Chromogenic smart materials

by Carl M. Lampert

Smart materials cover a wide and developing range of technologies. A particular type of smart material, known as chromogenics, can be used for large area glazing in buildings, automobiles, planes, and for certain types of electronic display. These technologies consist of electrically-driven media including electrochromism, suspended particle electrophoresis, polymer dispersed liquid crystals, electrically heated thermotropics, and gaschromics.

This review will look at each chromogenic technology, its characteristics, and potential applications set in the context of other competitive switchable technologies. It will cover the applications and market potential for a variety of media including mirror, glazing, and display products, such as low information content displays for banners and labels. The physics, electrochemistry, device design, and materials will be detailed. Performance comparisons will be made between several switchable technologies.

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Introduction to chromogenics

The chromogenic family of materials is ever expanding, with many types of new materials. Chromogenics cover any visibly switchable technology useful for glazing, mirrors, transparent displays, and a variety of other applications[1]. Common examples of electrically powered technologies are electrochromics, suspended particle devices (SPDs) – also known as electrophoretic media, phase dispersed liquid crystals (PDLCs), and cholesteric liquid crystals (ChLCs).

Other common chromogenic effects are photochromism and thermochromism. Photochromic materials change color upon exposure to ultraviolet (UV) illumination and have been used in ophthalmic products for many years. This type of material has evolved from alkali halide glass compounds to spirooxazines used in polymer-based lenses. Thermochromics, which change color with temperature, have been known for some time too, many based on transition metal oxides like VO_2. These materials have been used mainly by the

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aerospace industry to change the emissivity of surfaces upon heating. In addition, organic thermochromic inks are used as temperature indicators.

Another class of chromogenic material are thermotropics, which switch optically with temperature. Many of these materials are hydrogels or polymer blends that undergo large physical changes when heated. There are other hybrid types such as photoelectrochromics based on dye-sensitized nanomaterials.

Chromogenic markets

The markets for chromogenic smart materials cover automotive, architectural, aircraft, and information display. The use of flat glass is widespread with global production estimated at about 4.1 billion m^2 per year (in 2004) and an approximate value of $40 billion. The largest geographical producers[2] are Asia (1.76 billion m^2), the Americas (972 million m^2), and Europe (906 million m^2), with the rest of the world producing 472 million m^2. The North American market (1998) is split into three usage sectors for flat glass: 55% architectural, 28% automotive, and 17% other.

Low emittance (low-e) coated glass accounts for 40% of the insulated glass market, with total shipments of around 400 million m^2. Low-e is still one of the growth areas for coated glass. One form of low-e coating is fluorine-doped tin oxide, a degenerately doped transparent conductor. Tin oxide and indium tin oxide (ITO) are widely used as transparent electrical conductors for switchable glazing.

Research on new organic semiconductors arising from work on organic light emitting diodes (OLEDs) may lead to new classes of transparent semiconductors.

Automotive Market

Electrochromics have been very successful as dynamic antiglare automotive mirrors. About $300 million switchable mirrors are sold per year[3], representing ~10% of the total market. Switchable mirrors are now available for most major makes of cars. Many electrochromic mirrors are made by Gentex, with other makers including Magna Donnelly, Nikon, and Murakami-Kaimedo. Several companies are working on switchable sunroof glazing. Saint-Gobain has shown prototypes and is setting up a production facility in Germany[4,5].

Architectural Market

Architectural applications have dominated the research and development of smart switchable windows. The flat glass market for architectural glazing is one the most attractive because there are a wide range of possible applications for a variety of building types. The Flabeg Group has made and installed the largest electrochromic architectural windows. Switchable electrochromic skylights have been produced by SAGE Electrochromics working in collaboration with Apogee. PDLC glazing is currently made by UMU-Nippon Sheet Glass (NSG) in Japan and Saint-Gobain In France. SPD building glazing is available from Korean company SPD Inc. (SPDI), who are working with Research Frontiers, Inc. (RFI). The latter have commissioned a study from the Townsend Group on the acceptance of switchable glazing in the glazing industry[6]. Fig. 1 shows the percentage of companies introducing a switchable glazing product according to the added cost.

