Solar Energy Materials & Solar Cells 95 (2011) 2478–2484

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Nanostructured polyethylene glycol–titanium oxide composites as solvent-free viscous electrolytes for electrochromic devices

Narcizo Mendoza [a,b], Francisco Paraguay-Delgado [b], Liliana Hechavarría [a], Ma.Elena Nicho [c], Hailin Hu [a,*]

[a] Centro de Investigación en Energía, UNAM, Priv.Xochicalco S/N, Temixco, Morelos 62580, México
[b] Centro de Investigación en Materiales Avanzados, Miguel de Cervantes 120, 31109, Chihuahua, Chih, México
[c] Centro de Investigación en Ingeniería y Ciencias Aplicadas, UAEM, Av.Universidad 1001, Cuernavaca, Morelos 62210, México

ARTICLE INFO

Article history:
Received 3 February 2011
Accepted 22 April 2011
Available online 24 May 2011

Keywords:
Polymer composite electrolytes
Sol–gel method
Electron microscopy (STEM, TEM)
Tungsten oxide thin films
Electrochromic devices

ABSTRACT

Composites of polyethylene glycol (PEG) and titanium oxide compounds have been prepared by sol–gel method using different molar ratio between PEG and titanium isopropoxide. Transmission electron microscope (TEM) images and UV–vis absorption spectra of these composites indicate that titanium oxide particles or clusters were formed inside the composite materials and their maximum sizes were between 1.8 and 7 nm for PEG:Ti molar ratio changing from 24:1 to 4:1. Fourier Transform Infrared spectroscopy analysis of the same PEG–Ti composites suggests the presence of tetragonal titanium oxide compounds and its association with ether oxygen atoms of PEG molecules. As lithium iodide salt was added into PEG–Ti composites, iodide ions were oxidized into iodine and tri-iodides and, at the same time, titanium oxide compounds should be reduced. Color change speeds of tungsten oxide thin films were significantly improved when PEG–Ti–LiI composites were used as electrolytes compared to salt-in-polymer one (PEG–LiI); the bleaching time of tungsten oxide was reduced from 22 to 2.5 s under +1.0 V polarization, and the coloring time under −1.5 V lowered from 16 to 2.2 s. The transfer of negative charges from smaller iodide ions onto longer or crosslinked PEG–Ti macromolecules could be the origin of faster lithium ion transport/insertion speeds in PEG–Ti composite electrolyte based electrochromic devices.

1. Introduction

Electrolytes work as an ionic conductor-reservoir and as a separator of electrodes in electrochemical devices such as batteries, dye-sensitized solar cells, electrochromic windows, etc. They can be classified as liquid or solid according to their viscosity. Liquid electrolytes refer as salt-in-solvent, and the solvent usually consists in low vapor pressure small molecules. Although they have an excellent wet-ability on electrode surface and a good ionic conductivity which leads to rapid charge transfer process at electrode/electrolyte interfaces, the leak or evaporation of solvents is inevitable and their use requires a rigorous device sealing. Electrolytes without volatile solvents, or simply solvent-free electrolytes, are chemically stable and ideal for solar cell applications [1]. Polymeric electrolytes (PEs) can be solvent-free if they are polyelectrolytes such as Nafion®, or polymer–salt complexes like polyethylene oxide (PEO) with lithium ions. PEO is a commercially available polyether: HO–$(CH_2–CH_2–O)_nH$. As the lithium salt is added into it, the ether oxygen atoms of the repetitive unit are responsible to dissociate the salt, interact and transport lithium ions from one oxygen atom to another along the main chains of the polymer [2,3]. The ionic conductivity of PEO–Li^+ depends largely on molecular weight of the polymer and the type and concentration of lithium salt [4,5]. Classification and description about PEs can be found in [6,7].

