ORIGINAL PAPER

In situ formation of polyethylene glycol–titanium complexes as solvent-free electrolytes for electrochromic device application

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Abstract Transparent and ionic conductive polymeric electrolytes have been prepared through sol–gel method by adding titanium isopropoxide into an acidic polyethylene glycol (PEG) solution. After hydrolysis and condensation processes, new associations between titanium cations and ether oxygen atoms of PEG have been formed according to Fourier-transform infrared spectroscopy. Thermogravimetric analysis results of these hybrid materials indicate a better thermal stability with a less polydispersion of the molecular mass distribution in comparison with PEG. For the purpose of electrochromic or photoelectrochromic device applications, LiI was added into the hybrid materials to form solvent-free polymeric electrolytes. Optical transmittance spectra of these electrolytes show a red shift of the cutoff wavelength as a function of titanium isopropoxide percentage in the original sol–gel solutions. It is also observed that the amount of hydroxyl groups in the hybrid materials was reduced in comparison with the PEG one. This makes electrical conductivity of the hybrid electrolytes with LiI salt insensitive to humidity and solvents, which was about $2\times10^{-4}\ \Omega^{-1}\ cm^{-1}$ at room temperature. A solid WO_3-based electrochromic device with the hybrid electrolyte keeps the same optical transmittance value after 1,000 cycles of switching polarization potentials between −1 and +1 V.

Keywords Polyethylene glycol · Titanium compound · Hybrid materials · Solvent-free electrolytes · Solid electrochromic devices

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Introduction

Polyethylene glycol (PEG) is a commercially available polyether, $OH–(CH_2–CH_2–O)_n–H$. Although it is the synonymous of polyethylene oxide (PEO), PEG usually refers to oligomers and polymers with a molecular mass equal to or less than 20,000 and PEO to polymers with a molecular mass above 20,000. PEG is colorless and in liquid state at room temperature at atmosphere pressure; its viscosity increases with the molecular mass. Both low molecular mass PEG or its copolymer and high molecular mass PEO can form salt complexes, and they have been used as cationic conducting (Li^+) solid polymer electrolytes for electrochromic [1, 2] or anionic conducting (I_3^-/I^-) electrolytes for solar photovoltaic applications [3, 4]. But high molecular mass PEO needs plasticizer to increase its room temperature conductivity. It is reported in literature that a PEO (6×10^5 molecular weight) gel electrolyte with $LiClO_4$ can be formed with propylene carbonate (PC) and ethylene carbonate (EC) after the solvent of PEO, ethane nitrile is evaporated [1]. The conductivity of this PEO electrolyte maintains a stable value of 2.6 mS/cm after 3 days of gelation. The solid polymer matrix of PEO provides dimensional stability to the electrolyte while the high permittivity of solvents PC and EC enable extensive dissociation of the Li salts. The low viscosity of PC and EC provides an anionic environment that facilitates high ionic mobility.

The enhancement of the ionic conductivity is a very important issue in the research and development of polymer electrolytes for diverse applications. For example, both electrochromic switch speed and solar photovoltaic energy conversion efficiency are directly proportional to the ionic conductivity of the electrolytes. It is found that the addition of small metal oxide particles into PEG or PEO host can

increases the ionic conductivity of the resulting electrolytes [5–10]. Composite materials that have been used for electrolyte applications are: PEO-fumed silica [5], PEO-Al_2O_3 [6], PEG-$Mn0.03Zn0.97Al_2O_4$ [7], PEO-TiO_2 [8–10]. It is observed that the enhancement in the ionic conductivity of $(PEG)_{46}LiClO_4$ + $Mn0.03Zn0.97Al_2O_4$ system is attributed to the reduction in the glass transition temperature as well as in the degree of crystallinity of PEG [7]. The introduction of titanium oxide into the high-molecular mass PEO produces dramatic morphological changes to the host polymer structure [8]. The polymer chains separated by titania particles are arranged in a three-dimensional mechanically stable network that creates free space and voids into which the iodide/triodide anions can easily migrate. The addition of an adequate amount of TiO_2 nanotubes as fillers in high molecular mass PEG (100,000) increased the amorphous phase in the polymer network as indicated in DSC data, which resulted in an improved ionic conductivity [10].

