Combined Visible and Infrared Electrochromism Using Dual Polymer Devices**

By *Irina Schwendeman*, *Jungseek Hwang*, *Dean M. Welsh*, *David B. Tanner*, and *John R. Reynolds**

Electrochromic (EC) materials exhibit reversible and highly stable changes of their optical properties upon the application of a voltage.[1] Lately, the definition of electrochromism has been extended from that of a color change in the visible spectrum to a multi-spectral energy modulation that might cover ultraviolet (UV), near infrared (NIR), mid infrared (mid-IR), and microwave regions, with "color" corresponding to the response of detectors at these wavelengths.[2] There is a need for flexible flat-panel displays for use across a broad portion of the electromagnetic spectrum. The displays must be thin and able to cover objects of various shapes and sizes.[3] In addition, it can be useful when electrochromic materials exhibit large changes in reflectivity when switched between doped and undoped states, they should attain long lifetimes, and should display a rapid redox switching.[4]

There are several categories of EC materials that are capable of modulating both visible and IR light. Among them, highly disordered transition metal oxides have been studied frequently, due to their broad polaron absorption.[5] Difficulties encountered in processing, as well as relatively slow response times (many seconds to minutes), have opened up opportunities for the development of different types of EC materials.[6] Of these, redox electroactive and conducting

[*] Prof. J. R. Reynolds, I. Schwendeman, D. M. Welsh
Department of Chemistry
Center for Macromolecular Science and Engineering
University of Florida
Gainesville, FL 32611 (USA)
E-mail: reynolds@chem.ufl.edu

J. Hwang, Prof. D. B. Tanner
Department of Physics
University of Florida
Gainesville, FL 32611 (USA)

polymers represent a particularly attractive class of EC materials, as they are easily electrochemically deposited or spin-coated as thin films.[7] Some of the most promising conducting polymers for use in electrochromic devices (ECDs) are poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives.[8] These polymers exhibit a high degree of EC contrast in the visible region of the spectrum, extremely fast switching times, stability at elevated temperatures and an outstanding stability towards electrochemical cycling.[9] Moreover, their colorimetric properties can be tuned by chemical derivatization, opening up the possibility of obtaining a variety of materials with unique and complementary optical properties.[10]

Of the PEDOT derivatives synthesized in our laboratory, dimethyl substituted poly(3,4-propylenedioxythiophene) (PProDOT-Me$_2$) is an outstanding candidate for visible light ECDs.[11] PProDOT-Me$_2$ exhibits extremely high contrasts in visible light transmissive ECDs, with $\Delta\%T = 78\%$ at λ_{max} (578 nm) and a luminance change of 60%, measured by colorimetric analysis.[12] In addition, PProDOT-Me$_2$ switches quite rapidly, with the above noted optical changes occurring in 0.2–0.4 s. These enhanced EC properties, relative to the unsubstituted parents PEDOT and PProDOT, are probably due to a more open morphology of the films, allowing for a fast ion exchange during p-doping and undoping. The direct current (DC) conductivity is also somewhat smaller (about 40 S/cm at 300 K, compared with 70 S/cm for PProDOT). The decreased conductivity is likely due to repressed interchain interactions, which also serves to lower the intensity of the NIR tail throughout the visible region, commonly associated with highly conducting polymers. Furthermore, its high coloration efficiency (200 cm^2/C) translates into lower charge densities required to perform a switching cycle, thus providing longer device lifetimes.[11]

In this communication we address the optimization of ECDs that operate in the reflective mode and are able to modulate the reflectivity in the visible, NIR, and mid-IR regions of the spectrum.[13] As a device platform, which conveniently allows EC property characterization in a reflective mode, we have used an outward facing, active electrode device, sandwich structure originally described in the patent literature,[14] as shown schematically in Figure 1. This ECD structure has several benefits. Firstly, the properties of the EC material of interest can be probed through a window chosen to be highly transmissive over the wavelength range of interest. Secondly, all of the materials can be flexible, allowing significant mechanical deformation without hampering device operation. Finally, by using an especially-designed high-viscosity electrolyte, the device can be made self-sealing. In this construction, gold-coated Mylar sheets are used as both counter and working electrodes. The top electrode is cut with a series of parallel slits, separated by about 2 mm, across the active surface (see Fig. 2) making it porous to ion transport during switching. The cell was assembled using a high viscosity polymeric electrolyte composed of LiClO$_4$ dissolved in an acetonitrile (ACN)/propylene carbonate (PC) swollen poly(methyl methacrylate) (PMMA) matrix. At the edges of the device, the ACN in the
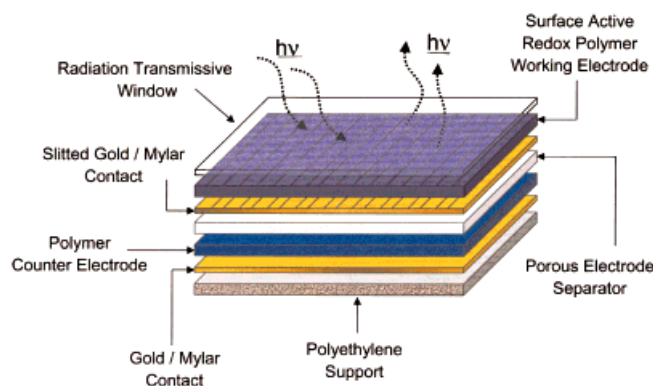

