Effect of Mixed Ions and Ion Irradiation on Ionic Conductivity of Solid Polymer Electrolytes

H Manjunatha¹, R Damle² and GN Kumaraswamy¹
¹Department of Physics, Amrita School of Engineering, Bengaluru, Amrita Vishwa Vidyapeetham, India
²Department of Physics, Bangalore University, Bengaluru, India

E-mail: gnk_swamy@blr.amrita.edu

Abstract. It is a well known fact that conductivity in case of solid polymer electrolytes (SPEs) is due to hopping of ions assisted by the segmental motion of polymer chains. It is observed that the ionic conductivity in SPEs increases with increase in the concentration of ions. After certain critical concentration the conductivity starts decreasing due to the formation of ion pairs. In this work, an attempt is made to identify the concentration at which ion pair formation occurs and hence improve conductivity by incorporating two different ions (salts) in the polymer matrix. SPEs with mixed conducting species PEOₓLiBrᵧNaBr with different concentration of salts have been prepared and investigated. Also an attempt is made to modify the crystalline phase of the host polymer by low energy ion beam (Oxygen ion, O⁺ with energy 100 keV) irradiation. These observations place ion irradiation as an effective tool in improving ionic conductivity in SPEs. Using X-ray diffraction spectra and the temperature dependent conductivity studies of SPEs, the effect of mixed ions and ion irradiation on the ionic conductivity of SPEs is investigated and presented.

1. Introduction
Solid polymer electrolytes [SPEs] acquired importance in the area of research and development, due to their applications in field of super capacitors, high energy- density batteries and sensors. Particularly in rechargeable batteries with lithium based solid polymer electrolytes. The flexibility in shape and size exhibited by the SPEs plays a vital role in miniaturization of battery technology. The fabrication of battery with high energy density along with high performance operation is the ultimate aim in the development of SPEs [1-3].

Unfortunately, most SPEs are known to have low ionic conductivity at ambient temperatures. The ionic conductivity may be enhanced through various approaches such as particle irradiation, variation in composition of conducting species, addition of inert nanosized fillers etc [4-7]. It is also known that, at higher concentration of conducting species high degree pairing of ions, formation of ion aggregates reduce ion mobility and hence the ionic conductivity to a large extent. Raman studies have shown the presence of ion pairs in several SPEs [8]. In this paper, we present the preliminary results of improved ionic conductivity in a PEO based SPEs by introducing two conducting ions in to polymer matrix. These composite SPEs show an enhancement in ionic conductivity by nearly one order over single ion conducting SPEs. Modifying the microstructure of the SPE systems through low energy ion irradiation is attempted in these studies. It has been observed that the conductivity of irradiated SPEs enhance by nearly one order compared to unirradiated SPEs.
2. Experimental details:

2.1. Preparation Technique

If Polymer–salt complexes, PEO,LiBr were prepared from Polyethylene oxide (Aldrich, molecular weight 100000g/mol), Lithium Bromide (Merck) and Sodium Bromide (Aldrich) by conventional solution cast technique. ‘x’ is number of ether oxygen’s in a monomer chain of polymer to each cation. The polymer-salt complexes were prepared by dissolving 1g of PEO and different weights of salt in 10 ml of Acetonitrile. The solution was stirred at room temperature for 24 hours. The thick viscous solution obtained was poured on to a petri dish; it is allowed to dry until the solvent gets evaporated at room temperature. Finally free standing polymer electrolyte films of 0.2-0.3mm thickness were obtained.

SPEs with two ionic conducting species (PEO,LiBr,NaBr) were prepared by following the above explained procedure, where ‘x’ is concentration of Li ions in the vicinity at which ionic conductivity is maximum and ion pair formation occurs for PEO,LiBr and ‘y’ is the concentration of Na ions in PEO,LiBr SPEs respectively. The samples were left at room temperature for 24 hours to remove residual solvent present in the samples and the samples were kept in vacuum desiccator for experimental investigation.

2.2. Characterization Techniques

Impedance spectra of the SPEs were recorded by placing them between two silver electrodes. Bulk resistance ‘R’ of the SPEs was evaluated from the impedance plots obtained from a Frequency Response Analyzer (Core Technology Group, USA). The dc conductivity exhibited by the SPEs was calculated using the relation $\sigma = 4l/\pi d^2$ where ‘l’ is sample thickness and ‘d’ is sample diameter. SPEs with mixed ion conducting species (PEO,LiBr,NaBr) which exhibits highest ionic conductivity is irradiated using low energy oxygen ion at Inter University Accelerator Centre (IUAC), New Delhi for fluencies $1 \times 10^{13}$, $5 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$, $1 \times 10^{15}$ and $5 \times 10^{15}$ ions/cm².