The big issue to be taken cared in composite materials is the dispersion of inorganic particles or nanoparticles in polymer hosts. A rigorous agitation and addition of solvents are common procedures to disperse the particles. Solvents are also used as plasticizers for high molecular mass PEO to form flexible and sometimes transparent electrolytes. Another way to prepare hybrid materials is the direct formation of the inorganic compound inside the polymer host through the sol–gel route. Usually a precursor of inorganic oxide is mixed with a polymer material. With the posterior hydrolysis and condensation processes, the inorganic oxide is formed inside the polymer host. Protonic conducting membranes [11, 12] or ionic conductors [13, 14] based on sol–gel prepared PEO-SiO hybrids have been reported during last 10 years. PEO-siliceous hybrids doped with lithium perchlorate have been used as electrolytes in solid state smart windows with thermally evaporated WO_3 as electrochromic active element [14]. The procedure used for the hybrids involved grafting a diamine containing approximately 15.5 oxyethylene repeat units onto the bridging agent, 3-isocyanatepropyltriethoxysilane precursor. This material was subsequently hydrolyzed and condensed in the sol–gel stage of synthesis to induce the growth of the siloxane framework. Xerogels with n (the salt content as the number of ether oxygen atoms per Li^+ cation) greater than five were obtained as flexible transparent, monolithic films with a yellowish color, whereas compounds with $n=$ 1 and 0.5 were rather brittle, powdery agglomerates. The maximum conductivity at 30°C was about 5×10^{-5} S cm^{-1} and the maximum transmittance contrast between bleached and colored states was close to 40% at 600–900 nm wavelength regions. The best electrochromic performance was obtained for compositions with the highest ionic conductivity.

Another inorganic oxide, titanium oxide compound, has also been incorporated into PEO by sol–gel method to form hybrid electrolytes. V. Ni Noto and collaborators prepared polyoligoethylene glycol (dihydroxytitanate) electrolytic systems by a polycondensation reaction between $Ti(OEt)_4$ and PEG 400 (I), as well as $Ti(OEt)_4$ and PEG 400/LiCl complex (II) [15]. The obtained polymers are rubbery solids with a cream-yellow color and showed conductivities at 25°C of ca. 3×10^{-6} and 4×10^{-6} S cm^{-1}, respectively. Both are inorganic–organic materials whose macromolecular chains consist of titanium atoms bonded together by PEG 400 bridges. Conductivity profiles obtained for these materials were fitted very well by the empirical Vogel–Tamman–Fulcher (VTF) equation, suggesting that both polymers conduct ionically and are strongly influenced by the segmental motions of polymer chains.

Whether the physical mixing or in situ sol–gel method is chosen for hybrid material preparation, the optical transmittance of the obtained electrolytes is largely dependent on the inorganic phase percentage in the hybrid materials. In cases of electrochromic or photoelectrochromic device development, the transparence of the electrolyte is an important property to be considered about. The objective of this work is looking for transparent or semitransparent solvent-free PEO–titanium compound electrolytes for electrohromic or photoelectrochromic applications because titanium compounds have interesting semiconductor and electrochromic properties. It is shown in the following sections that a slow hydrolysis and condensation process (sol–gel method) permits the formation of such electrolytes. Liquid PEG with different molecular mass haven been used as polymer hosts. Titanium isopropoxide has been used as the precursor of titanium compound in the hybrids. Electrical properties of the hybrid electrolytes have been studied as a function of temperature. Electrochromic devices based on these electrolytes and electrochemically deposited WO_3 films have also been analyzed.

Experimental

Liquid PEG products with different molecular mass are commercially available. Those of 600, 6,000, 8,000, and 20,000 have been used for preliminary test to prove their electrical conductivity as well as the formation of PEG–Ti complexes. Lithium salt complex formed from PEG 600 (Aldrich) and LiI shows the highest ionic conductivity in temperature range of 25–110°C compared with the rest of PEG products. Furthermore, when PEG products were mixed with the titanium isopropoxide ($Ti(OR)_4$, Aldrich 97%), the transparency of the resulting products decreases as the PEG molecular mass increases. It could be due to the precipitation of large PEG molecules as they are associated

with the titanium cations. As a result, PEG of 600 molecular mass was chosen in this work for hybrid electrolyte preparation and is referred as PEG.

To prepare hybrid materials, PEG was first diluted in 2-propanol. Concentrated HCl was added into the solution, followed by slow dripping of $Ti(OR)_4$. The mixture was under stirring for about 3 h at 40°C and then left at room temperature for 24 h to complete the hydrolysis (from $Ti(OR)_4$ into $Ti(OH)_4$) and condensation processes (from $Ti(OH)_4$ into titanium oxide compound). The solution composition of 3 g of PEG and 0.06 ml of $Ti(OR)_4$ corresponds to a molar proportion between the ethylene glycol (EG) monomer and titanium cation (EG/Ti) of 1:0.0043, and the resulting material was so-called PEG–Ti(0.0043). Other EG/Ti relations chosen in this work were: 1:0.01 (PEG–Ti(0.01)), 1:0.014 (PEG–Ti(0.014)), and 1:0.025 (PEG–Ti(0.025)). The amount of HCl was always kept as 1 ml to 3 g of PEG in the original PEG–$Ti(OR)_4$ solutions. Fourier-transform infrared (FT-IR) spectroscopy in ATR mode (Perkin-Elmer Spectrum GX) and thermogravimetric analysis (TGA; TGA Instruments Q500) were used to study the molecular interaction between hydroxyl groups of PEG and titanium species as well as the thermal stability of the PEG–Ti complexes with different $Ti(OR)_4$ concentration in the initial sol–gel solutions.

