Chem. Mater. **2001,** *13,* 4469−4472

Electrochromic Properties of Laminate Devices Fabricated from Polyaniline, Poly(ethylenedioxythiophene), and Poly(*N*-methylpyrrole)

Jeffrey L. Boehme,† Dhurjati S. K. Mudigonda, and John P. Ferraris*

Department of Chemistry, The University of Texas at Dallas, P.O. Box 830688,
Richardson, Texas 75083-0688

Received April 20, 2001. Revised Manuscript Received August 23, 2001

Electrochromic devices composed of laminated polymer layers, as the working electrode, and vanadium pentoxide, as the counter electrode, were prepared and evaluated. Three different laminate systems were investigated using various combinations of poly(3,4-ethylenedioxythiophene), poly(*N*-methylpyrrole), and polyaniline as the active electrochromes. The color change of the laminate devices was measured using spectrocolorimetric techniques and analyzed using Commission Internationale de l'Eclairage 1931 (*x*, *y*)-chromaticity coordinates. The device's observed colors in their fully doped and dedoped states are found to be linearly dependent on the color coordinates of the two individual polymers that comprise the laminate.

Introduction

Significant interest in electrochromic materials arises from their potential applications as active materials for smart windows, rearview mirrors, and large area displays.[1] Some of these applications have already been successfully commercialized. However, for many other potential applications, there remains a great need to achieve control over the relevant electrochromic colors. Although there have been some efforts in this direction, only a few systematic studies have been reported in the literature.[2−4] Our group has focused on achieving this control over electrochromic properties through various novel strategies.[5−8] These strategies can be classified into chemical and physical methods. Utilizing chemical methods such as copolymers or discrete electrochromes, we have shown that electrochromic properties of the parent system can be deliberately and systematically altered. Similar control over the electrochromic properties was achieved through a simple concept of making polymer blends of two homopolymers with distinct electrochromic properties.

Another way of combining properties of two materials is to form bilayers. Earlier reports on bilayers of conducting polymers have focused on studying the ion permeability of these layers.[9−15] In this paper, we discuss a technique based on the above concept to achieve tailorable electrochromism. When layers of polymers with well-defined electrochromic properties are placed on top of one another, the observed color should be different from those of the individual homopolymers. Furthermore, a device consisting of laminate layers should also exhibit visual properties that follow basic color subtraction theories. Thus, the resulting color could theoretically be determined even before a device is assembled. Recent investigations into tailoring electrochromic properties have focused around composite films of polyaniline and polythiophene derivatives.[16,17] We chose to investigate poly(ethylenedioxythiophene), PEDOT, poly(*N*-methylpyrrole), PN-MeP, and polyaniline, PANI, since their electrochromic properties have been extensively studied.[18,19] PEDOT exhibits a blue to transparent color change upon oxidation, whereas PN-MeP changes from transparent to brown, and PANI transforms from green to blue.

---

* To whom correspondence should be addressed.

† Current address: Physical Sciences Inc., 20 New England Business Center, Andover, MA 01810-1077.

(1) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism: Fundamentals and Applications*; VCH: New York, 1995.

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

(3) Reddinger, J. L.; Sotzing, G. A.; Reynolds, J. R. *J. Chem. Soc., Chem. Commun.* **1996**, 1777.

(4) Stilwell, D. E.; Park, S. *J. Electrochem. Soc.* **1989**, *136*, 427.

(5) Meeker, D.; Mudigonda, D.; Osborn, J.; Loveday, D.; Ferraris, J. *Macromolecules* **1998**, *31*, 2943.

(6) Mudigonda, D.; Loveday, D.; Ferraris, J. *Synth. Met.* **1997**, *84*, 349.

(7) Brotherston, D.; Mudigonda, D. S. K.; Osborn, J. M.; Belk, J.; Chen, J.; Loveday, D. C.; Boehme, J. L.; Ferraris, J. P.; Meeker, D. L. *Electrochim. Acta* **1999**, *44*, 2993.

