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New electrochromic materials

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A number of inorganic and organic materials exhibit redox states (reduced and/or oxidised forms) with distinct UV-Visible (electronic) absorption bands. When electrochemical switching of these redox states gives rise to different colours (i.e. new or different visible region bands), the material is described as being electrochromic. By virtue of their numerous applications, both of academic and commercial interest, electrochromic materials are currently attracting a great deal of interest. This review provides an introduction to the major classes of electrochromic materials, namely transition metal oxides, Prussian blue systems, viologens, conducting polymers, transition metal and lanthanide coordination complexes and metallopolymers, and metal phthalocyanines. Examples of some new materials and of prototype and commercial electrochromic devices are cited.

Introduction

Electrochromism is the reversible change in optical properties that can occur when a material is electrochemically oxidised (loss of electron(s)) or reduced (gain of electron(s)), and is of great academic and commercial interest. Traditionally, materials have been considered as being electrochromic when they displayed distinct visible colour changes, with the colour change commonly being between a transparent ('bleached') state and a coloured state, or between two



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coloured states. In cases where more than two redox states are electrochemically available, the electrochromic material may exhibit several colours and be described as polyelectrochromic. However, the working definition of electrochromism has now been extended to include devices for modulation of radiation in the near infrared, thermal infrared and microwave regions, so 'colour' can now mean a response by detectors at these wavelengths, and not just by the human eye.¹

Electrochromism enables the darkening of a window at the flick of a switch. This principle has already been demonstrated in electrochromic car rearview mirrors, which automatically darken at night, when a driver is 'dazzled' by the headlights of a car behind. These and many other applications make electrochromic materials highly sought after for commercial use, and a review on electrochromic systems and the prospects for devices has recently been published.²

There are a large number of materials that exhibit electrochromism, and a number of excellent recent reviews on various categories of electrochromic materials and their applications have been published, a few of which have been cited.¹⁻⁶ The most important classes of compounds which demonstrate this effect are: transition metal oxides, Prussian blue systems, viologens (1,1'-disubstituted-4,4'-bipyridinium salts), conducting polymers, transition metal and lanthanide coordination complexes and metallopolymers, and metal phthalocyanines (Table 1). These classes, and some new examples of materials within each class, will now be detailed. Additionally, examples of applications of the various classes of electrochromic materials will be given.

Table 1 Summary of applications of electrochromic materials discussed in this review

Class of electrochromic material	Examples and possible uses
Transition metal oxides	<i>e.g.</i> WO ₃ , MoO ₃ , V ₂ O ₅ , Nb ₂ O ₅ , Ir(OH) ₃ and NiO _x H _y . Potential use in smart windows, thermal control of satellites and electrochromic writing paper
Prussian blue systems	<i>e.g.</i> [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. Potential use in displays.
Viologens	1,1'-Disubstituted-4,4'-bipyridinium salts. Used in car rear view mirrors and potential use in displays
Conducting polymers	<i>e.g.</i> polypyrrole, polythiophene, polyaniline <i>etc.</i> Potential use in smart windows and displays.
Transition metal and lanthanide coordination complexes and metallopolymers	<i>e.g.</i> metal hydrides, nitrosyl and oxo molybdenum complexes, poly-[Ru ^{II} (vbpy) ₂ (py) ₂]Cl ₂ . Potential use in switchable mirrors, near-infrared switching
Metal phthalocyanines	<i>e.g.</i> [Lu(Pc) ₂], potential use in electrochromic displays

Transition metal oxides

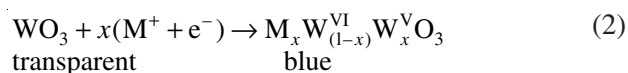
Electrochromism was first reported in thin films of WO_3 in 1969, and this material remains the most promising candidate for large-scale uses of electrochromic devices.^{3,4,6}

Electrochromism in WO_3 is conveniently introduced by reference to the simple reaction in equation (1).



where $\text{M}^+ = \text{H}^+, \text{Li}^+, \text{Na}^+, \text{or } \text{K}^+$, $0 < x \leq 1$ and e^- denoting electrons. Therefore, when a transparent thin film of WO_3 incorporates electrons and charge-balancing ions, it can be reversibly transformed into a material which is absorbing if the material is heavily disordered and infrared-reflecting if it is sufficiently crystalline.³ It must, however, be noted that equation (1) is a “gross oversimplification”³ and the thin films of practical interest are usually hydrous, *i.e.* contain some hydroxyl groups and incorporated water molecules, and may deviate to some extent from the stated WO_3 stoichiometry (relative proportions of constituent elements of the compound).^{2,3}

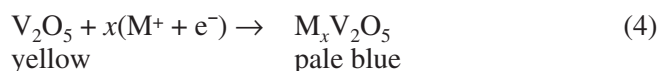
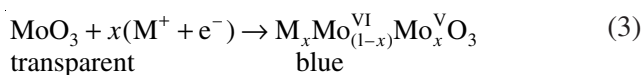
Tungsten trioxide, which, as indicated above, is transparent as a thin film, has all tungsten sites in oxidation state W^{VI} . Upon electrochemical reduction, W^{V} sites are generated to give the electrochromic effect. The detailed colouration mechanism is still controversial, but it is generally accepted that the injection and extraction of electrons and metal cations play a key role. More accurately, the reaction can be represented as shown in equation (2).



