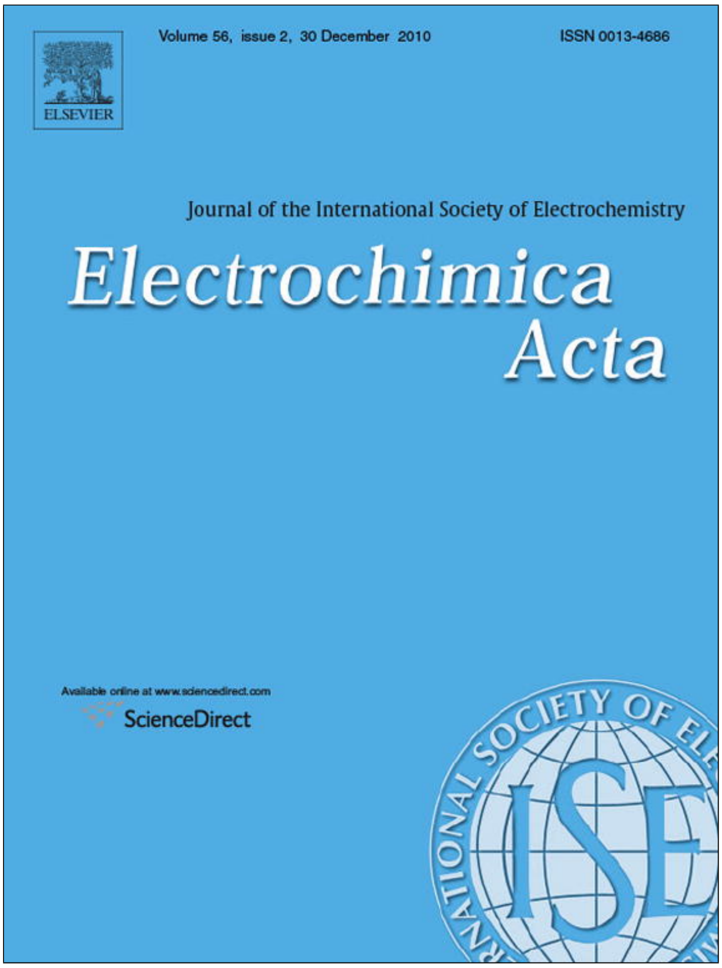
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High contrast asymmetric solid state electrochromic devices based on layer-by-layer deposition of polyaniline and poly(aniline sulfonic acid)

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ABSTRACT

Layer-by-layer (LbL) self-assembly was employed for alternating deposition of two electrochromic polymers to fabricate a single film composite. We report a wide spectral range, high contrast asymmetric solid state electrochromic device, fabricated by LbL assembly of the polycation polyaniline (emeraldine base) (PANI) and the polyanion poly(aniline sulfonic acid), (PASA). Detailed spectral and electrochemical investigation of the dual electrochrome thin film confirm that both electrochromic polymers contribute to the electrochromic and electrochemical characteristics of the composite. Under the application of ±2.3 V potential the system exhibited an average contrast of 49.7% across the full visible spectrum. The dual electrochrome system was compared to single electrochrome systems, and it was observed that PANI predominantly affects the electrochromic optical spectra of the composite, whereas PASA increases the switching speed.

1. Introduction

Due to variations in redox states, electrochromic (EC) devices exhibit changes in their optical transmittance. The variations in the redox states are caused by controlling the potential difference between the electrodes of the device. EC devices based on a variety of inorganic compounds [1–3], polymers [4–10] and phthalocyanines [11–13] have been previously studied. In this work we present EC devices based on a pair of electrochromic polymers.

Thin-films can be created through several methods including chemical vapor deposition, electron beam deposition, Langmuir–Blodgett technique, and layer-by-layer (LbL) self-assembly technique [14]. In the case of electronically functional thin-films, thinner films are generally preferred because of the shorter electron and ion transport path length.

