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Electrochromic materials and devices for energy efficiency and human comfort in buildings: a critical review

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Abstract

Electrochromic (EC) materials can be integrated in thin-film devices and used for modulating optical transmittance. The technology has recently been implemented in large-area glazing (windows and glass facades) in order to create buildings which combine energy efficiency with good indoor comfort. This critical review describes the basics of EC technology, provides a case study related to EC foils for glass lamination, and discusses a number of future aspects. Ample literature references are given with the object of providing an easy entrance to the burgeoning research field of electrochromics.

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1. Introduction

Electrochromic (EC) materials are characterized by properties that can be tuned, persistently and reversibly, through the application of electrical current or voltage [1,2]. These materials, and their associated device technologies, are rapidly evolving especially with regard to implementation in windows and glass facades—jointly known as glazing—for energy-efficient buildings with good indoor comfort. This paper outlines the state-of-the-art for oxide-based electrochromics and points at some recent advances and possible future developments.

Environmental challenges provide a driving force for many of today's (2017) studies of EC materials. Underlying these challenges is the fact that human actions lead to the injection of about 10 billion tonnes of carbon into the atmosphere per year [3] some half of which ends up in the air. It is therefore to be expected that the carbon dioxide content of the Earth's atmosphere is rising swiftly; this content was ~315 ppm in the late 1950s and currently exceeds ~400 ppm [4]. The increased amount of CO₂ originates from energy production—mostly the burning of coal, oil and gas—and is generally believed to affect life on Earth and yield global warming and rising sea levels [5]. There are also numerous secondary and harmful effects of climate change related to socio-economic effects and enhanced risk for violent conflict [6,7], health issues [8], and alterations of the biosphere [9,10] and geosphere [11]. Furthermore, it should be emphasized that the global population is rising and forecast to be 50% larger in 2100 than today [12], and this population is increasingly located in megacities which act as “urban heat islands” with temperatures several degrees higher of those in the neighbouring countryside [13].

The energy–population nexus makes it patently clear that the Earth's energy production must be decarbonized, which stresses the importance of better buildings. In fact, today's building stock is responsible for 30–40% of the global use of primary energy [14]. Furthermore, the role of buildings is currently growing in many countries, and their part of the energy consumption in the USA, to take one example, was 34% in 1980 but as large as 41% in 2010 [15].

Energy efficiency in the built environment has often been neglected as an opportunity for CO₂ abatement [16], but recent European developments [17] highlight its importance. In fact, there are many “green” technologies, often with nano features, that can be put to work in order to create better buildings [18–26] and which also can lead to economic growth [27], and energy-efficient glazing stands out as one of the most interesting possibilities. The glazing

often allows huge energy flows to enter or exit a building, which means that energy-guzzling cooling or heating must be used to create a comfortable indoor environment. One solution to this conundrum is to minimize the size of the glazing, but this leads to unacceptable losses of precious indoors–outdoors contact and day-lighting. However, energy efficiency can be reached with glazing allowing tunable transmittance of solar energy and visible light. This type of glazing is often called “smart” or “intelligent” [28] and is based on “chromogenic” materials [29,30], with EC materials currently being the most widely studied and important option [31].

EC materials can be altered electrically and can be used in devices for automatically adjusted as well as operator-controlled transmittance of solar energy and visible light [1,2]. These properties allow many benefits, as extensively investigated; current studies have focused on energy efficiency [32–39], lowered CO₂ emission [40], and on indoor comfort [41–43] for the users of buildings with EC glazing. These assets can be combined with financial benefits for the operators of the buildings [44]. EC glazing was proposed already in 1984 [45,46] and was introduced on the market during the 2010s. An increasing number of EC installations are currently used in real-life situations [31,47–49]. Oxide-based EC materials are far from the only alternatives for “smart” glazings [31], but it appears that they are currently the main ones used in buildings. Other options include devices based on reversible electroplating [50], suspended particles [51], polymer-dispersed liquid crystals [52], metal hydrides [53], plasmonic effects in wide-bandgap electrically conducting nanoparticles [54–56], and solution-based systems [57]. It should also be noted that oxide-based materials are far from the only ones with EC properties and, in particular, there are a plethora of organic EC materials [58–61]. The latter ones are particularly well suited for display devices but most probably lack sufficient durability for uses in buildings.

It is important to understand that EC-based glazing must be compatible with truly large-scale manufacturing. Thus flat-glass production, mostly by the float process, has been predicted to reach a stunning 11.5×10^9 square meters per year in 2018 [62]. Implementing EC-based functionality on only a very small fraction of the World’s glazing necessitates coating technology with manufacturing equipment capable of handling square kilometers each year.

