CHROMOGENIC MATERIALS, ELECTROCHROMIC

1. Introduction

A number of inorganic and organic materials exhibit redox states (reduced and/or oxidized forms) with distinct uv-visible (electronic) absorption bands. When electrochemical switching of these redox states is reversible and gives rise to different colors (ie, new or different visible region bands), the material is described as being electrochromic (1). The optical change is effected by a small electric current at low d-c potential.

The potential is usually on the order of 1V, and the electrochromic material sometimes exhibits good open-circuit memory. Unlike the well-known electrolytic coloration in alkali halide crystals, the electrochromic optical density change is often appreciable at ordinary temperatures. Where more than two redox states are electrochemically accessible in a given electrolyte solution, the electrochromic material may exhibit several colors and be termed polyelectrochromic (2).

By virtue of their numerous academic and commercial applications, electrochromic materials are currently attracting a great deal of interest.

Electrochromic antiglare car rearview mirrors have already been commercialized. Other proposed applications of electrochromic materials including their use in controllable light, reflective or light-transmissive devices for optical information and storage, sunglasses, protective eyewear for the military, controllable aircraft canopies, glare-reduction systems for offices and “smart windows” for use in cars and in buildings (3–5).

In the field of electrochromic data displays, present devices have insufficiently fast response times to be considered for such applications and cycle lives are probably also too low.

Accordingly the most exciting and attractive roles presently envisaged involve long-term display of information, such as at transport termini, reusable price labels, and advertising boards.

A large number of recent reviews on various categories of electrochromic materials and their applications have been published (2,5,6–9).

The major classes of electrochromic materials are metal oxides, Prussian blue systems, viologens, conducting polymers, transition metal and lanthanide coordination complexes metallopolymers and metal phthalocyanines. Although the latter two classes of metal coordination complexes might be considered as inorganic, they are included here because, mainly, the exhibited colors are a result of transitions that involve organic ligands. Table 1 characterizes the various classes of electrochromic materials and their main applications.

Table 1. **Summary of Applications of Electrochromic Materials**[a]

Material class	Examples	Possible uses
transition metal oxides	WO_3, MoO_3, V_2O_5, Nb_2O_5, $Ir(OH)_3$ and NiO_xH_y	smart windows, thermal control of satellites and electrochromic writing paper
Prussian blue systems	$[Fe^{III}Fe^{II}(CN)_6]^-$ Prussian blue; $[Fe^{III}Fe^{III}(CN)_6]^-$ Prussian brown; $[Fe^{III}_3\{Fe^{III}(CN)_6\}_2\{Fe^{II}(CN)_6\}]^-$ Prussian green and $[Fe^{II}Fe^{II}(CN)_6]^{2-}$, Prussian white	displays
viologens	1,1′-disubstituted-4,4′-bipyridinium salts[b]	car rearview mirrors and displays
conducting polymers	polypyrrole, polythiophene, polyaniline etc	smart windows and displays
transition metal and lanthanide coordination complexes and metallopolymers	metal hydrides, nitrosyl and oxo molybdenum complexes, poly-$[Ru^{II}(vbpy)_2(py)_2]Cl_2$	switchable mirrors, near-infrared switching
metal phthalocyanines	$[Lu(Pc)_2]$	electrochromic displays

[a] Ref. 1.

[b] Already used.

Coloration occurs both cathodically and anodically, as well as in both organic and inorganic materials. Compounds of all types may be classified within one or the other of two general groups based on the nature of charge balancing.

In one group, an electrolyte separates a cathode–anode pair, one or both of which may be chromogenically active. Typically the chromogenic material is a thin film on the cathode or anode.

As charge neutrality must be preserved, and the electrochromic cathode or anode is a solid, insertion–extraction of ions, often H^+ or alkaline metal, accompanies reduction-oxidation within the electrode surface layer. Insertion/extraction in the cathode or anode is the distinguishing feature of the group.

The second group is best described by referring to the viologens, a family of halides of quaternary ammonium bases derived from the 4,4′-bipyridinium structure.

Viologens are recognized as the first important organic electrochromic materials (10,11). Some of these color deeply within solution by simple reduction; others are distinguished by their deep coloration when electrodeposited from solution onto a cathode. These colorations are characteristic of the noninsertion group, although incidental insertion may accompany electrodeposition.

