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"Electrochromic Thin Film Devices"

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ELECTROCHROMISM AND ELECTROCHROMIC DEVICES

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Abstract

The first part of this paper reviews a large number of electrochromic devices for modulating transmittance and emittance. Data are given on all-solid-state devices as well as on polymer laminated devices, with and without self-powering by integrated solar cells. In the second part we turn to a specific, flexible polyester-based device incorporating electrochromic W oxide and Ni oxide and discuss, among other things, gas treatments for precharging of the individual electrochromic films in order to make them ready for facile device assembly, and enhancements of the bleached-state transmittance through addition of Al or Mg to the Ni oxide. [Based on C G Granqvist, A Avendaño and A Azens, "Electrochromic Coatings and Devices: Survey of Some Recent Advances", *Thin Solid Films* **442**, 201-211 (2003)].

1. Introduction

An electrochromic material is able to sustain reversible and persistent changes of its optical properties upon the application of a voltage. Integration of such materials – usually as thin films – in devices makes it possible to regulate the transmittance T , reflectance R , absorptance A , and emittance E between widely separated extrema [1,2]. This paper summarizes recent work on electrochromism with emphasis on devices for regulating T between a transparent (bleached) and an absorbing (colored) state. We mainly consider work carried out in the period 1998-2001 so that the present article complements earlier extensive reviews [1,2].

Fig. 1 illustrates a standard construction that allows basic features and operating principles to be introduced conveniently. The design embodies five superimposed layers on one substrate or positioned between two substrates in a laminate configuration. Normally the substrates are made of glass or flexible polyester foil. The central part of the five-layer construction is a pure ion conductor (electrolyte) that can be inorganic (often based on an oxide film) or organic (an adhesive polymer). The ions should be small in order to be mobile; protons (H^+) or lithium ions (Li^+) are normally preferred. This ion conductor bounds on an electrochromic film (WO_3 being a typical example) capable of conducting electrons as well as ions. On the other side of the ion conductor is a film serving as an ion storage, ideally with electrochromic properties complementary to those of the first electrochromic film. This central three-layer structure is positioned between electrically conducting transparent films; the best materials in terms of optical and electrical properties is $In_2O_3:Sn$ (known as Indium Tin Oxide,

ITO), while films of $SnO_2:F$ are less costly and readily available on large area glass panes [3,4]. Possibilities to replace these oxides with metal-based layers such as $ZnS/Ag/ZnS$ have been explored recently [5,6].

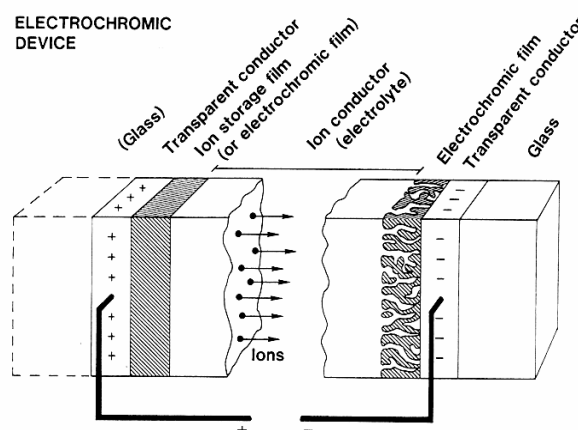


Fig. 1. Basic design of an electrochromic device, indicating transport of positive ions under the action of an electric field.

When a voltage of the order of one volt is applied between the transparent electrical conductors, ions will be shuttled between the ion storage film and the electrochromic film. The electrons injected from the transparent conductors then alter the optical properties. A reversal of the voltage, or short-circuiting, brings back the original properties. The coloration can be stopped at any intermediate level, and the device exhibits open-circuit memory so that the optical changes take place only when charge is moved. It is then apparent that the electrochromic device can be viewed as an electrical battery with a

charging state manifested as optical absorption. The transfer of battery-type work to the field of electrochromics has been attempted [7], but much remains to be done to fully exploit the analogies of the two technologies.

The basic reason for the optical absorption has been discussed extensively, especially for WO_3 . Recent work has lent credence to the well known polaron mechanism [8,9], implying that the inserted electrons enter localized states below the conduction band of WO_3 . These electrons cause a displacement of the atoms surrounding them and create a self-induced potential well; the ensuing strong electron-phonon interaction then leads to the formation of small polarons. Quantitative agreement was found with theory [10].

Electrochromism can lead to numerous applications. A few of these – such as architectural “smart windows”, rear-view mirrors for cars, and some display devices – are presently (2005) available on the market. More products are likely to appear in the future, especially when practical manufacturing techniques and more durable products become better established. We return to some of these aspects in Sec. 3 below. Fig. 2 summarizes a number of applications for electrochromic devices. Part (a) refers to non-emissive information displays. Such applications were envisaged for electrochromics already at the discovery of the phenomenon, but durability issues as well as progress in liquid-crystal-based devices has led to a total dominance of the latter. Presently electrochromics-based devices are reappearing in cont-emporary contexts such as “electronic paper” [11-13] and “printed” or “painted” displays [14-16]. Electrochromism can also be used for enhancing the contrast of emissive displays such as cathode ray tubes [17]. Fig. 2(b) illustrates an electrochromic variable-reflectance (anti-dazzling) mirror; such devices are in widespread use in cars. Fig. 2(c) depicts the most widely discussed electrochromic device: the “smart window” with variable through-put of luminous and solar radiation. Such windows are expected to be of large significance in architecture [18-20]; they are able to combine high energy efficiency with possibilities to achieve thermal and visual comfort to occupants of the building [21-24]. Fig. 2(d), finally, indicates that electrochromism can also be used – with a device design somewhat different from the one in Fig. 1 – for achieving surfaces with variable thermal emit-tance. Such surfaces can be used for temperature control of space vehicles, as well as for other applications.

