ADVANCED MATERIALS

Electrochromic Systems and the Prospects for Devices**

By *David R. Rosseinsky** and *Roger J. Mortimer*

Many inorganic and organic materials exhibit redox states with distinct electronic (UV-vis) absorption bands. When the switching of redox states generates new or different visible region bands, the material is electrochromic. Electrochromic materials are currently attracting much interest in academia and industry for both their fascinating spectroelectrochemical properties and their commercial applications. In this review some of the most important examples from the major classes of electrochromic materials are highlighted. Examples of their use in both prototype and commercial electrochromic devices are illustrated including car mirrors, windows and sun-roofs of cars, windows of buildings, displays (see Figure), printing, and frozen-food monitoring.

1. Introduction

Turn a switch and a window darkens—no extraneous curtains, shutters, or screens: how desirable, how simple, how neat. This is already achieved automatically in electrochromic rearview mirrors now widely available in cars. Extension of such controlled coloration to windows and displays is under widespread examination, and several firms now show demonstrator models of windows such as a switchable skylight. Adjustable-protection sunglasses, however, have, not surprisingly, failed as commercial items.

Electrochromism involves electroactive species (i.e., electron donor or acceptor, in the redox sense) and is the coloration of an electroactive surface film or of an electroactive solute, resulting from an electron-transfer reaction at an electrode. The electrodes are separated by electrolyte providing only ionic not electronic conduction, thus making up a typical electrochromic cell or device. The second electrode in some systems may also be electrochromic and in any case must undergo electron transfer in the reverse sense to that of the first electrode.[1]

The electrochemical reaction ensues from changing the potential applied between the electrodes, the system behaving as either an electrolytic or a current-producing cell, as determined by the intrinsic standard electrode potentials of the electrodes modified by the specific composition of the cell as used. On completion of the electrochemical coloration, the cell will usually retain its color—the "memory effect". An early review in this journal[2] focussed largely on solid-state devices. Two monographs[3,4] cover the subject to about 1994, and more recent updates include reviews of greater[5–8] or lesser[9] detail. Granqvist listed a total of 64 reviews published up to the year 2000, i.e., 65 including his own.[8]

Virtually all electrochemical reactions entail at least some visible change at the electrode,[10] but only a limited number are of sufficient intensity to be useful in devices, and a lower limit of color change or contrast specified to define usefulness could limit those described as electrochromic. While a system showing only changes of color is technically electrochromic, one of the states evoked in most applications needs to be a colorless one, though a weak yellow often suffices. Many recent papers address electrochromic efficiency, both as diminution of % transmittance and as coulombs consumed per unit area (e.g., ca. 30 mC$\,$cm^{-2} is acceptable); some include industrial/commercial viability.

New, only moderately colored, electrochromic systems can often still be improved by minor physical or chemical modification. Indium-doped tin oxide (ITO) is the transparent uncolored conductive coating on conductive glass and appears to be impregnable, thus non-colorable, by non-protonic cations, but ITO powder goes blue on apparent partial reduction.[11] Those systems now known need not remain dominant, and real innovation keeps breaking in: novel hydride systems (see Sec. 4.6) provide an outstanding example.

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[*] Dr. D. R. Rosseinsky[+]
Gintic Institute of Manufacturing Technology
71 Nanyang Drive, Singapore 638075 (Singapore)
E-mail: davidr@gintic.gov.sg

Dr. R. J. Mortimer
Department of Chemistry, Loughborough University
Loughborough, LE11 3TU (UK)

[+] Second address: School of Chemistry, University of Exeter, Exeter EX4 4QD, UK.

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2. Details of the Mechanism of Electrochromism

2.1. Fundamental Electrochemistry and the Optical Basis of Coloration

The key process is the evocation of a new species that exhibits color on an electrode by an electrochemical reaction that effects an electron transfer. Both states of the electroactive species are named "electrochrome".[4] The color itself, when under illumination, results from: a) an intervalence optical ($h\nu$) charge transfer where there are two centers of differing valence or oxidation state, or b) a moderate-energy internal electronic excitation effected by $h\nu$. In many systems, particularly the all-solid, once the coloring species has been evoked, no further charge injection is needed. This zero-current consumption after coloration, the "memory effect" of electrochromism, is often cited as a valuable desideratum of (large) electrochromic systems; it is practically irrelevant in small ones. A diagrammatic representation is given in Figure 1.

2.2. A Typical Electrochromic Assembly

Multilayer assembly, requiring good electrical contact between the layers, of a typical electrochromic window, with an indication of its operation, is as shown in Figure 1.[4] Electrochrome 2 may alternatively be a non-coloring redox material, when it is referred to as the "counter electrode" or, more irritatingly, as the "ion storage layer", which obscures the galvanic-cell basis of operation. Other devices, such as displays, need an appropriately modified construction. The "electrolyte" in the diagram may be a polymer adhesive in which the salt "MX" is dissolved. MX can be NaCl or $LiClO_4$ or another salt. For flexible devices, in the place of glass the ITO coated polymer PET (polyethylene-terephthalate) might be used.

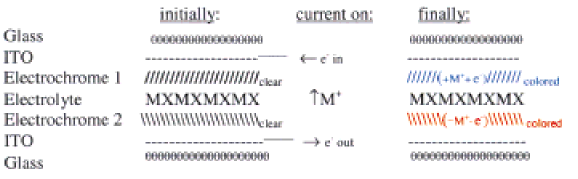
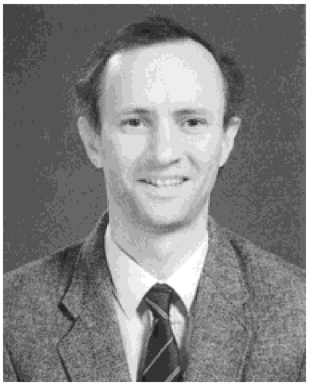


Fig. 1. Outline sketch of an electrochromic system. After current flow to inject/withdraw electrons in the colorizing process, subsequent open circuit leaves the electrochromes colored, until reversed current is allowed or made to flow.

