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High-Contrast Electrochromism from Layer-By-Layer Polymer Films

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Layer-by-layer (LBL) assembly is the ideal processing technique to combine two electrochromic polymers into a single thin film composite with fine control over morphology and composition. Here we present a very-high-contrast electrochromic composite developed from the LBL assembly of two readily available cathodically coloring electrochromic polymers: poly(hexyl viologen) (PXV) and the poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:SPS) colloid. Characterization of assembly reveals that film thickness increases exponentially with increasing layer-pair number, seemingly due to the globular nature of the PEDOT:SPS colloid. Elemental analysis confirmed the presence of both polymers in the final film and allowed the determination of a bulk composition profile. In detailed electrochemical and spectral investigations, the “dual electrochrome” was compared to single-electrochrome LBL films, confirming that both polymers contribute to electrochromic switching. Due to the unusual film architecture and complex interactions between PXV and PEDOT, a charge-trapping system is formed within the layers, resulting in a type of electrochemical rectification. The performance of PXV/PEDOT:SPS as a material for electrochromic applications was extremely competitive, with color-change response times ranging from 1 to 4 s and high contrast between a transmissive oxidized state and a deep purple/blue reduced state. The LBL approach was used to optimize the thickness of the polymer film, and a 45-layer pair PXV/PEDOT:SPS film was found to exhibit a transmittance change of 82.1% at 525 nm, one of the highest reported contrasts in polymer electrochromics. These results demonstrate the power of the LBL processing technique to create new electroactive materials with both unusual properties and unequalled potential for application. Future directions are illuminated for the LBL development of multiply colored, fast switching, and high contrast electrochromic materials from cheap and readily available electrochromic polyions.

Introduction

For the past half-century, there has been strong interest in developing low-cost elements with multiple reflective or transmissive colors suitable for flexible or wearable displays and smart windows.[1−3] Electrochromic materials may be ideally suited to meet the needs of these emerging applications: they are cheap and simple to produce, and they can provide reasonable contrast in multiple colors.[4−6] Electrochromics are particularly well suited to large area displays because of their low power consumption and forgiving manufacturing tolerances. Though electrochromics research has been ongoing for many decades, there has been a recent resurgence of interest as industries search for an “electronic paper” technology that is a cheap alternative to liquid-crystal and light-emitting-diode displays. This revitalized electrochromics research increasingly looks to polymer thin films for advancement. Color switching in an electrochromic polymer is caused by changes to its electron excitation energy profile following reduction or oxidation; specific examples are the formation of discrete charge-transfer complexes in poly(viologens),[7] or the doping/undoping of conducting polymers such as poly(thiophenes).[8−10] As is typical for most electroactive polymers, electrochromic polymers are customarily deposited on substrates by spin coating, electropolymerization, or surface polymerization by chemical means.

An alternative, innovative approach to film formation is the layer-by-layer (LBL) assembly technique. In the classical LBL method, a charged substrate is exposed alternately to dilute aqueous solutions of polycation and polyanion, enabling the deposition of a polyelectrolyte

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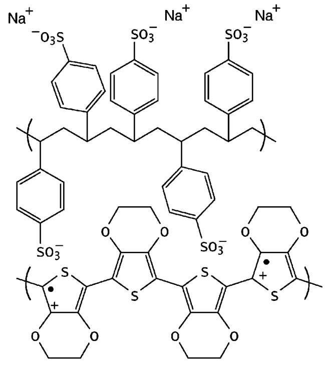
complex as a thin film with controlled thickness and composition.[11,12] The LBL technique results in smooth films that can include materials of any functionality, such as light-emitting polymers,[13] inorganic nanoparticles,[14] and biomaterials.[15] The technique can employ other assembly forces aside from electrostatics such as hydrogen bonding.[16−18] In addition, sophisticated patterning techniques have been developed to create three-dimensional micrometer-scale heterostructures of LBL films with ever-increasing complexity.[18−23] Typical LBL films consist of highly interpenetrated polymer layers that are regarded as a homogeneous composite film with a small alternating variation in polycation and polyanion density, though thicker, more stratified layers are made possible by varying assembly conditions.

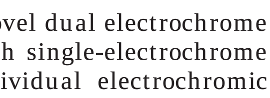
The LBL technique is the ideal tool for tailoring the properties of electroactive polymer films on the nanometer scale. Electronically conductive LBL films of exceptional homogeneity and high conductivity have been fabricated,[24−26] as well as other electroactive polymer systems. Very recently, the possibilities of using this versatile assembly approach to make electrochromic devices have been introduced. The earliest study of an LBL system containing a polymer electrochrome involved the investigation of charge transfer within polyelectrolyte LBL films containing polyviologens; these studies provided insight into ion transfer within the layers,[27,28] though the development of high-contrast electrochromic devices was not a focus of the work. The first complete electrochromic cell employing LBL films was recently developed in our research group; this device employed complementary coloring electrodes based on poly(3,4-ethylene dioxythiophene) (PEDOT) and polyaniline.[29] In the two years since the publication of this first device, there has been an increasingly strong interest in creating LBL electrochromic devices. LBL electrochrome systems studied in the past year include a conjugated polymer system developed in the Reynolds group incorporating a sulfonated PEDOT,[30] and inorganic electrochrome systems such as transition metal complexes[31] and poly(oxometalates).[32]

Despite the many advantages of these LBL electrochromics, in most functional LBL films an inert polymer is employed as the counterpolyion for the functional species. This counterpolyion is typically chosen from the short list of model polyelectrolytes: poly(diallyl dimethylammonium chloride) (PDAC), poly(allylamine hydrochloride) (PAH), poly(acrylic acid) (PAA), or poly(styrene sulfonate) (SPS). There have been previous successful efforts to create electroactive LBL films in which the polycation and polyanion are both conjugated,[33] however such efforts have not yet been extended to electrochromic composites. The inclusion of inert material reduces the performance of LBL electrochromics because inert polyions scatter or absorb light without contributing to contrast. Such polyions can also be resistive and can hinder electron or ion mobility within the film.

In this publication, we present for the first time a “dual electrochrome” composite in which the polycation and polyanion species within the LBL film are both cathodically coloring electrochromic species. The polycation species, poly(hexyl viologen) (PXV) is colored in the reduced state due to the formation of a charge-transfer complex,[7] while the polyanion species, the poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) colloidal dispersion (PEDOT:SPS, available as BAYTRON P from Bayer) derives color upon reduction from undoping of the conducting state.[34] Both electrochromic polymers switch from transparent oxidized states to dark blue reduced states. The chemical structures of these two electrochromic polymers are shown below.



PEDOT:SPS



PXV

Our investigation into this novel dual electrochrome composite first compares it with single-electrochrome LBL films containing the individual electrochromic polymers paired with inert polyions. Comparison of the PXV component was made by assembling a single-electrochrome LBL film from PXV and SPS, whereas

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comparison of the PEDOT component was made by assembling a single-electrochrome LBL film composed of linear poly(ethylene imine) (LPEI) and the PEDOT:SPS colloid. The electrochemical properties of these films were probed using cyclic voltammetry, and the optical properties were evaluated using spectroelectrochemistry.

The electrochemical and optical properties of the dual electrochrome system PXV/PEDOT:SPS were then elaborated using a variety of additional voltammetric and spectroscopic techniques, including voltage stepping and in situ monitoring of absorbance during switching. This study of the composite reveals complex behavior not found in single-electrochrome films that is caused by interactions between the two electrochromic polymers. After optimization, the contrast of this new electrochromic material actually surpasses that of almost all polymers synthesized specifically for electrochromic applications, and in fact, at this time there is only one polymeric electrochrome that has been reported to exhibit contrast higher than this dual electrochrome system.[35] These promising results further strengthen the position of this new assembly technique as a means of fabricating lightweight and flexible electrochromic films, as well as other types of redox-based devices.