2. Electrochromic devices and their properties: Results for 1998-2001

This section will revolve around Table I, which summarizes the designs of a number of

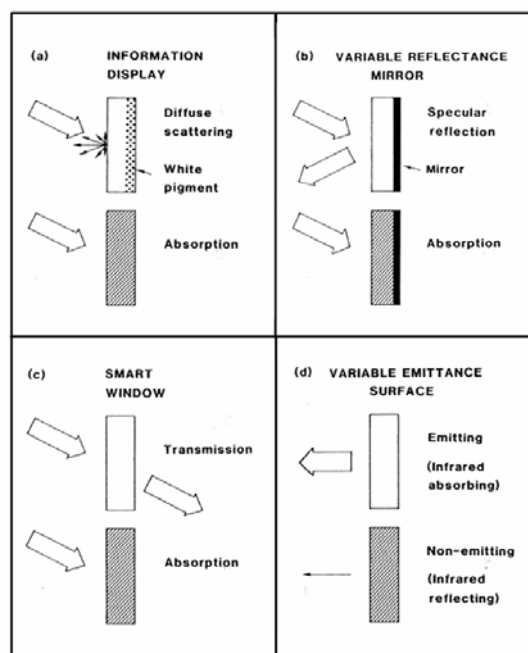


Fig. 2. Principles for four different applications of electrochromic devices. Arrows indicate incoming and outgoing electromagnetic radiation; the thickness of the arrow signifies radiation intensity.

electrochromic devices and lists some key numbers regarding their ability to modulate optical properties. Specifically, data are provided on the modulation range for T , R , and E , either at a specific wavelength or after an averaging over the eye’s sensitivity to obtain luminous (lum) properties, over a solar spectrum to obtain solar (sol) properties, or over a blackbody spectrum characteristic of room temperature to obtain thermal (therm) properties. Also given are the number of color/bleach (c/b) cycles the devices have been tested for, and a typical time for the full optical switching (τ_{sw}). The data should be regarded as typical only. The minimum value of T , say, depends on the charge transfer and, generally, a minimum T is obtained at the expense of a lowered number of c/b cycles before serious degradation sets in. The magnitude of τ_{sw} is strongly connected to the size of the electrochromic device, and a large device tends to have a long τ_{sw} . The maximum T is not subject to such uncertainties, though, and should be regarded more as an intrinsic property of the device. Table I can be directly compared with information in a previous survey covering 1993-1998 [2].

2.1 All-solid-state devices for transmittance modulation

Entries 1-4 in Table I show data for devices backed by a single glass or polyester substrate [25-28]. This work has been supported by industries in

different parts of the world. Entries 1 and 2 apply to devices operating by H^+ transport, while entries 3 and 4 refer to devices operating by Li^+ transport. The high transmittance, and the large modulation range, are noteworthy for devices incorporating NiO and IrO_2 ; these materials exhibit anodic electrochromism (color under charge extraction) and hence are complementary to the WO_3 which has cathodic electrochromism (colors under charge insertion). The device in entry 3 has a V_2O_5 counter electrode; this material has less favorable optical properties and is incapable of attaining a fully transparent state [29]. The device in entry 1 is intended to have an adhesive top layer, so that it can be fixed to a second glass substrate. More information on devices analogous to those in entry 2, also ones with NiO replacing the IrO_2 layer, was presented earlier [30]. The device in entry 4 is poorly specified; it is interesting, though, because it has undergone an elaborate testing program [28].

Entry 5 refers to a device employing a NiO counter electrode and H^+ transport [31,32]. The luminous transmittance is large in the bleached state. Data are available for non-normal transmittance [32]; such information is rarely given despite the fact that it is needed for reliable estimates of energy balances of buildings. The ZrP-based electrolyte has been studied in detail [33].

2.2 Polymer-laminated devices for transmittance modulation

We next turn to laminated devices and first consider, in entries 6-9, those operating with H^+ transport [34-40]. Specifically, the devices employed electrolytes based on polyethylene oxide (PEO), a copolymer of sodium vinylsulfonic acid and 1-vinyl-2-pyrrolidinone (PVSA-PVP) ion exchanged into an acidic form, and poly-2-acrylamido-2-methyl-propane sulfonic acid (PAMPS). The counter electrodes were IrO_2 , $K_3Fe(CN)_6$ (known as "Prussian Blue", PB), polyaniline (PANI), or a mixture of the latter two. The modulation range for visible light can be large, especially for the elaborated design in entry 7; devices with areas up to 1740 cm^2 were investigated in this work, and the relationship between coloring time and size was documented.

