EFFECT OF ION BEAM IRRADIATION ON SODIUM SALT BASED POLYMER NANO-COMPOSITE ELECTROLYTE FOR BATTERY APPLICATION

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INTRODUCTION

Rapidly developing state of the world today has led to an upsurge in use of energy sources. Heavy increase in demand for energy has led to the requirement for alternative and sustainable energy materials. Electrolyte materials and Electrode materials form the backbone of the electrochemical material research. In the present work, we deal with electrolyte materials. Liquid electrolytes are the best for when considering conductivity aspect of the electrolyte, but its mechanical complications motivate the researchers to develop better alternatives. Polymer electrolytes have mechanical stability like that of a solid and have conductivity comparable to that of liquid electrolyte materials and hence pose as an excellent class of electrolyte materials.

Armand (Armand, M et al., 1979) was the first to realize electrochemical importance of polymer materials. He reported that Polyethylene Oxide (PEO) can be used as a host material for solid electrolyte system. Ever since then tremendous research has been targeted in the field of solid polymer electrolyte materials. Successful commercial electrochemical devices based on polymer electrolyte materials have also been realized. Present commercial polymer based electrolyte materials however contain a small fraction of liquid material which is affiliated with issues such as volatility and explosion due to leakage. Hence it is important to consider non-volatility and non-in flammability parameters of electrolyte material. Synthesized system of polymer electrolytes can be employed to overcome the above mentioned safety issues and they also present an added advantage of design flexibility. Hence lab synthesized host matrix have become popular means of exploring the possible applications of conventional polymer-salt complexes.

Apart from developing new materials, recently research has also been focussed on understanding ion dynamics like dissociation of salt in polymer, correlation of ion motion with polymer segment, temperature dependence of various constants and the type of ion conduction mechanism. These studies are mandatory for understanding the future aisle for designing new materials. Impedance Spectroscopy is the most versatile tool which helps in understanding these crucial parameters in great detail. Impedance studies in conductivity, dielectric and modulus formalism yield important information about the ion dynamics. All the three formalisms go hand in hand and are synchronically employed to understand ion transport mechanism in disordered materials. In polymer-salt complex system ion transport is dominated by factors such as type of salt, its concentration and temperature dependence of the system. Scaling is used to understand the effect of these parameters on the conductivity of the system. In the present work, we have synthesized and characterized a novel polymer blend electrolyte system based on sodium salt.

Present Work

The main objective of the present work is to improve the ambient temperature ionic conductivity, mechanical stability, thermal and interfacial stability of the electrolytes.

However, it is difficult task for the researchers, in order to improve these basic requirements of the electrolytes simultaneously because the ionic conductivity and mechanical strength of a polymer electrolyte are disparate to each other, i.e., mechanical strength of the electrolyte decreases as conductivity increases.

Most of the solid polymer electrolytes (SPEs) are prepared by dissolving sodium salts in a solvating polymer using common solvent or by diffusion in the solid (or) molten state. If the polymer chains are helped for a charge transport of the ionic type, these are often called “polymer electrolyte”. Solid polymer electrolytes (SPEs) play two important roles in Li or Na-ion battery. 1) It is used as a separator in the battery system because of it rigid structure, at the same time to avoid the electrical contact between the anode and the cathode; 2) it is the medium in which the ions are transported between the anode and cathode during the cell operations. As a result, the polymer electrolyte should act as good electrical insulator but at the same time it should have high ionic conductivity.

The polymer-salt complexes are further classified into: i) Solid polymer electrolytes ii) Blend polymer electrolytes iii) Gel polymer electrolytes iv) Composite polymer electrolytes. Among the various polymer electrolytes which are used in Li or Na -ion batteries, solvent free polymer electrolytes are the most favourable for device fabrications. The solvent free polymer salt complexes are further classified into: i) Solid polymer electrolytes ii) Gel polymer electrolytes iii) Composite polymer electrolytes. In the present study, I have undertaken a solid and composite polymer electrolyte system which possesses ionic conductivity when modified by dissolving alkali salts, plasticizer and/or nano fillers in polymer matrix. They have several advantages when used in a battery and can be formed into thin films of large surface area giving high power levels.