2.3. Electrolyte

Easiest to use and reproduce and hitherto the most durable are liquid electrolytes. The salt used can be chosen for least electrochemical interference and greatest stability, and furthermore, high concentrations can aid in maintaining liquefaction for very low temperature operation. Liquid systems are often considered messy both in handling during manufacture and on breakage, but the highly successful Gentex[12] car-

David R. Rosseinsky, recently reader in Physical Chemistry at the University of Exeter, is now Honorary Research Fellow there. He finished his Ph.D. (Manchester, UK) on aquo ion electron transfer, and a postdoctorate at the University of Pennsylvania. He lectured for two years at the University of the Witwatersrand, South Africa, and after holding ICI and Leverhulme Research Fellowships, he was appointed lecturer at Exeter. He employs electrochemical probes in a wide variety of charge transfer processes, including electrochemical photovoltaism, electrochromism, and colloid electrodeposition. At present he is Visiting Senior Research Fellow at the Gintic Institute of Manufacturing Technology in Singapore.



Roger J. Mortimer is a senior lecturer in Physical Chemistry at Loughborough University of Technology. He received his Ph.D. in 1980 from Imperial College having studied heterogeneous catalysis at the solid-liquid interface. He then held a post-doctoral fellowship at the California Institute of Technology performing research on polymer-modified electrodes. After a demonstratorship at the University of Exeter and lecturing positions in Cambridge and Sheffield, he joined Loughborough in 1989. His research interests include electrochromism, electrochemical and optical sensors, and electrocatalysts for fuel cells.

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mirror system (Sec. 3.2) employs liquid, and its sealant has an excellent non-leakage record. In Gentex devices, one of the electrochromes being ionic provides all the electrolyte needed.

Solid electrolytes are sometimes a solid salt but either intrinsically ionically conductive polymers or polymers containing occluded salt are the most often used, the polymer acting here as solvent. Such mixtures are often in gel form. In the most sought-after applications the electrolyte must be transparent but if the front (visible) electrode in a display is conductive glass, at which electrochromism takes place, then in such displays the electrolyte can be unobtrusively opaque.

2.4. All-Liquid Electrochromes

The color-evoking electrode reaction involves the injection or removal of an electron and if this were the sole change, the region comprising the color-producing center would be left net negative or net positive respectively, and hence of raised energy relative to the final (colored) state. This final state is achieved: 1) by the migration to the color center of an oppositely charged "counter ion", or emigration away by a "co-ion" of the same charge as that acquired by the coloring electrochrome. The raised energy condition is further mitigated by two other factors. 2) In a spontaneously coloring system, extra stabilization is afforded by the orbital energy of the receiving orbital in a reducible system (correspondingly, by electron removal from a high-energy orbital in an oxidizable system). 3) Otherwise, the impressed applied potential adds stabilization. The migration (1) occurs readily if the electrochromes are dissolved species in an electrolyte solution where mobile counter-ions are practically omnipresent and where migration is thus of only secondary importance. (The electrolyte may moderately associate with the electrochrome if ionic.) This virtual removal of a major barrier to electrochromism is employed in all-liquid systems. An example is

$$\mathrm{Bipm}^{2+} + e^- \longrightarrow \mathrm{Bipm}^{+\bullet} \tag{1}$$

where Bipm^{2+} represents a colorless bipyridilium ion. The solubility of the $\mathrm{Bipm}^{+\bullet}$ and the color evoked depend on attached substituents. Addition of a second electron yields a weaker colorant, Bipm^0, and disproportionation of (dissolved) $\mathrm{Bipm}^{+\bullet}$ can be a complication. The chemistry has been compactly summarized[5] and comprehensively collated.[13]

Anodic solution-phase electrochromes like *N,N,N′,N′*-tetramethyl-*p*-phenylene-diamine (TMPD) are also available.[5]

2.5. Liquid/Solid Systems

An early example[4] (1920) involved the electrodeposition of Zn metal from Zn^{2+} in solution. In an organic example, the initially uncolored species may be dissolved but the colored state insoluble.[14] An example is found in the bipyridilium system comprising the so-called cyanophenylparaquat species CPQ^{2+}, the *N,N′*-di(*p*-cyanophenyl)-4,4′-bipyridilium cation, with solid-forming anions X^-,

$$\begin{array}{l} CPQ^{2+}(aq) + e^- + X^-(aq) \rightarrow CPQ^{+\bullet}\,X^-(\text{solid}) \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad (\text{deep green}) \end{array} \tag{2}$$

Here the solid formed must incorporate the counter ion, which thus assumes a markedly important role in the coloration mechanism, its individual physicochemical properties determining the mechanism and rate of deposition. A new example is the deposition of Bi or a Cu–Bi alloy from a Bi^{3+}/Cu^{2+} solution in a low-density information device,[15] where deposition onto conductive elements make up the display.

2.6. All-Solid Systems

Substantially different physics arises if the initial state itself is solid. Following Deb's work,[3,4] which revived modern electrochromism, the most widely studied system of this kind is[8]

$$\begin{array}{ll} WO_3 + \delta e^- + \delta M^+ \rightarrow & W^{VI}_{1-\delta}W^{V}_{\delta}O_3M_\delta \\ (\text{clear}) & \quad (\text{blue}) \end{array} \tag{3}$$

where $0 < \delta < 1$, i.e., a fraction of the W^{VI} population is converted; the product may be viewed as a solid solution. δ is the insertion coefficient. On coloration the counter-ion, for ingress or egress, must migrate through the lattice, a migration often greatly exceeding the purely electron-transfer factors in the energy requirements governing the rate, or indeed the possibility, of coloration. For a specific example, cation ingress from the electrolyte accompanies electron progress from the conductive electrode substrate, each charge species migrating at its own rate. Electrochromic coloration is sometimes considered as ion injection more-or-less accompanied by electron transfer, but all electrochromic coloration is fundamentally a consequence of the transfer of the electron (sometimes of two electrons), as outlined in Section 1 above. The WO_3 system is considered in more detail later (Sec. 4.4). Many oxides,[3,4] e.g., Nb_2O_5, NiO, MoO_3, and Ir_2O_3, mixed oxides, and polyoxometallates,[16] can all be made electrochromic.