EC materials and devices must be characterized as to their ability to transmit and reflect luminous (visible) and solar radiation. These properties can be introduced by considering the spectra shown in Fig. 1. Thermal radiation, in panel (a), is governed by blackbody curves—

which are shown for four temperatures—multiplied by an empirical emittance less than one; clearly this radiation is at $\lambda > 2 \mu\text{m}$ for normal ambient temperatures, where λ denotes wavelength. Solar radiation falling onto the Earth’s atmosphere can be represented by blackbody-like radiation for the Sun’s surface temperature (5505 °C) and lies at $0.2 < \lambda < 3 \mu\text{m}$. At ground level, and for normal clear weather, this radiation is as shown in Fig. 1(b); the distinct minima emanate from molecular absorption. Luminous radiation, finally, is described by the curve in Fig. 1(b) which covers the $0.4 < \lambda < 0.7 \mu\text{m}$ range and is peaked at $0.55 \mu\text{m}$. Quantitative luminous (lum) and solar (sol) transmittance, indicated by T_{lum} and T_{sol} , respectively, can be calculated from

$$T_{\text{lum,sol}} = \int d\lambda \phi_{\text{lum,sol}}(\lambda) T(\lambda) / \int d\lambda \phi_{\text{lum,sol}}(\lambda) , \quad (1)$$

where $T(\lambda)$ is spectral transmittance, ϕ_{lum} is the eye’s spectral sensitivity [63] and ϕ_{sol} signifies an “air mass 1.5” solar irradiance spectrum (with the sun being 37° above the horizon) [64].

Fig. 1. (a) Blackbody spectra for the shown temperatures (note that the vertical scales are different for blackbody and solar spectra). (b) Typical solar irradiance spectrum for clear weather, and relative spectral sensitivity of a light-adapted eye.

Many reviews have been written on EC materials and devices. The present paper is an update and extension of some recent surveys both regarding general content and references [31,65,66].

2. Operating principles and materials for electrochromics

2.1 Generic device design

Electrochromics is conveniently understood from a device perspective, and Fig. 2 illustrates a generic EC design [1,67] with five superimposed layers either on a single substrate or positioned between two substrates as a laminate. Glass is most commonly used as substrate material, but plastics is an alternative and flexible foils of polyethylene terephthalate (PET) allow device fabrication by roll-to-roll technology as discussed in Sec. 3 below [68–71].

Fig. 2. Generic EC device design; arrows illustrate the transport of positive ions in an electrical field. The dashed lines to the left indicate that the device can comprise either a five-layer stack on a single substrate or a laminate structure with two substrates. The ion storage film in a practical device may have EC properties.

The central part of an EC device conducts ions but is an insulator for electrons. It can be a polymer electrolyte layer [72,73] or a transparent thin film. The ions should be small in order to be easily transported in an electric field; protons (H^+) and lithium ions (Li^+) are by far the most common alternatives.

The ion conductor is in contact with an EC thin film which is a mixed conductor and conducts ions as well as electrons. Tungsten oxide is the premier example; it is the first widely known EC material [74] and is commonly employed in today's EC glazing [31]. The other side of the pure ion conductor has an ion storage film which again is a mixed conductor. It is preferable that the ion storage film has EC properties complementary to those of the first

EC film. The mentioned three-layer construction is located between transparent electrical conductors, which can be of many kinds and use thin films of doped wide-bandgap semiconductors or noble metals, carbon nanotubes or graphene layers, noble-metal nanowires, layers of some organics, or hybrids of two or more of the mentioned alternatives [31,75,76]. Certain interfacial layers can improve the EC functionality [77,78].

If a voltage is applied between the transparent conductors, there can be ion transport between the EC film and the ion storage film, and this charge is balanced by electrons introduced into or ejected from the EC film and the ion storage film by way of the transparent conductors. These electrons are responsible for the optical modulation of the EC film, as elaborated below. Reversing the voltage or, for some materials combinations, short-circuiting recovers the original optical properties. EC devices normally maintain their physical properties in the absence of an applied voltage—*i.e.*, under open-circuit conditions—so that the coloration can be aborted at any intermediate level between two extrema. It then follows that electrical power is needed solely to change the optical performance, which leads to energy efficiency of the EC glazing. Open-circuit memory is contingent on extremely low electron conductivity of the central ion-conducting layer, which is easier to reach with a polymer electrolyte, with a characteristic thickness of several micrometers, than in a usually much thinner inorganic ion-conducting film. The voltage needed for ion transport is typically only a few volt dc, which allows simple powering for example by photovoltaic cells integrated in the EC device [79].