Members of the ion-extraction group as inorganic or organic thin films, especially the former, have attracted the widest interest most recently. Tungsten trioxide was the earliest exploited inorganic compound (12), even before the mechanism of its electrochromic response was understood (13). It is still the best known of the important ion-insertion/extraction group.

Much of the earliest published work followed from research on displays, but opportunities for switchable mirrors and windows have been highlighted as well.

With one noteworthy exception, however, there has been no remarkable commercial success because the technology involves many complex scientific and engineering principles. Also, the competing liquid crystal technology has evolved successfully in some displays applications. The one commercial exception is an electrochromic automotive rearview mirror, which has been gaining popularity since 1988. The mirror contains an encapsulated solution of viologen, that undergoes optical switching without electrodeposition (14).

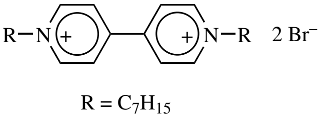
2. Oxidation–Reduction in the Noninsertion/Extraction Group

The best known examples in this group are organic dyes, and the vehicle in which the oxidation–reduction takes place is in general, a liquid electrolyte. For displays, however, it is preferred that color is not developed within the liquid itself, but rather by electrodeposition. Otherwise there is drifting of the coloration and poor memory, which are especially troublesome for displaying information with high resolution.

Earlier materials, which depended on oxidation–reduction in solution or on a pH indicating effect at an electrode, were abandoned (15). The drifting, however, has proven to be acceptable for a mirror (14).

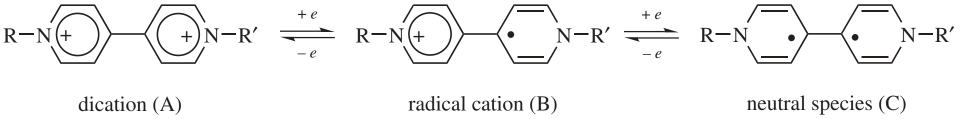
2.1. Organic Compounds.

Viologens. Viologens typically require a very low charge density of $2mc/cm^2$ to develop sufficient contrast for display applications. They are the only compounds of the group that have been studied extensively (16). The best known viologen is 1,1′-diheptyl-4,4′-bipyridinium dibromide [6159-05-3].



A cell is caused to switch from clear to bluish-purple when the divalent cation is univalently reduced in aqueous KBr solution and electrodeposited on the cathode as the bromide (10,11). The electrochromic response is visible with an applied potential more negative than −0−66V against the SCE. The peak of visible absorption is at 545 nm. The added electron is delocalized on the monovalent radical ion to which it is reduced (11). Various other viologen compounds have been mentioned (17,18).

The three common viologen redox states obtained by two successive electron transfer reactions could be represented in equation 1.



(1)

The dicationic form (A) is the most stable and is colorless when pure (unless optical charge transform with the counter anion occurs) (5). The developed colors are also depending on the substituents (19).

However, even with the flexibility for molecular synthesis with organic materials, the experience with viologens typifies two important difficulties.

Cycling instability associated with the onset of side reactions remains a consistent problem for displays, for which a lifetime $\geq 10^7$ cycles is generally required. Viologens suffer especially from a so-called recrystallization of the electrodeposit which impairs erasure of darkened state (20).

Efforts to alter the molecular structure of the radical ion halide salt have been without far-reaching success for display devices.

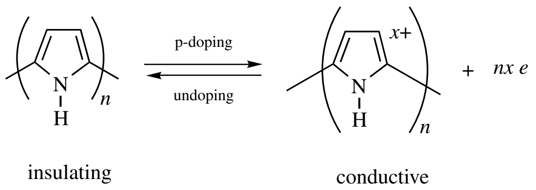
Besides this, susceptibility to degradative oxidation and photooxidation requires sealing out oxygen and minimizing exposure to uv frequencies of light. Clearly, this susceptibility to oxidation is an especially serious technical hurdle for switchable mirrors and windows exposed to outdoor conditions. When viologens are embedded in appropriate polymer matrices (eg, in poly(*N*-vinyl-2-pyrrolidone), they exhibit a photochromic behavior (21).