At low values of x , the films have an intense blue colour due to inter-valence electron transfer between adjacent W^{V} and W^{VI} sites stimulated by absorption of a visible photon. At higher values of x , insertion irreversibly forms a metallic ‘bronze’ that is red or golden in colour.⁶ The thin film microstructure of WO_3 is heavily dependent on the method of preparation. Gaseous processes include WO_3 sublimation, RF magnetron sputtering, or oxidation during chemical vapour deposition, whereas solution phase methods include electro-deposition, electrochemical oxidation of tungsten film, the sol-gel route from tungstic acid, or dip coating from colloidal WO_3 .⁷

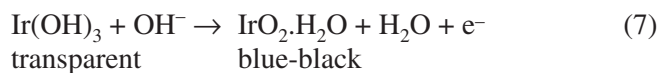
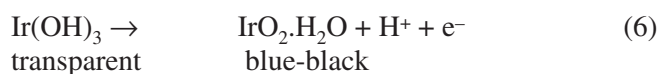
Several other thin-film transition metal oxides are also able to switch from a colourless oxidised state to an intensely coloured

reduced form, particularly the oxides of molybdenum, vanadium and niobium (equations 3–5).

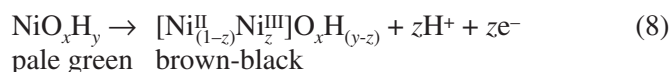


As in the case of WO_3 , this requires simultaneous ‘injection’ of electrons and small charge-compensating cations,⁷ and the more intensely absorbing redox state is produced on reduction (cathodic ion-insertion).⁶

Hydrated iridium oxide (strictly iridium hydroxide), in contrast, becomes coloured on electrochemical oxidation (anodic ion-insertion). The mechanism of colouration is uncertain, with both proton extraction and anion insertion routes being proposed (equations (6) and (7)).⁶



Nickel oxide, another commonly studied anodic ion-insertion material, is a material more commonly known for its use in secondary batteries. Nickel oxide (strictly nickel hydroxide) in basic electrolytes switches from pale green to brown-black (equation 8).^{6,7}



There are many reports of research into the electrochromic properties and uses of transition metal oxides in the scientific literature, and it is not possible to represent all of this work in the current review. A few examples have therefore been chosen to represent some recent findings.

Crystalline WO_3 is one of the most studied electrochromic materials – not only as a result of its transparent/intense blue electrochromism,

but, it also has some specific switching properties in the infrared region, of relevance to 'smart' windows technology.⁸ Switchable or 'smart' windows are now highly sought after, in order to save energy by reducing heat loss and avoiding overheating of buildings, and providing comfortable levels of daytime light. These conflicting demands can be achieved by smart windows, as their optical properties (transmittance and reflectance) can be varied between low and high transmitting states, and additionally such windows prevent the major visual discomfort caused by excessive glare.⁹ Smart windows therefore result in large energy savings by enabling the electrical control of the transfer of solar and thermal infrared radiations between the inside and outside of buildings and vehicles.^{1,8,9}

The preparation and performance of large area electrochromic films is being studied by a number of companies and research organisations, as this area is of vital importance for the preparation of commercially viable electrochromic windows for architectural applications.¹⁰ The most appropriate design for an electrochromic device for practical applications, such as windows, is similar to that found in a battery, comprising five active layers (Figure 1).⁹ The working electrode, ion conducting layer and counter electrode are sandwiched between two electronically conductive transparent electrodes coated on glass. Within smart window systems it is accepted that WO_3 films represent the best option for the working electrode, but the choice of the best counter electrode is still a matter of debate, and comparative studies of various counter electrodes have recently been reported.⁹ Upon application of a voltage,

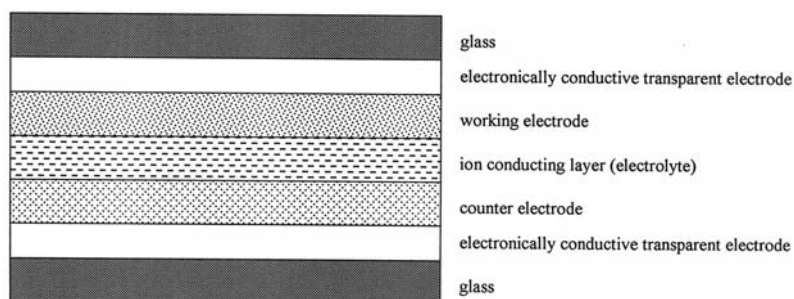


Fig. 1. Schematic design of an electrochromic device, suitable for a transmissive light-modulation application. The device can be thought of as a rechargeable electrochemical cell, in which the 'electrochromic electrode' (where the colour switching takes place) is separated from a charge-balancing counter electrode by an electrolyte. Colour changes occur by charging/discharging the device on application of an electrical potential.

simultaneous intercalation of ions (from the ionic conductor) and electrons (from the transparent electrode) into the electrochromic film occurs, inducing the colour change. During bleaching, this process is reversed.⁹

Present electrochromic devices take a long time to switch between transparent and coloured states, thereby hindering the realisation of their full potential.^{11,12} These devices fall into two categories. The first type change colour upon intercalation of small ions, *e.g.* Li⁺ and Na⁺, into a thin film of metal oxide, *e.g.* WO₃, V₂O₅ and TiO₂. These materials are typically deposited as amorphous or polycrystalline thin films onto conducting glass substrates, and the ions present in the electrolyte intercalated under an applied potential. Ion-intercalation must extend into the bulk of the metal oxide film, in order to obtain sufficient optical absorption. As a consequence, the rates of colouring and bleaching are limited by the rate of ion transport in to and out of the metal oxide film, leading to switching times of the order of tens of seconds even for relatively small area devices.¹²