Aircraft Market

In the aerospace market, there are likely to be many changes in the future. Over the next 20 years, about 35% of aging

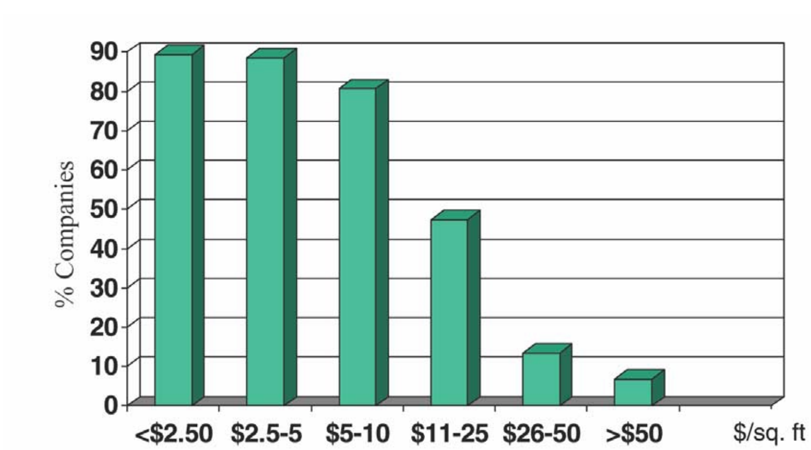

Fig. 1. The percentage of window companies adopting a switchable glazing according to the added cost of the switchable glazing (in $/sq. ft)[6].

aircraft will need to be replaced. In addition, aircraft stock will grow from 13 000 in 1999 to 28 000 in 2018[7]. The aerospace industry is interested in the development of visors and windows that can control glare for pilots and passengers. Airbus has announced that dimmable windows will be fitted to the first class cabin of its new A380 Airbus, due on the market 2004-2006. Saint-Gobain has already shown a prototype electrochromic cabin window[8], which has a 40:1 contrast ratio with deeply colored visible transmittance less than 1%. Boeing has announced that it too will fit switchable passenger windows to future aircraft.

SPD glazing can be seen in a variety of aircraft from InspecTech, where switchable plastic is being used for passenger window retrofits and upgrades to business jets and helicopters.

Information Display Market

The world market for displays is currently estimated at $60.9 billion, climbing to $86 billion in 2007[9]. An estimate of the future compared with the current market is shown in Table 1. The market is divided into two major product areas, cathode ray tubes (CRT) and liquid crystals. These displays are seen in a variety of electronic products from televisions to personal data assistants (PDAs). The major trend is toward thinner and lighter weight designs, based on flexible plastic substrates instead of glass. CRT technology is likely to retain a good portion of the display market, but its share has been in decline since 2001.

Three of the most dynamic areas of development are active matrix liquid crystal (AMLCD), plasma, and 'other' displays including OLED, electrochromic, and electroluminescent technologies. For flat panel displays (FPDs), the glass processing size is increasing and will soon exceed 2 m^2, while a thickness of 0.1-0.5 mm is becoming standard. In certain ways, we are beginning to see a bridge forming between the processing of large area glazing and display glass. Factories able to handle such large glass have been constructed, driven by demand for flat panel computer screens and large area FPD TVs.

Chromogenic materials are finding application in specialized displays. Electrophoretic technology is being used in electronic book, paper-like, and banner displays. Electrochromics can be found in low information content displays and indicators. Both PDLCs and ChLCs are being used. Many chromogenic materials can be fabricated on plastic substrates, which is an advantage for future display applications. The development of chromogenic for electrophoretic, electronic-paper displays, which can store and display information and graphics on a flexible substrate, is becoming increasingly important.

Table 1 *Current and estimated display market (in $ billion).*

Display Type	2003	2007
Liquid Crystal Displays	29.2	53.6
Plasma Display Panels	1.8	9.1
Microdisplays	1.4	1.7
Other FPDs and OLEDs	1.2	2.8
All Flat Panel Displays	**33.6**	**67.2**
Cathode Ray Tubes (CRT)	27.3	18.8
All Displays	**60.9**	**86.0**

The technology of electrochromics

Electrochromic devices are the most popular technology for large area switching devices. Much of this technology is being developed for building and automotive windows, as well as mirrors, as described above, but the history of chromogenics dates back to 1704, when Diesbach discovered the chemical coloration of Prussian Blue. In the 1930s, electrochemical coloration was noted in bulk tungsten oxide. Twenty years later, Kraus observed electrochemical coloration in thin films. The first electrochromic devices were made by Deb in 1969[10]. By the mid-1970s, electrochromic devices were being developed for displays. Electrochromics based on viologens and tungsten oxide followed in the 1980s for switchable mirrors in cars, which continues as a viable product to this day. In the 1990s, several companies began developing devices for glazing applications and the work still continues.