Fig. 1. Side-view schematic diagram of a dual polymer ECD for surface reflectivity control in both the visible and IR regions of the electromagnetic spectrum.
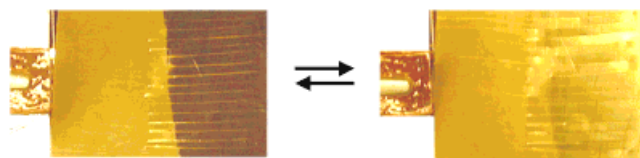

Fig. 2. Top-view photograph of a PProDOT-Me$_2$/PBEDOT-NMeCz dual polymer ECD in its two extreme states. Left: surface PProDOT-Me$_2$ in neutral state at –1.1 V, right: surface PProDOT-Me$_2$ in oxidized state at +1.1 V.

electrolyte evaporates, leaving behind the PMMA and LiClO$_4$ in PC. As the PMMA becomes insoluble, it seals the outer edges of the device and provides self-encapsulation. The use of this electrolyte minimizes further solvent evaporation, prevents leaking, and allows for long-term testing of the ECD. Both the active top layer and the counter polymer film were electrochemically deposited on the gold-coated Mylar electrodes from solutions of 10 mM monomer in 0.1 M LiClO$_4$ in ACN at constant potential. A separator paper, soaked in electrolyte, was used to isolate the back of the working electrode from the counter polymer layer. The top layer is in contact with a window, which is transmissive to the wavelengths of interest, allowing accurate measurements of the active layer reflectivity. We typically use ZnSe for NIR to mid-IR, glass in the NIR and visible, and polyethylene for visible through mid-IR, with a somewhat lower performance from the latter on account of IR absorption bands. With this design, only the outward facing electroactive polymer is responsible for the surface reflectivity modulation, while the counter electrode polymer is used for charge and coloration balance.

Figure 2 shows a photograph of a device based on PProDOT-Me$_2$ as the active top layer, and poly[3,6-bis(2-(3,4-ethylenedioxy)thienyl)-N-methylcarbazole] (PBEDOT-NMeCz) as the back layer. As the top film on the device is switched from its neutral, colored state, to its p-doped, bleached state, a gradual and controllable transition from a dark opaque violet to a pale transparent blue is observed (the polymer film is very transparent so that the gold electrode underneath is visible). This color change is due to the doping process that modifies the electronic band structure of the polymer, producing new electronic states in the gap and bleaching the π–π* transition; consequently the electronic absorptions are shifted toward lower

energies outside of the visible region. The PBEDOT-NMeCz counter electrode is electrochemically complementary to the PProDOT-Me$_2$. When the PProDOT-Me$_2$ is being oxidatively doped, the oxidized form of the carbazole polymer is being neutralized and vice versa.[8,9] As constructed, the device switches in 3 s between the two extreme electrochromic states shown. It should be noted that this switching time is due to the diffusion of the ions through the gel electrolyte and along the working electrode slits. Improving the design of the ECD, using a highly porous working electrode and increasing the electrolyte conductance will decrease the optical response time and may enhance the chromatic contrast of the device.

Figure 3 shows the reflectance of the sandwich structure over 0.3–5 μm (0.25–4 eV) at several cell voltages. The visible and NIR data were measured on a 150 nm thick polymer film
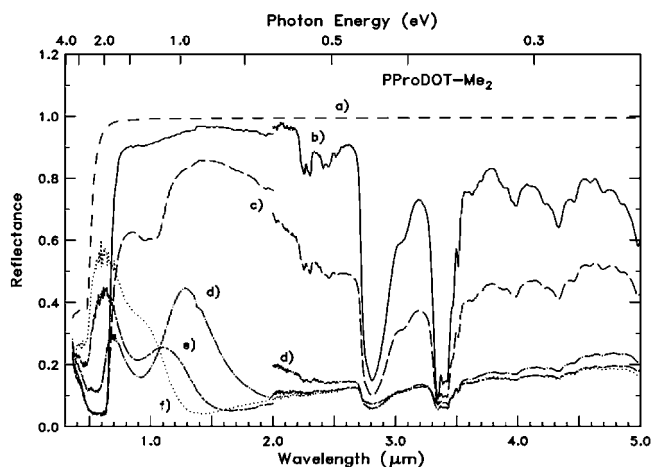

Fig. 3. Reflectance of the PProDOT-Me$_2$/PBEDOT-NMeCz dual polymer ECD spanning the visible to the mid-IR regions of the electromagnetic spectrum at various applied potentials. a) Uncoated gold surface; b) –1.5 V (PProDOT-Me$_2$ insulating, undoped); c) –1.0 V; d) –0.5 V; e) 0.0 V; f) +1.0 V (PProDOT-Me$_2$ conducting, p-doped).

