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Li^{3+} ion irradiation effects on ionic conduction in P(VDF–HFP)–(PC+DEC)–$LiClO_4$ gel polymer electrolyte system

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Abstract

Swift heavy ion irradiation of P(VDF–HFP)–(PC+DEC)–$LiClO_4$ gel polymer electrolyte system with 48 MeV Li^{3+} ions having five different fluences was investigated with a view to increase the Li^+ ion diffusivity in the electrolyte. Irradiation with swift heavy ion (SHI) shows enhancement of conductivity at lower fluences and decrease in conductivity at higher fluences with respect to unirradiated polymer electrolyte films. Maximum room temperature (303 K) ionic conductivity is found to be 2.2×10^{-2} S/cm after irradiation with fluence of 10^{11} ions/cm^2. This interesting result could be ascribed to the fluence-dependent change in porosity and to the fact that for a particular ion beam with a given energy higher fluence provides critical activation energy for cross-linking and crystallization to occur, which results in the decrease in ionic conductivity. The XRD results show decrease in the degree of crystallinity upon ion irradiation at low fluences ($\leq10^{11}$ ions/cm^2) and increase in crystallinity at high fluences ($>10^{11}$ ions/cm^2). The scanning electron micrographs (SEM) exhibit increased porosity of the polymer electrolyte films after low fluence ion irradiation.

Keywords: Polymer gel electrolyte; Ionic conductivity; Swift heavy ion irradiation; XRD; SEM

1. Introduction

Development of new polymer electrolytes has been an important area of research in the past three decades, driven by the need to find new electrolyte phases for applications in various electrochemical devices [1–3]. The field began with the intense research on polyethyleneoxide (PEO)-containing lithium salts. PEO-based polymer electrolytes, however, show poor room temperature ionic conductivity [4]. New polymer electrolyte systems have been investigated using different polymers and co-polymers wherein a polymer matrix is swollen in a plasticizer to get plasticized or gelled polymer electrolyte [5,6]. Compared to the solvent free PEO based polymer electrolytes, the gelled polymer electrolytes possess higher room temperature ionic conductivity of about 10^{-3} S/cm, good mechanical stability and could be useful for lithium and lithium ion battery applications. One of the gel polymeric electrolyte systems widely investigated is P(VDF–HFP)-based system [5,6].

Swift heavy ion irradiation is a novel technique for modification of properties of materials. High energy ion irradiation of polymers leads to remarkable changes in their physical and chemical properties [7]. Permanent modifications in the molecular weight distribution and solubility [8], electrical [9], optical [10] and mechanical properties [11] of polymers and other materials have been detected after ion irradiation. When an energetic ion traverses through a polymer, it loses its energy by interacting with target nuclei (nuclear stopping) and by interacting with target electrons (electronic stopping) processes. Nuclear stopping arises from collisions between the energetic ions and target nuclei, which cause atomic displacement and chain scission. Electronic stopping is mainly determined by the charge state of the ion and its velocity as the orbital electrons of the moving ion are stripped off to a varying degree depending upon the ion velocity [12]. Crystallinity is also affected by ion irradiation and most semi-crystalline polymers exhibit a

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decrease in crystallinity at high dose irradiation (≈1 MGy≈ 2×10^{12} ions/cm^2) [13]. Ordering of the molecular chains after low fluence (≈200 kGy≈4×10^{11} ions/cm^2) light ion irradiation has also been reported [14]. The recrystallization phenomena in polymers as a consequence of constructive phase transition, i.e., transition from amorphous to crystalline phase characterizing the growth of new crystallites or even formation of new lamellar stacks upon irradiation, is a relatively new area of research offering many potentials [15,16]. The crystallinity plays a crucial role in almost all polymer properties such as mechanical, optical, electrical and even thermal properties.

In the present paper, investigation of ionic transport in 48 MeV Li^{3+} ion-irradiated P(VDF–HFP)–(PC+DEC)–$LiClO_4$ gel polymer electrolyte system with different fluences has been reported. Energy of 48 MeV has been chosen for ensuring uniform irradiation of the about 30 μm thick samples. Ionic conductivities of the polymer gel electrolytes have been measured by complex impedance spectroscopy. XRD study has been carried out to quantify the degree of crystallinity of the polymer electrolytes. Scanning electron micrograph study has been conducted to observe the surface morphology and porosity of the polymer electrolyte films.

