

# Ionic Conductivity of Zn- Ferrite Doped Nanocomposite Polymer Electrolyte and Proton (H<sup>+</sup>) Conducting Solid State Rechargeable Battery Performance

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## Abstract:

In this context, nanocomposite polymer electrolytes are attracting scientific and technological importance due to their potential applications in many areas such as solid-state batteries, fuel cells, super capacitors and electrochromic devices etc. In general, nanocomposite polymer electrolytes are plasticized materials whose structure and properties can be tailored for specific needs namely in electrochemical devices like in solid-state ionic batteries. An attempt are made to develop and characterize the effect of salt in the improvement of ion transport property of polyethylene oxide (PEO)-based polymer electrolytes subsequent to dispersal of nanosized Zn-ferrite as a filler particles. The nanocomposite polymer electrolyte system [(1-x) PEO: xNH<sub>4</sub>SCN]: 1wt% Zn-ferrite films are prepared by solution cast technique. Zn-ferrite nano powder is synthesized through well-known sol-gel process at ambient temperature. The structural and morphological behaviors of NCPEs are studied with the help of XRD and OM measurements. Electrical conductivity measurements of nanocomposite polymer electrolytes samples are carried out using impedance spectroscopic technique. Dielectric relaxation studies are extracted by impedance data to assess ion conduction mechanism in electrolyte system. Electrochemical stability of NCPE is studied under the CV measurement and show better electrochemical response upon dispersal of Zn-ferrite. To check the utility of as synthesized NCPEs in electrochemical devices, solid state rechargeable proton conducting batteries are fabricated for optimally conducting electrolytes systems. The Solid State battery of sample containing 1wt% Zn ferrite in [93PEO-7NH<sub>4</sub>SCN]: polymer electrolyte gives better response of OCV (1.46V) and having energy density = 403 μWh/Kg.

**Keywords:** Nanocomposite polymer electrolyte, polymer-salt-ferrite interaction, ion conduction, PEO, Zn-ferrite, proton (H<sup>+</sup>) conducting solid state rechargeable battery.

## I. INTRODUCTION:

Solid state batteries built around polymer electrolytes are the new type of practical power sources that free from the problems associated with the escape of corrosive, flammable or toxic liquid, and they also offer the opportunity for a new continuous manufacturing process based on film formation technology. The urgent need for environmental control in highly populated urban areas has resulted in the call for the replacement of a large proportion of vehicles with internal-combustion engines by zero-emission battery. Rechargeable cells have beamed key components in mobile technology, pace makers, portable consumer electronics and electric vehicles in recent times. Search for batteries providing high energy density and multiple rechargeability has been the subjected of considerable attention over the decades. Several reviews have appeared in literature [1, 2]. It is worth mentioning here that within the umbrella of solid state ionic materials, polymer electrolytes have assumed considerable importance in battery research. Within the family of polymer electrolytes, nanocomposite polymer electrolytes have emerged as prominent class of material in solid state battery research after the advent of nano technology. Solid polymer electrolytes are prominent class of electrolyte materials for electrochemical device applications such as fuel cells, solid state ionic batteries, super capacitors, smart windows etc., possessing properties of good thermal, electrochemical stability and high electrical conductivity, mechanical strength, flexibility, optical density, corrosion toughness etc. Different cation/ anion conducting polymer electrolytes based on wide range of polymer hosts like Poly(ethylene oxide) PEO, Polyvinyl alcohol (PVA), Polyethylene glycol (PEG), Polymethylmethacrylate (PMMA), Polyvinylidene fluoride (PVdF) complex with few ammonium salts (NH<sub>4</sub>SCN, NH<sub>4</sub>HSO<sub>4</sub>, NH<sub>4</sub>ClO<sub>4</sub>, NH<sub>4</sub>I etc),

