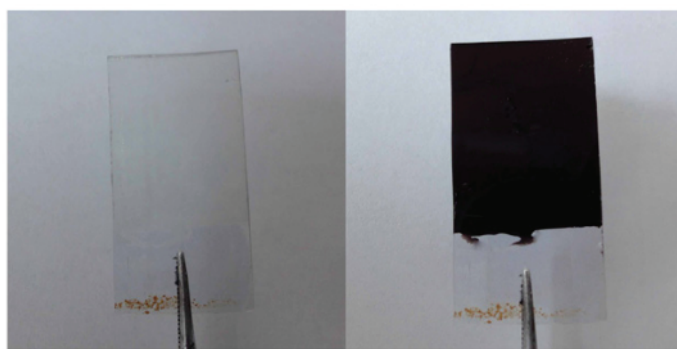


(a)



(b)

Bleached

Coloured

Figure 1.16 Spectral transmittance (a) and visual appearance (b) of an electroplated Ni oxide film on a substrate with and without a template layer consisting of polystyrene nanospheres. The film is in its fully coloured and bleached states. From Ref. [90].

consist of a mixture of amorphous WO_3 and nanocrystalline NiWO_4 , with equal amounts of W and Ni the structure was dominated by NiWO_4 , and nickel-rich films were made up of nanocrystalline NiO and NiWO_4 .

Figure 1.18 shows optical absorption coefficients at a mid-luminous wavelength of 550 nm for fully coloured and bleached films. The electrochromism is seen to be much stronger in W oxide than in Ni oxide. For W-rich films, the absorption coefficient drops as Ni fraction x is increased, except at the composition $x \approx 0.12$ where a pronounced peak can be seen in the absorption coefficient. For Ni-rich films, the absorption coefficient rises as x approaches unity. Films in the compositional range $0.3 < x < 0.7$ do not display electrochromism. Another important parameter

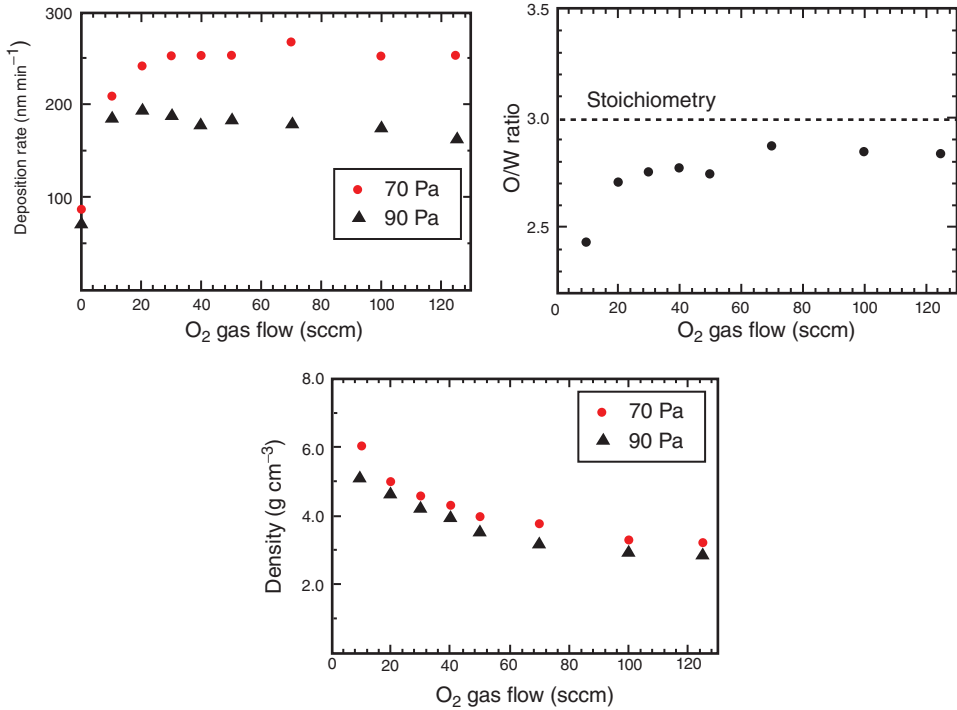


Figure 1.17 Deposition rate, oxygen/tungsten stoichiometry and density of thin films of electrochromic W oxide prepared by reactive-gas-flow sputtering at

different oxygen gas flows. The total gas pressure was 70 Pa, and for two of the data sets also 90 Pa. From Ref. [91].

for electrochromic films is coloration efficiency η , defined by $\eta = OD/\Delta Q$ where optical density (OD) is absorption coefficient multiplied by film thickness and ΔQ is inserted/extracted charge density. Figure 1.19 shows data on coloration efficiency and allows easy comparison with Figure 1.18. Obviously, η increases slightly for increasing values of x , except for compositions around $x \approx 0.5$ where η is approximately zero.