Use of Polymers Systems. A polymer electrochromic device (22) has been made, however the penalty for polymerization is a loss in device speed. Methyl viologen dichloride was dissolved in hydrated poly(2-acrylamido-2-methylpropanesulfonic acid), producing a tacky polymer electrolyte (23,24).

Poly(2-acrylamido-2-methylpropanesulfonic acid) was also used to immobilize methylene blue (22), which oxidizes from the colorless to neutral molecule by a one-electron transfer.

Chemical or electrochemical oxidation of many poly-conjugated compounds such as pyrrole, thiophene, aniline, furan, carbazole, azulene and indole produces polymer films of polypyrrole, polythiophene, or polyaniline etc. doped with counter-ions. The first stage of the polymerization mechanism involves radical cations. The doped polymers, which can adhere to the electrode surfaces are highly conducting, while the undoped, neutral forms are insulating. The oxidized (doped) and reduced (undoped) states of these polymers exhibit different colors, and electroactive conducting polymers are all potentially electrochromic as thin films (5,19).

For example polypyrrole as a thin film exhibits yellow-green (undoped) and blue-violet (doped) electrochromism (eq. 2) (5).



(2)

Polythiophenes (25) are of particular interest as electrochromic materials due to their chemical stability, ease of synthesis and processability. Polythiophene thin films are blue ($\lambda_{max} = 730$ nm) in their doped (oxidized) state and red ($\lambda_{max} = 470$ nm) in their undoped form. Tuning of color states is possible by suitable choice of the thiophene monomer, and this represents a major advantage of using conducting polymer for electrochromic applications. Suitable modifications to the monomer can significantly alter special properties. For example the colors available with polymer films prepared from 3-methylthiophene-based oligomer are strongly dependent on the relative position of methyl groups on the polymer back bone (26).

Colors available include pale blue, blue and violet in the oxidized form, and purple, yellow, red and orange in the reduced form. The color variations have been ascribed to changes in the effective conjugation length of the polymer chain.

Alkoxy-substituted polythiophenes are currently being intensively investigated for their electrochromic properties (27–34). Materials based on poly(3,4-(ethylenedioxy)thiophene) (PEDOT) have a band gap lower than polythiophene and alkyl-substituted polythiophenes, owing to the presence of the two electron-donating oxygen atoms adjacent to the thiophene unit. For example the band gap of PEDOT (Eg = 1.6eV) is 0.5eV lower than polythiophene which results in an absorbance maximum in the near infra-red region.

Generally the poly(3,4-alkylene dioxy thiophene)s (PXDOTS) are in a class of conducting and electroactive polymers that can exhibit high and quite stable conductivities, a high degree of optical transparency as a conductor, and the ability to be rapidly switched between conducting doped and insulating neutral states.

PXDOTS have attracted attention across academia and industry. In a recent review (35), fundamental aspects were investigated ranging from the electrochemical synthesis of PXDOTS, a variety of *in-situ* characterization techniques, the broad array of properties accessibles and morphological aspect.

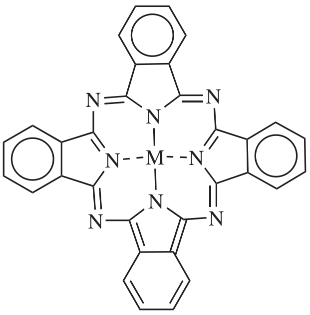
Finally two electrochemically driven applications, specifically electrochromism and chemical sensors of PXDOTS, are discussed.

Polyenes and oligomers of poly(*p*-phenylene vinylene) with well-defined length of the conjugated system were prepared by straightforward synthetic procedures based upon organometallic derivatives of silicon or boron (36). Fluorinated oligo(*p*-phenylenes) containing up to five aromatic rings were easily obtained by homocoupling reaction promoted by copper(I) thiophenecarboxylate.