The LbL assembly technique provides nanoscale thickness control for fabrication of thin films and is one of the most popular techniques for fabricating thin polymer films. The LbL technique consists of repeated cycles of alternating adsorption of cationic and anionic materials from aqueous solutions onto the substrate [15,16]. Varying the number of cycles results in a different number of bilayers and is one way to control the thickness of the thin film from the nanometer to micron scale. Other factors, such as pH and ionic strength of the ionic solutions, can also be used to tune the thickness of the material adsorbed into individual layers. Because of its low cost, high precision, and ease of production, the LbL technique is one of the easiest and simplest methods to implement [17–19]. Another significant advantage of using the LbL technique is that hypothetically any charged species can be incorporated into a thin film.

Polyaniline (PANI) is an electronically conductive and electrochemically active polymer. The optical and structural properties [20], switching speed [21], and optical properties of PANI in solid state EC devices [22] have been previously studied. Several forms of PANI exist. One is the emeraldine salt (ES) which is conductive and green in color, and another is the emeraldine base (EB) which is blue in color and an insulator [23]. PANI (ES) is not stable in the presence of moisture and converts into PANI (EB), which is the more oxidized form. PANI-based electrochromic devices have been previously studied by several groups. Hu et al. [23] studied the electrochromic properties of PANI along with poly(2-acrylamido 2-methylpropane sulfonic acid) (PAMPS) and reported maximum transmittance contrast of approximately 40% at a wavelength of approximately 580 nm and a switching time of 10 s under application of ±2.0 V. In a similar study, Hechavarría et al. [24] achieved maximum transmittance contrast of approximately 45% at approximately 580 nm. DeLongchamp and Hammond [25] performed a more in-depth study of PANI based EC devices fabricated through the LbL technique. They reported maximum transmittance contrast of 51.7% at a wavelength of 748 nm for an EC device consisting of 20

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bilayers of PANI and PAMPS and a contrast of 24% for a device consisting of 20 bilayers of PANI and PEDOT. The device exhibited fast switching speeds of 0.37 s and 1.22 s for bleaching and coloration, respectively.

In this study, we used PANI (EB) (Avg. M_w 10000, CAS 25233-30-1, Sigma Aldrich) as the polycation and poly(aniline sulfonic acid) (PASA) (Avg. M_w 10000, CAS 167860-86-8, Sigma Aldrich), as the polyanion. PASA is a self-doped fully sulfonated conducting polymer. Some of electrochemical behaviors of PASA is previously studied [26]; however, we were unable to find any in-depth study of electrochromic properties of PASA. By combining cationic and anionic polyaniline forms together into a single LbL film, we anticipated changes in electrochromic and electrochemical properties of the film compared to the films constructed of either PANI or PASA paired with a non-electrochromic polymer. In this work, we study the electrochromic and electrochemical properties of PANI/PASA solid state dual electrochrome EC devices with varying thickness and voltage. The thickness of the thin film can be easily controlled through the number of layer pairs, referred to as bilayers.

2. Experimental details

All solutions were freshly prepared prior to the LbL self-assembly process and were used within one week of the preparation date. All the chemicals used are commercially available (Sigma Aldrich). Deionized (DI) water was used for the immersion and rinsing solutions. Solutions were prepared at ambient conditions.

Since polyaniline is not soluble in water, a different technique, inspired by Cheung et al. [27], was used to prepare the solution. (1) Polyaniline was added to dimethylacetamide (DMAc) at ratio of 20 mg/ml; (2) the solution was then stirred overnight and (3) sonicated at 40 °C for 2 h. (4) The solution was slowly added to DI water nine times its volume with pH 3.25. (5) The pH of the solution was immediately reduced to 3.0. (6) The solution was then stirred for three more hours and then (7) filtered using filter paper with retention of 11 μm. The solution was kept at ambient temperature and used within seven days.

Aqueous solution of 10 mM PASA was made and left to stir for about 5 h. The pH of the solution was 2.9 and was increased to 4.2. The solution was kept at ambient temperature and used within seven days.

All devices were made using 25 mm × 75 mm × 0.7 mm unpolished float glass, with passivated SiO_2 and indium–tin oxide (ITO) coating on one side with sheet resistance R_s of 8–12 Ω/square (Delta Technologies Ltd.). Each slide was soaked in 1 M sodium hydroxide solution for 30 min to make a more hydrophilic surface. The non-ITO side of each substrate was covered with electrical tape to prevent formation of LbL film on that side.

