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# ELECTROCHROMIC MATERIALS AND DEVICES FOR ENERGY-EFFICIENT WINDOWS

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# ELECTROCHROMIC MATERIALS AND DEVICES FOR ENERGY-EFFICIENT WINDOWS

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# ELECTROCHROMIC MATERIALS AND DEVICES FOR ENERGY EFFICIENT WINDOWS*


## ABSTRACT

Numerous inorganic and organic electrochromic materials are discussed in the context of developing a film-based optical shutter for a window application. It is possible electronically to alter a window's transmission and reflection properties by use of electrochromic thin films. This allows regulation of conductive and radiative heat transfer rates, with variable optical attenuation. As a result, an aperture can be optically and thermally managed, reducing space heating and cooling loads. The properties of transition metal oxides, such as $WO_3$, $MoO_3$, $Ir_2O_3$ and $V_2O_5$ are detailed. Organic systems such as heptyl viologen and polytungsten anion are reviewed. Also, intercalated structures are discussed. Various designs of working devices are outlined with emphasis on solid-state configurations. From this quantification, materials and devices with appropriate deposition techniques for window applications are detailed.



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## 1. INTRODUCTION

The development of a dynamic adjustable optical shutter as an integral part of a window is extremely attractive from the viewpoint of improved building energy efficiency.

There is a wealth of technical literature and patents dealing with electrochromic materials and devices. However, primarily these are for electronic information display or other small-scale applications. As a result of this prior research, only minor attention has been paid to electrochromic devices as transmissive devices. Also, much study has emphasized very fast switching properties. In the selection process many compounds and device configurations have undoubtably been rejected or ignored. Historically, many promising technologies for electronic display purposes have yielded to select favored technologies. So, some cases, such as the electrochromic watch display, are abruptly abandoned to the reigning technology, liquid crystals.

In this study, we consider the technical properties and merits of known electrochromic phenomena and materials to determine their potential for architectural energy conservation and solar energy purposes. This application implies that such materials have a low or medium cost and characteristics which are appropriate for the control of light and heat. However, for many materials and devices insufficient data are available for a conclusive evaluation.

A switching device integrated in or attached to a window glazing offers adjustable control of the energy that flows through the window aperture. Energy management and favorable use (or rejection) of incident solar radiation for heating and lighting can reduce net energy consumption. Also, in certain cases, the insulating value of a window can be adjusted. Currently, windows have very poor energy management properties so they are responsible for at least 25% of net energy usage in buildings. Electrochromic optical shutter devices can eliminate elaborate internal and external shading devices and can provide daylighting for the workspace, reducing lighting energy loads. Also they assure privacy and glare control. If an optical shutter has high infrared reflectance in one of its optical states, it can have adjustable heat-mirror characteristics. An ideal optical shutter might be one that responds automatically to a changing ambient environment to provide comfort, visual needs, and energy savings. Such a device may be connected to a building's energy management system that adjusts heating, cooling, and even lighting to workplace needs. Electrochromism is not the only phenomenon which is useful for windows; a number of other chromogenic

and physio-optical techniques may be useful.[1,2] The optical switching effect can be ideally modeled by one of two processes: an adjustable transmission edge (Figure 1), or adjustable band transmission (Figure 2). In both cases, the admittance of the solar visible and near-infrared spectra in Figure 3 can be regulated as in Figure 4 schematic. For simplicity, absorptance is neglected in these idealized cases; in actual electrochromism, however, absorptance is a significant consideration. Also, such broadband responses may be limited to narrow regions of the visible or infrared energies. Actual modulation of near-infrared energy has been demonstrated in polycrystallines $WO_3$ films made by r.f. sputtering. This film is suitable for control of near infrared solar energy passing through windows.

As mentioned before, the electrochromic effect has been researched, with a few exceptions, entirely for electronic display devices. Display devices have important differences from optical switches. They are designed to be opaque rather than transmissive in their bleached form, either using a diffuse white electrolyte (or ion conductor) or a counter-electrode. A transparent counter electrode, required for an optical switch, is an unusual and restrictive requirement. Also, a display device when operated is either bleached or colored; for shutters, intermediate coloration is important. An advantage of electrochromic devices over other switching processes is that they exhibit open circuit memory in either the bleached or colored state. They are high-contrast devices and, in some cases, a metallic product is formed upon switching, enhancing the heat-mirror benefits. These devices are also useful in their absorptive form, as in photochromic glass. The speed of switching for a display and its power requirements determine whether it is viable. For a window shutter even very slow reactions, on the order of minutes, are acceptable. Also, power requirements are much less stringent than for a battery-operated display device. Lifetime and operating temperatures are probably more demanding for the window shutter than for the display.

Electrochromism for large-scale windows has been addressed in various publications,[1-4] including a review of materials.[5] Inorganic materials and devices for displays have been covered in past articles authored by workers at IBM Labs, Bell Labs, Brown-Bovari in Switzerland, Philips in The Netherlands,[6-8] and at RCA.[9] Much of the literature is concerned with mechanistic studies, with microscopic phenomena and importance of film hydration still subjects of controversy. However, since light-emitting diodes and liquid crystal devices dominate the display market, much electrochromic research has been discontinued. Regarding transmissive devices, some work has been reported in the United States for

passive solar uses.[3,10] Transmission devices have also been of interest in Japan. Research has been reported by Asahi Glass Labs on $WO_3$ devices.[11,12] There are several other firms in Japan interested in electrochromism: Sharp, Seiko, Sanyo, Matsushita, Toshiba, Canon, Nikon, and others.[13-15] Most, however, are electronics-oriented. In Europe, Ebauches SA, Asulab SA, Bosch, and Imperial College, among others, are interested. In the U.S. prior research has been reported from American Cyanamid, Bell Labs, RCA, Texas Instruments, IBM Labs, Optel, and others, all chiefly concerned with information display electronics. Also, some U.S. patents exist for $WO_3$ transmission displays and electrooptical modulators. These, among other general electrochromic devices, are tabulated in the Appendix.

Despite this work, sufficient research has not been performed on even the most popular $WO_3$-based device. Another consideration is whether to discount the liquid or gel electrolyte-containing device in favor of the solid-state one. Liquid devices have the best performance and are better characterized. When fast-ion-conductors are used, solid-state electrochromic development relies on progress in the allied field of solid electrolytes. Certain device configurations do not specify fast-ion conductors, an oxide layer may be used for slower devices. Because of potential sealant problems and liquid/ solid interface stability requirements, the solid-state device is generally favored, although it is the least mature. This study covers both liquid electrolyte and solid-state devices, mainly because liquid devices have played such a major role in the field. Up to this time, electrochromic devices have been fabricated on glass substrates. Also, it may be possible to deposit a flexible optical switching device onto plastic, much like present triple-layer heat-mirror films. Developments are underway to deposit transparent conductors onto polyester films; this may be a possibility. The characteristics of the best electrochromic device (liquid electrolyte) are: response time, 3-40 msec, cycle energy 8-50 $mJcm^{-2}$, 1 volt potential and lifetime $10^5$-$10^7$ cycles.[7]

## 2. ELECTROCHROMISM

Electrochromism and electrochemichromism* are exhibited by a number of materials, both inorganic and organic liquids and solids. Electrochromism is a reversible color change in a material caused by an applied

*Strictly speaking, electrochromism is a solid-state effect[16,17] electrochemichromism is an electrochemical effect.[18] Many of the systems described herein are based on electrochemichromism; however, no distinction will be made hereafter.

electric field or current. This change can be due to the formation of color centers (or defect complexes) or to an electrochemical reaction that produce a colored compound. Electrochromic coloration has been demonstrated in both anodic and cathodic devices. An electrochromic material must posses both ionic and electronic conduction. An electrochromic device can consist of many configurations depending on property requirements. The basic elements of an electrochromic device are: two (2) conductor layers to inject charge, an active electrochromic layer, an electrolyte or ion conductor (which may in some cases be an insulator), and an ion storage media which may be the electrolyte, another electrochromic layer, or even an integral part of the conductor layers. This sandwich configuration allows a reversible chemical reaction to cycle between the electrochromic material and ion storage media, with simultaneous injection of electrons or holes and proton or ions, depending on the material. For example, in an inorganic solid the ion-insertion reaction might be:

<u>Cathodic</u> $MO_y + xA^+ + xe^- \longleftrightarrow A_xMO_y$, colored when reduced
where: $A^+ = H^+, Li^+, Na^+, Ag^+$

<u>Anodic</u> $MO_y + xA^- + xh^+ \longleftrightarrow A_xMO_y$, colored when oxidized
where: $A^- = F^-, CN^-, OH^-/H^+$
and
x is generally $0 < x < 1$.

## 3. CLASSES OF ELECTROCHROMIC MATERIALS

There are three general classes of electrochromic materials: (1) transition-metal oxides (primarily hydrous), (2) organic, and (3) intercalated materials. Within each class there are differences in morphology, liquid or solid phase, crystal structure, degree of order, and stoichiometry for each electrochromic material. There are also differences in device configuration and whether a solid or liquid ion conductor is used.

The bulk of the research published to date concerns transition metal oxides. Within this large classification are some distinctions. The most popular system appears to contain the IV-B oxides. In this group are $WO_3$ and $MoO_3$. Also, the group VIII oxides are within this category where most of the parent metals belong to the platinum group (Pt, Ir, Os, Pd, Ru, Rh). Also, iron, cobalt, and nickel are in the group VIII category. Currently, four of the group VIII oxide materials are known to exhibit electrochromism, $IrO_x.nH_2O$, $Rh_2O_3.nH_2O$, $NiO.nH_2O$ and $Co_2O_3.nH_2O$.

Unrelated oxides such as $V_2O_5$ and doped $SrTiO_3$ also show electrochromism. The remaining oxides may have electrochromism that is yet to be demonstrated. Candidates are $Pt_2O_3.nH_2O$, $PtO_2.nH_2O$, $PdO.nH_2O$, and possibly $Fe_2O_3.nH_2O$. Other important categories are organic compounds and intercalated materials. For the organic groups, the viologen, pyrazoline, lanthanide phthalocyanine, anthraquinoide groups, and conductive organic polymers exhibit electrochromism.

