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Cycling and at-rest stabilities of a complementary electrochromic device containing poly(3,4-ethylenedioxythiophene) and Prussian blue[☆]

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Abstract

PEDOT-based electrochromic devices (ECDs) have been investigated intensively in recent years. In order to obtain an ECD having long cycle life, the counter electrode and electrolyte used should be compatible in the electrochemical environment. Prussian blue (PB) is proven to be electrochemically stable when cycling in non-aqueous solutions. Thus a new organic-inorganic complementary ECD was assembled in combination with a PMMA-based gel polymer electrolyte. This ECD exhibited deep blue-violet when applying -2.1 V and became light blue when applying 0.6 V. Under these conditions, the transmittance of the ECD at 590 nm changed from 13.8% (-2.1 V) to 60.5% ($+0.6$ V) with a coloration efficiency of 338 cm²/C. The cell retained 55% of its maximum transmittance window (ΔT_{\max}) after $50,640$ repeated cycles. Moreover, the at-rest stability test revealed a transmittance window (ΔT) decay of 9.6% over a period of 107 days. Therefore, the proposed PEDOT-PB ECD may have potential for practical applications.

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Keywords: At-rest stability; Coloration efficiency; Cycling stability; Electrochromic device; Poly(3,4-ethylenedioxythiophene); Prussian blue

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1. Introduction

Electrochromism [1] is a phenomenon with reversible and visible change in optical absorption in response to a DC voltage/current input. An electrochromic device (ECD) is composed of at least two layers of electrodes and one layer of electrolyte. The cell configuration may be solution, hybrid, or thin-film type [2]. If the two electrochromic (EC) materials offer an additive optical relationship, the ECD is referred to as complementary. During the last three decades, ECDs have been attractive for many applications such as displays [3], anti-glare rearview mirrors [4], secondary batteries [5], and solar-attenuated windows [6]. According to the types of EC materials, there are several systems reported in literature such as inorganic WO_3 -PB systems [7–9], inorganic–organic WO_3 -polyaniline systems [10,11], WO_3 -polypyrrole systems [12], organic solution system [13], and conducting polymers-based systems [14,15]. For comparison, conducting polymers-based systems have rapid optical response and high coloration efficiency (CE), while inorganic WO_3 -PB systems reported by Miyamoto et al. [7] and Ho [9] have larger transmittance window (ΔT). Except for some rare systems, most of the reported systems had problems of long-term cycling stability. Even if an ECD has good initial performance, such as high optical contrast or rapid response, it would limit the possibilities to bring the EC products to the markets before the cycling and at-rest stabilities are solved. Thus, resolving the stability issue is a crucial task. If an ECD is thought to be electrochemically and thermally stable over a long period of time, the good compatibility of the two EC materials with the electrolyte is required.

With the continuing development of the conducting polymers [16], many conducting polymers, such as polyaniline, polypyrrole, polythiophene and their derivatives, have been studied for the EC applications. Recently, a new conducting polymer, poly(3,4-ethylenedioxythiophene) (designated as PEDOT), was synthesized in Bayer AG research laboratories and commercialized. PEDOT possessed not only a high conductivity of 300 S/cm, but also exhibited good electrochemical and thermal stabilities [17,18]. With these attractive properties, PEDOT has been researched for many applications such as antistatic coatings [19], capacitors [18], light-emitting diodes [20], photoelectrochemical cells [21], biosensors [22], and ECDs [23–28]. PEDOT exhibits deep blue-violet in its neutral state. Upon doping, it changes to light blue, so it is EC in nature and is attractive to EC applications. Gustafsson et al. [23] was the first to report the PEDOT-based ECD with inorganic Li_yVO_x as the counter electrode in 1994. They reported that the transmittance of the ECD at 585 nm changed from 61% (+0.5 V) to 25% (–1.5 V), with a ΔT of 36% and a high CE of ca. 560 cm^2/C . The cell shows good reversibility, as evidenced by completing several thousand electrochemical cycles. In 1996, Sapp et al. [24] reported two dual-polymer ECDs based on PEDOT; the counter electrodes used were poly[3,6-bis(2-(3,4-ethylenedioxythiophene))-*N*-methylcarbazole] and polyaniline (PANI). The two cells were both opaque violet in the colored state and pale transparent green in the bleached state. The PEDOT-PANI ECD exhibited a ΔT of 45% at 620 nm with a limited cycle life of about 50–100 cycles. The symmetrical and wide range of

operating potentials may be what causes the serious ΔT decay. Subsequently, the same group assembled 12 kinds of cells by using PEDOT or PEDOT derivatives [25]. They claimed that one of the devices possessed an extremely high CE of up to $1413 \text{ cm}^2/\text{C}$ and retained 60% of the original optical response after 10^4 double potential steps. De Paoli et al. [26,27] reported PEDOT-based ECDs using polypyrrole and poly(*o*-methoxy aniline) as the counter electrodes. These two ECDs showed high ΔT (52% and 75%, respectively) at 640 nm. However, the decay of the ΔT was rapid over 100 cycles. In 2001, DeLongchamp and Hammond [28] proposed a new ECD using layer-by-layer method to form the EC electrodes. Although the ΔT of the device was low (24% at 660 nm), the optical response was retained after 35,000 cycles. Of those ECDs mentioned, only De Paoli et al. [27] reported spectra decay percentages. Table 1 summarizes the performance of the referenced PEDOT-based ECDs.

