



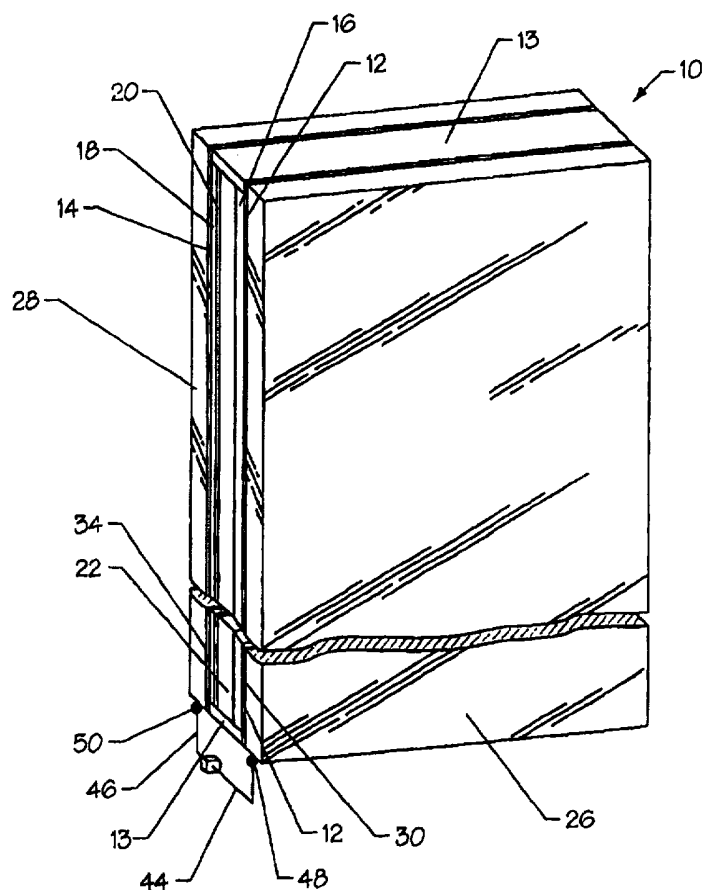
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<p>(21) International Application Number: PCT/US97/08773 (22) International Filing Date: 27 May 1997 (27.05.97) (30) Priority Data: 08/655,724 30 May 1996 (30.05.96) US (71) Applicant: MIDWEST RESEARCH INSTITUTE [US/US]; 425 Volker Boulevard, Kansas City, MO 64110 (US). (72) Inventors: BECHINGER, Clemens, S.; Hardergasse 14, D-78464 Konstanz (DE). GREGG, Brian, A.; 13940 Braun Drive, Golden, CO 80401 (US). (74) Agent: RICHARDSON, Ken; National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401 (US).</p>		<p>(81) Designated States: AU, BR, CA, CN, DE, DK, ES, GB, IL, JP, KP, KR, MX, NO, NZ, RU, SE, SG, VN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i></p>

(54) Title: PHOTOELECTROCHEMICAL-ELECTROCHROMIC DEVICE

(57) Abstract

A photoelectrochemical-electrochromic device is provided. The device comprises a first transparent electrode (12) and a second transparent electrode (14) in parallel, spaced relation to each other. The first transparent electrode (12) is electrically connected to the second transparent electrode (14). An electrochromic material (16) is applied to the first transparent electrode (12) and a semiconductor coating (18) is applied to the second transparent electrode (14). An electrolyte layer (22) contacts the electrochromic material (16) and the semiconductor coating (18). The electrolyte layer (22) has a redox couple whereby upon application of light, the semiconductor coating (18) absorbs the light and the redox couple oxidizes producing an electric field across the device modulating the effective light transmittance through the device.



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Photoelectrochemical-Electrochromic Device

The United States Government has rights in the invention under Contract No. DE-AC36-83CH10093 between the United States Department of Energy and the
5 National Renewable Energy Laboratory, a Division of the Midwest Research Institute.

Technical Field

The present invention relates to electrochromic devices which modulate the
10 transmittance of light entering a window depending on the incident solar intensity and, in particular, relates to electrochromic devices which are self-powered to modulate the transmittance of light entering a window without needing external power supplies.

Background Art

Presently there exists approximately 19 billion square feet of windows in commercial and residential buildings, and another 600 million square feet of windows are being installed in new buildings throughout the United States each year, culminating in enormous cost and energy demands for air conditioning to negate the
20 unwanted solar heat gains through these windows. Sometimes, static solar gain control coatings are applied to windows. This practice is disadvantageous, however, in that sunlight is blocked even when it is needed for lighting and heating during cold weather.

There have been some apparatus and methods developed for controlling the
25 transmittance of light through window panes. For example, Greenberg et al, U.S. Patent No. 4,768,865, discloses a conventional electrochromic film on a window that is responsive to the application of an electric field to change from a high-transmittance, non-absorbing state to a lower-transmittance, absorbing or reflecting state. Ito et al, U.S. Patent No. 4,958,917, discloses the use of an electrochromic
30 coating for dimming automobile windows, including a plurality of solid

electrochromic elements arranged in a horizontal abutting fashion and adhered to the glass window, each element being controllable independently of the others.

Hashimoto et al, U.S. Patent No. 4,958,917, discloses a specialized combination of two electrochromic cells which, together, are capable of reducing the transmittance of visible light to less than the usual lower limit of 7% for known electrochromic coatings.

While the Greenberg et al, Ito et al, and Hashimoto et al patents teach electrochromic coatings or controlling the transmittance of light through window panes, these coatings require external power supplies and, to be practical, the need for wiring into a building's electrical system.

The Mockovciak, U.S. Patent 4,475,031, discloses a self-contained sun-sensitive window made up of liquid nematic crystals (LC), sandwiched between two transparent sheets and powered directly by a solar cell. Liquid nematic crystals, however, are not effective in blocking heat radiation. Rather, they merely scatter light, thus making a window translucent, but not effectively blocking heat gain from the sun's rays. A further disadvantage of such liquid nematic crystal technology is that a constant source of energy is required to change the translucence of the window, thus requiring a substantial and continuous source of electric power as long as transparency instead of translucence is desired.

The Benson et al, U.S. Patent 5,384,653, assigned to the same assignee as the present application, describes a stand-alone photovoltaic powered electrochromic window. The window of the Benson et al patent includes an electrochromic material that has been deposited on one pane of the window in conjunction with an array of photovoltaic cells deposited along an edge of the pane to produce the required electric power necessary to vary the effective transmittance of the window. While providing a self-powered electrochromic window, the window of the Benson et al patent requires increased layers in the electrochromic material in addition to using a portion of the window space for the photovoltaic array along the periphery of the window. Use of only the periphery of the window for the photovoltaic cells could

result in the sunlight entering the building without actually contacting the photovoltaic cells.

