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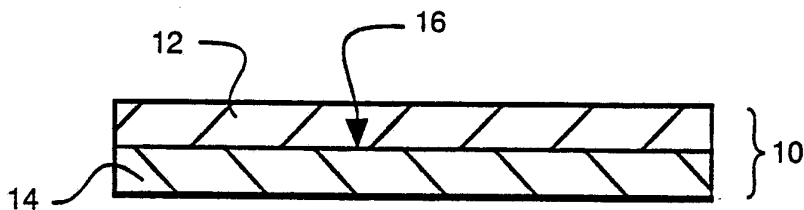
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(54) Title: ELECTROCHROMIC DEVICE USING MERCAPTANS AND ORGANOTHIOLATE COMPOUNDS



(57) Abstract

An electrochromic cell (10) is disclosed which comprises an electrochromic electrode (12) and a composite ion counter electrode (14) for transporting ions. The counter electrode (14) further comprises a polymer electrolyte material and an organosulfur material in which, in its discharged state, mercaptan or an organothioliolate. In one preferred embodiment, both the electrochromic electrode (12) and the counter electrode (14) are transparent either to visible light or to the entire electromagnetic spectrum in both charged and discharged states.

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ELECTROCHROMIC DEVICE USING MERCAPTANS
AND ORGANO THIOLATE COMPOUNDS

BACKGROUND OF THE INVENTION

The invention described herein arose in the course of, or
5 under, Contract No. DE-AC03-76SF00098 between the U.S.
Department of Energy and the University of California.

This is a continuation-in-part of co-pending U.S. patent
application Ser. No. 606,063 which was filed on October 30,
1990, and is incorporated herein by reference.

10 1. Field of the Invention

This invention relates to electrochromic films. More
particularly, this invention refers to electrodes comprising
reversible mercaptan or organothiolate films, and
electrochromic films which are used to form an
15 electrochromic cell. This invention also relates to the
formation of improved electrochromic devices from
electrochromic cells.

2. Description of the Prior Art

Electrochromism refers to a reversible color change which
20 occurs in certain materials in the presence of an applied
electric field or current. Devices that rely on
electrochromic switching mechanisms, such as electrochromic
films, are well known in the prior art. Typical uses for
such devices include: windows for watches, calculators and

computer display screens; eye protection such as eyeglasses, sunglasses and goggles of various types; switchable mirrors and sun visors; automobile, architectural, aircraft, marine, and spacecraft windows; large area information displays such as those used in airports, railway stations, motorways, and for stock exchange boards; voltage indicators; computer memory elements; and auto headlamp covers. Electrochromic films can also be used on opaque substrates including metallic or metal-like surfaces, and in combination with solar cells. The use of switchable windows, for instance, can provide greater flexibility for the control of daytime lighting. As a result, a reduction in power requirements for environmental heating and cooling can be realized. Electrochromic optical shutter devices can also assure privacy and provide glare control.

Not long ago, a basic electrochromic switching device was described in "Electrochromic Materials and Devices for Energy Efficient Windows", by Carl M. Lampert, in Solar Energy Materials, 11 (1984), pp. 1-27, North-Holland, Amsterdam. The article surveyed a number of compounds that are capable of functioning as electrochromic materials, and discussed their applicability for use in the construction of optical shutters for windows. More recently, in a chapter entitled "Chemical and Optical Studies of Electrochromic Hydrated Nickel Oxide Films and Devices", in Large Area Chromogenics: Materials and Devices for Transmittance Control, C.M. Lampert and C.G. Granqvist, Optical Engineering Press, Bellingham, WA (1989), the use of hydrated nickel oxide in the construction of electrochromic devices was discussed.

More recently, the use of polymerizable organosulfur compounds for electrode materials in rechargeable electrochromic cells was discovered. U.S. Patent 4,833,048 to De Jonghe, et al., describes and claims such a cell wherein polymerizable organosulfur material is used as the cathode. The organosulfur material described therein has

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the general formula, in its charged state, of $(R(S)_y)_n^-$ where $y = 1-6$, $n = 2-20$, and R is one or more of the same or different aliphatic or aromatic organic moieties having 1-20 carbon atoms. When the organosulfur electrode material is charged, one sulfur atom(s) of the $R-(S)_y^-$ monomer forms a sulfur-sulfur bond (S-S) with a sulfur atom of another $R-(S)_y^-$ monomer. This results, in the simplest case, in the formation of an R-S-S-R dimer moiety. Cells utilizing both liquid and solid versions, respectively, of such organosulfur electrodes are further described and claimed in U.S. Patent No. 4,917,974 and Application for Patent U.S. Ser. No. 07/421,091, filed October 13, 1989.

In co-pending application for patent U.S. Ser. No. 07/606,063 to Lampert and Visco, the construction of an electrochemical device using solid state reversible polymerization electrodes was first discussed. Solid polymerization electrodes have several advantages over many of the earlier electrochromic cell materials discussed above. One advantage is that they can exist in solid form at room temperature, and do not corrode other elements of electrochromic cells or degrade with time. Despite these advances, however, there are still a number of problems that persist.

One disadvantage of many electrochromic devices is that two different electrochromic electrodes must be fabricated that have complimentary or matching properties. Where transparent electrochromic devices are desired, for example, the counter electrode of the cell must be either a colorless or a matching electrode, i.e., one that will also become transparent at the same charge/discharge level as the first electrode. It is a non-trivial task to identify and generate two such seemingly disparate materials. It would greatly facilitate the construction of electrochromic devices, therefore, if matching electrodes were not required. This would result in the need for fewer

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fabrication steps, and ultimately reduce the cost of producing such electrochromic devices.

Another disadvantage of current solid-state electrochromic devices is occasionally observed where the device is incapable of uniformly returning to the transparency and color quality of that observed for the device in its original, uncharged state. This problem, mainly associated with large-area applications, may be referred to as "incomplete bleaching." An example of incomplete bleaching is seen where a material remains partially colorized in one region, while the surrounding area reverts to a completely colorless appearance upon discharge of the electrochromic cell. This inability to "bleach" the colored region may be due to such phenomena as the formation of competing or "parasitic" reactions that deplete the ions required to bleach/color the device. Such parasitic reactions are particularly problematic in applications where both the electrochromic and ion storage layers change color upon application of a potential.

Most of the electrochromic devices that are now known require a voltage drop across three layers of an electrochromic cell in order to effectively switch the device. In general, the three layers consist of an ion-conducting electrochromic material, a separator layer, and a counter electrode. The migration of ions across these layers is necessary for the observed color changes. For the most part, prior art electrochromic devices for information displays have involved relatively small-scale applications. This is partially due to the fact that it has been difficult to reliably generate electrochromic devices with greater surface area. The larger the area of the device, the harder it becomes to uniformly distribute a potential drop throughout the device. A commonly encountered problem with current large area electrochromic devices is that when the device is discharged, the potential required to completely

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bleach certain regions cannot be achieved in some areas because the potential is already at a maximum at others.

It is therefore an object of the current invention to provide an improved electrochromic device for transporting
5 ions that eliminates the need for two electrochromic electrodes with complimentary or matching properties.

It is also an object of the current invention to provide an improved electrochromic device that eliminates the need for a separation member between an electrochromic electrode and
10 a counter electrode.

It is a further object of the present invention is to provide an improved electrochromic device that will uniformly cycle between colored and uncolored or "bleached" states without loss of color uniformity in either state.

15 It is another object of the present invention to provide an improved electrochromic device in which balancing the capacity of an ion storage layer and an electrochromic layer is not necessary due to the fact that the ion storage layer does not change physical appearance upon application of a
20 potential.

These and other objects of the invention will become apparent to those skilled in the art from the following description and accompanying drawings.

SUMMARY OF THE INVENTION

25 The electrochromic device of the current invention comprises an electrochromic cell and electrical conductors. In one embodiment of the invention, the electrochromic cell comprises an electrochromic reservoir further comprising an electrochromic material and a redox material that serves
30 both as an electrolyte and an ion storage medium. The electrochromic material can be alternately electro-colored

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or de-colored ("bleached") by the dual passage of ions and electrons. It is an electron flow through the conductive path that provides the driving force for the coloration and bleaching of the electrochromic cell.

- 5 In an alternate embodiment of the current invention, the electrochromic cell comprises an electrochromic electrode further comprising an electrochromic material, and a composite counter electrode further comprising a redox material. In yet a third embodiment of the current
10 invention, a separator layer is used in conjunction with one or more electrochromic electrodes, or with an electrochromic reservoir and one or more electrochromic electrodes.

In one embodiment of the invention, the redox material is a dimerizable sulfur species contained in a polymer
15 electrolyte. In the preferred embodiment of the invention, the redox material comprises a mercaptan or an organothioliolate salt in a polymer electrolyte.

- Upon charging the electrochromic device, the sulfur-containing species dimerizes to form disulfide compounds.
20 This causes migration of cations and electrons produced by said dimerization, which in turn results in coloring of the electrochromic cell. Upon discharge of the electrochromic device, scission of the disulfide bonds occurs to regenerate the original sulfur-containing compound, thus resulting in
25 decolorization or bleaching of the electrochromic cell.

Further information to enable the practice of the device and method of the current invention by those skilled in the art will be apparent through the following discussion and description of the figures which follow.

30 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates an electrochromic cell of one embodiment of the current invention in its simplest form;

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Figure 2 shows a graph that contains optical switching data for a cell with a structure as shown in Figure 1;

Figure 3 illustrates an electrochromic device containing a two-layer electrochromic cell according to an alternate
5 embodiment of the current invention;

Figure 4 illustrates a more complete electrochromic device containing an electrochromic cell according to another embodiment of the current invention; and

Figure 5 illustrates an electrochromic device containing a
10 one-layer electrochromic cell according to yet another embodiment of the current invention.

DEFINITIONS

In the present specification and claims, reference will be made to phrases and terms of art which are expressly defined
15 for use herein as follows:

The term "bleached" as used herein describes an electrochromic cell that is in a discharged state. Bleached is therefore synonymous with de-colored or uncolored. An organosulfur material is described as existing in a bleached
20 state when it exists predominately in a monomeric form.