Although PEDOT has been proven to possess good electrochemical stability, a stable counter electrode pairing with PEDOT is needed in making the cell stable enough for long-term switching. The counter electrode acts not only as the charge compensating electrode but also should be compatible with the PEDOT in terms of electrochemical cycling in the same electrolyte. Although most of the counter electrodes shown in Table 1 are conducting polymers, the compatibility and cycling stability issues are still needed to be overcome. Apart from conducting polymers used as the counter electrode in ECDs, the inorganic Prussian blue (PB, iron (III) hexacyanoferrate (II)) [29,30] can be another choice. With regard to the use as a complementary EC material for ECDs, PB, which is characterized by a polyelectrochromic property and exhibits four corresponding redox states [31], has been investigated intensively. From the most reduced to the most oxidized state, the four redox states of PB are the colorless Everitt's salt (ES), PB, Berlin green (BG), and Prussian yellow (PY). PB can be cycled reversibly for several thousand times both in appropriate aqueous electrolyte [32] and in WO_3 -PB polymeric ECDs [9,33]. Moreover, PB has also proven to have good electrochemical stability in non-aqueous solvents [34,35]. In this work, a new organic-inorganic complementary ECD was assembled by using both PEDOT and PB thin-film electrodes.

A poly(methyl methacrylate)-based (PMMA-based) gel polymer electrolyte [36,37] was incorporated into the new PEDOT-PB ECD. The electrochemical and spectral properties of PEDOT and PB in 1 M LiClO_4 /propylene carbonate (PC) are discussed in this paper. The performance of the new ECD was characterized by the two-electrode chronoamperometry. The results show that PEDOT and PB exhibit good electrochemical stability in an organic environment, and the ECD has a ΔT value of ca. 47% at 590 nm. In addition, the PEDOT-PB ECD has a reasonable coloration efficiency of ca. $338 \text{ cm}^2/\text{C}$ at 590 nm. The ECD shows good dynamic cycling stability and at-rest stability. After a total of 50,640 cycling test, ΔT at 590 nm retained 55% of its maximum value. As for the at-rest test, the decay in ΔT was only 9.56% after a period of 107 days. The good long-term stability may provide the foundation for making this ECD into a real practice.

Table 1
A partial list of PEDOT-based ECDs reported in literature

Cell configuration Substrate/EC1/Electrolyte/EC2/Substrate	Operating condition Color state/bleach state	λ (nm)	T_c/T_b (ΔT) % Cycle life	CE (cm^2/C)	Ref.
ITO/PEDOT/ELE1 ^a /Li ₂ VO ₃ /ITO	–1.5 V(10 s)/0.5 V(10 s) opaque blue/pale sky blue	585	25/61 (36) > 10 ³ cycles	560	[23]
ITO/PEDOT/ELE2 ^b /PBEDOT-NCH ₃ Cz ^c /ITO	–0.8 V(30 s)/0.8 V(30 s) opaque violet/pale trans. green	535	37/68 (31) > 10 ⁴ cycles	—	[24]
ITO/PEDOT/ELE2 ^b /PANI ^d /ITO	–2.5 V(30 s)/2.5 V(30 s) opaque violet/pale trans. green	620	— (45) 50–100 cycles	—	[24]
ITO/PEDOT/ELE2 ^b /PBEDOT-NCH ₃ Cz ^c /ITO	–0.9 V(5 s)/0.9 V(5 s) opaque violet/trans. yellow-green	550	21/68 (47) > 10 ⁴ cycles	421	[25]
ITO/PEDOT/ELE2 ^b /PBEDOT-NC ₂₀ H ₄₁ Cz ^e /ITO	–0.9 V(5 s)/0.9 V(5 s) opaque violet/trans. yellow-green	560	21/53 (32) > 10 ⁴ cycles	—	[25]
ITO/PEDOT/ELE2 ^b /PBEDOT-BP ^c /ITO	–0.9 V(5 s)/0.9 V(5 s) opaque violet/trans. yellow-green	605	21/50 (29) > 10 ⁴ cycles	—	[25]
PET-ITO/PPy-DS-IC ^f /ELE3 ^g /PEDOT-PSS/PET-ITO	opaque violet/trans. yellow-green 1.5 V(–)/–1.5 V(–) ^h	640	> 10 ⁴ cycles 23/75 (52) ⁱ	360	[26]
PET-ITO/PEDOT-PSS/ELE4 ^g /PoAni ^h /PET-ITO	dark blue/pale yellow –0.8 V(20 s)/0.9 V(20 s)	640	15/90 (75) 100 cycles 43/85 (42)	—	[27]
ITO/(PEDOT-PSS/LPEI)/PAMPS/(PANI/PAMPS)/ITO	dark blue/trans. –0.8 V(–)/0.8 V(–)	660	25/49 (24) > 35,000 cycles	—	[28]
ITO/PEDOT/ELE5 ^k /PB/ITO	deep blue-green/pale yellow –2.1 V(10 s)/0.6 V(10 s) deep blue-violet/light blue	590	15/63 (48) 5 × 10 ⁴ cycles 34/60 (26)	338	This work

^aELE1 = LiClO₄ in POMOE-400.

^bELE2 = ACN+PC + PMMA + Li[(SO₂CF₃)₂] (70:20:7:3).

^cPBEDOT-NCH₃Cz = poly[3,6-bis(2-(3,4-ethylenedioxythiophene))-N-methylcarbazole]. PBEDOT-NC₂₀H₄₁Cz = poly[3,6-bis(2-(3,4-ethylenedioxythiophene))-N-oicosylcarbazole]. PBEDOT-BP = poly[4,4'-bis(2-(3,4-ethylenedioxythiophene))biphenyl].

^dPANI = polyaniline.

^ePPy-DS-IC = polypyrrole doped with dodecylsulfate and indigo carmine.

^fELE3 = poly(epichlorohydrin-co-ethylene oxide) + LiClO₄.

^gELE4 = THF + LiClO₄ + Epichtomer-16.

^hPoAni = poly(*o*-methoxy aniline).

ⁱ20 layers of films prepared with layer-by-layer method, LPEI = poly(ethylene imine).

^j20 layers of films prepared with layer-by-layer method, PAMPS = poly-2-acrylamido-2-methylpropane sulfonic acid.

^kELE5 = 1 M LiClO₄/PC + 10 wt% PMMA.

^lPEDOT-PSS EC electrode acts as the negative electrode in this ECD.

