

Research article

MOBILITY AND DIELECTRIC STUDY IN [PEO:(NH₄)₂(C₄H₈(COO)₂):LiFe₅O₈ ELECTROLYTE SYSTEM

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Abstract

Present work deals with findings on dielectric behavior and a.c. conduction in a ferrite doped polymer nano composite electrolyte system, namely [(100-x) PEO + x (NH₄)₂(C₄H₈(COO)₂): y LiFe₅O₈. The structural behavior of electrolytes studied by XRD, SEM and IR spectroscopy shows improvement in amorphous behavior on dispersal of Li-Ferrite nano fillers. The effect of ferrite dispersal on electrical behavior under isothermal conditions, has been investigated by the impedance spectroscopy.

Keywords: Polymer salt interaction, PEO, Polymer composite electrolyte, ionic conductivity

Introduction

Recently solid nano composite polymer electrolytes (NCPEs) have attracted lot of attention due to their potential application in solid state electrochemical devices. The ionic conductivity of these NCPE is strongly governed by the route of preparation, concentration of filler, type of salt and its concentration [1-2]. Among different polymer electrolytes, the PEO based electrolyte systems have been extensively investigated owing to the fact that PEO has a single helical structure which supports fast ion transport. Possibility of easy dissociation and large anionic site, forming high protonic conduction makes, Ammonium Adipate [(NH₄)₂C₄H₈(COO)₂] a favorable salt for development of highly conducting polymer electrolyte. Addition of fillers in these electrolytes is one of the several options to auger their structural, mechanical and ion transport properties. Within the family of inorganic fillers, ferrite is seen to be another probable better candidate for development of NCPEs [3-4]. Lithium ferrite is a good candidate for filler due to the abundance and low toxicity of Iron. It has stable frame work for electrodes in Lithium ion rechargeable batteries [5]. Further, it demonstrates super paramagnetic behavior opening new application areas for polymer electrolytes like drug delivery system, tissue engineering and biomedical applications [6]. Prompted by

these considerations, an innovative approach has been made to use nano sized Li ferrite materials as filler in developing the PEO based nanocomposite polymer electrolyte.

Experimental

Nanocomposite polymer electrolyte free standing films were prepared following well known solution cast technique. Polyethylene oxide [(PEO) (M.W.~ 6×10^5 , ACROS organics)] and Ammonium adipate $\{(NH_4)_2C_4H_8(COO)_2$ (Rankem, India) of AR grade} salt were used in synthesis of polymer electrolyte. Lithium ferrite filler, used in development of NCPE, was synthesized by sol-gel process [7]. Structural behavior of $[(100-x) PEO-x (NH_4)_2C_4H_8(COO)_2] : y LiFe_5O_8$ {where $x=5,10,20, 30$ and $y=0.5$ and 1 } systems were evaluated with the help of XRD, SEM and IR investigations. The XRD pattern was recorded between $2\theta=15-60^\circ$ at room temperature using Phillips X-pert diffractometer. EPMA model JXA-8100 instrument was used to obtain SEM images of electrolytes with stub coated with graphite to a thickness ~5-10 nm under vacuum using JEOL high vacuum evaporator. The coated samples were randomly scanned and photographs were taken with SEM. The infrared spectrum was recorded on Perkins Elmer IR spectrophotometer in a range $4000-400cm^{-1}$. The electrical conductivity was evaluated from complex impedance plot obtained using computer controlled Hioki (JAPAN)-LCZ HI Tester (model 3520-01) in the frequency range of 40Hz to 100KHz. The impedance spectrum was used to evaluate the bulk a.c. conductivity and other related parameters.

Result and Discussions

The XRD patterns of pristine and composite polymer electrolytes recorded at room temperature is shown in figure 1a and refined pattern (refined by GSAS program) are shown in figure 1b.

