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A complementary electrochromic device based on polyaniline and poly(3,4-ethylenedioxythiophene) [☆]

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Abstract

In this study, two conducting polymers, polyaniline (PANI) and poly(3,4-ethylenedioxythiophene) (PEDOT), were used to construct an electrochromic device (ECD). PANI was employed as the anodic coloring polymer while PEDOT was used as the cathodic coloring polymer. The electrochemical and optical properties of PANI, which has a coloration efficiency of $25 \text{ cm}^2/\text{C}$ at 570 nm, were coupled with the complementary coloring material, PEDOT, which has a coloration efficiency of $206 \text{ cm}^2/\text{C}$ at 570 nm. A suitable operating potential window was switched between -0.6 and 1.0 V to explore the cycle life of the ECD. We tested the PANI–PEDOT ECD, which consisted of PANI, PEDOT, and an organic electrolyte containing 0.1 M LiClO_4 in propylene carbonate and 1 mM HClO_4 . The transmittance of the ECD at 570 nm changed from 58% (-0.6 V) to 14% (1.0 V) with a coloration efficiency of $285 \text{ cm}^2/\text{C}$. Within the selected operating voltage range, the PANI–PEDOT ECD could be cycled for up to 2×10^4 cycles.

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Keywords: Coloration efficiency; Electrochromic device; Polyaniline; Poly(3,4-ethylenedioxythiophene); Cycling stability

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1. Introduction

Electrochromism is a phenomenon related to color change with a reversible electrochemical process due to the generation of different electronic absorption bands in the visible region [1–3]. The color change is usually between a colored state (darkened state) and a transparent state (bleached state), or between two colored states. One of the most important applications of electrochromic devices (ECDs) is in the construction of variably transmissive windows which can be used to boost the energy efficiency of buildings [4,5]. Other applications such as anti-glare rearview mirrors [6,7], sunglasses [8], and electrochromic displays [9] have also been proposed.

The use of conducting polymers in electrochromism has attracted much attention over the last few years due to their high color contrast, multiple color possibilities, rapid response times, and ease of processing. A complementary ECD is a device in which both anodic and cathodic electrochromic materials can simultaneously be darkened or bleached. Polyaniline (PANI), which has been extensively studied as a promising electrochromic material, has three main stable oxidation states: the fully reduced leucoemeraldine form, the 50% oxidized emeraldine form, and the fully oxidized pernigraniline form. Each of these states can exist in the form of its base or in the form of its protonated salt by subtracting or adding protons which does not modify its oxidation state; in this respect, PANI differs from other conducting polymers. PANI film is polyelectrochromic, i.e., transparent yellow for the leucoemeraldine form, green for the emeraldine salt form (ES), blue for the emeraldine base form (EB), and black for the pernigraniline form. This conducting polymer exhibits good electrochromic properties and is able to switch from a transparent yellow state when reduced to a green one when oxidized [10]. Other applications of PANI include batteries [11,12], capacitors [13], sensors [14], and electrochemical actuators [15].

Poly(3,4-ethylenedioxythiophene) (PEDOT) was developed in an attempt to produce an easily oxidized, stable conducting polymer that does not include the undesirable $\alpha - \beta'$ couplings often found in polythiophene. PEDOT was found to be cathodically colored and also exhibited a high optical density change (ΔOD) in the visible spectra. It switches from a transparent blue state when oxidized to a deep blue one when reduced [16]. In addition to electrochromic applications, PEDOT has also been applied in antistatic coatings [17] and capacitors [18].

An ECD composed of PANI and PEDOT films with a gel electrolyte was reported [19]. It exhibited a transmittance attenuation (ΔT) of 45% at 620 nm with a cycle life of about 50–100 cycles. The symmetrical and wide range of operating potentials may be what causes the serious ΔT decay. In this study, we investigated the electrochemical and optical properties of PANI, enhanced the stability of PANI by adding protons, chose PEDOT as the complementary coloring material, and tried to find a suitable operating potential window to improve the cycle life of the PANI–PEDOT ECD.

