Coloured electrochromic "paper-quality" displays based on modified mesoporous electrodes

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Abstract

Progress on the development and commercialisation of electrochromic displays that have comparable optical qualities to paper-based display media relies on several factors. The electronic display must meet key requirements of paper-based media in readability, switching speed, power consumption, and stability to seriously be considered as a replacement. In addition, broadening of the colour range of electrochromic pixels is a factor that is compelling to the commercial uptake and usage of electrochromic "paper-quality" displays. We report the progress that has been made in increasing the colour range and in assessing the lifetime of electrochromic displays based on modified mesoporous electrodes.
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1. Introduction

The electronic display industry can be broadly segregated so that two types of displays are defined. There are those displays that use materials that emit light such as light-emitting diodes, cathode ray tubes, plasma displays, field emission displays, vacuum fluorescent displays, and, more recently, organic light-emitting diode displays [1] based on small molecule and polymer emitting materials. Liquid crystal displays (LCDs) that require the use of backlighting may be included in the category of emissive displays. The second broad category includes reflective display media made up of various bistable liquid crystal technologies such as twisted nematic, super twist nematic, cholesteric [2], bistable nematic [3], and zenithal nematic-type [4] technologies. Also in this category are non-liquid crystal display technologies such as those utilising the rotation of two coloured microspheres [5] under the influence of an applied field and electrophoretic-type [6] display technologies.

Electrochromic displays, because of their ability to be operated in either transmissive or reflective modes, can, in addition to LCD, be included in both categories of displays. The benefit of using electrochromic displays is that in transmission mode, the displays can be transparent to over 70% [7], and in reflective mode, they can have diffusive white reflectance of up to 50% [8]. These benefits arise from the fact that electrochromics do not require the use of light polarisation, as in LCD.

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The category of reflective technologies includes technologies that can be potentially useful as "paper-quality" displays, or displays that can approach the optical qualities of paper. The optical qualities of paper are defined by its contrast ratio, in addition to its high diffusively reflective properties. Also, paper-based media demonstrate a high degree of independence of viewing angle and can be read under a wide range of illumination angles and intensities of ambient light. These qualities of paper are key targets in the development of an electronic paper-quality display.

Electronic displays are dynamically changeable and, therefore, switching speed, power consumption, colour range, lifetime, and manufacturability are other key considerations when developing a potential substitute for paper. Previous reports [7,8] on displays based on mesoporous, wide bandgap semiconductor electrodes or "NanoChromics™" have described the "paper-like" optical qualities of devices in addition to the good switching speed and manufacturability of the display devices. The structure of these devices is shown below in Fig. 1. For transparent devices, the white reflector layer is not included in the assembly.

The mesoporous electrodes are modified with viologens based on Fig. 2 and colour when an applied potential causes the accumulation of electrons in the bandgap of the semiconductor and the subsequent
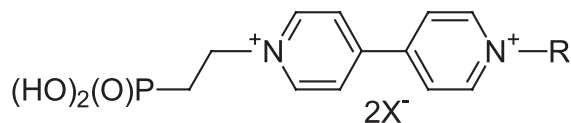

Fig. 2. General structure for viologens modifying the titania surface.

transfer of these electrons via the conduction band to the adsorbed viologen. The adsorption of the viologens enhances switching speed as the switching process is not limited by diffusion of viologens. The counter electrode of mesoporous $Sb:SnO_2$ acts as a mediator of the redox reaction and efficiently stores the charge.

Several publications have described these electrodes [9,10]. In addition, it has been reported in the past that electrochromic windows based on similar electrodes can be endowed with various colours [11]. For display applications, however, the colour range should be more broad. In particular, for paper-quality displays, a black-on-white contrast would be ideal. In the present communication, the range of colours achieved from the modification of viologen electrochromes and the data obtained from lifetime testing of devices are reported.

