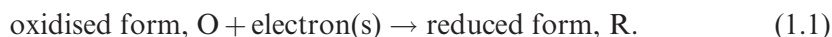


1

Introduction to electrochromism

1.1 Electrode reactions and colour: electrochromism

The terminology and basis of the phenomenon that we address are briefly outlined in this chapter. Although there are several usages of the term ‘electrochromism’, several being summarised later in this chapter, ‘electrochromes’ later in the present text are always ‘electroactive’, as follows. An electroactive species can undergo an electron uptake, i.e. ‘reduction’, Eq. (1.1), or electron release, i.e. ‘oxidation’, the reverse of Eq. (1.1) in a ‘redox’ reaction that takes place at an electrode. An electrode basically comprises a metal or other conductor, with external connections, in contact with forms O and R of an ‘electroactive’ material, and can be viewed as a ‘half-cell’:



Though in strict electrochemical parlance all the components, O and R and *the metallic or quasi-metallic conductor*, comprise ‘the electrode’, we and others often depart from this complete definition when we imply that ‘the electrode’ comprises the just-italicised component, which conforms with the following definition: ‘An electrode basically comprises a metal or metallic conductor or, especially in electrochromism, an adequately conductive semiconductor often as a thin film on glass.’ We thus usually refer to the ‘electrode substrate’ for the metal or metal-like component to make the distinction clear. Furthermore, in Chapter 3 it is emphasised that any electrode in a working system must be accompanied by a second electrode, with intervening electrolyte, in order to make up a cell allowing passage of current, in part comprising the flow of just those electrons depicted in Eq. (1.1).

An electroactive material may be an atom or ion, a molecule or radical, sometimes multiply bonded in a solid film, and must be in contact with the electrode substrate prior to successful electron transfer. It may be in

solution – solvated and/or complexed – in which case it must approach sufficiently closely to the electrode substrate and undergo the adjustments that contribute to the (sometimes low) activation energy accompanying electron transfer. In other systems, the electroactive material may be a solid or dispersed within a solid matrix, in which case that proportion of the electrochrome physically in contact with the electrode substrate undergoes the redox reaction most rapidly, the remainder of the electroactive material less so. The underlying theory of electrochemical electron-transfer reactions is treated elsewhere.¹

That part of a molecular system having or imparting a colour is termed a chromophore. White light comprises the wavelengths of all the colours, and colour becomes evident when photons from part of the spectrum are absorbed by chromophores; then the colour seen is in fact the colour *complementary* to that absorbed. Thus, for example, a blue colour is reflected (hence seen) if, on illumination with white light, the material absorbs red. Light absorption enables electrons to be promoted between quantised (i.e. wave-mechanically allowed) energy levels, such as the ground and first excited states. The wavelength of light absorbed, λ , is related to the magnitude of the energy gap \mathcal{E} between these levels according to the Planck relation, Eq. (1.2):

$$\mathcal{E} = h\nu = \frac{hc}{\lambda}, \quad (1.2)$$

where ν is the frequency, h is the Planck constant and c the speed of light in vacuo. The magnitude of \mathcal{E} thus relates to the colour since, when λ is the wavelength at the maximum (usually denoted as λ_{\max}) of the absorption band observed in the spectrum of a chromophore, its position in the spectrum clearly governs the observed colour. (To repeat, the colour arises from the non-absorbed wavelengths.) Most electrochromes colourise by reflection, as in displays; transmission-effective systems, as in windows, follow a corresponding mechanism.

Electroactive species comprise different numbers of electrons before and after the electron-transfer reaction (Eq. (1.1) or its reverse), so different redox states will necessarily exhibit different spectroscopic transitions, and hence will require different energies \mathcal{E} for electron promotion between the ground and excited states. Hence all materials will undergo change of spectra on redox change.

However, the colours of electroactive species only *may* be different before and after electron transfer because often the changes are not visible (except by suitable spectrometry) when the wavelengths involved fall outside the visible range. In other words, the spectral change accompanying a redox reaction is visually indiscernible if the optical absorptions by the two redox states fall in

the ultraviolet (UV) or near infrared (NIR). When the change is in the visible region, then a pragmatic definition of electrochromism may be formulated as follows. 'Electrochromism is a change, evocation, or bleaching, of colour as effected either by an electron-transfer (redox) process or by a sufficient electric potential. In many applications it is required to be reversible.' However, regarding intensity-modulation filters for, say, IR message-laser pulses in optical fibres, such terms as 'electrochromic switching or modulation' are increasingly being used for such invisible effects.

Visible electrochromism is of course only ever useful for display purposes if one of the colours is markedly different from the other, as for example when the absorption band of one redox state is in the visible region while the other is in the UV. If the colours are sufficiently intense and different, then the material is said to be electrochromic and the species undergoing change is usefully termed an 'electrochrome'.²

Simple laboratory demonstrations of electrochromism are legion.^{3,4} The website in ref. 5 contains a video sequence clearly demonstrating electrochromic coloration, here of a highly conjugated poly(thiophene) derivative. Many organic and inorganic materials are electrochromic; and even some biological species exhibit the phenomenon:⁶ *Bacteriorhodopsin* is said to exhibit very strong electrochromism with a colour change from bright blue to pale yellow.⁶

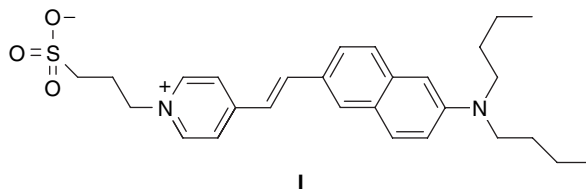
The applications of electrochromism are outlined in Chapter 13 and the general criteria of device fabrication are outlined in Chapter 14.