Laminated devices with Li^+ transport and inorganic counter electrodes have been subject to an impressive number of detailed investigations, reported in entries 10-22 [41-49]. The electrolytes were based on poly(methyl methacrylate) (PMMA) copolymerized with propylene carbonate (PC) or poly(propylene glycol) (PPG), polypyrrole (PPY), silane, glycidylxypropyl trimethoxysilane (GLYMO) copolymerized with tetraethylene glycol (TEG), ormolyte (inorganic-organic hybrid electrolyte), poly(ethylene glycol methacrylate)

(PEGMA) copolymerized with PEO, or poly(vinylidene fluoride) (PVDF); the polymers were made ion conducting by the addition of an appropriate Li salt. The counter electrodes were based on V_2O_5 , TiO_2 with or without additions of ZrO_2 or CeO_2 , SnO_2 doped with Mo and Sb, CoO deposited with Li, and NiO deposited with or without Li. A large range of optical modulation, together with durability and reasonable c/b response times, were observed in several cases. Entry 18 is noteworthy and shows that inorganic films other than WO_3 can be used to provide cathodic electrochromism in devices.

Table 1
Data for electrochromic devices investigated 1998-2001, showing materials, sample size, and modulation range for the transmittance (T), reflectance (R) and emittance (E). Also shown are the number of color/bleach (c/b) cycles, and the switching time (τ_{sw}). G denotes glass, P denotes polymer, and the subscript for T, R, or E signify the wavelength (in nm) or the averaging over wavelength to obtain luminous (lum), solar (sol) or thermal (therm) values. Optical density is denoted OD, an antireflection layer is denoted AR, and c- WO_3 signifies a crystalline state of the oxide. The abbreviations for the various polymers are explained in the main text. For some devices, no specification was given for the transparent electrical conductor (TC), ion conductor (IC), and counter electrode (CE).

| Entry | Device construction | Size (cm ²) | T (%) | c/b cycles | τ_{sw} (s) | Ref. |
|-------|--|-------------------------|--|-------------------|-----------------|---------|
| 1 | G/ITO/NiO/Ta ₂ O ₅ /WO ₃ /ITO | 2400 | $18 < T_{lum} < 73$ $11 < T_{sol} < 55$ | 10^5 | — | [25] |
| 2 | G or P/ITO/WO ₃ /Ta ₂ O ₅ /IrO ₂ /ITO | 30 | $18 < T_{350} < 70$ | 3.5×10^4 | — | [26] |
| 3 | G/ITO/WO ₃ /LiAlF ₄ /V ₂ O ₅ /ITO | 900 | $23 < T_{lum} < 55$ | — | — | [27] |
| 4 | G/TC/WO ₃ /IC-Li ⁺ /CE/TC | — | $8 < T_{lum} < 55$ | — | 150 | [28] |
| 5 | G/ITO/WO ₃ /ZrP-qH ₂ O/ZrO ₂ /NiO/ITO/G | 25 | $38 < T_{lum} < 74$ $25 < T_{sol} < 53$ | — | 60 | [31,32] |
| 6 | G/SnO ₂ /WO ₃ /PEO-H ⁺ /IrO ₂ /SnO ₂ /G | 130 | $10 < T_{350} < 48$ | — | — | [34] |
| 7 | G/SnO ₂ /WO ₃ /PVSA-PVP-H ⁺ /PB/SnO ₂ /G | 155 | $6 < T_{350} < 72$ | 2×10^4 | 30 | [35-37] |
| 8 | G/SnO ₂ /WO ₃ /PAMPS/PANI/SnO ₂ /G | 8 | $27 < T_{350} < 64$ | — | 26 | [38] |
| 9 | G/ITO/WO ₃ /PAMPS/PANI/PB/ITO/G | 2 | $23 < T_{sol} < 73$ | 3700 | 30 | [39,40] |
| 10 | P/ITO/WO ₃ /PMMA-PC-Li ⁺ /V ₂ O ₅ /ITO/P | — | $8 < T_{600} < 65$ | 3×10^4 | — | [41] |
| 11 | G/ITO/WO ₃ /PPY-Li ⁺ /V ₂ O ₅ /ITO/G | — | $\Delta T_{788} = 30$ | — | — | [42] |
| 12 | G/ITO/WO ₃ /PEO-Li ⁺ /TiO ₂ /ITO/G | — | $\Delta OD = 1$ | 10^6 | 2 | [43] |
| 13 | G/ITO/WO ₃ /PMMA-PPG-Li ⁺ /TiO ₂ -ZrO ₂ /ITO/G | 5 | $20 < T_{350} < 80$ | — | 200 | [44] |

Additional data on electrochromic devices for transmittance control are reported in entries 23-28 [7,50-57]. The device in entry 23 embodies a copolymer electrolyte of PVDF and hexafluoropropylene (HFP) between monohydrate tungsten oxide and PANI films; it also included reinforcing Al grids. Entry 24 is original in its use of 0.5-mm-diameter carbon dots, rather than a continuous film, as counter electrode. The obscuring effect of these dots may or may not be problematic, depending on

the application. The latter devices also included an ultraviolet filter whose purpose was to increase the long-term durability. Entry 25 represents a somewhat nondescript device; the transmittance data in Table I refer to the performance of an optically neutral device intended for building applications. A similar blue device was characterized by $10 < T_{lum} < 55\%$ and $6 < T_{sol} < 32\%$. Devices intended for automotive uses had $4 < T_{lum} < 40\%$ and $2 < T_{sol} < 18\%$. Entries 26 and 27 indicate the possibilities to make all-polymer devices (except for the ITO films). The polymers used were poly(3,4-ethylene-dioxythiophene) doped with polystyrene sulfonate (PEDT-PSS), polyepichlorohydrin copolymerized with PEO, PPY doped with dodecylsulfate (DS) and indigo carmine (IC), poly(*N,N'*-dimethyl-bipyrrole) doped with perchlorate (PNNDMBP), and poly(4,4'-dipentoxy-2-2'-bithiophene) doped with perchlorate (PET2). Another alternative is reported on in entry 28, where the device is based on anodically coloring poly[3,6-*bis*(2-(3,4-ethylenedioxythiophene))-*N*-methylcarbazole] (PBEDOT-NCH₃Cz) and a cathodically coloring alkyl derivative of poly(3,4-ethylenedioxythiophene) (PEDOT). Further work on similar materials is reported elsewhere [58,59]; a particularly interesting feature is their extremely large coloration efficiencies.

