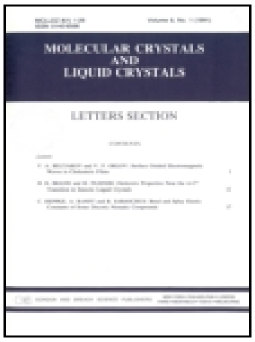

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Electrochromic Windows with PVB Electrolytes

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Electrochromic devices (ECDs) with WO_3/PVB electrolyte/CeO_2-TiO_2 configuration were assembled and characterized. The ECDs revealed charge density values of 2.9 and 7.8 mC/cm^2 with a cathodic/anodic ratio of 0.9 and 1.0 for the systems containing PVB-$LiClO_4$ and PVB-LiI electrolytes, respectively. The electrochemical stability showed a decrease of charge density, from 7.8 to 3.7 mC/cm^2 as a function of color/bleaching cycling being between 10 and 1,200th cycles for the ECD with PVB-LiI; and from initial 2.9 to 1.0 mC/cm^2 after 48,000 cycles for the ECD with PVB-$LiClO_4$. Moreover, a difference in transmittance of 30% between the ECD's colored and bleached states was also observed.

Keywords Electrochromic windows; sol-gel; PVB electrolytes

Introduction

The development of electrochromic devices (ECDs) have attracted attention during the last two decades due to the possibility of application related to the transmission and/or reflection of light [1, 2]. The ECDs belong to thermo-, photo- and electrochromic materials family and change their light absorption and/or reflection level and consequently their color as a function of light intensity (photochromic), temperature (thermochromic) and applied electric potential (electrochromic, EC). Depending on the application, there are already many described inorganic and organic systems used for electrochromic devices construction presenting different colors, but it should be stated that the predominant color is blue [1, 3–5]. Thus, ECDs, due to their controllable transmission, absorption and/or reflectance are systems of considerable commercial interest [1, 2] mainly applied as anti-glare rear-view car mirrors; there have been tentative to apply them as windows that can regulate the solar gains of buildings, cars, airplanes [6] or glasses [7].

The typical electrochromic devices usually consist of five layers called in sequence: glass/CT/CE/CI/RI/CT/glass, where CT is a transparent conducting substrate as ITO (indium tin oxide) or FTO (fluorine tin oxide); EC is electrochromic film; CI is an ionic conductor and RI is ions storage. There are some very well-known electrochromic and ion storage materials however the research on ionic conductors is still a scientific challenge. Different solid and gel electrolytes including polymeric ones are investigated [8, 9]. Also,

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gel polymer electrolytes based on natural macromolecules are prepared and characterized [10, 11].

One of the promising polymers for such an application is poly(vinyl butyrate) (PVB) widely used in glass industry laminates. In 1992 Ozer *et al* [12] showed electrochromic device with ITO/TiO_2/PVB-gel/ITO configuration that supported voltages of -2.8 V, evidenced 5 months memory in open circuit and almost 40% of difference between colored and bleached states. PVB was also used as a matrix for the ternary merged salts as ammonium benzoate and trimethyl(TEMAB)/lithium acetate (LiOAc)/bis(tri fluoro methylsulfonyl)imide lithium(LiTFSI) in order to obtain polymer electrolytes [13]. These electrolytes exhibited ionic conductivities of 10^{-5} S/cm at room temperature. Other ionically conductive membranes consisting of PVB-LiI with ionic conductivity of 10^{-5}–10^{-7} S/cm were investigated [14] and also applied in ECD that displayed almost 30% of difference between colored and bleached states. Moreover, Kobayashi *et al* [15] showed flexible ECDs with gel electrolyte containing PVB, tetra-n-butylammonium perchlorate (TBAP), N-methylpyrrolidone (NMP), ferrocene (Fc) and dimethyl phthalate (DMT) or diacetyl benzene (DAB) or diethyl ester of dicarboxylic biphenyl (DEB). However, those ECDs showed a short time memory of 80 s in an open circuit and its absorbance decreases from 0.45 to 0.35 after 120 cycles of coloration.

Other electrochromic glazing with up to 1.2×0.8 m^2 area and FTO/Prussian blue(PB)/PVB electrolyte/WO_3/FTO configuration was described [16]. This ECD exhibited color change from 80 to less than 30% in the 500 – 700 nm visible wavelenght. Similar configuration was used for innovative reflective ECD that changed the color from green to yellow [17].

