

# Electrochromic materials and devices: present and future

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## Abstract

The increase in the interaction between man and machine has made display devices indispensable for visual communication. The information which is to be communicated from a machine can be often in the form of color images. Electrochromic display device (ECD) is one of the most powerful candidate for this purpose and has various merits such as multicolor, high contrast, optical memory, and no visual dependence on viewing angle. A large number of electrochromic materials are available from almost all branches of synthetic chemistry. In this review, we have tried to describe the fundamentals of such electrochromic materials and their use in EDDs. The most important examples from major classes of electrochromic materials namely transition metal oxides, Prussian blue, phthalocyanines, viologens, fullerenes, dyes and conducting polymers (including gels) are described. Examples of their use in both prototype and commercial electrochromic devices are given. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Theoretical considerations suggest that the absorption and emission spectra of certain dyes may be shifted by hundreds of angstroms upon application of a strong electric field. This effect is called “electrochromism”, in analogy to “thermochromism” and “photochromism” which describe changes of color produced by heat and light. This definition of electrochromism does not, however, fit within the modern sense of the word. An electrochromic material is the one that changes color in a persistent but reversible manner by an electrochemical reaction and the phenomenon is called electrochromism. Electrochromism is the reversible and visible change in transmittance and/or reflectance that is associated with an electrochemically induced oxidation–reduction reaction. It results from the generation of different visible region electronic absorption bands on switching between redox states. The color change is commonly between a transparent (“bleached”) state and a colored state, or between two colored states. In case more than two redox states are electrochemically available, the electrochromic material may exhibit several colors and may be termed as polyelectrochromic or can be said to possess

multicolor-electrochromism. This optical change is effected by a small electric current at low dc potentials of the order of a fraction of volts to a few volts.

Electrochromic materials are generally first studied at a single working electrode, under potentiostatic or galvanostatic control, using three electrode circuitry. Electrochemical techniques such as cyclic voltammetry, coulometry, chronoamperometry, all with, as appropriate, in situ spectroscopic measurements are employed for characterization. An electrochromic device is essentially a rechargeable battery in which the electrochromic electrode is separated by a suitable solid or liquid electrolyte from a charge balancing counter electrode, and the color changes occur by charging and discharging the electrochemical cell with applied potential of a few volts. After the resulting pulse of current has decayed and the color change has been effected, the new redox state persists, with little or no input of power, in the so-called “memory effect”. Fig. 1 illustrates an electrochromic device configuration.

The electrochromic electrode of these devices, which can work either in the reflective or transmissive mode, is constituted by a conductive, transparent glass coated with electrochromic material. The counter electrode can be of any material that provides a reversible electrochemical reaction in devices operating in the reflective mode (like electrochromic displays); by contrast, in variable light transmission electrochromic devices (like electrochromic

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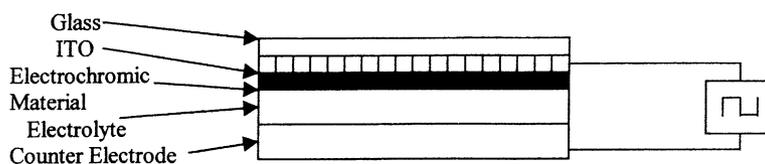


Fig. 1. Schematic diagram of the EDD.

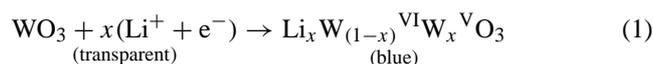
windows). In variable light transmissive electrochromic devices the counter electrode substrate also has to be transparent indium–tin–oxide (ITO) glass, with the counter electrode chemical species being either colorless in both its redox forms or electrochromic in a complementary mode to the primary electrochromic material, since the entire system is in the optical path. Hence, transparent electrolytes are required in the transmissive devices. For applications that are designed to operate in a reflective mode, such as displays, the counter electrode can be of any material with a suitable reversible redox reaction.

The purpose of this review is to give a flavor of the diversity of this fascinating subject by the description of some of the most important examples from the major classes of electrochromic materials, and to give some examples of their use in both prototype and commercial electrochromic display devices (ECDs).

## 2. Transition metal oxides (TMOs)

Recently, oxides of many transition metals (in the film form), e.g. iridium [1,2], rhodium [3], ruthenium [4], tungsten [5], manganese [6], cobalt [6], etc. have been shown to possess electrochromic property. This class of electrochromic (EC) materials have been classified under inorganic EC materials. The TMO films have been deposited by several techniques such as vacuum evaporation [7], sputtering [7], spray deposition [8], electrodeposition [9], electrochemical oxidation of tungsten metal [10], chemical vapor deposition (CVD) [10], sol–gel method [10], etc. The TMO films can be electrochemically switched to a non-stoichiometric redox state which has an intense electrochromic absorption band due to optical intervalence charge transfer [10–13]. A typical and most widely studied example is the tungsten trioxide ( $\text{WO}_3$ ) system, since its electrochromism was first reported in 1969 [10–13]. Tungsten oxide has a nearly cubic structure which may be simply described as an “empty-perovskite” type formed by  $\text{WO}_6$  octahedra that share corners. The empty space inside the cubes is considerable and this provides the availability of a large number of interstitial sites where the guest ions can be inserted. Tungsten trioxide, with all tungsten sites as oxidation state  $\text{W}^{\text{VI}}$ , is a transparent thin film. On electrochemical reduction,  $\text{W}^{\text{V}}$  sites are generated to give the electrochromic (blue coloration to the film) effect. Although, there is still controversy about the detailed coloration mechanism, it

is generally accepted that the injection and extraction of electrons and metal cations ( $\text{Li}^+$ ,  $\text{H}^+$ , etc.) play an important role.  $\text{WO}_3$  is a cathodically ion insertion material. The blue coloration in the thin film of  $\text{WO}_3$  can be erased by the electrochemical oxidation. In the case of  $\text{Li}^+$  cations the electrochemical reaction can be written as Eq. (1) and the generalized equation can be written as Eq. (2).



The fractional number of sites which are filled in the  $\text{WO}_3$  lattice is indicated by the subscript  $x$  in the general formula  $\text{M}_x \text{WO}_3$ . At low  $x$  the films have an intense blue color caused by photoeffected intervalence charge transfer (CT) between adjacent  $\text{W}^{\text{V}}$  and  $\text{W}^{\text{VI}}$  sites. At higher  $x$ , insertion irreversibly forms a metallic “bronze” which is red or golden in color. The process is promoted by cathodic polarization which induces ion insertion and electron injection: the inserted ions expand the lattice of the guest oxide while the compensating electrons modify its electronic structure and in turn its optical properties. It can be stated simply that the injected electrons are trapped by a  $\text{W}^{6+}$  forming a  $\text{W}^{5+}$  while  $\text{M}^+$  remains ionized in the interstitial sites of the  $\text{WO}_3$  lattice. This gives rise to the formation of tungsten bronze having electrical and optical properties different from those of the pristine oxide. In fact, the pristine state  $\text{WO}_3$  is a pale-yellow and a poor electrical conductor, while in the intercalated  $\text{M}_x \text{WO}_3$  state it becomes highly conducting and blue in color with absorption spectra around 0.5–0.6  $\mu\text{m}$ .

The above mentioned  $\text{W}^{6+}/\text{W}^{5+}$  intervalence transition model implies a certain delocalization of electrons which is consistent with the enhancement of the conductivity that accompanies the insertion processes. However, although this is the most accepted theory, other models, including a non-localized electron model are proposed to explain the electrochromic mechanism of tungsten oxide, in particular, and of inorganic ion insertion compounds in general.