2. Experimental

2.1. Substrate

Conducting indium tin oxide (ITO) glass substrates (RiTdisplay Corporation, Hsinchu Industrial Park, Taiwan, $R_{\text{sh}} = 20 \Omega/\square$) served as the optically transparent electrodes. Before use, the ITO substrates ($3.0 \times 4.0 \text{ cm}^2$) were ultrasonically cleaned in a 0.1 N hydrochloric acid (HCl, Merck, 32%) solution for 3 min and then in deionized water for 5 min. Finally, the substrates were dried in air. An active area of $2.0 \times 2.0 \text{ cm}^2$ was created on the ITO glass by attaching the epoxy tape (3 M Company, 0.14 mm thick). Conducting Cu tape (3 M Company, $3.0 \times 0.5 \text{ cm}^2$) was applied at one edge of the substrate as the bus bar.

2.2. Preparation of electrochromic thin films

2.2.1. Preparation of PANI film

Anodic electropolymerization of $\text{C}_6\text{H}_5\text{NH}_2$ (Lancaster, 99+ %) on the ITO glass substrate was used to form the PANI modified electrode. The bath solution was composed of 1.0 M $\text{C}_6\text{H}_5\text{NH}_2$, 2.0 M HCl, and deionized water. The current density and deposition time were set at 0.05 mA/cm^2 and 500 s, respectively. A platinum sheet ($4.0 \times 1.0 \text{ cm}^2$) served as the counter electrode. After electropolymerization, the PANI thin films were cleaned with 0.1 M HCl, dried with N_2 , and then stored in air. The average thickness of the PANI thin films was 160 nm, as measured with a profilometer (Sloan Dektak, model 3030).

2.2.2. Preparation of PEDOT films

The PEDOT thin films were electropolymerized on ITO as a working electrode by applying a potential at 1.2 V (vs Ag/Ag^+) with a platinum counter electrode ($4.0 \times 1.0 \text{ cm}^2$) until a charge capacity of 20 mC/cm^2 was reached. A homemade Ag/Ag^+ electrode, which contained a solution of 0.01 M AgNO_3 and 0.1 M tetrabutylammonium perchlorate in acetonitrile, was used as a reference electrode. The bath solution was acetonitrile (TEDIA, 99.95%, dehydrated with molecular sieves (Acros, 4 Å) before use) containing 0.1 M lithium perchlorate (LiClO_4 , Aldrich, 95+ %) and 0.01 M 3,4-ethylenedioxythiophene (EDOT, Aldrich). Nitrogen gas was used to purge the bath before electropolymerization. The as-deposited PEDOT thin films were then washed with acetonitrile and stored in air. The average thickness of the PEDOT thin films was 130 nm as measured using the same profilometer mentioned above.

2.3. Electrolyte solution

The electrolyte used was propylene carbonate (PC, Lancaster, 99%) containing 0.1 M LiClO_4 and 1 mM hydroperchlorate acid (HClO_4 , Fisher, 70%) and dehydrated using molecular sieves before use.

2.4. Electrochemical and spectroscopic measurements

A three-electrode system was used to characterize both the PANI- and PEDOT-modified electrodes. The working electrode was the modified ITO substrate, and the counter electrode was the platinum sheet mentioned above. Ag/Ag⁺ served as the reference electrode. The in situ spectroelectrochemical properties of both modified electrodes were recorded with a potentiostat/galvanostat (Autolab, model PGSTAT 30) and a spectrophotometer (Shimadzu, model UV-1601PC). The dynamic cycling stability test of the PANI–PEDOT ECD was conducted using an eight-channel battery tester (Maccor, model 2300).

2.5. Assembly and characterization of the ECD

Before assembling the cell, both the PANI- and PEDOT-modified electrodes were cycled several times in an electrolytic solution using the cyclic voltammetric (CV) method to ensure the proper function of ion insertion and extraction. After cycling, the PANI and PEDOT electrodes were stepped to the leucoemeraldine state and doping state by applying -0.5 and 0.3 V for 30 s, respectively. The ECD was finally sealed with a Torr Seal[®] (Varian, #9530001) around the four edges of the ITO glass, and the cell gap was set at 0.28 mm with a spacer tape. The equilibrated absorbance spectra of the ECD were also measured at different applied voltages (PEDOT vs. PANI) using a potentiostat/galvanostat and a spectrophotometer, as mentioned above.