1.2 Non-redox electrochromism

The word 'electrochromism' is applied to several, disparate, phenomena. Many are not electrochromic in the redox sense defined above.

Firstly, charged species such as 3-{4-[2-(6-dibutylamino-2-naphthyl)-*trans*-ethenyl] pyridinium} propane sulfonate ('di-4-ANEPPS') (**I**), called 'electrochromic probes', are employed in studies of biological membrane potentials.⁷ (A similar-looking but intrinsically different mechanism involving deprotonation is outlined below.) For a strongly localised system, such as a protein system where electron-donor and -acceptor sites are separated by large distances, the potential surfaces involved in optical electron excitation (see Eq. (1.2)) become highly asymmetrical.⁷ For this reason, the electronic spectrum of (**I**) is extraordinarily sensitive to its environment, demonstrating large solvent-dependent 'solvatochromic' shifts,⁸ so much information can be gained by quantitative analysis of its UV-vis spectra. In effect, it is possible to image the electrical activity of a cell membrane.⁷ Loew *et al.* first suggested this use of such

electrochromism in⁹ 1979; they pointed out how the best species for this type of work are compounds like (**I**), its 8-isomer, or nitroaminostilbene,¹⁰ both of which have large non-linear second-harmonic effects.⁹ In consequence, significant changes are induced by the environment in the dipole moment so on excitation from the ground to the excited states, different colours result.



This application is not electrochromism as effected by redox processes of the kind we concentrate on in the present work, but can alternatively be viewed as a molecular Stark effect¹¹ in which some of the UV-vis bands of polarisable molecules evince a spectroscopic shift in the presence of a strong electric field. Vredenberg¹² reviewed this aspect of electrochromism in 1997. Such a Stark effect was the original sense implied by ‘electrochromism’ when the word was coined in 1961.¹³

While many biological and biochemical references to ‘electrochromism’ mean a Stark effect of this type, some are electrochromic in the redox sense. For example, the (electrochromic) colours of quinone reduction products have been used to resolve the respective influences of electron and proton transfer processes in bacterial reactions.^{14,15,16} In some instances, however, this electrochromic effect is unreliable.¹⁷

A valuable electrochromic application has been employed by O’Shea¹⁸ to probe local potentials on *surfaces* of biological cell membranes. The effect of electric potential on acidity constants is employed: weak acids in solution are partly ionised into proton and (‘base’) residue to an extent governed ordinarily by the equilibrium constant particular to that acid, its acidity constant K_a . However, if the weak acid experiences an extraneous electric potential, the extent of ionisation is enhanced by further molecular scission (i.e. proton release) resulting from the increased stabilisation of the free-proton charge. With ‘p’ representing (negative) decadic logarithms, the outcome may be represented by the equation $pK_a(\varphi_s) = pK_a(0) - F\varphi_s/RT(\ln 10)$ where φ_s is the membrane surface potential.¹⁸ This result (a close parallel of the observed ‘second Wien effect’ in high-field conductimetry on weak acids) arises from combining the Boltzmann equation with the Henderson–Hasselbalch equation. The application proceeds as follows. A fluorescent molecule is chosen, that is a proton-bearing acid of suitable K_a , with only its deprotonated moiety

showing visible fluorescence, and then only when the potential experienced is high enough. The probe molecules are inserted by suitable chemistry into the surface of the cell membrane. Then it will fluoresce, in areas of sufficiently high electric potential, thus illuminating such areas of ϕ_s , and monitoring even rapid rates of change as can result from say cation acquisition by the surface. Suitable probe molecules are^{18,19} fluoresceinphosphatidyl-ethanolamine (FPE) and^{20,21,22} 1-(3-sulfonatopropyl)-4-[p[2-(di-n-octylamino)-6-naphthyl]-vinyl]-pyridinium betaine. To quote,²³ ‘Probe molecules such as FPE have proved to be particularly versatile indicators of the electrostatic nature of the membrane surface in both artificial and cellular membrane systems.’ This ingenious probe of electrical interactions underlying biological cell function thus relies unusually not on electron transfer but on proton transfer as effected by electric potential changes.

Secondly, the adjective ‘electrochromic’ is often applied to a widely differing variety of fenestrative and device applications. For example, a routine web search using the phrase ‘electrochromic window’ yielded many pages describing a suspended-particle-device (SPD) window. Some SPD windows are also termed ‘Smart Glass’²⁴ – a term that, until now, has related to genuine electrochromic systems. On occasion (as occurs also in some patents) a lack of scientific detail indicates that the claims of some manufacturers’ websites are perhaps excessively ambitious – a practice that may damage the reputation of electrochromic products should a device fail to respond to its advertised specifications.

