Microstructural, Relaxation and Transport Properties of Electron Irradiated Ion Conducting Polymer Electrolyte for Solid State Battery Applications

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Abstract. Poly (vinyl alcohol) (PVA) doped with KBr composite electrolytes was prepared by solvent casting method, prepared electrolyte films are irradiated with electron beam. The induced modification on the structure of the electrolyte has been confirmed by XRD studies. The XRD results reveal that the crystal structure of the electrolyte has disrupted, thus the amorphous nature increases upon electron irradiation and creates free radicals due to chain scission. Impedance analysis showed that the ionic conductivity increases upon electron irradiation and the maximum conductivity of $6.2388 \times 10^{-2}$ S/cm is attained for 300 kGy dose of electron irradiation at 373K. The ion transportation is determined by using Wagner’s polarization technique, and the TIC study confirms the presence of single ionic species within the electrolyte for both pristine and 300 kGy dose electron irradiated electrolyte. This study shows the ion transportation inside the polymer fabrics can be improved by electron beam irradiation method.

1. Introduction
In recent years, solid polymer electrolytes (SPE) particularly ion rechargeable batteries are attracted the researches due to its beneficial characteristics that encompass lightweight, high energy density, superior cycle performance. The traditional batteries consist of liquid electrolyte, which has some drawbacks such as volatile nature, sealing, explosion due to leakage, not stables at varying temperature. SPE hold numerous advantages than liquid electrolytes such as superior mechanical strength, high ionic conductivity, good transference number and better electrode/electrolyte interface stability. The technological influence of developing an SPE with enhanced ionic conductivity and mechanical strength is important and motivates for further exploration. Generally, ionic conductivity in polymers occurs due to migration of free charge carriers between the several coordinate sites of the host polymers or polymer chain segmental motion. Moreover, the cationic conductivity occurs usually in the amorphous phase via segmental motion [1-3]. Since the amorphous phase of the polymer enables faster ion transportation, hence attempt has been paid by the researchers to fabricate the polymer electrolyte that shows high amorphous nature using various methods [4]. Among various methods, electron irradiation gained much attention to design such type of electrolytes, because the
electron irradiation is free from chemicals so it is environmental friendly method to design high amorphous nature electrolytes [5]. This will facilitate more ions to the polymer matrix, which reduces the ionic relaxation and enhances the mobility of ions. It is known that the irradiation produces remarkable changes in their physical, chemical, structural and electrical properties of the polymers. Some of these modified properties are obtained due to crosslinking and/or scission of polymer chains and phase transition through electron irradiation, but the effect of electron irradiation is different for different materials [5]. Hitherto, different polymers had used to fabricate the efficient electrolyte using electron irradiation method. Among them PVA has gained much attention due to its peculiar properties like semi-crystalline nature, non-conducting it becomes conductive by doping with suitable dopant, significant dielectric and mechanical strength, rapid charge transport at electrode-electrolyte interface and other properties. Its physical and chemical properties can be tuned using doping and/or irradiation. Change in the properties depends on the type of dopant and its interaction with polymer as well as the irradiation condition. This is due to the fact that the chemical interaction of the dopant with hydroxyl group of PVA, through inter/intra molecular hydrogen bonding and forms charge transfer complex (CTC) [5]. Potassium salts in a polymer matrix are producing rapid ion transportation due to their small ionic radii (1.34Å), their addition alerts the microstructure and transport properties of polymers and further modifications can be done with the electron beam. The modifications imposed by the electron irradiation have probed by the X-ray diffraction analysis, impedance measurements, transport, and transient properties.

2. Experimental

PVA (M.W. 1,25,000) was procured from M/s. s. d. fine-Chem. Ltd, Mumbai and KBr was obtained from M/s. Sigma-Aldrich. The 5wt% of KBr/PVA films are prepared by solution casting method using double distilled water as a solvent [5, 6]. The prepared films are irradiated with 10MeV electron beam at RRCAT, Indore. Here 3x3 cm² sized films were sealed and staked in the conveyor belt with the help of thin transparent polyethylene sachets and placed perpendicular to the electron beam direction at room temperature. Dosimetric measurements were carried out using EPR alanine pellets (Bruker, Germany). The films were irradiated with 0, 50, 100, 150, 200, 250 and 300 kGy doses of electron beam of current 235 mA [5]. The irradiated films are examined with different experimental techniques. The microstructural changes have studied using Rigaku smartLab X-ray diffractometer with CuKα radiation. The impedance measurements have performed using Agilent 4294A precision Impedance Analyzer in the frequency range of 40Hz-5MHz. Using Wagner’s polarization technique, the ion transport parameters are determined in the configuration of Ag/PVA+KBr/Ag under a constant dc voltage of 1V with the help of Keithley-236 source measure unit.

