



# Incorporating paper matrix into flexible devices based on liquid electrochromic mixtures: Enhanced robustness, durability and multi-color versatility



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## ABSTRACT

Viologen-based liquid electrochromic mixtures provide high performance in terms of optical contrast and response time. However, their use in flexible ECDs is quite limited due to the risk of leakage and difficult manufacturing and handling. Herein, it is demonstrated that the incorporation of viologen-based electrochromic mixtures into paper-matrix is a promising solution to overcome the mentioned issues. The performance of flexible paper-based devices using both water-free and water-based formulations containing viologens is assessed for the first time and compared with paper-free devices. The benefits of using paper on the homogeneity, life-time (operating devices above 1000 redox cycles) and robustness against bending (operating devices above 200 bending cycles) is proven: while short-circuits, inhomogeneous coloration and ITO-etching usually occur in the paper-free devices, these concerns are avoided when the liquid mixtures are embedded within the paper-matrix while keeping the good electrochromic performance typically provided by liquid formulations. Additionally, a patterned bi-chromic (blue-green) device is presented as a proof-of-concept to show the potential of these paper-based systems in the field of flexible EC displays.

## 1. Introduction

Electrochromic devices (ECDs) change their optical properties reversibly as a result of redox reaction induced by a suitable external voltage [1]. A great deal of research regarding electrochromic materials and device architectures has been focused on commercial applications such as smart windows [2], anti-glare rear-view mirrors [3] and displays [4].

For future ECDs, further developments are in demand to allow devices to be highly flexible and wearable. Flexible ECDs comprising plastic substrates would have significant advantages over ECDs comprising glass substrates, including light-weight, being shape-able, low-cost and suitability for large-scale production e.g. by roll-to-roll. Thus, their low weight and adaptability to curved shapes would facilitate easy integration in building and automotive glazing, enabling adding them as a layer to existing windows and eliminating the need for full replacement of smart windows. Beyond smart windows, the development of flexible ECDs further extends their applications to those requiring bendability such as displays for smart labels/cards/packaging, etc.

Electrochromic (EC) materials include transition metal oxides,

Prussian blue (PB) systems, conducting polymers and viologens among others. Viologens are 1,1'-disubstituted-4,4'-bipyridinium salts ( $V^{2+}$ ), a class of redox chromophores that exhibit cathodic electrochromic behavior undergoing a reversible first reduction that leads to the formation of an intensely colored radical cation ( $V^{+•}$ ) [5]. For their integration in ECDs, the viologens can be either dispersed in the electrolyte, together with a suitable redox pair, or deposited over an electrode. ECDs based on viologens dissolved in liquid electrolytes usually offer very good performance in terms of optical contrast, switching speed, etc [3,6]. However, even if the use of liquid electrolytes is quite extensive, they are not suitable for flexible devices since the risk of leakage and of presence of bubbles increases, while being difficult to manipulate during manufacture.

A possible approach to enable the incorporation of the high performance liquid-state electrochromic materials into flexible devices avoiding such limitations would be absorbing/embedding them into paper. Indeed, even if challenging, the use of paper as functional part of electronic devices is emerging as a promising solution to generate sustainable, portable, reusable and/or disposable systems not only due to its easy and low-cost production but also because of being flexible, renewable and recyclable [7,8]. Previous studies in three-electrode cells

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(e.g. using metallic electrodes such as Pt plates) showed that viologens can be incorporated into paper (impregnating opaque filter or photocopy paper matrix by soaking in an aqueous solution containing the viologen and a supporting electrolyte), being their electrochemical response fairly similar to that in water alone, meaning that movement through paper is not inhibited to any large extent [9–11]. These previous works are focused on the assessment of the availability of the viologens for electron transfer (redox response) when embedded in the paper matrix. However, to the best of our knowledge, there are not reports on the incorporation of the viologen-impregnated paper matrix between two transparent electrodes in a sandwich architecture and the assessment of the performance of the resulting electrochromic devices. Furthermore, the use of transparent paper sheets to absorb the viologen-based formulations therefore enabling a proper optical characterization (e.g.  $\Delta\%$ T measurements) of these systems has not been reported neither.

The present article reports on flexible ECDs comprising a paper matrix (both opaque or transparent) impregnated with water-free or water-based electrochromic liquid mixtures, placed between transparent ITO/PET electrodes in a sandwich architecture. The utility of using the paper-matrix over placing the electrochromic liquid mixtures directly between the flexible electrodes is emphasized. In particular, the positive effect of this approach on the color homogeneity, stability upon redox cycling and stability upon bending is demonstrated. Additionally, a paper-based flexible system displaying bi-coloration in well-defined areas that can be switched separately is shown as a proof-of-concept to prove the potential of the paper in combination with viologen-based EC liquid mixtures in the field of flexible EC displays.

## 2. Material and methods

### 2.1. Materials

1,1'-diethyl-4,4'-bipyridinium dibromide (ethyl viologen dibromide, 99%), 1,1'-diethyl-4,4'-bipyridinium diperchlorate (ethyl viologen diperchlorate, 98%) and 1-Butyl-3-methylimidazolium tetrafluoroborate (98%) were purchased from Sigma-Aldrich and used without further purification. Hydroquinone (99.5%) was provided by Riedel-de-Häen and used as received. Organic solvents (propylene carbonate and dimethyl sulfoxide) were purchased from Scharlab. Indium tin oxide (ITO) coated-PET sheets (Rs 60  $\Omega\text{sq}^{-1}$ ) were provided by Sheldahl. Acrylic adhesive tape from TESA was purchased from RS Amidata.