The second type of devices change colour upon reduction or oxidation of a redox chromophore. The redox chromophore is either dissolved in solution or incorporated into a polymeric film deposited on a transparent conducting substrate. An example of such redox chromophores are the viologens, which give rise to a deep blue or green colour upon reduction. The rate of diffusion of the chromophore to the conducting substrates, or the rate of migration of electrons within the polymeric film therefore limit the rates of colouring and bleaching. The resultant switching times for such devices are typically of the order of tens of seconds, even for relatively small area devices.¹²

However, a new type of electrochromic system which shows promise of overcoming these problems has recently been reported.¹² The ultrafast electrochromic window gives rise to high-contrast images that can be rapidly generated and erased, and the optical appearance of the images does not depend on the viewing angle, of high relevance for use in display screens.¹¹ The electrochromic cell comprises two porous metal-oxide films sandwiched between glass electrodes. The negative electrode is coated with a layer of TiO₂ nanocrystals, with viologen molecules (which turn blue when reduced) attached to the surface of the nanocrystals. The positive electrode comprises a nanocrystalline antimony-doped tin oxide film, linked to phenothiazine molecules (which become red upon oxidation). The colour can be switched on and off in under 250 milliseconds upon filling the electrochromic cell with an electrolyte and application of a voltage.¹¹

There is additionally a strong interest in using electrochromic devices for the thermal control of satellites in orbit. This control is usually achieved by balancing the energy emitted by the satellite as infrared radiation against the energy dissipated by internal electrical components plus the energy absorbed from the environment. In low earth orbit, satellites are exposed not only to radiation from the sun and sunlight reflected from the earth's surface (earth's albedo), but additionally to infrared radiation emitted from the earth (earthshine).^{8,13} Indeed NASA is considering the use of electrochromic devices in the hope of replacing the venetian blind radiators in future low cost satellite systems.¹³ The venetian blind type radiator comprises a series of highly reflective vanes covering an emissive base plate, and the rate at which heat is radiated is controlled by opening and closing the vanes. Since electrochromic devices can change their optical properties by means of an applied voltage pulse, this would enable emittance modulation of surfaces and components without bulky blinds with moving parts. To ensure a good thermal conduction path, satellite components could even be coated directly.¹³ In an attempt to address such a potential use, a flexible electrochromic reflectance device based on tungsten oxide for infrared emissivity control has recently been reported.⁸

Polyoxometallates are discrete, molecularly-defined metal oxide clusters with an extensive range of structures and properties. They are also promising candidates for possible components of electrochromic devices, since they are able to act as an electron reservoir, and so give rise to coloured mixed-valence state entities while maintaining their structural integrity. $[\text{Eu}-(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110}]^{12-}$ has been shown to exhibit reversible electrochemical behaviour accompanied by a large electrochromic response (transparent to blue upon reduction), and a thin-film electrochromic device based on this polyoxometallate cluster has recently been reported.¹⁴

There is a recent report concerning the use of electrochromic materials incorporated into paper, in an attempt to produce 'electrochromic writing paper,' in which an electrochromic image is generated on paper when a stylus electrode touches it.¹⁵ A series of organic and inorganic electrochromic materials were dispersed in paper, and of the materials studied, tungsten trioxide yielded the best permanent electrochromic writing medium. It is interesting to note that the most intense electrochromic colour was that of methyl viologen in water, but the colour was not permanent, and that although Prussian blue is a good electrochromic material as a thin film on platinum, it was not electroactive enough in paper to warrant further investigation.¹⁵

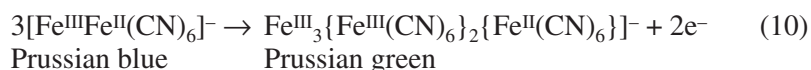
Prussian blue systems

Iron(III) hexacyanoferrate(II) is more commonly known as Prussian blue. Its intense blue colour is due to intervalence electron transfer, and it is the prototype of a number of related compounds, of general formula $M'_k[M''(\text{CN})_6]_l$ (k and l are integers; M' and M'' are transition metals with different formal oxidation numbers), that form an important class of insoluble mixed-valence compounds.⁶

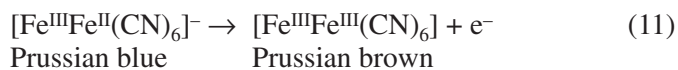
Thin films of Prussian blue are typically formed by the electrochemical reduction of solutions containing iron(III) and hexacyanoferrate(III) ions. Electrochemical reduction of the brown-yellow soluble complex Prussian brown, [iron(III) hexacyanoferrate(III)], present in equilibrium with iron(III) and hexacyanoferrate(III) ions] is the principal electron-transfer process in Prussian blue electrodeposition (equation (9)). It must be noted that charge-balancing cations (first Fe^{3+} , then K^+ on potential cycling in K^+ -containing supporting electrolyte) are present in the Prussian blue film to maintain electroneutrality.⁶



When Prussian blue is partially electrochemically oxidised, in pure supporting electrolyte, Prussian green (historically known as Berlin green), is produced (equation (10)).⁶