Tables 1-4 list electrochromic films reported to have either solid or liquid electrolytes. Only representative references are given here; others can be found in recent reviews.[5,7-9] Table 1 covers selected inorganic compounds from which devices have been fabricated using solid electrolytes. Recent research with hydrated polymer conductors has resulted in excellent electronic display characteristics. Hydrated polymers of polyvinylsulfonic Acid (Poly-VSA), polystyrensulfonic Acid (Poly-SSA), polyperfluorsulfonic Acid (Nafion), and poly-2-acrylamido-2-methylpropanesulfonic Acid (Poly-AMPS) have been investigated as electrolytes.[30-31,69] Both Poly-VSA and Poly-SSA suffer from yellowing with time. Poly-AMPS, a polymer electrolyte[31,69,70] is well suited to $WO_3$ display applications. It may be useful also for transmissive devices because it is normally a transparent polymer. Table 2 covers common electrochromic materials and Table 3 details less-researched electrochromic materials. Further research is needed to evaluate these systems properly. Table 4 catalogs the organic electrochromics. Electrochromism was first demonstrated in an organic viologen. The viologens (dipyridium salts) used as display materials tend to bleach irreversibly after a time, reducing their life. Other organic systems are the bipyridyls, pthalocyanines, anthraquinoids, tetrathiafulvalenes, and phenotiazines.[5] Phenotiazines have been dissolved directly in paste and gel electrolytes to give electrochromic effects.[71]

## 4. CATHODIC INORGANIC ELECTROCHROMICS

Both stoichiometric and sub-stoichiometric forms of some of the group VIB oxides such as $WO_3$ and $MoO_3$, along with various admixtures, exhibit electrochromism. The bulk of cathodic electrochromic research has been performed on the $WO_3$ compound, and to a lesser degree, $MoO_3$.

Traditionally, the $WO_3$, $MoO_3$, and $V_2O_5$ oxides are prepared by vacuum evaporation from heated boats of W, Ta, or Mo, under pressures of $10^{-4}$ - $10^{-6}$ Torr.[6,72] Also, $WO_3$ has been prepared by reactive sputtering and solution spraying or ions.[73] The general concern, in terms of deposited microstructure, is the material's ability to easily transport protons or ions.[74] Incorporation of water appears to dictate electrochromic

coloration speed.[75] Anodically-prepared films are generally much faster than others deposited by alternate techniques.[74,76] Also, there is some evidence that aged $WO_3$ cells can be regenerated by UV irradiation in the bleached mode.[77] Films formed by dry thermal oxidation in most oxide systems show poor electrochromism and require pretreatment to activate the material. Wet oxidation of metal film appears to be a promising fabrication technique.

## A. Tungsten Oxide Electrochromism

In tungsten oxide, ($WO_3$), amorphous and polycrystalline films have shown electrochromism, with switching performance improving with decrease in crystal size. Films of $WO_3$ can be converted from transparent into deeply-colored $H_xWO_3$ by proton injection from a suitable electrolyte or ion conductor. $H_xWO_3$ can be generalized to $M_xWO_3$, including other cations, namely, $Li^+$, $Na^+$, $K^+$, $Cs^+$, and $Mg^{2+}$.

Until about 1975 it was believed that a current applied to $WO_3$ produced a redox reaction to form a blue-colored oxide product. The reaction was proposed to be:

$$xWO_3 + 2\ yH^+ + 2\ ye^- \rightarrow W_xO^+_{3x-y} + yH_2O,$$

as mentioned in reviews on electrochromic displays.[18,59] A similar but more complex model for this system was proposed in 1975,[78] which resulted in a complex of $WO^+_x$ and $OH^-$ according to the following reaction:

$$WO_3 + yH^+ + ye^- \rightarrow WO_{3-y}(OH)_y.$$

Another model proposed at this time fit experimental data. It involved intervalence transition absorption for electrocoloration of $WO_3$.[40,72,79,80] Coloration of the film was achieved by simultaneous injection of electrons and cations into interstitial sites in the $WO_3$ atomic lattice, forming a tungsten bronze, according to the following equation:[72]

$$xM^+ + xe^- + WO_3 \rightarrow M_xWO_3 \quad (0 < x < 1),$$

where M is a positive ion, in the simplest case, a proton $H^+$. In amorphous films above $x = 0.32$ the tungsten bronze behaves as a metallic conductor,[81,82] and below that figure it semiconducts due to localization induced by inherent lattice disorder and disordered arrangement of

protons in the M sublattice.[81,83] This hypothesis accounted for coloration by intervalence transfer absorption[79] stated as:

$$W^{5+}(A) + W^{6+}(B) + h\nu \rightarrow W^{6+}(A) + W^{5+}(B),$$

where A and B are two different tungsten lattice sites. Closely related to this theory is small polaron absorption, which has also been suggested as an explanation of the coloration of $WO_3$ films.[36,37,84-86] In both models coloration is attributed to the tight localization of conduction band electrons to $W^{5+}$ sites. The $W^{+5}$ species form a defect band that is localized within the bandgap. However, coloration can be explained by delocalized electrons and free electron plasma absorption. This effect has been ruled out because in amorphous films a broad absorption peak is noted over the range 1.2 to 1.5 eV, rather than the sharp peak characteristic of plasma.[37,79]

Recent electron resonance studies argue against both intervalence transfer and small polaron models.[86a] Electrons are not uniquely localized in $H_xWO_3$ in either amorphous or polycrystalline forms. If $W^{5+}$ is formed during coloration, the donated hydrogen electron must be delocalized over a number of tungsten sites. In fine grained polycrystalline films a model has been proposed which follows Drude theory with consideration of localized electrons in deep donars in grain boundaries.[95]

Following the intervalence transfer and polaron models, we can make a model for device operation. An optical absorption transition from the valence band to the defect band can result from photon irradiation or an applied electric field. In the former case, population of the defect band causes color centers. For electrochromic films an external field is used to bend the bands sufficiently so injected electrons can fill the defect band. When the field is reversed the bands can bend in the opposite direction, allowing depletion of the defect band and film bleaching. There still exists considerable controversy regarding the coloration mechanism of $WO_3$. By various experiments including non-electrochemical ones, bleached and colored films do not appear to differ in their $H^+$, $H_2$ or $O_2$ content.[87-89] Therefore, the coloration reaction would consist of internal redistribution of hydrogen from site to site in the $WO_3$ lattice. These data don't explain the high charge injection levels needed to switch the device, compared to a much smaller amount needed to shift hydrogen[90].

## B. Properties of Protonated and Alkali Tungsten Bronzes

Electronic transport in amorphous $H_xWO_3$ films follows a variable range-hopping model for $x \leq 0.3$. Conductivity is $\sigma = 987\ (x - 0.31)^{1.6}$ $(ohm\text{-}cm)^{-1}$ for 4.2 $^oK$ and approximate for 300 $^oK$.[81] Electrochemical data have been measured on a wide x = 0.002-0.5 range of amorphous $H_xWO_3$ films.[91]

Stoichiometry was measured for amorphous films prepared by thermal evaporation in vacuum from $WO_3$ powder. Resulting films were measured by proton backscattering and revealed $H_xWO_{2.7}$ with $0.2 < x < 0.5$;[92] for x above 0.3 the films were metallic. However, these data have been criticized; oxygen to tungsten ratio may be 2.96-2.99.[93] In many cases in the literature, tungsten bronze is referred to as $H_xWO_3$ because its stoichiometry is unknown. The convention in this study is to state stoichiometric compounds if the exact stoichiometry is unknown.

Both sodium and lithium tungsten bronzes have been investigated as electro-coloring materials. Their properties and characteristics are similar to those of $H_xWO_3$. $Na_xWO_3$ shows a change from light green to deep blue. This material is made electrochromic by acid anodization of a deposited film.[41,42] Anodization creates a 1500-A thick sodium-depleted surface layer.[94] A proton then can occupy the empty Na site, resulting in the color center formation known for $H_xWO_3$. The electronic structure of $Na_xWO_3$ has been investigated also.[43]

For $Li_xWO_3$ it has been argued that the presence of $LI^+$ instead of $H^+$ may make a longer lifetime, as hydrogen tungsten bronze in acid electrolyte tends to discolor with time.[43] $Li_xWO_3$ shows a phase change at x = 0.4. When activated, symmetric cells of $LI_xWO_3$ and $WO_3$ show blue for $x < 0.4$ and pink for larger x.[43]

## C. Molybdenum Oxide

Color center phenomena have been noted in both crystalline and amorphous forms of $H_xMoO_3$. The absorption spectra of $H_xWO_3$ and $H_xMoO_3$ are similar; they peak in the red 0.87-micron wavelength.[44,45] When activated the characteristic color is purplish blue. Molybdenum bronze has a humidity threshold below which coloration will not take place.[96] The refractive index of $MoO_3$ as a thin film[45] is n = 2.30 for wavelengths greater than 0.8 microns and n = 2.2 for wavelengths greater than 0.5 microns.[34] Amorphous films are generally substoichiometric; possibly they are $MoO_{2.96}$.[46] They can be colored by ultraviolet light or by applied electric field. The mechanism of coloration is thought to be similar to that of tungsten oxide films, but has not been verified.[33]

D. Niobium and Vanadium Oxide

The group VB oxides, namely $Nb_2O_5$ and $V_2O_5$, exhibit electrochromism like that of $WO_3$. Electrochromic niobium oxide $Nb_2O_5$ films are formed by cyclic anodization. Large changes in optical absorption were noted when niobium electrodes were cycled; this was due to solution and ionization of hydrogen in the surface oxide. Only small refractive index changes occurred. The bandgap of this oxide is 3.18 eV.[53] The suggested reaction is:

$$Nb_2O_5 + 2H^+ + 2e^- \leftrightarrow Nb_2O_3(OH)_2 \text{ or } 2Nb_2O_2 \cdot H_2O.$$

Too little work has been performed on this system to qualify it for thin film use in optical shutters.

The vanadium oxide system performs much like $WO_3$ except water or alkaline electrolyte must be used due to $V_2O_5$'s high solubility in acid.[97] When $V_2O_5$ is immersed in water it changes from yellow to black.[53] Initially, amorphous $V_2O_5$ films are yellow and electrocolor to greenish-blue.[55] The peaks of the absorption bands are 1.6 microns and 0.690 microns in the yellow film. New bands appear at 0.525, 0.410, and 0.310 microns during activation.[33] During coloration in $V_2O_5$ films, $V^{5+}$ undergoes a reduction to $V^{4+}$.

Various vanadium bronzes may exhibit improved and tunable electrochromic behavior. An example might be $M_xV_2O_5$ where M = Li, Na, or Ag. $AgV_2O_5$ has been investigated as an electrode material.

