



## Prussian blue for electrochromic devices



L.M.N. Assis<sup>a</sup>, R. Leones<sup>b</sup>, J. Kanicki<sup>c</sup>, A. Pawlicka<sup>a,c</sup>, M.M. Silva<sup>b,\*</sup>

<sup>a</sup> IQSC, Universidade de São Paulo, São Carlos, 13566-590, SP, Brazil

<sup>b</sup> Centro de Química, Universidade do Minho, Gualtar, 4710-057 Braga, Portugal

<sup>c</sup> EECS-University of Michigan, Ann Arbor, MI 48109, USA

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### ABSTRACT

All solid electrochromic devices (ECDs) were prepared using Prussian blue (PB) as electrochromic layer, CeO<sub>2</sub>-TiO<sub>2</sub> as counter electrode, and either DNA-Er(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> or Agar-Eu(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> as ionic conductive membrane. The ECDs were assembled by combining the natural macromolecule-based electrolyte membrane placed between the glass-ITO/PB and CeO<sub>2</sub>-TiO<sub>2</sub>/ITO-glass electrodes. The two kind of electrochromic devices were characterized electrochemically and spectroscopically. The electrochemical measurements revealed that applying potentials of  $-3.0$  and  $+2.0$  V promoted the color change of the ECD from blue to transparent. The highest contrast of  $\Delta T_{VIS} = 25 \pm 2\%$  was at 686 nm after 60 s of applied potential for ECD with DNA-Er<sup>3+</sup>-based electrolyte. This ECD showed the charge density of  $-5.1$  mC cm<sup>-2</sup> after 15 s and  $-10.4$  mC cm<sup>-2</sup> after 60 s of potential application. Although a successive chronoamperometric (CA) cycling showed the insertion/extraction processes uniform, the  $\Delta T_{VIS}$  and charge density values dropped down to 5% and  $-1.6$  mC cm<sup>-2</sup> after 1000 CA cycles, respectively. The ECD with Agar-Eu<sup>3+</sup>-based electrolyte displayed almost the same charge density values of  $-5.1$  mC cm<sup>-2</sup> after 15 s and  $-10.5$  mC cm<sup>-2</sup> after 60 s of  $-3.0$  V potential application. This value decreased to  $-1.1$  mC cm<sup>-2</sup> after 1400 CA cycles. The best result of  $\Delta T_{VIS}$  was of  $35 \pm 2\%$  at  $\lambda = 686$  nm. All the presented results suggest the possibility of using PB as electrochromic coating and natural macromolecules as solid electrolyte in new ECDs development.

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### 1. Introduction

Electrochromic (EC) materials are very interesting because they change their color in a persistent but reversible way due to an electrochemical reaction [1]. This optical change is induced by a small electric current at low DC potentials in the range from a fraction of a volt to a few volts [2,3]. The EC inorganic materials are in general oxides divided in two groups. The first group consists of the materials that change the color under ions insertion, and are named cathodic ECs. The second group consists of materials that change the color during ions extraction, and consequently, they are named anodic ECs. In the last years, many transition metal oxides such as W, Ir, Mn, and Co have been studied for their electrochromic properties, and for their major stability when compared to the organic electrochromic compounds. WO<sub>3</sub> is one of the first studied electrochromic oxides. Usually, it is obtained by synthesis methods that vary from electrochemical [2], sol-gel [4], pulsed laser deposition techniques [5] to sputtering [6,7]. In the last five years, the number of published papers on EC materials has doubled confirming the great interest of the scientific community on this subject. The main reason for that is a possibility to develop new and modern devices such as electrochromic.

Different EC devices (ECDs) are today in the market with niche products in automotive, building windows, and displays sectors. For automotive industry, Gentex and Donnelly in the USA are producing auto

dimming rear mirrors [8]. For display industry, NTERA is producing iPod EC displays [9,10]. Unfortunately, these devices present several disadvantages such as the use of expensive deposition processes, the application of high flammable and low stability liquid electrolytes (e.g. PC-LiClO<sub>4</sub>), and the long switching times of the devices. The application of EC devices for thermal management for instance is limited to the Ferrari Superamerica roof panel [11]; nevertheless, its cost is extremely high. To overcome problems above, it is necessary to develop new electrochromic devices that will be less expensive and can be applied with success in several light transmitting and/or reflecting products [12].