In bulk form Prussian green is believed to have a fixed composition with anion composition as in equation (10). However, for thin films there is a continuous composition range between Prussian blue and Prussian brown, which becomes a golden yellow in the fully oxidised form. Prussian brown may be obtained by electrochemical oxidation of a particularly pure form of Prussian blue (equation (11)).⁶



Prussian white (Everitt's salt), which appears transparent as a thin film, is formed upon electrochemical reduction of Prussian blue (equation (12)).⁶



In all of the electrochromic redox reactions above (equations (9–12)), electroneutrality of the complexes (by means of charge compensating ions) must be maintained.⁶

Early Prussian blue electrochromic devices used Prussian blue as the only electrochromic material. For example, an electrochromic device using a single film of Prussian blue, sandwiched between two optically transparent electrodes in the absence of a conventional electrolyte, has been described. When an appropriate potential is applied across the film, oxidation occurs near the positive electrode (to produce Prussian brown) and reduction near the negative electrode (to produce Prussian white). The conversion of the outer portions of the film gives rise to a net bleaching of the device.⁶

It is also of interest to note that as Prussian blue and WO_3 have complementary electrochromic reactions (equations (12) and (2), respectively anodically and cathodically colouring), it is possible to use both together in a single device.

To construct such a device, thin films of the materials are deposited onto optically-transparent electrodes, that are separated by a layer of a transparent ionic conductor such as KCF_3SO_3 in poly(ethylene oxide). The films can be concomitantly coloured (deep blue) when sufficient voltage is applied between them as to render the WO_3 electrode as the cathode, and the Prussian blue electrode as the anode. Contrariwise, the coloured films can be bleached to transparency when the polarity is reversed.⁶

Viologens

1,1'-Disubstituted-4,4'-bipyridinium salts are better known as viologens. The dicationic form (Figure 2, **A**), is the most stable of the three common viologen redox states (Figure 2), and is colourless when pure (unless optical charge transfer with the counter anion occurs).⁶ Viologens can undergo two successive electron-transfer reactions, from the dication (Figure 2, **A**) to produce a radical cation (Figure 2, **B**), and then a neutral species (Figure 2, **C**), yielding differently coloured species at each step. The colours formed depend upon on the substituents.⁷

The radical cation in particular is highly coloured because of an intense intramolecular optical charge transfer. Radical cations containing short alkyl chains are blue (blue-purple in concentrated solution), becoming crimson as the alkyl chain length increases because of

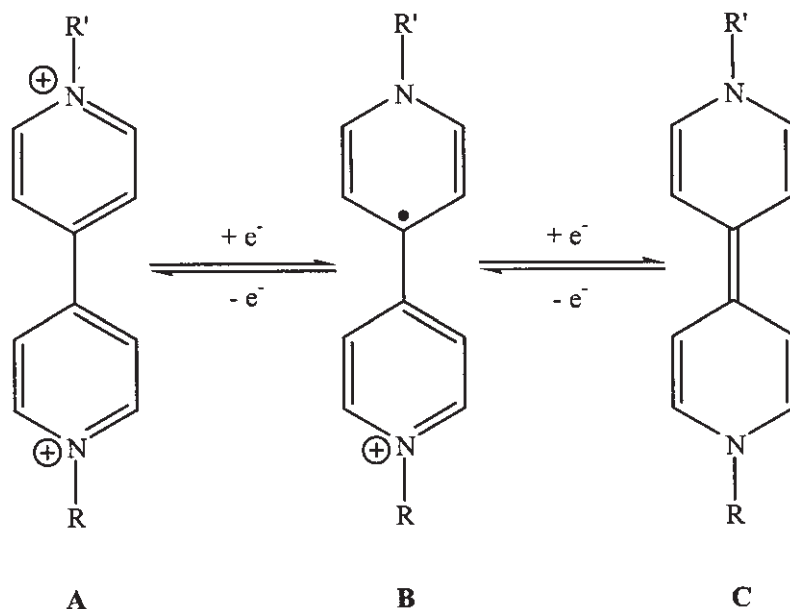


Fig. 2. The three common redox states of viologens, showing the two successive electron transfer reactions. **A**, dication; **B**, radical cation; **C**, neutral species.

increased dimerisation (the dimer is red).⁷

For use in display applications, the write-erase efficiency of electrochromic devices using short alkyl chain viologens, such as methyl viologen (1,1'-dimethyl-4,4'-bipyridinium), in aqueous electrolytes would be low due to the high solubility of both the dicationic and the radical cation states. Electrochromic devices based upon methyl viologen may be improved by retarding the rate at which the radical cation, produced by electron transfer, diffuses away from the electrode and into the bulk solution. This may be achieved either by tethering the dication to the surface of an electrode, or by immobilising the viologen species within a semi-solid electrolyte such as Nafion. When viologens having long alkyl-chain substituents are used, for which the coloured radical-cation is insoluble, the solubility-diffusion problem can be avoided. Heptyl viologen (1,1'-diheptyl-4,4'-bipyridinium) as the dibromide salt has been the most thoroughly studied of this type of viologen. The heptyl viologen dication is water-soluble, but, after a one-electron reduction, forms an insoluble film of crimson radical-cation salt, which adheres strongly to the electrode

surface. An electrochromic display, based upon the heptyl viologen system, was reported to have a response time of 10-50 ms, with a cycle life of $>10^5$ cycles between redox states.⁶