The Branz et al, U.S. Patent 5,377,037, assigned to the same assignee as the present application, describes an electrochromic-photovoltaic film for light-sensitive control of optical transmittance. The variable transmittance optical component of the
5 Branz et al patent includes an electrochromic material and a photovoltaic device-type thin film solar cell deposited in a tandem type, monolithic single coating over the component. A resistor is connected in series across the electrochromic material and photovoltaic device controlling the activation and deactivation of the electrochromic
10 material. The electrical conductivity between the electrochromic material and the photovoltaic device is enhanced by interposing a transparent electrically conductive layer.

In the Branz et al patent, an electrical connection exists between the electrochromic material and the photovoltaic device. While successfully providing a
15 variable transmittance optical component that does not require an external power supply, the optical component of the Branz et al patent requires at least eight thin layers to operate and is very complicated to construct due to the thin layers and delicacy of manufacture.

Regardless of the previous attempts to reduce the amount of solar energy entering a window, there remains a need for a self-darkening window coating which
20 modulates the transmittance of incoming light depending on the incident solar intensity without utilizing valuable window space. Furthermore, the need remains for a self-darkening window which modulates depending on the amount of light entering the window and not the amount of light striking the periphery of the window.

25

Disclosure of Invention

The present invention is a photoelectrochemical-electrochromic device. The device comprises a first transparent electrode and a second transparent electrode in a parallel, spaced relation to each other. The first transparent electrode is electrically
30 connected to the second transparent electrode.

The device of the present invention further comprises an electrochromic material applied to the first transparent electrode and a semiconductor coating applied to the second transparent electrode. An electrolyte layer contacts the electrochromic material and the semiconductor coating. The electrolyte layer has a redox couple whereby upon application of light, the semiconductor coating absorbs the light and the redox couple oxidizes producing an electric field across the device modulating the effective light transmittance through the device.

In a preferred embodiment, the device further comprises a first transparent substrate and a second transparent substrate. The first transparent electrode is applied to the first transparent substrate and the second transparent electrode is applied to the second transparent substrate. Preferably, the first and second transparent substrate comprises a material selected from the group consisting of glass and plastic.

In another embodiment of the device of the present application, the electrochromic material preferably comprises a material selected from the group consisting of WO_3 , IrO_x , V_2O_5 , and NiO and the semiconductor coating layer preferably comprises a porous material of metal oxide selected from the group consisting of TiO_2 , CdS , ZnS , ZnO , and WO_3 . Furthermore, the device of present invention preferably comprises a layer of dye applied on the surface and into the pores of the semiconductor coating layer. The dye preferably comprises transition metal complexes selected from the group consisting of ML_3 and ML_2X_2 wherein M is selected from the group consisting of Fe, Ru, Os, Cr, Mo and Mn, L comprises bipyridine-type ligand selected from the group consisting of 2,2'-bipyridine-4,4'-dicarboxylic acid and 4,4'-dimethyl-2,2'-bipyridine, and X comprises a monodentate ligand selected from the group consisting of CN, SCN, Cl, Br, I and H_2O ; porphyrins comprising zinc tetra(4-carboxyphenyl)porphyrin; phthalocyanines comprising 4,4',4'',4'''-tetraazaphthalocyanine; and perylenes comprising 3,4,9,10-perylene tetracarboxylic acid.

In yet another preferred embodiment, the electrolyte layer has a predetermined thickness to provide high lateral ionic conductivity to darken the entire

immediately adjacent electrochromic material. When the electrolyte layer's thickness is less than the predetermined thickness, high lateral conductivity does not occur and only those portions of the electrochromic material adjacent the electrolyte exposed to the light will actually darken.

5 The present invention is also a method of modulating the transmittance of light. The method comprises electrically connecting a first transparent electrode and a second transparent electrode in parallel, spaced relation to each other. Next, an electrochromic material is applied to the first transparent electrode and a semiconductor coating is applied to the second transparent electrode. Then, an electrolyte layer is positioned to contact the electrochromic material and the semiconductor coating. The electrolyte layer has a redox couple, whereby the first and second electrodes, the electrochromic material, the semiconductor coating, and the electrolyte layer form a photoelectrochemical-electrochromic device. Finally, the photoelectrochemical-electrochromic device is exposed to a light source wherein the semiconductor coating and/or the sensitizing dye absorbs the light and the redox couple becomes oxidized producing an electric field across the photoelectrochemical-electrochromic device to vary the effective light transmittance through the photoelectrochemical-electrochromic device.

15 In a preferred embodiment, the method further comprises applying the first transparent electrode to the first transparent substrate and applying the second transparent electrode to the second transparent substrate. Also, preferably, the light absorbing and transferring means comprises a dye substance, e.g., a monomolecular chromophore dye applied to the semiconductor layer. In yet another embodiment, the electrolyte layer has predetermined thickness to provide high lateral ionic conductivity.

Brief Description of the Drawings

20 The accompanying drawings, which are incorporated in and form a part of the specification, illustrate the preferred embodiments of the present invention, and together with the description serve to explain the principles of the invention.

Figure 1 illustrates a perspective view of a window incorporating the photoelectrochemical-electrochromic device of the present invention.

Figure 2 illustrates a diagrammatic cross sectional view of the photoelectrochemical-electrochromic device which constitutes the present invention;

5 Figure 3 illustrates a perspective view of a window incorporating the present invention wherein the electrolyte layer of the photoelectrochemical-electrochromic device comprises a thickness which provides low lateral conductivity

Figure 4 illustrates the transmission of light through the photoelectrochemical-electrochromic device of the present invention versus time.

10 The graph illustrated in Figure 4 is derived from the experimentations by the inventors of the present invention during the invention and reduction to practice of the present invention. The electrodes, electrochromic material, semiconductor coating, dye substance and electrolyte layer illustrated are representative of the types of materials available for use. Other materials, including the materials set forth
15 below, are within the scope of the present invention.

Figure 5 illustrates a graph of the relative transmittance of light through the photoelectrochemical-electrochromic device of the present invention.

Detailed Description of the Preferred Embodiments

20 The present invention is a photoelectrochemical-electrochromic light modulating assembly, indicated generally at 10, providing a self-powered electrochromic device which automatically or selectively modulates the transmittance of incoming light through a window without the need for an external power source. Basically, as will be described further below, the modulating assembly 10 of the
25 present invention combines an electrochromic coating with a semiconductor/electrolyte-type device providing the self-powered modulating assembly 10 of the present invention which reduces the actual number of layers typically needed for operation of an electrochromic coating compared to the prior art.

As illustrated in Figures 1 and 2, as an initial overview, in the present invention, the modulating assembly 10 comprises a first and second transparent electrode 12, 14. The first transparent electrode 12 is coated with an electrochromic material 16 and the second transparent electrode 14 is coated with a semiconductor coating 18 having an optional monomolecular layer of dye substance 20 applied thereon. The first and second transparent electrodes 12, 14 are spaced apart, joined together, and electrically connected. Then, an electrolyte 22, such as lithium iodide (LiI) propylene carbonate, is inserted between the first and second transparent electrodes 12, 14. As illustrated in Figure 4, when the modulating assembly 10 is exposed to white light source (approximately equal to one sun) (not shown), the transmittance of the light through the modulating assembly 10 is decreased within one minute by more than 70%. Each component of the modulating assembly 10 of the present invention will now be described in further detail.

