

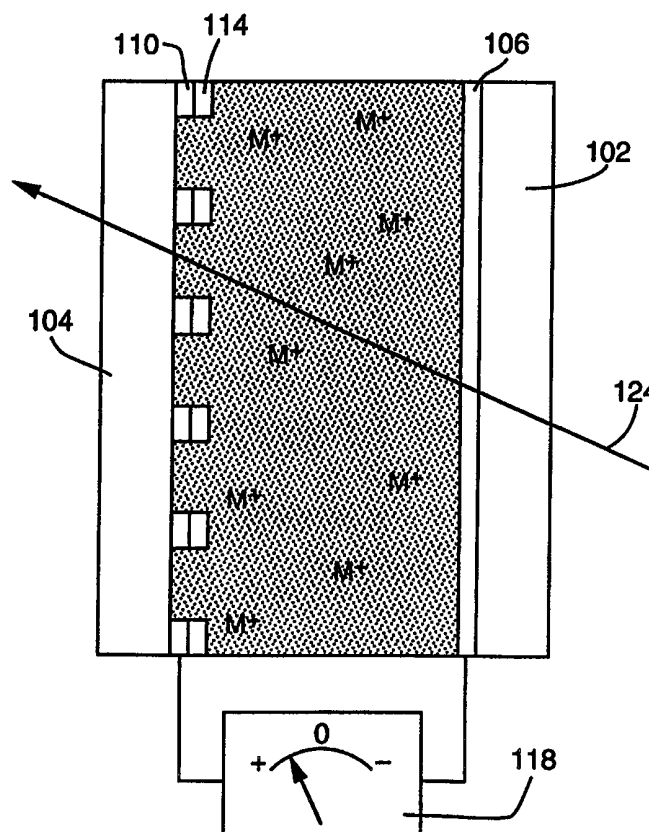


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(54) Title: ELECTRODEPOSITION CELL WITH HIGH LIGHT TRANSMISSION**(57) Abstract**

An electrochemical device includes a transparent first electrode (106) and a second electrode (110) distributed in localized areas. An electrolytic solution (112), disposed between and in electrical contact with the first and second electrodes, contains ions (116) of a metal which can electrodeposit on the first and second electrodes. Atoms of this metal (114) are deposited on the first or the second electrode. A negative electrical potential applied to the first electrode causes deposited metal to be dissolved from the second electrode into the electrolytic solution and to be electrodeposited from the solution onto the first electrode, thereby affecting the propagation of electromagnetic radiation (122) through the device. Conversely, a positive electrical potential applied to the first electrode causes deposited metal to be dissolved from the first electrode and electrodeposited from the solution onto the second electrode, thereby increasing the transmissivity of the device.



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ELECTRODEPOSITION CELL WITH HIGH LIGHT TRANSMISSION

BACKGROUND OF THE INVENTION

This invention is concerned with devices having controllable transmittance.

Sunlight transmitted through windows in buildings and transportation vehicles
5 can generate heat (via the greenhouse effect) that creates an uncomfortable
environment and increases air conditioning requirements and costs. Current
approaches to providing "smart windows" with adjustable transmission for use in
various sunlight conditions involve the use of light absorbing materials. These
approaches are only partially effective, since the window itself is heated and because
10 these devices, such as electrochromic devices, are relatively expensive and exhibit
limited durability and cycle life. Certain liquid crystal-based window systems switch
between transmissive and opaque/scattering states, but these systems require
substantial voltages to maintain the transparent state. There is an important need for
an inexpensive, durable low voltage device with variable transmissivity.

15 In prior art attempts to exploit reversible electrodeposition of a metal for light
modulation, the deposits obtained on transparent substrates presented a rough and
black, gray, or sometimes colored appearance (typical of finely-divided metals) and
exhibited poor reflectivity and high light absorbance, especially when thick. Such
deposits have been investigated for display applications involving reflectance from the
20 background, with white pigments often being added to improve contrast. Warszawski
(U.S. Patent No. 5,056,899), which is concerned with displays, teaches that reversible
metal electrodeposition is most appropriate for display applications, since significant
disadvantages for transmission devices were given (e.g., the possibility of metal
deposition at the counter electrode). Such teachings imply that the application of
25 reversible metal deposition to smart windows must involve light absorption by the
finely divided electrodeposited metal, which would result in heating of the device
itself and thus the space inside. The prior art literature also teaches that, for
transmission-type devices, reversible metal electrodeposition requires the use of an

auxiliary counter electrode reaction; otherwise, metal would plate on the counter electrode as the deposit was de-plated from the working electrode.

Electrolytes described in the prior art literature contain auxiliary redox species (e.g., bromide, iodide, or chloride) that are oxidized (e.g., to bromine, iodine, or chlorine) at the counter electrode during metal deposition, introducing chemistry-related instabilities during long term operation and greatly reducing the memory effect by causing dissolution of the metal deposit on open circuit, e.g., $2\text{Ag}^0 + \text{Br}_2 \rightarrow 2\text{AgBr}$. In most cases, this auxiliary redox process hinders metal deposition at the counter electrode during erasure, introducing a threshold voltage that is desirable for display applications. This auxiliary redox process represents a significant side reaction even when metal plating/deplating occurs at the counter electrode and a threshold voltage is not observed. See, e.g., Warszawski, Columns 3-4 (when copper or nickel were present in the counter electrode paste) and Duchene, et al., Electrolytic Display, IEEE Transactions on Electron Devices, Volume ED-26, Number 8, Pages 1243-1245 (August 1979); French Patent No. 2,504,290 (October 22, 1982). High switching voltages of at least 1 V were used for all the electrodeposition devices which have been found in the patent and literature prior art.