The disadvantage of polymeric solvent-free electrolytes, on the other hand, is their relatively low ionic conductivity and wet-ability. Several approaches have been reported to improve the ionic conductivity of PEs, and one of them is the use of composite materials to reduce the chain–chain interaction or increase amorphous phase percentage inside the polymeric matrix to create more room for ion mobility [8–11]: PEO composites with ceramic nanoparticles (TiO_2, SiO_2, etc.) have shown higher ionic conductivity than that of pure salt-in-polymer electrolytes. In a previous work we reported that the ionic conductivity of polyethylene glycol (PEG)–titanium oxide compound based electrolyte is higher than that of PEG only one [12]. PEG is low molecular weight specie of PEO and is in liquid state at temperature if its molecular weight is smaller than 10,000. By sol–gel method PEG(6 0 0)–titanium (PEG–Ti) composite material was formed and the bleaching speed of tungsten oxide with PEG–Ti–LiI as electrolyte was improved [12]. However, the chemical structure

---

[*] Corresponding author. Tel.: +52 55 5622 9747; fax: +52 55 5622 9742.
E-mail address: hzh@cie.unam.mx (H. Hu).

0927-0248/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2011.04.035

of the composite materials was not well verified and the origin of electrochromic property change was unclear and the coloring speed was still slow. In this work we show that nanoparticles of titanium oxide were formed inside the PEG–Ti composite materials and their sizes were a function of titanium precursor concentration in the original sol–gel solutions. The associations between PEG and titanium compounds can be observed by increasing considerably titanium molar proportion in the composites. A molecular structure of PEG–Ti nanocomposite electrolytes has been proposed to explain the chemical interaction between iodides and titanium oxide compounds and its effect on color change speeds in tungsten oxide, the most studied electrochromic device material [13], under electrical polarization.

2. Experimental

Tungsten oxide thin films were obtained from sol–gel prepared tungsten peroxy-ether solution [14]. Briefly, 6.5 g of metallic tungsten powder (Aldrich, 12 micron, 99.9%) was dissolved in solution of 40 ml of 30% hydrogen peroxide (Fermont, 30%, purified), 40 ml of acetic acid (Fermont, 99.9%) and 4 ml of distilled water. The mixture was maintained at 5 °C under stirring for 24 h. Then it was filtered and refluxed at 55 °C for 12 h. The obtained solution was yellow transparent, and dried at 60 °C in vacuum into yellow crystals called tungsten peroxy-acid (WPA). Then they were added into ethanol (J.T. Baker, 99.80%) with 1 g/3 ml relation together with 5 wt% oxalic acid (Sigma-Aldrich, 99%); the addition of oxalic acid helps to improve the electrochromic performance of tungsten oxide films, as reported in literature [15]. After stirring at room temperature for 24 h, the resulting solution was tungsten peroxy-ester (WPE), ready for spin-coating process. Detailed description about chemical processes involved in tungsten peroxy-ester formation can be found in Ref. [16]. Thin films of WPE were obtained from spin-coating the WPE solution on clean conductive glass (indium-tin oxide, ITO, Delta Technologies, 8–12 Ω/square) by 2000 rpm for 60 s, followed by the annealing in air at 250 °C for 1 h. The annealed films were ready to be used as electrochromic active layers. SEM images of the resulting films (not shown here) indicate a very compact morphology of tungsten oxide in comparison with electrodeposited ones [17]. XRD spectra (not shown here) show an amorphous structure of these 250 °C annealed films; samples with annealing at higher temperature (350–450 °C) were crystalline tungsten trioxide (WO_3), but the best electrochromic behavior was found when the samples were amorphous (annealed at 250 °C), as already mentioned in literature [18]. The film thickness was about 350 nm measured from SEM cross-section image of the annealed samples.