(8) Mudigonda, D. S. K.; Boehme, J. L.; Brotherston, I. D.; Ferraris, J. P.; Meeker, D. L. *Chem. Mater.* **2000**, *12*, 1508.

(9) Wojda, A.; Maksymiuk, K. *J. Electroanal. Chem.* **1997**, *424*, 93.

(10) Hillman, A. R.; Mallen, E. F. *J. Electroanal. Chem.* **1990**, *281*, 109.

(11) Hillman, A. R.; Mallen, E. F. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2209.

(12) Hillman, A. R.; Mallen, E. F. *J. Electroanal. Chem.* **1991**, *309*, 159.

(13) Torres, W.; Fox, M. A. *Chem. Mater.* **1990**, *2*, 306.

(14) Maksymiuk, K. *J. Electroanal. Chem.* **1994**, *373*, 97.

(15) Pyo, M.; Reynolds, J. R. *J. Chem. Soc., Chem. Commun.* **1993**, 258.

(16) Yamasaki, S.; Terayama, K.; Yano, J. *J. Electrochem. Soc.* **1996**, *143*, 9, L212.

(17) Morita, M. *Makromol. Chem.* **1993**, *194*, 2361.

(18) Pei, Q.; Zuccarello, G.; Ahlskog, M.; Inganas, O. *Polymer* **1994**, *35*, 7, 1347.

(19) Bjorklund R.; Lundtröm, I. *J. Electron. Mater.* **1985**, *14*, 1, 39.

10.1021/cm010346o CCC: $20.00

Colorimetric Theory

Color perception of an object is clearly different from observer to observer. This ambiguity can be attributed to changes in ambient lighting conditions and slight variations in the sensitivity of the eye from one observer to another. Therefore, colorimetry, a quantitative and repeatable means to measure color, must be applied to limit these uncertainties.

The retina is composed of photoreceptors, which create electrochemical signals that are transported to the visual cortex via the optic nerve resulting in the observer's perception of the color stimulus. According to opponent color theory, specialized cells in the visual cortex can either interpret red/green signals or blue/yellow signals.[20] The information acquired by the visual cortex allows one to describe an object's observed color stimulus as a vector, **Q**, in a color space.

In 1931, the Commission Internationale de l'Eclairage (CIE) standardized the tristimulus values *X*, *Y*, and *Z* whose unit vectors map a three-dimensional metric vector space (eq 1)

$$\vec{Q} = X\hat{X} + Y\hat{Y} + Z\hat{Z} \qquad (1)$$

The three tristimulus values, *X*, *Y*, and *Z*, are calculated by integrating the spectral reflectance of the object, the spectral power distribution of the illuminant, and the color-matching functions of the human eye over a defined wavelength range.[21] The color-matching functions and the spectral power distribution of the illuminant are standardized by the CIE and limit the ambiguities associated with a change in observers and lighting conditions.

The representation of color stimuli in *XYZ* tristimulus space as vectors is informative but usually not convenient in practice. Therefore, a two-dimensional representation is commonly preferred. One such representation is the 1931 CIE (*x*, *y*)-chromaticity space.

There is a region, or gamut, in a chromaticity diagram where all color stimuli must reside. This region's boundary is called the spectral locus and is dependent on the color-matching function of the human eye. The purple line is a line that connects the smallest wavelength detectable with the eye (blue) to the largest observable wavelength (red).

Some important predictability information can be acquired through the investigation of a (*x*, *y*)-chromaticity diagram. When two independent color stimuli are present, they are represented by two distinct points on the diagram. When one of these colors is subtracted from the other, the resulting chromaticity coordinates of the color stimulus must lie on the line joining the two original chromaticity coordinate pairs. Therefore, if one knows the chromaticity coordinates of two electrochromic polymers, one could determine the approximate hue of a device fabricated from laminate layers of these polymers.