Warszawski teaches that the use of a grid counter electrode would give a less uniform deposit since deposition on the transparent working electrode is highly localized in the vicinity of the counter electrode grid lines (a consequence of the very thin film of gel electrolyte used). Warszawski also teaches the use of an aqueous gel electrolyte to minimize sensitivity to atmospheric contaminants and to avoid the necessity of having a leak tight seal. Such electrolytes, however, have much more limited temperature and voltage operating ranges compared with organic-based electrolytes with high boiling solvents.

Prior art literature teaches that the memory effect is temporary. This is a consequence of the occurrence of a counter electrode reaction other than metal plating/deplating. The energetic oxidation products generated at the counter electrode

can cause dissolution of the metal deposit on the working electrode either chemically on open circuit (slow) or electrochemically during short circuit (fast).

Nishikitani et al. (European Patent No. 0,618,477) teaches that the counter electrode in electrochromic devices for smart window applications can be a metal grid which is substantially transparent. Since no metal electrodeposition occurs in electrochromic devices, however, the grid in this case is used to provide a transparent electrode, not to maintain transparency by localizing metal deposition. In addition, to provide adequate electrical capacity for electrochromic devices, Nishikitani's grid would need a very high surface area (at least $10 \text{ m}^2/\text{g}$ and preferably 50 to $5,000 \text{ m}^2/\text{g}$) and a line width of 50 to $5,000 \text{ }\mu\text{m}$; alternatively, a plurality of dots on a conducting substrate can be used, but the dots must contain fine particles having electrical capacitance of not less than 1 farad/g.

SUMMARY OF THE INVENTION

The electrodeposition device of this invention permits efficient and precise control over the propagation of visible light and other electromagnetic radiation. The device includes a transparent first electrode, with a second electrode distributed in localized areas. An electrolytic solution is disposed between the first and second electrodes such that ions of a metal which can electrodeposit on the electrodes are dissolved in the electrolytic solution. A plurality of atoms of the metal are deposited on either the first or second electrode.

When a negative electrical potential is applied to the first electrode relative to the second electrode, the applied potential tends to cause deposited metal to be dissolved from the second electrode into the electrolytic solution and to be electrodeposited from the solution onto the first electrode, thereby impeding the propagation of the radiation through the device. Conversely, when the polarity is reversed and a positive electrical potential is applied to the first electrode relative to the second electrode, the applied potential tends to cause deposited metal to be dissolved from the first electrode and electrodeposited from the solution onto the second electrode, thereby increasing the transmissivity of the device.

In various embodiments, the second electrode may be made substantially transparent to the radiation and may be distributed so as to block the radiation in a desired pattern, such as, for example, a graphic design. The second electrode may be a continuous electrical conductor, such as an electrochemically stable conductive mesh pattern on a glass substrate, or a discontinuous electrical conductor, such as a dot matrix pattern on a transparent conducting film on glass. An underlayer may be provided between the second electrode and the second substrate to improve adhesion.

The first electrode may be disposed uniformly on a first substrate, or may be disposed in a pattern. The electrolytic solution may include a gelling agent to form an aqueous or a non-aqueous gel electrolyte.

DESCRIPTION OF THE DRAWINGS

5 Figure 1 is a cross sectional view depicting the general design of an electrodeposition device constructed according to the invention.

 Figure 2 is a cross sectional view similar to Figure 1, but illustrating the configuration of the device when sufficient negative electrical potential has been applied to the first electrode relative to the second electrode to cause substantial
10 quantities of the metal to deposit onto the first electrode.

 Figure 3 is a cross sectional view similar to Figures 1 and 2, but depicting the status of the device when sufficient positive electrical potential has been applied to the first electrode relative to the second electrode to cause substantially all of the metal to deposit in distributed regions on the second electrode.

15 Figure 4 is a cross sectional view of a curtailed version of the device.

DESCRIPTION OF THE INVENTION

 Figure 1 is a cross sectional view depicting the general design of an electrochemical device constructed according to our invention (some dimensions, particularly layer thicknesses, are disproportionate in the drawings in order to more
20 effectively illustrate the structure and function of the invention). The device, which allows precise, reversible control over the transmission of electromagnetic radiation,

includes first and second substrates 102 and 104 which are substantially transparent to the radiation to be controlled. An electrically conducting and electrochemically stable film 106, which is also substantially transparent, is deposited on the first substrate. The film 106 functions as a first electrode. A second electrochemically stable
5 electrode 110 is deposited on the second substrate. Unlike the first electrode 106, however, the second electrode 110 is applied in a special configuration. Rather than being deposited in a uniform layer, the second electrode is distributed in localized areas on the second substrate.

