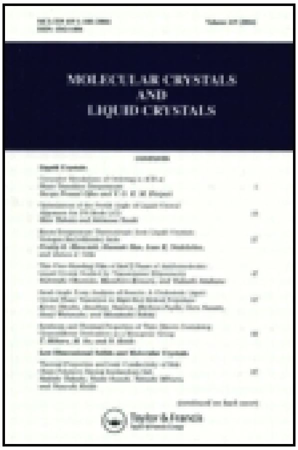

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# Electrochromic Devices with Solid Electrolytes based on Natural Polymers

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# ELECTROCHROMIC DEVICES WITH SOLID ELECTROLYTES BASED ON NATURAL POLYMERS

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*Solid-state electrochromic devices (ECDs) are of considerable technological and commercial interest because of their controllable transmission, absorption, and/or reflectance. For instance, a major application of these devices is in smart windows that can regulate the solar gains of buildings and also in glare attenuation in automobile rear view mirrors. A typical electrochromic device has a five-layer structure: GS/TC/EC/IC/IS/TC/GS, where GS is a glass substrate, TC is a transparent conductor, usually ITO (indium tin oxide) or FTO (fluorine tin oxide), EC is an electrochromic coating (typically* $WO_3$*,* $Nb_2O_5$*,* $Nb_2O_5{:}Li^+$ *or* $Nb_2O_5{-}TiO_2$*), IC is an ion conductor (solid or liquid electrolyte), in our case polymeric films based on natural polymers like starch or cellulose, and IS is an ion storage coating (typically* $CeO_2{-}TiO_2$*,* $CeO_2{-}ZrO_2$*, or* $CeO_2{-}TiO_2{-}ZrO_2$*).*

*This paper describes properties of two electrochromic devices with a* $WO_3$*/natural-polymer-based electrolyte/*$CeO_2{-}TiO_2$ *configuration.*

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

## INTRODUCTION

The development and applications of durable electrochromic devices (ECDs) has gained attention in recent years principally due to the growing use of automobile electrochromic rear view mirrors and electrochromic

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windows, called "smart windows" in architecture [1,2]. The main advantages of ECDs are the glare attenuation during night conduction for electrochromic mirrors and, the possibility of saving the energy in buildings through the control of sunlight transmission for electrochromic windows. ECD's may 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 [3] 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 [4].

The electrochromic devices can be fabricated with electrolytes of all-inorganic solid-state materials [5], organic-based materials [6] or organic-inorganic (ormolyte) based systems [7] that contain mobile species such as lithium or proton [8]. In the case of ormolytes and organic- or polymeric-based electrolytes, lithium salts are generally used as conductor species. These electrolytes are very interesting because of their low production cost and more appropriate mechanical properties than inorganic materials. Different solid polymeric electrolytes (SPEs) 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 [6] and natural polymers such as grafted hydroxyethylcellulose (HEC) [9] or modified starch [10].

Starch and cellulose are very attractive natural polymers as they are found in a wide variety in nature and obtained from renewable sources [11]. These polymers can be modified by chemical or physical plasticization with glycerol or by grafting through the condensation reaction of OH groups with mono or polyfunctional isocyanates, making possible the generation of a great variety of networks [12]. The conductivity values of some hydroxyethylcellulose (HEC) and hydroxypropylcellulose (HPC)-samples grafted with poly (ethylene oxide) diisocyanate (DPEO) and containing Li salt were about $2.08 \times 10^{-5}$ S/cm at 40°C and $8.8 \times 10^{-4}$ S/cm at 60°C [13,14]. The chemical structure of starch is very similar to that of cellulose and can be modified by either chemical or physical process like grafting with isocyanates [15] or plasticization with water or glycerol [11]. The addition of plasticizer to starch reduces its crystallinity and glass transition temperature, which is a very important parameter to obtain solid polymeric electrolytes. Solid polymeric electrolytes obtained from starch plasticized with 30% of ethylene glycol or glycerol present conductivity values of $1.29 \times 10^{-4}$ S/cm and $5.05 \times 10^{-5}$ S/cm at 30°C, respectively.

