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Electrochromics and thermochromics: towards a new paradigm for energy efficient buildings

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Abstract

Modern buildings normally have large windows and glass facades, known jointly as glazings, for achieving good day-lighting and indoors–outdoors contact. However, glazings are challenging for the buildings' energy efficiency and frequently let in or out too much energy, which has to be balanced by active cooling or heating. Cooling requirements, in particular, have soared recently. Emerging technologies based on thermochromics and/or electrochromics can regulate the inflow of visible light and solar energy between widely separated limits and yield better energy efficiency than static solutions. Thermochromic thin layers, based on vanadium dioxide, transmit less infrared solar radiation at high temperature than at low temperature. Electrochromic multilayer structures, normally based on thin films of tungsten oxide and nickel oxide, can regulate the transmittance of visible light and solar energy when a low-voltage is applied for a short time in order to move charge between the two oxide films. Importantly, the new fenestration technologies can improve indoor comfort. This brief review covers thermochromics and electrochromics and emphasizes that they are keys to a new paradigm for energy efficient buildings.

Keywords: Electrochromics; Thermochromics; Energy efficiency; Buildings; Oxide thin films

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1. Introduction

The atmospheric content of carbon dioxide has risen from ~315 ppm at the end of the 1950s to ~400 ppm in 2014, and the rate of increase has almost tripled [1]. The increasing amount of CO_2 is mainly due to the burning of coal, oil and gas; it is believed to have important consequences for life on Earth [2]. Clearly drastic measures must be taken in order to decarbonize the energy sector. Buildings are then of particular interest since they are responsible for 30–40% of the global use of primary energy [3].

Energy savings in buildings is a mostly untapped resource for CO_2 abatement [4]. A large number of "green" technologies, often with nanostructural features, can be employed [5] and energy efficient fenestration is particularly interesting. Frequently glazings let in or out too much energy with accompanying demands for active cooling and heating, and it is evident that "smart windows" with variable throughput of solar energy and visible light can lower the energy use. These windows employ chromogenic materials [6,7], specifically those with electrochromic (denoted EC and responding on electrical voltage or current) or thermochromic (denoted TC and changing with temperature) properties.

This paper surveys thermochromics and electrochromics. Both types of materials were proposed for glazings many years ago: TC materials in 1986/1987 by Jorgenson and Lee [8] and Babulanam *et al.* [9], and EC materials in 1984 by Lampert [10] and by Svensson and Granqvist [11]. EC-based fenestration is most advanced at present (2015), and products are currently being used in innovative buildings [12–15]; they achieve energy efficiency [16–18] as well as enhanced indoor comfort [19,20] and financial benefits. TC-based fenestration is not yet commercially available, but thermochromics has progressed very well recently and may be getting close to practical implementation [21–24]. The present brief survey, which is an abridged update of a recent review by the author [25] gives the essentials for TC- and EC-based fenestration and surveys some recent advances.
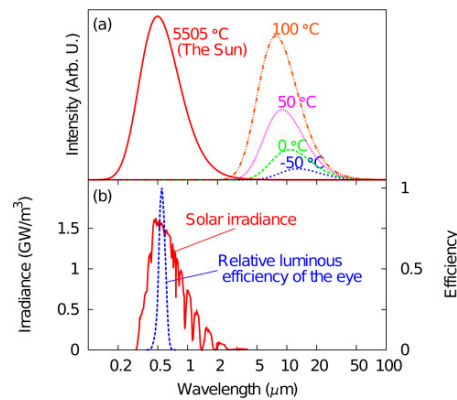

Fig. 1. Upper panel shows blackbody spectra for five temperatures (including the sun's surface temperature). Lower panel illustrates a typical solar irradiance spectrum during clear weather and at sea level, and the sensitivity of the light-adapted human eye.

A few background facts about visible light (luminous radiation), solar irradiance and thermal radiation should be provided, and Fig. 1 shows the basics: Thermal radiation, in panel (a), is given by blackbody curves (shown for four temperatures) multiplied by an empirical emittance that is less than unity; this radiation is at $\lambda > 2$ μm, where λ is wavelength. Solar irradiation onto the atmospheric envelope corresponds approximately to blackbody-like radiation from the sun's surface and lies at $0.2 < \lambda < 3$ μm. At ground level, the irradiation is typically the one shown in Fig. 1(b). Visible light is governed by the luminous efficiency of the human eye, which is represented by a bell-shaped curve for $0.4 < \lambda < 0.7$ μm with a peak at $\lambda = 0.55$ μm. Quantitative data on luminous (lum) and solar (sol) transmittance, denoted by T_{lum} and T_{sol}, are given by:

$$T_{lum,sol} = \int d\lambda \varphi_{lum,sol}(\lambda) T(\lambda) / \int d\lambda \varphi_{lum,sol}(\lambda) \tag{1}$$

where $T(\lambda)$ is spectral transmittance, φ_{lum} is the sensitivity of the light-adapted human eye [26] and φ_{sol} is the solar irradiance when the sun stands 37° above the horizon (known as "air mass 1.5") [27]. Analogous expressions can be used for reflectance R.

