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’:

$$\text{oxidised form, } O + \text{electron(s)} \rightarrow \text{reduced form, } R. \quad (1.1)$$

Though in strict electrochemical parlance all the components, $O$ and $R$ and the \textit{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, \( \lambda \), is related to the magnitude of the energy gap \( E \) between these levels according to the Planck relation, Eq. (1.2):

\[
E = h \nu = \frac{hc}{\lambda},
\]

where \( \nu \) is the frequency, \( h \) is the Planck constant and \( c \) the speed of light in vacuo. The magnitude of \( E \) thus relates to the colour since, when \( \lambda \) is the wavelength at the maximum (usually denoted as \( \lambda_{\text{max}} \)) 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 \( E \) 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 in 1979; they pointed out how the best species for this type of work are compounds like (I), its 8-isomer, or nitroaminostilbene, both of which have large non-linear second-harmonic effects. 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.

\[
\text{I} \quad \text{O} = \text{S} \quad \text{O} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{O} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N}
\]

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 effect in which some of the UV-vis bands of polarisable molecules evince a spectroscopic shift in the presence of a strong electric field. Vredenberg 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.

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. In some instances, however, this electrochromic effect is unreliable.

A valuable electrochromic application has been employed by O’Shea 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 $pK_a(\phi_s) = pK_a(0) - \frac{F\phi_s}{RT} (\ln 10)$ where $\phi_s$ is the membrane surface potential. 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 \( \varphi_s \), 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 smartglass 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 ‘SmartPaper\(^{TM}\)’. Gyricon is intended for products like electronic books, electronic newspapers, portable signs, and foldable, rollable displays. It comprises two plastic sheets, each of thickness \( ca. 140 \mu m \), 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 metallically conductive backing sheet; 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. 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 NanoChromics™ 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. 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, a thorough and detailed treatise covering solely inorganic materials.


Bowonder et al.’s 1994 review helps frame electrochromic displays within the wider corpus of display technology. Lampert’s 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 is 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 Gilbert 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):

\[ \text{MV}^{2+} (\text{aq}) + e^- \rightarrow \text{MV}^+ (\text{aq}) \]

\[ \text{colourless} \quad \text{intense blue} \]

\[ \text{H}_2\text{C} + \text{N} \quad + \quad \text{N} \quad \text{+} \quad \text{CH}_3 \quad 2\text{X}^- \]

\[ \text{II} \]

\[ \text{X}^- \] 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,\(^7^4,7^5,7^6\) Eq. (1.4):

\[ \text{CPQ}^{2+} (\text{aq}) + e^- + \text{X}^- (\text{aq}) \rightarrow [\text{CPQ}^+ \text{X}^-] (\text{solid}) \]

\[ \text{colourless} \quad \text{olive green} \]

\[ \text{III} \]

The solid material here is a salt of the radical cation product\(^7^4\) (the incorporation of the anionic charge \(\text{X}^-\) ensures electro-neutrality within the solid product).

Other type-II electrochromes commonly encountered include aqueous viologen systems such as heptyl or benzyl viologens,\(^7^7\) or methoxyfluorene compounds in acetonitrile solution.\(^7^8\) 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 Criteria and terminology for ECD operation

Type-III electrochromes remain solid at all times. Most inorganic electrochromes are type III, e.g. for metal oxides, Eq. (1.5),

\[
\text{MO}_y(s) + x\text{(H}^+(\text{soln.}) + e^-) \rightarrow \text{H}_x\text{MO}_y(s),
\]

(1.5)

where the metal M is most commonly a d-block element such as Mo, Ni or W, and the mobile counter ion (arbitrarily cited here as the proton) could also be lithium; \( y = 3 \) is commonly found, and \( \text{WO}_3 \) has been the most studied. The parameter \( x \), the ‘insertion coefficient’, indicates the proportion of metal sites that have been electro-reduced. The value of \( x \) usually lies in the approximate range \( 0 < x < 0.3 \).

Other inorganic type-III electrochromes include phthalocyanine complexes and metal hexacyanometallates such as Prussian blue. Organic type-III systems are typified by electroactive conducting polymers. The three groups of polymer encountered most often in the literature of electrochromism are generically termed poly(pyrrole), poly(thiophene) or poly(aniline) and relate to the parenthesised monomer from which the electrochromic solid is formed by electro-polymerisation, as discussed below.

1.4.2 Contrast ratio CR

The contrast ratio \( CR \) is a commonly employed measure denoting the intensity of colour formed electrochemically, as seen by eye, Eq. (1.6):

\[
CR = \left( \frac{R_o}{R_x} \right),
\]

(1.6)

where \( R_o \) is the intensity of light reflected diffusely though the coloured state of a display, and \( R_x \) is the intensity reflected similarly but from a non-shiny white card.\(^79\) The ratio \( CR \) is best quoted at a specific wavelength – usually at \( \lambda_{\text{max}} \) of the coloured state. As in practice, a \( CR \) of less than about 3 is almost impossible to see by eye. As high a value as possible is desirable.

The \( CR \) is commonly expressed as a ratio such as 7:1. A \( CR \) of 25:1 is cited for a type-II display involving electrodeposited bismuth metal,\(^80\) and as high\(^81\) as 60:1 for a system based on heptyl viologen radical cation, electrodeposited from aqueous solution with a charge\(^82\) of 1 mC cm\(^{-2}\), and 10:1 for the cell \( \text{WO}_3|\text{electrolyte}|\text{NiO} \).\(^83\)

More elaborate measures of coloration are outlined in Chapter 4.
1.4.3 Response time \( \tau \)

The response time \( \tau \) 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 \( \tau \). For example, \( \tau \) 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. For example, a film of WO\(_3\) (formed by spray pyrolysis of a solution generated by dissolving W powder in H\(_2\)O\(_2\)) became coloured in 15 min, and bleached in 3 min, 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.

However, applications such as display devices require a more rapid response. To this end, Sato reports an anodically formed film of iridium oxide with a response time of 50 ms; Canon made electrochromic oxide mixtures that undergo absorbance changes of 0.4 in 300 ms. Reynolds et al. 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 \( \text{ca.} 300 \text{ nm} \) 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 claimed \( \tau \) of 250 ms; the viologen bis(2-phosphonoethyl)-4,4'-bipyridilium (V), with a coloration efficiency \( \eta \) of 270 cm\(^2\) C\(^{-1}\) was employed as chromophore.