Metallopolymers. Transition metal coordination complexes of organic ligands are potentially useful electrochromic materials because of their intense coloration and redox reactivity. Chromophoric properties typically arise from low-enegy metal to ligand charge transfer (MLCT), intervalence CT, intraligand excitation, and related visible region electronic transitions. Because these transitions involve valence electrons, chromophoric characteristics are altered or eliminated upon oxidation or reduction of the complex (5). While these spectroscopic and redox properties alone would be sufficient for direct use of transition metal complexes in solution phase ECDS (electrochromic devices), polymers systems have also been investigated which have potential use in all-solid-state systems. Many schemes have been described for the preparation of thin-film "metallopolymers" (37) including both the reductive and oxidative electropolymerization of suitable polypyridyl complexes. Spatial electrochromism has been demonstrated in metallopolymer films (38). Photolysis of orange poly-$[Ru^{II}(vbpy)_2(Py)_2]Cl_2$ thin films (vbpy = 4-vinyl-4-methyl-2,2′-bipyridine) on ITO glass in the presence of chloride ions leads to photochemical loss of the photolabile pyridine ligands and squential formation of poly$[Ru^{II}(vbpy)_2(py)Cl]Cl$ (red) and poly$[Ru^{II}(vbpy)_2Cl_2]$ (purple).

By suitable choice of metal, the color of such metallopolymer films in the M(II) redox state may be selected (eg, M = Fe, red; M = Ru, orange; M = O_S, green). Electrochromicity results from loss of the metal-to-ligand charge transfer absorption band on switching between the M(II) and M(III) redox states (5).

Metal Phthalocyanines. Phthalocyanines (Pc) are tetraazatetrabenzo-derivatives of porphyrins with highly delocalized *II*-electron systems.



M= metal or H_2

Metallophthalocyanines are important industrial pigments used primarily in inks and coloring plastics and metal surfaces (39). The water soluble sulfonate derivatives are used as dyestuffs for clothing. The purity and depth of the color of metallophthalocyanines arise from the unique property of having an isolated, single band located in the far red end of the visible spectrum near 670 nm, with ε often exceeding 10^5 $dm^3mol^{-1}cm^{-1}$.The next most energetic set of transitions is generally much less intense, lying just to the blue of the visible region near 340 nm. Introduction of additional bands around 500 nm, eg, from charge transfer transitions between the metal and the phthalocyanine ring, allows tuning of the hue (39).

Polyelectrochromism of bis (phthalocyaninato)lutecium(III) ($[Lu(Pc)_2]$) thin films was first reported in 1970, and since that time this complex has received most attention, although numerous other (mainly rare earth) metallophthalocyanines have been investigated for their electrochromic properties (3).

In addition to the familiar applications in the area of dyestuffs, the metallophthalocyanines have been intensely investigated in many fields including catalysis, liquid crystals, gas sensors, electronic conductivity, photosensitizers, nonlinear optics and electrochromism (39).

2.2. Inorganic Electrodeposition. From a comprehensive analysis (40,41) of a variety of electrodepositable metals, the reversible cathodic electroplating of silver has been determined to be the best method. A preferred aqueous solution for light shutters and displays contains 3.0–3.5*M* Ag(I) and 7 M Ha(I). The complementary I_3^- anodic oxidation product contributes to the change in optical density. For the highest speeds and contrast intended at the time of analysis, several plating cells were required, back to back. Dependence on liquid-state electrolytes presents practical problems in cell assembly and scaling, so the solid-state is often prefered.

3. Insertion/Extraction Compounds

The seminal work on these materials began at American Cyanamid Co. in the 1960s (12,42), although these workers did not develop the ion-insertion/extraction model that has become widely accepted (13). Numerous patents were granted to American Cyanamid Co. as a result of its display-oriented work. Much of what others have written in the open literature either confirms or adds to what these patents disclosed. Important papers (23) about cathodic WO_3^--based insertion devices and others (24,43,44) summarize this activity. The so-called amorphous, or poorly crystallized, tungsten oxide thin film, which developed as the most important material, is, like the viologens, of great interest because of its reversible clear-to-deep-blue coloration in transmission. Coloration efficiency is high.