The term "broad band" is used with respect to any of the materials used in forming the electrochromic device of the current invention, including: the electrochromic material; the polymerizable organosulfur material; the separator, or
25 any other materials used in the device through which such radiation must pass for proper operation of the device; and refers to the solar transmission band of from about 300 nanometers (nm) to about 2500 nm.

The term "charged" as used herein is used to characterize an
30 electrochromic cell in which the electroactive or

organosulfur material exists in a dimeric form, and further wherein the electrochromic cell is colored.

The term "colored" is used with respect to an electrochromic cell that is in a charged state. An organosulfur material
5 is described as existing in a charged state when it exists predominately in a dimeric form.

The term "discharged" as used herein describes an electrochromic cell in which the electroactive or organosulfur material exists in a monomeric form, and
10 further wherein the electrochromic cell is decolored or uncolored.

The term "electrochromic material" is used to refer to a material in which a reversible color change occurs by the application of an electric field or current. More
15 particularly, an electrochromic material may be defined as a material having a charge capacity of about 10 to about 200 millicoulombs/cm² wherein application of a potential of from about 1 to about 10 volts--typically from about 1.5 to about 2.5 volts--results in a transmission change ranging from a
20 minimum change of about 20% up to a theoretical maximum of about 100% change in a particular electromagnetic radiation band. For example, a transmission change from a maximum of about 80% transmission down to a minimum of about 5% transmission (or vice versa), upon application of a
25 potential of from about 1 to about 2 volts, would represent a maximum of about 75% change in transmission.

The term "electrochromism" as used herein refers to a reversible color change which occurs in certain materials upon the application of an electric field or current.

30 The term "Group IA ion" as used herein refers to a cation, or positively charged ion, selected from the IA group of elements which consist of hydrogen, lithium, sodium, potassium, rubidium and cesium.

The term "mercaptan" is used to refer to a sulfur-containing organic compound of the general formula RSH, in which R is an organic moiety. A mercaptan is also the general name for an organothiolate or a thiol of the general formula RSM, in which case M = hydrogen (H). See also the definitions of "organothiolate" and "thiol" below.

The term "narrow band" is used with respect to any of the materials used in forming the electrochromic device of the current invention, including: the electrochromic material; the polymerizable organosulfur material; the separator, or any other materials used in the device through which such radiation must pass for proper operation of the device; and refers to the visible transmission band of from about 390 nm to about 760 nm.

The term "parasitic" is used herein to characterize reactions or other phenomena that have the effect of depleting the supply of ions responsible for the observed bleaching or coloring of an electrochromic cell or device.

The term "polyethylene oxide" (PEO) as used herein refers to PEO in any form, whether amorphous or not. Polyethylene oxide thus includes oxymethylene-linked polyethylene oxide or oxymethylene linked poly(oxyethylene), including the class of polymers having the general formula $(\text{CH}_2\text{CH}_2\text{O})_n(\text{X})_m$ where X can be any of a number of linking agents, such as oxymethylene (CH_2O). (Nicholas, C.V., et al., *Brit. Polym. J.* 20(1988) 289-292), and references cited therein.)

The term "organothiolate" or "thiol" is used to refer to a sulfur-containing organic compound of the general formula RSM, in which R is an organic moiety, and M is a Group IA element having an ionic charge of +1. In the case where M is hydrogen (H), the thiol is commonly referred to as a "mercaptan." See also the definition of "mercaptan" above.

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The term "semitransparent" as used herein refers to a material which will transmit approximately 20% to 70% of the electromagnetic radiation in a particular wavelength band. The wavelength band may be either a broad band or a
5 narrow band, or even a specific band or wavelength of light, e.g. red light or blue light.

The term "substrate" as used herein refers to a support member which may be glass or plastic or other such material as is appropriate for providing support for the
10 layers of an electrochromic cell or an electrochromic device.

The term "transparent" is used to refer to a material which will transmit at least about 70% of the electromagnetic radiation in a particular wavelength band.
15 The wavelength band may be either a broad band or a narrow band, or even a specific band or wavelength of light, e.g. red light or blue light. All of the organosulfur compounds of the current invention are transparent to electromagnetic radiation of at least a narrow visible
20 band and, preferably, are transparent to a broad band of light.

DETAILED DESCRIPTION OF THE INVENTION

An electrochromic cell according to the current invention is shown in its simplest form in Figure 1, and optical
25 switching data for such a device is shown in Figure 2. Figure 1 is a vertical cross-section of electrochromic cell 10 showing electrochromic film or layer 12, which comprises one electrode of the structure, and composite ion storage layer 14, which comprises a counter electrode
30 of the structure. Electrochromic layer 12 and composite ion storage layer 14 are coparallel layers, and are in mutual contact at common interface 16. In a preferred embodiment of the current invention, ion storage layer 14 is transparent, both in its charged and uncharged states,

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to visible light (narrow band) or to the entire electromagnetic spectrum (broad band).

Materials which may comprise electrochromic layer 12 include transition metal hydroxides and metal oxides such as (WO₃), molybdenum oxide (MoO₃), niobium oxide (Nb₂O₅), vanadium oxide (V₂O₅), titanium oxide (TiO₂ or Ti₂O₅), copper oxide (Cu₂O or uncolored CuO), bismuth oxide (Bi₂O₃), lead oxide (PbO or PbO₂), chromium oxide (Cr₂O₃), rhodium oxide (RhO, Rh(OH)_x, Rh₂O₃, or RhO₂), cobalt oxide (CoO), manganese oxide (MnO or Mn(OH)₂), ruthenium hydroxide (Ru(OH)_x), nickel oxide (NiO or Ni(OH)₂), osmium hydroxide (Os(OH)_x), and iridium oxide (IrO, IrO₂, or Ir(OH)₃).

Electrochromic layer 12 may also comprise mixtures of any of the above, especially tungsten oxide-vanadium oxide, tungsten oxide-titanium oxide, molybdenum oxide-vanadium oxide, molybdenum oxide-tungsten oxide, nickel oxide-manganese oxide, nickel oxide-cobalt oxide, iridium oxide-tin oxide (SnO₂), and iridium oxide-indium oxide (In₂O₃). Other compounds which may be used as electrochromic layer 12 include: heteropolyacids such as phospho-tungstic acid (H₃PO₄(WO₃)·xH₂O); redox compounds such as ferric ferrocyanide (Fe₄[Fe(CN)₆]₃)·xH₂O, lithium ferric ferrocyanide (Li_xFe_{4-x}[Fe(CN)₆]₃) or Prussian blue; and metal oxide cermets, such as gold tungstate (Au-WO₃) and platinum tungstate (Pt-WO₃).

Electrochromic layer 12 may also comprise organic electrochromic materials such: as viologens (halides of quaternary bases derived from 4,4'-dipyridinium ((C₅H₄N)₂), e.g., diheptylviologen-dibromide ((C₇H₁₅)₂(NC₅H₄)₂Br₂), (bis-4(-ethylpyridine-4'-yl)pyridium)-perchlorate; benzyl viologen; polyviologen dibromide mixtures such as 1,1'-dibenzyl-4,4'-bipyridinium difluoroborate, and 5,10-dihydro-5,10-dimethylphenazine; methylviologen compounds; pyridine (C₅H₅N); ortho-

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- toluidine ($C_{14}H_{18}N_2$), 4,4'-diamino-3,3'-dimethylbiphenyl; anthraquinones such as 2-tertiary butylanthraquinone ($C_{14}H_7O_2C(CH_3)_3$), phenothiazines such as methylene blue ($C_{16}H_{18}ClN_3S$); tetra thiafulvalene ($C_6H_4S_4$); polymers such as pyrazoline ($C_3H_6N_2$); polythiophene ($(C_4H_4S)_x$); polyaniline ($(C_6H_5NH_2)_x$); polytriphenylamine ($[C_6H_5)_3N]_x$); phthalocyanine lanthanides such as lutetium diphthalocyanine ($(C_{32}H_{16}N_8)_2Lu$); and tris(5,5'-dicarbo(3-acrylatoprop-1-oxy)-2,2'-bipyridine) ruthenium(II).
- 10 The thickness of electrochromic layer 12, which may be either in a solid or liquid state, should be sufficient, at a minimum, to provide a continuous film, i.e., usually at least about 100 Angstroms (10^{-8} meters). This thickness may be at least partially controlled by the
- 15 method used in forming the electrochromic electrode. The thickness of the electrochromic electrode will be further governed by the desired degree of light transmission as well as the desired amount of change in light transmission as the electrochromic material passes from either a
- 20 charged state to a discharged state or vice versa. A maximum thickness of about 1 micron (10^{-6} meters) for solid state materials should not be exceeded in order to avoid compromising the performance of the device due to longer ionic paths.
- 25 The electrochromic electrode may be formed by any one of a number of different and well-known methods. Examples of such methods include: sputtering or reactive sputtering of electrochromic materials onto a substrate; chemical deposition from a solution; electrochemical deposition; evaporation; spinning; spraying; chemical vapor deposition
- 30 (CVD), which includes plasma-enhanced CVD; vacuum evaporation which includes electron beam evaporation, or using a reactive gas such as O_2 ; and use of a sol-gel method. The electrochromic electrode may be made solely
- 35 of electrochromic material, i.e., in pure form, or an

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electrochromic material may be used in combination with a transparent carrier, such as polyethylene oxide.