Results and Discussion

Assembly. Electrochromic films were fabricated using the classical electrostatic LBL approach involving exposure of a bare ITO-coated float glass substrate to dilute aqueous solutions of polycation and polyanion in an alternating manner, followed by a copious water rinse between each deposition step. The electrochromic conjugated polymer complex PEDOT:SPS was assembled with LPEI at pH 4 as was described in our earlier publication.[29] A 40-layer-pair film of LPEI/PEDOT:SPS ($(\text{LPEI/PEDOT:SPS})_{40}$) with a total film thickness of approximately 780 nm was deposited onto ITO-coated glass. The total thickness of this film is more than four times greater than that reported for the 20-layer-pair film described in our earlier communication due to an exponential growth mechanism that has been observed in this and other LBL systems,[36−38] and will be described below for PEDOT:SPS-containing systems. For the second single-electrochrome film, the electrochromic polymer PXV was assembled with SPS in a manner similar to that described by Schlenoff and coworkers.[27,28]

As the LBL assembly of PXV/SPS has not been previously studied, initial LBL growth characterization was performed on oxygen-plasma-etched silica substrates exposed to pure, dilute aqueous solutions of the two polyions. The resultant films were on the order of ~0.4 nm per layer pair. To increase the electrochromic contrast of these ultrathin films, two methods were employed to increase film thickness: (1) ionic screening of PXV by adding NaCl to the PXV dipping solution, and (2) charge shielding of PXV by adding sodium dodecyl sulfate (SDS), an anionic surfactant, to the PXV dipping solution. The pH was in all cases held constant at pH 4. Ionic screening resulted in film thicknesses from 1.0 to 1.9 nm per layer pair, depending on salt concentration, and the maximum thickness was reached at 0.75 M NaCl. Thickness decreased at salt concentrations greater than 0.75 M due to screening-reduced adsorption. The maximum layer pair thickness of 1.9 nm is smaller than the 4.7 nm per layer pair observed by Laurent et al. for poly(butanyl viologen)/SPS LBL films at 0.5 M KBr,[27] a difference that may be explained by the lower electrostatic charge density per unit mass of PXV. The second approach of charge shielding with the surfactant SDS resulted in film thicknesses from 1.6 to 3.6 nm per layer pair, depending on SDS concentration, and a thickness plateau was reached at 10^{-4} M SDS. Film quality suffered at SDS concentrations greater than $5 \cdot 10^{-4}$ M due to a loss of PXV solubility, and precipitation occurs at 10^{-3} M SDS. The addition of SDS proved to be more effective than addition of salt for thickness enhancement because SDS binds and shields cationic sites on PXV and also presents a hydrophobic alkane tail to solution, drastically reducing the effective charge density of the polymer and increasing the extent of hydrophobic PXV deposition. The addition of 10^{-4} M SDS was thereafter chosen as a standard condition for PXV dipping solutions because of the resultant reproducibly thick LBL film. The single-electrochrome film $(\text{PXV/SPS})_{40}$ was assembled onto ITO-coated float glass at this condition. Unlike the PEDOT:SPS-containing systems, the growth of PXV/SPS proved to be linear with respect to layer-pair number, and the final thickness of a 40-layer-pair film was approximately 167 nm.

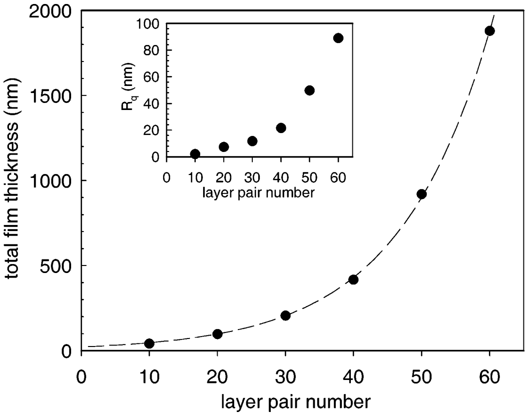

Figure 1. Total film thickness results for PXV/PEDOT:SPS films of increasing layer-pair number. The line connecting the points is an exponential regression. Inset shows RMS roughness with increasing layer-pair number.

The electrochromic polycation PXV and the electrochromic polyanion PEDOT:SPS were then combined in a dual electrochrome LBL composite. The PXV/PEDOT:SPS system was assembled in 10-, 20-, 30-, 40-, 50-, and 60-layer-pair systems onto ITO-coated float glass. The LBL growth profile for this system is shown in Figure 1. Rather than a linear growth profile, which is typical for most electrostatic LBL-assembled polymer films, the PXV/PEDOT:SPS system demonstrates an exponential growth profile, with total film thickness ranging from approximately 40 nm for a 10-layer-pair film to almost

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2 μm for a 60-layer-pair film. The per-layer-pair thickness for this system is not a single value, but rather increases from less than 4 nm/layer pair to greater than 100 nm/layer pair. Nonlinear regression gives the relation between t, the thickness in nm, and n, the layer-pair number, as $t = 22.7e^{0.0736 \cdot n}$ with an R^2 value over 0.999, indicating that the total thickness of a PXV/PEDOT:SPS film roughly doubles with every 10 layer pairs that are deposited. The regression line connects the film thickness points in Figure 1. A similar curve was obtained using quartz-crystal-microbalance monitored deposition (data not shown), confirming the deposition of exponentially increasing mass.

Nonlinear growth profiles in polyelectrolyte LBL films are a well-established phenomenon. In "model" polyelectrolyte LBL systems PAH/SPS[36] and PDAC/SPS,[37,38] superlinear growth has been observed when deposition solutions are at medium to high ionic strengths (>0.1−0.3 M). Exponential thickness growth appears to be especially common in the LBL assembly of many biologically derived polyelectrolytes even in the absence of added electrolyte.[39−41] Explanations of the exact exponential assembly mechanism vary. One explanation, offered for the case of high-ionic-strength deposition, suggests that the superlinear growth is due to increasing surface roughness, which in turn presents an increasing surface area that permits deposition of increasing amounts of material.[36] Increasing roughness in these systems is provided by the deposition of polyelectrolytes in the globular morphology that is assumed in solution at high ionic strengths. More recent efforts by other groups have suggested that the mechanism is related to polyelectrolyte diffusion in to and out of the film as well as surface interactions.[39−41] In the case of PXV/PEDOT:SPS, we believe the exponential growth to be a consequence of the nature of the PEDOT:SPS colloidal dispersion, which should deposit in a manner similar to that of globular polyelectrolytes, forming an increasingly rough and larger surface area. Our supposition of increasing "fractal" surface area is supported by roughness measurements shown in the Figure 1 inset, which increase approximately linearly with total film thickness and exponentially with layer-pair number. Regardless of the assembly mechanism, PXV/PEDOT:SPS films with this novel architecture display unique electrochemical and optical properties, as described in further detail below.

Compositional Analysis. Given the rather unusual architecture of these films, the composition was determined to better analyze the resultant film properties. Given the difficulties inherent in compositional estimation from simple thickness or mass measurements, sample scrapings were taken from multiple films of varying thickness and subjected to elemental analysis. Given the exponential growth of these films, the collected sample best represents the composition of the thickest films. Elemental analysis revealed a sulfur/nitrogen atomic ratio of 0.83. Assuming that PXV is the sole source of nitrogen and that the PEDOT:SPS complex is the sole source of sulfur, and given the PEDOT:SPS molar repeat unit ratio of 0.45:0.55 as provided by the manufacturer, a PXV:PEDOT:SPS molar repeat unit ratio of 0.38:0.28:0.34 was calculated. We assume that this bulk composition represents the film throughout growth, though we recognize that composition may vary at earlier or later stages of film deposition. Given that there are two quaternized, cationic ammonium sites on each PXV repeat, these results indicate that over half of these sites are not paired with SPS; this effect is consistent with the adsorption of PXV as loopy layers due to shielding of charged groups with either salt anions or hydrophobic surfactant. The sulfur/carbon and sulfur/hydrogen ratios indicate that these sites are *not* coordinated with the surfactant SDS − in fact there is no significant amount of SDS in the final film, confirming that PEDOT:SPS is the sole source of sulfur; thus, these cationic sites must remain paired with their bromide counterions. (This conclusion could not be confirmed, as a prohibitively large sample is required for bromide analysis). SPS is assumed to be fully ionically paired with either PEDOT or PXV, and PEDOT cationic sites are assumed to be electrostatically balanced by the SPS dopant.