Basic requirements of polymers and the salt for polymer electrolytes

1) Atoms or groups of atoms with sufficient electron donor power to form coordinate bonds with cations.
2) Low barriers to bond rotation so that segmental motion of the polymer chain can take Place easily.
4) Low glass transition temperature to increase the segmental motion.
5) The polymer should have amorphous phase which lowers the barrier for ionicmovement and yields high ionic conductivity.
7) The lattice energy of the salt should be low.

Although PEO still remains most investigated polymer for electrolyte applications, poor room temperature conductivity of PEO based electrolytes is a major drawback. Hence in addition to PEO we have chosen another polymer PAM to form a blend system. PAM is a commonly used matrix for nano-composite hydrogels (Sumathi, S et al., 2014) and is largely amorphous in nature. Presence of an amorphous polymer in the system along with PEO will hinder the effect of semi-crystalline and crystalline regions of PEO and increase the amorphous nature of the system. It is widely known and accepted fact that majorly, the conduction process of an ionically system occurs in the amorphous region and hence we target this particular area the most.

Sodium salt was chosen with the objective of coming up with an alternative to traditional commercial lithium ion based electrolytes. Sodium triflate has been chosen as the salt as it has a ligand in the form of anion. Large anions of the salt tend to combine with the polymer chains by settling in between the chains and thus breaking the rigid bonds. This leads to formation of conduction pathways for the smaller cation (Na^+ in the present case) to move easily thorough the matrix for conduction.

Addition of plasticizers in electrolyte systems to increase ionic conductivity is a well known practice. Organic diluents with high dielectric constant and low viscosity such as Ethylene Carbonate (EC), Propylene Carbonate (PC), Diethyl Carbonate (DEC) and Polyethylene Glylcol (PEG) are widely used plasticizing agents (Sharma et al., 2013; Gohel et al., 2018). Key role of a plasticizer in a system is to decrease the polymer-polymer interaction inside the matrix. This weakens the rigidity of the chains, increases the flexibility and also offers a stream-like medium to the charge carrier ions to move smoothly throughout the system 3. It is a common method of taking up one of the above mentioned agents as plasticizing medium in an electrolyte system. Understand the effect of presence of two plasticizers together would make a novel study and hence we have chosen a two-component plasticizing system consisting of Ethylene Carbonate (EC) and Propylene Carbonate (PC) for the present study.

Whereas plasticizer increases the conductivity of the system, it also leads to decrease in the mechanical strength of the system. Incorporating inert nano fillers such as Al_2O_3, SiO_2 and TiO_2 in the system help increase the conductivity and also stabilize the mechanical integrity of the matrix (Pitawala et al., 2008). We have selected SiO_2 as the filler material to form nano-composite electrolyte system.

Present study has been undertaken to understand the effect of SHI beam irradiation on sodium salt based polymer electrolyte systems diffused with plasticizers and nano fillers. Blend of polymers Polyethylene oxide (PEO) and Polyacrylamide (PAM), sodium triflate ($NaCF_3SO_3$) as salt for preparing primary blend electrolyte system, Ethylene Carbonate (EC) and Propylene Carbonate (PC) as plasticizers, Silicon dioxide (SiO_2) as nano filler. The prepared blend polymer electrolyte (BPE) samples have been subjected to irradiation by O^{6+} ion beam of 80 MeV energy.

Irradiation with Swift Heavy Ion (SHI) Beam

Irradiation by ion beams is another green technique of modifying the properties of polymer electrolytes. Large number of studies has reported that irradiation has led to a significant increase in the conductivity of the polymer system (Kumar et al., 2006). Swift heavy ions create a damage track on their way through the polymer matrix rupturing rigid polymer chains and hence help in increasing the amorphicity of the system. Irradiation by SHI beam has reported to show better ionic conductivity as compared to their un-irradiated counterparts (Kumar et al., 2006). Fluence, of irradiation plays a vital role in the enhancement of ionic conductivity. Every material added in a polymer electrolyte to increase its conductivity has a critical value above which it hinders the motion of the ions and hence leads to a decrease in the conductivity. Similarly there is a critical value of fluence after which it adversely affects the conductivity of the electrolyte. Critical fluence has different values for different materials i.e. critical fluence is dependent on the system of electrolyte material. It is a general observation that at lower fluencies, bonds of the polymer are broken and it undergoes chain scissioning process. This leads to faster ionic transport through the polymer matrix assisted by large segmental motion of the polymer backbone (Raghu et al., 2016).