Referring to Figure 2, preferably, the modulating assembly 10 further comprises a window 24 having a first glass plate 26 and a second glass plate 28, each having peripheral edges 40. The first glass plate 26 has an inner and an outer surface 30, 32 and the second glass plate 28 has an inner and outer surface 34, 36. The first and second plates 26, 28 are placed in a substantially parallel and spaced-apart relation to one another, separated by at least one spacer 38 and sealed around the peripheral edges 40 of the first and second plates 26, 28 to form a cavity 42 between the first and second plates 26, 28. While the modulating assembly 10 of the present invention will be described as having two plates, a first and a second plate, 26, 28, it is within the scope of the present invention to have additional plates, as needed. Furthermore, in the present invention, while the first and second plates 26, 28 preferably comprise glass, any other transparent electrically insulating material including, but not limited to, plastic is within the scope of the present invention.

In the present invention, as illustrated in Figure 2, the first transparent electrode 12 is deposited on the inner surface 30 of the first plate 26 and the second transparent electrode 14 is deposited on the inner surface 34 of the second plate 28 by known means including, but not limited to, physical vapor deposition, sputtering,

chemical vapor deposition, i.e., heat stimulated or radio frequency discharge or the like. The first and second transparent electrodes 12, 14 preferably comprise highly doped metal oxides such as $\text{SnO}_2:\text{F}$, $\text{SnO}_2:\text{Sb}$, $\text{In}_2\text{O}_3:\text{Sn}$ (ITO), Cd_2SnO_4 , $\text{ZnO}:\text{Al}$ and $\text{ZnO}:\text{In}$. Particularly suitable metal oxide semiconductors are oxides of the transition metals, and of elements of the third main group and of the fourth, fifth and sixth secondary groups (of the periodic system of elements) of titanium, zirconium, hafnium, strontium, zinc, indium, yttrium, lanthanum, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, or alternatively oxides of zinc, iron, nickel or silver, perovskites such as SrTiO_3 , CaTiO_3 or oxides of other metals of the second and third main groups or mixed oxides or oxide mixtures of these metals. Alternatively, any other conductive metal oxides or metal sulfides with semiconductor properties and a large energy gap (band gap) between the valence band and the conduction band can be used.

It is important that the first and second transparent electrodes 12, 14 be effectively transparent to the light so that the light can reach the semiconductor coating with the optional adsorbed dye 20 for conversion to electrical energy. Furthermore, preferably, the first and second transparent electrodes 12, 14 are each between approximately 1000 to approximately 5000 angstroms thick.

As illustrated in Figure 2, the electrochromic material 16 is deposited on the first transparent electrode 12 similar to the deposition of the first transparent electrode 12 on the first glass plate 26. In general, an electrochromic material is one that takes on and loses color, i.e., becomes opaque or transparent, in response to an electric field or current there through in the presence of an ion source adjacent to the electrochromic material, as will be discussed further below. The electrochromic material 16 can be anodic or cathodic in nature and can occur in two phases, liquids and solids. The electrochromic material 16 colors in a reduced state which can be induced by a DC electric current and includes, but is not limited to, WO_3 , IrO_x , NiO , V_2O_5 , MoO_3 , TiO_2 , U_2O_5 , Bi_2O_3 , PbO_2 , and CuO_x . The electrochromic material 16 of the present invention is preferably between approximately 1,000 to approximately 15,000 angstroms thick.

As stated above and as illustrated in Figure 2, the second transparent electrode 14 is coated with a semiconductor coating 18, preferably a porous specimen of TiO_2 , with the oxidizable sensitizer or chromophore (dye) 20, for example RuL_3^{4+} , applied to the semiconductor coating. The dye substance 20 is not required for operation of the device 10 if the semiconductor coating 18 absorbs sufficient light (operation of the device 10 of the present invention will be described further below). Also, preferably, nanoporous TiO_2 films prepared by either method 1 or by method 2 as described in Nazeeruddin et al (*J. Am Chem. Soc.*, 1993, 115, 6382) can be used in the present invention. Both methods produce satisfactory semiconductor films but method 1 produces films having better transparency.

In the case of the porous specimen of TiO_2 semiconductor coating 18, if the dye substance 20 is applied, the dye substance 20 actually enters the pores of the semiconductor coating 18 to thereby coat the pore surfaces with dye. It should be noted that different dye substances 20 have different spectral sensitivities. The dye substance 20 can thus be adapted to absorb light in a desired spectral region while transmitting light in other spectral regions. Examples of suitable dye substances 20, i.e., sensitizers, are complexes of transition metals of the type selected from the group consisting of ML_3 and ML_2X_2 wherein M is selected from the group consisting of Fe, Ru, Os, Cr, Mo and Mn, L comprises bipyridine-type ligand selected from the group consisting of 2,2'-bipyridine-4,4'-dicarboxylic acid and 4,4'-dimethyl-2,2'-bipyridine, and X comprises a monodentate ligand selected from the group consisting of CN, SCN, Cl, Br, I and H_2O ; porphyrins comprising zinc tetra(4-carboxyphenyl) porphyrin; phthalocyanines comprising 4,4',4'',4'''-tetraazaphthalocyanine; and perylenes comprising 3,4,9,10-perylene tetracarboxylic acid. The dye substance 20 can be chemisorbed, adsorbed or otherwise applied to the semiconductor 18 of the modulating assembly 10 of the present invention. It should be noted that the elements listed above for M, L, and X are merely representative of the types of elements available for use with the device of the present invention. Other elements are within the scope of the present invention.

The actual deposition of the electrochromic material 16 and the semiconductor coating 18 can be accomplished by evaporation techniques. Furthermore, the electrochromic material 16 and the semiconductor coating 18 can be deposited on the first and second transparent electrodes 12, 14, respectively, by dip coating, spray coating, spin coating, roll coating, or electroplating. The advantages of utilizing one of the above methods for application rather than by conventional vacuum techniques is the reduced cost factor in equipment and size when dealing with large sheets of material which are found, for example, in large windows for buildings and other uses.

Next, as illustrated in Figure 2, thin strips 13 of SURLYN brand adhesive strips are placed around the periphery of the first transparent electrode 12. The second transparent electrode 14 is then positioned and pressed against the thin strips 13 thereby forming a cavity 42 between the first and second transparent electrodes 12, 14. The lithium iodide (LiI) containing electrolyte 22 is then inserted between the first and second transparent electrodes 12, 14, e.g., through small holes (not shown) formed in the first plate 26 and/or the second plate 28, such that the electrolyte 22 contacts the electrochromic material 16 and the semiconductor coating 18. Upon filling of the cavity 42, the small holes are then sealed with an epoxy or medium (not shown).

