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

Executive Summary of the Thesis Submitted

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BRIEF RESEARCH METHODOLOGY

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

$$M^*(\omega) = \frac{1}{\varepsilon^*(\omega)}$$

$$= M'(\omega) + jM^{"}(\omega)$$

$$= M_{\infty}[1 - \int_{0}^{\infty} \exp(-j\omega t)(-\frac{d\phi(t)}{dt})dt]$$

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.

KEY FINDINGS

Present thesis is aimed at understanding basic mechanism lying behind the electrochemical response of blend polymer electrolyte systems of two polymers PEO (Polyethyleneoxide) and PAM (Polyacrylamide) irradiated with SHI beam. PEO is a semi-crystalline polymer which is widely investigated as polymer electrolyte host matrix. PAM is an amorphous hydrogel with high compatibility with many electrodes. In the present work, the combination of the polymers is optimized at 50-50 wt%. Sodium Triflate ($NaCF_3SO_3$) salt has been chosen to form the electrolyte samples. Our first system of samples (Polymer-Polymer-Salt (PPS)) is formed by varying $NaCF_3SO_3$ from 5 wt%-17.5 wt% in steps of 2.5. Addition of plasticizers in the electrolytes is a cost effective and promising technique of increasing the electrochemical performance of the electrolytes, hence we plasticized our blend electrolyte samples with EC+PC (1:1 w/w) plasticizers to form the second system of samples (Polymer-Polymer-Salt-Plasticizer (PPSP)) by varying the plasticizer content from 5 wt%-25 wt% in steps of 5. Another favourable method to increase the ionic conductivity is to add inert nano-fillers to the electrolytes and so we formed our third system of samples by dispersing silicon dioxide (SiO_2) nano particles to the plasticized blend electrolyte samples. In the third system (Polymer-Polymer-Salt-Plasticizer-Nanofiller (PPSPN)) amount of SiO_2 particles is varied from 5 wt%-15 wt% in steps of 2.5. Irradiation by swift heavy ion (SHI) beam has also been employed as a successful technique for enhancing the ion conduction in electrolytes, hence selected samples from each of the three systems were subjected to swift heavy oxygen (O^{6+}) ion beam of 80 MeV energy at four different fluence rates, namely 1×10^{11} ions/cm^2, 3×10^{11} ions/cm^2,1×10^{12} ions/cm^2 and 2×10^{12} ions/cm^2. To study thermal and surface properties and complexation of various contents of the electrolyte samples, we have used techniques like Differential Scanning Calorimetry (DSC), Fourier-Transform Infrared Spectroscopy (FT-IR), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Impedance spectroscopy technique has been applied to study the electrochemical properties of the samples.

The results of characterization techniques reveal that there is good complexation between all the components of the electrolytes. No added component remains as an individual entity in any of the systems.

The ionic conductivity of PPS system increases continuously with increase in amount of $NaCF_3SO_3$ from 5 wt% - 17.5 wt%. Maximum conductivity at room temperature is recorded to be 2.28×10^{-6} Scm^{-1} for PPS-17.5 sample. When the concentration of salt exceeds a certain optimal amount, re-association of ions takes place instead of dissociation and this leads to a decrease in the conductivity. But this is not true in the present case even after adding large amount (17.5 wt%) of $NaCF_3SO_3$. In case of PPSP system, Values of conductivity increase with increase in (EC+PC) content from 5 wt% - 15 wt% and slightly decrease for 20 wt% and 25 wt%. The room temperature conductivity value for PPSP-15 is recorded to be 9.26×10^{-6} Scm^{-1}. In the third system, the conductivity increases with increase in SiO_2 content upto 7.5 wt%, decreases at 10 wt%, and 15 wt% and again increases for 12.5 wt%. in case of PPSPN system, we observe two conductivity percolations, one at 7.5 wt% and the other at 12.5 wt%.

Electrical behaviour of a system can be probed using dielectric properties and modulus formalism also. Permittivity of a dielectric material is that property which measures the amount of energy stored in it. Modulus function is used to represent the frequency dependent dielectric or conductivity data. The dielectric properties of all the three systems trace the same path as that of their conductivities.

Irradiation by ion beam has successfully increased the ionic conductivity of all the systems up to a fluence of 1×10^{12} ions/cm^2 (critical fleunce) and then at 2×10^{12} ions/cm^2 fluence, electrochemical performance deteriorates.

CONCLUSION

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 15 wt% plasticizer and in the third series, sample with 12.5 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.

RECOMMENDATIONS

To summarize our entire work, we suggest that the blend of PEO-PAM polymers proves as an excellent host matrix for electrochemical investigations. The prepared blend electrolytes show good miscibility with all the additives in the system. The ionic conductivity increases by addition of plasticizer and nano-fillers in the system and irradiation further increase electrolytic properties of the films. Ionic contribution to the conductivity is maximum in each of the prepared blend electrolyte samples. However, we have not been able to reach a practically applicable conductivity value, further experiments are on to achieve a higher room temperature conductivity with better mechanical strength of the electrolytes for storage application.

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