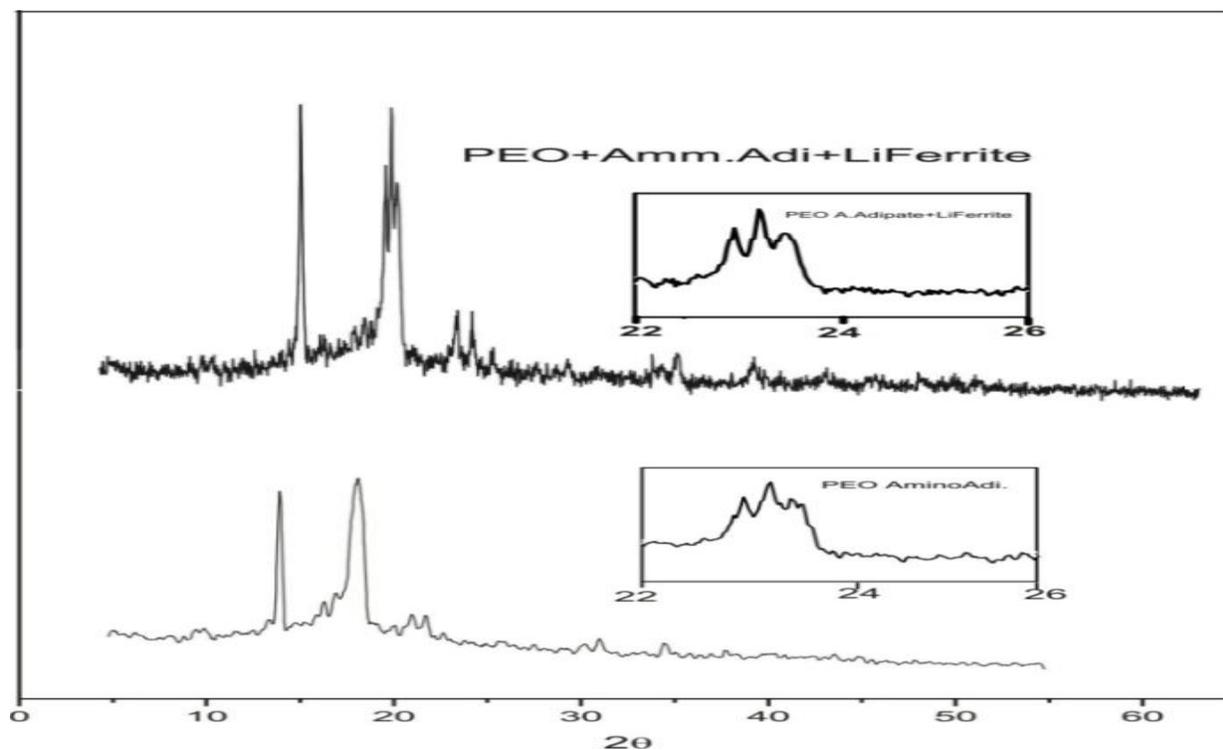


Fig. 1a: XRD Curves

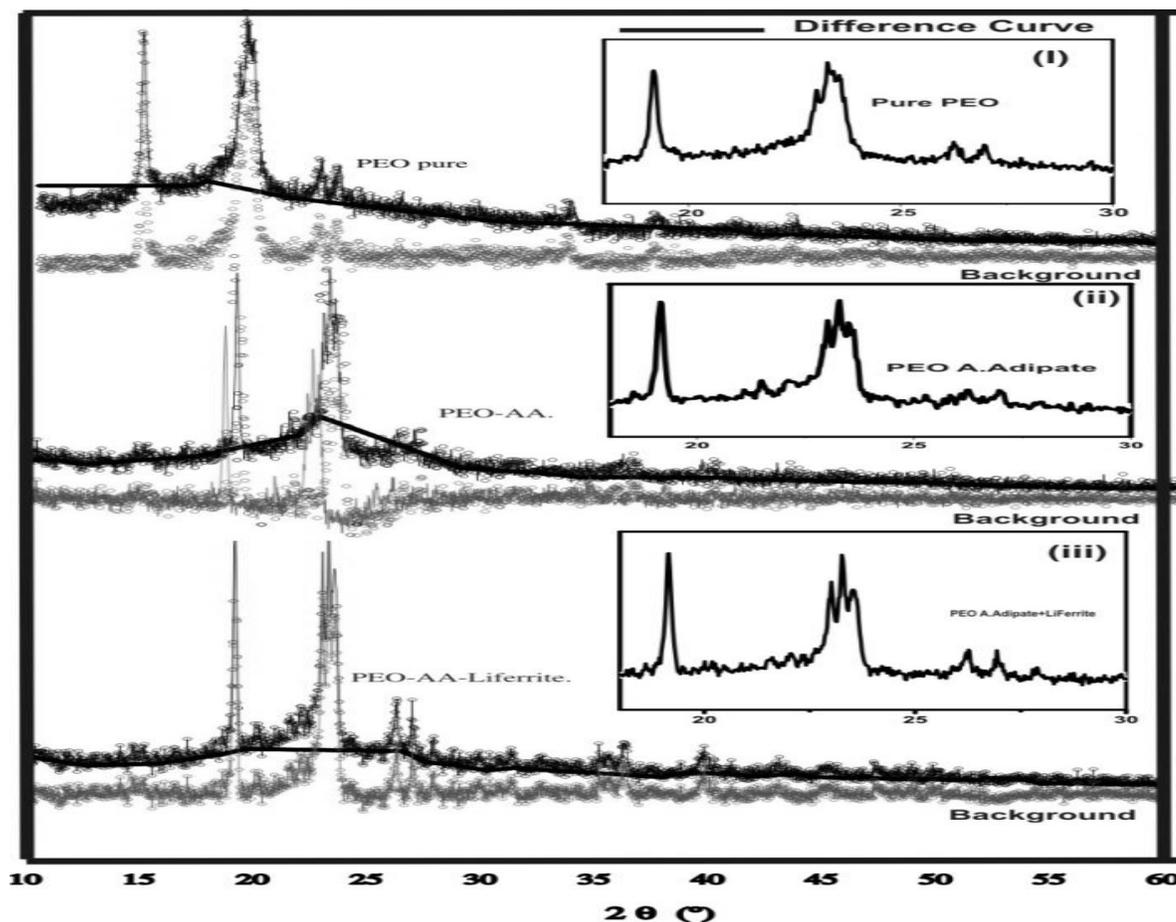


Fig. 1b: Refinement of XRD curves through GSAS program

In figure 1a comparison of XRD curves show interaction of salt/filler with polymer and increase in broadness of PEO related peak at 23° . This indicates the decrease in crystallinity of composite electrolyte film. To understand the interaction of salt / filler with polymer matrix, the main peak of PEO at 23° was enlarged (given in inset in all cases). It seems to consist of a triplet (one main peak and two spikes) having position at $2\theta = 23.0^\circ, 23.2^\circ,$ and 23.5° . The XRD curve of pristine [shown in figure 1a] also has the same nature with an additional peak at 23.4° . This additional peak corresponds to ammonium adipate [8]. After addition of Li Ferrite filler, peak at 23.4° and 23.5° merge and show a sharp triplet with enhancement in broadening of the main peak. It is found that broadness of peak increases as $\text{PEO} : (\text{NH}_4)_2\text{C}_4\text{H}_8(\text{COO})_2 + \text{Li ferrite} < \text{PEO} : (\text{NH}_4)_2\text{C}_4\text{H}_8(\text{COO})_2 < \text{PEO}$.

