Electrochromic device with Prussian blue and HPC-based electrolyte

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Given the importance of the development of electrochromic devices (ECDs) for technological applications, small devices with Prussian blue (PB)/hydroxypropyl cellulose (HPC) electrolyte/CeO₂–TiO₂ configuration were assembled and characterized. The films of PB were obtained galvanostatically by applying −0.45 mA for 300 s. The cyclic voltammetry, in 1 mol L⁻¹ KCl solution, of these films showed a redox pair peaks at well-defined potential of 0.16 V for oxidation and 0.4 V for reduction processes. The ECDs were assembled by combining the HPC-based membrane between the counter-electrode consisting of CeO₂–TiO₂ and the PB electrochromic layer. The devices were characterized by chromocoulo-meter coupled with UV–vis transmittance spectroscopy, open circuit properties, and voltammetry. The combination of PB with the transparent HPC electrolyte membrane resulted in an electrochromic device that switched between transparent and blue states by applying −2.6 and 2.0 V, respectively. The charge density measurements showed an increase from −6.0 to −8.4 mC cm⁻² when the potentials where applied for 15 and 60 s, respectively. The UV–vis spectra of the ECDs revealed that switching the ECD between −2.6 and 2.0 V for 15 s/15 s and 60 s/60 s resulted in 28% and 32% of transmittance difference between both states, respectively. The memory test, i.e., the changes of transmittance in open circuit after applying a potential of −2.6 V for 15 s revealed a decrease of transmittance from 60 to 59% in 3 h. The cyclic voltammetry measurements performed from 20 to 500 mV s⁻¹ showed better resolutions of the oxidation and reduction peaks for higher scan rates. Moreover, it was observed that after 2000 cycles, the charge density decreased from −6.0 to −1.5 mC cm⁻² and the difference of transmittance between colored and bleached state decreased from 28 to 5%.

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1. Introduction

For the past years, electrochromic devices (ECD) and chromic materials have attracted the attention of researchers because of their properties of changing color under certain circumstances, such as heat (thermochromic), light (photochromic), and electric potential (electrochromic). The interest on these materials is because of the development of modern devices [1,2]. For example, the electrochromic rearview mirrors for cars increase the night driving comfort as they darken automatically upon a strong light beam from the car behind [3]. Another example, are the electrochromic windows already applied in cars [4], buildings [5], Boeing 787 DreamLiner aircrafts [6], or sunglasses [7]. The basic configuration of an ECD is a sandwich type electrochemical cell (Fig. 1) composed by a conductive substrate, such as glass-ITO (indium tin oxide) or glass-FTO (fluorine tin oxide); an electrochromic (EC) layer, such as Prussian blue (PB) or WO₃; a solid, liquid or gel electrolyte, and finally counter electrode, such as CeO₂–TiO₂, deposited on the glass-conductive substrate.

Some ECD containing PB as electrochromatic layer were already reported. Deepa et al. [8] described an ECD using Prussian blue as EC layer, glass-FTO as a substrate, and poly(vinyl alcohol) (PVA) based electrolyte. This device presented fast times of coloration and discoloration, of around 2 s, a high value of chromic efficiency of 120 mC cm⁻² when −1.9 V was applied, and high reversibility of color changes, reaching 2000 cycles of coloration/discholoration. Barbosa et al. [9] described the ECD containing PB and poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) electrodeposited on PET-ITO (poly(ethylene terephthalate) coated with indium tin oxide). These cells required more than 600 s cycle times to reach full color switch, and had modest stability towards prolonged cycling tests. Another device, containing PB and poly(methyl metacrylate) (PMMA) as a gel electrolyte presented a ∆T of 46% upon applied potentials of −2.1 and 0.6 V [10]. These ECDs were tested for 50,640 color/bleaching cycles after which retained 55% of their maximum transmittance window. They also showed at-rest decay
of 9.6% after have been 107 days inactive. ECDs with PB as electrochromic layer were also assembled and analyzed in our labs [11–13]. The transmissive ECD with glass/ITO/ PB/PVC/PEDOT.PSS/ITO/glass configuration revealed a blue/ transparent color change of 35%, measured at 650 nm, and inserted/extracted charge of 1.7 mC cm⁻² after applied potentials of ±1.2 V [11]. The ECD with glass/ITO/PB/PVB-electrolyte/CeO₂–TiO₂/ITO/glass configuration was a reflective device changing a color from deep green to yellow under applied potentials of ±1.5 V [12,13].