2. Experimental methods

Poly(vinylidenefluoride-co-hexafluoropropylene) P(VDF–HFP) (MW≈400 000, Aldrich) as host copolymer, lithium perchlorate ($LiClO_4$, Aldrich) as salt, propylene carbonate (PC, E-Merck) and diethyl carbonate (DEC, E-Merck) as organic solvents were used without further treatment to prepare thin polymer electrolytes film. Samples were prepared by solution casting technique. An appropriate amount of the P(VDF–HFP) polymer was dissolved in acetone and the salt $LiClO_4$ was dissolved in a mixture of propylene carbonate and diethyl carbonate separately and then mixed together, stirred and heated at 50 °C for 12–14 h. PC has high dielectric constant (ε=64.6) but has high viscosity (η=2.53) also, whereas DEC has low dielectric constant (ε=2.82) but has low viscosity (η=0.748). PC+DEC (50% by volume each) solvent was used as a compromise for high dielectric constant (ε=33.71) and low viscosity (η=1.639) to achieve high ionic conductivity. The viscous solution thus obtained was cast onto glass plates and petri dishes and allowed to dry at room temperature. This procedure provided mechanically stable, free standing and flexible films of thickness in the range of 30–40 μm.

Ion irradiation of gel polymer electrolyte samples was performed at the 15 UD pelletron accelerator available at the Nuclear Science Centre, New Delhi, India using Material Science (MS) beam line facility. The gel polymer electrolyte samples were irradiated by 48 MeV Li^{3+} ion beam with five different fluences of 5×10^{10}, 10^{11}, 5×10^{11}, 10^{12} and 5×10^{12} ions/cm^2, mounted in the MS ultra high vacuum chamber. Energies of 48 MeV for Li^{3+} ion beams have been chosen so that the samples undergo uniform irradiation effects as the projected ion range (453 μm, according to stopping and ranges of ions in matter (SRIM) code [17]) was much larger than the polymer electrolyte film thickness (~30 μm). Ionic conductivities of both pristine (unirradiated) and irradiated polymer electrolytes were evaluated from the complex impedance analysis in the temperature range from 303 K to 343 K using a Hioki 3532-50 LCR Hitester in the frequency range of 42 Hz to 5 MHz. A symmetric stainless steel electrode system was used for ionic conductivity measurements. X-ray diffractograms have been taken by Phillips X'pert Pro diffractometer in the range of 2θ from 3° to 100°. Scanning electron micrographs (SEM) have been taken by JEOL JSM-35CF.

3. Results and discussion

3.1. Ionic conductivity measurements

The ionic conductivity of pristine (unirradiated) and Li^{3+} ion-irradiated P(VDF–HFP)–(PC+DEC)–$LiClO_4$ gel polymer electrolytes is calculated from the relation $\sigma = l/(R_b r^2 \pi)$, where l and r represent thickness and radius of the sample membrane discs, respectively. R_b is the bulk resistance of the electrolyte obtained from the complex impedance measurements. Fig. 1 shows the conductivity versus temperature inverse plots of pristine and Li^{3+} ion beam irradiated P(VDF–HFP)–(PC+DEC)–$LiClO_4$ gel polymer electrolytes. From the figure it is observed that the ionic conduction in ion-irradiated gel polymer electrolyte system obeys the VTF (Vogel–Tamman–Fulcher) relation [18–20], which describes the transport properties in a viscous matrix [21,22]. The interconnection between Arrhenius and VTF behavior of $\sigma(T)$ are widely reported and discussed in literature [23]. The VTF model is governed by the energy interval $k(T-T_0)$, whereas the Arrhenius behavior depends on the energy kT, T_0 being the idealized glass transition temperature of the polymer. At sufficiently higher temperature ($T \gg T_0$), VTF behavior approaches Arrhenius behavior [24].

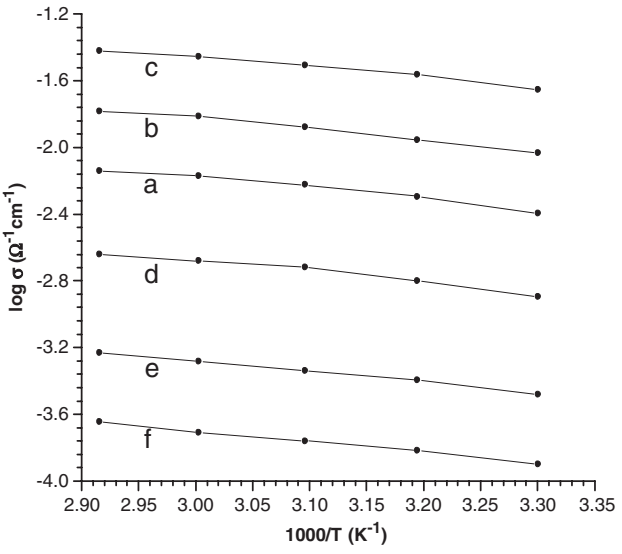

Fig. 1. Temperature dependence of ionic conductivity of Li^{3+} ion irradiated P(VDF–HFP)–(PC+DEC)–$LiClO_4$ (20:70:10 wt.%) gel polymer electrolyte (a) unirradiated, (b) 5×10^{10}, (c) 10^{11}, (d) 5×10^{11}, (e) 10^{12} and (f) 5×10^{12} ions/cm^2.