

SPECIFICATION

Electrochromic Display Device

This invention relates to electrochromic display devices.

- 5 Electrochromic display devices exhibit a phenomenon known as "persistent electrochromism" discussed, for example, in U.S. Patent Specification No. 3 521 941. The term "persistent electrochromism" denotes the
- 10 property of a material whereby its electromagnetic radiation absorption characteristics is altered, in most instances, even at ambient temperature, under the influence of an electric field. Such materials, for example, may
- 15 exhibit little or no absorption of visible wavelength in the absence of an electric field and therefore will be transparent or colourless, but when subjected to an electric field, effectively absorb in the red end of the spectrum, turning
- 20 blue in colour. Similar effects can be observed in other portions of the electromagnetic spectrum, invisible as well as visible.

- There have been numerous studies of the electrochromic process occurring at an
- 25 electrochromic electrode. Various electrochromic display devices, for example, for displaying numerals, have been made but most have defects, for example, slow colouring and bleaching response, short cycle lifetime of colouring and
- 30 bleaching, and problems with the method of driving the electrochromic display device.

- U.S. Patent Application Serial No. 953 596 discloses an electrochromic display device in which electrochromic layers deposited by oblique
- 35 evaporation have fast colouring and bleaching responses. This improvement makes it possible to replace a sulphuric acid (H_2SO_4) electrolyte with lithium perchlorate ($LiClO_4$) and to extend the cycle lifetime but the problems associated with
- 40 the method of driving an electrochromic display device have not been solved, because the colouring and bleaching responses depend upon on the area of the electrochromic layers and the ambient temperature so that the optical density of the coloured electrochromic layers differs. For
- 45 example, in the case of displaying the numeral 1 or the numeral 7, which occupy a relatively small display area, the display turns a deep colour immediately. However, in the case of displaying,
- 50 for example, the numerals 8, 9, 6 which have a relatively large display area, the display does not turn a deep colour immediately. Thus the colour shade of the display differs from numeral to numeral depending upon its display area. Thus it
- 55 is very complicated and difficult to control the driving of an electrochromic display device and to produce a driving circuit therefore as an integrated circuit.

- According to one aspect of the present
- 60 invention there is provided an electrochromic display device comprising: a substrate having an electrode thereon; an electrochromic layer consisting of a plurality of segments disposed on the electrode; an electrolyte disposed in contact

- 65 with the electrochromic layer; and means for applying a DC field between selected segments of the electrochromic layer to cause charge to be transferred therebetween.

- According to another aspect of the invention
- 70 there is provided an electrochromic display device comprising: a substrate having a first electrode thereon; an electrochromic layer consisting of a plurality of segments disposed on the first
- 75 electrode; a second electrode; an electrolyte disposed between the electrochromic layer and the second electrode; and means for applying a DC field between selected segments of the electrochromic layer to cause charge to be transferred therebetween.

- 80 The electrochromic display device may include means for applying a DC field between the first and second electrodes to inject charge into the electrochromic layer.

- Preferably the area of each segment is an
- 85 integer multiple of the segment with the smallest area.

- One or more segments may be arranged to produce a visible display and one or more other segments are arranged to produce no visible
- 90 display.

- The electrochromic display device preferably includes means for compensating for loss of charge by applying a DC field between the electrochromic layer and the second electrode.

- 95 The electrolyte may be an acid, for example, sulphuric acid or may be a salt, for example, lithium perchlorate. Alternatively said electrolyte may be an ionic conductive compound, such as lithium nitride.

- 100 Said electrochromic layer may be composed of tungsten oxide.

- The invention is illustrated, merely by way of example, in the accompanying drawings, in which:—

- 105 Figure 1 is a cross-section of an embodiment of an electrochromic display device according to the present invention;

- Figure 2 is a graph showing reflectance versus the charge density of various tungsten oxide
- 110 (WO_3) electrodes;

- Figure 3 is a graph showing the applied electric field between the tungsten oxide electrodes of Figure 2;

- Figure 4 is a graph showing the colouring and bleaching response as a function of the number of segments of a known electrochromic display device;
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- Figure 5 is a cyclic voltammogram at a scan rate of 50mV/sec for tungsten electrodes, initially holding a charge of 5mC/cm² on the coloured electrode;
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- Figure 6 is a graph showing the colouring and bleaching response by a charge transfer method of an electrochromic display device according to the present invention;
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- Figure 7 is a plan view showing an embodiment of a numerical electrochromic display device according to the present invention;
- Figure 8 shows waveforms of voltages, current

and reflectance to illustrate a drive method of an electrochromic display according to the present invention; and

Figure 9 is a graph showing the relationship between charge density and potential versus gold.