As the ECDs are multicomponent structures each one of them can influence the device performance. Consequently, there are problems to compare different devices because they are assembled with different components [11]. As it was shown above even though the ECDs have the same Prussian blue EC layer they display quite different electrochemical and spectroscopic performances probably due to the different electrolytes. Therefore, electrolyte is also an important part of an ECD, and among many different polymer electrolytes (SPEs) those based on natural polymers are investigated [14,15]. Besides many different natural macromolecules that were already reported as SPEs the new ones are being developed and described. For example, a new blend electrolyte based on poly(vinylidenefluoride-hexafluoropropylene) and hydroxypropyl methyl cellulose for lithium-ion battery was recently described [16]. This gel-type polymer electrolyte showed a great performance, with ionic conductivity of 0.38 × 10⁻² S cm⁻¹, an electrochemical window up to 5.0 V, and 5% loss of capacity after 45 cycles.

Aiming to advance in the SPEs research the present work shows the real time color changing of an electrochromic device obtained by using Prussian blue as electrochromic layer and HPC-based electrolyte. There are two main colors observed on the device: blue and transparent. The blue one results from the transparent color of the HPC based electrolyte with the blue color of Prussian blue, while the transparent state is a result of the reduced state of Prussian blue, which is transparent. According to the time of applied potential to the EC device, the observed color changes from deep blue to transparent (while EC become transparent).

2. Experimental

Electrochemical deposition was used to obtain PB films [13,17,18] from the solution composed by 5 mL of HCl (0.05 mol L⁻¹), 10 mL of K₃Fe(CN)₆ (0.05 mol L⁻¹), and 10 mL of FeCl₃-6H₂O (0.05 mol L⁻¹). ITO (Delta Technologies; CG-50IN–1507; 8–12 ohms) was used as working electrode, 1 cm² platinum plate as counter electrode, and Ag/AgCl as reference electrode. A controlled cathodic current density of −40 μA cm⁻² was applied for 300 s with an Autolab 302 N on ITO promoting the deposition of the PB. After that, the ITO/PB was rinsed with Milli-Q® water to remove the excess of solution.

The HPC-based electrolyte was prepared by dissolving 0.3 g of HPC (Aldrich) in 30 mL of acetone under a magnetic stirrer for about 5 h. After the complete dissolution, 10 wt% of acetic acid (Synth) were added and stirred for more 2 h. Next, the solution was placed inside the desiccator for 10 min under vacuum for air bubbles removal. Finally, the solution was poured on a Petri dish and dried at room temperature.

One cm² electrochromic devices (ECDs) and having the glass/ITO/PB/HPC-electrolyte/CeO₂–TiO₂/ITO/glass configuration (Fig. 1) were made by assembling the two pieces of coated glasses and polymer electrolyte membrane between them. The CeO₂–TiO₂ were obtained by sol–gel process by using titanium isopropylate, Ti (O′Pr)₄, and cerium nitrate hexahydrate, Ce(NO₃)₃ × 6H₂O, as precursors, and deposited by dip-coating method with the withdrawal rate of 20 cm min⁻¹ [19]. This method showed to produce films with reversible redox reaction during multiple chronoamperometric cycling. However, other precursors for sol–gel process or sputtering can be used to obtain CeO₂–TiO₂ coatings suitable for ECDs application [20,21]. One cm² free space was left on the upper edge of the glass/ITO for the electrical contact. Then the glass/ITO/CeO₂–TiO₂ was pressed against the PB/ITO/glass, having the HPC membrane in between, in such a way that the two coatings, CeO₂–TiO₂ and PB, faced each other inside the assembled window. A one cm wide Cu-conducting tape (3M®) was glued to the free edge of each substrate for electrical connections. The mounted cells were sealed with a protective, insulating Teflon® tape.