2. Experimental

Test devices were prepared on ultrasonically and UV ozone-treated F-doped SnO_2 (FTO)-coated float glass substrates (LOF TEC 15 $\Omega/\square$). Segmented cathodes were obtained by laser etching of the FTO transparent conducting layer in the pattern required. Mesoporous films of titanium dioxide of 3 μm thick were prepared by screen-printing the pattern from solvent-based paste and baking in air at 450 °C to burn off organic components. The viologen compounds were attached to the cathode by chemisorption from aqueous solution. Cathode and anode were sealed together using a thermocure epoxy sealant containing glass beads to define the cell gap, leaving a small entry port. The lithium ion-based electrolyte was introduced by vacuum backfilling before sealing the entry port with UV cure epoxy. UV/Vis spectra and reflectance measurements were made on an Ocean Optics SD2000 spectrometer equipped with an integrating sphere. Switching was controlled by a
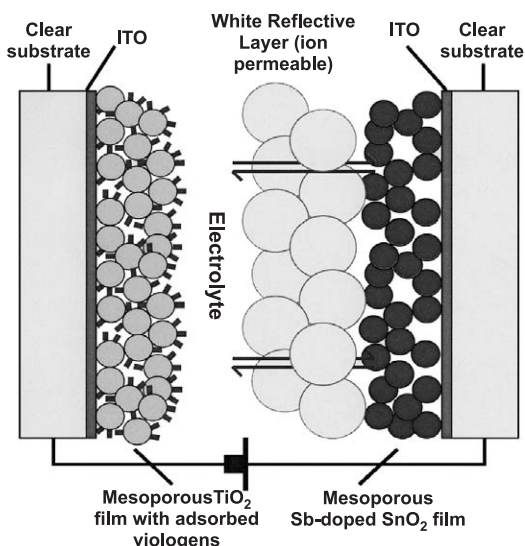

Fig. 1. Device cross-section of a NanoChromics™ display device.

computer running Igor Pro software and a Keithley source meter. Devices underwent electrochromic cycling on in-house built cycling apparatus with an "on" voltage of − 1.3 V vs. counter electrode and an "off" voltage of 0.0 V. Devices were cycled at higher temperatures in a Votsch VC4020 environmental chamber.

3. Results and discussion

3.1. Colour in NanoChromics™ technology

To obtain a broader colour range, viologens, as in Fig. 2, were modified with various R substituents. This gave rise to several materials, three of which are reported here. The contrast ratio spectra of the coloured devices are presented in Fig. 3. The devices were 50 × 50 mm in size, with a squared active area of 40 × 40 mm at the centre of the device. Spectrum (i) shows the broad absorbance of the viologen giving the "blackest" colouration. The cycling stability of this material is currently under investigation, although preliminary results have been promising. As previ-

ously mentioned, this material promises to give the appearance of the displays true "black-on-white" ink on paper quality. Spectrum (ii) is the characteristic UV/Vis response of the viologen, bis-2-(phosphonoethyl)-4,4′-bipyridinium dichloride.

Spectra (iii) and (iv) are attributable to one material. This material has two colour states due to the reduction of the viologen and, presumably, the reduction of the R substituent. The first state is green and is seen between 0.5 and 1.2 V as represented in Fig. 4. At voltages of higher magnitude (1.4–2.3 V), a hypsochromic shift from 600 to 530 nm is observed. This material and others under investigation offer the potential of creating colour displays from the technology without having to use colour filters which, by their use, would reduce the white state reflectance of a display device.

