# Thin Films for Electrochromic Devices

Annabeth Ryder Literature Seminar November 6, 2003

Electrochromism can be described as the modulation of the optical properties of a material upon application of a voltage across an electrochromic material.[1] The optical properties should be reversible such that the original state of a material is recovered upon reversing polarity of the applied voltage. Materials that exhibit electrochromism are under study as thin films for use in information displays, variable transmittance windows, variable reflectance mirrors, and variable emittance surfaces.[1-4] While both inorganic and organic electrochromic materials exist, the focus in research has been predominantly on inorganic oxides. In particular, tungsten trioxide has received much attention[1-9] as a result of its extensive characterization over several decades.

Tungsten trioxide exhibits a framework structure, with corner-sharing $WO_6$ octahedra shaping the lattice. Intercalation of cations such as $H^+$, $Li^+$, and $Na^+$ into holes in the "empty perovskite" structure is the process responsible for coloration from transparent to blue in $WO_3$ films. Figure 1 illustrates an $M_xWO_3$ tetragonal lattice structure, and Equation 1 represents the intercalation process.

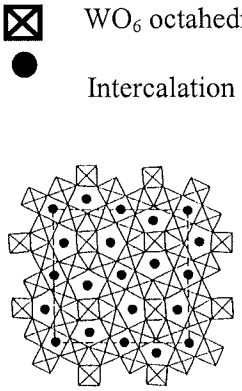


**Figure 1**

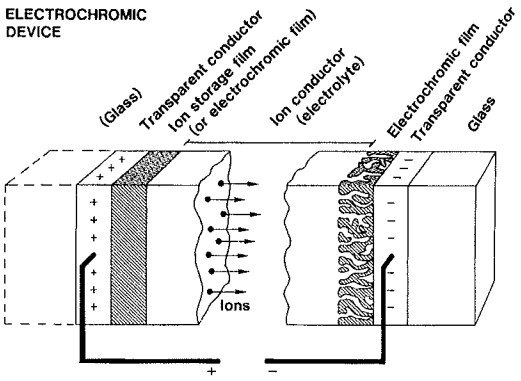


**Figure 2**

$$WO_3 + xM^+ + xe^- \rightarrow M_xWO_3 \; M^+ = H^+, Li^+, Na^+ \qquad (1)$$

A voltage applied across the electrochromic thin film and an ion storage thin film, separated by an electrolyte, provides the energy required for intercalation and deintercalation. A typical electrochromic device is illustrated in Figure 2.

Recent work concerning $WO_3$ has concentrated on the synthesis of mesoporous thin films using a surfactant[9] or block copolymer[5,10] as a template. The accompanying increase in surface area within the film leads to more facile ion intercalation from the

electrolyte. As a result, the time required to switch from the bleached state to the colored state decreases. The amount of inserted charge required to produce a given absorbance also decreases. Despite some successes in $WO_3$ electrochromic thin film research, limitations to the field do exist. For example, tungsten trioxide thin films lack flexibility and polyelectrochromism, as well as facile tuning of the electronic (and hence the optical) band gap.

Both polythiophenes and their isoelectronic analog polypyrroles[11] have been investigated for use in electrochromic devices as a superior alternative to inorganic oxides. While both of these polymers and their derivatives exhibit electrochromism when doped, most research has focused on polythiophene derivatives[12-18], particularly poly(3,4-ethylenedioxythiophene), referred to as PEDOT (Figure 3). In the mid 1980s, Bayer Corporation developed and made commercially available poly(styrene sulfonic acid) doped PEDOT, which has excellent mechanical properties and high conductivity.[12] The emergence of this system led to extensive study of PEDOT, as well as development of PEDOT derivatives.

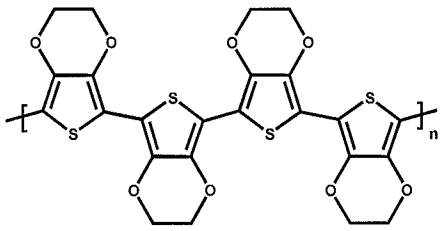

**Figure 3**

By functionalizing the PEDOT backbone, the electronic band gap may be selectively tuned, resulting in polymers with a wide range of accessible colors. PEDOT derivatives exhibit a large change in absorbance upon intercalation of small amounts of charge, resulting in high coloration efficiency (CE). The time required to switch from the colored state to the bleached state may be as little as milliseconds.[14] Integrally, these properties make electrochromic polymers superior to $WO_3$ films for use in electrochromic devices.

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