2. Thermochromics: Materials and devices

2.1. Vanadium dioxide coatings

Thermochromic materials are conveniently introduced by examining their electrical properties [8]. Abrupt changes in the conductivity, sometimes by several orders of magnitude, take place at well-defined values of a "critical" temperature τ_c and indicate reversible rearrangements in the crystal structure. Vanadium dioxide, VO_2, is of particular interest since $\tau_c \approx 68$ °C is not vastly different from room temperature. Switching occurs between a low-temperature monoclinic phase with semiconducting properties and high infrared transmittance and a high-temperature rutile phase with metallic-like conductivity and infrared reflectance. The physical nature of the metal–insulator transition has been much debated in the scientific literature.

VO_2 is the most promising of today's known materials and may be the basis for practically useful TC glazings. Its thermochromism was reported already in 1959 [28], and no alternative material is known today, especially when one considers that it must be "simple" enough to allow practical coating production on a huge scale. It is hardly surprising that VO_2 has attracted much attention for many years [9,21–24,29,30].
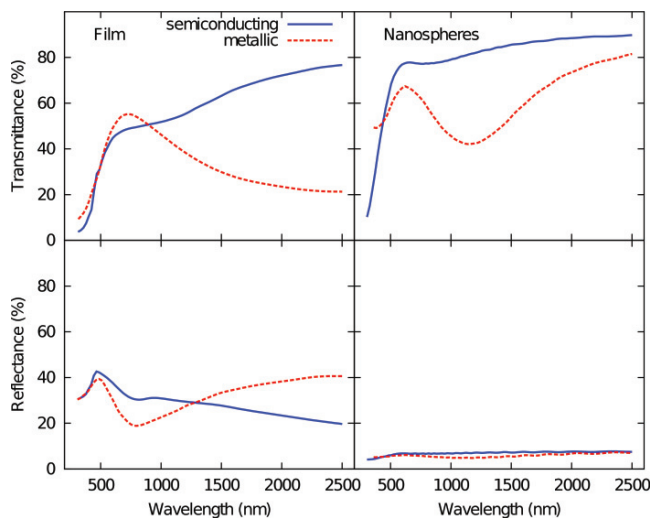

Fig. 2. Spectral transmittance (upper panels) and reflectance (lower panels) for a 50-nm-thick coating of VO_2 (left-hand panels) and for a layer being a dilute dispersion of VO_2 nanospheres, with an equivalent VO_2 thickness of 50 nm, in a medium characteristic of transparent glass and polymer.

Fig. 2 illustrates the most significant optical properties of VO_2-based materials. Left-hand panels report $T(\lambda)$ (upper) and $R(\lambda)$ (lower) for 50-nm-thick VO_2 coatings in the wavelength range for solar irradiance, and it is apparent that $T(\lambda)$ is much larger in the semiconducting state than in the metallic state—*i.e.*, below and above τ_c, respectively—when $\lambda > 1$ μm. The difference in $T(\lambda)$ between low and high temperature grows for increasing wavelength. Obviously this kind of variation in $T(\lambda)$ is the desired one, at least in principle, and a glazing with a TC coating of VO_2 lets through more energy at low temperature than at high temperature [22–24,31,32]. Fig. 2 also shows that the corresponding curve for $R(\lambda)$ increases monotonically towards long wavelengths for the metallic state, which is to be expected for a free-electron-like material. Right-hand panels in Fig. 2 refer to nanoparticles of VO_2 and are discussed later.

2.2. Towards practically useful VO$_2$-based coatings for glazings

We now examine $T(\lambda)$ for the VO$_2$ coating, shown in Fig. 2, in some detail. It is straight-forward to identify three challenges for practical implementation of these coatings on glazings, as done recently by Li *et al.* [29]:

- the shift between the semiconducting and metallic states occurs at ~68 °C, which obviously is too high for buildings,
- the visible transmittance is only ~40%, which is too small for most practical glazings; clearly the coating would be more transparent if it were thinner than 50 nm, but such coatings show lowered solar energy transmittance modulation between the semiconducting and metallic states, and
- the transmittance modulation is strong only for wavelengths where solar irradiation is rather weak (*cf.* Fig. 1), which limits the solar energy modulation to ~10% which is too small to be of much interest in practice.

These three challenges can be met. The first one is easiest, and replacing some percent of the V atoms with W to make W-doped VO$_2$ coatings can decrease τ_c to room temperature, as is well known for bulk materials as well as thin coatings.

The second challenge is related to unwanted optical absorption at short wavelengths, which is apparent in Fig. 2. This absorption occurs because VO$_2$ has a small optical band gap, and an at least partial solution can be achieved by adding a band gap widening agent such as Mg, as first reported by Mlyuka *et al.* [33]. Zn doping was found recently to have has a similar effect [34], and fluorine incorporation is another possibility [35–37]. The short-wavelength shift in Mg-doped VO$_2$ is definitely caused by band gap widening, as demonstrated in recent experimental [38] and computational [39] studies. The value of τ_c drops in proportion with the Mg content though not as fast as for W addition. T_{lum} in a 50-nm-thick coating increases from 39 to 51% when the Mg doping goes from zero to 7.2% [33].

