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# Chromogenic Switchable Glazing: Towards the Development of the Smart Window

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# Chromogenic Switchable Glazing: Towards the Development of the Smart Window

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## Abstract

The science and technology of chromogenic materials for switchable glazings in building applications is discussed. These glazings can be used for dynamic control of solar and visible energy. Currently many researchers and engineers are involved with the development of products in this field. A summary of activities in Japan, Europe, Australia, USA and Canada is made. The activities of the International Energy Agency are included. Both non-electrically activated and electrically activated glazings are discussed. Technologies covered in the first category are photochromics, and thermochromics and thermotropics. A discussion of electrically activated chromogenic glazings includes dispersed liquid crystals, dispersed particles and electrochromics. A selection of device structures and performance characteristics are compared. A discussion of transparent conductors is presented. Technical issues concerning large-area development of smart windows are discussed.

## 1. Introduction

Chromogenic switchable glazing or "smart windows" have an important role to play in future glazings. Chromogenics is probably one of the most exciting and complicated topics in the field of glazing. Over the last few years there has been growing interest in this technology and is expected to continue well into the next century for a variety of products [1-3]. The function of a smart window is to control the flow of light and heat into and out of a glazing, according to occupant comfort. Applications include glazings in buildings, vehicles, aircraft, spacecraft and ships. Chromogenic glazing can also regulate lighting and heating levels for energy load management. The smart window has a considerable energy advantage over that of a conventional bronze window. Energy modeling of electrochromic windows has shown that electrochromic windows can provide significant energy performance over that of conventional double glazed windows. The energy performance of a range of switchable windows is being studied at LBL [4-7].

There are various physical optical techniques that can be used for chromogenic glazing. The basic property of a chromogenic material is that it exhibits a large change in optical properties upon a change in either electrical field, charge, light intensity, spectral composition, or temperature. The change in optical properties can be in the form of absorptance, reflectance or scattering. This change can be either totally or partly over the visible and solar spectrum. The two major categories are non-electrically activated and electrically activated types. The non-electrically activated types include photochromics, and thermochromics and thermotropics. The most common of the electrically activated types are phase dispersed liquid crystals (PDLC), dispersed particle system (DPS) and electrochromics. These five categories will be summarized in this study. The most popular and most complicated is electrochromics. The electrically activated devices have the advantage of user or automatic control. The non-activated category has the advantage of being self-regulating with local control. Although, a version of a self-regulating photovoltaic powered electrochromic is being developed at National Renewable Energy Lab (NREL) [8].

One of the most significant issues with chromogenics is the cost of the glazing and the trade-offs between cost and benefit, and cost and lifetime. Current smart glazing development is aimed at long-life devices with durability similar to regular coated windows. A different approach is the development of low-cost limited-life switching devices. For the electronically switchable technologies, costs are probably in the range of 100-1000 US\$/m$^2$. Some companies have set cost goals of 100-250 US\$/m$^2$. There is growing investment by larger companies and national governments in promoting chromogenic technology. Specifically, some of the larger organized projects are in Japan, Europe, Australia and the U.S. In Table 1, are listed the organizations involved in all-non-electrochromic chromogenic glazing. In Table 2 are listed the organizations performing work on electrochromic glazing. These tables are not inclusive. The source of the names is from published papers, patents or trade articles.

**Table 1. World Research in Chromogenic Devices- Excluding Electrochromics**

**North America:**
PPG (Monroeville, PA)-Photochromic plastic
American Optical (Southbridge, MA)-Photochromic plastic
Corning (Corning, NY)- Photochromic glass
3M/Viracon/Marvin Windows (Minneapolis, MN)- PDLC
G.M. Research Labs (Warren, MI)- PDLC
Raychem/Taliq (Sunnyvale, CA)-PDLC
Kent State Univ.(Kent, OH)-PDLC
Research Frontiers (Woodbury, NY)- DPS
Suntek (Albuquerque, NM)- Thermotropic polymers
Meyer and Lonberg Assoc. (Brookline, MA)-Liquid crystals

**Europe:**
Glaverbel (Brussels, Belgium)-DPS
Saint Gobain Rech.(Paris, France)-PDLC, DPS
Pilkington (Lathom, UK)-PDLC
Isoclima (Este, Italy)-PDLC
Asulab-(Neuchatel, Switzerland)-LC
Schott Glass (Mainz, Germany)-Photochromic Glass
Interpane/BASF (Lauenforde, Germany)-Thermotropic polymers
Fraunhofer Inst. Building Physics (Freiburg, Germany)- Thermotropic polymers

**Japan & Asia:**
Asahi Glass (Yokohama, Japan)-PDLC
Nippon Sheet Glass (Itami City, Japan)- PDLC, DPS
Hankuk Glass (Korea)-DPS
Japan Steel Works (Fuchua, Japan)-DPS

## Table 2. World Research in Electrochromic Devices

**North America:**

Lawrence Berkeley Lab (LBL) (Berkeley, CA)
Tufts Univ. (Medford, MA)
OCLI/Andersen Windows (Santa Rosa, CA)
Donnelly Corp/Viracon (Holland, MI).
SAGE (Piscataway, NJ)
Ford Glass (Lincoln Park, MI)
Gumbs Assoc. (E. Brunswick, NJ)
University of Guelph (Guelph, Canada)
Inst. Nat. de la Rech.Sci. (Varennes,Canada)
EIC Labs (Norwood, MA),
NREL (Golden, CO).
3M (St. Paul, MN)
Gentex (Zeeland, MI)
LOF Glass (Toledo, OH)
Southwall Tech. (Palo Alto, CA)
Ashwin-Ushas (Freehold, NJ)
Enermodal Engin. Ltd. (Waterloo,Canada)
University of Moncton (Canada)

**South America:**

Univ. of Campinas (Campians, Brazil)
Univ. of Sao Palo (San Carlos, Brazil)
Univ. Nacional de Eng.(Lima, Peru)

**Europe:**

Univ. of Uppsala (Uppsala, Sweden)
Flachglas AG (Gelsenkirchen, Germany)
St. Gobain Recherche (Aubervilliers, France)
P. and M. Curie Univ. (Paris, France)
Imperial College (London, England)
Latvian State Univ. (Latvia)
University of Rome (Rome, Italy)
Oxford Brookes Univ. (Oxford, UK)
Elf Aqutaine (Lacq, France)
Corning Europe (Avon, France)
CRF Fiat (Orbassano, Italy)
Coat AB (Gothenburg, Sweden)
Conphoebus (Catania, Italy)
Isoclima (Este, Italy)
C.S.T.B. (Grenoble, France)
Schott Glass (Mainz, Germany)
Univ. of Catania (Catania, Italy)
Univ. of Lanquedoc (Montpellier, France)
Fraunhofer Inst. (Freiburg,Germany)
Leybold AG (Aahen,Germany)
Dornier (Friedrichshafen,Germany)
Pilkington (Lathom,UK)
Univ. of Bordeaux (Bordeaux, France)
SIV (San Salvo, Italy)
Univ. of Southamption (Southampton, UK)
Davionics AS (Odense, Denmark)
Norwegian Institute of Tech. (Trondheim)
ENEA (Rome, Italy)
Nat. Inst. of Chem. (Ljubljana, Slovenia)
Domaine Univ. (Grenoble, France)

