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Carl M. Lampert

October 1980

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THIN FILM ELECTROCHROMIC MATERIALS FOR ENERGY EFFICIENT WINDOWS*

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Abstract

Numerous inorganic and organic electrochromic materials are discussed in the context of developing a thin film energy efficient window. By use of electrochromic thin films, it is possible electronically to control transmission or reflection properties of a window, thus allowing it to be optically and thermally managed, thereby 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, Polytungsten anion are reviewed. Also, intercalated structures are discussed. The designs of working devices are outlined. From this quantification, materials, devices and appropriate deposition technology are selected for window applications.

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I. Introduction

Electrochromism and electrochemichromism* are exhibited in a widespread number of materials both inorganic and organic in nature. The electrochromic effect is of current interest because of its future utilization in electronic display devices. The electrochromic effect, in essence, is a material or material system which exhibits intense color change due to the formation of color centers when atomic defects are induced by an applied electric field. Also this effect can result from an electrochemical reaction, giving a colored compound. The electrochromic effect is very promising for optical shutter applications in conservation and passive solar energy window designs. Ideally, such a device with a flat panel configuration could provide a much needed heat management function in all types of buildings. It could offer adjustable or programable transmission or reflection properties, while maintaining an aesthetically pleasing building element. However, not all electrochromic compounds are acceptable for windows, as they require the material, in the bleached form, to be transparent or translucent. Current work on electrochromic devices is proprietary in nature and the bulk of the literature is concerned with mechanistic studies. Also, the theory about the manner in which a

*Strictly speaking, electrochromism is a solid state effect and electrochemichromism⁽¹⁾ is an electrochemical effect and most of the systems described herein are based on electrochemichromism; however, no distinction will be made beyond here.

particular material exhibits this phenomena is still in many cases a subject of controversy. The following treatise will review many types of electrochromic materials classes and develop specific materials which are most promising as optical shutters.

II. Electrochromic Classes

There are three general classes of electrochromic materials. They are (1) transition metal oxides (mainly hydrous) (2), organic and (3) intercalated materials. Of these systems both solid state and liquid electrolyte devices have been designed.

The bulk of the research published to date is on the transition metal oxides. Within this large classification, there are some distinctions. The most popular system appears to be the IV-B oxides. In this group are WO_3 , MoO_3 and also CrO_3 , which has not been investigated for electrochromic applications.

Another category is the group VIII oxides, where most of the parent metals belong to the platinum group (Pt, Ir, Os, Pd, Ru, Rh). Also, in the group VIII category are iron, cobalt and nickel. Currently three of the group VIII oxide materials have exhibited electrochromism, $\text{IrO}_x \cdot n\text{H}_2\text{O}$, $\text{Rh}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ and $\text{NiO} \cdot n\text{H}_2\text{O}$. For the remaining oxides there may be electrochromism yet to be demonstrated candidates are $\text{Co}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, $\text{Pt}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ or $\text{PtO}_2 \cdot n\text{H}_2\text{O}$, $\text{PdO}_2 \cdot n\text{H}_2\text{O}$ or $\text{PdO} \cdot n\text{H}_2\text{O}$ and possibly $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$. Still yet unrelated oxides such as V_2O_5 and doped SnTiO_3 show electrochromism.

Other important categories are intercalated materials and organic compounds. The viologens, pyrazoline, lanthanide phthalocyanines and anthraquinoides and conductive organic polymers have shown electrochromism.

Table I shows a listing of reported electrochromic films for reference.

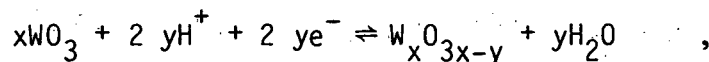
III. Group VIB Oxides--WO₃ and MoO₃ Systems

Both stoichiometric and substoichiometric forms of WO₃ and MoO₃, along with various admixtures, exhibit electrochromism. The bulk of prior research has been performed on the WO₃ compound and to a lesser degree MoO₃.

A. WO₃

In tungsten oxide (tungstic acid) WO₃, amorphous and crystalline films have shown electrochromism. Films of WO₃ can be converted from transparent into deeply colored H_xWO₃ by proton injection from a suitable electrolyte. H_xWO₃ can be generalized to M_xWO₃, including other ions, namely, Li⁺, Na⁺, K⁺, Cs⁺ and Mg²⁺.

It was believed up until about 1975 that WO₃ underwent a redox reaction to form a blue colored oxide product with applied current. The reaction was proposed to be,



as mentioned in recent reviews on the overall subject of electrochromic displays.^(1,11) A similar but more complex model for this system was

Table I. Electrochromic materials.

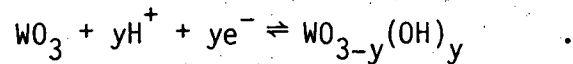
Material	Peak Absorption (eV)	Color Off/On	Prep. Tech.	References
a - M_xWO_3	1.4	Trans; Blue	Vac. Evap.	2-6, 79
a - $H_xWO_y; (y>2.5)$	1.38	Trans; Blue	Vac. Evap.	7
a - $WO_{2.5}$	1.38	Blue (at equilibrium)	Sputtering	7
c - $WO_{2.5}$	---	Blue (at equilibrium)	Vac. Evap.	8
c - H_xWO_y	0.72	Blue (at equilibrium)	---	7
a - WO_3	1.2	---	R. F. Sputt.	9, 79
c - WO_3	---	Yellow transp.	---	8
Au - M_xWO_3	1.4 - 2.15	Blue; red or pink	R. F. Co-sputt.	50,51
Pt - M_xWO_3	1.4 - 2.15	Blue, red or pink	R. F. Co-sputt.	50,51
$WO_3 - MoO_3$	1.5 - 2.0	---	Co-evap.	15
Na_xWO_3	---	Green; dark blue	---	30,31
Li_xWO_3	1.13- 1.55	Trans; Blue, pink	e-beam evap.	34
$H_3PO_4(WO_3)_{12} \cdot nH_2O$ (PWA)	---	White; blue	Powder	36
a - H_xMoO_3	1.42	Yellow; purplish blue	Evapor.	37,38,5
a - $H_xMoO_{2.96}$	---	Yellow; purplish blue	Evapor.	39
$IrO_x \cdot nH_2O$	---	Trans; blue black	Anod. RF Sputt.	41,43,44,46
Rh_2O_3 hydrous	---	Yellow; dk. green	Anod.	55,56
Rh_2O_3 hydrous	---	Yellow; brown-purple	Anod.	55,56
NiO_x hydrous	1.97	Trans; dk. bronze	Anod.	57
Nb_2O_5	$E_g = 3.18$	---	Anod.	60
V_2O_5	---	Yellow; black	Vac. evap.	62
V_2O_5	0.775, 1.8	Yellow; green, blue	Vac. evap.	58

Table I. Electrochromic materials (continued).

