



Effects of plasticizer and nanofiller on the dielectric dispersion and relaxation behaviour of polymer blend based solid polymer electrolytes



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ABSTRACT

Solid polymer electrolytes consisted of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) blend (50:50 wt/wt%) with lithium triflate (LiCF_3SO_3) as a dopant ionic salt at stoichiometric ratio $[\text{EO} + (\text{C}=\text{O})]:\text{Li}^+ = 9:1$, poly(ethylene glycol) (PEG) as plasticizer (10 wt%) and montmorillonite (MMT) clay as nanofiller (3 wt%) have been prepared by solution cast followed by melt–pressing method. The X–ray diffraction study infers that the (PEO–PMMA)– LiCF_3SO_3 electrolyte is predominantly amorphous, but (PEO–PMMA)– LiCF_3SO_3 –10 wt% PEG electrolyte has some PEO crystalline cluster, whereas (PEO–PMMA)– LiCF_3SO_3 –10 wt% PEG–3 wt% MMT electrolyte is an amorphous with intercalated and exfoliated MMT structures. The complex dielectric function, ac electrical conductivity, electric modulus and impedance spectra of these electrolytes have been investigated over the frequency range 20 Hz to 1 MHz. These spectra have been analysed in terms of the contribution of electrode polarization phenomenon in the low frequency region and the dynamics of cations coordinated polymer chain segments in the high frequency region, and also their variation on the addition of PEG and MMT in the electrolytes. The temperature dependent dc ionic conductivity, dielectric relaxation time and dielectric strength of the plasticized nanocomposite electrolyte obey the Arrhenius behaviour. The mechanism of ions transportation and the dependence of ionic conductivity on the segmental motion of polymer chain, dielectric strength, and amorphicity of these electrolytes have been explored. The room temperature ionic conductivity values of the electrolytes are found $\sim 10^{-5} \text{ S cm}^{-1}$, confirming their use in preparation of all-solid-state ion conducting devices.

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1. Introduction

Solid polymer electrolytes (SPEs) belong to one of the most important technological branch of novel materials owing to their promising properties over the liquid and ceramic electrolytes. The high flexibility, light weight, leak proof, good electrochemical performances and ease of preparation have established the SPEs as the most suitable material for the compact design of the all-solid-state ion conducting electrochromic devices, particularly in fabrication of the solid state high energy density rechargeable batteries to run portable electronic equipments for longer duration. These materials represent a fascinating class of solid–state coordinated complexes of polymer dipolar group/s with the cations of dopant salt, and

mostly have high amorphicity [1–17]. In these electrolytes, their amorphous structure and the dynamics of polymer chain segments in transient structures play an important role in the mechanism of the ions transportation. Therefore, the knowledge on how the transportation of ions coupled with the polymer chain dynamics occurred, and in what amount they contributed in the enhancement of room temperature (RT) ionic conductivity of a particular SPE material, are presently an intense topic of research and development, especially their characterization by the dielectric relaxation spectroscopy (DRS) [9–15,18,19].

The solid state complexes of poly(ethylene oxide) (PEO) matrix with different lithium salts have been frequently investigated owing to their better flexibility and good mechanical stability [1–3,6,7,10–15]. Although, PEO has high solvating power for the alkali salts but its crystalline phase limits the ionic conductivity of the SPE at RT. Therefore, in addition to semicrystalline PEO, several polymers of high amorphicity were also used as host matrix in the

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preparation of SPEs in order to achieve their RT ionic conductivity up to the realistic device applications. The poly(methyl methacrylate) (PMMA) matrix, which has amorphicity more than 96%, is preferred in preparation of SPE materials [4,5,19–22]. PMMA is a light weight polymer of high optical transparency, high strength and dimensional stability, but the brittle property under a loaded force limits its suitability in preparation of SPE materials of required flexibility.

In search of the novel SPE materials of moderate ionic conductivity and improved physico-chemical properties, work is in progress on the PEO-PMMA blend matrix based electrolytes [23–29]. The blending of PEO with PMMA matrix results in increase of PMMA flexibility and decreases its brittleness, whereas the PMMA environment reduces the crystallinity of PEO due to formation of some PEO-PMMA miscible phases in the blend. These properties of the PEO-PMMA blend make it a novel polymeric blend matrix for the preparation of SPEs. Our survey of literature reveals that the PEO-PMMA blend matrix is frequently used with lithium perchlorate [23–27] and silver nitrate [28,29] salts, and their ionic conductivity results seem highly interesting.

To the best of our knowledge, the PEO-PMMA matrix based electrolyte comprising lithium triflate (LiCF_3SO_3) salt, poly(ethylene glycol) (PEG) as plasticizer and montmorillonite (MMT) clay as inorganic nanofiller is yet to be studied in search of their possible applications in preparation of the ion conducting electrochromic devices. The small chain PEG molecule and large chain PEO macromolecules have same repeat unit in their structural backbone, and therefore it is interesting to explore the effect of PEG addition on the amorphicity of PEO based electrolyte in presence of MMT nanofiller. Further, the studies on PEO-MMT [30] and PMMA-MMT [31] nanocomposites have established that the addition of a small amount of MMT in the PEO and PMMA matrices significantly enhances their thermal, mechanical, gas barrier and corrosion protection properties. Such improvements in various properties of polymer matrix are needed for the safe working of the electrolytes at elevated temperature, hence the MMT nanofiller has been used in the present study. Therefore, in the light of above discussion, we have made an attempt to investigate the detailed dielectric and electrical properties of the (PEO-PMMA)- LiCF_3SO_3 -PEG-MMT electrolytes. This study has been carried out to gain insight into the effects of plasticizer and nanofiller on the amorphicity and ion transport mechanism in the complex polymeric electrolyte system by the comparative analysis of dielectric and electrical spectra.

