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Ionic conduction in 70 MeV C^{5+} ion-irradiated P(VDF–HFP)–(PC+DEC)–$LiCF_3SO_3$ gel polymer electrolyte system

A. Kumar[a,*], D. Saikia[a], F. Singh[b], D.K. Avasthi[b]

[a]Department of Physics, Tezpur University, Tezpur 784028, India
[b]Nuclear Science Centre, Aruna Asaf Ali Marg, New Delhi 110067, India

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Abstract

Swift heavy ion irradiation effects on ionic conduction in the P(VDF–HFP)–(PC+DEC)–$LiCF_3SO_3$ gel polymer electrolyte system have been investigated. Polymer gel electrolytes films were irradiated with 70 MeV C^{5+} ions with seven different fluences in the range of 10^{10}–10^{12} ions/cm^2. Irradiation of the polymer gel electrolyte films with swift heavy ions shows enhancement in conductivity at lower fluences ($\leq 10^{11}$ ions/cm^2) and decrease in conductivity at higher fluences. XRD results show decreased crystallinity below and increased crystallinity above the threshold fluence after ion irradiation. It appears that below the critical fluence, swift heavy ion irradiation increases Li^+ ion diffusivity in the polymer electrolyte. FTIR spectra suggest chain scission at low fluence and cross linking at higher fluence. Scanning electron micrographs exhibit increased porosity of the polymer electrolyte after ion irradiation.

Keywords: Swift heavy ion irradiation; Gel polymer electrolyte; Ionic conductivity; XRD; FTIR; SEM

1. Introduction

The development of new polymer electrolytes has been an important research area in the last three decades, driven by the need to find new electrolyte phases for applications in various electrochemical devices [1–4]. The field began with intense research on polyethyleneoxide (PEO)-containing lithium salts. PEO-based polymer electrolytes, however, show poor room temperature ionic conductivity [5]. New polymer electrolyte systems have been investigated using different polymers and copolymers. One of the polymeric electrolyte systems investigated is the P(VDF–HFP)-based system. Swift heavy ion irradiation is a novel technique for modification of properties of materials. In case of high energy ion irradiation of polymers, the nuclear and electronic energy losses of the incident swift heavy ion result into: (i) radiative decay; (ii) production of new reactive species (radicals, gases) and defects (unsaturation, scissions, cross links) and heat; and (iii) change in crystallinity [6–8].

In the present paper, in an attempt to increase the Li^+ ion diffusivity in polymers, investigation of ionic transport in 70 MeV C^{5+} ion-irradiated P(VDF–HFP)–(PC+DEC)–$LiCF_3SO_3$ gel polymer electrolyte system with different fluences has been reported. Ionic conductivities of the polymer gel electrolytes have been measured by complex impedance spectroscopy. Interaction between different gel components has been studied by FTIR. 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

Poly(vinylidenefluoride–co-hexafluoropropylene) P(VDF–HFP) ($M_w \approx 400{,}000$; Aldrich) as host copolymer, lithium

* Corresponding author.
E-mail address: ask@tezu.ernet.in (A. Kumar).

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trifluoromethane sulfonate ($LiCF_3SO_3$; Aldrich) as salt, and 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. In this technique, an appropriate amount of P(VDF–HFP) was dissolved in acetone and salt $LiCF_3SO_3$ 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. The viscous solution thus obtained was cast on 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.

Gel polymer electrolyte samples were irradiated with a swift heavy ion beam of C^{5+} of 70 MeV energy with seven different fluences (10^{10}, 2×10^{10}, 6×10^{10}, 10^{11}, 3×10^{11}, 7×10^{11}, and 10^{12} ions/cm^2). 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 42 Hz to 5 MHz. A symmetric stainless steel electrode system was used for ionic conductivity measurements. FTIR spectra were obtained using a Nicolet Impact 410 spectrophotometer. X-ray diffractograms have been taken by Phillips X'pert Pro diffractometer in the range of 2θ from 3° to 100°. Scanning electron micrographs have been taken by JEOL JSM-35CF.

