

Flexible displays for smart clothing: Part II— Electrochromic displays

Ludivine Meunier^{a,b}, Fern M Kelly^b, Cédric Cochrane^{a,b} & Vladan Koncar^{a,b,c},

^a Univ Lille Nord de France, F-59000 Lille, France

^b ENSAIT, GEMTEX, F-59100 Roubaix, France

Chromic materials have the ability to change their colour reversibly according to external environmental conditions. They are categorised by the stimulus that triggers the colour change. For example, thermochromic materials can be defined as those in which a colour change is induced by a change in temperature and electrochromic materials are those in which a colour change is induced when an electrical current is applied. Thermochromism is already a well-known application within the textile field, however electrochromism is not as common. In this paper, an overview of the field of electrochromic devices has been presented and the successful development of a first generation flexible textile electrochromic device, achieved by ourselves, is discussed. The flexible electrochromic textile display consists of a novel 4-layer sandwich structure containing a thin spacer fabric with electrochromic compound (Prussian blue), a conductive layer and two electrodes; bottom and upper (transparent). If powered with a low voltage battery, this structure is able to generate a reversible colour change. The switching times have been measured at ~ 5 s and 4.5 V. The colour changes are monitored via CIE L*, a*, b* values.

Keywords: Conducting polymer, Electrochromic display, Flexible display, Prussian blue

1 Introduction

Any change in the colour of an object, whether from white to black, colourless to coloured or from one colour to another, can be easily detected by the human eye, or by simple spectrophotometric instruments. Such changes in colour provide important visual signals that can be used to convey information to an observer, the most obvious being traffic control signals. Consequently, research into substances that undergo reversible colour changes upon the application of an external stimulus has been extensive.¹ Materials of this type are known as chromic materials. The ability to combine chromic materials with textiles therefore provides the opportunity to create a flexible communicative display for clothing, principally for protection and safety or for added fashion.

Chromic materials are classified based on the type of stimulus that induces their colour change. For example, an “electrochromic” material is one in which a reversible colour change is observed when an external voltage is applied. This phenomenon is an analogy to “photochromic” and “thermochromic” materials, whereby the change in colour is observed by a change in light or a change in heat respectively²⁻⁴.

Articles of clothing treated with photochromic materials were first introduced in the market in 1989, with the application intended for added fashion. However, the ability also exists to be applied in solar protection, by monitoring UV radiation. Photochromics are generally organic molecules that can reversibly change their molecular configuration with the influence of UV radiation. The molecular arrangement of the material affects the absorption spectra and hence its colour⁵.

Two types of thermochromic systems have been used successfully in textiles. These are the liquid crystal type and the molecular arrangement type. In both cases, the dyes are entrapped in microcapsules and applied to fabric like a pigment in a resin binder. Toray Industries commercially released in 1987, a line of clothing made from temperature sensitive chameleonic fabric, known by the name of “Sway”. The change of colour with temperature of these fabrics was designed to match the application. For example, ski-wear 11°–14°C, women’s clothing 13°–22°C and ‘temperature shades’ 24°–32°C (ref. 6). More recently, thermochromic materials have been implemented in fashionable flu-masks to monitor the body temperature of a person (Fig. 1a)⁷. Thermochromic paints also allow textiles to have a particular motif painted on them that will change colour. A wall paper painted with green plants in

[°]To whom all the correspondence should be addressed.
E-mail: vladan.koncar@numericable.fr



Fig. 1— Thermochromic textiles that change colour with temperature (a) fashionable flu-masks and (b) blossoming wallpaper

thermochromic paint, starts to blossom as soon as your room heater turns on, spreading wonderful roses all over your wall like magic (Fig. 1b)⁸.

In addition to photochromic and thermochromic materials, electrochromics are also currently attracting much interest in academia and industry for both their fascinating spectroelectrochemical properties and their commercial applications. However, unlike the photo- and thermo- analogues, clothing or interior textiles treated with electrochromics are not readily available on the market. Devices consisting of electrochromic materials, that are available, include glass windows of buildings which darken reversibly at the flip of a switch,⁹ and for anti-glare car windows; including the sun-roof and the rear-vision mirrors¹⁰. Other proposed applications include re-usable price labels, devices for frozen-food monitoring, camouflage materials and controllable light reflective or light-transmissive displays for optical information and storage¹¹. Developments are also being undertaken into electrochromically operated billboards, large-scale traffic direction boards, and rail and airport departure boards^{12, 13}.