3. Results and discussion

3.1. Electrochemical and spectral properties of PANI

3.1.1. Cyclic voltammetric (CV) analysis

The CV results of PANI in PC containing 0.1 M LiClO₄ and 1 mM HClO₄ are shown in Fig. 1. The operating potential was scanned between -0.5 and 1.0 V with a scan rate of 0.1 V/s. The oxidation peak at -0.04 V (A₁) corresponds to the change between the leucoemeraldine base (LB) and ES with anion doping upon oxidation and dedoping upon reduction to compensate for the charge of the PANI film. This can be represented by the following simplified reaction:

The oxidation peak at 0.91 V (A₂) corresponds to the change between EB and the pernigraniline salt (PS) with doping/dedoping of the anion processes. This can be represented by the following simplified reaction:

Fig. 1. Typical CV for a PANI thin film electrode scanned between -0.5 and 1.0 V in 0.1 M $\text{LiClO}_4 + 1$ mM $\text{HClO}_4 + \text{PC}$ at a scan rate of 100 mV/s. The active electrode area is 2.0×2.0 cm 2 .

The change between ES and EB due to protonation/deprotonation processes can be represented by the following reaction:

The middle peak at 0.46 V (A_m) probably corresponds to a side reaction that leads to an irreversible reaction of the PANI film at a high oxidation potential [20]. In order to obtain a stable electrochromic film, the operating potential was then chosen to be between -0.5 and 0.3 V to avoid the second redox reaction.

The CVs of PANI cycled between -0.5 and 0.3 V at a scan rate of 0.1 V/s, and results are shown in Fig. 2(a); the corresponding charge percentage during cycling calculated from the area of the CVs is shown in Fig. 2(b). The charge percentage is defined as the charge capacity at each cycle divided by the maximum charge capacity during the measurement. The reduction current upon the first scan corresponds to the expulsion of the Cl^- anion already incorporated into the PANI thin film during the preparation stage. With further cycling, both the oxidation and reduction currents increased. This was due to the replacement of Cl^- with ClO_4^- , thus enhancing the insertion and expulsion of the ClO_4^- electrolyte anions.

3.1.2. Effect of protons

Although the operating potential was controlled below 0.3 V, the equilibrium between ES and EB was affected by the presence of protons, according to the well-known redox path way of PANI [21]. The influence of protons, achieved by adding

Fig. 2. (a) CVs for a PANI thin film electrode scanned between -0.5 and 0.3 V in 0.1 M $\text{LiClO}_4 + 1$ mM $\text{HClO}_4 + \text{PC}$ at a scan rate of 100 mV/s. (b) The corresponding charge percentage as a function of cycle number. The charge percentage is defined as the charge capacity at each cycle divided by the maximum charge capacity during measurement.

Fig. 3. The effect of protons on the transmittance variation as a function of cycle number for a PANI thin film electrode switched between (a) -0.5 and 0.3 V, and (b) -0.5 and 0.6 V, with a step time of 30 s for both darkening and bleaching processes. The transmittances were measured at 570 nm.

1 mM HClO_4 , is shown in Fig. 3(a) and (b). In Fig. 3(a), the transmittance as PANI was switched between -0.5 and 0.3 V (30 s for each step) at 570 nm was plotted as a function of cycle number. The data marked with circular symbols were collected in an electrolyte containing 0.1 M LiClO_4 in PC only, while the triangular symbols represent data taken using the same electrolyte but with additional 1 mM HClO_4 added. The hollow and solid symbols denote PANI operated at -0.5 (bleached) and 0.3 V (darkened), respectively. We concluded that the optical stability of PANI was enhanced by adding protons; this was especially noticeable when the darkening potential was raised from 0.3 to 0.6 V, as shown in Fig. 3(b).