An important way to assess the many insertion/extraction films known is to compare spectral coloration efficiencies, CE(λ) for the visible region.

$$CE(\lambda) = \Delta OD(\lambda)/\mathrm{q} \tag{3}$$

where $\Delta OD(\lambda)$ represents the change in single-pass, transmitted optical density at the wavelength of interest λ, because of a transfer of charge q, as C/cm^2. 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 (45). The coloration efficiency is determined by spectroelectrochemistry, 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. For example, a 1 *N* $LiClO_4$–propylene carbonate electrolyte solution was used with a Li anode counter electrode strip to measure the optical density change in cathodic tungsten oxide and other films during galvanostatic switching (46). Li^+ was alternately inserted into and extracted from the films. The films were deposited on conductive glass by reactive RF sputtering. Others have used similar techniques to obtain electrochromic cycling data, and propylene carbonate has been commonly used as well. Often films have been deposited by other common methods in vacuum and sometimes by anodization of the metal.

3.1. Cathodically Colored Inorganic Films. The generalized cathodic, monovalent ion-insertion reaction for inorganic thin films is

$$M_nO_{my}H_2O + xe^- + xJ^+ \rightarrow J_xM_nO_{my} \cdot H_2O \tag{4}$$

where M is a multivalent cation of the electrochromic oxide with valence $2m/n$; both m and n are taken as integers here, though that may not always be so. J^+ is the ion being inserted, and usually $0 < x < 1$. The y moles of H_2O indicate that these materials are generally variably hydrated, depending on preparation technique. Hydration and porosity are required for rapid coloration (13,47–49). On the other hand, for amorphous tungsten oxide thin films, porosity and water content are known to be associated with accelerated dissolution in acid aqueous electrolyte (13,43,48,50). It is noteworthy that single-crystal WO_3 is essentially insoluble, while otherwise interesting MoO_3 films are soluble.

Dissolution of amorphous tungsten oxide films in sealed capsules has been reported to be 2.0–2.5 nm/d at 50°C in 10:1 glycerol/H_2SO_4 (43). Dissolution is much easier in water–H_2SO_4, an even earlier electrolyte choice. With more recently and successfully developed sulfonic acid-functionalized polymer electrolytes, cell stability depends on minimizing the water content of the polymer (24). As with the film itself, however, some minimum water content is necessary in the electrolyte for achieving rapid electrochromic response. A balance must be struck for the water content of both film and electrolyte. One other critical issue with proton-based electrolytes, which applies when they are used with any ion-insertion/extraction film, is the likelihood for the water-containing electrolyte to contribute to electrochemical H_2 or O_2 gas evolution. Because of these collective problems, most of the recently published work with amorphous tungsten oxide has been done with alkali-ion insertion from nonaqueous electrolytes. Generally, however, these electrolytes have relatively low ion conductivity.

Table 2 shows ion-insertion data for some of the better known vacuum-deposited thin films of this class. These grow as amorphous (α) or poorly crystallized films at indicated low substrate temperatures. The coloration efficiency data illustrate one reason why amorphous tungsten oxide remains of high interest, despite the constraints already mentioned. All of the alternatives, including polycrystalline c-WO_3, have lesser coloration efficiencies in the all important visible region. In the near infrared, however, c-WO_3 exhibits a relatively high

Table 2. **Some Cathodically Colored, Inorganic Insertion[a]/Extraction Films[b]**

Film	CAS Registry number	Growth parameter[c]	CE(λ),[d] cm^2/C	λ, nm
α-WO_3	[1314-35-8]	ambient	$30 < CE < 125$	400–700
α-WO_3[e]		240–660 nm	$30 < CE < 50$	633
α-WO_3[f]		150°C 1500 nm	55	633
c-WO_3	[1314-35-8]	310°C	$5 < CE < 50$	400–700
c-MoO_3	[1313-27-5]	351°C	$30 < CE < 90$	500–700
α-Nb_2O_5	[1313-96-8]	40°C	<12	400–700
α-TiO_2	[13463-67-7]	40°C	<5	400–700
α-Ta_2O_5	[1314-61-0]	40°C	<5	400–700

[a] Insertion ion is Li^+ unless otherwise noted.

[b] Ref. 46, unless otherwise noted.

[c] Besides grow temperature, the column includes films thickness when known.

[d] Given as a value at a λ or bracketed over the indicated λ range.

[e] Also H^+ as insertion ion; Ref. 51.