An electrolytic solution 112 is located between and in electrical contact with
10 the electrodes 106 and 110. In the configuration depicted by Figure 1, the device is initially charged by depositing a metallic layer 114 on the locally distributed electrode 110, i.e., the layer 114 is deposited on the electrode 110 prior to assembly of the device. As those skilled in the art will appreciate, and as further explained in the discussion below regarding the operation of the device, this metallic layer may be,
15 alternatively, initially deposited on the electrode 110, on the electrode 106, or divided between a partial deposit on the electrode 106 and a partial deposit on the electrode 110. The amount of metal in this initially deposited layer or layers establishes the maximum amount of metal which will be available for deposit, as explained in more detail below, to control the transmittance of the device. Metal ions 116, which contain
20 the same metal atoms as the layer 114, are dissolved within the electrolytic solution 112 such that the metal atoms in solution can be reversibly electrodeposited on and electrodisolved from the first and second electrodes.

The device is intended for use in conjunction with a source of electrical potential 118 which has a reversible polarity and an adjustable potential value. The
25 source 118 is connected between the first and second electrodes 106 and 110. When a negative electrical potential is applied to the first electrode 106 relative to the second electrode 110, metal 114 deposited on the second electrode 110 will tend to be dissolved from the second electrode into the electrolytic solution 112, while metal

ions 116 in the solution will tend to be electrodeposited from the solution onto the first electrode 106.

When the polarity of the applied potential is reversed, such that a positive potential is applied to the first electrode 106 relative to the second electrode 110,
5 deposited metal will tend to be dissolved from the first electrode into the solution 112 and dissolved metal will tend to be electrodeposited from the solution onto the second electrode.

The amount of deposited metal which remains on the first electrode will determine the impediment which the device presents to the radiation. Since the second
10 electrode is distributed in localized areas, metal deposited on the second electrode will not substantially impede the transmission of radiation through the device, much like the scene outside a window can be easily viewed through a window screen made of a grid of wire or fiberglass. The process is reversible and may be maintained at virtually any point between substantially complete deposition on and substantially complete
15 erasure from the first electrode. Thus the device may be adjusted to any transmissive value from approximately 0% to approximately 100%.

Figure 2 is a cross sectional view similar to Figure 1, but illustrating the performance of the device when sufficient negative electrical potential has been applied to the first electrode relative to the second electrode for a sufficient period of
20 time to cause a substantial layer of the metal to deposit onto the first electrode. In this condition, a layer 120, created by the deposited metal, will tend to impede the transmission of radiation, illustrated by the light beam 122, which impinges on the device, either by reflection or by absorption, as explained further below.

Figure 3 is a cross sectional view similar to Figures 1 and 2, but illustrating the
25 behavior of the device when sufficient positive electrical potential has been applied to the first electrode relative to the second electrode for a sufficient period of time to cause substantially all of the metal to dissolve from the first electrode and to deposit as the distributed metallic layer 114 on the second electrode. In this condition, the mirror will impose a minimal impediment to incoming radiation, thereby allowing

substantially all such incoming radiation to be transmitted through the device, as illustrated by the light beam 124.

Figure 4 is a cross sectional view of a "curtained" version of the device which is capable of forming both a reflective mirror layer and a black, absorbing curtain layer. In this embodiment, an electrically conducting transparent film 406a is deposited on a transparent substrate 402a, while another electrically conducting transparent film 406b is deposited on a transparent substrate 402b. Between these components, a substrate 404 has a locally distributed electrode 410a deposited on one side, with a similar locally distributed electrode 410b deposited on the other side. As explained above in connection with the embodiment depicted in Figures 1-3, the device is initially charged with metallic layers 114a and 114b deposited on electrodes 410a and 410b, respectively. Electrolyte solution 412a is positioned between and in electrical contact with the electrodes 406a and 410a, while an electrolyte solution 412b is positioned between and in electrical contact with the electrodes 406b and 410b. Metal ions 416a are dissolved within the solution 412a, while metal ions 416b are dissolved within the solution 412b. The solutions 412a and 412b may be the same or different, but should typically be chosen to optimize the operation of the respective sides of the device, as explained in more detail below. Similarly, the ions 416a and 416b may be identical or different, depending on the structural and operating parameters chosen for each side of the device. A surface modification layer 408 on the electrode 406a facilitates nucleation of electrodeposited metal on the electrode in a substantially uniform mirror layer.

A negative electrical potential applied to the electrode 406a, relative to the electrode 410a, will cause metal ions to deposit in a substantially uniform layer on the surface modification layer 408, forming a mirror surface which will reflect light passing through the device from the right side of Figure 4. A negative electrical potential applied to the electrode 406b, relative to the electrode 410b, will cause metal ions to deposit on the electrode 406b. Because of the design parameters chosen for this electrode, including the absence of a surface modification layer on the electrode

410b, however, the latter deposit will tend to be finely divided and porous, so that it appears black or gray. This deposit will thus tend to block the transmission of light through the device from the left by absorption. This embodiment thus provides the user with the option to employ both absorbing and reflecting layers, each of which
5 may be adjusted for the amount of absorption or reflection, respectively. One use for such a device would be in the sunroof of an automobile. When the device is configured to form a substantially reflecting mirror surface, the mirror surface will tend to reflect both light striking the surface from outside of the vehicle as well as from the interior of the vehicle. Since such a reflective panel might be undesirable on
10 the interior ceiling of the automobile, the curtain layer can be activated so that the sunroof would appear as a darkened non-reflective panel from the interior. The curtained embodiment may also be used where heating is desired, e.g., by means of heat radiated and/or conducted as a result of the light absorbed by the layer.