Electrochromic materials, which change their optical properties in response to an electric field and can be returned to their original state by a field reversal, have major advantages:

- A small switching voltage (1-5 V);
- Show specular reflection;
- Possess a gray scale;
- Require power only during switching;
- Exhibit adjustable memory, up to 12-48 hours.

Typical electrochromic devices have upper visible transmission of T_v = 70-50% and fully colored transmission of T_v = 25-10%. Levels of transmittance as low as 1% are possible. The range of shading coefficients (SC) for electrochromics is about 0.67-0.60 for the bleached condition, and 0.30-0.18 for the fully colored condition.

Electrochromic glazing has an interesting attractiveness, but laced with subtle complexities. The complexity comes from the fact that it has the structure of a transparent battery with a relatively thin large-area planar electrode. It differs from a battery in that the electrochromic is transparent, with very little optical scatter.

Typically, coloration ions such as Li^+, H^+, and $Ag^+$are used. An example of a Li^+ intercalation reaction for a cathodic coloring material is as follows:

WO_3 (colorless) + yLi^+ + ye^- $\leftrightarrow$ Li_yWO_3 (blue)

A complementary anodic nickel vanadium oxide reaction is:

$Li_yNi_zV_{2-z}O_5$ - yLi^+ (light gray) - ye^- $\leftrightarrow$ $Ni_zV_{2-z}O_5$ (colorless)

The electrochromic binary inorganic oxides of most interest are WO_3 (the most commonly used), NiO, IrO_x, V_2O_5, and MoO_3[11,12]. An electrochromic glazing device must have an ion-containing material (electrolyte) in close proximity to the electrochromic layer, as well as transparent layers for setting up a distributed electric field. Electrochemical stability can be increased by using interfacial layers. Devices are designed to shuttle ions back and forth into the electrochromic layer with applied potential. Electrochromic glazing can be fabricated from five (or less) layers consisting of two transparent conductors, an electrolyte or ion conductor, a counter electrode, and an electrochromic layer, as shown in Fig. 2.

Commercially, viologen derivatives are the most widely used organic electrochromics. Organic electrochromics tend to suffer from problems with secondary reactions during switching, but more stable organic systems have been developed, in particular, by Gentex. Some other companies are now researching polymer materials and flexible films. Devices based on poly(3,4-ethylenedioxythiophene) or PEDOT have shown 60% luminous transmission change[13].

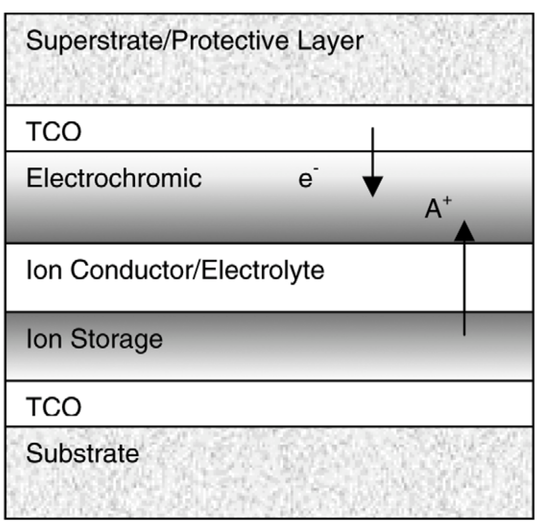

Fig. 2 Schematic of the layer structure of an electrochromic window (not to scale). The construction is similar to a battery. The condition shown is coloration in a cathodic material, such as tungsten oxide.

Fig. 3. South facing view of a portion of the 8 x 17 m electrochromic E-Control™ glass made by Flabeg and installed in the Stadtsparkasse Dresden am Altmarkt. The left portion of the window is colored. (Source: H. Wittkopf, Flabeg.)