An EC device is obviously akin to an electrical battery, whose charging state is manifested as optical absorption. This analogy can be useful—yet it is seldom taken advantage of sufficiently—and EC devices and electrical batteries often share the same limitations and idiosyncrasies. Thus both kinds of devices degrade rapidly upon overcharging but they can also show “self-repair”, and rejuvenation of several types of EC oxides has recently been demonstrated under galvanostatic and potentiostatic treatment, as further discussed in Sec. 4.2 [80,81]. Furthermore, both batteries and EC devices are unable to change their properties instantaneously, and a full-size EC glazing may take tens of minutes to transition from fully dark to fully transparent state.

As observed above, it is suitable to have a thin-film counter electrode whose optical properties complement those of the EC film. Such complementarity is possible since there are EC oxides of two types: some darkening under ion insertion and called “cathodic” and other ones darkening under ion extraction and referred to as “anodic”. Oxides based on W, Mo, Ti

and Nb are cathodic while oxides based on Ni and Ir are anodic [1,31]. An intermediate situation prevails for V_2O_5 which exhibits anodic and cathodic features in different wavelength ranges [82–84]. Oxides based on Cr, Mn, Fe, Co, Cu, Rh and Ta can display some electrochromism but are unable to reach a fully bleached state and/or have weak electrochromism and therefore are largely irrelevant for practical applications. Mixed EC oxides can exhibit properties better than those of the individual components. EC devices comprising W-oxide-based and Ni-oxide-based thin films are especially interesting [85,86] and are used in several varieties of EC glazing [31], including those discussed shortly in Sec. 3. Shuttling electrical charge from Ni oxide to W oxide makes both of these films dark, whereas both films become transparent when the charge is returned. Furthermore, the spectral coloration of W oxide and Ni oxide is complementary and can yield a fairly neutral color in an EC device, which is a desirable feature for most glazing.

2.2 The role of nanostructure

Nanostructure is important for EC materials and involves several length scales. These aspects are discussed next with particular reference to W oxide, which has been studied in depth. It is first observed that most of EC oxides can be viewed as being composed from octahedral structural units arranged with various degrees of corner-sharing and edge-sharing [1]. This is a benign structure since inter-octahedral spaces are large enough to allow at least some ion transport.

For stoichiometric WO_3 , the simplest structure comprises corner-sharing octahedra each with a centrally positioned tungsten atom surrounded by six oxygen atoms. However, this cubic structure is an oversimplification, and a monoclinic or triclinic structure is applicable for bulk-like WO_3 at normal temperature and pressure. The latter structures are more suitable for ion transport than the cubic one since the distances between the octahedral units are larger. Hexagonal structures are readily formed in thin films, nanorods and nanowires of W oxide [31], and this structure is even better for ion transport.

Empirical information on nanostructures in W oxide thin films have been reported many times in the scientific literature, and particularly clear information has been obtained for evaporated and sputter deposited W oxide films investigated by X-ray spectroscopy [87,88]. In the case of evaporated films, cluster-type structures were apparent and were based on hexagonal-like units which grew in size and interconnectivity for film deposition onto

substrates with successively higher temperatures [87]. These results are in agreement with the fact that trimeric W_3O_9 molecules tend to form during evaporation [89] and also with computed lowest-energy structures of $(WO_3)_q$ clusters [90]. Sputtered films appear to be even more disordered and detailed structural models have been obtained from reverse Monte-Carlo modelling of extended X-ray absorption fine structure data [88]; these films can be described as a mixture of corner-sharing and a small amount of edge-sharing polyhedra, with five-fold and a small number of four-fold coordinated W atoms present in addition to the six-fold ones. EC films are often described as “amorphous, but it is clear that some local order prevails, at least on the level of the polyhedral structural units, even when the films are deposited onto substrates at room temperature. Local order may be decreased under Li ion insertion [91].

Some ion transport is possible in the structures discussed above, but it is nevertheless important to prepare films with a sufficient degree of porosity in order to enable facile ion mobility. Many deposition techniques may be able to produce thin films with the desired properties, with greater or smaller difficulty. Considering sputter deposition, which is usually employed for the manufacturing of EC glazing, it is illustrative to consider “zone diagrams” which describe characteristic structural features as a function of deposition conditions such as the pressure of the sputter plasma and the substrate temperature in relation to the melting point of the deposited material [92–94]. Relatively high pressure in the sputter plasma, together with low substrate temperature, are appropriate and lead to films with what is known as “zone 1” structure with columnar features. Tungsten oxide films produced by sputter deposition under such conditions typically exhibits porosities of 20 to 30%. Even greater porosity can be achieved by oblique-angle deposition—with large angle between the direction of the impinging species and the substrate’s surface normal [95,96]—as clearly shown for W-oxide-based EC films [97]. Rapid EC dynamics is often reported for small-area coatings with “zone 1” character and is assigned to the nanostructure [98,99].