# EXPERIMENTAL

## $WO_3$ Thin Films

Tungsten trioxide ($WO_3$) thin films were prepared using the peroxo tungstenic route [16]. According to this method, metallic tungsten powder was dissolved in hydrogen peroxide (30%) and acetic acid at 0°C for 24 hours. Next, the solution was filtered and then dessicated, resulting in a transition-metal-peroxide ester derivative. This powder was then dissolved in ethanol, resulting in a transparent solution for film deposition by dip-coating method on ITO coated glass. The films were densified at 240°C for 1 h.

## $CeO_2-TiO_2$ Thin Films

Thin transparent films of $CeO_2-TiO_2$ were obtained by sol-gel process using $Ce(NH_4)(NO_3)_6$ and $Ti(OPr^i)_4$ and dip-coating technique for the deposition on ITO conducting glass [17].

## 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 down 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 $[O]/[Li] = 10$ when calculated for all starch and plasticizer oxygen atoms. The viscous solution was dispersed in Teflon plaque and dried for 48 h at 40°C. The resulting transparent film samples were stored in a dry box [10].

## Electrochromic Devices

Electrochromic devices were fabricated by a sandwich junction of glass/ITO/$WO_3$ with SPE based on natural polymer and $CeO_2-TiO_2$/ITO/glass. After isolating from ambient humidity, these devices were submitted to electrochemical measurements with a potentiostat galvanostat (Solartron 1286) controlled by a suitable software (CorrWare). *In-situ* visible spectra of the films were measured by a Hewlett-Packard spectrophotometer.

# RESULTS AND DISCUSSION

The changes in cyclic voltammograms of an ECD composed of $WO_3$/starch-glycerol/$CeO_2-TiO_2$ were observed as a function of number of

$WO_3$ deposited layers (Fig. 1). It can be seen that the cathodic and anodic peaks are better defined for the ECD with two layers of $WO_3$ films. An increase in cathodic and anodic current values with an increase of the number of $WO_3$ layers is also noted. The magnitude of cathodic current increases from $-0.234$ mA for a single $WO_3$-layer film to $-0.246$ mA for a double $WO_3$-layer film. Similarly, the anodic current increases from 0.197 mA for a single layer to 0.241 mA for an ECD with a double $WO_3$-layer film. It can be also observed that the current maxima occur at almost the same potentials for single or double layers of $WO_3$.

The results of measurements of change in transmittance at 550 nm as a function of time for ECDs composed of $WO_3$/starch-glycerol/$CeO_2-TiO_2$ during a potential step using a 100 s interval and between $-2.0$ V (colored state) and $+2.0$ V (bleaching state) are shown in Figure 2. A very fast response can be noted after potential application for both single- and double-$WO_3$-layer windows. In 10 s the window became dark and application of the reverse potential again made the window transparent in 5 s. Both windows show about 16% difference between bleached and colored states. However, it was observed that initially a single-$WO_3$-layer ECD is darker (~8% poorer transmittance) than a double-$WO_3$-layer ECD. Another remarkable difference between both types of ECDs is in the curves representing the coloring process. It seems that double-$WO_3$-layer ECDs reach the colored state much more easily. After 10 first seconds of the insertion of lithium ions that change the color of device, these ECDs became almost blue and there was no more charge insertion. On the other hand, single-$WO_3$-layer ECDs in the first 10 seconds of negative potential application became also colored, but this coloring process continued during the potential application. This performance difference between both types of devices is certainly due to the different $WO_3$ film thicknesses, as observed by Avellaneda *et al.* [18].

