

## **Electrochromic performance of WO<sub>3</sub> thin films with solvent-free viscous electrolytes based on polyethylene glycol-titanium oxide nanocomposites**

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### **ABSTRACT**

Polymeric nanocomposites of polyethylene glycol (PEG) with titanium oxide compound, PEG-Ti, have been prepared by sol-gel method from liquid PEG and titanium isopropoxide in acidic medium. Lithium salt (LiX) has been added into PEG-Ti to form PEG-Ti-LiX polymeric electrolytes. Electrochromic devices based on tungsten oxide thin films and PEG-Ti-LiX electrolyte may show excellent optical transmittance transient, however it depends on the type of lithium salt used during the sol-gel process. With LiI, the color change speed of the devices is very fast but they show a yellow color at bleaching state. The use of LiClO<sub>4</sub> makes the devices totally transparent in visible region but the optical contrast is small. Possible molecular structure model of these polymeric electrolytes have been analyzed to explain the relation between electrochromic performance of tungsten oxide and electrolyte chemical composition.

### **INTRODUCTION**

Electrolytes work as ionic conductor -reservoir and as a separator of electrodes in electrochemical devices such as lithium batteries, dye-sensitized solar cells, electrochromic windows and sensors [1,2]. They can be classified as liquid, viscous or solid according to their viscosity. An electrolyte with volatile solvents shows fast ionic conduction, but the leak or evaporation of solvents is inevitable. The use of this type of electrolytes obligates a rigorous device sealing to reduce or prevent solvent loss. On the other hand, electrolytes without volatile solvents, or simply solvent-free electrolytes, are chemically stable and easy to be handled, which is desirable for device applications.

A polymer electrolyte is usually prepared by dissolving a salt in a polymeric matrix. PEO is a commercially available polyether: HO-(CH<sub>2</sub>-CH<sub>2</sub>-O)<sub>n</sub>H. As the lithium salt is added into it, the ether oxygen atoms of the repetitive unit are responsible to dissociate such salt, interact with lithium ions and transport them from one to another. In comparison with those with solvents, the disadvantage of solvent-free electrolytes in comparison with those with solvents is their relatively low ionic conductivity, which can prejudice charge transfer process at electrode/electrolyte interfaces of electrochemical devices. Several approaches have been reported to improve the ionic conductivity of polymeric electrolytes, and one of them is the use of composite materials; those of PEO composites with ceramic nanoparticles (TiO<sub>2</sub>, SiO<sub>2</sub>, etc.) show better ionic conductivity than that of pure salt-in-polymer electrolytes [3-6]. In a recent work we reported a PEG-Ti nanocomposite made by sol-gel route. The electrochromic performance of tungsten oxide with PEG-Ti-LiI as electrolyte was improved [7,8]. In this work

we will show the effect of type of lithium salts as well as source of acid used in sol-gel process on the electrochromic performance of tungsten oxide thin films. Moreover we will analyze such effect along with a major change in titanium molar concentration in the polymeric composites.

## EXPERIMENTAL

Tungsten peroxy-ester solution was prepared by sol-gel method according to Cronin et. al. [9]. This solution was spin-coated onto clean conductive glass (ITO) by 2000 rpm for 60 s, followed by the annealing in air at 250 °C for 1 h. The obtained thin films by this process were amorphous tungsten oxide of about 350 nm thick ready for electrochromic device use. PEG-Ti composite materials were prepared by sol-gel method starting from dissolving titanium isopropoxide in an acidic solution with PEG of molecular weight equal to 600 and 2-propanol under stirring, as reported previously [7]. Either LiI or LiClO<sub>4</sub> was added in viscous PEG-Ti composites to form PEG-Ti-LiX electrolytes. The molar ration between an average PEG molecule and titanium atom was chosen as PEG:Ti = 24:1, 8:1 and 4:1. PEG-Ti-LiI and PEG-Ti-LiClO<sub>4</sub> electrolytes were prepared by dissolving LiI or LiClO<sub>4</sub> in viscous PEG-Ti complexes with a molar ratio of one atom of Li into 8 oxygen atoms in PEG. All of these electrolytes were vacuum-dried at 80 °C for 3 h before use.