The PEG–Ti complex preparation process used in this work was similar as reported before [12], except the molar ratio between PEG and titanium atoms had been widely varied. PEG of 600 molecular weight (Aldrich, 97%) was dissolved in 2-propanol (J.T. Baker, 99.92%) under stirring at 40 °C, followed by addition of concentrated HCl (J.T. Baker, 36.5%) and slow dripping of titanium isopropoxide, $Ti\{OCH(CH_3)_2\}_4$, (Aldrich, 97%). The molar ratio between PEG and HCl had kept constant for all composites, and the volume relation between HCl and 2-propanol was 1–10 ml/ml. The hydrolysis and condensation process was kept for 24 h at room temperature. Then the solution was dried at 110 °C for 3 h to obtain viscous PEG–Ti composite materials. The molar ratio between a PEG molecule (containing approximately 13 repetitive unit of CH_2CH_2O) and titanium atom was chosen as PEG:Ti = 24:1, 8:1, 4:1, 1:3.5 and 1:15. The first three of them were viscous and had been used as electrolytes in WO_3 electrochromic devices. The last two were solid and used only for material analysis. PEG–Ti–LiI electrolytes were prepared by dissolving LiI in viscous PEG–Ti complexes with a molar ratio of one atom of Li into 8 oxygen atoms of a PEG molecule. Tungsten oxide electrochromic devices were prepared by dropping polymer electrolyte (PE) onto free surface of tungsten oxide and putting another clean ITO on top of PE to form an electrochromic device of ITO/WO_3/PE/ITO. An electrical insulate spacer was used for electrolyte to make it as 100 μm thick. The final devices were of about 1 cm^2 effective area, sealed with a scholastic silicone to avoid the slipping of the electrodes.

PEG–Ti complexes as well as PEG–Ti–LiI electrolytes were analyzed by Fourier Transform Infrared Spectroscopy (FT-IR, Perkin-Elmer Spectrum GX) in ATR mode. Raman spectra of the same samples were obtained with Disperse Raman (Nicolet-Almega XR, excitation laser wavelength = 532 nm). Transmission Electron Microscope (TEM, Jeol model JEM 2200FS) operated at 200 KV with probe spherical aberration corrector was used in scanning transmission (STEM) mode to acquire images with high angle annular dark field (HAADF) and bright field (BF) detectors. Optical spectra were acquired with UV–vis spectroscopy (Shimadzu Spectrophotometer 3101 PC). Spectral and transient electrochromic performance of tungsten oxide based devices with different PEG–Ti–LiI electrolytes was determined by measuring their specular optical transmittance spectra under positive (+1.0 V) or negative (−1.5 V) bias. That is to say that the incident light was about 90° on the testing sample, and the measured transmitted light was also perpendicular to the sample surface. WO_3 films can change from transparent to blue at negative voltage of −1.0 or larger (more negative). The difference is that at smaller negative voltage the total transmittance change was smaller and the color change speed was slower. For bleaching process it is the same. On the other hand, if the voltage values are too large, undesirable electrochemical reactions could be occurred at WO_3/electrolyte interface and, as a result, WO_3 films could suffer chemical degradation, which would reflect in their electrochromic performance. Therefore, intermediate values of applied potentials were chosen (+1.0 and −1.5 V) for our electrochromic measurements.

Electrochemical impedance spectroscopy (EIS) study was realized at room temperature (20 °C) on tungsten oxide based electrochromic devices with different polymeric electrolytes by using a dynamic-EIS system (VoltaLab PGZ301). The DC potential was chosen as −1.5 V and the amplitude of the AC signal was 50 mV. The last one should be as small as possible, but smaller amplitude value also causes lower signal/noise ratio, which could lead to longer measurement time at low frequency region. The EIS results of our devices were similar for AC amplitude between 10 and 50 mV, therefore 50 mV was chosen in this work to save testing time. The frequency range for EIS test was between 100 mHz and 100 kHz.

3. Results and discussion

3.1. Molecular structure of PEG–Ti composites

The incorporation of titanium oxide compounds in PEG changes its physical appearance. The transparency and viscosity of PEG–Ti complexes depend on PEG:Ti molar ratio for a fixed amount of HCl in the starting sol–gel solution. In the case of PEG with 600 molecular weight, if PEG:Ti molar ratio was equal to or higher than 4:1 the obtained PEG–Ti composites were transparent and viscous, and their viscosity increased with the initial titanium precursor concentration in the sol–gel solution. If it is smaller than 1:1, the compound becomes solid and opaque material, useless for electrochromic device application. In an acidic sol–gel