

Actuation increase in polypyrrole bilayer by photo-activated dopants

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ABSTRACT

A new methodology to increase the polypyrrole (PPy) bilayer actuation displacement is presented, based on photo-activated dopants generating secondary charges. Two dopants, dodecyl benzenesulfonate (DBS) and the photo-active dopant 2-diazo-1-naphthol-5-sulfonic acid (DNSA), were compared in this study. PPy/DBS, PPy/DBS-DNSA and PPy/DNSA bilayers on polyethylene terephthalate were formed and their actuation properties in aqueous electrolyte were investigated applying cyclic voltammetry and square wave potential steps. Exposure to solar irradiation increased PPy/DBS-DNSA and PPy/DNSA bilayer bending displacements by two and three times, respectively, accompanied by increased charge density during the reversible redox cycles. UV-vis and Fourier transform infrared (FTIR) measurements were also performed to follow the photo reaction of the photo-active dopants.

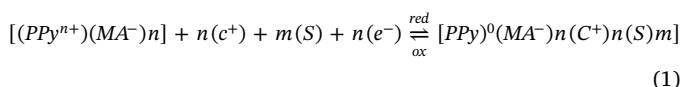
1. Introduction

Conducting polymer actuators have been studied over the last two decades to increase actuation properties for potential applications in smart textiles [1], micro-actuators [2], robotics [3,4] and biomedical devices [5,6]. In general, the formation conditions of the working conducting polymer, often polypyrrole (PPy), is optimized with the aim of increasing actuation properties [7]. Additional investigations have been made using different electrolytes [8,9] and solvents [10,11] or including highly charged anions such as polyoxometalates [12] or carbon particles [13], as electrolyte substitutes to obtain conducting polymer composites with improved maximum strain and stress [14].

However, little attention has been given to the treatment of conducting polymer actuators after their formation. In this study, we present a novel methodology to increase actuation properties by using solar irradiation to activate 2-diazo-1-naphthol-5-sulfonic acid (DNSA) [15], which is embedded within the PPy network during electropolymerization. The inclusion of DNSA in Novolac resins [16] in combination with conducting polymers such as thiophenes [17], with inclusion of a chemical oxidant, has been studied recently [18], in order to achieve interpenetrated networks that can be patterned over photolithography, resulting in micro-structures with conductivities up to 20

S cm^{-1} . To our knowledge, DNSA have not been applied before as the supporting electrolyte during electropolymerization with the goal to subsequently activate the film. The main reason to do so relies on the properties of the PPy bilayer, where actuation properties decrease after long term cycling [7]. Therefore, PPy bilayer systems with embedded DNSA have been produced, their actuation properties studied and on the second treatment, the photo-active molecule activated with the same repeated actuation cycles.

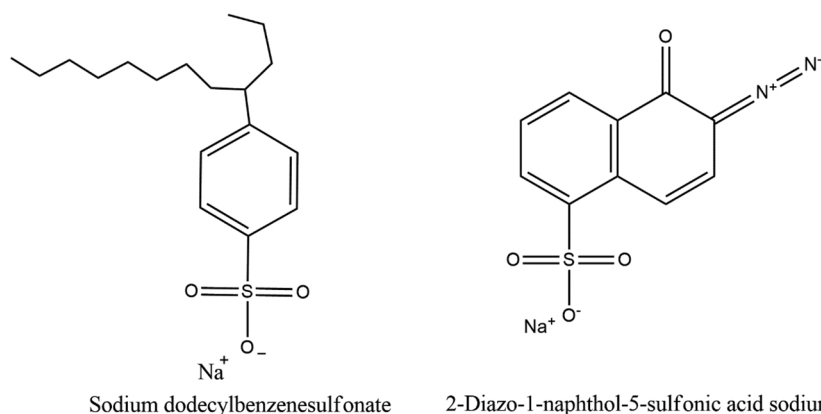
The best known and most studied conducting polymer actuator system with immobile anions is PPy containing dodecylbenzenesulfonate (DBS) anions [19] as dopants, leading to expansion upon reduction, due to the residual negative charge of the immobile anions being compensated by the ingress of solvated cations. Such actuators are called cation-driven, and following equation 1 [20].



Several studies have been carried out to understand why macro-anions such as DBS^- stay immobile within the PPy network. Khalkhalia et al. [21] investigated PPy doping with different large anions using quartz crystal microbalance. They concluded that while *p*-toluene

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Scheme 1. Structures of NaDBS (sodium dodecylbenzenesulfonate) and NaDNSA (2-Diazo-1-naphthol-5-sulfonic acid sodium salt).

sulfonate and dodecylsulfate showed mixed ion behavior, DBS^- doping resulted in purely cationic activity. The immobile character of DBS^- anions in PPy was attributed to the hydrophobic properties of DBS^- and their large size [21]. Earlier studies indicated that the bulky amphiphilic anions such as DBS^- form micelles where the hydrophobic pyrrole monomer dissolves [22]. In the case of DBS^- anions, more pyrrole monomers are dissolved in the micelles near the critical micelle concentration (CMC), and when electropolymerization starts, the pyrrole polymerizes around those anions and deposits on the working electrode [22]. Another assumption of immobilized DBS^- anions was presented based on their aromatic character [23] with similar features seen in NaDNSA compounds (Scheme 1).