Prussian Blue (PB) and its analogues,[3,4] phthalocyanines,[5] electroactive organic polymers, and polymers containing transition metal ions[5] provide further classes of solid electrochromes.

While the blue material is the "natural" form, PB can be thought to colorize in devices as follows. (We carefully omit the cationic counter ion which in the blue form can be K^+ or $1/3Fe^{3+}$, or indeed a combination, or even other cations.)

$$\begin{array}{cccc} Fe^{II}[Fe^{II}(CN)_6]^{2-} & \rightarrow & Fe^{III}[Fe^{II}(CN)_6]^- & + \; e^- \\ \text{"Prussian White"} & & \text{"Prussian Blue"} & \\ \text{clear} & & \text{blue} & \end{array} \tag{4}$$

Further (partial) oxidation of the PB gives a green, and total oxidation (i.e., stoichiometric one-electron abstraction from PB) gives a golden-yellow final color, but these latter steps have not been explored much for device application. The green is largely a solid solution of blue and yellow but with additional specific interaction, since the absorption peaks originating from those for the blue and yellow colorations shift somewhat with extent of oxidation.

2.7. Other Electrically Driven Darkening Systems

There are other electrically-driven systems for achieving darkening in operation, hence calling for no elaboration here, some being liquid crystalline.[17] Mechanisms falling between those of liquid-crystalline devices and truly electrochromic ones occur in systems[18] employing suspended particle display (SPD) devices. These are said[18] to rely on the field-effected parallel orientation of near-colloidal platelets to allow passage of light through otherwise darkened suspensions of the randomly oriented particles at zero field, as mentioned in Section 3.3 below, but even in the "clear" mode the visual field is still particulate and most unlikely to approach 100 % transmittance.

3. Applications and Devices, Extant and Future

3.1. Availability of Information Regarding Compositions

The commercial promise of electrochromism is such that, for patent reasons, details of real working systems are often not disclosed in research papers, or, if they are, they are not necessarily the final system of choice for device application. For apparently imminent systems, in this review we have to contend sometimes with a real and inescapable ignorance of detailed compositions and physical states; and faute de mieux we need to refer to commercial websites. Studies of the seminal WO_3 system have however been widely published and now the theoretical and experimental materials bases are well established and quite profound,[8] as detailed in Section 4.4.

3.2. Car Rear-View Mirrors

The only widespread commercially available device at present is the car rear-view mirror (Nikon's costly electrochromically adjustable dark glasses on sale around 1990 were soon withdrawn). The all-solid mirror described in the literature[2] has not yet achieved distribution, but of liquid-state devices, more than 25 million Gentex mirrors[12a] (now 27 million) have been sold since inception, from work started in 1974. Excellent illustrations of their operation appear elsewhere.[9] The reflecting surface adjoins one of the two facing conductive-glass electrodes. These, spaced in parallel, make up the cell, which contains the all-liquid system; the two dissolved electrochromes colorize on oxidation and reduction respectively, one at each electrode, so that both electrodes are electrochromic.

The cathodic coloring reaction is outlined in Equation 1, where the ionic species is ohmically driven to the cathode, in an ingenious accelerating ploy. The anodically coloring species, which may be of the Wurster's Blue type,[5] is neutral in charge and thus diffuses to the electrode in a chemical-potential gradient created by the driven process at the cathode. The resulting intensely dark blue-green color permits only the outline of otherwise dazzling headlights to appear. Each colored species—one now electron-deficient, the other electron-rich, compared to their initial states—diffuses away from its color-conferring electrode, and some molecules collide in solution in mid-cell to undergo mutual electron transfer, both thereby losing color. Maintenance of color intensity hence requires a small current, negligible in a car, to continuously generate the colored species. This lack of memory effect—the fading of color on disconnection of current—is an advantage: the fail-safe mode required by US law is the clear mirror. A minor chemical complication is that both electroactive species undergo some disproportionation, e.g., for bipyridiliums,[13]

$$2\,\mathrm{Bipm}^{+\bullet} \longrightarrow \mathrm{Bipm}^{2+} + \mathrm{Bipm}^{0} \qquad (5)$$

thus the particular bipyridilium or oxidizable species used requires a stable di-reduced (here Bipm^0) or di-oxidized byproduct to avoid material loss. Reversible cyclic voltammograms are indicative of long-term device stability.[12b] Segregation of the colorants under gravity, and the potential gradients that occur down (or up) from the external connections along the conductive surfaces of the glass plates, are minimized by appropriate top and bottom contacts to the conductive surfaces. Here the anode connection is made to the top and the cathode to the bottom contact. The control system ensures that it is only at night that the darkening reaction is effected. For external mirrors a single glass plate is employed, the second electrode being an inert metal, acting also as reflector.

The Donnelly firm[17] also makes a self-darkening mirror that is said to operate via a liquid-crystal system, which they call "electrochromic", not our definition of the term. (A solid-state device from Donnelly, which we presume comprises a WO_3 electroactive, is reported as imminent.)

3.3. Windows

A compelling motivation for achieving the manufacture of electrochromic windows either for cars (including sunroofs), but more importantly for buildings, is the huge possible saving in air-conditioner fuel costs—worth many billions of dollars per annum. It has been noted earlier[4] that only the totally reflective state, as can be attained in WO_3 (alas irreversibly) by heavy (>20 %) reduction, completely prevents heat inflow. The merely colored state of ordinary electrochromism, as with lightly reduced WO_3, acts by absorbing the radiation and hence itself becoming heated. Liquid systems present problems on the large scale and polymer gels are needed. Similar electrochromes to those in their mirrors we surmise are in use

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by Gentex.[12] For window purposes the systems are undergoing extensive sunlight-exposure tests in Arizona on larger expanses of the double-wall glass cells of size 11″ × 14″, i.e., 28 × 35 cm^2 (Fig. 2); these dim from 80 % transmission to 4 % transmission in a few minutes, and a sample tested for over a year in Florida appears in Figure 3.