An automated dipping robot (Nanostrata 6) was used to deposit the LbL films on the ITO slide. PANI and poly(allylamine hydrochloride) (PAH) (Sigma Aldrich) were used as polycations and PASA and PAMPS (Sigma Aldrich) as polyanions. The immersion time for each layer of polymer was set to 6 min, followed by three consecutive washings of 45 s each. Thin films with different numbers of bilayers were fabricated. The thickness of films of different number of bilayers was measured by scanning electron microscope (SEM) of the cross-section of the thin films.

Asymmetric devices were fabricated using the ITO-coated slide with LbL film as the primary electrode and an ITO-coated slide without LbL film as the counter electrode. A few drops of PAMPS conductive gel was used to bind the two electrodes together and close the circuit.

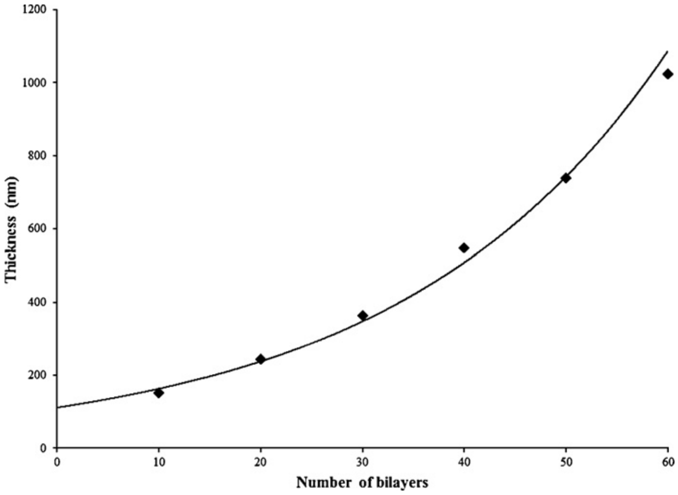

Fig. 1. Film thickness of PANI/PASA LbL films vs. number of bilayers. The curve is an exponential fit to the data.

3. Results

3.1. Thickness

Films with different numbers of bilayers were made in order to examine the contrast of the film with respect to the number of bilayers. As shown in Fig. 1, the thickness of PANI/PASA films followed an exponential behavior. While LbL films generally exhibit linear growth with the number of bilayers, exponential growth has also been observed in several cases [28–30]. The mechanism for exponential growth is not yet fully understood. The absolute change in transmittance (|Δ%T|) between the oxidized and reduced states (i.e. contrast) of each sample, under application of ±2.3 V, is shown in Fig. 2. The contrast of the devices is increased with the number of bilayers up to 40 bilayers. The contrast of the 50 bilayers device essentially overlaps that of 40 bilayers device, and the contrast of the 60 bilayers device is only slightly improved; thus, 40 was chosen as the number of bilayers for optimum thickness of EC films studied in this work.

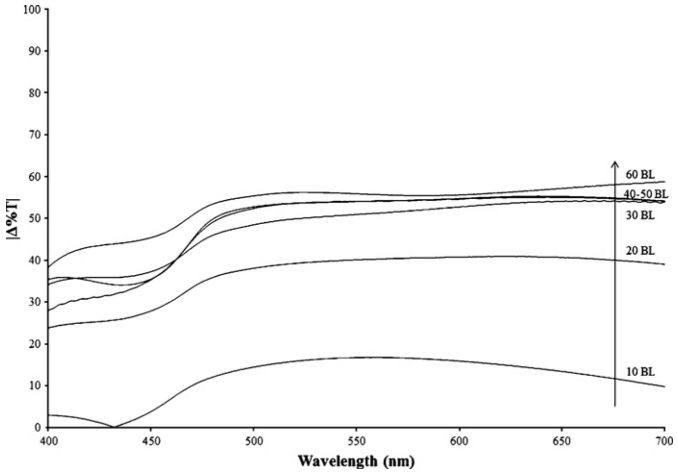

Fig. 2. The absolute of the change in transmittance between +2.3 V and −2.3 V of PANI/PASA devices with different numbers of bilayers for 10–60 bilayers with 10 bilayers intervals. The arrow indicates increasing number of bilayers.