Applications such as electrochromic car rear view mirrors and smart windows do not necessarily require such high response times. It is of interest to note that Gentex's commercialised automatic-dimming interior 'Night Vision Safety' (NVS) mirror functions wholly by solution electrochromism. In this system, an ITO (tin-doped indium oxide)-glass surface (conductive side inwards) and the reflective metallic surface, spaced a fraction of a millimetre apart, form the two electrodes of the cell, with a solvent containing two electroactive chemical species that function both as electrochromic materials and supporting electrolyte. The two electroactive chemical species comprise a substituted (cationic) viologen, which serves as the cathodic-colouring electrochromic material, and a negatively charged (possibly) phenylene diamine as the anodically colouring electrochromic material. After switching the mirror on, the species migrate to their respective electrodes. Once the dual electrochromic colouration process has begun, the products will diffuse away from their respective electrodes and meet in the intervening solution, where a mutual reaction regenerating the original uncoloured species takes place. This type of electrochromic device therefore requires application of a continuous small current for replenishment of the coloured electroactive species lost by their mutual redox reaction in solution. Bleaching occurs at short or open circuit by homogeneous electron transfer in the bulk of the solution. Although not an electrochromic phenomenon, the ingenious control system for this device is noteworthy. A photosensitive detector is placed facing rearward to monitor any dazzling incident light. However, this would also be triggered in daylight, resulting in an unwanted darkening of the mirror. This problem is avoided by a second forward-looking detector, which, on seeing daylight, is programmed to cancel any operation of the controlling sensor, which therefore only responds at night.⁶

Recently, a new coupled bipyridinium-based dye system, of potential use in smart window applications, and which demonstrates excellent daylight, long term and cycle stability has been reported.¹⁶ Cells with the coupled system show a stable switching performance for more than 4000 hours.

Conducting polymers

Chemical or electrochemical oxidation of many aromatic compounds, such as pyrrole, thiophene, aniline, furan, carbazole, azulene and

indole (Figure 3), produces polymer films of polypyrrole, polythiophene or polyaniline, *etc.*, doped with counter-anions.

These doped polymers, which can adhere to the electrode surfaces, are highly conducting, while the undoped, neutral forms are insulating. The oxidised (doped) and reduced (undoped) states of these polymers exhibit different colours, and electroactive conducting polymers are all potentially electrochromic as thin films.^{6,7}

Polyaniline films undergo many reversible colour changes with variation of potential (transparent yellow \leftrightarrow green \leftrightarrow dark blue \leftrightarrow black, Figure 4). However, the most stable polyaniline electrochromic devices use a restricted potential range, to allow only the yellow and green states.⁷

Similarly, polypyrrole as a thin film exhibits yellow-green (undoped) and blue-violet (doped) electrochromism (Figure 5).⁶

The colours of conductive polymers can be 'tuned' by choosing a suitable aromatic substituent. Polythiophene, for example, is red when undoped, but blue when oxidised, whereas polymethylthiophene is purple when neutral, and turns pale blue on oxidation. Polymers made from variously-substituted dimers or tetramers of thiophene give a "designer choice"⁷ of electrochromism; the neutral polymers

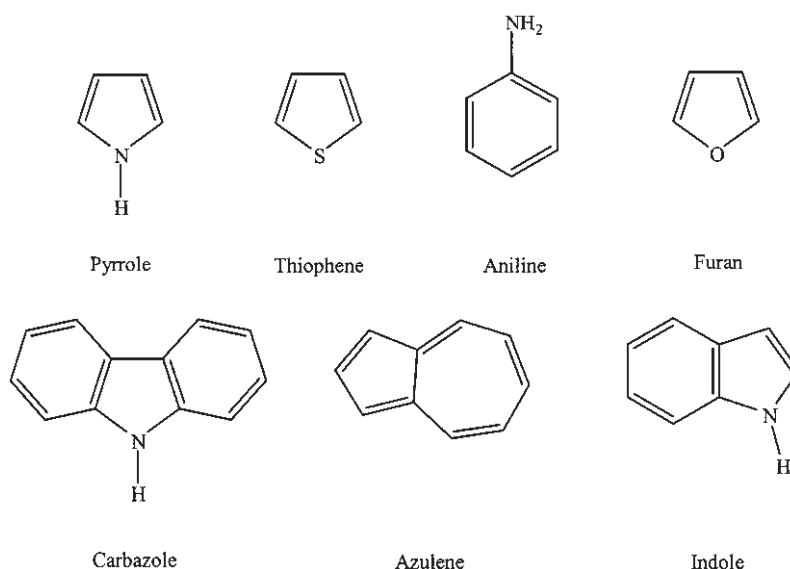


Fig. 3. Structures of various aromatic compounds that can undergo chemical or electrochemical oxidation to produce conducting polymers. All have conjugated ring structures, which allow ease of oxidation to produce radical cations, in the first stage of the polymerisation mechanism.