3. Results and discussion

3.1. Ionic conductivity measurements

The ionic conductivity of unirradiated and C^{5+} ion-irradiated P(VDF–HFP)–(PC+DEC)–$LiCF_3SO_3$ (20:70:10 wt.%) gel polymer electrolytes is calculated from $\sigma = l/(R_b r^2\pi)$ relation, where l and r represent the thickness and radius of the sample membrane discs, respectively. R_b is the bulk resistance of the gel polymer electrolyte obtained from complex impedance measurements. It is widely accepted that R_b could be obtained from the intercept on the real axis at the high-frequency end of the Nyquist plot of complex impedance [9]. Fig. 1 shows the conductivity versus temperature inverse plots of C^{5+} ion-irradiated P(VDF–HFP)–(PC+DEC)–$LiCF_3SO_3$ (20:70:10 wt.%) gel polymer electrolyte system. From the figure, it is observed that the ionic conduction in ion-irradiated gel polymer electrolyte system obeys the VTF (Vogel–Tamman–Fulcher) relation [10–12], which describes the transport properties in a viscous matrix [13–16]. It supports the idea that the ions move through the plasticizer rich phase, which is the conducting medium and involves the salt and plasticizer. If the conductivity versus temperature dependence curve is linear in a larger temperature region, then it is said to be Arrhenius behavior. VTF (curved) behavior can be modeled as Arrhenius (linear) behavior by dividing the entire temperature regime into smaller temperature regions. The interconnection between Arrhenius and VTF behavior of $\sigma(T)$ is widely reported and

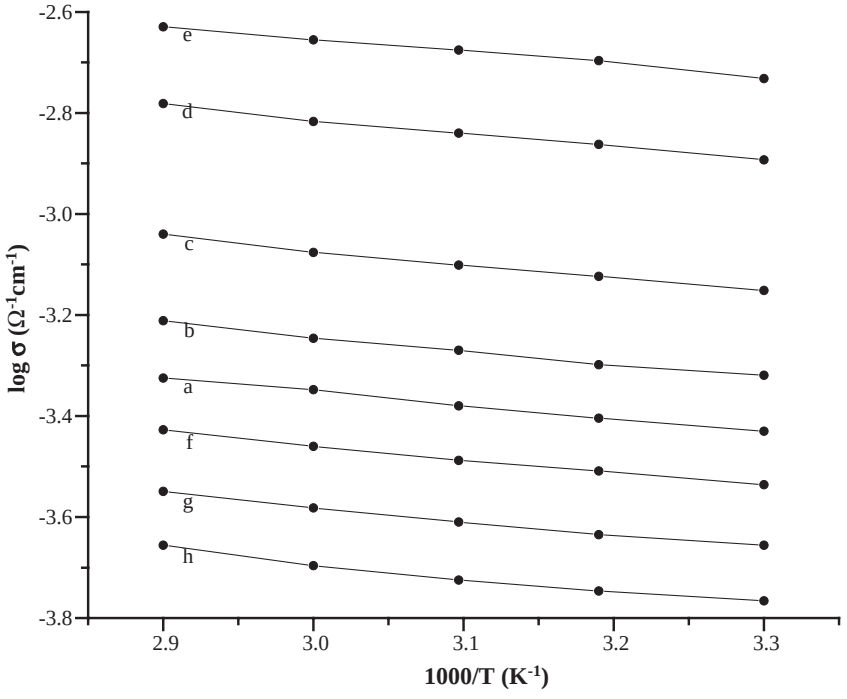

Fig. 1. Temperature dependence of ionic conductivity of C^{5+} ion-irradiated P(VDF–HFP)–(PC+DEC)–$LiCF_3SO_3$ (20:70:10 wt.%) gel polymer electrolyte: (a) pristine, (b) 10^{10}, (c) 2×10^{10}, (d) 6×10^{10}, (e) 10^{11}, (f) 3×10^{11}, (g) 7×10^{11}, and (h) 10^{12} ions/cm^2.