Seven segment display devices were prepared with these chromophores, pictures of which are presented in Fig. 5. The transparent conductor was etched such that each segment could be addressed individually. It is evident from the displays that a high degree of saturation is achieved by each of the colours. The red colour is achieved by doubly reducing the material via
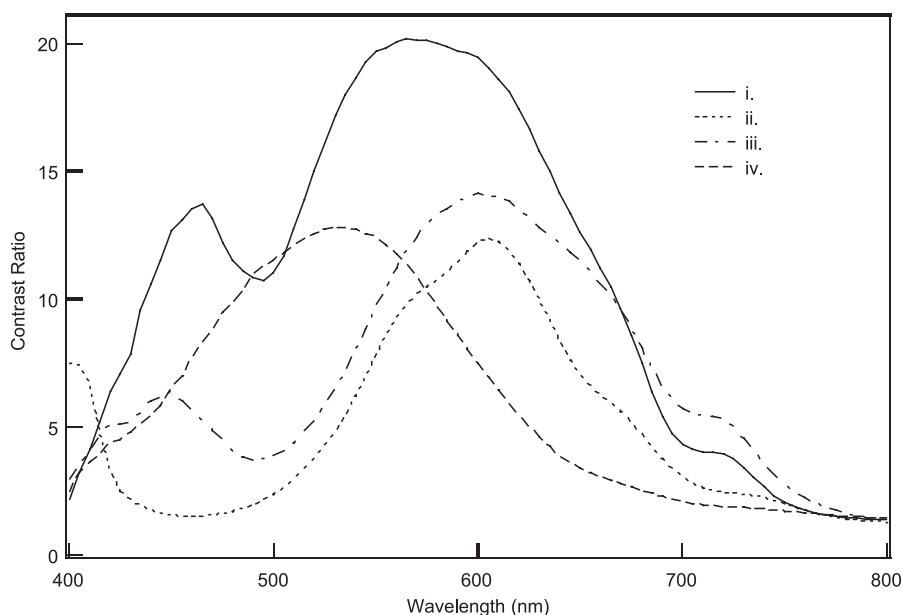
Fig. 3. Contrast ratio spectra for different viologens chemisorbed on mesoporous anatase titanium dioxide showing black (i), blue (ii), green (iii), and red (iv) colouration in the reduced state.
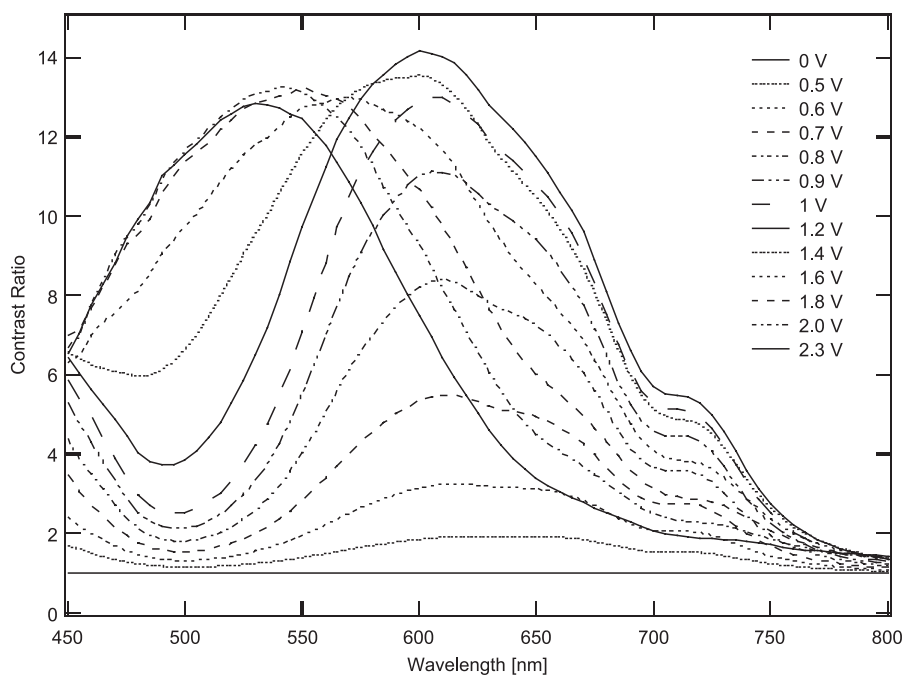
Fig. 4. Voltage-dependent contrast ratio spectra of a viologen with two coloured reduced states.

the green singly reduced species and shows surprising stability undergoing several thousand cycles. Several potential candidates were investigated in an attempt to obtain a material that may be reduced to a red colour

Fig. 5. Pictures of coloured NanoChromics™ devices.

from a colourless state. This investigation is ongoing and materials outside the class of the viologens are showing promise.

