A chromogenic device with a chromogenic material (102) facing a conductive layer (11-m) in which the transmission of incident radiation through the conductive layer (11-m) and the chromogenic material (10-2) is enhanced. The enhancement is achieved by adjusting indices of refraction of layers (11a/11b) embracing the conductive layer.
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ELECTROCHROMIC DEVICES HAVING REFRACTIVE INDEX-MATCHED STRUCTURE AND METHODS OF OPERATING AND MANUFACTURING

Background of the Invention

This invention relates to electrochromic structures through which energy, including light, can be transmitted under controlled conditions, and more particularly, to large-area electrochromic structures for controlled energy transmission.

A variety of electrochromic materials are available for controlling the through-passage of energy. Such devices operate "chromatically" by producing a change in coloration in accordance with an applied stimulus or excitation.

Thus, a thermochromic device produces a color change in response to temperature. The resultant coloration of, for example, a sheet of material, depends upon the temperature to which the sheet is subjected. There is, however, the objection that a user has only limited control over the coloration since it is temperature dependent.

Another chromogenic device is "photochromic" in that its coloration depends upon the intensity of light that falls upon the device. When glass or other translucent materials are doped with iron oxide, a light-induced reaction produces increased darkening with increased intensity of light. Here again, the degree of coloration is dependent upon external effects.
Still another chromogenic device depends upon the extent to which an electrical stimulus is applied, and is said to be "electrochromic". In such devices the nature and extent of coloration depends upon an electrical effect.

Unfortunately, it has been difficult to produce economical large-scale chromogenic devices with useful optical properties. Thus, small-area devices have been produced for lenses (photochromic) and mirrors (electrochromic). However, it has been difficult to produce panels with large surfaces of the kind needed for vision applications such as windows and skylights.

Accordingly, it is an object of the invention to facilitate the manufacture and use of chromogenic structures. A related object is to facilitate large-scale chromogenic applications in which appreciable surface areas are required.

Still another object of the invention is to adapt chromogenic devices to light transmissive structures such as skylights and other arrangements that are intended to provide large-area control over natural illumination.

A further object of the invention is to facilitate the manufacture and use of electrochromic structures, particularly for relatively large-scale applications. In addition, the entrapment of radiant energy can produce a greenhouse effect. Accordingly, it is another object of the invention to provide electrochromic devices with a
capability for reducing the extent to which sunlight and other forms of radiation produce solar heat gain in buildings and other structures.

Another object of the invention is to adapt electrochromic devices for widespread architectural and automotive applications, as well as aeronautic structures such as cockpits and avionic viewing surfaces.

Studies have been undertaken which relate various parameters of materials, and device configurations (e.g., area), to switching speed. Such studies are reported by J.P. Randine in Proc. SPIE 154, 539 (1989) and Messrs. K-C. Ho, D.E. Singleton and C.B. Greenberg in Proc. Electrochem Soc. 90-2, 349 (1990). It has been predicted that as device area increases, the resistance of its transparent conducting layer is the major factor limiting switching time and uniformity of coloration or bleaching.

Accordingly, it is another object of the invention to counteract the increase in switching time and nonuniformity of coloration and bleaching in electrochromic devices as their areas increase.

One approach has been to add an electrically conducting grid structure in accordance with U.S. Patent 4,768,865 of Greenberg and Singleton issued September 6, 1988. This approach degrades the transmission of light and may be unsuitable where the objective is to attain high percentage transmission. The adverse effect of a grid structure can be
significant, especially if multiple grids, one on top of each transparent conduction layer, are used to obtain the desired switching speed. It also is difficult to form grids on non-planar surfaces.

Accordingly, a further object of the invention is to increase switching speeds for electrochromic structures and eliminate or minimize the use of electrical grids.

Accordingly, yet another object of the invention is to achieve fast switching, while maintaining a high light transmission, and relatively low cost and ease of manufacture.