In the present study, all electrolyte samples were irradiated with 80 MeV O^{6+} oxygen ion beam.

1. First system (PPS – system) (Variation of Sodium triflate)

[PEO_{50} – PAM_{50}] + *x* wt% $NaCF_3SO_3$

x = 5 wt% - 17.5 wt% in steps of 2.5

In this series, effect of variation of salt sodium triflate is studied on blend system of polymers PEO and PAM

2. Second system (PPSP – system) (Variation of EC-PC Plasticizer)

[PEO_{50} – PAM_{50} – 12.5 wt% $NaCF_3SO_3$] + *x* wt% 1: 1 (*w/w*) EC-PC

x = 5 wt% - 25 wt% in steps of 5

In this system, effect of variation of plasticizer combination EC-PC is studies on optimized blend electrolyte system of PEO_{50} – PAM_{50} – 12.5 wt% $NaCF_3SO_3$.

3. Third system (PPSPN – system) (Variation of nano filler SiO_2)

[PEO_{50} – PAM_{50} – 12.5 wt% $NaCF_3SO_3$ – 20 wt% EC – PC] + *x* wt% SiO_2

x = 5 wt% -15 wt% in steps of 2.5

In the third series we observed the effect of variation of nano filler SiO_2 on optimized plasticized blend electrolyte system of PEO_{50} – PAM_{50} – 12.5 wt% $NaCF_3SO_3$ – 20 wt% EC – PC

These systems will be known as PPS, PPSP and PPSPN respectively.

Polymer electrolyte samples were prepared as mentioned above and then subjected to irradiation. For ion beam irradiation, free standing films were cut into 1 cm × 1 cm segments and mounted on the ladder maintaining a distance of 1 cm between all the samples. Irradiation with 80 MeV swift heavy O^{6+} ion beam is carried out using material science beam line facility of pelletron accelerator at IUAC, New Delhi. Irradiation has taken place at room temperature for four different fluences of 1×10^{11}, 3×10^{11}, 1×10^{12} and 2×10^{12} ions/cm^2 and a constant current of 4 nA is maintained throughout the experiment. After this un-irradiated and irradiated samples were characterized using the different techniques such as X-ray diffraction Analysis (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM) and to study conduction mechanism Electrochemical Impedance Spectroscopy is employed. For this the electrolyte samples were sandwiched between two blocking electrodes and the impedance spectrum was recorded from ambient up to 333 K temperature in the frequency range from 20 Hz- 2MHz. Fundamentally, a small ac signal is applied across the system under study and its voltage response is studied.

Entire work of the thesis is divided into 6 chapters as briefly discussed below.

Chapter 1: Introduction

Subject of the thesis is based on solid state ionics which is briefly introduced here. Background of development of solid electrolytes, polymer electrolytes and its classification are discussed in this chapter. Techniques of enhancing ionic conductivity such as blending of polymers, addition of organic solvents, incorporation of nano fillers and irradiation by swift heavy ion beam are described in here. Various electrochemical applications of the polymer electrolytes are also discussed.

Chapter 2: Theoretical Details

In this chapter we discuss various theories that have been developed to understand the ion dynamics of the electrolyte materials. Some of the models which are relevant to the present study are discussed in detail.

Free Volume Theory, Static Bond Percolation Model and Dynamic Bond Percolation model explain conduction mechanism as correlated to the structure of the matrix.

Frequency dependence of conductivity is explained by Quantum Mechanical Tunnelling Model (QMTM), Small Polaron Tunnelling Model (SPTM), Correlated Barrier Hopping Model (CBH), Jump Relaxation Model (JRM) and Dynamic Structural Model and Jonscher's Universal Power Law dependence of the conductivity is also explained.

Temperature dependence of conductivity is studied using Arrhenius theory, Vogel-Tammann-Fulcher (VTF) theory and Williams, Landel and Ferry (WLF) model. Modulus Formalism and Dielectric Relaxation are also discussed in detail.

Chapter 3 Experimental Techniques

In this chapter description of the materials used, preparation of the blend electrolyte samples and various characterization techniques used are described in detail. X-ray diffraction analysis had been carried out at ambient temperature to understand the complexation and structural modifications.DSC thermograms were recorded to observe the changes in melting temperature with respect to change in concentration of the various additives in the system. Vibrational spectroscopy (FT-IR) was used for studying the modifications occurring in materials and understanding the change in molecular bond lengths of the polymers or interaction between the constituents, if any. SEM was employed to study surface modifications in the electrolyte system. Wagner's dc polarization method had been undertaken to find the ionic transport number of the BPE samples. All the characterizations are performed for samples before and after irradiation and any modifications recorded in the parameters are explained accordingly.