The characteristics of the electrochromic process can be conventionally examined by directly comparing the optical and electrochemical response of the  $\text{WO}_3$  electrode. Fig. 2 shows the cyclic voltammetry and the optical transmittance of a  $\text{WO}_3$  electrode measured in a cell having  $\text{Li}^+$  ion conducting electrolyte and a Li metal counter electrode. The cathodic scan promotes the development of the process: current flows in the  $\text{WO}_3$  electrode and the blue color  $\text{L}_x \text{WO}_3$

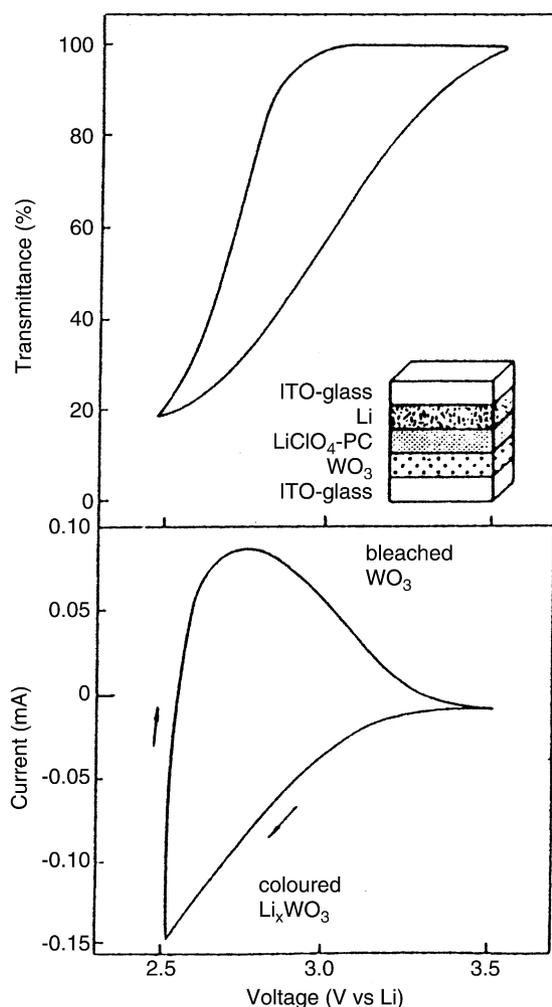


Fig. 2. Cyclic voltammetry and optical transmittance of a  $\text{WO}_3$  electrode in a  $\text{LiClO}_4\text{-PC}$  solution. Light source: He-Ne laser ( $6328 \text{ \AA}$ ); scan rate:  $20 \text{ mV/s}$ , sample thickness:  $600 \text{ \AA}$  [14b].

bronze develops. Accordingly, the optical transmittance decays to reach a minimum at the voltammetric peak. Reversing the scan results in the removal of the  $\text{Li}^+$  ions with the restoration of the pale-yellow-colored  $\text{WO}_3$  pristine oxide and the transmittance increases to reach nearly 100%. Although the process is readily reversible and can be repeated a large number of times, a careful observation of the voltammograms reveals some slight differences between the initial cycle and the subsequent cycling. Fig. 3 shows that the development of the electrochromic effect requires a sort of preliminary “activation” process. Such a process which is commonly encountered in insertion compounds may be described as an initial and permanent uptake of  $\text{M}^+$  ions which somewhat opens the route for the following fast and reversible insertion–withdrawal reactions. The extent of the process may vary from material to material and for some insertion ECMs it appears crucial in establishing prolonged cyclability [14]. A very good, informative review “Electrochromic tungsten oxide films” has been written by Granqvist [15].

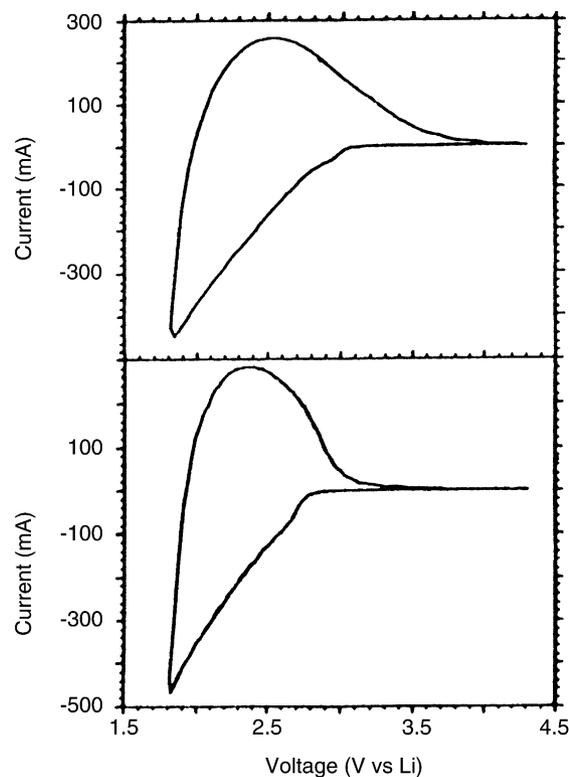


Fig. 3. Initial (upper curve) and stabilized (lower curve) voltammetric response of a  $\text{WO}_3$  electrode in a  $\text{LiClO}_4\text{-PC}$  solution. Scan rate:  $20 \text{ mV/s}$ ; sample thickness:  $2500 \text{ \AA}$  [14b].

The electrochromic properties of tungsten trioxide films have also been studied by combining it with other electrochromic materials such as  $\text{Nb}_2\text{O}_5$ , conducting polymers (CPs), etc. and the ECDs were made and studied [16–21]. Tungsten trioxide research has always been driven by the many possible commercial applications and prototype alphanumeric displays; and electrochromic mirrors were also reported. The so-called amorphous, or poorly crystallized tungsten oxide thin films have developed as the most important EC material, like the viologens is of great interest because of its reversible clear to deep blue coloration in transmission and high coloration efficiency. An important way to assess the many insertion/extraction films known is to compare spectral coloration efficiencies,  $\text{CE}(\lambda)$ , for the visible region

$$\text{CE}(\lambda) = \frac{\Delta\text{OD}(\lambda)}{q} \quad (3)$$

where  $\Delta\text{OD}(\lambda)$  represents the change in single-pass, transmitted optical density at the wavelength of interest  $\lambda$ , because of transfer of charge  $q$ , as  $\text{cm}^2 \text{C}^{-1}$ . The coloration efficiency, also called as electrochromic efficiency (EE) depends strongly on the sample preparation. The EE may vary from  $40$  to  $100 \text{ cm}^2 \text{C}^{-1}$  and accordingly the response time (i.e. the coloration–decoloration switching time) may vary from milliseconds up to few seconds. The cycle life (i.e. the number of coloration–decoloration cycles) depends upon the electrolyte used and can reach up to  $10^6$  cycles.

Table 1  
Electrochromic TMOs

Serial number	Cathodically ion insertion materials	Anodically ion insertion materials	Color	
			Oxidized state	Reduced state
<i>Part A</i>				
1	MoO <sub>3</sub>		Transparent	Blue
2	V <sub>2</sub> O <sub>5</sub>		Yellow	Blue-black
3	Nb <sub>2</sub> O <sub>5</sub>		Yellow	Blue
4	WO <sub>3</sub>		Transparent	Blue
<i>Part B</i>				
1		Ir(OH) <sub>3</sub>	Blue-black	Transparent
2		Ni(OH) <sub>2</sub>	Brown-bronze	Transparent or pale-green

Adherence to Lambert's law must either be assumed or tested to avoid pitfalls with thin films; cathodic coloration is well described by  $CE(\lambda)$  at moderate values of  $q$  for many inorganic amorphous films [22]. The coloration efficiency is determined spectro-electrochemically, using a cell which employs a cathode–anode pair in a liquid electrolyte. The cell is operated such that only the electrode of interest is in the light path of a spectrophotometer.

At present the major aim is the development of “smart windows” for control of thermal conditions within a building, thereby reducing winter heating and summer cooling requirements. Glass manufacturers have recognized this opportunity a long back. Pilkington Technology Center have produced a prototype electrochromic window (dimensions: 0.7 m × 1 m) which when colored is capable of reducing light transmittance by a factor of four [12]. Also, it is worthwhile to mention here that numerous patents were granted to American Cyanamid as a result of its display oriented work. Such electrochromic systems are of a simple two-electrode sandwich device construction as described above. In the development of such variable transmission windows, glass companies favor the sputtering technique because it is already in place for the production of a range of coatings for architectural glazings [23].

Many other TMOs in the thin film form are electrochromic, e.g. the oxides of molybdenum and vanadium given in Table 1. All the above materials of TMOs given in Table 1 are cathodically ion insertion materials, i.e. the more intensely absorbing redox state is produced on reduction. In contrast, group VIII metal oxides become colored on electrochemical oxidation (anodic ion insertion materials). The typical examples are given in Table 1 (Part B) [24–32].

### 3. Prussian blue

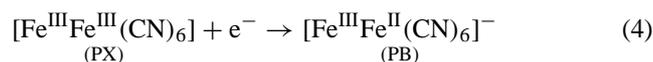
Prussian blue [PB, iron(III) hexacyanoferrate(II)] is the prototype of a number of polynuclear transition metal hexacyanometallates which forms an important class of insoluble mixed valance compounds. They have the general formula  $M'_k [M''(\text{CN})_6]_l$  ( $l, k$  integral), where  $M'$  and  $M''$  are transition metals with different formal oxidation numbers. In these compounds, a given element exists in two oxidation

states with the possibility of charge/electron transfer between them. PB is ferric ferrocyanide. A high spin ferric ion is coupled to a low spin ferrous ion by a cyanide bridge. The coupling is  $\text{Fe(III)}-\text{N}\equiv\text{C}\equiv\text{Fe(II)}$ , i.e. the first ferric ion couples to the nitrogen and the ferrous ion to the carbon. Robin [33] has shown that the electrons has a 99% probability of being on the low spin ion coordinated to the carbon.