3.1.3. Absorbance spectra and coloration efficiency

The absorbance spectra of PANI at different applied potentials are shown in Fig. 4. The absorbance increased upon oxidation (darkened state) and decreased upon reduction (bleached state). The transmittance at 570 nm for PANI was 91% (nearly transparent) at -0.5 V and 79% (light green) at 0.1 V. It was found that the bleached state of PANI was very transparent. The higher the transmittance of the electrochromic material in the bleached state was, the larger the transmittance attenuation of the ECD that could be achieved. A plot of the optical density change (ΔOD) at 570 nm vs. the charge density of PANI is shown in Fig. 5. The reference state was set to -0.5 V. The slope of this plot was defined as the coloration efficiency. Three coloration efficiencies can be observed from this figure. The coloration efficiency between -0.5 and 0.1 V was $25 \text{ cm}^2/\text{C}$, corresponding to the change from the LS state to the ES state; and that between 0.1 and 0.6 V was $76 \text{ cm}^2/\text{C}$, which is related to the change from the ES state to the EB state because of deprotonation. The coloration efficiency between 0.6 and 0.8 V was $37 \text{ cm}^2/\text{C}$, corresponding to the change from the EB state to the PS state. When a higher potential is reached, the second redox reaction occurs, as well as the degradation of PANI. Eventually, the PANI film dissolved into the electrolytic solution, and a decrease in ΔOD was observed to occur at about 0.9 V.

3.2. Electrochemical and spectral properties of PEDOT

As mentioned before, the stability of PANI was improved by selecting a suitable operating potential window and adding HClO_4 . From Fig. 5, the coloration

Fig. 4. In situ UV-Vis absorption spectra of a PANI thin film electrode switched in $0.1 \text{ M LiClO}_4 + 1 \text{ mM HClO}_4 + \text{PC}$ solution at different equilibrium potentials: $E = -0.5, 0.1, 0.6$, and 1.0 V (vs Ag/Ag^+).

Fig. 5. The optical density change (ΔOD) at 570 nm for a PANI thin film electrode at different equilibrium potentials. The reference state is set at -0.5 V.

efficiency of PANI operating between -0.5 and 0.1 V was only $25 \text{ cm}^2/\text{C}$, with transmittances ranging from 91% to 79%. It is necessary to choose a complementary cathodic coloring material that has a high coloration efficiency in order to enhance the transmissive performance of the ECD. PEDOT, which has recently attracted much attention, has a coloration efficiency of $183 \text{ cm}^2/\text{C}$ at 585 nm [22]. It was chosen as the cathodic coloring material because of its high coloration efficiency for the ECD proposed in this study.

3.2.1. Cyclic voltammetric (CV) analysis

Results of a typical CV analysis of PEDOT in PC containing 0.1 M LiClO_4 and 1 mM HClO_4 are shown in Fig. 6. The operating potential was scanned between -1.2 and 0.3 V with a scan rate of 0.1 V/s . PEDOT was controlled at -1.2 and 0.3 V, which correspond to its undoping and doping states, respectively. The reaction of PEDOT, which involves anion diffusion into and out of the polymer matrix to compensate for the charge, can be represented by the following simplified reaction:

3.2.2. Absorbance spectra and coloration efficiency

The absorbance spectra of PEDOT at different applied potentials are shown in Fig. 7. The absorbance decreases upon oxidation (bleached state) and increases upon reduction (darkened state). A plot of the optical density change (ΔOD) at 570 nm vs

Fig. 6. Typical CV for a PEDOT thin film electrode scanned between -1.2 and 0.3 V in 0.1 M $\text{LiClO}_4 + 1$ mM $\text{HClO}_4 + \text{PC}$ at a scan rate of 100 mV/s. The active electrode area is 2.0×2.0 cm².