2. Experimental

2.1. Materials

The solvents, acetonitrile (ACN) and PC, used in this work were purified before using. They were bubbled with nitrogen gas (N_2) for 10 min, dehydrated with 4 Å molecular sieves and stored in N_2 atmosphere prior to use. Lithium perchlorate ($LiClO_4$) was dissolved into ACN and melted at 110 °C, under vacuum for 24 h. PMMA (weight average MW = 996,000) was dried at 100 °C under vacuum for 15 h. The recrystallized $LiClO_4$ and dehydrated PMMA were stored in N_2 atmosphere prior to use. Other chemicals (tetrabutylammonium perchlorate (TBAP), $AgNO_3$, KCl, HCl, $FeCl_3 \cdot 6H_2O$, and $K_3Fe(CN)_6$) were used as received. The electrode potential recorded was against a homemade Ag/Ag^+ non-aqueous reference electrode. The Ag/Ag^+ reference electrode contains a solution of 10 mM $AgNO_3$ and 0.1 M TBAP in ACN. The calibrated potential of the Ag/Ag^+ reference electrode is 0.48 V vs. NHE.

2.2. Preparation of the electrochromic thin-film electrodes

Optically transparent ITO glass substrates ($R_{sh} = 20 \Omega/sq.$, RiTdisplay Corporation, Hsinchu Industrial Park, Taiwan) were used for the deposition of EC films. Before use, the ITO substrates ($3.0 \times 4.0 \times 0.2 \text{ cm}^3$) were ultrasonically cleaned in a 0.1 M HCl solution for 3 min. They were ultrasonically re-cleaned for 3 min in deionized water (DIW) and dried in air. The insulating epoxy tapes (3 M Company, 0.14 mm thick) were pasted around the four edges of the ITO glass to maintain the same electroactive area of $2.0 \times 2.0 \text{ cm}^2$ on each electrode. Later, a piece of Cu tape (3 M Company, $3.0 \times 0.5 \text{ cm}^2$) was applied at one edge of the ITO surface as the bus bar. A three-electrode electrochemical cell was set up to deposit the EC thin films using the ITO glass substrate as the working electrode, a platinum plate counter electrode and the Ag/Ag^+ reference electrode. The experiments were conducted in air at room temperature and controlled by a potentiostat/galvanostat (Eco-Chemie, Autolab, PGSTAT30). The deposition solution for PEDOT was composed of 10 mM 3,4-ethylenedioxythiophene (EDOT) monomer and 0.1 M $LiClO_4$ in ACN. The PEDOT thin films were electropolymerized onto the ITO glass substrates by applying a potential at 1.2 V (vs. Ag/Ag^+) with a platinum counter electrode until a charge capacity of 25 mC/cm^2 was passed, in order to control the film thickness. The average thickness of the PEDOT films was 155 nm as measured using a profilometer (Sloan Dektak, model 3030). The as-deposited PEDOT thin-film electrodes were rinsed with ACN and dried in air prior to use. The PB thin-film electrodes were deposited galvanostatically. The composition of the plating solution was 10 mM $FeCl_3 \cdot 6H_2O_{(aq)}$, 10 mM $K_3Fe(CN)_{6(aq)}$, 0.1 M $KCl_{(aq)}$, and 0.1 M $HCl_{(aq)}$. Before the deposition, the mixed plating solution was bubbled with N_2 for 10 min to reduce the O_2 content of the solution. The deposition was done by applying a cathodic current density of $20 \mu A/cm^2$ onto the ITO glass substrates and the deposition time was controlled either at 120 s for

the use in cell assembly or 300 s for the measurement of the absorbance spectra. The as-deposited PB electrodes were rinsed with DIW, dried under the flow of N₂, and stored in air for at least one day before using.

2.3. Preparation of gel polymer electrolytes and cell assembly

The ECD was assembled with the PEDOT and PB electrodes by incorporating a PMMA-based gel polymer electrolyte under N₂ atmosphere. The PMMA-based gel polymer electrolyte was prepared according to the literatures [36,37]. LiClO₄ salt was dissolved into PC. Then 10 wt% PMMA, which was based on 1.0 M LiClO₄/PC solution, was added and well-stirred. Finally, the solution was slowly heated until a transparent gel was formed. Before the cell assembly, both the PEDOT and PB electrodes were cycled several times by the cyclic voltammetric (CV) method in 1.0 M LiClO₄/PC solution under N₂ atmosphere to ensure the proper function of the ion insertion and extraction. After the cycles, the PEDOT and the PB electrodes were stepped to doping state and colorless ES state by applying 0.3 V and −0.9 V for 60 s, respectively. Following this potential pretreatment, the transparent gel polymer electrolyte was poured onto the PEDOT electrode, and the PB electrode was placed on top. Subsequently, the three layers were carefully sandwiched together to form a solid-state EC cell. The cell gap was controlled at 0.28 mm with a spacer tape. Finally, the cell was sealed with a Torr Seal[®] (Varian) cement around the four edges of the ITO glass.

2.4. Electrochemical and spectral measurements for the electrodes and stability tests for the ECD

The PEDOT and PB EC electrodes were characterized electrochemically in 1.0 M LiClO₄/PC by the three-electrode CV method. The CV was performed by using the above-mentioned potentiostat/galvanostat. Both the PEDOT and PB thin-film electrodes were separately connected to a potentiostat/galvanostat and placed in a spectrophotometer (Shimadzu, model UV-1601PC) to collect the absorbance spectra ranging between 350 and 1100 nm at different equilibrated potentials in 1.0 M LiClO₄/PC solution. In the same manner, the absorbance spectra of the ECD were also measured at different equilibrated applied voltages (PEDOT vs. PB). The dynamic transmittance responses of the PEDOT electrode and the ECD at 590 nm were measured in situ by a double potential method. The dynamic cycling stability test of the ECD was characterized by the two-electrode chronoamperometry with a multi-channel battery testing system (Maccor, model 2300). The applied voltage (PEDOT vs. PB) was −2.1 V for 10 s and changed to 0.6 V for 10 s at each cycle. The in situ transmittance spectra at 590 nm were recorded continuously for the first 1000 cycles, and the spectra were collected at specific cycle after 1000 cycles. Additionally, the at-rest stability of the ECD was characterized by the same method. The only difference was that the switching time was 30 s for each step, and the transmittance data were collected at specific day.