Fabrication of a Preferred Embodiment

15 The preferred first electrode utilizes a glass or plastic substrate which is uniformly coated on one side with a transparent, high conductivity ($\leq 10 \Omega/\text{square}$) ITO (indium tin oxide) film. An electrical bus connection is formed around the perimeter of the ITO coating with conducting Ag epoxy or a vacuum evaporated metal strip.

20 The preferred second electrode includes an adherent, electrochemically inert metal grid pattern, e.g., Ti/Au or Cr/Au, deposited on a glass or plastic substrate via vacuum deposition. A square, electrically continuous grid pattern with 25 μm wide lines 500 μm apart will provide $\sim 90\%$ light transmission. The grid is electrically connected through a Ag epoxy or evaporated metal bus around the perimeter of the
25 substrate. Prior to cell assembly, the grid is plated with a quantity of metal, an excess being preferable. (Alternatively, the first electrode can be plated in this fashion).

The preferred electrolyte is an optically clear gel electrolyte with the following components:

1. An appropriate solvent with a low freezing point, high boiling point, and high dielectric constant, e.g., propylene carbonate (f.p. -49°C , b.p. 241°C), or γ -butyrolactone (f.p. -43°C , b.p. 202°C). These solvents have large windows of electrochemical potential stability and are used in commercial batteries and electrolytic capacitors.
2. A supporting electrolyte salt, such as a lithium salt with a strongly acidic anion, e.g., perchlorate, hexafluorophosphate, trifluoromethanesulfonate, bistrifluoromethanesulfonimide, etc., to provide conductivity to the electrolyte. Electrolytes of such lithium salts ($\sim 1\text{ M}$) in a propylene carbonate (PC) or γ -butyrolactone (GBL) solvent are highly conductive and are used in advanced batteries and capacitors. Other soluble supporting electrolyte salts, e.g., containing other alkali metal ions or tetraalkylammonium ions, can also be used.
3. An active metal salt or complex which is soluble ($\sim 0.1 - 1\text{ M}$), and thermally/photolytically stable in the above lithium salt electrolyte, to enable the reversible plating of the metal layer onto the first and second electrodes. This salt can be based on various metal ions, e.g., silver(I), copper(I), bismuth(III), or other metal systems. Examples include silver perchlorate and silver trifluoromethanesulfonate.
4. An additive to complex the metal ions, which may be required by some systems to stabilize them with respect to thermal or photolytic decomposition to the elemental metals and increase the voltage required for electrodeposition (thus improving the plating quality). For example, Ag(I) and Cu(I) can be stabilized by nitriles, amines, phosphines, sulfur donors, etc., e.g. $[\text{Cu}(\text{nitrile})_4]\text{CF}_3\text{SO}_3$. Additives may also be desirable for preventing dendrite growth, which can lead to electrical shorting.
5. An electrochemically inert polymer stiffener, e.g., polymethylmethacrylate (PMMA) or polyacrylonitrile (PAN), which dissolves in the liquid electrolyte to form a transparent plastic-like gel at room temperature. With an appropriate

amount of stiffener, the resulting gel electrolyte can retain the conductivity of the liquid electrolyte, yet be cut and applied as a "solid state" component. A typical gel electrolyte composition which is free-standing at room temperature contains about 6% (by weight) lithium salt ($\sim 0.5 - 1\text{M}$), 4% silver salt ($\sim 0.1 - 0.5\text{ M}$), 20% PMMA, and 70% solvent (e.g., PC + benzonitrile stabilizer). This composition may be cast onto a glass sheet (at elevated temperature or with excess volatile solvent), allowed to cool or evaporate to the desired level, peeled off of the glass, and then sandwiched between the two electrodes.

The electrochemical device of this invention can be fabricated using a liquid (without the polymer stiffener) or a gel electrolyte, with the latter being preferred. In both cases, the two electrodes may be separated by a gasket or O-ring of appropriate chemical compatibility (e.g., silicone rubber). The preferred electrode separation is about $0.5 - 3.0\text{ mm}$ and contains either the liquid or gelled electrolyte. Electrical contact is made to the metal/silver epoxy bus on each electrode and connected to a voltage source for switching.

Examples

1. An electrolyte was prepared containing 1.35 g silver perchlorate ($\sim 0.2\text{ M}$), 1.91 g lithium perchlorate ($\sim 0.6\text{ M}$), and 7.62 g PMMA in 7.5 ml BN and 22.5 ml PC. The first electrode was a 7.6 cm diameter glass disk with a $10\ \Omega/\text{square}$ ITO coating and a $15\ \text{\AA}$ titanium/ $40\ \text{\AA}$ gold flash. (The titanium underlayer enhanced the adhesion of the gold to the ITO). The second electrode was fashioned from a glass substrate with a fine evaporated Ti/Au $\sim 1,000\ \text{\AA}$ square grid pattern with $25\ \mu\text{m}$ thick lines separated by $500\ \mu\text{m}$ spacings; 5 coulombs ($\sim 5.6\text{ mg}$) of silver were electroplated onto the grid. Electrical contacts were made to both electrodes via peripheral strips of silver epoxy which were located outside of and not in contact with the electrolyte. Cell fabrication was carried out by sandwiching the electrolyte (which flowed slowly at 100°C) between the electrodes, using a 2.4 mm thick silicone rubber O-ring spacer/seal, and clamping the assembly together

in a circular frame; excess electrolyte was rinsed away with acetone. The cell was switched at ± 0.3 V between transparency and a mirror.