The strong optical absorption at $x \approx 0.12$ is interesting for electrochromic device applications, and Figure 1.20 reports spectral coloration efficiency for films of pure W oxide and for Ni_xW_{1-x} oxide films with two values of x . It is evident that good performance of films with $x \approx 0.12$ is found in the whole luminous wavelength range, that is, for 400–700 nm.

1.4 Transparent Electrical Conductors and Electrolytes

An electrochromic device does not only include electrochromic thin films but also incorporates transparent electrical conductors and an electrolyte, as seen

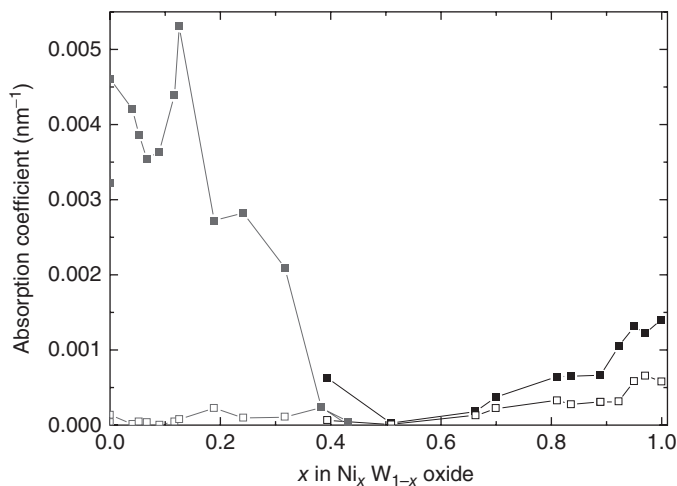


Figure 1.18 Mid-luminous absorption coefficient as a function of composition for electrochromic thin films of W–Ni oxide. Filled and open symbols denote fully coloured and bleached states, respectively. From Ref. [95].

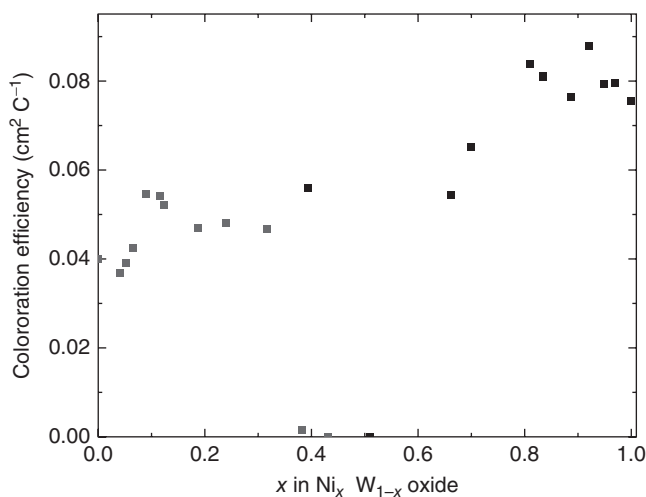


Figure 1.19 Mid-luminous coloration efficiency as a function of composition for electrochromic thin films of W–Ni oxide. From Ref. [95].

in Figure 1.1. The transparent electrical conductors may be the most costly part in the device – especially if they are based on an indium-containing oxide – and clearly deserve attention. They are of critical importance not only in electrochromics but also for thin-film solar cells, light emitting devices and so on. There are several recent reviews covering the field of transparent conductors [32, 99–101], and therefore only a bird’s-eye view is given here, though with some