Experimental Section

Model devices were fabricated in a three-step process. The first step involves the formation of the working electrode, which contains the electroactive material(s). The construction of the laminated working electrodes was dictated by the processability of the polymers. Each polymer was deposited by the most convenient method. The thickness of one of the polymer layers was kept constant, and that of the other was varied in a systematic way to afford fine-tuning of the observed color in the resulting laminate devices. Film thickness measurements were performed on a Sloan Dektak IIA profilometer. Average thickness was calculated by performing measurements across the films. Three systems consisting of a total of nine different solid-state electrochromic devices were fabricated and investigated: system 1, three devices containing PEDOT as the outer layer on top of varying thicknesses of the inner layer, PN-MeP; system 2, three devices containing various amounts of the outer layer, PANI, on top of the inner layer, PEDOT; system 3, three devices containing the outer layer PANI on top of varying thicknesses of the inner layer, PN-MeP.

Also, three devices consisting of only the individual polymers, PEDOT, PANI, and PN-MeP, as the working electrodes were fabricated. UV−vis absorption spectra were obtained on a Perkin-Elmer Lambda 9 spectrophotometer on all working electrodes before device assembly to ensure the presence of both homopolymers.

System 1: Poly(ethylenedioxythiophene)/Poly(*N*-methylpyrrole). N-MeP was electrochemically polymerized onto a piece of indium tin oxide coated with poly(ethylene terephthalate), PET (Altair O, Southwall Technologies, Inc.), in a three-electrode cell. An aqueous solution containing the monomer (0.05 M N-MeP) and the electrolyte (0.01 M sodium polystyrene sulfonate, Aldrich, Na-PSS) was used for polymerization. With the use of an EG&G PARC 273A potentiostat, a constant potential of 1.0 V was applied with respect to a Ag/Ag^+ reference for different lengths of time to vary the thickness of the polymer film. Deposition times of 60, 120, and 180 s were used in this study. Before the PN-MeP electrode was removed from the electrolyte, the potential was reduced to 0 V. The resulting neutral polymer films were air-dried overnight. Baytron P, a suspension containing PEDOT and Na-PSS in water, was obtained from Bayer. This solution was then cast onto the dried PN-MeP electrodes. The resulting laminated electrodes were then dried again in atmospheric conditions.

System 2: Polyaniline/Poly(ethylenedioxythiophene). Baytron P was cast onto ITO/PET and allowed to air-dry. A mixture of 38% polyaniline, 51% xylene, and 11% butylcellusolve was obtained from Monsanto (currently available from DuPont as Zypan). This mixture was too viscous for spin-coating and was therefore further diluted using xylene in a 6:1 volumetric ratio of xylene to the PANI mixture. A 0.5 mL portion of the resulting diluted mixture was then deposited onto the PEDOT electrodes using a spin-coater. To vary the thickness of the PANI layer, depositions occurred at 1000, 1500, and 2000 rpm for 1 min. The resulting electrodes were allowed to air-dry overnight.

System 3: Polyaniline/Poly(*N*-methylpyrrole). N-MeP was electrochemically polymerized onto ITO/PET at a constant potential of 1 V for 60, 120, and 180 s. The growth solution was composed of 0.05 M N-MeP and 0.01 M Na-PSS in water. After polymerization, the films were returned to their neutral state by applying a 0 V potential until the cell current dropped to zero. The films were then removed from the growth solution and air-dried overnight. PANI was spin-coated over the air-dried PN-MeP films using 0.5 mL of the diluted Monsanto mixture at 1500 rpm. The resulting laminate electrodes were dried overnight in atmospheric conditions.

Counter Electrodes. Since the electroactive materials deposited on the working electrode undergo an oxidative process, a corresponding reductive process must occur in the finished devices to ensure charge neutrality. Therefore, the second step in the device fabrication involves the construction of the counter electrode. For these studies, a vanadium pentoxide film was used as the counter electrode material. The vanadium oxide, which can be easily formed by a sol−gel process, exhibited slight color change upon doping and inter-

---

[20] Zelanski, P.; Fisher, M. P. *Color*; Prentice-Hall: Englewood Cliffs, NJ, 1989.