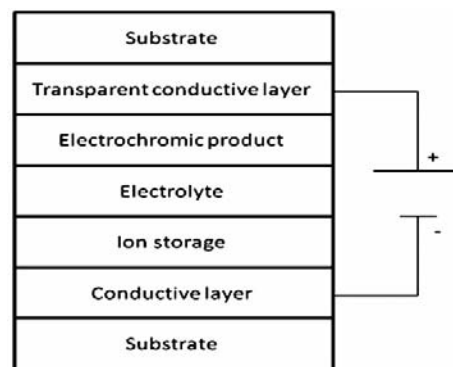


Fig. 2— An ECD with a seven-layer sandwich structure

However, the products listed above are rigid in their structure due to glass commonly being applied as the base substrate^{12,14-17}. An opportunity therefore exists to alternatively combine the desired spectrochemical properties of electrochromic materials with a flexible textile substrate, in order to achieve a display that is flexible. This would give rise to a technology that could be applied to a suite of products that would have the ability to change its pattern or print. Not only could communicative clothing be created, but also communicative flags and interior furnishings, including upholstery and drapery.

Many materials express these chromic properties, and can be assigned to one of three general categories^{18, 19}. Type I materials are soluble in a given electrolyte solution in both reduced and oxidised states, e.g. 1,1'-di-methyl-4,4'-bipyridilium ('methyl viologen'). Type II materials are soluble in one redox state, but form a solid film on the surface of an electrode following electron transfer, e.g. 1,1'diheptyl-4,4'bipyridilium dication in water. Type III materials, in both the reduced and oxidised states, are solids. All-solid systems are the most common for electrochromic displays. They include all conducting polymer systems, metal oxides, Prussian blue and its analogues, and rare earth phthalocyanines.

Electrochromic devices (ECDs) themselves may have one of many alternative compositions³. The traditional structure of an ECD, however, is that of a seven-layer electrochemical cell with the rigid sandwich structure (Fig. 2). An electrochromic material is coupled to both a suitable solid or liquid electrolyte (ionic conductor) and an ionic storage layer. These three layers are sandwiched between two conductors (electrodes), with at least one of these, also requiring transparency. These are then sandwiched between two substrates, typically glass, completing the device. Colour changes observed in

ECDs occur by charging and discharging the electrochemical cell with an applied potential of a few volts (typically 1 - 5 V)²⁰. After the resulting current has decayed, the colour change will be effected with the simultaneous redox reaction. The new redox state (and colour) remains due to the so-called “memory” effect, without the requirement of further electrical input³.

A number of academic and commercial research groups, including the engineering conglomerate (Siemens), are currently working on the development of ECDs that are flexible (Fig. 3)^{4, 21-30}. The Siemens display consists of a layer of electrochromic material sandwiched between two electrode layers. The ECD structure or the electrochromic mixture used by Siemens, which enables the screen to work so rapidly, however has not been disclosed. Moreover, Mecerreyes *et.al.*²⁶ have proposed a simplified alternative to that of the seven-layer structure described above. By using a plastic substrate, they have successfully created a flexible all-polymer ECD. Poly(3,4-ethylenedioxythiophene) (PEDOT) has been utilized, demonstrating that conducting polymers can act simultaneously as both the electrode and the electrochromic material. The transparent conducting layer of the classical configuration is therefore eliminated, resulting in a device requiring only five-layers (Fig. 4).

This article discusses the preparation of a flexible electrochromic display for application in smart clothing. The five-layer electrochromic device, considered above, has been simplified further to a four-layer device, by suspending a solution of an inorganic Type III electrochromic material (Prussian Blue) within a spacer fabric. The pros and cons of this device are discussed and the ways in which it may be improved are proposed.

2 Materials and Methods

Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 97 %) and potassium ferricyanide [$\text{K}_3\text{Fe}(\text{CN})_6$, 98 %] of analytical grade were purchased from Sigma-Aldrich Chemicals. Carbon black and silver were purchased from Dupont de Nemours. PET/ITO films were purchased from Sigma-Aldrich. Polyurethane-coated polyester was provided by Mediama. The specific spacer employed, consisted of 100 % polyester, was prepared in the GEMTEX laboratory of ENSAIT.