Summary of the Invention

In accomplishing the foregoing and related objects, the invention provides a relatively large-scale chromogenic device, with planar and non-planar by incorporating an index-adjusted structure to serve as at least one electrode of the device. Such a device can meet switching time and optical transmission requirements for architectural windows and other visual effects. Devices in accordance with the invention are easy to manufacture at low cost.

In accordance with another aspect of the invention, materials and process parameters for the electrodes are selected to adjust refractive indices and thicknesses in a layered index-adjusted structure (LIAS) having desirable electrical conductivity and optical transmission.
In accordance with a further aspect of the invention, materials are selected for an enhanced LIAS, along with materials, parameters and materials for counterelectrodes (CE’s), electrochromic electrodes (ECE’s) and ion conductors (IC’s) which will meet desirable switching speeds and transmission requirements for large-area electrochromic devices.

The invention includes provision for energizing individual electrochromic panels. Each such panel can be laminated to a transparent superstrate by, for example, an adhesive. The adhesive can be selected from a wide variety of substances including ethylene vinylacetate and polyvinyl butyl.

Each panel can be formed of successive layers on a substrate beginning with a transparent conductor, which desirably is a layered index-adjusted structure, which can include the electrochromic electrode. The next layer is an ion conductor, which is followed by a counterelectrode that also is desirably a part of a layered index-adjusted structure formed from transparent metallic and ceramic layers. Separate layered index-adjusted structures can form upper and lower components of the device. Alternatively, a single, or multiple index-adjusted structures can be incorporated into the overall device as desired.
The electrochromic layer changes color when subjected to an electrical effect and faces the ion conducting layer. The counterelectrode is on the opposite face of the ion conducting layer and adjacent the transparent conductive material upon the counterelectrode.

The ion conductor is transparent in the visible range, preferably solid, with high electronic resistivity, and high ionic conduction. Lithium or hydrogen ion conductors are suitable. The lithium ion conductors include lithium silicates, lithium aluminum silicates, lithium borosilicates, lithium borates, lithium zirconium silicates, lithium niobates, and various lithium ion conducting polymer electrolytes. The hydrogen ion conductors are derived from such oxides such as tantalum pentoxide ($\text{Ta}_2\text{O}_5$) and silicon dioxide ($\text{SiO}_2$). The counterelectrode can be nickel oxide, iridium oxide, vanadium pentoxide, molybdenum oxide, or various mixed oxides.

In a method of manufacturing a relatively large-scale non-planar electrochromic device according to the invention, a non-planar substrate is combined with a set of layers, including an ion conducting layer and an electrochromic layer. The layers may be formed upon the substrate by chemical dipping, sputtering, thermal evaporation or thin
film deposition techniques. These procedures can be combined and the resulting structure joined to a superstrate by adhesive lamination.

In a method of operating a relatively large-scale electrochromic device, electrical energy is applied between exterior and interior transparent conductive layers. This causes a migration of ions among a counterelectrode, an ion conductor and an electrically responsive coloration layer. Exterior energy, such as light, ultraviolet and infrared radiation, is transmitted through a transparent substrate to the interior transparent conductive layer. The voltage controlled coloration determines the extent to which the exterior energy is further transmitted from the interior transparent conductive layer through the electrically responsive coloration layer, the ion conductor, the counterelectrode and out of the exterior transparent conductive layer.

Description of the Drawings

Other aspects of the invention will become apparent after considering several illustrative embodiments, taken in conjunction with the drawings in which:

Fig. 1 is a cross-sectional view of an electrochromic device incorporating the constituent layers of the invention;
Fig. 2 is a cross-sectional view of an alternative electrochromic device incorporating constituent layers of the invention; and

Fig. 3 is a cross-sectional view of a modified electrode in accordance with the invention.

**Detailed Description**

With reference to the drawings a cross-section of a window 10 in accordance with the invention is shown in Fig. 1.