### 2.2. Methods

#### 2.2.1. Instrumentation and measurements

UV/Vis spectra were obtained on a Jasco V-570 spectrophotometer using air as the background, while the devices were connected to Biologic MPG potentiostat-galvanostat as a direct current source. The spectra in transmission (%T) mode were registered using a films holder accessory for solid samples. The spectra in reflectance (%R) mode were registered using a two ports integrating sphere. Before recording the spectra measurement of the ECDs (%T or %R as a function of the wavelength), the devices were exposed to the same voltage during 40 s with the aim of reaching the maximum colored state before starting the measurement.

$^1\text{H}$  NMR spectra was measured on a Bruker 500 MHz spectrometer in DMSO-*d*<sub>6</sub>, using tetramethylsilane as an internal reference.

Fourier transform infrared (FT-IR) spectra were recorded on a 4100LE FTIR from Jasco. The IR spectra were obtained using the attenuated total reflectance (ATR) technique on the pure solid.

ITO-etching was made by laser scribing with a Rofin Powerline E-Air 25 at 1064 nm (25 W, 25 A) at a frequency of 10 kHz and a speed of 700 mm/s.

#### 2.2.2. Synthesis of 1,1'-bis-(*p*-cyanophenyl)-4,4'-bipyridinium dichloride

1,1'-bis-(*p*-cyanophenyl)-4,4'-bipyridinium dichloride (*p*-cyanophenyl viologen dichloride) was synthesized according to previously reported procedure [12].  $^1\text{H}$  NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 9.77 and 9.18 (d of d, 4 H and 4 H, Ar H), 8.35 and 8.23 (d of d, 4H and 4H, bipyridine); IR (bulk ATR):  $\nu$ =3091 (C-H), 2227 (-CN), 1629, 1603 (C=C, C=N), 830  $\text{cm}^{-1}$  (*o*-phenylene H).

#### 2.2.3. Preparation of the EC mixtures

Water-free mixture (A): ethyl viologen diperchlorate (2.16 wt%), hydroquinone (0.54 wt%), 1-butyl-3-methylimidazolium tetrafluoroborate (43.25 wt%) and propylene carbonate (54.05 wt%) were mixed for 1 h at room temperature.

Water-based mixtures (B): The following mixtures were prepared and stirred for 1 h at room temperature:

**B1:** ethyl viologen dibromide (0.99 wt%), hydroquinone (0.25 wt%), dimethyl sulfoxide (79.01 wt%) and water (19.75 wt%).

**B2:** ethyl viologen dibromide (0.98 wt%), hydroquinone (0.73 wt%), dimethyl sulfoxide (78.62 wt%) and water (19.65 wt%).

**B3:** ethyl viologen dibromide (0.98 wt%), hydroquinone (0.73 wt%), dimethyl sulfoxide (49.14 wt%) and water (49.14 wt%).

**B4:** *p*-cyanophenyl viologen dichloride (0.25 wt%), hydroquinone (0.13 wt%), dimethyl sulfoxide (49.81 wt%) and water (49.81 wt%).

#### 2.2.4. Devices assembly

**2.2.4.1. Paper-free devices.** ITO/PET cells were prepared by joining two ITO-coated PET substrates (2 cm x 4 cm) through a double adhesive tape (thickness: 220  $\mu\text{m}$ ) placed along the whole perimeter, but leaving two small openings (1 mm wide) placed in opposite corners. The internal cavity of the cell was filled with the EC liquid mixtures (A or B1-B4) through one of the openings by surface capillarity. Once the cell was fully filled with the EC mixture, the openings were sealed with a transparent silicone (Loctite 595).

**2.2.4.2. Paper matrix-based devices.** Paper (100% cellulose) pieces (1.5 cm x 1.5 cm and 2 cm x 2 cm) of Filter-lab® (opaque filter paper (Fig. S1a and c), 60  $\text{g}/\text{m}^2$ ; thickness: 130  $\mu\text{m}$ ) and ALEDINHA (transparent cigarette paper, %T: ~90% in the whole visible range (Fig. S1b and c); thickness: 20  $\mu\text{m}$ ) were pre-soaked in the water-free (A) or in the water-based (B1-B4) mixtures for ca. 5 min and then placed on the ITO-coated side of an ITO/PET substrates. Then they were covered with another ITO/PET and an adhesive tape was placed in the perimeter to avoid device disassembly.

The devices were sealed in a vacuum sealer Lerica Levac 3 using vacuum seal channeled bags.

A schematic illustration of the devices architectures is depicted in Fig. 1.

## 3. Results and discussion

Water-free mixture (A) was first used to impregnate opaque filter paper (herein after named **OP**), leading to ECDs that provided homogeneous and deep blue coloration at applied potentials above -1.8 V (Fig. S2a). However, when transparent paper (hereinafter named **TP**) was used, the mixture was not absorbed even after long immersion times (> 1 h), probably due to a lower porosity and higher hydrophilic character of **TP** compared to **OP** (Fig. S2b), which might hinder the absorption of the liquid A mixture based on organic solvents. In order to obtain transparent flexible ECDs, a new EC mixture containing water (**B1**) was formulated. While ethyl viologen diperchlorate was used as electrochromophore in the water-free EC

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