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Study of time-ageing effect on the ionic conduction and structural dynamics in solid polymer electrolytes by dielectric relaxation spectroscopy

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ABSTRACT

This research work demonstrates the effect of time-ageing on the dielectric and electrical properties, and also the structural dynamics of solid polymer electrolyte (SPE) and nanocomposite solid polymer electrolyte (NSPE) films over a period of one-year. The SPE and NSPE films based on polymer blend matrix of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) (50/50 wt%) with lithium triflate ($LiCF_3SO_3$) as dopant ionic salt (22 wt %) and montmorillonite (MMT) clay (3 wt%) as inorganic nanofiller have been prepared by solution-cast method followed by melt-pressing technique. These films are characterized by employing scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), dielectric relaxation spectroscopy (DRS) and electrochemical analysis (ECA) techniques. The influence of MMT filler on the polymer-ion interactions was confirmed from comparative analysis of the structural and electrochemical properties of the SPE and NSPE films. The XRD and DRS measurements on these films were repeated at various time intervals over one-year duration in order to explore the time-ageing effect on the structural properties, dielectric parameters, and ionic conduction mechanisms in the electrolyte samples. The XRD study reveals the irregular variation of PEO crystalline phase in these films and also the intercalated/exfoliated MMT phases in the NSPE film with time-ageing. The ionic conductivity of the SPE and NSPE films increases by about one order of magnitude over the time-ageing period of 2 to 3 months of these films, whereas it drops by more than one order of magnitude at the one-year ageing in comparison to that of the freshly prepared films measured on day first. It is found that the ionic conductivity of these materials has a correlation with the relaxation time of polymers cooperative chain segmental motion which validates the fact that the ions transport in the solid ion-dipolar complexes occurs through hopping mechanism coupled with polymers structural dynamics not only for the freshly prepared electrolyte films but also for the films with time-ageing. Further, these electrolyte films have good electrochemical stability, better reversibility and cyclability, and the ion transference number close to unity.

1. Introduction

In the advancement of materials science and engineering, the solid polymer electrolytes (SPEs) and gel polymer electrolytes (GPEs), and these materials based ion-conducting solid-state devices remain one of the most attractive research areas in the past decade from academic and technological points of view [1–6]. So far, the lithium ion conducting SPE materials have established their promising properties in the design and development of rechargeable lithium-ion batteries (LIBs) and also for the ion conducting electrochromic devices and sensors [1–10]. The striking features of SPEs like light weight, high flexibility, compact size, ease of preparation, safe working over a wide temperature range, and high energy storing ability are much superior properties over those offered either by the liquid or ceramic electrolytes. So far, multiple-objective based studies on the SPE materials have been performed mainly focused on tailoring the suitable composition of the polymer, ionic salt, plasticizer and/or inorganic nanofiller with a change in sample preparation methods in order to achieve the desired ionic conductivity and their electrochemical compatibility with the cathode materials. Additionally, the high mechanical flexibility, thermal and chemical stabilities, and also a deep understanding of various factors responsible for the ion transportation process in the SPE materials are required in order to confirm their applications in ion-conducting devices.

For the preparation of novel SPE materials, various semicrystalline and/or amorphous polymer matrices, numerous ionic salts and a

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variety of additives i.e., inorganic nanofillers and high dielectric permittivity plasticizers have been used in order to achieve an encouraging value of ionic conductivity at room temperature. Poly(ethylene oxide) (PEO) is a frequently used polymer host matrix for the preparation of SPEs from their initial stage of discovery [11] to continuous thereafter till date [5–8, 12–20]. PEO matrix has become the most popular choice to the researchers because of its high solvating power for the ionic salts in the solid-state SPE preparation process in addition to the good flexible-type stable film forming ability and also the low values of its lattice energy and glass transition temperature [8]. But as a consequence of the semicrystalline nature of the PEO matrix at room temperature, the SPEs based on it exhibit relatively low ionic conductivity because the ordered crystalline structure is jam-packed and does not leave much vacant spaces required for accelerating the ion transportation through hopping mechanism. To reduce the crystalline phase in the PEO based SPE materials, several liquid plasticizers were added in the PEO matrix during the preparation of electrolytes which confirmed a greater increase in ionic conductivity of the plasticized SPEs [13, 16, 18]. In addition to these materials, amorphous poly(methyl methacrylate) (PMMA) matrix is also attempted by several researchers for the preparation of novel amorphous SPE materials [21–26]. But, it was realized that the side pendent groups of PMMA chain cause it to become dynamically more rigid, and also its film shows brittle behaviour and has relatively high value of the glass transition temperature, so the PMMA matrix is used with plasticizers for preparation of SPEs having suitable physicochemical properties in addition to enhanced ionic conductivity [21, 24, 26].

Meanwhile, it was noted that the use of PEO–PMMA blend matrix can overcome the unsought properties of the individual polymers and exhibits better combined physicochemical properties which are fundamentally needed for the preparation of novel SPE materials [27–35]. The DRS studies on the PEO–PMMA blend matrix based various SPEs revealed that the ions transport in transient-type ion-dipolar complexes of these materials occurs coupled with cooperative polymer chain segmental dynamics through hopping mechanism [30–33]. In the recent years, a lot of work has been done in our laboratory on the NSPE materials based on PEO–PMMA blend matrix with $LiCF_3SO_3$ as dopant ionic salt and montmorillonite (MMT) clay as an inorganic nanofiller [30, 32–34]. The dispersion of MMT in the SPEs is of special interest because it forms intercalated and exfoliated phases which promotes the cation transportation and also restricts the ion-pairing effect in the NSPE materials [25, 30, 32, 33, 36, 37].