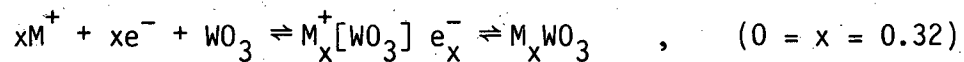
Material	Peak Absorption (eV)	Color Off; On ^a	Prep. Tech.	References
a - TiO ₂	Eg = 2.88, 2.99		Anod.	60
C ₆ Li-C ₂ Li		Black; blue, green, yellow, gold	Disol.	62
Pyrazoline	1.9, 3.1	Yellow; blue, green	Disol.	90
dimethyl viologen dichloride	---	---	Disol.	11
diheptyl viologen-dibromide	2.28	Trans, blue-purple	Disol.	65
benzyl viologen + poly viologen dibromide	2.07, 2.25	Whitish blue; red purple	Disol.	67
GaAs/viologen	---	---	Disol.	71
Polytungsten anion + ZnCdS	---	Trans, violet	Disol.	72
Polytungsten anion (PTA)	1.77	Trans, violet	Disol.	72, 11, 1
benzyl viologen	3.1, 4.77	Trans, blue	Disol.	66
Pyradine + Pyradinium viologen salts	2.16	---		74
o-Tolidine	---	--- ; white, reddish		11, 1
Lutetium diphthalocyanine	---	green, red, violet, blue, yellow-red	Vac. Dep.	75, 76
2-tertiary butyl Anthraquinoide	2.25	red; white	Paste	77
2-tertiary butyl Anthraquinoide	---	red; blue, green	Paste	77
Tetrathiafulvalene (TTF)	---	pale yellow; green, purple	Spin cast	78

Codes: Anod. = anodized; Disol. = dissolved in solvent; R. F. Sputt. = R. F. Sputtered; Vac. Evap. = vacuum evaporated (deposited); Electrochem. = electrochemical deposition; e-beam evap. = electron beam evaporation.

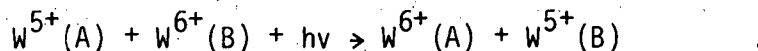
proposed in 1975,⁽¹²⁾ which resulted in a complex of WO_x^+ and OH^- according to the following reaction:



Another model proposed at this time which fit experimental data was an intervalence transition absorption mechanism for electro-coloration of WO_3 .⁽¹³⁻¹⁶⁾ Coloration of the film was achieved by simultaneous injection of electrons and protons (or cations) into WO_3 , forming a tungsten bronze, according to the following equation:⁽¹³⁾



where M is a positive ion, the simplest case, a proton, H^+ . In amorphous film above $x = 0.32$ the tungsten bronze becomes metallic,⁽²⁰⁻²¹⁾ and below it semiconducts due to localization induced by inherent lattice disorder and disordered arrangement of protons in the M sublattice.^(19,20) with this hypothesis the phenomena of coloration was accounted for by intervalence transfer absorption⁽¹⁴⁾ stated as,



where A and B are two different tungsten lattice sites. Closely related to this theory is small polaron absorption which has also been

suggested to explain coloration of WO_3 films. (7,9,22-24) In both these 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 since in amorphous films a broad absorption peak is noted over the range 1.2 to 1.5 eV^(9,14) rather than a sharp characteristic plasma peak.

Recent electron resonance studies argue against both intervalence transfer and small polaron models. It was found that the electrons are not uniquely localized in H_xWO_3 in either amorphous or crystalline forms. If W^{5+} is formed during coloration the donated hydrogen electron must be delocalized over a number of tungsten sites.

Following the intervalence transfer and polaron models, a model for device operation can be made. An optical absorption transition from the valence band to the defect band can result generally from photon irradiation or an applied electric field. In the former manner population of the defect band causes what are known as color centers. For electrochromic films an external field is used to sufficiently bend the bands so injected electrons can fill the defect band. By reversing the field the bands are allowed to bend in the opposite direction allowing depletion of the defect band and film bleaching.

1. H_xWO_3

Electronic transport in amorphous H_xWO_3 films is by a variable range hopping model for $x \leq 0.3$. Conductivity is $\sigma = 987 (x - 0.31)^{1.6}$ for 4.2°K and approximate for 300°K. (20)

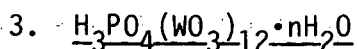
Stoichiometry was measured for amorphous films prepared by thermal evaporation in vacuum from WO_3 powder. Resulting films were measured by proton backscattering and revealed $\text{H}_x\text{WO}_{2.7}$ with $0.2 < x < 0.5$; (26) for x above 0.3 the films were metallic. However, this data has been criticized and oxygen to tungsten ratio may be 2.96 - 2.99. (28) In many cases in the literature, tungsten bronze is referred to as H_xWO_3 , because its stoichiometry is unknown. The convention used in this study is to state stoichiometric compounds if the exact stoichiometry is unknown.

Electrochemical data has been measured on a wide $x = 0.002-0.5$ range of amorphous H_xWO_3 films. (29)

2. Na_xWO_3 and Li_xWO_3

Both sodium and lithium tungsten bronzes have been investigated as electro-coloring material. Their properties and characteristics are similar to H_xWO_3 . Na_xWO_3 shows a change from light green to deep blue. This material is made electrochromic by acid anodization of an as deposited film. (30,31) Anodization creates a 1500Å thick sodium depleted surface layer. (32) A proton then can occupy the empty Na site, thereby resulting in the color center formation known to H_xWO_3 . The electronic structure of Na_xWO_3 has been investigated also. (33)

For Li_xWO_3 it has been argued that the presence of Li^+ instead of H^+ may make a longer lifetime cell, as hydrogen tungsten bronze in acid electrolyte tends to discolor with time.⁽³⁴⁾ Li_xWO_3 shows a phase change at $x = 0.4$. Symmetric cells of Li_xWO_3 and WO_3 when activated show blue for $x < 0.4$ and pink for larger x .⁽³⁴⁾



Phosphotungstic acid ($\text{H}_3\text{PO}_4(\text{WO}_3)_{12} \cdot n\text{H}_2\text{O}$) is a member of a group of compounds known as heteropolyacids. Within this classification several materials have been known to exhibit coloration upon reduction. The electrochromic properties in solution have been noted elsewhere.⁽³⁵⁾ However, phosphotungstic acid exhibits electrocoloration in its solid form. This material serves also as a proton conductor, eliminating the need for an ionic electrolyte. In the bleached state this compound is white (as a compressed powder) and activated, it is blue.⁽³⁶⁾ This substance would be useful only in windows, possibly sky lights, if it were translucent. If this material could be formed into thin films rather than being used as a powder, it may have promise.