Also to be noted, ‘gasochromic windows’ (also called gasochromic smart-glass windows) are generally not electrochromic, although sometimes described as such, because the change in colour is wholly attributable to a direct chemical gas + solid redox reaction, with no externally applied potential, and no measurable current flow. The huge complication of the requisite gaseous plumbing is rarely addressed, while electrochromic devices require only cables. (The most studied gasochromic material is, perhaps confusingly, tungsten oxide, which is also a favoured electrochrome.) The gasochromic devices in refs. 25,26,27,28,29,30,31,32 are not electrochromic in the sense adopted by this book.

Thirdly, several new products are described as ‘electrochromic’ but are in fact electrokinetic–colloidal systems, somewhat like SPDs with micro-encapsulation of the active particles. A good example is Gyricon ‘electrochromic paper’,³³ developed by Xerox. Lucent and Philips are developing similar products. Such paper is now being marketed as ‘SmartPaperTM’. Gyricon is intended for products like electronic books, electronic newspapers, portable signs, and foldable, rollable displays. It comprises two plastic sheets, each of thickness *ca.* 140 μm , between which are millions of ‘bichromal’ (i.e. two colour) highly

dipolar spheres of diameter 0.1 μm , and are suspended within minute oil-filled pockets. The spheres rotate following exposure to an electric field, as from a 'pencil' tip attached to a battery also connected to a metallicly conductive backing sheet;³⁴ the spheres rotate fully to display either black or white, or partially (in response to weaker electrical pulses), to display a range of grey shades.³³ Similar mechanisms operate in embedded sacs of sol in which charged black particles are 'suspended' (when in the colourless state) but on application of a potential by an 'electric pencil', black particles visibly deposit on the upper surface of the sacs. Some of these systems being deletable and re-usable promise substantial saving of paper.

Note that the NanoChromicsTM paper described on page 347, marketed by NTERa of Eire, is genuinely electrochromic in the redox sense.

1.3 Previous reviews of electrochromism and electrochromic work

The broadest overview of all aspects of redox electrochromism is *Electrochromism: Fundamentals and Applications*, by Monk, Mortimer and Rosseinsky.² It includes criteria for electrochromic application, the preparation of electrochromes and devices, and encompasses all types of electrochromic materials considered in the present book, both organic and inorganic. A major review of redox electrochromism appears in *Handbook of Inorganic Electrochromic Materials* by Granqvist,³⁵ a thorough and detailed treatise covering solely inorganic materials.

Other reviews of electrochromism appearing within the last fifteen years include (in alphabetical order) those of: Agnihotry³⁶ in 1996, Bange *et al.*³⁷ in 1995, Granqvist (sometimes with co-workers) in 1992,³⁸ 1993,^{39,40} 1997,^{41,42} 1998,^{43,44,45} 2000,⁴⁶ 2003,^{47,48} and 2004,⁴⁹ Green⁵⁰ in 1996, Greenberg in 1991⁵¹ and 1994,⁵² Lampert in 1998,⁵³ 2001⁵⁴ and 2004,⁵⁵ Monk in 2001⁵⁶ and 2003,⁵⁷ Mortimer⁵⁸ in 1997, Mortimer and Rosseinsky⁵⁹ in 2001, Mortimer and Rowley⁶⁰ in 2002, Mortimer, Dyer and Reynolds⁶¹ in 2006, Scrosati, Passerini and Pileggi⁶² and Scrosati,⁶³ 1992, Somani and Radhakrishnan⁶⁴ in 2003 and Yamamoto and Hayashida⁶⁵ in 1998.

Bamfield's book⁸ *Chromic Phenomena*, published in 2001, includes a substantial review of electrochromism. Non-English reviews include that by Volke and Volkeova⁶⁶ (in Czech: 1996). McGourty (in 1991),⁶⁷ Hadfield (in 1993),⁶⁸ Hunkin (in 1993)⁶⁹ and Monk, Mortimer and Rosseinsky (in 1995)⁷⁰ have all written 'popular-science' articles on electrochromism.

Bowonder *et al.*'s 1994 review⁷¹ helps frame electrochromic displays within the wider corpus of display technology. Lampert's⁵⁵ 2004 review 'Chromogenic materials' similarly helps place electrochromism within the wider scope of

other forms of driven colour change, such as thermochromism. Lampert's review, shorter, crammed with acronyms but more up-to-date, includes other forms of display device, such as liquid crystal displays (LCDs), phase-dispersed liquid crystals (PDLCs), cholesteric liquid crystals (ChLCs) and suspended particle devices (SPDs).

There are also many dozen reviews concerning specific electrochromes, electrochromic-device applications and preparative methodologies, which we cite in relevant chapters. The now huge numbers of patents on materials, processes or devices are usually excluded, the reliability – often just the plausibility – of patents being judged by different, not always scientific, criteria.