Survey of the literature reveals that a variety of SPEs and NSPEs has been extensively investigated from academic and technological points of view. But the study of time-ageing effect on the structural, dielectric and electrical properties of the PEO–PMMA blend based SPE and NSPE materials still remain untouched. The time-ageing properties of such electrolyte materials may be interesting in regards to understand the performance with the ageing of the SPE based electrochemical devices. Previous works on the physical ageing of the polymer electrolyte films as a function of time have been done mainly focusing on the increment of interfacial stability between electrolyte and lithium metal electrode in a cell, and also on how to minimize the formation of the lithium passivation layer with time to maintain the device performance [38–44]. These studies have established that the use of solvent-free electrolyte as well as the dispersion of ceramic nanofillers lead to better interfacial properties and lessen the chemical and structural degradation with the physical ageing. Recently, the time-ageing effect on the ionic conductivity and glass transition temperature of polymer-in-salt type electrolyte films based on poly(acrylonitrile-*co*-butyl acrylate) and lithium salts has been investigated for the longer ageing duration [45]. This study revealed that there is a decrease of ionic conductivity by a factor of about 10 after 60 days of storage of the electrolyte film comprising poly(AN-*co*-BuA) matrix with 65 wt% LiTFSI. Further, a huge decrease in lithium-ion conductivity was observed after 170 days of films storage duration which also depends on the nature of ionic salt and different types of mixed salts used in the preparation of polymer-in-salt type SPEs [45].

In this paper, an attempt has been made to explore the effect of time-ageing on the ionic conductivity and structural dynamics of PEO–PMMA blend matrix based SPE and the MMT dispersed NSPE films. This work is a novel approach to broaden the current knowledge in deciding the ion conduction efficiency of an electrolyte material with its time evolution. Although, the present work does not extend to the study of electrode-electrolyte interfacial stability and the effect of electrolyte material on the behaviour of lithium passivation layer in a lithium-ion battery with time-ageing as investigated earlier [39–43], but it mainly focuses on the time-ageing dependent structural properties, dielectric dispersion, ionic conductivity and the dynamical relaxation processes in the (PEO–PMMA)–$LiCF_3SO_3$ film (SPE) and (PEO–PMMA)–$LiCF_3SO_3$–3 wt% MMT film (NSPE) at room temperature. The MMT has been considered as an inorganic nanofiller in order to understand the consequences of its intercalated and exfoliated phases on the dielectric and electrical behaviour of NSPE as a function of time-ageing by comparing its properties with the SPE material.

2. Experimental

2.1. Sample preparation

PEO granular powder ($M_w = 600{,}000\ g\ mol^{-1}$), and PMMA powder ($M_w = 350{,}000\ g\ mol^{-1}$), MMT clay nanopowder (hydrophilic 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, and the same were used as solvents. The classical solution-casting method followed by melt-pressing technique was employed for the preparation of SPE and NSPE films. The polymer blend having equal weight amounts of PEO and PMMA (50/50 wt%) was used as the base matrix. 22 wt% $LiCF_3SO_3$ amount to the weight of polymer blend was used as ionic dopant salt for the fixed stoichiometric molar ratio 12:1 of polymers functional groups [EO + (C=O); where EO is the total number of ethylene oxide units of PEO and C=O is the carbonyl groups of PMMA in the prepared polymer blend] to the $LiCF_3SO_3$ cations (Li^+) in the electrolyte samples. The 3 wt% MMT amount to the weight amount of PEO–PMMA blend was used as nanofiller.

For the preparation of SPE film (i.e., (PEO–PMMA)–$LiCF_3SO_3$), initially, the PEO and PMMA, each of 1 g amount were dissolved in acetonitrile and tetrahydrofuran, respectively, in separate conical flasks and then mixed together to achieve the PEO–PMMA blend solution. After that, the required amount (0.4425 g) of $LiCF_3SO_3$ was added to the polymer blend solution and dissolved under magnetic stirring process. This homogeneous (PEO–PMMA)–$LiCF_3SO_3$ electrolyte solution was cast on to a Teflon petri dish which results in the SPE film by slow evaporation of the solvents at room temperature. Same steps were performed for the preparation of the solution-cast NSPE film (i.e., (PEO–PMMA)–$LiCF_3SO_3$–3 wt% MMT) with the dispersion of 0.06 g MMT into the separately prepared same composition solution as used for the preparation of (PEO–PMMA)–$LiCF_3SO_3$ film. The surfaces of these solution-cast prepared films were achieved smooth by following the melt-pressing technique as described elsewhere [32]. The thickness of these SPE and NSPE films were 0.031 cm and 0.029 cm, respectively, and these films were vacuum dried for 12 h at 40 °C prior to their characterizations. After the initial measurements (first day), these films were sealed in poly propylene ziplock bags and stored in the desiccator. The films were taken out from the bags only during their XRD and DRS characterization at different time-age periods up to one-year duration. The films were vacuum dried every time prior to the measurements at their different aged periods.