2. Experimental

2.1. Sample preparation

The PEO ($M_w = 6 \times 10^5 \text{ g mol}^{-1}$), PMMA ($M_w = 3.5 \times 10^5 \text{ g mol}^{-1}$), PEG ($M_w = 200 \text{ g mol}^{-1}$), hydrophilic MMT (Nanoclay, PGV, a product of Nanocor[®]) and LiCF_3SO_3 were obtained from Sigma-Aldrich, USA. The anhydrous acetonitrile and tetrahydrofuran of spectroscopic grade were purchased from Loba Chemie, India. All the chemicals were dried at the standard temperatures before their use. For the preparation of PEO-PMMA blend based electrolyte films, the 50:50 wt/wt% blend of PEO and PMMA was used. The average stoichiometric ratio $[\text{EO} + (\text{C}=\text{O})]:\text{Li}^+ = 9:1$ was used, where $\text{EO} + (\text{C}=\text{O})$ is the number of ethylene oxide unit (EO) and the carbonyl group ($\text{C}=\text{O}$) of the (PEO-PMMA) blend with respect to the lithium cations (Li^+) of the LiCF_3SO_3 . The concentration of the salt has been kept low in order to minimize the possibility of ion-pairing effect. The 10 wt% and 3 wt% concentrations of PEG and MMT, respectively, to the weight of PEO-PMMA blend were used for the preparation of plasticized

nanocomposite electrolytes. These PEG and MMT concentrations are adequate to explore their effects on the dielectric properties of the electrolytes.

The electrolyte films having three different compositions were prepared by classical solution casting method.

- (i) SPE film: For the preparation of solid polymer electrolyte (SPE) film of (PEO-PMMA)- LiCF_3SO_3 , initially, the required amounts of PEO and PMMA were dissolved in acetonitrile and tetrahydrofuran, respectively, in separate glass bottles. After that, LiCF_3SO_3 was added in the PEO solution which was dissolved and mixed homogeneously under magnetic stirring. Subsequently, the PEO- LiCF_3SO_3 electrolyte solution was mixed with PMMA solution by magnetic stirring for 2 h at room temperature which resulted in the homogeneous (PEO-PMMA)- LiCF_3SO_3 electrolyte solution. The solution was casted onto Teflon petri dish and by slow evaporation of solvent at room temperature, the (PEO-PMMA)- LiCF_3SO_3 film was achieved.
- (ii) PSPE film: For the preparation of plasticized solid polymer electrolyte (PSPE) film, initially, the (PEO-PMMA)- LiCF_3SO_3 electrolyte solution was prepared following the steps as mentioned above, and after that the amount of PEG for 10 wt % concentration, with respect to weight of PEO-PMMA blend, was added and homogeneously mixed, which resulted in the (PEO-PMMA)- LiCF_3SO_3 -10 wt% PEG solution. Using this solution, the (PEO-PMMA)- LiCF_3SO_3 -10 wt% PEG electrolyte film was achieved by solution casting method.
- (iii) PNSPE film: For the preparation of plasticized nanocomposite solid polymer electrolyte (PNSPE) film, initially, the (PEO-PMMA)- LiCF_3SO_3 -10 wt% PEG solution was prepared and after that the required amount of MMT for 3 wt% concentration, with respect to weight of PEO-PMMA blend, swelled in acetonitrile was added and stirred, which resulted in the (PEO-PMMA)- LiCF_3SO_3 -10 wt% PEG-3 wt% MMT electrolyte solution. This solution was casted onto Teflon petri dish and the film of (PEO-PMMA)- LiCF_3SO_3 -10 wt% PEG-3 wt% MMT plasticized nanocomposite electrolyte was achieved after solvent evaporation.

The solvent evaporated surfaces of these solution casted SPE, PSPE and PNSPE films were found uneven at micro scale level, which were made smooth by melt-pressing technique using polymer press film making equipment. In this technique, each film was initially melted at 70°C in circular stainless steel die of 60 mm diameter with 0.45 mm thickness spacer, and subsequently pressed under 2 tons of pressure per unit area. Cooling the material slowly up to room temperature, the solution cast melt-pressed electrolyte films of 0.45 mm thickness and having smooth surfaces were achieved. The smooth surfaces of the films at micro scale level were needed to achieve proper physical contact between the film and the dielectric test fixture electrodes surfaces in order to eliminate the formation of tiny air-gap pockets to minimize the measurement error.

2.2. Characterizations

The X-ray diffraction (XRD) patterns of the PEO-PMMA blend based various SPE films and their constituents were recorded in reflection mode using a PANalytical X'pert Pro MPD diffractometer of $\text{Cu K}\alpha$ radiation (1.5406 \AA) operated at 45 kV and 40 mA with a scanned step size of $0.05^\circ/\text{s}$. The dielectric relaxation spectroscopy (DRS) of the electrolyte films was carried out using Agilent technologies 4284A precision LCR meter frequency f range 20 Hz to 1 MHz having 1 V electric signal, along with Agilent 16451B solid

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