3. Results and discussion

3.1. Electrochemical and spectral properties of PEDOT and PB thin-film electrodes

3.1.1. Electrochemical properties of PEDOT and PB thin-film electrodes

The typical CVs of PEDOT and PB EC electrodes are shown in Fig. 1. They were cycled in 1.0 M LiClO₄/PC solution under N₂ atmosphere at a scan rate of 100 mV/s. According to Fig. 1, PEDOT thin-film electrodes show two oxidative and reductive peaks in the cycling potential range. The two oxidative peaks locate at ca. -0.89 and -0.12 V, and the reductive peaks locate at ca. -1.04 and -0.29 V. However, the first oxidative peak at -0.89 V is not obvious. The electrochemical behavior is similar to the results reported in the literature [38]. When PEDOT is doped in the positive potential range, the charge compensation of anions occurs and exhibits a capacitive characteristic. PEDOT is a cathodically coloring EC material; it shows deep blue in the neutral state, while upon doping, it changes to light blue. On the other hand, PB is colorless in the ES state at -0.9 V and blue in the PB state at 0.4 V. To avoid the second redox couple formation in PB, the upper oxidative potential is controlled at 0.4 V. With the results of the CVs, PEDOT and PB thin-film electrodes fulfill the requirement of a complementary ECD. Moreover, the simplified working principle of the complementary PEDOT-PB ECD containing LiClO₄ salt can be represented by Eqs. (1) and (2) for PEDOT and PB electrodes,

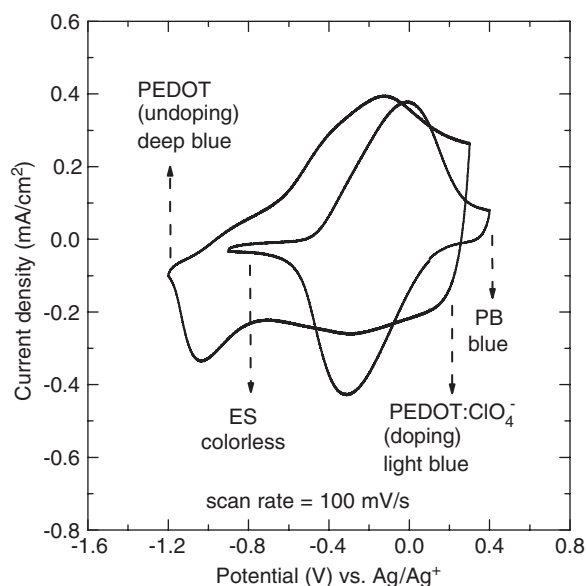
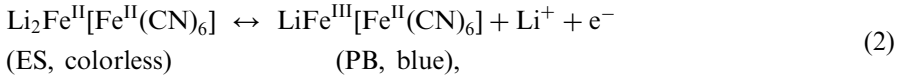
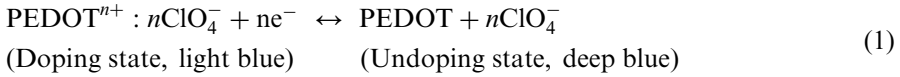


Fig. 1. CVs for the PEDOT and PB electrodes scanned in 1.0 M LiClO₄/PC under N₂ atmosphere at a scan rate of 100 mV/s. The area of the electrode is 2.0×2.0 cm².

respectively, as follows:



where ES is the Everitt's salt, n is the stoichiometric number of the counter ions. Thus the overall EC process in the ECD can be represented by adding Eqs. (1) and (2), as



3.1.2. Spectral properties of PEDOT and PB thin-film electrodes

Fig. 2 shows the results of the absorbance spectra for the PB thin-film electrode equilibrated at different potentials in a 1.0 M LiClO_4/PC solution. In the visible region, the intensity of the absorbance peak increases as the applied potential increases. The maximum absorption occurs at 690 nm, which is the same characteristic wavelength when switching PB in an aqueous electrolyte [31]. The

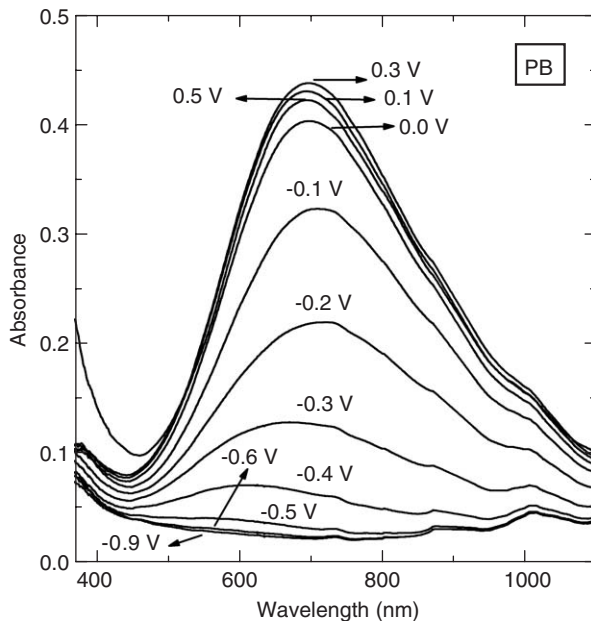


Fig. 2. Absorbance spectra of the PB electrode equilibrated in 1 M LiClO_4/PC at different applied potentials. The PB film was deposited at a constant current density of $20 \mu\text{A}/\text{cm}^2$ for 300 s.