3.2. Switching and temperature stability of devices

As there are many different applications and environments in which electronic displays are used, the levels of stability required vary quite considerably. For indoor environments, operating temperature ranges may be acceptable between -10 and $+40$ °C, whilst outdoor environments may require operating stabilities of -40 to $+70$ °C. The lifetimes of devices depend on the application but most would require 5 years. In terms of cycling, at least 10^6 on/off cycles would be required, with 10^7 being the acceptable level for most applications in which "paper-like" optical requirements are necessary.

Devices based on the blue viologen were prepared and subjected to electrochromic cycling of 2 s on and 2 s off at an applied potential of -1.3 V. The switching speed of the devices has previously been reported at these voltages to be less than 1 s [1]. It can therefore be accepted that 2 s of on/off constitutes deep cycling for
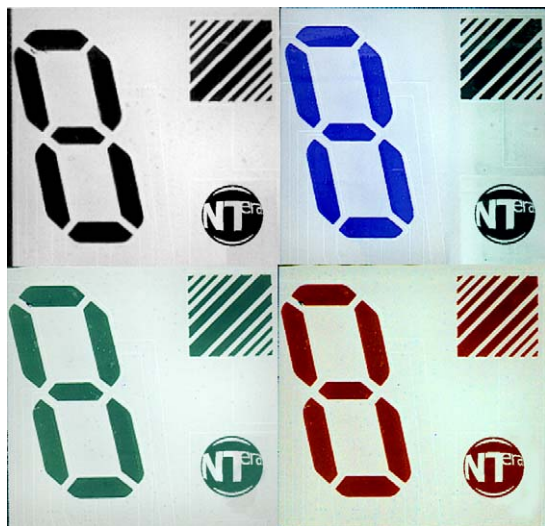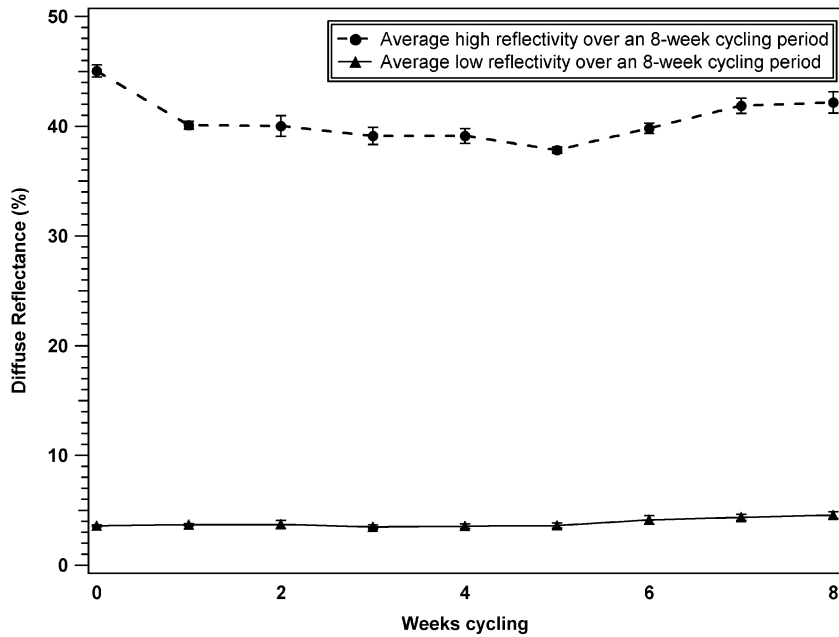
Fig. 6. High and low diffuse reflective values for a blue electrochromic display with the viologen, bis-2-(phosphonoethyl)-4,4′-bipyridinium dichloride, during cycling up to 1.2 million on/off cycles ($n = 4$).
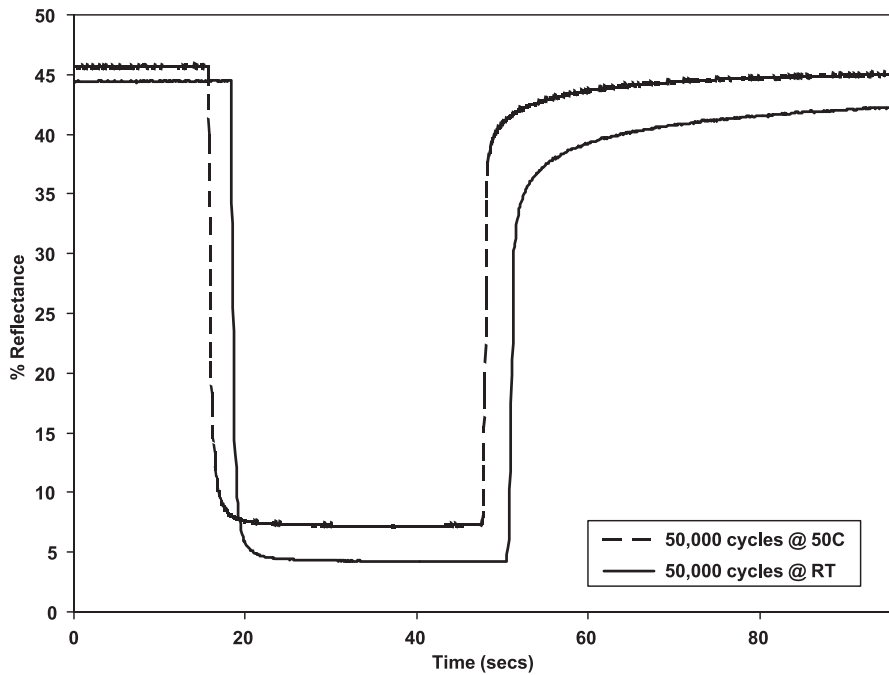