Fig. 2. Gentex windows being tested in Florida. A man is visible beneath the nearest.

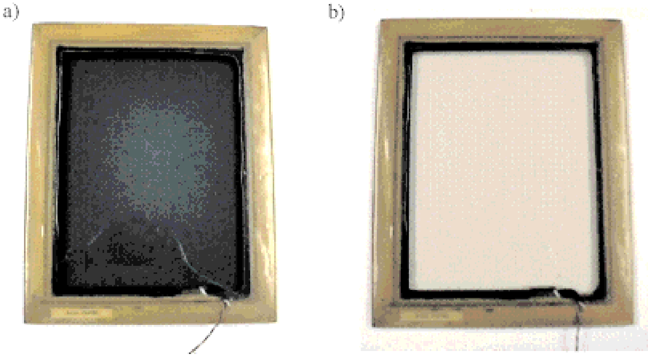

Fig. 3. Close-up of Gentex window: a) switched on; b) switched off.

Specimens twice this area are also under test, and a large 1 × 2 m^2 prototype window has been constructed (Fig. 4). The small sized samples shown in "on" and "off" states in Figure 5 illustrate the variety of colors accessible from chemical modifications of the molecules used by Gentex.

Schott–Donnelly have a demonstration electrochromic skylight of about 30 cm diameter called Ucolite,[19] to be fitted as an indoor ceiling fixture closing the base of a 40 cm diameter tube to a window in the external roofing.

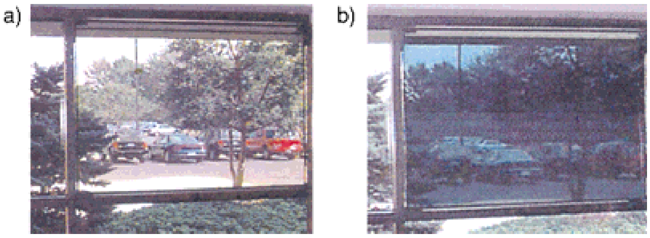

Fig. 4. Gentex window 1 × 2 m^2: a) clear and b) darkened.

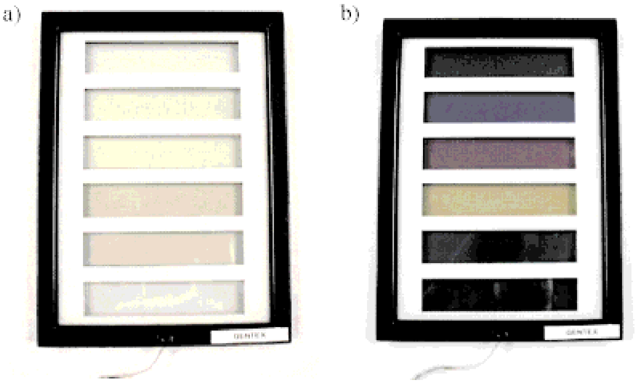

Fig. 5. Available Gentex colors, in off (a) and on (b) states.

The SPD-based system outlined in Section 2.7 is also claimed to operate in window form but neither the durability nor stability to switching are noted.[18] The website emphasizes the speculative nature of the information given. Other websites such as that of Sustainable Technologies Australia Ltd.[20] advertise well-functioning electrochromic windows cutting out 95 % of solar infrared (IR) and saving 30 % of working-environment costs. Flabeg GmbH, successors to Pilkington for electrochromic windows, portray a triple-glass construction comprising the extra adjunct of a conventional gas-filled double-glazing window.[21]

Some papers[22,23] devoted to testing procedures with sample results for electrochromics, exemplify the technical and architectural approaches now being applied.

3.4. Displays

The requirement for addressable pixels, each comprising separate potentially electrochromic electrodes, is a complexity being tackled at present, e.g., Figure 6, where dissolved electrochromes at a 3 × 3 matrix of electrodes with six inputs operate without cross-talk, the unconnected pixels experiencing insufficient potential for coloration spread to ensue,[24] even though the electrochromes (TMPD and heptylviologen) are always in solution.

Large-scale traffic direction boards, rail and airport departure boards, and the myriad advertisements seen about sports-

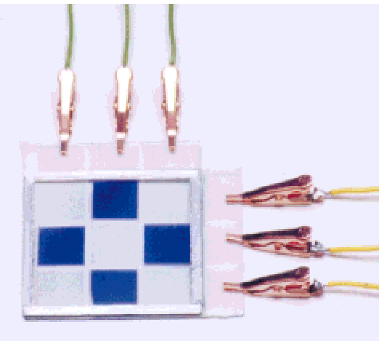

Fig. 6. Pixel array showing no cross-talk between close pixel elements, with solution-phase electrochromes [21]. (Reproduced from [24] with permission of the Electrochemical Society.)

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fields and elsewhere could ultimately be electrochromically operated. Nanomat[25] have a small demo device available with ~1 cm^2 pixels.

3.5. Remarkable Display and Actuator

A remarkable display system of polypyrrole (PPy) on silicon has been devised[26] in which a pixel comprises a platelet of Si segregated by suitable etching processes from its surrounding parent wafer (Fig. 7). It is attached to the wafer by the gold layer of a PPy/gold bilayer abutting both pixel and its surround; the PPy (previously electrodeposited) is outermost. This bilayer prospectively forms a hinge between Si surround and Si platelet. In contact with electrolyte in a cell the PPy can be oxidized and reduced, allowing the change in volume of this side of the bilayer to cause the Si platelet to rotate from the plane of the wafer. The gold is etched so that connection to the hinge is separate from connection to the colorizing PPy^+ deposited on the face of the platelet. The angle of rotation (up to at least 170°) alters the depth of PPy^+ viewed, which thereby changes its perceived color.