Applications of electrochromics

The projected price for electrochromic glazing is within the \$100-250/m^2 range. However, most prototypes are currently a factor of ten higher than this in cost. An example of an application is Flabeg's prototype E-Control™ switchable glazing comprising an insulated glass unit with two panes, which have low-e coatings and a transmittance range of T_v = 50-15%[14]. E-Control™ windows covering an area of 8 x 17 m have been installed in the Stadtsparkasse Dresden am Altmarkt (Fig. 3).

The recently established spin-off company from Uppsala University, ChromoGenics Sweden, is developing a flexible electrochromic on plastic for visors on motorcycle helmets[15]. A prototype visor, with transmittance T (550 nm) = 70-25%, is shown in Fig. 4. Eclipse Energy Systems, Inc. is also working on flexible plastic electrochromics using plasma-enhanced chemical vapor deposition (PECVD).

Saint-Gobain, as mentioned above, is developing a production plant in Germany to produce electrochromic

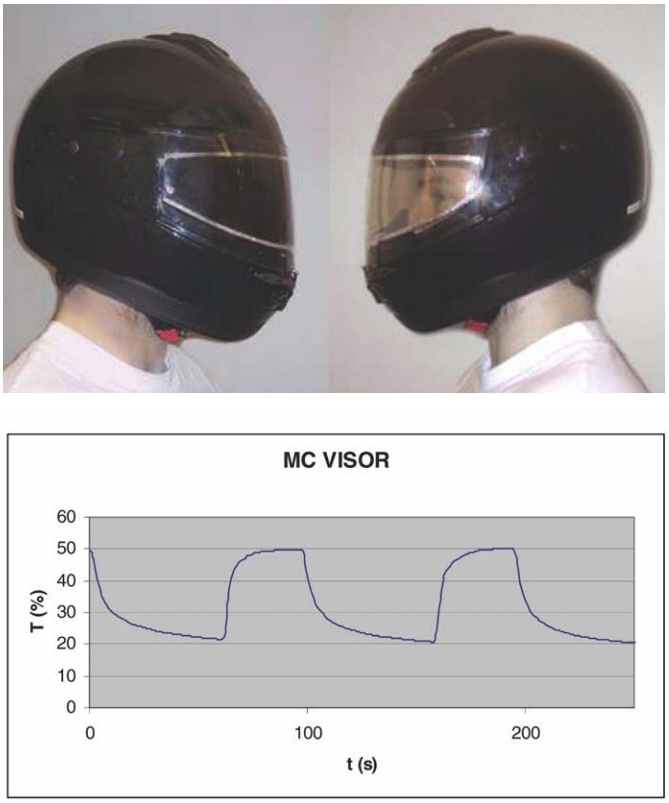

Fig. 4 Switchable motorcycle helmet visor made by ChromoGenics. Shown (top) are two colorations of the visor. The spectra (bottom) shows the change in visible properties with an applied voltage of 1.6 V. (Credit: C. Granqvist, ChromoGenics.)

automotive sunroof glazing[4] with T_v = 40-4%, T_s = 20-2%, T_v = 15-1%, and T_s = 8-0.6%. The switching speed is 20 s for 0.3 m x 0.3 m glazing. SAGE and Apogee Enterprises are jointly developing a ~1 m x 0.6 m SageGlass™ switchable skylight. The prototype windows have a visible switching range of ~70-4%. AFG Industries is also in the process of commercializing an electrochromic window technology.

Philips and Lawrence Berkeley National Laboratory are investigating metal hydride materials that switch from a transparent to a reflective state[16,17]. While another US government lab, the National Renewable Energy Laboratory (NREL), is testing the lifetime and durability of electrochromic devices.

Another type of electrochromic structure is the 'Nanocell'. This device is fashioned from photovoltaic cells so that the electrochromic can self-color when exposed to sunlight. The cell relies on a dye-sensitized anatase titanium oxide layer, which forms a distributed *pn*-junction. Its optical density can be regulated by resistively shunting the anode and cathode of the cell. IVT in Sweden, NREL, and NTERA in Ireland are working with École Polytechnique Fédérale de Lausanne (EPFL) in Switzerland to develop this type of photo-electrochromic. Nanocell designs can be electrochromic too.