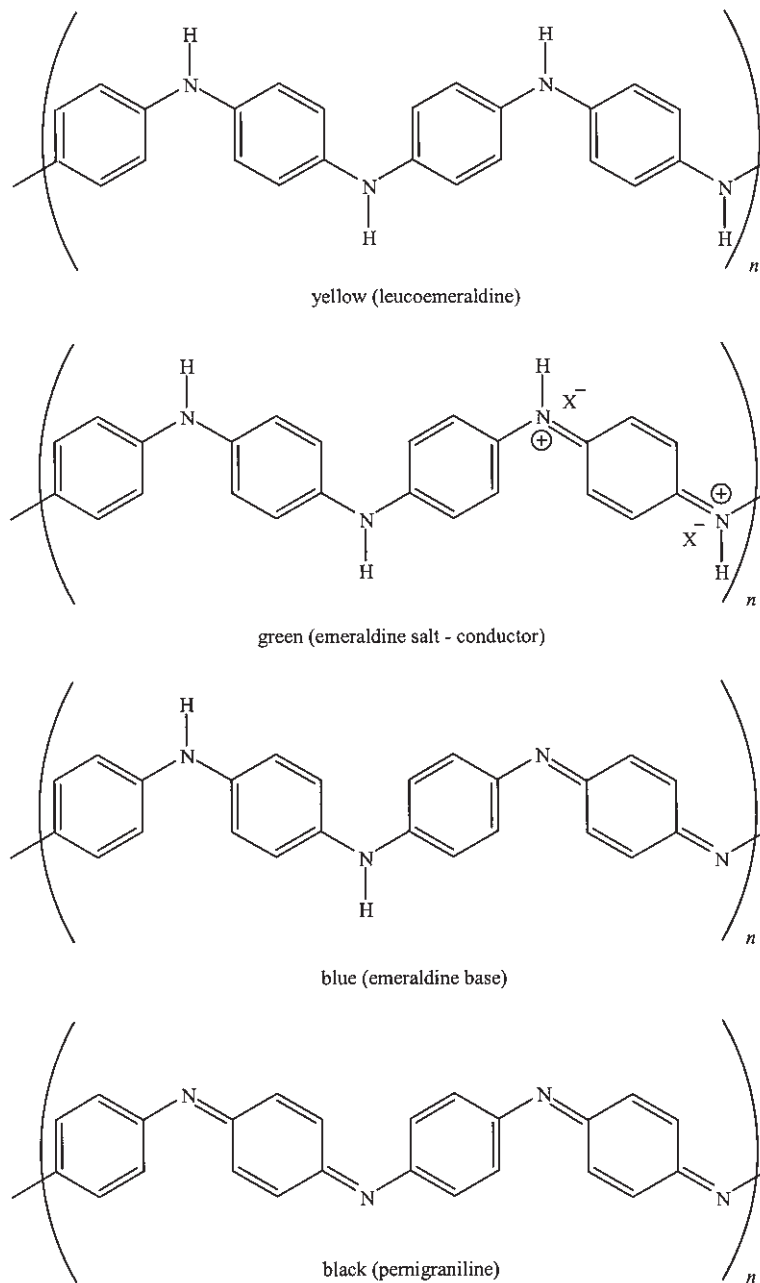


Fig. 4. Proposed composition of some of the redox states of polyaniline, from the fully reduced (leucoemeraldine) through to the fully oxidised (permigraniline) forms. X^- is a charge-balancing anion.

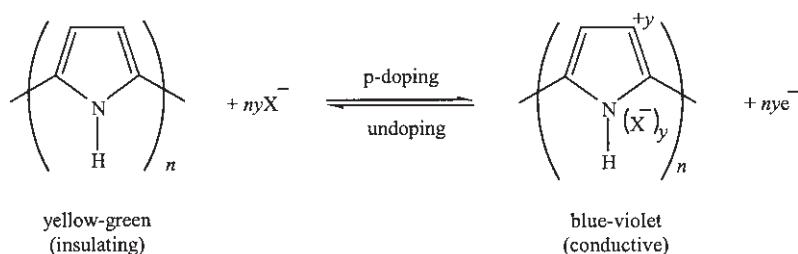
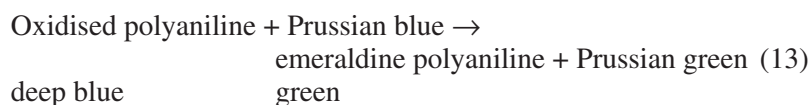


Fig. 5. Electrochromism in polypyrrole. The yellow-green (undoped) form undergoes reversible oxidation to the blue-violet (conductive) form, with insertion of a charge-compensation anion (X^-).

can be yellow, orange, red, or purple, turning either blue or violet on oxidation.^{6,7}

Polyaniline has been combined with Prussian blue in complementary electrochromic devices that exhibit deep blue \rightleftharpoons green electrochromism. Electrochromic compatibility is obtained by combining the coloured oxidised state of the polymer with the blue Prussian blue and the bleached reduced state of the polymer with Prussian green (Equation 13).



Both liquid electrolyte and solid-state configurations have been described.⁶ Such hybrid organic-inorganic materials are an area of rapid growth and have recently been reviewed.¹⁷

Poly(3,4-ethylenedioxythiophene) PEDOT (or PEDT) and its derivatives have been some of the most successful conducting polymers and these have been the subject of a recent review.¹⁸ PEDOT has proven to be a promising electrochromic polymer, as it exhibits long term stability, a low oxidation potential, high contrast ratios, and fast switching times. This polymer also has the advantage that it is cathodically colouring, *i.e.* in the reduced state the film is deep blue (highly absorbing to visible light) and in the oxidised state it is sky blue transparent (highly transmissive). This change in transmissivity could lend itself to applications in smart windows and displays.¹⁹

