CHROMOGENIC COATINGS FOR GLAZING: TOWARD A NEW PARADIGM FOR BUILDINGS

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The world’s population is expected to increase 50% by 2100[1] and more than 70% of all people will live in urban areas by 2050[2]. Consequently, huge numbers of new and refurbished buildings will be needed in the future, requiring a great deal of energy to construct and operate. The total energy expenditure of buildings is large and growing. In the U.S., for example, it was 34% in 1980 and increased to 41% in 2010[3]. Today’s energy production is mainly based on fossil fuels and is expected to remain so for decades. Burning fossil fuels leads to increasing amounts of carbon dioxide in the atmosphere—the concentration has grown from ~315 ppm in the 1950s and now regularly exceeds 400 ppm[4]—leading to harmful effects, such as climate change and rising sea levels. Clearly there is an urgent need for improved buildings that use less energy and are sustainable. Glazing in windows and glass facades are particularly important and more often than not they let out or in too much energy so that heating or cooling is required; this is a major reason why buildings are energy guzzlers. From a strictly energy-related point of view, it makes sense to remove the glazing altogether, or at least to make them very small. However, this is highly undesirable from a human perspective because precious visual indoor-outdoor contact, as well as daylight, are subsequently lost.

So what can be done? One important development is “smart” or “intelligent” glazing that adapts to varying ambient conditions—to let in solar energy when there is a need for such, to avoid solar inflow under other conditions, to eliminate glare so that floor areas can be used rationally—and to do these things while ensuring that the glazing can be looked through easily. Such glazing exists today and includes coatings of chromogenic materials with optical properties that can be altered by an external stimulus. The significance of these materials for glazing was pointed out in the late 1980s, and the term “chromogenic” was coined[5]. Two types of chromogenic coatings will be discussed here: thermochromic with strongly temperature-dependent optical transmittance and electrochromic, which allow electrical control of the transmittance. Electrochromic glazing is produced on a small but growing industrial scale and is currently being installed mainly in commercial buildings in the U.S. and Europe[6].
**Thermal Radiation, Solar Energy, and Visible Light**

Chromogenic coatings are able to control the throughput of electromagnetic radiation of different wavelengths, and it is important to understand what wavelengths apply to thermal radiation (heat), solar energy, and visible light (Fig. 1).

Thermal radiation, illustrated in Fig. 1(a), is governed by blackbody curves—reported for four temperatures—multiplied by a materials-specific emittance less than unity. Clearly this radiation lies at wavelengths longer than 2 μm for normal ambient temperatures. Solar radiation outside the Earth’s atmosphere is approximately blackbody-like if the sun’s surface temperature is taken to be 5505°C and falls in the 0.2–3.0 μm range. At ground level, and for typical clear-weather conditions, this radiation is typically the one in Fig. 1(b), where the narrow minima are caused by absorption due to molecules in the air. Visible light is represented by the bell-shaped curve in Fig. 1(b), which extends over the 0.4–0.7 μm wavelength range and is peaked at 0.55 μm. Quantitative data on visible (luminous) and solar transmittance, referred to as $T_{\text{lum}}$ and $T_{\text{sol}}$, are obtained by integration over the eye’s spectral sensitivity and over a typical solar irradiance spectrum, respectively. Thermochromic coatings mostly affect the solar energy performance, while their luminous performance is rather temperature-independent. The solar energy modulation ($\Delta T_{\text{sol}}$) is quantified as the difference of $T_{\text{sol}}$ below and above a certain temperature where the change takes place.

**Thermochromic Coatings**

There are many thermochromic materials, but only a few are appropriate for glazing, especially oxide-based coatings and nanoparticle composites\(^7,8\). Vanadium dioxide (VO\(_2\)) is of special interest and exhibits an abrupt and reversible property change at about ~68°C, i.e., not very far from room temperature. The transformation takes place between a low-temperature semiconducting phase with small absorption in the 0.7–3.0 μm range—and therefore high infrared transmittance—as a thin coating—and a high-temperature metal-like phase with large infrared reflectance.