Although, PB has been an important inorganic pigment and has been manufactured on a large scale for use in paints, lacquers, printing inks and other color uses, not much was known about the electrochemistry of PB. This might be due to the lack of knowledge for the preparation of the thin films of PB. Neff et al. [34,35] have shown a method for preparation of thin films of PB on platinum (Pt) and gold (Au) electrodes and demonstrated the redox behavior of PB. The first report [34] concerning the electrochemistry and electrochromism of PB promoted numerous investigations in to the properties of PB thin films. We have used PB as a sensitizer to improve the electrochromic response of CPs (particularly polypyrrole and polyaniline) and for photosensitivity [36,37]. Also, we have constructed EDDs (lab scale) and studied their electrochromic responses in liquid electrolytes, which are explained later in this review.

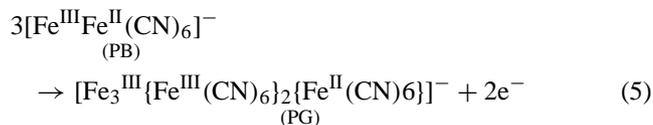
As is well known, there are two proposed formulae of PB, which have been called as “water insoluble PB”  $[\text{Fe}^{\text{III}}_4\{\text{Fe}^{\text{II}}(\text{CN})_6\}_3]$  and “water soluble PB”  $[\text{KFe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6]$  [38–40]. It is shown that the electrochemical reduction and oxidation of PB can lead to the “Prussian white” (PW, Everitt's Salt) and “Prussian green” (PG, Berlin green), respectively.

PB thin films are generally formed by electrochemical reduction of solutions containing iron(III) and hexacyanoferrate(III) ions [41–44]. Reduction of the brown-yellow soluble complex Prussian brown [PX, iron(III) hexacyanoferrate(III), present in equilibrium with the iron(III) and hexacyanoferrate(III) ions], is the principal electron-transfer process in PB electrodeposition as shown in the equation below



charge compensating cations (initially  $\text{Fe}^{3+}$ , then  $\text{K}^+$  on potential cycling in  $\text{K}^+$ -containing supporting electrolyte)

are present in the PB film for electroneutrality [45]. Partial electrochemical oxidation of PB in pure supporting electrolyte yields PG, a species historically known as Berlin green (BG), as can be presented by



Although in bulk form PG is believed to have a fixed composition with anion composition as above, for thin films there is a continuous composition range between PB and PX, which becomes a golden yellow in the fully oxidized form [45]. The latter may be obtained by electrochemical oxidation of a particularly pure form of PB [41,45],

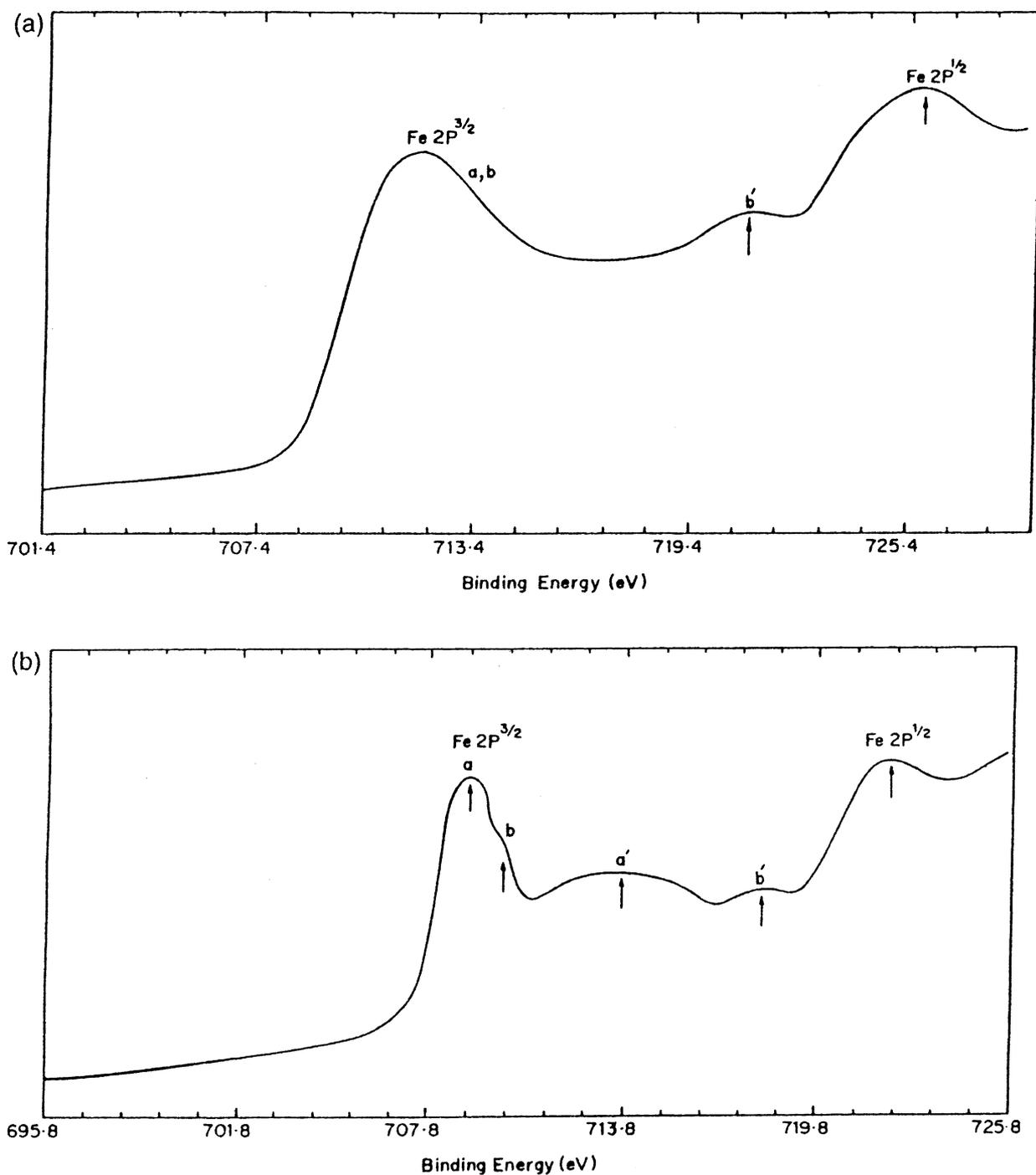
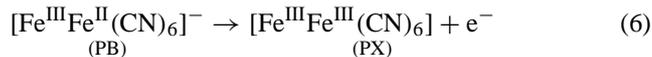
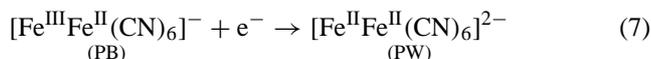


Fig. 4. XPS spectrum of the electrochemically deposited PB film and the reduced film obtained by applying a reducing potential of  $-0.5$  V vs. SCE for 60 s in 0.01 M aqueous KCl electrolyte [42].

Reduction of PB yields PW, also known as Everitt's salt, which appears transparent as a thin film, Eq. (7):



For all above electrochromic redox reactions, there is a concomitant ion ingress/egress in the films for electroneutrality. The PB film deposited electrochemically on an ITO electrode shows a color change from blue to transparent when reduced by applying a potential of 0.5 V versus SCE in an aqueous (0.01 M) KCl electrolyte for 60 s. Our XPS results, shown in Fig. 4 confirms Eq. (7).

Early PB-ECD employed PB as a sole electrochromic material. An example includes a seven segment display using PB modified SnO<sub>2</sub> working and counter electrode at 1 mm separation and an ITO/PB–Nafion/ITO solid state devices [46,47]. For the solid state system, device fabrication involved chemical rather than electrochemical formation of PB on immersion of a membrane of the solid polymer electrolyte (SPE) Nafion in aqueous solutions of FeCl<sub>3</sub>, than K<sub>3</sub>Fe(CN)<sub>6</sub>. The resulting PB-containing Nafion composite film was sandwiched between two ITO electrodes. The construction and optical behavior of an ECD utilizing a single film of PB, without addition of conventional electrolyte, has also been described [48]. In such designs, a film of PB is sandwiched between two optically transparent electrodes (OTEs) (Fig. 5a). Upon application of an appropriate potential across the film, oxidation occurs near the positive electrode and the reduction occurs near the negative electrode to yield PX and PW, respectively (Fig. 5b). The conversion of the outer portions of the film results in a net bleaching of the device. The functioning of the device relies on the fact that PB can be bleached both anodically (to the yellow state) and cathodically (to the transparent state) and that it is a mixed conductor through which the potassium ions can move to provide charge compensation required for the electrochromic redox reactions.

