Microporous Patterned Electrodes for Color-Matched Electrochromic Polymer Displays

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The emergence of electroactive and conducting polymers offers new opportunities for the design of materials for electrochromic devices (ECDs). Of these, poly(3,4-alkylenedioxy-thiophene)s (PXDOTs) and their derivatives exhibit the most promising electrochromic (EC) properties. Here, we report the use of highly porous metallized membranes which allow the production of patterned, rapid-switching, reflective ECDs. Using poly(3,4-ethylene-dioxithiophene) (PEDOT), poly(3,4-propylenedioxythiophene) (PProDOT), and the dimethyl-substituted derivative PProDOT-Me$_2$ as the active EC materials, we have obtained switching times of 0.1−0.2 s (5−10 Hz) to achieve full EC contrast. These polymers yield reflective contrast values of up to 90% in the NIR and ~60% in the visible regions. In addition, the ECDs were switched repetitively 180 000 times with less than 10% contrast loss. We have also demonstrated a 2 × 2 pixelated display device built using shadow mask patterning. Two cathodically coloring polymers which exhibit two distinct colors in their neutral states (blue and red) are patterned on a porous metallized electrode to yield a highly contrasted surface. Upon simultaneous oxidation of these polymers, the bi-color surface is rapidly bleached presenting a uniform shiny gold surface.

Introduction

Electrochromic (EC) materials exhibit a reversible change in their electronic absorption properties, with corresponding distinctive color changes, driven by a change in the electrochemical potential. Transition metal oxides have been intensively studied as electrochromic materials because of their switchable absorptive properties in both the visible and near-infrared (NIR).[1−3] The emergence of electroactive and conducting polymers (EAPs) where the band gap can be tuned through the full visible spectrum offers new opportunities for the design of materials for electrochromic devices (ECDs).[3−7] Polymeric EC materials are promising candidates for applications such as information displays, advertising, switchable windows, and thermal mirrors. The broad spectral absorbances of EAPs, which can range from the UV through the visible, NIR, mid-IR, far IR, and into the microwave region, have resulted in the need to modify the definition of electrochromism to include this multi-spectral window of photon energies.[8,9]

Our group has developed a number of EC polymers based on polythiophenes and polypyrroles[10−14] with band gaps ranging from ca. 1.0 eV (1200 nm) to over 3.0 eV (400 nm), effectively spanning the full visible region. Of these, the poly(3,4-alkylenedioxythiophene)s (PXDOTs) and poly(3,4-alkylenedioxypyrrole)s (PX-DOPs) and their derivatives exhibit the most promising electrochromic properties because their electron-rich nature gives them especially low redox switching potentials.[15−20] These polymers allow electrochemically stable transmissive/absorptive ECDs that exhibit fast switching times and high contrast ratios in the visible and NIR range. Band gap control is an important strategic key in the construction of dual-polymer-based ECDs in which a low band gap (cathodically coloring) polymer is matched with a high band gap (anodically

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coloring) polymer to obtain a high degree of contrast during the switching process.[21]

Poly(3,4-ethylenedioxythiophene) (PEDOT), poly(3,4-propylenedioxythiophene) (PProDOT), and the dimethyl derivative of PProDOT (PProDOT-Me$_2$) have emerged as promising candidates for polymeric ECDs. As an example, PProDOT-Me$_2$ exhibits a high transmittance contrast in the visible region (350−800 nm) with a $\Delta\%T = 78\%$ at $\lambda_{max} = 578$ nm and a colorimetrically measured luminance contrast of 60%. Electrochromic switching of films of PProDOT-Me$_2$ tuned for optimal contrast occurs in less than 400 ms.[12,20]

Recently, others and we have utilized a dual-polymer configuration for the construction of reflective ECDs.[22−24] The outward-facing active electrode is convenient for obtaining reflectance characterizations and for modifying the optical response from a surface. In our initial studies, gold-coated Mylar with parallel slits cut to allow for ion transport between the polymer film and a counter electrode hidden beneath were used. These reflective ECDs exhibit high EC contrasts in the visible, NIR, and mid-IR regions of 55, 80, and 50% (specular response), respectively, and maintain their electroactivity for tens of thousands of redox switching cycles.[24] In our slitted devices, we found that the switching was quite slow. This type of device construction is applicable to thin and flexible electrochromic platforms.[25]

Here, we report the use of highly porous metallized membranes in patterned reflective ECDs that switch rapidly. Figure 1 illustrates the device design as initially developed by Bennet and Chandrasekhar.[22,23] Gold-patterned porous electrodes were prepared by means of a shutter mask during the metal vapor deposition process (MVD) allowing the deposition and independent addressing of more than one active electrode. With PEDOT, PProDOT, or PProDOT-Me$_2$ as the active EC materials, switching times were 0.1−0.2 s (5−10 Hz) to achieve full EC contrast. During the redox switching process, the charge-carrying ions easily migrate from the polymer through the thin porous membrane, giving a small distance between electrodes.