Aiming to progress in ECDs development small electrochromic devices with ITO/WO_3/PVB electrolyte/CeO_2-TiO_2/ITO configuration were assembled and characterized by electrochemical and spectroscopic methods.

Experimental

Peroxotungstic acid was obtained by dissolving 3.5 g of metallic tungsten in a mixture of 15 ml of 30% solution of hydrogen peroxide, 15 ml of anhydrous ethanol and 15 mL of glacial acetic acid at 0°C for 12 h [18]. Next, the peroxotungstic acid was filtered, dried and dissolved in anhydrous ethanol resulting in a sol for WO_3 thin film deposition. The sol for CeO_2-TiO_2 thin film deposition was prepared by reacting 2.05 g of $Ce(NH_4)_2(NO_3)_6$ in 15 ml of isopropanol and 1.06 g of $Ti(OPr^i)_4$ under ultrasound irradiation using Branson Digital Sonifier 450 operating at 95 W and 20 kHz ultrasonic irradiation and equipped with a disruptor horn. As a result a transparent and dark red solution was obtained. After aging this solution for about 3 days its color changed to pale yellow and was transferred to the refrigerator [19, 20].

The films of CeO_2-TiO_2 and WO_3 were deposited by dip-coating on conducting glass ITO (Delta Technologies 8 $\Omega/\Box$) previously cleaned and rinsed with bidistilled water, ethanol and then dried at room temperature. The ITO substrates were withdrawn from the CeO_2-TiO_2 and WO_3 solutions in dry box (RH $< 40\%$) at a speed of 20 and 6 cm/min, respectively. Finally, the gel films of CeO_2-TiO_2 were densified at 450°C for 15 min and of WO_3 at 120°C for 1 h.

The electrolyte was obtained by dissolving 1.0 g of poly(vinyl butyrate) (PVB; BUTVAR B-98) in 20 mL of propanone under magnetic stirring and at a constant temperature of 50°C until complete dissolution [17]. Then, to this mixture was added either a solution of LiI/I_2 (10:1) or 0.4 g of $LiClO_4$ and stirred for more 2 h. The solutions were then poured

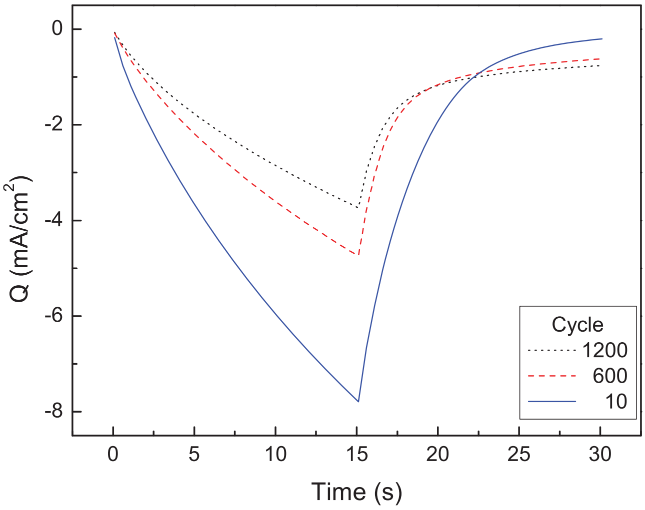

Figure 1. Charge densities of ECD with WO_3/PVB-LiI/CeO_2-TiO_2 configuration after applying −2.0 and +1.8 V for 15/15 s. (——) 10, (- - - -) 600 and (····) 1200th cycle.

into glass Petri dishes and dried in an oven at 40 °C resulting membranes formation. The samples were named PVB-LiI and PVB-$LiClO_4$ and stored in a vacuum desiccator over silica gel.

The electrochromic devices (ECDs), with one cm^2 area and having the glass/ITO/WO_3/PVB-electrolyte/CeO_2-TiO_2/ITO/glass configuration were obtained by assembling the two pieces of coated glasses. One cm free space was left for the electrical contact. Then, the CeO_2-TiO_2/ITO/glass and WO_3/ITO/glass substrates were pressed onto the PVB-membrane in such a way that the two coatings faced each other inside the assembled window. A 1 cm wide Cu-conducting tape (3M) was glued to the free edge of each substrate for electrical connections. The mounted cells were finally sealed with a protective, insulating tape (3M).