Referring initially to Figure 1, an electrochromic display device according to the present invention is generally designated by the reference numeral 10. The electrochromic display device includes a transparent substrate 11, e.g. of glass or plastics material, and a first transparent electrode 12, for example of tin-doped indium oxide or antimony-doped tin oxide, on the substrate 11. An electrochromic layer 13 consisting of segments 13a, 13b for example, of tungsten oxide (WO_3), molybdenum oxide (MoO_3) or vanadium pentoxide (V_2O_5) is deposited on the first electrode 12.

An electrolyte 18, such as sulphuric acid, lithium perchlorate in propylene carbonate, lithium nitride, calcium fluoride (CaF_2), magnesium fluoride (MgF_2) or $\text{Na}_{1-x}\text{Zr}_x\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, is in contact with a surface of the electrochromic layer 13. The electrolyte 18 is partially contained by a spacer 17. It is preferable that the spacer 17 be of a material which is inert with respect to the electrochromic environment of the electrochromic display device 10, e.g. of a plastics material. A second counter electrode 16 is in contact with the electrolyte 18 such that the electrolyte 18 is completely contained by the electrochromic layer 13, spacer 17 and the second electrode 16. The second electrode 16 may comprise a gold film deposited on a substrate 15 of, for example, glass or plastics material.

The colouring mechanism of the electrochromic material is not clear but when the electrochromic material is tungsten oxide (WO_3), the colouring process is believed to occur with the simultaneous injection of electrons and positive ions into colourless tungsten oxide forming a so-called "tungsten bronze" by the following reaction:



where M^+ is a positive ion and x has a value between 0 and 1.

Colouring and bleaching responses are measured as follows. Reflectance of the electrochromic layer decreases as charge is injected into it. The reflectance of the light from a halogen lamp is measured by a photomultiplier through a filter designed so as to correspond to a visibility curve.

Figure 4 shows the colouring and bleaching responses by means of reflectance when a 1.5V DC field is applied between tungsten electrodes and a counter electrode in a known electrochromic display device. In Figure 4, curves a, b, c show the reflectance of the tungsten electrodes where the tungsten electrodes to be coloured or bleached have 1, 2 and 3 segments respectively. Each of the segments has a uniform area. As shown in Figure 4, the response depends

on the number of segments involved. Therefore, when the numeral displayed by the known electrochromic display device changes, the pulse width of the applied voltage must change depending upon the number of segments which change from a colourless state to a coloured state and vice versa. Moreover, compensation for temperature dependence is necessary to maintain fixed the reflectance of coloured segments.

A driving circuit for this known electrochromic display device is very complicated and difficult to manufacture because there are various restrictions imposed upon it especially when it is used in an electronic wristwatch, such as IC chip size, battery voltage and so on.

A new driving method for an electrochromic display device referred to as "charge transfer" solves these problems as follows. The coloured segments hold charges (electron and positive ions) but the colourless segments do not. When a DC field is applied between both segments so that the colourless segments are negative, the coloured segments, from which charge is extracted, bleach, while the colourless segments, into which charge is injected, colour. In a word, charges are transferred from the initially coloured and bleaching segments to the initially colourless and colouring segments. As shown in Figure 5, after all charge primarily held in the coloured segments is transferred, no electric current flows. Therefore, the optical density of the coloured segments is determined by the density of the charge held in them and is constant and independent of temperature.

Figure 6 shows the colouring and bleaching responses by the charge transfer method with a 1.5V DC field. The response is substantially unaffected by the number of segments. Also the optical density of the coloured segments is fixed by the density of the charge injected and is independent of temperature. Therefore, there is no need to compensate for these factors and the driving circuit for an electrochromic display device using the charge transfer method is greatly simplified.

In a first embodiment of an electrochromic display device according to the present invention having the structure shown in Figure 1, the transparent electrode 12 is composed of tin-doped indium oxide deposited by vacuum evaporation on a transparent glass substrate 11. Electrochromic segments 13a, 13b are of tungsten oxide (WO_3) deposited by vacuum evaporation on the transparent electrode 12. On the part of the transparent electrode 12 where tungsten oxide is not deposited, an insulating layer 14 of aluminium oxide (Al_2O_3) is deposited. The counter electrode 16 is a gold film deposited on the substrate 15 which is made of glass. In the space between the substrates 11, 15 is arranged a porous ceramic sheet 19 acting as a background. The electrolyte 18 is lithium perchlorate (LiClO_4) in propylene carbonate.

Initially a 1.5V DC field was applied from the electrochromic display device so that the segment

13a was negative relative to the counter electrode 16, and a charge 5mC/cm^2 was injected into the segment 13a which turned blue with reflectance of 42% (a reflectance of 100% means a fully bleached colourless state).