**Japan & Asia:**

Asahi Glass (Yokohama)
Central Glass (Tokyo)
Toyota -Cars (Nagakute)
Shizuoka Univ.
Tokyo Metro. Univ. (Tokyo)
Takai-Rika-Cars
Carmate-Cars
NIRIN-(Nagoya)
Tokyo Univ. (Tokyo)
Ichikoh-Cars (Tokyo)
Nikon-Cars/Eyeglasses (Tokyo)
Nagoya Univ. (Nagoya)
Murakami Kaimeido-Cars

**Australia**

University of Technology (Sydney)
Silicon Technologies Australia (Queensland West)
Glassform (Victoria)
Monash Univ. (Melbourne)

## 2. Non-Electrically Activated Chromogenics

### A. Photochromic Materials

Photochromic materials have potential in advanced glazings. It is one of the oldest phenomena in switching and dates back to the 1880's. Photochromism occurs a wide variety of organic and inorganic materials [9-13]. For glazings there are two types of photochromic materials (1) photochromic glass based on metal halides and (2) photochromic plastics. There exist other classes of photochromics, but they are unexplored for glazings, such as photochromic insulating aerogels. Photochromic materials change their optical properties when exposed to the UV portion of sunlight and revert to their original properties in the dark. Generally, photochromic materials are energy-absorptive. Basically, the phenomenon is the reversible change of a single chemical species between two energy states having different absorption spectra. This change in states can be induced by electromagnetic radiation (usually UV light).

Of the inorganic materials, the best known commercial photochromic is photochromic eyeglasses [14-17]. To become photochromic a special glass containing metal halides such as AgCl or AgBr is made. A special heat treatment of this composition causes the formation of photosensitive silver halide crystals of about 15 nm in size. When UV light of the wavelength between 300-400 nm illuminates the glass, the metal halide crystals disassociate into metallic silver and the halide. This effect causes a visible absorption to take place. When the UV light is removed, the metal-halide molecule recombines thermally to its original form and as a result the glass becomes more transparent. Because of this process the coloration rate is strongly thermal dependent. Glasses that exhibit photochromism contain silver halide, hackmanite, and rare earth elements. The most widely known companies that make opthalmic photochromics are Corning, Schott, Pilkington, Desag (Germany), and Asahi. The typical optical response for a photochromic glass in the bleached and colored state is shown in Fig. 1. The glass shows good durability and fatigue-resistance during color/bleach cycling [18]. Typical values for a Corning gray-brown eyeglasses (Photosolar Super) are $T_v$(uncolored) = 89% and $T_v$(colored) = 26%. Fading of the colored state to about $T_v = 57\%$ takes 3-4 minutes at room temperature [19]. A typical solar value is $T_s = 85\text{-}50\%$. Photochromic glass is not presently produced in sufficient sizes or at low enough cost to allow its use in buildings or cars. Thin prototype sheets (approximately 1 $m^2$) have been made by Corning for use as a glass laminate to regular float glass. To be effective the photochromic glass must be at least 1 mm thick. Lamination is one of the ways to reduce the cost of the glass. The glass is now manufactured by rolling, drawing and fusing, followed by a special heat-treatment process. The float process has not been demonstrated for photochromic glass. Durability under extended color/bleach cycling, and resistance to chemical attack, are excellent for photochromic glass and probably this is the most chemically stable of all the chromogenic materials.

Another large class of photochromics are the organics. They include certain dyes, stereoisomers, and polynuclear aromatic hydrocarbons. Photochromism in organic materials is associated with heterolytic and homolytic cleavage, cis-trans isomerisation and tautomerism. The most suitable glazing material in this class are the derivatives of spirooxazine applied to plastic [20, 21]. The photochromic compound is applied to the substrate by a surface treatment process. In the spirooxazine molecule photochromism also occurs during UV exposure. Upon exposure, bond scission occurs in the molecule and as a result a chromophore forms in the visible region. Again, as in the inorganics, bond reformation occurs thermally and bleaching occurs. A photochromic plastic product has been developed by PPG for eyeglasses called "Transitions". This material has been developed for ophthalmic use but with future research may become useful for energy regulating glazings for solar energy control. The polymer host material is CR-39 poly(diethylene glycol bis(allyl carbonate)). It is temperature sensitive, and loses its switching range at elevated temperature. The photochromic material is sensitive to UV over the long term giving about 3-5 years life in opthalmic products. It has a visible switching range of $T_V$=83-33%, with a blue color. The spectral properties of the Transitions plastic are shown in Fig. 2. Improvement is needed in durability, and loss of photochromism at elevated temperatures, before it can be used in glazings for any extended period of time. What is most interesting is it is possible to apply the photochromic organic treatments to flexible plastics. These could be laminated or used as suspended glazing.

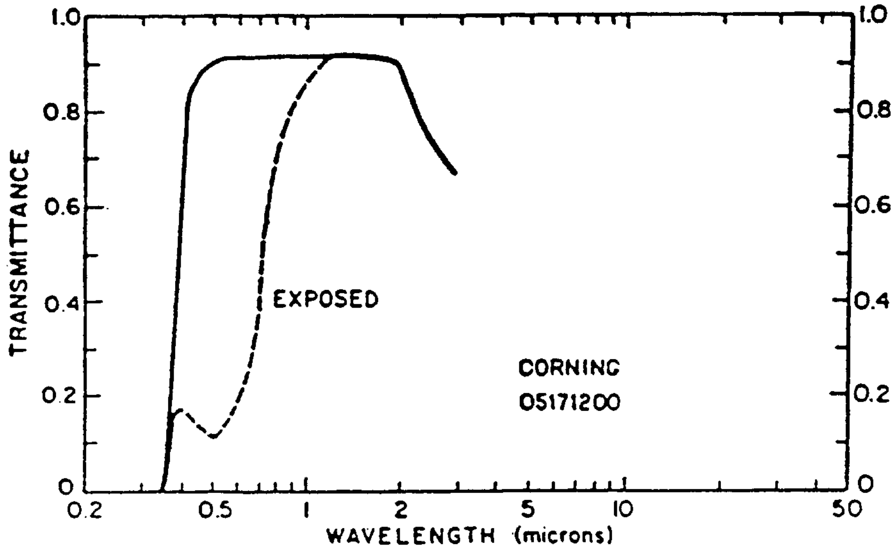

**Fig.1.** The spectral transmittance properties of a Corning photochromic glass. Shown are the fully bleached and fully colored conditions.

