Study of EDOT/benzothiadiazole copolymer electropolymerization for application in electrochromic devices

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Abstract
Electrochromic (EC) materials have a wide range of applications including anti-glare car rear-view mirrors, smart windows etc. In conducting polymers, electrochromism is related to their doping-dedoping process, which leads to the creation of different absorption bands in the visible region. A standard EC device (ECD) is essentially an electrochemical cell composed of two transparent electrodes (e.g. ITO coated glass), with at least one of them coated with a thin EC film. In single layer ECDs the EC film is the anode, the other ITO is the cathode and the two electrodes are sandwiched together with a proper electrolyte. In dual ECDs, apart from the main EC layer (cathode), there is another EC layer (secondary or ion storage layer) deposited on ITO, which is the anode; between the two EC layers there is the electrolyte. Initially, the EC layer is in the reduced state, whereas the secondary one is in the oxidized. The changes of the colour occur by charging and discharging the cell (i.e. applying potential).

One of the greatest challenges for polymer ECDs is to improve the performance and the stability of the ECDs. To this direction, the current research has shown that the 3,4-ethylenedioxythiophene (EDOT) can be used as the basis for synthesizing new EC copolymers that combine very good EC properties and adequate stability in both dedoped and doped states. The aim of this work is to study the effect of the electropolymerization conditions on the morphology, optical and nanomechanical properties of one such EDOT derivative, namely poly(4,7-bis(7-methyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole)/poly (bEDOTBThAZ) films as well as on the performance of their corresponding EC devices.

The poly(bEDOTBThAZ) films were deposited on ITO electrodes by electropolymerization using cyclic voltammetry or potentiostatic conditions by varying the deposition parameters. The films exhibited good EC properties, switching their colour from green (reduced state) to transparent sky blue (oxidized state). The different electropolymerization conditions affect the morphology, optical and nanomechanical properties of the EC polymers. Single layer ECDs were constructed using the poly(bEDOTBThAZ) film on ITO using gel electrolyte consisting of propylene carbonate, PMMA and tetrabutylammonium tetrafluoroborate (TBABF4). The ECDs switched successfully their colour between the dedoped and doped state (Figure 1). In order to find the optimum EC films, the operational performance of the devices (specifically the response time, current, optical properties and stability) was thoroughly investigated and correlated with the corresponding electropolymerization conditions used for the deposition.

![EC device at -1 V](image1)

![EC device at +2 V](image2)

Figure 1. EC devices based on poly(bEDOTBThAZ) in dedoped (-1 V) and doped state (at +2 V)