Cyclic Voltammetry. The first electrochemical test that was applied to the electroactive LBL films assembled in this study, cyclic voltammetry (CV), was used to identify redox potential ranges and elucidate general electrochemical behavior. Because PEDOT and PXV have very different redox potentials, the scanning range was quite large: between −0.9 V and 0.5 V vs SCE, in a supporting electrolyte of aqueous 0.1 M NH_4Cl. Working electrodes consisted of LBL films assembled onto ITO-coated float glass. To assess the electrochemical accessibility of the redox polymers within the films, the CV dependency on scan rate was determined for each film. CV was first applied to the $(PXV/SPS)_{40}$ and $(LPEI/PEDOT:SPS)_{40}$ films, with results shown in Figure 2.

Single Electrochrome Films. The redox behavior of the $(PXV/SPS)_{40}$ composite as shown in Figure 2a is similar to that of viologen-containing LBL films studied by Schlenoff.[27,28] A sharp redox wave appears with $E°' = -0.66$ V, corresponding to the first reduction of bispyridyl moieties in the PXV polymer backbone. The peak is sharp due to the insulating nature of the alkyl spacer; the polymer is a covalently bonded collection of discrete redox centers each with a well-defined redox potential. The hysteresis between oxidative and reductive peaks increases with scan rate, from $\Delta E_p = 0.17$ V at 0.025 V/s to $\Delta E_p = 0.25$ V at 0.2 V/s. This increasing hysteresis indicates a non-Nernstian condition at the reactive front, possibly due to slow electron transfer from ITO to the polyviologen or more likely resistance to redox propagation in the bulk of the film. Oxidation and reduction peak heights do not scale linearly with scan rate and instead scale almost perfectly with the square root of scan rate, indicating slow ion diffusion into the film. This in turn suggests that the LBL film does not have an open, ion-permeable morphology, but rather a more tightly knit, hydrophobic interior. This character would be expected for a LBL film such as PXV/SPS which contains two highly charged polyelectro-

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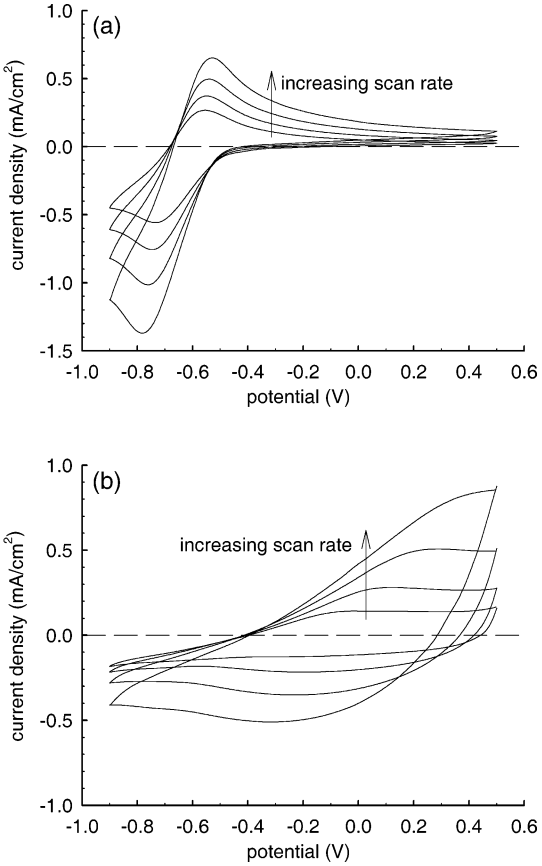

Figure 2. Cyclic voltammograms of (a) $(PXV/SPS)_{40}$ and (b) $(LPEI/PEDOT{:}SPS)_{40}$. Scans were at 0.025, 0.05, 0.1, and 0.2 V/s; increasing peak height indicates increasing scan rate. Electrolyte was 0.1 M NH_4Cl; reference was K-SCE.

lytes;[42] in particular as SPS presents a very hydrophobic main-chain.

The CV characterization of $(LPEI/PEDOT{:}SPS)_{40}$ as shown in Figure 2b is similar to that published by us previously.[29] A broad redox wave is visible centered at $E^{\circ\prime} \approx 0.0$ V, corresponding to the reductive elimination and oxidative creation of distributed cationic polaron charge carriers on the PEDOT polymer backbone. The broad nature of these peaks is due to the extended conjugation of PEDOT; redox potential varies depending on polaron environment and proximity to other charge carriers. This redox behavior is qualitatively similar to that of the poly(allylamine hydrochloride)/sulfonated PEDOT LBL system recently described by Cutler and Reynolds,[30] though LPEI/PEDOT:SPS displays a more capacitative response, most likely due to the additional redox-inert material present in the film. Like PXV/SPS, this system displays an increasing hysteresis between oxidation and reduction peaks with increasing scan rate, again indicating internal resistance in the film. High internal resistance in this system is not surprising considering the low PEDOT “loading” that we have observed in this and previous work[29] — the film is composed primarily of resistive polyions LPEI and SPS (a primary motivation for considering the dual electrochrome approach). However, unlike the PXV/SPS CV, the oxidation and reduction peak heights for LPEI/PEDOT:SPS scale nearly linearly with scan rate, indicating less ion resistance and a more open film morphology.

Dual Electrochrome Films. Films of PXV/PEDOT:SPS ranging from 20 layer pairs to 60 layer pairs were subjected to CV under the same experimental conditions as the single-electrochrome films. As shown in Figure 3, the CV curves exhibit electrochemical signatures of both the polyviologen and the PEDOT. In particular, a sharp PXV peak centered at approximately 0.65 V and a broader PEDOT peak centered near 0.0 V are clearly visible, and correspond to peaks obtained from the separate CV scans shown in Figure 2. In the dual electrochrome scans, the polyviologen peak predominates in thinner films, whereas the PEDOT contribution appears to become larger at higher layer-pair numbers. Thus, both materials are electrochemically accessible, though the relative contributions of the two materials vary with the total layer-pair number and film thickness. Furthermore, the PEDOT peak is partially obscured by the presence of a strong new peak that appears in the oxidative scan. Thus, the combination is successful, though the behavior of the combined composite is far more complex than that of simpler single-electrochrome systems.

The new oxidation peak does not appear in CVs of the single-electrochrome composites, suggesting that it is the product of interactions between PEDOT:SPS and PXV. The new peak first appears as a sloping shoulder in the 0.2 V/s CV scan of $(PXV/PEDOT{:}SPS)_{30}$, and it grows broader and more prominent in scans of films with more layer pairs. There is no reductive wave for this peak, and the peak location and height are extremely scan-rate dependent. One explanation for this behavior is that PXV might facilitate PEDOT oxidation as has been observed for other conjugated polymers,[43,44] resulting in a more localized and stronger PEDOT oxidation peak. This hypothesis does not, however, explain the large size of the peak or its appearance only in thicker films. Furthermore, the new peak should also appear in CV scans at potentials too anodic for PXV reduction, as shown in Figure 4; however, such a peak does not appear in these scans. A more consistent hypothesis is that the new peak is due to the release of charge-trapped states within the LBL construct. Charge-trapping is a phenomenon that has been observed in spatially separated heterogeneous redox-active systems consisting of a bilayer film of two different materials.[45] The oxidation state of the inner layer controls electron transfer to the outer layer and thus regulates the outer layer oxidation state. One model charge-trapping system that has been studied in detail is composed of a polythiophene inner layer and a polyviologen outer layer.[46] Although charge-trapping has not yet been described within polyelectrolyte LBL films, it stands to reason that the PXV/PEDOT:SPS LBL system might be considered as a “stack” of charge-trapping bilayers. However, the growth profile for this system is almost