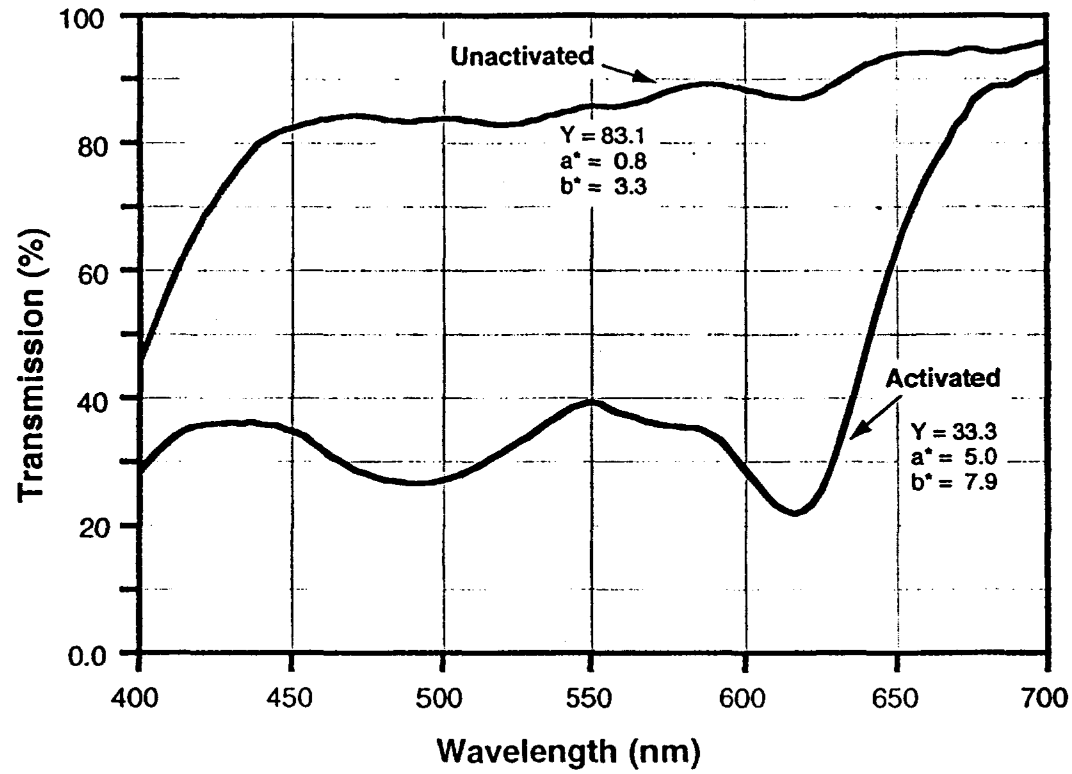

**Fig. 2.** The transmittance spectra for PPG photochromic plastic known as Transitions. The unexposed and exposed states are shown.

## B. Thermochromic and Thermotropic Materials

Thermochromic and thermotropic materials show a large optical property change with change in temperature, such as with heating. Thermochromic materials have been known since the 1870's. Like photochromism, this phenomena is one of the oldest of the chromogenic processes. Thermochromic materials change color by going through a thermally induced chemical reaction or by a phase transformation. Thermotropic materials go through a physical phase transformation, making a radical property change, causing scattering or multiple absorption of light. The phase change in a thermotropic material can also be a large electronic change such as an insulator to semiconductor transition. They return to their original condition when they go back to the starting temperature. Some materials exhibit hysterisis during their heating and cooling cycle.

Thermochromism can be due to equilibria between different molecular species, cis-trans isomerization, crystal phase transitions, etc. Thermochromism is seen in a large number of organic and certain inorganic compounds [22-24]. Organic compounds in the anil, spiropyrans, polyvinyl acetal resins, and hydroxide groups readily exhibit thermochromism. A wide range of inorganic compounds have been identified as being thermochromic [25-26]. Inorganic thermochromic compounds include AgI, $Ag_2HgI_4$, $Cd_3P_3Cl$, HgI, $HgI_2$, $SrTiO_3$, along with several cobalt, copper and tin complexes.

Themotropic switching occurs as an electronic transformation in specific transition metal oxides and related compounds, which transform from semiconducting to metallic state when a "critical" temperature is exceeded. Some of these compounds are $Fe_3O_4$, $FeSi_2$, $NbO_2$, NiS, $Ti_2O_3$, $Ti_4O_7$, $Ti_5O_9$, $VO_2$, and $V_2O_3$ [27]. These are known as the Mott transition compounds [28-29]. Such materials, can be used to control both transmittance and infrared emissivity of a glazing or a building skin. The major issue with these materials is their transition temperature. Many of the transition temperatures of these materials are not in the proper range. For glazing use they have to be modified to switch in the human comfort range. Modification to the transition temperature can be made by doping, although in many cases the overall reflectivity intensity is lessened. Vanadium dioxide, $VO_2$ has been considered for window applications [30]. By substitutional doping of vanadium in $VO_2$, alteration of the transformation temperature can be achieved. Compounds of $V_{1-x}W_xO_2$ have shown large changes in transition temperature but unfortunately smaller changes in conductivity during switching compared to $VO_2$ [31-32]. In Japan, NIRIN is studying the doping of $VO_2$ themochromics. It may be possible to directly incorporate thermochromic materials into polymer films and coatings. Such materials could have a wide use in shading devices and greenhouse glazings. Inorganic thermotropic coatings have the potential for large-area devices, but have not been demonstrated. Another classic thermotropic are the inorganic fiber/liquid composites can show thermochromism using the Christiansen effect. [33].

Three commercial thermotropics, developed for glazings, are the polymer hydrogels [34-35]. "Cloud Gel" by Suntek is the earliest example of this type of film [36] Other glazings are known as "TALD" (Fraunhofer Institute for Building Physics), and a product under development at Interpane with BASF. A example of a thermotropic polymer gel is polyether/ethylene oxide/carboxyvinyl. The gel switches from transparent to translucent with increasing temperature. It has privacy characteristics. The Suntek Cloud Gel (1 mm film between PET polyester films) has optical properties of $T_{v\ (25\text{-}50C)}$=92-6% and $T_{s(25\text{-}50C)}$=82-5% with $R_{v(25\text{-}50C)}$=6-79% and $R_{s(25\text{-}50C)}$=6-69% [35]. Fig. 3. shows the optical properties of a polymer gel material for a window application under development by Interpane/BASF [37]. This film has optical characteristics of $T_{v\ (25\text{-}60C)}$=79-4% and $T_{s(25\text{-}60C)}$=63-3% with $R_{v(25\text{-}60C)}$=8-49% and $R_{s(25\text{-}60C)}$=7-39%. For the TALD films the integrated hemispherical visible transmission change with temperature, for different gel thicknesses, are 85-40% (1 mm), and 65-15% (10 mm). The spectral range for the TALD glazing is about 350-1400 nm. In thin films, some partial transparency is seen from 1600-1900 nm. The transition temperature is easy to adjust in these gels by compositional change. For the TALD glazing, the transition temperature range is 9-90 C ±1.5 C. The technical problems with the gels are UV stability, cyclic lifetime, and inhomogeneity during switching. Another class of gels are the polymer blends that avoid the use of water in the system. These are under development at BASF [35]. A modification to the gel window is the addition of a transparent conductor that can be heated to induce the transformation, so it could be switched on command.