A discussion on suitable nanostructures for EC thin films also have to include the influence of the surface of the film, and recent work has pointed to the importance of surface features, including deposition-dependent exposed crystal facets, for anodically coloring Ni oxide immersed in Li-ion conducting electrolytes [100].

2.3 Optical properties

The origin of the optical absorption in EC oxides has been investigated for many years. This is a complicated topic for various reasons and only a simplified view, capturing the most salient features, is given here. The complications ensue from the absence of a well-defined crystal structure, as observed above, and also from oxygen deficiency and inclusion of mobile ions and water molecules. Nevertheless, a detailed picture has been presented for W oxide [101–105], while much less is known for Ni oxide and other EC oxides.

Insertion and extraction of protons (H^+) and electrons (e^-) in WO_3 can be described by the highly simplified electrochemical reaction

where H^+ can be replaced by Li^+ or some other ion [1]. Complete reversibility can only be achieved for partial reactions [80,106,107], which implies that the colored material should be written H_xWO_3 or Li_xWO_3 with $x < 0.5$. For Ni oxide, the corresponding reaction is

where the reaction is believed to take place on hydrous grain boundaries [108,109]. If Li^+ is the mobile ionic species, the reaction is confined to the surface [100], as already observed.

The fact that most EC oxides can be represented as being constructed from octahedra-like structural units makes it possible to put forward a schematic model for the occurrence of cathodic and anodic electrochromism [1]. The oxides can be characterized by oxygen $2p$ bands well separated from the metal d band, and octahedral symmetry leads to a splitting of the latter band into sub-bands with the conventional designations e_g and t_{2g} [110]. Fig. 3 shows three cases of relevance for EC oxides. Specifically, the left-hand panel, for H_xWO_3 , shows an $O2p$ band that is separated from a split d band by an energy gap. Stoichiometric WO_3 has a full $O2p$ band and an empty d band, and the band gap is wide enough to give luminous transmittance for thin films. Insertion of ions and charge balancing electrons yields partial filling of the d band along with optical absorption as discussed shortly. Middle panel of Fig. 3 pertains to anodically coloring EC oxides, such as IrO_2 and overstoichiometric Ni oxide (NiO_x with $x > 1$), which can be described as having unoccupied t_{2g} states, and the insertion of ions and electrons may fill these states to the top of the band implying that the material displays a gap between the e_g and t_{2g} sub-bands. The material then becomes transparent, assuming that the band gap is sufficiently large. Finally, the right-hand part of Fig. 3 indicates that V_2O_5 , with both cathodic and anodic characteristics, has a principally different electronic structure. The departure from octahedral coordination is large enough that the d band exhibits

a narrow split-off part in the band gap. Insertion of ions and electrons into V_2O_5 can fill this narrow band so that the optical band gap is broadened. This feature of the band structure can account for electrochromism in V_2O_5 [82] as well as band gap widening upon photo-injection of hydrogen into V_2O_5 [111].

Fig. 3. Schematic band structures for different types of EC oxides. Shaded areas indicate filled states and E is energy. The pertinent chemical species are indicated at the top; some uncertainty prevails for the Ni-containing species.

The detailed mechanism of optical absorption is considered next, again with particular consideration of W oxide. When ions and electrons are inserted, the electrons become localized on tungsten sites, and some of the W^{6+} sites turn into W^{5+} sites. By absorption of a photon, the inserted electrons can obtain sufficient energy to be transferred to a neighboring site. Transfer between two sites, denoted i and j , can be described, schematically, as [1,112,113]

More specifically, the electrons are believed to enter localized states positioned 0.1–0.2 eV below the conduction band. The atoms are displaced so that a potential well is formed, and pronounced electron–phonon interaction leads to the formation of polarons with an extent of 0.5–0.6 nm [86]. More detailed descriptions can be found in recent work [102], and the effect of W^{4+} has sometimes been emphasized [114,115]. Polaron-induced optical absorption in W oxide produces a broad band centered at $\lambda \approx 0.85 \mu\text{m}$ and extending into the luminous part of the spectrum so that thin films attain a blue color in transmission. The spectral dependence of the absorption can be described in detail by theory [103,116,117].

