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Effect of different acid and lithium salt used in polyethylene glycol–titanium oxide based solvent-free electrolytes on electrochromic performance of WO_3 thin films

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Abstract

Polymeric nanocomposites of polyethylene glycol (PEG) with titanium oxide compound, PEG–Ti, are solvent-free viscous materials obtained by sol–gel method 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 contrast in the wavelength range from 300 to 2500 nm, however it depends on the type of lithium salt as well as the acid source 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 $LiClO_4$ makes the devices totally transparent in visible region, and the optical contrast is small. On the other hand, hydrochloric acid is good catalyst for hydrolysis of the titanium precursor during the sol–gel process, but it also originates the yellowish appearance of the devices. The substitution of HCl by acetic acid makes the devices more transparent in 250–500 nm, but the optical contrast as well as color change speed were deteriorated. Possible chemical reaction mechanisms during the formation of these polymeric electrolytes have been proposed to explain the relation between electrochromic performance of tungsten oxide and chemical composition of the electrolytes.

Keywords: Nanocomposite electrolytes; Polyethylene glycol; Titanium oxide; Tungsten oxide; Electrochromic performance

1. Introduction

A polymer electrolyte is usually prepared by dissolving a salt in a polymeric matrix. The dissociation of the salt can be achieved either by using some volatile solvents or by the same polymer whose atoms can interact with cations and separate them from the corresponding anions. The latter case is called solvent-free polymer electrolyte and its advantage is the chemical stability; polymer cannot be evaporated as volatile solvent and the ionic conductivity of the electrolyte will be stable during its use. Polyethylene oxide (PEO) or polyethylene glycol (PEG) is one of those macromolecules whose ether oxygen atoms can dissociate lithium, for example. It has been widely studied due to their potential applications in lithium batteries, electrochemical display devices and sensors (Schultze and Karabulut, 2005; Granqvist et al., 1998). Most of the previous studies were focused on complexes of PEO with lithium salts such as $LiClO_4$, $LiCF_3SO_3$, and $LiAsF_6$ (Petersen et al., 1993, 1994), and their electrical conductivity was determined as a function of salt concentration. The variation in salt concentration is described in terms of the ratio of the number of ether oxygen atom to the metal ion (e.g., Li^+). The high molecular weight PEO resumes much attention as the host for the polymer electrolytes, because of its ability to dissolve a variety of alkali salts MX (M = alkali metal, X = anion),

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electrochemical stability and beneficial structure for supporting ion migration (Ratner and Shriever, 1988).

The ionic conductivity of polymer electrolytes, on the other hand, is generally lower than that of liquid ones which contain small volatile solvents. To increase the ionic conductivity of those it is necessary to decrease the glass transition temperature or crystallinity of the polymer in order to give more room for molecular motion. In this aspect, most of the studies have been directed to the preparation and characterization of sol–gel polymer electrolytes which exhibit higher ionic conductivity than that of polymer-salt only electrolytes at ambient temperature. Some of sol–gel polymer electrolytes are prepared by incorporating ceramic fillers into the matrix polymer such as Al_2O_3, SiO_2, TiO_2, $CaSiO_3$, and $BaTiO_3$ (Choi et al., 1997; Wen et al., 2003; Quartarone et al., 1998; Sun et al., 1999, 2000; Croce et al., 1998; Lan et al., 2007). Adding ceramics develops PEO–ceramic–LiX composite polymer electrolytes of nanoscale particle size having both excellent mechanical stability (promoted by the network of the fillers into the polymer bulk) and high ionic conductivity (promoted by the high surface area of the dispersed fillers). In a recent work we reported a PEG–Ti nanocomposite made by sol–gel route, and the electrochromic performance of tungsten oxide with PEG–Ti–LiI as electrolyte was improved (Hechavarria et al., 2010; Mendoza et al., 2011). 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 composite electrolytes.

2. Experimental

Tungsten peroxy-ether solution was prepared by sol–gel method according to Cronin et al. (1994). 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 were amorphous tungsten oxide of about 350 nm thick measured by SEM and ready for electrochromic device use. Detailed description about synthesis and characterization of WO_3 thin films can be found in our previous work (Mendoza et al., 2011). 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 (Hechavarria et al., 2010; Mendoza et al., 2011). The following modifications were made in this work: (a) either hydrochloric acid or acetic acid was used for sol–gel process, (b) either LiI or $LiClO_4$ was added into 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–$LiClO_4$ electrolytes were prepared by dissolving LiI or $LiClO_4$ in viscous PEG–Ti complexes with a molar ratio of one atom of Li into eight oxygen atoms in PEG. Since the average number of repetitive units in a PEG (600) molecule is about 13, there would be 13 ether molecules per each PEG molecule, then the molar ratio between PEG and Li ion would be PEG:Li = 1:1.62. All of these electrolytes were vacuum-dried at 80 °C for 3 h before use.

Tungsten oxide electrochromic devices (WO_3–ECDs) were prepared by collocating polymer electrolyte (PE) between ITO glass and WO_3 coating on ITO to form a device configuration of ITO/WO_3/PE/ITO. An electrical insulated spacer was used for electrolyte to keep it as 100 μm thick. The final device was sealed with a scholastic silicone with an effective area of about 1 cm^2. Spectral and transient optical transmittance curves of WO_3–ECDs 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 WO_3–ECDs 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.

3. Results and discussion

3.1. Electrochromic stability of WO_3–ECDs as a function of molar ratio of PEG:Ti

As reported before, the oxidation reversibility of WO_3–ECDs was 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 (Hechavarria et al., 2010). In this work the titanium percentage in the polymer composites has been increased up to four molecules of PEG vs. one atom of titanium. Fig. 1a shows optical spectra of ITO/WO_3/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, 8:1 and 4:1. It is observed that the bleaching and coloring curves of the three devices are similar in 300–2500 nm region, with small variation in cut-off wavelength around 400 nm. The transient optical transmittance curves at 650 nm (it could be any other wavelength from 500 to 1000 nm for a notable transmittance contrast) of the same devices exhibited in Fig. 1b indicate that the more the titanium percentage, the faster the color change speed of the devices. If we analyze the reproducibility of optical contrast after several cycles of alternative polarizations, the most stable device is made with PEG:Ti equal to 4:1. Fig. 1c depicts the maximum (oxidation) and minimum transmittance values of the three devices from cycle number 1 up to 30.

The redox speed as well as optical contrast stability with number of redox cycles in electrochromic devices is related to the ion storage capacity inside the electrolyte or at the counter electrode (León-Silva et al., 2008). It is known that color change is occurred in WO_3 as the lithium ions are