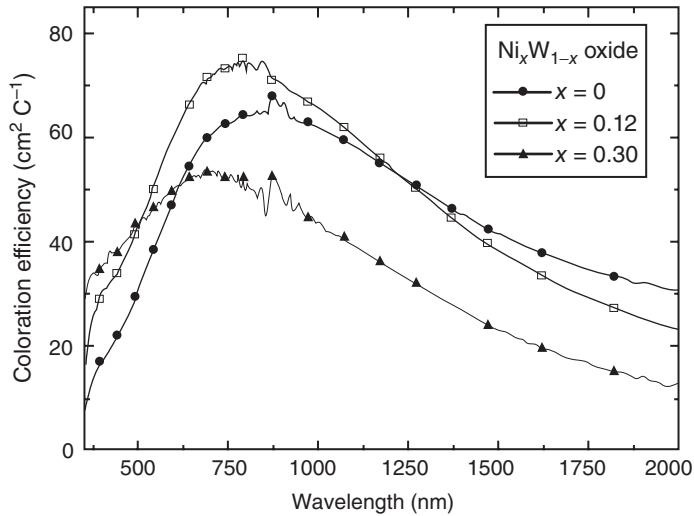


Figure 1.20 Spectral coloration efficiency for W–Ni oxide films with the shown compositions. From Ref. [94].

attention to very recent work and to transparent conductors suitable for flexible substrates. There are several types of transparent conductors with specific pros and cons; semiconductor-based films are treated in Section 1.4.1, metal-based films in Section 1.4.2 and nanowire-based and other alternatives in Section 1.4.3. Electrolytes for electrochromic devices are surveyed in Section 1.4.4 with foci on thin films and polymer layers.

1.4.1

Transparent Electrical Conductors: Oxide Films

Thin films of heavily doped wide-bandgap conducting oxides are commonly used in electrochromic devices. These materials include $\text{In}_2\text{O}_3:\text{Sn}$ (ITO), $\text{In}_2\text{O}_3:\text{Zn}$, $\text{ZnO}:\text{Al}$, $\text{ZnO}:\text{Ga}$, $\text{ZnO}:\text{In}$, $\text{ZnO}:\text{Si}$, $\text{ZnO}:\text{B}$, $\text{SnO}_2:\text{F}$ (FTO), $\text{SnO}_2:\text{Sb}$ and $\text{TiO}_2:\text{Nb}$; their doping levels are typically a few atomic percent. Several of the oxides can combine a resistivity as low as $\sim 1 \times 10^{-4} \Omega \text{ cm}$ with excellent luminous transmittance and durability. Films of ITO, $\text{ZnO}:\text{Al}$ and $\text{ZnO}:\text{Ga}$ deposited by reactive DC magnetron sputtering onto glass and PET typically have a resistivity of $\sim 2 \times 10^{-4}$ and $\sim 4 \times 10^{-4} \Omega \text{ cm}$, respectively. High-quality FTO films are normally made by spray pyrolysis in conjunction with float glass production, and high temperatures are necessary also for $\text{TiO}_2:\text{Nb}$ films. All of these oxides are transparent across most of the solar spectrum, as seen in Figure 1.21 for FTO-coated glass [102]. The oxide-based transparent conductors are very well understood theoretically [103–105], which means that detailed and accurate simulations of optical properties can be made for multilayer configurations such as electrochromic devices.

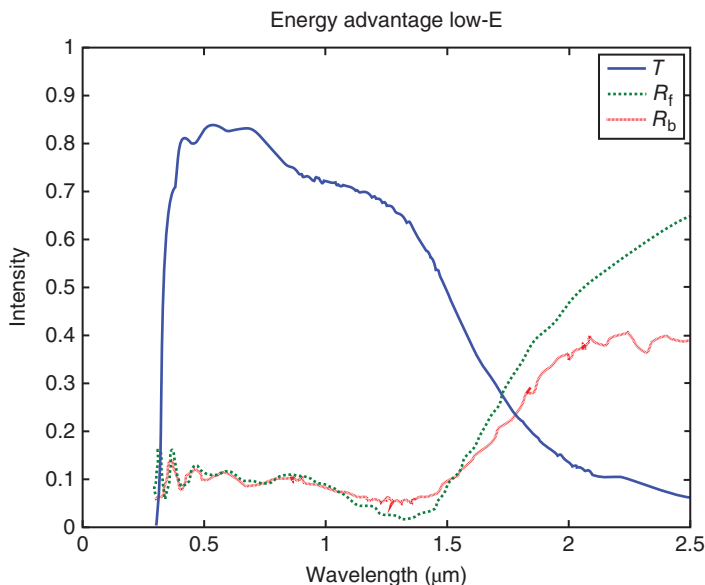


Figure 1.21 Spectral transmittance T and reflectance from the front (coated) side (R_f) and the back side (R_b) for commercial FTO-coated glass. The luminous transmittance is 83% and the solar energy transmittance is 71%. From Ref. [102].