[21] Wyszecki, G.; Stiles, W. *Color Science: Concepts and Methods, Quantitative Data and Formulae*, 2nd ed.; John Wiley & Sons: New York, 1982.

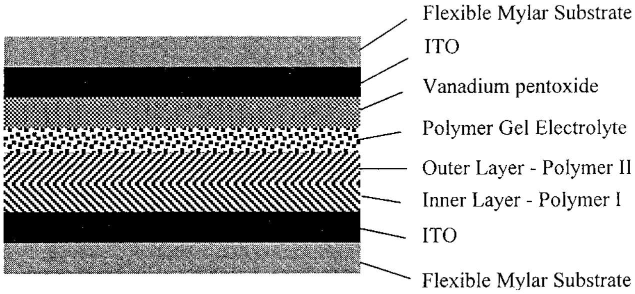

Figure 1. Typical laminate device construction.

calated lithium ions quite readily. To fabricate the vanadium oxide film, a solution containing vanadium isopropoxide (Alfa chemicals) and isopropyl alcohol in a 1:150 volumetric ratio was formed. A 1 mL portion of the resulting sol−gel was then spin-coated onto a blank ITO/PET substrate at 2000 rpm. The resulting film was then dried in a vacuum oven at 50 °C overnight.

Polymer Electrolyte. The final step in the device fabrication is the deposition of the polymer gel electrolyte. The polymer electrolyte used in this investigation was prepared by mixing poly(methyl methacrylate) ($M_w = 120\,000$) (500 mg), propylene carbonate (1 mL), and ethylene carbonate (2 g) in acetonitrile (3 mL). Lithium tetrafluoroborate (100 mg) was then added, and the mixture was stirred overnight. Model devices were fabricated by first spin-coating 0.2 mL of the gel electrolyte onto the vanadium oxide counter electrodes at 1000 rpm for 1 min. The resulting electrodes were air-dried for 20 min to allow the acetonitrile to evaporate. The devices were then assembled in a sandwich fashion as shown in Figure 1.

Color Measurements. Colorimetric measurements were performed on a HunterLab MiniScan XE spectrocolorimeter with the large view area option with a D_{65} (daylight) illuminant. The MiniScan system was controlled through a computer interface using HunterLab Universal software. The color data were given in CIE 1931 *XYZ* tristimulus values using the 10° standard observer model. The tristimulus coordinates were then converted into (x, y)-chromaticity coordinates using eqs 2 and 3

$$x = \frac{X}{X + Y + Z} \tag{2}$$

$$y = \frac{Y}{X + Y + Z} \tag{3}$$

Results and Discussion

For all the systems used in the study, polymers were deposited onto the ITO/PET either by electrochemical polymerization from aqueous monomer solutions or by spin-casting the polymer solution. Both these techniques resulted in homogeneous polymer films. The thickness of the films deposited depended on the deposition time for electrochemical polymerization and spin rate for the process of spin-casting. It has been shown earlier that the amount of polymer deposited during the process of electropolymerization is directly proportional to the deposition time.[24] For the process of spin-casting, the spin rate determines the thickness of the polymer film. The film thickness h is inversely proportional to the spinning speed f ($h \propto 1/f$) for solutions whose viscosity is constant during spinning, and for solutions whose viscosity changes during spinning, the relation is $h \propto 1/f^{1/2}$.[25] The average thickness values for each of these laminate electrodes is listed in Table 1. As expected, in case of electrochemical deposition, the average film thickness increases with deposition time and in case of spin-casting, the average film thickness decreases with spinning speed. The solid-state UV−vis absorption spectra of the laminate electrodes and the individual polymer electrodes were recorded in the wavelength range of 350−1200 nm. The absorption spectra of the laminate electrodes were found to be a simple sum of the spectra of the two individual polymers that make up the laminate, thus indicating the presence of both the polymers in the laminate.

