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Ultrathin electrochemically driven conducting polymer actuators: fabrication and electrochemomechanical characterization

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ABSTRACT

Electronic conducting polymer based-actuators have attracted lots of interest as alternative materials to traditional piezoelectric and electrostatic actuators. Their specific characteristics such as their low operating voltages and large strains should allow them to adapt better to soft microstructures. Recently, poly (3,4-ethylenedioxythiophene) (PEDOT) – based ionic actuators have overcome some initial stumbling blocks to widespread applications in the microfabricated devices field. These trilayer bending microactuators were fabricated (i) by sequential stacking, using a layer by layer polymerization (LbL) of conducting polymer electrodes and a solid polymer electrolyte and (ii) by micro-patterning, using standard microsystems processes. While microfabrication processing of a trilayer actuator, involving no manual handling has been demonstrated, their bending performances remain limited for practical applications. Moreover, the complete characterization of their electrical, electrochemical, and mechanical properties has never been investigated. This paper describes the optimization of PEDOT electroactive electrodes synthesized with a vapor phase polymerization process. Influence of synthesis parameters on thickness, electronic conductivity and volumetric charge density were studied to determine the guidelines for synthesizing highly efficient electrodes. Afterwards, these parameters are used to guide the LbL synthesis process of ultrathin trilayer actuators. Electrochemical and mechanical properties of the resulting microactuators have been thoroughly characterized. Bending deformation and output force generation have been measured and reached 0.5% and 11 μN respectively. This constitutes the first characterization of ionic PEDOT-based microactuators operating in air of such a thin thickness (11 μm dry and 18.3 μm swelled in 1-Ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMImTFSI)). These actuators and their actuation properties are promising for future soft microsystem devices where the use of polymer actuators should be essential.

1. Introduction

Ionic electroactive polymer (IEAP) actuators have attracted a lot of interest of researchers from different domains since they can be used in a variety of applications: locomotion systems [1], Braille displays [2], steerable micro catheters [3], micro pumps [4,5], microactuators [6–8]. IEAP actuators have many attractive features including low operating voltages and large strains when compared to conventional materials [9]. Among different types of IEAPs, poly(3,4-ethylenedioxythiopene) (PEDOT) based-actuators have received significant attention because of their highly reversible, fast switching redox processes [10]. Also, they are lightweight, biocompatible, produce high stress (~10 MPa) [9], high power/weight ratio [11], significant strain (up to 1%), require low operating voltages (typically < 3 Vpeak-peak (Vpp)) [12] in solutions or in open-air condition [13], can be electronically controlled with reasonable frequency response (>50 Hz) and are potentially suitable for microscale applications [13,14]. The actuation is obtained when the electronic conducting polymer (ECP) is oxidized or reduced electrochemically [15–19]: ions and solvent molecules, coming from a surrounding electrolyte, are inserted or expelled from the ECP in order to insure the overall electroneutrality which results in a variation of the ECP volume, or in short, this ECP

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actuator responses to the consumed charge. For a particular case, where the ionic liquid (EMImTFSI) is used, the electrochemical reactions driving the actuator displacement under an electrical stimulation is:

$$\underset{\text{Neutral chains}}{\left[\left(\text{PEDOT}^0\right), n\left(\text{TFSI}^-\right), n\left(\text{EMIm}^+\right)\right]} \underset{\text{Reduction}}{\overset{\text{Oxidation}}{\rightleftarrows}} \times \underset{\text{Oxidized chain}}{\left[\left(\text{PEDOT}^{n+}\right), n\left(\text{TFSI}^-\right)\right]} + n\left(\text{EMIm}^+\right) + n(e^-),$$

where $TFSI^-$ are immobilized anions which are trapped between PEDOT backbone chains in oxidized state, and $EMIm^+$ are mobilized cations driving the actuation [20].

To operate in open-air, a trilayer configuration [21–23] is the most described: two ECP electrodes sandwiching a solid polymer electrolyte (SPE) layer that will act as an ion reservoir.

For microscale actuators, the thickness must be less than 20 μm to be compatible with microsystem technologies (photolithography, etching process …) which is the reason why the layer-by-layer (LbL) approach has been developed recently [24]. The bending microactuators were fabricated by sequentially stacking layers using a layer by layer polymerization of conducting polymer electrodes and a SPE. Each layer was deposited by spin-coating to accurately control the thicknesses. PEDOT can be fabricated in-situ via electropolymerization [25] or via vapor phase polymerization (VPP) [26]. In this work the first and last layers of the actuators were obtained using VPP of 3,4-ethylenedioxythiophene (EDOT). The intermediate SPE layer was synthesized as a semi-interpenetrating polymer network (semi-IPN) combining poly(-ethylene oxide) (PEO) network for ionic conductivity and nitrile butadiene rubber (NBR) for mechanical strength [23,27].