under a glass window; the mid infrared data on a 200 nm thick polymer film with a ZnSe window. The parasitic reflectivity of the window has been subtracted in these spectra. Several layers in our device influence these spectra: the EC polymer, the electrolyte gel, and the gold electrode. Two strong absorption bands from water (2.8 μm) and C–H stretching (3.3–3.4 μm) are seen in all of the spectra; these arise from both the polymer and the gel electrolyte, and are relatively constant as the polymer is oxidized and reduced. The fully reduced polymer (–1.5 V; solid line) is strongly absorbing in the visible region (0.4–0.65 μm) and, thus the reflectance of the device is low in this region. At wavelengths longer than 0.9 μm (1.4 eV) this polymer layer becomes quite transparent, so the gold layer underneath the polymer dominates the reflectance. At still longer wavelengths vibrational features in the polymer become evident, and the device reflectance is diminished. When fully oxidized, i.e., doped, (+1.0 V, dotted line), the visible absorption is bleached; at the same voltage a strong infrared absorption appears, hiding the underlying gold electrode. The infrared absorption (and the contrast of our device) is strongest at ca. 1.8 μm. At this wavelength, we

detect a reflectance contrast, ΔR, greater than 90 %. This contrast ratio is highly enhanced when compared to results for PEDOT (ΔR = 50–55 %) and polyaniline derivatives.[14] At longer wavelengths (4–5 μm), the reflectance of the device increases somewhat for the polymer in the doped state, and decreases for the polymer in the undoped state, reducing the contrast to ΔR = 60 %. At intermediate oxidation states (0 V, –0.5 V, and –1 V) the device has a reflectance that is generally intermediate between that of the fully oxidized and fully reduced states. The exception to this behavior is the doping-induced band around 1–1.2 μm (1–1.2 eV), which is strongest at these intermediate doping levels. The physical interpretation of these spectra is that the undoped insulating polymer has its π–π* interband transition in the visible, and is transparent (except for vibrational absorptions) in the IR region. Light doping produces two sub-gap absorption bands, due to the presence of polaron states, and partial bleaching of the interband transition. At full doping, bipolarons are formed, and the polaron interband transition is absent.

A key characteristic of an ECD of this type for displays or for thermal control applications is the lifetime of the device, i.e., the number of switching cycles can undergo before degradation sets in. The redox stability of the cell was determined by continuously switching the device between its fully absorptive and transmissive states using a switching period of 25 s. After several double potential steps, the reflectivity was measured at a fixed wavelength where the contrast is high. The PProDOT-Me$_2$ based cell, using the LiClO$_4$ electrolyte, performs hundreds of switches without any degradation of the working electrode. After 1500 switches, the reflectivity of the oxidized form of the polymer has the same initial value, but the neutral form exhibits a decrease in reflectivity. As the device was assembled in air, the oxygen-sensitive neutral form is likely to be irreversibly oxidized during switching. Preparing the device in an oxygen and water free environment should drastically increase its cycle life-time, while also opening up a further window in the 2.7–3.1 μm region. By changing to a lithium trifluoromethylsulfonylimide (3 M salt) based electrolyte we have constructed devices that could be switched 10 000 times over a period of 6 days with only approximately 20 % loss in contrast.

In conclusion, we have shown that PProDOT-Me$_2$ provides high EC contrast in the visible, NIR, and mid-IR regions of the electromagnetic spectrum. Contrast ratios of 55 % at 0.6 μm in the visible, greater than 80 % between 1.3–2.2 μm in the NIR, and greater than 50 % between 3.5–5.0 μm demonstrate that these conducting polymers are excellent materials for redox switchable reflectivity for a metallic surface over a broad range of spectral energies.

Experimental

PProDOT-Me$_2$ was synthesized and fully characterized according to previously published procedures [11]. The high viscosity electrolyte based on poly(methyl methacrylate) and lithium perchlorate was plasticized by propylene carbonate to form a highly conducting and transparent gel. To ease the gel synthesis, the PMMA and LiClO$_4$ were first dissolved in acetonitrile. The composition of the casting solution was LiClO$_4$/PMMA/PC/ACN in a ratio of 3:7:20:70 by weight.

Electrochemical deposition of the polymer layers was carried out using an EG&G Model 273A potentiostat/galvanostat. A three electrode cell with Ag/Ag$^+$ as the reference, gold coated Mylar as the working, and platinum flag as the counter electrode was used for electrosynthesizing the polymer films.

The reflectance of the sandwich structure was measured over the IR and visible regions using a Bruker 113v Fourier transform IR (FTIR) spectrometer and a Zeiss MPM 800 microscope photometer. In the mid-IR we used a ZnSe window over the polymer and the device was enclosed in a sealed cell to isolate it from the atmosphere. A glass window was used in the visible and near infrared region. Electrical leads attached to the electrodes allowed the polymer to be oxidized and reduced in situ.

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