2.4 Comments on mixed oxides

Mixed oxides can sometimes have better EC properties than pure oxides, one reason being that additional optical transitions are possible and can produce an intermixing of polaron-induced absorption bands. Much work has been devoted recently on oxides based on W–Ti, W–V, W–Ni, W–Nb, W–Mo, W–Ta, Mo–Ti, Mo–V, Mo–Nb, Mo–Ce, Ti–V, Ti–Zr, Ir–Sn, Ir–Ta, Ni–Al, Ni–Ti, Ni–V, and many others [31]. Complexation between WO₃ and an organic substance is another option [118]. Recent studies have been reported on W–Ti oxide [119] and Ni–Ir oxide [120,121], for which a minor amount of Ti or Ir produced strongly enhanced electrochemical durability.

Further optimization of EC oxides can be accomplished in ternary compositions, and a comprehensive study was recently performed on thin films of W_{1-x-y}Ti_xMo_yO₃ with $x < 0.2$ and $y < 0.2$ [122]. The well-established ability of Ti addition to give electrochemical durability for WO₃ [119,123,124] could be combined with the also well-known capability of Mo addition to provide color neutrality to WO₃ [125–127]. Fig. 4 shows chromaticity coordinates for several oxides with Ti contents of ~10 at.% and demonstrates that approximate color neutrality can be obtained [122]. Electrochemical durability was impeded at excessive Mo contents, and it was appropriate to maintain the amount of Mo below ~6 at.%. Complex oxides of anodically coloring EC oxides have been investigated recently too, and interesting results have been reported for oxides of Ni–W–Li [128], Ni–Al–Li [129], Ni–Zr–Li [130], Ni–Fe–C [131] and Ni–Ti–Li [132] as well as on Ni–LiPON [133].

Fig. 4. CIE 1931 chromaticity diagram with (x,y) coordinates for ~ 300 -nm-thick $W_{1-x-y}Ti_xMo_yO_3$ films with the shown compositions. Numbers along the curve denote wavelengths in nm. From Arvizu et al. [122].

3. Case study: flexible EC foil

Several variations are possible for the generic EC design reported in Sec. 2.1, and the present section presents data for one of these, specifically for a mechanically flexible foil which can be produced by low-cost high-productivity roll-to-roll processing. The design is illustrated in Fig. 5 and comprises (i) a 0.175-mm-thick PET foil with a transparent electrically conducting $In_2O_3:Sn$ film and a film of EC W oxide, (ii) another PET foil with a transparent electrically conducting $In_2O_3:Sn$ film and a film of EC Ni oxide, and (iii) a polymer electrolyte joining the two EC oxides. The foil can be used in different ways: it can be fixed onto the surface of an existing glass pane, it can be suspended between two glass panes in glazing thus effectively altering it from a double-glazed to a triple-glazed construction without significantly increasing the weight, and it can be used for glass lamination as delineated in the left-hand part of Fig. 5. Some of these constructions can give added functionalities to the EC device and impart spall shielding, burglar protection, etc.

Fig. 5. Principle design of a foil-based EC device (cf. Fig. 2). Arrows indicate ion transport when a voltage is applied between the transparent electrical conductors. The entire foil can be employed to laminate glass panes, as shown in the left-hand part.

Fig. 6 gives some background for understanding the optical properties of an EC foil [134]. Upper panel shows $T(\lambda)$ in the luminous spectral range after charge exchange to the stated levels and demonstrates that the transmittance can be modulated within a wide range. The middle and lower panels in Fig. 6 illustrate the optical modulation of the individual W-oxide-based and Ni-oxide-based components after the device has been disassembled. Clearly the oxide films are optically complementary with the W-oxide-based film showing cathodic coloration mainly in the long-wavelength part of the luminous spectrum while the Ni-oxide-based film displays anodic coloration mainly at short wavelengths.

Fig. 6. Spectral transmittance for an as-prepared EC foil device of the kind shown in Fig. 5 (upper panel), and similar data for the W-oxide-based (middle panel) and Ni-oxide-based (bottom panel) parts of the device. From Granqvist et al. [134].

Fig. 7 shows optical modulation under extended coloration and bleaching of a 240-cm²-size EC foil device [134]. Upper panel demonstrates mid-luminous ($\lambda = 0.55 \mu\text{m}$) transmittance for two consecutive cycles adjusted to give a transmittance modulation ΔT of 55%. Half of the transmittance range (from point 1 to 2) took ~ 10 s, 90% of this interval (from point 1 to 3) took ~ 20 s, while the full range (from point 1 to 4) took ~ 30 s. Slower cycling could yield a larger value of ΔT . Lower panel of Fig. 7 shows evolution of maximum and minimum transmittance during the initial color–bleach cycles. The optical modulation range remained almost unchanged for thousands of cycles.