PB spectra show no absorption characteristics when the applied potential is more negative than -0.6 V , which is consistent with the results of CVs. In contrast, when the applied potential is more positive than 0.3 V , the absorption starts to decrease due to the formation of BG. That is why one needs to control the potential, only to allow for the formation of the first redox couple. Similarly, the spectra of PEDOT equilibrated at different potentials are shown in Fig. 3. The spectral behavior is similar to those reported in Ref. [39]. The absorbance in the neutral state, which starts to increase at 760 nm , implies that the band gap of PEDOT is ca. 1.6 eV . The neutral PEDOT exhibits a high absorbance throughout the visible region, and the maximum absorptive peaks locate at 590 and 620 nm . The wavelengths, correspond to deep blue-violet region, are especially sensitive to human eyes. Upon doping, the absorption in the visible region decreases; however, another absorption peak appears at ca. 885 nm . Carlberg et al. [40] explained this as the formation of the bipolaron state of PEDOT. As the applied potential is increased further, the absorption peaks at 620 and 885 nm disappear and another low-energy absorption increases in the IR region. These are the characteristics of the low band-gap conducting polymers, making PEDOT a good cathodically EC material attractive to ECD applications. When the applied potential is more positive than 0.2 V , it is also found that PEDOT results in a capacitive charging and does not change the absorbance in the visible region.

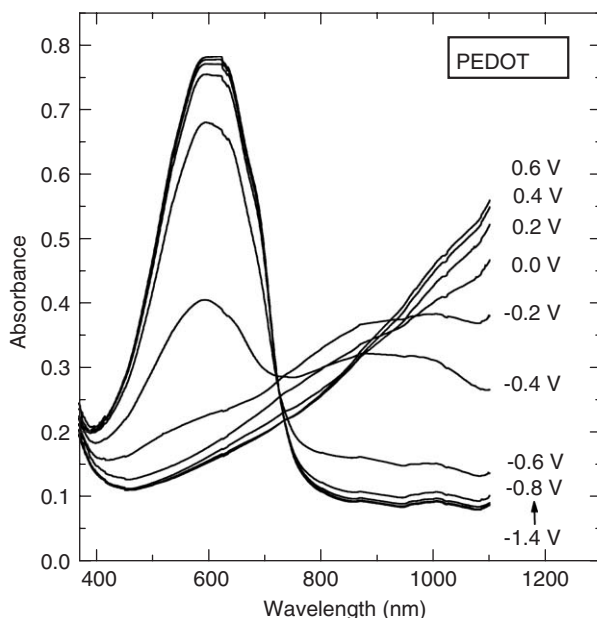


Fig. 3. Absorbance spectra of the PEDOT electrode equilibrated in $1.0\text{ M LiClO}_4/\text{PC}$ at different applied potentials. The PEDOT film was deposited by applying a potential of 1.2 V (vs. Ag/Ag^+), with a controlled charge density of $25\text{ mC}/\text{cm}^2$.

3.1.3. Transmittance response and coloration efficiency of PEDOT

As the deposited charge capacity of PB used in the ECD is only 2.40 mC/cm^2 , the EC contribution of PB in the PEDOT-PB ECD is less important, as compared to that of PEDOT. In this section, we will discuss the dynamic transmittance and coloration efficiency of the PEDOT electrode only. Because the maximum absorbance change for PEDOT occurs at ca. 590 nm, Fig. 4 shows the in situ transmittance change at 590 nm in response to the applied potentials. The coloring potential (V_c) was set to -1.2 V , and the bleaching potential (V_b) was set to 1.0 V , with switching intervals of 10 s. From the figure, the maximum ΔT at 590 nm is ca. 50%. This value is close to those reported in Refs. [41,42]. The response of the doping process is faster than that of the undoping one. Moreover, as the current response of the EC material is rapid, the estimation of the inserted charge should be recorded with extra care [23]. Under certain circumstances, if the inserted charge is underestimated, it is very likely that the calculated coloration efficiency would be overestimated by two or three times. Thus we have recorded data for the current–time ($I-t$) response with an interval of 0.01 s by the above-mentioned potentiostat/galvanostat to avoid the underestimation of the inserted charge. The inserted charge density was obtained from the integration of the $I-t$ curve and was ca. 2.40 mC/cm^2 , which was very close to the reported value of 2.68 mC/cm^2 at 95% of the full switch [42]. The charge density passed at 95% of the full optical density change is used for reporting the coloration efficiency since the majority of the color change has taken place and the last 5% is difficult to perceive with the naked eye.

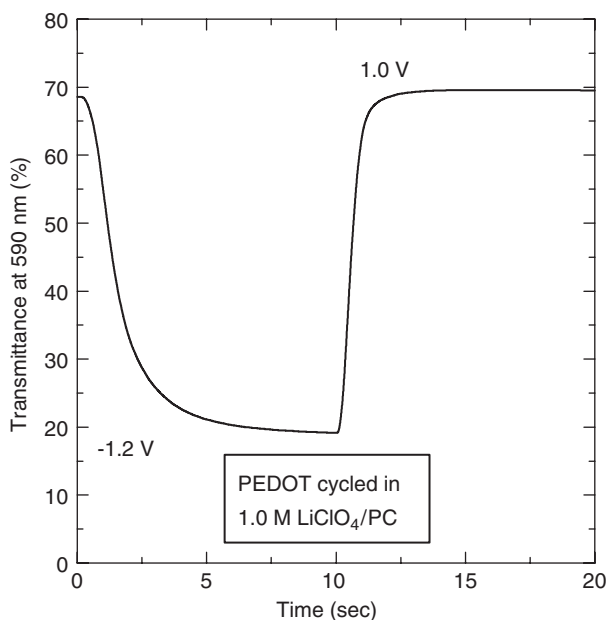


Fig. 4. The transmittance response at 590 nm for a PEDOT electrode cycled in 1.0 M LiClO_4/PC . The applied potentials were -1.2 V (10 s) for coloring and 1.0 V (10 s) for bleaching.

Following this practical observation, the anodic coloration efficiency of PEDOT at 590 nm was calculated to be ca. $225 \text{ cm}^2/\text{C}$ (equilibrated at -1.2 V for 10 s, then stepped to 1.0 V), and that of the cathodic one was ca. $120 \text{ cm}^2/\text{C}$ (equilibrated at 0.6 V for 10 s, then stepped to -1.2 V). Such lower cathodic coloration efficiency may be attributed to the extra charge consumed by side reactions in the negative applied potential.