Table 1

laminate system	avg film thickness (μm)
System 1: PEDOT/PNMeP	
PEDOT on PNMeP (deposition time 60 s)	1.08
PEDOT on PNMeP (deposition time 120 s)	1.15
PEDOT on PNMeP (deposition time 180 s)	1.24
System 2: PANI/PEDOT	
PANI (spin rate 2000 rpm) on PEDOT	1.58
PANI (spin rate 1500 rpm) on PEDOT	1.71
PANI (spin rate 1000 rpm) on PEDOT	1.8
System 1: PANI/PNMeP	
PANI on PNMeP (deposition time 60 s)	1.61
PANI on PNMeP (deposition time 120 s)	1.74
PANI on PNMeP (deposition time 180 s)	1.82

Table 2

polymer	E_{ox} (V) vs NHE
PANI[22]	0.3
PEDOT[23]	0.39
PN-MeP[9]	0.54

The three polymers used in the present study have oxidation potentials (E_{ox}) that are similar (Table 2). Ideally, choosing polymers with similar oxidation potentials would help in avoiding electrochemical side reactions that can occur with over oxidation. Previous studies on the rectifying properties of bilayers of polypyrrole/polybithiophene and polybithiophene/polypyrrole have found that the outer layer can be oxidized only when the inner layer is in a conducting state.[13] For the laminates studied here, the maximum difference in oxidation potential between two polymers was ~0.2 V. Since we simultaneously switch both polymers on or off in the devices (±2 V, vide infra), we were not concerned as much with the relative placement of the layers as we were about potential over oxidation of the more easily oxidized material. The latter also proved to be a non issue as the devices could be repeatedly cycled between their doped and undoped states. Among the three homopolymers used for the study, PANI exhibits the lowest oxidation potential. PN-MeP, on the other hand, exhibits the highest oxidation potential (Table 2). Thus, the absorption spectra of single electrodes of PANI were recorded with increasing applied potential. The absorption spectra did not show any variance at values above the oxidation potential of PANI (0−0.6 V vs NHE).

Color measurements of the individual polymer devices and laminate devices were taken in the doped and

---

(22) Malinauska, A.; Holze, R. *J. Electroanal. Chem.* **1999**, *461*, 184.

(23) Lapkowski, M.; Pron, A. *Synth. Met.* **2000**, *110*, 79.

(24) Rudge, A.; Raistrick, I.; Gottesfeld, S.; Ferraris, J. P. *Electrochim. Acta* **1994**, *39*, 273.

(25) Hikita, M.; Yoshimura, R.; Usui, M.; Tomaru, S.; Imamura, S. *Thin Solid Films* **1998**, *331*, 303.

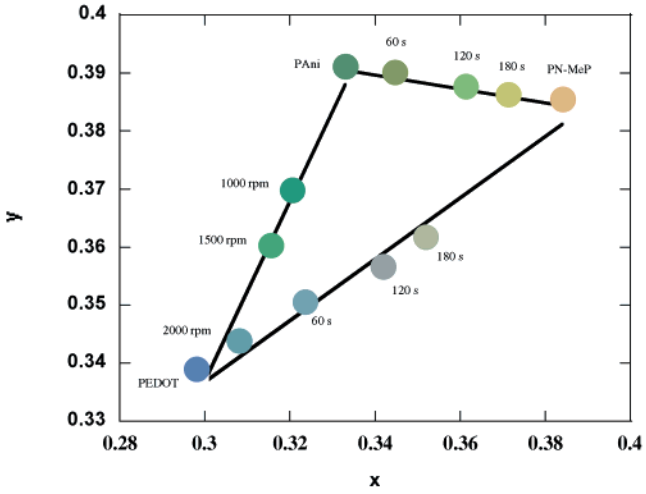

Figure 2. The (*x*, *y*)-chromaticity coordinates for homopolymers and laminate devices in their neutral states with their corresponding colors.