The cyclic voltammetry and chronoamperometric measurements of ECDs were performed with an Autolab 302N apparatus applying a potentials ranging from −2.0 to +1.8 V with the electric field scan step of 20 mV/s.

The UV–Vis spectroscopy measurements in transmittance mode were recorded with an Agilent 8453 spectrophotometer between 200 and 1100 nm.

Results and Discussions

Aiming to evaluate the reversibility of the ECD with PVB-LiI electrolyte, the samples were subjected to chronoamperometric cycling by applying the potentials of −2.0 V and +1.8 V for 15s/15s. Figure 1 shows the results of the charge density for the 10, 600 and 1200th cycles with color change from pale blue to transparent. The variation between the blue color and transparent showed a change during the test, where a decrease of the charge density, from −7.8 to −3.7 mC/cm^2 was observed after 1200 color/bleaching cycles. However, comparing this result with the results already published it can be stated that the values of the initial sweeps were higher than −1.8 mC/cm^2 at −2.5 V reported for the ECD with DNA-based electrolytes [21, 22].

Typical cyclic voltammograms of ECD with PVB-LiI-based membranes are shown in Fig. 2. Two cathodic peaks centered at −1.1 and 0.7 V and an increase of the cathodic

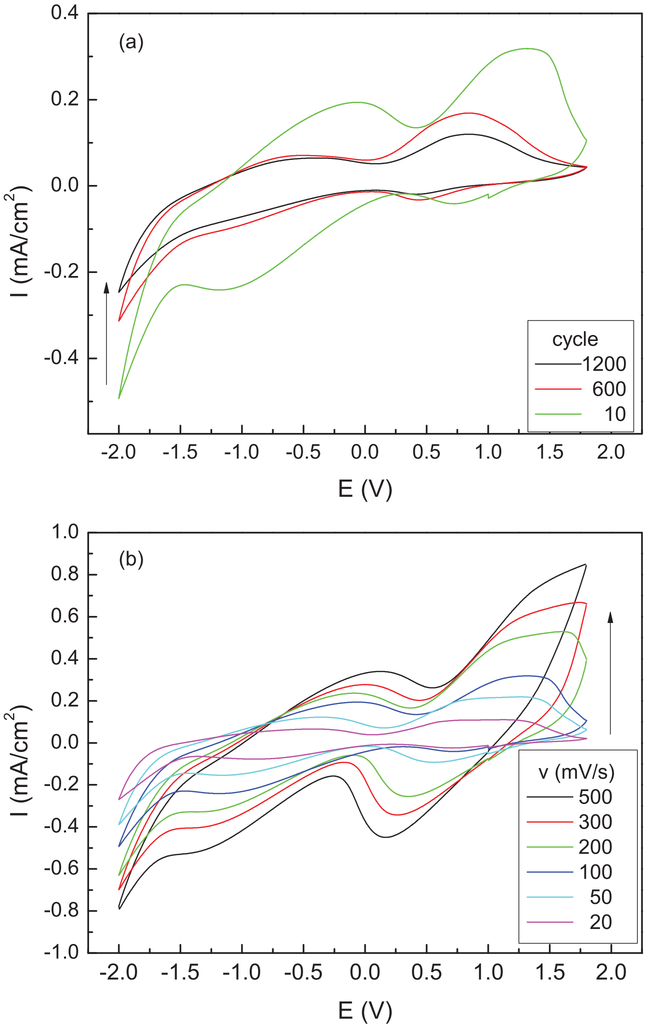

Figure 2. Cyclic voltammetries of ECD with WO_3/PVB-LiI/CeO_2-TiO_2 configuration recorded for 10, 600 and 1200th cycle (a) and at 20 to 500 mV/s (b).

current starting at −1.5 V is observed in 10th cycle votammogram (Figure 1a). Cathodic peak at −1.1 V as well as an increase of the cathodic current are characteristic to the blue color process due to the reduction of WO_3 coating and explained as an intervalence optical charge-transfer (CT) transition between adjacent W^{VI} and W^{V} centers [1]. The anodic electrochemical response of the ECDs with PVB-LiI membrane is also composed by two peaks, centered at 0.0 and 1.3 V, where the peak at 0.0 V is responsible for the bleaching process of ECD. The presence of this additional oxidation/reduction process can be due to I^-/I_3^- redox pair present in the PVB-LiI electrolyte formulation [23]. Additional anodic peaks were already observed for ECDs with gelatin- [24] and agar-based electrolyte [25]. Consecutive color/bleaching cycling promotes changes in the voltammograms and decrease of the intensity of all peaks.