Deposition onto flexible substrates introduces risks for cracking and delamination, and thereby lowered electrical conductivity, if the bending radius is smaller than a few centimetres [106, 107]. In general, the fracture behaviour is dependent on film thickness and bending direction. If needed, several techniques can be used to diminish the propensity for cracking.

ITO films are widely used but expensive, even if indium is not one of the rarer elements in the earth's crust [108], and its deposition requires careful process control. ZnO:Al and ZnO:Ga films can reach similar optical and electrical properties but tend to demand even more stringent process supervision, and good FTO and TiO₂:Nb films must be deposited onto hot glass. Clearly, each type of transparent conducting oxide films presents particular challenges, and there is no 'best' option for electrochromic-based and other devices.

Health aspects of indium-based films require attention, and their preparation can lead to pulmonary disorders [109]. This affliction is named 'indium lung' and obviously is a concern for large-scale production of ITO films and particles.

1.4.2

Transparent Electrical Conductors: Metal-Based Films

Metal-based transparent conductors can show excellent properties and avoid the electronic activation barrier that may exist between, for example, W oxide and ITO [110]. Coinage metals (Cu, Ag and Au) have electrical conductivities around 2

orders of magnitude higher than for the best transparent conducting oxide, which means that they can be thin enough that the luminous absorption is only some per cent. Metal films are stretchable to a much larger degree than oxide-based films.

Metal films to be used in transparent conductors must be extremely thin, which means that their properties are strongly affected by the peculiarities of thin-film growth. When metal is deposited onto a substrate of glass or polymer, the condensate goes through a number of more or less distinct growth stages [111]: tiny metallic nuclei form initially; they grow and create increasingly irregular 'islands'; these 'islands' interconnect and produce a contiguous meandering (percolating) network at a thickness that corresponds to 'large-scale coalescence'; the network is then transformed to a film comprising holes; and finally, a well-defined metallic film may be created. The relevant films have thicknesses of the order of 5–10 nm [112].

Interface reflectance limits the luminous transmittance of the coinage metal film to ~50%, but this transmittance can be radically enhanced if the metal film is positioned between high-refractive-index transparent layers anti-reflecting the metal. This effect is shown in Figure 1.22 for an 8.0-nm-thick Au film and for such a film between 55-nm-thick TiO₂ layers, from the work by Lansåker *et al.* [113]. The anti-reflection increases the transmittance to ~80%. This figure also indicates that computations based on thin-film optics can model the optical properties accurately except in the infrared. The ultrathin Au films were durable enough to be used in electrochromic devices [113]. Many other combinations of materials can be employed as alternatives to the one illustrated here, and transparent conductors based on oxide/metal/oxide are of intense interest not only for energy-related applications but also for transparent and flexible electronics and so on.

Silver-based coatings are used on a massive scale in today's fenestration, and it is possible to devise multilayer structures with a luminous transmittance of 80% and minimum throughput of solar energy (known as a 'solar-control' coating) [114, 115]. These coatings may combine two or more metal films in an advanced construction with more than 10 individual layers. Figure 1.23 shows an example of a commercial coating of this type on glass [102]. The figure allows direct comparison with data for the semiconductor-based coating in Figure 1.21.

1.4.3

Transparent Electrical Conductors: Nanowire-Based Coatings and Other Alternatives

Numerous alternatives to transparent conductors based on thin films of oxides and metals are currently investigated. Carbon-based materials are one of these [116]. We first consider graphite, which consists of loosely bound layers of carbon atoms on a honeycomb lattice. Such layers can create nanoparticles, for example, 60-atom units called 'fullerene molecules' as well as *carbon nanotubes* [117]. Single-wall carbon nanotubes can be several centimetres in length and consist of one layer of carbon atoms rolled into a seamless cylinder with a radius up to a few nanometres. There are two types of such carbon nanotubes, with metallic and semiconducting properties; the two fractions can be separated by several