Fig. 7. Mid-luminous transmittance for an EC foil device of the kind shown in Fig. 5 adjusted to give a transmittance modulation ΔT of 55%. Upper panel shows transmittance for two consecutive color-bleach cycles (numbers 1–4 are used in the main text) and lower panel shows evolution of maximum and minimum transmittance during several color-bleach cycles. From Granqvist et al. [134].

EC foils for glazing are prone to be exposed to ultraviolet irradiation, which can give a photochromic effect in addition to the electrochromism [135,136]. If so desired, photochromism can be avoided by over-coating the W oxide film with Ta_2O_5 [137]. Photochromism has been noted also in Ni-oxide based films [138].

Color-bleach dynamics can be an important property for EC devices. For small devices, the time for going from dark to fully transparent states, or vice versa, can be as little as a few seconds, but large devices are slower since greater quantities of electrical charge must be inserted or extracted through electrical contacts (known as “bus bars”) at one or, preferably, several of the devices’ edges. EC devices can show an “iris effect” with the color change

being faster at the edge than in the center, but this often unwanted feature may be compensated via the electrical drive circuitry.

The preferred range of optical modulation depends on the intended application of the EC foil. In buildings, it is often desirable to have glazing with large bleached-state transmittance, and antireflection coatings can then be used provided they do display excessive light scattering (“haze”) [136,139]. If instead glare control is most important, it is feasible to decrease the colored-state transmittance radically through superimposed foils. Thus if the transmittance is 10% in the dark state for an EC foil, then two superimposed foils give a transmittance of only ~1%. Long-term durability is another essential parameter, which is discussed in more detail in Sec. 4.

Foil-type EC devices include a layer of a polymer electrolyte, which can be functionalized by nanoparticles. Most research on this aspect of EC devices used a “model electrolyte” of polyethyleneimine–lithium bis(trifluoromethylsulfonyl) (PEI–LiTFSI) [140,141], but similar functionalization can be implemented for the electrolyte of the EC foil device in Fig. 5 [142]. One interesting option is based on nanoparticles of a transparent electrical conductor such as $\text{In}_2\text{O}_3\text{:Sn}$, in which case it is possible to achieve near-infrared plasmon-based absorption and diminish T_{sol} without appreciably affecting T_{lum} [141]. This property is important for EC glazing particularly in warm climates. Fig. 8 shows $T(\lambda)$ and proves that strong near-infrared absorption occurs when the amount of nanoparticles is increased. Using 7 wt.% of $\text{In}_2\text{O}_3\text{:Sn}$, the EC foil has $T_{\text{lum}} = 83.3\%$ and $T_{\text{sol}} = 56.3\%$, while the electrolyte stays essentially free from haze. The measured data on $T(\lambda)$ can be reconciled with quantitative calculations, as shown by the symbols in Fig. 8, which follows from the detailed theoretical understanding of the properties of $\text{In}_2\text{O}_3\text{:Sn}$ [143] and of accurate descriptions (“effective-medium models”) for the optical properties of not too concentrated suspensions of nanoparticles [144].

Fig. 8. Spectral transmittance vs. the amount of of $\text{In}_2\text{O}_3\text{:Sn}$ nanoparticles in electrolytes of $(\text{PEI}-\text{In}_2\text{O}_3\text{:Sn})\text{:LiTFSI}$. Experimental data (curves) and calculations (symbols) are shown. From Bayrak Pehlivan et al. [141].

The EC foil in Fig. 5 can be produced by roll-to-roll web coating [71,145], which is well known to be a technology combining low cost with high productivity [146,147], and this thin-film deposition process can be combined with continuous lamination of W-oxide-coated and Ni-oxide-coated PET foils by use of the polymer electrolyte. The end products are then large flexible sheets for glass lamination, which can be cut to any size and shape after which “bus bars” are applied. Consequently, manufacturing of the final foil-based device—for example an EC-based glazing—can be removed from the site for foil production.

Fig. 9 shows installations of full-size glazing with EC-based foil laminated between large glass panes. Two of the windows in the upper panel are dark and look distinctly different from the adjacent clear window. The time for going from fully dark to fully colored states is of the order of ten minutes, which is appropriate for allowing the eye to light-adapt. No visible haze or other imperfections were noted. The lower panel of Fig. 9 depicts a commercial building with foil-based EC glazing on the lower two floors.

