

CHAPTER 18

Electrochromic Materials

18.1 Introduction

A set of materials exhibit *electrochromic activity* when constituted as a thin film structure whose coloration can be changed reversibly by electrical charging and discharging. There are two types of such *electrochromic materials*. The first type is uncolored when unpowered and changes to a colored state when a voltage is applied and returns to its uncolored state when the voltage is removed. In the second type, an opposite voltage is required to be applied for *bleaching* (or *decoloration*). The *degree of coloration* is a direct visual indication of the state of charging present in the material.

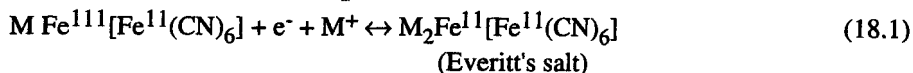
Electrochromic devices are constituted by multilayered structures consisting of an electrochromic electrode, a transparent electrolyte, and a transparent counter or complementary electrochromic electrode.

The phenomenon of coloration (or decoloration) in an electrochromic material is a result of two possible reactions set forth by electrical energization, namely, the *reduction* of an electrochromic electrode and the *oxidation* of a counter/complementary electrode. This phenomenon warrants the flow of compensating ions (typically alkali ions or protons) across the electrolytic layer in order to maintain the charge neutrality of the system.

A well-known electrochromic material is Prussian blue (PB) which in conjunction with WO_3 can be used as a primary or as a complementary electrochromic window [1].

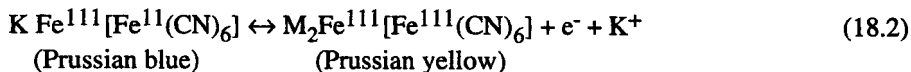
There are two types of PB, namely, soluble PB $[\text{KFeFe}(\text{CN})_6]$ and insoluble PB, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. Both versions have cyanide-bridge iron atoms forming a nominally cubic molecular framework with distinct iron sites. The soluble or insoluble property refers to the relative peptization of each type.

The soluble type is an N-bounded Fe^{3+} -type iron site and in an electrochromic reaction, the reduction of N-bounded Fe^{3+} yields the transparent Everitt's salt (ES). The relevant reaction is as follows:



where M^+ is an alkaline ion (such as potassium ion). Thus the reduction of soluble PB leads to a (reversible) bleached condition, inasmuch as ES is optically transparent.

The oxidation of soluble PB is also an electrochromic reaction:



Since Prussian yellow (PY) absorbs light much less than PB, PB is bleached (reversibly) by this reaction. Thus soluble PB offers reversible bleaching both by reduction as well as by oxidation.

A single film electrochromic device is a simple way to get dark and bright effects by application of external voltage. Relevant structure consists of a PB kept between two transparent conducting plates as shown in Figure 18.1a. When voltage is applied, oxidation occurs near the positive electrode and reduction near the negative electrode to yield PY and ES, respectively, as indicated in Figure 18.1b. This conversion of the outer portions of the film results in the net bleaching of the device. A single film of PB is thus made to function as both electrochromic and complementary electrodes as well as an electrolyte. Materials like PB are known as *ion insertion electrochromic materials*.

Water plays a major role in the electrochromic mechanism. For example, tungsten oxide (WO_3) colors cathodically in aqueous solution. When nickel oxide (NiO) is used as a

positive electrode, it colors anodically only in its hydrated form in aqueous electrolytes [2,3]. Under appropriate conditions, NiO can undergo a reversal lithium intercalation-deintercalation process in aprotic nonaqueous electrolytes. This type of electrochromic effect may be described by the following reaction:



Under this circumstance, the oxide is electrochromic in a complementary mode with respect to Tungsten oxide whose reaction is given by:



Hence, WO_3 and LiO can be used in order to create efficient electrochromic windows provided that the two materials are adjoined by a suitable electrolyte.

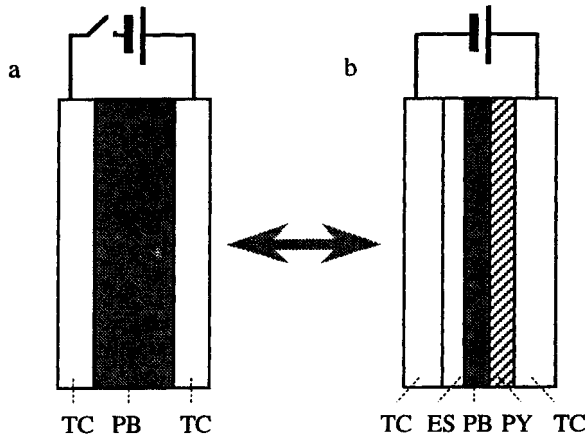


Figure 18.1 SFPB Cell. A: With no bias voltage. B: With bias voltage applied. (TC: Transparent conductor; PB: Prussian blue; ES: Everitt's salt; PY: Prussian yellow).