Experimental Section

Chemicals. Propylene carbonate and acetonitrile were purchased from Aldrich, distilled, and dried before use. LiClO$_4$ (99%, purity) was purchased from Fluka and used without further purification. 3,4-Ethylenedioxythiophene (EDOT) was obtained from Agfa Gaevert and distilled prior to use. 3,4-Propylenedioxythiophene (ProDOT), its dimethyl derivative (ProDOT-Me$_2$), and 1,4-bis(2-ethylenedioxythiophene)-2,5-di-dodecyloxybenzene [BEDOT-B(OC$_{12}$H$_{25}$)] were synthesized as reported previously.[11,12,26,27]

Electrochemistry. A three-electrode cell containing a gold-coated membrane as the working electrode, a platinum flag as the counter electrode, and a silver wire as the pseudo-
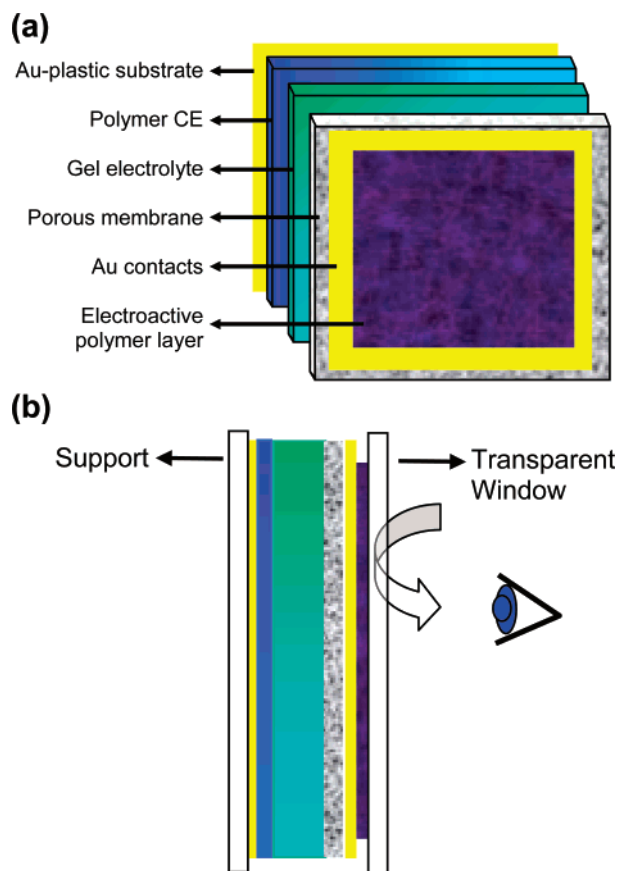
Figure 1. (a) Schematic representation of a reflective-type electrochromic device (ECD) using a porous membrane electrode. (b) Cross section of the ECD.

reference electrode were used for electrodeposition of polymer films via potentiostatic or potentiodynamic methods. All electrochemistry was performed using an EG&G PAR model 273A potentiostat/galvanostat. The pseudo-reference electrode was calibrated vs. ferrocene and the PXDOT films deposited at 1.27 V vs. Fc/Fc$^+$ from a 0.01 M monomer solution in 0.1 M LiClO$_4$/PC electrolyte.

Metal Vapor Deposition. Gold deposition (99.99%) on porous membranes (polycarbonate, 10-μm pore size, Osmonics Inc.) was carried out using a high-vacuum thermal evaporator (Denton DV-502A). During the metallization process, the membrane (5 × 5 cm) was sandwiched between a clean piece of glass (5 × 5 cm) and a shutter mask to pattern the membrane surface. The metallization was carried out at 10^{-6} to 10^{-5} Torr with a deposition rate of 5.0 Å/s to yield shiny Au surfaces with a thickness of 50 nm, as measured by a DEKTAK 3030 profilometer.

Gel Electrolyte. The gel electrolyte was prepared from an acetonitrile solution containing poly(methyl methacrylate) and LiClO$_4$ as described previously.[24] The acetonitrile was slowly evaporated under stirring and a few drops of propylene carbonate were added to decrease the vapor pressure of the gel electrolyte, yielding a highly conducting transparent gel (~3 mS/cm).

Device Construction. Films of either PEDOT or PPro-DOT-Me$_2$ were electrochemically deposited onto the counter electrode (CE) consisting of a 1.5 × 2.0 cm Au-coated plastic sheet using a deposition charge of ~150 mC from a 0.1 M LiClO$_4$/PC electrolyte. The active layer of PEDOT, PProDOT, or PProDOT-Me$_2$ for the front working electrode (WE) was deposited using 100 mC on a metallized porous membrane. The CE was placed, face-up, onto a transparent plastic substrate and a thin layer of gel electrolyte was homogeneously applied, and the polymer-coated membrane was placed face up on the CE. A few drops of gel electrolyte were also added on top of the active layer to ensure adequate swelling of the