The refinement was performed on the basis of experimental and calculated data of PEO, $\text{PEO} : (\text{NH}_4)_2\text{C}_4\text{H}_8(\text{COO})_2$ and $\text{PEO} : (\text{NH}_4)_2\text{C}_4\text{H}_8(\text{COO})_2 + \text{Li ferrite}$ by least square method [9]. The aim of least-squares refinement is to minimize the difference between the observed and calculated structural amplitudes. Through various steps we are reducing or filtering the zero point error. Figure 1b shows the reduction in composite volume. The change in peak intensity is observed after the refinement. The calculated average particle size in pristine and composite electrolytes is 47 nm and 43 nm respectively. In order to distinguish the effect of crystallite size induced broadening in FWHM of XRD profile, W-H plot [10] (shown in figure 2) was drawn and found crystallite size to be nearly 20nm size in both cases. The infrared spectra of $[90\text{PEO} : 10(\text{NH}_4)_2\text{C}_4\text{H}_8(\text{COO})_2]$ and $[90\text{PEO} : 10(\text{NH}_4)_2\text{C}_4\text{H}_8(\text{COO})_2] + 1\% \text{LiFe}_5\text{O}_8$ electrolyte system (recorded in the range $4000\text{-}400\text{cm}^{-1}$) is shown in figure 3.