| Entry | Device construction | Size (cm ²) | T (%) | c/b cycles | t ₉₀ (s) | Ref. |
|-------|--|-------------------------|---|---------------------|---------------------|------------|
| 14 | G/ITO/WO ₃ /SiIame-Li ⁺ /TiO ₂ -CeO ₂ /ITO/G | 1225 | 20 < T ₃₀₀₋₈₀₀ < 80 | — | >100 | [45] |
| 15 | G/ITO/GLYMO-TEG-Li ⁺ /SnO ₂ (Mo ₆ Sb)/ITO/G | 5 | 25 < T ₃₅₀ < 75 | 500 | 30 | [46] |
| 16 | G/SnO ₂ /WO ₃ /Ormolyle-Li ⁺ /SnO ₂ (Mo ₆ Sb)/SnO ₂ /G | 9 | 20 < T ₃₅₀ < 60 | 500 | ~100 | [47] |
| 17 | G/SnO ₂ /WO ₃ /Ormolyle-Li ⁺ /CoO-Li ⁺ /SnO ₂ /G | 9 | 20 < T ₃₅₀ < 65 | — | — | [47] |
| 18 | G/SnO ₂ /Nb ₂ O ₅ /Li/Ormolyle-Li ⁺ /SnO ₂ (Mo ₆ Sb)/SnO ₂ /G | 9 | 20 < T ₃₅₀ < 70 | — | — | [47] |
| 19 | G/SnO ₂ /WO ₃ /PEGMA-PEO-Li ⁺ /NiO-Li ⁺ /SnO ₂ /G | 144 | 27 < T _{lum} < 70 | — | ~120 | [48] |
| 20 | G/SnO ₂ /WO ₃ /PVDF-Li ⁺ /NiO-Li ⁺ /SnO ₂ /G | 7 | 2 < T _{lum} < 75 | — | — | [49] |
| 21 | G/ITO/WO ₃ /PMMA-PC-Li ⁺ /NiO/ITO/G | — | 31 < T ₆₀₀ < 78 | 10 ⁴ | — | [41] |
| 22 | P/ITO/WO ₃ /PMMA-PPG-Li ⁺ /NiO/ITO/P | 220 | 35 < T ₃₅₀ < 70 | 5000 | ~200 | This work |
| 23 | P/ITO/WO ₃ /H ₂ O/PVDF-HFP-Li ⁺ /PANI/ITO/P | — | 2 < T ₆₀₀ < 12 | — | — | [7] |
| 24 | G/TC/WO ₃ /IC/C-dots/TC/G | 25 | 2 < T _{lum} < 55 | 3 x 10 ⁵ | ~20 | [50,51] |
| 25 | G/TC/WO ₃ /IC/CE/TC/G | 4800 | 13 < T _{lum} < 58 7 < T _{sol} < 37 | — | — | [52] |
| 26 | P/ITO/PEDT-PSS/PEPI-PEO-Li ⁺ /PPY-DS-IC/ITO/P | — | 23 < T ₆₀₀ < 75 | — | 4 | [53,54] |
| 27 | P/ITO/PNNDMBP-PEPI-PEO/PEPI-PEO-Li ⁺ /PET2-PEPI-PEO/ITO/P | — | 27 < T ₆₀₀ < 64 | 1000 | 7 | [53,55,56] |
| 28 | G/ITO/PBEDOT-NCH ₃ Cz/PMMA-PC-Li ⁺ /PEDOT-C ₆ H ₅ /ITO/G | — | 8 < T ₆₀₀ < 68 | 10 ⁴ | 1 | [57] |
| 29 | G/ITO/dye-TiO ₂ /IC/WO ₃ /ITO/G | — | 54 < T ₇₈₀ < 70 | — | — | [60] |

Table I (continuation)

| | | | | | | |
|----|--|----|---|-----|-----|---------|
| 30 | G/TC/WO ₃ /dye-TiO ₂ /IC/TC | 25 | 3 < T _{lum} < 8 2 < T _{sol} < 26 | — | 120 | [61] |
| 31 | P/ITO/dye-TiO ₂ /PEGMA-Li ⁺ /WO ₃ /ITO/P | 8 | 30 < T ₃₅₀ < 40 | — | — | [62,63] |
| 32 | G/TC/SiC:H/TC/V ₂ O ₅ /Li/LiAF ₄ /WO ₃ /TC | 16 | 8 < T _{lum} < 25 | — | 120 | [63,64] |
| 33 | CaF ₂ or Si/grid/c-WO ₃ /IC/CE/TC | — | 40 < R ₁₀₀₀ < 66 | — | — | [67,68] |
| 34 | G/Al/WO ₃ /Ta ₂ O ₅ /c-WO ₃ /grid | — | 40 < E _{lum} < 58 | — | — | [69,70] |
| 35 | G/grid/WO ₃ /Ta ₂ O ₅ /c-WO ₃ /grid | — | 64 < E _{lum} < 80 | — | — | [70] |
| 36 | G/ITO/NiO/PAMPS-DMA-Li ⁺ /c-WO ₃ /Si/AR | — | 60 < E _{lum} < 68 | — | — | [70,71] |
| 37 | G/ITO/WO ₃ /PAMPS-Li ⁺ /PANI-CSA/grid/AR/ZnSe/AR | — | 22 < R ₁₂₀₀ < 65 | 900 | 9 | [72] |
| 38 | G/ITO/NiO/PMMA-TFSI-Li ⁺ /WO ₃ /grid/Si | 11 | 56 < E _{lum} < 65 | — | — | [73] |