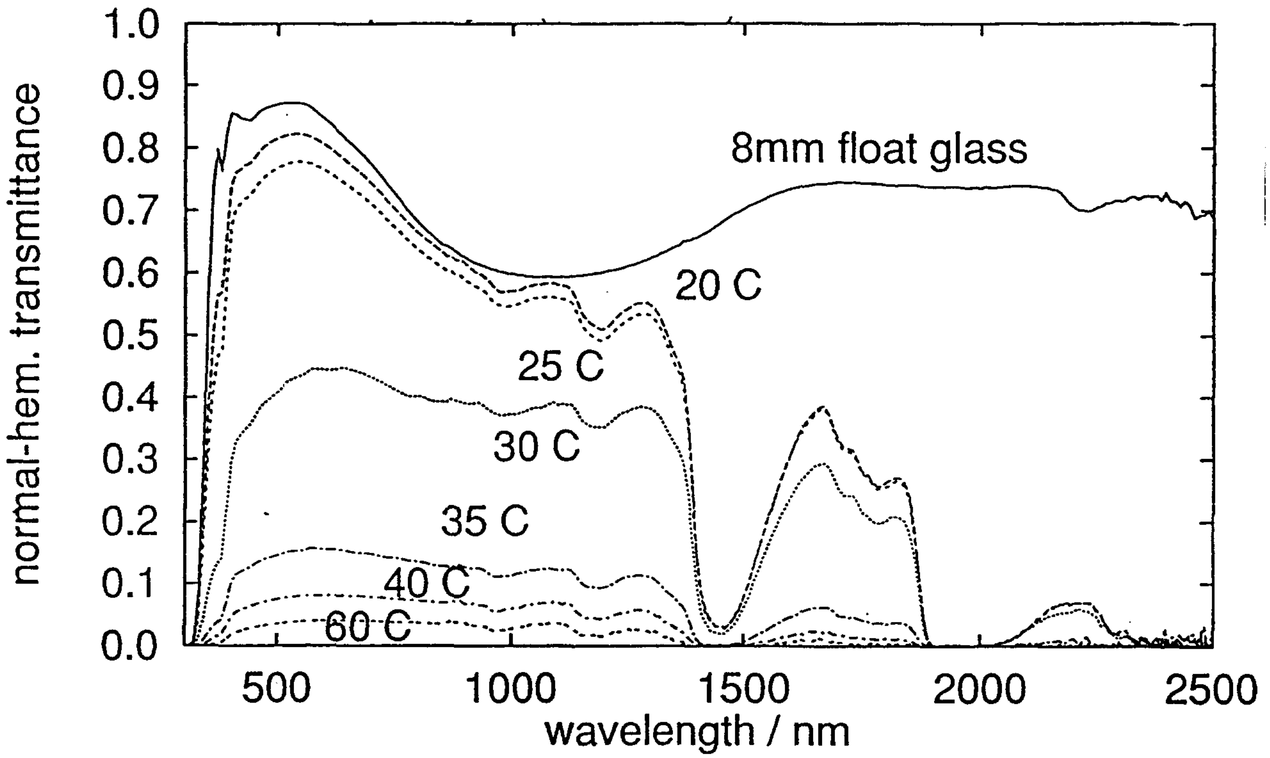

Fig. 3. Optical properties of the Interpane/BASF, prototype thermochromic hydrogel window [37]. It consists of a 1 mm thickness of gel between two 4 mm panes of float glass. The change in $T_v$ (25-60C)=79-4% and $T_s$(25-60C)=63-3% with $R_v$(25-60C)=8-49% and $R_s$(25-60C)=7-39%.

## 3. Electrically Activated Chromogenics

The electrically activated chromogenics are comprised of electrochromic, dispersed liquid crystal, and suspended particles. A significant issue for all electrically activated devices is the quality and cost of transparent conductors. The most common examples are $In_2O_3$:Sn (also known as ITO) $SnO_2$:F and SnO:Sb [38,39]. Another conductor under development is ZnO:Al. Zinc oxide is softer than the other transparent conductors but it does absorb UV light, which is a useful protection property. ITO is produced commercially on both glass and flexible plastic for electronic applications. The transparent conductors are a dominate cost of the switchable glazing, and necessary for all device types [40, 41].There are fairly new coated glass products for Low-e surfaces, e.g., Tech 15, Tech 20 Glass (LOF Glass) and K-Glass (Pilkington) can be used for electrochromic windows. The cost in quantity is about $15/m$^2$ which is considerably less than electronic grade ITO/glass. The coatings consist of a low resistivity layer (15-20 ohms/sq.) of doped tin oxide produced by thermal pyrolysis directly on the glass float line. Pilkington uses this material for their prototype electrochromic windows. For much larger electrochromic windows, greater than 1m$^2$, even lower sheet resistance transparent conductors are required. Asahi glass (Yokohama, Japan) has shown a very large area ITO glass, over 2 m$^2$ with 1 ohm/sq. and low haze. Unfortunately it is expensive. For the field effect devices: liquid crystals and dispersed particles, the need for the lowest resistivity for large areas is less than for electrochromics.

## A. Liquid Crystals

Liquid crystal based systems offer one approach to electrically switchable glazings. The basic classes of liquid crystals are the twisted nematic, guest-host, surface stabilized ferroelectric, and dispersed liquid crystals. The mechanism of optical switching in liquid crystals is to change the orientation of liquid crystal molecules interspersed between two conductive electrodes with an applied electric field. The orientation of the liquid crystals change with the field strength that alters the overall optical properties of the window. Open circuit memory is not possible with liquid crystals. So far dispersed liquid crystals are the only liquid crystal type used for commercial glazings. The largest size of any chromogenic glazing in the market place is the dispersed liquid crystal glazing. This glazing is currently produced by 3M. Also, Raychem (formerly under Taliq), along with other licencees including Isoclima, St. Gobain and Nippon Sheet Glass, produce a glazing called NCAP for products known as "Varilite", "Umu" (Japan) and "Vision Panel" for specialty automotive and building applications. The guest-host liquid crystals are another choice for large-area glazing [42]. Of the dispersed liquid crystals, there are two types the polymer dispersed liquid crystal (PDLC) and encapsulated liquid crystal (NCAP-nematic curvilinear aligned phase) which consists of nematic liquid crystals distributed in microcavities [43, 44]. PDLC and NCAP materials have very similar characteristics but are defined in the patent literature differently according to preparation procedure. NCAP films are formed from an emulsion and PDLC films are formed from an isotropic solution which phase separates during curing. 3M with General Motors Research Labs., and Kent State University have developed PDLC technology for automotive glazing [45]. The 3M product is alo used in speciality architectural windows by Viracon and Marvin Windows.

