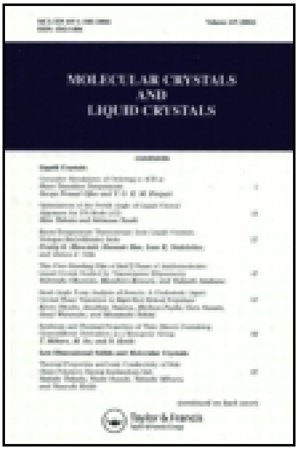

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Optoelectrochemical Characterization of Electrochromic Devices with Starch Based Solid Electrolytes

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This paper describes the manufacturing and spectroelectrochemical characterization of all solid electrochromic devices (ECD). Both electrochromic (WO_3) and storage ion (CeO_2-TiO_2) thin films were obtained by sol-gel method and deposited by dip-coating technique. The electrolytes were obtained by plasticization of starch with glycerol and addition of $LiClO_4$ salt. The spectroelectrochemical measurements were performed with the complete devices as a function of the applied potential. The obtained results revealed that the color/bleaching process was reversible and the inserted/extracted charge was about 4.6 mC/cm^2 for the applied potential of –2.0 V and increased up to 5.3 mC/cm^2 for –2.3 V. This value was stable up to –2.5 V applied. The transmittance change at 630 nm was about 30% for 2.3 V applied and the optical density was about 0.25. The memory tests showed that the colored device bleached completely in open circuit in about 500 min.

All the obtained results show that the presented devices are very good candidates to be tested as smart windows for architectural applications.

Keywords: counter-electrode; electrochromic devices; electrochromism; solid electrolyte; thin films; starch based electrolyte

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INTRODUCTION

One of the possible applications of the electrochromic properties of some materials is in durable electrochromic devices (ECD), which continue to be a very promising technological solution to “smart windows” [1,2], displays and others. Over the last years “smart windows” has gained a lot of attention principally in the architecture area, due to the possibility of saving energy in buildings through the very intense control of sunlight transmission in tropical countries. These ECDs should have a large area, but contrarily to the display’s applications, electrochromic windows require switching response of few minutes and contrast ratio of about 30–50% [3].

The ECDs have different compositions and technologies, but most of them are based on inorganic materials with WO_3 as electrochromic thin films. There also exist other alternatives, like all polymeric solid-state electrochromic devices based on modified conducting polymers [4] that change their transmission values from 90% to 50% in 2 s. However until now the best results have been achieved with inorganic materials that are now in the focus of several durability tests important for different applications [5].

The electrochromic devices can be performed with electrolytes of all-inorganic solid-state materials [6], organic compound-based materials [7] or organic-inorganic (ormolyte) based systems [8] that contain mobile species, such as lithium or proton [9]. In the case of ormolytes and organic or polymeric based electrolytes, lithium salts are generally used as conductor species. The polymeric electrolytes are very interesting due to their low production cost and more appropriate mechanical properties than inorganic materials. Different solid polymeric electrolytes have been recently proposed based on poly(amide 6-b-ethylene oxide), whose conductivity is in the range of 10^{-4} S/cm at 100°C [7] and natural polymers, which can be either grafted hydroxyetlhycellulose (HEC) [10–12] or modified starch [13,14].

Solid polymeric electrolytes obtained from starch plasticized with 30% of ethylene glycol (EG) or glycerol present conductivity values of $1.29 \cdot 10^{-4}$ S/cm and $5.05 \cdot 10^{-5}$ S/cm at 30°C, respectively. These conductivity values also depend strongly on the salt quantity, where it is observed that the best ionic conductivity values are obtained for $[O]/[Li] = 6{,}5$ and 11 for the samples with glycerol and (EG), respectively [15].

Most of the described ECDs contain ormolytes as ionic conductors and only few of them have polymeric electrolytes. Many different examples are cited by Heusing and Aegerter [16], where it can be observed that few ECDs with polymeric electrolytes achieve the color/bleaching difference of about 30%. On the other hand this difference is observed in many ECDs with ormolytes. However the comparison between them is difficult due to their different compositions.