Thin films of WO_3 (about 250 nm thick) were obtained by electrodeposition in a peroxytungstic acid solution contained in a three-electrode electrochemical cell with a platinum sheet as the auxiliary electrode, an indium-tin-oxide-coated glass sheet (ITO, 8–12 Ω/square, Delta Technologies) as the working electrode and SCE electrode as reference [16]. The working electrode was subjected to a constant cathodic potential of −0.5 V, and the total deposition time was about 10 min. The obtained WO_3 films were homogenous, stable, and transparent in air. They were amorphous materials, and the morphology of the films was sensitive to post thermal treatment. They can change the color, from transparent to blue color, as they are reduced in electrochemical cells [16]. A 100-µm spacer (an electrically insulator tape) was collocated on the surface of clean ITO glass, and the electrolyte was applied into it. The electrolyte with the same thickness was obtained after the WO_3-coated ITO slide was placed on top of the electrolyte. The final electrochromic devices were sealed with a scholastic silicone gun. The silicon bar was transparent and thermoplastic, which melted at about 70°C. The effective area of the devices was about 1 cm^2.

As for PEG electrolyte preparation, LiI was added into the PEG as well as PEG–Ti hybrid systems with a lithium salt content $n=8$, that is, eight ether oxygen atoms per each Li^+ cation. Electrical conductivity of the PE, sandwiched between two ITO substrates, was measured as a function of temperature between room temperature and 110°C with the

electrochemical impedance spectroscopy (VoltaLab PGZ301, Dynamic-EIS) in the frequency range from 1 to 100 kHz. Optical transmission modulation or transient optical transmittance curves (ΔT, %) of ITO/WO_3/PE/ITO as well as optical transmittance spectra of these and ITO/PE/ITO samples were recorded on an UV-VIS spectrophotometer (Shimadzu 3101 PC). A homemade voltage source was used to apply a DC potential to the electrochromic devices.

Results and discussion

It is well known that during the process of sol–gel, the hydrolysis of $Ti(OR)_4$ with water leads to the formation of titanium hydroxide, which in turn transforms into titanium oxide by condensation under acidic condition. The presence of PEG in HCl aqueous titanium isopropoxide solution could induce the interaction between PEG and the titanium compound through the hydroxyl groups at the same time as the latter was undergoing the hydrolysis-condensation process. The association of PEG and titanium compound can be determined by FT-IR and TGA techniques. Figure 1 shows the FT-IR spectra of PEG and PEG–Ti hybrid materials with different PEG/Ti molar proportions. The products were analyzed without drying in vacuum. In the low wavenumber region (Fig. 1a), it is observed that the deformation mode of water molecules (1,650 cm^{-1}) decreases as the $Ti(OR)_4$ concentration increases in the original polymer solution. The appearance of a new absorption band around 884 cm^{-1} in PEG–Ti systems, as well as its intensity increase with respect to the increase of $Ti(OR)_4$ concentration, suggests the existence of an interaction between PEG and titanium compound. Actually, according to the literature [17] the observed vibrational modes around 860–870 cm^{-1} are associated with the cation–ether oxygen interactions in PEO-based systems. The same conclusion could be obtained from Fig. 1, and the slightly red-shifted value was probably due to the particular titanium cations and the specific polymer environment in this hybrid material. On the other hand, the vibration band around 1,079 cm^{-1} usually is assigned to the stretching of C–O–H groups [18], which is present in PEG molecules. The increase of its intensity in the PEG–Ti complex systems should be related to the appearance of a strong CH group stretching at 2,866 cm^{-1} (Fig. 1b), functional groups that only appeared in 2-propanol, solvent used for sol–gel process. It suggests that trace of 2-propanol is present in hybrid systems before a rigorous vacuum drying. Since the 2-propanol contains also hydroxyl groups, they may originate the vibration band in the region of 3,420 cm^{-1}. Another important feature of PEG–Ti hybrid materials is that water content is considerably reduced in these new compounds. It
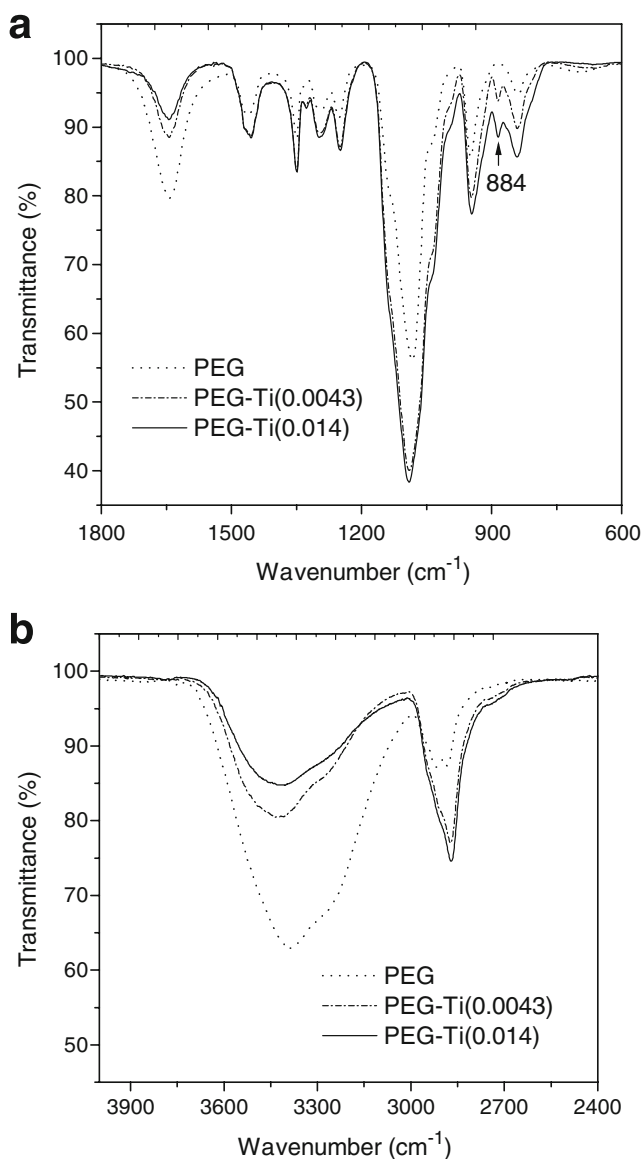
Fig. 1 FT-IR spectra in ATR mode of PEG and PEG–Ti complexes in **a** 1,800–600 cm^{-1} and **b** 4,000–2,400 cm^{-1} wavenumber regions