As previously described, a sandwich structure is the desired structure for the formation of an electrochromic device. The five-layer structure,



Fig. 3—A flexible electrochromic display, as developed by Siemens

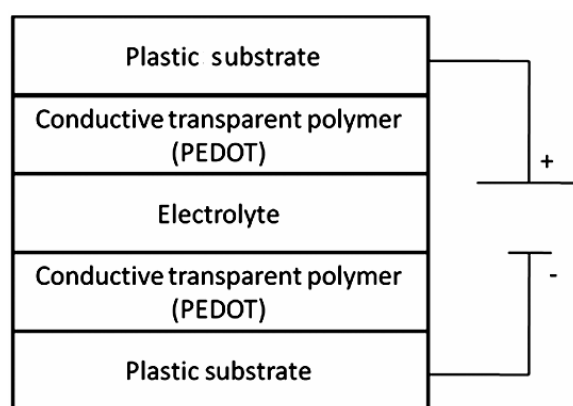


Fig. 4—An ECD with a five-layer sandwich structure

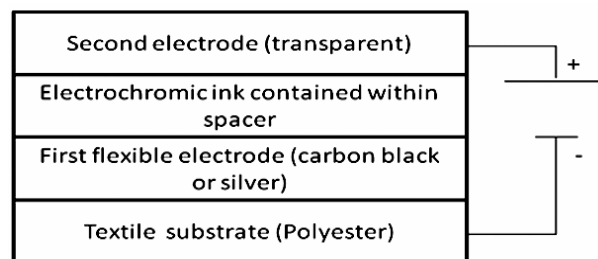


Fig. 5— Four-layer sandwich structure of the flexible electrochromic display prototype

developed by Mecerreyes *et al.*²⁶ (Fig. 4), has been adapted to prepare the flexible electrochromic device, giving rise to a simplified four-layer structure (Fig. 5). Figure 6 outlines the step-by-step preparation of the display. Polyester, pre-coated with polyurethane to provide a waterproof surface, was used as the textile substrate. The first conductive layer typically used is carbon black or silver. Prussian blue, $\text{K}_4[\text{Fe}(\text{CN})_6]$, has been selected as the electrochromic compound for the prototype due to its availability and its ease of synthesis via electrochemical reaction. The preparation includes combining two precursors, namely $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10 cm^{-3} , 0.05 mol.dm^{-3}) and

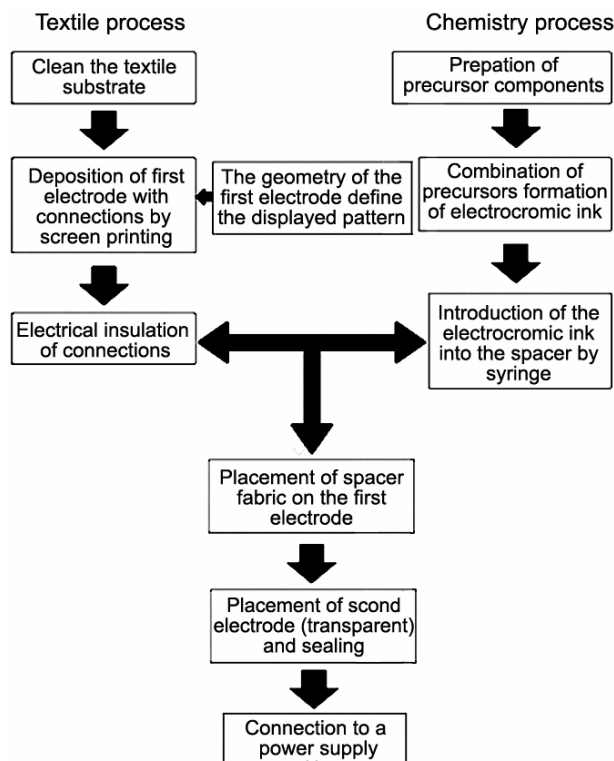


Fig. 6— Steps for flexible display preparation

$K_3Fe(CN)_6$ (10 cm^{-3} , $0.05\text{ mol}\cdot\text{dm}^{-3}$). An oxidation-reduction reaction ensues and $K_4[Fe(CN)_6]$ is formed. The colour of the $K_4[Fe(CN)_6]$ solution is orange-red. When the solution is introduced to the white spacer fabric, the fabric becomes orange-yellow in colour. The thickness of the spacer can be set between 0.5 mm and 1 mm. The device is sealed by joining the upper electrode (transparent and flexible PET/ITO) to the textile substrate using neoprene glue. A 4.5 V power supply is utilised to initiate the redox cycling of the electrochromic material.

To characterize the colour change, a spectrophotometer by Data Color International, Spectraflash SF600 Plus, was employed, and L^* , a^* , b^* co-ordinates obtained. To compare results, the CIELab colour space was implemented (Fig. 7).