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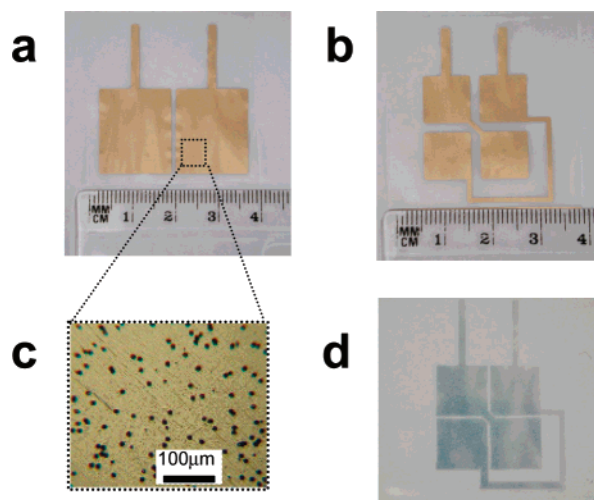
Figure 2. (a) Two gold pixels (1.5 × 2 cm) patterned on a polycarbonate (PC) membrane. (b) A 2 × 2 gold pattern (2 × 2 cm) on PC. (c) Magnification (80×) of the metallized membrane to show the unfilled pores. (d) Image of the pattern on the glass backing plate used during the evaporation process indicating that the gold passes through the membrane during deposition.

polymer. Finally, a transmissive window was placed over the outward facing active electrode to protect the polymer film.

Device Characterization. The characterization of the devices' optical properties was carried out in reflectance mode using a Cary 500 Varian UV−Vis−NIR spectrophotometer mounted to an integration sphere. A device without the active polymer layer, but otherwise with the same construction, was used as a reference. This reference accounts for the relatively low reflectance of gold at shorter wavelengths.

Results and Discussion

Electrode Patterning. To prepare porous, yet highly reflective, gold metal contacts for the electroactive polymers, vapor deposition was used through shadow masks onto polycarbonate membranes. Figure 2a and b shows two examples of patterned electrodes demonstrating the ease with which pixels of 1 × 1 cm could be attained. It is important to note that the pores within the membrane are not clogged during the deposition process because the film thickness (50 nm) is small compared to the pore size (10 μm). Figure 2c demonstrates this with a reflective optical micrograph of a membrane after the metallization process, clearly showing that the pores (black holes) are preserved. Figure 2d shows a photograph of the glass substrate on which the membrane had been placed during the gold deposition process. It is covered by the residue, or ghost image, of the gold which passed through the pores of the membrane. The gold surface has a total reflectance (%R) of ~90% throughout the NIR region with a measured diffuse reflectance (%R_d) of ~70% and a specular reflectance (%R_s) of ~20%. Although the PC substrate is quite transmissive in this region (~50%), the transmissivity drops to ~3% following the gold deposition. The films are conducting, with a surface resistance of $R \approx 5$ Ω/sq as measured by a two point probe conductivity meter. The resistance through the gold-coated porous membrane is >20 000 Ω.

Electroactive Polymer Deposition. Potentiostatic methods, where a constant potential is applied in a three-electrode cell configuration until the desired

**Table 1. Components Used in Construction of the Reflective Electrochromic Devices**

device	active layer	working electrode	counter electrode	environment
D1	PProDOT-Me$_2$	slitted	PEDOT	air
D2	PEDOT	porous	PEDOT	air
D3	PProDOT	porous	PEDOT	air
D4	PProDOT	porous	PProDOT	air
D5	PProDOT-Me$_2$	porous	PProDOT-Me$_2$	air
D5-inert	PProDOT-Me$_2$	porous	PProDOT-Me$_2$	argon
D6	PEDOT and P(BEDOT-B)	porous	PEDOT	air

amount of charge is passed, are the most convenient techniques for the electrochemical deposition of dioxythiophene-based polymers (PXDOTs) onto metallized membranes. Resulting films are well-adhered and have high integrity. PBEDOT-B(OC$_{12}$H$_{25}$)$_2$ was deposited more effectively using a potentiodynamic multi-sweep method between −0.6 and 0.9 V vs. Fc/Fc$^+$. The metallized membranes have low surface resistance values (5 Ω/sq), which minimize the effect of the ohmic drop along the electrode surface. The polymers are doped/dedoped easily on these highly conducting surfaces. In all cases the electrochemical behavior of the EC polymers was found to be stable upon several thousands of switches as reported previously.[24]

Device Design and Construction. To obtain good performance of the ECDs in terms of color contrast, it is necessary to pair the front WE active layer with a CE containing a higher amount of electroactive polymer. This combination allows the CE to serve as an electron sink and ion storage layer for the WE so that the electrochemical properties of the CE do not limit the optical contrast of the active layer. The identity of the polymer deposited onto the CE does affect the kinetic performance of the devices (for example, PEDOT switches more slowly than PProDOT-Me$_2$), yet has no influence on the steady-state properties of the devices (such as Δ%R) in the visible−NIR regions. Table 1 lists the components used in six poly(3,4-alkylenedioxythiophene)-based devices (D1−D6) examined in this study. D1 refers to results from a device that utilized a slitted WE previously published by our group.[24] D2, D3/D4, and D5 refer to devices constructed with PEDOT, PProDOT, and PProDOT-Me$_2$ as the active layers, respectively. Finally, D6 represents a dual-polymer PEDOT and PBEDOT-B(OC$_{12}$H$_{25}$)$_2$ reflective device with a 2 × 2 pixel configuration.

