



Effect of intercalated and exfoliated montmorillonite clay on the structural, dielectric and electrical properties of plasticized nanocomposite solid polymer electrolytes



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ABSTRACT

Plasticized nanocomposite solid polymer electrolyte (PNSPE) films, consisted of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) polymer blend matrix (50/50 wt%) with lithium tetrafluoroborate (LiBF₄) as dopant ionic salt (10 wt%), ethylene carbonate (EC) as plasticizer (10 wt%) and montmorillonite (MMT) clay as nanofiller (3 wt%), have been prepared by classical solution-cast (SC) and the ultrasonic-microwave irradiated (US–MW) solution-cast methods. X-ray diffraction (XRD) study confirms that these PNSPE films are predominantly amorphous and contain very small amount of PEO crystallites. The SC method prepared PNSPE film bears highly ordered intercalated MMT structures, whereas, the US–MW method prepared PNSPE film has large amount of disordered exfoliated MMT structures. Dielectric relaxation spectroscopy (DRS) from 20 Hz to 1 MHz has been employed for characterization of complex dielectric permittivity, alternating current electrical conductivity and complex impedance spectra of the films. Three relaxation processes corresponding to the electric double layers dynamics, polymer chain segmental motion and ionic conductivity have been explored. It has been observed that the dielectric and electrical properties of the PNSPE films change notably with the film preparation methods. Results reveal that the exfoliated MMT decreases the dielectric polarization and creates hindrance to the polymer chain segmental dynamics which causes decrease of ionic conductivity in comparison to the ion-dipolar complexes containing intercalated MMT. The room temperature dc ionic conductivity of the PNSPE films have been found about 10^{-5} S cm⁻¹, which confirms these materials as potential candidate for design and development of flexible-type all-solid-state lithium-ion conducting electrochromic devices.

1. Introduction

The solid polymer electrolytes (SPEs) are flexible-type solid-state ion-dipolar complexes which are recognized as the most suitable light weight ion-conducting dielectric materials for the design and development of dry-state high energy density rechargeable batteries, supercapacitors, ion sensors, electrochromic windows, dye-sensitized solar cells and fuel cells [1–8]. In the designing of dry-state secondary ion battery, besides the anode and cathode materials, an indispensable SPE also has a major role in the conduction of ions to control the resultant power density. So far, researchers have used various kinds of synthetic semicrystalline- and amorphous-type polar polymers as host matrices with a variety of alkali metal ionic salts for the preparation of high-performance SPEs to fulfill the future requirements of flexible-type ion-conducting electronic devices. Lithium tetrafluoroborate (LiBF₄) is one of the low dissociation energy ionic salts suitable in preparation of SPE

materials. Several aprotic and non-volatile dipolar liquids of high dielectric permittivity have been considered as plasticizers in order to increase the ionic conductivity value of such plasticized SPEs (PSPEs) [9–14]. Further, inorganic nano materials have also been dispersed into the SPEs for the enhancement of their ionic conductivity and also improvement of mechanical, thermal and chemical stabilities of the nanocomposite SPE (NSPE) materials [3,7–10,14–18]. The use of polymers blend matrix in preparation of SPEs remains the choice of researchers because of the superior properties of the blend matrix over the individual polymers matrices [14–16,19–22].

The polymer blend matrix consisted of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) has received much attention in preparation of SPEs for the enhancement of lithium-ion conduction processes [14–16,19,20,23–25]. In the PEO–PMMA blend based SPEs, the ether oxygen (–O–) of PEO and the carbonyl group (C=O) of PMMA present in the repeat units of their backbone chains mainly act as

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functional groups in the formation of ion-dipolar complexes i.e., $\ddot{O}\cdots Li^+$, $C=\ddot{O}\cdots Li^+$ and $C=\ddot{O}\cdots Li^+\cdots\ddot{O}$. Further, there is continuous breaking and reforming of these coordinations along with the polymer chain segmental dynamics which results in acceleration of the ions transportation process mainly through hopping mechanism [14–16,25]. In the last few years, we have prepared and characterized several types of SPE materials based on PEO, PMMA and PEO–PMMA blend as host matrices with doping of lithium ions in order to explore their suitability as electrolyte for the development of lithium-ion batteries and also in other ion conducting electrochromic devices [14–16,25–28].

Among the various liquid plasticizers, ethylene carbonate (EC) of static dielectric permittivity $\epsilon_s = 89.78$ [5], has been frequently used for the preparation of PSPEs [9–12]. It enhances the amorphous phase and simultaneously creates more free volume in the host polymer matrix favouring the increase of polymer chain segmental dynamics due to which there is enhancement of ionic conductivity of the PSPEs. In regards to the inorganic nanofillers, the montmorillonite (MMT) clay is one of the most frequently used nano material in preparation of polymer nanocomposites by dispersing it with a state-of-the-art in the PEO and PMMA matrices and such composites have greatly improved thermal and mechanical properties [29–32]. The hydrophilic MMT material has one nanometer thick layered sheets stacked by weak dipolar and van der Waals forces, and it forms intercalated and exfoliated structures in the polar polymers matrices due to formation of electrostatic and transient-type interactions between the functional dipolar groups of polymer chains and the charges present on layered sheets [32–34]. For safer working of SPEs in the rechargeable solid-state batteries at elevated temperature, the MMT clay has been preferred as inorganic nanofiller for the preparation of NSPEs [15,16,18,25,35–39]. The intercalated and exfoliated MMT structures play important role in the improvement of thermo-physical properties, formation of relatively favourable ions transportation paths and also in the restriction of the ion-pairing effect in the MMT dispersed NSPE materials.