3.2. Operational performance of the PEDOT-PB ECD

3.2.1. Spectral characterization and dynamical response of the ECD

The high coloration efficiency of PEDOT would make it very attractive to ECD applications from the viewpoint of the low-required power consumption. However, in order to obtain a workable and stable ECD, the choices of counter electrode and electrolyte are crucial. As outlined in Table 1, there are many PEDOT-based ECDs reported in recent years using a wide variety of counter electrodes. Most of them are organic, thus forming the dual polymer ECDs. Nevertheless, long-term stability may still be a problem. In this work, PB was chosen as the counter electrode because it is electrochemically active and stable, not only in aqueous systems [32] but also in non-aqueous systems [34,35]. The PMMA-based gel polymer electrolyte has been proven to possess high ionic conductivity; stable electrochemically and thermally [36,37] when the LiClO_4 salt and PC are used. In addition to the advantageous properties of the gel, the lithium salt in non-aqueous solvents does not have the insertion and extraction problem that seems to cause irreversibility for PB in aqueous solutions, in which serious hydration of lithium ions occurs [34]. Therefore, an ECD made of PEDOT and PB thin films with a PMMA-based gel electrolyte was successfully fabricated. Fig. 5 shows the in situ spectra of the ECD recorded between 370 and 1000 nm. The voltages reported in Fig. 5, and the rest of the device, are PEDOT with respect to PB. In order to achieve the charge balance between the two electrodes in the cell, the thickness of PB was carefully controlled, as mentioned in the Experimental section. The spectra of the assembled PEDOT-PB ECD, as shown in Fig. 5, were similar to those of the PEDOT in Fig. 3. From Fig. 5, the maximum absorption occurs at 625 nm, while the maximum absorbance change is at 590 nm. According to Fig. 1, when PEDOT thin-film electrode acts as the positive electrode in the assembled ECD, the cell exhibits deep blue-violet when the applied voltage is more negative. At a negative applied cell voltage, PEDOT is at its neutral state, and the negative electrode (PB) is in the blue state; so both are in the colored states. In addition, absorbance in the visible region reaches a maximum when the applied voltage is ca. -2.1 V . On the other hand, the ECD exhibits light blue as the applied voltage is higher than 0.0 V , and reaches a saturated absorbance at 0.6 V . It is therefore expected that when the ECD is stepped between -2.1 and 0.6 V , a maximum ΔT at 590 nm can be achieved.

3.2.2. Credible measurement for the coloration efficiency of the ECD

The typical in-situ transmittance response measured at 590 nm and the corresponding $I-t$ transient response of the ECD are shown in Fig. 6(a) and (b),

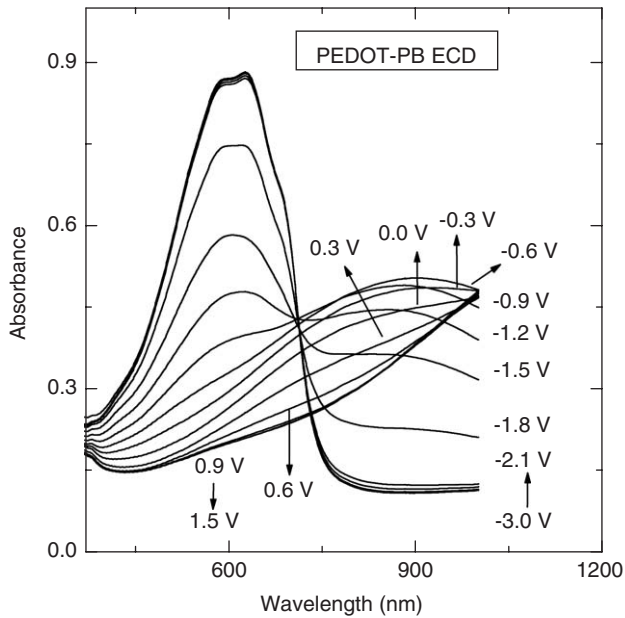


Fig. 5. Absorbance spectra of the PEDOT-PB ECD switched at different applied voltages. The voltage is the potential difference between the PEDOT electrode and the PB electrode (PEDOT vs. PB). The PEDOT electrode acts as the positive electrode.

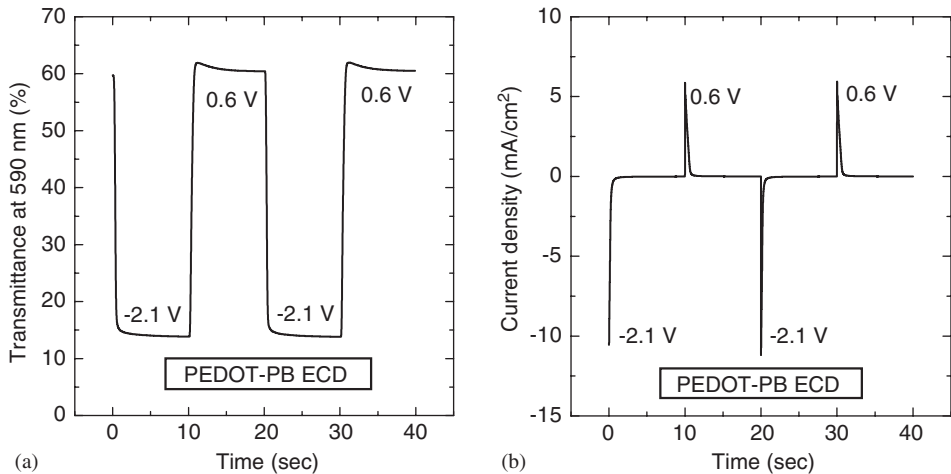


Fig. 6. (a) The in situ transmittance response of the cell at 590 nm. The applied voltages were $V_c = -2.1$ V (10 s) for coloring and $V_b = 0.6$ V (10 s) for bleaching and (b) the corresponding current density–time relationship of the cell in response to the applied voltages. The data were recorded with a time interval of 0.005 s.