Spectroelectrochemical Characterization. Reflectance spectroelectrochemistry gives us the ability to probe the attenuation of reflectance from the metal electrode induced by the electroactive polymer in both the visible and near-infrared regions of the electromagnetic spectrum. Figure 3a demonstrates this by showing the reflectance (%R) of a PProDOT active layer (D3) device from 400 to 1600 nm in which the PProDOT is held in its two extreme redox states. This behavior is visually evident in Figure 3b and c. Photographs of the active layer in its neutral and oxidized forms show a deep blue/purple color or the gold metallic reflectivity, respectively. In the neutral state, the visible light reflectivity is low, with %R_{vis} approaching a minimum of ~20% at 600 nm, while the NIR reflectivity is high, with %R_{NIR} reaching values greater than 90%. Upon oxidation, the visible reflectivity increases. In this state,
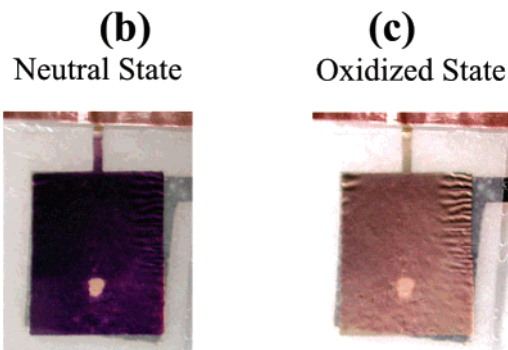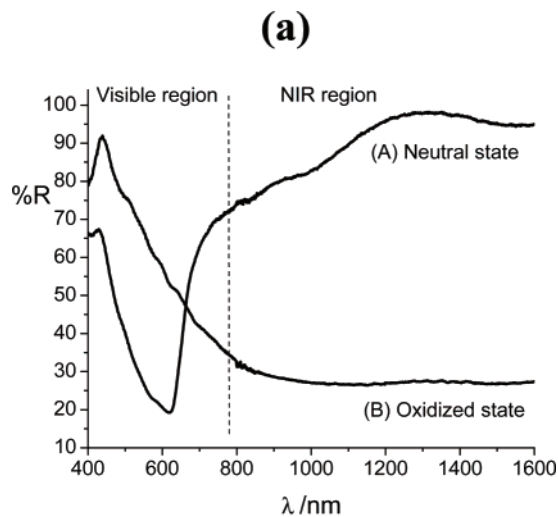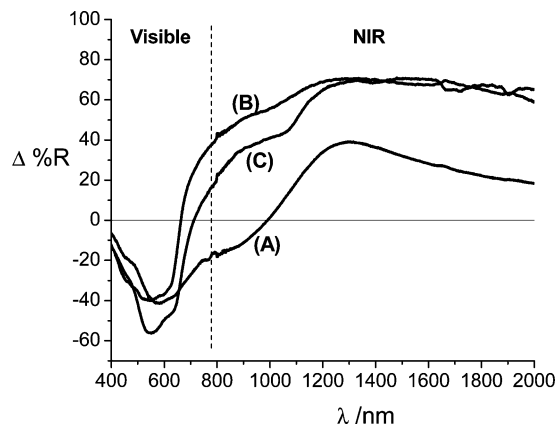
Figure 3. (a) Percent reflectivity (%R) of the neutral (A) and the oxidized (B) states of an active PProDOT layer device (D3 type) in the visible and the NIR region. The two photographs represent (b) the neutral and (c) the oxidized appearance of the active layer.

Figure 4. Reflectivity contrast ($\Delta\%R = \%R_{neutral} - \%R_{oxidized}$) spectra of D2 PEDOT (A), D3 PProDOT (B), and D5 PProDOT-Me$_2$ (C) devices. The CE polymer is the same as the active layer in each case.

Table 2. Optical Reflectivity Contrast in the Visible ($\Delta\%R_{VIS}$) and the NIR Range ($\Delta\%R_{NIR}$) for the Devices D1−D5[a]

	D1	D2	D3/D4	D5/D5-inert
VIS contrast ($\Delta\%R_{VIS}$)	55%	40%	40%	55%
λ (ΔR_{max}) (nm)	600	573	534	549
NIR contrast ($\Delta\%R_{NIR}$)	80%	40%	70%	70%
λ (ΔR_{max}) (nm)	~1750	1265	1260	1540
η^b (cm^2 C^{-1})	N/A	259	372	607
switching time[b] (ms)	3000	1050	400/170	100/90

[a] Also given are the composite coloration efficiency (CCE) and switching time values. [b] Data taken at 95% of the full %ΔR.

the gold surface becomes visible to the human eye. A concurrent drop in the reflectance through the NIR region is observed, leveling off between 20 and 25%. This inversion of the electrochromic response in the two regions of the spectrum is due to the depletion of the interband transition (in the visible) with oxidative doping of the polymer and transfer of the absorbance to longer wavelength, often referred to as polaron and bipolaron transitions.[28]