The window 10 is electrochromic in the sense that the transparency of the area exposed to external illumination or radiation is controlled electrically or electronically. For that purpose the occupant of a room or compartment containing the window can operate electrical controls in the manner described in detail below in order to achieve a desired degree of darkness or lightness. It will be appreciated that although the invention is illustrated in terms of a window, it is equally applicable to other areas that admit illumination into the interior of a room or compartment, i.e., vision applications. By virtue of electrical control, the transparency of a window, for example, can be adjusted as desired.
As shown in the cross-sectional view of Fig. 1, the window 10 of Fig. 1 includes constituents 10-1 through 10-3. It will be appreciated that the size of the window is relative, and that very large electrochromic structures can be realized in accordance with the invention.

The constituents 10-1 through 10-3 of Fig. 1 are mounted on a base or substrate 12 and are adhered to the substrate 12 in suitable fashion. A convenient medium (not shown) can be a laminating transparent adhesive such as ethylene vinylacetate or polyvinylbutyral.

Alternatively, the constituents 10-1 through 10-3 may be adhered to the substrate 12 by a dipping technique in which the materials of the various layers are dissolved in an organic solvent and reacted as desired, after which the solvent is evaporated to form a precipitate which is heated to realize the desired layer. In this way successive layers can be formed.

The cross-section of Fig. 1 also illustrates the substituent layers of the constituents 10-1 through 10-3 of the window 10.

The constituent 10-1 includes a transparent oxide 11-a, a contact electrode 11-m and an active electrochromic layer 11-b for the window 10. In effect, the contact electrode 11-m is embraced between the transparent oxide 11-a and the electrochromic layer 11-b. Also included are thin metallic layers 11-1 and 11-2 which sandwich the contact electrode 11-m.
The purpose of the transparent oxide is to admit radiation, while the contact electrode carries electrical charge into and out of the electrochromic device. The transparent oxide is a film of high refractive index. Suitable oxides are doped zinc oxide, tungsten, nickel oxide, cobalt oxide and indium tin oxide. The higher the refractive index of the oxide, the greater the suitability.

Included in the constituent 10-1 is an active electrochromic or colorant layer 11-b, illustratively of tungsten trioxide (Wo). The colorant layer is optically active and permits the reversible flow of both positive ions and negative ions. The layer’s ability to change color and transmit light is a direct function of the number of ions and electrons contained in the layers. While tungsten trioxide is a standard electrochromic layer, other suitable layers include molybdenum trioxide, nickel oxide and iridium oxide, as well as mixed oxides of vanadium, tungsten, titanium and molybdenum.

Adjoining the colorant layer 11-b of the structure 10-1 is a transparent and electrically insulating ion conductor layer 10-2, which isolates the electrochromic layer 11-b of the structure 10-1 from the counter electrode layer 13-a of the structure 10-3, which also includes an underlying oxide layer 13-b.
The ion conducting layer 10-2 allows ions, but not electrons to pass through it and provides the device with "memory". There are many suitable ion conductor electrolytes including, but not limited to, lithium-based ceramics such as lithium silicate, lithium aluminum silicate, lithium niobate, lithium nitride and lithium aluminum fluoride. Suitable hydrogen ion conductors are derived from tantalum pentoxide and silicon dioxide.

The counterelectrode layer 13-a of the structure 10-3 "inserts" and stores ions when they are not employed in the electrochromic layer of the structure 10-2. Some counterelectrode materials are also electrochromic in that they modulate incident radiation, including certain infrared and visible components of solar radiation. Such materials complement the modulation by the electrochromic layer in the structure 10-2. Suitable insertion compounds for the counterelectrode 11-b include vanadium pentoxide, niobium oxide, indium oxide, nickel oxide, cobalt oxide and molybdenum oxide, and mixed oxides.

Prior to completion of the window 10, at least one of the constituents 10-1 and 10-3 is inserted with lithium or hydrogen, unless there is already a source of lithium or hydrogen ions within one of the constituents. The insertion may be accomplished by treating one or more of the constituents 10-1 and 10-3 with a suitable reducing agent. For example n-butyl lithium can be used for lithium
insertion, or aqueous sulfuric acid can be used for hydrogen insertion. Alternatively, the insertion may take place in vacuum processing by sputtering from a target serving as a source of suitable ions, for example, a lithium target that decomposes to produce lithium atoms in the vapor phase. Additionally, a plasma may be used for the insertion, for example, a hydrogen plasma to produce hydrogen insertion. Another technique is vapor deposition using a source of the desired composition. Another technique is electrochemical intercalation into one of the structures, for example, lithium intercalation into either 10-1 or 10-3 constituent.

