

STUDIES ON QUASI SOLID STATE ELECTROCHROMIC SMART WINDOWS BASED ON TiO_2 AND SnO_2

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INTRODUCTION

Electrochromic devices (ECDs) are opto-electrochemical systems that change their optical properties, mainly their transmittance, when a voltage is applied to them. This interesting behavior leads to many applications, such as windows, sunroofs, shades, visor or rear view mirrors for automotive and mass transportation applications, architectural windows, skylight, displays, light filter and screens for light pipes, displays and other electro-optical devices (Barbadosa 2008). Electrochromic phenomena result from the electrochemical insertion/extraction of electrons and ions (singly charged small ions such as H^+ or Li^+) into inorganic materials. Even after many years of development the main research effort in this domain continues to be focused on using thin tungsten oxide layers as electrochromic components (Avellaneda 2008). The favorable characteristics of this material include reversible transmittance modulation when the electric field is established, reversibility to cycle operation and high stability during operation, particularly in devices based on polymer electrolytes doped with lithium ions (Sonmez 2005).

However, all these devices generally consist of expensive oxides such as WO_3 , and CeO_2 as electrochromic and counter electrodes respectively with electrolytes consisting with volatile solvents. These factors, especially the fact that the liquid electrolyte causes significant technological problems associated with device sealing and stability, affect the commercial application of ECDs. Therefore, there is a considerable interest in both the development of a solid-state electrolyte for these devices and replacement of expensive oxide materials with inexpensive and readily available materials.

Therefore, in this paper we describe the possible assembly of new prototype quasi solid state electrochromic device based on a four layer sandwich structure with the FTO glass/ TiO_2 /Poly(methyl methacrylate) (PMMA) polymer electrolyte/ SnO_2 /FTO glass configuration as an alternative system for these expensive devices.

METHODOLOGY

The electrolyte used for the ECD has been prepared according to the following recipe. One gram of PMMA was dispersed in 4.5 g of propylene carbonate (PC), 3 g of ethylene carbonate (EC) and heated under magnetic stirring for a few minutes up to 50 °C to complete dissolution. Then, 0.5 g of LiClO_4 , 0.5 g of LiCF_3SO_3 and 0.33g (one drop) of ionic liquid EMITFSI were added to this solution under stirring. This viscous solution was then cooled down to 30 °C and poured on Petri plates to form transparent films.

Electrochromic mesoporous TiO_2 films were prepared on fluorine-doped conducting tin oxide (FTO) glasses (sheet resistance $\sim 16 \Omega/\square$) by the “doctor blade” method using a TiO_2 paste

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from Solaronix nanoxide (Solaronix T) and then sintered at 500 °C for 1 h. The thicknesses of the TiO₂ electrodes were found to be ~ 4–5 µm (Dektak profilometer, Veeco, Dektack 3). Transparent conductive SnO₂ oxide films were deposited on FTO glass substrates by spin coating a colloidal solution of SnO₂ at 5000 rpm for 1 minute and sintered at 500 °C for 1 hour and cooled down to room temperature. Electrochromic devices having the configuration FTO glass/TiO₂/polymer electrolyte /SnO₂/FTO glass and a size of 5x5 cm² were fabricated by sandwiching the two pieces of the above thin film coated glasses with the polymer electrolytes. Devices were tested by cycling between potentials of 0V and +4.0 V and obtained the transmissions at each voltage using Shimadzu 5800 spectrophotometer in the wavelength range between 350 and 1000 nm.

Total ionic conductivities of electrolyte samples were determined using a sample holder equipped with gold blocking electrodes and located within a Buchi TO 50 oven. The sample temperature was evaluated by means of a type K thermocouple placed close to the electrolyte film and impedance measurements were carried out at frequencies between 96 kHz and 500 mHz with a Solartron 1250 FRA and 1286 ECI, over a temperature range of 20–100 °C.