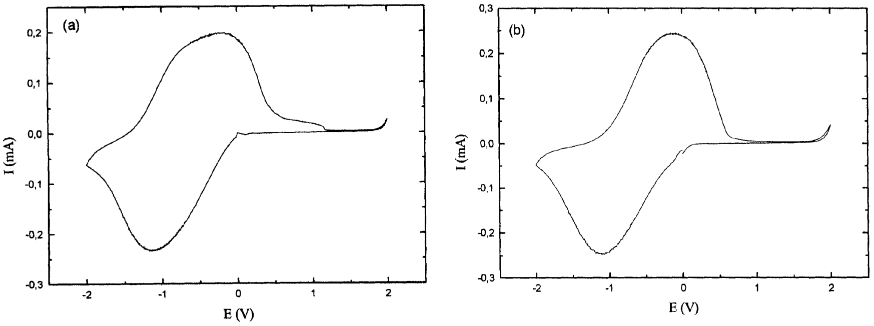

**FIGURE 1** Cyclic voltammograms for ECDs composed of $WO_3$/starch-glycerol/$CeO_2-TiO_2$ with (a) single and (b) double layers of $WO_3$ films.

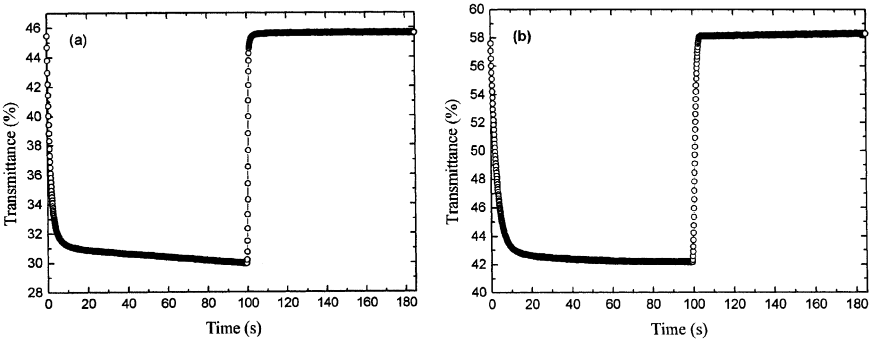

**FIGURE 2** Transmittance versus time for ECD composed of $WO_3$/starch-glycerol/$CeO_2$–$TiO_2$ with (a) single and (b) double layers of $WO_3$ films.

The transmission difference between transparent and blue color states was about 30% (Fig. 3) in the spectral range from 700 to 1500 nm for the electrochromic window made with two layers of $WO_3$ films.

Figure 4 shows the current and charge response of an ECD containing solid electrolyte based on starch plasticized with ethylene glycol (EG) as a function of time in a step-like applied potential switching cycle. As can be observed, the insertion (coloration) and extraction (bleaching) processes are very fast. In 10 s the inserted charge reaches the value of about $-6.8\,\mathrm{mC/cm^2}$ and during the next 50 s further increases to $-17.3\,\mathrm{mC/cm^2}$.

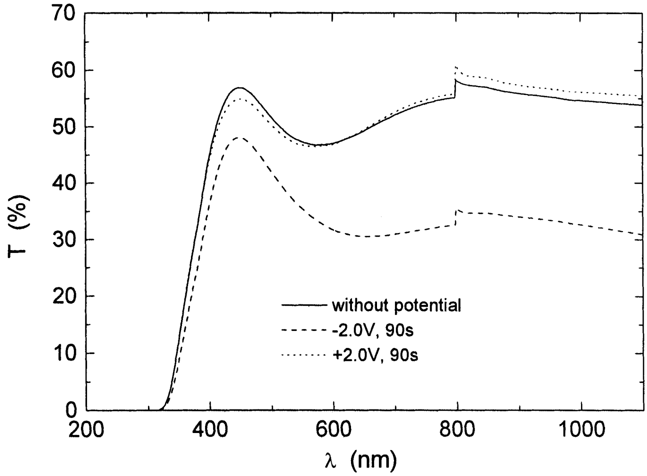

**FIGURE 3** UV-Vis-NIR spectra for ECD composed of $WO_3$/starch-glycerol/$CeO_2$–$TiO_2$ with two layers of $WO_3$ films.