Next, a 1.5V DC field was applied between the segments 13a, 13b so that the segment 13b was negative relative to the segment 13a. The segment 13b coloured with a reflectance of 42% and the segment 13a bleached and returned to its original, colourless state with a reflectance of 100%. As a result, the charge primarily injected into the segment 13a was transferred to the segment 13b. Then, when the polarity of the applied electric field was reversed, the segments 13a, 13b exchanged their colourless and coloured states.

Thus, when a voltage periodically alternating in polarity as shown in Figure 3 was applied between the segments 13a, 13b the segments coloured alternately with the same optical density.

A second embodiment of an electrochromic display device according to the present invention had the same structure as the first embodiment, the electrochromic layer 13 being arranged to produce a numerical display as shown in Figure 7. Eight segments 71 to 78 were used to display numerals and segments 79 to 81 were used as auxiliary segments and could be hidden by, for example, a cover plate.

The area of each segment 71 to 77, 79 is S, the area of the segments 78, 80 is 2S respectively, and the area of the segment 81 is 3S, where S is 1mm^2 .

Initially, a 1.5V DC field was applied between the eight segments 71 to 77, 79 and the counter electrode 16, so that the eight segments were negative relative to the counter electrode. The eight segments turned blue with a reflectance of 42% due to an injected charge of 5mC/cm^2 . The segments 78, 80, 81 were colourless with no charge. The 7 segments 71 to 77 displayed the numeral 8.

Next a 1.5V DC field was applied between the segments 75, 79 and the segment 80. The charge which had been held in the segments 75, 79 was transferred to the segment 80 and as the total area of the segments 75, 79 was 2S and equal to the area of the segment 80, the reflectance of the coloured segment 80 was also 42%. Therefore, the numeral 9, uniformly coloured, was displayed.

By repeating the application of an electric field in the same way, the charge on the segments 77, 80 was transferred to the segments 75, 78 and the numeral 10 was displayed.

As described above, by applying a DC voltage between segments, the charge initially held in the coloured segments was transferred to the primarily colourless segments and the display changes. Thus the colouring and bleaching responses were substantially independent of the number or the area of the segments even in a practical numerical display. Moreover, even if the response varies with ambient temperature, the

optical density of coloured segments does not vary and is constant.

A third embodiment of an electrochromic display device according to the present invention has the same structure as the first embodiment. Initially a 1.5V DC field was applied across the electrochromic display device so that segment 13a was negative relative to the counter electrode 16, and a charge of 4.8mC/cm^2 was injected into the segment 13a which turned blue with a reflectance of 45%. The segment 13a remained in the coloured state even after the removal of the applied electric field.

Next, a 1.5V DC field was applied between the segments 13a, 13b so that the segment 13b was negative relative to the segment 13a. The segment 13b coloured with a reflectance of 45% and the segment 13a bleached and returned to its original, colourless state with a reflectance of 100%.

When the polarity of the applied electric field was reversed, the segments 13a, 13b exchanged their colourless and coloured states.

Thus when a voltage alternating in polarity was applied between the segments 13a, 13b as shown in Figure 8(A) the segments 13a, 13b coloured alternately with the same optical density and the cycle of colouring and bleaching was continually repeated.

However, during many cycles of colouring and bleaching the charge held in the coloured segments was gradually lost and after 10^3 cycles of colouring and bleaching the charge density decreased to 4.1mC/cm^2 and the reflectance rose to 50%. After 10^4 cycles, the charge density decreased to 3.3mC/cm^2 and the reflectance rose to 55%.

Therefore, it is necessary to compensate for loss of charge density over a long period. Figure 8(B) is a graph showing the applied electric field between the coloured segments and the counter electrode to compensate the loss of charge density. The first pulse voltage F_0 is used to inject charge initially into the segment 13a. Figure 8(C) is a graph showing the electric current and Figure 8(D) is a graph showing the reflectance of the segment 13a. As the cycle of colouring and bleaching is repeated the charge held in the coloured segments is gradually lost and decreases. The electric current when the charge is transferred decreases as shown in Figure 8(C) and the reflectance rises as shown in Figure 8(D). Therefore, compensating voltage pulses F_1 to F_3 in Figure 8(B) are provided to compensate for the loss of charge and the reflectance rises as shown in Figures 8(C) and 8(D).

The compensating pulses were applied every 1000 to 5000 cycles. In an electrochromic display device of an electronic watch displaying hours and minutes, it was found sufficient to apply a compensating pulse once a day.