Most recently, a dual cathodically and anodically colouring electrochromic polymer, based on a new alkylendioxythiophene derivative [poly(spiroBiProDOT)], exhibiting three colour states has been reported. Luminance studies showed that the polymer was initially

cathodically colouring, exhibiting a dark red film in the neutral state. As the film became oxidised, the luminance increased until the potential reached 0.45 V. Here the film had a transparent blue-grey colour, and showed a 30% change in luminance. As the potential was increased beyond 0.51 V, the luminance decreased, making the polymer unique relative to any other alkylenedioxythiophene derivative. At 1.1V, the polymer exhibited a third electrochromic state which was dark blue.¹⁹

Transition metal and lanthanide coordination complexes and metallopolymers

Due to their intense colouration and redox activity, transition metal coordination complexes are potentially useful electrochromic materials. Chromophoric properties typically arise from low-energy metal-to-ligand charge transfer (MLCT), intervalence charge transfer, intraligand excitation, and related visible region electronic transitions. Since these transitions involve valence electrons, chromophoric characteristics are altered or eliminated upon oxidation or reduction of the complex.⁶

Since the striking discovery that yttrium thin films could be reversibly switched with hydrogen gas between reflective and transparent states, researchers are investigating electrochromic rare-earth hydride-forming thin film electrodes. Reversible optical switching can also be achieved by electrochemical means, and switchable mirror properties can be adjusted by alloying.²⁰

There is a recent report of research towards solid-state switchable mirrors using a 'symmetric-GdMg' all solid-state device deposited on a glass substrate. It comprised a GdMgH_x/Pd bottom electrode, a ZrO₂·(H₂O)_x·[H₂]_y proton conductor and a Pd/GdMgH_x/Pd storage top electrode. When exposed to a hydrogen atmosphere, this device showed reversible optical switching.²¹

A number of nitrosyl and oxo molybdenum complexes containing the tris(3,5-dimethylpyrazolyl)borato ligand which exhibit electrochromism in the near-infrared region have recently been described.²² During the course of spectroelectrochemical studies it became apparent that some of the complexes behaved as electrochromic near-infrared dyes, since the complexes developed strong charge transfer transitions in the near-infrared region (800–1500 nm) following reversible redox processes. This is of technological importance, as materials which display near-infrared switching can be used to modulate lasers that operate in this region of the spectrum, of particular relevance to telecommunications applications. As a consequence,

the near-infrared electrochromism has been recently exploited in a prototypical optical switching device.²³

Novel ferrocene-naphthalimide compounds which can act as dual-mode chemical (protons) / electrochromic molecular switches have been reported.²⁴ These systems operate due to the ability to switch off the photo-induced electron transfer path (from the ferrocenyl unit to the naphthalimide moiety) both by oxidation of the ferrocene unit and by the protonation of the alkylated amine group.²⁴

In addition to the spectroscopic and redox properties, which warrant the use of transition metal complexes directly in solution phase electrochromic devices, polymeric systems have been investigated. Numerous schemes detail the preparation of thin-film metallopolymers. The reductive electropolymerisation of suitable polypyridyl complexes is a particularly versatile technique, relying on the ligand-centred nature of the three successive reductions of complexes such as $[\text{Ru}^{\text{II}}(\text{vbpy})_3]^{2+}$ (vbpy = 4-vinyl-4'-methyl-2,2'-bipyridine, Figure 6), in combination with the anionic polymerisability of suitable ligands. Vinyl-substituted pyridyl ligands are generally used, although metallopolymers have also been formed from chloro-substituted pyridyl ligands, *via* electrochemically initiated carbon-halide bond cleavage. Electrochemical reduction of the metal complexes produced from either route gives rise to radicals, which in turn leads to carbon-carbon bond formation and the subsequent formation of oligomers. Oligomers above a certain size are insoluble, and therefore thin films of the metallopolymer are formed on the electrode surface.⁶

By suitable choice of metal, the colour of such metallopolymer films in the M^{II} redox state may be selected (*e.g.* $\text{M} = \text{Fe}$, red; $\text{M} = \text{Ru}$, orange; $\text{M} = \text{Os}$, green). Electrochromicity results from loss of the metal-to-ligand charge transfer absorption band on switching

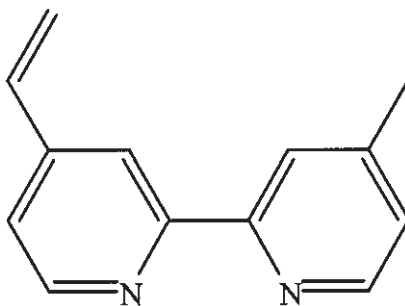


Fig. 6. Structure of 4-vinyl-4'-methyl-2,2'-bipyridine (vbpy). Complexes of vbpy, such as $[\text{Ru}^{\text{II}}(\text{vbpy})_3]^{2+}$ undergo reductive electropolymerisation to produce electrochromic thin films.

between the M^{II} and M^{III} redox states.⁶

Spatial electrochromism has recently been demonstrated in metallo-polymeric films. Photolysis of poly- $[Ru^{II}(vbpy)_2(py)_2]Cl_2$ thin films on ITO glass in the presence of chloride ions leads to photochemical loss of the photolabile pyridine (py) ligands and sequential formation of poly $[Ru^{II}(vbpy)_2(py)Cl]Cl$ and poly $[Ru^{II}(vbpy)_2Cl_2]$. Contact lithography can be used to spatially control the photosubstitution process, forming laterally-resolved bicomponent films. Due to the dramatic changes which occur in the colour and redox potentials of such ruthenium(II) complexes upon substitution of chloride for the pyridine ligands, striped patterns of variable colours are produced on addressing such films with a sequence of potentials.⁶

Metal phthalocyanines

Phthalocyanines are tetraazatetrabenzo-derivatives of porphyrins with highly delocalised π -electron systems (Figure 7).