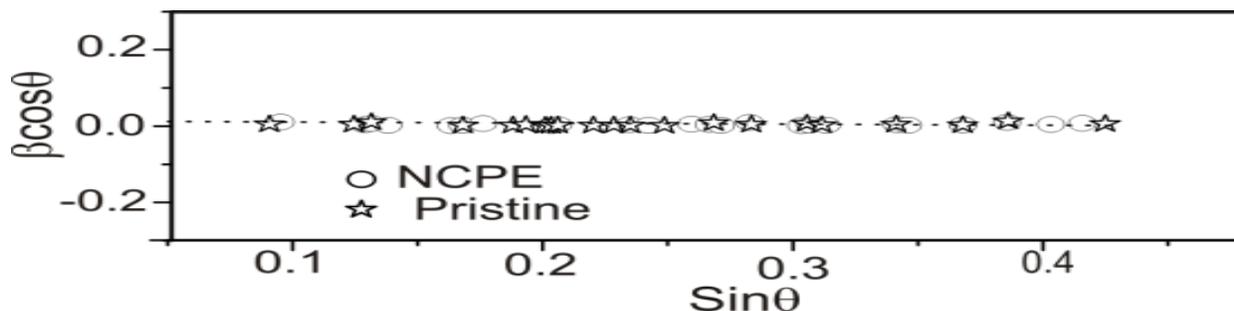


Fig. 2: W-H Plot of polymer electrolytes

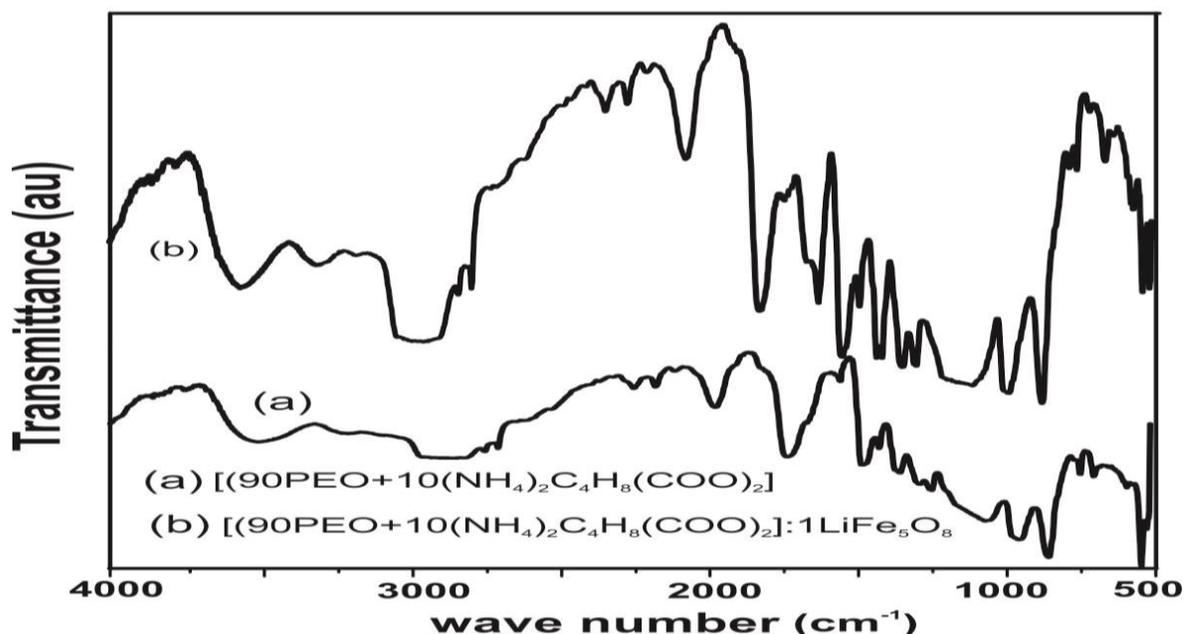


Fig. 3: IR spectrums of polymer electrolyte systems

The IR spectrum of NCPE shows formation of few new peaks in the low frequency region with other peaks become same as in case of polymer salt electrolyte. In both the cases $-\text{OH}$ stretching ($\sim 3500\text{cm}^{-1}$, broad in nature) and $-\text{OH}$ bending ($\sim 1650\text{cm}^{-1}$) are present and change in intensity after complexation with filler. In the pristine electrolyte system, the stretching modes of PEO chain i.e. C-H stretching ($\sim 2860\text{cm}^{-1}$) and asymmetric C=C=C stretching ($\sim 2240\text{cm}^{-1}$) are modified in intensity with a small shift due to the presence of $(\text{NH}_4)_2\text{C}_4\text{H}_8(\text{COO})_2$ in the PEO matrix. New peak forms at 1720 and 1965cm^{-1} (C=O stretching) appear in the IR spectra of present electrolyte to on account of polymer-salt interaction. In IR spectra NCPE, new peaks at 2100 and 1774cm^{-1} were recorded along with the shift in peak positions of other new peaks toward the higher wave number side (e.g. peaks on 1303cm^{-1} to 1400cm^{-1} , 1343cm^{-1} to 1465cm^{-1} and 1065cm^{-1} to 1054cm^{-1}) due to change of local environment. Formations of new peaks clearly indicate the interaction of filler with polymer-salt composite. The detail of IR spectra of Li ferrite is reported elsewhere [11-12]. Another important feature of IR spectra is the increase of intensity and merging of two peaks in a single peak (at 1231cm^{-1}), which shows the disintegration of crystalline phase of original pristine

sample. Variation of conductivity with frequency for different compositions of [90PEO-10(NH₄)₂(C₄H₈(COO)₂)₂]:
 yLiFe₅O₈ (where y=0.1.2.3.4 and 5 wt %) system is shown in figure 4a.