acids ( $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  etc.) and a number of alkali, alkaline and transition metal salts (e.g.  $\text{LiClO}_4$ ,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{LiI}$ ,  $\text{NaI}$ ,  $\text{AgNO}_3$  etc. have been developed over the years [3-4]. Among these polymer hosts, Poly (ethylene oxide) PEO based polymeric electrolytes is extensively investigated owing to fact that PEO has a single helical structure which supports fast ion transport [1]. Further PEO has good complexation properties and high solvating behavior [5], partial crystalline/amorphous nature, low melting point ( $65\text{-}69^\circ\text{C}$ ) and low glass transition temperature [1, 4]. However, due to high crystalline phase concentration, the conductivity of PEO based electrolyte is limited. This is essentially due to basic requirement for ionic conduction viz., ionic motion coupled to the segmental motion (relaxation) of flexible amorphous polymer phases [4]. Recently, particular attention has been devoted to introduce some structural modification in polymer electrolyte in order to increase their electrical conductivity and improve their thermal, mechanical and electrochemical properties to provide commercial acceptability in electrochemical devices. Various techniques (like plasticization, co-polymerization, etc.) have been adopted to achieve the desired objective-high ionic conductivity in polymer electrolytes [6, 7]. In this process, another class of polymer electrolyte referred to as "Nanocomposite polymer electrolyte (NCPE)" has been developed. In this regards, various attempts have been made in the past decade, to enhance the ionic and mechanical properties with the addition of different organic and inorganic fillers leading to formation of composite polymer electrolyte [CPE] [8, 9].  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SnO}_2$  and ferroelectric fillers ( $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$ ) etc. are few inorganic inert fillers that have been tried over the years to attain high ionic conductivity [8-12]. Scaling down of these inert inorganic fillers to nanometric sizes have been shown to improve significantly the ion conducting properties of the composite polymer electrolyte in recent past leading to emergence of NCPE [13, 14].

Within the family of inorganic fillers, ferrite is seen to be another probable candidate for development of NCPE, as they possess interesting structural and electrical features. Ferrite do exhibits high dielectric constant below Curie temperature-a feature desired by filler particles. Further, it demonstrates super paramagnetic behavior opening new applications for polymer electrolytes like drug delivery system, tissue engineering, biomedical application [15, 16].

Prompted by these considerations, an innovative approach has been made in this investigation to use nanosized Zn-ferrites material as filler in development of PEO- $\text{NH}_4\text{SCN}$  based nano composite polymer electrolyte and its characterization. Further the pristine electrolyte system PEO- $\text{NH}_4\text{SCN}$  is synthesized with the objective of developing proton ( $\text{H}^+$ ) conducting batteries. In order to understand the structural behavior of these electrolytes, the effect additive salt ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ ) and Zn-ferrites on PEO, with respect to morphology have been investigated via X-ray diffraction (XRD) and Optical microscopy. These experimental tools have been also used to ascertain nanometric dimensions of the electrolytes besides understanding the structural behavior. Once of the basic requirements of these entire polymer electrolytes is high ionic conductivity over a wide temperature window to establish their worth in electrochemical devices. Thus, besides structural & electrochemical characterizations, electrical characterization of NCPE is yet another important factor. Keeping this in mind electrical characterization on the developed nanocomposite polymer electrolytes was pursued and the results have been presented in this work. Ion transport properties have been examined under dc and as well as ac condition i.e. bulk ionic and ac conductivity.

The change in ionic conductivity with frequency and temperature were studied by impedance spectroscopic investigations. The effect of salt on dielectric parameters of NCPEs was also extracted from impedance spectroscopic data to explore underlying ion dynamics. The applicability of these smart materials (better conducting NCPE system) has also been studied through fabrication of solid state rechargeable proton ( $\text{H}^+$ ) conducting batteries and performance studies.

## II. EXPERIMENTAL:

### I. SYNTHESIS:

The polymer PEO (M.W.  $\sim 6 \times 10^5$ , ACROS Organics) and the salt Ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ , Rankem India) of AR grade were used in the synthesis of nanocomposite polymer electrolytes. For the synthesis of filler, tetraethyl orthosilicate (TEOS, Aldrich) was used as precursor material, ethanol as solvent and Ammonia solution as a catalyst. The Zn-ferrite powders were also synthesized by the well known sol-gel technique. Nitrates like  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  AR grade) were used as the starting chemicals to obtain  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$  ions in aqueous solution [17]. The aqueous solutions were obtained by dissolving precursors Zn, and Fe nitrates (Rankem India) in water-ethanol mixture followed by addition of tetraethoxysilane (TEOS) drop by drop while stirring it at room temperature for 50-60 hours in the molar ratio  $\text{EtOH}:\text{TEOS}:\text{H}_2\text{O} = 3:1:10$ . The pH of solution was fixed within 2-3 range. The sols were allowed to formation of gel at  $40^\circ\text{C}$ . After gellification gel were kept for drying at  $150^\circ\text{C}$  for 50 hrs. Subsequently, the powdered gels were subjected to thermal treatment at  $700^\circ\text{C}$  (for 3 hrs) and  $1000^\circ\text{C}$  (for 2 hrs) in a Kenthal high temperature furnace. The dried materials were crushed to obtain fine powder of

ferrites (Zn-ferrite nano powder). Solution cast technique was then developed to synthesize nanocomposite polymer electrolytes (NCPEs). Solution cast electrolyte films were dried at constant 30°C in BOD incubator before finally drying them in vacuum to obtain the solvent free standing films of NCPEs.

