



Effect of TiO₂ nanoparticles on structural, thermal, mechanical and ionic conductivity studies of PEO₁₂–LiTDI solid polymer electrolyte



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ABSTRACT

In the present study, poly(ethylene oxide) (PEO) complexed with lithium 2-trifluoromethyl-4,5-dicyanoimidazole (LiTDI) nanocomposite solid polymer electrolyte membranes (NSPEMs) have been prepared by solution cast technique using different weight percent of nano-sized TiO₂ ceramic filler. The effect of filler incorporation on the structural, thermal, mechanical and ionic conductivity properties of solid polymer electrolytes have analyzed. X-ray diffraction (XRD) and polarized optical microscopy (POM) results indicated that the crystallinity has been reduced remarkably with the incorporation of TiO₂ nanofiller. The thermal stability and mechanical integrity of the nanocomposite polymer electrolyte system increased significantly compared to filler free electrolytes. The maximum ionic conductivity is found to be in the range of $2.11 \times 10^{-5} \text{ S cm}^{-1}$ for 8 wt% TiO₂ nanofiller in PEO₁₂–LiTDI electrolyte system. These results indicated that the prepared TiO₂ based nanocomposite membrane would be a promising alternative separator for rechargeable lithium-ion battery applications.

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Introduction

Solid polymer electrolyte membranes (SPEMs) have received extensive attention in the past few decades for their potential applications in solid state ionic devices such as lithium batteries, fuel cells, solar cells, etc. [1–3]. Lithium batteries have attracted a great deal of attention due to its higher energy density, improved safety hazards, and good processability [4,5]. As it is well known, SPEMs have several advantages over the liquid counterpart such as desirable shape mouldability, light-weight, free from leakage, mechanical strength, high physical and chemical stability and flexibility of design, thereby permitting miniaturization [6]. One of the most important properties of high-performance polymer electrolytes is their ionic conductivity. In polymer electrolyte membranes, ionic conduction depends on the dissociation of the ionic conductor and the structure of the polymer matrix. High molecular weight poly(ethylene oxide) (PEO) based polymer electrolytes containing lithium salts have been studied extensively due to its compatibility with a wide range of ionic conducting salts

while maintaining an acceptable chemical and electrochemical stability [7].

Recent success of imidazole-derived lithium salts [8] and stressed as “tailor made” salts, notably LiTDI (lithium 4,5-dicyano-2-(trifluoromethyl)imidazole), has encouraged us for lithium battery applications [9]. For exploring the properties of this salt, only a few publications are available [10,11]. In compare with many other lithium salts, LiTDI is fully stable in the presence of moisture [12]. In addition, this LiTDI electrolyte is thermally stable up to 250 °C far more than boiling point of any solvent or stability of many other organic lithium salts. The safety, stability information of LiTDI and its parameters in solvent mixtures are available elsewhere [13]. However, a major drawback of these poly(ethylene oxide)–lithium salt electrolyte membranes for practical applications is that they tend to crystallize at ambient temperatures resulting low ionic conductivity [14].

Generally two ways have been used to enhance the room temperature ionic conductivity of the polymer electrolytes; one is the incorporation of nano-sized ceramic fillers such as TiO₂, CeO₂, SiO₂ and Al₂O₃ [15] in the polymer matrix and the other is the addition of plasticizers such as ethylene carbonate (EC), propylene carbonate (PC) and polyethylene glycol (PEG) [16]. These plasticizers can improve the room-temperature ionic conductivity of the polymer electrolytes, but decrease the mechanical properties and the potential stability of these polymer membranes [17]. The

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incorporation of ceramic nano-fillers reduces the crystalline character, improve the ionic conductivity as well as promote the thermal behaviors, mechanical stability and electrochemical properties of the polymer membrane [18]. Among the several fillers in polymer electrolyte membranes, nano-sized titanium oxide (TiO_2) supports the ionic mobility due to its substrate characteristics, such as shape and surface nature, which effectively disturbs the order packing tendency of the host polymer chains [19]. The effects of TiO_2 , Al_2O_3 and SiO_2 in PEO– LiClO_4 polymer electrolyte has been studied by Chung et al. [20] and identified TiO_2 as the filler with greatest enhancement in ionic conductivity due to the weakened interactions between the polymer chain and the Li^+ ions. To the best of our knowledge, there are no reports available in the literature on the ionic conductivity, thermal stability and mechanical stability enhancement of PEO–LiTDI polymer electrolyte due to the incorporation of nano-sized TiO_2 ceramic filler.

In this work, we have studied the effect of TiO_2 nano-filler incorporation on structural, thermal, mechanical and electrical properties of PEO₁₂–LiTDI polymer electrolyte membrane. X-ray diffraction (XRD), polarized optical microscopy (POM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and universal testing machine (UTM) were employed to characterize the physical and chemical properties of the nanocomposite solid polymer electrolyte membranes (NSPEMs). Impedance spectroscopy was used to study the ionic conductivity of the NSPEMs at various temperatures. Cyclic voltammetry was used to examine the electrochemical potential window of the NSPEM.

Experimental details

Materials used

High molecular weight PEO (MW = 4×10^6 g/mole), TiO_2 nanopowder (21 nm) and anhydrous acetonitrile were purchased from Sigma–Aldrich (St. Louis, USA). Lithium 2-trifluoromethyl-4,5-dicyanoimidazole (LiTDI) obtained from Alfa Aesar.