The cyclic voltammetry and chronoamperometric measurements of ECDs were performed with an Autolab 302N apparatus by applying potentials ranging from −2.6 to +2.0 V and the electric field scan step of 100 mV s⁻¹. The UV–vis spectroscopy measurements in transmittance mode were recorded with a spectrophotometer Agilent 8453 between 200 and 1100 nm, and the memory test was realized by measuring the transmittance at 686 nm of the ECD in open circuit after application of −2.6 V for 15 s.

3. Results and discussion

Fig. 2 shows the result of the galvanostatic electrodeposition of the PB thin film obtained by applying −.40 μA cm⁻² for 300 s. As can be seen in this figure the values of potential drop almost instantly in the first five seconds, proving the reduction of FeCl₃ and K₃Fe(CN)₆ near the ITO electrode has occurred [13]. After that, the constant behavior is explained by the diffusion control of the
electrodeposition [22]. It also should be noted that since the very first moment of PB electrodeposition the ITO becomes blue colored. The intensity of this color depends on the time of electroosynthesis [13,23]. The PB coating deposit for 300 s at 40 μA cm⁻² had a dark blue color as shown in inset of Fig. 2.

Freshly electrodeposited PB coating is mechanically instable [23], but upon the redox cycling, between −0.2 and 0.6 V, in 1 mol L⁻¹ KCl electrolyte, the PB becomes more stable. This procedure performed soon after PB electrodeposition is called stabilization of the film [24,25], and is important for the PB good adhesion properties to the ITO substrate [26]. As an example, Fig. 3 shows the 3rd voltammetric cycle of the PB stabilization process performed in −0.2 to 0.6 V range and at the scan rate of 20 mV s⁻¹. The Fe³⁺/Fe²⁺ redox pair can be seen at 0.17 and 0.33 V, and is attributed to the PB → PW reaction (Eq. (1)) [27]. It means that PB film switches between blue and transparent states in oxidation and reduction processes, respectively.

\[
\text{KFe}^{3+}\text{Fe}^{2+}(\text{CN})_6 + e^- + \text{K}^+ \rightarrow \text{K}_2\text{Fe}^{2+}\text{Fe}^{2+}(\text{CN})_6
\]  

(1)

insoluble PB → Everitt’s salt

The stabilized PB films were then used to assemble ECDs with glass/ITO/PB/HPC-electrolyte/CeO₂–TiO₂/ITO/glass configuration. Fig. 4 shows the results of transmittance of this ECD after applied potentials of −2.6 and 2.0 V for 15, 30 and 60 s, where it is clearly seen that the biggest difference between transparent and blue color occurs between 600 and 800 nm. The most transparent state of 62% of transmittance at 686 nm, called Everitt’s salt [Eq. (1)] [17] is achieved after 30 and 60 s of applied potential of −2.6 V. This value is almost the same as the value of 60% for only 15 s of this negative potential application. The blue colored state is obtained after 2.0 V application after which the transmittance value at 686 nm drops to 28% after 15 s and to 27% for 30 and 60 s of positive potential application. Consequently, the color changes at 686 nm are of ΔT = 32% for 15 s and of 35% for 30 and 60 s of applied potentials. Comparing these values with some other ECDs that contain natural-polymer-based electrolytes it can be stated that they are very similar to ΔT = 35% registered for the ECD with glass/ITO/WO₃/agar-CH₃COOH/CeO₂–TiO₂/ITO/glass configuration [28]. The color changes from transparent to blue are shown on pictures of measured ECD (Fig. 4 insets) and are due to the PB → PW (Prussian blue → Prussian white) transitions (Eq. (1)).