## II. CHARACTERIZATION:

The structural behavior of NCPEs was studied by X-ray diffractometer (Phillips X-pert model). The diffraction pattern were recorded at room temperature in the Bragg's angle range ( $2\theta=15-60^\circ$ ) using Cu-K $\alpha$  radiation ( $\lambda=1.542 \text{ \AA}$ ). The optical micrographs of the films were recorded using computer controlled Leica DMLP polarizing microscope.

The electrical behavior of solid polymer composite electrolyte samples was studied through impedance spectroscopy on application of small a.c. signal (200mV) across the sample cell with Pt blocking electrodes. The complex impedance parameters were measured with impedance analyzer (HIOKI LCR Hi-tester, model: 3520, Japan) under varying temperature conditions. Study of dielectric relaxation, a.c. conductivity and modulus spectra was carried out using impedance spectroscopic data.

CV measurements on NCPEs were performed on CH-electrochemical workstation model-608D at room temperature making use of two electrode system in a specially designed sample holder. The cyclic voltammetry has been performed for the "Pt/NCPEs/Pt" cell with a scan rate 0.1volt/ sec for 10 cycles. Last but not the least proton conducting battery for best conducting electrolytes was assembled for investigating battery performance.

## III. RESULTS AND DISCUSSION:

### I. STRUCTURAL CHARACTERIZATION:

The X-ray diffraction (XRD) patterns of the different nanocomposite electrolyte system [(1-x) PEO-xNH<sub>4</sub>SCN]:1wt% Zn-ferrite are shown in figure-1. The XRD pattern of as synthesized Zn ferrite sample show peaks at  $2\theta$  value  $18.2^\circ$  (111),  $29.9^\circ$  (220),  $32.0^\circ$ ,  $34.5^\circ$ ,  $35.3^\circ$  (311),  $36.9^\circ$  (222) and  $42.8^\circ$  (400) alongwith crystal plane. These values ( $18.2^\circ$ ) ascertain formation of cubic Zn ferrite with spinel structure [18]. All peaks match well with the characteristic reflection of zinc ferrite (ref. JCPDS card 22-1012). No peaks attributable to other phases were observed, indicating the single existence of phase zinc ferrite. The average size of crystallites was calculated by the well known Scherer's formula [19]. The evaluated average crystallite size of Zn-ferrite powder was found to 25nm. In XRD pattern of nanocomposite electrolyte system two main peaks at  $19^\circ$  and  $23^\circ$  (PEO characteristic peaks) with few other weak reflections were observed. Addition of salt and filler in polymeric host changes the intensity and broadness of existing original peaks. The increase in broadness or reduction in intensity is an indication of change (decrease) in crystalline of pristine electrolyte which leads to an increase in amorphous behavior of nano composite electrolyte system. The splitting and broadening of polymer chain upon doping of salt and Zn ferrite filler indicates intercalation of salt and filler in polymer mother chain [13]. This feature usually enhances the interlayer spacing which symbolizes enhancement of amorphousness of NCPEs. These also support the interaction of PEO with NH<sub>4</sub>SCN and zinc ferrite. The evaluated average crystallite sizes for different electrolytes were found to 45nm. To understand the effect of salt on the structural behavior of NCPE, X-ray diffraction (XRD) patterns of fixed 1wt% Zn-ferrite and with variable salt content in the nanocomposite polymer electrolytes system are shown in figure-1. The addition of salt in 99PEO:1Zn-ferrite nanocomposite system increases the broadness of another mother PEO peak ( $23^\circ$ ) and increase the sharpness of the former ( $19^\circ$ ) peak. Above 2wt% of salt (NH<sub>4</sub>SCN) content, increase in peak area of PEO peaks at  $23^\circ$  gives further indication of intercalation of filler and salt in polymer chain. This increase in broadness further ascertains increase in amorphousness of electrolyte system. At higher wt% of salt, NCPE (containing 8wt% NH<sub>4</sub>SCN) shows optimum amorphous behavior for ion conduction. This result can be correlated to change morphology in optical micrograph after the enhancement of salt (NH<sub>4</sub>SCN) [13].