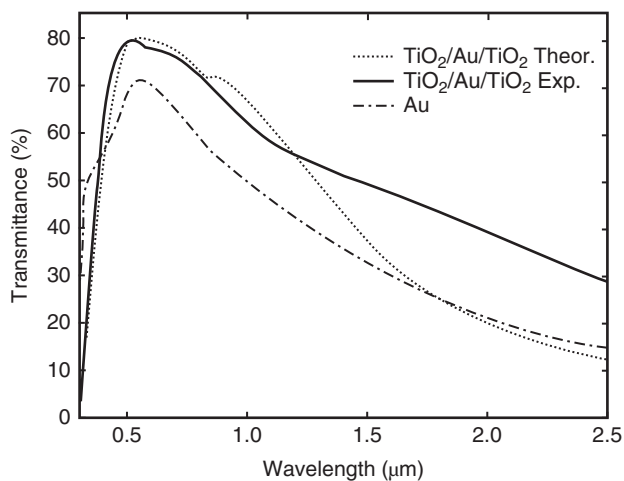


Figure 1.22 Experimental and computed spectral transmittance for Au and $\text{TiO}_2/\text{Au}/\text{TiO}_2$ films. Film thicknesses were 8 nm for Au and 55 nm for TiO_2 . From Ref. [113].

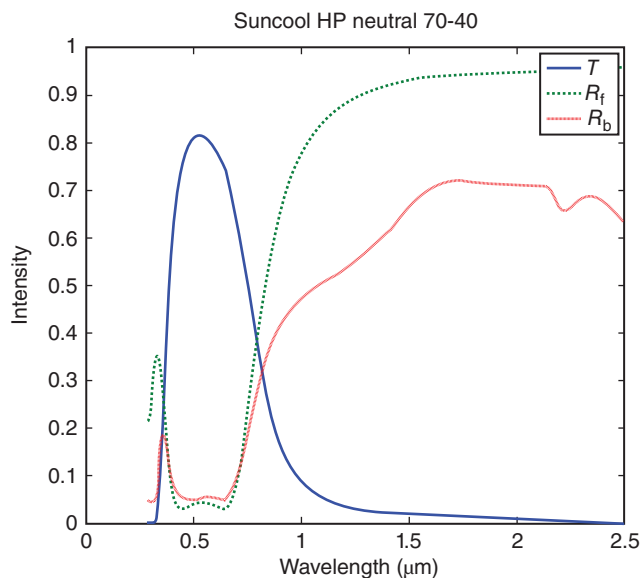


Figure 1.23 Spectral transmittance T and reflectance from the front (coated) side (R_f) and the back side (R_b) for a commercial glass with an Ag-based coating. The luminous transmittance is 80% and the solar energy transmittance is 41%. From Ref. [102].

techniques. Carbon nanotube meshes can be used as transparent conductors and attached to substrates by roll-to-roll coating [118].

Another carbon-based alternative is *graphene*, which consists of atomically thin layers of sp^2 -hybridised carbon atoms arranged on a honeycomb lattice [119]. Graphene layers are usually prepared via mechanical or chemical exfoliation of graphite into individual sheets [120] or by chemical vapour deposition [121]; doping can be used to enhance the properties. Roll-to-roll production of graphene coatings have been demonstrated, and up to 30-in.-wide ribbons yielded a sheet resistance as low as $\sim 30 \Omega$ along with $\sim 90\%$ optical transmittance for films comprising four graphene layers [122]. Hot-press lamination onto PET and ink-jet printing are other techniques that can be used for large-area manufacturing.

Meshes of *metal-based nanowires* are another possibility. They can be prepared cheaply by wet-chemical techniques and applied to substrates by ‘simple’ techniques such as electro spraying and brush painting. A vast amount of research has been performed recently, mainly on silver-based nanowires. The electrical connection between the nanowires can be improved by different techniques such as ‘nanowelding’ and application of electrical fields. Recent work on metal ‘nanotrough’ networks demonstrated particularly good optical and electrical properties [123]. It should be noted that nanowire assemblies can have good electrical properties, but the physical dimensions of the individual nanowires make it hard to avoid some diffuse light scattering, as studied recently for silver nanowires [124]. This haze tends to limit applications in electrochromic devices for see-through applications.

Some *organic materials* can be used as transparent conductors, and a good example is poly(3,4-ethylenedioxythiophene) (PEDOT) (see Chapter 5). This material cannot quite compete with the other alternatives with regard to performance but is nevertheless of considerable interest since preparation is possible by printing at very low cost [125].

A number of *hybrid transparent conductors* have attracted attention during recent years; they combine at least two of the options discussed earlier. One may include the oxide/metal/oxide coatings in this class, provided that the oxide is a transparent conductor in its own right. Other alternatives of this rapidly growing group of transparent conductors include silver nanowires combined with ITO films or nanoparticles or with carbon nanotubes, graphene and so on. Furthermore, *macroscopic metal meshes, grids and arrays* can be of interest, although they may lead to unwanted optical scattering.