Fig. 2 a Original and **b** derivative of TGA curves of PEG, PEG–Ti (0.0043), and PEG–Ti(0.014)

is observed in Fig. 1b that the original hydroxyl group stretching of water in PEG (around 3,260 cm^{-1}) decreases as the Ti(OR)$_4$ percentage increases, congruent with the same tendency observed in the deformation mode of water molecules (Fig. 1a).

The formation of new associations in PEG–Ti complexes is also confirmed by TGA. Figure 2 shows the weight loss (ΔW) curves as a function of temperature (Fig. 2a) as well as the corresponding first derivative of ΔW with respect to temperature (Fig. 2b) of the same three samples of Fig. 1: PEG, PEG–Ti(0.0043), and PEG–Ti(0.014) without vacuum drying. The mass loss below 150°C in PEG sample was due to water, whereas in PEG–Ti complexes, it should come from the presence of 2-propanol. With temperature higher than 150°C, PEG sample starts to lose its weight at about 175°C in a slow
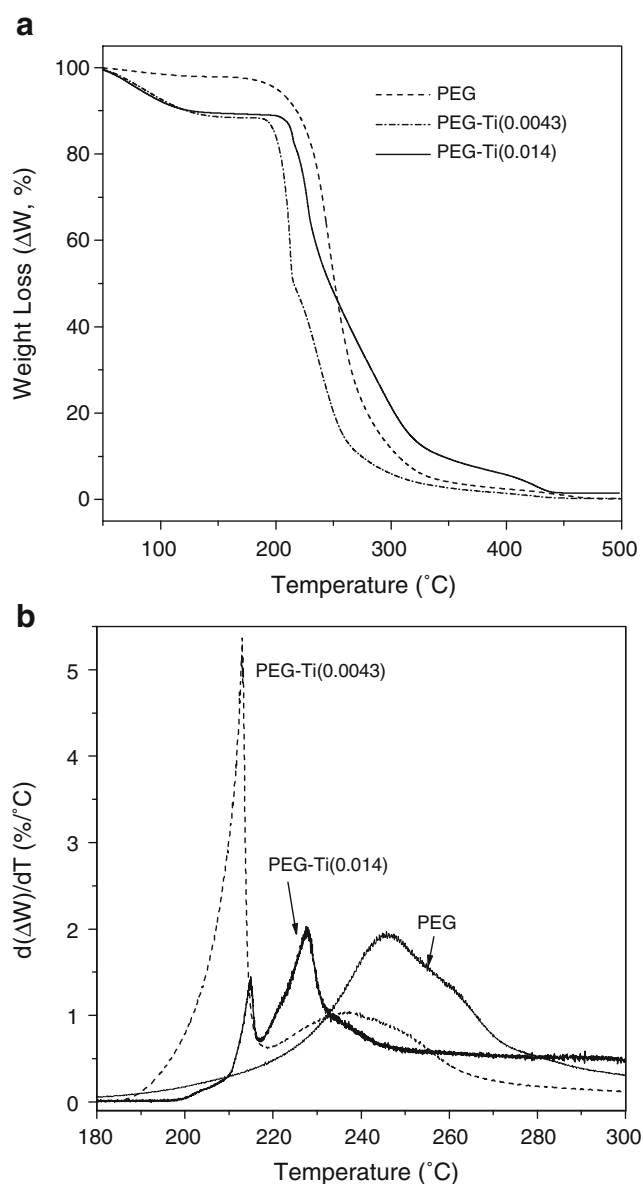
rate , reaching to its maximum loss at about 245 °C (Fig. 2b). The broad decomposition temperature range in PEG is due to the broad distribution of molecular mass. On the other hand, the starting decomposition temperature of PEG–Ti compounds is higher compared with the single PEG: for PEG–Ti(0.0043) sample, it was at about 190°C and for PEG–Ti(0.014) one, at around 200°C. Namely, the hybrid materials are thermally more stable than the single PEG because of the new associations formed between PEG and titanium complex. Furthermore, the mass loss of the hybrid materials occurs in a relatively narrow range of temperature with two different loss rates (Fig. 2b). In the PEG–Ti(0.0043) sample, the highest and sharpest decomposition peak occurs between 200 and 216°C range, which should