The chemical reactions depicted by Equations 18.3 and 18.4 show that the NiO film becomes transparent in the cathodic cycle (Li insertion) and dark brown in the anodic cycle (Li extraction). The WO_3 film becomes transparent in the anodic cycle (Li extraction) and blue in the cathodic cycle (Li insertion).

Figures 18.2a and 18.2b illustrate the electrochromic properties of individual (electrochromic) layers by depicting the cyclic voltametric curves for NiO and WO_3 immersed in a typical nonaqueous electrolyte.

The coloring and bleaching mechanism for WO_3 and NiO can be specified by the following reactions:



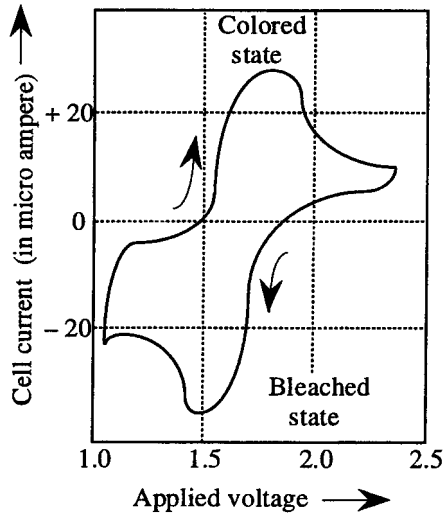


Figure 18.2a Cyclic volt-ammogram of a typical NiO-based electrochromic layer.

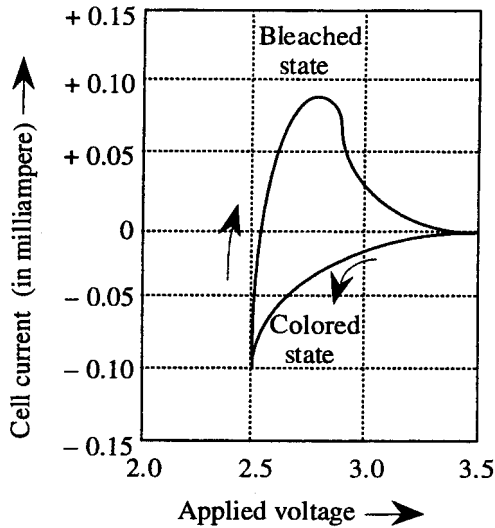


Figure 18.2b Cyclic volt-ammogram of a typical WO₃-base electrochromic layer.

Thus, the observed coloration is due to the formation of hydrogen-tungsten bronze with the inclusion of protons into the tungsten oxide layer with electrons from an external voltage source. Simultaneously, the nickel oxide absorbs an hydroxide ion to form a nickel hydroxide compound with the release of an electron into the external maintaining a charge neutrality.

18.2 Electrochromic Mirror Systems

An application of an EC device is to control the passage of the incoming light. That is accomplished by an EC window which is transparent in one state and colored in another state with appropriate application of electrical voltage. This switching phenomenon can be effected by an EC mirror whose reflectivity can be changed by introducing or removing an electric field. This effect is prevalent in two types of materials, namely:

- Liquid crystal (LC) materials
- Electrochromic (EC) materials

The most popular LC mirror is a *guest-host liquid-crystal mirror* shown in Figure 18.3. In this type of material, specialized dyes (the *guest*) are combined with the liquid crystal material (the *host*) which acts as a matrix to orient the dye molecules. The host material reorients the dye molecules when an electric field is applied to it and causes a change in the amount of light that can be absorbed. The darkness depends on the dye efficiency and dye concentration. In the dimmed mode, higher concentrations lead to a darker mirror and also it results in higher residual coloration due to incomplete ordering of the dye molecules.