Optical micrograph of pure PEO and different composition (100-x) PEO-xNH<sub>4</sub>SCN: 1wt% Zn ferrite (where x= 2 and 4 wt %) are shown in figure-2. In this image spherulites of different format are seen in pure PEO image and as well as in nanocomposite polymer electrolyte system of low concentration of NH<sub>4</sub>SCN in PEO matrix respectively. The presence of spherulites indicates that complexed material which is partially crystalline phases. The sample containing 2wt% of NH<sub>4</sub>SCN salt concentration, these spherulites do not appear and some boundaries separating a few large regions are observed. The dark areas between spherulites are seen to increase in optical image which signify enhancement in amorphous behavior of NCPEs. At higher concentration of salt, spherulites grow in size along with some tiny crystals of NH<sub>4</sub>SCN and ferrite in between the spherulites. Further the existence of tiny crystals of NH<sub>4</sub>SCN/ferrite suggests that the solubility/complexation of NH<sub>4</sub>SCN in PEO is limited in ratio and NH<sub>4</sub>SCN and ferrite seems to be segregating beyond this wt%. These results have also been confirmed in XRD and SEM measurements of NCPEs [13].

## II. ELECTRICAL CHARACTERIZATION:

The changes in bulk electrical conductivity of pristine polymer electrolyte film as a function of variation of salt ( $\text{NH}_4\text{SCN}$ ) are given in figure -3(a). With the addition of salt the figure indicates an increase in the electrical conductivity to reach an optimum at 7wt% of salt and thereafter it decreases. Beyond 10% salt concentration the film becomes fully sticky and is extremely difficult to handle for further measurements. It is clear from basic relation of electrical conductivity that it is influenced either by the number of transporting charge carrier or their mobility or both. Therefore the increase in bulk electrical conductivity of pristine electrolyte with salt concentration can be attributed to the increase in number of charge carriers and enhancement in amorphous behavior (factor influencing mobility) of the system. Contradictory explanations have been found in the understanding of conduction of PEO- $\text{NH}_4\text{SCN}$  [20, 21]. Prusinowska et al [21] have shown through DSC and IR measurements that complexation of ammonium cation with PEO takes place via hydrogen bonding to ether oxygen. This interaction can be qualitatively discussed by the figure-3(b). They have further shown that cations are strongly bonded to polyether chains where as anions are free to move giving rise to ionic conduction via anion movement. This argument has been contradicted by Stainer et al [22]. They have shown  $\text{NH}_4^+$  ion is the mobile charge carrier rather than  $\text{H}^+$  ion in PEO- $\text{NH}_4\text{SCN}$  matrix. Srivastava et al [20, 22 & 23] have implicated protonic charge transport in PEO- $\text{NH}_4\text{SCN}$  system through gas chromatography measurement coupled with IR studies. They have suggested that both cation ( $\text{H}^+$ ) and anion ( $\text{SCN}^-$ ) are mobile in the matrix electrolyte though  $\text{SCN}^-$  ion being heavier its movement is low as compared to protons and so protons are the main ion conduction species in PEO- $\text{NH}_4\text{SCN}$  electrolyte. The anion contribution to the total ionic transference number ( $t_{\text{anion}} = 0.18$ ) has also been evaluated by Srivastava et al. In the present investigations too similar results have been obtained which corroborates the result of Srivastava et al and Zhang and Wang [20, 22]. Zhang and Wang have also shown that hydrogen bond of PEO and  $\text{NH}_4\text{SCN}$  exert great effect of ionic association at high salt concentration and which varies with salt content. Thus variation in ionic conductivity of electrolyte is logical so isothermal conductivity behavior can be best described by ion association [22, 23]. The initial increase in conductivity with salt concentration support correlated to enhancement in concentration of free charge carriers and mobility which depends upon morphology of the system. This in turn enhances ionic mobility. However, the decrease in conductivity at higher salt concentration can be explained with help of ion association effect in PEO chain [21-25]. The mechanism of proton transport is given in figure- 3(b) Scheme of ion conduction mechanism in PEO:  $\text{NH}_4\text{SCN}$  electrolyte system.