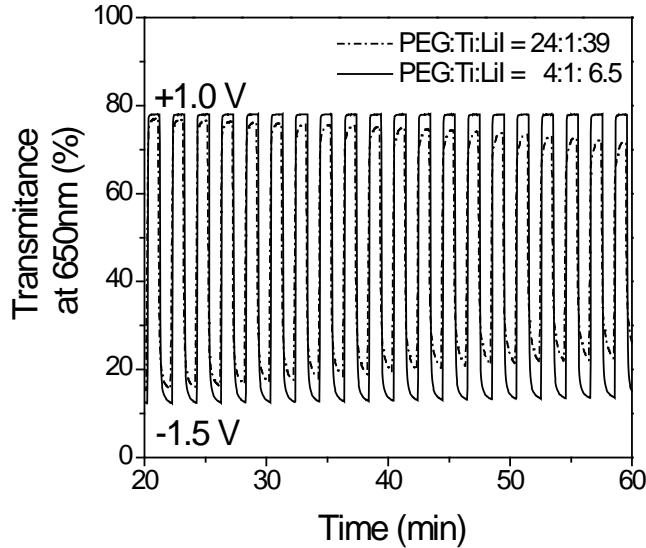
Tungsten oxide electrochromic devices were prepared by collocating polymer electrolyte (PE) between ITO glass and WO<sub>3</sub> coating on ITO to form a device configuration of ITO/WO<sub>3</sub>/PE/ITO. Transient optical transmittance curves of tungsten oxide based devices with different PEG-Ti-LiX electrolytes were determined under positive and negative potential bias. Electrochemical impedance spectroscopy (EIS) study was realized at room temperature (25 °C) on tungsten oxide based electrochromic devices with different polymeric electrolytes by using a VoltaLab PGZ301, Dynamic-EIS system. The DC potential was -1.5 or -2.0 V and the amplitude of the AC signal was 50 mV. The frequency varied from 100 mHz to 100 kHz.

## RESULTS AND DISCUSSION

The incorporation of titanium oxide compound in PEG changes its physical appearance. The increasing viscosity of PEG-Ti composite materials with the increasing titanium precursor amount in original sol-gel solution is a clear evidence of the formation of longer or crosslinked molecular chains of PEG by titanium compounds in polymeric composites. The formation of titanium oxide compounds in viscous PEG-Ti (8:1) complexes was observed by Transmission Electron Microscope (not shown here). The image shows a kind of dark pots that are related to interferences of crystalline planes (Moire bands), which indicate that those particles or clusters are crystalline. The average diameter of those dark areas was about 1.8 to 7 nm.

As reported before, the oxidation reversibility of tungsten oxide has improved considerably by introducing titanium oxide compound inside the PEG-LiI electrolytes with a PEG:Ti molar ratio equal to 24:1, but the reduction one was still poor [7]. Now the titanium percentage in the polymer composites has been increased up to four molecules of PEG vs. one atom of titanium. Figure 1 shows the transient optical transmittance curves at 650 nm of ITO/WO<sub>3</sub>/PE/ITO devices under oxidation (+1.0 V) and reduction (-1.5 V) bias, in which PE were PEG-Ti-LiI with PEG:Ti

molar ratio as 24:1 and 4:1. This curve indicates that the more the titanium percentage, the faster the color change speed of the devices.

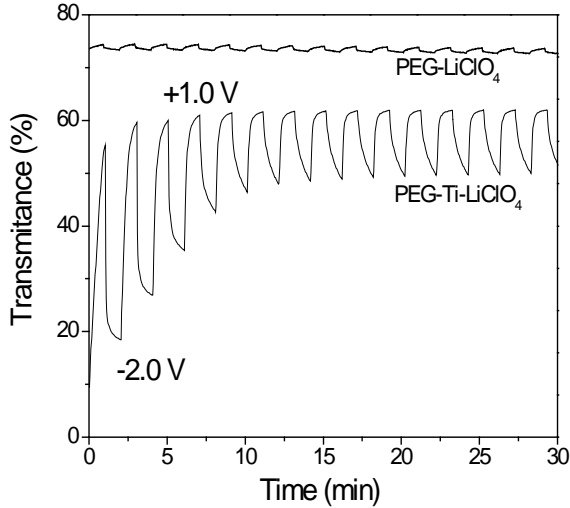


**Figure 1.** Optical transmittance transients at 650 nm of ITO/WO<sub>3</sub>/PE/ITO devices with polymer electrolyte (PE) as PEG-Ti-LiI with PEG:Ti molar ratio of 4:1 and 24:1.