E. Titanium Oxide

Amorphous titanium oxide undergoes an electrochromic reaction after the following:[53]

$$TiO_2 + H^+ + e^- \leftrightarrow TiOOH.$$

This was noted for Ti metal electrode material made by anodic cycling. The bandgap for amorphous $TiO_x$ is 2.88 eV with absorption edge at 0.43 microns. After coloration, the bandgap moved to 2.99 eV and absorption edge decreased to 0.415 microns.[53]

F. Tungsten Heteropolyacids

Phosphototungstic acid ($H_3PO_4(WO_3)_{12} \cdot nH_2O$) is a member of a group of compounds known as heteropolyacids. Within this class several materials exhibit coloration upon reduction. Electrochromic properties in solution have been noted elsewhere.[98] However, phosphototungstic acid exhibits electrocoloration in its solid form. This material also serves as a proton conductor, eliminating the need for an ionic electrolyte. In the bleached state this compound is white (as a compressed powder) and is blue when activated.[99] This substance would be useful only in windows, and possibly skylights, if it were translucent. If this material can be formed into thin films rather than being used as a powder, it could have promise.

The polytungsten anion (PTA) system exhibits a deep violet in its reduced state. PTA is made from a solution of $CaWO_4$ and $H_3PO_4$ at high temperature. It can exist as an electrochromic material or if it is mixed with photosensitive material such as ZnCdS, it can exhibit photoactivation. The mixed system will darken with incident light intensity but can be lightened by applied potential. In a research cell it takes 4 minutes to achieve an optical density change of 40 at 3 volts.[62] The concept of this cell is important to window shutters, since it combines both passive and active effects. Its long reaction time is a drawback, however.

PTA has also been used, exclusively as an electrochromic display.[59] The working electrolyte consists of $Na_2WO_4$ + $ClCH_3COOH$. PTA undergoes a simple redox reaction. By the addition of $H_2O_2$, a redox reaction coupled with an independent reaction is obtained for this system.

## G. Metal-Oxide Cermets and Mixed Oxide Composites

Au-$WO_3$ cermets and Pt-$WO_3$ cermets have been formulated as electrochromic materials. Au and Pt were added in the hope "tuning" the color of the electrochromic material. The characteristics of 20-120 angstrom diameter gold particles in amorphous $WO_3$ produce a material that is blue initially and becomes red or pink when electrochromically excited.[38,39] In a polycrystalline $WO_3$ matrix the colored state is dark blue.

The purpose in developing mixed oxides was to create an electrochromic system that better suited the human eye's peak response at 2.25 eV.[100,101] (The peak for $WO_3$ is 1.4 eV and for $MoO_3$ is 1.56 eV.) For highly-colored films a peak of 2.15 eV can be obtained with a mix of 50 atomic $MoO_3$.[40]

For most designs, conductive transparent oxide films of doped $SnO_2$ or $In_2O_3$ or commercially precoated glass are available. Composite systems such as $WO_3$-$MoO_3$ are made by co-evaporation[40] or RF reactive co-sputtering.[38,39,100]

## 5. ANODIC INORGANIC ELECTROCHROMICS

The hydrous oxides in group VIII, the platinum group, have been investigated for electrochromism. Ion injection into oxides of iridium, rhodium, nickel, and cobalt causes optical absorption changes in these materials.[7,47] They color by anodic transfer of electrons out of the film coupled with cation ejection or anion injection from the electrolyte.[50] One potential drawback with large scale devices based on iridium and rhodium is their high materials cost. Anodic display devices are constructed in a similar fashion as cathodic devices. These oxides are formed by anodization of metal electrodes as films. Also, oxides can be made by reactive sputtering and evaporation. Very little work has been done on solid-state or optical switching devices based on the platinum group oxides.[51]

### A. Iridium Oxide

Hydrated iridium oxide shows a transparent to blue-black electrochromism with ion injection. These films can be made by a variety of methods. The most promising technique is reactive sputtering of iridium metal in oxygen to make what is known as the sputtered iridium oxide film (SIROD) device.[102] Cyclic anodization is used to make films from iridium electrodes, known as anodic iridium oxide films (AIROF). These electrodes are cycled in a bath of $H_2SO_4$ at 85°C to be converted to oxide[47,102,103]. Also, iridium can be vacuum evaporated on conductive glass and subsequently anodized to make an oxide film.[104] The bulk of the research on these films was done at Bell Laboratories.

The structure and exact composition of these films is still unknown. AIROF films show poor chemical stability when cycled in common electrolytes. However, SIROF films show excellent durability. The structure of SIROF films is identified as densely amorphous, while AIROF's have highly porous crystalline or amorphous structures.[105,106]

A proposed reaction for coloration is based on one of two mechanisms a) proton extraction from the films b) hydroxide ion insertion. There exists experimental evidence for either mechanism. The reaction can be interpreted as:

$$Ir(OH)_3 - H_+ + h^+ \longleftrightarrow IrO_2 \cdot H_2O \text{ , proton extraction or}$$

$$Ir(OH)_3 + OH^- + h^+ \longleftrightarrow IrO_2 \cdot H_2O + H_2O \text{, hydroxide injection}$$

For hydroxide injection the second $H_2O$ is unbound interstitial water. The colored compound is $IrO_2 \cdot H_2O$ and uncolored is $Ir(OH)_3$.[48] During this transformation reflectance contrast changes 60:1.[107] The presence of bound water is important for fast coloration and bleaching of the film.[108] Iridium films formed by dry oxidation are electrochromically inactive. In terms of switching time, coloration efficiency and temperature, iridium oxide is comparable or better than tungsten oxide films.

B. Rhodium Oxide

A two-color electrochromic film can be formed from $Rh_2O_3$ (hydrous) by anodic pulsing. Both yellow to dark green and yellow to brown-purple colorations can be invoked in either 1M or 5M KOH solutions.[51] Coloration reaction is suggested as:

$$1/2\ Rh_2O_3\text{(hydrous)} + OH^- + h^+ \longleftrightarrow IrO_{RhO_2}\ \text{(hydrous)} + 1/2\ H_2O,$$

where $Rh_2O_3$ is yellow and $RhO_2$ is dark green in color.[51,52] The reaction to form a brownish-purple product has not been identified.

C. Nickel Oxide

Electrochromic films of $NiO_x$ (hydrous) have been found by cycling the potential of a nickel electrode in an alkaline electrolyte. The hydrous nickel oxide film can also be electrodeposited. During coloration the film changes from transparent to a dark bronze color, resulting in a reflective contrast ratio of 100:1. Coloration and bleaching times are 50 msec and 19 msec respectively in 1M KOH electrolyte. These fast times are due to the incorporation of water molecules between oxide layers. The general reaction of coloration[52] is:

$$Ni^{+2}\ \text{(hydroxide)} \rightarrow Ni^{+3}\ \text{(hydroxide)} + e^-.$$

The colorization and bleaching potentials are separated by 0.4 V.[52] This work is in progress at present and may lead to a fairly inexpensive material for windows.

## 6. ORGANIC ELECTROCHROMIC MATERIALS

A number of organic materials can exhibit electrochromism. Historically, the viologens have been researched for electrochromic display devices. Within the organics, coloration of a liquid is achieved by an oxidation-reduction reaction, which may be coupled with a chemical reaction; the product reaction is a highly-colored species. Also, substances in groups, such as pyrazoline, biphenyl anthraquinoides, and tetrathiafulvalence system exhibit electrochromism. Organmetallics, such as phthalocyanines of lanthanides and polytungsten anions, have also been researched. The basic organic electrochromic reactions have been listed by type: type 1, a simple redox reaction, which gives a colored species; type 2, also a redox reaction but coupled with an independent reaction resulting in variable color persistence; and type 3, a redox reaction with a chemical reaction producing an insoluble colored species, which affords a memory effect. The type 1 systems are the simplest of the electrochemical electrochromic process. The drawbacks are that the induced colored species tends to drift or diffuse from the electrode structure; however, this is not a serious problem for window applications. A gel electrolyte can be used to suppress drifting. For type 2, color drift is eliminated by conversion back to the uncolored material, for example by oxidation. This system requires refreshing to maintain the colored state so its intrinsic efficiency is reduced. This type is not well suited for a window shutter. The third category involves a colored species that is insoluble in the electrolyte, which makes the display stable. However, reverse leakage current exists, and leakage paths should be eliminated for long-term coloration. The last group is probably the most attractive for optical shutters because the colored state need not be refreshed, resulting in energy and color savings.

Organic electrochromic molecules can be chemically attached to polymer coated electrodes. Various systems have been demonstrated. Polyelectrolyte complexes, polyaromatics, (polypyrrole) and polymerized hetrocyclic compound (thiophenes) have been coupled with tetrathiofulvalene and pyrozaline.[109-112]

A. Viologens

The viologens are a family of chlorides of specific quarternary bases derived from 4, 4,′-depyridinium ($C_{10}H_8N_2$). Viologens are commonly used for oxidation-reduction indicators. They are unusual indicators because they color in reduction rather than in oxidation and the redox potential is independent of pH. A popular electrochromic viologen is diheptylviologen-dibromide ($A^2Br_2^-$) in water. With applied potential above -0.66 V, the organic ion may absorb an electron of the cell cathode to form the $A^+$ radical, resulting in a deep blue color. Also, a second reaction may take place, forming A and giving a yellow color, which reacts with $A^{2+}$ to form more $A^+$ again.[113] The result is a bluish-purple cathode layer of bromide salt that is insoluble in water. The optical density of the resulting colored product peaks at 545 nm and has an absorption coefficient of a = 26000/cm.[60] The reaction is reversed (oxidized) by reversing the current or shorting electrodes, the latter being slower. The difficulty with reversing the current is knowing when to stop, as the same coloration reaction can take place on the counter-electrode. Another method of erasure is by using a reference electrode which allows only the proper voltage to be used. Erasure times can be 10-50 msec. Since an oxidation-reduction reaction is used, hermetic sealing of the device from the air is very important; this may be a drawback for a window shutter. An advantage to this cell is that contrast ratio is independent of viewing angle.

Benzyl viologen halides have also been studied; they have a lower threshold potential than the heptyl derivative. Also, benzyl viologen has been mixed with a polymerized viologen dibromide to make a two-color display.[102] In this system, colors can range from a whitish blue to reddish purple, the color being controlled by the applied voltage. Other modified viologens have been compounded to avoid aging problems associated with the second-stage reaction of heptyl viologen salt formation. It has been shown that $SnO_2$ electrodes will improve aging.[114] Also, stable films has been formed with tetramethylene [bis-4 (-ethylpridine -4′-y) pyridinium] perchlorate.[115] Speed of switching for viologen displays has been detailed elsewhere[116] but is of little concern to windows development. A GaAs-viologen device has been fabricated using photo-electrochemical principles.[117] This cell can be colored by photoreduction or electroreduction. This new cell might in principle be ideal for use as a window device. For instance, at high solar illumination the panel could turn dark, while one could manually override this effect for daylighting. However, GaAs would be impractical for this application due to its materials cost and high visible absorption.