Applications of SPDs

RFI and its licensees are developing SPDs for goggles, eyeglasses, and windows. Recent activities have been directed toward polymer sheet development. SPDI, one of several companies with RFI licenses, has been very innovative in developing a factory for producing large area flexible plastic sheeting. Fig. 5 shows prototype SPD windows in four conditions of coloration. The glazing consists of three layers. An active layer of needle-shaped dipole particles (<1 mm long) suspended in a polymer is laminated or filled between two transparent conductors on polyester. In the off condition, the particles are random and light absorbing. When an electric field is applied, the particles align and increase transmission. Typical transmission ranges are 6-75% and 15-60% with switching speeds of 100-200 ms, respectively[18]. The device requires 100 V and a low current for operation.

Electrophoretic electronic paper displays are being developed by E Ink in the US and at NOK in Japan. The display consists of electrophoretic inks encapsulated in

Fig. 5. SPD composite glazing (3 m x 3 m) in four levels of coloration. These windows were shown at the National Glass Association 2002 show in Houston, USA.

polymer bubbles embedded in a flexible polymer matrix. Depending on the applied field, the white or black electrophoretic ink particles move to the top or bottom of the bubble, producing a contrast effect. The displays operate at ~15 V and have contrast ratios of at least 6:1[19]. They are also bistable and exhibit a memory effect. A reverse emulsion nanosize electrophoretic display is also being developed by Zikon. The display appears transparent in one state and reflective under an applied potential.

Applications of PDLCs and ChLCs

Liquid crystals are the largest area of development in FPDs. Properties are rapidly improving, which is lowering the overall cost of flat panels.

Liquid crystals come in nematic, smectic, twisted nematic, ChLCs, guest-host, and ferroelectric types. For displays, twisted nematic liquid crystals are the most commonly used. The mechanism of optical switching in these materials is a change in the orientation or twist of liquid crystal molecules interspersed between two conductive electrodes with an applied electric field. The orientation of the liquid crystals alters the overall optical reflectivity properties of the window or display. Kent Displays has developed large area displays for signage using ChLCs. A glazing using this technology has also been demonstrated by US company Chelix.

One unusual version of a liquid crystal system takes an emulsion of a polymer and liquid crystal to form a film. This emulsion is called a PDLC or nematic curvalinear aligned phase (NCAP)[20] and has been commercialized in switchable glazings. There are some preparation and structural differences between a PDLC and an NCAP, but here they will be treated without distinction since their performance is similar. The PDLC film can be fabricated between two sheets of transparent conductor-coated polyester or glass, which serve as electrodes. The switching effect of the device spans the entire solar spectrum, up to the absorption edge of glass. In the off-state, the device appears translucent white. When an electric field is applied, the liquid crystal droplets align with the field and the device becomes transparent. Typically, the devices operate between 24-120 V and power consumption is less than 20 W/m^2. However, since the devices require continuous power to be clear, the power consumption is higher than for electrochromics. The typical integrated hemispherical visible transmission values for a PDLC device are T_v (off-on) = 50-80% and the SC changes by 0.63-0.79. Pleochroic dyes can be added to darken the device in the off-state, which provides considerable control over visible transmittance compared with an undyed film.

UMU-NSG, who licenses NCAP processes from Raychem, produces a PDLC product known as Umu™ for specialty automotive and building applications. Umu glazing can be used as a window projection screen in the off condition. The large area PDLC glazing can be fabricated in 1 m x 2.5 m sheets (Fig. 6). Open circuit memory is generally not possible with dispersed liquid crystals but, by adding dipoles to the liquid, a memory effect can be achieved. Long-term UV stability and cost (~\$750-950/m^2 for glazing) remain issues.

Applications of thermotropics

Thermotropics, which exhibit large physical changes at certain temperatures, have also been studied and developed for glazing. These materials appear clear at lower temperatures, but become opaque at higher temperatures. They can be used for skylights, inclined glazing, and upper windows where view is not important. They can be totally passive, changing with ambient temperature for solar heating.

Fig 6. Example of PDLC-based Switch Lite glass. The glazing was produced by Pulp Studios (Los Angeles, USA) and the base PDLC film was made by UMU-NSG.

Some designs use a resistive heating layer made from thin film metals or transparent conductors, which enables electrical control of the physical change. Thermotropics scatter light like PDLC materials, although PDLCs tend to be more isotropic scatterers. Most thermotropics are based on hydrogels, and polymer blends have been studied for higher temperature performance. One example of a thermotropic polymer gel is polyether/ethylene oxide/carboxyvinyl.