The electrolyte 22 is designed to store ions and shuttle the ions back and forth into the electrochromic material 16 with applied potential. The first transparent electrode 12 operates as an electron delivery system to transfer electrons into the electrochromic material 16 upon application of the potential produced upon light exposure. Therefore, to operate properly, the electrochromic material 16 requires the ion delivery and storage electrolyte 22 to be contacting the electrochromic material 16. The electrolyte can be either liquid or solid. Solid thin-film electrolytes are made of fast-ion conductor materials in which lithium, sodium or hydrogen ions diffuse readily. In the preferred embodiment, the electrolyte 22 includes Li, which will be described further below. Examples of other materials which are within the scope of the present invention include Li_3N , Li_2NH , and $\text{Li}_{1-x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$, where M

represents another metal, such as aluminum, chromium, gallium, or the like. A solid thin-film electrolyte may be, for example, 500 to 10,000 angstroms thick.

In order to darken the entire electrochromic material 16 of the modulating assembly 10 when light strikes any portion of the electrolyte 22 therein, the thickness of the electrolyte 22 must exceed a certain predetermined thickness to provide a high lateral ionic conductivity to darken the entire immediately adjacent electrochromic material 16. If the thickness of the electrolyte 22 is less than the predetermined thickness, then only those portions of the electrolyte 22 which have light applied thereto will actually darken the immediately adjacent electrochromic material 16. As illustrated in Figure 3, a thinner electrolyte layer 22 allows the modulating assembly 10 of the present invention to be used for storing images by writing on the modulating assembly 10 with a laser or other light generating device (not shown). Furthermore, a thinner electrolyte layer 22 provides the modulating assembly 10 to be utilized as an imaging storage device. Images 23 can be applied to the modulating assembly 10 by an imaging projection device or similar equipment (not shown), stored thereon and then erased when desired. With the use of LiI as the electrolyte 22 in the modulating assembly 10 of the present invention, the thickness must be greater than approximately 0.5 mm to cause high lateral ionic conductivity.

As illustrated in Figure 2, a first lead 44 and a second lead 46 are connected to a first terminal 48 and a second terminal 50, respectively, on the first transparent electrode 12 and the second transparent electrode 14, respectively, to provide the electrical circuit across the modulating assembly 10. With the first and second leads 44, 46 connected to the first and second terminals 48, 50, and connected to each other, the electric potential across the electrochromic material 16 upon application of light causes the electrochromic material 16 to convert from essentially transparent to opaque. With the first and second leads 44, 46 disconnected, coloration of the electrochromic material 16 will not occur.

With the electric potential reversed, such as by attaching a battery to the first and second leads 44, 46, or by connecting the leads to each other in the absence of illumination, the electrochromic material will lighten back to its original state.

Furthermore, a variable resistor element can be inserted between the first and second leads 44, 46 in order to change the dynamics of the modulating assembly 10. The variable resistor controls the amount of potential across the first and second leads 44, 46 such that electrochromic material 16 can be made more or less dark or overridden altogether.

In the present invention, light absorption by the semiconductor coating 18 directly, or by the sensitizing dye substance 20, results in electrons appearing in the second electrode 14 and the oxidation of the redox couple in the electrolyte 22 such as iodide to iodine. When the electrode leads 44 and 46 are connected to each other, electrons flow from the second electrode 14 to the first electrode 12 and then into the electrochromic layer 16. Another species in the electrolyte 22, such as lithium, also enters the electrochromic layer 16 causing a decrease in light transmission through the electrochromic layer 16.

In operation, as the sun or other light source shines through the window 24, a chemical reaction takes place in the modulating assembly 10. As the sun contacts the dye substance 20, the dye substance 20 absorbs the photons from the sun and electrons are injected from the dye substance 20 into the semiconductor coating 18. A potential travels through the second transparent electrode 14 and into the first transparent electrode 12 through the first and second leads 44, 46. The first transparent electrode 12 injects electrons into the electrochromic material 16. As the charged dye substance 20 oxidizes the electrolyte 22, the electrolyte 22 injects ions into the electrochromic material 16. Injection of ions and electrons into the electrochromic material 16 causes the electrochromic material 16 to darken. Removal of the sun or use of a battery as discussed above causes a reverse chemical reaction to cause the electrochromic material 16 to lighten.

Examples

In the examples below, all TiO_2 films were prepared on 10 Ω /square tin oxide-coated glass from Libby Owens Ford. The WO_3 films were prepared on 12 Ω /square indium tin oxide-coated glass. For purposes of the examples, a

photoelectrochemical-electrochromic device was constructed according to the teachings of the present application.

Example 1

5 Tris(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) was adsorbed from ethanol solution onto a approximately 4 μm thick nanoporous TiO_2 film by soaking overnight. The dye-sensitized electrode was then rinsed with ethanol and dried in a nitrogen stream. The WO_3 electrode was prepared by thermal evaporation of 500 nm of WO_3 onto In_2O_3 -coated glass. The two electrodes were clamped together
10 separated by a gasket made of TYGON tubing with a hole cut therethrough. A solution of LiI in acetonitrile was injected through the gasket to fill the internal space. Upon illumination with white light from a 75 W Xe arc lamp, the cell generated an open circuit photovoltage of 0.25V. This was not sufficient to color the WO_3 electrode by itself, but decreased the externally applied voltage necessary to color the
15 cell.

Example 2

Bis(4,4'-dicarboxy-2,2'-bipyridine)-bis(thiocyanate)ruthenium(II) was adsorbed onto a TiO_2 film as in *Example 1*. A cell constructed in the same fashion as
20 in *Example 1* gave a photovoltage of 0.5 V. This led to the coloration of the WO_3 electrode at short circuit resulting in a change of transmittance of approximately 40% over 100 seconds. The spontaneous bleaching process upon removal of the light was slower, recovering about 20% of its original transparency in 2.5 minutes. Addition of I_2 solution to the original LiI electrolyte decreased the photovoltage to 0.45V but did
25 not increase the bleaching rate. After about 10 minutes of illumination, the open circuit voltage of the cell was approximately 0 V, consistent with the WO_3 electrode being charged up to a voltage equal and opposite to the dye-sensitized TiO_2 electrode. When the light was blocked, the cell voltage was 0.45 V of the opposite polarity as the original photovoltage, consistent with the discharging of the colored
30 WO_3 electrode.

Example 3

A solid polymer electrolyte was made (similar to that described by Zhang et al, J. Electrochem. Soc. 1994, 141, 2795) by dissolving 2 g poly(methylmethacrylate) (MW = 120,000) in 10 mL ethyl acetate, and then mixing in 10 mL of 0.5 M LiI in propylene carbonate. A few drops of this solution were placed on the TiO₂ film and the WO₃ electrode was pressed on top. The cell was baked at 80°C for four hours. Exposing this cell to white light resulted in a 7% decrease in transmittance over 10 minutes.