Since PB and WO<sub>3</sub> are respectively anodically and cathodically coloring electrochromic materials, used together in a single device so that their electrochromic reactions are complementary [49]. Our results on polypyrrole/PB (Ppy/PB) and polyaniline/PB (PANI/PB) composite films shows that the use of PB not only enhances the electrochromic response of the CPs but also extends the electrochromic response to wider region of the visible spectrum, thus acting as a sensitizer. The EDDs constructed by us using Ppy/PB and PANI/PB films have been shown in latter sections of this review.

#### 4. Phthalocyanines

Since the first report of the multicolor electrochromism of thin films of lutetium bis(phthalocyanine) ([Lu(Pc)<sub>2</sub>]) in 1970, numerous metal phthalocyanines have been investigated for their electrochromic properties. Such compounds have a metal ion either at the center of a single phthalocyanine (Pc) ring or between two rings in a sandwich type compound. Solid state electrochromism has been observed in phthalocyanine compounds of more than 30 metals, predominantly, among the sandwich-type diphtalocyanine (bisphthalocyanine) of the lanthanide and actinide rare earths and the related Group III elements lanthanide, yttrium and scandium. It also occurs in diphtalocyanines of the Group IV elements tin, zirconium and hafnium. Single ring electrochromic phthalocyanines include the metal free and magnesium compounds and those of transition elements, including divalent iron, cobalt, nickel, copper, zinc and molybdenum [50–56]. Because lutetium diphtalocyanine provides a full range of colors from orange or reddish-orange to violet and the films are easily prepared by vacuum sublimation, this compound has been most extensively studied among the lanthanide complexes. Lutetium diphtalocyanine [Lu(Pc)<sub>2</sub>]<sup>+</sup> is generally formed as a vivid

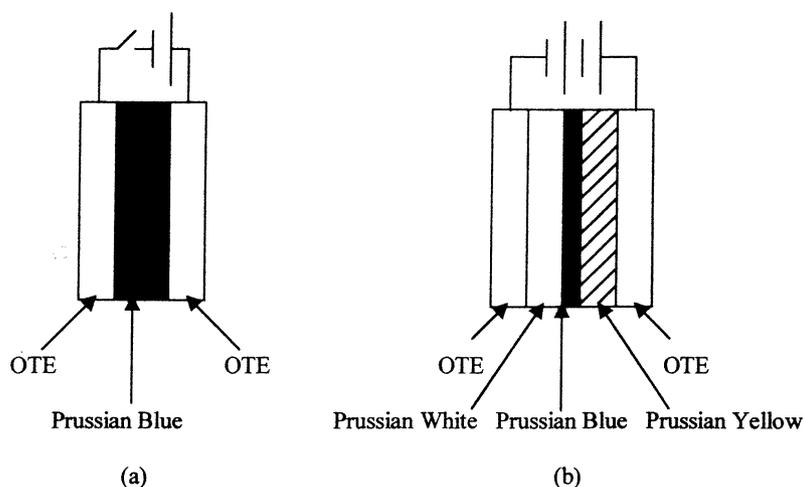


Fig. 5. ECD using PB film only [48].



ligand-centered. In the case of nickel polymer, both redox processes are ligand-based.

A further alternative to vacuum deposition method is the Langmuir–Blodgett (LB) technique, which is suitable for both monolayer and multilayer film formation. The electrochemical properties of a variety of substituted and unsubstituted phthalocyanine metal complexes as multilayer LB films have been studied. The first paper on this subject reported the electrochemical study of alkoxy-substituted  $[\text{Lu}(\text{Pc})_2]$ . LB films exhibited a one electron reversible reduction and one electron reversible oxidation corresponding to a transition from green to orange and blue forms, respectively, with the electron transport through the multilayers being, at least in parts, diffusion controlled. An explanation of the relatively facile redox reaction in such multilayers is that the Pc ring is large compared with the alkyl tail projected area, with enough space and channels present in the LB films to allow ion transport. High quality LB films of  $\text{M}^{\text{II}}$ tetrakis[(3,3'-dimethyl-1-butoxy)carbonyl]phthalocyanine ( $\text{M} = \text{Cu}, \text{Ni}$ ) have been reported. Ellipsometric and polarized optical absorption measurements suggests that the Pc molecules are oriented with their large faces perpendicular to the dipping direction and to the substrate plane. That the LB technique is amenable to the fabrication of ECDs is supported by recent report of a new thin film display based on LB films of the praseodymium bisphthalocyanine complex. The electrochromic electrode in the display was fabricated by the deposition of multilayers (10–20 layers, ca. 100–200 Å) of praseodymium bisphthalocyanine on to ITO-coated glass (7 cm × 4 cm) slides. The display exhibit blue–green–yellow–red polyelectrochromicity when a potential ranging from –2 to +2 V is applied. After,  $10^5$  cycles, no significant changes are observed in the spectra of these color states. The high stability of the device was ascribed to the preparation of well-ordered monolayers (by LB technique) which seems to allow better diffusion of the counterions into the film and improve the reversibility and stability of the system [58].

## 5. Viologens

Viologen family (4,4'-dipyridinium compounds) has the general chemical formula as shown in Fig. 7a, where R may be an alkyl, cyclo-alkyl or other substitute and X is a halogen. The name viologen was coined by Michaelis and Hills for 4,4'-dipyridium compounds because they become deeply blue-purple on reduction. The viologen ion (as shown in Fig. 7b) can have a two step reduction, i.e. one electron or

two electron reduction. The most extensively studied material from viologen family is the methyl viologen (MV). Elofson and Edsberg reported the first electron reduction of MV at –0.6 V versus SCE. It is reversible (the co-planarity of the two heterocyclic nuclei facilitates the reversible reduction) and independent of pH. The second electron reduction is not electrochemically reversible, but MV can be reoxidized by air. The second reduction was reported at –1.038 V versus SCE in the range of pH = 5–13 and slightly pH dependent below pH = 5. A polarograph of MV dichloride in an aqueous solution with pH = 5.3 clearly exhibit a two-step reduction with two half wave potentials located at –0.68 and –1.07 V versus SCE, respectively, confirming the results of Elofson and Edsberg and the cyclic voltammetry results.

The scope for viologen systems is indicated by the following observations [59,60,61a]:

- The color of the precipitate is a function of the nitrogen substituent. For example, if the substituent is *n*-heptyl then a purple deposit is obtained; if it is *p*-cyano-phenyl then a green deposit results.
- The electrical properties of the deposit can be tailored by selection of the anion. With *n*-heptyl viologen dication and bromide anions the deposit is conducting; substitution of the bromide by dihydrogen phosphate anions results in an insulating deposit.
- Electrodes can be functionalized with electrochemically active polymeric materials derived from, e.g., the hydrolytically unstable viologen, *N,N'*-bis[-3-(trimethoxysilyl)propyl]-4,4'-bipyridinium dibromide, potentially realizing solid state EC devices.
- Conventionally, EC displays achieve the contrast change by modulating light using the optical absorption of the electrodeposited film. A technique which uses light scattering of the viologen deposit to achieve very high contrast in short times, has recently been described.

## 6. Buckminsterfullerene

A change in color of  $\text{C}_{60}$  thin films from yellow-brown (undoped state) to silver-black when doped with alkali metals has been observed. Cordoba de Torresi et al. [61b,61c] report (absorbance and current versus potential data) the reversible color change of  $\text{C}_{60}$  thin films produced by electrochemical  $\text{Li}^+$  insertion. Undoped film is light brown, doped is dark brown.

It will be interesting to know whether the thin films of higher fullerenes such as  $\text{C}_{70}$  are showing electrochromism.



Fig. 7. (a) General chemical formulae of viologen; (b) viologen ion.

## 7. CPs

Chemical and electrochemical polymerization of various organic aromatic molecules such as pyrrole, aniline, thiophene, furan, carbazole, etc. produces novel electronically CPs. In their oxidized forms, such CPs are “doped” with counter anions (p-doping) and possess a delocalized  $\pi$ -electron band structure. The energy gap ( $E_g$ ) between the highest occupied  $\pi$ -electron band (valance band) and the lowest unoccupied band (conduction band) determines the intrinsic optical (and of course electrical) properties of these materials. It is well known that we can tune the optical properties of these materials by controlled doping (and/or dedoping). The doping process (oxidation) introduces polarons, which are the major charge carriers. Other charge carriers such as solitons, bipolarons, etc. are also very important in such systems (as shown in Fig. 8). The introduction of new states in the band gap (or forbidden gap) with doping process is the main reason for the changes in the optical properties of CPs and is the main cause for the electrochromism of such materials. Reduction of CPs with concurrent counter anion exit removes the electronic conjugation, to give the “undoped” (neutral) electrically insulating form. CPs can also undergo cathodic doping with cation insertion (n-doping). However, n-doped forms are less stable than p-doped forms. There are few reports on the electrochromism of the n-doped CPs.