Large-area NCAP glazings have been fabricated in 1 m x 2.5 m sheets. With NCAP the liquid crystals are encapsulated within an index matched polymer matrix. The composite polymer is fabricated between two sheets of ITO coated polyester (PET) that serves as electrodes. A schematic of the construction and operation is shown in Fig. 4. The device can also be fabricated between one sheet of glass and one sheet of plastic or two sheets of conductive glass.

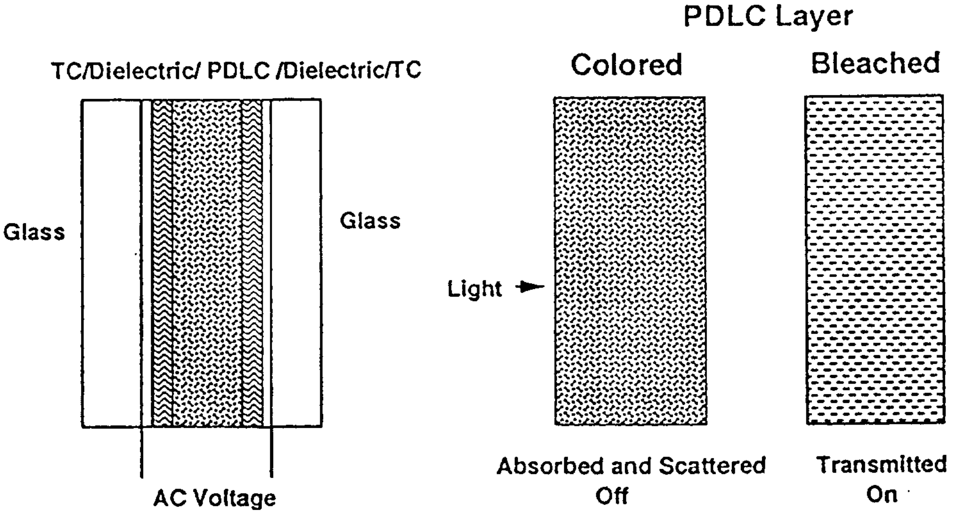

**Fig. 4.** Schematic of the construction of a dispersed liquid crystal glazing. Film thicknesses are not to scale. Shown are the off (diffusing) and on (specular) states.

The switching effect of this device spans the entire solar spectrum, up to the absorption edge of glass. In the off-state, the device appears translucent white. Since the off-state in these devices is diffusely transmitting, the device has application for privacy and security. When an electric field is applied, the liquid crystal droplets align with the field and the device becomes transparent. Typically these devices operate between 60-120 V a.c., (potentially lower in the future). Their power consumption is less than 20 $W/m^2$ but require continuous power to be clear [45]. In general, compared to electrochromics, the power consumption is higher for liquid crystals because of the need for continuous power in the activated state. The typical integrated hemispherical visible transmission values for a 3M-PDLC device are $T_{visible(off-on)}$= 0.49-0.80. The shading coefficient changes by SC=0.63-0.79 [46]. Pleochroic dyes can be added to darken the device in the off-state [47]. The dyed film shows considerable control over visible transmittance compared to an undyed film. The spectral properties of a Raychem dyed film are shown in Fig. 5. These films were evaluated in IEA SH&C Task 10 activities [48]. Dispersed liquid crystal devices have a very good future but are restricted by three characteristics: the unpowered state is diffuse, haze remains in the activated (transparent) state and UV stability is poor. Also, for widespread use of NCAP and PDLC devices the cost will have to decline.

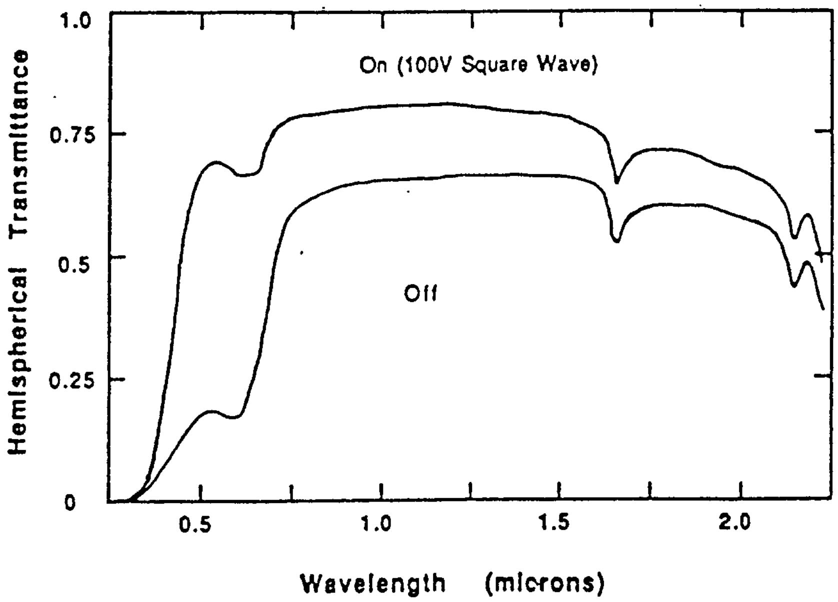

**Fig. 5.** Spectral transmittance of a dispersed dyed liquid crystal glazing made by Raychem. Shown are the unpowered and powered states (100V a.c.)

## B. Dispersed Particles

The development of suspended particle device has spanned many years. Some of the earliest work was done by Edwin Land of Polaroid in 1934. The development of suspended particle devices has been slowed by a number of technological problems including long-term stability, cyclic durability, particle settling and agglomeration, and gap spacing control for larger glazing. In recent years, many of these problems have been reduced or controlled [49-51]. Commercial development of these devices for goggles, eye glasses and windows is being done chiefly by Research Frontiers Inc. (RFI) and licensees. Recent developments have been to encapsulate the particles in a polymer sheet. A group of 50 RFI liquid based windows (0.46 m x 0.46 m) have been installed as a demonstration in the Japan Steel Works Building (Fuchua, Japan). Gloverbel, S.A. is working to develop mirrors and visors for cars. Commercial groups working on this technology are Hankuk Glass Industries, St. Gobain Glass for arcitectural windows and Sanyo Electric for flat panels [52]. Another version of this device is being developed by Nippon Sheet Glass in Japan. [53]

A suspended particle device consists of 3-5 layers. The active layer has needle shaped particles of polyiodides (dihyrocinchonidine bisulfate polyiodide) or heraphathite (<1µm long) suspended in an organic fluid or film This layer is laminated or filled between two parallel conductors. A schematic of this structure is shown in Fig. 6.