Another technique for ion insertion is to use a volatile species and ignite a discharge to dissociate the insertion ion from the precursor. Thus an organic lithium compound in the form of a precursor gas is caused to dissociate so that insertable lithium atoms come into contact with the material to be charged. It is desirable to use a species that will not react in the gas flow channel.

When the host material "intercalates" ions, for example lithium ions, the host intercalation compound accepts lithium ions and release them when exposed to an electric field. The lithium atoms exit into the ion conductor. Lithium ions in the ion conductor meet electrons in the outside circuit. When the lithium ion and associated electrons are in an electrochromic insertion compound, e.g. tungsten trioxide, there is a change in optical properties.
Attached to the constituents 10-1 and 10-3 are respective leads 21 and 22 that extend to a control circuit 25 including a battery and a potentiometer for regulating the voltage applied to the window 10 through the leads 21 and 22. It is advantageous for the battery in the control circuit 25 to be rechargeable. In addition, it is desirable for the window 10 to be used in conjunction with solar panels (not shown) by which the battery can be recharged during daylight hours.

When a voltage of low magnitude, typically a direct current voltage, is applied across the outer leads 21 and 22, charge compensating ions, such as lithium atoms stored in the counterelectrode of the constituent 10-3, are oxidized by the electric field between the electrodes of the constituents 10-1 and 10-3, with the result that positively charged ions are drawn by the field through the ion conducting layer 10-2 to the active electrochromic layer of the constituent 10-1.

In the active layer of the constituent 10-1, positively charged ions join with electrons supplied through the outer circuit. This combination in the electrochromic layer brings about a change in optical properties and makes the electrochromic layer light-absorbing. The amount of light absorbed, i.e., degree of shading, is variable and controlled by the ions and electrons injected in accordance with the magnitude and polarity of the applied voltage.
In addition, the device has "memory" so that when voltage is removed, shading remains for extended periods.

It will be appreciated that although the ion conductor layer 10-2 is desirably a lithium based inorganic film, a lithium on hydrogen ion conducting polymer electrolyte may be used in place of a solid inorganic electrolyte.

In order to achieve an advantageous current distribution for the device 10, the embodiment of Fig. 2 includes a modified constituent 33, corresponding to the constituent 10-3 of Fig. 1. The constituent 33 includes a combination of electrode and electrochromic or counterelectrode layers which form a layered electrode 33 by sandwiching a thin film of metal 33-m between thinner films of metal 33-1 and 33-2, such as nickel, iron, tungsten, zirconium or titanium. The resulting metal sandwich is further embraced between oxide films 33-a and 33-b of high refractive index. The metallic film 33-m provides electrical conductivity and reflectivity of incident energy in the near infrared region. A suitable metallic film 33-m is of silver, aluminum or copper.

As noted above, the layers 33-1 and 33-2 are of nickel, iron, tungsten, zirconium or titanium. The further layers 33-a and 33-b may be of doped or undoped zinc oxide, tungsten oxide, indium tin oxide, nickel oxide and cobalt oxide, vanadium oxide, titanium oxide molybdenum oxide, niobium oxide, iron ferro- cyanide, and mixtures thereof.
The remaining layered electrode 31 of Fig. 2 corresponds to the structure 10-1 of Fig. 1. In addition, while the electrochromic layer 11-b of Fig. 1 was included in the component 10-1, and may correspond to the layer 31-b of Fig. 2, it will be appreciated that the layer 31-b may be a counterelectrode, in which case the electrochromic layer of Fig. 2 becomes the layer 33-a.

