controlled by a CH Instruments electrochemical workstation (model CHI440). The polymerization process was carried out for 40,000 s (11.1 h) at a constant temperature of −18 °C. The polymerization solution consisted of 0.2 M Py and 0.2 M NaDBS in a 50:50 (v/v) mixture of deionized water and ethylene glycol. The electrochemically deposited films were peeled off the electrode, washed in ethanol to remove excess of pyrrole and washed in deionized water to remove excess of NaDBS. The films were dried in an oven and stored for further use. PPy/DBS and PPy-PEO/DBS films had thickness of 37 μm and 40 μm, respectively, with weight of 244 ± 20 μg for PPy/DBS and 319.5 μg for PPy-PEO/DBS.

2.3. Electro-chemo-mechanical deformation (ECMD) measurements

PPy/DBS and PPy-PEO/DBS films were cut in length of 10 mm and 1 mm width. For each system, 3 samples were measured and the presented values reflect the mean values. The films were connected to the force sensor (TRI202PAD, Panlab) with a fixed arm that served as a working electrode in a linear muscle analyzer set up [29] presented in Fig. 1.

Platinum sheet was used as the counter electrode and Ag/AgCl (3 M KCl, 0.23 V *vs*. SHE) as the reference electrode in the measurement cell containing 0.2 M solution of LiTFSI in water. The initial length of the films between the clamps was 1 mm. The films were immersed in the electrolyte, pre-stretched in range of 2% (equivalent to 400 mg) and left immersed in the electrolyte for 4 h before the measurements commenced. While keeping the film under constant load (isotonic, force of 4 mN), the length change under the driving signal was measured from the force changes compensated by the moveable arm, controlled by in-house software. The strain ε in % was obtained from the formula $\varepsilon = \Delta L/L^*100\%$. The difference of the length change is $\Delta L = L - L_1$, where L is the original length of the film, and L_1 the changed length obtained under the isotonic ECMD measurements. Within a voltage range of 0.6 V to −0.65 V, the cyclic voltammetry (scan rate 5 mV s^{-1}) and the chronoamperometry at frequencies 0.0025 Hz, 0.005 Hz, 0.01 Hz, 0.025 Hz, 0.05 Hz and 0.1 Hz were performed.

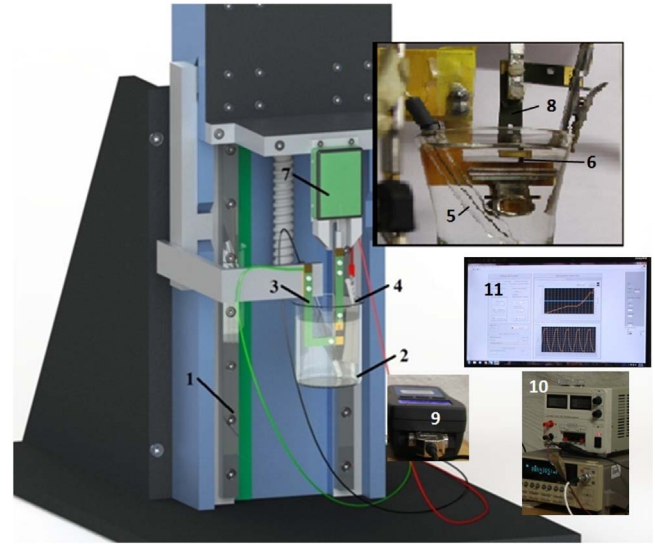

Fig. 1. Experimental set-up of linear muscle analyzer with precision stage (1), measurement cell (2) including the working electrode (3), counter electrode (4) and reference electrode (5). The film (6) is fixed attached to the working electrode (3) and the force sensor (7) via the upper clamp (8). The setup is driven by a potentiostat (9) with a controller (10) run by a PC with in-house software (11).

2.4. Characterization by FTIR, SEM, EDX and conductivity

PPy/DBS and PPy-PEO/DBS films were analyzed by FTIR (Alpha, Bruker) after the actuation cycles. The films were characterized by using scanning electron microscopy (Helios NanoLab 600, FEI) and EDX analysis. The conductivity of the films was determined by four-point probe method with a surface resistivity meter (Guardian SRM).

3. Results and discussion

3.1. Electropolymerization of PPy/DBS and PPy-PEO/DBS

The potential developed at the beginning of the polymerization of the pristine PPy decreased to a certain value and then increased to ca. 0.94 V for the remaining of the polymerization. When PEO was present in the polymerization solution, the chronopotentiogram looked rather similar, but with slightly lower potentials developed that plateaued at ca. 0.88 V (Fig. 2).

In both cases, the initial decrease in potential was followed by a steady increase and then ultimately a steady potential was developed, stable throughout the polymerization period. Such chronopotentiogram

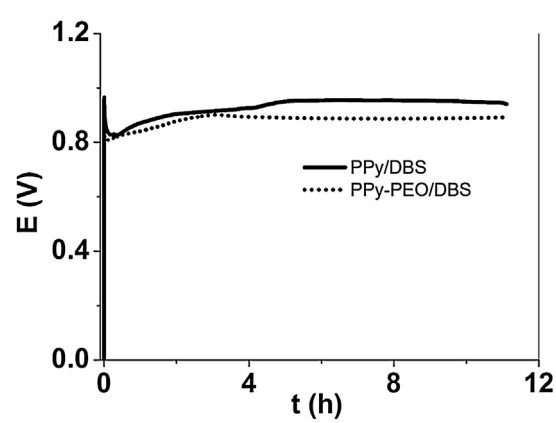

Fig. 2. Electropolymerization of PPy/DBS (solid) and PPy-PEO/DBS (dashed) (galvanostatic, 0.1 mA/cm^2, 11.1 h, −18 °C) in a three-electrode cell with stainless steel working electrode, platinum woven mesh counter electrode and Ag/AgCl reference electrode.