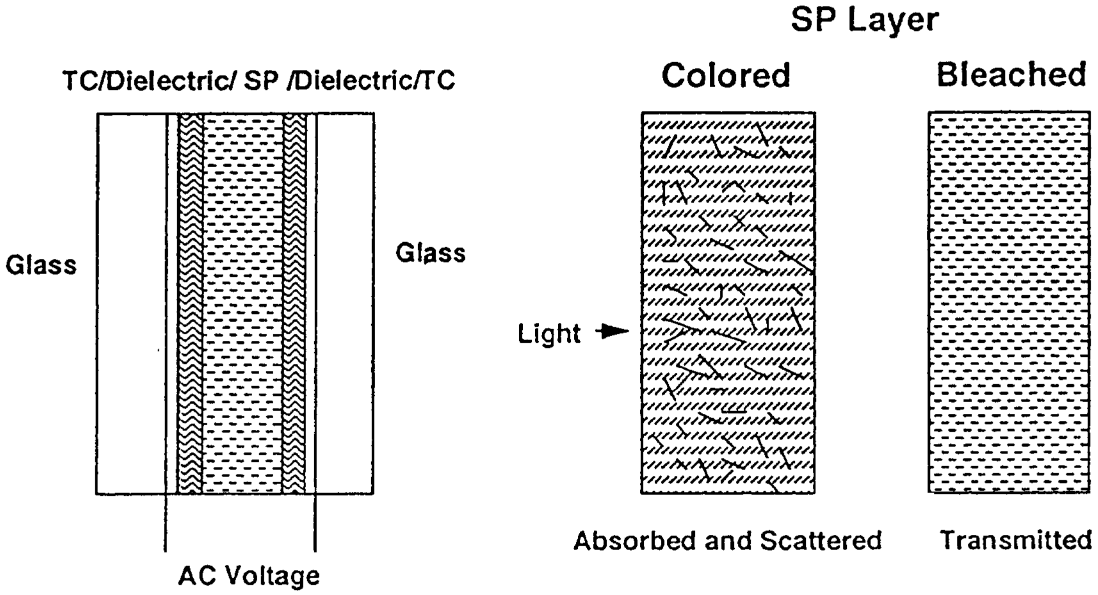

**Fig. 6.** Schematic of the construction of a dispersed particle glazing. The films are not shown to scale. Shown are the off condition (highly absorbing) and the fully on condition (less absorbing).

In the off-condition the particles are random and light absorbing. When the electric field is applied, the particles align with the field, causing transmission to increase. Typical transmission ranges are 6-75%,0.1-30%, with switching speeds of 100-200 ms and several seconds for films. The voltage required for the device depends on thickness and ranges from 0-20V to above 150 V a.c.

## C. Electrochromics

Electrochromic glazing are the most popular and most complex area of all switching technology. Electrochromism occurs in organic, inorganic and polymer materials [54-57]. The electrochromic relies on a dual injection or ejection of electrons and ions to color. Because of this dual process the device is more complicated that the other electrically switchable glazing. Over the last ten years about 200 U.S. and international patents on electrochromics have been granted per year. The major advantages of electrochromic materials are: (1) require a small voltage to switch (1-5 V); (2) are specular under all conditions; (3) they only require power during switching; (4) have continuous dimming; (5) many designs have a long term memory (12-48 h). Electrochromic products currently in the marketplace are automobile and truck mirrors, and sunglasses. The mirrors are designed to automatically regulate glare in response to incident light levels. Both the Gentex Corporation and and Donnelly Corporation have commercially developed organic electrochromic materials for automotive mirrors. The truck mirror commercialized by Donnelly is based on inorganic $H_yWO_x/Ta_2O_5/NiO_x$. Mirrors are the most commercially developed electrochromic product to date. Gentex has produced over 5.5 million mirrors over the last few years. Prototype electrochromic glazing panels are being tested for automobile sun-roofs and visors. St. Gobain Glass is developing electrochromic sunroofs for French automakers. Donnelly has developed a sunroof for the Ford Motor Co. This is an ideal large-area entry market because of the smaller size and shorter lifetime required of the window compared to building glazings. Although the upper temperature limits are higher (90-120 C).

Electrochromic materials change their optical properties due to the action of an electric field and can be changed back to the original state by a field reversal. Organic electrochromics are based on the viologens, anthraquinones, diphthalocyanines, and tetrathiafulvalenes. With organic compounds, coloration is achieved by an oxidation-reduction reaction, which may be coupled to a chemical reaction. The viologens are the most studied and commercially used of the organic electrochromics. Originally, organic electrochromics tended to suffer from problems with secondary reactions during switching, but recently more stable organic systems have been developed. The electrochromic effect occurs in inorganic metal oxides by dual injection (cathodic) or ejection (anodic) of ions (A) and electrons ($e^-$). A typical reaction for a cathodic coloring material is:

$WO_3$ (transparent) + $yH^+$ + $ye^-$ <-> $H_yWO_3$ (blue)

A typical coloring anodic reaction is:

$Ni(OH)_2$ (transparent) <-> NiOOH (bronze) + $H^+$ + $e^-$

Also, other ions such as, $Li^+$, $H^+$, $Na^+$, $Ag^+$, can be used for coloration. The two most popular devices use protons or lithium ions. The inorganic materials that have gained the most research interest are various forms of $WO_3$, NiO, $MoO_3$, and $IrO_x$. These compounds, among other transition metal oxides, are the subject of several technology reviews [58-60]. Other compounds such nanocrystalline $TiO_2$ and $NbO_2$ have been studied [61, 62] An electrochromic device must be in contact with an ion-containing or conducting material (electrolyte) as well as transparent layers for setting up a distributed electric field. Devices are designed in such a way that they shuttle ions back and forth into the electrochromic layer with applied potential. An electrochromic window can be fabricated from five (or less) layers consisting of two transparent conductors, electrolyte or ion conductor, counter electrode, and electrochromic layer. A schematic of the structure is shown in Fig. 7. Uniform films of polythiophene, polyaniline and polypyrrole have been deposited by a oxidation polymerization technique. Polyaniline is one of the favored organic polymer electrochromics [63, 64]. Depending on the components used in devices, some of the layers can be combined serving dual functions. Some devices use even more layers depending on design. Ion conductors and solid electrolytes also require further development for this technology. The most promising ion conductors are certain immobile solvent polymer systems (a-poly(ethylene oxide)), ionic glasses and open channel metal oxide structures such as Perovskites. Typical electrochromic devices have upper visible transmission of $T_V$=0.65-0.50 and fully colored transmittance $T_V$=0.25-0.10. Lower levels of transmittance have been noted below 1%, but only in very specialized devices. The shading coefficient change is about SC=0.67-0.60 for the bleached condition, and SC=0.30-0.18 for the fully colored condition. A example spectral response is shown in Fig. 8.