The fast oxidation speed should come from a fast lithium ion insertion into the electrochromic element as it was positively polarized. A faster cation insertion should be related to better lithium iodide dissociation inside the polymer matrix. The formation of iodine and tri-iodide inside the PEG-Ti composite materials after addition of LiI indicates that iodide ions have been oxidized and, at the same time, titanium oxide compounds should be partially negative, which is chemically possible considering that tetragonal titanium element has two available molecular orbitals in 3d electron level that permit the incorporation of two electrons with opposite spins. Since the titanium oxide compounds are associated with PEG macromolecules to form crosslinked network or larger molecular chains, the average size of negative charges in the composite electrolytes becomes much larger than that of iodides in PEG. Under external polarization, the separation of lithium ions from negative charges inside the composite polymer should be easier and, as a result, the cation insertion process should be faster. In the case of reduction, the improvement of colouring speed is also notable but not so large, because of different mechanisms of charge transfers in each process [7].

The formation of iodine and tri-iodides inside the PEG-Ti composites after the dissolution of LiI makes the suggestion of substitution this by some other lithium salt that is free of iodides and may avoid the yellow color of tungsten oxide during the bleaching process. Lithium perchlorate (LiClO<sub>4</sub>) was chosen to be added into PEG-Ti composites to form PEG-Ti-LiClO<sub>4</sub> electrolytes due to its colorless appearance and its good solubility in most of the solvents. Effectively the substitution of LiI by LiClO<sub>4</sub> leads to more transparent PEG-Ti-LiClO<sub>4</sub> composite electrolytes. However, the WO<sub>3</sub> electrochromic devices with PEG-LiClO<sub>4</sub> electrolyte (without titanium oxide compound) show very small electrochromic capacity under +1 V and -2 V bias (Figure 2); with -1.5 V the tungsten oxide could not be colored in this case. When titanium oxide compounds are incorporated in the electrolytes, the electrochromic performance of the corresponding WO<sub>3</sub> devices is improved, although the coloring process is not quite completed under -2V reduction

polarization, and color change speeds are slow. Although Figure 2 only exhibits the electrochromic performance of one PEG-Ti-LiClO<sub>4</sub> device (PEG:Ti:LiClO<sub>4</sub> = 8:1:13), the variation in titanium concentration did not improved the observed electrochromic properties in these devices.



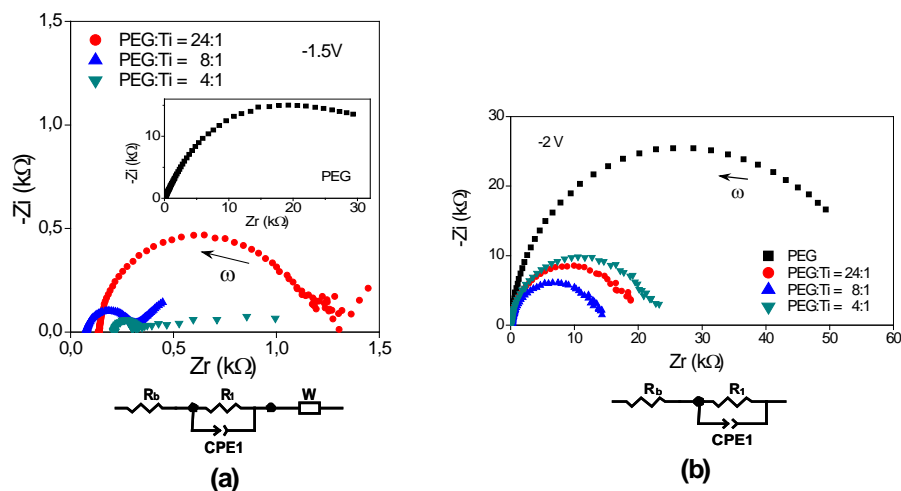
**Figure 2.** Optical transmittance transients at 650 nm of ITO/WO<sub>3</sub>/PE/ITO devices with polymer electrolyte (PE) as PEG-LiClO<sub>4</sub> or PEG-Ti-LiClO<sub>4</sub> with PEG:Ti molar ratio of 8:1.

The poor electrochromic performance of WO<sub>3</sub> with lithium perchlorate comes first from the lower dissociation of LiClO<sub>4</sub> in PEG; it took longer time to dissolve this than LiI in the polymer as well as in the PEG-Ti composites. Secondly, there must be some kind of interactions between titanium oxide compounds with ClO<sub>4</sub><sup>-</sup> ions that results in a better dissociation of LiClO<sub>4</sub> in comparison with that in PEG only, provided the electrochromic performance of the devices has been improved again with the presence of titanium oxide compounds. However, these interactions are not sufficiently strong to lead charge transfer between perchlorate ions and titanium complexes, and as a result, the electrochromic performance improvement of tungsten oxide devices is limited.