In an illustrative embodiment of the invention, the metallic films 31-m have a refractive index less than 1.0, namely about 0.2, and the embracing oxide films 31-a and 31-b have similar refractive indices on the order of 2.0.

One possible explanation of the effect of adjusting refractive indices in accordance with the invention is that incident radiation reflected from the metallic film 31-m into the overlying oxide layer 31-a is substantially canceled by an out-of-phase reflection from the underlying oxide layer 31-b.

Similarly, the counterelectrode constituent 10-3 of Fig. 1 is desirably a thin film structure 33, as shown in Fig. 2 with a metallic layer 33-m embraced between oxide layers 33-a and 33-b.

In the fabrication of the device 10 of Fig. 1, one technique is to coat the substrate 12 with successive films that can be deposited, for example, by reactive sputtering from a metal or metal-alloy target using a rotatable
magnetron cathode to sputter deposit the material. Alternative thin film deposition techniques include thermal evaporation, sol-gel, chemical vapor deposition (CVD) and plasma enhanced CVD.

In forming, for example, the layered electrode 31 by magnetron sputtering, the deposition of doped or undoped metal oxide layers 31-b takes place using a metal or alloy target. This is followed by the deposition of a thin layer (less than 50 angstroms) of metal 31-2 to obtain a suitable nucleation surface for the subsequent deposition of an electrically conducting metal 31-m. The latter is deposited as a continuous film of less than 300 angstroms. This is followed by deposition of a protective metallic layer 31-1 to preserve the electrically conducting layer from exposure to oxygen plasma in subsequent oxide deposition. The protective metallic layer can be used for the partial formation of oxide, which is supplemented by the deposition of another doped or undoped oxide layer, for example, the ZnO or TiO$_2$ layer 31-a.

To form the ion conducting layer 10-2, a deposition is made of an amorphous lithium silicate containing elements such as aluminum or titanium to increase ionic conductivity. For example, a substrate with the layers 10-3 or 33 is dipped into a solution formed by mixing alkoxides of silicon and alkoxides and/or salts of lithium, in
alcohol or water. The solution may contain salts or alkoxides of aluminum or titanium. The substrate is then withdrawn from the solution at a controlled rate. After removal of the substrate, a thin film remains which is completed by simultaneous hydrolysis and drying, followed by annealing.

The device is completed with the layers 10-1, or 31, by sputtering upon the ion conducting layer 10-2, with lithium added to the counterelectrode film 31-b by simultaneous or sequential sputtering from a lithium containing target such as lithium carbonate. A thin layer of metal 31-2, such as nickel in which lithium solid has low solubility, is deposited to prevent the lithium in the counterelectrode from diffusing into and reacting with the electrically conducting metallic layer. In the next step, an electrically conducting layer, for example silver, is deposited, followed by deposition of a protective layer of metal 31-1 and the oxide film 31-a.

The electrode contacts 21 and 22 are made by masking and deposition of a low resistance metal such as copper. In addition, a "capping" layer, for example of silicon nitride, is formed by sputtering. In practice, the device 10 is on a substrate that is laminated to a second superstrate of the same size and shape of the substrate, with an edge sealant applied to eliminate contact with air and moisture.
In Figs. 1 and 2 the metallic layers 11-m, 31-m and 33-m are planar, but it is advantageous to provide these conductors with a variable cross-section, as shown in Fig. 3 where the conductor 11-m' (31-m') has minimum thickness t at the center and maximum thickness T at the outer edges. This is to promote uniform current flow through the metallic layers by having the greatest thickness of the layer at the edges where contact is made with external conductors such as the conductors 21 and 22 of Figs. 1 and 2. When the overall structure is cylindrical, the variable cross-section conductor 11-m' of Fig. 3 takes the form of a surface of revolution about the center where the thickness is minimum. In those cases where the overall structure is rectangular in cross-section, the conductor 11-m' simply extends in the depth direction of the structure while maintaining the cross-section shown in Fig. 3. For the particular embodiment of Fig. 3, only the upper surface U of the conductor 11-m' is tapered, with a corresponding taper in the overlying buffer metallic film 11-1'. A countertaper is therefore provided in the overlying oxide layer 11-a'.