B. Pyridine and o-Tolidine Systems

The terminology "electrochromism" originated from field-induced spectra shifts shown in pyridine.[118] Most of the data on the pyridine system are in patent literature.

O-tolidine ($C_{14}H_{116}N_2$; 4,4′ diamine-3; 3′ dimethyl biphenyl) exhibits electrochromism. Upon oxidation it can turn white or reddish in color.[6]

C. Phthalocyanine Lanthanides

The phthalocyanine lanthanides form a large series of new electrochromic materials. Lutetium diphthalocyanine is currently receiving attention.[64,65] The original film coloration is green and can be transformed to red, violet, blue, or yellowish red depending on the magnitude of applied current. Electrolytes such as dimethylformamide and potassium chloride can be used. The coloration mechanisms, along with device design, currently are under development. The variety of colors shown by this last group of materials is promising for aesthetically pleasing optical shutters.

D. Anthraquinoide and Polymer Tetrathiafulvalene System

Anthraquinoides of oxygen compounds can form colored salts with cations when in the divalent anion state.[66] This is opposite to the formation of colored anions for the viologens in the monovalent cation state. A cell has been fabricated using 2-tertiary butyl anthraquionone with other materials to form a paste material. The peak absorption is at 0.55 microns and will color reversibly from red to white. Blue and green are also obtainable by changing the solvent.

The last group of organic materials includes polymers. Films of yellow tetrathiafulvalene (TTF) can be oxidized to green or purple.[67] Switching times for TTF bound to polystyrene are on the order of 50 msec. It is thought that other, similar electroactive polymer films may exhibit electrochromism.[67]

E. Pyrazoline

The color-producing reaction in pyrazoline can be triggered by blue or UV radiation. By application of voltage the cell an be b eached or intensified in less than 1 sec. These coupled effects are known as photo-induced electrochromism (PIE). The pyrazoline cell is made from a sandwich of ITO-coated glass plates with an overcoating of $Zn(NO_3)_2$

polyamide barrier on one plate. A solution of M-DEASP pyrazoline and chloroform is between the plates. It is possible to develop a flexible PIE cell using a thermoplastic material.[58]

## 7. REDOX FERRIC FERROCYANIDE

Ferric ferrocyanide, known as Prussion blue exhibits bicolor electrochromism and UV photochromism. Ferric ferrocyanide can be deposited onto a conductive electrode from a solution of potassium ferrocyanide, $K_3Fe(CN)_6$, and iron chloride, $FeCl_3$.[119] It exhibits three color states depending upon the conditions of oxidation and reduction. Colors can range from dark blue, transparent (reduced), to light green (oxidized).[102,121] In aqueous media, it has been shown to be stable for greater than $10^6$ cycles.[122] Also using ferric ferrocyanide a transmitting switching film for potential window use has been demonstrated.[123]

## 8. INTERCALATED ELECTROCHROMIC MATERIALS

Intercalated graphite has been investigated for electrochromism[54] although, since graphite is opaque, it is not useful as an optical window material. However, it is of technical interest because the intercalated structure might be useful to synthesize new electrochromic materials.

Historically, intercalation of graphite is performed by a gas-phase reaction with alkaline metals. These metals intercalate between layers of graphite lattice without changing the crystallographic order in the graphite planes. Between these layers different stoichiometric compounds can form, including $C_6Li$, $C_{12}Li$, $C_8M$, $C_{24}M$, and $C_{36}M$ where M = K, Rb, and Cs. These compounds are commonly characterized by their golden or brass-like appearance. Intercalation can be performed in phases where, at higher (first) stages, fewer interlayer spaces are occupied by metallic compounds. The stage number is the number of carbon planes between intercalate planes; the lowest is 1, which is characteristic of $C_6Li$ and $C_8M$. The electrochromic system relies on the different colorations and optical properties these stages can exhibit.

For an electrochromic device, intercalation compounds are formed by electrochemical means and in stages, depending on the applied potential. The general reaction follows:[124]

$$C_z + e^- + M^+ \longleftrightarrow C_z^- M^+,$$

where $M^+$ = alkali metal ion and
$z$ = stage parameter

The cell is composed of a graphite back electrode and a front counterelectrode made of metal, graphite, or a conductive transparent oxide. Between the electrodes is a water-free aprotic electrolyte such as dimethyl sulfoxide. By controlling the applied voltage from 3-5 V, induced color can range from black or blue to green and golden yellow.[54] By reverse polarity the color reverts back to black. The writing and erase times are 0.2 sec; power consumption is equivalent to other electrochromic devices. It is believed that, by use of fast ionic conductors such as $Li_3N$, a solid-state display can be fabricated using these principles.

DEVICE TECHNOLOGY

As noted before, electrochromic optical switching devices can use either a liquid or a solid electrolyte. Example configurations are shown in Figures 7-8. Selected patents on these devices are detailed in the References - Patents section. (There are many other configurations and device considerations embodied in these patents than covered here). An alternate design for Figure 7a is to use oxide layers to isolate the fast-ion-conductor. Generally, the electrochromic device operates between two electrode layers. These can be semi-transparent metals, such as 50-100 A of gold or transparent conductors, such as indium-tin-oxide (ITO), doped tin oxide, or cadmium stannate. Generally, transparent electrodes should be as transparent as possible (unless attenuation is desired) and highly conductive. For a large-area window shutter it is important to keep electrical resistance as low as possible to minimize current loss and heating of the window. In both liquid and solid electrolyte devices, it is important that the electrolyte or fast-ion-conductor not react chemically with the electrodes. In insulator devices, it is important that the electrodes not serve as catalytic surfaces for oxygen evolution, which will act to mechanically break up the electrodes. For the insulator devices shown in Figure 8, the insulator layer can generally be any ion-conductive oxide such as, SiO, $MgF_2$ $CaF_2$, $Ta_2O_5$, or $ZrO_2$ at a thickness of about 100A. the active electrochromic layer is typically 0.2 - 0.5 microns; however, other thicknesses have been used.

There are only two general types of solid-state devices, one dependent on and one independent of the presence of water. Early work on devices,[34,125] was with the configuration shown in Figure 8a. Since no coloration was observed in vacuum of $10^{-5}$ Torr, it was realized that the action of adsorption and desorption of ambient water played a significant role in producing coloration. Another device was designed to depend only on trapped water. Its configuration is shown in Figure 8b.

Devices have been made consisting of $In_2O_3/p\text{-}Cr_2O_3/n\text{-}WO_3/Au$. In this configuration mixed $Cr_2O_3$ oxides have been studied.[15]

Up to now, anodic and cathodic electrochromic layers were discussed separately. These films can be placed together to function as an anodic-cathodic electrochromic cell. For example, Japanese research has shown that a transmission cell can be made up of $ITO/WO_3/TaO/MOH/ITO$ where ITO serves as an electrical contact and MOH is one of the platinum hydroxides.[13] These systems look promising as optical shutters for windows and need further research.

Solid-state devices do not have to depend on water (or protons) for their operation. Cells can rely on the transport of $Li^+$,$Na^+$, or $Ag^+$ cations. Due to the ionic size and slow solid-state diffusion rates, these devices use fast-ion-conductors to decrease switching time.

Temperature response is another consideration for using electrochromics as window shutters. It is well known that the response time of $WO_3$ electrochromics slows down below room temperature. Iridium oxide devices have been shown to have superior response at - 10°C to times better than one second.

Liquid electrolyte devices generally switch faster than solid-state devices due to increased ionic mobility. Traditionally, $H_2SO_4$ in a water-glycerol mixture has provided a satisfactory electrolyte in liquid and paste form. For displays, a white pigment is also added. Sulfuric acid provides a large reservoir of protons. Because an aqueous electrolyte has been shown to limit the lifetime of the $WO_3$ layer,[126] various aprotic electrolytes with other ions such as $Li^+$ and $Na^+$ are used. From the basic reaction to the device properties, this new ion alters the device performance. At high concentrations, ionic precipitation onto the $WO_3$ is also a problem. A typical aprotic electrolyte is $LiClO_4$ in propylene carbonate or ethylene-glycol.

Counter-electrodes also offer challenges, particularly in optical switching devices, because they must be nonpolarizing to ionic current flow. Positive ions, in the case of $WO_3$, leave the electrolyte from the $WO_3$-electrolyte interface and go to electrolyte-counterelectrode interface upon bleaching. Most metals are not suitable unless high voltages are used, which generally cause gas evolution at the electrode and surfaces, degrading the device. In practice, for display devices, a graphite electrode, graphite paper, or another electrochromic is used.

## 8. SUMMARY AND CONCLUSIONS

This paper has decribed the state of the art in electrochromic material and device design. Although most of the referenced work addresses display devices rather than large-area window shutter systems, this paper places it in context of window applications. Historically, the drawbacks of electrochromic devices have been image drift and slow response. The development of light-emitting diodes and liquid crystal displays has suppressed electrochromic research. The advantages of an electrochromic display (with memory) are principally high-contrast ratios, low-power memory, and wide viewing angles. For energy-efficient window shutters the important characteristics are solar-matched spectral response, low power, wide operating temperature and provide a wide range of intensity response. Shutters should also be programmable and manually-controlled according to heating and cooling needs and should be stable to solar radiation, weather, and cleaning. Last of all, the fabrication of material or device needs to be cost-effective.

Electrochromic devices can consist of inorganic, organic, or polymeric materials in the form of films or liquids. Many cell configurations call for a liquid electrolyte, which may be less suitable for an electrochromic window. Solid-state ion injectors (electrolytes) are probably the best for large-scale fabrication. The transition color or coloration sequence and uniformity of color are very important for a window. Human engineering for optical response and preference is important if these devices are ever to become part of large-scale construction. Other potential problems that have not been addressed in detail are the lifetime of the electrochromic panel and how it looks upon aging and degradation.

In terms of basic electrochromic materials, those that show potential as solid-state devices and exhibit memory, that is, those that do not need refreshing, are favored. Certainly the $H_yWO_x$ systems are the most researched; by replacing hydrogen with an alkali metal element, coloration can also be altered. The solid heteropolyacids hold promise because they do not need electrolytes. By forming refractory bronze cermets and metal bronzes, color tuning can be performed on these systems, which is very important for windows. A number of anodically-created platinum group oxides, including nickel, have shown electrochromic effects. These groups offer potentially inexpensive electrochemical methods of making electrochromic films. Solid-state cells have also been fabricated. Another method of film formation is reactive sputtering, which is presently being developed for high-rate coatings for other uses. Intercalated structures offer a unique electrochromic material; however,

currently graphite is used as a basis and it is opaque and therefore inappropriate for windows.