Coatings to be used in glazings must be durable enough to last for many years without losing their desired performance more than marginally. This requirement needs careful consideration for TC-based glazings since vanadium pentoxide (V$_2$O$_5$), and not VO$_2$, is the thermodynamically stable oxide [40]. However, it was shown recently by Ji *et al.* [41] that sputter deposited over-coatings of Al$_2$O$_3$ can give excellent protection of underlying VO$_2$ and maintain the TC properties for long times at elevated temperature and high humidity.

2.3. Nanothermochromism in composite materials with VO$_2$-based nanoparticles

The limited modulation of T_{sol} between the semiconducting and metallic states in VO$_2$ has been the most persistent challenge for reaching TC glazings of practical interest. However, it was recently discovered by Li *et al.* [42,43] that a layer comprising VO$_2$ nanoparticles, rather than a continuous VO$_2$ coating, can give radical improvements. Calculations have demonstrated that the particle size should be ~20 nm or less in order not to produce optical scattering [44]. Such "nanothermochromism" [42] was introduced in the right-hand panels in Fig. 2, which show $T(\lambda)$ and $R(\lambda)$ for a 5-μm-thick layer of a transparent medium, with properties typical for glass and polymers, containing 1 vol.% of well-dispersed VO$_2$ nanospheres with diameters much smaller than any relevant wavelength. This choice of parameters gives an equivalent VO$_2$ thickness of 50 nm and makes the data for the nanospheres and the continuous coating easily comparable.

It is evident that several important features distinguish the two sets of data:

- the nanosphere-containing material is much more transparent than the corresponding coating,
- the metallic nanoparticles show a distinct transmittance minimum in the $0.7 < \lambda < 1.5$ μm range, which strongly curtails the solar transmittance which is intense at these wavelengths, while the visible optical properties hardly are affected at all, and
- the nanospheres absorb rather than reflect.

The striking transmittance minimum—*i.e.*, absorption maximum—in the infrared is due to plasmon resonance among the free electrons in VO$_2$ and lies at a wavelength which is almost ideally located for solar control (*cf.* Fig. 1). The plasmonic nature of the near-infrared absorption was first discussed by Lopez *et al.* [45]. VO$_2$-based nanoparticles and nanorods can be made by many different chemical and physical techniques, and numerous parameters affect the nanofeatures [46,47].

2.4. Approximate performance limits for thermochromic glazings

It is clear from the discussion above that various combinations of T_{lum} and solar energy modulation ΔT_{sol}, defined as

$$\Delta T_{sol} \equiv T_{sol}(\tau < \tau_c) - T_{sol}(\tau > \tau_c) \tag{2}$$

can be achieved in VO$_2$-based materials. Fig. 3, reproduced from Li *et al.* [23], gives a bird's eye view of today's (2015) state-of-the-art with regard to $T_{lum}(\tau < \tau_c)$ and ΔT_{sol}. We note that T_{lum} does not depend strongly on temperature, and data on $T_{lum}(\tau < \tau_c)$ were chosen only to be specific.

Pure VO$_2$ films give the lowest values of T_{lum} and ΔT_{sol}, but the optical data can be boosted by antireflection (AR) layers. Especially good properties were observed with multilayers of TiO$_2$ and VO$_2$ [48,49]. "Bio-inspired" cone-shaped surfaces represent another possibility to enhance T_{lum} [30]. Mg-containing VO$_2$ films have superior properties, which can be further improved by antireflection. However, the best performance is obtained with VO$_2$ nanoparticles which can give $T_{lum} \approx 60\%$ together with $\Delta T_{sol} > 20\%$. It should be noted that Mg-containing nanoparticles do not give better performance than nanoparticles of pure VO$_2$, the reason being that the addition of Mg leads to an erosion of solar energy modulation that is not balanced by enlarged transmittance at short wavelengths. Some improvements of T_{lum} and ΔT_{sol} might be possible by selecting nanoparticles with optimized shape and orientation [42] and with core–shell structures [43].
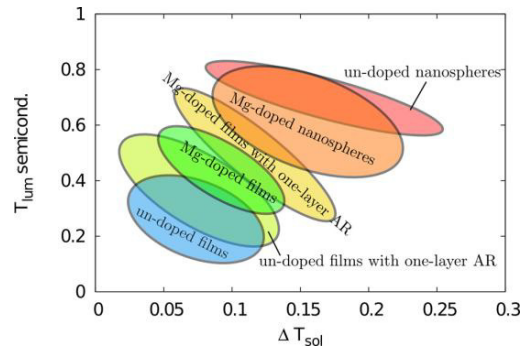

Fig. 3. Schematic performance limits of various VO$_2$-based materials for thermochromic glazings. From Li *et al.* [23].