[f] Ref. 52.

reflectance when darkened (53,54). The data in Table 2 have been used to propose an all solid-state window based on Li^+ insertion/extraction in cathodically coloring WO_3 (46). A low coloration, insertion/extraction oxide film such as α-Nb_2O_5 is deposited on conductive glass and serves as the counter electrode. A transparent thin film such as $LiAlF_4$ overlies it and is the nonliquid electrolyte. Deposited first on top of the electrolyte is a Li^+-precharged WO_3 film, and then a conductive and transparent film. During cycling, the α-Nb_2O_5 does not contribute much coloration in the WO_3-bleach cycle, as desired, when it assumes a cathodic role. As ideal as this seems in principle, however, it has not yet been reduced to a practical art.

By way of contrast, using proton conductivity, at least two other workable solid-state designs have actually been demonstrated at scale. The function of neither one is dictated by the coloration efficiency of a counter electrode. These use sulfonic acid-functionalized polymer electrolytes and depend on unique counter electrodes. One has a high surface area carbon paper counter electrode for reversible proton storage in a display configuration (23). The other has a very fine, reversibly oxidized copper grid that permits vision through a large-area transparency (55,56).

3.2. Anodically Colored Inorganic Films. The important electrochromic films of this class have been discussed in the open literature since 1978 and include Prussian blue (PB) (57) and the highly hydrated (h) oxides of iridium (59) and nickel (60). Data for these are shown in Table 3. Of lesser significance are the hydrous oxides of rhodium and cobalt (61,66,67). Like the cathodically coloring insertion films, the anodically coloring films depend, for useful darkening and bleaching rates, on having open porosity and hydration. Various colors have been reported qualitatively, though full coloration is limited sometimes by the onset of O_2 evolution (61). As Table 3 shows, Prussian blue is especially interesting because of its relatively high coloration efficiency. Except for Prussian blue, a common method of film preparation is potential cycling (pc) on either a bulk

Table 3. **Some Anodically Colored, Inorganic Insertion/Extraction Films**

Film	CAS Registry number	Growth method	Insertion ion	CE(λ), cm^2/C	λ, nm	References
h-IrO_x	[12645-46-4]	pc[a]	H^+/OH^-	15	633	60
h-IrO_x		rs	H^+/OH^-	18,12	633,600	61,62
h-NiO_x	[11099-02-8]	ged	H^+/OH^-	~50	~440 peak	63,64
Prussian blue	[12240-15-1][b]	ged	K^+	68	633	65

[a] ~180 nm.
[b] CI Pigment Blue 27.

metal or a conductive film. Reactive sputtering (rs) and galvanostatic electrodeposition (ged) have also been used for these electrochromic films. In the case of Prussian blue, the film has been grown by electroless reduction, by the sacrificial anode method or by galvanostatic electrodeposition (68–72).

Despite the considerable progress made in the few years in which anodic insertion/extraction films have been known, neither film compositions, film properties, nor electrochemical reactions are sufficiently well characterized. There have been disagreements, as indicated for h-IrO_x and h-NiO_x in Table 3, as to whether H^+ is being extracted or OH^- inserted during coloration. The general problem is best illustrated by the important example of Prussian blue. Early work (68–71) resulted in two different sets of equations for electrochromic reduction:

$$KFe^{3+}[Fe^{2+}(CN)_6] + e^- + K^+ \rightarrow K_2Fe^{2+}[Fe^{2+}(CN)_6] \tag{5}$$

$$Fe_4^{3+}[Fe^{2+}(CN)_6]_3 + 4\ e^- + 4K^+ \rightarrow K_4Fe^{2+}[Fe_4^{2+}(CN)_6]_3 \tag{6}$$