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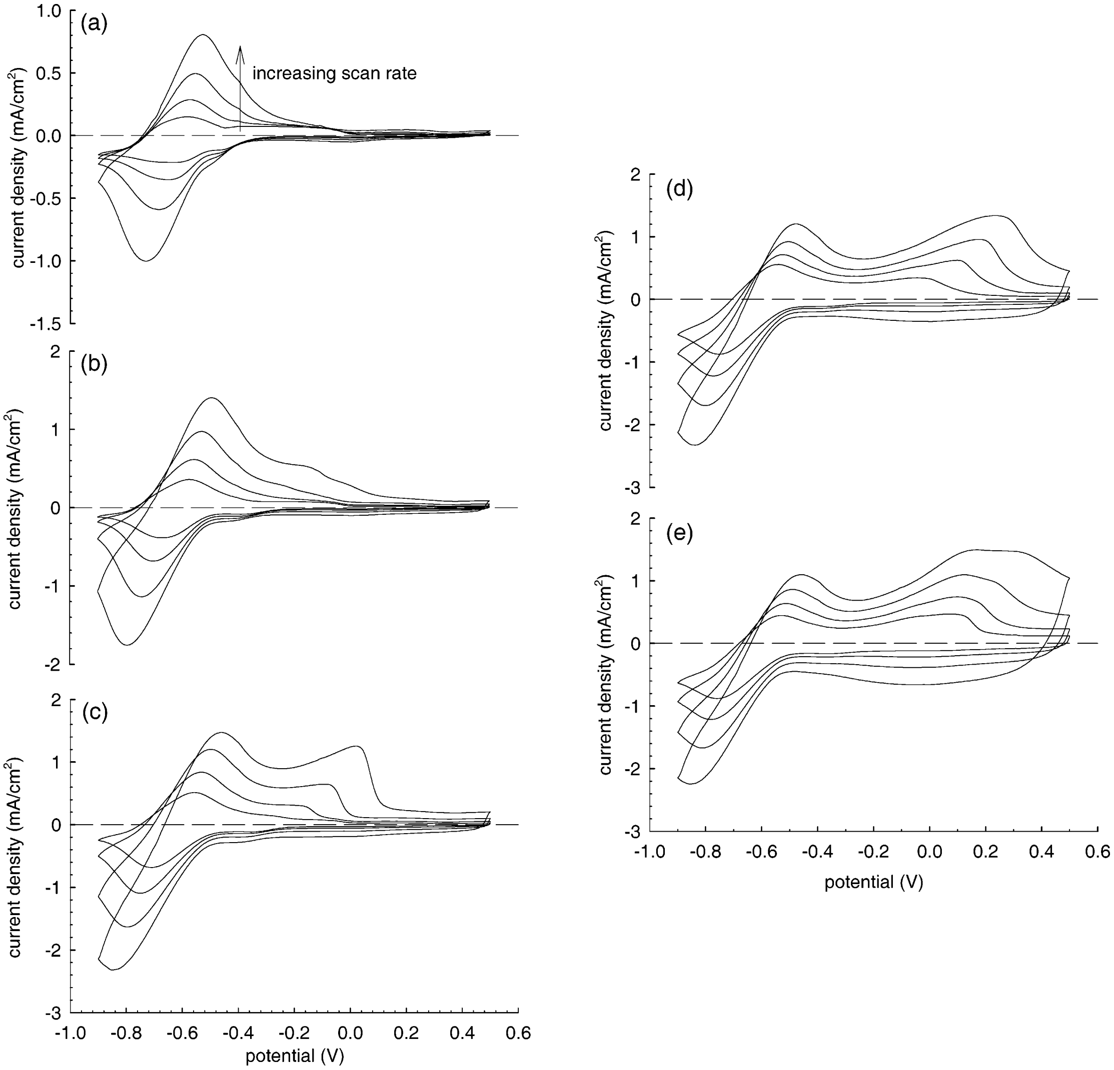

Figure 3. Cyclic voltammograms of PXV/PEDOT:SPS LBL films. Films of 20-, 30-, 40-, 50-, and 60-layer pairs were tested, corresponding to plots (a)−(e), respectively. Scans were at 0.025, 0.05, 100, and 0.2 V/s; increasing peak height indicates increasing scan rate. Electrolyte was 0.1 M NH_4Cl; reference was K-SCE.

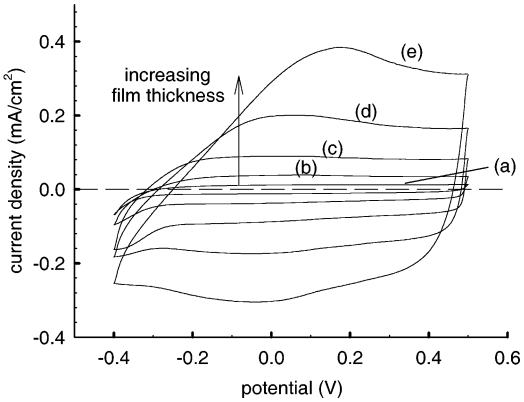

Figure 4. Cyclic voltammograms of PXV/PEDOT:SPS films between 0.5 V and −0.4 V. Films of 20-, 30-, 40-, 50-, and 60-layer pairs were tested, corresponding to curves (a)−(e), respectively. Scans were at 0.1 V/s; increasing peak height indicates increasing film thickness/layer-pair number.

perfectly exponential, so that the thin, highly interpenetrated inner layers of PXV/PEDOT:SPS should behave as a homogeneous blend with no charge-trapping, while much thicker outer layers should behave as more well-defined domains and allow for redox mediation. The fact that these large domains are stacked in series within the LBL film should further enhance charge-trapping, allowing for greater mediation with each subsequent layer pair. This hypothesis explains why the new oxidation peak is not observed in thinner PXV/PEDOT:SPS films, yet becomes prominent in films of greater thickness, where the individual layers are thicker and presumably more discrete.

The charge-trapping mechanism is illustrated in Figure 5, which compares CV curves of PXV/PEDOT:SPS films of 20-, 40-, and 60-layer-pair thickness at a scan rate of 0.2 V/s. The cathodic scan begins at point **A** where all films are oxidized. From point **A** to point **B**, PEDOT reduction occurs, which appears to be essentially complete by −0.5 V. PEDOT appears to be electrochemically accessible even in thick films as this reduction wave appears to increase proportional to film thickness. From point **B** to point **C**, PXV becomes reduced, though in the thick 60-layer-pair film, PXV appears to be only partially accessible and outer portions may not become reduced — this is especially clear as the 40- and 60-layer-pair films show reduction peaks of similar magnitude, even though the 60-layer-pair film contains nearly four times more PXV. Point **C** is the endpoint of the cathodic scan.

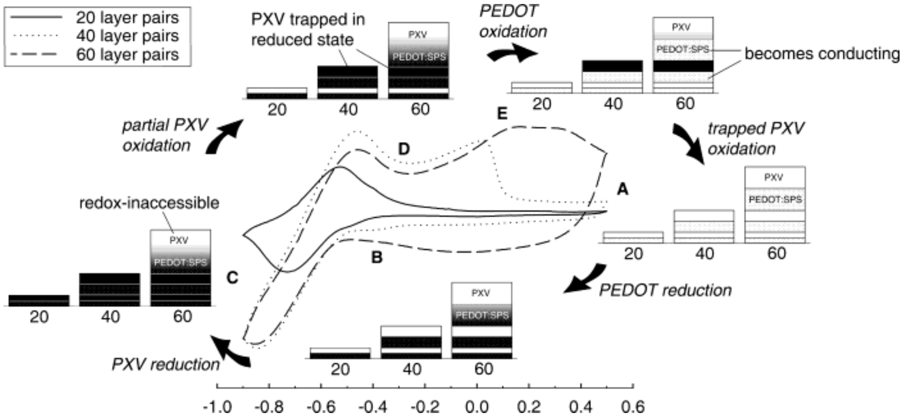

Figure 5. Suspected charge-trapping mechanism. Depicted are cyclic voltammograms (extracted from Figure 3) of PXV/PEDOT:SPS films of 20-, 40- and 60-layer-pair thickness at 0.2 V/s. Illustrations representing the suspected state of the films at different points on the CV curves accompany the voltammograms. In these drawings, white color indicates oxidized film and black color indicates reduced film. Cyclic voltammetry begins at point **A** and proceeds clockwise through points **A**−**E** following the discussion in the text.