The X-ray diffraction patterns of samples were recorded using X-ray diffractometer (Bruker AXS model D8 ADVANCE). The XRD patterns were used to confirm the complexation in all SPEs. Structural changes in the polymer matrix due to incorporation of salts and irradiation with low energy oxygen ions was also analyzed using XRD patterns.

The dependence of ionic conductivity on temperature was studied using a low temperature cryostat with temperature controller and sample holder. Scanning Electron Microscope (Carl Zeiss SEM model EVO MA15) was used to understand the surface morphology of SPEs.

3. Results and Discussions:

3.1. Transport properties

The conductivity due to ions in SPE systems is evaluated by impedance analysis using complex impedance spectrum. The impedance spectra for SPE systems PEO₉₀LiBr and PEO₃₀LiBr₁₀₀NaBr (unirradiated and irradiated) are shown in ‘figure 1’. The impedance spectrum at high frequency is a semicircle which is followed by a spike in the region of low frequency. The semicircle corresponds to the physical properties of the SPEs [9]. Bulk resistance (R) of the SPEs is known by the intercept of semicircle with real axis.

‘Figure 2’ shows variation of log (σ) as function of salt composition in SPE with Li species. It can be observed that, conductivity in the system depends on the concentration of salt. The conductivity shows a continuous increase up to O/Li concentration of 30, which is due to increase in number of charge carriers. For O/Li concentrations more than 30, there is a decrease in conductivity. The decrease in ionic conductivity is attributed to the formation of ion pairs at higher carrier (salt) concentration and thus reduction in the mobility of the carriers [4]. The maximum conductivity of $3.33 \times 10^{-6}$ Scm⁻¹ is observed in PEO₉₀LiBr system.
In the current study, we have tried to investigate the effect of the presence of a second charge carrier ‘Na’ in PEO-LiBr systems at the limiting composition beyond which the ion pair formation sets off. Varying concentrations of NaBr is added to PEO\_30LiBr, which has the maximum conductivity and the conductivity of these composite systems is presented as function of NaBr concentration in ‘figure 3’. From the figure we observe an enhancement in conductivity nearly by one order (9.76 x 10\(^{-6}\) Scm\(^{-1}\)) when a second carrier (Na) is incorporated into PEO\_30LiSPEs. However, at higher concentrations of Na, the ionic conductivity exhibits continuous decrease, which needs further investigation to ascertain the possible charge complexation.

The incorporation of Na ions in to PEO\_30LiBr system has enhanced the concentration at which ion pairs are formed, which has lead to increase in ionic conductivity. The conductivity in SPEs is because of segmental motion of polymer chains as well as movement of ions between and along the polymer chains. This fact has been ascertained through temperature dependant studies of the conductivity. Also,
it has been observed that, the conductivity varies as the molecular weight of the polymer. In both the above situations, the segmental motion is altered by modifying the morphology of the SPE system. The segmental movement in polymer matrix is much restricted to amorphous region. Therefore, higher amorphous regions in a polymer ensure higher ionic conductivity. Ion irradiation technique has been employed by us to modify the morphology of the polymer matrix and its effect on the conductivity; is presented in ‘figure 4’. In the irradiated SPEs we observe an increase in ionic conductivity as function of ion fluence up to $10^{15}$ ions/cm$^2$. The maximum ionic conductivity is found to be 7.07x10$^{-5}$ Scm$^{-1}$ for $10^{15}$ ions/cm$^2$. The increase in conductivity suggests the change in polymer morphology towards amorphous nature through chain scissions by the incident ions [5]. The fluence above $10^{15}$ ions/cm$^2$ seems to induce the cross linking of polymer chains thus setting off decrease in conductivity. The values of resistance, ionic conductivity and activation energy of the SPEs PEO$_{30}$LiBr and PEO$_{30}$LiBr$_{100}$NaBr (unirradiated and irradiated) are tabulated in table 1.

3.2. Structural studies

The XRD patterns of different compositions of salts in polymer matrix and that of pure salts (LiBr and NaBr), polymer (PEO), PEO$_{30}$LiBr and PEO$_{30}$LiBr$_{100}$NaBr are presented in ‘figure 5’. The absence of the peaks related to the salts LiBr (peaks at 20 = 23.37°, 24.8°, 29.4° and 37.18°) and NaBr (peaks at 20 = 42.88°, 43.88° and 50.72°) in the complexes suggests formation of polymer electrolyte due to dissociation of salt in to ions. The two diffraction peaks at 20 equal to 19.1° and 23.3° in the XRD spectra of pure PEO show reduction in intensity and were broadened with the incorporation of salt LiBr suggests reduction in crystalline phase in the system. The width and intensity of these peaks are found to be decreased further by the addition of second salt NaBr in to SPE PEO$_{30}$LiBr indicated further reduction in the ordered phase of the systems.