In the recent years, CPs have gained a lot of attention for ECDs. This is due to the fact that all electroactive and CPs are potentially electrochromic materials, and are more processable than inorganic electrochromic materials and offer the advantage of a high degree of color tailorability. This tailorability has been achieved through the modification of various polymer systems via monomer functionalization and copolymerization as well as with the use of blends, laminates and composites. Complex colors are achieved by mixing two existing colors in a dual polymer device.

In CPs, electrochromic changes are induced by redox processes which are accompanied by ion insertion/expulsion and results in a modification of the polymer’s electronic properties giving rise to changes in color of the material. The color exhibited by the polymer is closely related to the band gap and the dopant ions. A major focus in the study of electrochromic polymeric materials has been that of controlling their colors by main-chain and pendant group structural modification. Polyheterocycles have proven to be of special interest for this due to their environmental stability under ambient and in use conditions.

Three major strategies of color control are used with electrochromic properties. The polymer’s band gap (defined as the onset of the  $\pi$ - $\pi^*$  transition) is directly related to the relative energies of the HOMO and the LUMO. By judiciously substituting the polymer’s repeat unit, the electrochromic properties can be controlled by the induced steric and electronic effects. These substituents determine the effective conjugation length and the electron density of the polymer backbone. Copolymers offer a second means of controlling the electrochromic properties of the CPs. Copolymerization of distinct monomers or homopolymerization of hybrid monomers containing several distinct units, can lead to an interesting combination of the properties observed in the corresponding homopolymers. Indeed, it has been observed that the color of copolymers based on carbazole, thiophene and pyrrole derivatives can be controlled by altering the ratio of the respective monomers. Blends, laminates and composites offer a third method, similar to copolymers, for combining the electrochromic properties of several systems. The use of two polymers covering different color regions is a simplest way to achieve multicolor electrochromism [62–65].

### 7.1. Polypyrrole

The electrochromic properties of polypyrrole were investigated in the thin film form. Polypyrrole (Ppy) thin

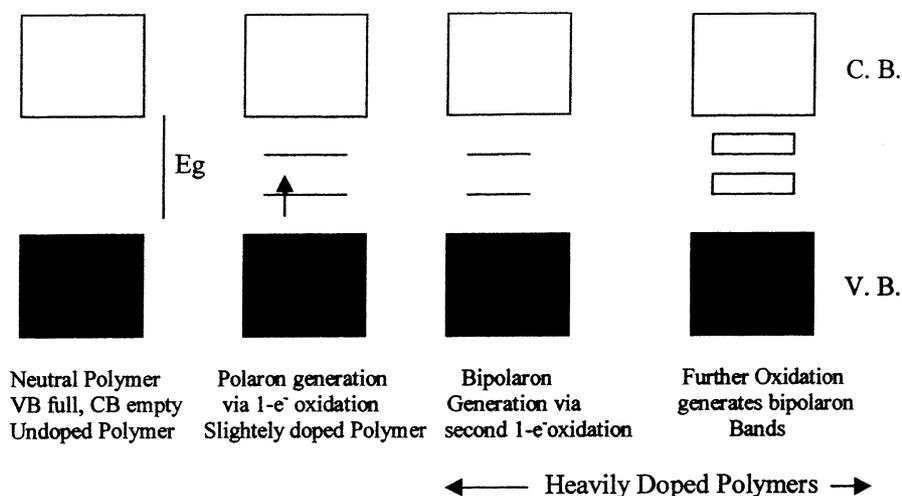
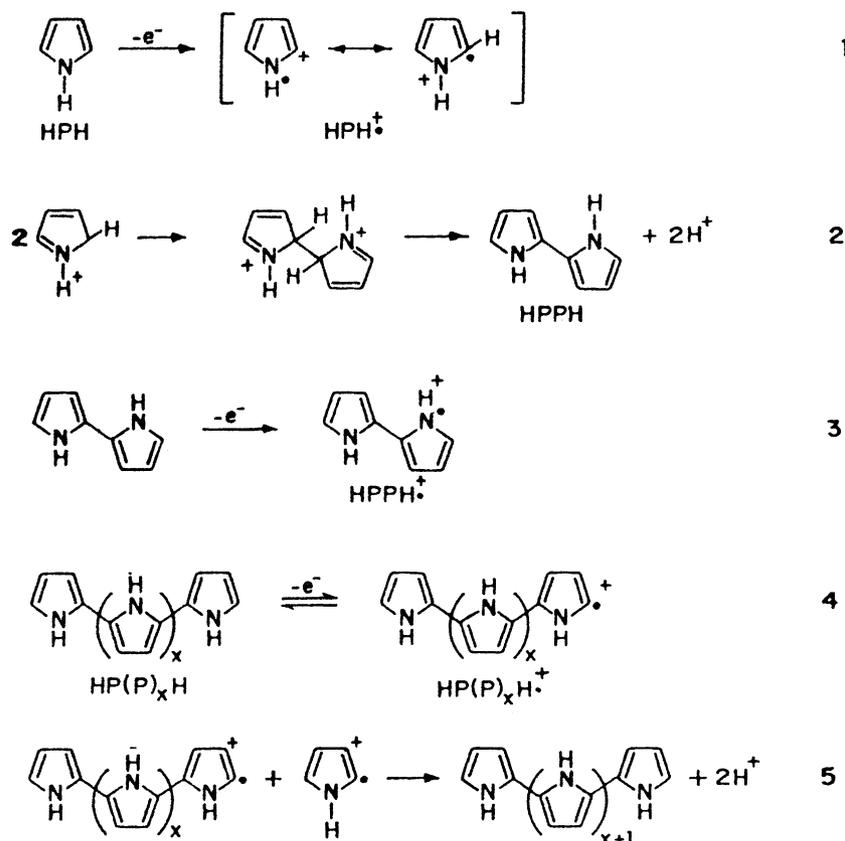


Fig. 8. Polarons and bipolarons in CPs.



Scheme 1. Mechanism for the electrochemical polymerization of the polypyrrole.

films were prepared usually by electrochemical polymerization of pyrrole (either in aqueous or organic solvent solution such as acetonitrile together with suitable electrolyte). The mechanism for electrochemical polymerization of pyrrole is shown in Scheme 1. It involves oxidation and dimerization of pyrrole followed by aromatization and oxidation of the dimer. The aromatic dimer and the higher molecular weight oligomers are known to oxidize more easily than the monomer. By extension of these reactions, the steps for the polymerization process can be described as in Eqs. (4) and (5) of the Scheme 1. The polymerization reaction has been shown to involve two electrons/molecule of pyrrole reacted and the resulting polymer is produced in the oxidized state with 0.25–0.33 cation centers per pyrrole unit depending on the electrolyte anion used. Ppy thickness is controlled through the charge passed.

Doped (oxidized) polypyrrole film is blue-violet ( $\lambda_{\max} = 670$  nm). Electrochemical reduction yields the yellow-green ( $\lambda_{\max} = 420$  nm) “undoped” form. The schematic of the doping/dedoping process can be given as



Removal of all dopant anions from polypyrrole yields a pale-yellow film. However, complete dedoping is only

achieved if the Ppy films are extremely thin. This means that Ppy of thickness commensurate with device construction ( $>1 \mu\text{m}$ ) has a low contrast ratio.

The electrochromism of Ppy is unlikely to be exploited, mainly due to the degradation of the film on repetitive color switching. CPs with improved electrochromic properties are, however, formed on electrochemical polymerization of 3,4-disubstituted pyrrole.

We have combined PB films with polypyrrole films and constructed ECDs. Our results show that the use of PB not only enhances the electrochromic response (contrast) but also extends the response to wider region of the visible spectrum thus acting as a sensitizer for improving the electrochromic response of Ppy (Fig. 9). We have also found that the electrochromic contrast of such composite films is strongly dependent on the size of the counterions, electronegativity and thickness of the films.

