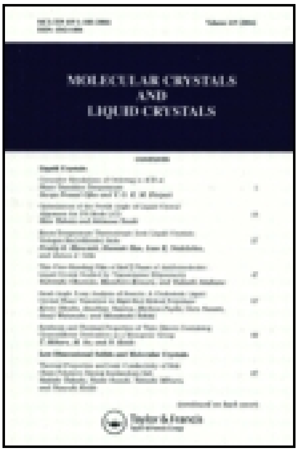

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

All Sol-Gel Electrochromic Smart Windows:CeO 2 -TiO 2 /Ormolyte/WO 3

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Version of record first published: 29 Oct 2010

To cite this article: C. O. Avellaneda, K. Dahmouche & L. O. S. Bulhões (2002): All Sol-Gel Electrochromic Smart Windows:CeO 2 -TiO 2 /Ormolyte/WO 3, Molecular Crystals and Liquid Crystals, 374:1, 113-118

To link to this article: http://dx.doi.org/10.1080/10587250210437

Mol. Cryst. Liq. Cryst., Vol. 374, pp. 113-118

1058-725X/02 $12.00 + .00

All Sol-Gel Electrochromic Smart Windows: CeO_2-TiO_2/Ormolyte/WO_3

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A solid state system having the configuration WO_3/Ormolyte/CeO_2-TiO_2 has been assembled. Syntheses routes for tungsten oxide WO_3, and cerium-titanium CeO_2-TiO_2 oxide sols, were developed.
A novel solid electrolyte - Ormolyte is reported, which were obtained by the sol-gel process, they have a chemical stability due to the covalent bonds between the inorganic and organic phase, and were prepared with different [O]/[L] ratios, being the best for [O]/[L]=15.
The variation of transmittance of the electrochromic device using the ormolyte [O]/[L]=15 was 35 % (colored state) and 77 % (bleached state).

Keywords: Smart windows, WO_3, CeO_2-TiO_2, Ormolyte.

INTRODUCTION

There is a growing `interest in the development of solid state electrochromic devices (ECD) for application in smart windows, large area displays and rear view mirror due to their technological interest

[1]. The sol-gel process is a less expensive route to produce thin films over large areas and offers the advantage of controlling the film microstructure, which strongly affects the kinetics, durability and coloring efficiency.

Tungsten trioxide (WO_3) is the most studied electrochromic material and it is considered one of the best materials for electrochromic devices. Several sol-gel routes have been developed to produce WO_3 thin films such as acidification of sodium tunsgtate, peroxopolytungstic acid, tungsten alkoxide and peroxotungstenic route [2].

Thin films of CeO_2-TiO_2 are a promising material to be used in ECD as counter-electrode, due to their electro-optical response. Baudry *et al.* [3] have reported the first results concerning cerium-titanium sols prepared dissolving ammonium hexanitratocerate and titanium alkoxide in different alcohols. Keómany *et al.* [4] have obtained sols of CeO_2-TiO_2 by alkoxides $Ce(OBu^s)_4$ and $Ti(OBu^s)_4$, also in our laboratory film of CeO_2-TiO_2 was prepared using the sonocatalytic route [5].

One of the most important part of an electrochromic device is the ion-conductive electrolyte. Recently, several systems using ormolytes have been developed. Munro *et al.* [6] and Orel *et al.* [7] developed an electrochromic device using electrolytes obtained from the hydrolysis of organically modified silane precursors such as glycidocypropyltrimethoxysilane (GPTS) or glycidyloxypropyltrimethoxysilane (GLYMO).

A promising family for use in electrochromic windows is constituted by silica-polyethyleneglycol Ormolytes [8]. These materials exhibit good ionic conductivity, high transparency and satisfactory mechanical properties such as good flexibility and high Young modulus.

The aim of the present paper is to describe the development of a new all sol-gel electrochromic device based on WO_3/Silica-PEG/CeO_2-TiO_2. The synthesis of the electrochromic electrode (WO_3), the counter-electrode (CeO_2-TiO_2) and the silica-polyethyleneglycol Ormolyte is presented. The electrochemical and optical properties of each coating is analyzed.

EXPERIMENTAL

WO_3 sol was prepared according to a previous paper [9]. Metallic tungsten was dissolved in hydrogen peroxyde (30%) and acetic acid at 0°C during 24 hours. The solution was filtered and then evaporated to dryness, resulting in a transition metal-peroxyde ester derivative. The film was deposited by dip-coating technique on ITO-(Asahi Glass, 20Ω/□) at a speed of 10 cm/min. Coatings were dried in air at room temperature and heat-treated at 240°C during 1h.