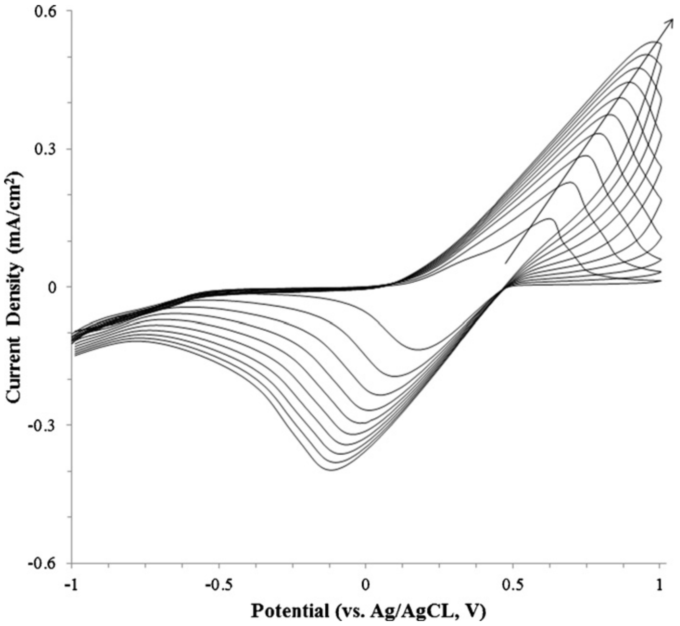

Fig. 3. Cyclic voltammograms of (PAH/PASA)$_{40}$ taken at 10–100 mV/s scan rates (10 mV/s increments). Arrow indicates increasing scan rate.

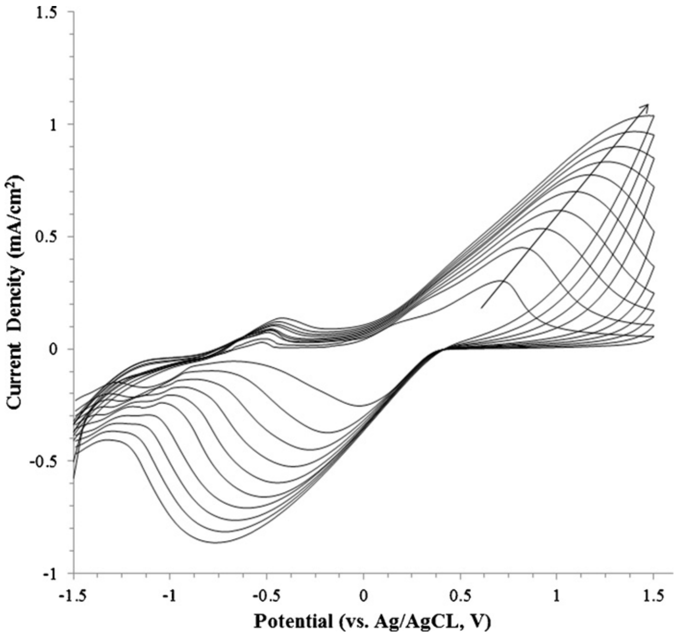

Fig. 4. Cyclic voltammograms of (PANI/PAMPS)$_{40}$ taken at 10–100 mV/s scan rates (10 mV/s increments). Arrow indicates increasing scan rate.

3.2. Cyclic voltammetry

Cyclic voltammetry (CV) measurements were made on 40 bilayer films assembled on ITO-coated glass (working electrode) to identify redox potential ranges and clarify the general electrochemical behavior of electroactive polymer films. The scanning ranges were quiet large to include most redox peaks at different scan rates. The range was between $\pm$1.0 V for (PAH/PASA)$_{40}$ and $\pm$1.5 V for other films vs. silver chloride electrode (Ag/AgCl), in a supporting aqueous electrolyte solution of 1 mM PAMPS (pH 3.5), the same electrolyte used in assembled devices. Measurements were taken at different scan rates ranging from 10 mV/s to 100 mV/s, increasing in 10 mV/s increments, to characterize redox process of the films.