## 7.2. Polyaniline

The electrical and electrochromic properties of polyaniline depend not only on its oxidation state but also on its protonation state, and hence the pH value of the electrolyte used. The electrochemistry of polyaniline thin films were extensively investigated in aqueous acid solutions and in organic media, and several redox mechanisms involving

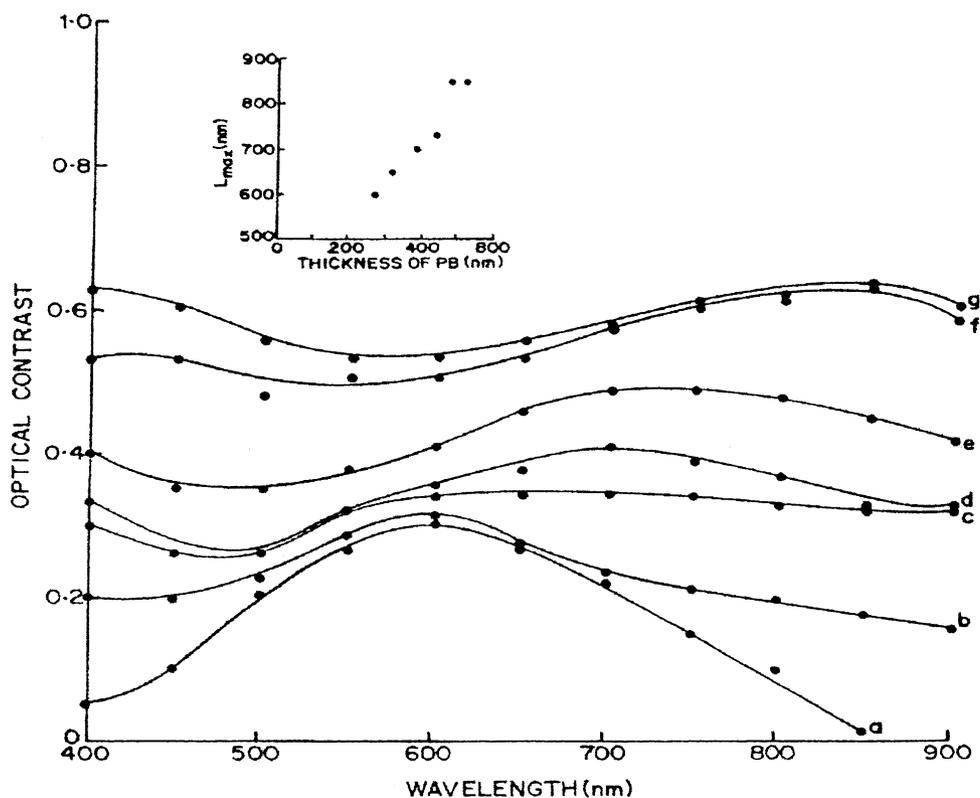


Fig. 9. Effect of PB films on the electrochromic contrast of polypyrrole films in 0.01 M aqueous  $\text{LiClO}_4$  electrolyte. Curves (a)–(g) correspond to the PB film thickness of 0, 280, 315, 380, 435, 475, 520 nm, respectively. The inset shows the shift in wavelength of maximum contrast  $L_{\text{max}}$  with the PB film layer thickness [44].

protonation–deprotonation and/or anion ingress/egress have been proposed. Fig. 10 shows various polyaniline forms and their interconversions. Polyaniline (PANI) films are poly-electrochromic (transparent yellow to green, dark blue and

black), the yellow–green transition being durable to repetitive color switching.

Kaneko et al. have prepared the PANI films by electropolymerization of aniline on a platinum or Nesa glass at

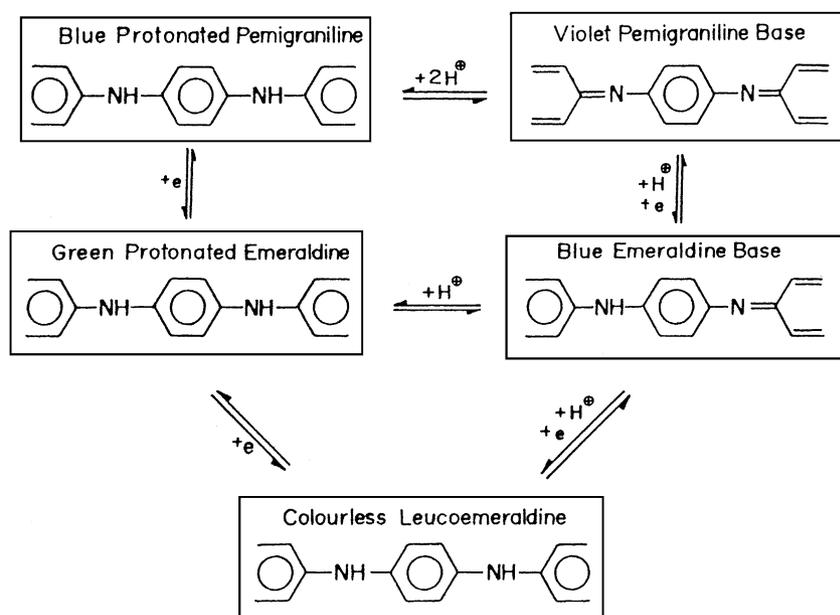


Fig. 10. PANI forms and their interconversions.

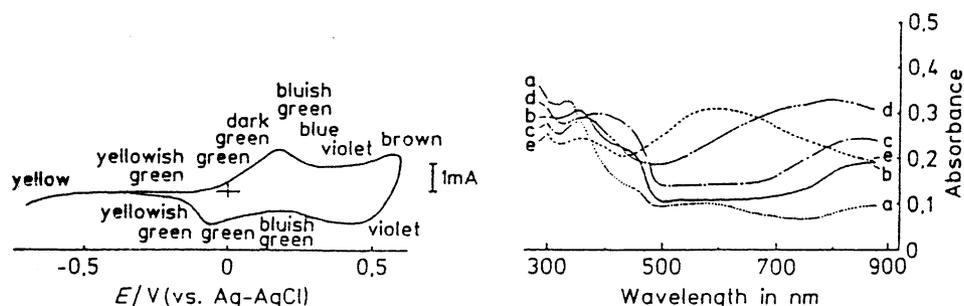
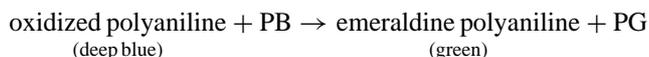


Fig. 11. (a) Cyclic voltammogram and the color changes in the PANI film coated on Pt and dipped in a  $10^{-2}$  M aqueous HCl solution containing  $0.2 \text{ mol/dm}^3$  LiCl, scan rate:  $10 \text{ mV/s}$ . (b) Absorption spectra of PANI film coated on a Nesa glass dipped in a  $10^{-2}$  aqueous HCl solution containing  $0.2 \text{ mol/dm}^3$  LiCl measured after applying potentials of: (a)  $-0.7 \text{ V}$ , (b)  $0 \text{ V}$ , (c)  $0.2 \text{ V}$ , (d)  $0.5 \text{ V}$  and (e)  $0.7 \text{ V}$  vs. Ag–AgCl electrode [72].

$1 \text{ V}$  versus Ag–AgCl using  $1 \text{ Mol/dm}^3$  aniline dissolved in  $2 \text{ M}$  aqueous HCl solution for  $15 \text{ s}$ . The results shows that under neutral to basic conditions, the PANI film prepared was black and do not show any electrochromism studied by visible spectroscopy. The PANI film prepared under acidic conditions as described above showed reversible multicolor electrochromism. The cyclic voltammogram and the color changes under continuous scanning of the applied potential from  $-0.7$  to  $0.6 \text{ V}$  versus Ag–AgCl are shown in Fig. 11a. It shows reversible color changes from yellow, yellowish green, green, dark green, bluish green, blue and violet to brown, depending on the applied potential. Fig. 11b shows the visible absorption spectrum measured after applying a potential to a PANI film coated on a Nesa glass. They show two major absorption regions around  $300\text{--}500 \text{ nm}$  and above  $500 \text{ nm}$ . The absorption at the wavelength above  $500 \text{ nm}$  shifts to a shorter wavelength when the applied potential is changed from  $-0.7$  to  $0.7 \text{ V}$  versus Ag–AgCl electrode. This blue shift of the absorption corresponds to color changes of yellow ( $-0.7 \text{ V}$ ), green ( $0 \text{ V}$ ), blue ( $0.2\text{--}0.3 \text{ V}$ ), violet ( $0.5 \text{ V}$ ) and brown ( $0.7 \text{ V}$ ). If the absorption maximum shifts to around  $500 \text{ nm}$ , as is expected when the applied potential is above  $0.7 \text{ V}$  versus Ag–AgCl, the PANI film must exhibit a red color. However, application of a potential above this value indicated an irreversible color change of the PANI film.