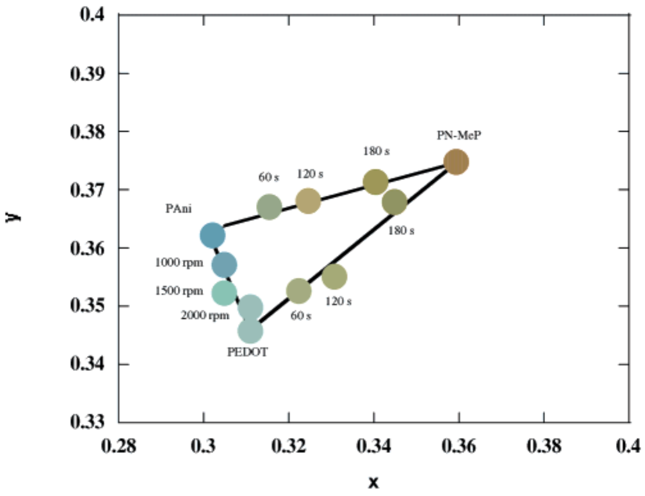

Figure 3. The (x,y)-chromaticity coordinates for homopolymers and laminate devices in their doped states with their corresponding colors.

dedoped states. This was achieved by switching the applied potential from 2.0 to −2.0 V. Devices subjected to applied potentials above or below these levels showed no apparent change in their observed color. Thus, the maximum and minimum potentials for each device correlate to fully doping and fully dedoping the devices, respectively.

Figure 2 shows a CIE 1931 (*x*, *y*)-chromaticity diagram of devices of all three systems in their neutral state. The thickness of the deposited polymer film is controlled either by increasing the electrochemical deposition time or by changing the spin rate. The time shown in seconds corresponds to the electrochemical deposition length of N-MeP. Similarly, the revolutions per minute represent the spin-coater's velocity upon deposition of PANI. The data show that the (*x*, *y*) coordinates of the laminate devices in each system lie between the individual polymers making up the laminate, as expected. Therefore, the observed color of the laminated devices is the subtractive color combination of the two individual polymers. Furthermore, as the amount of one of the polymers increases, the color coordinates of the laminate approach the coordinate pair of that polymer. The coordinates of the individual polymers and their laminates in each case vary linearly with composition with correlations higher than $R = 0.98$. The results shown in Figure 2 demonstrate the applicability of laminates to tailor, in a controlled and predictable way, the observed color of electrochromic devices.

Similar arguments are true for these devices in their doped state. Figure 3 displays the chromaticity coordinates of the individual polymer and laminate devices. Again, the laminates lie between the coordinates of the homopolymers and the trend is linear in nature with correlations greater than 0.94. Figure 3 indicates that under potential control, the laminated device's observed color can also be considered as an apparent subtractive color combination of the two individual doped polymers. Using this technique, one could access a precise location in the triangular (*x*, *y*)-chromaticity space formed by the color coordinates of the individual polymers and laminates. This could be possible with laminates utilizing all three components in a specific ratio. Further efforts are underway to show the control of electrochromic properties through multiple-layered laminates.

Conclusions

Electrochromic devices composed of laminated layers of polyaniline, poly(ethylenedioxythiophene), and poly(*N*-methylpyrrole) were constructed. The observed color of these devices was measured by spectrocolorimetric techniques and analyzed in terms of their 1931 CIE (*x*, *y*)-chromaticity coordinates. The color coordinates were then compared to nonlaminated devices, each containing a single, homogeneous layer of PANI, PEDOT, and PN-MeP as the working electrode. As is evident from the strong linear correlation in the CIE 1931 (*x*, *y*)-chromaticity diagrams for both the fully doped and dedoped states, the fabrication of devices with laminate layers of electrochromic polymers with known properties is a viable and predictable means to adjust the observed color of an electrochromic device. Furthermore, by varying the thickness of one of the electrochromic polymers, different shades of the observed color can be achieved.

Acknowledgment. We gratefully acknowledge the financial support of the Office of the Secretary of Defense Augmentation Award for Science and Engineering Research Training (AASERT).

CM010346O