Neutral PEDOT, PProDOT, and PProDOT-Me$_2$ have similar electronic band gaps and λ_{max} values, giving them very similar colors. When these polymers are held in their neutral forms on the devices, they are difficult to distinguish. This behavior is evident in the visible region of the $\Delta\%R$ results of Figure 4 (here, $\Delta\%R = \%R_{neutral} - \%R_{oxidized}$, is the reflectivity contrast) which presents data for devices D2 (curve A), D3 (curve B), and D5 (curve C). At the same time, there is a difference in the NIR reflectivity contrast among the samples. PProDOT and PProDOT-Me$_2$ devices D3 and D5 have a higher contrast in the NIR ($\Delta\%R_{NIR}$ reaching 70%) relative to the PEDOT device D2. This improvement may be attributed to a more open morphology in the ProDOTs induced by the more sterically demanding rings, which allows higher levels of doping and, thus, higher contrast ratios.[29] The optical and electrochemical

switching properties for these devices are presented in Table 2. The PProDOT-Me$_2$ based devices, D1 and D5, possess higher $\Delta\%R$ values in the visible and NIR regions than the PEDOT and PProDOT based devices, D2 and D3. The similarity in the reflectivity contrast values observed for D1 and D5 is reassuring because two different substrates were used for the working electrode, specifically Au on slitted Mylar layer (used for D1) and an Au-coated porous polycarbonate membrane (used for D5). The enhanced reflectance contrast of the PProDOT-Me$_2$ device, relative to the PEDOT and unsubustituted PProDOT device, is consistent with earlier studies showing the dimethyl derivitization provides enhanced EC contrast in the polymer film.

One D5 type device (D5-inert in Table 1) was also constructed in a glovebox to ensure the absence of any oxygen and water. The spectroelectrochemistry of this PProDOT-Me$_2$ based device, shown in Figure 5, exhibits the same optical properties as the device built on the desktop, i.e. $\Delta\%R_{VIS} = 55\%$ and $\Delta\%R_{NIR} = 70\%$. When reduced (curve a), the spectrum exhibits a sharp absorption peak at $\lambda = 620$ nm (minimum of %R_{VIS}) corresponding to the $\pi-\pi^*$ transition of the polymer. Upon initial oxidation, at voltages between −1.0 and −0.4 V (curves a−d) there is little change in the color of the device ($\Delta\%R_{VIS}$ is low), whereas the 750−1200-nm NIR absorption increases. This band is attributed to absorption by the upper polaron band of the lightly doped polymer.[28] The visible absorption then decreases concurrently with further increase of NIR absorption

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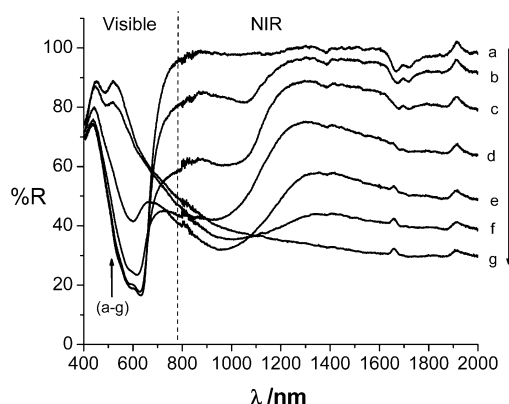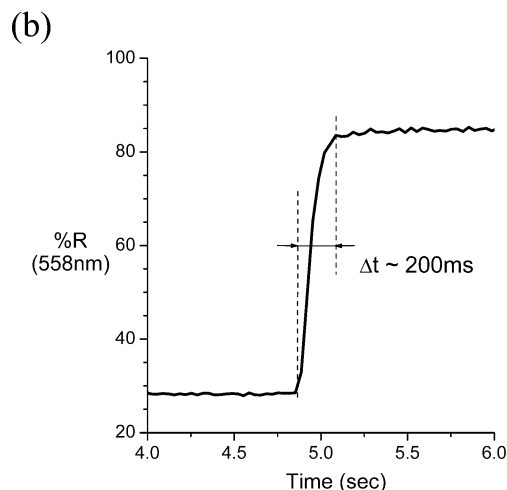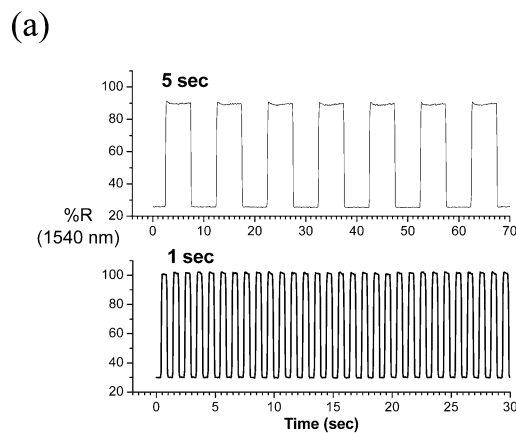
Figure 5. Spectroelectrochemistry of a PProDOT-Me$_2$ active layer in a D5-inert type reflective device: (a) −0.8, (b) −0.6, (c) −0.4, (d) −0.2, (e) 0.0, (f) +0.2, and (g) +0.4 V.

due to the bipolaron band and free charge carriers (curves d−g). The unusual behavior observed in the initial electrochromic switching properties of the device has also been reported using spray-cast films of soluble PProDOT derivatives on porous electrodes.[30] The first change in reflectivity in the visible window appears at −0.2 V ($\Delta\%R_{VIS}$ = 5%, compared to $\Delta\%R_{NIR}$ = 50%). This effect has also been reported by Chandrasekhar et al.[8,25] who attributed this particular behavior to a micrometer-scale morphology transition of the polymer during the redox switching which alters the scattering component of the reflected light at comparable wavelengths (1∼3 μm).