DNSA compounds applied in Novolac resin [16] are photo-reactive molecules, which upon irradiation (UV or Sun light) undergo a change in molecular structure (Wolff rearrangement [24]) by releasing nitrogen and forming a secondary charge (carboxylate) in the presence of water. Under the assumption that DNSA acts as an immobile species like DBS^- , bilayers were made from PPy doped with DNSA (PPy/DNSA), PPy doped with DBS and DNSA (PPy/DBS-DNSA), and PPy/DBS as a pure reference. The main goal of this study was to activate DNSA using photoreactions in the solid PPy films. Cyclic voltammetry measurements and square wave potential steps were performed. The reactivity of DNSA was tested in solution and in polyacrylonitrile membranes using UV-vis spectroscopy. Scanning electron microscopy (SEM) images of the bilayer samples are performed.

2. Materials and methods

2.1. Chemicals

2-Diazo-1-naphthol-5-sulfonic acid sodium salt (DNSA, 97%, Sigma), polyacrylonitrile (PAN pellets, Sigma), dimethylsulfoxide (DMSO, 99%, Sigma), methanol (technical grade, Sigma) sodium dodecylbenzenesulfonate (NaDBS, 99%, Sigma), tetramethylammonium chloride (TMACl, 98%, Fluka), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT-PSS, 1 wt% in Milli-Q, H. C. Stock (PH500)), multi-wall carbon nanotubes (95%, Bayer) were used as supplied. Pyrrole (98%, Sigma) was distilled and stored under nitrogen at -20°C . Polyethylene terephthalate (PET, 12 μm thickness) foil was supplied by Melitta.

2.2. Conductive coatings

The PET foil surfaces were cleaned (dust free) and treated with 0.1 M HCl, washed with Milli-Q and acetone to produce a hydrophilic surface. PEDOT:PSS/MWCNT at the ratio of 3.6 (wt%) (3.6 wt% PEDOT:PSS/1 wt% MWCNT in aqueous solution) was spin-coated (5000 rpm, 2 min) on one side of the PET foil [25]. The coated PET was

dried in an oven at 100°C . The thickness of the PEDOT:PSS/MWCNT was around 500 nm with surface resistivity of $400 \pm 34 \Omega$ ($16.6 \pm 1.1 \text{ S cm}^{-1}$).

2.3. Electro-polymerization

The PET-foil with one side coated by PEDOT:PSS/MWCNT was applied as the working electrode (a platinum sheet counter electrode, with reference electrode Ag/AgCl (3 M KCl)) in an aqueous solution of pyrrole (0.1 M) and 0.05 M of the supporting electrolyte under galvanostatic conditions (0.2 mA cm^{-2} , 2000s, 25°C , Eco Chemie Autolab). For PPy/DBS, 0.05 M NaDBS was applied as the dopant, for PPy/DBS-DNSA, 0.025 M NaDBS and 0.025 M NaDNSA were used, and in the case of PPy/DNSA, 0.05 M NaDNSA was applied. Since NaDNSA is light sensitive, polymerization was performed in the dark. The thickness of the PPy layers with different doping anions (DBS^- , DNSA^-) was around $1.9 \pm 0.2 \mu\text{m}$.

2.4. Actuation studies

PPy/DBS-, PPy/DBS-DNSA- and PPy/DNSA-bilayers were applied as the working electrodes in aqueous actuation solution containing 0.2 M TMACl (counter electrode Pt sheet, reference electrode Ag/AgCl (3 M KCl)). The bilayers were cut into strips 2.5 cm in length and 0.5 cm in width. The bilayer samples were connected to a metal clamp on the conductive coatings, and electrochemical stimulations were applied (Eco Chemie Autolab). Cyclic voltammetry was undertaken at a scan rate of 10 mV s^{-1} ; while square wave potential steps were applied at frequencies of 0.0167 Hz, 0.05 Hz, 0.1 Hz, 0.5 Hz and 1 Hz, using an applied potential of $\pm 0.85 \text{ V}$. The movement of the bilayers was recorded with a CCD (Sony Cyber-shot DSC-F717) camera connected to a PC installed frame grabber card and set to begin recording at the same time as the cyclic voltammetric and chronoamperometric experiments. Individual frames were captured from the recorded video frames and the displacement of the bilayer was calculated at 1 cm from top outer edge. An example of the screenshots are shown in Fig. 1 for the PPy/DBS-DNSA bilayer sample before and after solar irradiation.

From each bilayer system, the displacements, calculated charge density, diffusion coefficients and actuation speed were determined as mean values of more than three samples. Bilayer screenshots for PPy/DBS and PPy/DNSA are shown in Fig. S1a,b. After the first actuation studies, the PPy bilayers were washed and dried in an oven at 40°C (2 mbar) for 24 h. During the next step, the PPy bilayers were placed under solar irradiation for 1 min to activate DNSA, and the actuation cycles were then repeated. From each PPy bilayer system 4 samples were polymerized and measured independently.

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