The chronocoulometry measurements were performed by applying potentials of −2.6 and 2.0 V, and the obtained results are shown in Fig. 5. From this figure, one can observe that after applying potential of −2.6 V the charge density values decrease to −6.0, 7.2 and −8.4 mC cm⁻² after 15, 30 and 60 s, respectively. The reverse potential application of 2.0 V promotes an increase of charge density values up to 16.2, 25.3 and 3.3 mC cm⁻² after 15, 30 and 60 s, respectively. The obtained charge density values are similar to the reported ones of −5.16 mC cm⁻² for the ECD with glass/ITO/WO₃/starch-Li/CeO₂–TiO₂/ITO/glass configuration [29].

![Fig. 2](image1.png)

**Fig. 2.** Electrodeposition curve of PB at −40 μA cm⁻² for 300 s.

![Fig. 3](image2.png)

**Fig. 3.** Cyclic voltammetry of PB film in 1 mol L⁻¹ KCl solution, −0.2 to 0.6 V potential range, and scan rate of 20 mV s⁻¹.

![Fig. 4](image3.png)

**Fig. 4.** Transmittance versus wavelength for ECD with glass/ITO/PB/HPC-electrolyte/CeO₂–TiO₂/ITO/glass configuration for applied potentials of −2.6 to +2.0 V. Images of ECD in colored and transparent states (insets).

![Fig. 5](image4.png)

**Fig. 5.** Charge density versus time for electrochromic device with glass/ITO/PB/HPC-electrolyte/CeO₂–TiO₂/ITO/glass configuration for applied potentials of −2.6 to +2.0 V.
Fig. 6 shows the cyclic voltammetry for applied potential from -2.6 to 2.0 V and scan rates of 20, 50, 100, 200, 300, 400, and 500 mVs⁻¹. Analyzing Fig. 6 (inset) there are observed two reduction peaks at ~0.5 and 1.0 V, and three oxidation peaks at 0.5, 1.4 and 1.7 V. The obtained voltammograms are much different than those presented for ECD with glass/SnO₂/PEDOT/electrolyte/PB/SnO₂/glass configuration [8], which resemble the ECD with WO₃ and gelatin-based electrolyte [30,31]. However, they are similar to the voltammograms obtained for ECD with poly(vinyl butyrate) (PVB) electrolyte [32]. The presence of these additional peaks can be due to the PB redox properties, described in Eq. (2), where transition PB → PG (Prussian blue → Prussian green) can occur due to the applied potentials of -2.6 to 2.0 V during this analysis [13]. The voltammogram of PB (not shown here), in the experiment with CeO₂–TiO₂ as counter electrode and 10% acetic acid solution, is very similar (peaks at 0.2 and 0.35 V) to the voltammogram of PB shown in Fig. 3, so HPC-electrolyte can contribute to the final ECD voltammogram. Additional anodic peaks were already observed for ECDs with gelatin- and agar-based electrolyte [28]. Moreover, the kinetic parameters concerning the charge transport in HPC-electrolyte and interface of HPC-electrolyte and ITO surface are different from the solution. It was stated that higher scan rates provided better resolutions and higher values of peak currents of the oxidation and reduction processes. 

\[
\text{Fe}^{3+} \text{[Fe}^{2+}(\text{CN})_{6}]^3^+ K^+ + e^- \rightarrow \text{K}_2\text{Fe}^{2+}[\text{Fe(CN)}_6]^2^-
\]  

(2)

soluble PB → Everitt’s salt (PG)