The variation of bulk electrical conductivity of 1wt% zinc ferrite filler with variation of salt concentration is shown in figure-3(c). At low filler concentration, the filler particles which are scattered within the matrix electrolyte heterogeneously provide new hopping sites for ion transport through polymer salt filler interaction. This tends to increase the number of transporting ions and also increase in amorphousness of the system. When the salt concentration in 99PEO-1Zn ferrite beyond 2wt%, formation of non conducting ion pairs as a result of ferrite salt interaction starts predominating and the conductivity increases significantly upto 8%wt of  $\text{NH}_4\text{SCN}$ . Ferrite salt interaction has been confirmed from XRD. Further thermal studies along with  $T_m$ ,  $T_g$ . A rise in conductivity at concentration (above 2wt %) is on account of the dominance of system morphology over the decreasing trend of n- the number of transporting ions causing increase of conductivity. Finally at very high concentrations of salt, agglomeration of insulating grains and ion association effect results in ultimate fall in ionic conductivity.

## III. ELECTROCHEMICAL STUDIES:

The electrochemical stability of PEO based polymer electrolyte has been studied by cyclic voltammetry. Figure-4(a) represents the cyclic voltammogram of 93PEO-7 $\text{NH}_4\text{SCN}$  polymer electrolyte. The cyclic voltammetry has been performed for the "Pt/93PEO-7 $\text{NH}_4\text{SCN}$  /Pt" cell with a scan rate 0.1volt/ sec for 10 cycles to check its reversibility. Following inference has been drawn from the cyclic voltammogram of figure-4 (a). The electrochemical window has been obtained in between -2.0 to +2.0 volt for pristine polymer electrolyte system. Small cathodic and anodic peaks were also observed around  $\pm 0.5$  V in each of the cycles. The appearance of these peaks may be possibly due to oxidation/ reduction of uncomplexed ( $\text{NH}_4\text{SCN}$ ) salt in the polymer electrolyte as also evidenced in IR investigations [28]. It can be seen from voltammogram that the decomposition voltage of polymer electrolyte is around  $\pm 2.0$  Volt. A sudden rise in the Faradaic current corresponding to an increase in electrochemical decomposition of electrolytes was observed during potential the variation. The pristine electrolyte exhibits electrochemical stability over a potential range extending in between  $\pm 0.9$ V. The electrochemical stability region is defined as a potential region where no appreciable Faradaic current flows ( $< 10\mu\text{A}$ ). As indicated earlier reversibility of electrolyte has been enhanced by repeated CV measurement. It is observed that the area under the curve decreases after 10 cycles which indicates that ion extraction takes place in cycling process. The redox potential ( $E^\circ$ ) of pristine electrolyte were found to be 0.181V. The large electrochemical window with wide stability regime for the pristine electrolyte suggest its utility in practical devices, because most of electrochemical devices are essentially operated in the range of 0.8- 2.8 V [1, 2].

Cyclic voltogram of [93PEO-7NH<sub>4</sub>SCN]:1wt% Zn-ferrite nanocomposite polymer electrolyte is given in figure-4(b). The cyclic voltammetry has been performed for the “Pt/ NCEMP /Pt” cell with a scan rate 0.1volt/ sec for 10 cycles to evaluate reversible nature of electrolyte. Following inference have been drawn from the cyclic voltogram of figure 4(b). The electrochemical window has been evaluated from -3.0 to +3.0 volt for NCPE. Broad shoulder around -0.4 volt and small peak around +0.5 volt were found on closer examination of curves during anodic and cathodic cycles respectively. These anodic and cathodic potential essentially correspond to oxidation/reduction potential of zinc in nanocomposite polymer electrolyte. The broadness might be due attachment of PEO chain with Zn-ferrite. Such an attachment has been evidenced in IR studies [28]. Further careful examination of voltogram reveals an increase of decomposition potential of NCPE increases with respect to pristine electrolyte figure 4(a). CV curve show that Zn ferrite based NCPE has good window stability between  $\pm 1.0$  volt. It can be seen from voltogram that the decomposition voltage of polymer electrolyte is around  $\pm 2.6$  Volt. Thus electrochemical window for Zn-ferrite based NCPE is seen to increase by  $\pm 0.8$  V with respect to pristine electrolyte (figure 4(a)).

