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Construction of electrochromic devices using thiophene based conducting polymers

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Abstract Dual type polymer electrochromic devices (ECDs) based on poly(terepthalic acid bis-(2-thiophen-3-yl-ethyl)ester) (PTATE), its copolymer with thiophene P(TATE-co-Th) and poly(3,4-ethylenedioxythiophene) (PEDOT) have been constructed. Spectroelectrochemistry, switching ability and stability of the devices were investigated by UV-Vis Spectrophotometer and Cyclic voltammetry. These devices exhibit low switching voltages (between 0.0 V and +1.6 V), short switching times with reasonable switching stability under atmospheric conditions.

Introduction

An electrochromic material is the one that changes color reversibly by an electrochemical reaction, and the phenomenon is called electrochromism [1]. New electrochromic materials attract great interest, due to their rapid response times, long term stability, and high contrast [2, 3]. Conducting polymers represent an attractive class of electrochromic materials owing to their facile switching properties and controllable optical properties [4–8].

Electrochromic devices take part in various applications, such as display panels [9], camouflage materials [10], variable reflectance mirrors [11] and variable transmissive windows [12]. An electrochromic device is essentially a battery in which the electrochromic electrode is separated by a suitable solid or liquid electrolyte from a charge balancing suitable electrode, and the color changes occur by charging and discharging the electrochemical cell with applied potential [1]. Some of the most promising conducting polymers for use in ECD's are based on poly(3,4-ethylenedioxythiophene) and its derivatives as they exhibit high electrochromic contrast, low oxidation potentials, and high conductivity as well as good electrochemical and thermal stability [13]. The low band gap of PEDOT allows the polymer to be almost transparent in the doped state and blue in neutral state [14].

In this study, we constructed dual-type electrochromic devices based on poly(terepthalic acid bis-(2-thiophen-3-yl-ethyl)ester), its copolymer with thiophene, and poly(3,4-ethylenedioxythiophene). Devices were assembled in sandwich configuration of electrochromic materials deposited on ITO glass electrodes and a gel electrolyte. For the construction of the devices, PEDOT was used as the cathodically coloring, PTATE and P(TATE-co-Th) were used as the anodically coloring materials.

Experimental

Chemicals

Propylene carbonate (PC), tetrabutylammonium tetrafluoroborate (TBAFB), Polymethylmethacrylate (PMMA) were purchased from Aldrich and used without further purification. Borontrifloride ethylether (BFEE) was purchased from Sigma. Acetonitrile (AN) (Merck) and thiophene (Th) (Aldrich) were distilled prior to

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use. 3,4-Ethylenedioxythiophene (EDOT), was purchased from Aldrich and used as received. Terepthalic acid bis-(2-thiophen-3-yl-ethyl)ester and its copolymer with thiophene were synthesized as reported previously [15].

Electrochemistry

A three-electrode cell containing an ITO-coated glass slide as the working electrode, a platinum flag as the counter electrode, and a silver wire as the pseudo-reference electrode were used for electrodeposition of polymer films via potentiostatic or potentiodynamic methods. All electrochemistry experiments were carried out using a Solatron 1285 model potentiostat/galvanostat. PEDOT films were deposited on ITO from a 0.1 mol L^{-1} monomer solution in (0.1 mol L^{-1}) TBAFB/AN electrolyte-solvent couple. PTATE was coated on ITO electrode via cyclic voltammetry scanning between –0.5 V and + 1.6 V in DCM/BFEE (8:2, v/v) solution containing 0.01 mol L^{-1} TATE and 0.1 mol L^{-1} TBAFB. P(TATE-co-Th) was prepared in the same solution that contains 5×10^{-3} mol L^{-1} thiophene.

Gel electrolyte preparation

AN was used to dissolve the PMMA and TBAFB. While the homogeneous mixture was prepared by stirring and heating, the mixture was plasticized by PC introduced in the medium. Stirring and heating continued until honey-like gel obtained. The weight ratio of ACN:PC:PMMA:TBAFB was 70:20:7:3.