In Fig. 3 is presented the CV of (PAH/PASA)$_{40}$. This single electrochrome film shows a pair of sharp redox peaks in the $\pm$1.0 V potential range. The oxidation peak occurred at +0.6 V and the corresponding reduction peak at +0.2 V for a scan rate of 10 mV/s and shifted in opposite directions with increasing scan rate. The redox process was accompanied by color change from light gray to dark green during oxidation and back to light gray through the reduction scan. Both oxidation and reduction peak current densities rise linearly with the square root of the scan rate, which implies a primarily diffusion controlled electrochemical reaction.

CV measurement of (PANI/PAMPS)$_{40}$ was performed under the same experimental conditions as (PAH/PASA)$_{40}$, except for the potential range which was broadened to $\pm$1.5 V. As shown in Fig. 4, during the oxidative scan two oxidation peaks were observed at $-$0.55 V and +0.7 V at 10 mV/s scan rate. The color of the film changes from pale blue ($-$1.5 V) to dark green ($-$0.55 V) to dark blue (+0.7 V) and under reversed potential (reductive scan) the film changes color from dark blue to dark green to pale blue. The primary reduction peak was observed at 0 V, which corresponds to the oxidation peak at +0.7 V, and a second smaller peak was observed at $-$1.1 V. Both oxidation and reduction peak heights rise linearly with the square root of scan rate, which implies slow diffusion of ions into the film and confirms a primarily diffusion controlled process.

A dual electrochrome film of (PANI/PASA)$_{40}$ was subjected to CV measurements under the same experimental conditions as the (PANI/PAMPS)$_{40}$ film. As shown in Fig. 5, a small oxidation curve occurred at $-$0.53 V followed by a sharp peak at +0.75 V. The peak at $-$0.53 V is the electrochemical fingerprint of PANI and corresponds to the oxidation peak at $-$0.55 V in Fig. 4. The larger peak shows electrochemical signatures of both PANI and PASA.

In the reductive scan, only one reduction peak is observed at $-$0.12 V which corresponds to the +0.75 V oxidation peak. The peak is significantly broadened compare to reduction peaks of PASA or PANI alone, possibly because of the difference in diffusion rate between dual and single electrochrome films. The hysteresis between oxidation and reduction peaks was increased with increasing scan rate, indicating a non-Nernstian condition in the reactive front, due to either slow electron transfer between ITO and electrochrome film, or the internal resistance of the bulk of the film [18]. The increasing hysteresis between redox peaks was observed

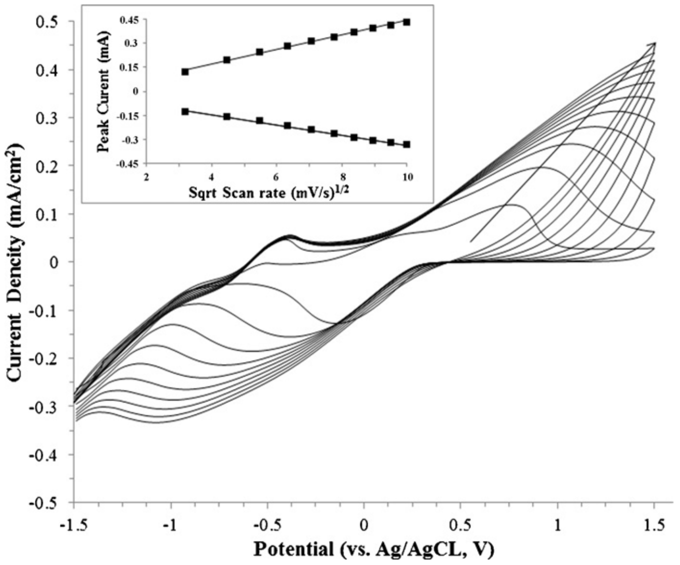

Fig. 5. Cyclic voltammogram of (PANI/PASA)$_{40}$ taken at 10–100 mV/s scan rates (10 mV/s increments). Arrow indicates increasing scan rate. Contribution of both electrochromic materials to the electrochemical behavior of the dual electrochrome film was confirmed. Inset: peak current density vs. square root of scan rate indicates diffusion controlled process.