Considering practical implementation in TC glazings, VO$_2$-based coatings can be applied in insulated glass units (IGUs) in the same way as for today's technology which employs metal-based coatings with static properties [5]. TC nanoparticles—perhaps with protective shells surrounding VO$_2$ cores—might be dispersed in polymers and used for glass lamination, as sketched in Fig. 4.

3. Electrochromics: Materials, devices and glazings

EC glazings are presently (2015) making their appearance on a limited scale and are expected to become more common in the future [12–14,50]. They can give energy efficiency along with indoor comfort, as shown several times [16–19,51–53].

3.1. General device design

Fig. 5 shows the operating principle of an EC device [54,55]. A transparent electrolyte—for example an ion-conducting polymer or an inorganic ion conductor—is positioned in the center and joins two nanoporous oxide films, typically of W oxide and Ni oxide [56,57]. This three-layer stack is located between transparent electrical

conductors which can be of several types and based on coinage metals, wide band gap oxide semiconductors, nanowires of carbon or coinage metals, graphene, certain organics, or hybrids combining two or more of these types of materials [13,58]. Thin films of In_2O_3:Sn [59], known as ITO, are commonly used. Application of a voltage between the transparent conductors, typically a few volts DC, shuttles charge between the W oxide and Ni oxide.

The function of an EC device is similar to that of an electrical battery with W oxide and Ni oxide serving as cathode and anode, respectively, and it is instructive to regard the EC device as an electrical battery with optical absorption depending on charging state. The device absorbs across the solar spectrum when the mobile charge resides in the W oxide and is transparent when this charge is in the Ni oxide. The optical properties can stay unaltered—dark, bleached or intermediary—for days under open-circuit conditions, which allows highly energy-efficient operation. The optical changes are gradual and take place at a rate that depends on the size of the device. An area of a few square centimeters may darken and bleach in seconds, whereas the response time can be tens of minutes for a large glazing. Time constants of this latter order of magnitude may be desirable since they allow the eye to light-adapt, and the optical modulation of the glazing therefore is unlikely to be perceived as disturbing.
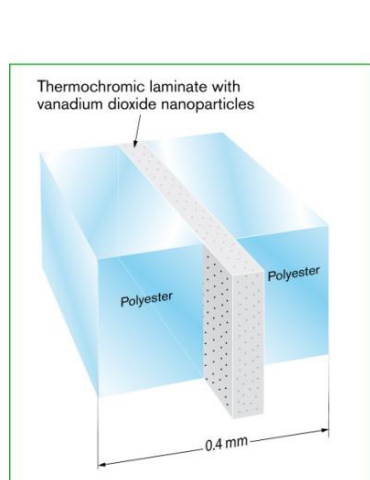

Fig. 4. Construction principles for lamination foil incorporating thermochromic nanoparticles.
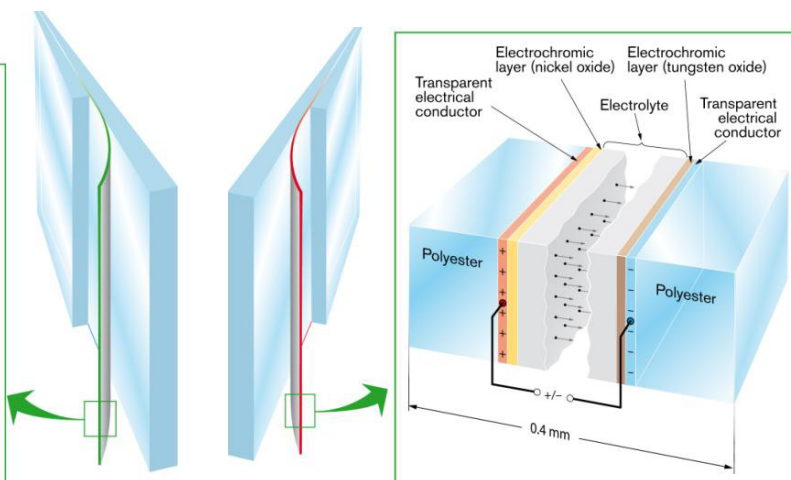
Fig. 5. Construction principle for an electrochromic foil-type device implemented as a laminate between glass panes. From Bayrak Pehlivan *et al.* [55].

3.2. How does an electrochromic device work?

Electrochromism takes place in a number of oxides that serve as mixed conductors for electron and ions [54]. Tungsten oxide is a particularly well studied EC material which comprises corner-sharing octahedral structural units, each with a centrally positioned W atom surrounded by six oxygen atoms so that the overall composition is WO_3. The EC oxides have a propensity for oxygen deficiency, which implies that some of the octahedra are edge-sharing. This atomic arrangement yields extended three-dimensional "tunnel structures" between the octahedra. The "tunnels" are wide enough to be able to easily transport mobile ions in an electrical field. The most suitable mobile species are hydrogen ions ("protons", H^+) and lithium ions (Li^+). The nanoporous nature of the oxide, and therefore its ability to transport ions, can be improved if it is strongly disordered on a length scale larger than that of the individual octahedra. Such nanostructures can be accomplished by a careful choice of parameters for making EC coatings; in the case of reactive sputtering, nanoporosity demands higher gas pressures in the sputter plasma and larger target–substrate separations than in conventional sputtering.