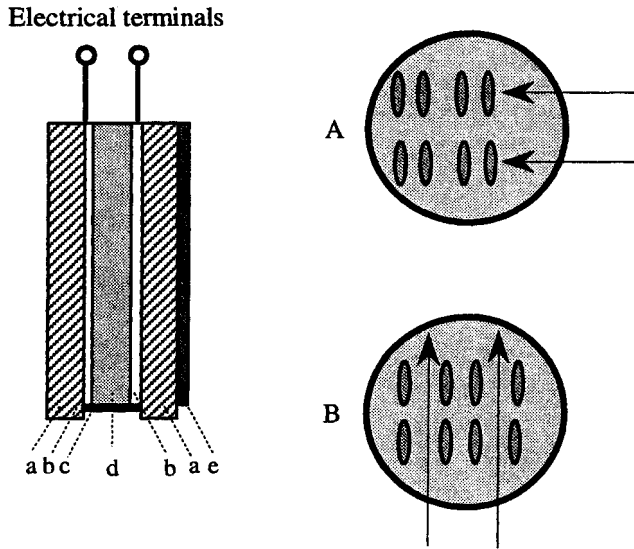


Figure 18.3 A guest-host liquid-crystal mirror.

A: Dark-mode wherein the dye absorbs the light.

B: Bright-mode wherein the passage of light is not inhibited.

(a: Glass substrates; b: Transparent conductors; c: Seal; d: Liquid-crystal/dye solution; e: Silver reflector.)

Hence, *guest-host mirror* can be classified as negative or positive guest-host mirror. The negative one is bright when powered and dark when unpowered and the positive-type mirror is bright when unpowered and dark when the electric field is present. Thus by applying an electric field, the reflectivity of the mirror can be changed and it acts as a switching device yielding a chopped square wave corresponding to the incoming light falling on the mirror.

Another type of mirror is the electrochromic mirror [4-7] which changes its color in the presence of an electric field typically through the injection of ions and electrons or through electrochemical reactions.

EC mirrors are typically constructed in two ways. In one type, the reaction takes place in a chemical solution. In the other construction, the reaction takes place within thin solid films. The first type of mirror uses a solution which contains two EC materials; one colors cathodically and the other colors anodically. The solution is sealed between two sheets of conductive coated glass as shown in Figure 18.4.

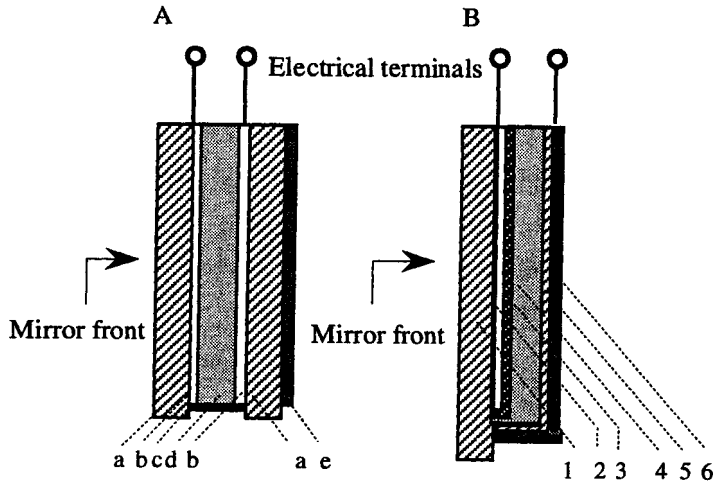


Figure 18.4 Electrochromic mirrors.

A: Using electrochromic solution.

B: Solid-state type.

(a: Glass substrates; b: Transparent conductors; c: Seal; d: Liquid-crystal/dye solution; e: Silver reflector.)

(1: Glass substrate; 2: Transparent conductors; 3: Anodic electrochromic layer; 4: Solid-state electrolyte; 5: Cathodic electrochromic layer; 6: Silver reflector.)

A piece of glass is coated with a reflective film to form the mirror. The EC material is uncolored when unpowered. When a voltage is applied between the two glass sheets, one material is cathodically reduced and the other is anodically oxidized to convert them to the colored state. On removing the voltage, the system spontaneously returns to the uncolored state.

The second type of mirror refers to a multilayer structure which consists of a stack of thin films deposited on a single piece of glass as shown in Figure 18.4. An electric field is set up between the transparent conductive material and the metallic layer by an external bias. Sandwiched between these layers, is a layer of anodic and a layer of cathodic electrochromic materials. When a voltage is applied, both the anodic and cathodic layers get colored and the mirror darkens. When the voltage is removed, the thin film electrochromic layers retain their color. An opposite voltage is required to reverse the electrochromic reactions and return the mirror to full brightness.

18.3 Optical Switching Applications of Electrochromic Materials

Inasmuch as an electrochromic mirror or a window offers optical transparency or opacity to the incoming light, it is possible to produce a square wave corresponding to the light absorbed or transmitted by it. The rate of optical switching depends on the dynamic/transient (switching) characteristics of the ER material used.