ECDs construction

ECD's were constructed by sandwiching the gel electrolyte between conducting polymers deposited on ITO. While constructing the device one polymer was oxidatively doped, the other was neutral. Before construction, in order to improve the optical stability during redox process, it is important to equilibrate the charge on the electrodes [16]. TATE and P(TATE-co-Th) coated electrodes were polarized to + 1.6 V in TBAFB/ACN electrolyte-solvent couple. Same procedure was applied to PEDOT coated ITO at –1.0 V.

Device characterization

The characterization of the devices, optical properties was carried out using a Agilent 8453 UV-Vis spectrophotometer. A device without the electrochromic polymer layer, but otherwise with the same assembly, was used as a reference. Stability of the devices upon repeated switching was also investigated by cyclic voltammetry experiments.

Results and discussion

PTATE, P(TATE-co-Th) and PEDOT (structures shown in Fig. 1) were coated onto ITO-coated glass slides potentiodynamically. Once the PTATE film was fully oxidized and reduced back to the neutral state, the color changed from blue to yellow. P(TATE-co-Th) film was blue in its oxidized state and orange in its neutral state. Two dual electrochromic devices, namely PTATE/ PEDOT and P(TATE-co-Th)/ PEDOT were constructed with these polymers.

Spectroelectrochemistry

In order to obtain more insight into the relationship between structure and electrochemical properties, spectroelectrochemical series of both PTATE/PEDOT and P(TATE-co-Th)/PEDOT devices were examined [17].

Spectroelectrochemical study of PTATE/PEDOT device at voltages varying between –0.2 V and + 1.6 V are shown in Fig. 2a. When negative potential was applied to PTATE layer, due to π–π^* transition there was a maximum absorption at 420 nm revealing the yellow color. In that state PEDOT layer was in transparent blue color and device revealed yellow color. When the applied potential increased, due to reduction of PEDOT layer, blue color became dominant and maximum absorption observed at 620 nm.

Spectroelectrochemical study of P(TATE-co-Th)/PEDOT device was carried out varying the voltage between 0.0 V and + 1.5 V (Fig. 2b). At 0.0 V, when the PEDOT layer was in oxidized form and reveals the transparent sky blue color, P(TATE-co-Th) layer