Of the organic materials, most is known about the viologens. Heptyl viologen exhibits a desirable memory effect. Some semiconductor viologen displays show photo-activation, along with electrochromic effects; a passive/active device such as this might be useful as a shutter. This is because it has built-in darkening in response to increased solar radiation, which can be overriden electrically. This effect, which is also seen in pyrazoline, requires more research. The group of pythalocyanine lanthanides offer hope of multicolored electrochromics. A variety of colors might be best and would allow versatility for architectural use. Electro-active polymers such a tetrathiafulvalene might be filmed onto plastic window materials, although present devices require a liquid electrolyte. The most cost-effective technique might be to incorporate electrochromic material directly into the plastic or glass-making process or use a related treatment.

Critical materials research issues for transmitting electrochromic devices are: 1) understanding the electrochromic phenomena and its relationship to interfaces, microstructure and chemistry of thin films, 2) determination of the solar optical properties and the range of properties for several materials, 3) development of transparent proton or ion storing counter-electrodes, 4) development of simplified device structures.

Issues of performance of optical shutter materials include: reasonable switching time, optical density range, optical homogeneity, spectral characteristics, and long cyclic lifetime. Other considerations are chemical ones: photothermal stability, no irreversible reactions, limited interdiffusion, and resistance to atmospheric attack and corrosion. Other concerns are economic, or production- and installation-oriented. For many of the materials described here, insufficient information is available to address these considerations properly. Directed, concentrated basic research is still required to arrive at meaningful and timely solutions.

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## APPENDIX

### ADDITIONAL REFERENCES-ELECTROCHROMIC RELATED PATENTS (SELECTED)


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Table 1. Selected Electrochromic Materials having Solid Electrolytes

| Material | Preparation Technique | Electrolyte | Color off/on | Insertion Ion | Ref. |
|---|---|---|---|---|---|
| $WO_3$ | Vac. Evap. | HUP(1) | -/blue | $H^+$ | 19 |
| a-$WO_3$ | Vac. Evap. | $RbAg_4I_5$ | trans./blue | $Ag^+$ | 20 |
| $WO_3$ | Vac. Evap. | Nasicon(2) | trans./blue | $Na^+$ | 21 |
| a-$WO_3$ | Evap. Sputt. | $Na^+$-β-$Al_2O_3$ | trans./blue | $Na^+$ | 22 |
| a-$WO_3$ | Evap. Sputt. | $Li_3N$ | trans./blue | $Li^+$ | 23 |
| $IrO_x$ | Anodization | $PbSnF_4$,$PbF_2$ | trans./blue-black | $F^-$ | 24 |
| $IrO_x$ | Anodization | NAFION(3) | /blue-black | $H^+/OH^-$ | 25 |
| PWA(4) | pressed powder | none | white/blue | $H^+$ | 26 |
| $WO_3$ | e-b Evap. | $ZrO_2$ | trans/blue | $H^+$ | 27 |
| $WO_3$ | e-b Evap. | $Ta_2O$(5) | trans/blue | $H^+$ | 27 |
| $Na_xWO_3$ | Vac. Evap. | $Na^+$-β-$Al_2O_3$5 | white/blue | $Na^+$ | 28 |
| a-$WO_3$ | e-b Evap. | p-TsOH/urea(6) | trans/blue | $H^+$ | 29 |
| $WO_3$ | Vac. Evap. | a-$LiAlF_4$ | trans/blue | $Li^+$ | 30 |
| $WO_3$ | Vac. Evap. | poly-AMPS(7) | white/blue | $H^+$ | 31 |

1. Also known as $HUO_2PO_4 \cdot 4H_2O$, hydronium-β-alumina.
2. Nasicon is also known as $Na_{1+x}\ Zr_2Si_xP_{3-x}O_{12}$.
3. Nafion is a DuPont trademark for polyperfluorosulfonic acid.
4. PWA is phosphototungstic acid, $H_3PO_4\ (WO_3)_{12}\ 29H_2O$.
5. $Na^+$-β-$Al_2O_3$ is in this case $Na_2O \cdot 8Al_2O_3$.
6. P-TsOH is p-tolenesulfonic acid.
7. Polymerized, 2-acrylamideo-2methylpropane sulfonic acid.

Abbreviations:
r.f. sputt. = r.f. sputtered,
vac. evap. = vacuum evaporation,
electrochem. = electrochemical deposition,
e-b evap. = electron-beam evaporation.

Table 2. Electrochromic materials having liquid electrolytes.

| Material | Prep. Tech. | Peak Absorption (eV) | Color off/on | Ref. |
|---|---|---|---|---|
| a - $M_xWO_3$ | Vac. Evap. | 1.4 | trans.; blue | 32-35 |
| a _ $H_xWO_y$; (y>2.5) | Vac. Evap. | 1.38 | trans.; blue | 36 |
| a - $WO_{2.5}$ | Sputt. | 1.38 | blue (at equilibrium) | 36 |
| c - $H_xWO_y$ | ---- | 0.72 | blue (at equilibrium) | --- |
| a - $WO_3$ | R.F. Sputt | 1.2 | ---. | 37 |
| Au - $M_xWO_3$ | R.F. Co-sputt. | 1.4 - 2.15 | blue; red or pink | 38,39 |
| Pt - $M_xWO_3$ | R.F. Co-sputt. | 1.4 - 2.15 | blue; red or pink | 38,39 |
| $WO_3$ - $MoO_3$ | Co-evap. | 1.5 - 2.0 | --- | 40 |
| $Na_xWO_3$ | --- | Green; dark blue | --- | 41,42 |
| $Li_xWO_3$ | e-beam evap. | 1.13- 1.55 | trans.; blue, pink | 43 |
| a - $H_xMoO_3$ | Evap. | 1.42 | yellow; purplish blue | 33,44,45 |
| a - $H_xMoO_{2.96}$ | Evap. | Yellow; purplish blue | ---- | 46 |
| $IrO_xnH_2O$ | Anod. RF Sputt. | --- | trans.; blue-black | 47-50 |

Table 3. Less Common Inorganic Electrochromic Materials

| Material | Preparation Technique | Electrolyte | Color on/off | Ref. |
|---|---|---|---|---|
| Au-$MxWO_3$ | Co-sputt. | ACID | blue/red-pink | 38 |
| Pt-$MxWO_3$ | Co-sputt. | ACID | blue/red-pink | 38 |
| $WO_3$-$MoO_3$ | Co-Evap. | ACID | - | 40 |
| a-$HxMoO_3$ | Vac. Evap. | ACID | Yellow/blue-pink | 46 |
| $Rh_2O_3 \cdot nH_2O$ | Anodization | KOH | yellow/green, brown, purple | 51 |
| $NiO_x \cdot nH_2O$ | Anodization | $LiClO_4$/ ACID | trans./dark bronze | 52 |
| $Nb_2O_5 \cdot nH_2O$ | Anodization | | trans./dark blue | 53 |
| $V_2O_5$ | Vac. Evap. | $H_2O$ | yellow/black | 54 |
| $V_2O_5$ | Vac. Evap. | LiCl+MeOH | yellow/green,black | 55 |
| a-$TiO_2H$ | Anodization | ACID | /blue | 53 |
| $W_9Nb_8O_{47}$ | Sputt. | ACID | - | 56 |
| $CoO_x$ | Anodization | - | red-purple/ grey-black | 57 |
| $Fe_4(Fe(CN)_6)_3$ | Electrod. | KCl | trans./green/blue | 119-123 |

Table 4. Organic Electrochromic Materials

| Material | Preparation Technique | Color Off/On | Ref. |
|---|---|---|---|
| Pyrazoline | Dissolved | yellow;blue,green | 58 |
| dimethy viologen dichloride | Dissolved | --- | 59 |
| diheptyl viologen dibromide | Dissolved | trans./blue-purple | 60 |
| benzyl viologen + poly viologen dibromide | Dissolved | Whitish blue/ red-purple | 61 |
| Polytungsten anion + ZnCdS | Dissolved | trans./violet | 62 |
| Polytungsten anion (PTA) | Dissolved | trans./violet | 18,59,62 |
| benzyl viologen | Dissolved | trans./blue | 61 |
| Lutetium diphthalocyanine | Vac. Dep. | green/red/violet blue,yellow/red | 63-65 |
| 2-tertiary butyl Anthraquinoide | Paste | red;white | 66 |
| 2-tertiary butyl Anthraquinoide | Paste | red/blue/green | 66 |
| Tetrathiafulvalene (TIF) | Spin cast | pale yellow; green, purple | 67 |
| $C_6Li-C_2Li$ | Dissolved | black/blue,green, yellow,gold | 54 |
| Pyradine + Pyradinium viologen salts | Dissolved | - | 68 |
| $\sigma$ -Tolidine | Dissolved | /white,reddish | 18,59 |