The effect of different lithium salts in electrolytes on electrochromic behavior of tungsten oxide thin films can be compared by studying the charge transfer phenomena at electrolyte/electrode interfaces observed with electrochemical impedance spectroscopy (EIS). Figure 3a shows Nyquist plots of tungsten oxide based electrochromic devices (ECDs) with PEG-Ti-LiI as electrolytes at -1.5 V polarization on WO<sub>3</sub> electrode and its equivalent circuit, and Figure 3b the same plots for ECDs with PEG-Ti-LiClO<sub>4</sub> as electrolytes.

In all cases semicircle form of the plots at middle-low frequency range is observed, indicating a charge transfer process occurred at interface of electrolyte with tungsten oxide electrode under reduction process by negative bias. It is observed that ionic resistance in electrolyte (high frequency resistance **R<sub>b</sub>**) is lower with LiI than with LiClO<sub>4</sub>, as well as the charge transfer resistance at the interface of electrolyte/tungsten oxide electrode (**R<sub>1</sub>**). The charge storage capacity at the same interface (**CPE1**) is larger with LiI than with LiClO<sub>4</sub>. It is observed also from Figure 3a that at -1.5 V the impedance resistances of those ECDs with LiI, reduce by more than one order of magnitude after the introduction of titanium oxide compounds, and the more the titanium percentage, the larger the reduction of impedance. In the case of

polyelectrolytes with  $\text{LiClO}_4$ , this reduction is only about 40-70 percentage at  $-2\text{V}$  polarization. The less the values of impedance, the faster the charge transfer processes occurred in tungsten oxide electrodes under negative bias, just as observed through the color change in this electrochromic material. Similar EIS results were obtained for the same ECDs under positive polarization ( $+1\text{V}$ ).



**Figure 3.** Nyquist plots and equivalent circuits of ITO/ $\text{WO}_3$ /PE/ITO with PE as: (a) PEG-Ti-LiI at  $-1.5\text{V}$  and (b) PEG-Ti- $\text{LiClO}_4$  at  $-2\text{V}$  for PEG:Ti molar ratio of 24:1, 8:1, 4:1 and 1:0.

## CONCLUSIONS

Titanium oxide compounds of maximum size of 1.8 to 7 nm have been formed inside the polyethylene glycol (PEG) by sol-gel method as the molar ratio between PEG and titanium precursor (PEG:Ti) varied from 24:1 to 4:1. For molar ratio of PEG:Ti from 24:1 to 4:1, the larger the concentration of titanium, the better the  $\text{WO}_3$  color change speed as well as its optical contrast and stability. They are associated with PEG molecules through hydroxyl-oxygen interactions and form longer or crosslinked molecular chains. As the lithium iodide salt was added into the PEG-Ti composite polymer, part of the iodide ions were oxidized into iodine and tri-iodides. At the same time, titanium oxide compounds inside the PEG-Ti complexes should be negatively charged, leading to a faster lithium ion insertion in positively polarized tungsten oxide thin films. When LiI was substituted by  $\text{LiClO}_4$ , both optical contrast and color change speeds were reduced. Electrochemical impedance spectroscopy study confirms the fast charge transfer process occurred in those polymeric composite electrolytes with LiI salt.

## REFERENCES

- [1] J. W. Schultze and H. Karabulut, *Electrochim. Acta* **50**, 1739 (2005).
- [2] M. Grätzel, *J. Photochem. & Photobiology C: Photochemistry Reviews* **4** 145 (2003).
- [3] L. M. Bronstein, J. C. Karlinsey, A. Ryder, and J. M. Zwanziger, *Chem. Materials* **13**, 3678 (2001).

- [4] G. Katsaros, T. Stergiopoulos, I. M. Arabatzis, K. G. Papadokostaki, and P. Falaras, *J. Photochemistry and Photobiology A. Chemistry* **149**, 191 (2002).
- [5] V. Di Noto, R. Gliubizzi, E. Negro, and G. Pace, *J. Phys. Chem. B* **110**, 24972 (2006).
- [6] M. S. Akhtar, J. M. Chun, and O. B. Yang, *Electrochem. Commun.* **9**, 2933 (2007).
- [7] L. Hechavarria, N. Mendoza, P. Altuzar, and H. Hu *J. Solid State Electrochem.* **14**, 323 (2010).
- [8] N. Mendoza, F. Paraguay-Delgado, L. Hechavarría, M. E. Nicho, and H. Hu, submitted.
- [9] J. P. Cronin, D. J. Tarico, A. Agrawal, and R. L. Zhang *USA Patent* 5,277,986 (1994).