Ion insertion into tungsten oxide (WO_3) is accompanied by an inflow of charge-balancing electrons from the transparent electrodes in the EC device. These electrons change the valency of the W atoms, and some of them are transformed from W^{6+} to W^{5+}. A photon impinging on a W oxide layer can have sufficient energy to transfer an electron between two neighboring tungsten ions (on sites *i* and *j*, say) which can be expressed, schematically, as

$$W_i^{5+} + W_j^{6+} + photon \rightarrow W_i^{6+} + W_j^{5+} \tag{3}$$

This means that the photon's energy is used to transfer an electron while optical absorption occurs. The intensity of the overall absorption in the W oxide is determined by the density of inserted electrons, which in its turn is proportional to the charging state. A more detailed and quantitative description of the optical absorption can be formulated by considering the explicit role of small polarons [60,61].

W oxide becomes optically absorbing under charge insertion, and oxides of Mo, Ti and Nb are alternatives, although with lower optical efficiency. There are also oxides that darken under charge extraction, such as Ni oxide and Ir oxide. Ni is much more abundant in the earth's crust, so clearly Ni oxide is preferred at least for large-scale applications.

It is clearly advantageous to have EC devices that combine oxides of the two types, for example W oxide and Ni oxide, since charge transfer from Ni oxide into W oxide darkens both of them, while charge transfer in the opposite direction bleaches them both [57]. This device design was shown in Fig. 5 above.

3.3. Six hurdles for device manufacturing, and two practical device types

EC technology is not easy, and six hurdles have been identified [12,13,62,63]. All of them need to be overcome in order to have a functioning device. The list can be given as follows:

- the EC coatings need to be nanoporous over their full areas, which may require non-standard deposition technology,
- the transparent conductors must show a good combination of optical transparency and electrical conductivity, which is particularly challenging for heat-sensitive (polymer) substrates,
- charge insertion/extraction and charge balancing must be handled in an industrial environment, which may call for special techniques such as ozone exposure [64–66],
- the electrolyte must be transparent, combine high ion conductivity with extremely small electronic conductivity, be durable under solar irradiation and, depending on device design, be a good adhesive,
- long-term cycling durability is necessary, and
- obviously, large scale manufacturing must be possible at a low enough cost.

Fig. 5 is an example of how EC glazings can be implemented in practice. It is possible to start with two flexible polymer foils, for example of polyethylene terephthalate (PET), and coat them with two layers each, which can be conveniently done by roll-to-roll deposition. The thin EC oxide coatings serving as anode and cathode are then connected via the polymer electrolyte, and the complete EC device is employed as a laminate to join two glass panes.

This is not the only way to construct an EC device, however, and another option, that is currently being commercialized, is to apply the full five-layer stack shown in Fig. 5 directly onto the surface of a single glass pane by sequential depositions so as to make a "monolithic" construction. This latter technology must assure that the anodes and cathodes are well separated by a thin layer serving as electrolyte. The five-layer monolithic configuration is delicate and must be protected against mechanical and chemical damage, most conveniently by integrating the coated glass in an insulated glass unit (IGU).

The laminated and the monolithic device designs differ in several ways. The laminated construction allows production of a generic EC foil that can be cut to any size and shape and applied, in principle, to any flat or singly-curved glazing. It therefore separates the EC functionality from the window manufacturing. Lamination may be desirable also for other reasons and can give spall shielding, burglar protection and more. It may even be feasible to incorporate nanoparticles in the laminate in order to achieve infrared absorption or even thermomochromism.

3.4. Some data on foil-based electrochromic devices

Fig. 6 shows optical modulation under extended color/bleach cycling [63]. Left-hand panel shows mid-luminous transmittance for two consecutive color/bleach cycles adjusted so that the transmittance modulation is 55%. For a

240-cm^2-size EC foil device, half of the transmittance range (from point 1 to 2) took ~10 s, 90% of this range (from point 1 to 3) took ~20s, while the full range (from point 1 to 4) took ~30 s. Slower cycling could in principle have yielded a larger modulation span. Right-hand panel of Fig. 6 illustrates typical transmittance modulation of an EC device and shows that the mid-luminous transmittance goes between 17 and 68%. This operation can be extended to many thousands of cycles.
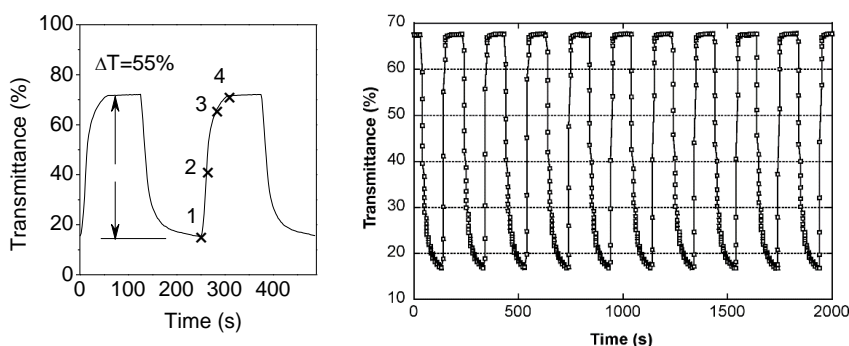