A thermotropic called ThermoSEE has been introduced by US company Pleotint. The activation temperature can be set from -10°C to 50°C and the material is stable to 85°C. Fig. 7 shows examples of ThermoSEE in the off- and on-state.

Some early thermotropic work was performed by Suntek on 'Cloud Gel', a hydrogel film laminated between two pieces of glass. Hydrogel and polymer gels are being developed in a joint project between Interpane Glas Industrie, BASF, and the Fraunhofer Institute for Solar Energy Systems in Germany. The film has optical characteristics of T_v (25-60°C) = 79-4% and T_s (25-60°C) = 63-3% with R_v (25-60°C) = 8-49% and R_s (25-60°C) = 7-39%[21]. Affinity Corp. in Japan has developed a similar hydrogel glazing[22]. The technical problems with the hydrogels, however, are cyclic lifetime and inhomogeneity during switching.

Applications of gaschromics

Gaschromics are based on the property of tungsten oxide thin films to color in the presence of hydrogen gas with a suitable catalyst. The reaction is as follows:
WO_3 (colorless) + $xH_2 \rightarrow 2xH^+ + WO_3 \rightarrow H_{2x}WO_3$ (blue).

Gaschromic window construction follows a double pane model with a gap between the two panes. On one pane, a film of tungsten oxide is deposited with a thin layer of catalyst on top. Hydrogen gas is fed into the gap producing coloration of the tungsten oxide layer. To switch back, the gap is purged with another gas. An example of a gaschromic window is shown in Fig. 8. Transmittance of 75-18% and T_s = 74-14% have been obtained, which is better than most electrochromic windows. The windows can color with 0.1-10% hydrogen, which is below the flammability concentration. The Fraunhofer Institute for Solar Energy Systems and Interpane have built a pilot production plant that can produce 1.5 m x 2 m windows[23]. They have developed a small gas generator that can be incorporated into a wall, but the plumbing of the gas tubes for the window remains an issue.

Summary and conclusion

Chromogenics have unique properties for applications such as glazing, large area displays, and electronic paper. In this review, selected technologies have been outlined including electrochromics, SPDs including electrophoretic displays, liquid crystals, thermotropics, and gaschromics.

Electrochromics are favored for many applications because they remain specular and nonscattering when switched. This means they can be used for a variety of view or see-through applications. In addition, electrochromics can be easily powered because of their low voltage. They have been commercialized for automotive mirrors and large

Fig. 7 ThermoSEE thermotropic glazing. The off-state is shown on the left and the heated on-state is shown on the right. (Credit: F. Millett, Pleotint, USA.)

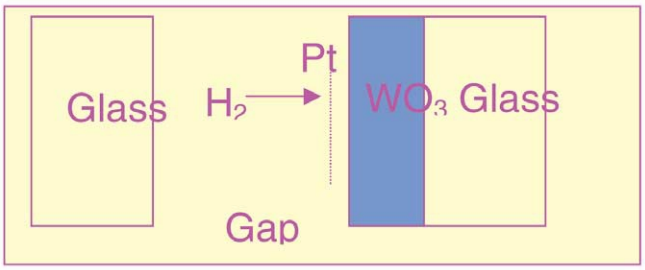

Fig. 8 Gaschromic glazing developed at the Fraunhofer Institute for Solar Energy Systems (Freiburg, Germany). Both the colored and bleached conditions are shown. Schematic shows the cross-section of the glazing.

composite windows for buildings. Many companies are working on the introduction of glazing products for architectural and automotive sunroof applications. Production costs and process simplification are major issues for large area switchables.

SPDs are more absorbing in the off-state compared with the on-state. They have the advantage of much lower scattering in the off-state compared with PDLCs. SPDs can be made into a flexible sheet form for use in a variety of laminated applications. Various companies are producing flexible window films. For example, SPDI has shown prototypes of displays, sunroofs, and architectural windows. SPD windows are also being installed in aircraft.

PDLCs are being marketed for glazing applications, particularly security windows and office dividers, because of their unique privacy properties. PDLC can also be made in a flexible sheet form. PDLCs are also being developed for exterior glazing.

Several chromogenic technologies are being developed for the display market. Electrophoretics, for example, are being used in electronic paper displays by E Ink, NOK, and Zikon.

The future is likely to hold some exciting developments in displays and windows, but there are great challenges ahead for the chromogenic community. MT

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