Fig. 7. In situ UV-Vis absorption spectra of a PEDOT thin film electrode switched in 0.1 M $\text{LiClO}_4 + 1$ mM $\text{HClO}_4 + \text{PC}$ solution at different equilibrium potentials. The potentials were changed from 0.2 to -0.8 V (vs Ag/Ag^+) with a decrement of 0.1 V.

the charge density of PEDOT is shown in Fig. 8. The reference state was set to 0.3 V which corresponds to a transmittance of 78% at 570 nm. The coloration efficiency of PEDOT at 570 nm was the slope obtained from the origin to a voltage-dependent

Fig. 8. The optical density change (ΔOD) at 570 nm as a function of charge density for a PEDOT thin film electrode equilibrated at different potentials. The reference state is set at 0.3 V. The straight line is obtained from the origin to a voltage-dependent data point corresponding to an injected charge density of 2.14 mC/cm².

data point corresponding to an injected charge density of 2.14 mC/cm² in Fig. 8. This charge density value for PEDOT is resulted from the consumed charge per unit area of the PANI–PEDOT ECD, which is 2.14 mC/cm² as measured later in Fig. 12(b). The coloration efficiency of PEDOT at 570 nm was calculated to be 206 cm²/C (with $\Delta OD = 0.44$ and injected charge density = 2.14 mC/cm²). Similar concept was developed by Reynolds group [22], who reported a method to quantify the composite coloration efficiency of organic electrochromic polymers at 95% of the total ΔOD measured at $\lambda_{\max}$. Here we calculate the coloration efficiency of PEDOT based on the consumed charge density in the PANI–PEDOT ECD. The reason for the nonlinear graph is that organic polymers possess many states while being doped, such as polarons, bipolarons, π -dimers, and even the conformational changes occurring along the polymer backbone will influence the overall properties of organic electrochromic polymers [23,24].

3.3. PANI–PEDOT ECD

3.3.1. Cyclic voltammetric (CV) analysis

Results of a typical CV analysis of the PANI–PEDOT ECD are shown in Fig. 9. The cell configuration of the ECD is denoted as PANI/0.1 M LiClO₄ + 1 mM HClO₄ + PC/PEDOT, and the corresponding reaction of the complementary ECD

Fig. 9. Typical CV for a PANI/0.1 M LiClO₄ + 1 mM HClO₄ + PC/PEDOT ECD scanned between −0.6 and 1.2 V at a scan rate of 100 mV/s. The active electrode area of the PANI–PEDOT ECD is 2.0 × 2.0 cm².

can be represented by adding Eq. (1) and Eq. (4):

The two-electrode CV was scanned between −0.6 (light blue, bleached) and 1.2 V (deep blue, darkened) with a scan rate of 0.1 V/s. The reported cell voltage is that of PANI with respect to PEDOT. In a comparison of the CV results of the ECD to that of PEDOT, the peaks at 1.0 and 0 V corresponded to the characteristic peaks of PEDOT at −1.0 and 0 V, respectively, as shown in Fig. 6. The redox peaks of PANI did not appear in the CV of the ECD, but they broadened the redox peak of the CV results for the ECD. Since the CV results of the ECD are a simple combination of the CV results of PANI and PEDOT, and because there are no other peaks present due to side reactions, the operating potential window of the ECD was thus chosen to be between −0.6 and 1.2 V.

3.3.2. Absorbance spectra and coloration efficiency

The equilibrated spectra of the ECD are shown in Fig. 10 for different applied voltages. The contribution of PANI was mainly from 400 to 480 nm; and the contribution of both PEDOT and PANI was from 480 to 800 nm, with PEDOT being the major one. The cycling stability of the ECD, cycled at −0.6 and 1.2 V for bleaching and darkening, respectively, with a step time of 10 s for each process, is shown in Fig. 11. The bleached state transmittance of the ECD decreased with repeated cycles. This was probably due to over-reduction of PEDOT in its reduced state (when a voltage of 1.2 V was applied to the ECD), and because the PEDOT

Fig. 10. In situ UV-Vis absorption spectra of the PANI/0.1 M LiClO₄ + 1 mM HClO₄ + PC/PEDOT ECD switched at different equilibrium potentials: $E = 0.8$ to -1.0 V (PANI vs PEDOT). The spectral data show a potential difference of 0.2 V for the two nearest neighboring curves.

Fig. 11. Transmittance in the bleached state (T_b), transmittance in the colored state (T_d), and the transmittance window (ΔT) as a function of cycle number, showing the dynamic cycling stability of the PANI/0.1 M LiClO₄ + 1 mM HClO₄ + PC/PEDOT ECD. The PANI–PEDOT ECD was cycled at -0.6 and 1.2 V for bleaching and darkening, respectively, with a step time of 10 s for each process.