RESULTS AND DISCUSSION

Figure 1 shows the average transmittance of the electrochromic devices with the configuration, FTO glass/TiO₂/polymer electrolyte /SnO₂/FTO glass at different status in the visible region. Electrochemical status of this device was changed by applying several voltages for 30 seconds using an external power supply. As depicted in the figure 1 and 2, the colour of the active layer of these devices was subjected to change from its transparent state to blue, associated with the reduction of TiO₂ and the simultaneous insertion of Li⁺ due to the external applied voltage. Polarity changes of this external voltage resulted in oxidation of TiO₂ and device returned to its initial state. As can be seen from the figure 1, as prepared devices showed more than 65% transmittance in the visible region of the spectrum.

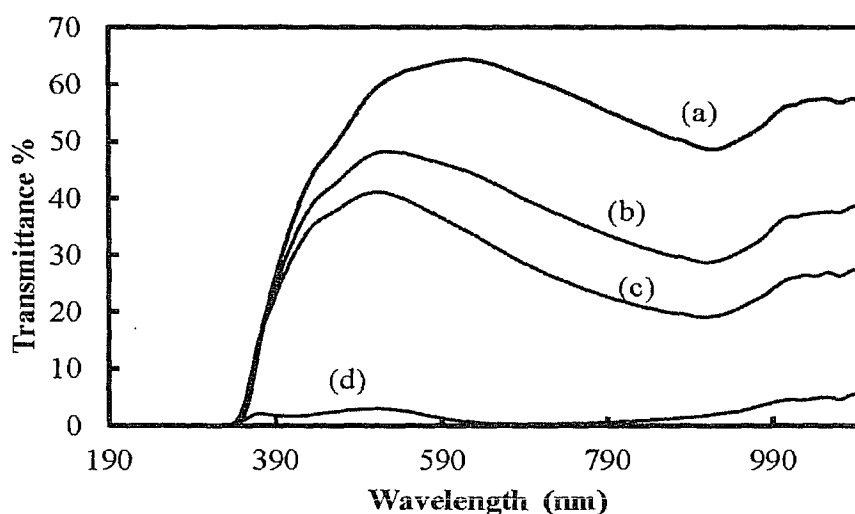


Fig 1. UV-vis-NIR spectra for the ECD measured at different voltages (a) 0 V, (b) 3.5 V (c) 3.75 V(d) 4.0 V

Fig. 3 shows the variation of the conductivity of the polymer electrolyte as a function of temperature in the range 26 °C to 80 °C. The conductivity value increases from $1.74 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature to $7.11 \times 10^{-4} \text{ S cm}^{-1}$ at 70 °C and follows an Arrhenius thermally activated process expressed as $\sigma(T) = \sigma_0 \exp(-E_a/kT)$, where k is the Boltzmann constant, T is the temperature and E_a is the activation energy. The value extracted from the data is $E_a = 49.5 \text{ kJ/mol}$.

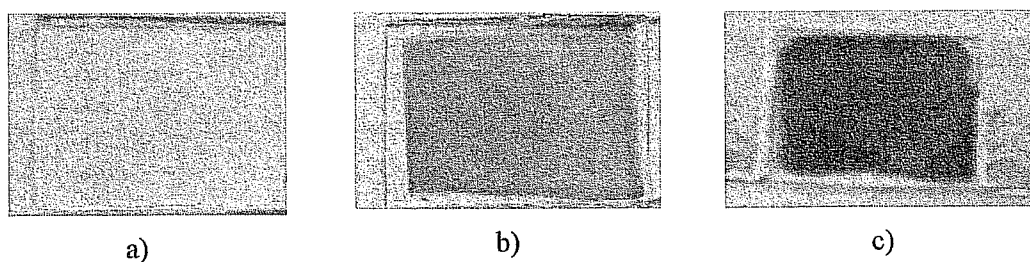


Fig.2 Different electrochemical statues of the device FTO/TiO₂/PMMA electrolyte/SnO₂/TiO₂ (a) as prepared (b) coloured (partially reduced) (c) Highly reduced .