The counter electrode, composite ion storage layer 14, may comprise a polymeric electrolyte material and an
5 organothiol (or mercaptan) material, the former serving as an electrolyte, and the latter serving as an ion storage medium. The organosulfur material further comprises a compound having the general formula, in its uncharged or monomeric state, of RSH or RSM , where $\text{M} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Cs}^+, \text{Rb}^+$, etc.. In its charged or dimer state, the
10 organosulfur material comprises a compound having the formula of $(\text{R}(\text{S})_y)_2$ wherein y is 1 to 6, and preferably 2. R is one or more of the same or different aliphatic or aromatic organic moieties having 1 to 100 carbon atoms,
15 and may include one or more oxygen, sulfur, or nitrogen heteroatoms when R comprises one or more aromatic rings, or one or more oxygen, sulfur, nitrogen or fluorine atoms associated with the chain when R comprises an aliphatic chain, wherein the aliphatic chain may be linear,
20 branched, saturated or unsaturated, and wherein either the aliphatic chain or the aromatic ring may have substituted groups thereon.

In its simplest form, the organosulfur material is a mercaptan or organothiolate compound, the basic or
25 backbone formula of which is RSM . In its dimerized state, when the device is colored, the sulfur atom (or atoms) forms an S-S bond with a sulfur atom of another RSM group forming the dimer RS-SR . Upon bleaching of the device, the S-S bond is broken, and each RS- group forms a salt
30 with a metal ion or proton. The result is a monomer species containing sodium or lithium, for example, to form RSNa or RSLi , respectively, or a mercaptan, if the RS- group recombines with a proton.

In certain instances, the organosulfur material may have
35 the formula RS-SR' in its dimerized state. In other

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words, both the R and R' may comprise the same or different organic moieties as described above. It will, of course, be understood that the foregoing description showing formation of a dimer with RS-SR can also indicate the mixed dimer form RS-SR', or formation of dimers containing sulfur atoms (such as RSS-SSSR') and is principally for illustrative purposes. Such organosulfur compounds and others which are useful in the practice of the invention are further described in the aforesaid U.S. Patents No. 4,833,048 and 4,917,974 to De Jonghe, et al., and application for patent U.S. Ser. No. 07/421,091 to Visco, et al.

The organosulfur material may be formed into an electrode consisting solely of an organosulfur material, or it may be combined in a transparent and ionically conductive matrix. Generally, any suitable transparent material that is stable in the presence of the electrochromic electrode and conducts ions may be used in storage layer 14. In the preferred embodiment of the invention, composite ion storage layer 14 comprises an organosulfur material and a polymeric electrolyte such as polyethylene oxide. The organosulfur material or the polymeric electrolyte may be used as a liquid or a solid, but preferably both are used in a solid state.

Examples of polymeric electrolyte materials which may be used in the practice of the invention include: polyethylene oxide (PEO); polyethylene glycol and polyethylene glycols linked with groups such as oxymethylene or oxypropylene such as oxymethylene-linked polyethylene oxide; polypropylene oxide (PPO); polyvinyl alcohol; polypropylene glycol; and poly[bis((methoxyethoxy)ethoxy)] phosphazene (MEEP). Of the foregoing materials, amorphous polyethylene oxide is a particularly preferred compound because although it is a solid and has no vapor pressure, it has a sticky or gooey

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characteristic which results in good adherence and contact with the electrochromic electrode.

While the composite ion storage electrode in the preferred embodiment is described as a transparent electrode, it
5 should be noted that for certain applications, e.g. displays, this counter electrode need not be transparent. Nontransparent materials, such as powdered carbon, may be added to the above list of polymeric electrolyte materials as desired for certain applications. Similarly,
10 the addition of other transparent or nontransparent additives that render the electrochromic electrode nontransparent is also anticipated. The use of such nontransparent counter electrodes should be apparent to one skilled in the relevant art, and are deemed to be
15 within the scope of the invention.

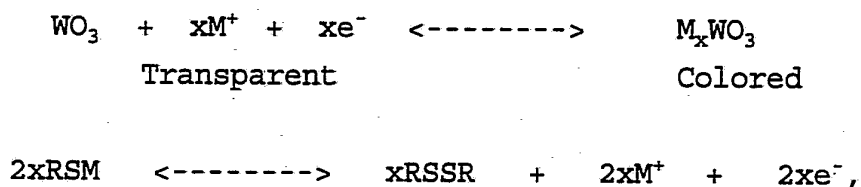
Dispersed through the composite ion storage layer there may also be dispersed an electrolyte in the form of a salt, an acid or a base. The cation of the salt may comprise an alkali metal such as lithium, sodium,
20 potassium, rubidium, and cesium, while the anion may comprise any element or compound such as triflate (CF_3SO_3^-) borate ($\text{B}_4\text{O}_7^{2-}$), carbonate (CO_3^{2-}) silanate (RSiO^-), silicate ($\text{SiO}_{2.5-1}^{2-}$), phosphate (HPO_4^{2-}) chlorate (ClO_4^-), chlorine (Cl^-), or hydroxide (OH^-), which will not
25 interfere with operation of the device. It should be noted that, in some instances, oxides may also be used as the anion if they are sufficiently soluble, and such oxide usage is intended to be included in the use of the terms "anion" and "salt". Examples of ion storage layers
30 include 2-mercapto-1-methyl imidazole in polyethylene oxide, or a lithium salt of dimercapto-thiadiazole in polyethylene oxide and lithium triflate.

Thus, the electrolyte may include at least one Group IA element selected from the class consisting of hydrogen,
35 lithium, sodium, potassium, rubidium, and cesium. When

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the electrolyte is in the form of an acid or a base, it may comprise, for example, H_3PO_4 , $(\text{C}_2\text{H}_5)_4\text{NOH}$, or $\text{HN}(\text{CF}_3\text{SO}_2)_2$. The amount of electrolyte used in the counter electrode may range from about one molecule of electrolyte per 20 units of monomer (PEO) up to about one molecule of electrolyte per 6 units of monomer.

In operation of the device, the electrochromic film is switched from transparent to colored, and reversed, by ion transfer. A reversible reaction for tungsten oxide with a generalized mercaptan is shown as follows:



Where: $\text{M}^+ = \text{H}^+, \text{Li}^+, \text{etc.}, \text{ and}$
 $\text{R} = \text{organic}$

The counter electrode layer may be formed, for example, when using polyethylene oxide (PEO), by mixing about 3 parts by weight of PEO powder with about 97 parts by weight of a solvent such as acetonitrile and then adding sufficient electrolyte to achieve the aforementioned ratio of electrolyte molecules to units of monomer. Mercaptan or organothiolate is then added so that the final solid electrode contains about 10 - 30 weight percent of the mercaptan or organothiolate electroactive material. The thickness of the composite ion storage layer counter electrode may range from about 0.01 millimeters (10^{-5} meters) to about 0.1 millimeters (10^{-4} meters).

Overall, the minimum concentration of organosulfur material in the electrode is governed by the amount of ions needed to cause the electrochromic material to color. This minimum amount of organosulfur material (i.e., minimum amount of charge capacity) may be calculated based

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The first tin oxide layer, in mutual contact with the electrochromic electrode, was then connected to the negative terminal of a variable DC potential source, and the second tin oxide layer, in mutual contact with the organosulfur electrode, was connected to the positive terminal. The voltage was then gradually raised until it reached a potential difference, between the electrodes, of about 1.3 volts, at which point a color change from transparent to deep blue was visually observed. Upon removing the connections to the power source, the device gradually bleached. Alternately, the device could be bleached more rapidly by reversing the potential (0.4 volts). Similar results were obtained by forming a tungsten oxide film (WO₃) over the conductive layer by reactive sputtering, and by electrochemically depositing molybdenum oxide-tungsten oxide (MoO₃-WO₃) films.

Example II

A device similar to that in Example I was constructed, with the addition of a separator layer between the electrochromic electrode and the ion storage layer. The separator layer was cast directly over the electrochromic layer from a solution of 1 gram of amorphous PEO dissolved in water. This was allowed to dry, and the ion storage layer was then cast over it. Similar procedure to those described in Example I above were then followed.

From the forgoing discussion and examples, one skilled in the art can recognize that the current invention provides an improved electrochromic structure. The use of a composite ion counter electrode and an electrochromic electrode, for example, permits construction of an inexpensive device. Further, the electrochromic electrode and the composite ion counter electrode may exist as discrete and/or separated layers, or may be combined into a singular complex matrix. According to the current device, materials may be used which may be in the solid state, and are chemically compatible with one another.

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Transport elements which can be used include hydrogen, lithium, sodium and other ionic elements. Furthermore, the use of a composite ion counter electrode in both the charged and discharged states, which may or may not be transparent, makes matching the characteristics of prior art positive and negative electrochromic electrodes unnecessary. The current invention also affords an opportunity to adjust the charge storage capacity of the counter electrode to meet the requirements of the particular electrochromic electrode used.

The foregoing disclosures and descriptions of the invention are illustrative and explanatory of the invention, and various changes in the size, shape, materials and components, as well as in the details of the illustrated construction, placement method, and configuration may be made without departing from the spirit of the invention, all of which are contemplated as falling within the scope of the specification and appended claims. Without further elaboration, it is believed that one of ordinary skill in the art can, using the preceding description, utilize the present invention to its fullest extent.

REFERENCES

The following references have been cited in the present specification, and are expressly incorporated by reference herein.

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4. US Patent No. 4,833,048 to L.C. De Jonghe, S.J. Visco, C.C. Mailhe, and M.B. Armand, issued May 23, 1989, for
5 "Metal-Sulfur Type Cell Having Improved Positive Electrode."
5. US Patent No. 4,917,974 to L.C. De Jonghe, S.J. Visco, M. Liu, C.C. Mailhe, issued April 17, 1990, for
10 "Lithium/Organosulfur Redox Cell Having Protective Solid Electrolyte Barrier Formed on Anode and Method of Making Same."
6. US Ser. No. 07/421,091 to S.J. Visco, M. Liu and L.C. De Jonghe, filed October 13, 1989, for "Cell for Making Secondary Batteries."
- 15 7. US Ser. No. 07/606,063 to C.M. Lampert and S.J. Visco, filed October 30, 1990, for "Electrochromic Optical Switching Device."