The PPy had been deposited together with the large dodecylbenzenesulphonate (DBS) anion that remains lodged within the polymer, thus compelling the redox process to be

$$PPy^+(DBS^-) + Na^+ + e^- \longrightarrow PPy^0(NaDBS) \qquad (6)$$

A number of applications besides electrochromism is envisaged.[26]

3.6. Displays Constructed by Printing Processes

Coleman et al.[27,28] report a notable process for printing displays, which could find a wide range of applications. It employs the highly electrochromic and rapidly responding antimony-doped tin oxide, ATO (Sec. 4.5), where the requisite layers and their topography are laid down by printing processes. The high surface area and hence accessibility to ions of the ATO nanocrystals, formed in the deposition, account for the rapidity of response.

3.7. 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.[29] Electrochromic darkening is preferable to direct electrical control as color values are thereby better preserved.

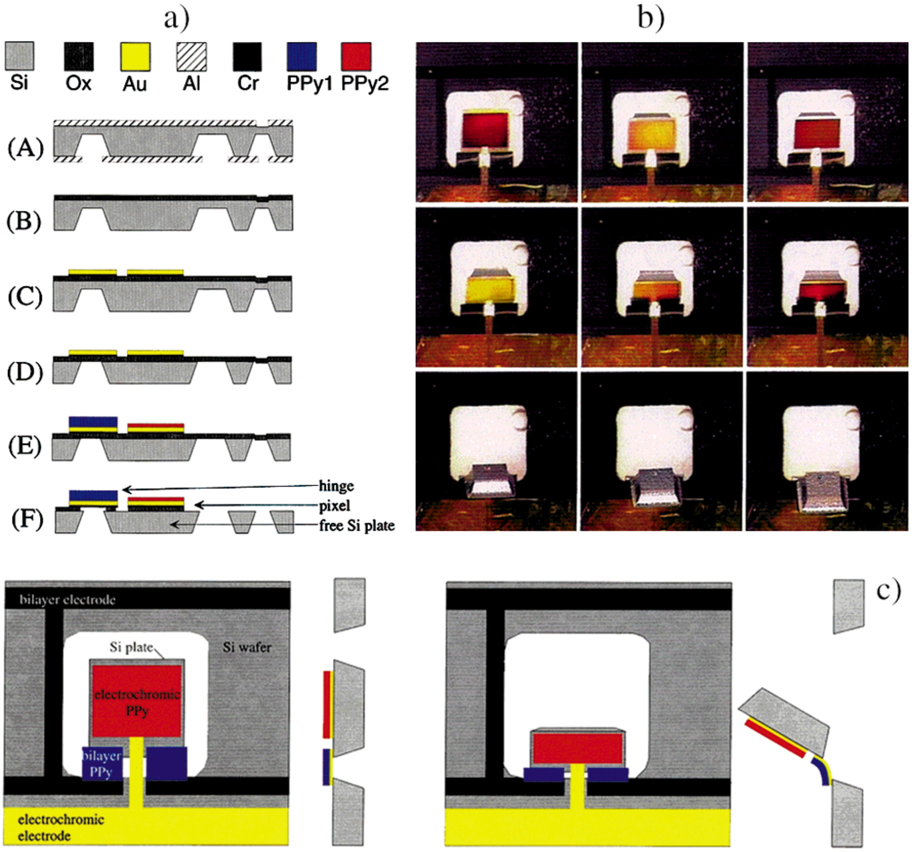

Fig. 7. The "hinged silicon flap" coated with PPy, constructed on a silicon chip. The hinge is a gold/PPy bilayer, operated by redox reaction of PPy, which has different molar volumes in the two redox states, hence effecting opening and closing of the hinge [26]. a) Schematic of the fabrication, b) snapshots taken during operation, and c) operating principle. (Reproduced from [26]).

3.8. A Thermal-Exposure Indicator for Frozen Foodstuffs[30]

A thin electrochromic cell can be attached as part of the labeling of frozen foodstuffs. The cell could have dual-layer conductive electrodes, one possibly a metal segment, the other transparent, either one bearing an electrochrome, WO_3, with an intervening ion-bearing polymer electrolyte, $LiClO_4$ or ZnI_2, in oxomethylene-linked polyethylene glycol. The composition of the cell is chosen so that it remains in the uncolored state when the foodstuff is frozen: the polymer electrolyte is such as to be virtually non-conductive at low temperature. The composition of the polymer electrolyte is chosen to have just the right temperature coefficient of conductivity so that, on warming, increased conductivity allows electrochromism to set in, thus warning of the thermal deterioration of the goods. The higher the temperature

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and/or the longer the exposure, the more intense could the color become and hence the greater the deterioration demonstrated. After accidental thermal exposure, re-freezing does not dispel the coloration.

The conductivity temperature-coefficient of the electrolyte, expressible as an activation energy E_a, is adjusted by choice of polymer length and the kind and concentration of salt content to match the robustness or sensitivity of the sample goods to thermal deterioration.

The degree of deterioration D relates directly to the extent of coloration by integrating the rate expressed in Arrhenius form over time t:

$$D = \int_{t_1}^{t_2} A \exp(-E_a/RT)\,\mathrm{d}t \qquad (7)$$

The prototype constructed[30] did not indicate exposure via color intensity; rather, the deterioration was shown by the length turned blue on a WO_3 strip (Fig. 8), thus avoiding the need of a calibration chart. Furthermore, in order to furnish the cell with its own driving potential, reactive metals Li or Zn were employed, to drive electrons to the WO_3 when warming of the polymer electrolyte allowed sufficient ionic conduction. This device prototype in our view represents a highly ingenious and exceedingly promising application of electrochromism.