Certain forms of crystalline $WO_3$ can have substantial near-infrared modulation. This material has the potential to control part of the infrared portion of the solar spectrum. The more common amorphous form, used by most developers, has only a little effect in the near-infrared. Crystalline $WO_3$ is being studied by several investigators [65-67]. Peak near-infrared switching levels from 20% to greater than 75% have been achieved with crystalline tungsten oxide. The reflectance properties of tungsten oxide films produced so far seem to lie far from the theoretically limiting behavior.

Several international research groups are investigating electrochromic materials and devices for building windows [68]. Many of these are organized under government funded programs. Also, many of the participants have other parallel chromogenic projects. Also, some of these researchers participate in the International Energy Agency SH&C Task 18 Annex on Advanced Glazing Materials-Chromogenics (B3) Project.

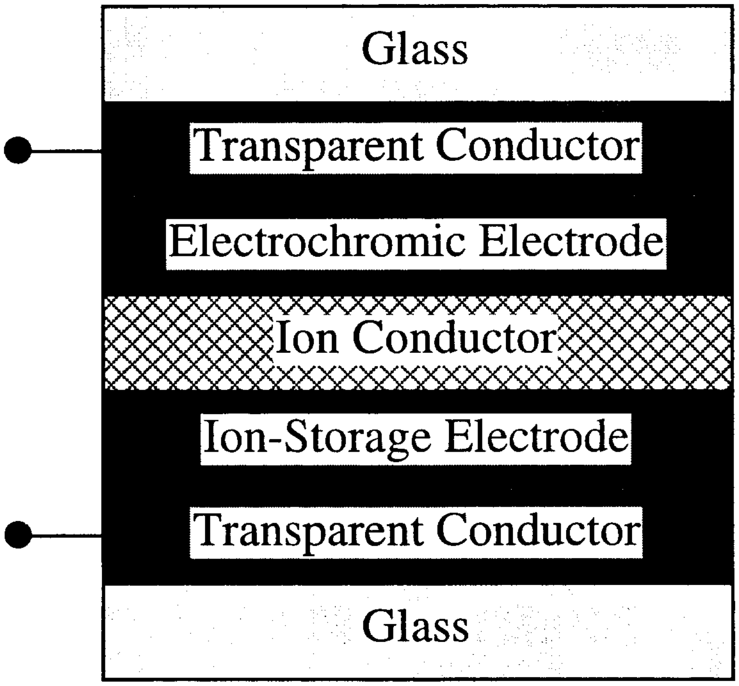

**Fig. 7.** Schematic of an electrochromic glazing showing the various layers.

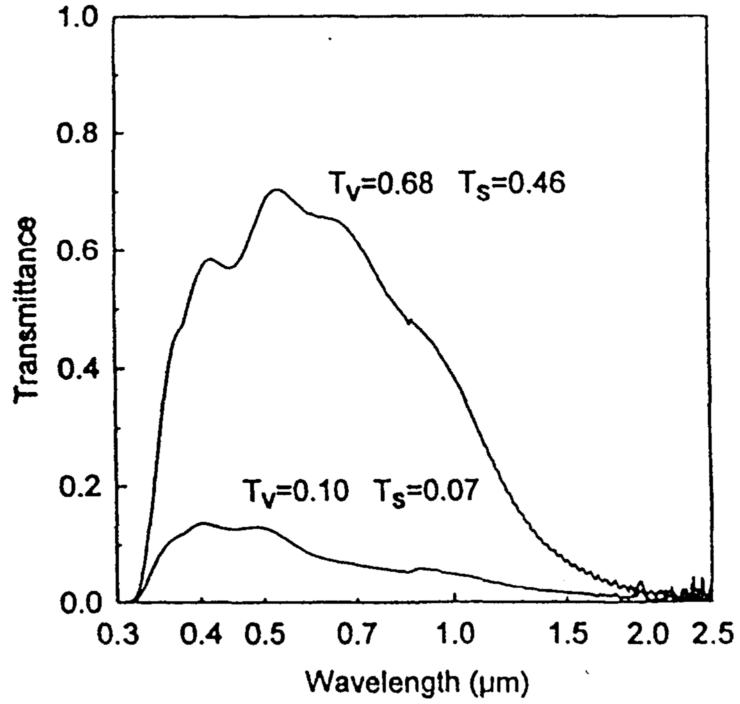

**Fig. 8.** Spectral transmittance of an electrochromic glazing based on tungsten oxide and nickel oxide laminated with a lithium polymer ion conductor.

One of the bigger multinational projects is the Joule II Commission of the European Communities (CEC) project. Pilkington PLC has a multiyear project electrochromic glazing under the JOULE II program. This project involves several organizations, including Flachglas AG and Danionics AS, Oxford Brookes University and the University of Southampton. The Oxford group is known for their work on electrochromic nickel oxide. Flachglas has recently shown a prototype switchable glazing of 0.80 m x 1.2 m. For their window they obtained a range of $T_V$=65-20% and $T_S$=45-10% [69]. The glazing takes a few minutes to change color and to bleach. Flachglas has also made prototype sunroofs for cars (46 cm x 78 cm) with a $T_V$=70-14%. Under this project, laminated glazings have been developed based on $Li_xWO_3$/Li-polymer/metal oxide structure. Other participants in CEC projects are the Granqvist group at the University of Uppsala working with Coat AB and Leybold AG. In France, St. Gobain, Corning Europe, and C.S.T.B and the University of Domaine are working with electrochromic devices and components. In Italy there are several groups involved in electrochromic devices testing and development. They are listed in Table 2.

In Japan, Asahi Glass has been steadily developing prototype electrochromic windows (0.4 m x 0.6 m and 0.6 x 0.8 m) based on $Li_xWO_3$/metal oxide/$NiO_x$ for testing and evaluation. Part of Asahi's work has been funded by the Japanese government-Sunshine project under MITI. The project goals are to develop a glazing by Spring 1996, with 50 % visible change, 10 year projected lifetime and $10^5$ cycle lifetime [70]. For this glazing they have obtained optical properties of $T_V$=73-18% and $T_S$=55-11% withstanding 25-60 C long term cycling. The transmission properties are shown in Fig. 9. About two hundred (0.4 x 0.4 m size) of an early prototype electrochromic window have been installed in the Seto Bridge Museum (Kojima, Okayama-Pref., Japan).These prototypes were evaluated in the IEA SH&C Task 10 activities [48]. Another Japanese Government funded project is at NIRIN, on basic electrochromic materials for devices including characterization.

