Electrochromic Organic Polymers and Devices

Matthew Dalton Materials Literature Seminar December 9, 2004

Electrochromic (EC) materials are those which reversibly modulate electromagnetic radiation (UV/Vis/NIR) based on their redox state.[1] Many transition metal oxides, small organic dyes called viologens, and conducting organic polymers are known to exhibit electrochromism and have been studied as materials for use in electrochromic devices (ECDs). ECDs have potential applications in display panels, variable transmittance windows, variable reflectance mirrors, spacecraft thermal control, and visible/IR camouflage.[1-7] Conducting polymers have received much attention during the last decade due to high coloration efficiencies, fast switching times between redox states, and ease of processing.[6,8] Their colors (band gaps) can also be adjusted through slight structural changes or copolymerization.[2,8,9,10]

Conjugated polymers are semiconductors in their neutral, reduced state with a π-electron band gap generally around 2 eV, which is in the visible region; upon electrochemical oxidation, charge carriers called polarons (radical cations) are generated along the polymer backbone with concomitant influx of counter anions from the electrolyte. This produces a partially "doped" and conducting state. The doping process generates a lower energy intraband transition in the near IR at the expense of the π- π^* transition. Further oxidation leads to the generation of bipolarons (dications), which further reduce the band gap and generate a new absorption of even lower energy. This completely eliminates the visible absorption and produces a highly transmissive polymer. Reversal of the electrochemical potential then reduces and de-dopes the polymer, returning it to its neutral colored state.[11]

Poly(thiophene), poly(pyrrole), poly(aniline), and their derivatives have all been studied extensively,[1] though poly(thiophene) derivatives (especially poly(ethylenedioxythiophene), or PEDOT, and its derivatives) have received the most attention due to promise as materials for ECDs.[6-10,12]

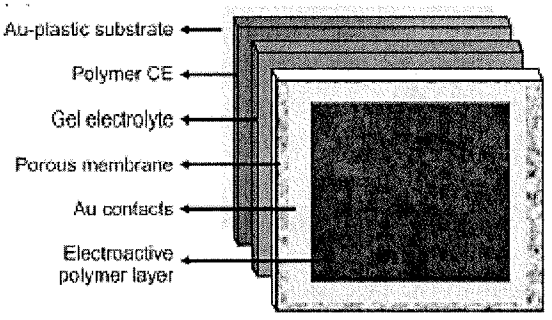

Figure 1

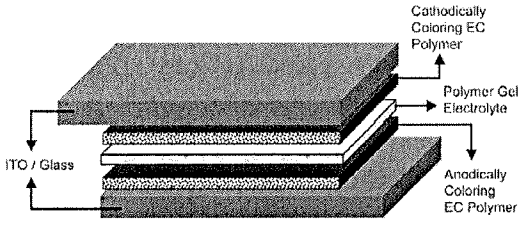

Figure 2

The newest ECDs utilize two complementary EC polymers and can be of two general types: absorptive/transmissive for window-type applications[12-14] (Figure 1) or reflective for mirror or display applications[4-7,15] (Figure 2). A second complementary EC polymer or ion storage layer must be present in these devices to provide an effective counter reaction, otherwise electrolyte degradation products build up and severely limit device lifetimes. To allow for effective operation of the device in Figure 2, one polymer must be anodically coloring while the other is cathodically coloring; i.e., one is colored in its oxidized, doped state, and the other is colored while neutral.[14] The nature of the counter electrode in the reflective device is less important because reflected radiation is being modulated.

Device performance is highly dependent on the EC materials and the electrolyte, but a series of poly(alkylenedioxythiophene)-based ECDs developed recently by Reynolds and coworkers is illustrative.[7] These devices utilize the design in Figure 1 and can switch at 5-10 Hz. They display reflectance contrasts of up to 90% in the NIR and 60% in the visible with less than 10% contrast loss upon 180,000 switches. One of the actual devices in both its reduced and oxidized form is shown in Figure 3.

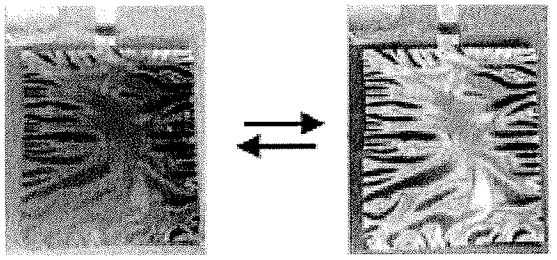

Figure 3

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