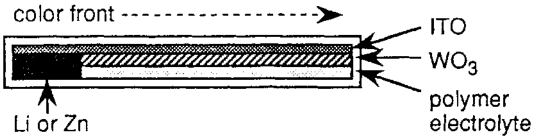

Fig. 8. Construction and operation of frozen-food exposure indicator [30] (Reproduced from [30] with permission from the Society of Chemical Industry).

3.9. Electrochromic Printing

As outlined in our monograph,[4] electrochromic printing has been and can be effected by impregnating paper with uncolored electrochrome + electrolyte solution, the paper resting on a large backing electrode below, with a fine printhead electrode making contact on the viewed surface. Multicolor printing requires quite elaborate sophistication. Earlier studies[4] of evoking PB coloration, and that of bipyridilium species, in paper, have been clarified:[31] PB needs to be retained in the paper by a film of Nafion. Methylviologen (1,1′-dimethyl-4,4′-bipyridilium) bromide, and the diheptyl analogue, soon lose color on reaction of the radical-ion with oxygen, but a host of colorable/bleaching redox indicators is available for study. The di-*N*-hexyl bipyridilium layer, in Nafion conductive polymer superimposed on PB, yields (at negative potentials) a pink color in addition to the clear/blue/green/yellow (at ever more positive potentials) of PB.[32]

An ingenious application to entry-ticket security has been devised.[33,34] Besides the overt label, the ticket card is invisibly printed with electrochrome, in an authenticating pattern that emerges when the ticket on submission is passed between two electrodes for endorsement. Nil response exposes counterfeits.

3.10. Other Applications

The control of device light intensities has been considered,[35] (CPQ^{2+} again),[13,14] though heat problems usually arise in cases of intense illumination, e.g., for theatrical lighting. The coating of stealth aircraft with switchable electrochromes has been mooted, but considering the care needed simply to coat such aircraft with ordinary anti-radar paint, one may perhaps view this application to be, as it were, a long shot.[36]

4. Some Aspects of Electrochromic Systems

4.1. Counter Electrodes

In conjunction with a chosen electrochromic electrode, a counter-electrode of comparable efficiency and rate is required. Many non-coloring electrodes have been studied, often comprising oxide or mixed-oxide[37] electroactive substances, but important though these are, being a sub-plot to the theme of coloration, we omit them but for one comment. Ho[38] points out that to maximize overall efficiency, a complementarity of response is required from a counter electrode, i.e., the amount of electroactive species must match or exceed that of the electrochrome (matching brings material economy), and similar considerations apply to rate.

4.2. Electrolytes

Transparent electrolytes comprise either polymers like polyethylene oxide (PEO) loaded with electrolytes such as $LiClO_4$ or PAMPS (poly-2-acrylamido-2-methyl-propane sulfonic acid), which provides its own H^+ ions.[8] Such materials can be employed in flexible devices, since ITO can now be coated onto polymer substrates.[39]

Electron-blocking inorganic salts providing ionic but no electronic conductivity are alternatives, and zirconium phosphate has been advocated as an example.[4]

4.3. Viologens

Amongst the most widely studied of electrochromes, the properties of these bipyridilium compounds are encompassed in great detail in the literature.[17] One-electron reduction produces intense coloration of either solid or solution-state species, whereas a two-electron uptake yields a less intensely colored product. The specific properties of color and solubility can be adjusted chemically by suitable choice of attached substituents. An interesting cell comprising a variety of viologens attached to TiO_2 sintered onto ITO, with a PB complementary electrode, exhibits huge absorbances and 1–3 s switching times.[40] Further details of mechanisms and applications are referred to in Sections 2.4, 2.5, 3.2, 3.4, and 3.9 above.

4.4. Tungsten Trioxide, WO_3, and an Ion-Diffusion Barrier Exemplified in TiO_2

With 626 references, a comprehensive, impressive update of his 1995 overview[3] has recently been provided by Granqvist,[8] who even so needed to be selective; our simplified summary here no doubt has attendant inaccuracies.

Porosity is a desideratum for rapid coloration–bleaching responses. WO_3 may be prepared by evaporation or sputtering of oxide, by sol–gel deposition, by spin-coating, dipping or spraying, by chemical vapor deposition (CVD), by the anodizing of metal, and other methods. Special attention[8] was given to examining the role of experimental parameters in determining product properties in the sputtering of W in Ar + O_2 + CF_4. The variation in properties and structures depending on preparation is impressive. Electrodeposited material from $Na_2WO_4{\cdot}2H_2O$ is shown by X-ray photoelectron spectroscopy (XPS) to comprise W^{IV}, W^{V}, and W^{VI}, the W^{IV} being suggested by other authors[41] to participate in the optical event giving the electrochromic coloration.

With M = H, Li, Na, or K in Equation 3, modified, the electrochromic reaction is

$$WO_3 + xM^+ + xe^- \longrightarrow M_xWO_3 \qquad (8)$$

This reaction is in fact a "gross oversimplification"[8] of the hydrous nature of the initial solid, H_2O and –OH also being involved. The latter affects the "insertion coefficient" x. Many crystal structures plus amorphism appear in WO_3; defect-perovskite is the simplest, but the cubic form,[8] orthorhombic, monoclinic, hexagonal (two forms), and pyrochlore structures plus a supermetastable phase are also listed; there are mixed-oxide variants, and a sub-stoichiometric form short of oxygen. Numerous counter-ion species M including divalents in the product M_xWO_3 have been studied.

Different roles of W^{IV}, W^{V}, and W^{VI} in optical charge-transfer processes (= "the intrinsic color effects") may arise in O-deficient compared with the stoichiometric material. A theoretical model[42] employing density-functional calculations argues for W^{V}–W^{V} dimers rather than W^{IV} in such situations. The electrochromic and photochromic properties of O-deficient WO_3 have been found to depend on similar W^{IV} participation in both mechanisms.[43]

Detailed density-of-state and associated structural calculations on initial and totally mono-reduced forms of MWO_3 give some insight into the bonding and the disposition of the transferred electron. Incorporated Li^+ (also Na^+) turns out, realistically, to be nearly totally ionic, but H^+ becomes attached to O; the transferred electron, acquired in the electrochemical coloration process, is in a conduction band largely comprising the W d orbitals.