1.4 Criteria and terminology for ECD operation

The jargon used in discussions of the operation of electrochromic devices (ECD) is complicated, hence the criteria and terminology cited below, necessarily abridged, might aid clarification. The terms comply with the 1997 IUPAC recommended list of terms on chemically modified electrodes (CMEs). A CME is⁷²

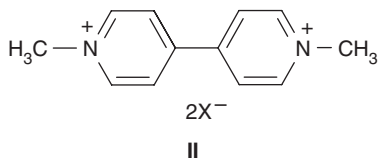
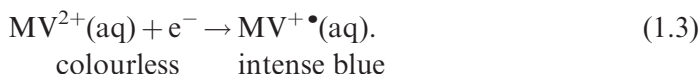
an electrode made up of a conducting or semi conducting material that is coated with a selected monomolecular, multimolecular, ionic or polymeric film of a chemical modifier and that, by means of faradaic . . . reactions or interfacial potential differences . . . exhibits chemical, electrochemical and/or optical properties of the film.

Chemically modified electrodes are often referred to as being derivatised, especially but not necessarily when the modifier is organic or polymeric. *All* electrochromic electrodes comprise some element of modification, but are rarely referred to as CMEs; this is simply to be understood.

1.4.1 Electrochrome type

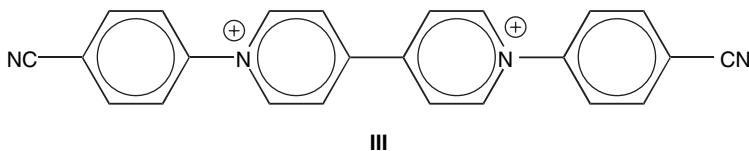
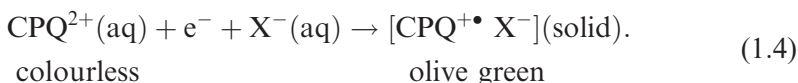
In the early days of ECD development, the kinetics of electrochromic coloration were discussed in terms of 'types' as in the seminal work of Chang, Sun and Gilbert⁷³ in 1975. Such types are classified in terms of the phases, present initially and thence formed electrochemically, which dictate the precise form of the current–time relationships evinced during coloration, and thus affect the coloration–time relationships. While the original classifications are somewhat dated, they remain useful and are followed here throughout. A **type-I** electrochrome is soluble, and remains in solution at all times during electrochromic usage. A good example is aqueous methyl viologen

(1,1'-dimethyl-4,4'-bipyridilium – **II**), which colours during a reductive electrode reaction, Eq. (1.3):



X^{-} can be a halide or complex anion such as BF_4^{-} . The cation is abbreviated to MV^{2+} . Other type-I electrochromes include any viologen often soluble in aqueous solution, or a phenathiazine (such as Methylene Blue), in non-aqueous solutions.

Type-II electrochromes are soluble in their colourless forms but form a coloured *solid* on the surface of the electrode following electron transfer. This phase change increases the write-erase efficiency and speeds the response time of the electrochromic bleaching. A suitable example of a type-II system is cyanophenyl paraquat (**III**), again in water,^{74,75,76} Eq. (1.4):



The solid material here is a salt of the radical cation product⁷⁴ (the incorporation of the anionic charge X^{-} ensures electro-neutrality within the solid product).

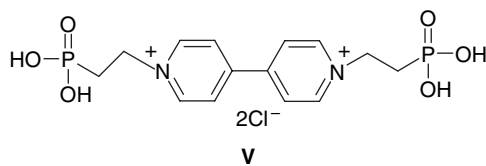
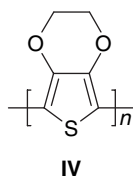
Other type-II electrochromes commonly encountered include aqueous viologen systems such as heptyl or benzyl viologens,⁷⁷ or methoxyfluorene compounds in acetonitrile solution.⁷⁸ Inorganic examples include the solid products of electrodeposited metals such as bismuth (often deposited as a finely divided solid), or a mirror of metallic lead or silver (Section 9.3), in which the electrode reaction is generally reduction of an aquo ion or of a cation in a complex with attached organic or inorganic moieties ('ligands').

1.4.3 Response time τ

The response time τ is the time required for an ECD to change from its bleached to its coloured state (or vice versa). It is generally unlikely that $\tau_{(\text{coloration})} = \tau_{(\text{bleach})}$. At present, there are few *reliable* response times in the literature since there is no consistency in the reporting and determination of cited data, and especially in the way different kinetic criteria are involved when determining τ . For example, τ may represent the time required for some fraction of the colour (defined or arbitrary) to form, or it may relate to the time required for an amount of charge (again defined or arbitrary) to be consumed in forming colour at the electrode of interest.