2. An example of a system which forms a mirror deposit using an ITO first electrode without a nucleating layer is based on a silver cyanide electrolyte composition: 15 g/L AgNO_3 , 23.5 g KCN, 15 g K_2CO_3 , in 400 ml of water. A mirror deposit forms on the ITO second electrode when biased at -0.6V versus $\text{Ag}/\text{Ag}(\text{CN})_2^-$. The silver erases upon biasing at +0.6V.
3. If a mirror deposit is not required, one could construct a device employing a locally distributed electrode and an electrolyte, without a nucleating layer. Such a device can be designed to yield a finely divided, black or gray deposit. The aqueous bismuth electrolyte reported by Howard and Ziegler (Solar Energy Materials and Solar Cells, Volume 39, Pages 309-316 (1995)), for example, provides such a deposit which will tend to absorb rather than reflect light propagating through the device.

Features of the Invention

It may be desirable for some applications to use a second electrode with an inert metal pattern which is not electrically continuous. Since the overvoltage for metal deposition on conducting oxides like ITO is much greater than on a metal, inert metal islands distributed on a conducting oxide film, which lowers the sheet resistance, will behave like localized isolated electrodes with respect to the metal deposition. In this embodiment of the invention, current is conducted through the conducting substrate film (e.g., ITO) to the metallic islands without causing metal electrodeposition elsewhere. The voltage is chosen so that the metal electrodeposits only on the isolated metal sites, although current to the sites is carried by the underlying conducting oxide film. A second electrode pattern could thus be chosen to be less perceptible to the eye, e.g., a fine dot matrix. Conversely, a pattern could be selected to be intentionally visible for aesthetic effects, e.g., an array patterned to represent an image.

The second electrode, which can be in the form of a fine inert metal mesh, like a window screen, enables most of the light to be transmitted. Such a fine grid, which localizes the metal deposit for maximum light transmission, permits the use of the same reversible electrochemical reaction (metal electrodeposition/dissolution) at both electrodes, greatly simplifying the overall system, eliminating the need for a cell separator, and avoiding high voltages. Thus, the system involves a net reversible transfer of the same metal from a plated layer at one electrode to a distributed localized state at the other, with no net chemical change in the overall system. Very little voltage is required for switching and it is not necessary to maintain an applied voltage to preserve a given switched state. This is attained by excluding redox species other than the metal ions to be deposited from the electrolyte and by limiting the operating voltage so that solvent/counterion breakdown is thermodynamically not possible. A fine grid counter electrode localizes the second electrode deposit for maximum light transmission.

No highly energetic species are produced at the electrodes. As a result, a particular switched state is maintained indefinitely at open circuit.

The device of this invention requires neither a high electrode surface area nor high electrical capacity, so that metal traces (having high electrical conductivity) can be used and much greater window transparency can be attained via finer line widths, greater spacing, or smaller dot diameters.

High light transmission through the second electrode is attained via a fine electrochemically stable metal mesh pattern (deposited on glass or plastic) to localize the metal deposit.

The electrochemical device is operated well within the electrolyte stability region, so that excessive metal plating or deplating is not harmful. In fact, the device is self-limiting for both electrodes when biased within the voltage stability region, since the current will practically cease when the deposited metal is depleted at either electrode. By limiting the amount of metal deposited on the second electrode prior to

cell assembly, overplating of the first electrode under a protracted applied voltage is precluded.

No cell separator is needed since the same redox couple (metal deposition/dissolution) involving a solid product is used at both electrodes and side
5 reactions are avoided.

A wide temperature operating range is obtained by using electrolytes based on high boiling organic solvents, e.g., propylene carbonate, sulfolane, γ -butyrolactone, tetraglyme, etc.). Use of mixtures of these solvents can extend the temperature range to lower operating temperatures.

10 Use of a "solid state" gel electrolyte which incorporates an electrochemically inert polymer stiffener facilitates device fabrication and minimizes sensitivity to atmospheric contamination by preventing convectional transport (diffusion is a very slow process) as well as cell leakage.

The preferred embodiments of this invention have been illustrated and
15 described above. Modifications and additional embodiments, however, will undoubtedly be apparent to those skilled in the art. Furthermore, equivalent elements may be substituted for those illustrated and described herein, parts or connections might be reversed or otherwise interchanged, and certain features of the invention may be utilized independently of other features. Consequently, the exemplary
20 embodiments should be considered illustrative, rather than inclusive, while the appended claims are more indicative of the full scope of the invention.

CLAIMS:

- 1 1. An electrochemical device for reversibly controlling the propagation of
2 electromagnetic radiation, comprising:
3 a first electrode (106) which is substantially transparent to the radiation;
4 a second electrode (110) which is distributed in localized areas;
5 an electrolytic solution (112) disposed between and in electrical contact with
6 the first and second electrodes;
7 a plurality of ions (116) of a metal capable of electrodeposition on the first and
8 second electrodes, the ions being soluble in the electrolytic solution; and
9 a plurality of atoms of said metal (114) deposited on either the first or the
10 second electrode,
11 such that a negative electrical potential (118) applied to the first electrode
12 relative to the second electrode tends to cause deposited metal to be dissolved from
13 the second electrode into the solution and to be electrodeposited from the solution
14 onto the first electrode, and
15 such that a positive electrical potential (118) applied to the first electrode
16 relative to the second electrode tends to cause deposited metal to be dissolved from
17 the first electrode and electrodeposited from the solution onto the second electrode,
18 the amount of deposited metal subsisting on the first electrode affecting the
19 propagation of the radiation (122) through the device.
- 1 2. The device of Claim 1, wherein the second electrode is substantially
2 transparent to the radiation.
- 1 3. The device of Claim 1, wherein the second electrode is distributed so as to
2 block the radiation in a desired pattern.
- 1 4. The device of Claim 1, further comprising:

2 a first substrate (102) which is substantially transparent to the radiation, the
3 first electrode being disposed on the first substrate; and

4 a second substrate (104) which is substantially transparent to the radiation, the
5 second electrode being distributed in localized areas on the second substrate.

1 5. The device of Claim 4, wherein
2 the second substrate is an electrically insulating substrate and
3 wherein the second electrode is a continuous electrical conductor.

1 6. The device of Claim 5, wherein the second electrode is arranged in a
2 conductive mesh pattern.

1 7. The device of Claim 4, wherein the second substrate is an electrically
2 conducting substrate and the second electrode is a discontinuous electrical conductor
3 having a relatively low overvoltage for electrodeposition of the metal relative to the
4 second substrate.

1 8. The device of Claim 7, wherein the second electrode is arranged in a dot
2 matrix pattern.

1 9. The device of Claim 5, wherein the second electrode is an electrically
2 continuous grid of an electrochemically stable metal deposited on the second
3 substrate.

1 10. The device of Claim 4, further comprising an underlayer between the second
2 electrode and the second substrate to improve adhesion between the second electrode
3 and the second substrate.

1 11. The device of Claim 4, wherein the first electrode is disposed uniformly on the
2 first substrate.

1 12. The device of Claim 4, wherein the first electrode is disposed in a pattern on
2 the first substrate.

1 13. The device of Claim 4, wherein the first electrode is an electrically conductive
2 oxide coating deposited on the first substrate.

1 14. The device of Claim 4, wherein the first and second substrates are glass.

1 15. The device of Claim 4, wherein the first and second substrates are a plastic.

1 16. The device of Claim 4, wherein the electrolytic solution comprises a gelling
2 agent to form a gel electrolyte.

1 17. The device of Claim 16, wherein the gel electrolyte includes an
2 electrochemically inert polymer stiffener.

1 18. The device of Claim 4, wherein the electrolytic solution is a solvent selected
2 from the group consisting of benzonitrile, dimethylcarbonate, dimethylsulfoxide,
3 ethylene carbonate, ethylene glycol, γ -butyrolactone, glycerol, propylene carbonate,
4 sulfolane, and tetraglyme.

1 19. The device of Claim 4, wherein the electrolytic solution further comprises a
2 complexing species for chemically stabilizing the electrodepositable metal ion in
3 solution, thereby facilitating the electrodeposition of a substantially uniform layer of
4 the metal on the first electrode.