Electroactive layers compose all solid-state ECDs, and electrochromic materials are separate from counter electrode by polymer electrolyte. Prussian blue (PB) is a well-known EC material that changes the color from blue to transparent [13]. The two forms of PB are called insoluble Fe<sup>III</sup><sub>4</sub>[Fe<sup>II</sup>(CN)<sub>6</sub>]<sub>3</sub> and the soluble MFe<sup>III</sup>Fe<sup>II</sup>(CN)<sub>6</sub>, where M is an alkaline metal. The simple method to obtain the PB is by electrodeposition [14]. The nature of the counter electrode will have direct impact on ECD properties [1,15]. As already shown in several publications, CeO<sub>2</sub>-TiO<sub>2</sub> is a good counter electrode thin film. It can reversibly undergo redox reactions without changing the color. It can be also obtained by simple sol-gel method coupled to dip-coating technique deposition [16].

Aiming to develop new all solid-state ECDs windows with glass/ITO/PB/electrolyte membrane/CeO<sub>2</sub>-TiO<sub>2</sub>/ITO/glass configuration were assembled and characterized by electrochemical and spectroscopic methods.

## 2. Experimental section

### 2.1. Polymer electrolyte membrane preparation

The polymer electrolytes membrane were synthesized according to the method described by Leones et al. [17]. Salmon sperm-DNA (0.5 g, Ogata Research Laboratory, Japan) was dispersed in 20 mL of Milli-Q® water, and heated under magnetic stirring up to 60 °C for a few minutes for complete dissolution. To this solution were added different quantities of erbium triflate (Er(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>) [18] and glycerol (Himedia, 99.5%) as plasticizer.

The polymer electrolytes membrane were synthesized according to the method described by Raphael et al. [19]. Samples of Agar<sub>n</sub>Eu(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> were prepared by dissolving 0.5 g of agar (Sigma-Aldrich) in 30 mL of Milli-Q® water under heating up to 100 °C and magnetic stirring for a few minutes for complete dissolution. 0.5 g of glycerol (Himedia, 99.5% of purity) acting as plasticizer and Eu(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (Sigma Aldrich, 98% of purity) were added to this solution under stirring.

The resulting solutions were poured on Petri dishes, cooled at room temperature, and then dried in a Büchi oven at 60 °C for 8 to 12 days to form transparent membranes of about 0.9 mm of thickness [20,21].

### 2.2. Glass/ITO/Prussian blue and glass/ITO/CeO<sub>2</sub>-TiO<sub>2</sub> electrodes preparation

Prussian blue (PB) films with thickness of about 217 nm [22] were electrodeposited from a solution containing 5 mL of HCl (0.05 mol L<sup>-1</sup>), 10 mL of K<sub>3</sub>Fe(CN)<sub>6</sub> (0.05 mol L<sup>-1</sup>), and 10 mL of FeCl<sub>3</sub>·6H<sub>2</sub>O (0.05 mol L<sup>-1</sup>) over glass/ITO (Delta Technologies; CG-50IN-1507; 8–12 Ω) substrates; this was a working electrode. One square centimeter platinum plate as counter electrode and Ag/AgCl as reference electrode were used. A cathodic current density of -40 μA cm<sup>-2</sup> was applied for 300 s with an Autolab 302N on between ITO and Pt promoting a deposition of the Prussian blue coating. Next, the glass/ITO/PB was removed from the solution and washed with Milli-Q® water.

The CeO<sub>2</sub>-TiO<sub>2</sub> thin films were deposited from sol-gel solution over glass/ITO substrate. The dip-coating method was used with the withdrawal rate of 20 cm min<sup>-1</sup> and final annealing temperature of 450 °C for 15 min, as described previously [16].

### 2.3. ECD cell assembly

The electrochromic devices (ECDs) with one square centimeter area and having the configuration glass/ITO/PB/electrolyte membrane/CeO<sub>2</sub>-TiO<sub>2</sub>/ITO/glass were assembled. Two electrodes previously prepared faced each other and were separated by polymer electrolyte membrane of thickness of 0.9 mm. The thickness of the electrolyte controlled the cell thickness. Electrical contacts were applied to ITO surface. Aiming to improve this contact a one cm wide Cu-conducting tape (3 M) was glued to the ITO. The edges of the mounted cells were sealed with a protective and insulating tape (3 M).