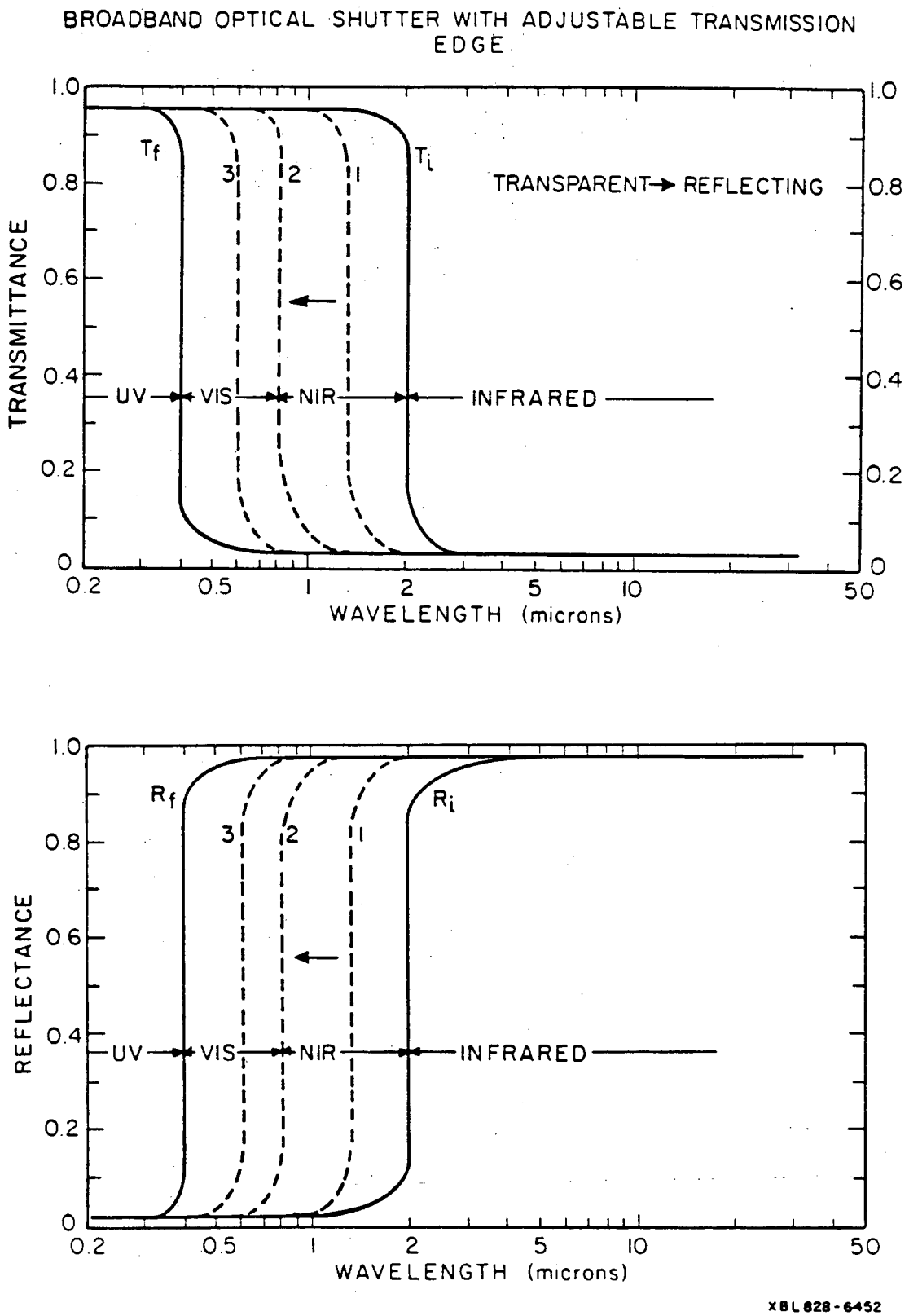



Figure 1. **Spectral response of an idealized optical shutter with an adjustable transmission edge (absorption is neglected).**

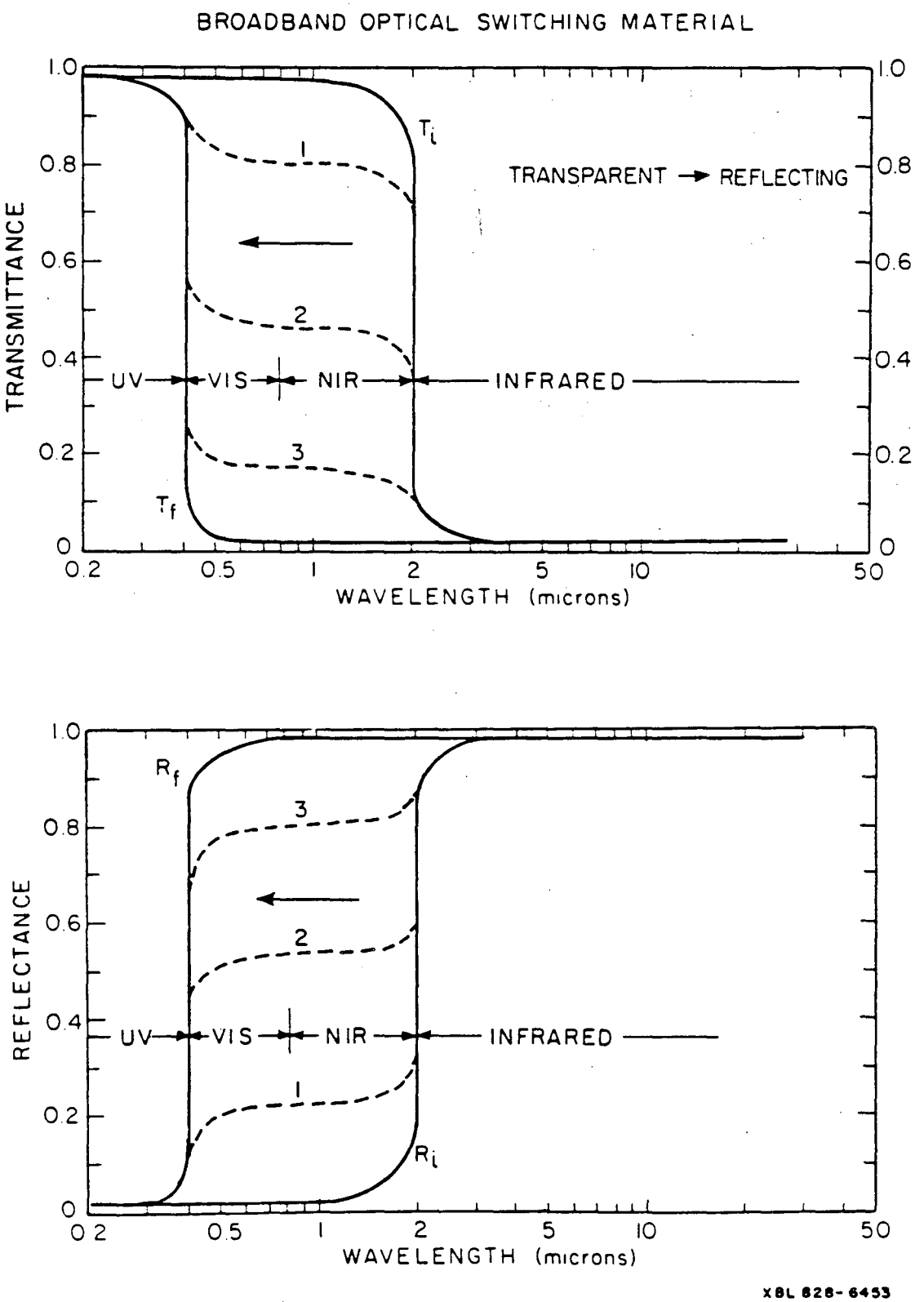
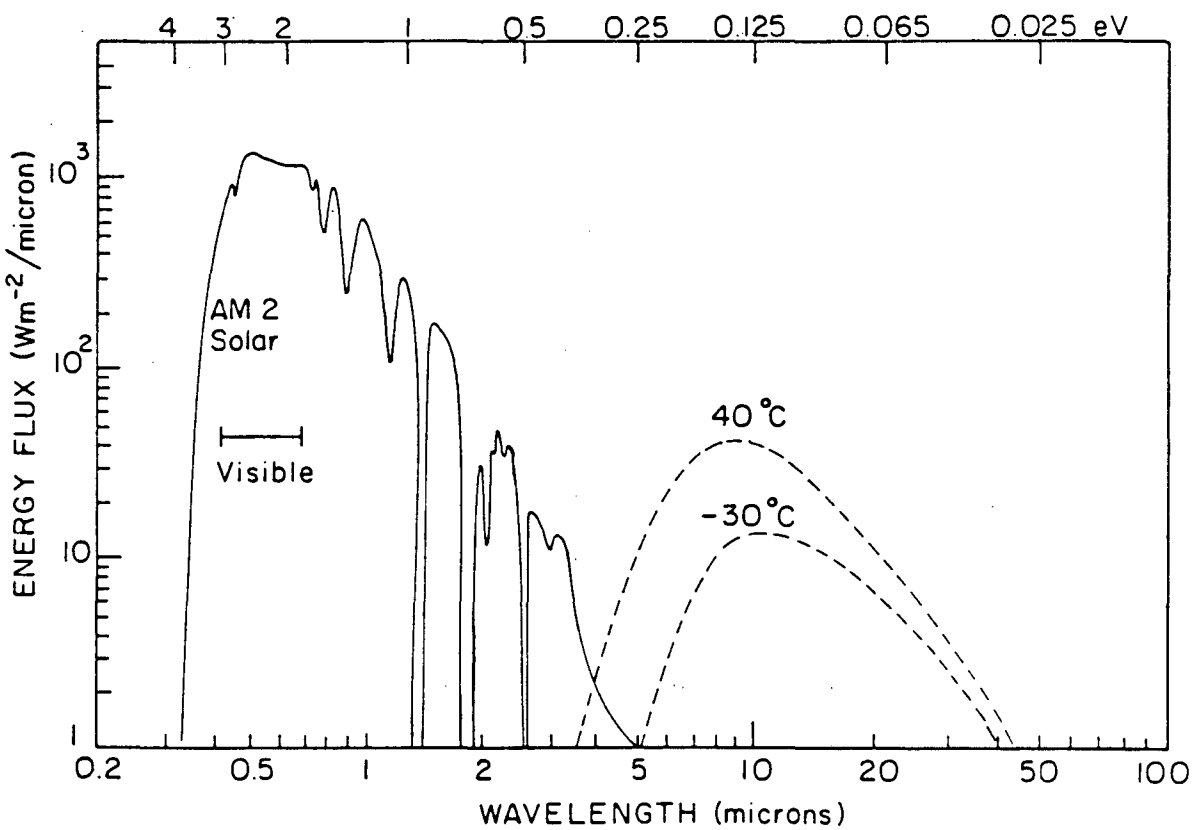



Figure 2 Optical response of idealized broadband optical switching film with adjustable reflection over an entire band of wavelengths, successive intervals of transformation are shown (absorption is neglected).