In the present work, keeping all the above mentioned facts in mind, an attempt has been made to investigate the effects of intercalated and exfoliated MMT on the structural, dielectric and electrical properties of the plasticized nanocomposite solid polymer electrolyte (PNSPE) films i.e., (PEO–PMMA)–LiBF₄–10 wt% EC–3 wt% MMT, which were prepared by two different types of methods. The dielectric relaxation spectroscopy (DRS) and X-ray diffraction (XRD) techniques were employed for the characterization of dielectric and structural properties of the PNSPE films in order to explore the effects of sample preparation methods and the MMT structures on these properties of the PNSPEs. The DRS measurements were made over the frequency range from 20 Hz to 1 MHz, at room temperature (27 °C). The study of dielectric and electrical spectra in this frequency range is most appropriate because the solid polymer electrolytes, at room temperature, exhibit relaxation processes corresponding to their structural dynamics, ionic conductivity and electrical double layers (EDLs) dynamics over the same frequency range. These relaxation processes are important in analysis of ions transportation mechanism in the solid ion-dipolar complexes. The XRD patterns of the PNSPE films were recorded in the angular range from 3.8 to 30° because the semicrystalline PEO and the MMT, which are constituents of the films exhibit their characteristic diffraction peaks in this range.

2. Experimental

2.1. Materials and sample preparation

The PEO ($M_w = 6 \times 10^5 \text{ g mol}^{-1}$), PMMA ($M_w = 3.5 \times 10^5 \text{ g mol}^{-1}$), LiBF₄ and MMT clay (Nanoclay, PGV, a product of Nanocor®) were obtained from Sigma–Aldrich, USA. The ethylene carbonate (EC), anhydrous acetonitrile and tetrahydrofuran of spectroscopic grade were purchased from Loba Chemie, India. Equal weight

amounts of PEO and PMMA each of 1 g, along with 0.2 g amounts individually of LiBF₄ and EC for their 10 wt% concentrations and 0.06 g MMT for its 3 wt% concentration with respect to the 2 g amount of polymer blend (PEO–PMMA) were used for the preparation of (PEO–PMMA)–LiBF₄–10 wt% EC–3 wt% MMT films by two different sample preparation methods. The 10 wt% concentration of LiBF₄ in the films is corresponding to the stoichiometry 16:1 of the polymers dipolar groups ($E\ddot{O} + (C=\ddot{O})$) to the salt ions (Li^+), which is kept low in order to avoid the ion-pairing effect. The PNSPE films were prepared by classical solution-cast (SC) method and the ultrasonic-microwave (US–MW) irradiated solution-cast method. The surfaces of these PNSPE films were made smooth by employing hot-press technique using polymer press film making unit (Technosearch Instruments; Model PF-M15). The steps followed during the preparation of these PNSPE films by both the methods are same as reported in detail in our earlier publication [15].

2.2. Instruments and characterizations

2.2.1. Structural

The structures of PNSPE films were characterized using a PANalytical X'pert Pro MPD X-ray diffractometer (XRD) operated at 1800 W (45 kV and 40 mA). The Cu K α radiation of wavelength $\lambda = 1.5406 \text{ \AA}$ was used for recording the XRD patterns in reflection mode over the angular range $3.8^\circ \leq 2\theta \leq 30^\circ$ with a scan rate of $0.05^\circ/\text{s}$, at room temperature.

2.2.2. Dielectric and electrical

The DRS measurements of the PNSPE films were carried out using an Agilent technologies 4284A precision LCR meter equipped with Agilent 16451B solid dielectric test fixture in the frequency range from 20 Hz to 1 MHz, at 27 °C. The frequency dependent values of capacitance C_p , resistance R_p and dielectric loss tangent $\tan\delta$ (dissipation factor D) of each PNSPE film sandwiched between the electrodes of the dielectric test fixture were measured in the parallel mode circuit operation with increasing frequency of the applied alternating current (ac) electric field of 1 V. These measured values of C_p , R_p and $\tan\delta$ were used for evaluation of complex dielectric function $\epsilon^*(\omega) = \epsilon' - j\epsilon''$, ac electrical conductivity $\sigma^*(\omega) = \sigma' + j\sigma''$ and complex impedance $Z^*(\omega) = Z' - jZ''$ spectra for the PNSPE films using the expressions described in detail elsewhere [28].

3. Results and discussion

3.1. Structural analysis

The XRD patterns of MMT clay nanopowder and (PEO–PMMA)–LiBF₄–10 wt% EC–3 wt% MMT films prepared by SC and US–MW methods are shown in Fig. 1. The MMT nanopowder exhibits its main characteristic diffraction peak at $2\theta = 7.03^\circ$, which is corresponding to its (001) reflection plane [33]. The SC method prepared PNSPE film also exhibits the intense MMT diffraction peak at $2\theta = 4.91^\circ$. In addition to the MMT peak, this film has peaks at $2\theta = 19.43^\circ$ and $2\theta = 23.57^\circ$, which are the main characteristic diffraction peaks of PEO crystallites corresponding to its reflection planes (120) and concerted (112),(032), respectively, as reported earlier for the pristine PEO film [33]. The other polymer PMMA is amorphous and has broad and diffused hump around $2\theta = 16^\circ$ [28]. Although, LiBF₄ is crystalline and has the main intense diffraction peak at $2\theta = 26.33^\circ$ [40], but it is not exhibited in these PNSPE films which confirms the complete dissolution of the added salt due to its participation in the formation of large scale ion-dipolar complexes. In case of US–MW method prepared PNSPE film, there is appearance of diffused-type MMT diffraction peak at $2\theta = 4.46^\circ$, and also of relatively low intensity PEO peaks are exhibited as compared to that of the SC method prepared PNSPE film. The observed low intensity diffraction peaks of PNSPEs in

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