Preparation of nanocomposite solid polymer electrolyte membranes

The NSPEMs have been prepared by using solution cast technique. The high molecular weight PEO, TiO_2 nanopowder and LiTDI have been dried at 50, 100 and 100 °C under vacuum for 24 h respectively. The high molecular weight PEO and LiTDI was dissolved in anhydrous acetonitrile, followed by the addition of different weight percentages of TiO_2 nanofiller. The relative amounts of PEO and LiTDI are taken at the EO/Li = 12 based only on the amount of ethylene oxide in the PEO and lithium in the LiTDI. The mixture was stirred for 24 h to obtain a homogeneous viscous solution. This solution was cast onto Teflon plates followed by the evaporation of the solvent in a dry box for about 1 day. The resulting films were further dried in vacuum oven at 40 °C for 24 h. After that the films shifted to nitrogen-filled glove box and left undisturbed for 5 days to remove residual acetonitrile. The NSPE membrane synthesis process and the interaction scheme among PEO, LiTDI and TiO_2 are displayed in Fig. 1.

Characterization

The X-ray diffraction spectra of polymer electrolyte membranes were carried out using an X-ray diffractometer (D-MAX 2500, Rigaku) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at ambient temperature in the range $2\theta = 5\text{--}50^\circ$. Surface morphology and microscopic feature of the polymer films were examined using polarized optical microscope (Optiphot-2 Pol, Nikon) at room temperature. The thermogravimetry (TG) measurements were carried out on a

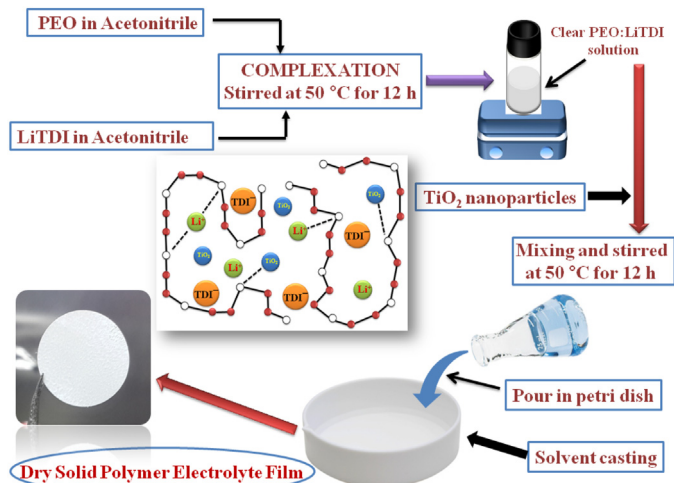


Fig. 1. The NSPE membrane synthesis process and the interaction scheme among PEO, LiTDI and TiO_2 .

TGA-2950 thermal analyzer (Hi-Res, TA instruments) by heating from 25 to 500 °C under a N_2 atmosphere at a heating rate of 20 °C/min, with a sample about 7 mg. The formation of polymer–salt–nanofiller complexes and interaction among polymer, salt, and ceramic nanofiller were determined by Fourier transform infrared spectroscopy (FTIR) using Nicolet 380 FT-IR spectrometer (Thermo Electron) in the region 4000–400 cm^{-1} at a resolution 1 cm^{-1} . Universal materials testing machine (Lloyd instruments, LR5K Plus) has been used to measure the mechanical stability of the solid polymer electrolytes. Impedance and conductivity of the samples were determined using an Iviumstat (Ivium Technologies, Netherlands). The measurements were done in the frequency range from 1 Hz to 1 MHz by varying temperature from 23 to 60 °C. The impedance studies were carried out by sandwiching the solid polymer electrolyte membrane between two gold electrodes under spring pressure. The thickness of each sample was measured using a micrometer screw gauge. The electrochemical studies were carried out by cyclic voltammetry using an electrochemical analyzer (WonA tech WBCS 3000L battery cyler system) in the potential range 0–5 V (vs. Li^+/Li) at a scanning rate of 5 mV s^{-1} .

Results and discussion

XRD analysis

The XRD patterns of pure PEO, pure LiTDI, pure TiO_2 and PEO₁₂–LiTDI– TiO_2 polymer electrolytes at various TiO_2 concentrations are shown in Fig. 2. The X-ray diffraction pattern of pristine PEO shows two high intensity diffraction peaks at 19.36° and 23.72° which are assigned to set of planes (1 2 0) and (1 1 2) [21]. The XRD pattern of LiTDI salt exhibits sharp peaks centered at 2θ angle of 10.4°, 11.2°, 15.5°, 23.4°, 24.7°, 27.2°, 31.3°, 33.5°, 40.3° due to the crystalline nature of the salt. After LiTDI inclusion, the peaks of PEO shifted to lower 2θ values due to increase of the interplanar crystal spacing of PEO which may have occurred from the insertion of large TDI anions into PEO lattice. In XRD pattern of PEO₁₂–LiTDI polymer electrolyte (0 wt% TiO_2), no diffraction peak of LiTDI is found, demonstrating that the added lithium salt has well dissolved into the PEO matrix. With the incorporation of LiTDI decreased the intensity of the peaks and broader than pure PEO. This can be attributed to a destruction effect of the lithium salt on the ordered arrangement of the polymer chains, and hence an enhancement in the amorphous phase and led to increase in ionic conductivity [22].

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