respectively. The applied voltages are $V_c = -2.1$ V for coloring and $V_b = 0.6$ V for bleaching, with an interval of 10 s each. The ECD exhibits a reversible transmittance response of ca. 13.8% in the colored state and ca. 60.5% in the bleached state, resulting in a ΔT of 46.7%. There is only a small ΔT loss compared to that of the PEDOT, as revealed in Fig. 4. The reductive peak current is larger than that of the anodic one, as judged by Fig. 6(b). This implies that the electron transfer is faster in the undoping process due to the metallic state of PEDOT. In addition, the integrated area under the $I-t$ curve (recorded time interval = 0.005 s) gives the inserted charge density of ca. 1.9 mC/cm² for the doping process and 2.0 mC/cm² for the undoping process. The calculated coloration efficiencies of the ECD at 590 nm, both in doping and undoping processes, are 338 cm²/C ($\log(60.5/13.8)/0.0019 = 338$ cm²/C) and 321 cm²/C ($\log(60.5/13.8)/0.002 = 321$ cm²/C), respectively, as calculated from Fig. 6(a) and (b). In order to avoid the underestimation of the inserted charge of the ECD, the choice of the time interval for the recorded current is important. Fig. 7(a) and (b) reveal that both the inserted charge density and the calculated coloration efficiency of another ECD, being operated under the same condition ($V_c = -2.1$ V (10 s) and $V_b = 0.6$ V (10 s)) as that of the ECD in Fig. 6, are dependent of the time interval of the recorded data taken in the $I-t$ response. From Fig. 7(a), one finds that the inserted charge density reaches a near constant value as the recorded time interval decreases. The faster the current response of the ECD, the smaller the recorded time interval is needed to capture the peak current and obtain the exact inserted charge. From Fig. 7(b), one sees that the calculated coloration efficiency approaches a constant value as the recorded time interval decreases, and we concluded that the calculated coloration efficiency of our ECD is reasonable. Although the high coloration efficiency obtained in the PEDOT-PB ECD is

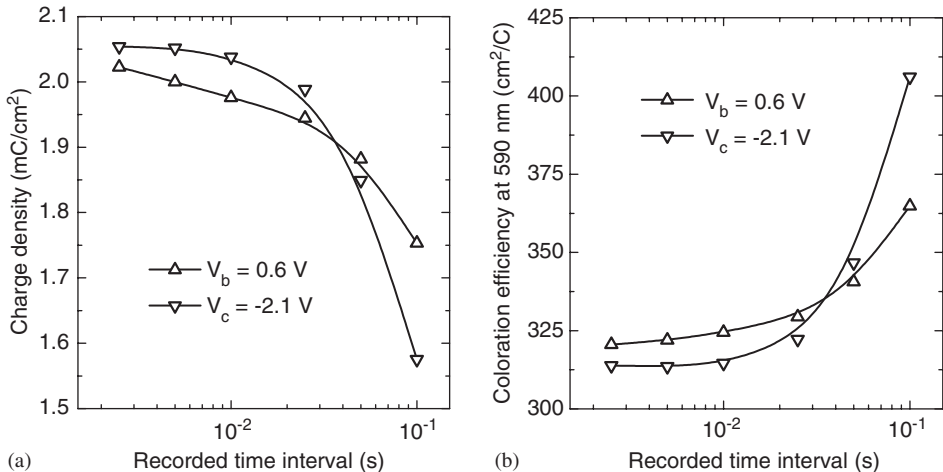


Fig. 7. (a) The passed charge densities of the ECD as a function of the recorded time interval in the $I-t$ response and (b) the calculated coloration efficiencies of the ECD as a function of the time interval recorded in the $I-t$ response.

attractive, cycling and at-rest stabilities are even more important in real practice. The results of the long-term stability for the PEDOT-PB ECD are discussed below.

3.3. Long-term cycling stability and at-rest stability of the ECD

3.3.1. Long-term cycling stability of the ECD

Fig. 8 plots the in situ transmittances in the bleached state (T_b), colored state (T_c), and transmittance window (ΔT) of the ECD at 590 nm as a function of the cycling number (N). The ECD was tested up to 50,640 cycles. During the cycling tests, the applied voltages were set at $V_c = -2.1$ V for coloring and $V_b = 0.6$ V for bleaching, with the time interval of each step being set at 10 s. It is apparent that the variation of the ΔT can be divided into four stages. During the first 60 cycles ($N \leq 60$), because the cycling tests started right after the cell assembly, it took longer time for the cell reaction to complete and reach equilibrium, and ΔT remained very stable during the second stage ($60 \leq N \leq 300$). However, at ca. 300 cycles, the ΔT of the cell fell off rapidly from 49.7% to 33.5%. It was noticed that the extent of the increase of T_c was much larger than that of the decrease of T_b in the third stage, up to $N = 540$. The