Color center phenomena has been noted in both crystalline and amorphous forms of H_xMoO_3 . The absorption spectra of H_xWO_3 , and H_xMoO_3 is very similar; it peaks in the red 0.87 micron wavelength.^(37,38) Its characteristic color when activated is purplish blue. This molybdenum bronze has a humidity threshold below which coloration will not take place.⁽⁴⁰⁾ The refractive index of MoO_3

as a thin film⁽³⁸⁾ is $n = 2.30$ for wavelengths greater than 0.8 microns (at 0.35 microns $n = 2.2$ for wavelengths greater than 0.5 microns.⁽⁶⁾ Amorphous films are generally substoichiometric; possibly they are $\text{MoO}_{2.96}$.⁽³⁹⁾ They can be colored by ultraviolet light or by applied electric field. The mechanism of coloration is thought to be similar to the tungsten oxide films, but has yet to be verified.⁽⁵⁾

C. M-WO₃ Cermets and WO₃-MoO₃ Composites

Au-WO₃ and Pt-WO₃ cermets have been formulated as electrochromic materials. The additions of Au and Pt were made in the hope of being able to "tune" the color of the electrochromic material. The characteristics of 20-120Å gold particles in amorphous WO₃ results in a material which was blue initially and became red or pink when electrochromically excited.^(50,51) In a polycrystalline WO₃ matrix the colored state is dark blue.

The purpose in developing mixed oxides was to create an electrochromic system which was better suited to the human eye peak response at 2.25 eV.^(52,53) (The peak for WO₃ is 1.4 eV and MoO₃ is 1.56 eV.) For highly colored films a peak of 2.15 eV can be obtained with a mix of 50 at.% MoO₃.⁽⁵⁴⁾

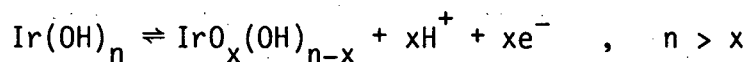
IV. Group VIII Oxides—Hydrated IrO_x , Rh_2O_3 , NiO

The hydrous group of the oxides in VIII has recently been investigated for electrochromism.⁽⁴¹⁾ Currently it is known that oxides of iridium, rhodium and nickel⁽⁴¹⁾ can be electrochromic. All of these oxides are generally formed by anodization of a metal film or by reactive sputtering. Also, they are believed to color by anode transfer of a electron into the metal substrate coupled with a cation ejection into or an anion injection from the electrolyte.⁽⁴⁶⁾

A. IrO_x (Hydroxide)

There are two basic methods of creating electrochromic IrO_x by reactive sputtering and cyclic anodization. The resulting films are known as SIROF⁽⁴²⁾ and AIROF,⁽⁴³⁾ respectively. Anodized films have been prepared from bulk and evaporated iridium films.

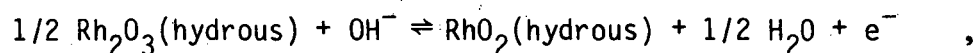
The overall coloration reaction was given as:



where Ir(OH)_n is transparent and $\text{IrO}_x(\text{OH})_{n-x}$ is colored blue black.⁽⁴⁴⁾ During this transformation reflectance contrast changes 60:1. This system competes well with WO_3 .⁽⁴⁹⁾ The presence of bound water is important for fast coloration and bleaching of the Ir(OH)_n film.⁽⁴⁵⁾ Iridium films formed by dry oxidation are inactive electrochromically. Iridium oxide films can be grown directly on transparent SnO_2 coated substrates.⁽⁴⁸⁾ Solid state cells can be fabricated using this film, to be discussed subsequently.⁽⁴⁷⁾

B. Rh₂O₃ (Hydrous)

A two color electrochromic film can be found by anodic pulsing. Both yellow to dark green or yellow to brown purple colorations can be invoked in either 1M or 5M KOH solutions.⁽⁵⁶⁾ Coloration reaction is suggested as:

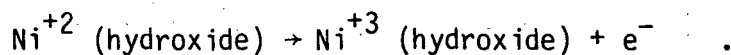


where Rh₂O₃ is yellow and RhO₂ is dark green in color.^(55,56)

The reaction to form a brownish purple product has not been identified.

C. NiO_x (hydrous)

Electrochromic films of NiO_x 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 the 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⁽⁵⁷⁾ is:

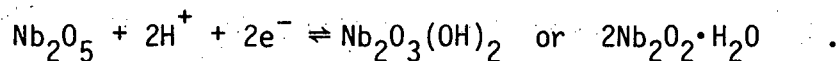


The colorization and bleaching potentials are separated by 0.4 volts. (57) This work is in progress at present and may lead to a fairly inexpensive material for windows.

V. Group VB Oxides, Nb₂O₅ and V₂O₅

A. Nb₂O₅

Electrochromic niobium oxide films are found 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 band gap of this oxide is 3.18 eV. (60) The suggested reaction:



Obviously not enough work has been performed on this system to qualify it for thin film use in optical shutters.

B. V₂O₅

The vanadium oxide system performs much like WO₃ (Ref. 61) except water or alkaline electrolyte has to be used due to V₂O₅ high solubility in acid. When V₂O₅ is immersed in water it changes from yellow to black in color. (62) Initially, amorphous V₂O₅ films are yellow and electrocolor to greenish-blue. (58)

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. (5) During coloration, in V₂O₅ films, V⁵⁺ undergoes a reduction to V⁴⁺.

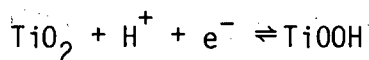
Various vanadium bronzes may exhibit improved and tunable electrochromic behavior. Examples might be $M_xV_2O_5$ where $M = Li, Na$ or Ag . AgV_2O_5 has been investigated as an electrode material. For the V_2O_5 system, the initial coloration must be yellow and transparent, not opaque, if it is used in windows. Also the V_2O_5 reaction with moisture may deem it unsuitable for window applications.