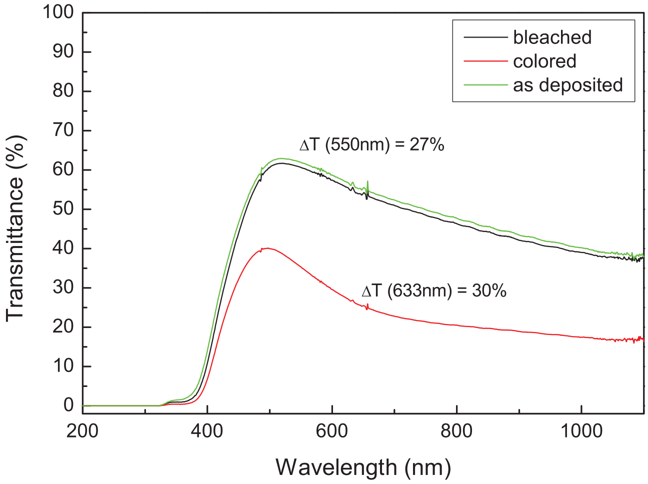

Figure 3. Transmittance of ECD with WO_3/PVB-LiI/CeO_2-TiO_2 after 10th cycle.

An increase in current density with increasing scanning rate from 20 to 500 mV/s of ECD with PVB-LiI electrolyte voltammograms is shown on Fig. 2b. This figure also reveal a shift of both cathodic waves to lower potentials with increasing voltammetric scanning rate and a shift to higher potentials for both anodic waves after increasing the voltammetric scan rate from 20 to 500 mV/s.

The UV–Vis transmission spectra of the ECD with WO_3/PVB-LiI/CeO_2-TiO_2 configurations in the range from 200 to 1100 nm for the 10th cycle are shown in Fig. 3. A transmittance variation of 27% at 550 nm and 30% at 633 nm between the bleached and colored state is observed, similarly to data reported for ECD with PVB-LiI electrolytes [26]. The transmittance variation decrease slowly with an increase of the wavelength and in the near infrared region the difference between the colored and bleached states is lower than 20% at $\lambda = 1100$ nm. These results are comparable to those obtained with electrochromic devices built with gelatin- and DNA-based electrolytes [25]. The transmittance data as a function of number of color/bleaching cycles confirm the electrochemical data and the transmittance difference of 3.5% between the colored and bleached states for the 1,200th cycle was recorded.

Aiming to evaluate the reversibility of the ECD, the samples were subjected to chronoamperometric cycling coupled to a spectral analysis by applying the potentials of -2.0 V and $+1.8$ V for 15s/15s. Figure 4 shows the results of the absorbance during 1,200 (Figure 4a) and the last 32 cycles (Figure 4b) where one can observe a continuous decrease in the optical density difference (ΔOD) between color (OD_c) and bleached (OD_b) states ($\Delta OD = OD_c\text{-}OD_b$). The absorbance of color state device drop from 0.58 to 0.49 and bleached device increase from 0.31 to 0.47. Thus, ΔOD decreases from 0.27 to 0.02 during 1,200 color/bleaching cycles. There are no results to compare however Kobayashi *et al* [15] reported on the ECD with a PVB-based electrolyte, where a drop in absorbance value of 0.45 to 0.35 after 120 color/bleaching cycles of 20 s of applied potential between 0 and 3.0 V was observed.

Figure 4b shows last 32 color/bleaching cycles of 1,200 cycles recorded at 633 nm, where one can observe regular waves between absorbance values of 0.49 and 0.47.

