

Full Length Article

Effects of oxidation potential and retention time on electrochromic stability of poly (3-hexyl thiophene) films

Tae-Ho Kim^a, Seok Hyun Song^b, Hyo-Jae Kim^b, Seong-Hyeon Oh^b, Song-Yi Han^b, Goung Kim^b, Yoon-Chae Nah^{a,b,*}^a Interdisciplinary Program in Creative Engineering, Materials Research Center, Korea University of Technology and Education, Cheonan, Chungnam 31253, Republic of Korea^b School of Energy, Materials, and Chemical Engineering, Korea University of Technology and Education, Cheonan, Chungnam 31253, Republic of Korea

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ABSTRACT

Herein, we report the effects of applied voltage on the electrochromic (EC) stability of poly(3-hexylthiophene) (P3HT) films during EC reactions. The transmittance difference and cycling stability of these films were monitored to optimize the oxidation voltage, and their chemical compositions were analyzed by X-ray photoelectron spectroscopy after long-term electrochemical cycling. High oxidation voltages increased the color contrast of P3HT films but decreased their cycling stability due to facilitating chemical degradation. Furthermore, at an optimized oxidation voltage, the retention time during potential pulsing was adjusted utilizing the optical memory of P3HT, revealing that the decreased voltage application time reduced power consumption by 9.6% and enhanced EC stability without loss of color contrast.

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1. Introduction

Electrochromism refers to a reversible change of material optical properties when during electrochemical reactions [1]. Electrochromic (EC) devices are different from other passive chromogenic devices such as thermochromic [2,3], photochromic [4,5], and gasochromic ones [6] due to being active systems controlling color intensity/opacity by working purpose of users. Furthermore, compared to other optoelectronic devices, EC devices can be operated by applying voltages of only several volts and maintain their colors for certain time periods under open-circuit conditions, exhibiting the so-called memory effect [7]. Due to these advantages, EC devices find prospective applications in smart window [8–10], switchable mirrors [11,12], information displays [13,14], and optical shutters [15].

Among EC materials, electrochemically active conjugated polymers such as polythiophene [16], polyaniline [17], polypyrrole [18] have received much attention due to their high switching speed and multiple coloration. However, the low cycling stability of these materials during electrochemical reactions hinders the development of next-generation EC devices, necessitating the exploitation of methods for prolonging EC cyclability. For example, the cycling

stability of EC polymers can be enhanced by the incorporation of carbon nanomaterials such as functionalized graphene [19,20] and graphene oxide [21,22]. Moreover, the adhesion of EC polymers to transparent electrodes (e.g., indium tin oxide (ITO)) can be improved by covalent bonding between them, resulting in high EC stability [23]. Hybrids of EC polymers and inorganic nanomaterials have shown suitable long-term stability [24–26], which can be further enhanced by choosing an appropriate electrolyte anion [27].

The electrode and electrolyte modification increases the importance of carefully adjusting the driving voltage to attain sufficient stability during EC reactions, with unreasonable voltages often inducing irreversible electrochemical reactions and thus decreasing the stability of EC materials [28]. However, although the above stability issues have been receiving much attention, the corresponding voltage conditions have not been systematically studied. Herein, the effects of oxidation voltage and retention time on EC reactions were investigated for poly(3-hexylthiophene) (P3HT) films, with their long-term cyclability achieved by optimizing the above parameters. Furthermore, the stable optical memory of P3HT enabled the control of voltage retention time during EC reactions and thus reduced power consumption by 9.6%.

2. Experimental

P3HT ($M_w = 85,000$) was obtained from EM INDEX (Electronic Materials Index Co., Ltd.). All solvents were purchased from

* Corresponding author at: Interdisciplinary Program in Creative Engineering, Materials Research Center, Korea University of Technology and Education, Cheonan, Chungnam 31253, Republic of Korea.

E-mail address: ycnah@koreatech.ac.kr (Y.-C. Nah).

Sigma-Aldrich and used without further purification. ITO glass (Geomatec, <math><10 \Omega/\text{sq}</math>) was cleaned by sequential sonication in acetone, isopropanol, and ethanol, rinsed in deionized (DI) water, and dried under N_2 . The cleaned ITO substrate was spin-coated with a 0.7 wt% solution of P3HT in chlorobenzene (1500 rpm, 15 s) and dried on a hot plate (60 °C, 10 min), with the thickness of the thus obtained P3HT film (~45 nm) measured using ellipsometry (SE MG-1000 UV, Nano-View Co., Ltd.). For electrochemical characterization of the samples, electrochemical cells were assembled using P3HT on ITO glass as a working electrode, Pt wire as a counter electrode, and Ag wire as a reference electrode, with measurements conducted in 0.5 M LiClO_4 in propylene carbonate. Cyclic voltammetry (CV) curves were recorded under various conditions at a scan rate of 50 mV/s. EC properties were evaluated by recording optical transmittances at a wavelength of 550 nm using a UV/Vis spectrophotometer (Cary 100, Agilent Technologies Inc.), with a background spectrum of blank ITO/glass in the above electrolyte recorded in a standard quartz cell for all measurements. The chemical compositions of samples were determined using X-ray photoelectron spectroscopy (XPS, K-ALPHA; Thermo Instruments Inc.).