1.4.4

Electrolytes: Some Examples

Three types of electrolytes are of importance for electrochromic devices: thin solid films, polymer layers and ionic liquids. Electrolytes are generally proprietary in devices, and little is known about the ones that are used in practice.

Concerning thin solid films, those of porous oxide can be made H^+ or Li^+ conducting by co-deposition, by chemical or electrochemical post-treatment or by

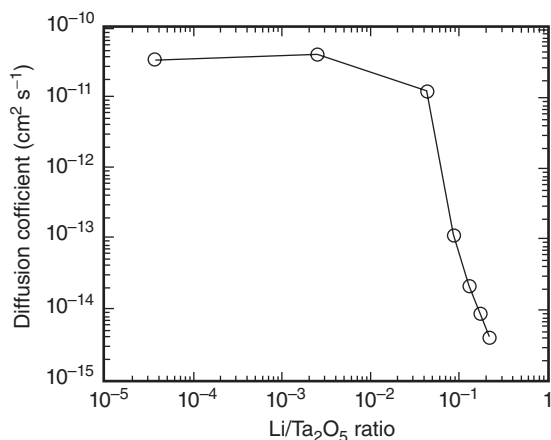


Figure 1.24 Diffusion coefficient for Ta oxide films with different amounts of Li⁺. After Ref. [126].

exposure to humidity. A particularly well-studied example is tantalum pentoxide, whose applicability in electrochromic devices has been investigated in detail. For example, proton-conducting films have been prepared by sputter deposition of Ta in the presence of O₂ and H₂O and have shown an ion conductivity of $\sim 10^{-9}$ S cm⁻¹ for as-deposited films; heat treatment led to a rapid decrease in their ion conductivity. Electrochemical lithium incorporation is another possibility and can yield amorphous-like films with Li⁺ diffusion constants of 10^{-10} to 10^{-11} cm² s⁻¹, at least for Li/Ta₂O₅ ratios below 0.01, as evidenced in Figure 1.24, which reproduces data from Frenning *et al.* [126]. More complex thin-film electrolytes have been investigated in other work, such as LiPON [127] and LiBO₂-Li₂SO₄ (known as LiBSO) [128].

Polymers and ionic liquids can be used in electrochromic devices that are more rugged than those possible with thin-film ion conductors. There are almost innumerable options. *In situ* polymerisation may be required for sealing purposes, and research with this object has been reported for polymer electrolytes [129] and ionic-liquid-based gel electrolytes [130]. Polymer electrolytes are discussed further in Chapter 10.

1.5

Towards Devices

Electrochromic device technology has been under development for many years, as noted in Section 1.1.2. There may be several reasons why this development has taken so many years, one being that electrochromic operation is 'difficult' and combines electrochemistry with optical technology and often also with

thin-film science in order to produce devices that should work for decades under harsh conditions while being observed by persons used to benchmarking against today's high-quality optical products (such as windows). Section 1.5.1 below considers a number of hurdles that must be overcome in order to have functional EC 'smart' windows. Section 1.5.2 then surveys some practical oxide-based devices. More in-depth discussions of device performance are presented elsewhere in this book.

1.5.1

Six Hurdles for Device Manufacturing

The first hurdle is that the electrochromic and the counter electrode films, shown in Figure 1.1, must have well-developed *nanoporosity* over their full areas, which may require that thin films are produced under non-standard conditions. These aspects were treated briefly in Section 1.3.5.

Secondly, the *transparent conductors* connecting electrochromic and counter electrode films must combine excellent electrical conductivity and high optical transparency, which is demanding particularly for polymer substrates. Transparent conductors of several different types were discussed in Sections 1.4.1–1.4.3.

The third difficulty is easily understood by considering the electrochromic device as a thin-film battery, which highlights that *charge insertion/extraction and charge balancing* are essential. In practical manufacturing, these processes must be accomplished by highly controllable and industrially viable techniques. Ozone exposure is one of several possible techniques [49, 131, 132].

Fourth, the *electrolyte* in the centre of the electrochromic device must combine good ion conductivity with very low electronic conductivity and high durability under solar irradiation. In some devices, it must also serve as an adhesive and reliably join two parts of the device.