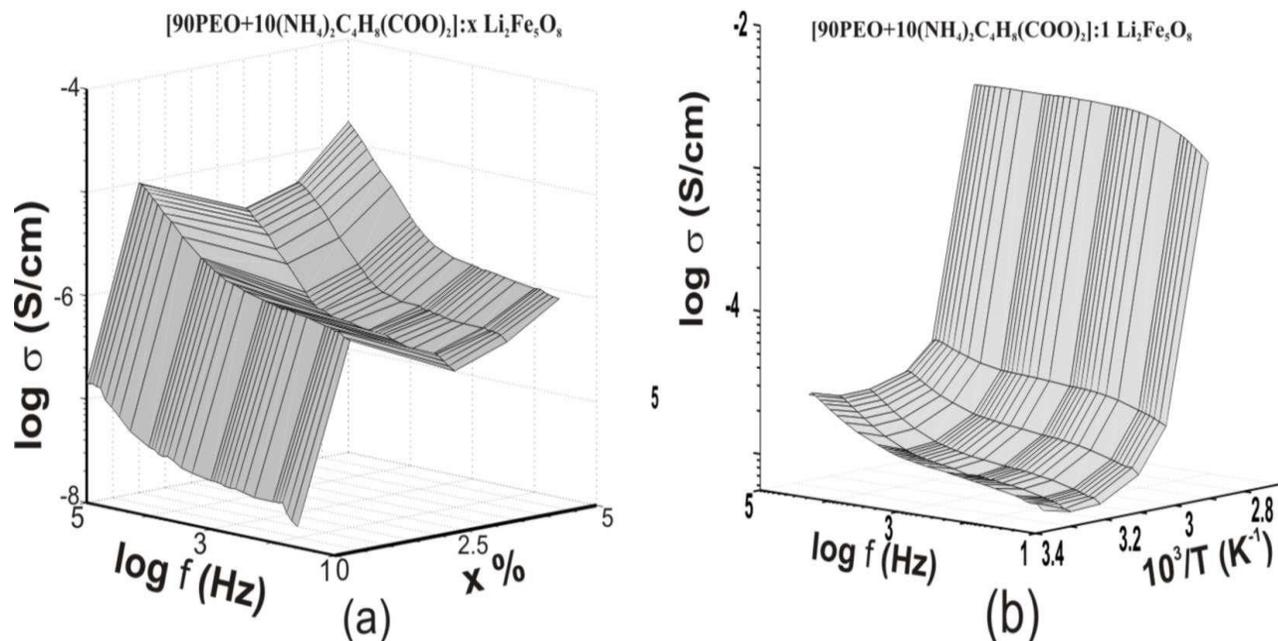


Fig. 4: A.C. conductivity of electrolytes

The a. c. conductivity of electrolyte system has been evaluated using the relation

$$\sigma_{ac} = \epsilon' \epsilon_0 \omega \tan \delta$$

where ϵ_0 is the vacuum permittivity and ω is the angular frequency.

The conductivity of NCP systems is seen to increase rapidly at lower ferrite contents, to attain a maxima at (1wt %); this is followed by a decrease and later on again increases with filler content. Initial increase in conductivity is due to salt dissociation in the presence of ferrite particles. Decrease in conductivity is related to disorderliness of the composite system with increasing amount of filler. The final increase shows segregation or unacceptability of filler in the pristine system. This is a common nature of polymer-salt-filler composite electrolyte system. The conductivity is nearly unchanged with frequency in low frequency region (display plateau type behavior for all compositions), but in higher frequency region it increases with frequency. The appearance of low frequency plateau is due to blocking effect of grain boundaries and in the high frequency region charge carriers become free to follow the changing electric field, therefore increasing conductivity with frequency. The change of a. c. conductivity with frequency at different temperatures for [90PEO-10 (NH₄)₂(C₄H₈(COO)₂)₂]: 1% LiFe₅O₈ film is given in figure 4b. The conductivity of the NCP film increases with increasing frequency at each temperature. It is interesting to note that the increase in conductivity before the T_m of the host polymer (PEO) is extremely low but beyond T_m the increase appears to become rapid. This nature is due to phase transformation in the polymeric matrix.