Chapter 4 Results and Discussion of Characterizations

This chapter describes in detail the results of applied characterization techniques on the samples and discusses the principles behind observed effects.XRD Analysis reveals that structural modifications in the electrolyte samples with increase in slat concentration, or plasticizer, or nano filler. Effect of irradiation on the structural properties is distinctively observed in the diffractograms. Calculated values of XRD parameters such as inter chain separation, crystallite size and percentage crystallinity are compiled in the form of table.

Presence of broad humps in the XRD pattern of Electrolyte confirms the complete amorphous nature of the polymer. It is observed that the characteristic peaks corresponding to the sodium salt in their respective electrolyte systems were absent and it confirms the complete dissolution of the sodium salts in the complex matrix which implies that the salt do not have any separate phase in the electrolytes. Addition of plasticizer in the blend complex enhances the amorphous region thus permitting the free flow of ions from one site to another site. Ionic conduction in the polymer electrolytes occurs mostly in the amorphous region and it has been achieved by the addition of low molecular weight plasticizer. Further addition of inorganic filler into the polymer salt matrix would increase the dissolution of the charge carriers in the matrix; hence, the ionic conductivity was improved.

Infrared spectral (IR) analysis is a powerful tool for identifying the nature of bonding and different functional groups present in a sample by monitoring the vibrational energy levels of the molecules, which are essentially the fingerprint of different molecules. The FTIR transmittance spectra in the range 400-4000 cm^{-1} has been taken for blend electrolyte with the incorporation of plasticizer, salt and the filler. Results of FT-IR spectroscopy show that there is a good complexation between all the constituent components of the three electrolyte systems. Shifting of vibrational peaks and decrease in their intensity physically depict these interactions. Irradiation has led to degradation the polymer and breaking down of polymer chains results in chemical changes and interactions which are manifested in the form of shifting of peaks and lowering of the intensity. These trivial changes observed in the IR-spectra of BPE samples, suggest that the irradiation has definitely caused important modifications but not caused a complete wipe-out of the overall structure of the polymer host matrix.

DSC thermograms are studied to understand thermal response of the BPE systems. It is observed that with increase in salt, plasticizer, nano filler and fluence of irradiation we observe a decrease in melting temperature. Lowering of melting temperature is suggestive of decrease in crystallinity of the system. Melting temperatures and degree of crystallinity of the electrolyte samples are presented in a table.

The scanning electron microscope (SEM) is one of the most versatile instruments available for the examination and analysis of the microstructure morphology of the conducting surfaces. Scanning electron microscope (SEM) image of present polymer electrolytes clearly show smooth and uniform surface morphology. This smooth morphology confirms the complete amorphous nature of PAM polymer and complete dissolution of the sodium salt. SEM micrographs show evident surface modifications with variation in amounts of salt, plasticizer and nano filler. Apparent changes in the microstructure of the samples are observed after irradiation. Results of all characterizations are in good agreement with each other.

Chaper-5 Electrochemical Impedance Spectroscopy Studies

AC studies are similar to the DC techniques in that the ratio of voltage to current is measured. For DC, this ratio provides the value of the resistance, R, measured in ohms. For AC the ratio gives an analogous quantity, the impedance, Z, also measured in ohms. The impedance contains four main contributions; these are from resistance, capacitance and constant phase elements. The induction is not an important factor for the polymer electrolytes although it can play a role in other electro-chemical applications of polymers. Measurement of the impedance as a function of frequency is called impedance spectroscopy. In general, impedance is complex quantity, in which the real and the imaginary parts are labelled Z' and Z'' respectively. In the complex impedance plot, the real quantity Z′ (X-axis) is plotted against Z″ (Y-axis) which displayed the polymer electrolytes characteristics as an arc followed by the linear spike is straight line inclined to the real axis. From the plotted graph, we can easily read the bulk resistance of the electrolyte system.