Example 4

A solid polymer electrolyte was obtained by combining 430 mg poly(ethylene glycol) monomethylether (MW = 2000) with 47.3 mg LiI. These were heated together above the melting point of the polymer until much of the LiI had dissolved. Then a piece of this polymer was placed onto a heated dye-sensitized TiO₂ electrode prepared as in *Example 2*. When the polymer electrolyte had melted, a WO₃ electrode was pressed tightly on top and the cell was cooled to room temperature. The polymer electrolyte also acted as an adhesive to bond the two electrodes together. Upon illumination with white light, the cell transmittance decreased 23% over eight minutes.

20

Example 5

A cell was constructed as in *Example 2* but using 0.1 M LiI in propylene carbonate containing several drops of 4-*tert*-butylpyridine as the electrolyte. The transmission decreased 66% over 1.5 minutes exposure to white light.

25

Example 6

A nanoporous TiO₂ film without any sensitizing dye was used as the semiconductor electrode in a cell made up as in *Example 5*. This cell developed an open circuit photovoltage of 600 mV when illuminated with white light. The transmission decreased by 35% over 12 minutes. A filter cutting out only the UV

30

light eliminated the photoeffect in this cell consistent with a photoeffect resulting from direct excitation of the TiO_2 .

Example 7

5 A TiO_2 coated electrode was soaked overnight in an ethanol solution containing 138 μM bis(4,4'-dicarboxy-2,2'-bipyridine)(4,4'-dimethyl-2,2'-bipyridine)ruthenium(II) and 25 mM chenodeoxycholic acid. A cell made from this electrode following the procedure of *Example 5* showed a photovoltage of 680 mV upon exposure to white light and a change in transmission of about 70% as shown in
10 Figure 4.

Example 8

 A TiO_2 coated electrode was soaked overnight in an ethanol solution containing 69 μM bis(4,4'-dicarboxy-2,2'-bipyridine)(4,4'-dimethyl-2,2'-
15 bipyridine)ruthenium(II) and 12.5 mM chenodeoxycholic acid. A cell made from this electrode following the procedure of *Example 5* showed a photovoltage of 580 mV upon exposure to white light and a change in transmission of about 30% within 100 seconds. After blocking the white light with a shutter, spontaneous bleaching occurred leading back to the transparent state after about 200 seconds as shown in
20 Figure 5.

Example 9

 A 5 cm x 5 cm dye-sensitized TiO_2 film was prepared by soaking overnight in an ethanol solution containing 8.3 μM bis(4,4'-dicarboxy-2,2'-bipyridine)(4,4'-
25 dimethyl-2,2'-bipyridine)ruthenium(II) and 29 mM chenodeoxycholic acid. The WO_3 electrode was prepared by thermal evaporation of 500 nm of WO_3 onto indium tin oxide-coated glass at a temperature of 50°. The TiO_2 and the WO_3 electrodes were sealed together using SURLYN 1601 strips with a thickness of about 30 microns. The strips were arranged around the edges of one electrode. The other electrode was
30 placed on top of the first and the whole cell was heated to about 100°C to melt the

SURLYN and seal the cell. The cell was then filled with the electrolyte of *Example 5* through small holes drilled through the WO_3 substrates. The fill holes were later sealed with epoxy cement. The open circuit voltage upon exposure to white light was around 880 mV. In the bleached state the white light transmission was about 80%. The transmission upon exposure to white light decreased by about 40%. Shading a part of the TiO during light exposure results in a pattern on the device. The blue coloration is obtained only where the dye-sensitized electrode was directly illuminated, the other parts stayed in the transparent state. The partial coloration can be preserved for more than 24 hours if the cell is stored with open-circuited electrodes.

Example 10

An electrolyte solution was made up containing 0.1 M LiClO_4 and 0.1 M tetrabutylammonium bromide in propylene carbonate with about 1% 4-*tert*-butylpyridine. This was filled into a cell made up as in *Example 9* but using a TYGON gasket instead of SURLYN. This cell developed an open circuit photovoltage of about 230 mV.

END OF EXAMPLES

Spontaneous back reaction, i.e., bleaching, of the electrochromic material 16 occurs when the light source is no longer available to reach the modulating assembly 10. Since only a small current is required to change the light transmission of the modulating assembly 10, an external battery can be also charged during operation and used to speed up the bleaching process.

When the electrochromic material 16 is in the substantially transparent state, radiation from the sun is substantially transmitted through the first and second plates 26, 28 of the window 24 into the interior of the building. Of course, some amount of the radiation is always reflected and some is absorbed by the first and second plates 26, 28, but, with the electrochromic material 16 in the substantially transparent state,

most of the radiation in the near infrared and visible light portions of the spectrum is admitted into the interior of the building. Inside the building, the sun's radiation, of course, provides light and is eventually absorbed by interior walls, floors, furnishings, and the like, where the electromagnetic radiation is converted to heat energy. In
5 certain ambient weather conditions, the sun's radiation is not desired and often has to be dissipated or removed by ventilation, air conditioning, or the like to maintain the interior of the building at temperatures that are comfortable to humans.

The modulating assembly 10 of the present invention is effective in substantially decreasing such undesirable heat gain inside a building from the sun's
10 radiation by a combination of features and without the need for an external power source. The electrochromic material 16 on the inner surface 30 of the first plate 26 of the window 24 changes to a substantially opaque state, thus blocking rather than transmitting the sun's radiation. With most of the sun's radiation blocked in this manner, the sun's radiation does not reach the interior of the building to be absorbed
15 and converted to interior heat.

Of course, as mentioned above, when heat gain in the building is desired, the electrochromic material 16 can be changed back to its substantially transparent state to admit the sun's radiation into the building. The extent of opacity or transparency
20 of the electrochromic material 16 can be varied and set at any desired state between the two limits, so, for example, enough light can be admitted to be able to see through the modulating assembly while minimizing the amount of energy transmitted.

The modulating assembly 10 of the present invention can be used in windows of commercial and institutional buildings, automobile glass, airplane and aerospace applications, sunglasses, and protection of solar concentrators.

25 Therefore, the usefulness of the modulating assembly 10 of the present invention is that the modulating assembly 10 reduces air conditioning costs, glare and UV damage while increasing comfort and thus, productivity of the persons inside the building. Furthermore, the modulating assembly 10 of the present invention is a self-powered system requiring no external electrical wiring. Irradiation sensors are not
30 required. Continuously variable transmission is also available.

The foregoing exemplary descriptions and the illustrative preferred embodiments of the present invention have been explained in the drawings and described in detail, with varying modifications and alternative embodiments being taught. While the invention has been so shown, described and illustrated, it should be understood by those skilled in the art that equivalent changes in form and detail may be made therein without departing from the true spirit and scope of the invention, and that the scope of the present invention is to be limited only to the claims except as precluded by the prior art. Moreover, the invention as disclosed herein, may be suitably practiced in the absence of the specific elements which are disclosed herein.