VI. Other Inorganic Systems

Under this category there is a range of unusual materials which are not associated with a chemical group in behavior; many are transition metal oxides but some are not.

A. TiO₂

Amorphous titanium oxide undergoes an electrochromic reaction after the following: (60)



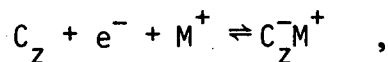
This was noted for Ti metal electrode material made by anodic cycling. The bandgap for amorphous TiO_x is 2.88 eV with absorption edge at 0.43 microns. After coloration, the bandgap moved to 2.99 eV and absorption edge decreased to 0.415 microns. (60) Normally, since TiO_2 is a white opaque oxide, it may not be suitable for optical shutters.

V. Intercalated Electrochromic Materials

Intercalated graphite has been investigated for electrochromism⁽⁶²⁾ although since graphite is opaque it does not have use as an optical window material. However, since the intercalated structure can possibly be applied to other materials systems, it is of technical interest.

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 , $C_{12}Li$ and C_8M , $C_{24}M$, and $C_{36}M$ where $M = K, Rb, \text{ and } Cs$. These compounds commonly are characterized by their golden or brass like appearance. Intercalation can be performed in stages where, at higher (first) stages, fewer inter-layer spaces are occupied by metallic compounds. The stage number is the number of carbon planes between intercalate planes; the lowest is 1 and characteristic of C_6Li and C_8M . The electrochromic system relies upon 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 upon the applied potential. The general reaction follows:⁽⁶⁴⁾



where M^+ = alkali metal ion.

z = stage parameter

The cell is composed of a graphite back electrode and a front counter electrode 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 volts, color can be induced ranging from black, blue, green and golden yellow.⁽⁶²⁾ By reverse polarity the color reverts back to black.

The writing and erase times are 0.2 sec and power consumption equivalent to other electrochromic devices. It is felt that by use of fast ionic conductors, such as Li_3N , a solid state display can be fabricated using these principles.

VI. Organic Electrochromic Materials

These are a number of organic materials which 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. Organometallics, such as phthalocyanines of lanthanides and polytungsten anions have also been researched. The basic types of 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 by far the simplest type of 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. Also, a gel electrolyte can be used to suppress drifting. For type 2, color drift is eliminated by conversion back to the uncolored material, by oxidation for example. This system requires refreshing to maintain the colored state and its intrinsic efficiency is reduced. This type is not well suited for a window shutter. The third category involves a colored species which is insoluble in the electrolyte, which makes the display stable. However, reverse leakage current does exist and leakage paths should be eliminated for long term coloration. The last group probably is the most attractive to optical shutters since the colored state need not be refreshed, resulting in energy and color savings.

A. Viologens

The viologens are a family of chlorides of specific quaternary bases derived from $\gamma\gamma'$ -dipyridyl, ($C_{10}H_8N_2$). Commonly viologens are used for oxidation-reduction indicators. As indicators they are unusual because they color in reduction rather than in oxidation and the redox potential is independent of pH. A popular electrochromic viologen is diheptylviologen-dibromide ($A^{2+}Br_2^-$) 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, giving a yellow color, which reacts with A^{2+} to form more A^+ again. The result is a bluish purple cathode layer of bromide salt which is insoluble in water. The optical density of the resulting colored product, peaks at 545 nm and has an absorption coefficient of $a = 26000/\text{cm}$.⁽⁶⁵⁾ The reaction is reversed (oxidized) by current reversal, or shorting electrodes, the latter being slower. The problem with reverse current is to know when a stop, as the same coloration reaction can take place on the counter-electrode. Another method of erasure is by using a reference electrode which would only allow the proper voltage to be used to decolor. 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 not dependent upon viewing angle. The basic heptyl viologen reaction⁽⁶⁶⁾ is shown in Figure 1.

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.⁽⁶⁷⁾ 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 heptyl viologen salt formation second stage

reaction. It has been shown that SnO_2 electrodes will improve aging.⁽⁶⁹⁾ Also, stable films have been formed with tetramethylene [bis-4 (-ethylpyridine -4'-y) pyridinium] perchlorate.⁽⁶⁸⁾ Speed of switching for viologen displays have been detailed elsewhere⁽⁷⁰⁾ but are of little concern to windows development. Another GaAs viologen device has been fabricated using photo-electrochemical principles.⁽⁷¹⁾ This cell can be colored by photoreduction or electroreduction. For use as a window device this new cell might be ideal in principle. For instance, at high solar illumination the panel could turn dark, while manually one could over ride this effect for daylighting purposes. However, use of GaAs is not recommended for this application due to its poor availability and high cost.

B. Polytungsten Anions (PTA)

The polytungsten anion system (PTA) exhibits a deep violet in its reduced state. It can exist as an electrochromic material or if it is mixed with photosensitive material such as ZnCdS, it can exhibit photo-activation. 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.⁽⁷²⁾ The concept of this cell is important to window shutters, since it combines both passive and active effects. The drawback is its long reaction times.

PTA has been used also, exclusively as an electrochromic display.⁽¹¹⁾ The working electrolyte consists of $\text{Na}_2\text{WO}_4 + \text{ClCH}_2\text{COOH}$. PTA undergoes a type 1 reaction. By the addition of H_2O_2 , a type 2 reaction is obtained for this system.

C. Pyradine, Perylium and o-Tolidine Systems

The terminology "electrochromism" originated from field induced spectra shifts shown in pyridine.⁽⁷³⁾ Most of the data on the pyradine system is in the patent literature.

Perylium has been mixed with pyridinium (viologan) to form an electrochromic material. It has a coloration time of 5-180 seconds, depending upon solute composition. The peak absorption spectra ranges from 405-508 nm,⁽⁷⁴⁾ depending upon composition.

o-tolidine ($C_{14}H_{16}N_2$; 4,4' diamine-3, 3' dimethyl biphenyl) exhibit electrochromism. Upon oxidation it can turn white or reddish in color.

D. Phthalocyanine Lanthanides

The phthalocyanine lanthanides form a large series of new electrochromic materials. Lutetium diphtalocyanine is currently receiving attention.^(75,76) The original film coloration is green and can be transformed to red, violet, blue or yellowish red depending upon 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 has very promising utility as optical shutters while being aesthetically pleasing.