Fig. 9. Examples of interior (upper panel) and exterior (lower panel) views of EC glazing based on web-coated foils.

4. Towards superior EC glazing

4.1 Long-term durability assessment of EC films

Long-term durability is an obvious requirement for most EC devices, and this property has been investigated repeatedly [1,148–153]. Durability is multi-faceted and includes the ability to maintain charge transport between the two thin films in an EC device for many thousands of cycles without major loss of performance, resistance against degradation by solar irradiation for extended times, chemical ruggedness especially with regard to interfaces, sufficient shelf-life, etc.

Recent work studied the decrease in the charge density Q —and therefore of the coloration—for films of EC Ni oxide [154,155] and W oxide [156]. Fig. 10 shows data recorded under electrochemical cycling for up to 10^4 cycles. Panel (a) reports current density as the voltage applied to the films was swept between set endpoints and demonstrates cycle-dependent differences. The encircled areas correspond to charge density exchange, whose

evolution is given in Fig. 10(b); it can be represented as an almost linear drop when the number of cycles x as well as Q are expressed on logarithmic scales.

Fig. 10. Current density vs. voltage during long-time electrochemical cycling (a) and associated charge density exchange (b) for a Ni-oxide-based EC film immersed in a Li-ion-conducting electrolyte. Dots in panel (b) show experimental data and the curve was drawn as a fit to Eq. (5). Panel (b) is reproduced from Wen et al. [154].

Several functional dependencies were implemented to fit the data in Fig. 10(b), and it was found that a power-law or, alternatively, a stretched-exponential expression could accurately represent the decline of the charge density [155]. Specifically the fittings used the expression

$$Q = A_2 + \frac{A_1 - A_2}{1 + \left(\frac{x}{x_0}\right)^p} \quad (5)$$

for the power law, where A_1 and A_2 are the initial and final charge capacities, x_0 is the cycle number at which the charge density has declined to the average of its initial and final value, and p is a kinetic exponent. The fitting parameters depended on film composition and voltage range for ion insertion/extraction. The underlying model for degradation may be connected

with dispersive chemical kinetics [157] and involve a variety of diffusion-limited reactions that still are poorly understood.

4.2 Rejuvenation of degraded EC films

Another recent discovery demonstrated unambiguously that degraded EC films could be rejuvenated so that they recover their original properties [80]. This may open new ways for long-term use of EC devices, and the finding may also be relevant for other ionics-based devices such as electrical batteries. Most studies of rejuvenation have so far been carried out on W oxide and have encompassed galvanostatic [80] as well as potentiostatic [81] treatment. Rejuvenation can be performed many times [158] and has been demonstrated also for other EC materials such as Ti oxide [159] and Mo oxide [160]. Fig. 11 shows data from a study of sputter deposited WO_3 thin films immersed in a Li-conducting electrolyte and serves as a clear demonstration of rejuvenation. Panel (a) shows data on electrochemical cycling of a film after the initial and the 400th cycle in the stated voltage interval. There is an apparent drop of the charge density exchange, and Fig. 10(c) demonstrates a corresponding decrease of the optical modulation.

Fig. 11. Galvanostatic rejuvenation of an EC W oxide film, showing electrochemical cycling data performed in a Li-conducting electrolyte (a), open-circuit voltage during galvanostatic expulsion of trapped ions (b), mid-luminous optical transmittance (c) and in the entire luminous wavelength range (d). Spectral transmittance data overlap partly for bleached films. From Wen et al. [80].

Device degradation can be assigned to trapping of Li ions by following notions assuming that W oxide can be represented as a network of connected sites with low inter-site barriers, and allowing fast ion diffusion throughout the host material, and other sites with higher energy barriers which are capable of trapping diffusing ions [161–164]. The trapping hypothesis was probed by applying a constant current density of $10^{-5} \text{ A cm}^{-2}$ through a W oxide film for 20 h in the “bleaching direction”. The potential then grew from ~ 2.8 to ~ 5.5 V, as apparent from Fig. 11(b), while the optical transmittance remained high and virtually unchanged. Subsequent to this galvanostatic treatment, the open-circuit potential returned to its initial value of ~ 3.3 V, thus indicating that the original properties were recovered. Optical transmittance provided further proof that the film was indeed rejuvenated, which is clear from the information in Fig. 11(c) and also for data on $T(\lambda)$ in Fig. 11(d). Furthermore, the electrochemical cycling data returned to those for the pristine film, as indicated in Fig. 11(a). Potentiostatic rejuvenation revealed some additional features, and a conspicuous peak in the current density was associated with a rapid change in the optical transmittance [81].