While most applications do not require a rapid colour change, some such as for electrochromic office windows actually require a very slow response, as workers can feel ill when the colour changes too rapidly.⁸⁴ For example, a film of WO_3 (formed by spray pyrolysis of a solution generated by dissolving W powder in H_2O_2) became coloured in 15 min, and bleached in 3 min,⁸⁵ but the choice of both potential and preparative method was made to engender such slowness. In contrast, a film of sol-gel-derived titanium dioxide is coloured by reductive insertion of Li^+ ions at a potential of about -2 V with a response time of about 40 s.⁸⁶

However, applications such as display devices require a more rapid response. To this end, Sato⁸⁷ reports an anodically formed film of iridium oxide with a response time of 50 ms; Canon⁸⁸ made electrochromic oxide mixtures that undergo absorbance changes of 0.4 in 300 ms. Reynolds *et al.*⁸⁹ prepared a series of polymers based on poly(3,4-alkylenedioxythiophene) ‘PEDOT’ (IV); multiple switching studies, monitoring the electrochromic contrast, showed that films of polymer of thickness *ca.* 300 nm could be fully switched between reduced and oxidised forms in 0.8–2.2 s with a modest transmittance change of 44–63%. Similarly, a recently fabricated electrochromic device was described as ‘ultra fast’, with a claimed⁹⁰ τ of 250 ms; the viologen bis(2-phosphonoethyl)-4,4'-bipyridilium (V), with a coloration efficiency η of $270\text{ cm}^2\text{ C}^{-1}$ was employed as chromophore.



Furthermore, the electrochrome–electrolyte interface has a capacitance C . Such capacitances are well known in electrochemistry to arise from ionic ‘double layer’ effects in which the field at (or charge on) the electrode attracts a ‘layer’ – really just an excess – of oppositely charged electrolyte ions from the bulk solution. The so-called ‘rise time’ of any electrochemical system denotes the time needed to set up (i.e. fully charge) this interfacial capacitance prior to successful transfer of electronic charge across the interface. Coloration will not commence between instigation of the colouring potential and completion of the rise time, a time that may be tens of milliseconds.

Applying a *pulsed* potential has been shown^{91,92,93,94,95,96,97,98} to enhance significantly the rate at which electrochromic colour is generated, relative to potential-jump (or linear potential-increase) coloration. Although a quantitative explanation is not readily formulated, in essence the pulsing modifies the mass transport of electrochrome, eliminating kinetic ‘bottle-necks’, as outlined in Chapter 5. Pulsing is reported to speed up the response of viologen-based displays, enhancing the rate of electrochromic colour formation for ‘viologens’,⁹¹ methyl,⁹² heptyl⁹³ and aryl-substituted viologens;⁹⁴ pulsing also enhances the rates of electro-coloration ECDs based on TiO_2 ,⁹⁵ WO_3 ^{96,97} and ‘oxides’.⁹⁸ The Donnelly mirror in ref. 97 operates with a pulse sequence of frequency 10–20 Hz.

Substrate resistance

The indium–tin oxide (ITO) electrode substrate in an ECD has an appreciable electrical resistance R , although its effects will be ignored here. References 98 and 99 present a detailed discussion of the implications.

In many chemical systems, the uncoloured form of the electrochrome also has a high resistance R : poly(thiophene), poly(aniline), WO_3 and MoO_3 are a few examples. Sudden decreases in R during electro-coloration can cause unusual effects in the current time profiles.^{100,101}

1.4.4 Write–erase efficiency

The write–erase efficiency is the fraction (percentage) of the originally formed coloration that can be subsequently electro-bleached. The efficiency must approach 100% for a successful display, which is a stringent test of design and construction.

The write–erase efficiency of an ECD of aqueous methyl viologen MV^{2+} as the electrochrome will always be low on a realistic time scale owing to the slowness of diffusion to and from the electrode through solution. The kinetics of electrochrome diffusion here are complicated since this electrochrome is

extremely soluble in all applicable solvents for both its dicationic (uncoloured) and radical-cation (coloured) forms. Electrochrome diffusion is discussed in Chapters 4 and 5.

The simplest means of increasing the write–erase efficiency is to employ a type-II or type-III electrochrome, since between the write and erase parts of the coloration cycle the coloured form of the electrochrome is not lost from the electrode by diffusion. The write–erase efficiency of a type-I ECD may be improved by retarding the rate at which the solution-phase electrochrome can diffuse away from the electrode and into the solution bulk. Such retardation is achieved either by *tethering* the species to the surface of an electrode (then termed a ‘derivatised’ electrode), with, e.g., chemical bonding of viologens to the surface of particulate¹⁰² TiO₂, or by immobilising the viologen species within a semi-solid electrolyte such as poly(AMPS). This is amplified in Section 14.2. Such modified type-I systems are effectively ‘quasi type-III’ electrochromes. While embedding in this way engenders an excellent long-term write–erase efficiency and a good electrochromic memory, it will also cause all response times to be extremely slow, perhaps unusably so.

1.4.5 Cycle life

An adjunct to the write–erase efficiency is the electrochromic device’s cycle life which represents the number of write–erase cycles that can be performed by the ECD before any significant extent of degradation has occurred. (Such a write–erase cycle is sometimes termed a ‘double potential step’.) The cycle life is therefore an experimental measure of the ECD durability. Figure 1.1 shows such a series of double potential steps, describing the response of hydrous nickel oxide immersed in KOH solution (0.1 mol dm⁻³). The effect of film degradation over an extended time is clear. However, a 50% deterioration is often tolerable in a display.