From point **C** to point **D**, the anodic scan begins and PXV becomes reoxidized. In thicker films (40 and 60 layer pairs), it is clear that reoxidation is only partial because the oxidation peak is far smaller than the reduction peak. The PXV that remains reduced is suspected to reside in a trapped state located in the outer portions of the film, insulated by reduced PEDOT:SPS. From point **D** to point **E**, PEDOT becomes reoxidized. After oxidation, PEDOT becomes electronically conducting, and reduced PXV remaining in the outer portions of the film becomes immediately redox-accessible and reoxidizes. The reoxidation of trapped PXV takes place between point **E** and point **A**, and follows immediately or is simultaneous with PEDOT oxidation, resulting in the appearance of the strong new CV peak in thicker films.

Cyclic Absorptometry. The charge-trapping effect was also investigated spectroelectrochemically by performing fast spectral scans of films in situ while applying the potential ramp waveform used for CV. This technique provides information about the hysteresis of light absorbance during CV, which directly correlates to the polymer film oxidation state. A single wavelength of 560 nm was chosen to represent the oxidation state of both PEDOT and PXV. This wavelength was isolated from the fast spectral scans, resulting in the cyclic absorptometry shown in Figure 6. These scans were performed at a scan rate of 0.1 V/s; slower scans produced less hysteresis, though it was not eliminated. The cathodic scan shows two regions of increasing absorbance: one near the PEDOT reduction onset at 0.2 V, and one near the polyviologen reduction onset at −0.6 V. The anodic scan also shows two vertical inflections: one small decrease in absorbance at −0.7 V and one very large decrease in absorbance at −0.1 V. The differences in the location and magnitude of these inflections between the anodic and cathodic scans create two regions of hysteresis. These hystereses are not observed in the $(PXV/PEDOT:SPS)_{20}$ scan, but become significant in thicker films.

The hysteresis at negative potentials is clear evidence of the existence of charge-trapped states. As was elaborated by electrochemical means, charge-trapping does not appear in the 20-layer-pair film but is significant within 40- and 60-layer-pair films. During the anodic scan, starting at point **C**, the PXV undergoes a small oxidation at −0.7 V (point **D**) but remains substantially reduced until the sudden inflection at −0.1 V (point **D** to point **E**, corresponding to PEDOT oxidation), where light absorbance suddenly decreases as the charge-trapped states are released (point **D** through point **A**). The second and opposite hysteresis at positive potentials is due to the fact that the PEDOT oxidation proceeds much faster and at lower potential than the initial PEDOT reduction (point **A** to point **B**). The oxidative bleaching of PEDOT is typically far faster than its reductive coloration, yet it is also possible that PXV is indeed facilitating PEDOT oxidation, as was previously suggested.

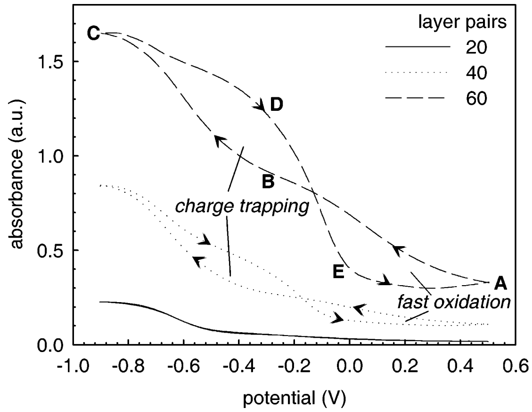

Figure 6. Cyclic absorptometry of PXV/PEDOT:SPS LBL films. The labels **A**−**E** correlate to the labeled CV points in Figure 5. Absorbance shown is at 560 nm. Scan rate was 0.1 V/s.

Double Potential Step Chrono-Amperometry. The electrochemical properties of the PXV/PEDOT:SPS system were further investigated using double potential step chrono-amperometry (DPSCA) in order to confirm the results of CV and to investigate the response time and charge capacity (columbic charge uptake/removal) of each film. In the DPSCA scans, the PXV/PEDOT:SPS films were subjected to a continuous square-wave pulse that switched the film potential between 0.5 V and −0.9 V with a period of 20 s and a duration of 10 s at each potential. A current wave was reproduced with every step, which was found to not vary significantly over at least 100 full cycles. A single current wave was isolated

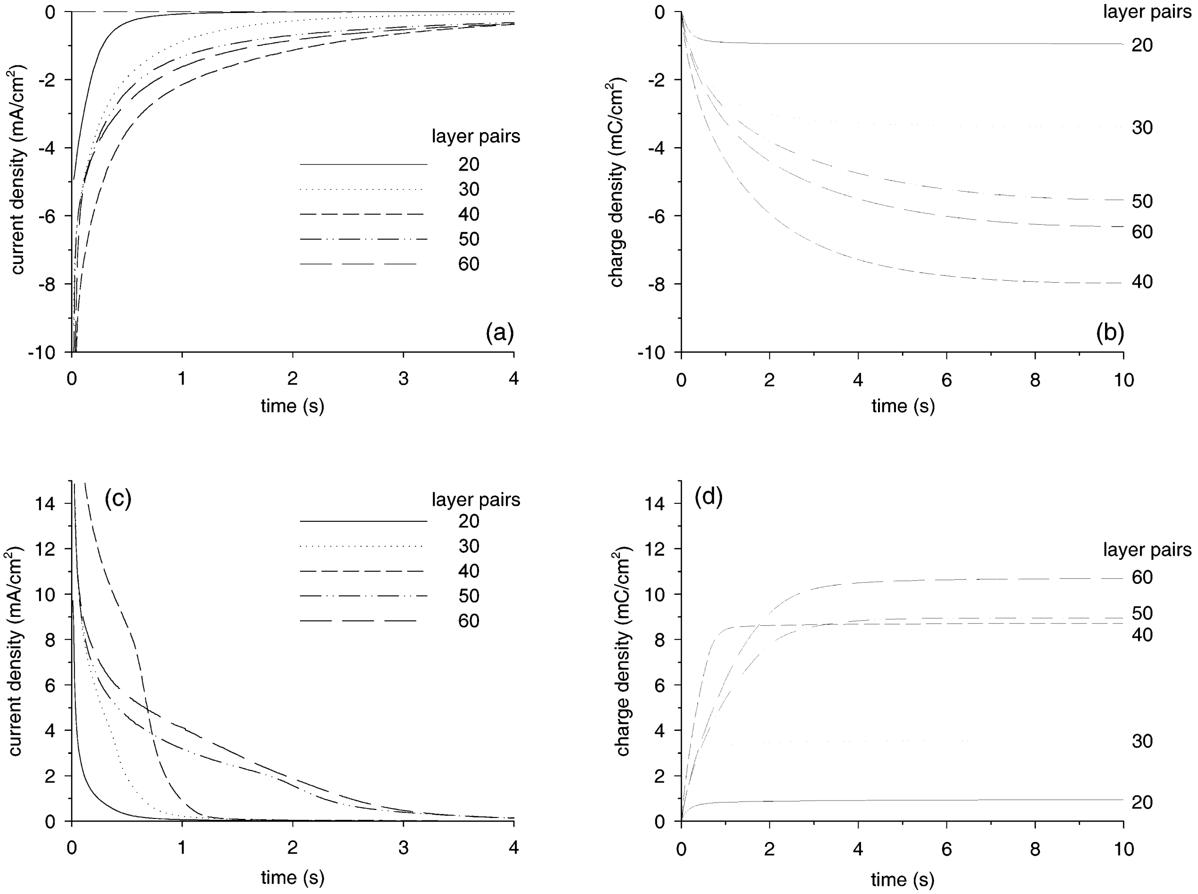

Figure 7. Reductive (a) current and (b) charge profile during switching from 0.5 V to −0.9 V for PXV/PEDOT:SPS films of 20-, 30-, 40-, 50-, and 60-layer pairs. Oxidative (c) current and (d) charge profile during switching from −0.9 V to 0.5 V for the same films.