### 2.4. Measurements

The electrochemical measurements of ECDs were performed with an Autolab 302N apparatus. The cyclic voltammeteries were registered during applied potentials ranging from -3.0 to +2.0 V with the electric field scan step of 100 mV s<sup>-1</sup>. The chronoamperometric (CA) measurements were done using a square wave of -3.0 and +2.0 V for 15, 30, and 60 s each. It means that one CA cycle was composed of application

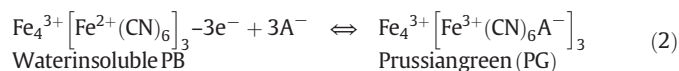
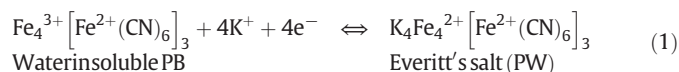
of -3.0 V for 60 s and +2.0 V for next 60 s (Fig. 2a). The same procedure was used for 15 and 30 s of applied potentials.

The UV-vis spectroscopy measurements of electrochemical cell were recorded with an Agilent 8453 between 200 and 1100 nm after application of -3.0 and +2.0 V for 15, 30, and 60 s.

## 3. Results and discussion

### 3.1. ECD with the DNA-Er<sup>3+</sup>

The voltammograms for ECD were registered between -3.0 and +2.0 V at a scan rate of 100 mV s<sup>-1</sup>, and a representative curve is displayed in Fig. 1. It is possible to observe in this figure that the application of an increasingly negative voltage to the ECD in the dark blue color state leads to an increase in the cathodic current, and it is accompanied by a simultaneous change to bleached state (transparent). Three peaks are observed in the voltammogram instead of four peaks characteristic to the PB [23]. Two cathodic peaks at -0.8 and 0.9 V and one anodic peak at 1.0 V are observed and can be attributed to PW, PB, and PG, respectively. The anodic peak was responsible for the blue coloring of the PB and the ECD. From this figure, it seems that the reactions described in Eqs. (1) and (2) [23,24] that are ascribed to PW to soluble PB and PG to PB transitions, respectively are not very clear in ECD voltammogram; consequently, peak at 1.0 V can be either of PG or insoluble PB shifted to more positive potential. The shape of ECD voltammogram in Fig. 1 is probably due to electrolyte composition, where no additional potassium and iron ions are present, rather than to the PB film. Finally, the redox processes seem to be not fully reversible [25].



Aiming to verify the possibility of use of the DNA-erbium triflate as ionic conducting membrane, small ECDs with glass/ITO/PB/DNA-Er(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>/CeO<sub>2</sub>-TiO<sub>2</sub>/ITO/glass configuration were assembled and characterized. The charge density ( $Q = \int_0^t i dt$ ) / A (I-current, t-time, and A-area) responses measured by applying -3.0 V/+2.0 V in the three time intervals of 15, 30, and 60 s of this ECD is shown in Fig. 2a.

From Fig. 2a it can be stated that the insertion of charge ( $Q_{in}$ ) for 15 s at -3.0 V of applied voltage reached -5.1 mC cm<sup>-2</sup>, and the inverse potential application of 2.0 V during next 15 s promoted the extraction

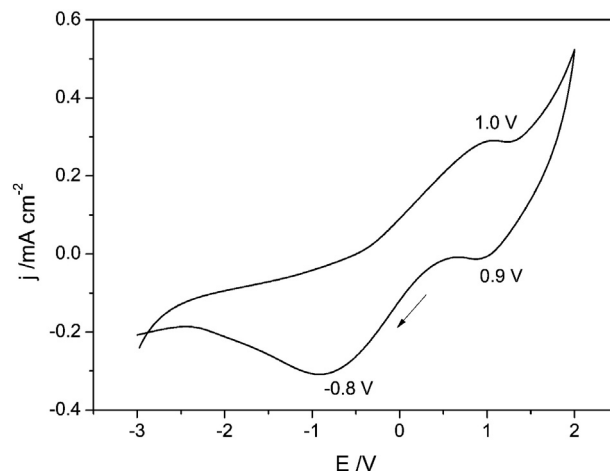


Fig. 1. Cyclic voltammograms at  $v = 100 \text{ mV s}^{-1}$  of the ECD with glass/ITO/PB/DNA-Er<sup>3+</sup>/CeO<sub>2</sub>-TiO<sub>2</sub>/ITO/glass configuration after 3rd CA cycle.

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