The above results suggest strongly that Li ion de-trapping is possible, and conclusive evidence on this matter was obtained by analyzing the Li content—including its depth profile—by time-of-flight elastic recoil detection analysis (ToF-ERDA) [165] and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) [166]. Fig. 12 shows that the optical transmittance modulation is rapidly diminished during electrochemical cycling until it reaches the point denoted II at which the Li content was investigated and found to be much greater than in the pristine film. Galvanostatic rejuvenation according to the procedures delineated above led to abrupt onset of high transmittance after ~ 9 h, which could be correlated with de-trapping of Li ions as evident from the absence of Li in the ToF-ERDA data corresponding to point III in Fig. 12.

Fig. 12. Mid-luminous optical transmittance vs. time during galvanostatic rejuvenation of a W oxide film. Inset shows ToF-ERDA depth profiles for Li ions corresponding to points II and III as well as for a reference sample that only had been immersed in the electrolyte. From Arvizu et al. [165].

Very recent results show that electrochemical rejuvenation can be accomplished also in anodically coloring EC Ni oxide films immersed in an electrolyte of LiClO_4 in propylene carbonate, and that ion accumulation and ion release again takes place and, interestingly, involves Li as well as Cl [167]. Fig. 13 reports some characteristic transmittance data and shows that the optical modulation drops during 500 electrochemical cycles (corresponding to 11 h of treatment). Potentiostatic rejuvenation was then applied during a period of 20 h, during which the transmittance reached a low level, and this treatment was followed by a resting period of 2 h. Finally, the data in the right-hand part of Fig. 13 indicate that the initial optical performance was regained, at least approximately. The new results for Ni oxide show that both the cathodic and anodic components of a typical EC device can be rejuvenated, but work is still needed to demonstrate rejuvenation of a complete device. It should be emphasized that the physics and chemistry for the rejuvenation processes still are not well understood.

Fig. 13. Mid-luminous optical transmittance vs. time of an EC Ni oxide film subjected to electrochemical cycling and degradation, potentiostatic rejuvenation followed by a brief resting period, and resumed electrochemical cycling. Selected time-resolved data are shown in the insets.

5. Some conclusions and perspectives

EC glazing has progressed dramatically since its feeble beginnings in 1984 [45,46]. Such glazing is presently (2017) manufactured by at least four companies and is installed in buildings, especially in Europe and the USA, where it yields energy efficiency along with indoor comfort and other amenities. Low-cost manufacturing and long-term durability are keys to successful products and, as discussed in this article, web-coating can be implemented to create light-weight, rugged EC devices in the form of large sheets or on a roll suitable for glass lamination and incorporation in glazing. Reactive DC magnetron sputtering appears to be a preferred deposition technology, but other options, for example based on sol-gel deposition [168] or inkjet printing [169], may be used. In contrast with many other “green” technologies, electrochromism does not rely on “critical” rare-earth elements with questionable availability [170]. The electrolyte in the EC device can be based on an eco-friendly biohybrid [171,172], which strengthens the notion that electrochromic technology is environmentally benign.

Predictions about future developments are notoriously difficult, but here follow some perspectives on multifunctionality in conjunction with electrochromics, which may become a key issue [173,174]. Thus it is possible to combine energy generation [175,176], energy storage [177–181], or light-emission [182] with electrochromism, and another aspect of

multifunctionality regards “dual-band” EC devices that are capable of separately modulating luminous radiation and near-infrared solar radiation [54,183–187]. Still another possible—perhaps even likely—future development of EC technology concerns thermochromic (temperature-dependent) control of solar energy throughput, which can be added to electrochromism via VO₂-based nanoparticles [188–190] in the electrolyte in analogy with the application of nanoparticles discussed in Sec. 3 above [191]. Furthermore, it is feasible to invoke photocatalytic remediation of indoor air [192,193] in conjunction with EC glazing; the temperature increase caused by optical absorption in a darkened EC device can contribute significantly to the efficiency of the air purification.

The discussion in this paper was centered on glass-based products, but this is not the only option for web-coated EC devices, which may be employed in membrane architecture of a kind that already is well-established in sports stadiums, function halls, etc. [194,195]. The membranes are based on transparent or translucent ethylene tetrafluoroethylene (ETFE), which has proven durability for many decades even under full solar irradiation. Coating ETFE with a transparent electrical conductor is a critical step, but recent advances in thin-film deposition [196] and sub-second heat treatment of thin films on polymer substrates [197,198] strongly indicate that the technical challenges can be met. Flexible web-coated EC membranes therefore stand out as an interesting possibility for future innovative architecture.

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