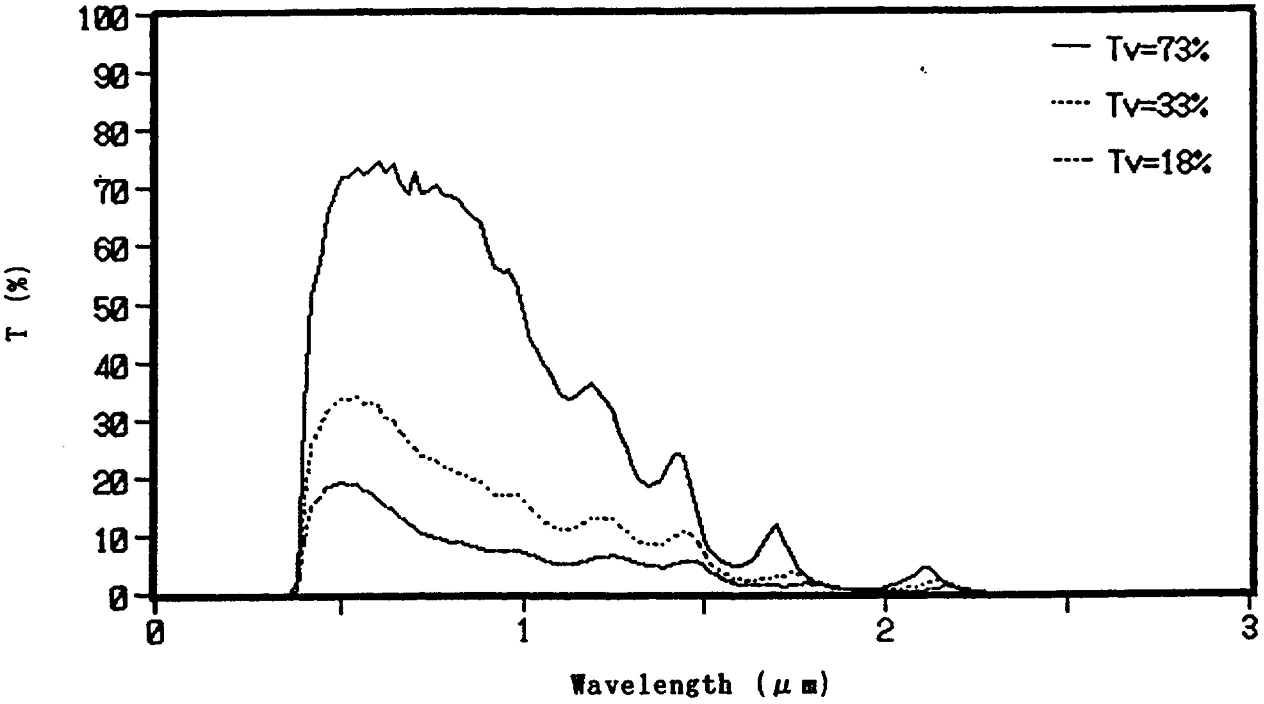

**Fig. 9.** Spectral transmittance of an Asahi prototype electrochromic glazing based on tungsten oxide/metal oxide/nickel oxide using lithium as a coloration ion.

In Australia, a government grant has funded the Univ. of Technology, Monash University, Glassform and Silicon Technologies Australia to develop sol-gel deposited electrochromic devices. These devices are based on laminated structures using $WO_3$, so far prototypes of 10 cm x 10 cm have been produced.

In Canada, the National program through, Energy Mines and Resources, funds work at Enermodal Engineering to determine performance characteristic of electrochromic windows. The program funds basic work at Univ. of Moncton on monolithic lithium coloring electrochromic devices based on tungsten oxide. This group has a long history of basic work on electrochromic films. Also, work is funded at INRS on making laminated electrochromic devices by dip and roll coating using their lithium polymer. INRS is well known for their battery development work.

Under the U.S. DOE (Dept. of Energy) "Electrochromics Initiative" both Donnelly, and OCLI in partnership with EIC Labs. and Andersen Windows have contracts to develop large-area electrochrochromic glazing. Also, under the U.S. Dept. of Commerce, NIST grant, the partnership of 3M and SAGE Corp. was awarded a sizable grant to develop electrochromics on plastics. At LBL we serve as the lead lab for the U.S. Dept. of Energy Program. At LBL devices and components for mainly laminated devices based on $WO_3$, NiO, $NbO_x$ and $Li_xNiO$ have been studied.[71-73] Another development at LBL has been on polymer ion storage layers for lithium and proton storage [74]. The development of testing and evaluation procedures has been done through IEA under Task 10 [75] and at NREL [76]. Another approach is the development of low-cost switching devices based on plastic substrates. Southwall Technologies (Palo Alto, CA) has produced electrochromic electrodes of tungsten oxide/ITO on polyester.

## 4. Conclusions

Switchable glazings will ultimately lead to better glazings for buildings. In a number of applications, it will add to the comfort and well-being of its users. Smart windows will help lower of the demands on precious non-renewable fuels for lighting and cooling. The prospects are great with many major companies involved in the development of switchable glazings worldwide. Also, the scientific and technological challenges of the development of these complex glazings are great, creating a specialized area of research. In this study, chromogenic glazing materials were discussed. The discussion included non-electrically activated materials covering phochromic and thermochromics. Under electrically activated devices dispersed liquid crystals, and suspended particle devices and electrochromic devices were covered. For the non-electrically activated glazing the best specular response comes from photochromic glass or plastic. Unfortunately the glass is very expensive and the plastic is not very UV stable. The best thermotropics for glazing appear to be the hydrogels which are commercially or near commercially available. The hydrogels suffer from stability with time due to their dependence on water. But they offer a strong switching effect from a bleached to translucent condition. Work is ongoing on the Mott transition materials such as doped $VO_2$. Possibly a breakthrough might come from this area in the future. Of the three major types of electronically activated glazings, all three have their particular applications. Dispersed liquid crystal devices have a very good future but are restricted by three characteristics: (1) UV stability is poor. (2) haze remains in the activated (transparent) state, and (3) the unpowered state is diffuse. The development in dispersed particle devices is moving forward with a number of commercial activities and demonstration windows. These devices are colored in the off-state and become transparent in the on-state. With further improvements in processing and the development of a sheet form of this material, these devices could see widespread use. There are several promising electrochromic devices for window glazings. For the electrochromic layer, tungsten trioxide, nickel oxide, iridium oxide and viologens are the most developed for devices. In the future, the developments will lie in the designing of the appropriate ionic and electronic materials to make devices durable over many years and cycles. Durability is of importance for all smart window devices, and an expected lifetime of at least 5-15 years must be assured. The great challenge is to make these technologies, with low-cost fabrication techniques, in the 100-250 $\$/m^2$ price range.

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