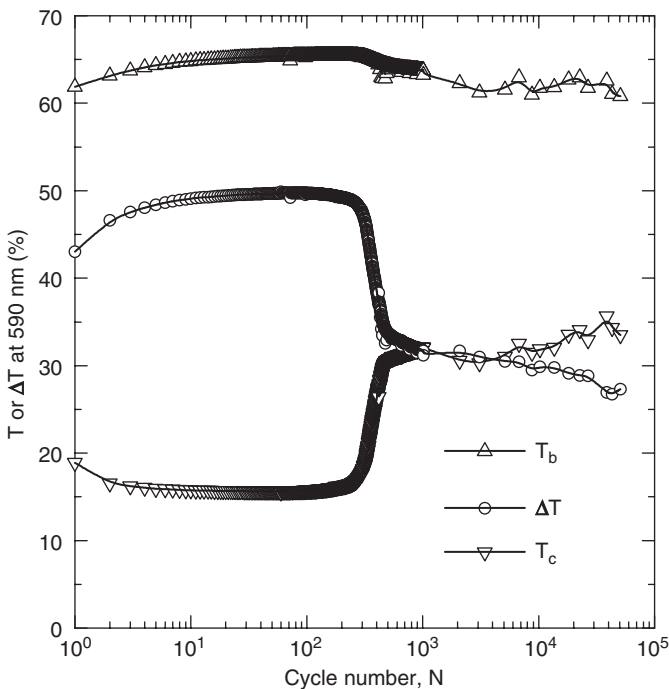


Fig. 8. Dynamic cycling stability of the cell: transmittance in the bleached state (T_b), transmittance in the colored state (T_c), and the transmittance window (ΔT) as a function of cycling number. The applied were $V_c = -2.1$ V (10 s) for coloring and $V_b = 0.6$ V (10 s) for bleaching. The spectra data were recorded continuously during the first 1000 cycles and recorded at some specific cycles after 1000 cycles. The total cycle number was 50,640.

percentage of ΔT loss, based on the ΔT_{\max} , is ca. 32.6% during the third stage. In the last stage ($540 \leq N \leq 50,640$), ΔT decreased slowly. The decay of the ΔT was only 6.2% or at an average decay rate of 0.00012% per cycle in the last stage. After a total of 50,640 cycles, the cell was still partially electroactive and the percentage of ΔT loss, based on the ΔT_{\max} , was ca. 45.1% or 0.0009% per cycle. The rapid decay of ΔT between 300 and 540 cycles could be attributed to the high operating voltages. Although a maximum ΔT (at 590 nm) was obtained at $V_c = -2.1$ V and $V_b = 0.6$ V, applying too negative of a voltage V_c at -2.1 V may cause the degradation of the PEDOT film. Besides, when a too negative V_c is applied to the cell, the PB shifts to the second redox couple, resulting in side reactions at the PEDOT electrode. This explanation is consistent with Fig. 8, which reveals that T_c increases dramatically in the third stage. Therefore, it is important to search for a safe operating voltage range before switching an ECD. The effect of operating voltage on the cell performance is discussed in a separate paper [43].

3.3.2. Long-term at-rest stability of the ECD

In addition to the dynamic cycling stability, the at-rest stability of the ECD is equally important. Another identical ECD was assembled and tested for its at-rest stability over a period of 107 days. The cell was cycled twice each day and stored in

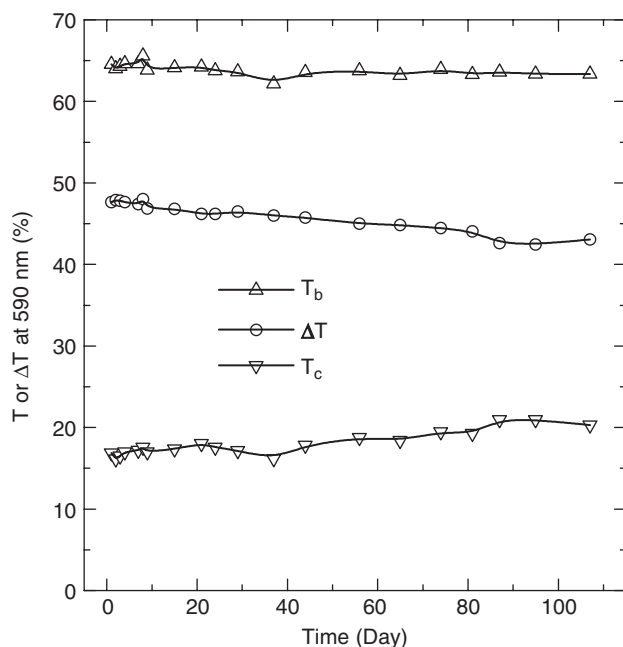


Fig. 9. At-rest stability of the cell: transmittance in the bleached state (T_b), transmittance in the colored state (T_c), and the transmittance window (ΔT) as a function of the time after assembling the cell. The applied voltages were $V_c = -2.1$ V (30 s) for coloring and $V_b = 0.6$ V (30 s) for bleaching at each measurement. The total testing time was 107 days.

the bleached state when at-rest. The results of the at-rest stability are shown in Fig. 9. The cell was switched at $V_c = -2.1$ V and $V_b = 0.6$ V, with each step lasting for 30 s. It was found that ΔT decayed slowly over the testing period. The decay of ΔT is only ca. 9.6% over a period of 107 days. From the above results, it is inferred that this novel organic–inorganic complementary ECD not only exhibits a relatively good cycling stability but also possesses good at-rest stability. With more careful control over the coloring voltage, the system may provide opportunities for possible EC applications.

4. Conclusions

In this work, a new organic–inorganic complementary ECD based on PEDOT and PB in combination with the PMMA-based gel polymer electrolyte was proposed and tested. PEDOT is electrochemically stable in 1 M LiClO₄/PC and reaches an anodic coloration efficiency of ca. 225 cm²/C at 590 nm. It has also been proven that PB is electrochemically stable for cycling in the same organic environment, and PB is chosen as the counter electrode in the new ECD. With the application of $V_c = -2.1$ V and $V_b = 0.6$ V, the PEDOT-PB ECD exhibited a deep blue-violet-to-light blue electrochromism. The transmittance window of the ECD measured at 590 nm was ca. 47% and a relatively high coloration efficiency of ca. 338 cm²/C was obtained. In comparison to the PEDOT-based ECDs reported in literature, the calculated coloration efficiency was reasonable, as judged by the careful recording and analysis of the current data. In addition to the high coloration efficiency, the new ECD exhibited good long-term cycling stability. In the dynamic cycling test, the value of ΔT still remained ca. 55% of its maximum value after 50,640 cycles. Moreover, the results of the at-rest stability test showed that the decay of the ΔT was only 9.6% over a period of 107 days. It is hoped that the high coloration efficiency and the good cycling and at-rest stabilities of the PEDOT-PB ECD will make it attractive for real world applications.

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