correspond to the degradation of low molecular mass chains. The followed smaller and broader one with the peak around 233°C should come from the loss of higher molecular mass chains. The sharp decomposition peak suggests that the associations of titanium cations and ether oxygen atoms of PEG occurred basically in the shorter molecules of the polymer, leading to a less polydispersion in lower molecular mass population of PEG–Ti(0.0043) sample. In the case of PEG–Ti(0.014) sample, these associations occur within two groups of molecular mass: one with lower molecular mass which decomposes at around 213°C as that in the PEG–Ti(0.0043) sample, and another one of higher molecular mass that degrades at around 226°C.

The formation of new associations in the hybrid PEG–Ti materials affects on their optical properties. Figure 3 shows the optical transmittance spectra of PEG–LiI complexes. It is showed that the addition of only HCl in PEG–LiI electrolytes, without the presence of titanium isopropoxide, induced the red shift of the optical cutoff of PEG–LiI electrolytes, and this red-shift value is relatively insensitive to the HCl concentration in the solutions (not showed here). It suggests that HCl molecules could oxidize iodide anions into the iodine molecules in the electrolytes, and the amount of iodine molecules that could be formed depends on the equilibrium between lithium salt, iodide, and iodine and not on HCl amount. In the cases of PEG–Ti–LiI complex samples, the lithium salt was added into the PEG–Ti solutions after the hydrolysis and condensation processes as well as the evaporation of the HCl molecules. Therefore, the red-shift of the optical cutoff observed in PEG–Ti–LiI electrolytes is mostly due to the new associations formed

between PEG and titanium complexes. They behave like short wavelength dispersion centers; with longer chelating (PEG–Ti(0.014), for example), the starting dispersed wavelength is longer than that of the shorter one (PEG–Ti (0.0043), for example), congruent with the TGA results.

For the electrochromic device application purpose, a lower concentration of Ti complexes in hybrid materials is more desirable due to a larger transparency of the resulting electrolyte. Two PEG–Ti complex systems with low titanium concentration were chosen to study their electrical conductivity as well as to be electrolytes in WO_3-based electrochromic devices: PEG–Ti(0.0043) and PEG–Ti (0.01). The electrical conductivity of the polymeric electrolytes was measured by the electrochemical impedance spectroscopy (EIS) at different temperatures with frequency range from 1 to 100 kHz. Since the electrolyte sample was sandwiched between two ITO slides, it is expected that no reduction–oxidation would be occurred at the interface between the electrolyte and the ITO surface. Consequently the results of EIS of the ITO/PE/ITO samples should indicate a blocked electrode behavior, namely a line almost parallel to the $-Z''$ at low frequency range and a bulk resistance of the electrolyte at high frequency range should be appeared in their Nyquist plots. Actually, all the electrolyte samples studied in this work, PEG and PEG–Ti systems, showed similar Nyquist plots. Figure 4 exhibits two of them, corresponding to the vacuum-dried ITO/PEG–Ti(0.0043)–LiI/ITO sample at 25 and 100°C. The intersection of the spoon-like curve with x-axis gives the electrolyte resistance, from which the electrical conductivity of the electrolyte (σ) was obtained by taking into account the thickness of the electrolyte (100 μm). The equivalent circuit in this case is a resistor (bulk electrolyte) in series with a capacitor (electrolyte/electrode).
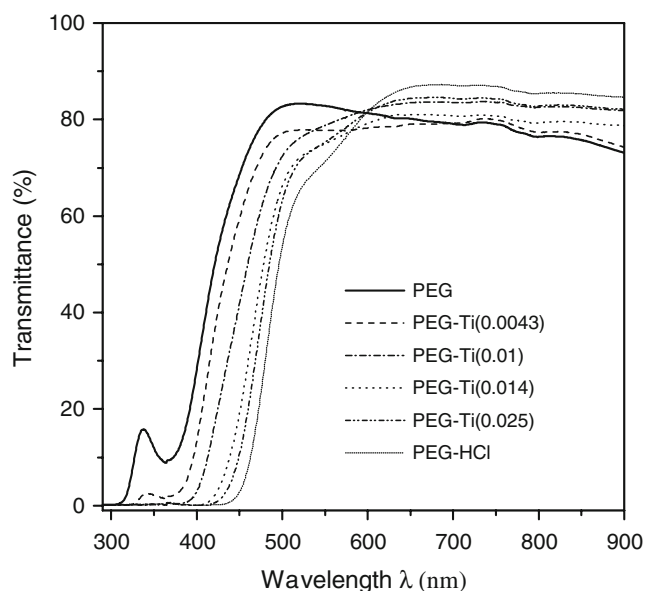