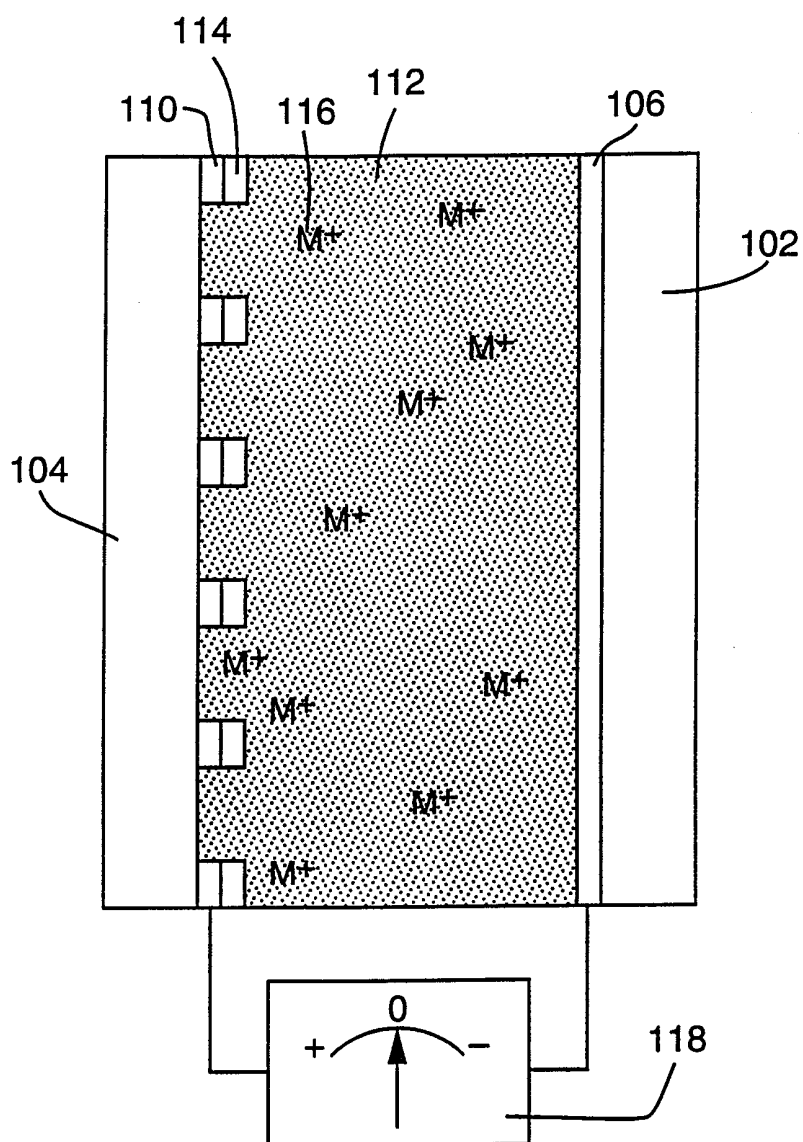


FIGURE 1

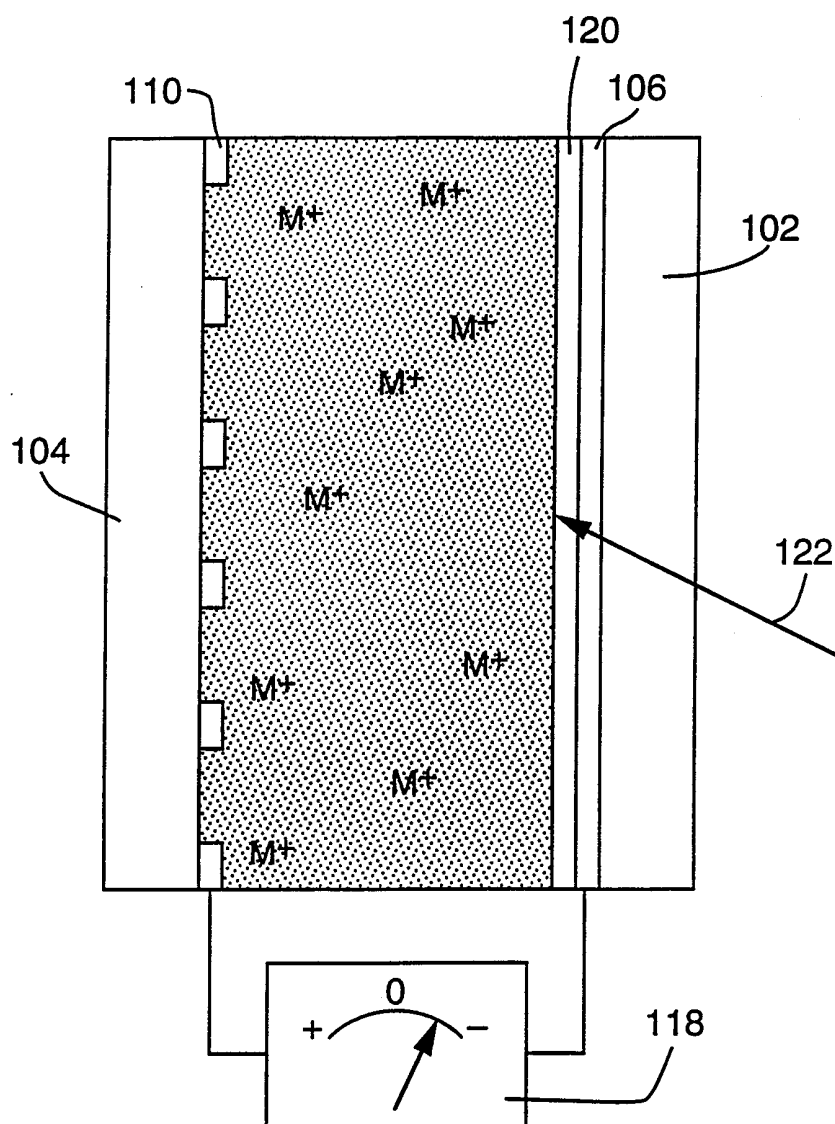


FIGURE 2

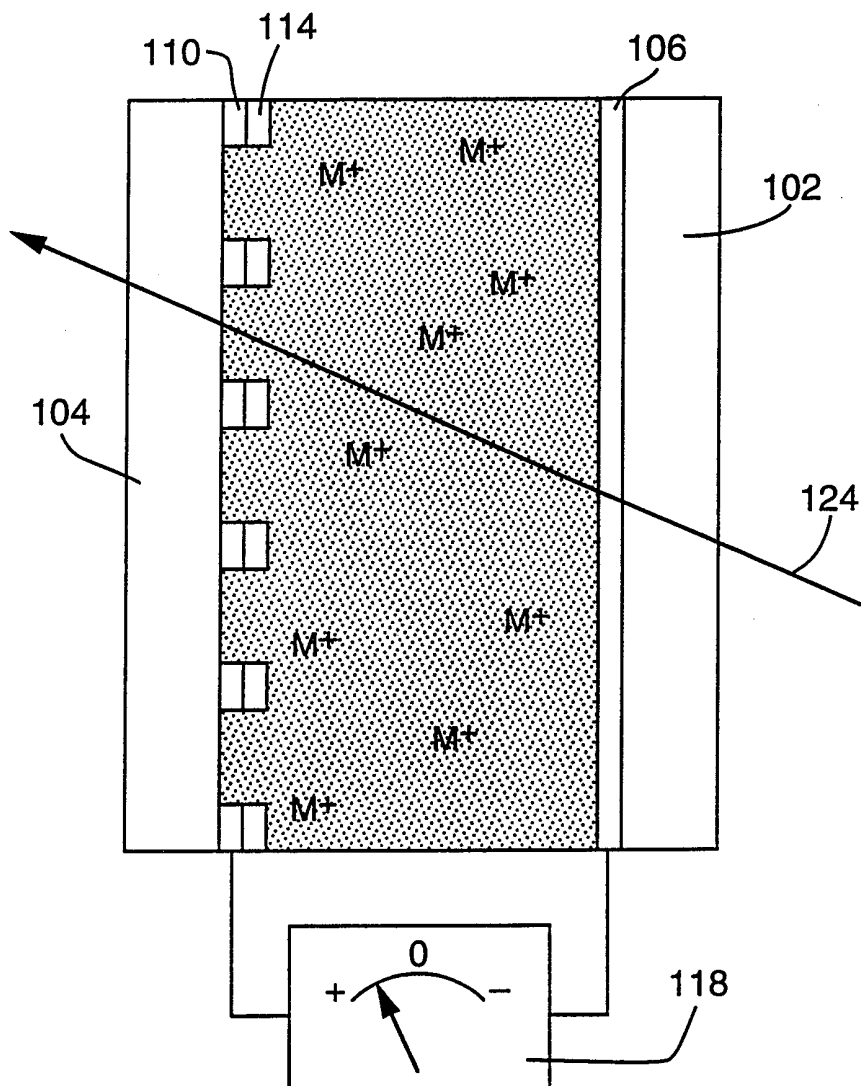


FIGURE 3

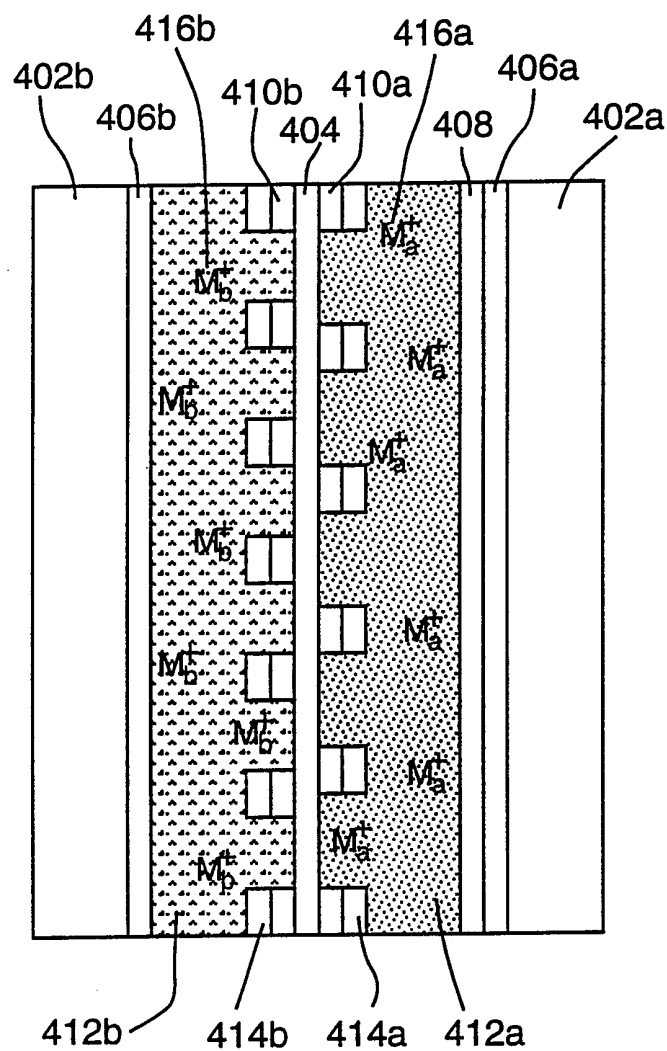


FIGURE 4

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/US98/26610

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : G02F 1/15, 1/155, 1/153

US CL : 359/265-275

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. : 359/265-275

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
noneElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
none

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,768,865 A (GREENBERG ET AL) 06 September 1988 (06/09/88), see entire document.	1-19
A	US 4,902,108 A (BYKER) 20 February 1990 (20/02/90), see entire document.	1-19
A	US 5,161,048 A (RUKAVINA) 03 November 1992 (03/11/92), see entire document.	1-19
A	US 5,210,638 A (EID ET AL) 11 May 1993 (11/05/93), see entire document.	1-19
A	US 5,239,405 A (VARAPRASAD ET AL) 24 August 1993 (24/08/93), see entire document.	1-19
A	US 5,293,546 A (TADROS ET AL) 08 March 1994 (08/03/94), see entire document.	1-19

☒ 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
B 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)	*G* 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

29 JANUARY 1999

Date of mailing of the international search report

22 FEB 1999

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/26610

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	✓ US 5,294,376 A (BYKER) 15 March 1994 (15/03/94), see entire document.	1-19
A	✓ US 5,332,530 A (EID ET AL) 26 July 1994 (26/07/94), see entire document.	1-19
A	✓ US 5,472,643 A (VARAPRASAD ET AL) 05 December 1995 (05/12/95), see entire document.	1-19
A	✓ US 5,671,082 A (BABINEC) 23 September 1997 (23/09/97), see entire document.	1-19
A,P	✓ US 5,760,945 A (COLEMAN) 02 June 1998 (02/06/98), see entire document.	1-19