3. Results and discussion

Fig. 1(a) shows CV curves of P3HT films on ITO glass (P3HT/ITO) obtained at various voltage conditions, with the lowest voltage fixed at $E_0 = -0.2$ V, and the highest voltage (E_1) varied between 0.6 and 1.0 V. During the electrochemical reactions of P3HT, oxidation peaks were observed at 0.2 and 0.6 V, with reduction peaks observed at 0.1 and 0.5 V, implying polaronic and bipolaronic P3HT transition states [29]. Furthermore, during the E_0 to E_1 voltage sweep, the color of the P3HT layer was gradually bleached from red to pale blue, with a reverse sweep from E_1 to E_0 resulting in original color restoration. Thus, the above results implied that

P3HT underwent the following chemical reaction during voltage sweeping [29,30]:



To determine appropriate E_1 values for the EC reactions of P3HT films, we initially monitored their transmittance (T) at 550 nm as a function of E_1 (Fig. 1(b)), revealing that T linearly increased from 68.5 to 87.6% ($\Delta T = 19.1\%$) as the voltage was swept from 0.2 to 0.6 V, with the latter voltage corresponding to maximal oxidation current. However, above 0.6 V, the transmittance increase slowed down, with only marginal changes observed upon going from 0.8 V ($T = 91.2\%$) to 1.0 V ($T = 92.6\%$). Combining the results of Fig. 1(a) and (b), we concluded that the rapid change of P3HT color occurred until the current density reached its maximum and the EC reaction was gradually saturated. Experiments featuring 20-s potential pulses between E_0 and E_1 clearly showed the dependence of transmittance changes (ΔT) on E_1 (Fig. 1(c)), with a ΔT of 23.4% observed for colored/bleached states at $E_1 = 0.6$ V (Table 1). At $E_1 = 0.8$ V, the transmittance of the bleached state significantly increased, resulting in $\Delta T = 26.8\%$. However, for higher E_1 (0.8–

Table 1

Electrochemical and electrochromic data for P3HT films at different E_1 . (The τ_b and τ_c are the response times during the bleaching and coloring processes, respectively, which were estimated as the time required for 90% of the total transmittance difference to be reached.)

E_1 (V)	ΔT (%)	τ_b (s)	τ_c (s)	Q_c (mC/cm ²)	Q_a (mC/cm ²)	Q_c/Q_a
0.6	23.4	0.90	0.52	0.307	0.310	0.990
0.8	26.8	0.80	0.65	0.519	0.530	0.979
0.9	27.3	0.81	0.66	0.565	0.582	0.971
1.0	27.6	0.79	0.68	0.613	0.639	0.959

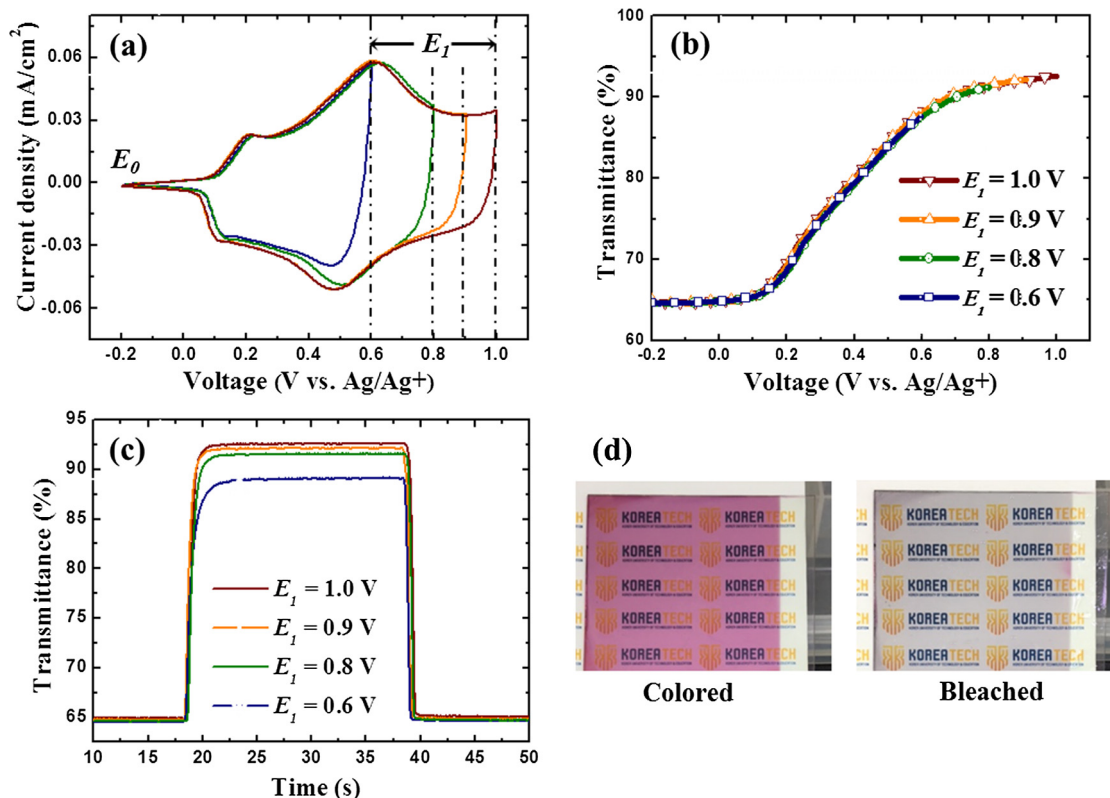


Fig. 1. (a) CV curves of P3HT films recorded between E_0 (-0.2 V) and E_1 (0.6, 0.8, 0.9, and 1.0 V). Transmittance changes during (b) CV measurements and (c) potential pulsing. (d) Images of bleached and colored states for P3HT films on ITO.

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