3. Results and Discussions

3.1. X-Ray Diffraction Analysis

The recorded wide-angle X-ray diffractogram of pristine and electron irradiated PVA/KBr SPEs are shown in Fig. 1. (a). The observed diffractogram shows a relatively sharp and well-defined peak at 2θ = 19.51° for pristine. This peak intensity increases up to 150 kGy dose with small variation in peak position. After 150 kGy of irradiation, it is noticed that a new peak appears at 2θ = 28.59°, (characteristic peak for KBr [3]) and the intensity of the first peak decreases drastically and the second peak intensity increases. Appearance of new peak after 150 kGy may be due to the creation of K⁺ ion free radicals within the film. Using XRD results the degree of crystallinity is calculated and it shows (Fig. 1. (a)) that the degree of crystallinity increase at lower dose (up to 150 kGy) and then it decreases at higher dose. This decrease in the intensity of first peak and increase in the intensity of the second peak at high dose has assigned to the onset of chain scissoring and formation of K⁺ ion free radicals respectively. As a result of this chain scission, the amorphous nature of the film increases. Therefore the crosslinking process is predominant at lower dose and chain scission is predominant at higher
dose, this is attributed to the interaction of K⁺ ions with carbonyl (C=O) and hydroxyl (O-H) group of polymer electrolytes and creates charge transfer complex (CTC).

Figure 1. (a) X-ray diffractogram (b) Cole-Cole plot of pristine and electron irradiated electrolytes respectively, (c) Cole-Cole plot of 300 kGy dose electron irradiated electrolyte with varying temperature.

3.2. Impedance Measurement Analysis

The observed real and imaginary part of complex impedance (Cole-Cole) plot for pristine and electron irradiated SPEs at 303K are as shown in Fig. 1. (b). The figure show the partial semicircular nature of the curves at high frequency region suggests the ionic conductivity occurs due to the bulk of the polymers electrolytes and it is differs from the Debye process. At lower frequency, the observed linear portion indicates the heterogeneity of the electrode/electrolyte interface or double layer at the blocking electrode. Here the ions within the electrolyte get drifting through free volume site within the amorphous phase (expressed by the resistive portion) and the stagnant polymer chains get polarized in the presence of applied field (represented by capacitor). Both these phenomena occur simultaneously in parallel and hence a broad imperfect semicircle has noticed. For electron irradiated films the partial semicircular shape decreases, indicates the structural modification of the electrolyte upon irradiation (confirmed from XRD). This structural modifications are attributed to the poly-dispersive nature (0 < α < 1) of the amorphous electrolyte and it suggests the decrease of resistive component and increase in conductive part within the electrolyte, which helps in enhancing mobile charge carrier concentration and of the dipoles. Moreover, in this amorphous structure, the flexibility of polymer chain backbones increases and the ionic conductivity increase through segmental motion due to electron irradiation. The highest ionic conductivity is obtained for 300 kGy dose irradiated SPE. To examine this feature temperature dependence of the ionic conductivity has been studied for highest conduction SPE and the observed variation is given in Fig. 1. (c). Figure shows that the partial semicircle modifies in to semicircle at high frequency region with rise in temperature but it is vanish at higher temperature and results in to a spike. It suggests that bulk resistance of the electrolyte decreases with increase in temperature: the electrolyte becomes less resistive and more conductive. The observed spike (parallel to Y-axis) shape at higher temperature reflects that the conductivity of these SPEs is purely due to ions [2]. From the figure, it is noticed that for irradiated films, the intercept between semicircle and spike decreases with increase of temperature, which indicates the decrease in bulk resistance largely with temperature, is due to the increase of flexibility and dynamic segmental motion of polymer chains in the amorphous region. Hence, the conductivity of the SPEs increases with temperature due to segmental motion, which in turns increases the free volume around the polymer chains [7]. Here the segmental motion of the polymer chain promotes the translational ionic mobility.
within the SPE and hence the ionic conductivity (maximum ionic conductivity \(6.2388 \times 10^{-2} \text{ S/cm}\)).

To understand this mechanism further the relaxation time for charge carriers has been estimated from Fig. 2. (a) using method explained in reference 2. Fig. 2. (a) show the variation of imaginary part of impedance with frequency for electron irradiated SPE. Using the figure the relaxation peak \(f_{\text{max}}\) is identified and the observed \(f_{\text{max}}\) decreases along with a shift towards higher frequency region with electron irradiation, which indicates the non-Debye nature of relaxation mechanism. Using the \(f_{\text{max}}\) value the relaxation time is calculated and it is shown in Fig. 2. (b). Here the figure shows that the relaxation time decreases with electron irradiation indicates that the electron irradiation creates the free radicals due to scission and contributes to the ionic conductivity. The relaxation time decreases with rise in temperature facilitates the faster ionic mobility leading to the enhancement in conductivity. To understand the relaxation process in 300 kGy dose electron irradiated films, the temperature dependence of the imaginary part with frequency has been studied and the observed results are shown in Fig. 2. (c). From the Fig. 2. (c) it is clear that the value of relaxation frequency \(f_{\text{max}}\) further declines and shifted towards higher frequency side with increase of temperature and at higher temperature, it becomes independent of frequency, it indicates the relaxation time decreases with temperature (Fig. 3. (a)). This shows that the irradiation induces defects and affects strongly to the magnitude of relaxation phenomenon.