E. Anthraquinoides and Polymer Tetrathiafulvalene System

Anthraquinoides of oxygen compounds can form colored salts with cations when in the divalent anion state.⁽⁷⁷⁾ 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 anthraquinone with other materials to form a paste material. The peak absorption is at 0.55 microns and will color reversibly from red to white. By solvent change, blue and green are also obtainable.

The last grouping of organic materials deals with polymers. Films of yellow tetrathiafulvalene (TTF) can be oxidized to green or purple.⁽⁷⁸⁾ Switching times for TTF bound to polystyrene of the order of 50 msec. It is thought that other similar electroactive polymer films may exhibit electrochromism.⁽⁷⁸⁾

F. Pyrazoline

The color producing reaction occurring in pyrazoline can be triggered by blue or UV radiation. By application of voltage the cell can be bleached or intensified in less than 1 second. 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 over coating of $Zn(NO_3)_2$ polyamide barrier layer on one plate. Between the plates is a solution of M-DEASP pyrazoline and chloroform. It is possible to develop a flexible PIE cell using a thermoplastic material.⁽⁹⁰⁾

VII. Cell Design

Many electrochromic cells or structural designs stem from the historic conductive glass/electrolyte/electronic material/contact configuration. Solid state systems differ by using a solid ion

injector instead of a liquid electrolyte. Many instabilities associated with these displays center around cycle speed, lifetime and drifting (diffusion) effects.

A. Deposition

Traditionally, the WO_3 , MoO_3 and V_2O_5 oxides are prepared by vacuum evaporation,⁽⁸⁰⁾ from heated boats of W, Ta or Mo^5 , under pressures of 10^{-4} - 10^{-6} Torr.⁽⁸¹⁾ Also, WO_3 has been prepared by reactive sputtering⁽⁷⁹⁾ and solution spraying.⁽⁸⁵⁾ The general regard in terms of deposited microstructure, is the ability of the material to easily transport protons.⁽⁸⁷⁾ The incorporation of water appears to dictate the electrochromic coloration speed.⁽⁸⁴⁾ Anodically prepared films are generally much faster than others deposited by alternate techniques.^(83,86) Also, there is some evidence that aged WO_3 cells can be regenerated by UV irradiation in the bleached mode.⁽⁸²⁾ Films formed by dry thermal oxidation in most oxide systems show poor electrochromism and required a pre-treatment to activate the material. Wet oxidation appears to be promising as a fabrication technique.

Oxide films on polished Ti and Nb are grown anodically in a solution of ammonium hydrogen tetraborate.⁽⁶⁰⁾ Iridium oxide can be formed by potential cycling of a metal electrode in an anodizing bath made up of H_2SO_4 at 85°C .^(41,43,44) Also, iridium films can be formed by reactive sputtering in oxygen,⁽⁴⁷⁾ and by vacuum evaporation of Ir metal on SnO_2 coated glass with subsequent anodization.⁽⁴⁸⁾ Possibly, other platinum oxides can be formed in

this manner. Most organic electrochromics are in the liquid phase so deposition technique is an unnecessary consideration. For most of the designs, conductive transparent oxide films of doped SnO_2 or In_2O_3 or commercially precoated glass are available. Composite systems such as $\text{WO}_3\text{-MoO}_3$ are made by co-evaporation⁽⁵⁴⁾ or RF reactive do-sputtering.⁽⁵⁰⁻⁵²⁾

B. Configurations

1. Solid State Cell

SP/Metal/FIC/ECM, TC (see Fig. 2) where

SP = scratch protection overcoat (i.e., SiO_2 , Si_3N_4)

metal = Au, Ag, Al

ECM = electrochromic material; e.g., WO_3 , MoO_3

TC = transparent conductor: In_2O_3 , doped SnO_2 , CdO,
 Cd_2SnO_4

FIC = Fast ion conductor: SiO , MgF_2 , ZrO_2 , Ta_2O_5 , or

$\text{Na}_{1-x}\text{Zn}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}/\text{Na}_{0.3}\text{WO}_3$, or

RbAg_4I_5 or $\text{M-B-N}_2\text{O}_3$ (Ref. 18, 89, 90, 91).

2. Liquid Cell

Metal/ELY/ECM/TC (see Fig. 3) where

ELY: Liquid Electrolyte, ion injector, e.g., H_2SO_4 .

3. Anodizing Cell

TC/AECM/ELY or Metal or TC or IN (see Fig. 4) where

AECM: Anodized electrochromic material;

e.g., Ir_2O_3 , NiO, Rh_2O_3 .

IN: NAFTON (Ref. 84).

4. Organic Liquid Cell

Metal or TC/OELY, OCEM/Metal or TC (see Fig. 5) where

OELY: organic solvent electrolyte

OCEM: organic electrochromic material, e.g., viologen, pyrazoline, etc.

5. PWA Cell—No Electrolyte (Ref. 36)

SnO_2 /PWA/Ag or SnO_2

PWA: Phosphotungstic acid.

VIII. Summary and Conclusions

The preceding developed the state of the art in electrochromic material and device design. Although all of the referenced work addressed display devices and not large area window shutter systems, it was placed in context of such applications. Historically, the drawbacks of electrochromic devices have been image drift and slow response times; also the development of light emitting diodes (LED) and liquid crystal displays (LCD) stifled electrochromic research. The advantages of an electrochromic display (with memory) are principally high contrast ratios, low power memory and wide viewing angles; thus research is continued. For energy efficient window shutters the important characteristics are solar matched spectral response, low power, wide operating temperature and gradient response, programable and manually controlled according to heating and cooling needs, and should be stable to solar radiation, weather and cleaning. Last of all, the material or device needs to be cost effective in materials and fabrication.

Electrochromic devices can consist of inorganic, organic and 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) probably are the best for large scale fabrication. The transition color or coloration sequence is very important for a window. A certain amount of human engineering in terms of optical response and preference is important for these devices ever to become part of large scale construction. Other potential problems 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 showing potential as solid state devices and exhibit memory, that is, no need for refreshing, are favored. Certainly the H_yWO_x systems are the most researched; by replacing hydrogen with an alkali metal element coloration can be altered. The solid heteropolyacids hold promise because they have no need for electrolytes. By forming refractory bronze cermets and metal bronzes various color tuning can be performed on these systems, which is very important for windows. A number of recent anodically created platinum group oxides, including nickel, have shown electrochromic effects. These groups offer potentially inexpensive electrochemical methods of making electrochromic films. Also, solid state cells have been fabricated. Another method of film formation is reactive sputtering, which is presently being developed for high rate coating applications for other uses. Intercalated

structures offer a unique electrochromic material; however, currently graphite is used as a basis and it is, of course, opaque.