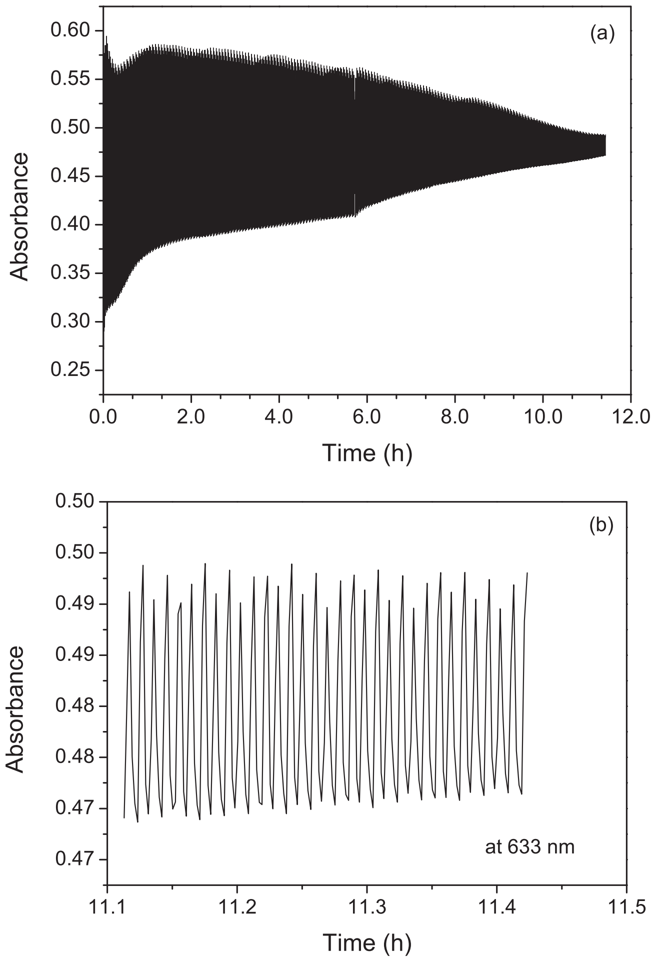

Figure 4. Absorbance in function of the chronoamperometric cycles of insertion and extraction of charges for ECD with WO_3/PVB-LiI/CeO_2–TiO_2 configuration. Applied potentials were of −2.0 and 1.8 V during 15s/15s; 1,200 (a) and last 32 (b) color/bleaching cycles.

The charge density response measured by chronoamperometry (−2.0/+1.8 V; 15 s/15 s) of ECD containing PVB-$LiClO_4$ electrolyte is shown in Fig. 5. From these measurements it can be stated that the insertion (coloration) is fast. For instance, for the 10th color/bleaching cycle, the inserted charge at –2.0 V reaches –2.9 mC/cm^2 in 15 s. The charge extraction occurs faster and the ECD is already discolored after applying +1.8 V potential during 5 s. As can be observed on this Fig. 5 whenever the devices become transparent fast and completely, the successive color/bleaching processes promote a decrease in the inserted charges. This can be observed when after 10,000 color/bleaching cycles the inserted charge value drop to −1.5 mC/cm^2. More cycling promote again a decrease in charge density values reaching −1.0 mC/cm^2 for 48,000th cycle. It is also interesting to note that extraction continue very fast during all 48,000 cycles.

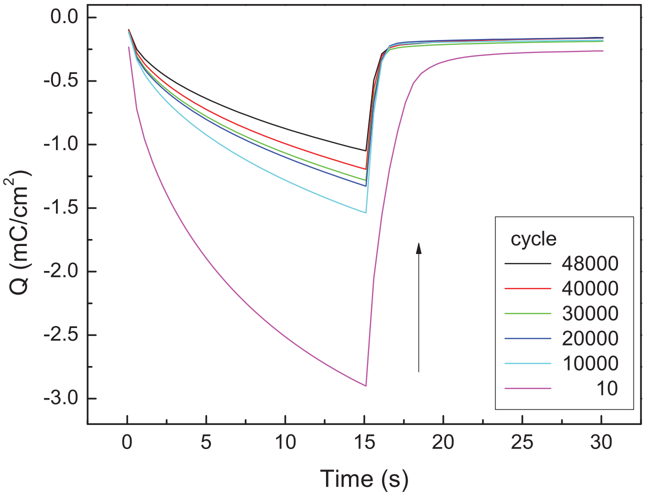

Figure 5. Charge densities of ECD with WO_3/PVB-LiIClO$_4$/CeO_2-TiO_2 configuration recorded after applying −2.0 and +1.8 V for 15s/15 s.