Figure 18.5 illustrates the dynamic performance of the current and photonic reflectance of an EC mirror for a coloring voltage of 1.8 volt d.c. followed by a bleach voltage of -0.8 volt (d.c.). The reflectance varies between 75 to 10 percent with a switching time of < 20 second.

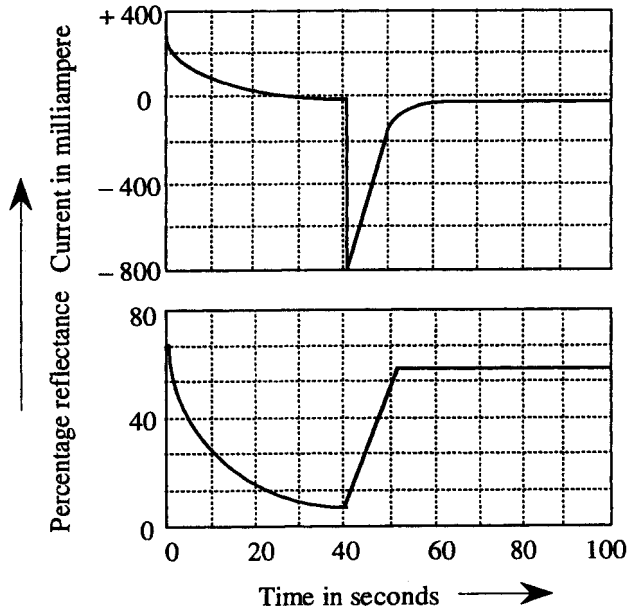


Figure 18.5 Time-response characteristics of an electrochromic mirror.

In the colored state the mirror becomes deep blue; therefore reflectance drops. The spectral response of an EC mirror is shown in Figure 18.6 in both clear and colored state. The EC material adopted is same as the tungsten oxide (WO_3) and nickel oxide (NiO) combination as the active cathodic and active anodic part, respectively, as discussed earlier.

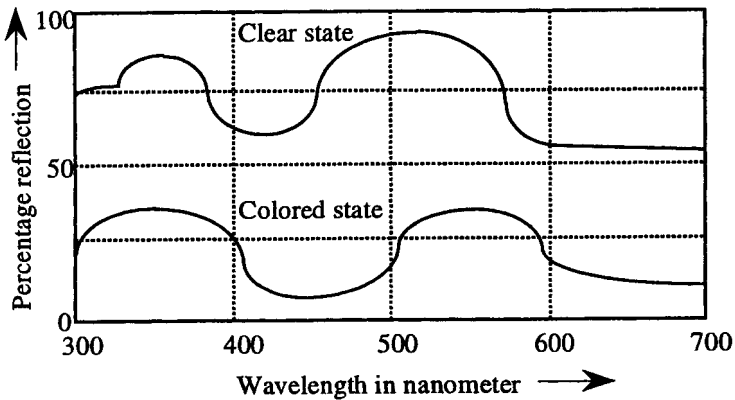


Figure 18.6 Visible reflectance at the electrochromic mirror under clear and colored states.

18.4 Characteristics of Constituent Materials in an EC System

The electrolyte in a conventional cell is an electrochromic insulator which prevents electron flow between the two electrodes whereas the electrolyte in an EC device such as the single film Prussian blue (SFPB) is a mixed conductor with enough electronic conductivity to allow the system to equilibrate rapidly after removal of the driving voltage. Therefore an electrochromic device repeatedly bleached by the application of a voltage across it would result in partial oxidation near the anode and partial reduction near the cathode. The applied voltage determines the extent of bleaching of the device. In addition, the response of the device is also sensitive to the amount of pressure applied to it.

The optical absorbance spectra of a single film Prussian blue (SFPB) device for different voltage is shown in Figure 18.7. Significant absorbance changes in the SFPB cell occur over a wide spectral range (550-900 nm). It is seen that the open-circuit state, when no voltage is applied, corresponds to maximum absorbance and the absorbance decreases with an increase in the applied voltage. Hence the more voltage is applied, the more it is bleached.