This paper presents the results of ECDs composed of WO_3 electrochromic layer and CeO_2-TiO_2 thin films and polymeric electrolytes based on plasticized starch with $LiClO_4$ salt in the concentration of $[O]/[Li] = 8$.

EXPERIMENTAL

WO_3 and CeO_2-TiO_2 Thin Films

Tungsten oxide (WO_3) sol was produced in INM-Germany using a modified synthesis based on the reaction of tungsten metal powder with an excess of hydrogen peroxide (30% solution) to yield peroxotungstic acid, in the presence of ethanol and glacial acetic acid as described elsewhere [17–21].

$(CeO_2)_x(TiO_2)_{1-x}$ sol ($x = 0.45$) was also prepared in INM-Germany by dissolving $Ce(NO_3)_3 \cdot 6H_2O$ (0.056 mol) and $Ti(O^iPr)_4$ (0.069 mol) in 250 ml ethanol followed by stirring the sol at 30°C for 4 days [22,23].

The K-glass substrates (glass coated with transparent conducting layer of SnO_2:F, (17 Ω/■) were washed, dried and heat treated at 450°C for 15 min. The $(CeO_2)_x(TiO_2)_{1-x}$ layers were deposited on these substrates by the dip-coating technique with a withdrawing rate of 4 mm/s at 20°C with 38% air humidity. The layers were then heated in air from room temperature up to 450°C with a heating rate of 2.5 K/min, kept for 15 min at 450°C and then cooled to room temperature in the oven for 5 hours. The WO_3 layers were deposited on K-glass by the same technique under the same experimental conditions and then heat-treated at 240°C for 1 hour.

Solid Polymeric Electrolytes

The samples of amylopectin-rich starch (Amidex 4001 Corn products Brasil Ingredientes Industriais Ltda.) were dispersed in water (2% w/v) and heated for 2 hours at 100°C. Next, the solution was cooled to room temperature and then glycerol (Synth) or ethylene glycol was added with 30% of starch mass. Lithium perchlorate ($LiClO_4$) was also added resulting in the concentrations of $[O]/[Li] = 8$ when calculated for all starch and plasticizer oxygens. The viscous solution was dispersed in a Teflon plate and dried for 48 h at 40°C. The resulting transparent film samples were stored in a dry box [13].

Electrochromic Devices

Electrochromic devices were obtained by a sandwich junction of glass/ITO/WO_3 with SPE based on natural polymer and CeO_2-TiO_2/ITO/glass. After isolated from ambient humidity these devices of 7.02 cm^2 of area were subjected to electrochemical measurements with a potentiostat/galvanostat (Solartron 1286) controlled by CorrWare software. *In situ* Visible spectra of the films were measured by an HP spectrophotometer.

RESULTS AND DISCUSSION

The cyclic voltammogram of ECD composed of WO_3/starch-glycerol/CeO_2-TiO_2 is showed in Figure 1, where it can be observed that the cathodic and anodic peaks are large and not so well defined as in the author's previous study [24]. This difference may be due to the coating methods preparation or to the salt quantity of SPE. In the present case the SPE was prepared with higher salt quantity than