XBL 808- 5758E

Figure 3. **Spectral distribution of solar radiation (Air Mass 2) and thermal blackbody spectra (-30°C, 40°C); an optical shutter material will operate to thermally isolate these spectra while having adjustable properties over the range of 0.3-3 microns wavelength.**

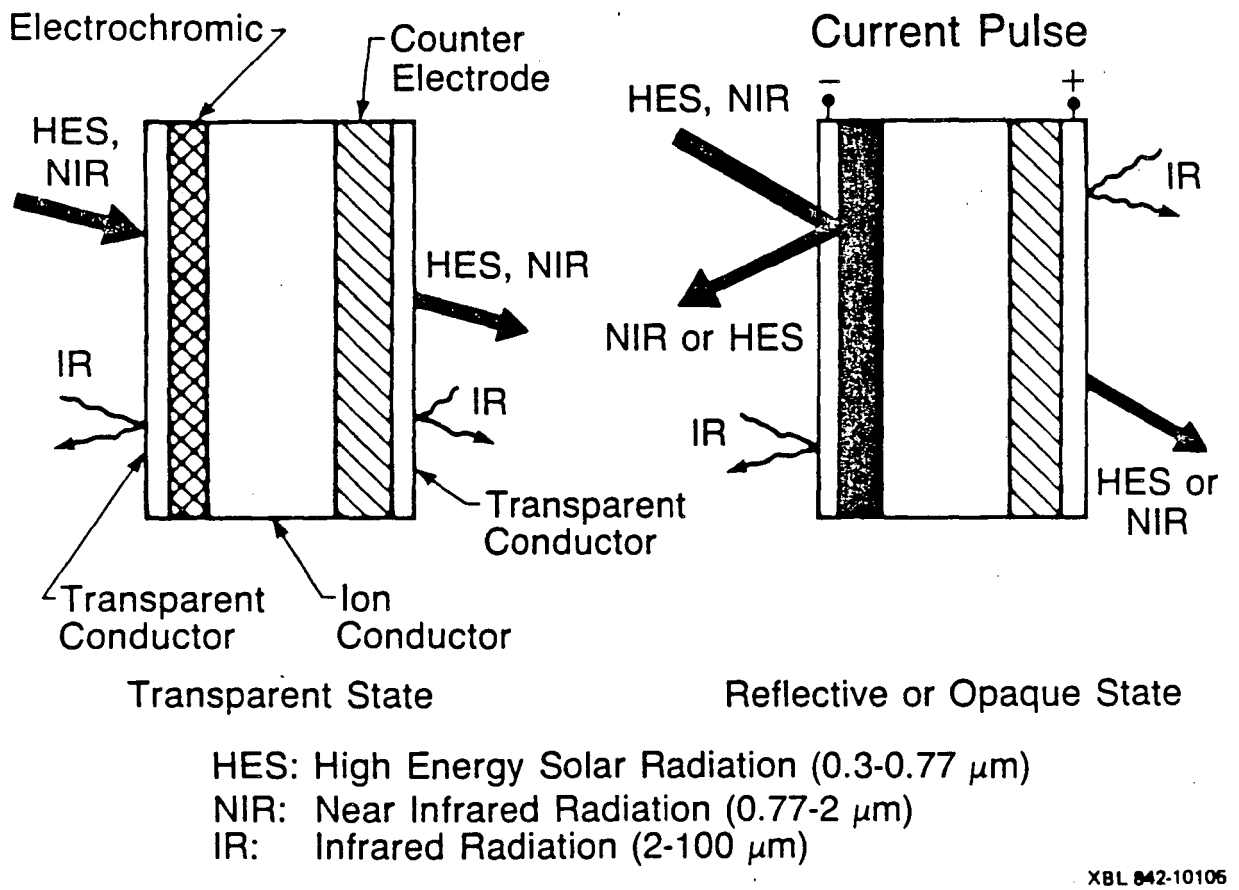
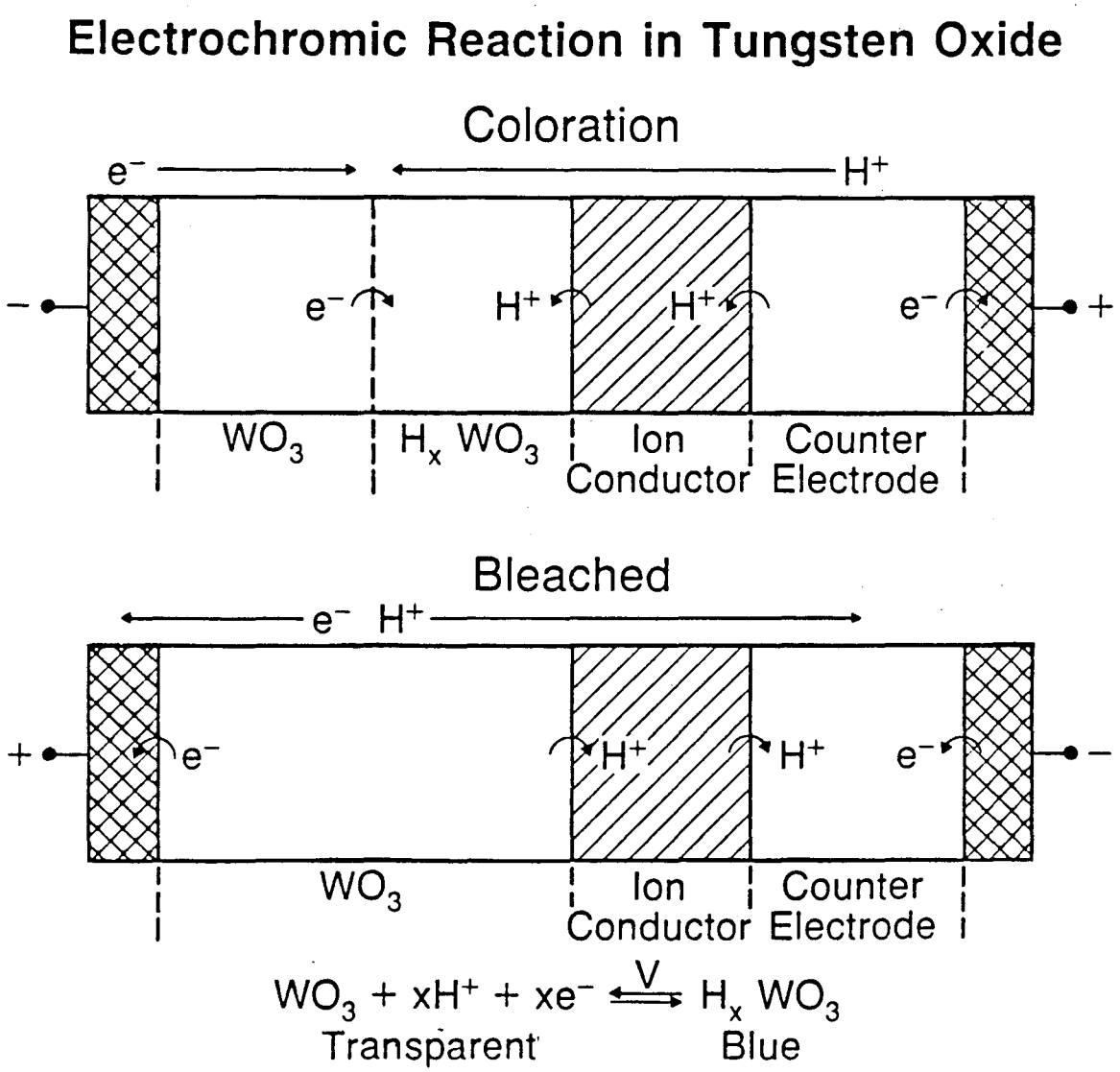
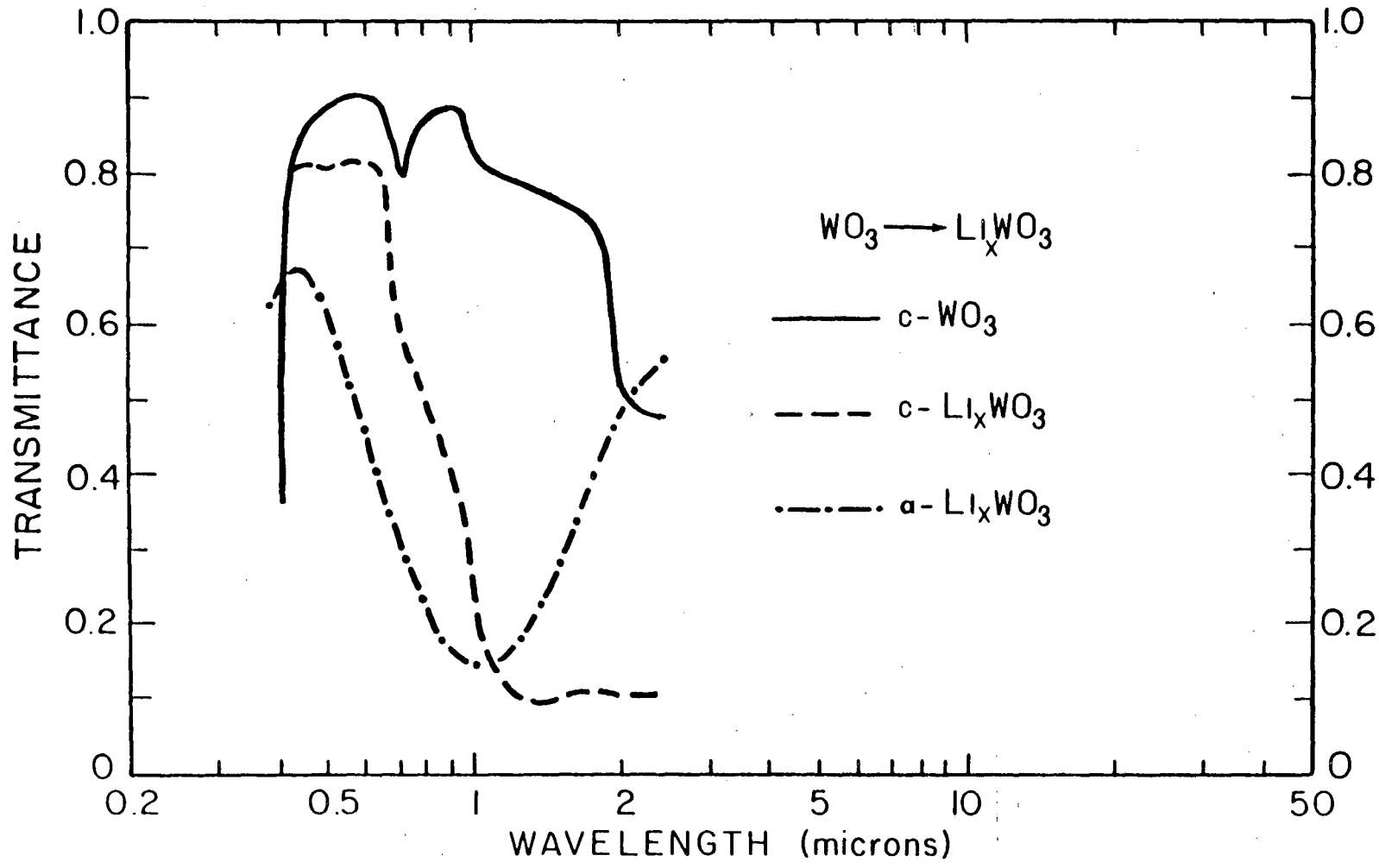



Figure 4. Schematic of a switchable window showing the bleached, and fully darkened state.