Probably the most important barrier in oxide processes is ion-insertion and its reversal. An interesting study of this problem in TiO_2 has been summarized;[44] the requisite parameters for WO_3 are presumably lacking. The activation energy E_c for transfer of M^+ (of charge z_+ and radius r_+) over a distance d from an oxygen ligand (of radius r_-), to a vacancy near a similar oxygen (each bearing a charge z_-) is[45,46]

$$E_c = B\,z_+ z_- e^2/\varepsilon(r_+ + r_-) - 2\,z_+ z_- e^2/\varepsilon(d/2) + \pi l \Gamma (r_+ - r_d)^2/2 \qquad (9)$$

where B is the Madelung-constant/$4\pi\varepsilon_0$, z_+ and z_- the charge numbers on cation and non-bonded oxygen, respectively, while r_+ and r_- are the corresponding radii. The relative permittivity of the material is ε and the shear modulus Γ. l is the jump length and r_d is half the distance between bridging oxygens forming the "doorway" needing enlargement to r_+ to enable M^+ to pass. Inserting data for TiO_2(anatase) and the observed E_c for cation migration gave a value of d of 0.4 nm, which matches well the unit cell dimensions of the corresponding anatase, and orthorhombic $Li_{0.5}TiO_2$. The Na^+ doped oxide also accords, but the larger K^+ containing material could not be thus accommodated. The expression encompasses the loss by M^+ of lattice interaction (first term), its stabilization by gain of interaction with two oxygens (second term), plus (final term) the work of lattice expansion at the push-through situation. (It is intriguing that ε appears in the first term, unusual for Madelung-type calculations; and the loss implies a longer relaxation time for the lattice interaction than the jump time of M^+, which is unexpected.) This simple expression appears to be of potentially wide applicability.

From a multiplicity of devices, Granqvist[8] picked out the system studied by Ho et al.,[47] G/ITO/WO_3/PAMPS/PB/ITO/G, where ITO/G is indium tin oxide coated glass, PAMPS the polymeric electrolyte, and PB the second electrochromic electrode, comprising iron(III)hexacyano-ferrate(II) in its colored form, colorless when reduced—see Section 2.6. The data are: size: 400 cm^2; transmittance at 550 nm: 5 % to 65 %; cycles survived without serious degradation: 2 × 10^4; coloration switching time: 60 s.

A 100 cm^2 sample of different composition gave a comparable performance, while others could be cycled 10^4 to 10^5 times but were somewhat different in other regards.[48]

In a survey of the four compositions at which WO_3 changes (decreases in) coloration efficiency, namely x = 0.035, 0.34, 0.44, and >0.44, Monk[49] provides an astonishingly simple geometric model for the first two, that predicts x = 0.037 [=1/27] for the first and x = 0.375 [=3/8] for the second value. The model requires non-neighbor interactions to be forbidden at particular distributions of W^{V} in simple lattice configurations.

4.5. Antimony-Doped Tin Oxide—A Notable New Mixed Oxide

A highly promising new electrochrome meriting special mention is Coleman et al.'s[27,28] ATO, of which the applicability in printable displays on polyester film has already been noted in Section 3.6.

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4.6. The Remarkable New Hydride Reversible Mirrors-or-Windows Systems

In research on lanthanide hydrides made by hydrogenation, research student Huiberts at the Vrije Universiteit, Amsterdam, discovered that, on hydride formation from the reflecting-mirror metallic state of Y, La, and Y/La alloys, a transparent semiconductor phase ensued.[50] A thin Pd layer seems to be necessary, possibly allowing hydride formation from H_2 gas. Originally effected by exposure to gaseous hydrogen, the process is electrochemically induced[51,52] at highly cathodic potentials in aqueous 1 M to 5 M hydroxide solution, and also with Gd/Mg and other Mg/lanthanide alloys. Does the hydride ion have any role as solution-phase intermediate? The effect is remarkable, and a half-reflecting half-transparent state can be observed at intermediate compositions. New work is burgeoning[52,53] and an excellent overview is available by Notten (Philips),[53] where much of the development has been undertaken. While highly attractive in the remarkable clarity of both states, such hydride solids will need effective anti-atmospheric protection and a huge downward hike in cost to become widely useable. Even so, pixel systems are being contemplated. Space-station applications requiring electrochromic protection seem a possibility. An excellent video of the switching, from mirror to window and back, is given on the website.[54]

4.7. Electroactive Polymers

All conducting polymers, such as the PPys, polyanilines, and polythiophenes, are latently electrochromic in thin-film form, redox switching giving rise to new optical absorption bands in accompaniment with transfer of electrons and counter anions. In their oxidized states, conducting polymers are "doped" with counter anions ("p-doping") and contain a delocalized π-electron band structure, the energy gap between the highest occupied π electron band (valence band) and the lowest unoccupied band (the conduction band) determining the intrinsic optical properties. Reduction of conducting polymers with concurrent counter-anion exit removes the electronic conjugation, to give the "undoped" (neutral) electrically insulating form.

While these polymers can be of questionable chemical stability in the conductive state, polythiophene(s)[55] are of particular interest as electrochromic materials owing 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 achieved by the suitable choice of thiophene monomer, representing a major advantage of using conducting polymers for electrochromic applications. Subtle modification can significantly alter spectral properties. For example, the colors available with polymer films prepared from 3-methyl-thiophene based oligomers are strongly dependent on the relative positions of methyl groups on the polymer backbone.[56] Colors available include pale blue, blue, and violet in the oxidized form, and purple, yellow, red, and orange in the reduced form, with often only weak yellow as the best "clear" form. The color variations have been ascribed to changes in the effective conjugation length of the polymer chain.