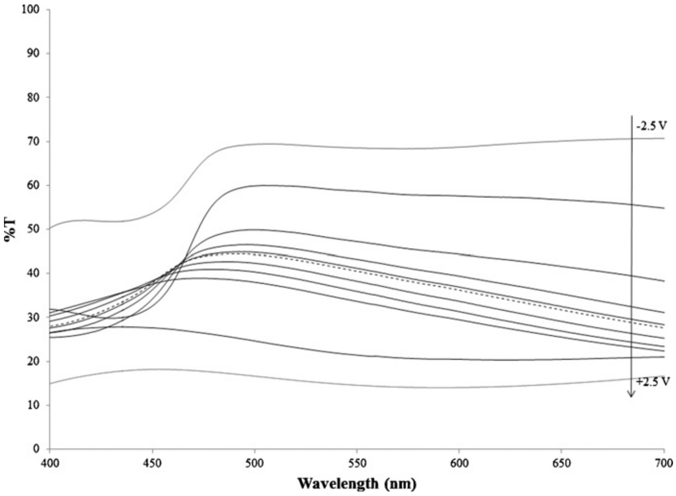

Fig. 6. Spectra of $(PANI/PASA)_{40}$ asymmetric EC device taken from −2.5 V to +2.5 V at 0.5 V intervals. Dashed line indicates 0 V data, and the arrow indicates increasing potential.

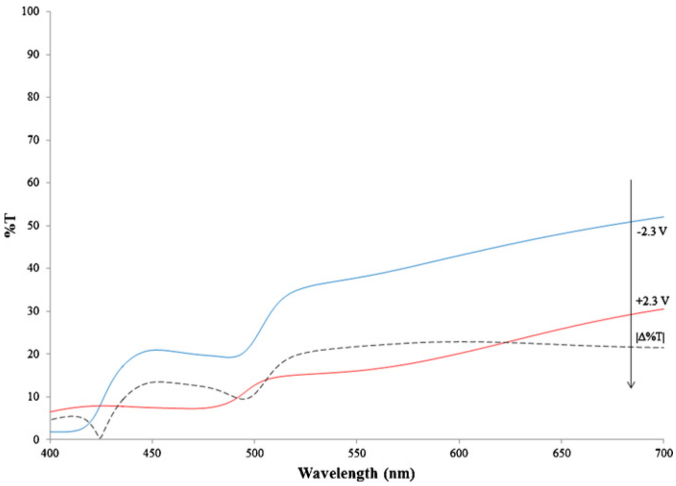

Fig. 8. Spectra of $(PAH/PASA)_{40}$ asymmetric EC device taken at −2.3 and +2.3 V. The dashed line indicates the absolute of the change in transmittance between −2.3 V spectra and +2.3 V spectra. The arrow indicates increasing potential.

for both single and dual electrochrome films. Similar to single electrochrome films, the $(PANI/PASA)_{40}$ film exhibited a linear trend on increasing peak current vs. square root of scan rate, confirming that the process in primarily diffusion controlled.

The redox peak potentials and current densities along with increasing rate of hysteresis of redox curves show signature of both electrochromic materials, confirming that both materials are electrochemically active and accessible and contribute to the electrochemical properties of the dual electrochrome film.

3.3. Contrast

Asymmetric solid state EC devices were used to investigate the optical properties in the visible spectrum at different potentials. The transmittance curves of a $(PANI/PASA)_{40}$ EC device shown in Fig. 6 have significant changes in transmittance beyond ±1.5 V.

In Fig. 7 we show the spectra of the $(PANI/PASA)_{40}$ EC device at ±2.3 V along with the contrast plot. At positive potential the film is strongly colored (dark blue), and this coloration is in response to the oxidation of the composite. Upon application of negative potential, the composite undergoes reduction resulting in a decoloration of the film (pale yellow). One of the most significant properties of the PANI/PASA composite is the large and relatively flat change in transmittance over the entire visible spectrum. The average contrast between the colored and bleached states of the composite at ±2.3 V over the visible spectrum (400–700 nm) is 49.7%. The average contrast between 500 and 700 nm is 54.4%.