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

Appendix. Reversible Electrodeposition

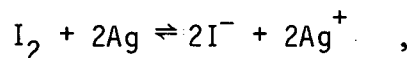
1. Introduction

The term "electrochromic" is often misused and even in this work it has been used to describe liquid state displays. Reversible electrodeposition actually is a form of metallic electrochromism, broadly defined.⁽¹⁻³⁾ Reversible electrodeposition is directly related to liquid electrochromic cells, for example, where a redox reaction forms a colored compound which is, in essence, electro-deposited on an electrode film. Devices utilizing the reversible electrodeposition process, per se, are referred to as Reversible Electroplating Light Modulators (REIM) or Electrolytic Displays. Principally, the AgI system has been investigated for electronic display devices; however, if the liquid or paste electrolyte systems can be tolerated for an energy efficient window design, it may be appropriate there, also. Then, an added feature with the basically metallic deposition systems, reflectance and absorptance can both be varied.

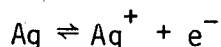
2. Devices

The AgI devices rely upon a electro-redox reaction wherein metal ions are reduced or iodide ions are oxidized and deposited on an electrode, forming a solid reflecting layer. The basic theory behind reversible electrodeposition devices has been detailed.⁴ In an original survey work it was found that tin, silver and gold gave the highest variation of absorption coefficient with thickness. In that study AgI

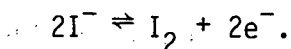
solutions were favored.⁴ A plated thickness of 50 - 150 Å of silver was found to be satisfactory for display applications.⁽⁵⁾ A simplified plating reaction for this solution is⁵:



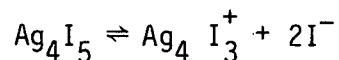
where



and



Recently, a new cell electrolyte has been devised governed by the following reaction:



This system exhibits a transparent to metallic gold or silver white color. Electrolytes for these devices consist of organic solvents such as methanol acetonitrile and dimethyl sulfoxide, diethyl malonate, also alkali metal halides. The presence of the alkali halide,^{3,6} NaI, KI improves conduction and complexing of AgI.

This type of cell efficiency is $50 \text{ cm}^2/\text{q}$, compared to the WO_3 electrochromic devices, $25\text{--}100 \text{ cm}^2/\text{q}$. Efficiency is defined as the ratio of optical density change to charge injected per cm^2 . However, the power consumption for the reversible deposition cell is roughly 10 times that of electrochromic devices.

The suitability of such devices for window systems depends mainly upon the ease in deplating after the metal film has aged for some time in the plated mode. Also, one must consider the refresh cycles, their interval and power consumption.

3. Configurations (See Fig. A1)

System I. (Ref. 6)

Electrolyte 1M AgI, 1M NaOH, 5M NaI

System II. (Ref. 5) Electrolyte: AgI, NaI, Methanol or acetonitrile

1. Refresh every 10 min. to keep opacity
2. $V_{\text{max}} = 0.8$ volts continuous, $I_{\text{min}} = 0.4 \text{ mA/mm}^2$
3. Write erase time $50\text{--}200$ in sec.
4. Lifetime $> 10^7$ cycles and one year (research devices)
5. Operating temperature -40° to 80°C

System III. (Ref. 3) Electrolyte: AgI, KI, I_2 , dimethyl sulfoxide

1. $V_{\text{min}} < 2$ volts, $V_{\text{max}} = 100$ volts, pulsed
2. Matte Reflectivity
3. Lifetime $> 10^6$ cycles

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Figure Captions

Fig. 1. Electrochemical Heptyl Viologen Reduction reaction with substituents: $R = C_3H_7, C_6H_{13}, C_7H_{15}, C_8H_{17},$ phenyl- CH_2 ; $X = Br, Cl, I.$

Fig. 2. Solid state cell where a fast ion conduction (FIC) is used as an electrolyte.

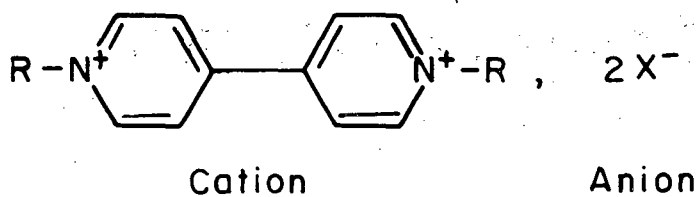
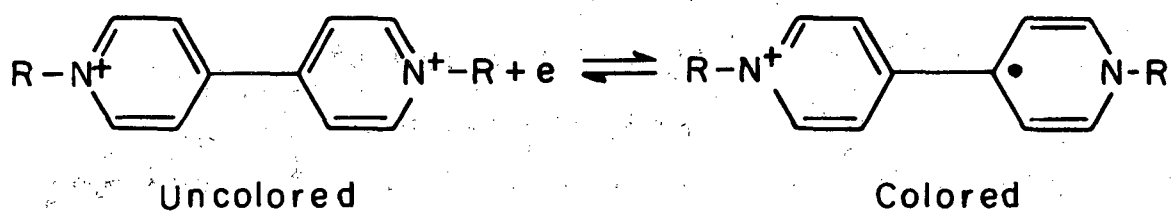
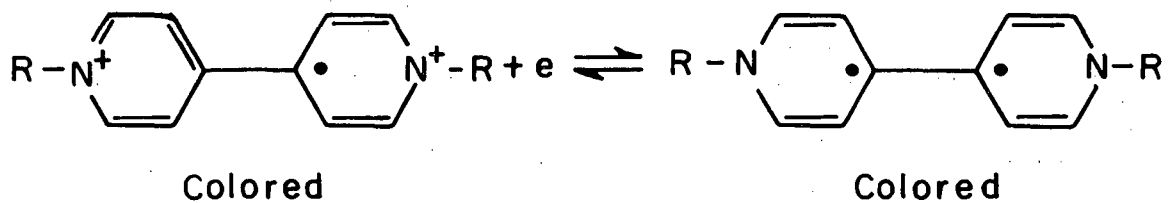
Fig. 3. Liquid electrolyte cell used with solid inorganic electrochromic films

Fig. 4. Electrochromic cell where an inorganic electrochromic film is colored by anodization.