2.3 Self-powered devices for transmittance modulation

Modulation of the optical properties requires the application of a DC voltage of a magnitude that is conveniently obtained from solar cells. These cells can be external to the electrochromic device. Alternatively, if semitransparent cells are used, they can be integrated in a multilayer construction comprising a superimposed solar cell and electrochromic tandem configuration. A number of such designs are described in entries 29-32 [60-64]. The solar cells are of two types: a dye sensitized nanocrystalline cell employing TiO₂, Ru-containing dye, iodine-containing electrolyte, and a transparent conductor with a very thin Pt layer. Entry 30 is interesting in that it incorporates a non-liquid PEGMA electrolyte. This device shows slow dynamics, though, and full bleaching takes 12 h. Entry 32 reports an all-solid-state device with a wide-bandgap solar cell based on doped amorphous SiC:H operating in conjunction with an electrochromic device similar to the one in entry 3. All of the solar-cell-powered tandem devices exhibit a small range of optical modulation, and most of them have a low transmittance in the bleached state, which gives a significant limitation for these applications. In the absence of the SiC:H, the

electrochromic structure in entry 32 has a performance similar to the one in entry 3. Electrochromic devices with redox chromophores associated with nanocrystalline TiO_2 have been discussed recently [65,66].

2.4 Devices for emittance modulation

The final set of data reported in Table I regards electrochromic devices for modulating the thermal emittance; see entries 33-38 [67-73]. Most of the devices exploit the fact that crystalline tungsten oxide ($c\text{-WO}_3$) is able to modify its infrared reflectance upon charge insertion/extraction. This surface must be exposed to the ambience either directly or via an infrared-transparent substrate such as CaF_2 , Si, or ZnSe. Charge is introduced via a grid electrode, normally of Al or Au, with a large open fraction. Antireflection (AR) treatments can diminish the infrared reflectance, *i.e.*, enhance the emittance. The counter electrode can be normal “amorphous” WO_3 , NiO, or a polymer electrolyte. The modulation of E_{therm} remains less than 20%. The device in entry 37 uses the electrochromism of a copolymer of PANI and camphor sulfonic acid (CSA) to modulate the reflectance at one specific wavelength within a rather wide range. The device in entry 38 employed a polymer which contains PMMA and Li^+ -incorporated trifluorosulfonyl imide (TFSI).

3. Electrochromic foil: Specific design features and properties

This section discusses in some detail the preparation of a flexible electrochromic device (entry 22 in Table I). Particular attention is given to practical manufacturing technology and to optimization of the bleached-state transmittance. More details on this novel electrochromic device can be found elsewhere [74,75].

3.1 Deposition of thin films

Electrochromic films of WO_3 and NiO were made by DC magnetron sputtering onto 0.175-mm-thick polyester foil, precoated with an ITO layer having a resistance/square of 60 Ω , using a large box-type coater with 50 x 12.5 cm^2 targets [76]. For research purposes we also employed a smaller coater with 5-cm-targets [77] and prepared films on glass plates with ITO layers having a resistance/square of 15 Ω . The targets were plates of W, Ni, Mg, $\text{NiV}_{0.08}$, and $\text{NiAl}_{0.56}$ with purities between 99.95 and 99.99%. The additions to the Ni target rendered it non-magnetic and hence convenient for magnetron sputtering. Carbon substrates were used for compositional determinations using Rutherford Backscattering Spectrometry (RBS). Sputtering took place in Ar/O_2 or $\text{Ar}/\text{O}_2/\text{H}_2$ with optimised mixing ratios. The target-substrate distance lay

between 13 cm for the small deposition unit and 20 to 25 cm for the large unit, and the total gas pressure was in the 30 to 40 mTorr range. Typical deposition rates and film thicknesses were 0.4 nm/s and 200 to 300 nm, respectively. Specifics on the depositions can be found elsewhere [74,75,78-80].

With regard to manufacturing, it is preferable to be able to deposit the films under conditions that make them ready for device lamination, or to have convenient processes for making the as-deposited films prepared for this. In the case of W oxide, one can carry out the deposition in $\text{Ar}/\text{O}_2/\text{H}_2$ according to principles described in the literature [81]. The hydrogen produces a blue color for the as-deposited films, and the key issue with regard to optimizing the gas mixture is to incorporate hydrogen into the film without creating oxygen deficiency.