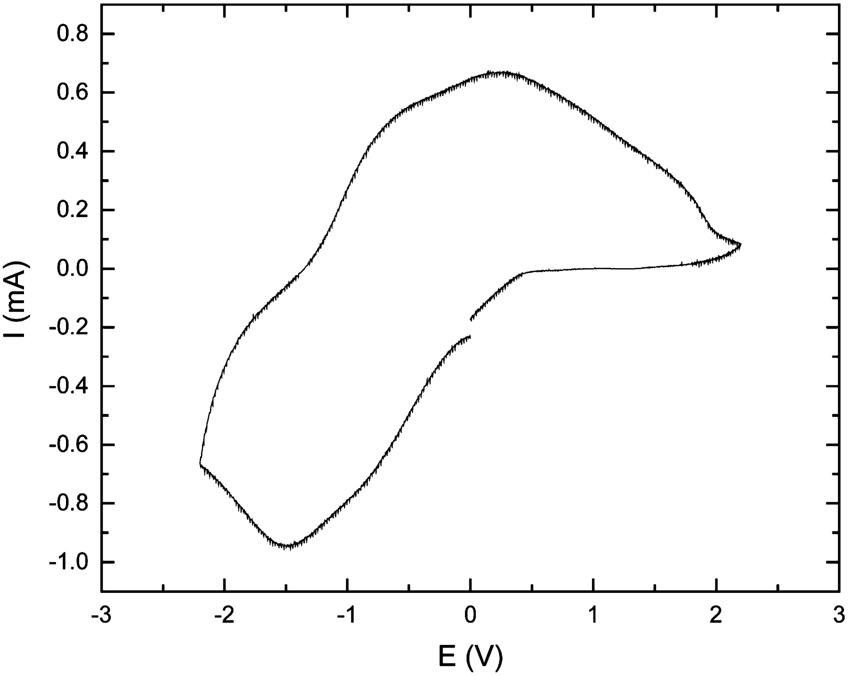
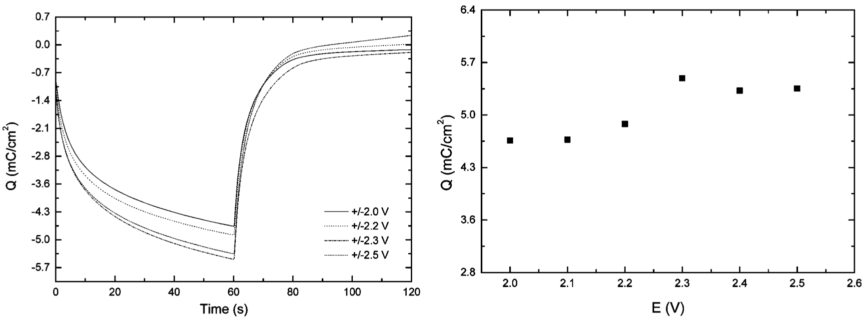


FIGURE 1 Cyclic voltammograms for ECD composed of WO_3/starch-glycerol/CeO_2-TiO_2.

in the previous work [24]. The present results show the maximum of the cathodic peak at –1.5 V and the maximum of the anodic peak at 0.25 V. The cathodic current value was –0.97 mA and the anodic current value was 0.73 mA. As it can be observed in this graph the redox process is completely reversible during 100 tested voltammetric cycles.

Figure 2 shows the charge density response of ECD containing solid electrolyte based on starch plasticized with glycerol as a function of the time for different applied potentials. As it can be observed in this figure the insertion (coloration) and extraction (bleaching) processes are very fast. In 10 s the inserted charge at –2.3 V reaches the value of about –3.6 mC/cm^2 and the next 50 s increase this value to up to –5.6 mC/cm^2, which is lower when compared with similar devices with electrolytes based on starch plasticized with ethylene glycol [24] and ECDs with PVA complexed with H_3PO_4 and H_2SO_4 [25]. However, these low charge density values promote high optical density (ΔOD) ranging from 0.24 to 0.27, depending on the applied potential during 60 s. The colouration efficiency obtained from these results is about 50 cm^2/C, which is much higher than the one observed in the devices described by Singh *et al.* [25]. The extraction occurs faster and the ECD is already transparent after 10 s of inverse potential applied. The evolution of charge density maxima for a different potential applied is shown in Figure 2b, where one can observe that for lower potentials the charge density was about 4.8 mC/cm^2 from 2.0 V to 2.2 V. The small increase in the applied potential promoted an increase in the charge density values of ECD to 5.6 mC/cm^2, after which this value is almost the same for higher potentials.

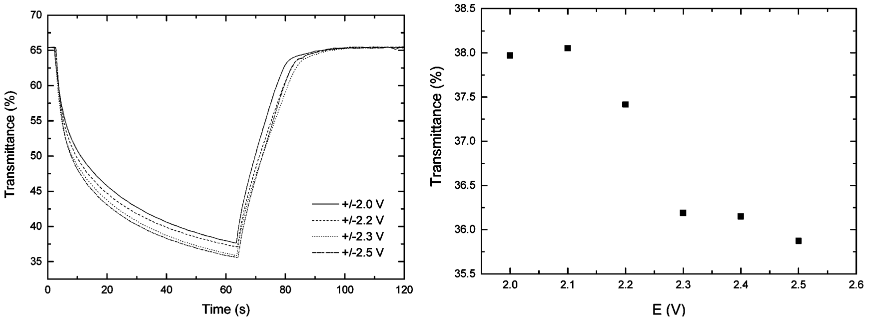


(a) (b)

FIGURE 2 Charge density versus time for ECD composed of WO_3/starch-glycerol/CeO_2-TiO_2 for different applied potentials (a) and the maximum of charge density for different potentials (b).