The compounds $KFe^{3+}[Fe^{2+}(CN)_6]$ [25869-98-1] and $Fe^{3+}{}_4[Fe^{2+}(CN)_6]_3$ [14038-43-8] are both called Prussian blue. The first is known as the water-soluble form, though actually it only peptizes easily, and the second as the insoluble form. The reduced compounds $K_2Fe^{2+}[Fe^{2+}(CN)_6]$ and $K_4Fe^{2+}{}_4[Fe^{2+}(CN)_6]_3$ are known as Everitt's salt [15362-86-4] and Prussian white [81681-39-2] respectively. A similar lack of specificity occurs when Prussian blue is oxidized to Berlin green [14433-93-3]. This has led to propositions that film composition depends on the K^+ concentration of the growth solution (71) and on cycling (73,75). A film that is in the insoluble form initially, prior to cycling, is said thereafter to develop an intermediate K^+ content between the two forms of Prussian blue. The radius of the hydrated insertion ion is believed to be the key factor that dictates the reversibility of ion injection/extraction for the zeolite structure of Prussian blue. Reversibility has been shown to be best for K^+, Rb^+, Cs^+ and $NH_4{}^+$; hydrated radii were determined to be in the range 0.118–0.125 nm (70).

3.3. Doped/Undoped Organic Films. This class of electrochromic materials is probably the youngest and least thoroughly explored from a practical viewpoint. There has been more interest generally in the very high, metal-like conductivity of the oxidized state of some of its members than in the insertion/extraction electrochromism accompanying oxidation–reduction. Of interest have been applications for lightweight and moldable batteries and also for antistatic and electromagnetic shielding. On the other hand, there is not enough

Table 4. **Some Organic Insertion/Extraction Films**

Film	CAS Registry number	Growth method[a]	Possible dopants	Oxidizing color shift[b]	References
polyaniline	[25233-30-1]	ep	H^+, Br^-	lt yel–grn–bl	77–81
polypyrrole	[30604-81-0]	ep	ClO_4^-, BF_4^-, Li^+	yel/grn–gr/br	75,76,82–86
polythiophene	[25233-34-5]	ep	ClO_4^-, BF_4^-	red–bl	76,86,89
poly(isothianaphthene)	[91201-85-3]	ep	ClO_4^-, BF_4^-,	bl/blk–lt grn/yel	76,90,91
TTF-functionalized polymer		spin-cast	ClO_4^-, BF_4^-,	orange–brown	92,93
TNF-MN	[1172-02-7]	vacuum	K^+	grn–transparent	94

[a] ep = electropolymerization.

[b] lt = light; yel = yellow; grn = green; bl = blue; gr = gray; br = brown; blk = black.

reported in the open literature to permit good comparisons of coloration efficiencies. Also, although the films themselves are solid state, almost all electrochromic work has been done with liquid electrolytes. This suggests that research and development are still at a fundamental stage. Nevertheless, two excellent reviews (75,76) do emphasize optical properties and color switching. Some of this is summarized in Table 4, though the dopant column should be considered with care. Analytical work using the quartz–crystal microbalance (81,84,85) suggests that charge balancing may sometimes involve both anions and cations in complicated ways. The first four materials in Table 4 are best known for the e^- conductivity that is associated with a conjugated π-electron structure. These are usually deposited by electropolymerization. Tetrathiafulvalene [31366-25-3] (TTF) and 2,4,7-trinitro-9-fluorenylidene malononitrile [1172-02-7] (TNF-MN) demonstrate some variety in the growth method for this electrochromic class. TNF-MN is also different because coloration only occurs in the reduced state. Generally, the whole class is characterized by a wide variety of transmitted colors in both the oxidized and nonoxidized forms. Some of the colors reported are shown in Table 4, though these colors are known only qualitatively and without specification of viewing conditions. They are only indicated here to show the breadth possible. Even wider color variety is possible with structural substitutions (75). Some degree of predictability may be possible because solid-state colors seem to be similar to those reported for solutions (76,94).

The same color variety is not typical with inorganic insertion/extraction materials; blue is a common transmitted color. However, rare-earth diphthalocyanine complexes have been discussed, and these exhibit a wide variety of colors as a function of potential (95–97). Lutetium diphthalocyanine has been studied the most. It is an ion-insertion/extraction material that does not fit into any one of the groups herein but has been classed with the organics in reviews. Films of this complex, and also erbium diphthalocyanine, have been prepared successfully by vacuum sublimation and even embodied in solid-state cells (98,99).