Electrochromic Switching and Stability. The use of a porous WE affords a homogeneous color change of the EC film as the device switches, as opposed to that observed for the device D1 in which the color change initiates at the slits and moves laterally across the surface of the electrode. The highly porous membranes allow the devices to be switched quite rapidly. In potential-step experiments performed on D4 shown in Figure 6a, the switching time is set every 5 s (upper) and 1 s (lower) between neutral and oxidized states. The reflectivity recorded in the NIR (1540 nm) shows the identical contrast at these two switching rates. The optical switch is fast and fully reversible. Examining a single transition more closely (Figure 6b), shows that the switching time between these two extreme redox states is ∼200 ms. Table 2 lists the switching times for the different devices. In general, when using the porous membrane electrodes the switching times are subsecond. Using the slitted electrode with 1−2 mm separation, a few seconds is required to attain the full transition. By replacing the slitted gold−Mylar electrode with a porous metallized substrate where ion diffusion lengths are minimized, a substantial improvement of the device's switching speed is obtained.

We investigated device stability by switching D5-inert (constructed and sealed under argon) 180 000 times between −1 and +1 V every 3 s while monitoring the %R at 1540 nm as shown in Figure 7. The initial contrast of the device is 75%, and throughout the experiment the oxidized form of the active layer gives a stable reflectivity of %R_{NIR} = 20%. At the same time,

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(a)

(b)

Figure 6. (a) Temporal change in %R (1540 nm) during electrochromic switching of a D3 type reflective device between −1 and +1 V every 5 (upper) and 1 (lower) seconds. (b) A single transition illustrating the switching time of the same device (−1 to +1 V, λ = 558 nm).
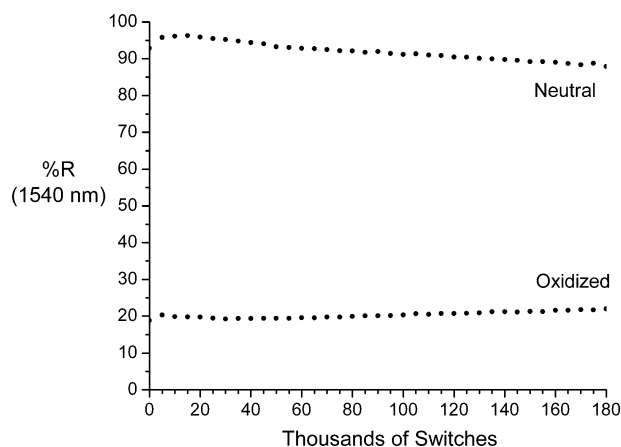
Figure 7. Long-term switching stability of a D5-inert type device switching from −1 to +1 V every 3 s.
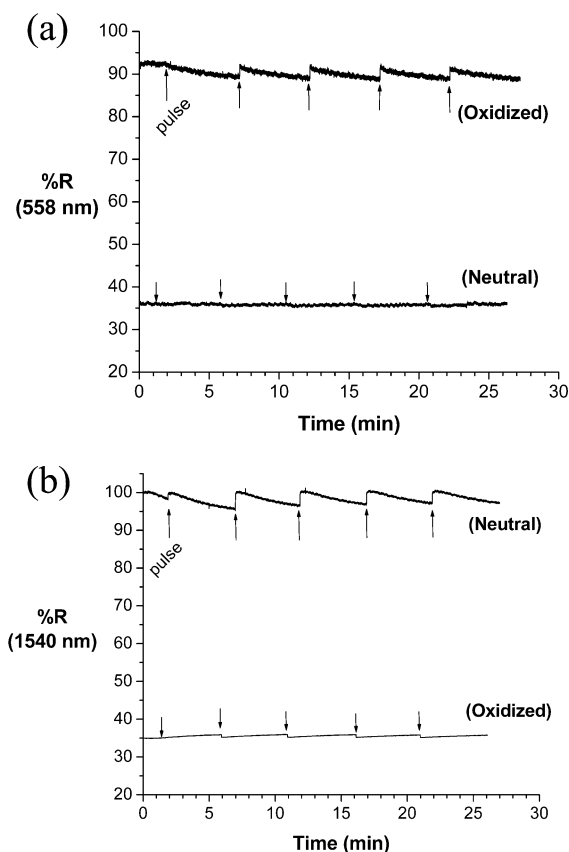
the reflectivity of the neutral form of the active layer slowly decreased from 95 to 89%. Following the completion of the 180 000 switches, the device was held at a constant voltage for an extended period of time and the initial contrast value was recovered in ca. one minute. Subsequently beginning the multiple switching process again shows this loss of contrast to be permanent as the contrast quickly drops to the value observed before the applied voltage annealing. By slowing the switching

speed to >3 s, the full original contrast could be retained. If the device contains air (oxygen and water) as in D5, the decrease in reflectance contrast occurs at a faster rate, with $\Delta\%R = 15\%$ after only 35 000 switches. Speculating on this issue, we note that this is a kinetic phenomenon and not an irreversible oxidation of the neutral polymer in air. Possible explanations include a decrease in the ionic conductivity in the cell due to slow evaporation of the solvent and a reorganization of the polymer film morphology slowing ion movement in the cell.