Table 1. Estimated Redox Accessibility of Films of Varying Thickness

layer-pair number	est. sites (mC/cm^2)	reduced sites (mC/cm^2)	oxidized sites (mC/cm^2)
30	7.0	3.4 (48%)	3.5 (50%)
40	14	7.8 (54%)	8.7 (61%)
50	31	5.5 (18%)	9.0 (29%)
60	64	6.3 (10%)	10 (17%)

for oxidation and reduction of each film, and integrated to show the charge response. These results are compared in Figure 7. The reduction step shown in Figure 7a and b shows a generally slower response time with increasing layer-pair number. The final charge density at 10 s from Figure 7b indicates the total charge capacity of the film.

Given the compositional data obtained through elemental analysis, it is possible to estimate the percentage of redox-accessible sites in the finished film at various film thicknesses. Assuming a thin film density of 1.2 g/cm^3, as has been previously verified for similar polyelectrolyte LBL-assembled films,[47,48] and assuming that each PXV repeat unit remains coordinated to one bromide anion, an estimated number of total redox sites and percent accessed were calculated, with results shown in Table 1. The estimated sites were based on the sum of PXV and PEDOT repeat units, a calculation which considers a single PXV reduction and complete PEDOT reduction/oxidation, though one would not expect full oxidation or reduction of every monomer unit on the PEDOT chain. Results shown are for 30−60-layer pairs, where bulk composition data are most accurate. Initially half of the redox sites present are accessible; this number decreases above 40-layer pairs due to increasing electronic resistance and ion impermeability in the thicker films.

Spectroelectrochemistry. Following the electrochemical tests, the optical properties of the electrochromic LBL composites were evaluated using spectroelectrochemistry. For these investigations, LBL films assembled onto transparent working electrodes were inserted into a cuvette electrochemical cell and a UV−Vis spectrum was measured through the films at different potentials. The results are presented as a series of UV−Vis absorbance curves correlated to film potential. The potential range and other electrochemical experimental conditions were identical to those used for CV and DPSCA. The scan for spectroelectrochemistry was made cathodically, proceeding from 0.5 V to −0.9 V, and two-minute equilibration at each stepped potential was employed to minimize transient effects.

Single Electrochrome Films. First measured were the single-electrochrome films, with results shown in Figure 8a and b. In Figure 8a, the characteristic visible absorbance of the singly reduced state of PXV can be observed at 550 nm. The reduction appears to begin suddenly at −0.5 V and continues essentially to comple-

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(47) Caruso, F.; Niikura, K.; Furlong, D. N.; Okahata, Y. *Langmuir* **1997**, *13*, 3422−3426.

(48) Caruso, F.; Furlong, D. N.; Ariga, K.; Ichinose, I.; Kunitake, T. *Langmuir* **1998**, *14*, 4559−4565.

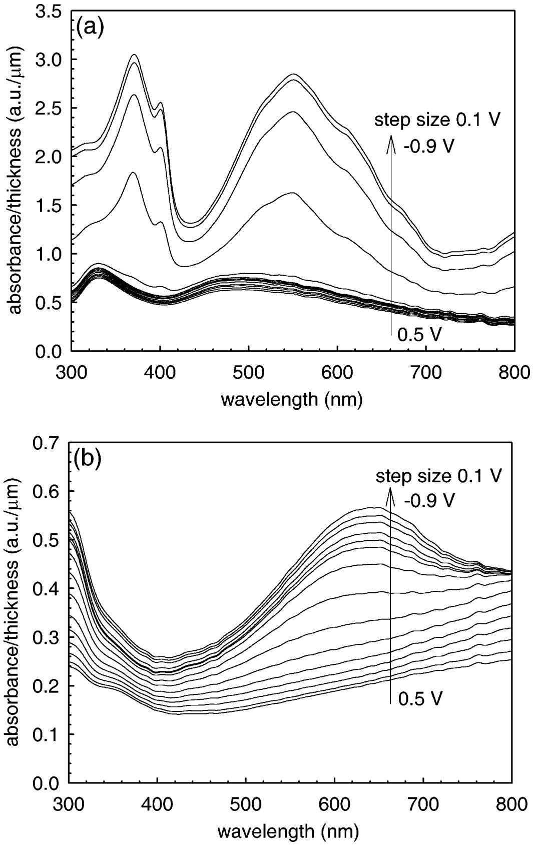

Figure 8. Spectroelectrochemistry of (a) $(PXV/SPS)_{40}$ and (b) $(LPEI/PEDOT{:}SPS)_{40}$. Spectra were taken from 0.5 V to −0.9 V at 0.1-V intervals. Arrows indicate increasing reduction. Electrolyte was 0.1 M NH_4Cl; reference was K-SCE.

tion by −0.8 V. The sharp transition from bleached to colored state is consistent with the sharp nature of the CV peak shown in Figure 2a, and the potential of the optical absorbance increase is in good agreement with the reduction potential determined from the CV scan. The spectroelectrochemistry of PEDOT reduction as shown in Figure 8b proceeds quite differently, with a much more gradual transition over the entire potential range. A substantial portion of the reaction appears to take place between 0.3 V and −0.4 V. This behavior is again consistent with a broad CV peak and is expected for a polymer with extended conjugation.

Dual Electrochrome Films. In Figure 9, we present spectroelectrochemistry of the dual electrochrome $(PXV/PEDOT{:}SPS)_{40}$, which clearly shows absorbance features of both PEDOT and PXV. At positive potentials, the entire composite is bleached. Immediately on applying a more cathodic potential, the film begins to color. From 0.5 V to −0.5 V, the gradual coloration is primarily due to the reduction of PEDOT. In fact, at −0.5 V, the spectrum of $(PXV/PEDOT{:}SPS)_{40}$ appears nearly identical to that of $(LPEI/PEDOT{:}SPS)_{40}$. At negative potentials beyond −0.5 V, the reduction of PXV suddenly begins, and absorbance increases profoundly. The final colored state clearly displays three broad absorbance peaks: two due to PXV at 550 and 620 nm, and one due to PEDOT at approximately 670 nm. The separation of redox potentials within this composite provides a unique breadth of gray-scale control, with adjustable absorbance over the entire potential range studied. The inclusion of PXV with PEDOT provides significantly more coloration than PEDOT alone, and the combination clearly provides broader absorbance throughout the visible range. Because of this wide band absorbance, very thick PXV/PEDOT:SPS films appear nearly black at negative potentials.

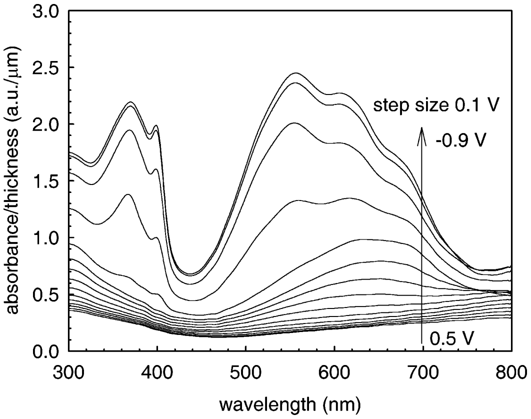

Figure 9. Spectroelectrochemistry of $(PXV/PEDOT{:}SPS)_{40}$. Spectra were taken from 0.5 V to −0.9 V at 0.1-V intervals. Arrow indicates increasing reduction. Electrolyte was 0.1 M NH_4Cl; reference was K-SCE.

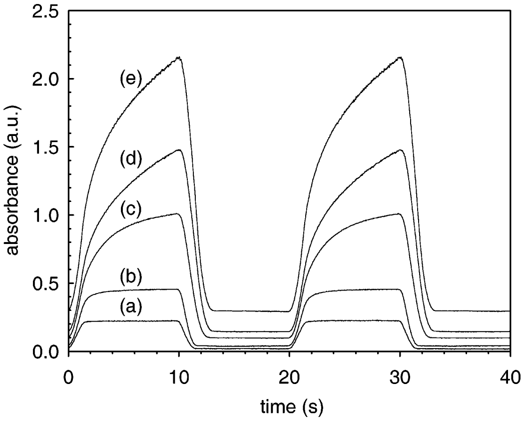

Figure 10. Potential step absorptometry of PXV/PEDOT:SPS films. Films of 20-, 30-, 40-, 50-, and 60-layer pairs were tested, corresponding to plots (a)−(e), respectively. Absorbance shown is for 560 nm. Switching was performed between 0.5 V and −0.9 V with a 20-s period and 10-s duration at each potential.