There is tangible support for ion insertion/extraction in some materials, such as polypyrrole, polyaniline, and Prussian blue, from analyses with the mass-sensitive quartz-crystal microbalance (81,84,85,100). This relatively new technique is developing as an important one for electrochromic materials generally. It increases the standard electrochemical analyses, especially cyclic voltammetry, that have been effectively used up to now. Its further use, for charge-balancing ion insertion/extraction, should give growth to the analytical technique, and also help speed along developments in electrochromism, which is still a young science.

4. Sol-Gel Systems

Gelling an electrolyte layer, which includes an electrochromic layer, has been suggested as a means of eliminating hydrostatic pressure concerns (101–103). However, not everything that is termed a gel is self-supporting, free-standing, and capable of eliminating hydrostatic pressure. Figure 1 provides a qualitative comparison of polymer thickener, polymer gels, purepolymer electrolytes and their variation viscosity. The viscosity as a function of polymer content is highly dependent on crosslink density. In the illustration, one starts with a low viscosity liquid and adds some soluble uncrosslinked polymer thickeners to increase viscosity.

If the crosslinking is provided by chemical bond formation the resulting gel can be termed a chemical gel by contrast to a physical gel.

5. Applications

The increase in the interaction between humans 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

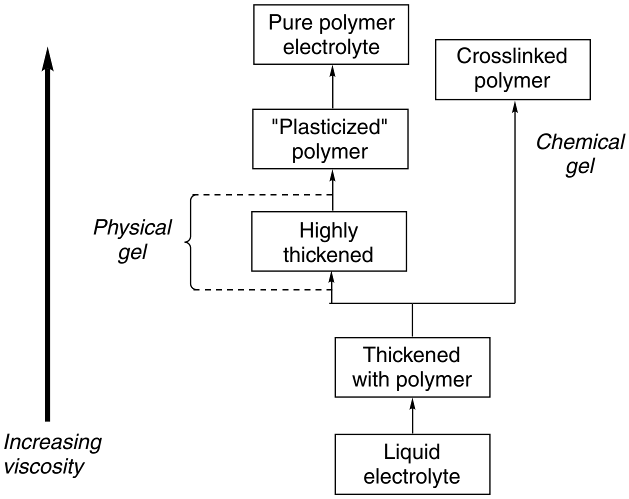


Fig. 1. Illustration of polymer thickeners, polymer gels, and polymer electrolytes as a function of viscosity and polymer crosslinking (101).

this purpose and has various merits such as multicolor, high contrast, optical memory and no visual dependence on viewing angle. A large number of electronic materials are avoidable from almost all branches of synthetic chemistry. The most important examples from major classes of electrochromic materials namely transitions metal oxides, Prussian blue, phthalocyanines, viologens, fullerenes, dyes and conducting polymers (including gels) are described (104).

In the recent years, a lot of attention has been paid to understanding the physical and chemical properties of various electrochromic materials, particularly on conducting polymer (CPs) the focus is not only on basic research, but also on commercial aspects (104,105). It has brought various electrochromic materials and devices actually into the market. In the automobile sector rear view mirrors and several parts such as sunroofs and visors are under prototype production.

Alphanumeric displays and electrochromic mirrors have also been produced. Widespread applications of ECDs (electrochromic displays) particularly for architectural applications, depend 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 change color electrochemically, but only after being illuminated may be more appropriate candidates for smart windows (105,106).

Windows are divided into three classes : battery-like, with open circuit minory and solution phase and hybrid designs, which are self erasing and require a maintenance current during coloration.

Construction of windows includes all thin films state structures and devices containing polymer or gel electrolytes (6).

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.

Electrochromic coatings, thin films such as WO_3 that change their optical absorbance or reflectance as a function of injected ions (typically H^+or Li^+ species) is an area of research and development that has received considerable attention from academia, industry and government laboratories, involving manufacturing challenge (108–110).

The production of moving electrochromic images (such as moving pixels and alphanumeric displays etc) is the next step in the research and development of electrochromic materials and hence needs more efforts to be done in that direction. Recent interest for electrochromic devices for multispectral energy modulation by reflectance and absorbance has extenced the working definition. Electrochromic devices are now being studied for modulation of radiation in the near infrared, thermal infrared and micro wave regions and “color” can mean response of detectors of these wavelengths, not just the human eye (104).

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