Since ECDs are usually intended for use in windows or data display units, deterioration is best gauged by eye and with the same illumination, environment and cell driving conditions, that would be employed during normal cell operation. While it may seem obvious that the cycle life should be cited this way, many tests of cell durability in the literature of electrochromism involve cycles of much shorter duration than the ECD response time τ . Such partial tests are clearly of dubious value, but studies of cycle life are legion. Some workers have attempted to address this problem of variation in severity of the cycle test by borrowing terminology devised for the technology of battery discharge and describing a write–erase cycle as ‘deep’ or ‘shallow’ (i.e. the cycle length being greater than τ or less than τ , respectively).

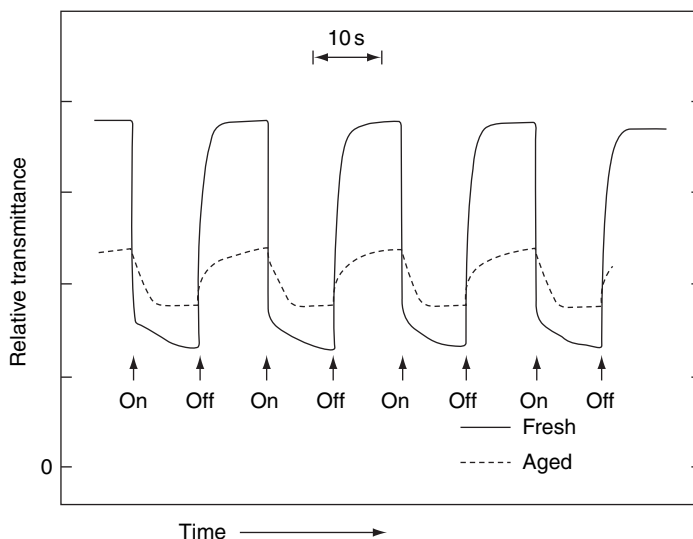


Figure 1.1 Optical switching behaviour of a fresh and an aged film of NiO electrodeposited onto ITO. The potential was stepped between 0 V (representing 'off') and 0.6 V (as 'on'). The aged film had undergone about 500 write-erase cycles. (Figure reproduced from Carpenter, M. K., Conell, R. S. and Corrigan, D.A. 'The electrochromic properties of hydrous nickel oxide'. *Sol. Energy Mater.* **16**, 1987, 333–46, by permission of Elsevier Science.)

The maximising of the cycle life is an obvious aim of device fabrication. A working minimum of about 10^5 is often stipulated.

There are several common reasons why devices fail: the conducting electrodes fail, the electrolyte fails, or one or both of the electrochromic layers fail. The electrolyte layers are discussed in Section 14.2, and overall device stability is discussed in Chapter 16. An individual device may fail for any or all of these reasons. Briefly, the most common causes of low cycle life are photodegradation of organic components within a device, either of the solvent or the electrochrome itself; and also the repeated recrystallisations within solid electrochromes associated with the ionic ingress and egress⁹⁹ that necessarily accompany redox processes of type-II and -III electrochromes.

1.4.6 Power consumption

An electrochromic display consumes no power between write or erase cycles, this retention of coloration being called the 'memory effect'. The intense colour of a sample of viologen radical cation remains undimmed for many months in the absence of chemical oxidising agents, such as molecular oxygen.

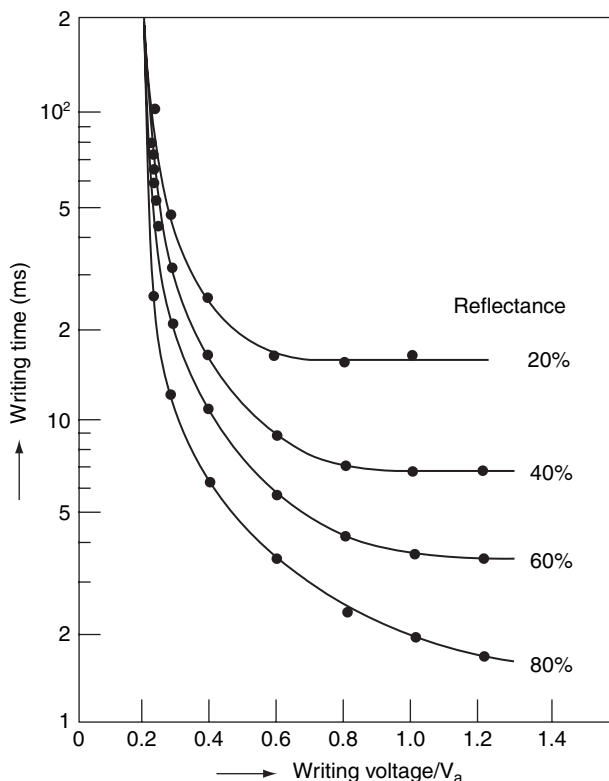
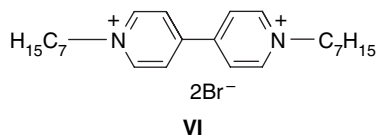


Figure 1.2 Calibration curve of electrochromic response time τ against the potentiostatically applied 'writing' potential V_a (cited against SCE) for heptyl viologen dibromide (VI) (0.1 mol dm^{-3}) in aqueous KBr (0.3 mol dm^{-3}). It is assumed that $\tau_{(\text{bleaching})} = \tau_{(\text{coloration})}$. (Figure reproduced from Schoot, C. J., Ponjeć, J. J., van Dam, H. T., van Doorn, R. A. and Bolwijn, P. J. 'New electrochromic memory device.' *Appl. Phys. Lett.*, **23**, 1973, 64, by permission of the American Institute of Physics.)