The electrochromic colors shown by the PANI films are very close to the three primary colors (i.e. green, blue and red) except for red. If the absorption maximum could be shifted to a shorter wavelength up to  $500 \text{ nm}$ , it would show all three primary colors. Introduction of a substituent or another monomeric unit might lead to an electrochromic device which can show all colors.

PANI has been combined with PB in complementary ECDs that exhibit deep blue  $\leftrightarrow$  green electrochromism. The electrochromic compatibility is obtained by combining the colored oxidized state of the polymer with the blue PB and the bleached reduced state of the polymer with PG



(9)

both liquid electrolyte and solid state configurations have been described.

Whilst electrochemical polymerization is a suitable method for the preparation of relatively low surface area electrochromic CP films, it may not be suitable for fabricating large area electrochromic displays. Efforts have been made to synthesize soluble CPs such as poly(*o*-methoxyaniline) which can then be deposited as thin film by casting from solution, by relatively easier techniques such as dip coating, spin coating, etc. In a novel approach, large area electrochromic coatings have been prepared by incorporating PANI into polyacrylate–silica hybrid sol–gel networks using suspended particles or solutions and then spray or brush-coating onto ITO surfaces [66–72].

### 7.3. Polythiophene

Like Ppy, polythiophene thin films can be prepared by electrochemical polymerization of thiophene. Electrochromic properties of polythiophene and of the polymers of several substituted thiophenes are reported in Table 2.

Tuning of color states is possible by suitable choice of thiophene monomer. For example, the electrochromic properties of polymer films prepared from 3-methylthiophene based oligomers are strongly dependent on the relative positions of the methyl groups on the polymer backbone.

When a multicolor EDD is constructed by combination of different species of electrochromic CPs, an electrochromic CP is often combined with a second electrochromic polymer showing a different specific color at a quite different

Table 2  
Polythiophenes

Serial number	Monomer	Polymer $\lambda_{\text{max}}$ (nm) and color	
		Oxidized state	Reduced state
1	Thiophene	730 (blue)	470 (red)
2	3-Methylthiophene	750 (deep blue)	480 (red)
3	3,4-Dimethylthiophene	750 (dark blue)	620 (pale-brown)
4	2,2'-Bithiophene	680 (blue-grey)	460 (red-orange)

Table 3  
Electrochromism observed in CPs

Serial number	Polymer	Anion	Color of the film		Response time (ms)
			Oxidized state (doped)	Reduced state (undoped)	
1	Polypyrrole	$\text{ClO}_4^-$	Brown	Yellow	20
2	Polythiophene	$\text{ClO}_4^-$	Brown	Green	45
3	Polymethylthiophene	$\text{BF}_4^-$	Blue	Red	12
4	Poly-3,4-dimethylthiophene	$\text{ClO}_4^-$	Dark blue	Blue	60
5	Poly-2,2'-bithiophene	$\text{CF}_3^-$ , $\text{SO}_3^-$	Blue/grey	Red	40
6	Octacyanophthalocyanine	$\text{H}^+$	Green	Blue	1
7	PANI	$\text{Cl}^-$	Green/blue	Yellow	100

operation potential. Poly(aniline)–poly(sodium acrylate)–poly(thiophene) and poly(aniline)–poly(sodium acrylate)–poly(3-methylthiophene) combined films are constructed by combining poly(aniline)–poly(sodium acrylate), which shows its specific color in the oxidized state, with poly(thiophene) and poly(3-methyl thiophene), which show their specific color in the reduced state. An electroactive polymer laminate for use in an EDD comprises a conductive substrate, a first layer of an electroactive polymer, and a second layer of an electroactive polymer prepared from a second monomer having an oxidation potential higher than that of the first monomer and adhering to the first layer [73–75].

Table 3 gives the comparison of electrochromism observed in most studied CPs.

#### 7.4. Other CPs and gels

Polyisothianaphthene (PITN) is the first example of the transparent CP. It exhibits reversible p-type electrochemical doping with an associated high contrast color change with an excellent stability. Doped thin films of PITN have very low optical density. Reversible electrochromism with a characteristic switching time of a few hundred milliseconds have been found. The experimental results demonstrate that the rate limiting step in the electrochromic switching process involves diffusion of dopant counterions into the polymer structure. Also, it has been shown that the polymer morphology plays an important role in determining the electrochromic switching. By controlling the morphology, so as to minimize the diffusion distance in CPs, it should be possible to achieve sufficient speed to be of interest for a variety of technological applications [76].

Poly(*o*-aminophenol) (PAP)—a ladder polymer with phenoxazine rings as electroactive sites—can be prepared by electrooxidative polymerization of *o*-aminophenol in an acidic solution. The PAP film is strongly adhesive to the electrode surfaces, with very uniform, semiconducting, and display electrochromic properties. The oxidative form is bronzy brown and reduced one is pale-green (almost colorless). The maximum absorption peak of the oxidized form was observed at 440 nm and that of the reduced one at ca. 600 nm. A reversible color change of the film between brown and pale-green (almost colorless) was observed when the electrode potential was cycled between  $-0.7$  and

$+0.7$  V versus SCE. The brown color of the oxidized form remains substantially unchanged even after standing it in air at open circuit for a long period (of about 6 months), i.e. the film possessed the “memory effect”. On the other hand, the reduced form was gradually oxidized by oxygen in air and consequently becomes colored. The colorlessness of the reduced form can be held under an atmosphere of nitrogen gas. The response time is somewhat high, i.e. several seconds were required to complete the coloring of the film and then to bleach it completely [77].

It has been observed that, under certain experimental conditions, the electrochemical reduction of *o*-chloranil (*o*-CA) yields electrode adherent blue films which can be bleached by oxidation. The writing/erasing lifetime of the *o*-CA/*o*-CA<sup>−</sup> system on a Pt electrode, greater than  $10^5$  cycles, deteriorates if the reduction potential allows the formation of *o*-CA<sup>2−</sup> dianions. The electrochemical reduction of *p*-chloranil under similar experimental conditions produces a yellow color at the electrode which diffuses into the solution. Hence, ortho-quinones seem better suited for electrochromic applications than *para*-compounds [78].

Polymer gel films [poly(1-vinyl-2-pyrrolidin-one-co-*N*,*N*'methylenebisacrylamide (PVPD))] which contain simple organic electrochromics [*p*-diacetylbenzene (*p*-DAP), dimethyl- or diethyl terephthalate (*p*-DMP or *p*-DEP)] have been prepared and their electrochromic response is being investigated. A single film ECD has been prepared and studied. Its simple construction is suitable for large area displays [79].

## 8. Comparison between inorganic and polymeric EC materials

Table 4 gives a comparison between inorganic and polymeric electrochromic materials.

## 9. Current status and use of electrochromic devices

### 9.1. A moving electrochromic pixel

A microfabricated, movable electrochromic “pixel” based on conducting Ppy has been prepared and demonstrated

Table 4  
Comparison between inorganic and polymeric EC materials

Serial number	Property	Inorganic materials	Polymers
1	Method of preparation	Needs sophisticated techniques such as vacuum evaporation, spray pyrolysis, sputtering, etc.	The material can be easily prepared by simple chemical, electrochemical polymerization and the films can be obtained by simple techniques such as dip-coating, spin coating, etc.
2	Processibility of the materials	The materials are poor in processibility	The materials can be processed very easily
3	Cost for making the final product (device)	High as compared to the polymer based devices	Low cost as compared to the inorganic materials
4	Colors obtainable	Limited number of colors are available from a given material	Colors depends on the doping percentage, choice of the monomer, operating potential, etc. Hence, large number of colors are available with the polymeric materials
5	Contrast	Contrast is moderate	Very high contrast can be obtained
6	Switching time (ms)	10–750	10–120
7	Lifetime	$10^3$ – $10^5$	$10^4$ – $10^6$ cycles

by Elisabeth Smela, which uses the fact that the conjugated polymers undergo a volume change of several percent and color change when its oxidation state is changed electrochemically. This demonstration shows that, in principle, many different kinds of electronic, optical and micromechanical devices could be put on movable platforms. One can envision moving light emitting diodes or semiconductor lasers, e.g., or a comb-drive microgrippers being moved into position to grasp a small object.

A particular application one can pursue is a chip for the study of living cells or single-celled organisms. A cavity etched in silicon with a sealable lid could be used to capture a cell, and both the cavity floor and the lid could carry devices for measuring a property of interest. For example, there could be electrodes on them so that the resistance could be measured or a potential applied. Alternatively, a light source on the lid could be coupled with a light detector on the floor for optical measurements. Chemical sensors could monitor the response of the cell. A wafer could be covered with thousands of such devices so that information could be gathered from the great many cells. Such devices are one step on the way to such goals [80].