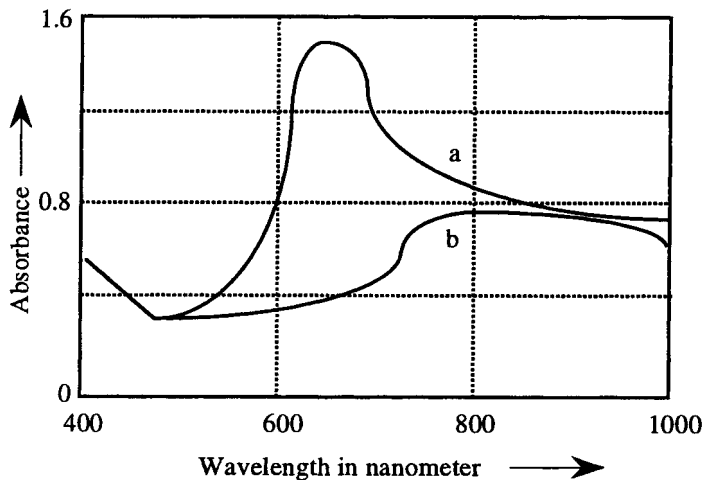


Figure 18.7 Optical absorbance of a typical SFPB device. (a: Zero bias voltage; b: Bias voltage \approx 8 volts.)

Figure 18.8 shows the typical absorbance (at 690 nm) of a cell during repeated switching. The cell is alternately powered over 15 seconds at 12 volts and turned off with open-circuit state for 15 seconds. The absorbance changes between 0.92 (when voltage is 12 volt) and 1.85 (when no voltage is applied). It could be seen from the figure (Figure 18.8) that both coloration and bleaching occur within the first 5 seconds of the transient state of the voltage.

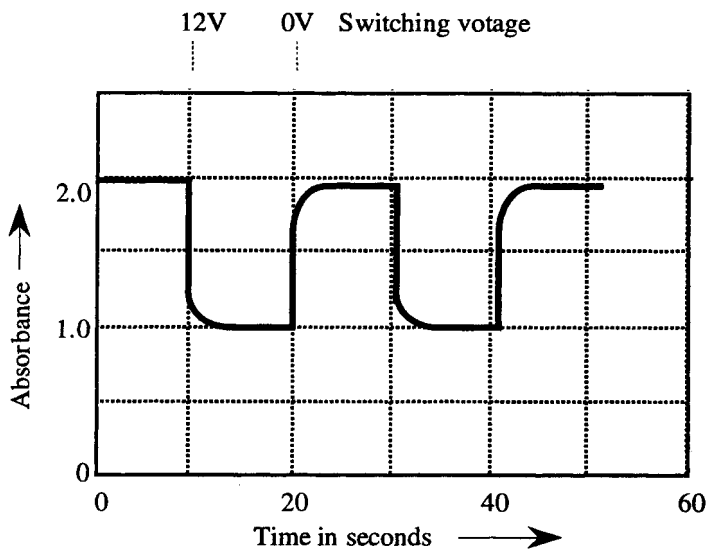


Figure 18.8 Optical transients of a SFPB device in response to an applied switching voltage.

The various aspects of electrochromic materials discussed so far indicate that an EC device can be used as an optical switch whose switching state can be alternated by changing the voltage applied to it. That is, by changing the voltage applied to an EC material, the incoming light can be alternately blocked or allowed to pass. This principle can be used in the *reticle* design to chop an incoming beam of light. In the conventional reticles a rotating disk is used to modulate the light at a desired rate and modulation profile (such as amplitude modulation, frequency modulation etc.). Such reticles (or *choppers*) find useful applications in passive homing systems in pursuing a target *via* tracking the heat (infrared) emissions from the target. The infrared emission intercepted at the seeker is chopped (modulated) by a rotating disk reticle, to acquire position information of the target [8]. The rotating disk systems, however, is rather cumbersome *vis-a-vis* considering the vibrations involved, mounting of the motor, wobbling of the disk, etc.

In order to overcome the shortcomings of rotating reticles, a *stationary chopper/reticle* can be used as an alternative. This stationary reticle can be designed [9] with EC materials making use of the electronically controllable optical transparency/opacity characteristics of the EC device as discussed earlier.

Other applications of the EC principle include the design of rear view mirrors [10-13] with glare control abilities and high resolution flat panel display technology for cockpit applications.

18.5 Concluding Remarks

Electrochromic materials refer to one of newest breeds of electromagnetic media. Though successful studies have been made and some potential applications have been put into practice, still the material science aspects and possible technological innovations are many to be explored *vis-a-vis* electrochromic materials. In the applications of EC materials, several technological desirabilities such as contrast (in color changing display), grey shades involved, switching speed, lifetime, resolution of the displays etc. pose persistent problems yet to be addressed in detail. Nevertheless, EC materials constitute a set of the most promising items of material science and technology of the future.

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Defining Terms

Electrochromic material: An electrochromic material changing its color, when subjected to an external electric field.

Electrochromic mirror: A mirror system with variable transmittance/reflective characteristics constituted by electrochromic materials.

Static reticles: An optically, nonmoving chopper system using electrochromic materials.