Comparing the Figs. 1 and 5 it should be noted that the ECD with PVB-$LiClO_4$ displayed much lower charge density as ECD with PVB-LiI. As the only difference was the used salt so this difference can be explained in terms of larger $LiClO_4$ than LiI/I_2 lattice energy. Consequently, the probability of formation of ion pairs and clusters in the system PVB-$LiClO_4$ is higher [27] affecting ionic and electronic conduction of electrolyte and operation of the device [28].

Figure 6 shows typical voltammogram of ECD with WO_3/PVB-$LiClO_4$/CeO_2-TiO_2 configuration. As can be seen on this Fig. 6a the voltammograms reveal one cathodic peak centered around −1.0 V and attributed to the WO_3 coloration process [29]. The anodic peak at −0.3 V for 10th color/bleaching cycle shift to −0.6 V after 10,000 cycles and is attributed to bleaching of the device. The second anodic peak centered at 0.7 V is small during the first 10 cycles and during the chronoamperometric cycling shifts to 0.6 V and its intensity increases. The presence of this peak was already reported in other studies and is probably related to some other oxidation process occurring in the system [23, 25].

Figure 6b shows voltammograms of ECD with WO_3/PVB-$LiClO_4$/CeO_2-TiO_2 configuration where one can observe an increase in current density with increasing scanning rate from 20 to 500 mV/s. Moreover, small shift from −1.0 to −1.3 V of the cathodic peak and corresponding anodic peak remains almost at the same potential of −0.3 V. The second anodic peak shifts from 0.6 to 1.2 V after increasing the voltammetric scan rate from 20 to 500 mV/s.

The UV-Vis spectra of ECD with WO_3/PVB-$LiClO_4$/CeO_2-TiO_2 configuration in the 200 to 1100 nm range are shown in Fig. 7. As in the case of the devices with PVB-LiI ionically conducting membranes the application of negative potential to WO_3 electrode promotes the darkening of the devices to blue color and consequently a decrease of the transmittance. The ECD with PVB-$LiClO_4$ membrane shows transmittance change of 16% at the wavelength of 550 nm that increases to 21% at 633 nm and then decreases to 13% at 1100 nm. Moreover, the obtained results are comparable to those observed with

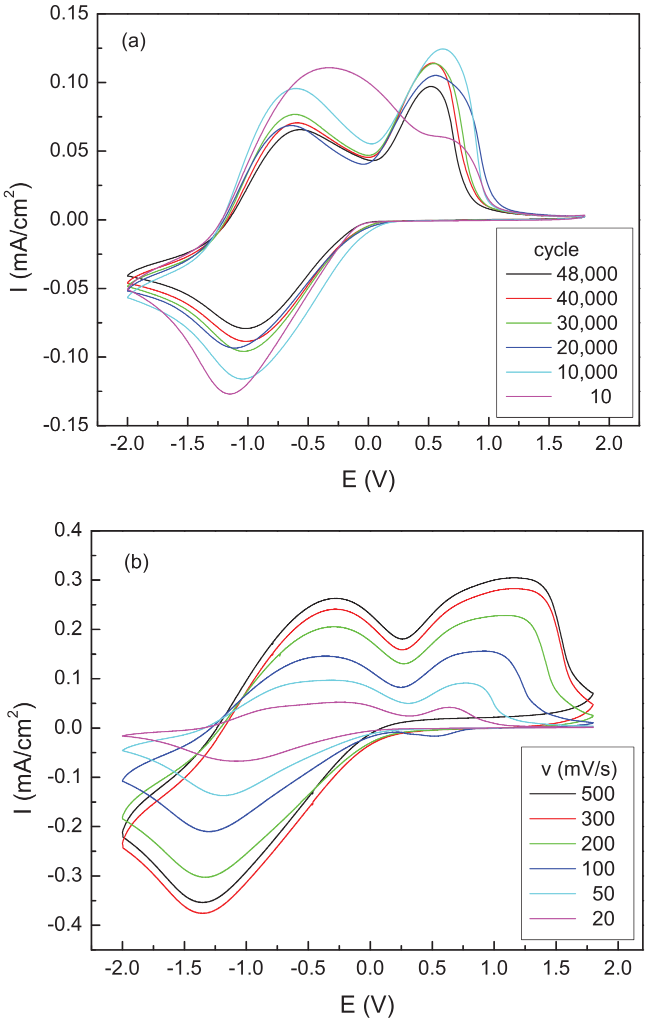

Figure 6. Cyclic voltammetries of ECD with WO_3/PVB-$LiClO_4$/CeO_2-TiO_2 configuration recorded for 10, 1000, 30000, 40000 and 48000th cycle (a) and at 20 to 500 mV/s (b).