In order to determine the relative contributions of PANI and PASA to the composite device, we also fabricated EC devices in which PANI and PASA were each paired with the electrochromically inactive polyelectrolytes PAMPS and PAH, respectively. Comparison of the spectra of $(PANI/PASA)_{40}$ with that of $(PAH/PASA)_{40}$ and $(PANI/PAMPS)_{40}$ (shown in Figs. 8 and 9, respectively) suggests that the transmittance of the PANI/PASA composite is largely influenced by PANI. While PASA has little effect on the shape of the $(PANI/PASA)_{40}$ spectra, the $(PANI/PASA)_{40}$ spectra are shifted to 10–20% higher transmittance values than the $(PANI/PAMPS)_{40}$ spectra. More importantly, the incorporation of PASA results in faster electrochromic switching, as shown below.

3.4. Switching speed

The switching speeds of $(PANI/PAMPS)_{40}$ and $(PANI/PASA)_{40}$ devices were monitored over time with a He–Ne laser (λ = 633 nm). A ±2.3 V square wave was applied at 0.25 Hz. As shown in

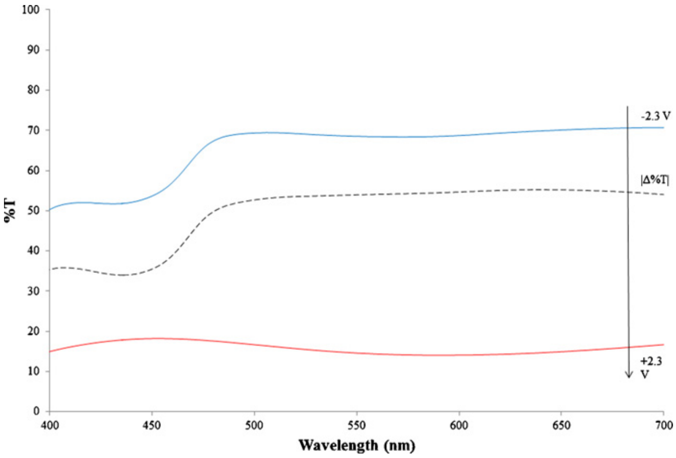

Fig. 7. Spectra of $(PANI/PASA)_{40}$ asymmetric EC device taken at −2.3 and +2.3 V. The dashed line indicates the absolute of the change in transmittance between −2.3 V spectra and +2.3 V spectra. Arrow indicates increasing potential.

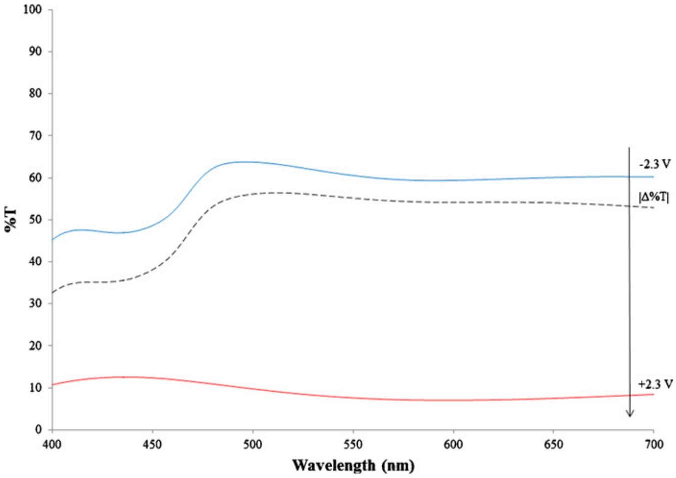

Fig. 9. Spectra of $(PANI/PAMPS)_{40}$ asymmetric EC device taken at −2.3 and +2.3 V. The dashed line indicates the absolute of the change in transmittance between −2.3 V spectra and +2.3 V spectra. Arrow indicates increasing potential.