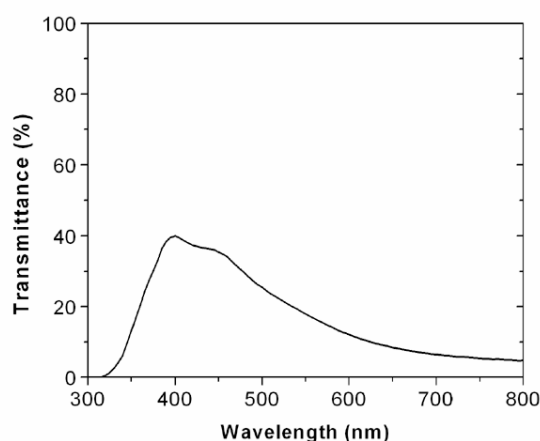


Fig. 3. Spectral transmittance of a 300-nm-thick W oxide film produced by sputtering in $\text{Ar}/\text{O}_2/\text{H}_2$ under conditions making it ready for device lamination.

In practice, the optimization of the WO_3 films can be made by measuring their color in the as-deposited state. Color properties are conveniently specified by use of chromaticity coordinates – corresponding to red (x), green (y), and blue (z) primaries, respectively – using the CIE Colorimetric System [82]. Color neutrality is represented by $(x,y,z) = (0.333, 0.333, 0.333)$. Fig. 3 illustrates the spectral transmittance for a film made in an optimized mixture of $\text{Ar}/\text{O}_2/\text{H}_2$.

3.2 Transmittance enhancement of Ni oxide films

A number of recent electrochromic device designs include NiO films operating in conjunction with WO_3 , as found in Table I and elsewhere [30,83]. This combination of materials is favorable with regard to electrochemical potentials and the option for achieving chemical compatibility to the electrolyte [84]. A long-standing problem with NiO, however, has been the residual optical absorption in the $400 < \lambda < 500$ nm wavelength interval, which has precluded a fully transparent state. This limi-

tation has been detrimental to architectural applications [18]. As shown next, the absorption in Ni oxide and Ni-V oxide can be significantly lowered by an addition of Al or Mg.

The study on the electrochemical and optical properties used cyclic voltammetry in a 1 M KOH electrolyte at a scan rate of 10 mV/s with a three-electrode configuration including a counter electrode of Pt and a reference electrode of Ag/AgCl. Typical data were obtained with a lower (bleaching) potential of -0.5 V and an upper (coloring) potential, denoted U_{col} , of 0.6 V. Spectrophotometric measurements were conducted on films that had been withdrawn from the electrolyte and cleaned. Specifically, we measured normal T and near-normal R and evaluated spectral absorbance from $A(\lambda) = 1 - T(\lambda) - R(\lambda)$.

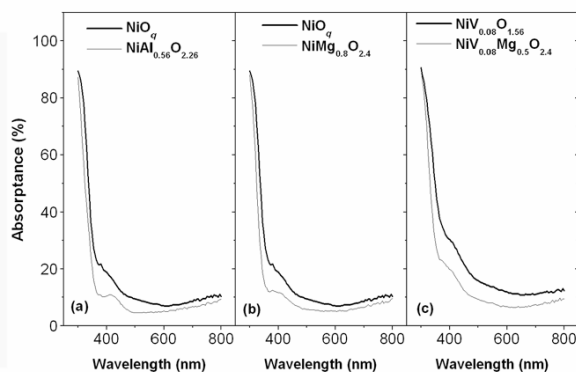


Fig. 4. Spectral absorbance for 200-nm-thick Ni-oxide-based films of the shown compositions. The films were in their states of maximum transmittance. q denotes an unknown amount of oxygen.

Fig. 4 compares bleached-state data on $A(\lambda)$ in the $300 < \lambda < 800$ nm range for films of $\text{NiAl}_{0.56}\text{O}_{2.26}$ (part a), $\text{NiMg}_{0.8}\text{O}_{2.4}$ (part b), and $\text{NiV}_{0.08}\text{Mg}_{0.5}\text{O}_{2.4}$ (part c). Absorbance is also shown for analogous films lacking Al or Mg, *i.e.*, NiO_q and $\text{NiV}_{0.08}\text{O}_{1.56}$, where q signifies that the oxygen content has not yet been determined. With the films in their states of maximum transmittance, the absorbance is found to be significantly smaller for the films containing Al or Mg. This difference prevails across the full spectral range and is particularly large at $\lambda < 500$ nm. The strong absorbance at $\lambda < 350$ nm is due to the semiconductor band-gap, which appears to be widened as a consequence of the addition of Al or Mg. Some weak absorption features can be discerned in the spectral data; they are possibly associated with crystal-field effects [85,86]. Similar beneficial effects were found for Mg addition to electrochromic IrO_2 [87].

Corresponding data on $T(\lambda)$ are shown in Fig. 5 for the films of $\text{NiAl}_{0.56}\text{O}_{2.26}$ and $\text{NiV}_{0.08}\text{O}_{1.56}$. The transmittance-enhancing effect of the Al is apparent

once again. The latter film has a T_{lum} of 82 % and chromaticity coordinates equal to (0.347, 0.347, 0.306), whereas the Al-containing film is characterized by $T_{\text{lum}} = 85$ % and chromaticity coordinates being (0.334, 0.339, 0.328). An analogous analysis for the data in Fig. 4(b) yielded that the films of NiO_q and $\text{NiMg}_{0.8}\text{O}_{2.4}$ have chromaticity coordinates (0.339, 0.342, 0.319) and (0.337, 0.336, 0.327), respectively. It is thus clear that the addition of Al or Mg alters the visual appearance towards a more color-neutral state primarily by increasing the contribution from the blue part of the spectrum.