The foregoing description is illustrative only. Other modifications and adaptations of the invention will readily occur to those of ordinary skill in the art.
What is claimed:

1. An electrochromic device comprising
   an electrochromic material,
   a metallic conductive layer, and
   and means for enhancing the transmission of radiation
   through said metallic conductive layer and said chromogenic
   material.

2. An electrochromic device as defined in claim 1
   wherein the enhancing means comprises means for adjusting
   the refractive indices of layers embracing said conductive
   layer to enhance transmission of incident radiation.

3. An electrochromic device as defined in claim 1
   further including
   a transparent substrate.

4. An electrochromic device as defined in claim 1
   wherein said metallic conductor is sandwiched between
   thinner metal films and can serve as a lithium barrier.

5. An electrochromic device as defined in claim 1
   wherein said electrochromic material, said conductive layer
   and the enhancing means form a refractive index-matched
   structure which conducts electrons with a high degree of
   light transmission.
6. An electrochromic device as defined in claim 4 wherein the thin metal films are of a different metal than said metallic conductor.

7. An electrochromic device as defined in claim 1 further including an ion conducting layer facing said electrochromic material which changes color during the insertion of charge compensating ions and electrons flowing into said chromogenic material change the refractive index thereof.

8. An electrochromic device as defined in claim 7 further including index-adjusting means facing said ion conducting layer.

9. An electrochromic device as defined in claim 2 laminated to a superstrate by an adhesive.

10. An electrochromic device as defined in claim 9 wherein said adhesive is selected from the class consisting of ethylene vinylacetate and polyvinyl butyral.

11. An electrochromic device as defined in claim 7 comprising a layer of transparent oxide material, a first metallic layer upon said transparent oxide material, a chromatic layer upon said metallic layer containing an
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electrochromic substance which changes color when subjected to an electrical effect, an ion conducting layer upon said chromatic layer, a counterelectrode layer upon said ion conducting layer, a second metallic layer upon said counterelectrode layer and a transparent material upon said second metallic layer.

12. An electrochromic device as defined in claim 11 wherein said ion conductor is selected from the class consisting of lithium silicate, lithium aluminum silicate, lithium borate, lithium zirconium silicate and lithium niobate; said counterelectrode is selected from the class consisting of vanadium pentoxide, molybdenum oxide, nickel oxide and iridium oxide; said transparent material is a transparent oxide selected from the class of metallic oxides.

13. A method of manufacturing an electrochromic device which comprises the steps of:
   (A) providing a substrate; and
   (B) depositing upon said substrate an index-adjusting structure including an electrochromic layer.

14. A method as defined in claim 13 wherein said electrochromic member is combined with an ion conducting layer.
15. A method as defined in claim 14 wherein said ion conducting layer is combined with an index-adjusted structure.

16. A method as defined in claim 15 wherein said electrochromic device is electrically energized by contacts to the index-adjusted structure.

17. A method as defined in claim 16 wherein each index-adjusted structure includes a metallic film embraced between oxide layers and each contact is connected to a respective metallic film.

18. A method of operating an electrochromic device which comprises the steps of

(A) applying electrical energy to metallic layers, each embraced by oxide layers, one of which is an electrochromic electrode facing one of said metallic layers and another of the oxide layers being a counterelectrode facing another of said metallic layers; and

(B) causing a migration of ions between said counterelectrode and said electrochromic electrode.
19. A method as defined in claim 11 wherein the layer of transparent oxide is a conductor and said metallic layer is a barrier to lithium diffusion, including nickel, tungsten, iron and metal-like or electronically conducting layers such as silicon nitride.

20. An electrochromic device as defined in claim 1 wherein said metallic conductive layer has a variable cross-section, including a taper.
### A. CLASSIFICATION OF SUBJECT MATTER
IPC(5) : C02F 1/115, 1/155, 1/01
US CL : 359/265.266.275
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. : 359/273.274
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 practical, search terms used
NONE

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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