However, no-one has ever invented a perfect battery of infinite shelf life, and any ECD (all of which follow battery operation) will eventually fade unless the colour is renewed by further charging.

The charge consumed during one write-erase cycle is a function of the amount of colour formed (and removed) at an electrode during coloration (and decoloration). Schoot *et al.*¹⁰³ state that a contrast ratio of 20:1 may be achieved with a device employing heptyl viologen (1,1'-di-*n*-heptyl-4,4'-bipyridilium dibromide, VI) with a charge of 2 mC cm^{-2} , yielding an optical reflectance of 20%. Figure 1.2 shows a plot of response time for electrochromic coloration for $\text{HV}^{2+} 2\text{Br}^-$ in water as a function of electrochemical driving voltage.



Displays operating via cathode ray tubes (CRTs) and mechanical devices consume proportionately much more power than do ECDs. The amount of power consumed is so small that a solar-powered ECD has recently been reported,¹⁰⁴ the driving power coming from a single small cell of amorphous silicon. Such photoelectrochromic systems are discussed further in Chapter 15.

The power consumption of light-emitting diodes (LEDs) is relatively low, usually less than that of an ECD. Furthermore, ECDs consume considerably more power than liquid crystal displays, although a LCD-based display requires an applied field at all times if an image is to be permanent, i.e. it has no ‘memory effect.’ For this reason, Cohen asserts that ECD power consumption rivals that of LCDs;¹⁰⁵ he cites 7 or 8 mC cm⁻² during the short periods of coloration or bleaching, and a zero consumption of charge during the longer periods when the optical density remains constant. This last criterion is overstated: a miniscule current is usually necessary to maintain the coloured state against the ‘self-bleaching’ processes mentioned earlier, comparable to battery deterioration (see p. 54).

1.4.7 Coloration efficiency η

The amount of electrochromic colour formed by the charge consumed is characteristic of the electrochrome. Its value depends on the wavelength chosen for study. The optimum value is the absorbance formed per unit charge density measured at λ_{\max} of the optical absorption band. The coloration efficiency η is defined according to Eq. (1.7):

$$Abs = \eta Q, \quad (1.7)$$

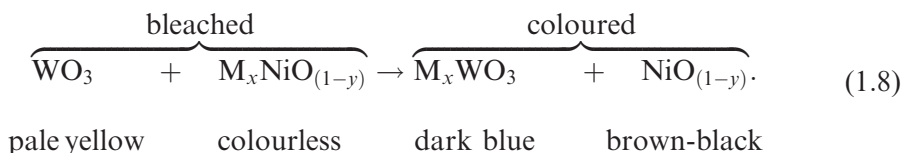
where *Abs* is the absorbance formed by passing a charge density of *Q*. A graph of *Abs* against *Q* accurately gives η as the gradient. For a detailed discussion of the way such optical data may be determined; see Section 4.3.

The majority of values cited in the literature relate to metal oxides; few are for organic electrochromes. A comprehensive list of coloration efficiencies is included in Section 4.3; additional values are sometimes cited in discussions of individual electrochromes.

1.4.8 Primary and secondary electrochromism

To repeat the definition, a cell comprises two half-cells. Each half-cell comprises a redox couple, needing the second electrode to allow the passage of charge through cell and electrodes. As ECDs are electrochemical cells, so each ECD requires a minimum of two electrodes. The simplest electrochromic light modulators have two electrodes directly in the path of the light beam. Solid-state electrochromic displays are, in practice, multi-layer devices (often called ‘sandwiches’; see Chapter 14). If both electrodes bear an electrochromic layer, then the colour formation within the two should operate in a *complementary* sense, as illustrated below using the example of tungsten and nickel oxides. The WO_3 becomes strongly blue-coloured during reduction, while being effectively colourless when oxidised. However, sub-stoichiometric nickel oxide is dark brown-black when oxidised and effectively colourless when reduced.

When an ECD is constructed with these two oxides – each as a thin film (see Chapter 15) – one electrochrome film is initially reduced while the other is oxidised; accordingly, the operation of the device is that portrayed in Eq. (1.8):



The tungsten oxide in this example is the more strongly coloured material, so is termed the primary electrochrome, and the $\text{NiO}_{(1-y)}$ acts as the secondary (or counter) electrode layer. Ideally, the secondary electrochrome is chosen in order to complement the primary electrochrome, one colouring on insertion of counter ions while the other *loses* that ionic charge (or gains an oppositely charged ion) concurrently with its own coloration reaction, i.e. their respective values of η are of different sign. Note the way that charge passes through the cell from left to right and back again during electrochromic operation – ‘electrochromism via the rocking chair mechanism’, an uninformative phrase coined by Goldner *et al.* in 1984.¹⁰⁶ Nuclear-reaction analysis (NRA) is said to confirm this mechanistic mode,¹⁰⁷ but it is difficult to conceive of any other mechanism. In perhaps a majority of recent investigations, tungsten trioxide has been the primary electrochrome chosen owing to its high coloration efficiency, while the secondary layer has been an oxide of, e.g., iridium, nickel or vanadium.