### 9.2. All plastic and flexible electrochromic devices

The production of all plastic and flexible electrochromic device, is in progress, which facilitates new technological applications. Two factors prompted the assembly of all plastic electrochromic devices

- Commercial production of transparent electrodes with thermoplastics (i.e. ITO–PET, where PET is poly(ethylene terephthalate));
- Synthesis of new CPs with low energy band gap.

Most of the so-called “all plastic” electrochromic devices described in the literature comprise not only plastic components, but also inorganic compounds as one of the

electrochromic materials. Moreover, most of these materials, including those polymers with low energy band gap, do not show the high flexibility and elasticity inherent to polymeric materials. One exception is PANI-doped with dodecylbenzene sulfonic acid or phosphoric acid diesters, which shows “plastic” characteristics.

Hence, in order to assemble an all-plastic and flexible electrochromic device it is necessary to improve the mechanical properties of the CPs used as electrochromic materials. This problem can be overcome by mixing the CPs with thermoplastics or elastomers to produce polymeric blends which show the electrochromic properties of the CPs associated with the mechanical properties of common polymers.

All plastic and flexible electrochromic devices have been fabricated and described by De Paoli et al. using two optically complementary conductive polymer blends deposited on ITO–PET and a polymeric electrolyte. Two polymer blends were prepared by mixing the CPs poly(ET2) and poly(4,4'-dipentoxo-2,2'-bithiophene) (poly(NNDMBP)) with the elastomer poly(epichlorohydrin-Co-ethylene oxide) (Hydrin-C). The SPE was a mixture of Hydrin-C and  $\text{LiClO}_4$ . The results show that blending with Hydrin-C improves not only the mechanical properties of the CPs, but also their electrochromic properties. Such devices show good optical characteristics, such as stability to successive electrochromic cycling, short optical response time and a good optical contrast. Scale-up of such devices is in progress [81].

### 9.3. ECD for time–temperature integration

An attempt has been made to use an electrochromic device for time–temperature integration. Such a device could be used for “smart” labeling of frozen food. A “use by” date is valid only if the product has been stored and transported under correct conditions. There is a heavy interest in sensors that could be incorporated into packaging and provide

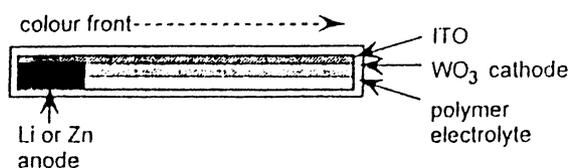


Fig. 12. Schematic diagram of the ECD used for time-temperature monitoring. [83].

a visual indication of whether an item has experienced conditions that cause deterioration.

In a simple case, the rate of deterioration may be expressed by an Arrhenius equation and the cumulative effect over time is given by an expression of the form

$$\text{Degree of deterioration} = \int A \exp(-E_a/RT) dt \quad (10)$$

For an electrochromic device incorporating a polymer electrolyte and operating under a condition of constant potential across the electrolyte, the current depends upon the temperature according to the Arrhenius expression, at least over a small temperature range, and the total charge passed in a given time is given by an expression similar to the integral of Eq. (10). It should, therefore, be feasible for a polymer electrolyte and device configuration to be tailored to match the time/temperature profile for decay of a particular foodstuff.

Budd et al. have prepared a polymer electrolyte suitable for use at subambient temperatures and investigated its behavior in a simple prototype electrochromic device, as shown in Fig. 12. The electrochromic layer is  $\text{WO}_3$ , which becomes blue on intercalation with lithium or hydrogen, e.g.



the anode is a metal foil, and the polymer electrolyte incorporates an appropriate salt. The circuit is completed by

a conducting ITO layer. Coloration occurs initially in the region closest to the anode and, as that region becomes saturated, the color front progresses along the device at a rate dependent on the conductivity of the electrolyte, and consequently on the temperature. The polymer studied by him is the poly[oxymethylene-oligo(oxyethylene)] [82,83].

#### 9.4. Electrochromic (smart) windows

An electrochromic window (EW) is an ECD which allows electrochemically driven modulations of light transmission and reflections. Such electrochromic optical switching device is usually called as “smart window”. It can be used for a variety of applications where the optical modulation effect can be used significantly. For example, regulation of incident solar energy and glare for the improvement of energy efficiency of buildings, vehicles, aircraft, spacecraft and ships. The potential market for smart windows is very large and includes in the automobile sector rear-view mirrors (which are already in the marketplace), sun-roofs and visors, side and smart windows. Other uses are large area information displays to be used in airport and railway stations as well as electrochromic eyeglasses and sunglasses.

In EW, the entire system is in the optical path unlike ECD which puts some restrictions on the electrolyte to be used. Either it should be transparent or electrochromic in a complementary mode with respect to primary electrochromic electrode. These requirements are not easy to be fulfilled and hence most of the efforts have been devoted to the characterization of the materials capable of assuring the desired complementary switchable optical function. Such EWs can be combined with the solar cells so that the power required to bring the electrochromic color change can be obtained from the solar cells.

Table 5  
A comparison of ECDs with other non-emissive displays

Serial number	Property	Electro chromic displays (ECDs)	Electro phoretic (EP) displays	Field effect liquid crystal (FELC) displays	Dynamic scattering liquid crystal (DSLCL) displays	Dipole suspension (DS) displays
1	Viewing angle	Wide	Wide	Narrow	Narrow	Narrow
2	Optical mode	T <sup>a</sup> , R <sup>b</sup> , P <sup>c</sup>	R	T, R, P	T, R, P	T, R
3	Color	Two or more	Two	B/W or dye	B/W	B/W
4	Resolution	Electrode limited	Electrode limited	Electrode limited	Electrode limited	Electrode limited
5	Operating mode	dc pulse	dc pulse	ac	ac	ac
6	Voltage (V)	0.25–20	30–80	2–10	10–30	2–30
7	Power ( $\mu\text{W}/\text{cm}^2$ )	1–10	15	<0.1	1–10	1–10
8	Energy ( $\text{mJ}/\text{cm}^2$ )	10–100	$6 \times 10^{-4}$			
9	Memory	Yes	Yes	No/yes	No/yes	No
10	Threshold	Poor	No	Poor	Poor	Poor
11	Contrast					
12	Write time (ms)	100–1000	60	20	20	20
13	Erase time (ms)	100–500	30	1–500	100	30
14	Operating life	$10^5$ – $10^6$ cycles		$>2 \times 10^4$ h	$>1 \times 10^4$ h	

<sup>a</sup> Transmission.

<sup>b</sup> Reflection.

<sup>c</sup> Projection.

### 9.5. Cathode ray tubes with variable transmittance

An alternative to the common “brilliance” adjustments of TV tubes, when room illumination alters, is an electrochromically darkening cathode ray tube (CRT) screen employing oxides, which is being studied at Philips [84]. Electrochromic darkening is preferable to direct electrical control as color values are thereby better preserved.

Other applications of electrochromic materials such as for entry-ticket security [85,86], etc. are quite interesting.

## 10. A comparison of ECDs with other non-emissive displays

A comparison of ECDs with other non-emissive displays is given in Table 5. It can be seen that ECD is comparable in properties with that of LCD with the added advantages that it can be made into different colors without the addition of external dye or window, does not depend upon the viewing angle and can be easily prepared in the form of large area windows.

## 11. Conclusions and future prospects of electrochromic materials and devices

In the recent years, a lot of attention is being paid in understanding the physical and chemical properties of various electrochromic materials and particularly on CPs not only from basic research point of view but also from the commercial view. It has brought various electrochromic materials and devices actually in the market also, such as, in automobile sector rear view mirrors and several others like sunroofs and visors are under prototype production. Alphanumeric displays and electrochromic mirrors have also been produced. Widespread applications of ECDs, particularly, for architectural applications depends on reducing costs, increasing device lifetime and overcoming the problem of ECD degradation. Further, existing smart windows require an external power source for their operation. Photo-electrochromic systems which changes color electrochemically but only on being illuminated may be more appropriate candidates for smart windows. The study and development of photo-electrochromic materials and devices for large area window applications are in progress. Commercial production of all plastic electrochromic devices, smart windows, for monitoring time–temperature application has been already achieved.

The production of moving electrochromic images (such as moving pixels as described in this paper and alphanumeric displays, etc.) is the next step in the research and development of EC materials and hence needs more efforts to be done in that direction.

In this review, we consigned non-visible electrochromic responses, important in both solar screening and optical fiber

systems. Recent interest for electrochromic devices for multispectral energy modulation by reflectance and absorbance has extended the working definition. Electrochromic devices are now being studied for modulation of radiation in the near infrared, thermal infrared and microwave regions and “color” can mean response of detectors of these wavelengths, not just the human eye.

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