Potential Step Absorptometry. The kinetics of color change within PXV/PEDOT:SPS films were investigated spectroelectrochemically by performing fast spectral scans in situ while applying the potential step DPSCA waveform. This technique provides information about the kinetics of color-switching as shown in Figure 10, which demonstrates the absorbance change of an isolated wavelength (560 nm) from the fast spectral scans. The 20-, 30-, and 40-layer-pair films all display minimum and maximum absorbance that is linear with respect to film thickness and exponential with respect to layer-pair number. The thicker films such as 50- and 60- layer-pair films do not have this linear relationship, confirming the inaccessibility of PXV in outer regions of the film that was determined by electrochemical means.

The absorbance profiles shown in Figure 10, as well as the charge density DPSCA response presented in Figure 7 can be used to determine switching time, an important figure of merit for electrochromic composites. Different metrics are often used to define the switching

Table 2. Switching Times for PXV/PEDOT:SPS Composites

layer-pair number	bleaching time (s)			coloring time (s)		
	%T^b	abs	charge^c	%T^b	abs	charge^c
20	1.2	1.2	1.2	1.3	1.3	0.6
30	1.1	1.2	0.6	1.8	2.2	2.2
40	2.2	1.9	0.7	3.1	5.5	3.7
50	2.6	2.3	2.2	3.1	7.3	4.8
60	2.7	2.3	2.3	2.0	7.4	4.6

[a] Values were based on the time required to reach 90% of the full change in the indicated property. Absorbance and transmittance were evaluated at 560 nm. [b] From Figure 10. [c] From Figure 7.

time. If switching time were defined as the time that is required to reach 90% of the full change in absorbance after switching the potential, then these composites would require 1.3−7.4 s for coloration, and 1.2−2.3 s for bleaching. If the definition were changed to refer to reaching 90% of the full change in *transmittance*, then coloration would require 1.3−3.1 s and bleaching would require 1.2−2.7 s. Switching time can also be based on the charge response of the film. A full tabulation of switching times is reported in Table 2.

Switching times of 1−2 s are typical for electrochromic polymer films, though the times shown here are somewhat slower than the subsecond switching times reported for some high-contrast electrochromic polymers.[9] Importantly, the PXV/PEDOT:SPS films are far thicker than those with subsecond switching,[9] and the slower switching of this composite is thought to be due to slow ion permeation and internal resistance in thicker films that was described earlier by electrochemical investigation. This slight disadvantage in thicker films is by no means prohibitive. Furthermore, the application possibilities for static displays are undiminished due to the coloration and high contrast that can be achieved with this composite.

Coloration Study. Coloration in PXV/PEDOT:SPS is demonstrated in Figure 11, which shows digital images of films at different potentials. The composite switches from a transmissive, sky-blue color when oxidized, to a deeply absorptive purple/blue color when reduced. Increasing the composite thickness results in a slightly darker color in the bleached state, and a far more saturated colored state. The gray scale of this composite is demonstrated at −0.4 V, where most of the PEDOT is reduced, but PXV remains oxidized. Aside from saturation, there is a slight difference in color between −0.4 V and −0.9 V because reduced PEDOT only absorbs in the red portion of the visible spectrum, producing a pure blue color, while the PXV features an additional, higher energy visible absorbance (Figures 8 and 9) that produces a more purple color. Due to the dramatic coloration to an intensely saturated purple/blue at full reduction, these films have obvious applications as electronic inks or in other types of static display technologies.

Optimization for Electrochromic Applications. The most important figure of merit for electrochromic materials is the contrast between oxidation and reduction. From examination of the plot shown in Figure 10 and the images of Figure 11, it is clear that the contrast achieved is strongly dependent on the number of layer pairs. Furthermore, both colored and bleached absorbance increase with increasing layer number, so there must exist an optimum film thickness at which the contrast is maximized. The probable location of this maximum can be determined by comparing the contrast of the films studied spectroelectrochemically using a suitable metric. There are several metrics for contrast determination, however the most commonly used are $\Delta\%T(\lambda)$ and the optical density, OD(λ). One rather recent criterion has been the comparison of colorimetric luminance, which we may pursue in future studies.[49] The quantity $\Delta\%T(\lambda)$ is the change in transmittance between the colored and bleached states at a specific wavelength. The OD(λ) is the logarithm of the ratio of bleached transmittance to colored transmittance at a specific wavelength − *not* a suitable measure for evaluating strongly coloring films such as PXV/PEDOT:SPS because thicker films invariably have a greater OD. Instead of OD, the quantity $\Delta\%T_{\max}$, the maximum value of $\Delta\%T(\lambda)$, was determined for each of the PXV/PEDOT:SPS films. The values of this measure are shown in Figure 12, along with the transmittance of bleached and colored states at the $\Delta\%T_{\max}$ wavelength. The value of $\Delta\%T_{\max}$ increases from about 35% for a 20-layer-pair film to a maximum of greater than 70% for a 40-layer-pair film. Although these contrast values are already quite high, it is clear that an even greater maximum contrast might be achievable in a film of thickness between 40- and 50-layer-pairs.

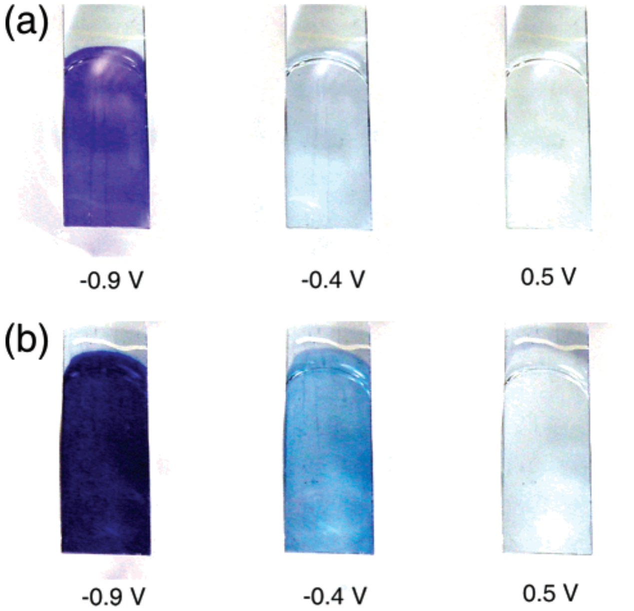

Figure 11. Digital photographs of the coloration and bleaching of (a) (PXV/PEDOT:SPS)$_{40}$, and (b) (PXV/PEDOT:SPS)$_{50}$. The films as shown are immersed in 0.1 M NH_4Cl within an electrochemical cell. Shadows and lighting gradients are responsible for the variations in brightness on the film surface as the films are smooth and uniform.

To achieve this maximum, several PXV/PEDOT:SPS films were assembled in the range of 40−50-layer-pairs, fine-tuning the optimum film thickness. A (PXV/PEDOT:SPS)$_{45}$ film with a thickness of approximately 550 nm was found to display higher contrast than either the 40- or 50-layer-pair films. The spectroelectrochemistry of this film is shown from the transmittance perspective

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(49) Thompson, B. C.; Schottland, P.; Zong, K.; Reynolds, J. R. *Chem. Mater.* **2000**, *12*, 1563−1571.

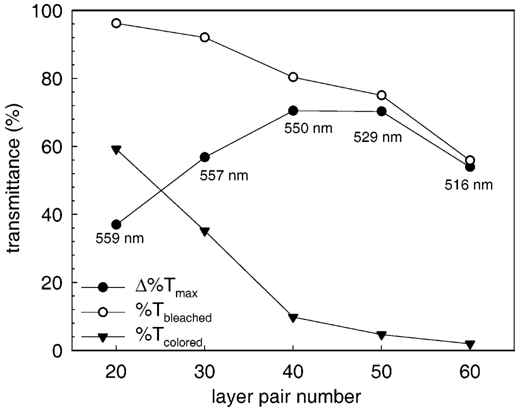

Figure 12. Optimization of PXV/PEDOT:SPS film thickness and layer-pair number. Maximum $\Delta\%T$ was determined at each film thickness. The wavelength of $\Delta\%T_{max}$ is recorded for each point, and the $\%T_{bleached}$ and $\%T_{colored}$ at that wavelength (wavelength of $\Delta\%T_{max}$) are also plotted.