WHAT IS CLAIMED IS:

1. An electrochromic cell comprising an ion storage/dispersed electrochromic reservoir further comprising:
 - 5 a) an electrochromic material; and
 - b) a redox material, further wherein said redox material serves as an ion storage medium.
2. The electrochromic cell of Claim 1 wherein said ion storage/dispersed electrochromic reservoir is
10 semitransparent.
3. The electrochromic cell of Claim 1 wherein said ion storage/dispersed electrochromic reservoir is transparent to electromagnetic radiation of at least a narrow band.
- 15 4. The electrochromic cell of Claim 1 which further comprises a first transparent electrical conductor in electrical contact with a first surface of said ion storage/dispersed electrochromic reservoir and a second transparent electrical conductor in contact with a second
20 surface of said ion storage/dispersed electrochromic reservoir.
5. The electrochromic cell of Claim 4 wherein said transparent electrical conductors are in electrical communication with electrical contact members to permit
25 charge and discharge of said ion storage/dispersed electrochromic reservoir by a potential source.
6. An electrochromic cell comprising:
 - a) an electrochromic electrode further comprising an electrochromic material; and
 - 30 b) a composite ion counter electrode comprised of a redox material, further wherein said redox material serves as an ion storage medium.

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upon the amount of electrochromic material used in the device, or determined empirically based on observation of the change in light transmission of the electrochromic material. It should be noted, however, that the use of an
5 amount of organosulfur electrode material in excess of this minimum amount is not considered to be harmful, although it may be economically wasteful.

The minimum thickness of counter electrode 14 must be sufficient to permit formation of a continuous film,
10 usually at least about 100 Angstroms. The maximum thickness of the counter electrode is not critical and is normally governed by the attenuation in transparency or transmission which occurs if the electrode is formed of excessive thickness. For most applications, a maximum
15 thickness of about 0.1 millimeters (10^{-4} meters) should not be exceeded in order to avoid degrading the performance of the device.

Turning now to Figure 3, a more complete embodiment or version of the electrochromic structure or device of the
20 present invention is illustrated. Figure 3 shows electrochromic cell 20 placed between first transparent conductor layer 22 and second transparent conductor layer 24. Conductor layer 22 is located on the outer surface of electrochromic layer 28 with which it is in mutual
25 contact along common interface 26, and conductor layer 24 is located on the outer surface of composite ion storage layer 32 with which it is in mutual contact along common interface 30.

Transparent conductor layers 22 and 24 may comprise from
30 about 0.01 to about 0.5 microns (10^{-8} to 5×10^{-7} meters) of the same or different conductive material such as: tin oxide (SnO_2) doped with antimony or fluorine ($\text{SnO}_2:\text{F}, \text{Sb}$); indium oxide (In_2O_3 (5-15% Sn); zinc oxide (ZnO); zinc oxide and indium ($\text{ZnO}:\text{In}$); zinc oxide and aluminum
35 ($\text{ZnO}:\text{Al}$); cadmium stannate (Cd_2SnO_4); cadmium stannite

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(CdSnO₃); cadmium oxide (CdO); copper sulfide (Cu₂S); titanium nitride (TiN); or titanium oxynitride (TiO_xNi_{1-x}). Metals such as copper, silver, gold, aluminum, nickel, stainless steel, chromium, titanium, rhodium, and brass may also be used as transparent conductive layers 26 and 28 in thicknesses ranging from about 30 to about 1000 Angstroms (about 3×10^{-9} to about 10^{-7} meters). Conductor layers 22 and 24 provide electrical contact to the electrochromic electrode and the counter electrode, providing a sheet resistance typically of about 10 to about 15 ohms/square.

As is well known to those skilled in the art, transparent conductor layers can be produced by any one of several techniques. Examples of such techniques include, but are not limited to, vacuum deposition, sputtering, evaporation, solution dipping, chemical vapor deposition, electrochemical deposition, sol-gel techniques, and spraying. Furthermore, the conductor layers may be in the form of a continuous film, discontinuous film, dispersed conductor, or grid conductor.

In Figure 4, the construction of an electrochromic device is illustrated, utilizing the structure or cell shown in Figure 3. First glass or plastic substrate 40 is coated with a layer of transparent electrically conductive material to form first transparent electrical conductor 42 thereon. Electrically conductive connector 44 is then attached to conductor 42 to provide an external connection for the device to potential source 46. A layer of electrochromic material is then applied over transparent conductor 42 to form electrochromic electrode 48 thereon. In another embodiment of the invention, the electrochromic material may be dispersed throughout the ion storage medium.

Continuing with respect to Figure 4, second glass or plastic substrate 50 is coated with the same or different

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- transparent electrically conductive material to form second transparent conductor 52, and second electrically conductive connector 54 is then attached to conductor 52 to provide external electrical connection to the other terminal of potential source 46. A layer of composite or composite ion counter electrode material is then formed over conductor 52 to form composite ion storage layer 56. The two portions of the structure may then be placed together to form the device shown in Figure 4.
- 10 It should be noted, in this regard, that the various layers need not be formed in the manner just described. For example, after forming transparent conductor 42 on glass or plastic substrate 40, and forming electrochromic electrode 48 over conductor 42, counter electrode 56 can be formed over electrochromic electrode 48. Second transparent conductor 52 can then be formed as a layer over electrode 56, followed by application of second glass or plastic substrate 50 over conductor 52 to complete formation of the composite structure of the device.
- 20 The edges of the layers and/or the interfaces at the edges of the device may be sealed by using sealing material 58. Sealing material 58 can comprise any insulating material which is sufficiently non-porous to prevent entrance of foreign materials, including moisture, at such interfaces between the various layers of the composite structure. For example, an epoxy, a silicone, or a butyl rubber sealant compound, or a combination of the same can be utilized for this purpose. In addition, if desired, a rigid frame such as a wood or metal frame can be fitted around the edges of the device to impart more mechanical strength to the device. If a metal frame is used, care is needed to prevent any electrical shorting of the layers. In such instances, insulating sealing material 58 will provide sufficient electrical isolation and insulation of such a metal frame from the active layers of the device. It should be noted that the preference for using solid

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state materials in all the layers of the device does not require sealing the interface edges between the layers. Rather, sealing can be used to exclude foreign materials from penetrating into the structure, which would otherwise interfere with the performance or shorten the lifetime of the device.

An alternate embodiment of the current invention is shown in Figure 5. Electrochromic device 60 represents a minimum structure according to the current invention.

Device 60 contains first and second glass or plastic substrates 62 and 64 in contact with first and second electrical conductors 66 and 68, respectively. The active electrochromic component of the device is shown at ion storage/dispersed electrochromic layer or electrochromic reservoir 70. Electrochromic reservoir 70 may be formed by dispersing an electrochromic material into the ion storage layer formed as described above. Electrically conductive connectors 72 and 74, power source 76, and sealing material 78 then comprise additional elements of electrochromic device 60.

For certain applications not illustrated here, the electrochromic electrode may be separated from the composite ion storage layer. In such instances, a separator layer may be employed. Such a separator layer is claimed and described in co-pending application U.S. Ser. No. 606,063.

In another embodiment of the invention, also not shown, the electrochromic device may comprise one electrochromic electrode further comprising a composite ion storage/dispersed electrochromic region, and a second electrochromic electrode. Such a device may or may not feature the separation layer described above. Each of the above embodiments are for purposes of illustration only, and further combinations of layers, which will become apparent to those skilled in the art, are

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understood to fall within the scope of the claimed invention.

With reference again to Figure 4, the actual operation of the depicted device will be described in greater detail.

5 Electrical connector 44 is connected to one terminal, either negative or positive, of potential source 46. The terminal to which conductor 44 is attached depends upon the type of electrochromic material used at electrode 48. Similarly, electrical connector 54 will be attached to a
10 second terminal of potential source 46 in order to change the transmission characteristics of the electrochromic material forming electrode 48 when a potential is applied. For example, when electrochromic electrode 48 is comprised of WO_3 , connecting contact 54 to the negative terminal of
15 potential source 46 and connecting contact 54 to the positive terminal of potential source 46 will cause the electrochromic material in electrode 48 to darken upon the application of a potential, i.e., lower the transmission of light through electrode 48.

20 When this occurs, i.e. upon the application of a potential, it should be noted that counter electrode 56 remains transparent to light. This comprises one of the many advantages of the structure of the current invention over the prior art. As mentioned earlier, one advantage
25 of the current invention is that there is no need to try to match the transmission change characteristics of two different materials as is required with currently known electrochromic devices.

Glass or plastic substrates 40 and 50 will normally
30 comprise transparent materials, with plastic comprising the preferred material if greater flexibility is desired. Such substrates need not both be transparent if the type of device being constructed is one wherein transparency through the entire device is not needed or desired. One
35 such example might be a display device. For such

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applications, other substrate materials, such as metal substrates, for example, may also be utilized.

It should be further noted that where each of the above layers or components of the electrochromic cell have been described as discrete or separate components or layers, single layers may be formed which are capable of more than one function. The use of such composite layers should be deemed to fall within the scope of the invention. For example, either the electrochromic electrode or the composite ion counter electrode can comprise the transparent conductor material. Similarly, either the electrochromic electrode or the composite ion counter electrode can also comprise an ionic separator layer. It is also possible, for instance, to construct the device of the invention with a second electrochromic material in order to achieve special effects.

The following examples will serve to further illustrate the invention.

Example I

Onto a glass plate coated with a 4000 Ångstrom thick transparent layer of tin oxide (SnO_2) was applied a 3000 Ångstrom layer of tungstate (WO_3) electrochromic material. The tungstate was electrochemically deposited from a saturated tungsten peroxide solution made by dissolving tungsten metal in 10 ml of H_2O_2 , which was then diluted to 200 ml total volume with water.

A 0.01 mm thick transparent organosulfur electrode was cast directly over the above electrochromic layer from a mixture of 1 gram of amorphous PEO and 1.5 grams of 2-mercapto-1-methylimidazole dissolved in 10 ml of water. A second tin oxide coated glass plate, such as previously described, was then placed over the organosulfur electrode.