Alkoxy-substituted polythiophenes especially are now intensively investigated for their electrochromic properties.[57–64] Materials based on poly(3,4-(ethylenedioxy)-thiophene) (PEDOT) have a bandgap lower than polythiophene and alkyl-substituted polythiophenes, due to their two electron-donating oxygen atoms adjacent to the thiophene unit. Thus the bandgap of PEDOT (E_g = 1.6 eV) is 0.5 eV lower than polythiophene, giving an absorbance maximum in the near IR region. Relative to other substituted polythiophenes these materials exhibit an exceptional stability in the highly conductive doped state. Doped PEDOT is almost transparent in the visible region (with a sky-blue tint) and the neutral polymer is blue-black. As PEDOT and its alkyl derivatives are cathodically coloring electrochromic materials they are suitable for use with anodically-coloring conducting polymers in the construction of dual polymer electrochromic devices.[61] Some polymers are both n- and p-dopable, e.g., polymerized dithienothiophenes; this allows the same material to be employed for both electrodes of electrochromic windows.[65]

Enhanced contrast ratios and rapid electrochromic switching are shown in substances based on poly(3,4-propylenedioxythiophene) derivatives.[66] The highly stable electrochromic polymer poly(3,4-ethylene-dioxypyrrole) (PEDOP) is an electron-rich conjugated polymer especially useful for the formation of stable conducting polymer complexes that can be switched between their oxidized (doped) and charge-compensated (neutral) states rapidly over many redox cycles.[67] PEDOP switches between a bright red neutral form and a highly transmissive blue-gray doped conducting form. Rapidly switchable electrochromic polymers are based on new poly(3,4-alkylenedioxy-thiophene) derivatives.[68] A Reynolds review summarizes the developments of his group's work.[69] A solid state electrochromic device based on two optically complementary conducting polymers has been made.[70]

4.8. Composite Systems of Electroactive Polymers with Electro-Inert Polymers, or with Included Dyes or Dopants

The electropolymerization of monomers to include additives with electrochromic or other properties has furthered the preparation of "design" materials. Shannon and Fernandez prepared a water-soluble poly(styrenesulphonic acid)-doped polyaniline both by persulphate oxidative coupling and anodic oxidation of aniline in aqueous dialyzed poly(styrenesulphonic acid) solution.[71] De Paoli et al.[72] made composites of polyaniline and cellulose acetate both by casting of films from a suspension of polyaniline in a cellulose acetate solution and deposition of cellulose acetate films onto electrochemically prepared polyaniline films. The electrochromic

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properties of these films, studied spectroelectrochemically, showed that the included cellulose acetate did not impede the redox processes of the polyaniline. Tassi et al.[73] studied the electroactivity and electrochromism of the graft copolymer of polyaniline and nitrilic rubber using stress–strain measurements, cyclic voltammetry, frequency response analysis, and visible range spectroelectrochemistry, finding that the graft copolymer exhibits mechanical properties similar to a cross-linked elastomer but with the electrochromic and electrochemical properties typical of polyaniline.

The encapsulation of the redox indicator dye indigo carmine within a PPy matrix[74,75] provides an example of the additive itself being electrochromic. Girotto and De Paoli,[76] informatively represented in quasi-3D the potential dependence of absorbance and current data acquired during cyclic voltammetry, and showed that enhancement and modulation of the color change is effected by indigo carmine insertion into polypyrrole or PPy/dodecyl-sulfonate films. The anionic indigo carmine as dopant improves the electrochromic contrast ratio of the film.

4.9. Electrochromism in Fullerene C_{60}

A change in color of C_{60} thin films from yellow-brown (undoped state) to silver-black when doped with alkali metals has been observed.[77] Now Córdoba de Torresi et al.[78] report (absorbance and current vs. potential data) the reversible color change of C_{60} thin films produced by electrochemical Li^+ insertion. Undoped film is light brown, doped is dark brown.

5. Conclusions

The field of electrochromism is rapidly expanding both in novel systems or applications, and in forums and their publications. Thus, perhaps more so than usual, the views and selections of topics presented here are personal to the authors, being neither objective nor—within so short a review—complete. Thus, we have with regret consigned non-visible electrochromic responses, important in both solar screening and optical-fiber systems, to a later forum. To quote Rauh's first paragraph:[79] "Electrochromism, the reversible change in optical properties when a material is electrochemically oxidized or reduced, has a long history of fundamental and practical interest. While materials were considered "electrochromic" when they showed marked visible color changes, recent interest in 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."

For comprehensive surveys, readers should scan the now compendious literature, proceedings of conferences, the extensive patent literature (quite neglected here) and the web. A number of specialist meetings take place in the USA under the auspices of the Electrochemical Society, appearing as *"Proceedings of Symposium on Electrochromic Materials"* I, II, and III extracted from ECS Symposia in 1990, 1994,[47] and 1996. Other sponsors also participate, for example the American Institute of Chemical Engineers at the Annual Meeting held in Chicago, 11–16 November 1990 ("Fundamentals of Electrochromic Devices") also published,[80] and many, often under the "Displays" heading, in the UK and Europe. The International Meeting on Electrochromism (IME) series started in Venice. The Second International Meeting on Electrochromism (IME-2) in 1997 in San Diego, USA, was reported in a special (and belated) issue of *Solar Energy Materials and Solar Cells*.[8] IME-3 in 1998 in London, UK, appeared in *Electrochimica Acta*,[6] while IME-4, which took place in Uppsala, Sweden (21–23 August 2000), was also reported in *Electrochimica Acta*[81].

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[1] In principle the second electrode need not necessarily undergo electron transfer since an excess or dearth of electrons in the metal of the second electrode, forming a space charge, might in principle be counterbalanced by an opposing space charge of oppositely charged ions in the contacting electrolyte at that electrode. Substantially larger potentials would need to be applied, and (probably irreversible) electron transfer involving the solvent or electrolysis would practically always intervene before an appreciable space charge accumulated. However, a solid electron-blocking proton conductor like hydrogen uranyl phosphate as electrolyte could conceivably allow a space charge mechanism at an anode of an electrochromic cell.

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