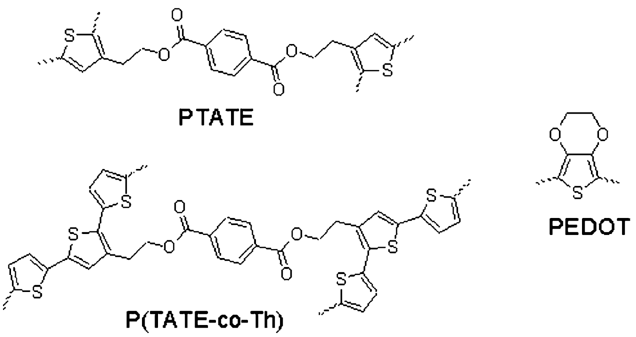

Fig. 1 Structures of electrochromic polymers used in this work

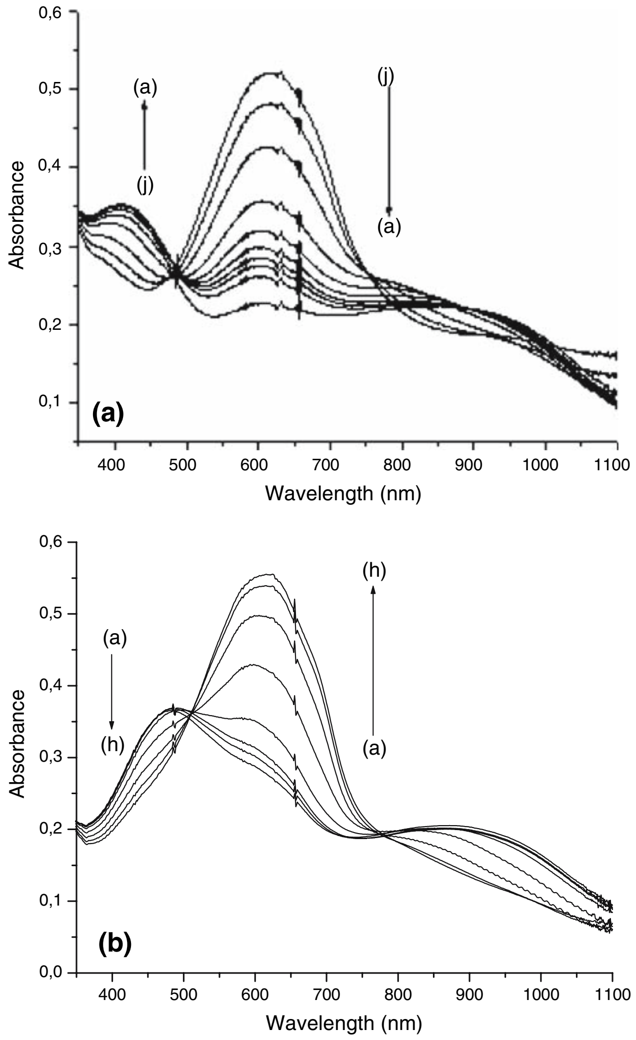

Fig. 2 Spectroelectrochemistry of **(a)** PTATE/PEDOT device at applied potentials between –0.2 V and 1.6 V. (a) –0.2 V (b) 0.0 V (c) + 0.2 V (d) + 0.4 V (e) + 0.6 V (f) + 0.8 V (g) + 1.0 V (h) + 1.2 V (i) + 1.4 V (j) + 1.6 V **(b)** P(TATE-co-Th)/PEDOT device at applied potentials between 0.0 V and + 1.4 V. (a) 0.0 V (b) + 0.4 V (c) + 0.6 V (d) + 0.8 V (e) + 1.0 V (f) + 1.2 V (g) + 1.4 V (h) + 1.5 V

reveals the orange color. λmax value due to π–π* transition was observed at 450 nm in that state. As the applied potential increased, especially beginning from + 0.8 V, PEDOT layer become dominant, λmax value was observed at 640 nm.

Switching

To investigate switching characteristics of the ECD's, the transmission and the response time at the maximum contrast wavelength was monitored during repeated redox stepping experiments. For PTATE/PEDOT device, maximum contrast (Δ%T) was measured as 12.9 and switching time was less than 2 s (Fig. 3a) by stepping potential between 0.0 V and + 1.6 V with a residence time of 5 s. For the case of P(TATE-co-Th)/PEDOT device, switching time and Δ%T values were measured as less than 1.1 s and 20.9 respectively (Fig. 3b) while stepping the potential between 0.0 V and + 1.6 V. Consequently, copolymerization procedure in device processing not only decreases the response time, but also increases the Δ%T.

Stability

Redox stability is an important requirement for production of reliable electrochromic devices with long lifetimes. Main reasons for device failure are different applied voltages and environmental conditions of the