\[ Z' \]

\[ f_{\text{max}} \]

\[ \text{Relaxation Time} = \frac{1}{f_{\text{max}}} \]

3.3. Transport and Transient Properties

To understand the nature of ionic transportation within the SPE, transport and transient properties of ions both in pristine and 300 kGy dose irradiated (highest conducting) were estimated using Wagner’s polarization technique [2, 8]. Using the method explained in ref. 2, both pristine and 300 kGy dose irradiated SPEs films are sandwiched separately between two Ag electrodes and a steady DC potential of 1V is applied, current in the circuit was recorded as a function of time and the same is shown in Fig. 3. (b). It is clear from the figure that a high spontaneous current flow with the application of small DC voltage, it disintegrates with time and after long duration, it reaches steady state. Therefore, the initial current \(I_i\) is responsible for both ions as well as electrons and the final current \(I_f\) is only due to electrons. The ionic and electronic transparency number is calculated [2] and is recorded in table 1. From the table it is observed that the ionic transparency number for both pristine and 300 kGy dose irradiated SPEs are 0.9975 and 0.9986 respectively, which are more compare to that of electronic transparency number (0.0025 and 0.0014). Here the observed ionic transparency number is less then unity because of the fact that the increment in the number of anionic repetitive units decreases the polyanion contribution to ionic transport in both cases. Therefore, the cationic transport number never reaches unity. Here it suggests that even with the existence of very large number cations within a SPE, still there is an anionic contribution to the total ionic conductivity. However, the attained ionic transference number is very much closer to unity and in electron irradiated (300 kGy dose) SPE is
more ionic transference than that of pristine SPE. This is due to scission of polymer chains due to irradiation, which facilitates faster ionic mobility through the segmental motion. Hence, more ionic transference number is obtained for 300 kGy electron irradiated SPE than pristine. The mobility of ions in pristine and 300 kGy dose electron irradiated SPE are determined by reversing the polarity of the applied voltage using transient ionic current (TIC) technique [2]. Here TIC has measured as a function of time until it reaches steady state. The observed TIC spectra is displayed in Fig. 3. (c). From the figure we can see single peak throughout the spectra for both pristine and 300 kGy dose irradiated SPEs which indicates the existence of single ionic species in the SPEs. Using time of flight method the mobility of ions is determined for both pristine as well as 300 kGy dose irradiated SPEs [2] and the estimated motilities are 6.2745×10⁻⁷ cm² V⁻¹ S⁻¹ and 7.7939×10⁻⁷ cm² V⁻¹ S⁻¹. The observed total mobility is resolved into cationic and anionic mobility and the diffusion coefficient of K⁺ ion have been determined using the formulas described in literature [2] and the estimated transport parameters are given in table 1. From the table it is clear that the cation mobility (µ⁺) and cation diffusion coefficient (D⁺) in 300 kGy dose electron irradiated SPE are much more than that of pristine SPE. These results indicate that the irradiation enhances the amorphous nature of SPE due to chain scission, which contributes more number of ion transportation as compared to pristine and hence the enhancement of conductivity. This transference number measurements leads to the conclusion that the conductivity has mainly caused by µ⁺ and D⁺. This study suggests that the observed value of transport parameters as well as conductivity is higher than the reported values in literature and it may be useful in solid-state batteries.

Figure 3. (a) Variation of relaxation time with temperature for 300 kGy dose irradiated electrolyte, (b) Variation of polarization current (c) variation of Transient current as a function of time for pristine and 300 kGy dose irradiated electrolytes.

Table 1. Transport parameters of pristine and 300 kGy dose electron irradiated SPEs

| EB Dose (kGy) | n (cm⁻³) ×10²⁰ | t⁺ | t⁻ | µ⁺ (cm² V⁻¹ S⁻¹) ×10⁻⁷ | µ⁻ (cm² V⁻¹ S⁻¹) ×10⁻⁷ | D⁺ (cm² S⁻¹) ×10⁴ | D⁻ (cm² S⁻¹) ×10⁴ |
|--------------|----------------|----|----|------------------|------------------|----------------|----------------|
| Pristine     | 5.4526         | 0.9975 | 0.0025 | 6.2588           | 0.0157           | 1.6541          | 0.0041          |
| 300          | 14.3672        | 0.9986 | 0.0014 | 7.7939           | 0.0110           | 2.0350          | 0.0029          |

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