Fig. 7. Transient plots of a device (geometric surface area $= 16$ cm^2) cycled for 50,000 cycles at room temperatures (20–25 °C) at λ_{max} of the viologen [608 nm, bis-2-(phosphonoethyl)-4,4′-bipyridinium dichloride] with -1.3 V vs. counter electrode applied to colour.

these fast switching devices. Fig. 6 illustrates the high and low reflectances of the devices at points during 1.2 million of these cycles at room temperature. The data show that no significant degradation of the contrast ratio was seen under these conditions and the results are consistent with earlier reports of systems utilising modified mesoporous electrodes [12]. The devices were cycled at 50 °C for 50,000 cycles, 2 s on and 2 s off, in addition to the testing as described above. Fig. 7 is a comparison of the devices having undergone 50,000 cycles at room temperature and 50,000 cycles at 50 °C. A slight loss in the contrast ratio is observed under this testing as the lower reflectance value increases from 4.5% to 7.1%. This is within acceptable margins for several display applications.

In addition to cycling on and off for large numbers of cycles and a range of temperatures, display devices used in the field may have to be powered on for some time. A device based on a novel blue colouring viologen was thus maintained in a state with a constant potential of -1.3 V applied. The data for a typical device from this test are illustrated in Fig. 8.

The contrast ratio of the device was maintained for 888 h of constant applied potential.