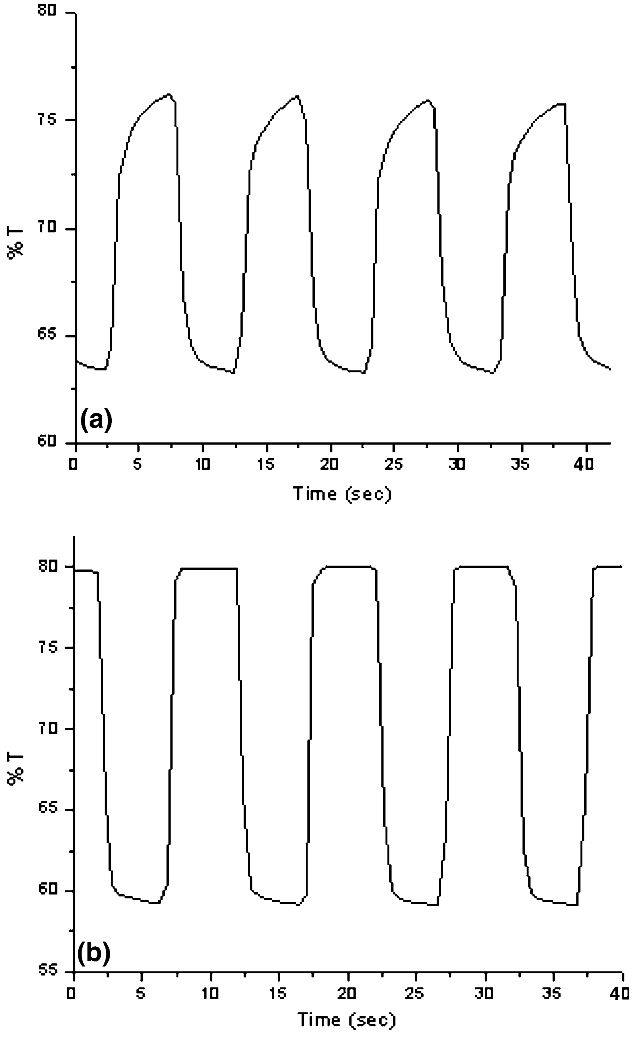

Fig. 3 Electrochromic transmittance changes during redox switching of **(a)** PTATE/PEDOT device at 620 nm between 0.0 V and + 1.6 V **(b)** P(TATE-co-Th)/PEDOT device at 640 nm between –1.0 V and + 1.7 V, with a step time of 5 s

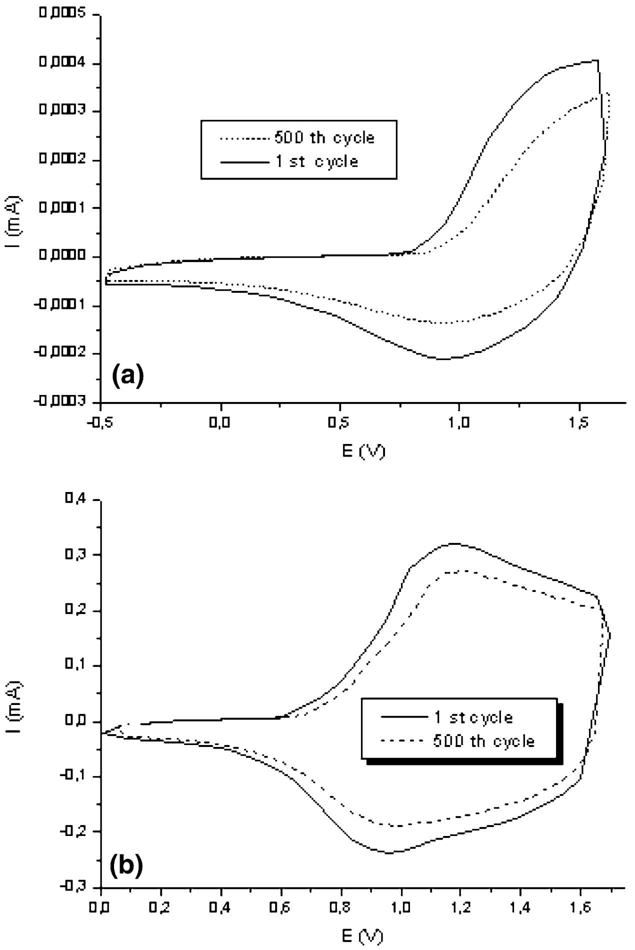

Fig. 4 Switching stability of **(a)** PTATE/PEDOT device sweeping the potential between –0.5 V and + 1.6 V. **(b)** P(TATE-co-Th)/PEDOT device sweeping the potential between 0.0 V and + 1.7 V