The charge capacity – and hence the electrochromism – is influenced by the potentiodynamic range, particularly the magnitude of U_{col} . This effect was studied with regard to $\text{NiV}_{0.08}\text{Mg}_{0.5}\text{O}_{2.4}$, $\text{NiAl}_{0.56}\text{O}_{2.26}$, and $\text{NiV}_{0.08}\text{O}_{1.56}$, *i.e.*, films reported on in Fig 4, for $0.45 < U_{\text{col}} < 0.65$ V vs. Ag/AgCl. It was found that similar charge capacities could be obtained provided that U_{col} was set at a potential that was 0.05 to 0.1 V higher when Mg is present. This shift is insignificant for electrochromic device applications.

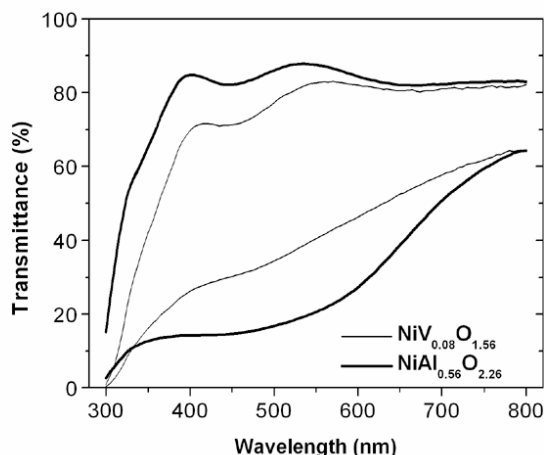


Fig. 5. Spectral colored-state and bleached-state transmittance for 200-nm-thick Ni-oxide-based films made by sputtering from $\text{NiAl}_{0.56}$ and $\text{NiV}_{0.08}$ targets. Coloration and bleaching were accomplished in 1 M KOH at 0.6 and -0.5 V vs. Ag/AgCl, respectively. The coloration charges were 15 and 12 mC/cm^2 for the two films; this difference accounts for part of the difference in the optical performance.

3.3 Pre-assembly charge balancing, and device lamination

WO_3 films can be made dark (*i.e.*, charge inserted) by sputtering in the presence of hydrogen [81], as mentioned above. If these films are to operate in conjunction with NiO films, the latter, ideally, should be made so that they are prepared for charge insertion prior to device assembly. Such discharged

films are dark. However, the NiO films normally are transparent in their as-deposited state and hence require pre-treatment before device lamination. Charge insertion via an electrochemical procedure is possible, in principle, but obviously unwieldy and not suited for practical fabrication. An alternative method for discharging was developed in earlier work of ours [88]. Essentially, this new method employs exposure to ozone obtained by ultraviolet irradiation of the film in the presence of oxygen.

Fig. 6 displays the decrease of T_{lum} as a function time when a conventional ozone photo-reactor was used to illuminate a 220-nm-thick NiV_{0.08} oxide film. The transmittance drops by some 50 % during a few minutes, and a further decrease takes place for extended exposure times. Fig. 7 illustrates a typical spectral transmittance plot for this film prior to device lamination.

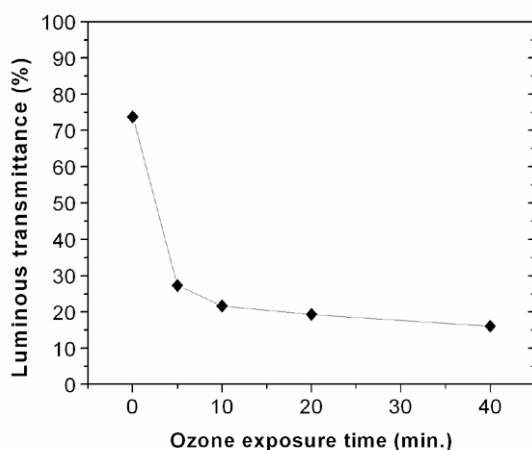


Fig. 6. Luminous transmittance vs. post-deposition ozone exposure time for 220-nm-thick Ni-V oxide films produced by sputtering in Ar/O₂/H₂.

Polyester-based foils – one with a WO₃ film colored by sputtering in the presence of hydrogen (*cf.* Fig. 3) and another with a NiO film colored by post-deposition ozone exposure (*cf.* Fig. 7) – were laminated together by a PMMA-based electrolyte of a type described elsewhere [89] using roll-pressing at a temperature of 80 °C. The edges of the double foil were then sealed by a two-component epoxy glue, electrical contacts were attached, and the electrochromic device was ready for testing and use.

3.4 Device tests

Devices of the type described above were cycled between colored and bleached states using trapezoidal voltage pulses between -1.6 and +1.5 V, respectively. Durability tests, that are currently going on, are discussed next.

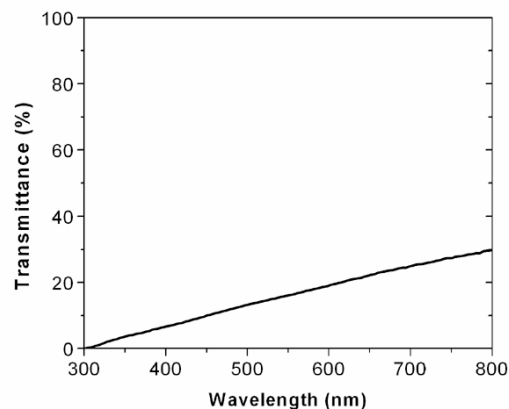


Fig. 7. Spectral transmittance of a 220-nm-thick Ni-V oxide film produced by sputtering in Ar/O₂/H₂ and post-treated in ozone under conditions making it ready for device lamination.