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7. The electrochromic cell of Claim 6 wherein said counter electrode is semitransparent.
8. The electrochromic cell of Claim 6 wherein said counter electrode is transparent to electromagnetic
5 radiation of at least a narrow band.
9. The electrochromic cell of Claim 6 further comprising a first transparent electrical conductor in electrical contact with said electrochromic electrode and a second transparent electrical conductor in electrical
10 contact with said composite ion counter electrode.
10. The electrochromic cell of Claim 9 wherein said transparent electrical conductors are in electrical communication with electrical contact members to permit charge and discharge of said electrodes by a potential
15 source.
11. The electrochromic cell of Claim 1 or Claim 6 wherein said redox material further comprises an organosulfur material and an electrolyte material.
12. The electrochromic cell of Claim 11 wherein said
20 electrolyte material further comprises a polymer electrolyte.
13. The electrochromic cell of Claim 12 wherein said polymer electrolyte further comprises a material selected from the group consisting of polyethylene oxide,
25 oxymethylene-linked polyethylene oxide, amorphous polyethylene oxide, linked polyethylene glycols, polypropylene oxide, polyvinyl alcohol, polyethylene glycol, polypropylene glycol, and poly[bis((methoxyethoxy)ethoxy)] phosphazene.
- 30 14. The electrochromic cell of Claim 12 wherein said polymer electrolyte comprises polyethylene oxide.

15. The electrochromic device of Claim 11 wherein said electrolyte material further comprises an electrolyte material in the form of a salt, an acid, or a base.
16. The electrochromic device of Claim 11 wherein said
5 electrolyte material further comprises a Group IA ion selected from the group consisting of hydrogen, lithium, sodium, potassium, rubidium and cesium.
17. The electrochromic cell of Claim 11 wherein said
10 organosulfur material further comprises a mercaptan or an organothiolate.
18. The electrochromic cell of Claim 11 wherein said organosulfur material further comprises a compound having the general formula, in its dimeric state, of $(R(S)_y)_2$ wherein y is 1 to 6, and R is one or more of the same or
15 different aliphatic or aromatic organic moieties having 1 to 100 carbon atoms which may include one or more oxygen, sulfur, or nitrogen heteroatoms when R comprises one or more aromatic rings, or one or more oxygen, sulfur, nitrogen or fluorine atoms associated with the chain when
20 R comprises an aliphatic chain, wherein the aliphatic chain may be linear, branched, saturated or unsaturated, and wherein either the aliphatic chain or the aromatic ring may have substituted groups thereon.
19. The electrochromic cell of Claim 18 wherein said
25 organosulfur material comprising said compound having the general formula, in the charged state, of $(R(S)_y)_2$ has a value of y of from 2 to 4.
20. The electrochromic cell of Claim 11 wherein said organosulfur material is further characterized by a
30 sulfur-sulfur bond when said device is in a charged state which, upon discharge of said electrochromic cell, is broken to form a mercaptan or an organothiolate with a Group IA ion in said cell, further wherein said Group IA

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ion is selected from the group consisting of hydrogen, lithium, sodium, potassium, rubidium, and cesium.

21. The electrochromic cell of Claim 1 or Claim 6 wherein said electrochromic material and said redox material all comprise materials in a solid state.

22. The electrochromic cell of Claim 1 or Claim 6 wherein said electrochromic material is capable of passing from a nontransparent state to a transparent or semitransparent state, depending upon the state of charge of said material, and further wherein said electrochromic material is selected from the group comprising transition metal oxides, heteropolyacids, metal-oxide cermets, mixed oxide composites, hydrous Group VIII metal oxides, organic electrochromic materials, and redox compounds.

23. The electrochromic cell of Claim 1 or Claim 6 wherein said electrochromic material is capable of existing in a transparent or semitransparent state and a nontransparent state, depending upon the state of charge of said material, further wherein said electrochromic material is selected from the group consisting of tungsten oxide (WO_3), molybdenum oxide (MoO_3), niobium oxide (Nb_2O_5), vanadium oxide (V_2O_5), titanium oxide (TiO_2 or Ti_2O_5), copper oxide (Cu_2O or uncolored CuO), bismuth oxide (Bi_2O_3), lead oxide (PbO or PbO_2), chromium oxide (Cr_2O_3), rhodium oxide (RhO , $\text{Rh}(\text{OH})_x$, Rh_2O_3 , or RhO_2), cobalt oxide (CoO), manganese oxide (MnO or $\text{Mn}(\text{OH})_2$), ruthenium hydroxide ($\text{Ru}(\text{OH})_x$), nickel oxide (NiO or $\text{Ni}(\text{OH})_2$), osmium hydroxide ($\text{Os}(\text{OH})_x$), iridium oxide (IrO , IrO_2 , or $\text{Ir}(\text{OH})_3$), tungsten oxide-vanadium oxide, tungsten oxide-titanium oxide, molybdenum oxide-vanadium oxide, molybdenum oxide-tungsten oxide, nickel oxide-manganese oxide, iridium oxide-tin oxide (SnO_2), iridium oxide-indium oxide (In_2O_3), phospho-tungstic acid ($\text{H}_3\text{PO}_4(\text{WO}_3) \cdot x\text{H}_2\text{O}$), ferric ferrocyanide ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$), lithium ferric ferrocyanide ($\text{Li}_x\text{Fe}_{4-x}[\text{Fe}(\text{CN})_6]_3$), gold

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- tungstate (Au-WO_3), platinum tungstate (Pt-WO_3), 4,4'-dipyridinium ($(\text{C}_5\text{H}_4\text{N})_2$), diheptylviologen-dibromide ($(\text{C}_7\text{H}_{15})_2(\text{NC}_5\text{H}_4)_2\text{Br}_2$) (bis-4-ethylpyridine-4'-yl)pyridium perchlorate, 1,1'-dibenzyl-4,4'-bipyridinium
- 5 difluoroborate, 5,10-dihydro-5,10-dimethylphenazine, methylviologen compounds, pyridine ($\text{C}_5\text{H}_5\text{N}$), 4,4'-diamino-3,3'-dimethylbiphenyl, ortho-toluidine ($\text{C}_{14}\text{H}_{18}\text{N}_2$), anthraquinone, 2-tertiary butylanthraquinone ($\text{C}_{14}\text{H}_7\text{O}_2\text{C}(\text{CH}_3)_3$), phenothiazines, methylene blue
- 10 ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$), tetra thiafulvalene ($\text{C}_6\text{H}_4\text{S}_4$), pyrazoline ($\text{C}_3\text{H}_6\text{N}_2$), polythiophene ($(\text{C}_4\text{H}_4\text{S})_x$) polyaniline ($(\text{C}_6\text{H}_5\text{NH}_2)_x$), polytriphenylamine ($([\text{C}_6\text{H}_5)_3\text{N}]_x$), lutetium diphthalocyanine ($(\text{C}_{32}\text{H}_{16}\text{N}_8)_2\text{Lu}$), and tris(5,5'-dicarbo(3-acrylatoprop-1-oxy)-2,2'-bipyridine) ruthenium(II).
- 15 24. The electrochromic cell of Claim 1 or Claim 6 further comprising a separator layer.
25. The electrochromic cell of Claim 4 or Claim 9 wherein one of said transparent electrical conductors is selected from the group consisting of tin oxide (SnO_2),
- 20 tin oxide doped with antimony and fluorine ($\text{SnO}_2:\text{F},\text{Sb}$), indium oxide (In_2O_3), indium oxide and tin ($\text{In}_2\text{O}_3:\text{Sn}$) (5-15% Sn), zinc oxide (ZnO), zinc oxide and indium ($\text{ZnO}:\text{In}$), zinc oxide and aluminum ($\text{ZnO}:\text{Al}$), cadmium stannate (Cd_2SnO_4), cadmium stannite (CdSnO_3), cadmium oxide (CdO),
- 25 copper sulfide (Cu_2S), titanium nitride (TiN), titanium oxynitride ($\text{TiO}_x\text{N}_{1-x}$), copper, silver, gold, aluminum, nickel, stainless steel, chromium, titanium, rhodium, and brass.
26. The electrochromic cell of Claim 4 or Claim 9
- 30 wherein at least one of said transparent electrical conductors is in contact with a substrate selected from the group comprising glass or plastic substrates.

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27. An electrochromic device comprising:

a) an ion storage/dispersed electrochromic reservoir capable of existing in a transparent electrical charge state, said reservoir further comprising:

- 5 i) an electrochromic material;
 ii) an organosulfur material further comprising a compound having the general formula, in its charged state, of $(R(S)_y)_2$ wherein y is 2 to 4, and R is one or more of the same or different aliphatic or
10 aromatic organic moieties having 1 to 100 carbon atoms which may include one or more oxygen, sulfur, or nitrogen heteroatoms when R comprises one or more aromatic rings, or one or more oxygen, sulfur, nitrogen, or fluorine atoms associated with the chain
15 when R comprises an aliphatic chain, wherein the aliphatic chain may be linear, branched, saturated or unsaturated, and wherein either the aliphatic chain or the aromatic ring may have substituted groups thereon; and

- 20 iii) a polymer electrolyte material;
 b) a first transparent electrically conductive film in electrical contact with a first surface of said ion storage/dispersed electrochromic reservoir;
 c) a second transparent electrically conductive
25 film in electrical contact with a second surface of said ion storage/dispersed electrochromic reservoir; and
 d) a first substrate in contact with one of said transparent electrically conductive films.

28. The electrochromic device of Claim 27 wherein said
30 ion storage/dispersed electrochromic reservoir comprises materials in a solid state.