Fig. 3 Optical transmittance spectra of PEG, PEG–Ti(0.0043), PEG–Ti(0.01), PEG–Ti(0.014), PEG–Ti(0.025), and PEG–HCl electrolytes. All of them contain the same LiI content ($n=8$)
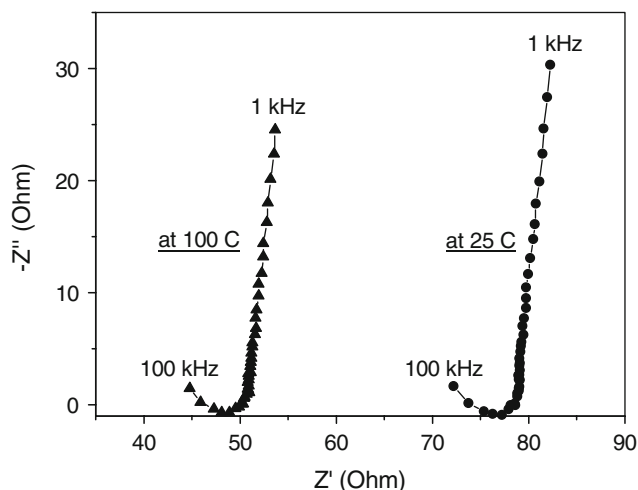

Fig. 4 Nyquist plots of vacuum dried ITO/PEG–Ti(0.0043)–LiI/ITO sample at 25 and 100°C

By using the above-mentioned method, electrical conductivity values of four electrolyte samples were obtained and resumed in Fig. 5 as a function of temperature: PEG alone, PEG–LiI, PEG–Ti(0.0043)–LiI, and PEG–Ti(0.01)–LiI. Since the presence of solvent (2-propanol) or humidity could influence the electrical properties of the electrolytes, the σ values were taken before (Fig. 5a) and after drying in vacuum at 80°C for 3 h (Fig. 5b). The effect of humidity in PEG and PEG–LiI electrolytes is quite notable; for PEG alone sample the room temperature σ increases by more than one order of magnitude after vacuum drying, and for PEG–LiI sample the increase in σ was about 50% after the same drying. The hygroscopic properties of PEG–LiI electrolytes deteriorate their electrical conductivity. However, data from Fig. 5 indicate that the electrical conductivity of PEG–Ti complex systems is insensitive to the presence of solvent and humidity, keeping at about $2\times10^{-4}\ \Omega^{-1}\ cm^{-1}$ at room temperature with or without vacuum drying. It implies that the PEG–Ti hybrid material based electrolytes are ambient stable, and there is no need for a rigorous sealing to avoid their contact with oxygen and humidity. This insensitivity towards humidity should come from the less concentration of hydroxyl groups inside the hybrid materials (Fig. 1). As for the ionic conduction mechanism, $\log\sigma$ vs. $1/T$ curves of all the four samples are not linear and cannot be fitted by the Arrhenius equation. They look like the VTF relationship, $\sigma \propto T^{-1/2}\exp(-E_a/k(T-T_0))$, as reported in the polyoligoethylene glycol (dihydroxytitanate) complexes [15], which suggests a segmental motion in polymeric materials during the ionic conduction. The value of activation energy, E_a, could be obtained by fitting the curves in Fig. 5 with the mentioned expression. In the case of the vacuum-dried PEG–Ti(0.0043)–LiI sample, the T_0 value was

taken as 260 K from [15] and the corresponding E_a value was about 0.122 kJ/mol. This is quite small compared with other PEG–Ti systems reported in [15] in the same temperature range, typically about 0.8 kJ/mol. It suggests a low energy barrier for ionic conduction in the hybrid electrolytes studied in this work.

As mentioned earlier, the electrochromic device performance is intimately related to the electrical properties of the electrolyte. Optical spectra of three ITO/WO$_3$/PE/ITO devices under oxidation (+1 V) and reduction polarizations (−1 V) are showed in Fig. 6: one with PEG–LiI and the other two with PEG–Ti(0.0043)–LiI or PEG–Ti(0.01)–LiI as PE. As indicated by their optical spectra (Fig. 3), the two hybrid electrolytes show a red-shift of the optical transmittance cutoff in comparison with the PEG one. When the corresponding WO$_3$-based electrochromic devices were under redox polarizations, the red-shift value is increased with the titanium compound concentration in the original sol–gel solution (Fig. 6). At the same time, the reduction capacity of the devices is also improved with the hybrid electrolytes; it increases with the amount of titanium compound. Since the reduction process in WO$_3$-based devices involves the intercalation of lithium ions into the WO$_3$ film, a larger degree of reduction implies a larger amount of lithium ions incorporated into the WO$_3$ film, and consequently a larger degree of dissociation of LiI salts in the hybrid electrolyte. Namely, titanium cations in the hybrid electrolytes may attract the iodide anions to make more effective the LiI dissociation under polarizations.