Fig. 12. The responses of the PANI/0.1M LiClO₄+1mM HClO₄+PC/PEDOT ECD by applying potentials at -0.6 V (bleached) and 1.0 V (colored). (a) The in situ transmittance response of the PANI–PEDOT ECD at 570 nm. (b) The corresponding current density transient, showing an averaged injection charge density of 2.14 mC/cm².

thin film cannot be gradually bleached. In order to obtain an ECD with long-term stability, the applied darkening potential was reduced to 1.0 V.

The transmittance transient of the device at 570 nm and the corresponding current density transient, in response to a double potential step change between -0.6 and 1.0 V, are shown in Fig. 12(a) and (b), respectively. The bleached state transmittance of the ECD was 58.6% when a potential of -0.6 V was applied. When a potential of 1.0 V was applied, the darkened state transmittance of the ECD was 14.2% . It is convenient to define the time it takes to reach 95% of the total transmittance change as the response time. Under this definition, both the bleaching and darkening times for the ECD were less than 1 s. Values of ΔOD and the averaged injection charge density of the ECD were 0.61 and 2.14 mC/cm², respectively, from which the coloration efficiency of the ECD at 570 nm was calculated to be 285 cm²/C. This value is very close to the coloration efficiency calculated by adding the coloration efficiency of PANI (25 cm²/C) and that of PEDOT (206 cm²/C). In addition, the coloring and bleaching potentials applied to the ECD were also confirmed by the corresponding input charge densities of both thin-film electrodes and the ECD. Theoretically speaking, the bleaching and coloring potentials of the ECD could be expressed by the bleaching and coloring potentials of both electrodes: $E_{\text{bleach,ECD}} = E_{\text{bleach,PANI}} - E_{\text{bleach,PEDOT}} = (-0.5 \text{ V}) - (0.3 \text{ V}) = -0.8 \text{ V}$, and $E_{\text{color,ECD}} = E_{\text{color,PANI}} - E_{\text{color,PEDOT}} = (0 \text{ V}) - (-1.0 \text{ V}) = 1.0 \text{ V}$. The calculated coloring and bleaching potentials were very close to the applied potentials of the ECD.

3.3.3. Cycling stability

The cycling stability of the ECD is shown in Fig. 13. The ECD was cycled at -0.6 and 1.0 V for bleaching and darkening, respectively, with a step time of 10 s for each

Fig. 13. Transmittance in the bleached state (T_b), transmittance in the colored state (T_d), and the transmittance window (ΔT) as a function of cycle number, showing the dynamic cycling stability of the PANI/0.1 M LiClO₄ + 1 mM HClO₄ + PC/PEDOT ECD. The PANI-PEDOT ECD was cycled at -0.6 and 1.0 V for bleaching and darkening, respectively, with a step time of 10 s for each process.

process. The ECD had transmittance attenuation (ΔT) of about 43% for the initial cycle, which increased to a maximum value of about 47% with further cycling to the 2,600th cycle. The ΔT of the ECD then decreased to 42% and 34% for the 11th, 400th and 23,200th cycles, respectively. Thus, an asymmetric, narrower operating potential window did enhance the cycling stability and prevented side reactions on both electrodes.

4. Conclusions

In this study, the electrochemical and optical properties of both PANI and PEDOT thin films were studied. A suitable operating potential window of between -0.6 and 1.0 V was chosen to explore the cycle life of the ECD consisting of PANI and PEDOT. An ECD based on PANI and PEDOT with an organic PC electrolyte containing 0.1 M LiClO₄ and 1 mM HClO₄ was evaluated. The initial transmittance at 570 nm changed from 58% (-0.6 V) to 14% (1.0 V). The coloration efficiency of the ECD was calculated to be 285 cm²/C, and the value was verified by summing the coloration efficiencies of PANI and PEDOT. Within the selected operating voltage range, the PANI-PEDOT ECD could be cycled up to 2×10^4 times.

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