The second electrode need not acquire colour at all. So-called ‘optically passive’ materials (where ‘passive’ here implies visibly non-electrochromic) are often the choice of counter electrode for an ECD. Examples of optically

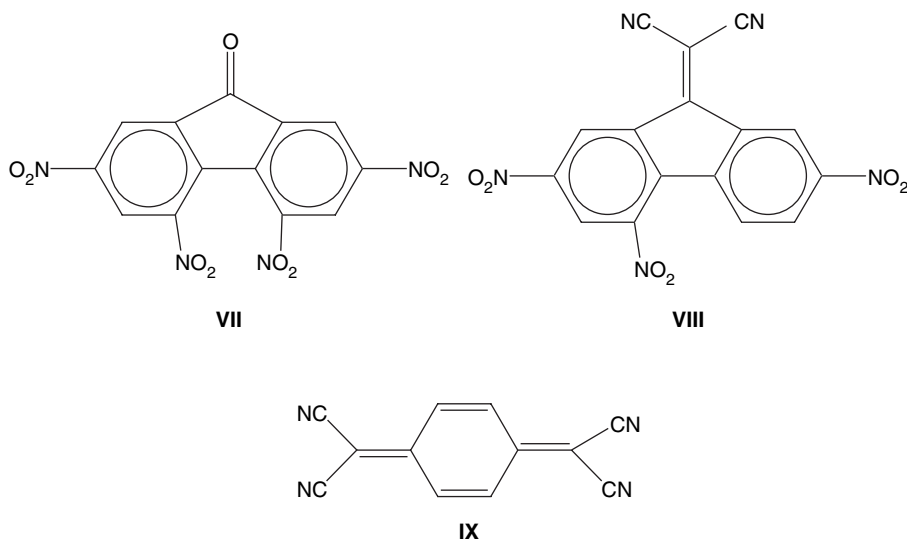
passive oxide layers include indium–tin oxide and niobium pentoxide. In an unusual design, if the counter electrode is a mirror-finish metal that is very thin and porous to ions, then ECDs can be made with one electroactive layer *behind* this electrode. In such a case, the layer behind the mirror electrode can be either strongly (but ineffectively) coloured or quite optically passive. Chapter 14 cites examples of such counter electrodes.

In devices operating in a complementary sense, both electrodes form their colour concurrently, although it is often impossible to deconvolute the optical response of a whole device into those of the two constituent electrochromic couples. When the electrochrome is a permanently solid in both forms (that is, type III), an approximate deconvolution is possible. This requires sophisticated apparatus such as *in situ* ellipsometry¹⁰⁸ and accompanying mathematical transformations. Recently, however, the group of Hagen and Jelle^{109,110,111,112,113,114,115,116} have devised an ingenious and valuable means of overcoming this fundamental problem of distinguishing the optical contributions of each electrode. Devices were fabricated in which each constituent film had a narrow ‘hole’ (a bare area) of diameter *ca.* 5 mm, the hole in each film being positioned at a different portion of each film. By careful positioning of a narrow spectrometer beam through the ECD, the optical response of each individual layer is obtainable, while simultaneously the electrochemical response of the *overall* ECD is obtained concurrently via chronoamperometry in real time. This simple yet powerful ‘hole’ method has led to otherwise irresolvable analyses of these complicated, multi layer systems. For optimal results, the holes should not exceed about one hundredth of the overall active electrode area.

1.5 Multiple-colour systems: electropolychromism

While single-colour electrochromic transformations are usually considered elsewhere in this book, applications may be envisaged in which one electrochrome, or more together, evince a whole series of different colours, each coloured state generated at a characteristic applied potential. For a single-species electrochrome, a series of oxidation states, or charge states – each with its own colour – could be produced. Each state forms at a particular potential if each such state can be sustained, that is, if the species is ‘multi-valent’ in chemical parlance. Such systems should be called electropolychromic (but ‘polyelectrochromic’ prevails). A suitable example is methyl viologen, which is colourless as a dication, MV^{2+} (**II**), blue as a radical cation, and red–brown as a di-reduced neutral species, as described in Chapter 11. Electrochromic viologens with as many as six colours have been synthesised.¹¹⁷

Other systems that are electropolychromic are actually mixtures of several electrochromes. An example is Yasuda and Seto's¹¹⁸ trichromic device comprising individual pixels addressed independently, each encapsulated to contain a different electrochrome. For example, the red electrochrome was 2,4,5,7-tetranitro-9-fluorenone (**VII**); a product from 2,4,7-trinitro-9-fluorenylidene malononitrile (**VIII**) is green, and reduction of TCNQ (tetracyanoquinodimethane, **IX**) yields the blue radical anion $\text{TCNQ}^{\bullet-}$. The chromophores in this system always remained in solution, i.e. were type I.



The colour evinced is a simple function of the potential applied, provided that each chromophore generates colour at a different potential (i.e. differs in E^{\ominus} value: see Chapter 3) and there is no chemical interaction (that can be prevented by encapsulation).

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