The optical stability of any electrochromic device can be analyzed by studying its transient optical transmittance curves. Figure 7a shows the first six optical contrast modulations (coloration and bleaching characteristics) at

Fig. 5 σ vs. $1/T$ of PEG, PEG–LiI, PEG–Ti(0.0043)–LiI, and PEG–Ti(0.01)–LiI electrolytes **a** before and **b** after drying in vacuum at 80°C for 3 h
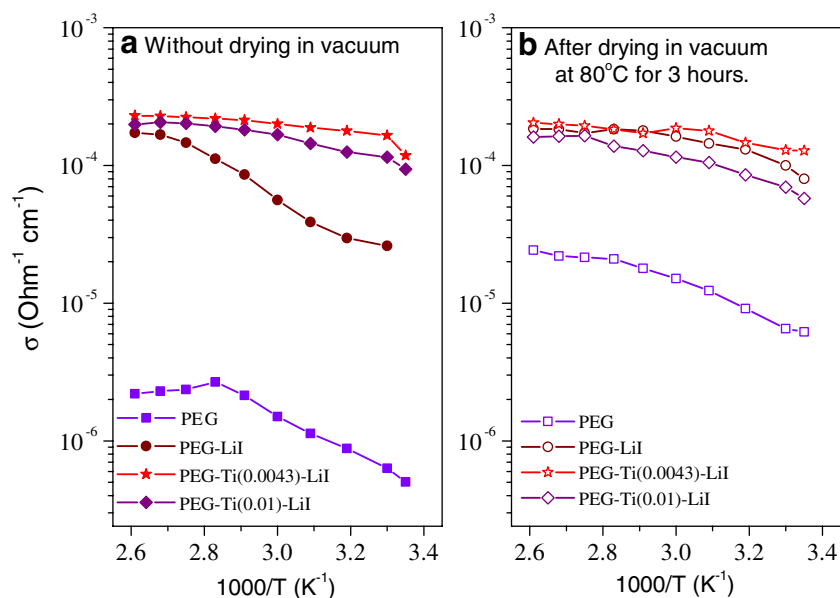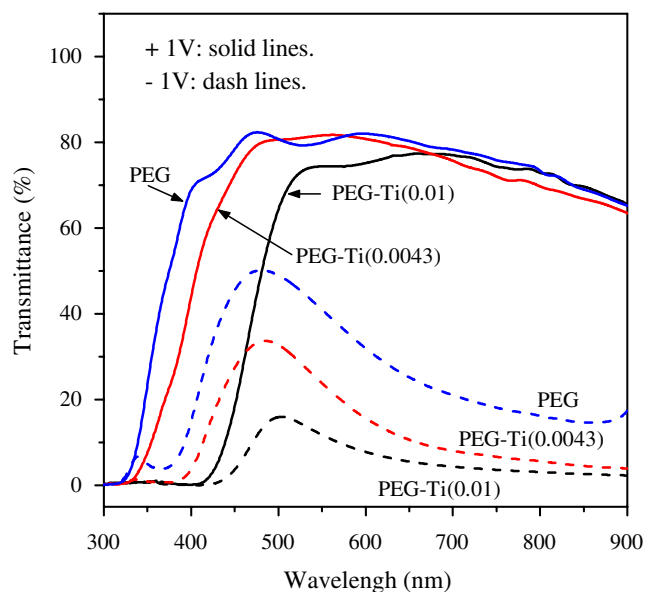
Fig. 6 Optical spectra of ITO/WO$_3$/PE/ITO under +1 V (oxidation) and −1 V (reduction) polarizations with PE of PEG–LiI, PEG–Ti(0.0043)–LiI, and PEG–Ti(0.01)–LiI. The electrolytes were not dried in vacuum before use