The X-ray diffractograms of SPEs shown in ‘figure 6’ reveals that, the intensity of the peaks of irradiated SPEs has decreased representing the decrease in crystalline phase. This indicates the modification of the microstructure of SPEs due to ion irradiation.

3.3. Temperature dependent conductivity studies

The temperature dependence of ionic conductivity in SPEs suggests that it as an activated process.
‘Figure 7’ shows temperature dependence studies of SPEs PEO\textsubscript{30}LiBr and PEO\textsubscript{30}LiBr\textsubscript{100}NaBr (unirradiated and irradiated) in the temperature range 270-340 K. All the plots of log (σ) versus 1000/T fit well to Arrhenius equation

\[ \sigma = \sigma_0 \exp \left( \frac{-E_a}{kT} \right) \]

Where ‘\( \sigma_0 \)’ is a constant, ‘k’ is the Boltzmann constant, ‘\( E_a \)’ is the activation energy and ‘T’ is absolute temperature [10]. The vibrational energy of the polymer segments matrix increases with the increase in temperature leading to enhancement of free volume and hence amorphous phase. The activation energies in case of PEO\textsubscript{30}LiBr and PEO\textsubscript{30}LiBr\textsubscript{100}NaBr (unirradiated and irradiated) are tabulated in Table 1. The decline in activation energy in systems due incorporation of two cations and further due to irradiation may be attributed to improved amorphous phase in the systems.

![Arrhenius plots](image)

**Figure 7.** Arrhenius plots for (a) PEO\textsubscript{30}LiBr, PEO\textsubscript{30}LiBr\textsubscript{100}NaBr (b) un-irradiated, (c) irradiated to 10\textsuperscript{14} ions/cm\textsuperscript{2}, (d) irradiated to 10\textsuperscript{15} ions/cm\textsuperscript{2}.

| Solid polymer electrolyte | Resistance (Ω) | Ionic Conductivity ‘σ’ (Scm\textsuperscript{-1}) at 303K | Activation energy (\( E_a \)) in eV |
|---------------------------|----------------|---------------------------------|-------------------------------|
| PEO\textsubscript{30}LiBr  | 6912           | 3.33E-6                         | 0.634                         |
| PEO\textsubscript{30}LiBr\textsubscript{100}NaBr [Un-irradiated] | 2110           | 1.45E-5                         | 0.479                         |
| PEO\textsubscript{30}LiBr\textsubscript{100}NaBr [Irradiated with fluence 1x10\textsuperscript{14} ions/cm\textsuperscript{2}] | 1226           | 4.57E-5                         | 0.371                         |
| PEO\textsubscript{30}LiBr\textsubscript{100}NaBr [Irradiated with fluence 1x10\textsuperscript{15} ions/cm\textsuperscript{2}] | 848.9          | 7.05E-5                         | 0.290                         |

3.4. Morphological studies
The morphological changes in irradiated SPEs were analyzed using SEM. Figure 8 (a–c) shows the SEM images of PEO\textsubscript{30}LiBr\textsubscript{100}NaBr (unirradiated) and PEO\textsubscript{30}LiBr\textsubscript{100}NaBr irradiated with 10\textsuperscript{14} and 10\textsuperscript{15} oxygen ions/cm\textsuperscript{2}, surface morphological changes were observed in irradiated SPEs. These morphological changes may be due to dissipation of energy processed by the ions while passing all the
way through the matrix of the polymer. These changes raise the disordered phase in the matrix, which enhance the ion mobility and hence the ionic conductivity.

Figure 8. SEM images of (a) un-irradiated PEO$_{30}$LiBr$_{100}$NaBr and PEO$_{30}$LiBr$_{100}$NaBr irradiated with fluence of (b) $10^{14}$ ions/cm$^2$ and (c) $10^{15}$ ions/cm$^2$.

4. Conclusions
The hindrance caused to the ionic conductivity through formation of ion pairs could be balanced by the introduction of mixed carrier species, which evident from the increase in conductivity by one order. Further, it is shown, the microstructure of the SPEs could be modified using low energy ion beam to improve the conductivity. The irradiation of SPEs by low energy ion beam was observed to alter the crystallinity of the systems.

5. References
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