ECDs containing gelatin-based electrolyte [24, 25]. Generally, the all obtained results are comparable to ECDs made with different polymeric electrolytes compiled by Heusing and Aegerter [30]. As in previous case, i.e., in ECD with PVB-LiI electrolyte the consecutive chronoamperometric cycling promotes a decrease in the transmittance of the device that drop to 4% at 550 nm and to 6% at 633 nm between the colored and bleached state for the 48,000th cycle. This result also corroborates the charge density and voltammetric analysis confirming not completely reversible processes occurring during the device switching.

As in the case of the ECD with PVB-LiI also the ECD with PVB-$LiClO_4$ electrolyte was subjected to spectral analysis at $\lambda = 633$ nm during 48,000 chronoamperometric cycles at -2.0 and $+1.8$ V for 15s/15s. The ΔOD decrease from 0.10 recorded for the first cycles to 0.05 after 48,000 cycles. At his point it should be stated that still after 48,000 cycles slightly blue color is observed when the devices is polarized at -2.0 V.

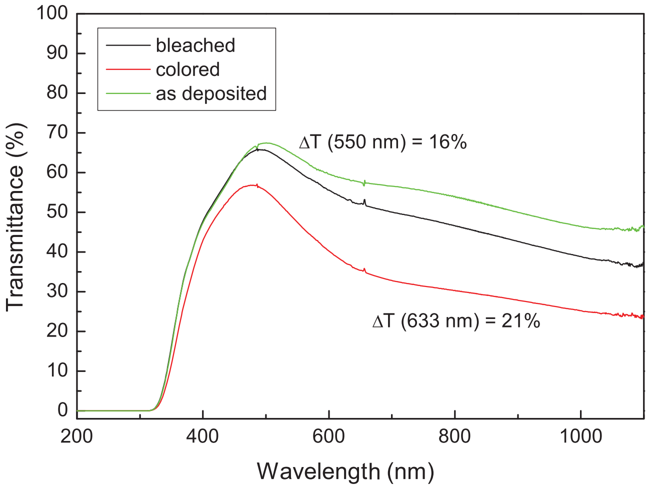

Figure 7. Transmittance of ECD with WO_3/PVB-$LiClO_4$/CeO_2-TiO_2 configuration recorded after 10th cycle.

Conclusions

Electrochromic devices (ECDs) with WO_3/PVB electrolyte/CeO_2-TiO_2 configuration were assembled and characterized. The chronocoulometry measurements revealed that ECD with PVB-LiI electrolyte displays higher charge density, i.e., of 7.8 mC/cm^2 than ECD with PVB-$LiClO_4$, that shows 2.9 mC/cm^2 after applying −2.0 V for 15 s. The color/bleaching processes are almost reversible and the cathodic/anodic charge rate is 1.0 for ECD with PVB-LiI and 0.9 for ECD with PVB-$LiClO_4$. Also the transmittance variation for ECD with PVB-LiI_2 is 30% at 633 nm while, the transmittance variation for ECD with PVB-$LiClO_4$ is 21% in the same wavelength. As possible explanation for the differences in the devices performance is fact that $LiClO_4$ have larger lattice energy when compared with LiI. Consequently, probability of ion pairs and clusters formation in $LiClO_4$ system is higher and affects the ionic and electronic properties of electrolyte. Another difference that can also influence on the device performance is I^-/I_3^- redox property evidenced on cyclic voltammograms of ECD with PVB-LiI electrolyte. However, both devices, i.e., with PVB-LiI and PVB-$LiClO_4$ show good spectral and electrochemical properties switching between color and bleaching states during 1,200 and 48,000 cycles, respectively.

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