Figure 5 shows the variation of emf generated by the cell Zn / PCE /Zn with temperature [13]. In pristine electrolyte system PEO+ Ammonium Adipate thermovoltametric curve shows that the emf decreases after 48°C due to removal of adsorbed water then it becomes linear and again decreases after 71°C. The second decrease is possibly due to phase transition of host polymer. In the composite electrolyte only second decrease is prominent. The absence of first peak is an indication of less absorption of humidity (or humidity resistant nature) in the electrolyte due to dispersal

of ferrite filler. The temperature dependence of conductivity for pristine and NCPE support the nature of thermovoltametry. In the phase transition region conductivity increases due to more amorphousness of the electrolyte.

The temperature dependence conductivity shows the Arrhenius type behavior followed by VTF nature [14] of thermally activated process. In order to understand the dynamics of mobile ions the conductivity spectra at different temperature may be presented in terms of scaling law, which compares the ion dynamics. The conductivity is scaled according to the following expression:

$$[\sigma(\omega)/\sigma_{dc}] = F(\omega/\omega_p)$$

Where $F(\omega/\omega_p) = (1 + (\omega/\omega_p)^n)^{-1}$ and ω_p is the characteristic hopping frequency dependent on temperature. Scaled conductivity plot with frequency of 90 PEO-10(NH₄)₂(C₄H₈(COO)₂) and [90PEO-10 (NH₄)₂(C₄H₈(COO)₂):1%LiFe₅O₈ systems are shown in figure 6. From the figure it is apparent that scaled conductivity spectra of pristine electrolyte sample do not coincides with each other, but in the NCPE, scaled conductivity spectra at different temperature merge on a single master curve in the complete frequency range (40Hz-100KHz). This type of process is called "Time-temperature superimposition principle". It implies that the relaxation dynamics upon addition of Li-ferrite filler changes and forced to follow similar relaxation dynamics at all temperatures in the range (RT- 373K).

The activation energy (E_a) of each system was calculated from the slop of the curve shown in figure 7. The increase in conductivity with temperature is also explained by the Rice and Roth model that express the ionic conductivity σ as

$$\sigma = 2/3 [(Ze)^2 / K_B T m] n E_A \tau \exp[-E_A/KT]$$

Where Z is valency, m is the mass of the conducting ion, e is electronic charge and τ is time of flight between the sites. In the equation, number of charge carriers (n), ionic mobility (μ) and diffusion coefficient (D) can be identified.

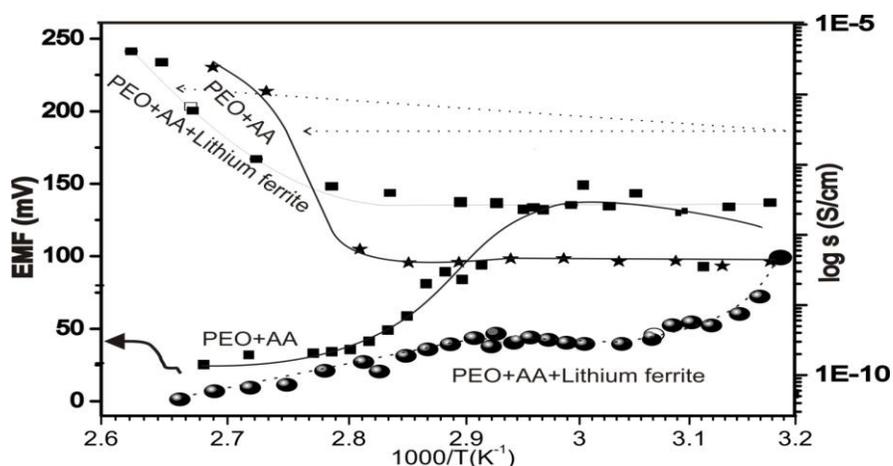


Fig. 5: Comparison of voltage and conductivity

Variation of dielectric parameters (real & imaginary part of relaxation) with frequency at different temperature for pristine and nanocomposite polymer electrolyte system are shown in figure 8. The dielectric parameters (ϵ' & ϵ'') show low frequency dispersive nature in both the cases. In the low frequency region, ions jump in the field direction and pile up at sites with high energy barrier. In pristine sample this effect is also observed at intermediate temperatures (Figure 8a, 8b). However at higher frequencies dielectric parameters (ϵ' & ϵ'') remain low and constant, as the orientation of polarization due to chain motion of polymer cannot keep pace with rapidly oscillating applied electric field of nano composite electrolyte. In general the electrode polarization is attributed to the blocking charge