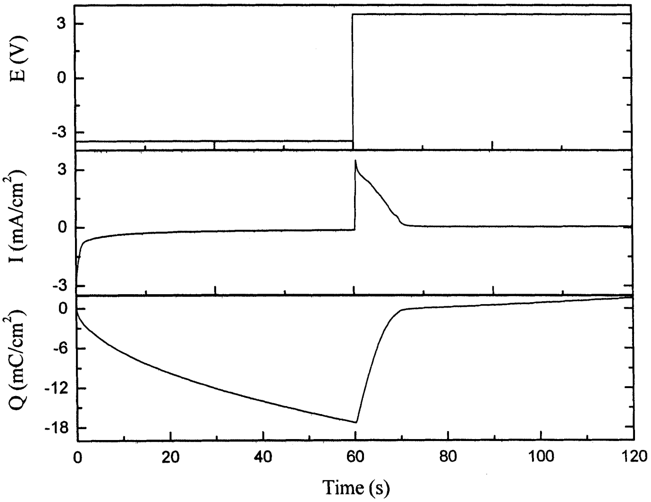

**FIGURE 4** Electrochemical measurements for ECD composed by $WO_3$/starch-EG/$CeO_2-TiO_2$ with two layers of $WO_3$ films.

The extraction occurs faster, and after 10 s of inverse potential applied to the ECD, the device is already transparent. In this case it seems that the kinetics of insertion/extraction processes is faster in ECDs containing starch plasticized with EG, even though both types of ECDs were made with double-$WO_3$-layer films.

Under application of potential scan, the films exhibit coloring (−3.0 V) and bleaching (+3.0 V) changes from blue to transparent. The transmission difference between blue and transparent color states was ~30% in the spectral range from 500 to 650 nm, and 50% in the spectral range from 700 to 1100 nm (Figure 5). This electrochromic performance is very similar to the results reported by Orel *et al.* [5]. Both types of films showed excellent performance, with the original transmittance value restored in the transparent state.

## CONCLUSION

Small-area ECDs were fabricated in the form of sandwich junctions of thin films deposited on ITO-coated glass and transparent solid polymeric electrolyte. $WO_3$ was used as electrochromic film and $CeO_2-TiO_2$ was used as counter electrode film. Solid polymeric electrolytes were obtained form starch plasticized with glycerol or ethylene glycol and containing $LiClO_4$ salt. The ECD samples characterized by electrochemical and optical

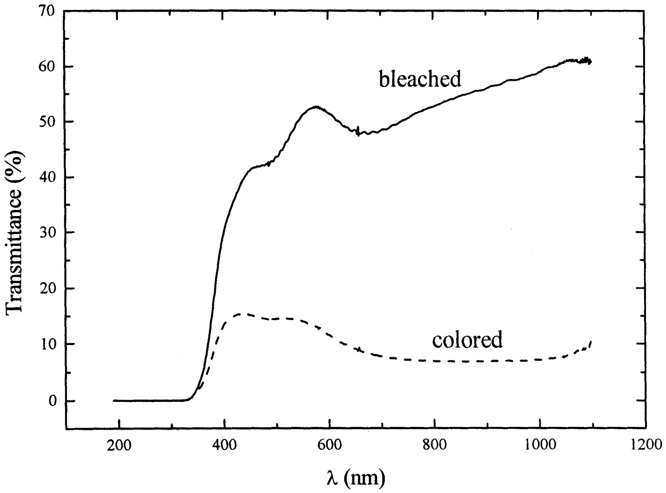

**FIGURE 5** UV-Vis-NIR spectra for an ECD composed of $WO_3$/starch-EG/$CeO_2$–$TiO_2$ with two layers of $WO_3$ films.

measurements, the latter in the range from 200 to 1100 nm, showed very good response. The difference in transmittance between colored and transparent states was 30% for ECD with starch plasticized with glycerol and 50% for starch plasticized with ethylene glycol. It was also observed that the ECDs became blue after 10 s when negative potential was applied and that this process was slower than the extraction process. The best results were achieved with ECDs made with two layers of $WO_3$ films. These preliminary results show that starch-based electrolytes are very promising materials to be applied in electrochromic devices. They are also very interesting due to the abundance of starch in nature, its renewable sources, low cost, and very simple preparation method.

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