3 Results and Discussion

The flexible electrochromic display developed is a four-layer sandwich structure (Fig. 5). The flexible textile substrate employed, and the first layer of the device, is a polyurethane coated polyester fabric. Deposited on this fabric, via screen printing, is the first flexible electrode of carbon black or silver. The third layer consists of the electrochromic ink (Prussian blue), dispersed within a spacer fabric. The

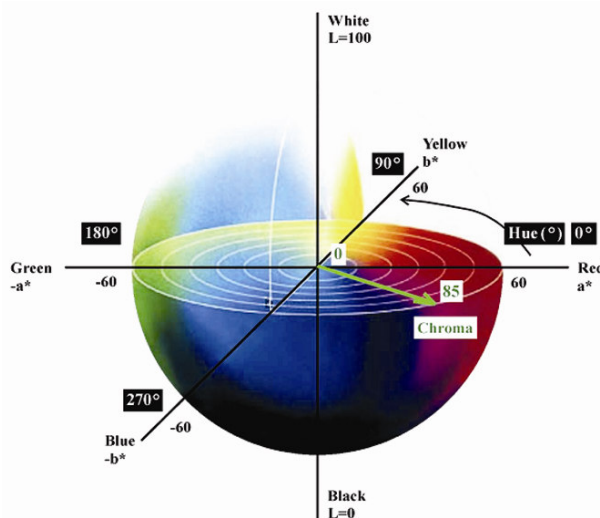


Fig. 7— CIELab colour space

second electrode (PET/ITO) and final layer of the device is transparent, so that the colour-switching of the electrochromic ink may be observed, and completes the device as the fourth layer. On sealing of the device, the PET/ITO layer also acts in protecting the electrochromic material from the atmosphere and thus slows the oxidation process. The solution of Prussian blue employed is both electrochromic ink and electrolyte. As it is in liquid form, it is mobile within the spacer. For this reason the two electrochromic layers, divided by an electrolyte, that are present in the five-layer device developed by Mecerreyes *et al.*²⁶ (Fig. 4), may be combined and the structure can be simplified to the proposed four-layer structure.

Following the successful construction of a flexible electrochromic device in the shape of the letter X (Figs 8 and 9), an electrical current was applied. A colour change from orange/yellow (Fig. 8a) to blue (Fig. 8b) is observed in less than one minute. The CIE L^* , a^* , b^* results, characterising the change in colour, are provided in Table 1. Of particular interest is the measured b^* coordinates, as these values describe the colour hue of the material between pure yellow (90°) and pure blue (270°). Before an electrical current was pulsed through the flexible display the X was yellow/orange, confirmed by a measured b^* value of 68.86° . The consequent change in colour to blue after the passage of electricity is noted from the b^* value changing to 243.84° .

Prussian blue is widely used in ECDs, either as the sole electrochrome or as an auxiliary electrode^{3, 31-34}. However, in the literature they are typically applied in

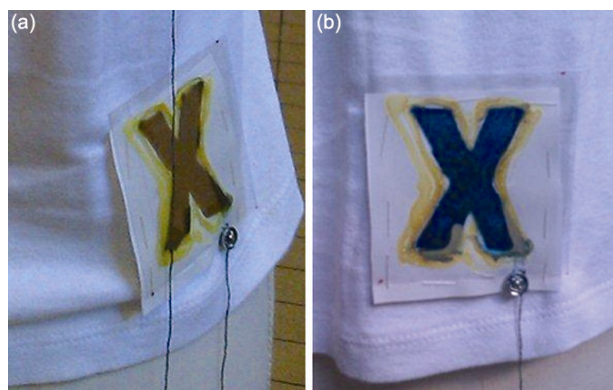


Fig. 8— The flexible electrochromic device (a) before and (b) after an electrical current has been applied



Fig. 9— Showing the flexible nature of the electrochromic device the form of solid films or solutions on a rigid electrode and substrate. Retention of a solid film or solution of Prussian blue on a flexible substrate is a very difficult task, due to the movement of the fabric. Thus, dispersing a liquid Prussian blue suspension in a spacer fabric is a novel idea. However, a number of challenges exist when using a solution phase electrochromic material in a flexible display. Due to the nature of the spacer fabric and the EC compound being a solution, the exact volume required by the spacer is difficult to determine. Additionally, when pressure is applied to seal the device, retaining the entirety of the dispersed solution within the structure is challenging. In the device discussed above, the Prussian blue solution has a tendency to leak with tilting and flexing of the display. Therefore, adequate sealing of the device by means of selecting the correct adhesive and sufficient contact between upper electrode and substrate is of utmost importance. A complete seal is also required as atmospheric exposure leads to oxidation of the inorganic electrochromic material Prussian blue, hence

Table I— Characterisation of the colour of electrochromic device, via CIE L^* , a^* , b^* values, before and after application of a current