Figure 2 summarizes the most important optical properties of VO\(_2\) coatings and nanoparticle composites. The left-hand panels illustrate spectral transmittance (upper) and reflectance (lower) for 50-nm thick VO\(_2\) coatings on glass in the wavelength range for solar radiation. Transmittance for wavelengths larger than 1 μm is much greater in the semiconducting low-temperature state than in the metallic high-temperature state, which is clearly desirable for glazing in buildings. The figure also illustrates that the spectral reflectance increases monotonically toward long wavelengths for the metallic state. Reflectance seems to level off at ~40% for the 50-nm-thick coating, but will be higher in a thicker coating.

The spectra in the left-hand panels of Fig. 2 are interesting, but the performance is not good enough for practical implementation in glazing. Nevertheless, the properties of VO\(_2\) coatings are sufficiently close to the desired ones that it is meaningful to make a concerted attempt to improve this material\(^9\). In particular, a number of challenges need
consideration, and great strides have been taken to address them during the last decade. These challenges include:

- The property change in VO$_2$ is at ~68°C, which is too high for buildings, but this temperature can be decreased to room temperature by replacing some percent of the vanadium atoms with tungsten atoms[9].

- $T_{	ext{lum}}$ is only ~40% and too low for most glazing ($T_{	ext{lum}}$ would be higher for a thinner coating but consequently $\Delta T_{\text{sol}}$ becomes minuscule)—which can be alleviated by introducing some magnesium[10,11].

- Temperature-dependent transmittance modulation is large mainly for wavelengths at which solar irradiation is weak, limiting $\Delta T_{\text{sol}}$ to ~10%. However, the situation can be significantly improved by using nanoparticles of VO$_2$ rather than uniform coatings[12], as is apparent from the right-hand panels in Fig. 2. The most striking feature of the nanoparticles’ transmittance data is the broad minimum centered at a wavelength of ~1.2 μm, which appears in the metallic state but is absent in the semiconducting state. This minimum corresponds to an absorptance peak and is caused by the electrons responsible for the electrical conduction in the metallic state of VO$_2$.

- VO$_2$ is not stable and further oxidation yields non-thermochromic V$_2$O$_5$. However, VO$_2$ can be passivated by a thin overcoating of alumina, for example[13].

VO$_2$-based coatings and nanoparticle composites can be made by many techniques, and Fig. 3 shows preliminary data for a VO$_2$–SiO$_2$ composite prepared by reactive dc magnetron sputtering[14]. Scanning electron microscopy images (left) displayed rounded nanoparticles with sizes of 0.1–0.3 μm, and energy-dispersive x-ray data indicated that these particles were vanadium-rich.

Various combinations of $T_{\text{lum}}$ and $\Delta T_{\text{sol}}$ can be obtained in VO$_2$-based materials. Figure 4 illustrates the current state of the art[15]; ($T_{\text{lum}}$ is approximately the same in the semiconducting and metallic states). Thin coatings of pure VO$_2$ give the lowest magnitudes of $T_{\text{lum}}$ and $\Delta T_{\text{sol}}$, but the optical performance can be boosted by antireflection (AR) layers. Magnesium-containing VO$_2$ coatings have improved properties, which can be further enhanced by AR layers. However, optimum performance can be reached with VO$_2$ nanoparticles which, for example, can give $T_{\text{lum}} \approx 60\%$ and $\Delta T_{\text{sol}} > 20\%$. Perhaps surprisingly, magnesium-containing nanoparticles are not superior to nanoparticles of pure VO$_2$.
Electrochromic Coatings and Devices

Electrochromics is conveniently understood from a device perspective and Fig. 5 shows a generic design[16,17]. Five functional layers are either positioned between two substrates as a laminate (illustrated) or are backed by a single substrate. Glass is commonly used as a substrate but polymer is an alternative, and flexible films of polyethylene terephthalate (PET) allow manufacturing by low-cost roll-to-roll technology[17].

The central part of the device conducts ions but is an insulator for electrons. It can be a polymer electrolyte, preferably with adhesive properties, or it can be a transparent inorganic ion-conducting coating. In most cases, the ions are protons (H⁺) or lithium (Li⁺). The ion conductor is in contact with an electrochromic coating that conducts both ions and electrons. Tungsten oxide is the primary example and is widely used in today’s electrochromic glazing[6]. The other side of the pure ion conductor is in contact with an ion-storage coating, which also is a conductor for ions as well as electrons. The entire three-layer stack is positioned between two coatings of transparent electrical conductors, which in principle can be of several different types[6,18], but in practice often consists of an oxide based on tin or indium. Applying a voltage between the two transparent conductors leads to ion transport between the electrochromic coating and the ion-storage coating, and the displaced charge is balanced by electrons inserted into or extracted from the electrochromic coating and the ion-storage coating via the transparent conductors. These electrons are the actual cause of the optical changes in the electrochromic coating. If the voltage is reversed—or sometimes by short-circuiting—one recovers the original optical performance.