Fig. 6. Mid-luminous transmittance for an electrochromic foil device of the kind shown in Fig. 5. Left-hand panel shows transmittance for two consecutive color/bleach cycles (numbers 1–4 are explained in the main text) for which the modulation span was set to 55%. Right-hand panel shows transmittance modulation under repeated charge insertion/extraction. From Granqvist *et al*. [63].

Color/bleach dynamics is of obvious importance for EC devices. For small constructions, time constants can be as short as a few seconds whereas bigger devices are slower since larger amounts of electrical charge must be inserted/extracted via electrical contacts at one or more of the edges of the device. EC devices may show an "iris effect", *i.e*., the color change is more rapid at the edge than in the center of a device. However, this effect can be counteracted by adequate powering of the EC device. EC foils in practical fenestration are likely to be exposed to ultraviolet irradiation, which can give a photochromic effect that adds to the electrochromism [62,67].

The desired optical modulation span depends on the intended application. In buildings, it may often be suitable to have glazings with large bleached-state transmittance, and antireflective (AR) layers can then be used as long as they do not scatter light too much [62,68]. If glare control is of prime importance, rather than high bleached-state transmittance, it is possible to diminish the colored-state transmittance radically by use of superimposed foils. If, for example, the transmittance is 10% in the dark state for one EC device, then two devices on top of each other yield a transmittance of only ~1%.

Finally, Fig. 7 shows a practical installation of full-size windows with EC-based foil laminated between glass panes by use of standard procedures. Two panes are dark and display strong contrast to the adjacent clear window. The time for going between fully dark and colored states is of the order of ten minutes. No visible haze or other optical defects were apparent.

Fig. 7. Part of an office equipped with electrochromic glazing, with one window in its transparent state and two windows in their dark state.

4. Conclusions and comments

This brief article has surveyed thermochromic and electrochromic glazings for energy efficient buildings. Thermochromics has progressed rapidly during the past few years, and the discovery of new doped VO_2-based oxides has led to more transparent thin films than those used in the past. The realization that nanoparticles of VO_2 offer great performance gains represents a distinct step forward, and thermochromic fenestration may be approaching a state where practical implementation is feasible.

Electrochromic glazings have shown a gradual evolution during many years. These glazings have sometimes been portrayed as inherently expensive. However, important steps that have been taken recently, both in Industry and Academia, which have led to solutions that are sound as regards technical performance, cost and business model. There are many electrochromic materials that can be used in devices, but combinations of W-oxide-based and Ni-oxide-based films are most advanced. Mixed oxides are likely to be used increasingly in the future. An interesting recent development has shown that degraded EC films, both based on W oxide and Ti oxide, can be rejuvenated by a galvanostatic treatment [69,70].

Thermochromic and electrochromic glazings offer possibilities to improve energy efficiency as well as indoor comfort in buildings. These improvement is not only incremental but can lead to a new paradigm for buildings, which are no longer static entities in the built environment but areable to adapt to the dynamic needs. Furthermore, the emerging possibilities with thermochromic and electrochromic foils may be implemented in innovative membrane architecture and offer attractive environments that blur the zone between indoors and outdoors.