Claims

1. A photoelectrochemical-electrochromic device, the device comprising:
5 a first transparent electrode and a second transparent electrode in parallel, spaced relation to each other, the first transparent electrode electrically connected to the second transparent electrode;
an electrochromic material applied to the first transparent electrode;
a semiconductor coating applied to the second transparent electrode;
10 an electrolyte layer contacting the electrochromic material and the semiconductor coating, the electrolyte layer having a redox couple whereby upon application of light, the semiconductor absorbs the light and the redox couple oxidizes producing an electric field across the device modulating the effective light transmittance through the device.
2. The device of claim 1 and further comprising a first transparent substrate and a second transparent substrate, the first transparent electrode being applied to the first transparent substrate, the second transparent electrode being applied to the second transparent substrate.
3. The device of claim 1 wherein the first and second transparent substrate comprises a material selected from the group consisting of glass and plastic.
4. The device of claim 1 wherein the electrochromic material comprises a material selected from the group consisting of WO_3 , IrO_x , V_2O_5 , and NiO .
5. The device of claim 1 wherein the semiconductor coating layer comprises a metal oxide or metal sulfide selected from the group consisting of TiO_2 , CdS , ZnS , ZnO , and WO_3 .
6. The device of claim 1 and further comprising a dye substance applied to the semiconductor coating, the dye substance enhancing the absorption of light in a specific spectral range.
7. The device of claim 6 wherein the dye substance comprises transition metal complexes selected from the group consisting of ML_3 and ML_2X_2 , wherein M is

selected from the group consisting of Fe, Ru, Os, Cr, Mo and Mn, wherein L comprises bipyridine-type ligand selected from the group consisting of 2,2'-bipyridine-4,4'-dicarboxylic acid and 4,4'-dimethyl-2,2'-bipyridine, and wherein X comprises monodentate ligand selected from the group consisting of CN, SCN, Cl, Br, I and H₂O.

8. The device of claim 6 wherein the dye substance is selected from the group consisting of porphyrins, perylenes, phthalocyanines and RHODAMINES.

9. The device of claim 1 wherein the electrolyte layer includes Li ions.

10. The device of claim 1 wherein the electrolyte layer has predetermined thickness to provide low lateral ionic conductance whereby images are storable within the device.

11. The device of claim 1 wherein the electrolyte layer is selected from the group consisting of a liquid, a polymer and an ionic solid.

12. A method of modulating the transmittance of light, the method comprising: electrically connecting a first transparent electrode and a second transparent electrode in parallel, spaced relation to each other;

applying an electrochromic material to the first transparent electrode;

applying a semiconductor coating to the second transparent electrode;

positioning an electrolyte layer between the electrochromic material and the semiconductor coating, the electrolyte layer having a redox couple, whereby the first and second electrodes, the electrochromic material, the semiconductor coating, and the electrolyte layer form a photoelectrochemical-electrochromic device; and

exposing the photoelectrochemical-electrochromic device to a light source wherein the semiconductor coating absorbs the light and the redox couple oxidizes producing an electric field across the photo-electrochemical-electrochromic device to vary the effective light transmittance through the photoelectrochemical-electrochromic device.

13. The method of claim 12 and further comprising applying the first transparent electrode to the first transparent substrate and applying the second transparent electrode to the second transparent substrate.

14. The method of claim 12 and further comprising applying a dye substance to the semiconductor coating.
15. The method of claim 14 wherein the dye substance comprises transition metal complexes.
16. The method of claim 12 wherein the electrolyte layer has predetermined thickness to provide high lateral ionic conductance.