The complex impedance plot of the polymer electrolyte shows the semicircular portion which is mainly due to the parallel combination of the geometrical capacitance, C_g and the bulk resistance, R_b. When adding the plasticizer and the filler into the electrolyte matrix, the impedance spectra shows only a linear spike which corresponds to the lower frequency region. It confirms the idea that the current carriers are ions and the majority of the conduction only by the ions not by the electrons. From the obtained bulk resistance value, we can estimate the ionic conductivity value of the electrolyte system which depend on R_b, the bulk resistance of the electrolyte film, A the area of the electrode surface and t, the thickness of the electrolyte. Addition of plasticizer (such as ethylene carbonate) in to the polymer salt matrix greatly being reduced the bulk resistance of the system; this is because of the high dielectric nature of the low molecular weight plasticizer. The addition of plasticizer would considerably enhance the amorphous phase of the polymer electrolyte which will improve the ionic conductivity of the system. However, the gain in conductivity is adversely associated with a loss of the mechanical properties. So it is necessary to identify the solid additives which would not affect the mechanical stability and interfacial stability of the electrolyte, at the same time will enhances the ionic conductivity. Solid additives should improve the amorphicity of the electrolyte at room temperature. Addition of solid additives in the present study, such as nano filler have enhanced the amorphicity of the electrolyte medium, hence the room temperature ionic conductivity and the interfacial stability of the electrode-electrolyte interface is increased.

The ceramic dispersed electrolytes show good thermal stability. The temperature dependence of the conductivity is given by the Vogel–Tamman–Fulcher (VTF) equation

$$\sigma = AT^{(-1/2)}\left(-\frac{B}{K(T-T_0)}\right)$$

where, A is the pre-exponential factor, B should not be confused with an activation energy in the Arrhenius expression and T_0 is related to the so called thermodynamic T_g. Plots of log σ vs 1/T are curved because of the reduced temperature ($T-T_0$). Dispersive nature of conductivity with frequency can be well interpreted from Jonscher’s Universal Power law (Jonscher, 1977) given as

$$\sigma(\omega) = \sigma_0 + A\omega^n$$

where, $\sigma(\omega)$ is the value of AC conductivity, σ_0 depicts DC conductivity, A is a constant for particular temperature and n is the power law exponent related to degree of interaction amongst mobile ions and lattice around them.

Permittivity of dielectric materials is the measure the energy stored by them. Real and imaginary parts of complex impedance Z* can be used to evaluate real and imaginary parts of the permittivity.

$$\varepsilon' = \frac{-Z_i}{\omega C_0(Z_r^2 + Z_i^2)}$$

$$\varepsilon'' = \frac{-Z_r}{\omega C_0(Z_r^2 + Z_i^2)}$$

where, C_0 is the capacitance of the material in vaccum, ε_0 is the permittivity of free space and has the value of $8.854\times10^{-12} F/m$, $\omega = 2\pi f$ is the angular frequency and f is the frequency of the applied electric field. Real part of permittivity ε' corresponds to ordinary dielectric constant of the material which measures the amount of elastic energy stored in the material during every cycle of applied alternating field and the energy responded back to the field at the end cycle.

Modulus formalism has been employed to have a better insight into the electrical relaxation process. Modulus formalism $M^*(f)$ can be well extracted from complex permittivity by the following relationships

$$\begin{aligned} M^*(\omega) &= \frac{1}{\varepsilon^*(\omega)} \\ &= M'(\omega) + jM''(\omega) \\ &= M_\infty[1 - \int_0^\infty \exp(-j\omega t)(-\frac{d\phi(t)}{dt})dt] \end{aligned}$$

where, $M'$and M'' are the real and imaginary parts of the complex modulus M^*. The function $\varphi(t)$ gives the time evolution of the electric field within the material and $\omega = 2\pi f$ is the angular frequency.

Ionic conductivity and dielectric properties of the system enhance with respect to increase in amount of the additives as well as temperature. Results of characterizations combined with electrochemical behaviour of the system led us to identify one optimized sample in each of the three series. For first series, sample with 17.5 wt% salt, in the second series, sample with 20 wt% plasticizer and in the third series, sample with 15 wt% nano filler have been identified as optimized samples. In case of irradiated samples, 1×10^{12} ions/cm^2 was established as the optimized value of fluence.

Chapter 6 Conclusion

This chapter contains a summary of investigations of the blend polymer electrolyte materials. A list of publications is included at the end of chapter 6.

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