Composite Coloration Efficiency. The coloration efficiency is an efficient and practical tool to measure the power requirements of a device. In essence, it determines the amount of optical density change (ΔOD) induced as a function of the injected/ejected electronic charge (Q_d) during a potential step, i.e., the amount of charge necessary to produce the optical change in the polymer.[20] This concept has been used in electrochromic studies to compare ECDs containing different materials.[31,32] ΔOD is directly related to the amount of the doping/dedoping charge (Q_d) by the equation: ΔOD $= \eta\Delta Q_d$ where η (cm²/C) is the coloration efficiency at a given λ. We have developed[29] a practical method for measuring coloration efficiency, termed composite coloration efficiency (CCE), where the ΔOD during an electrochromic switch with a predetermined OD or color change desired for an application is used. The CCE experiment employed here consisted of a series of potentiostatic steps from the neutral state (-1 V) to the oxidized state ($+1$ V) while both the charge passing through the cell and the reflectivity are monitored as was shown in Figure 6b. Although these CCE experiments have previously been performed on transmissive-type devices, for this study we obtained values for reflective devices. To the best of our knowledge, these are the first coloration efficiency experiments performed with reflected light as opposed to transmitted light. For comparison, the coloration efficiencies (η) calculated for a 95% optical change and the associated switching times are listed in Table 2. The ΔOD = 95% switching times of the poly(3,4-alkylenedioxythiophene) derivatives decrease from PEDOT (1.05 s), to PProDOT (170 ms), to PProDOT-Me₂ (90 ms), and the CCE values of 259, 372, and 607 cm² C⁻¹, respectively, increase. These values are consistent with the transmission/absorption optical contrast ranking as published previously,[12] demonstrating the utility of this method for device studies. PProDOT-Me₂ exhibits a full contrast in ~200 ms in a porous-type device, as shown in Figure 6b. By using the thin porous membranes, the working and counter electrode distance is relatively small (50–100 μm), reducing ion diffusion lengths and shortening switching times. This device platform serves as an improved configuration for a reflective electrochromic cell.

Open Circuit Memory. One of the benefits of using an electrochromic material in a display as opposed to a light-emitting material is the EC memory effect. After setting the device in one color state and removing the electric field, it should retain that color with no further

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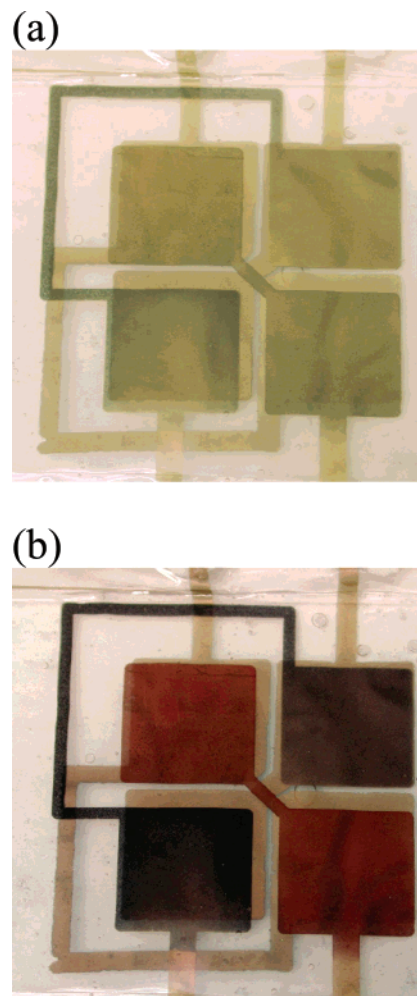

Figure 8. Open circuit memory of a D5-inert type device monitored by single-wavelength reflectance spectroscopy. A ±1 V pulse is applied for 1 s every 300 s to recover the initial reflectance. (a) Visible memory at 558 nm, and (b) NIR memory at 1540 nm.

current required; thus giving the device an open-circuit memory. In reality, ECDs require small refreshing charges to maintain the charge state because side reactions change the desired color. Figure 8 illustrates the variation of the reflectivity (%R) in the visible (a) and NIR (b) regions for both the oxidized and neutral states of PProDOT-Me₂ as the active layer for a device constructed and sealed under argon (D5-inert). In this experiment, we applied a pulse (-1 or $+1$ V for 1 s) and then held the cell in an open-circuit condition for 300 s while the reflectivity was monitored as a function of time. The change in %R tends to move the device to an equilibrium state and represents a loss of memory, i.e., the ability of the device to retain the reflectivity imposed by the pulse. We observe that the reflectivity of the neutral state is highly stable in the visible region (Figure 8a) and the oxidized state exhibited a $d(\% R_{VIS})/dt = 0.4\%$ min⁻¹ loss while being held at open circuit. The short 1-s pulse ($+1$ V) fully recovers the initial %R. This behavior is opposite in the NIR region. A $d(\% R_{NIR})/dt = 1\%$ min⁻¹ at open circuit is recorded when the device is set to its neutral state. However, the reflectivity loss is easily regained by a new voltage pulse. This study reveals that the sealed device can exhibit its full reflective properties with a brief supply of energy. Devices constructed and tested under ambient atmosphere exhibit similar behavior with a more rapid decrease in NIR reflectivity contrast ($d(\% R_{NIR})/dt > 1\%$ min⁻¹); again the 1 s: 1 V pulse recovers the initial electrochromic states.