29. An electrochromic device comprising:

a) a first transparent electrically conductive film;

- 35 b) an electrochromic electrode further comprising an electrochromic material, said electrochromic

electrode capable of existing in a transparent electrical charge state, further wherein said electrochromic electrode is in electrical contact with said first transparent electrically conductive film;

- 5 c) a composite ion counter electrode for transporting ions, said counter electrode comprised of a redox material which further comprises:

 i) a polymer electrolyte material; and

 ii) an organosulfur material further

- 10 comprising a compound having the general formula, in its charged state, of $(R(S)_y)_2$ wherein y is 2 to 4, and R is one or more of the same or different aliphatic or aromatic organic moieties having 1 to 20 carbon atoms which may include one or more oxygen, sulfur, or
15 nitrogen heteroatoms when R comprises one or more aromatic rings, or one or more oxygen, sulfur, nitrogen, or fluorine atoms associated with the chain when R comprises an aliphatic chain, wherein the aliphatic chain may be linear, branched, saturated or
20 unsaturated, and wherein either the aliphatic chain or the aromatic ring may have substituted groups thereon;

 d) a second transparent electrically conductive film in electrical contact with said composite ion counter electrode; and

- 25 e) a substrate in contact with one of said transparent electrically conductive films, said substrate selected from the group comprising glass or plastic substrates.

30. The electrochromic device of Claim 29 wherein said
30 electrochromic electrode and said composite ion counter electrode all comprise materials in a solid state.

31. The electrochromic device of Claim 27 or Claim 29 wherein said polymer electrolyte material further
comprises a material selected from the group consisting of
35 polyethylene oxide, oxymethylene-linked polyethylene oxide, amorphous polyethylene oxide, linked polyethylene

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glycols, polypropylene oxide, polyvinyl alcohol, polyethylene glycol, polypropylene glycol, and poly[bis((methoxyethoxy)ethoxy)] phosphazene.

32. The electrochromic device of Claim 27 or Claim 29
5 wherein said polymer electrolyte material further comprises polyethylene oxide.

33. The electrochromic device of Claim 27 or Claim 29 which further includes sealing means for sealing end edges of said device.

10 34. The electrochromic device of Claim 27 or Claim 29, wherein said organosulfur material is further characterized by a sulfur-sulfur bond when said device is in the charged state which, upon discharge of said electrochromic device, is broken to form a mercaptan or an
15 organothiolate with a Group IA ion in said cell, further wherein said Group IA ion is an ion selected from the group consisting of hydrogen, lithium, sodium, potassium, rubidium, and cesium.

35. The electrochromic device of Claim 27 or Claim 29
20 which further comprises a second substrate in contact with the other of said transparent electrically conductive films.

36. The electrochromic device of Claim 35 which further comprises electrical contact members electrically
25 connected to said first and said second transparent electrically conductive films, respectively.

37. The electrochromic device of Claim 27 or Claim 29 wherein said transparent electrically conductive films comprise indium oxide and tin.

30 38. The electrochromic device of Claim 27 or Claim 29 further comprising a separator layer.

39. An electrochromic device having one level of transparency when in a charged state and a second level of transparency when in a discharged state comprising:
- a) a first transparent electrically conductive planar film including an electrical contact member;
 - b) a planar ion storage/dispersed electrochromic reservoir capable of existing in a transparent electrical charge state having a first surface in electrical contact with said first transparent electrically conductive film, said reservoir further comprising:
 - i) an electrochromic material comprising one or more materials selected from the group consisting of transition metal oxides, heteropolyacids, metal-oxide cermets, mixed oxide composites, hydrous Group VIII metal oxides, organic electrochromic materials, and redox compounds;
 - ii) an organosulfur material further comprising a compound having the general formula, in its charged state, of $(R(S)_y)_2$ wherein y is 2 to 4, and R is one or more of the same or different aliphatic or aromatic organic moieties having 1 to 100 carbon atoms which may include one or more oxygen, sulfur, or nitrogen heteroatoms when R comprises one or more aromatic rings, or one or more oxygen, sulfur, nitrogen, or fluorine atoms associated with the chain when R comprises an aliphatic chain, wherein the aliphatic chain may be linear, branched, saturated or unsaturated, and wherein either the aliphatic chain or the aromatic ring may have substituted groups thereon; and
 - iii) a polymer electrolyte material;
 - c) a second transparent electrically conductive planar film having a first surface in contact with a second surface of said planar ion storage/dispersed electrochromic reservoir;
 - d) planar substrates in contact with said transparent electrically conductive films, said substrates

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selected from the group comprising plastic or glass substrates; and

e) sealing means for sealing end edges of said planar members of said electrochromic device.

5 40. The electrochromic device of Claim 39 wherein said ion storage/dispersed electrochromic reservoir is semitransparent, in both the charged and discharged states.

10 41. The electrochromic device of Claim 39 wherein said ion storage/dispersed electrochromic reservoir is transparent, in both the charged and discharged states, to electromagnetic radiation of at least a narrow band.

15 42. An electrochromic device having one level of transparency when in a charged state and a second level of transparency when in a discharged state comprising:

a) a first transparent electrically conductive planar film including an electrical contact member;

b) a planar solid state electrochromic electrode capable of existing in a transparent electrical charge
20 state, said electrochromic electrode having a surface in electrical contact with said first transparent electrically conductive film, and said electrochromic electrode comprising an electrochromic material that further comprises one or more materials selected from the
25 group consisting of transition metal oxides, heteropolyacids, metal-oxide cermets, mixed oxide composites, hydrous Group VIII metal oxides, organic electrochromic materials, and redox compounds;

c) a transparent planar solid state composite
30 ion counter electrode for transporting ions, further comprising:

i) a polymer electrolyte material; and

ii) an organosulfur material further comprising a compound having the general formula, when
35 in a charged state, of $(R(S)_y)_2$ wherein y is 2 to 4,

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and R is one or more of the same or different aliphatic or aromatic organic moieties having 1 to 100 carbon atoms which may include one or more oxygen, sulfur, or nitrogen heteroatoms when R comprises one or more aromatic rings, or one or more oxygen, sulfur, nitrogen, or fluorine atoms associated with the chain when R comprises an aliphatic chain, wherein the aliphatic chain may be linear, branched, saturated or unsaturated, and wherein either the aliphatic chain or the aromatic ring may have substituted groups thereon;

d) a second transparent electrically conductive film in contact with said composite ion counter electrode, including an electrical contact member;

e) planar substrates in contact with said transparent electrically conductive films, said substrates selected from the group comprising plastic or glass substrates; and

f) sealing means for sealing end edges of said planar members of said electrochromic device.

43. The electrochromic device of Claim 42 wherein said composite ion counter electrode is semitransparent, in both the charged and discharged states.

44. The electrochromic device of Claim 42 wherein said composite ion counter electrode is transparent, in both the charged and discharged states, to electromagnetic radiation of at least a narrow band.

45. The electrochromic device of Claim 39 or Claim 42 wherein said electrically conductive film is selected from the group consisting of tin oxide (SnO_2), tin oxide doped with antimony and fluorine ($\text{SnO}_2:\text{F}, \text{Sb}$), indium oxide (In_2O_3), indium oxide and tin ($\text{In}_2\text{O}_3:\text{Sn}$) (5-15% Sn), zinc oxide (ZnO), zinc oxide and indium ($\text{ZnO}:\text{In}$), zinc oxide and aluminum ($\text{ZnO}:\text{Al}$), cadmium stannate (Cd_2SnO_4), cadmium stannite (CdSnO_3), cadmium oxide (CdO), copper sulfide (Cu_2S), titanium nitride (TiN), titanium oxynitride

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($\text{TiO}_x\text{N}_{1-x}$), copper, silver, gold, aluminum, nickel, stainless steel, chromium, titanium, rhodium, and brass.

46. The electrochromic device of Claim 39 or Claim 42 wherein said polymer electrolyte material further
5 comprises a material selected from the group consisting of polyethylene oxide, oxymethylene-linked polyethylene oxide, amorphous polyethylene oxide, linked polyethylene glycols, polypropylene oxide, polyvinyl alcohol, polyethylene glycol, polypropylene glycol, and
10 poly[bis((methoxyethoxy)ethoxy)] phosphazene.

47. The electrochromic device of Claim 39 or Claim 42 wherein said polymer electrolyte material comprises polyethylene oxide.

48. The electrochromic device of Claim 39 or Claim 42
15 wherein said organosulfur material is further characterized by a sulfur-sulfur bond when said device in a charged state which, upon discharge of said electrochromic device, is broken to form a mercaptan or an organothiolate with a Group IA ion in said cell, further
20 wherein said Group IA ion is selected from the group consisting of hydrogen, lithium, sodium, potassium, rubidium, and cesium.

49. The electrochromic device of Claim 39 or Claim 42 further comprising a separator layer.

25 50. An electrochromic device comprising:
a) an electrochromic electrode; and
b) a composite ion counter electrode for transporting ions, which further comprises an organosulfur material characterized by the formation of sulfur-sulfur
30 bonds in the charged state which, upon discharge of said electrochromic device, are broken to form a mercaptan or an organothiolate with a Group IA ion in said cell, further wherein said Group IA ion is selected from the

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group consisting of hydrogen, lithium, sodium, potassium, rubidium, and cesium.

51. The electrochromic device of Claim 50 further comprising a polymer electrolyte.

5 52. The electrochromic device of Claim 50 further comprising a separator layer.

53. A method for reversibly coloring an electrochromic device, comprising the steps of:

a) reversibly generating and transporting ions
10 across an ion storage/dispersed electrochromic reservoir, wherein said ion storage/dispersed electrochromic reservoir further comprises:

i) an electrochromic material;

ii) a polymer electrolyte material further
15 comprising a material selected from the group consisting of polyethylene oxide, oxymethylene-linked polyethylene oxide, amorphous polyethylene oxide, linked polyethylene glycols, polypropylene oxide, polyvinyl alcohol, polyethylene glycol, polypropylene glycol, and poly[bis((methoxyethoxy)ethoxy)]
20 phosphazene; and

iii) an organosulfur material further comprising a compound having the general formula, in its charged state, of $(R(S)_y)_2$ wherein y is 1 to 6, and
25 R is one or more of the same or different aliphatic or aromatic organic moieties having 1 to 100 carbon atoms which may include one or more oxygen, sulfur, or nitrogen heteroatoms when R comprises one or more aromatic rings, or one or more oxygen, sulfur, nitrogen
30 or fluorine atoms associated with the chain when R comprises an aliphatic chain, wherein the aliphatic chain may be linear, branched, saturated or unsaturated, and wherein either the aliphatic chain or the aromatic ring may have substituted groups thereon;

b) transporting electrons at a first transparent electrically conductive film, wherein said first conductive film is in electrical contact with a first surface of said ion storage/dispersed electrochromic reservoir; and

c) transporting electrons at a second transparent electrically conductive film, wherein said second conductive film is in electrical contact with a second surface of said ion storage/dispersed electrochromic reservoir.