XBL 842-10104

Figure 5. Schematic of coloration and bleaching reactions within $WO_3$. During coloration the reaction proceeds with injection of protons and electrons. During bleaching protons and electrons are depleted from the $H_xWO_3$ layer.




XBL 8210-3127

Figure 6. Spectral response of amorphous and crystalline phases of $WO_3$ with injection of $Li^+$, the $Li_xWO_3$ compounds are fully colored.

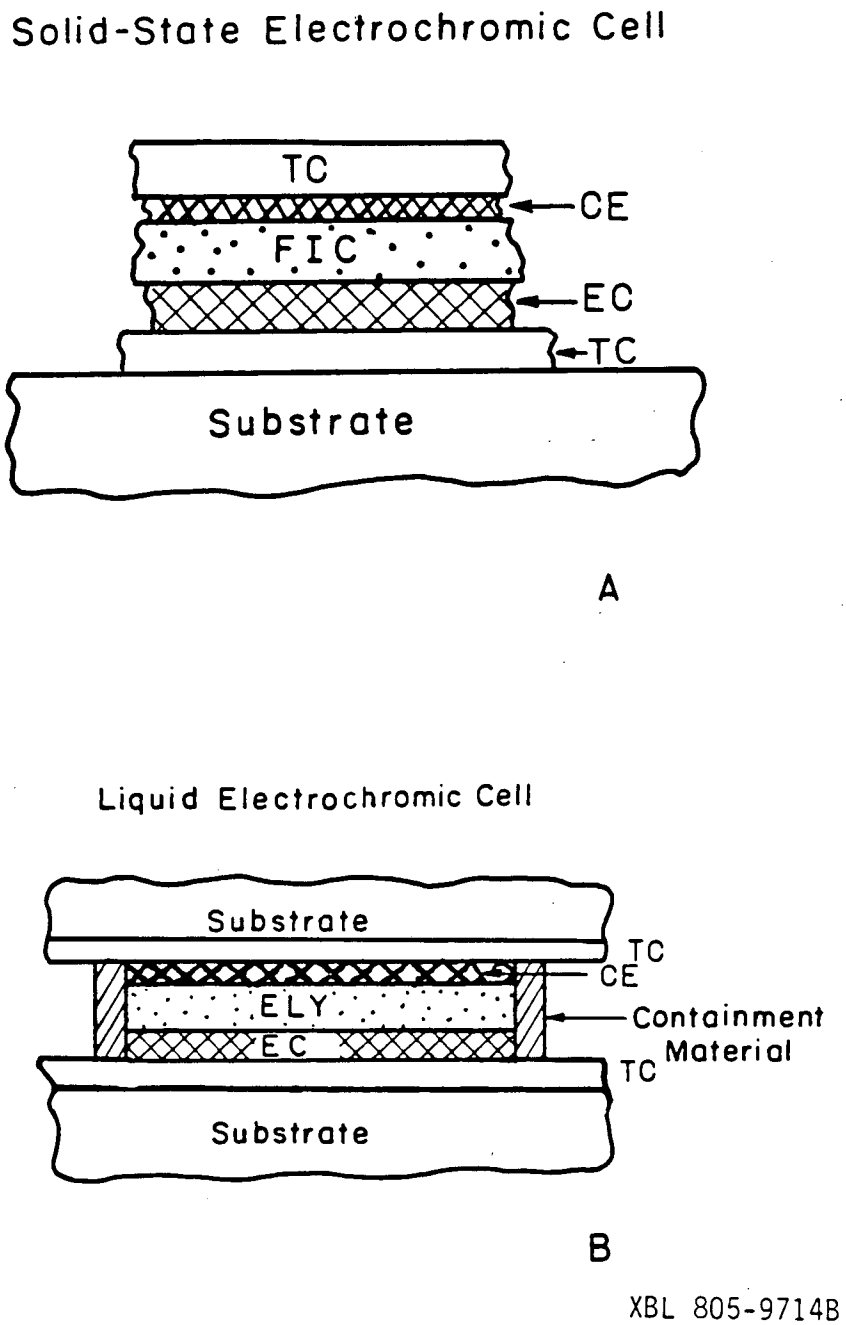
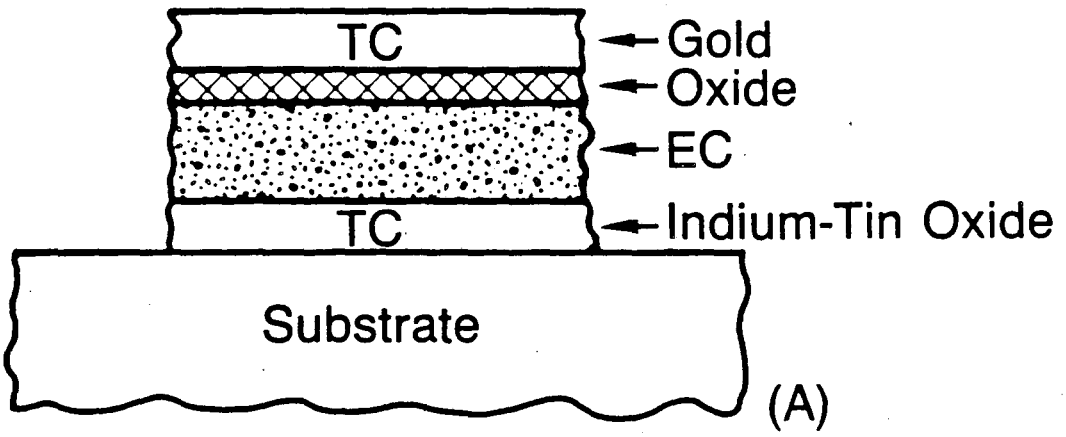
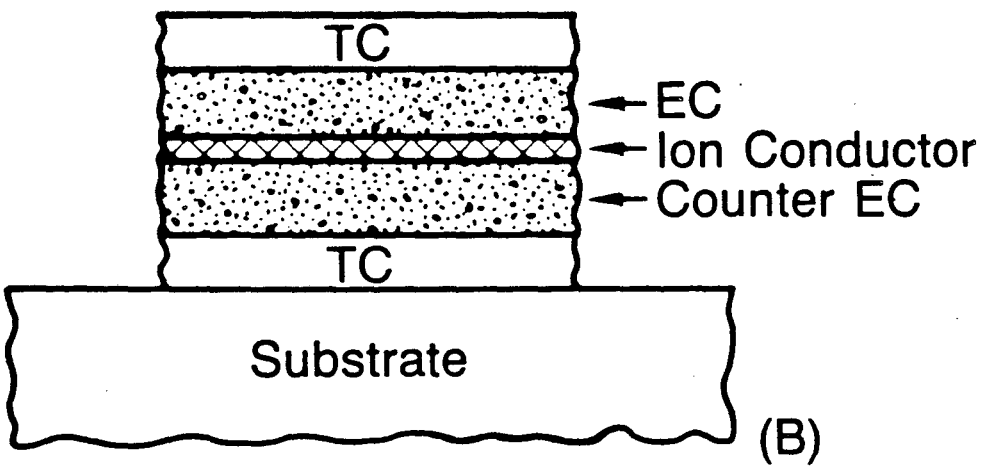



Figure 7. Two configurations of electrochromic cells showing the various layers: TC = transparent contact, CE = counter electrode, FIC = fast ion conductor, ELY = electrolyte.




Trapped Water Design




XBL 842-10107

Figure 8. **Two solid-state electrochromic cell designs using oxide ion conductors.**

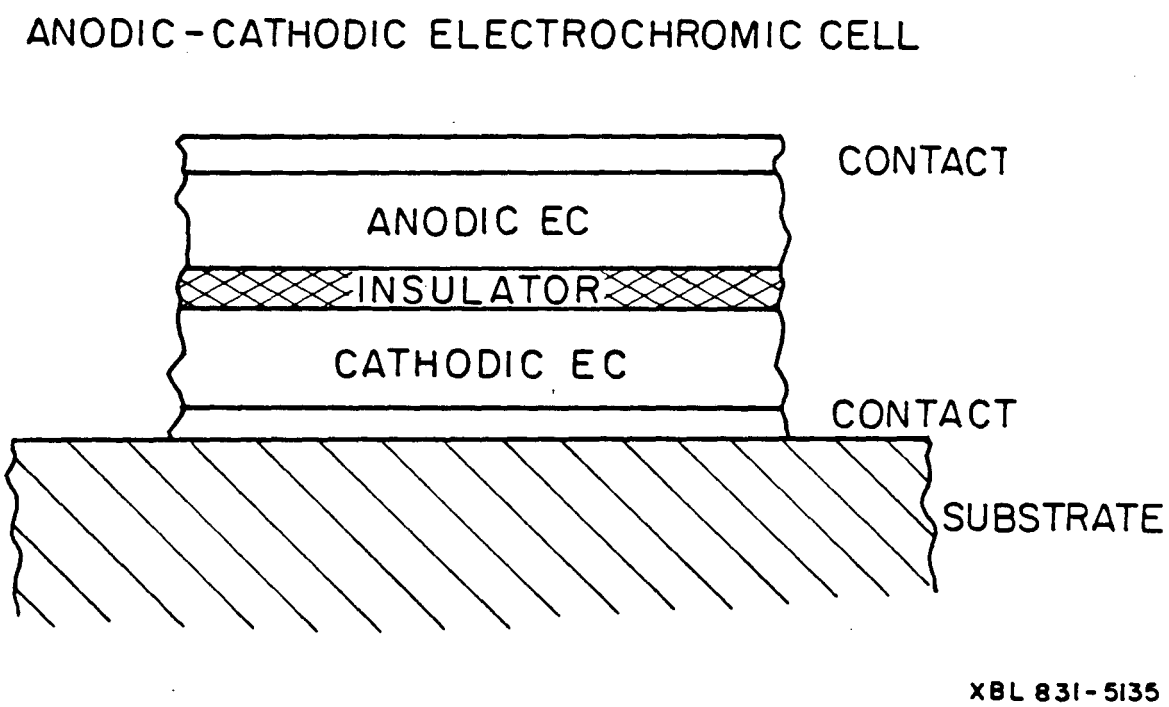



Figure 9. **Solid-state electrochromic using an anodic and cathodic electrochromic material separated by an oxide barrier.**

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