carriers at electrode interface due to existence of crystallinity, absorbed water and presence of heterogeneity. In the pristine sample the change of tangent loss ($\tan\delta$) with frequency at different temperature show a peak at the frequency region $\sim 1\text{KHz}$. After the addition of ferrite filler in the pristine sample, we observe an additional peak with the broadness of the original peak. Two peaks in nanocomposite systems are possibly due to two phases or two types of mobile charge carriers (i.e. proton and/or Li^+). The loss occurring due to such interaction depends on a number of factors like the number/ type of constituents in the matrix, the number of repeat units and its mobility, molecular (intra/ inter) interaction and their relaxation time. The shift in loss peak in NCPE toward the higher frequency side is an evidence of manifestation of polymer chain mobility and its interaction with relaxing dipoles.

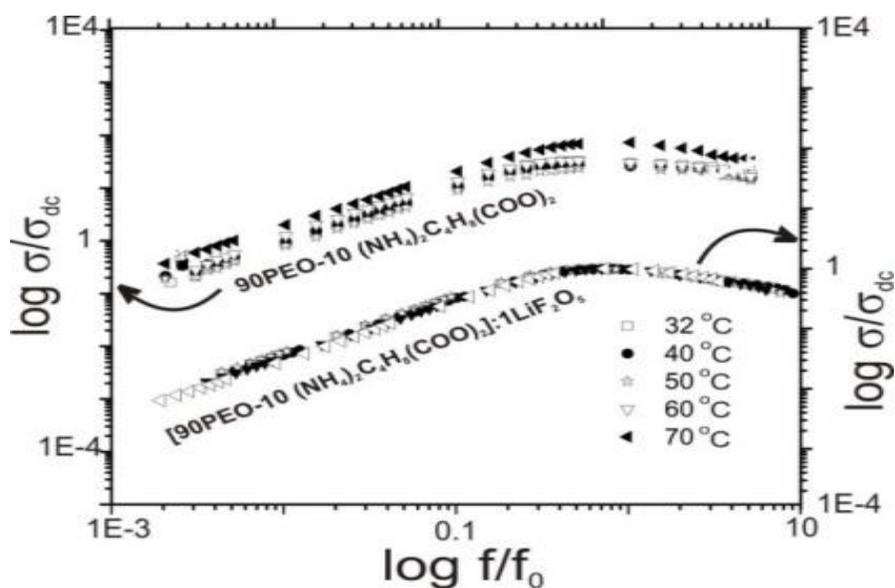


Fig. 6: Scaling behavior of conductivity with temperature in electrolytes

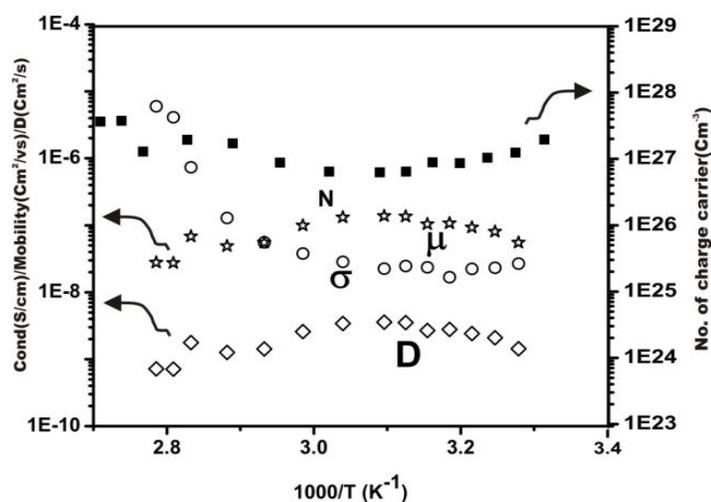


Fig. 7: Ionic Mobility Vs Inverse temperature

The ionic conductivity is represented by

$$\sigma = \sum n_i e_i \mu_i$$

Where n_i , e_i , and μ_i are the charge carriers density of ionic charge and ionic mobility of the i^{th} ion respectively. In general an increase of ionic conductivity of the complex system is due to an increase of number of mobile charge carriers introduced/ produced in the material with a change of constituent concentration. On the basis of the transport parameter calculated by Rice & Roth model [15], it is contrary that the combinations of Lithium Ferrite provide a better medium for mobility in the matrix. The deviation from ideal behavior is somewhat greater for the ion mobility than for the conductivity because the mobile ion content increases with temperature. The changes in number of charge carriers are not noteworthy in the present case.