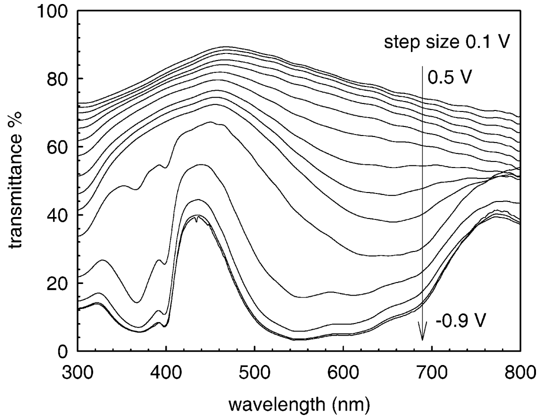

Figure 13. Spectroelectrochemistry of $(PXV/PEDOT:SPS)_{45}$, presented from the transmittance perspective. Spectra were taken from 0.5 V to −0.9 V at 0.1-V intervals. Arrow indicates increasing reduction.

in Figure 13. The bleached state of this film transmitted more light than $(PXV/PEDOT:SPS)_{40}$ due to the addition of a ultrasonic rinsing step during the deposition process that resulted in a smoother film. As expected, the colored state transmittance of $(PXV/PEDOT:SPS)_{45}$ was between that of the 40- and 50-layer-pair films. The maximum contrast of $(PXV/PEDOT:SPS)_{45}$ is $\Delta\%T_{max}$ = **82.1%** at 525 nm; this contrast is higher than that of any reported electrochromic polymer film with the exception of one.[35] Because of the very wide band absorbance, $\Delta\%T$ is greater than 50% over the range of 450 nm to 700 nm. The fact that PXV/PEDOT:SPS can provide a greater contrast than many specially synthesized materials is a testament to the power of the LBL processing technique to provide new high-performance electrochromic composites. We anticipate that elegant monomer design and polymer synthesis efforts to provide water-soluble electrochromic polymers that are capable of aqueous assembly by electrostatic or other forces will broaden the color and performance capabilities of these exciting new LBL composite materials. A combination of new materials design and innovative polymer processing using the LBL assembly process as a means of tailoring these systems will lead to new advancements in this area.

Conclusion

A new high-contrast dual-electrochrome composite has been developed based on the LBL assembly of two cathodic electrochromic polymers: PXV, a discrete electrochromic polymer that colors based on charge transfer complex formation, and PEDOT, a conjugated polymer doped with SPS that colors based on the reduction of electronically conducting polaron and bipolaron states. Unlike most LBL films, the PXV/PEDOT:SPS system grows exponentially in thickness with increasing layer-pair number, providing smooth and robust films that double in thickness every 10 layer pairs. As the PXV/PEDOT:SPS films become thicker, PXV becomes less electrochemically available and charge-trapping appears where PEDOT controls the PXV oxidation state in the outlying portions of the film. In contrast to PXV, PEDOT appears to remain redox-accessible even in very thick films. Spectroelectrochemical investigations confirm that both PXV and PEDOT contribute to electrochromic coloration, and additional optical/electrochemical investigation corroborates the charge-trapping effect and also reveals accelerated PEDOT oxidation. These interaction effects do not negatively impact performance and in fact may be positive; charge-trapping enhances colored-state stability, and accelerated oxidation causes faster electrochromic bleaching.

The performance of PXV/PEDOT:SPS as an electrochromic material was extremely competitive. Color-change response times vary depending on metric, but in general range from 1 to 4 s for coloration and bleaching, which is similar to other electrochromic polymers, but slower than the fastest-switching. PXV/PEDOT:SPS provides high contrast, switching between a transmissive light-blue oxidized state to a deeply saturated purple/blue reduced state. The LBL approach provides a convenient means to optimize the thickness of the polymer film based on layer-pair number, and optimum contrast performance was manifested by $(PXV/PEDOT:SPS)_{45}$, which exhibited a maximum transmittance change of 82.1% at 525 nm, exceeding that of all but one electrochromic polymer film reported to date.

Future directions of this work involve enhancing the response time of LBL electrochromic composites by evaluating the effects of different assembly mechanisms and morphologies. In addition, the LBL method provides a simple processing platform to create complex composites with multiple colored states from assembly of simpler electrochromics with a single bleached/colored transition. Development in this area will be accelerated with the realization that aqueous solubility and functionality for intermolecular interactions are worthy of consideration by the synthetic polymer chemist regardless of application, because investigators can then avail themselves of this and other similar processing techniques to extend the utility and application of newly synthesized and/or existing electrooptical materials.

Experimental Section

Polycations included LPEI (25k, Polysciences), and PXV, which was synthesized in dry, boiling acetonitrile from 1,6-bromohexane and 4,4′-bipyridine (both from Sigma-Aldrich) and then recrystallized from cold methanol with an overall yield of approximately 50%. PXV is fully oxidized at ambient conditions, providing two positive charges per monomer repeat unit. Polyanions included SPS (70k, Aldrich), and PEDOT:SPS (BAYTRON P, Bayer Corporation). BAYTRON P is described by the manufacturer as roughly 0.8% SPS and 0.5% PEDOT by mass, indicating approximately equimolar monomer amounts with a slight (~22%) SPS excess. As PEDOT doping does not involve oxidation of every PEDOT repeat, there is a substantial excess of unpaired SPS, providing stabilization and enabling Coulombic interactions with polycations in LBL assembly.

Polymer solutions were made using Milli-Q (Millipore deionized, >18.2 Ωcm, 0.22-μm-filtered) water, and adjusted to pH 5 using NaOH or HCl. PEDOT:SPS colloidal suspsension was diluted 1:10 with an aqueous cosolvent. The cosolvent was 90% water and 10% dimethylacetamide as described by Rubner.[26] LPEI and SPS solutions were 0.02 M, and PXV solutions were 0.01 M (polymer concentrations with respect to repeat unit). ITO-coated float glass substrates with dimensions 0.7 cm × 5 cm (Delta Technologies, 6 Ω/square) were cleaned by ultrasonication in a series of solvents including dichloromethane, methanol, acetone, and Milli-Q water at 15 min each, followed by a 5-minute oxygen plasma cleaning (Harrick PCD 32G). Silicon substrates (research grade ⟨100⟩, SiTech) were similarly etched to provide a hydrophilic silica surface.

Film assembly was automated with a Carl Zeiss HMS DS-50 slide stainer. The substrates were exposed to polycation solution for 15 min, rinsed for 4 min in several Milli-Q water baths, then exposed to polyanion solution for 15 min and again rinsed. This cycle was repeated for the desired number of layer pairs. (PXV/SPS) systems employed a base coat of $(LPEI/SPS)_2$ and (PXV/PEDOT:SPS) systems employed a base coat of $(LPEI/PEDOT:SPS)_2$ to promote adhesion. After assembly, a ~1-mg sample was collected from films of several thicknesses by scraping, dried under vacuum at 150 °C for 48 h, and then sent for C−H−N−S elemental analysis at Desert Analytics, Inc.

Electrochemical potential control and current sensing were performed using an EG&G 263A potentiostat/galvanostat. Electrolyte was 0.1 M NH_4Cl, counter electrode was 4 cm^2 platinum foil, and reference was K-SCE. CV was performed by cyclic between 0.5 V and −0.9 V at 0.025 V/s, 0.05 V/s, 0.1 V/s, and 0.2 V/s. DPSCA was performed by stepping between −0.9 V and 0.5 V vs SCE, with 10 s per step and 20 s per cycle. Approximately 20 cycles were performed sequentially before the measurement cycle. Spectral characterization was performed with a rail-mounted Oriel UV−Vis spectrophotometer with a 300 L/mm, 300 nm blaze grating and InstaSpec IV CCD. Films assembled atop ITO were positioned in a quartz cell with electrolyte, platinum working electrode, and SCE.

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