54. The method for reversibly coloring an electrochromic device of Claim 53, further comprising the steps of:

a) exchanging electrons between said first electrically conductive film and said ion storage/dispersed electrochromic reservoir; and

b) exchanging electrons between said second electrically conductive film and said ion storage/dispersed electrochromic reservoir.

55. A method for reversibly coloring an electrochromic device, comprising the steps of:

a) reversibly transporting ions at an electrochromic electrode, said electrochromic electrode comprising electrochromic material;

b) reversibly generating ions at a composite ion counter electrode capable of ionic exchange with said electrochromic electrode, in which said composite ion counter electrode further comprises:

i) a polymer electrolyte material further comprising a material selected from the group consisting of polyethylene oxide, oxymethylene-linked polyethylene oxide, amorphous polyethylene oxide, linked polyethylene glycols, polypropylene oxide, polyvinyl alcohol, polyethylene glycol, polypropylene glycol, and poly[bis((methoxyethoxy)ethoxy)] phosphazene; and

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- ii) an organosulfur material comprising a compound having the general formula, in its charged state, of $(R(S)_y)_2$ wherein y is 1 to 6, and R is one or more of the same or different aliphatic or aromatic organic moieties having 1 to 100 carbon atoms which may include one or more oxygen, sulfur, or nitrogen heteroatoms when R comprises one or more aromatic rings, or one or more oxygen, sulfur, nitrogen or fluorine atoms associated with the chain when R comprises an aliphatic chain, wherein the aliphatic chain may be linear, branched, saturated or unsaturated, and wherein either the aliphatic chain or the aromatic ring may have substituted groups thereon;
- c) exchanging ions between said electrochromic electrode and said counter electrode;
- d) transporting electrons at a first transparent electrically conductive film, wherein said first conductive film is in electrical contact with said electrochromic electrode; and
- e) transporting electrons at a second transparent electrically conductive film, wherein said second conductive is in electrical contact with said composite ion counter electrode.

56. The method for reversibly coloring an electrochromic device of Claim 55, further comprising the steps of:

- a) exchanging electrons between said first electrically conductive film and said electrochromic electrode;
- b) exchanging electrons between said second electrically conductive film and said composite ion counter electrode.

57. The method for reversibly coloring an electrochromic device of Claim 53 or Claim 55 wherein said organosulfur material is further characterized by a sulfur-sulfur bond in the charged state which, upon

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discharge of said electrochromic device, is broken to form a mercaptan or an organothiolate with a Group IA ion in said cell, further wherein said Group IA ion is selected from the group consisting of hydrogen, lithium, sodium, potassium, rubidium, and cesium.

58. The method for reversibly coloring an electrochromic device of Claim 53 or Claim 55, wherein said organosulfur material comprises a compound having the general formula, in the charged state, of $(R(S)_y)_2$ has a value of y from 2 to 4.

59. The method for reversibly coloring an electrochromic device of Claim 55 wherein said counter electrode is semitransparent, in both the charged and discharged states.

60. The method for reversibly coloring an electrochromic device of Claim 53 wherein said composite ion/dispersed electrochromic reservoir is semitransparent, in both the charged and discharged states.

61. The method for reversibly coloring an electrochromic device of Claim 55 wherein said counter electrode is transparent, in both the charged and discharged states, to electromagnetic radiation of at least a narrow band.

62. The method for reversibly coloring an electrochromic device of Claim 53 wherein said composite ion/dispersed electrochromic reservoir is transparent, in both the charged and discharged states, to electromagnetic radiation of at least a narrow band.

63. The method for reversibly coloring an electrochromic device of Claim 53 or Claim 55, wherein said electrochromic material is capable of passing from a nontransparent state to a transparent or semitransparent

state depending upon the state of charge of said material, further in which said electrochromic material is selected from the group consisting of transition metal oxides, heteropolyacids, metal-oxide cermets, mixed oxide
5 composites, hydrous Group VIII metal oxides, organic electrochromic materials, and redox compounds.

64. The method for reversibly coloring an electrochromic device of Claim 55 wherein said composite ion counter electrode further comprises an electrolyte
10 selected from the group consisting of hydrogen, lithium, sodium, potassium, rubidium and cesium.

65. The method for reversibly coloring an electrochromic device of Claim 53 wherein said composite ion/dispersed electrochromic reservoir further comprises
15 an electrolyte selected from the group consisting of hydrogen, lithium, sodium, potassium, rubidium and cesium.

66. The method for reversibly coloring an electrochromic device of Claim 53 or Claim 55 wherein one of said transparent electrically conductive films is
20 selected from the group consisting of tin oxide (SnO_2), tin oxide doped with antimony and fluorine ($\text{SnO}_2:\text{F}, \text{Sb}$), indium oxide (In_2O_3), indium oxide and tin ($\text{In}_2\text{O}_3:\text{Sn}$) (5-15% Sn), zinc oxide (ZnO), zinc oxide and indium ($\text{ZnO}:\text{In}$), zinc oxide and aluminum ($\text{ZnO}:\text{Al}$), cadmium stannate
25 (Cd_2SnO_4), cadmium stannite (CdSnO_3), cadmium oxide (CdO), copper sulfide (Cu_2S), titanium nitride (TiN), titanium oxynitride ($\text{TiO}_x\text{N}_{1-x}$), copper, silver, gold, aluminum, nickel, stainless steel, chromium, titanium, rhodium, and brass.

30 67. The method for reversibly coloring an electrochromic device of Claim 53 or Claim 55 wherein at least one of said transparent electrically conductive films is in contact with a substrate selected from the group consisting of glass and plastic substrates.

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68. The method for reversibly coloring an electrochromic device of Claim 53 or Claim 55 which further comprises the steps of charging and discharging said electrically conductive films by a potential source,
5 wherein said potential source is in electrical communication with said electrically conductive films.

69. The method for reversibly coloring an electrochromic device of Claim 53 or Claim 55 wherein said polymer electrolyte material comprises polyethylene oxide.

10 70. The method for reversibly coloring an electrochromic device of Claim 53 or Claim 55 further comprising a separator layer.

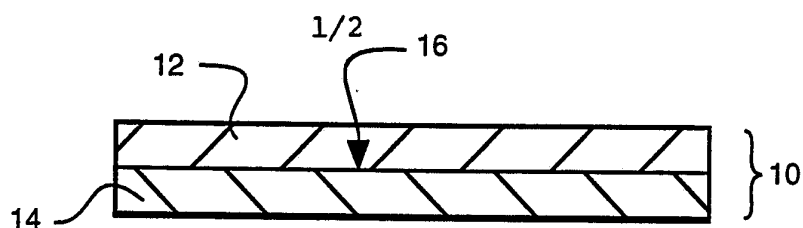


FIG. 1

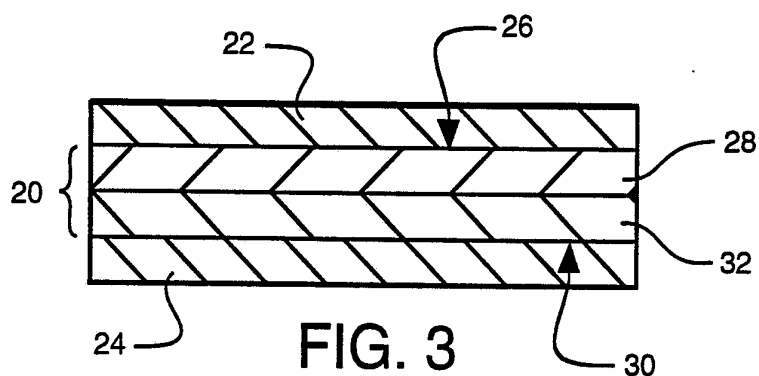
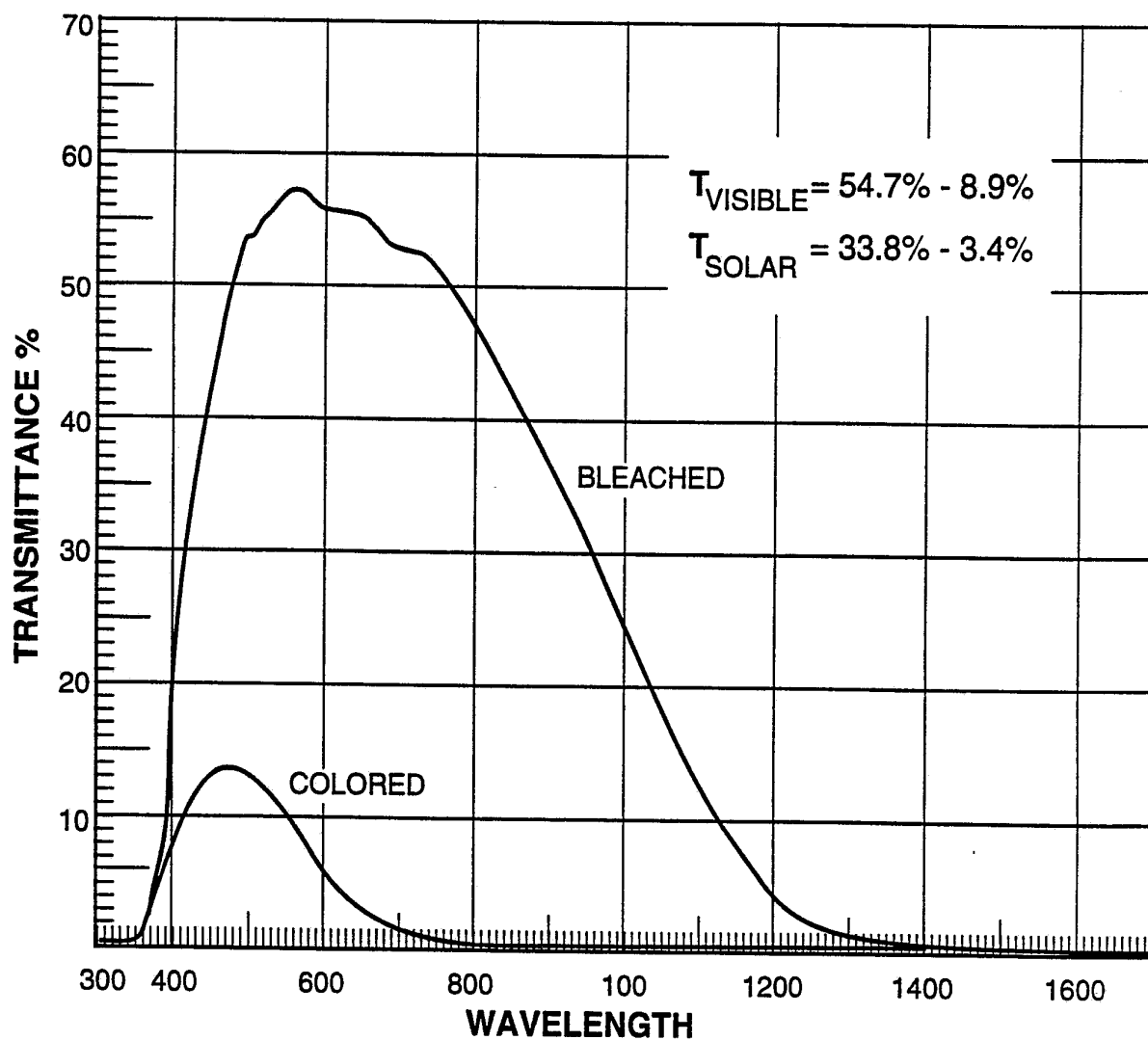