Acknowledgements

References

[1] NOAA, U.S. Department of Commerce, National Oceanic and Atmospheric Administration, Earthscan System Research Laboratory, Global Monitoring Division, http://www.esrl.noaa.gov/gmd/ccgg/trends/index.html
[2] Intergovernmental Panel on Climatic Change (2014), https://www.ipcc.ch
[3] UNEP, Buildings and Climate Change: Challenges and Opportunities, United Nations Environmental Programme, Paris, France, 2007.
[4] B. Richter, D. Goldston, G. Crabtree, L. Glicksman, D. Goldstein, D. Greene, D. Kammen, M. Levine, M. Lubell, M. Savitz, D. Sperling, F. Schlachter, J. Scofield, J. Dawson, Rev. Mod. Phys. 80 (2008) S1.
[5] G.B. Smith, C.G. Granqvist, Green Nanotechnology: Solutions for Sustainability and Energy in the Built Environment (CRC Press, Boca Raton, FL, USA, 2010)
[6] C.G. Granqvist, Crit. Rev. Solid State Phys. Mater. Sci. 16 (1990) 291.
[7] C.M. Lampert, C.G. Granqvist, editors, Large-Area Chromogenics: Materials and Devices for Transmittance Control, SPIE Institutes for Advanced Optical Technologies, Vol. 4 (SPIE Optical Engineering Press, Bellingham, WA, USA, 1990).
[8] G.V. Jorgenson, J.C. Lee, Sol. Energy Mater. 14 (1986) 205.
[9] S.M. Babulanam, T.S. Eriksson, G.A. Niklasson, C.G. Granqvist, Sol. Energy Mater. Sol. Cells 16 (1987) 347.
[10] C.M. Lampert, Sol. Energy Mater. 11 (1984) 1.
[11] J.S.E.M. Svensson, C.G. Granqvist, Sol. Energy Mater. 11 (1984) 29.
[12] C.G. Granqvist, Sol. Energy Mater. Sol. Cells 99 (2012) 1.
[13] C.G. Granqvist, Thin Solid Films 564 (2014) 1.
[14] B.P. Jelle, A. Hynd, A. Gustavsen, D. Arasteh, H. Goudey, R. Hart, Sol. Energy Mater. Sol. Cells 96 (2012) 1.
[15] B.P. Jelle, Sol. Energy Mater. Sol. Cells 116 (2013) 291.
[16] A. Azens, C.G. Granqvist, J. Solid State Electrochem. 7 (2003) 64.
[17] E.S. Lee, S.E. Selkowitz, R.D. Clear, D.L. DiBartolomeo, J.H. Klems, L.L. Fernandes, G.J. Ward, V. Inkarojrit, M. Yazdanian, Advancement of Electrochromic Windows (California Energy Commission, PIER, Publication number CEC-500-2006-052, 2006).
[18] M. Pittaluga, in F. Pacheco-Torgal, J. Labrincha, L.F. Cabeza, C.G. Granqvist, editors, Eco-Efficient Materials for Mitigating Building Cooling Needs: Design, Properties and Applications (Woodhead, Cambridge, UK, 2014).
[19] R.D. Clear, V. Inkarojrit, E.S. Lee, Energy Buildings 38 (2006) 758.
[20] M. Zinzi, Building Environment 41 (2006) 1262.
[21] Y. Gao, H. Luo, Z. Zhang, L. Kang, Z. Chen, J. Du, M. Kanehira, C. Cao, Nano Energy 1 (2012) 221.
[22] S. Hoffmann, E.S. Lee, C. Clavero, Sol. Energy Mater. Sol. Cells 123 (2014) 6.
[23] S.-Y. Li. G.A. Niklasson, C.G. Granqvist, J. Appl. Phys. 115 (2014) 053513.
[24] M.E.A. Warwick, R. Binions, J. Mater. Chem. A 2 (2014) 3275.
[25] C.G. Granqvist, J. Vac. Sci. Technol. B 32 (2014) 060801.