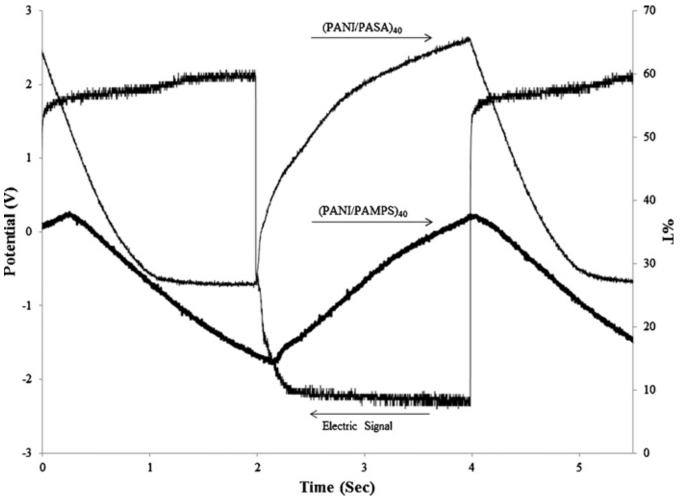

Fig. 10. Switching speed response of single electrochrome $(PANI/PAMPS)_{40}$ and dual electrochrome $(PANI/PASA)_{40}$ asymmetric EC devices during application of ±2.3 V square wave at 0.25 Hz.

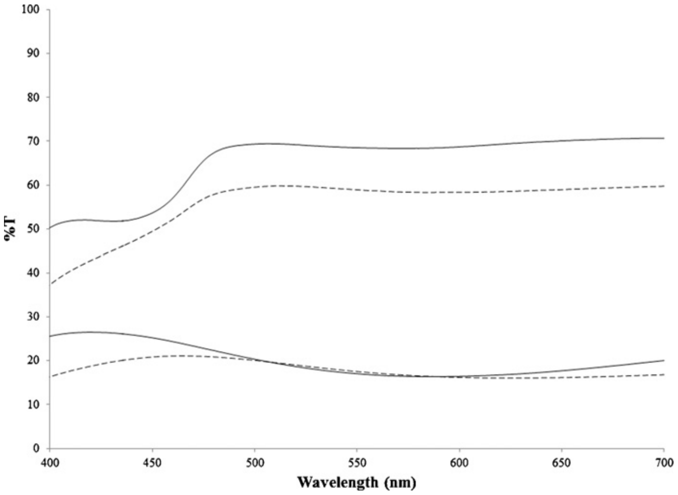

Fig. 11. Spectra of $(PANI/PASA)_{40}$ taken at −2.3 V and +2.3 V, before (solid line) and after (dotted line) going through more than 1000 switching cycles.

Fig. 10, $(PANI/PASA)_{40}$ showed faster electrochromic switching than $(PANI/PAMPS)_{40}$, as indicated by the transmittance nearly reaching its asymptotic value over the switching period for both coloration and decoloration. As a result, the PANI/PASA device also achieved a higher change in transmittance in the given period. The PANI/PASA sample reached a change in transmittance of 39.6% at 633 nm while the PANI/PAMPS sample reached a change in transmittance of 23.6%. Although the PANI/PASA device exhibits a faster coloration, neither of the devices achieves 75% of the full coloration state within the switching period of 2 s. For decoloration, PANI/PAMPS exhibited a similar curve to its coloration process with reversed slope while the PANI/PASA device reached 75% of full decoloration in approximately 700 ms.

3.5. *Lifespan*

PANI/PAMPS LbL films have been reported to degrade under application of ±2.0 V potential [24]. In our study on PANI/PASA composites, the films showed reasonably long lifespan with little drop in performance. As shown in Fig. 11, the contrast dropped by approximately 10% after undergoing more than one thousand cycles at an arbitrary sequence of $f = 1$ Hz and 0.25 Hz frequencies. The addition of PASA appears to have improved the lifespan of the system, yet more in-depth study is needed to confirm this hypothesis.

4. Conclusion

Dual electrochrome solid state electrochromic devices based on PANI and PASA were constructed based on LbL self-assembly. The devices exhibited high optical contrast over a wide range of wavelengths covering the entire visible spectrum. The average contrast of the 40-bilayer device in the visible spectrum was 49.7%. CV studies of the composite confirmed that both electrochromic polymers contribute to the electrochromic and electrochemical properties of the system, however PANI is primarily responsible for the observed transmittance changes. Comparison of PANI/PAMPS devices with PANI/PASA devices showed that the incorporation of PASA to the composite increases the switching speed and lifespan of the device. The response time performance of the device was significantly improved by addition of PASA. Under application of ±2.0 V square wave at 0.25 Hz, the PANI/PASA device reached more than double the contrast compared to the PANI/PAMPS device. Thus, the addition of the conducting and electrochromically active PASA significantly improved the electrochromic and electrochemical properties of the composite.

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