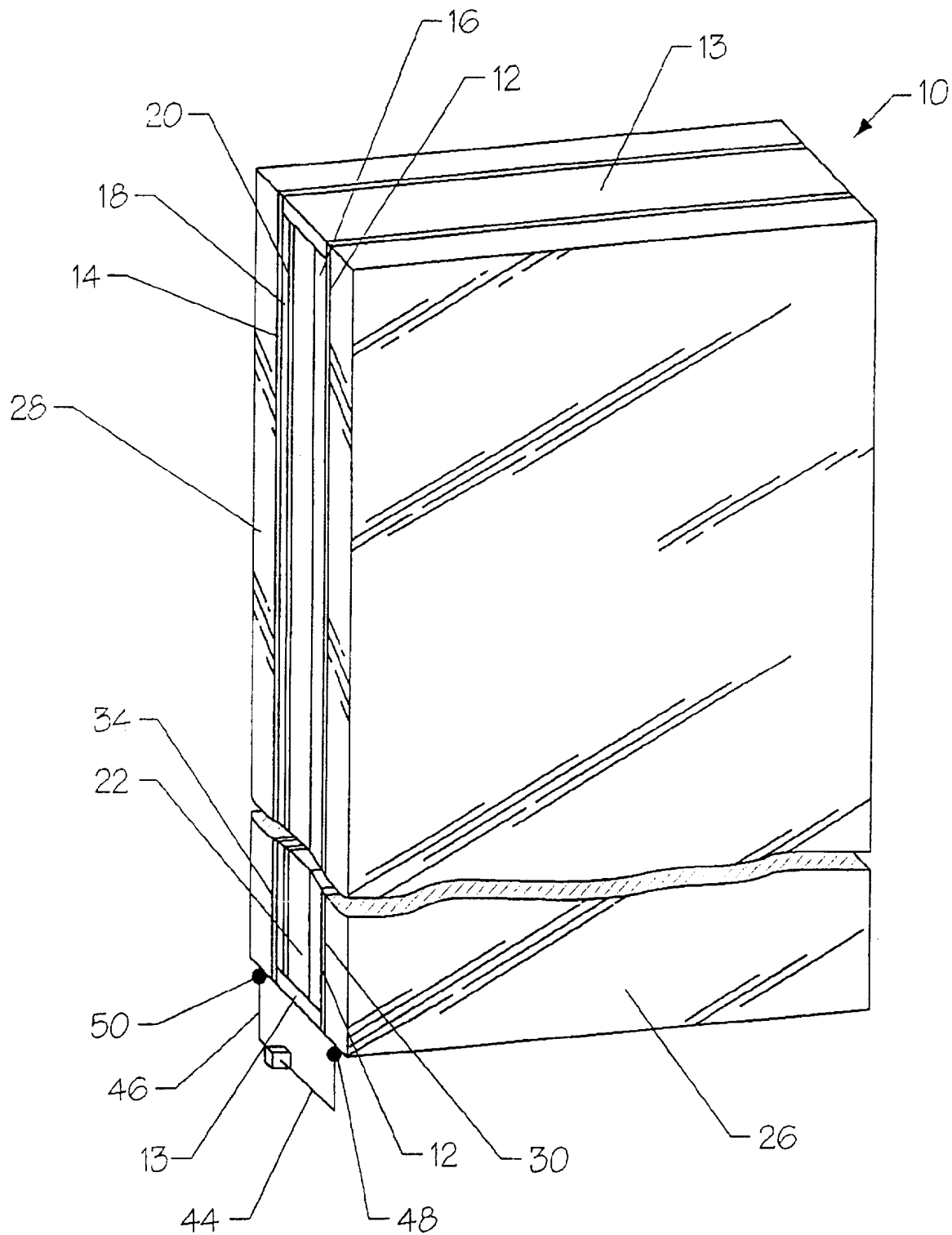


Fig. 1

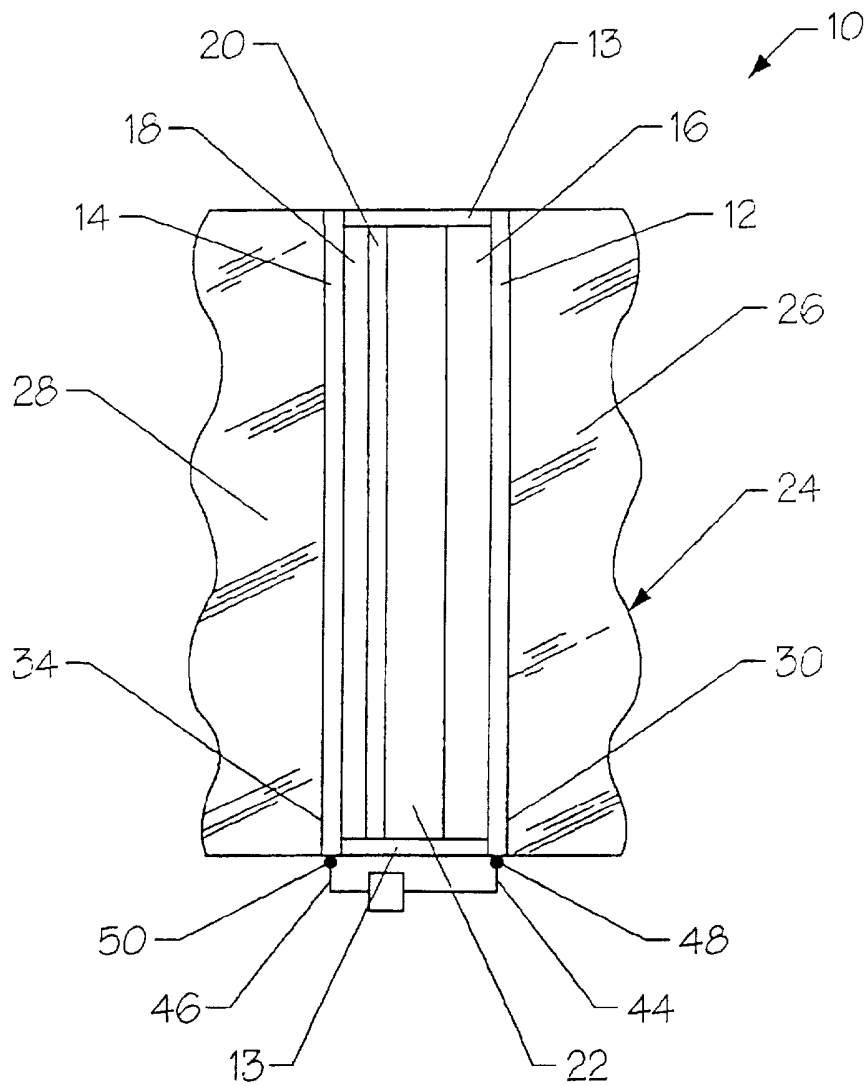


Fig. 2

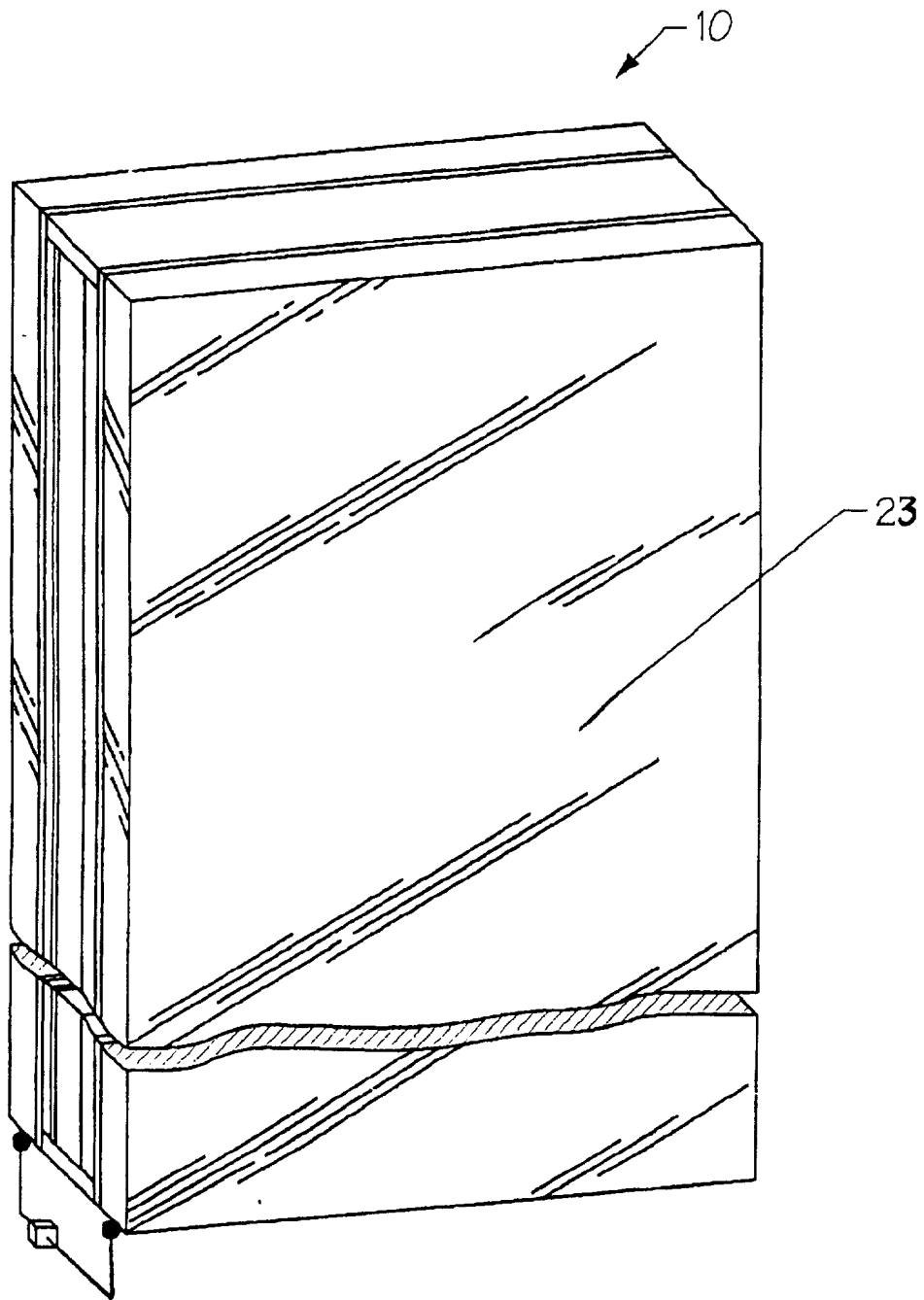


Fig. 3

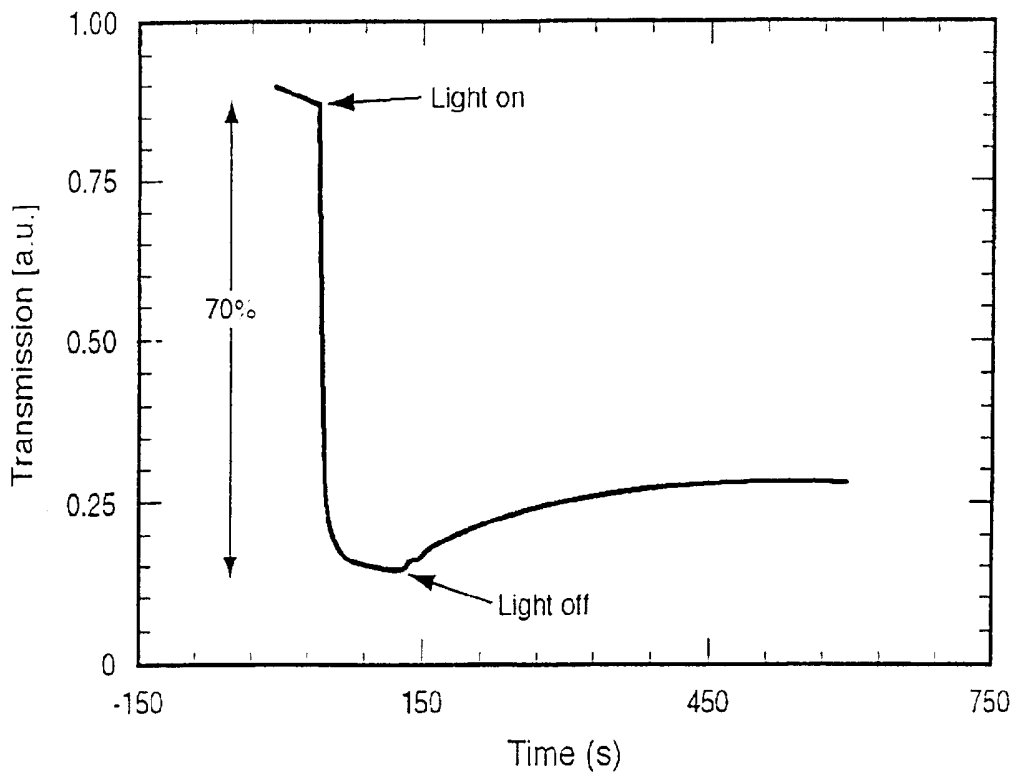


Fig. 4

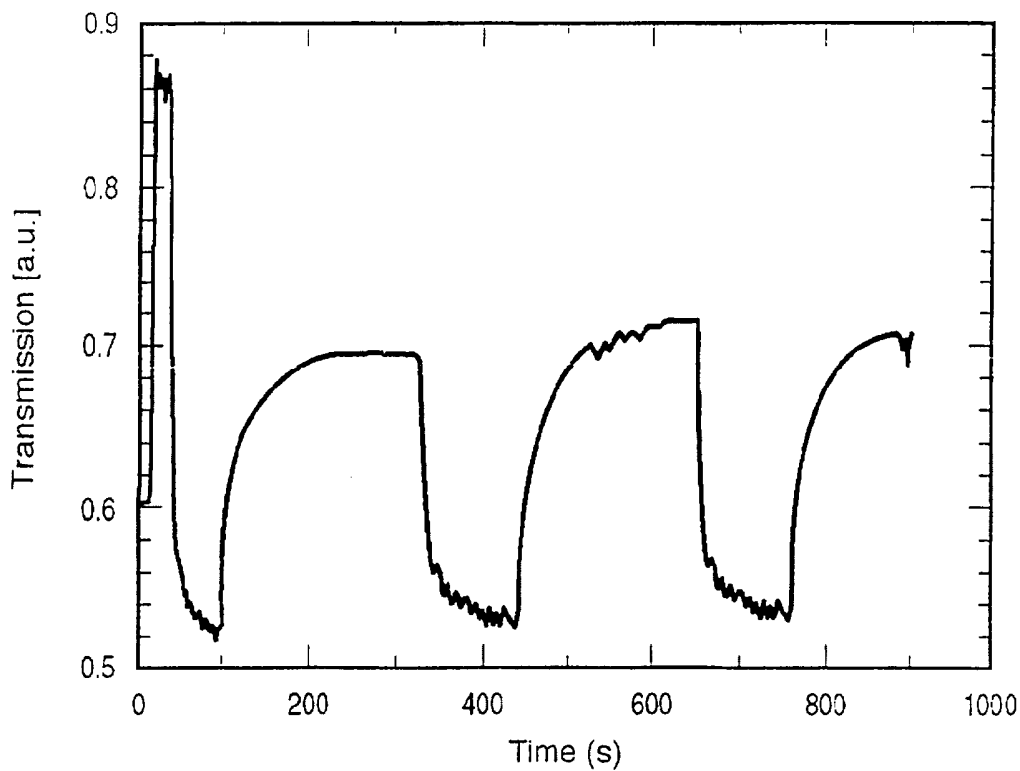


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/08773

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :G02F 1/15.

US CL :204/157.15; 359/265,275; 429/111.

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. : 204/157.15; 359/265,275; 429/111.

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US 5,604,626 A (TEOWEE et al) 18 February 1997, see Fig. 1(A); col. 6, line 9 through col. 10, line 45.	1-16
X	MONK et al, "Electrochromic Display Devices of Tungstic Oxide Containing Vanadium Oxide or Cadmium Sulphide as a Light-Sensitive Layer", Electrochemica Acta, Vol. 38, No. 18, pp. 2759-2764, 1993.	1-5, 9-13 and 16
X	LAMPERT C. A., "Towards large-area photovoltaic nanocells: experiences learned from smart window technology", Solar Energy Materials and Solar Cells 32 (1994) pp. 307-321.	1-16

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 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
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"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

04 SEPTEMBER 1997

Date of mailing of the international search report

17 SEP 1997

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