Electrochromic devices may have open-circuit memory and their coloration can be stopped at any intermediate level between fully colored and fully bleached. The voltage for transporting the ions is in the order of a few volts dc, which allows facile powering for example by solar cells[19]. The electrochromic device can be described as an electrical battery with a charge state that corresponds to optical absorption. Neither electrochromic glazing nor batteries can change their properties instantaneously; a full-size electrochromic glazing may take minutes or more to transition between fully colored and bleached states.

It is useful to have an ion-storage coating with optical properties that are complementary to those of the primary electrochromic coating. Devices combining tungsten-oxide-based and nickel-oxide-based coatings are particularly interesting[20] and are employed in several types of electrochromic glazing[6]. Moving charge from nickel oxide to tungsten oxide makes both coatings dark and both coatings bleach when charge is returned. This leads to a rather neutral color, as is desirable for most electrochromic glazing. Figure 6 shows spectral transmittance data for an electrochromic device such as that in Fig. 5. If the colored-state appearance is not appropriate, it is possible to improve it by use of mixed oxides. Figure 7 indicates that coatings incorporating tungsten, titanium, and molybdenum are able to achieve approximate color neutrality[21]. These coatings have excellent durability as a consequence of their titanium content. The electrolyte in a laminated electrochromic glazing can be functionalized by well-dispersed electrically conducting nanoparticles in order to lower $T_{Sol}$ without affecting $T_{Lum}$ more than marginally, if this property is desired[22].

Fig. 5—Principle construction of a foil-based electrochromic device. Arrows indicate ion movement when a voltage is applied between the transparent electrical conductors. The entire film construction can be used to laminate glass panes, as shown in the left-hand side.

Fig. 6—Spectral transmittance of an electrochromic film device, including a glass substrate, shown under different levels of injected charge, following the construction in Fig. 5.

Fig. 7—CIE 1931 Color space chromaticity diagram (x,y). Color coordinates for electrochromic coatings with their respective compositions are shown. Wavelengths (nm) are indicated along the circumference of the colored area.
The electrochromic film shown in Fig. 5 can be manufactured by magnetron sputtering using a roll-to-roll coating chamber, combined with continuous lamination of tungsten-oxide-coated and nickel-oxide-coated PET by use of a polymer electrolyte, and with subsequent cross-linking of this electrolyte. The end product is large flexible sheets for glass lamination. Sheets can be cut to any size and shape and electrical contacts can be applied. Figure 8 depicts an installation of full-size windows with electrochromic film laminated between glass panes. Two of the panes are dark and look distinctly different from the adjacent clear window. The time for going from fully dark to fully colored states is approximately 10 minutes.

Conclusion

Due to recent research, oxide-based thermochromic glazing now have properties that make them very interesting for buildings, and electrochromic glazing are already proving themselves on the market. These developments lead to buildings with a number of desired features, such as improved energy efficiency and indoor comfort. Chromogenic technologies, such as those discussed here, may lead to a paradigm shift in the concept of a building[23], which no longer is static and in need of vast amounts of energy to achieve an adequate indoor environment, but instead is dynamic and able to adapt to varying ambient conditions.

References


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Claes-Göran Granqvist is emeritus professor of Solid State Physics at the Department of Engineering Sciences, the Ångström Laboratory, Uppsala University, Sweden, since 1993. Granqvist’s research during the past several years has covered materials, mostly thin surface coatings, for energy efficiency and solar energy applications particularly in the built environment. Variable-transmittance “smart” windows are one example, which also forms the basis of ChromoGenics Sweden AB, a company founded by Granqvist and his collaborators and presently employs 20 people. Other research interests include nano-science and sensor science. Granqvist has published about 600 scientific papers and many books and proceedings volumes. He is a member of the Royal Swedish Academy of Sciences and the Royal Swedish Academy of Engineering Sciences. For more information, contact Claes Granqvist at claes-goran.granqvist@angstrom.uu.se.

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