The color/bleaching performance of the studied ECD was analyzed throughout the chronoamperometric cycling coupled to a spectral analysis under applied potentials of -2.6 and +2.0 V for 15 s each. Fig. 7 shows the results of the charge density (Fig. 7a) and the transmittance (Fig. 7b) for cycles 1, 500, and 2000 of device that changed alternatively the color from deep blue to transparent. Confirming the previous spectral analysis (Fig. 4), it was observed that the application of -2.6 and 2.0 V for 15 s each caused the discoloration and coloration of the Prussian blue, respectively. The variation between the transparent and blue colors showed a decrease of the cathodic (-2.6 V) charge density, from -6.1 to -1.9 mCcm⁻² after 2000 blue/transparent color cycles, respectively (Fig. 7a). During the chronoamperometric cycling of ECD UV–vis spectra were taken, and it was observed that the charge density values drop was accompanied by a transmittance values drop. The UV–vis values recorded at 686 nm and measured between 1 and 2000 cycles decreased from 60 to 39% for transparent state (-2.6 V) and from 28 to 33% for a blue colored ECD (2.0 V) (Fig. 7b). Su, Fang, Xiao and Lu [33] reported on complementary ECD with PB/PMMA/WO₃ configuration, i.e., with two electrochromic layers, which worked during 5000 color/bleaching cycles upon applied potentials of −0.5 and 1.0 V and lost only 10% of its initial transmittance. Kuo, Hsu, Lee and Ho [34] described another complementary ECD with PBV/succinonitrile-LiBF₄/PB configuration that changed its transmittance from bleached (73%) to colored (8%) after −1.0 to 0.7 V potential application. This ECD worked for 4000 color/bleaching cycles, and remained 86% of its transmittance attenuation initial value.

Cyclic voltammetry was also recorded for 1, 500, and 2000 cycles during the chronoamperometric (CA) measurements. Fig. 8 repeats from Fig. 6 the 1st cycle voltammogram where two cathodic and three anodic peaks are observed. After consecutive chronoamperometric cycling by applying -2.6 and 2.0 V for 15 s each, the voltammograms shapes change. Although the two cathodic peaks remain at the same potentials (~0.5 and 1.0 V) and shapes after 500 CA cycles, their current density values decrease considerably when compared with the values of the 1st cycle. Contrarily to the cathodic peaks, the anodic ones change the shape and the positions. The peak that was at 0.5 V shifted to 0.8 V, and peak assigned at 1.4 V merged with the peak at 1.7 V. After 200 cycles, the cathodic peaks reveal more decrease of the current density values, but maintain their potentials at ~0.5 and 1.0 V. However, the anodic peaks almost completely disappear, and only an increase of the anodic current density is observed at 2.0 V. The changes of cyclic voltammograms observed during CA cycling of ECD with PB as electrochromic coating and HPC as electrolyte point clearly that PB redox reactions are not completely reversible. As a result, there’s a decrease of the charge density values and, consequently, decrease of transmittance.
difference between color and bleached states were observed. This can be caused by the lack of K⁺ ions in the HPC-based electrolyte that are desired to the color/bleaching process [25], which is related to the changeover [24]. Although changeover process is preferentially dependent of K⁺ other species such as H⁺ and/or H₂O⁺, which are present in HPC-based electrolyte, are also exchanged during changeover [35].

Finally, the ECDs with PB/HPC-electrolyte/Co₃O₄–TiO₂ composition were subjected to the memory test, which means to the transmittance recording at 686 nm in open circuit after polarization at −2.6 V for 15 s. The results of these measurements are shown in Fig. 9, where one can observe a continue decrease of transmittance values from 61 to 59% during 10,800 s, i.e., 3 h of experiment. This low decrease of transmittance in the transparent state of device as a function of time in open circuit conditions showed that the investigated ECD has as good memory as the ECDs with WO₃ electrochromic coating [36]; however, in present case the natural state of the device is blue, while for the devices with WO₃ is transparent.

4. Conclusions

All solid state blue-transparent electrochromic devices containing Prussian blue (PB) as electrochromic layer, Co₃O₄–TiO₂ as counter-electrode thin film, and HPC-based membrane as electrolyte were assembled and characterized. The PB film was deposited by chronopotentiometric method and stabilized by cyclic voltammetry. This film evidenced redox peaks assigned to Prussian blue and Prussian white (Everitt’s salt). The change of ECD transmittance at 686 nm varies from 60% (at −2.6 V) to 27% (at +2.0 V). The 2000 chronoamperometric cycles performed between −2.6 and +2.0 V showed a decrease of the charge density, from −6.1 to −1.9 mC/m². A memory test indicated a decrease of the transmittance from 60% to about 59% after 10,800 s. All the results suggest that the investigated ECD that change its transmittance from blue to transparent presents good performance/properties and can be a promising solution for practical applications.

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