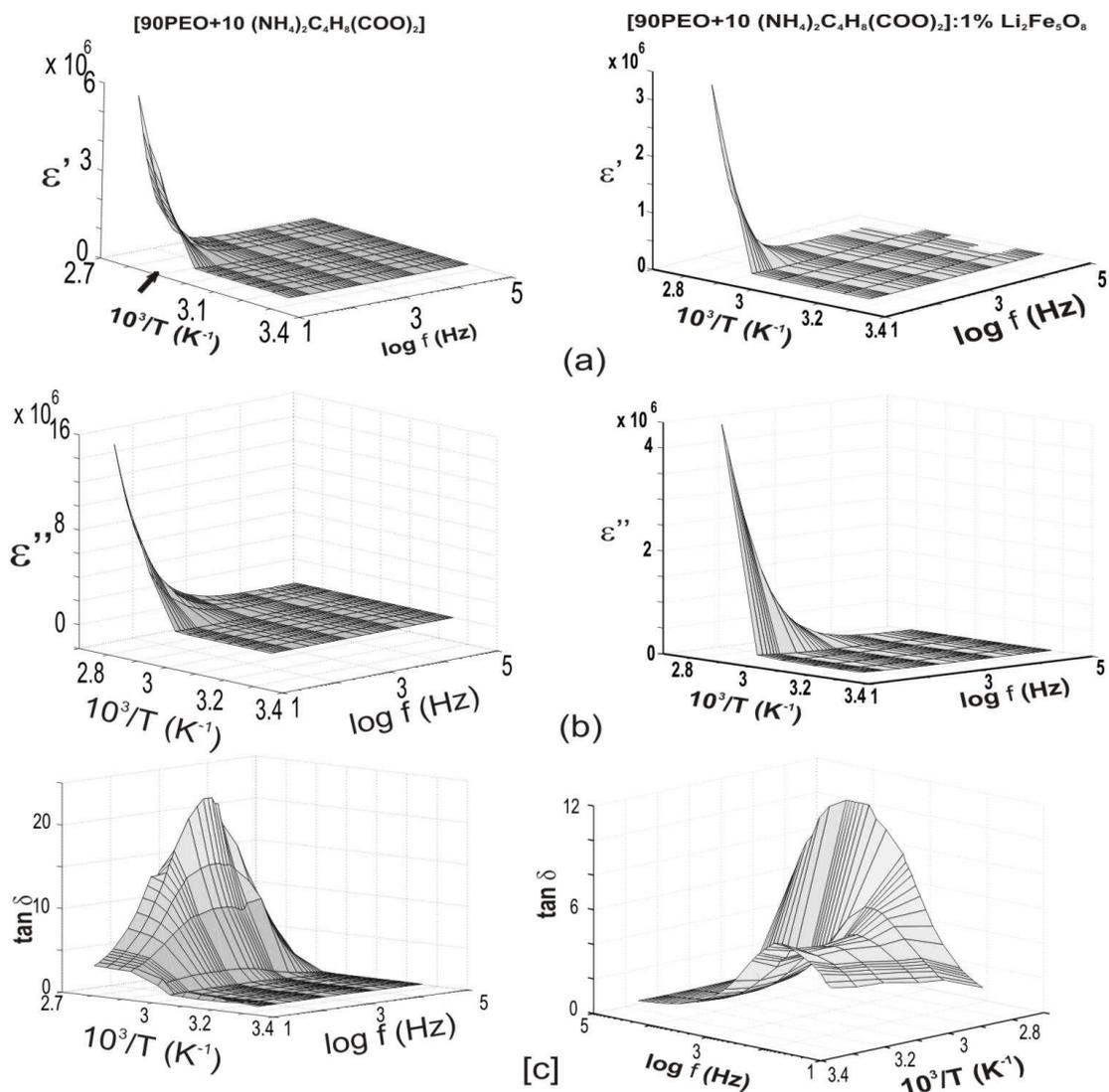


Fig. 8: Dielectric parameters of pristine and nano Composite polymer electrolyte

Conclusion

The experimental studies by XRD, IR, Impedance showed that addition of Li ferrite filler in [(100-x)(PEO-10(NH₄)₂(C₄H₈(COO)₂)] decreases the crystalline nature of polymer composite electrolyte due to intercalation of salt/ Li ferrite in PEO Polymer. It also produces better mechanical property of solid composite electrolyte film with nano size crystallite format for the device application. The conductivity of NCPE film became one order higher than the composite film.

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