State	Colour	L^* d65/10	a^*	b^*
Before current	Yellow	64.06°	43.1°	68.86°
After current	Blue	30.12°	36.52°	243.84°

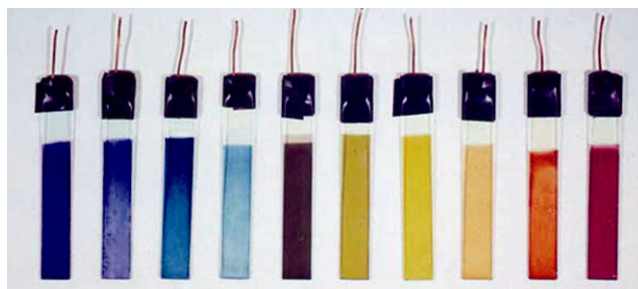


Fig. 10— EDOT and B-arylene EDOT electrochromic polymer films on ITO/glass

decreasing the life cycle duration of the device. Neoprene glue was applied to the four-layer device discussed above and it is found to be a valid choice due to its contact properties and flexibility. It takes about 10 min to successfully connect and seal the upper electrode to the lower substrate using the yellow coloured glue. The requirement is there for a transparent glue with immediate sealing properties. Future tests look towards using a fine line of epoxy resin. Sealing of the device by means of ultrasonic thermowelding is another option. This would essentially create a sealed pixel that could be manipulated in an individual manner.

Alternatively, a solid electrochromic material could replace the Prussian blue suspension within the spacer. Grafting a conducting polymer to the spacer fabric would be a favourable substitute. In comparison to Prussian blue, by using solid conducting polymers, the issues with the loss of electrochromic material during device formation, i.e. leaking of the electrochromic would be removed. Also, conducting polymers, in particular the polythiophene family, are known for their high cycle lifetime. Poly(3,4-ethylenedioxythiophene) or PEDOT, for example, shows no significant loss in performance after more than 5000 cycles²⁶.

Although the colours produced by Prussian blue are limited (either yellow or blue), the use of conjugated polymers in ECDs allows the possibility of developing other desirable colours. Subtle modifications to the monomer in the preparation of the conducting polymer can significantly alter the spectral properties of the material²⁰, and for this

reason the conducting polymers have become the most commonly used materials for ECD applications. Polythiophene and the family of polythiophene-derived polymers are a good example of how by tailoring the thiophene monomer, a rainbow of colours can be achieved. Polythiophene is blue in its oxidised state and red in its reduced state. However, by manipulating the monomer a large number of substituted thiophenes have been synthesized, leading to materials varying along a broad spectrum. Figure 10 presents a series of neutral EDOT and B-arylene EDOT electrochromic polymer films on ITO/glass illustrating the range of colors available³⁵.

Polypyrrole (PPy) and polyaniline (PAni) are two more examples of conducting polymers subject to wide investigation. PAni is polyelectrochromic, showing several colours for the various redox states in which it may exist. The redox states include leucoemeraldine (yellow), emeraldine salt (green), emeraldine base (blue) and pernigraniline (dark purple)^{36, 37}. PPy is blue/violet in colour in its oxidized state and yellow when reduced³⁷. As with thiophenes, by altering the monomer prior to polymerization, the colour of the pyrrole-derived polymer can also be manipulated. For example, poly(3,4-ethylenedioxyppyrole) (PEDOP) is pink when reduced and transparent light blue when oxidized. However, because PPy presents lower cycle lifetimes, its use in ECDs, as a reliable medium, is not as common as that for the thiophene family².

It is proposed to develop a second generation of flexible ECDs. These would be prepared by grafting conducting polymers, such as those listed above, to a spacer fabric in an analogous 4-layer structure to that described. This will remove issues relating to the solution phase and open the door to flexible ECDs capable of showing an array of colours.

4 Conclusion

The structure of a classical electrochromic device and a summary of electrochromic materials have been described. The process of creating an ECD whereby the substrate is a flexible textile is a challenging task, but a first generation device, consisting of four-layers, has been successfully prepared on a t-shirt. The four layers are: a pre-coated textile substrate, the first electrode of carbon black, a Prussian blue solution dispersed within a spacer fabric and finally a second electrode of PET/ITO. The solution phase electrochromic dye has not proved to be the best

solution for the preparation of a flexible ECD. However, ways in which the device can be improved, relating to sealing processes have been proposed. The second generation of flexible ECDs will look towards using solid organic conducting polymers, replacing the Prussian blue, so as to overcome the drawbacks of inorganic electrochromics.

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