4. Conclusions

The colour range in electrochromic devices utilising viologen-modified mesoporous films has been expanded. Other reflective display technologies require the use of colour filters to provide a range of colours; these filters reduce the amount of light reflected from the devices. The fact that the colours achievable by this electrochomic technology are intrinsic properties of the organic modifiers of the mesoporous layers means that there is no compromise between loss in optical quality as colour filters may not be required. In addition, the ability of these devices to be assembled in transparent mode, reflective mode, or a combination of both (i.e., transflective) opens up the possibility of using backlighting, and thus full colour mixing is somewhat simplified.
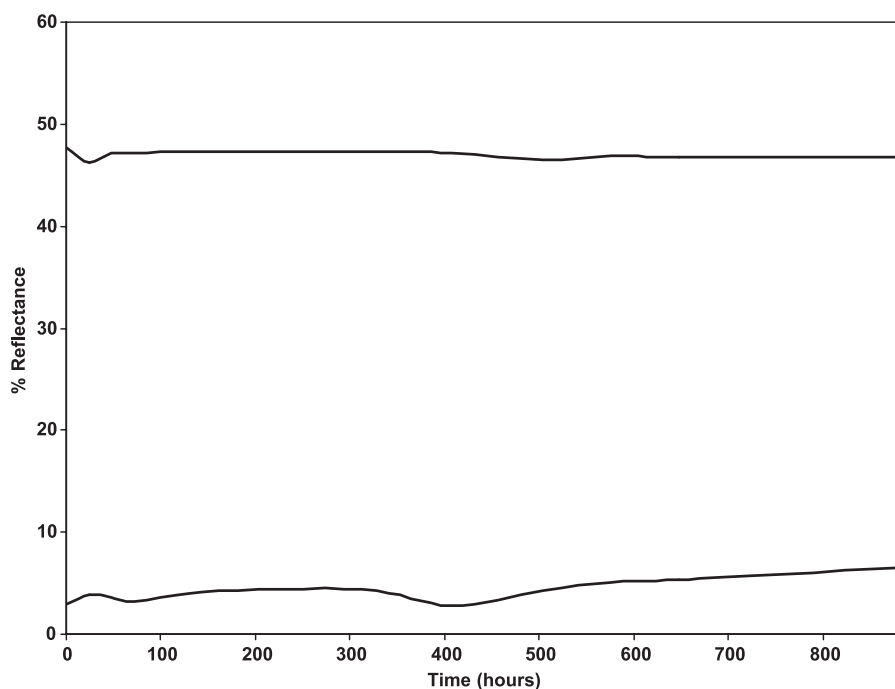

Fig. 8. High and low diffuse reflectance values for a device maintained in the coloured state for 888 h with an applied potential of -1.3 V vs. counter electrode.

The stability of these electrochromic devices is approaching the necessary requirements of commercial applications, and, indeed, some have largely been met. These results, in combination with the benefits of fast switching and ease of manufacture reported earlier, make the possibility of commercialisation of NanoChromics™ a real and near-term possibility.

References

[1] T. Tohma, Recent progress in development of organic electro-luminescent display devices, Dig. Tech. Pap.—Int. Display Res. Conf. (IDRC) (1997) F1.1.

[2] J.L. West, The challenge of new applications to liquid crystal displays, Liq. Cryst. Complex Geom. (1996) 255–264.

[3] C. Joubert, J. Angele, A. Boissier, P. Davi, I. Dozov, T. Elbhar, B. Pecout, D. Stoenescu, R. Vercelletto, P. Martinot-Legarde, SID Dig. Tech. Pap. (2002) 30.

[4] E.L. Wood, P.J. Brett, G.P. Bryan-Brown, A. Graham, R.M. Amos, S. Beldon, E. Cubero, J.C. Jones, SID Dig. Tech. Pap. (2002) 91.

[5] T. Pham, N. Sheridon, R. Sprague, SID Dig. Tech. Pap. (2002) 119.

[6] Y. Chen, K. Denis, P. Kazlas, P. Drzaic, SID Dig. Tech. Pap. (2001) 157–159.

[7] D. Cummins, G. Boschloo, M. Ryan, D. Corr, S. Nagaraja Rao, D. Fitzmaurice, J. Phys. Chem., B 104 (2000) 11449.

[8] U. Bach, D. Corr, D. Lupo, F. Pichot, M. Ryan, Adv. Mater. 14 (11) (2002) 845.

[9] P. Bonhôte, E. Gogniat, F. Campus, L. Walder, M. Grätzel, Displays 137 (1999) 20.

[10] R. Cinnsealach, G. Boschloo, S. Nagaraja Rao, D. Fitzmaurice, Sol. Energy Mater. Sol. Cells 55 (1998) 215.

[11] R. Cinnsealach, G. Boschloo, S. Nagaraja Rao, D. Fitzmaurice, Sol. Energy Mater. Sol. Cells 57 (1999) 107.

[12] H. Pettersson, T. Gruszecki, L.H. Johansson, A. Norberg, M.O.M. Edwards, A. Hagfeldt, SID Dig. Tech. Pap. (2002) 123.