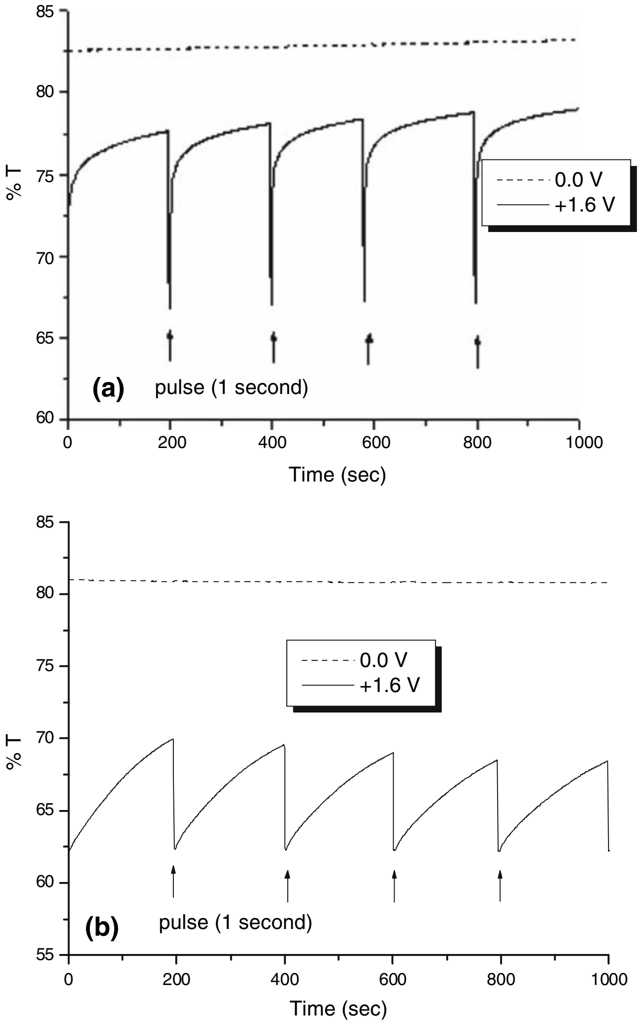

Fig. 5 Open circuit memory of **(a)** PTATE/PEDOT device monitored at 620 nm **(b)** P(TATE-co-Th)/PEDOT device monitored at 640 nm

materials. To test the stability of devices, potential between –0.5 V and + 1.6 V, 0.0 V and + 1.7 V for PTATE/PEDOT and P(TATE-co-Th)/PEDOT devices respectively sweeped repeatedly with a scan rate of 500 mV/s. Between 1st and 500th cycles only limited decrease in the current response was observed (Fig. 4 a, b), which show that ECD's have good environmental and redox stability with an average of 10% transmittance loss.

Memory effect

After setting the device in one color state and removing the applied voltage, it should retain that color with no further current required; thus giving the device an open circuit memory. Figure 5(a) and (b) show the variation of the transmittance (ΔT%) of 620 nm for yellow and blue states of PTATE/PEDOT device and 640 nm for blue and orange states of P(TATE-co-Th)/PEDOT device. We applied a pulse (0.0 V or + 1.6 V) for 1 s and held the cell in an open-circuit condition for 200 s while the transmittance was monitored as a function of time. We observe that the transmittance of the yellow state of the PTATE/PEDOT device is highly stable at 620 nm while blue state exhibits a 11 T% loss and at 640 nm the transmittance of the orange state of the P(TATE-co-Th)/PEDOT device is highly stable while blue state exhibits a 8 T% loss.

Colorimetry

Colorimetry analysis provides accurate and quantitative measure of the color for an electrochromic material. Luminance (L), hue (a) and saturation (b) are three attributes that are used to describe the color

Table 1. Electrochromic properties

Electrochromic devices	Color (ox)	Color (neut)	L	a	b
PTATE/PEDOT	Blue	Yellow	55	–2	3
			38	–1	–24
P(TATE-co-Th)/ PEDOT	Intense blue	Orange	36	6	26
			20	7	–34

ox: oxidized state

neut: neutral state

according to the CIE system [11, 17]. The L, a, b values measured at 0.0 V and + 1.6 V were given in table 1.

Conclusion

The dual polymer ECD's were constructed by separating complementary pairs of electrochromic polymer films deposited on ITO-coated glass slides with a gel electrolyte consisting of an inorganic salt and plasticized PMMA. Device contrast ratios (measured as Δ%T) and switching time of devices were 12.9% and less that 2 s for PTATE/PEDOT device, 20.9% and less than 1.1 s for P(TATE-co-Th)/PEDOT device. Stability studies show that devices have reasonable stability. According to open circuit memory studies, yellow state of the PTATE/PEDOT device is highly stable while the transmittance of blue state exhibits a 11%T loss and orange state of the P(TATE-co-Th)/PEDOT device is highly stable while the transmittance of blue state exhibits a 8%T loss. Compare to such devices constructed using thiophene derivatives, this one is quite good in terms of switching time, however, better contrast values (Δ%T) were reported.

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