FIG. 3



SUBSTITUTE SHEET FIG. 2

2/2

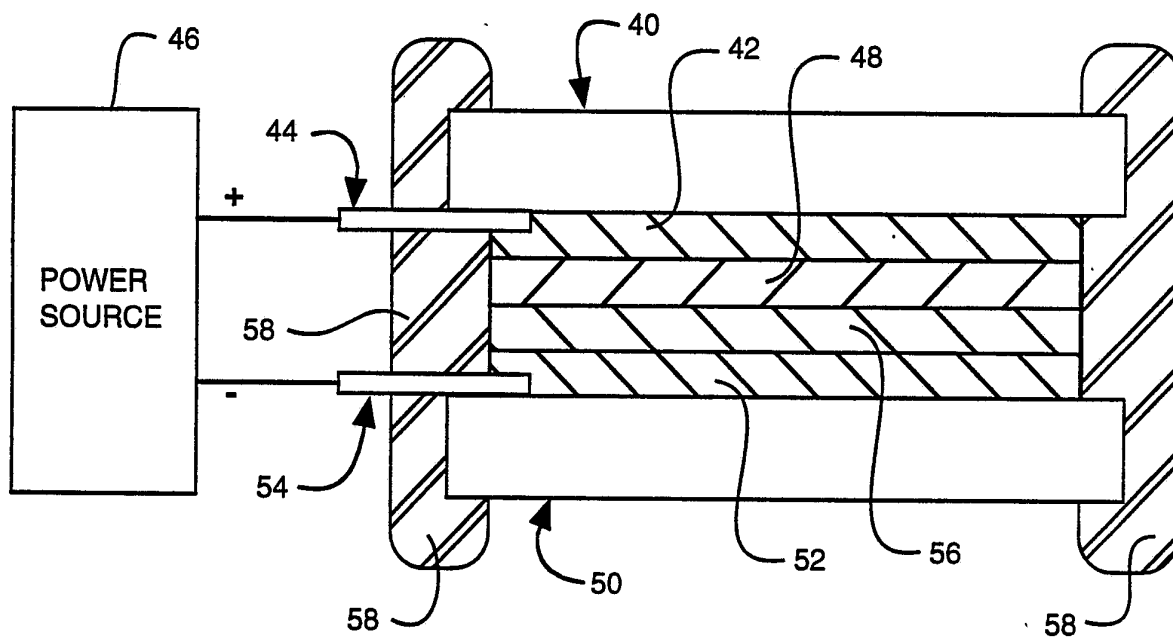


FIG. 4

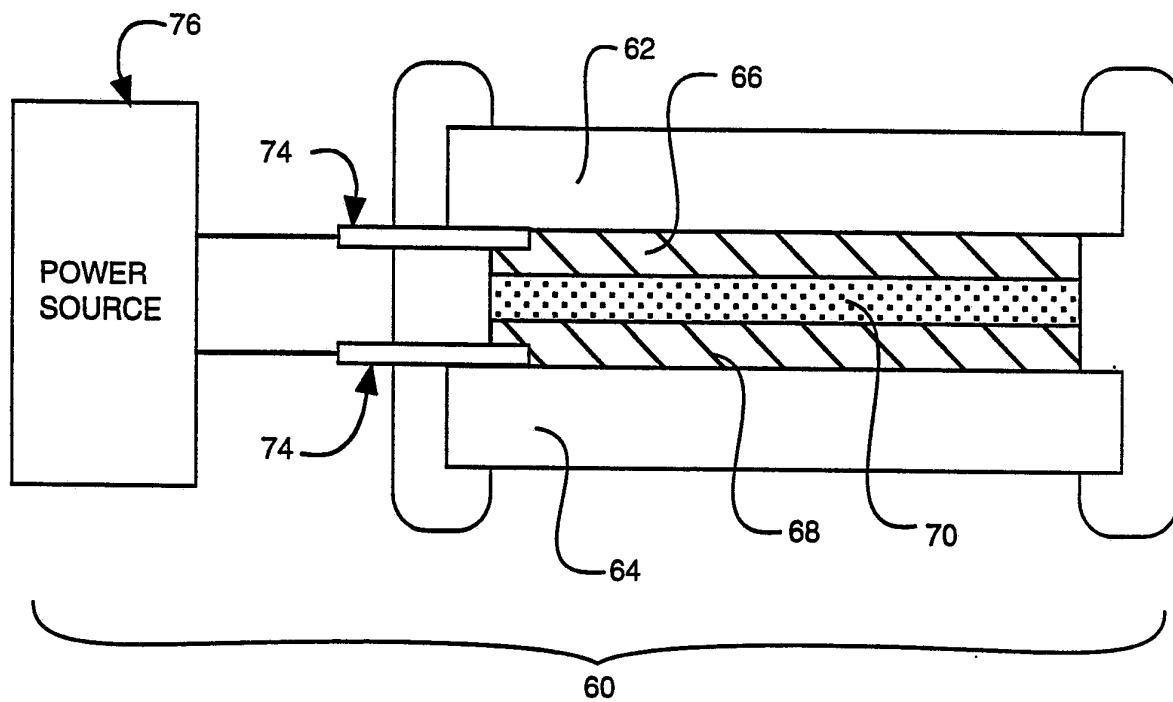


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/03675**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) :G02F 01/153, 01/15

US CL :359/269, 270, 275, 268, 265

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 359/269, 270, 275, 268, 265

NONE

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|------------------------------|
| X | US, A, 3,451,741 (MANOS) 24 June 1969 see column 6 and column 19 | 1 - 5 22,23,25,26 |
| X,P | US, A, 5,128,799 (BYKER) 07 July 1992 see entire document | 1 - 5 22,23,25,26 |
| X,E | US, A, 5,206,756 (CHESHIRE) 27 April 1993 see entire document | 6-10, 21-23, 25,26 |
| X,E | US, A, 5,215,684 (OKABAYASHI ET AL) 01 June 1993, see detailed description | 6-10, 21-23, 25,26 |
| X,P | US, A, 5,124,080 (SHABRANG ET AL) 23 June 1992 see entire document | 6-10, 15,16, 21-23,25, 26 |

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

| | | |
|---|-----|--|
| * Special categories of cited documents: | *T | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
| *A* document defining the general state of the art which is not considered to be part of particular relevance | *X* | document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone |
| *E* earlier document published on or after the international filing date | *Y* | document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | *Z* | document member of the same patent family |
| *O* document referring to an oral disclosure, use, exhibition or other means | | |
| *P* document published prior to the international filing date but later than the priority date claimed | | |

Date of the actual completion of the international search

11 AUGUST 1993

Date of mailing of the international search report

23 AUG 1993

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/03675

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| Y | US, A, 4,992,559 (KATHIRGAMANATHAN ET AL) 12 February 1991, see entire document | 1-70 |
| Y | US, A, 4,781,443 (GILES) 01 November 1988 see beginning column 6, line 42 | 1-70 |

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/03675

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

L₁ electrochrom? or electro chrom?L₂ redoxL₃ L₁ and L₂L₄ ion storageL₅ L₃ and L₄L₆ reservoirL₇ L₆ and L₃**BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING**

This ISA found multiple inventions as follows:

I. Claims 1-5, (11-24)/1, 25/4, 26/4, 27, 28, (31-38)/27, 39-41, (45-49)/39, 53, 54, 57/53, 58/53, 63/53, 60, 62, 65 and (66-70)/53, drawn to an electrochromic cell utilizing an electrochromic reservoir to accomplish the chromatic operation of the cell, classified in Class 359, subclass 274.

II. Claims 6-10, (11-24)/6, 25/9, 26/9, 29, 30 (31-38)/29, 42-44, (45-49)/42, 50-52, 55, 56, 57/55, 58/55, 63/55, 61, 64 and (66-70)/55, drawn to an electrochromic cell utilizing an electrochromic layer and an ion counter electrode operating in conjunction with each other to accomplish the chromatic operation of the cell, classified in Class 359, subclass 270.