Polyelectrochromism of lutetium bis(phthalocyanine) $[Lu(Pc)_2]$ thin films was first reported in 1970, and since that time numerous other metallophthalocyanines have been investigated for their electrochromic properties. Such compounds have a metal ion either at the centre of a single phthalocyanine (Pc) ring, or between two rings in a sandwich-type compound, *e.g.* $[Lu(Pc)_2]$. Vivid green films, probably of $[(Pc)Lu(Pc)H]$, can be oxidised to a yellow-tan form, $[(Pc)Lu(Pc)H]^+Cl^-$, and further oxidised to a red form, $[(Pc)Lu(Pc)H]^{2+} \cdot 2Cl^-$. Upon reduction, the green state can be switched first to a blue redox form, $[(Pc)Lu(Pc)H] \cdot Li^+$, and then to a violet-blue form, $[(Pc)Lu(Pc)H]_{n+1}$, where $2 \leq n \leq 4$.⁷

Although, as described, $[Lu(Pc)_2]$ films can exhibit five colours, only the blue-green transition is used in most prototype electrochromic devices. There are mechanical problems associated with the use of $[Lu(Pc)_2]$ -based films, but in spite of such difficulties, electrochromic displays with good reversibility, fast response times, and little degradation over $>5 \times 10^6$ cycles have been described.⁶

Polymeric phthalocyanine networks are also of interest, due to their rigidity, high stability and strong, well-defined coupling of the electronic π -systems. However, polymeric phthalocyanines are not soluble and cannot be vaporised, hence new methods of thin film formation were needed. Electropolymerisation is now commonly used to produce thin films of polymers of phthalocyanines, and also of the related macrocyclic compounds, porphyrins. The electropolymerisation technique is advantageous since a wide variety of conducting

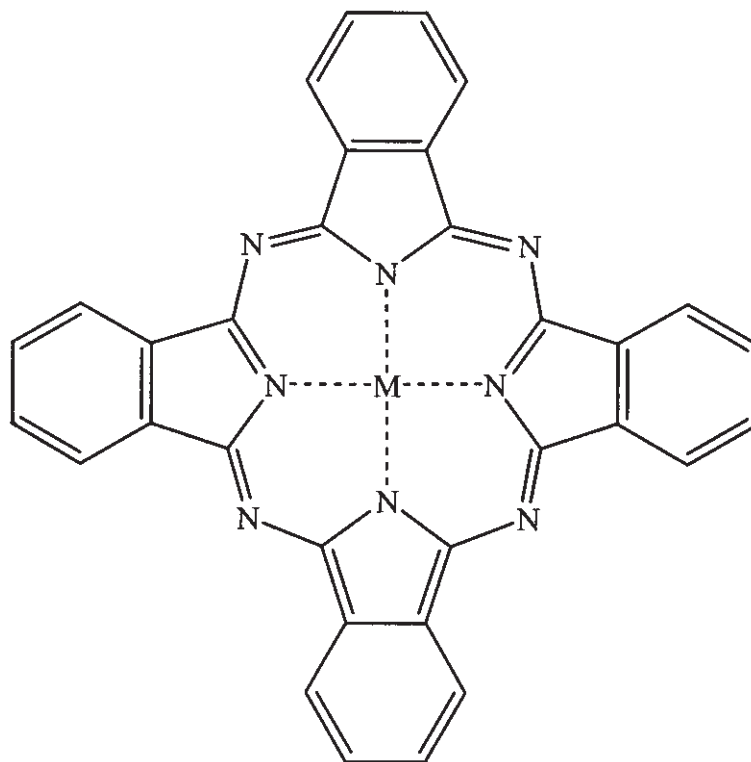


Fig. 7. Structure of phthalocyanine ($M = H_2$ or various metals), the tetraazatetrabenzoporphyrin derivative of porphyrin. Thin films of metal phthalocyanines, such as lutetium bis(phthalocyanine) are polyelectrochromic.

surfaces can be used, and the film thickness can be directly controlled by the polymerisation conditions. Most of the polymeric phthalocyanines have been produced by electropolymerisation of a group such as an aromatic amino group directly attached to the macrocyclic ring, therefore polymers have been produced in which the phthalocyanine electronic system is included in the conjugated system, influencing the optical and electronic properties of the thin films produced. Very recently a phthalocyanine with a polymerisable group which is separated by an electronically insulating alkylene spacer from the phthalocyanine macrocycle has been reported, thus efficiently separating the conjugated polymer chain from the chromophore. This polymer displayed a reversible electrochromic colour change.²⁵

Conclusion

It has not been possible, within the scope of this paper, to provide a comprehensive review of the large area of new electrochromic materials, and the authors have had to use their discretion in choosing up-to-date findings to illustrate the exciting area. The field of electrochromism is rapidly expanding and there is a vast array of reports concerning the phenomenon, both in the scientific literature and in the patent literature, as well as on the web, to which the reader should be directed for more in-depth and comprehensive information.

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