Fig. 8 shows T at three different wavelengths for cycling with one full color-bleach cycle each 200 s. The optical modulation is pronounced, especially for mid-luminous and red light. Most of the changes take place within a few tens of seconds after application of the pulse, but the coloration has not reached saturation even after several minutes. Fig. 9 reports on the transmittance in fully colored and bleached states after cycling in the same way as in Fig. 8. The foils are seen to change between a high level of about 70 % and a low level of 35 to 40 % at a wavelength of 550 nm, which is agreement with the data in Fig. 8. The span between the colored and bleached states remains practically unaltered for at least 5000 cycles. Lower transmittance levels, down to 25 % or less in the colored state, could be reached for longer coloration times. It should be noted that the possibility of increasing T_{lum} by adding Al or Mg to the Ni oxide has not yet been implemented for the investigations reported on in this section; however, such work is currently under way.

The devices have open circuit memory, which is an asset since electrical power must be drawn only to effect changes in the optical properties. For example, it was found that the transmittance at a wavelength of 550 nm for a device colored to a transmittance equal to 20 % increased only up to about 30 % after a time as long as 160 h. Keeping the device in the colored state for an extended time influenced the bleaching time, and a device with an initial bleaching time of about one minute attained a bleaching time of some 20 minutes after being maintained in the colored state for 160 h.

The work reported above has demonstrated techniques to make flexible electrochromic foils with sufficient optical modulation range, dynamics,

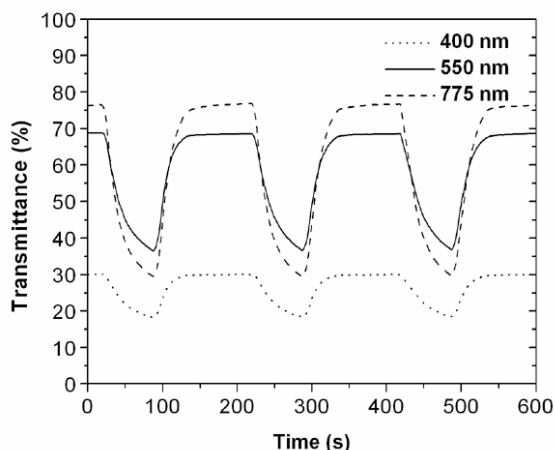


Fig. 8. Transmittance at three wavelengths vs. time for electrochromic switching of a laminated device described in the main text.

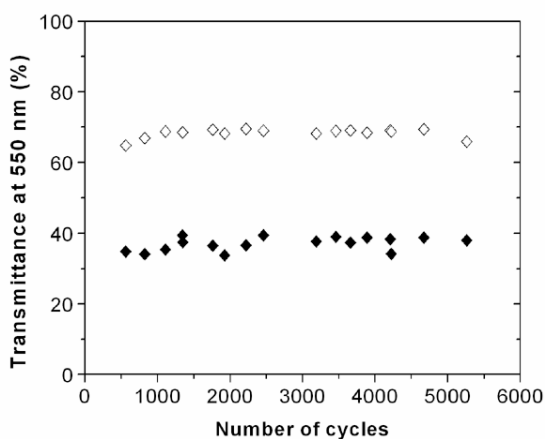


Fig. 9. Transmittance at a wavelength of 550 nm vs. number of color/bleach cycles for a laminated electrochromic foil device in colored and bleached states.

and durability for making them interesting for a range of applications. Facile manufacturing was found to be possible by a combination of different technologies, and the potentially cumbersome pre-lamination treatments of the films was avoided by sputtering the WO_3 film in the presence of hydrogen and by post-deposition treatment of the NiO film in ozone for a few minutes. New materials were developed for enhancing the bleached-state transmittance, specifically employing additions of Al or Mg to Ni oxide. The electrochromic foils can be used to achieve smart windows with large energy efficiency, provided that their control strategy is adequate. In particular, the window in a room should be set for minimum/maximum transmittance, when this room is unoccupied, if the building is dominated by space cooling / heating [21,24].

Another application concerns electrochromic foils in variable-transmittance visors for motorcycle helmets. Driving or riding safety requires different transmittance levels for varying lighting conditions, and properties such as those illustrated in Figs. 8 and 9 are excellent for these applications [90].

4. Conclusion

In the first part of this paper we reviewed a large number of electrochromic devices for modulating transmittance and emittance. Data were given on all-solid-state devices as well as on polymer laminated devices, with and without self-powering by integrated solar cells. A number of designs were shown capable of large optical modulation, as well as dynamics and durability sufficient for applications. The information was presented in a way that allowed direct comparison with earlier reviews [1,2]. It should be realized that no tabulation of this kind can be expected to be complete. For example device-like constructions incorporating hydride-based switchable mirrors [91-97] and variable-electroplating-based systems were not included. The second part of the paper considered a specific, flexible polyester-based device incorporating electrochromic W oxide and Ni oxide and discussed, among other things, gas treatments for precharging of the individual electrochromic films in order to make them ready for facile device assembly, and enhancements of the bleached-state transmittance through additions of Al or Mg to the Ni oxide.

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