Thin films of CeO_2-TiO_2: with [Ce]/[Ti] = 0.5was prepared as previous paper [5], which show a good electrochemical and optical responses.

The preparation of the electrolyte has already been described [19]. Equimolar amounts of 3-isocyanatopropyltriethoxysilane and O,O'Bis (2aminopropyl)polyethyleneglycol$_{500}$, were stirred together in tetrahydrofuran (THF) under reflux for 6 h. THF was then evaporated and a pure hybrid precursor $_3$(OEt)Si-PEG$_{500}$-Si(OEt)$_3$ was obtained.

RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammograms obtained for WO_3:5 %Li^+ films. When a more negative potential is applied, an increase of the cathodic current is observed being this process associated with oxide reduction and lithium ions intercalation. In the cathodic region from –0.1 V to –0.7 V and after the reversal of the potential at –0.7 V, anodic current starts to flow which corresponds to the deintercalation process with an anodic peak at –0.1V. The changes of color of the WO_3 film was analyzed by *in situ* visible transmittance measurements in the wavelength range from 350nm to 800nm (Figure 1). The results show that the film had a different transmission, giving a 25 % in the colored state and 80 % for the bleached state.

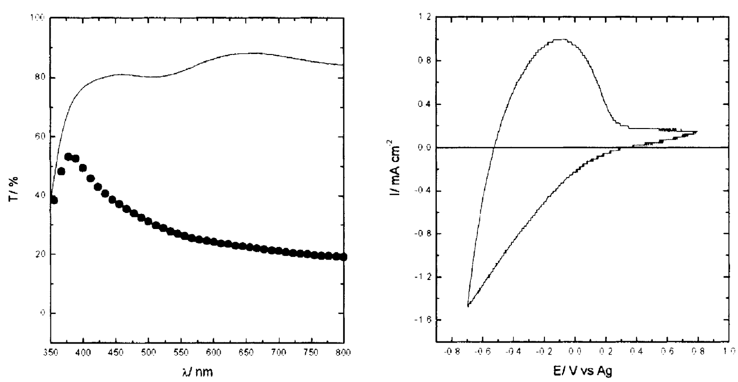

FIGURE 1. Optical transmittance (– oxidized and ••• reduced film) and cyclic voltammetry (v= 50 mV/s) of the WO_3 thin film doped with 5 % of lithium in 0.1M, $LiClO_4$ in propylene carbonate solutions.

The insertion/extraction process for the CeO_2-TiO_2 films does not exhibit a color change, remaining transparent. A density charge of 16 mC/cm^2 was obtained for one dip layer.

The ionic conductivity for the ormolyte was 10^{-5} – 10^{-6} S/cm at room temperature. The ratio [O]/[Li]=15, where the oxygen is from the ether of the PEG corresponds to the maximum of ionic conductivity, while for [O]/[Li]=8 a maximum of ionic conduction is the value obtained for pure organic polymers [9].

An ECD was prepared using as Silica-PEG_{500}: with [O]/[Li]=15. The color change of this was analyzed by transmittance measurements in the wavelength range from 350 nm to 800nm (Figure 2).

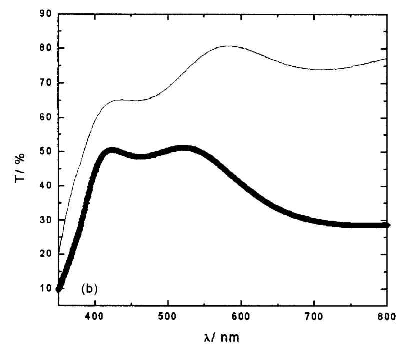

FIGURE 2. Optical transmittance of the ECD for the ormolyte [O]/[Li] =15.

The results shown that ECD display a different spectral transmission modulation, where the device with [O]/[Li]=15 exhibits a electrochromic transmission, giving a 35% (colored state) and 77% (bleaching state) at at λ=633 nm. The results are associated with the performance of the ionic conductor, which exhibits the best ionic conductivity for the ratio [O]/[Li]=15.

CONCLUSION

The sol-gel process was used to produce a new all sol-gel ECD, where the all components WO_3, CeO_2-TiO_2 and electrolyte showed good properties.. Tests on smaller ECD gave a change in transmission from 77 % (bleaching state) to 35 % (colored state) at λ=633 nm.

Acknowledgment

The authors thank FAPESP, CNPq and FINEP for financial support

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