[26] G. Wyszecki, W.S. Stiles, Color Science: Concepts and Methods, Quantitative Data and Formulae, 2nd ed. (Wiley, New York, NY, USA, 2000).
[27] ASTM G173-03 Standard Tables of Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on a 37° Tilted Surface, in Annual Book of ASTM Standards (American Society for Testing and Materials, Philadelphia, PA, USA, 2008), Vol. 14.04; http://rredc.nrel.gov/solar/spectra/ am1.5
[28] F.J. Morin, Phys. Rev. Lett. 3 (1959) 34.
[29] S.-Y. Li, G.A. Niklasson, C.G. Granqvist, Thin Solid Films 520 (2012) 3823.
[30] A. Taylor, I. Parkin I, N. Noor, C. Tummeltshammer, M.S. Brown, I. Papakonstantinou, Opt. Expr. 21 (2013) A750.
[31] M. Saeli, C. Piccirillo, I.P. Parkin, R. Binions, I. Ridley, Energy Buildings 42 (2010) 1666.
[32] M. Saeli, C. Piccirillo, I.P. Parkin, I. Ridley, R. Binions, Sol. Energy Mater. Sol. Cells 94 (2010) 141.
[33] N.R. Mlyuka, G.A. Niklasson, C.G. Granqvist, Appl. Phys. Lett. 94 (2009) 171909.
[34] M. Jiang, S. Bao, X. Cao, Y. Li, S. Li, H. Zhou, H. Luo, P. Jin, Ceram. Int. 40 (2014) 6331.
[35] K.A. Khan, C.G. Granqvist, Appl. Phys. Lett. 55 (1989) 4.
[36] W. Burkhardt, T. Christmann, S. Franke, W. Kriegseis, D. Meister, B.K. Meyer, W. Niessner, D. Schalch, A. Scharmann, Thin Solid Films 402 (2002) 226.
[37] P. Kiri, M.E.A. Warwick, I. Ridley, R. Binions, Thin Solid Films 520 (2011)1363.
[38] S.-Y. Li, N.R. Mlyuka, D. Primetzhofer, A. Hallén, G. Possnert , G.A. Niklasson, C.G. Granqvist, Appl. Phys. Lett. 103 (2013) 161907.
[39] S. Hu, S.-Y. Li, R. Ahuja, C.G. Granqvist, K. Hermansson, G.A. Niklasson, R.H. Scheicher, Appl. Phys. Lett. 101 (2012) 201902.
[40] H.A. Wriedt, Bull. Alloy Phase Diagr. 10 (1989) 271.
[41] Y.-X. Ji, S.-Y. Li, G. A. Niklasson, C.G. Granqvist, Thin Solid Films 562 (2014) 568.
[42] S.-Y. Li, G.A. Niklasson, C.G. Granqvist, J. Appl. Phys. 108 (2010) 063525.
[43] S.-Y. Li, G.A. Niklasson, C.G. Granqvist, J. Appl. Phys. 109 (2011) 113515.
[44] K. Laaksonen, S.-Y. Li, S.R. Puisto, N.K.J. Rostedt, T. Ala-Nissila, C.G. Granqvist, R.M. Nieminen, G.A. Niklasson, Sol. Energy Mater. Sol. Cells 130 (2014) 132.
[45] R. Lopez, T.E. Haynes, L.A. Boatner, L.C. Feldman, R.F. Haglund, Jr., Opt. Lett. 27 (2002) 1327.
[46] S.-Y. Li, K. Namura, M. Suzuki, G.A. Niklasson, C.G. Granqvist, J. Appl. Phys. 114 (2013) 033516.
[47] J. Montero, Y.-X. Ji, S.-Y. Li, G.A. Niklasson, C.G. Granqvist, J. Vac. Sci. Technol. B 33 (2015) 031805.
[48] N.R. Mlyuka, G.A. Niklasson, C.G. Granqvist, Phys. Status Solidi A 206 (2009) 2155.
[49] Z. Chen, Y. Gao. L. Kang, J. Du, Z. Zhang, H. Luo, H. Miao, G. Tan, Sol. Energy Mater. Sol. Cells 95 (2013) 2677.
[50] R. Baetens, B.P. Jelle, A. Gustavsen, Sol. Energy Mater. Sol. Cells 94 (2010) 87.
[51] E.S. Lee, D.L. DiBartolomeo, S.E. Selkowitz, Energy Buildings 38 (2006) 30.
[52] E.S. Lee, E.S. Claybaugh, M. LaFrance, Energy Buildings 47 (2012) 267.
[53] P.F. Tavares, A.R. Gaspar, A.G. Martins, F. Frontini, Energy Policy 67 (2014) 68.
[54] C.G. Granqvist, Handbook of Inorganic Electrochromic Materials (Elsevier, Amsterdam, The Netherlands, 1995).
[55] İ. Bayrak Pehlivan, R. Marsal, E. Pehlivan, E.L. Runnerstrom, D.J. Milliron, C.G. Granqvist, G.A. Niklasson, Sol. Energy Mater. Sol. Cells 126 (2014) 241.
[56] A. Azens, G. Vaivars, M. Veszelei, L. Kullman, C.G. Granqvist, J. Appl. Phys. 89 (2001) 7885.
[57] G.A. Niklasson, C.G. Granqvist, J. Mater. Chem. 17 (2007) 127.
[58] C.G. Granqvist, Sol. Energy Mater. Sol. Cells 91 (2007) 1529.
[59] I. Hamberg I, C.G. Granqvist, J. Appl. Phys. 60 (1986) R123.
[60] V.V. Bryksin, Fiz. Tverd. Tela (Leningrad) 24 (1982) 1110 [Sov. Phys. Solid State 24 (1982) 627].
[61] C.A. Triana, C.G. Granqvist, G.A. Niklasson, J. Appl. Phys. 118 (2015) 024901.
[62] C.G. Granqvist, S. Green, E.K. Jonson, R. Marsal, G.A. Niklasson, A. Roos, Z. Topalian, A. Azens, P. Georén, G. Gustavsson, R. Karmhag, J. Smulko, L.B. Kish, Thin Solid Films 516 (2008) 5921.
[63] C.G. Granqvist, S. Green, G.A. Niklasson, N.R. Mlyuka, S. von Kræmer, P. Georén, Thin Solid Films 518 (2010) 3046.
[64] A. Azens, L. Kullman, C.G. Granqvist, Sol. Energy Mater. Sol. Cells 76 (2003) 147.
[65] G.H. Aydogdu, D. Ruzmetov, S. Ramanathan, J. Appl. Phys. 108 (2010) 113702.
[66] F. Lin, D. Nordlund, T.-C. Weng, R.G. Moore, D.T. Gillaspie, A.C. Dillon, R.M. Richards, C. Engtrakul, ASC Appl. Mater. Interfaces 5 (2013) 301.
[67] Y. Zhang, S.-H. Lee, A. Mascarenhas, S.K. Deb, Appl. Phys. Lett. 93 (2008) 203508.
[68] A. Jonsson, A. Roos, E.K. Jonson, Sol. Energy Mater. Sol. Cells 94 (2010) 992.
[69] R.-T. Wen, C.G. Granqvist, G.A. Niklasson. Nat. Mater. DOI:10.1038/NMAT4368 (2015).
[70] R.-T. Wen, G.A. Niklasson, C.G. Granqvist, to be published.