The reproducibility of recorded conductivities was confirmed by comparing the results obtained for a sample subjected to two heating–cooling–heating cycles. This procedure demonstrated the accurate operation of the electrolyte and the mechanical stability of it.

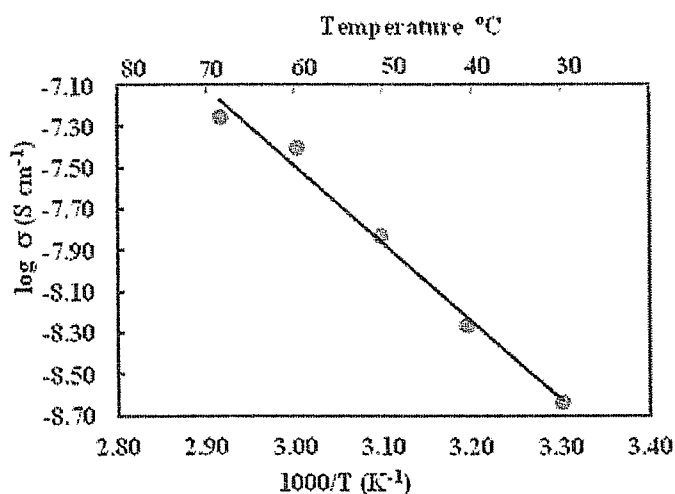


Fig. 3. Temperature dependence of the Li⁺ conductivity of the PMMA based electrolyte.

Fig. 4 shows a typical X-ray diffraction pattern obtained for the PMMA based electrolyte measured at room temperature. No crystalline peaks were observed and only a broad weak peak was seen at 2θ~22°, with a shoulder at 2θ~48°. This means that the electrolyte has an X-ray amorphous structure.

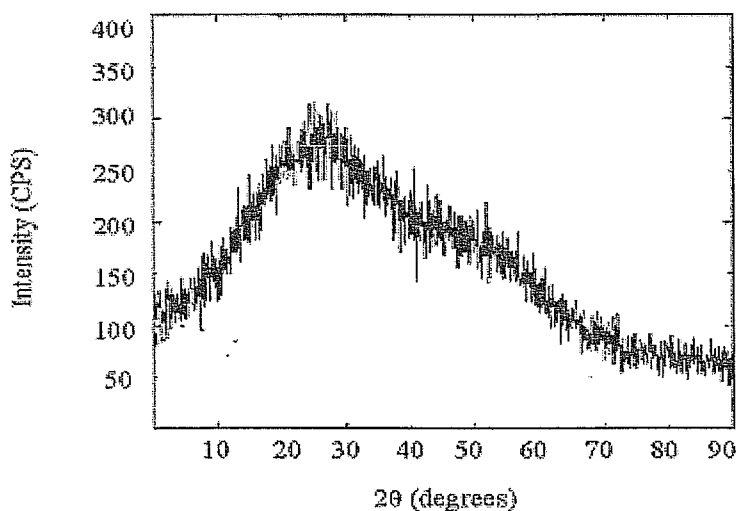


Fig. 4. Typical X-ray diffraction pattern of the gelatin-based electrolyte.

CONCLUSIONS/RECOMMENDATIONS

In order to explore the possibilities of replacing expensive oxide semiconductors in electrochromic devices, readily available low cost TiO_2 and SnO_2 were employed in the fabrication of ECDs and tested their performances. A reversible color change between blue and colorless was observed when an appropriate voltage was applied repeatedly to the electrochromic device. A difference in the absorbance between the coloring and bleaching states was clearly found. The kinetics of the bleaching of the device is faster than the coloration. The electrochromic characteristics were consequently evaluated with the transmittance change. On the other hand, PMMA based electrolytes are promising materials to be applied in ECDs because, it is cheap, easy to handle and easy to prepare. The samples were found predominantly amorphous with ionic conductivity values increasing according to an Arrhenius law as a function of temperature.

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