For the LbL process, while the proof of concept has been demonstrated previously, then the resulting performances remained relatively poor (0.13% strain and 0.75 μN of generated force) [24] mainly due to the low electroactivity of PEDOT electrodes obtained by VPP. Practical use of such microactuators and integration into innovative microelectromechanical systems requires improved performances. Moreover, any real application requires precise control and prediction of the performances. While models have been developed [28–30], they require precise electrical, electrochemical and mechanical characterizations of actuators, which have never been performed on these materials.

In this paper, we will first describe the VPP synthesis for optimization of PEDOT electrodes to provide highly electroactive electrodes, suitable for efficient microactuators. Microbeams of the actuators will be then prepared using the LbL approach and the resulting devices will be thoroughly characterized. More specifically, electrochemical parameters such as the volumetric capacitance, the ionic conductivity of the SPE, and the electronic conductivity of the ECP, will be measured. The Young's modulus, the curvature and the blocking force will describe the mechanical and electromechanical properties. Large improvement in actuator's performances and the first complete characteristics have been obtained, setting the stage for a potential integration into a micromechanical structure.

2. Trilayer synthesis

2.1. Materials

Poly(ethylene glycol) methyl ether methacrylate (PEGM, $M_n = 500\ g\ mol^{-1}$), poly(ethylene glycol) dimethacrylate (PEGDM, $M_n = 750\ g\ mol^{-1}$), cyclohexanone (>99.8%) and 3,4-ethylenedioxythiophene (EDOT, distilled under reduced pressure) were obtained from Sigma Aldrich. Iron(III) p-toluene sulfonate Clevios™ CB 55 V2 (55 wt% in butanol, $Fe(OTs)_3$ in BuOH) was purchased from HERAEUS. 1-butanol (99%), initiator dicyclohexyl peroxydicarbonate (DCPD), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMImTFSI 99.9%) and nitrile-butadiene rubber, were used as supplied from Alfa Aesar, Groupe Arnaud, Solvionic and LANXESS, respectively.

2.2. PEDOT electrode fabrication

The fabrication process of the PEDOT electrodes was performed as described in the work of Maziz [31] and is depicted in Fig. 1. The PEDOT electrode layers were obtained from EDOT VPP, first described by Winther-Jensen [26]. The VPP of EDOT was carried out with a direct chemical oxidation using the commercial solution of Iron(III) tosylate $Fe(OTs)_3$ (55 wt% in butanol). PEO precursors (mPEG) composed of 50 wt% of PEGM and 50 wt% of PEGDM were added as a monomer and a crosslinker, respectively, to the $Fe(OTs)_3$ solution. Additionally, DCPD (3 wt% vs mPEG) as the radical initiator for mPEG polymerization was introduced to the solution. The latter was then stirred until dissolution and degassed. The oxidant solution was then spin-coated onto a substrate and exposed to EDOT vapor for a fixed time at a fixed temperature. EDOT VPP was carried out under primary vacuum by heating liquid EDOT monomers that evaporate and polymerize on the oxidant solution. The EDOT VPP was followed by the final heat treatment for mPEG polymerization/crosslinking (3 h at 50 °C) to obtain PEDOT/PEO composite electrodes. PEDOT electrodes were swollen in ionic liquid (EMImTFSI) for further characterization.

The final properties (thickness, electronic conductivity and volumetric charge density (VCD)) of the PEDOT electrodes were studied as a function of: composition of oxidant solution (content of mPEG), rotation speed of spin-coater for deposition of oxidant solution, EDOT VPP time and temperature. The synthesis initial conditions for PEDOT electrode study were 55% $Fe(OTs)_3$ in BuOH, 10% mPEG in the oxidant solution, the spin coating speed, acceleration and duration were 2500 rpm, 1000 rpm s^{-1}, and 30 s, respectively, the EDOT VPP time of 30 min and temperature of 40 °C were used. When one parameter was changed, the others remained the same as in the initial parameters. The range of values for each parameter varied is presented in Table 1.

The volumetric charge density, ρ, was calculated using the expression:

$$\rho = \frac{\int_0^{T/2} i(t)dt}{lbh}\ (\text{C/m3}),$$

where $i(t)$ is the measured current using setup in Fig. SI1a (refer to the supporting information), T is the duration of one cycle of applied voltage, and l, b, h are the length, width, and thickness of the PEDOT electrode, respectively.

2.3. Microactuator fabrication

The trilayer actuator was synthesized using a LbL method. In this process, all the layers are spin-coated on top of the previous layers and the thickness can be controlled extremely accurately by adapting the speed of rotation. The oxidant solution was prepared by adding PEO precursors (50 wt% PEGM and 50 wt% PEGDM) into a commercial $Fe(OTs)_3$ solution. The PEO precursors (mPEG) were added to each layer and polymerized at the end of the process throughout the trilayer structure to improve adhesion between the layers. The solution was then stirred for 10 min and spin-coated onto a two-inch silicon wafer. The EDOT VPP was carried out in