Long-term *cycling durability* is of obvious interest for most electrochromic devices and is the fifth item. It hinges on good strategies for voltage and current control, which points at analogies between electrochromics and electrical batteries. These strategies, and their implementations via electronic drive circuitry design, are another area where proprietary considerations are dominating. However, it is evident that simple switching of voltage levels between two set values is far from an optimised strategy.

The sixth and final item is *large-scale manufacturability*, which is an obvious key to cost-effective electrochromic devices and hence to their acceptance on the consumer market. Clearly, it is necessary to avoid time-consuming production steps such as protracted thin-film deposition, long post-treatment times, elaborate steps for electrochemical charge insertion and extraction and so on. Life-cycle assessment is an important ingredient for judging the suitability of a specific manufacturing technology [133, 134]; these aspects are discussed in Chapter 18.

1.5.2

Practical Constructions of Electrochromic Devices

An uncritical reading of the scientific and technical literature may give an impression that many types of oxide-based electrochromic devices are available, but few of these are ready for practical use. However, there are some full-scale products and prototypes, especially for ‘smart window’ applications [115, 135–137], and those currently (2014) delivered to early adopters and other customers are introduced next. This presentation also allows a view of practical device designs and some insights into their pros and cons. The following literature references are to scientific journals, and some of these papers are rather old and probably more or less outdated. Thin films of tungsten oxide are a significant part of the electrochromic functionality for all of these devices.

We first consider a *five-layer ‘monolithic’ design* based on a single glass pane and developed by Sage Electrochromics Inc. in the United States [138] and Saint-Gobain Recherche in France [139]. Details are obscure, but it is clear that the electrolyte is a thin solid film. Such an arrangement makes it hard to avoid some leakage current between the electrochromic films through structural imperfections, and repeated electrical ‘refresh’ pulses may be needed to maintain the device in its dark state and transmittance changes can develop unevenly over large surfaces. The design may also lead to visible ‘pin holes’. A related construction was developed by the US company View (earlier known as Soladigm Inc.). Somewhat analogous work was performed at the Optical Coating Laboratory Inc. (OCLI) in the United States during the 1990s [140, 141].

A laminated design embodying two double-layer-coated glass panes, joined by a polymer electrolyte, has been developed by Flabeg/EControl Glass GmbH in Germany. Some data are available for this device [142]. The electrolyte is injected in fluid form in a millimetre-wide gap between the glass panes via vacuum filling [143].

Another laminated device has been presented by Gesimat GmbH in Germany [144]. Here, the electrolyte is based on poly vinyl butyral (PVB), which is a standard material for glass lamination, and the transparent electrical conductors are produced by low-cost spray pyrolysis during float-glass production. The complementary electrochromic material is a film of iron(III) hexacyanoferrate(II) (‘ferric ferrocyanide’ or ‘Prussian Blue’; see Chapter 2) prepared by electrodeposition.

A principally different *polymer-foil-based laminated design* has been developed by ChromoGenics AB in Sweden. It employs flexible PET foil substrates and allows roll-to-roll web coating [33, 145], that is, production by low-cost technology [146]. Another distinguishing feature is that the foil-based electrochromic device allows ‘free-form design’, which implies that product definition can be made at a later stage of device manufacturing. One PET foil is coated with a transparent and electrically conducting thin film and W oxide, another PET foil is coated with a transparent conductor and Ni oxide and the electrochromic-film-coated surfaces of the two foils are joined by an electrolyte via continuous lamination with an adhesive polymer. This type of electrochromic foil is discussed in more detail in Chapter 17.

1.6

Conclusions

This chapter has presented the conceptual and materials-oriented basis of oxide-based electrochromics with special attention to thin films of tungsten oxide and nickel oxide. The connection to the electronic properties and to nanostructural features was emphasised, and the importance of the thin-film manufacturing technology was stressed. Transparent electrical conductors and electrolytes were discussed too as were some general manufacturing aspects.

The electrochromic properties of a number of transition metal oxides have been known for decades and their application in devices have been attempted for many years. Promises of applications in ‘smart windows’ and elsewhere have been made repeatedly by many, but few products have emerged some products have swiftly been retracted. Nevertheless, research and development have progressed at a steady pace, and oxide-based electrochromic technology may finally (2015) be ready for market introduction on a massive scale.

Acknowledgement

Financial support during the writing of this chapter was received from the European Research Council under the European Community’s Seventh Framework Program (FP7/2007–2013)/ERC Grant Agreement No. 267234 (GRINDOOR).

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