Figure 3 shows the change in transmittance measurements as a function of time at 630 nm for ECD composed of WO_3/starch-glycerol/CeO_2-TiO_2 during a potential step using a 60s-interval for different applied potentials and between –/+ 2.0 and –/+ 2.5 V (colored/bleached states). In this figure a very fast response can be noted after a different potential application. In 15 s the window became blue (the transmittance values decreased 20%) and the next 45 s of applied potential promoted a more intensive blue color, decreasing in more 10%. Again the reverse potential application made the window transparent in 10 s. The results of these measurements revealed that after 60 s of the application of voltage of –2 V the window darkened from 65% to 38% of transmittance, which is much more than the similar windows with smaller salt quantity in the electrolyte composition [24]. A similar color/bleaching difference was observed by Ozer and Lampert [26], where a 2.25 cm^2 device composed of glass/FTO/WO_3/polymer electrolyte (α-PEO)/NiO_xH_y/FTO/glass presented 30% and switching time of about 50 s. In the present devices a small difference was also observed in the colored state transmittance when higher potentials were applied. The increase from –2 V to –2.5 V in the applied potential promoted a small decrease in the transmittance values of up to 35.7% for the window in the colored state (Figure 3b).

The UV-Vis spectra in the range from 250 to 2500 nm for ECD can be seen in Figure 4. The windows investigated in this research presented a difference between the bleached and colored states of about 18% in the shortest wavelength (550 nm) and of about 30% for the longest wavelength (800 nm). This result is better when compared



(a) (b)

FIGURE 3 Transmittance versus time for ECD composed of WO_3/starch-glycerol/CeO_2-TiO_2 for different applied potentials (a) transmittance maxima reached after 60 s of different applied potentials (b).

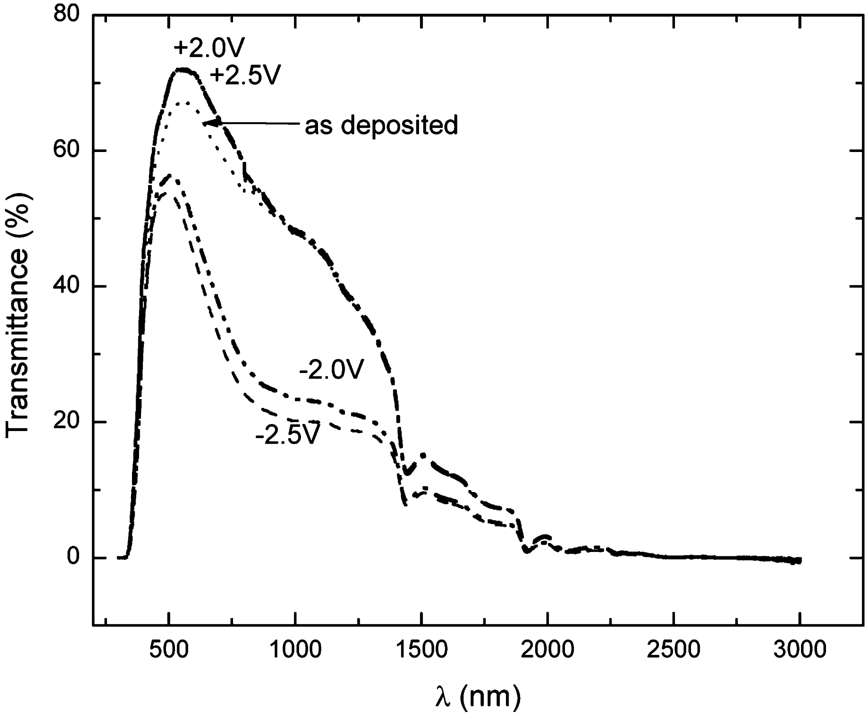


FIGURE 4 UV-Vis-NIR spectra for ECD composed of WO_3/starch-glycerol/CeO_2-TiO_2 for different applied potentials.

with ECD containing starch-based electrolyte with smaller lithium salt quantity [24] and comparable with ECDs with polymeric electrolytes listed by Heusing and Aegerter [16].