Fig. 5. Liquid electrolyte cell for use with liquid organic electrochromic compounds.

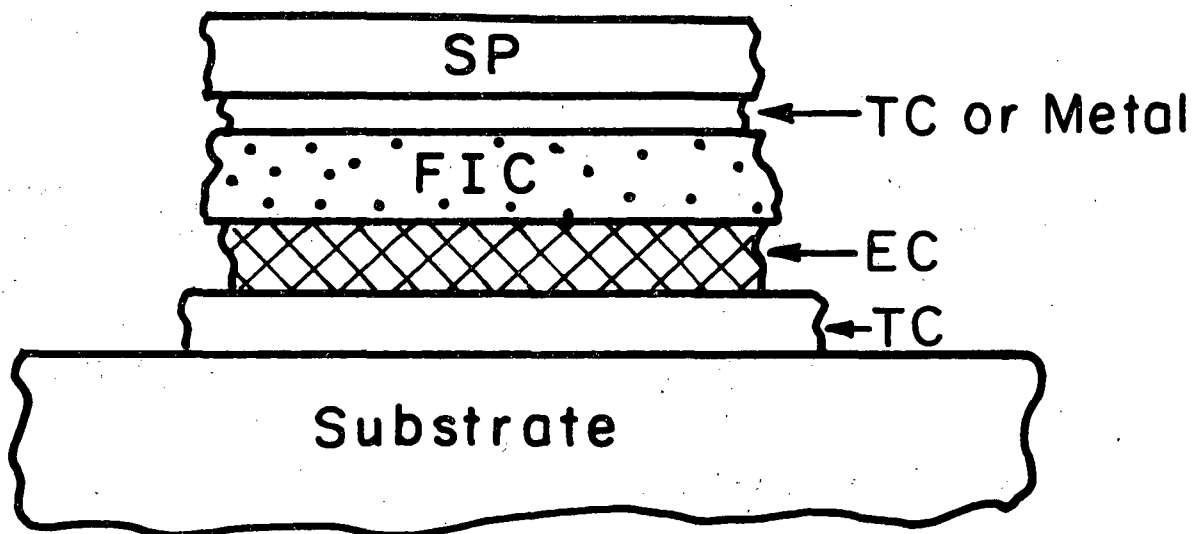
Fig. 6. Solid state cell designed for PWA. For this unusual case PWA serves both as electrochromic material and fast ion conductor.

Fig. A-1. Reversible electrodeposition cell. It is designed to reversibly deposit a silver film with applied potential.