650 nm of two ITO/WO$_3$/PE/ITO devices with PEG–LiI or PEG–Ti(0.0043)–LiI as electrolyte. None of these two electrolytes was vacuum-dried before use. It must be mentioned that the observed slower reduction (coloring) speed compared with the faster oxidation (bleaching) one has been observed in similar single WO$_3$ devices based on both liquid and polymeric electrolytes with solvents (PMMA-PC-LiI) [16] (The word "single" means that there is only one electrochromic element in the device). This is due to the different mechanisms that govern the two processes proved by numerical fitting: the exchange of current density at the WO$_3$/electrolyte interface controls the reduction (coloration) process, whereas the space charge-limited Li$^+$ ion diffusion current governs the oxidation (bleaching) one. As for the effect of titanium compound on the optical stability of the same devices, Fig. 7b showed that after 200 modulations, the equilibrium value of the oxidation transmittance at 650 nm of the PEG–LiI-based device starts to decrease, whereas the PEG–Ti(0.0043)–LiI one keeps the same transparency at +1 V after 1,000 cycles. In this case, the bleaching process implies the transformation of the colored Li$_x$WO$_3$ phase into the colorless WO$_3$ by expulsing tungsten ions from the solid electrochromic electrode to the electrolyte. But the amount of the lithium cations that the electrolyte can accept depends on the amount of iodide anions available in the ionic conductor. Possibly part of iodide anions inside the PEG–LiI electrolyte is converted into iodine molecules after polarization potential cycling because of its hygroscopic properties. The less absorption of water molecules together with the
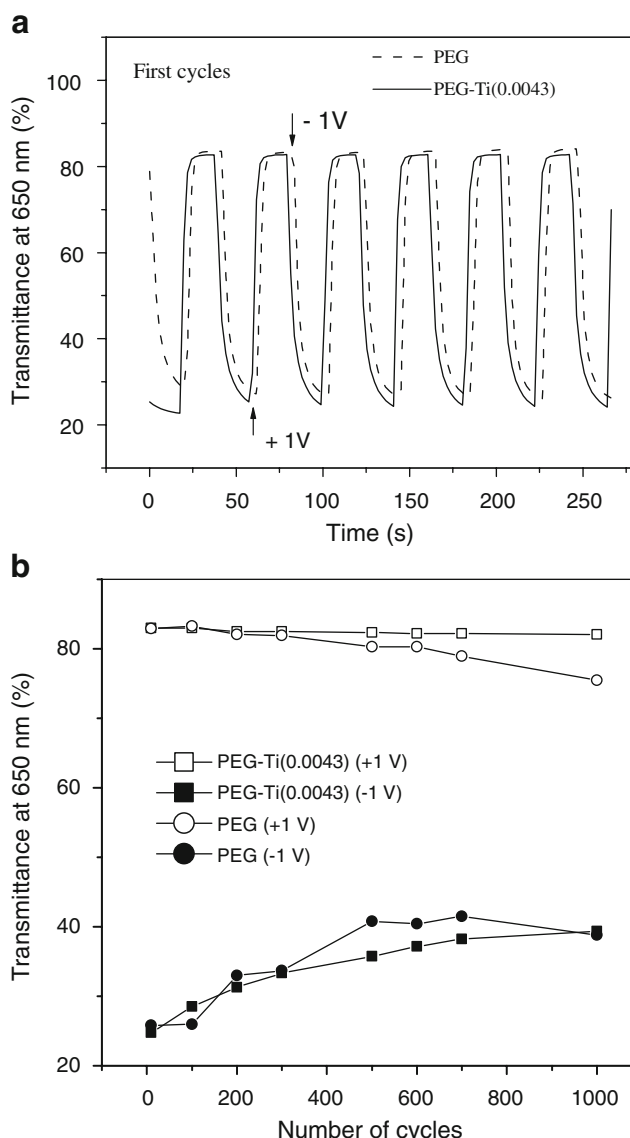

Fig. 7 **a** First six optical transmittance modulations and **b** equilibrium values of optical transmittance at 650 nm after cycling of two ITO/WO$_3$/PE/ITO devices with PE as PEG–LiI and PEG–Ti(0.0043)–LiI. The electrolytes were not dried in vacuum before use

presence of titanium cations in the hybrid electrolytes may keep the iodide anions not to be reduced during oxidation process. Finally, both devices show a similar tendency of apparent deterioration under the reduction polarization (Fig. 7b). From the previous work about the single vs. dual electrochromic devices with polyaniline and poly3-methylthiophene as electroactive elements [19], it is observed that this decreasing redox capacity with cycling (and the slower switch speed as well) comes from the inherent low ion storage capacity in electrolyte/ITO interface of the electrochromic devices with only one electrochemically active electrode. The storage capacity of the counter electrode (ITO) as well as the polymer

electrolyte (100 μm thick) was too low compared with a liquid electrolyte in a three electrode-electrochemical cell. If this counter ITO electrode is coated by a second and complementary electrochromic element with respect to the primary one, the optical switch speeds are largely increased, and the apparent optical contrast deterioration is disappeared. It is expected that the same result would be obtained if the bare ITO electrode could be replaced by an optically complementary secondary electrochromic element. Research works about the use of hybrid electrolytes in WO_3-based electrochromic and photoelectrochromic devices are carrying on and the preliminary tests are compromising, showing a better device performance with the hybrid electrolytes than with the PEG one.

Conclusions

Hybrid materials can be synthesized from PEG and $Ti(OR)_4$ by a sol–gel process. FT-IR analysis of the hybrid materials indicates the formation of a new association between the titanium ions and ether oxygen atoms of PEG. The TGA curves of the same materials show an improved thermal stability and suggest a more narrow distributed molecular mass in them by the chelating between the shorter PEG chains and titanium ions. Results of electrical conductivity measurements of PEG and PEG–Ti-based electrolytes exhibit a humidity-insensitive behavior for hybrid materials in contrast with the single PEG one in a temperature range from 25 to 110°C. The ambient stable hybrid PEG–Ti materials give optically stable WO_3-based electrochromic devices which keep the same transparency and optical contrast after 1,000 cycles of oxidation–reduction polarizations.

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