Table 3. Energy Consumption Data for D1 and D5 Devices

	D1 slitted-type device	D5 porous-membrane device
ΔV	1 V	1 V
charge, Q	15 mC	2 mC
area	10 cm^2	3 cm^2
pulse time, t	10 s	1 s
energy, E/area	1.5 mJ/cm^2	0.67 mJ/cm^2

Energy Consumption. To establish the energy consumption of these devices, we compared the power necessary to switch a porous-type ECD (D5) to a slitted-type ECD (D1) with the slits separated by 2−3 mm. Table 3 contains the electrical characteristics of D1 and D5 used to calculate the energy (E) per unit area of ECD necessary to switch from one redox state to another. The energy is given by $E = \int \Delta V i(t) dt$, where ΔV is the pulse (1 V) applied to switch the device and $i(t)$ is the time-dependent current. Under these conditions, $E = \Delta V \int i(t) dt = \Delta V Q(t)$ with $Q(t)$ being the charge passed during the pulse. It is evident that using the porous electrodes substantially reduces the energy consumption when compared to a working electrode that has been prepared with slits. These data allow us to theoretically estimate the energy requirements of a large-area ECD assuming the iR losses are scalable to large areas. We consider a 1-m^2 surface-active device (mass of ca. 600 g/m^2) connected to a state-of-the-art 1-kg Li battery (400 kJ kg^{-1}, 111 W kg^{-1}).[33,34] A device like D5 will hold 8000 hours (1 year) in any single state. Then, a 1-m^2 ECD constructed as D1 and D5 will switch 26 000 and 60 000 times, respectively, using this battery. If switched 500 times during a day and held between switches in either one redox state, the 1-kg battery can operate a D5-type device for 50 days. As another example, we consider a device operation as described in the previous section where the ECD is refreshed with 1 s: 1 V pulses every 300 s to maintain either a bleached or colored state. The 1-kg battery can then refresh the same D5-type device ($A = 1$ m^2) 600 000 times (operation time of ~2100 days) with an energy consumption of only 0.67 J/pulse. For smaller devices, we consider operation of a 4 × 4 cm ECD display running on a lightweight (1.5 g) button-type alkaline battery (1.5 V, 100 mAh). Using this battery, the D5-type device will switch ~34 000 times. These numerous practical considerations suggest this reflective device platform based on PXDOT polymers can be considered for numerous applications.

Pixelated Lateral ECDs. The adaptability of the dual-polymer concept previously published for transmissive ECDs[21] to the lateral reflective ECDs was further explored. As a demonstration, we have developed a device where a high contrast active area and color matching concepts are simultaneously used (D6). Specifically, a patterned porous substrate composed of the 2 × 2 gold-square pattern originally shown in Figure 2b, is coated by two different polymers PEDOT and poly-[1,4-bis(2-(3,4- ethylenedioxythienyl))-2,5-didodecyloxy-benzene] [PBEDOT-B(OC$_{12}$H$_{25}$)$_2$]. In this instance, the electrodeposition of each polymer was first performed

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Figure 9. A 2 × 2 pixels patterned device (D6 type) comprising two cathodically coloring electrochromic polymers to provide color match/contrast. (a) Both polymers oxidized (bleached), and (b) both polymers reduced (colored).

on the separate electrodes and the films were reduced to provide the colors evident in Figure 9b. This device was constructed in a manner similar to that previously described, using a PEDOT counter electrode. When both polymers are oxidized they are visibly transmissive, presenting a uniform shiny gold surface. When they are reduced, they reveal the colors of the two polymers so that the device exhibits an optical surface contrast. PEDOT appears deep blue in its neutral form, whereas PBEDOT-B(OR)$_2$ is red. The PXDOT-based electrochromic polymer family (developed in our group) offers many possibilities to use dual-polymer lateral reflective ECDs where the materials can be matched for multicolored displays applications.

Conclusions

This paper presents the design of reflective platforms in which one or two electrochromic polymer(s) cover a reflective gold surface mounted onto a uniformly porous membrane using patterning techniques. Using a multilayer configuration, the electro-active platform was paired to a polymeric counter-electrode to realize reflective ECDs. The alkylenedioxythiophene-based polymers are suitable materials for broadband electrochromic

applications. Our goal was to utilize these materials on a porous ECD architecture to attain fast switching and high switching stability, and to have a low energy consumption for maintaining a specific color state. An interesting potential feature is to bring this technology to a smaller size level (submillimeter) with the goal of constructing a set of micro-pixels independently addressable in order to be more applicable to multicolor displays.

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