Basic Viologen SaltStage 1 ReactionStage 2 Reaction

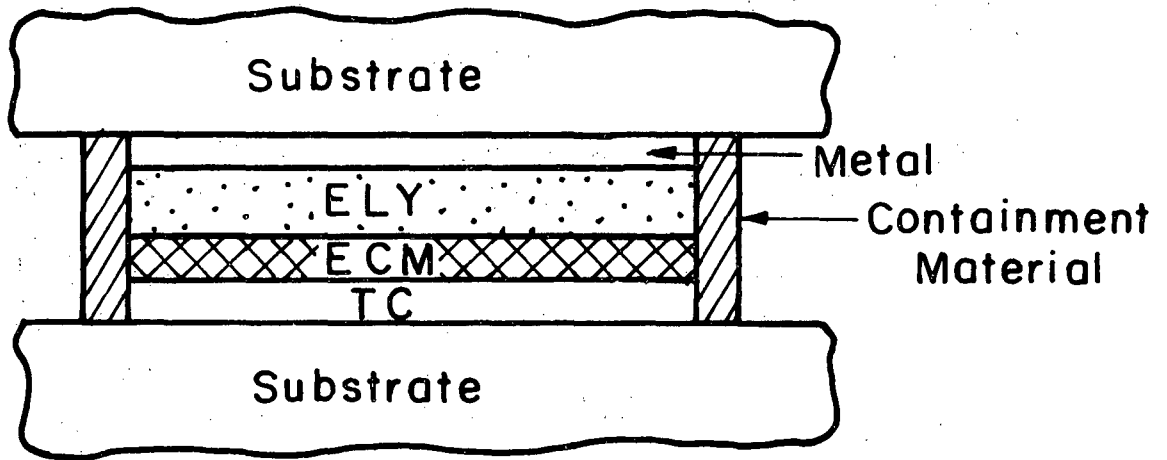
XBL 805-9716

Solid State Electrochromic Cell

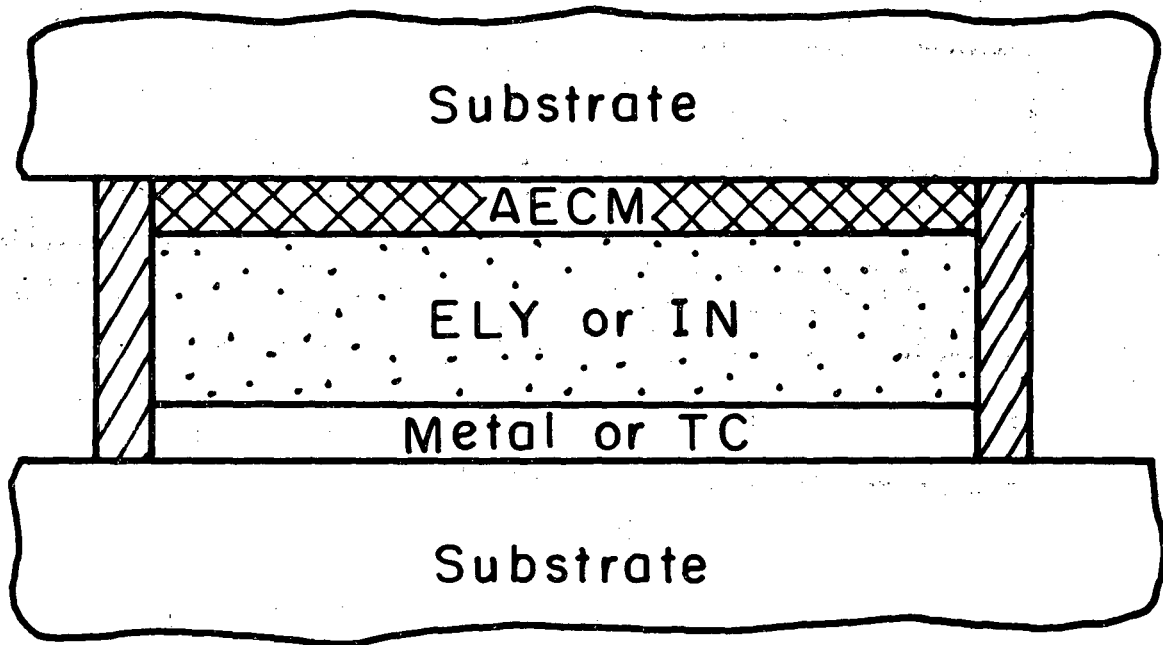


XBL 805-9713

Liquid Electrochromic Cell

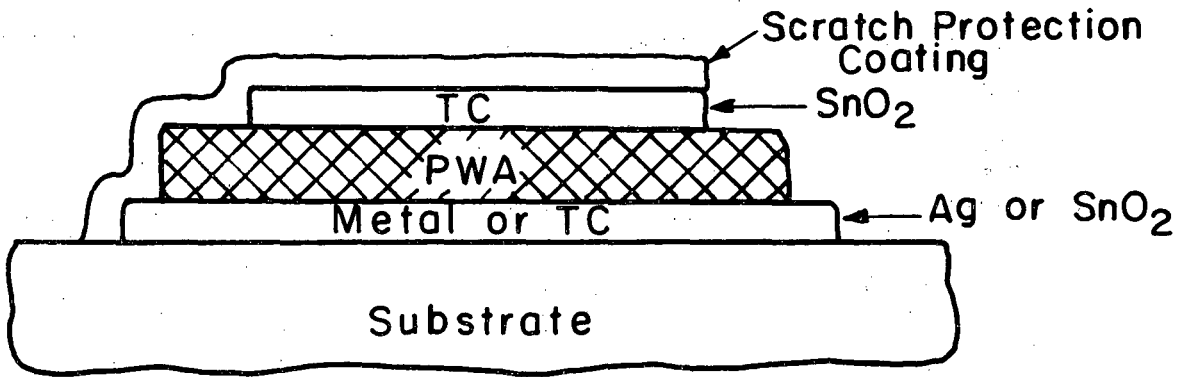


Anodizing Cell

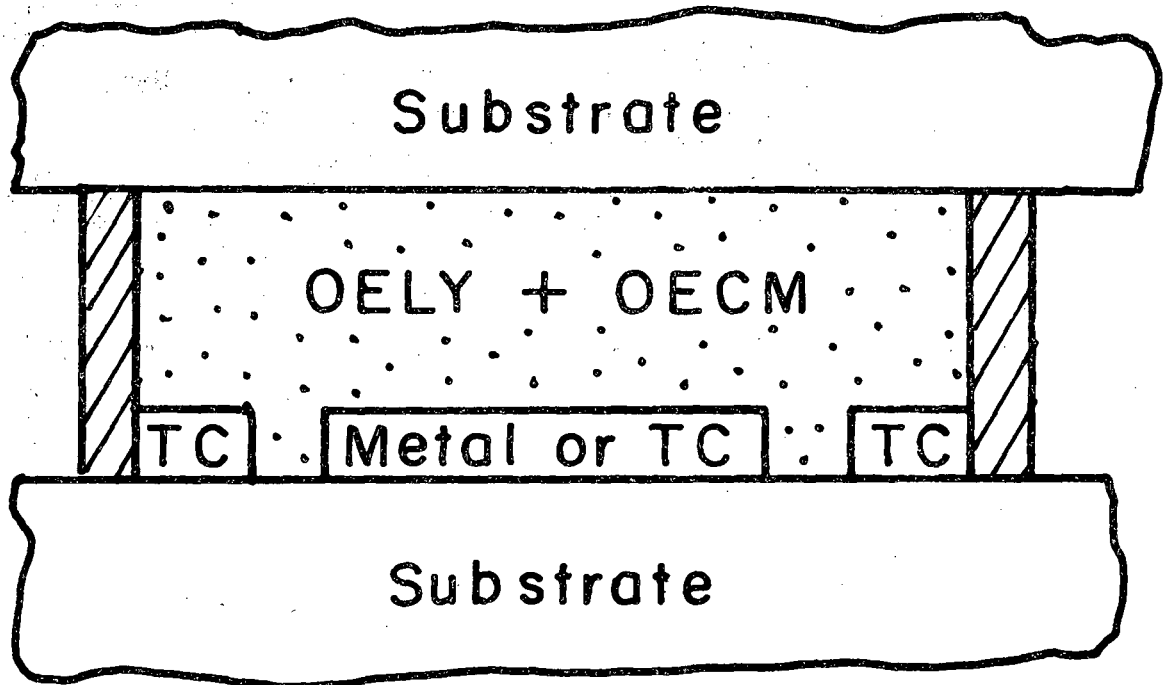


XBL 805-9711

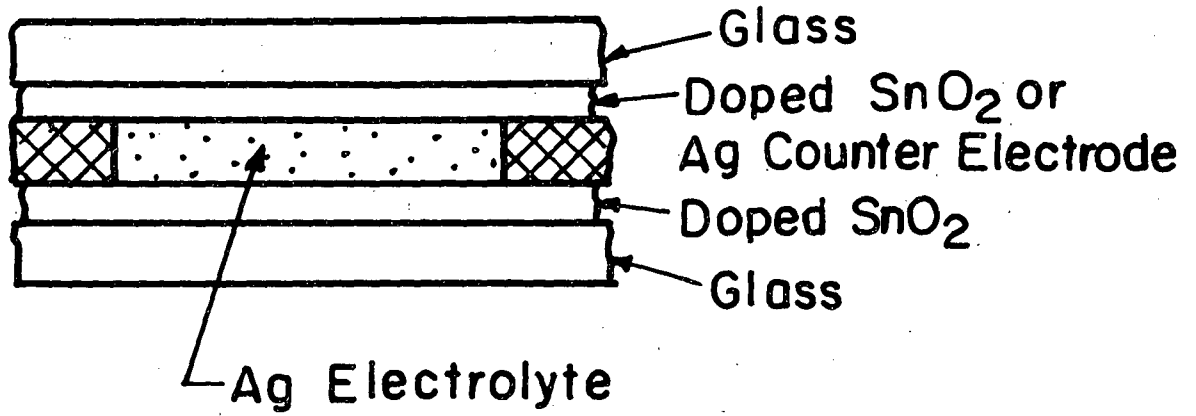
Non Electrolyte Cell - PWA Cell



Liquid Organic Electrochromic Cell



XBL 805-9715



XBL 805-9710

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