Finally the investigated ECD was subjected to the memory test showed in Figure 5. As it can be observed in this figure the sample showed a continuous decrease in the transmittance values in open circuit after polarization at –2.2 V for 120 s. The transmittance values increased from about 35% (colored state) to about 62% (bleached state) in 9 hours of open circuit. This test showed that the investigated ECD has good memory and can be very promising to be applied as electrochromic windows for architectural applications.

CONCLUSIONS

Small ECDs of 7.02 cm^2 area were performed by sandwich junctions of thin films deposited on ITO coated glass and transparent solid

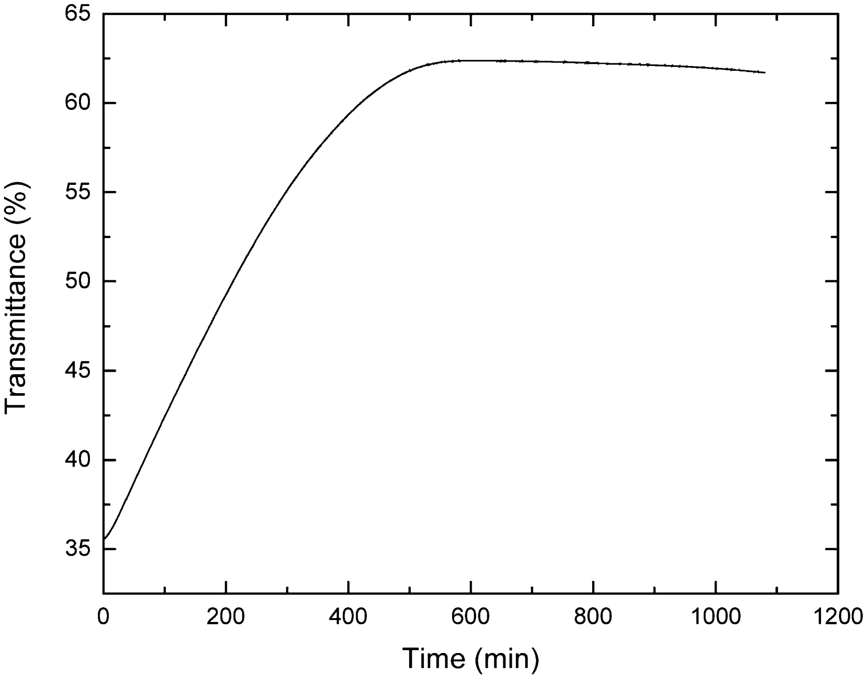


FIGURE 5 Transmittance versus time for ECD composed of WO_3/starch-glycerol/CeO_2-TiO_2 in open circuit after applying potential of –2.2 V during 120 s.

polymeric electrolyte. The ECD samples characterized by optical and electrochemical measurements, in the range from 250 to 2500 nm, showed a difference between the colored and transparent states of 18% for the shortest wavelength (550 nm) and of about 30% for the longest wavelength (800 nm). From the transmittance measurements as a function of time of ECD it was observed that the transmittance value of the window decreases 20% i.e., the window becomes blue after 15 s of applied potential and the next 45 s of applied potential promote more 10% of decrease of transmittance value. Again the reverse potential application made the window transparent in 10 s. The charge density of the devices was about 5 mC/cm^2 and the ΔOD of 0.25 yielded a colouration efficiency (η) of about 50 cm^2/C.

These results show that starch-based electrolytes are very promising materials to be applied in electrochromic devices. They are also very interesting due to the richness of starch in nature, its renewable source, low cost and very simple preparation method.

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