A fourth embodiment of an electrochromic display device according to the present invention was identical to the third embodiment except for the compensating pulses. The pulse voltage was



determined by the relation between the charge density and the potential versus the gold counter electrode as shown in Figure 9. The potential versus gold is -0.5V for a charge density of 5mC/cm^2 . The cycle of colouring and bleaching was repeated with a -0.5V compensating pulse and over 10^6 cycles the charge held in the coloured segments hardly varied and was about 5mC/cm^2 independent of the compensating pulse width and the interval between compensation.

Claims

1. An electrochromic display device comprising: a substrate having an electrode thereon; an electrochromic layer consisting of a plurality of segments disposed on the electrode; an electrolyte disposed in contact with the electrochromic layer; and means for applying a DC field between selected segments of the electrochromic layer to cause charge to be transferred therebetween.
2. An electrochromic display device comprising: a substrate having a first electrode thereon; an electrochromic layer consisting of a plurality of segments disposed on the first electrode; a second electrode; an electrolyte disposed between the electrochromic layer and the second electrode; and means for applying a DC field between selected segments of the electrochromic layer to cause charge to be transferred therebetween.
3. An electrochromic display device as claimed in claim 2 including means for applying a DC field between the first and second electrodes to inject charge into the electrochromic layer.
4. An electrochromic display device as claimed in any preceding claim in which the area of each

segment is an integer multiple of the segment with the smallest area.

5. An electrochromic display device as claimed in claim 4 in which one or more segments are arranged to produce a visible display and one or more other segments are arranged to produce no visible display.
6. An electrochromic display device as claimed in claim 2 or any of claims 3 to 5 when dependent thereon including means for compensating for loss of charge by applying a DC field between the electrochromic layer and the second electrode.
7. An electrochromic display device as claimed in any preceding claim in which the electrolyte is an acid.
8. An electrochromic display device as claimed in claim 7 in which the acid is sulphuric acid.
9. An electrochromic display device as claimed in any of claims 1 to 6 in which the electrolyte is a salt.
10. An electrochromic display device as claimed in claim 9 in which the salt is lithium perchlorate.
11. An electrochromic display device as claimed in any of claims 1 to 6 in which said electrolyte is an ionic conductive compound.
12. An electrochromic display device as claimed in claim 11 in which said ionic conductive compound is lithium nitride.
13. An electrochromic display device as claimed in any preceding claim in which said electrochromic layer is composed of tungsten oxide.
14. An electrochromic display device substantially as herein described with reference to and as shown in the accompanying drawings.

determined by the relation between the charge density and the potential versus the gold counter electrode as shown in Figure 9. The potential versus gold is $-0.5V$ for a charge density of $5mC/cm^2$. The cycle of colouring and bleaching was repeated with a $-0.5V$ compensating pulse and over 10^6 cycles the charge held in the coloured segments hardly varied and was about $5mC/cm^2$ independent of the compensating pulse width and the interval between compensation.

Claims

1. An electrochromic display device comprising: a substrate having an electrode thereon; an electrochromic layer consisting of a plurality of segments disposed on the electrode; an electrolyte disposed in contact with the electrochromic layer; and means for applying a DC field between selected segments of the electrochromic layer to cause charge to be transferred therebetween.
2. An electrochromic display device comprising: a substrate having a first electrode thereon; an electrochromic layer consisting of a plurality of segments disposed on the first electrode; a second electrode; an electrolyte disposed between the electrochromic layer and the second electrode; and means for applying a DC field between selected segments of the electrochromic layer to cause charge to be transferred therebetween.
3. An electrochromic display device as claimed in claim 2 including means for applying a DC field between the first and second electrodes to inject charge into the electrochromic layer.
4. An electrochromic display device as claimed in any preceding claim in which the area of each segment is an integer multiple of the segment with the smallest area.
5. An electrochromic display device as claimed in claim 4 in which one or more segments are arranged to produce a visible display and one or more other segments are arranged to produce no visible display.
6. An electrochromic display device as claimed in claim 2 or any of claims 3 to 5 when dependent thereon including means for compensating for loss of charge by applying a DC field between the electrochromic layer and the second electrode.
7. An electrochromic display device as claimed in any preceding claim in which the electrolyte is an acid.
8. An electrochromic display device as claimed in claim 7 in which the acid is sulphuric acid.
9. An electrochromic display device as claimed in any of claims 1 to 6 in which the electrolyte is a salt.
10. An electrochromic display device as claimed in claim 9 in which the salt is lithium perchlorate.
11. An electrochromic display device as claimed in any of claims 1 to 6 in which said electrolyte is an ionic conductive compound.
12. An electrochromic display device as claimed in claim 11 in which said ionic conductive compound is lithium nitride.
13. An electrochromic display device as claimed in any preceding claim in which said electrochromic layer is composed of tungsten oxide.
14. An electrochromic display device substantially as herein described with reference to and as shown in the accompanying drawings.