#### IV. DIELECTRIC STUDIES:

Figure-5 (a) & (b) shows the variation of dielectric parameters with frequency of 99PEO:1Zn-ferrite]:xNH<sub>4</sub>SCN nanocomposite polymer electrolyte system. The permittivity ( $\epsilon'$  &  $\epsilon''$ ) of nanocomposite electrolyte appears to increase with increasing salt content upto 6wt% after this dip down and attained to minimum value due ion association effect at higher concentration of salt, it's also decreases with increasing frequency. This effect might be due to existence of an electrode and interfacial polarization. In general, the electrode polarization is attributed to the blocking charge carriers at electrode, which is clarifying the abnormal increase of the real permittivity at low frequencies. On the other hand, an interfacial polarization means the polarization take place at interface of existence of crystallinity, absorbed water and presence of heterogeneity. The origin of an interfacial polarization is may be trapped water in electrolyte matrix, due to the presence of different dielectric media. Another possibilities of the origin of value of  $\epsilon'$  and  $\epsilon''$  in electrolyte system may be traced to the presence of dipolar interaction between proton (H<sup>+</sup>) coordinated to the either oxygen (-O-) of polymer host and anion (SCN<sup>-</sup>) present in the polymer electrolyte network which separated by finite distance with polymer network acting as space in the matrix. A sharp increase in  $\epsilon'$  and  $\epsilon''$  value with rise in NH<sub>4</sub>SCN may be increased the possibility of the formation of transient dipolar due to ion-ion pair formation in the amorphous electrolyte phase when crystalline to amorphous phase transition have occurred. However, at the higher frequencies, dielectric parameters ( $\epsilon'$  and  $\epsilon''$ ) factor is low and remains constant, because the orientation of polarization due to chain motion of polymer cannot keep phase the rapidly oscillating applied electric field.

Figure 5(c) shows the variation of dielectric loss tangent ( $\tan \delta$ ) [99PEO:1Zn-ferrite]:xNH<sub>4</sub>SCN polymer nanocomposite electrolyte as function of frequency, the  $\tan \delta$  follows to increasing pattern achieving at higher frequency and is directly a manifestation of polymer chain mobility and its interaction with relaxing dipoles present in the polymer-salt complex. Such a type relaxation phenomena termed as  $\beta$ -relaxation may be attributed to the dipole-polymer segment interaction effect observed normally at temperature above the glass transition temperature (T<sub>g</sub>). The loss occurring due to such interaction depends on a number of factors i.e. the number/ type of constituents in the matrix, the number of repeat units and its mobility, molecular (intra/ inter) interaction and their relaxation time. A strong interaction among sample constituents is expected to reduce the molecular motion in the matrix resulting in a shift of loss peak towards higher frequency side. This shift occurs with increasing frequency together with enhancement in the magnitude of loss factor. This infers to based on the fact of PEO exhibits three type of relaxation [26] namely,  $\alpha$ ,  $\beta$  and  $\gamma$  relaxations. The  $\alpha$ -relaxation is observed near to melting point of PEO (T<sub>m</sub>~ 338 K) and attributed to motion of the chains associated with crystalline phase and segmental motion of host polymer chain [26]. The  $\beta$ - relaxation is usually detected in the temperature 250-350K and related to with local motion of chain segment or side group.

#### V. A.C. CONDUCTIVITY & MODULUS STUDIES:

Figure-6 (a) & (b) shows the variation of a.c. conductivity ( $\sigma'$  &  $\sigma''$ ) of [99PEO-1Zn ferrite]:xNH<sub>4</sub>SCN nanocomposite polymer electrolyte with frequency. It is nothing but sum of two parts; one is frequency independent part and second frequency dependent part. The frequency independent of conductivity is called d.c. conductivity and frequency dependent behavior shows the a.c. conduction in nanocomposite polymer electrolyte. This can be easily shown by the Jonscher Power law relation. The frequency dependent conductivity in solid polymer electrolyte system is seen to follow Universal Power law [27].

$$\sigma_{ac} = \sigma_o + A\omega^n \quad (1)$$

where,  $\sigma_o$  is the dc conductivity (extrapolation of the frequency dependent region to zero frequency gives the d. c. ionic conductivity), A the pre-exponential factor and n the fraction exponent laying between 0&1. This means that the charge carriers are sufficiently free to follow the changing electric field and therefore conductivity frequency

dependent. The increase in conductivity at higher temperature might be due to presence of more free ions in NCPE. At higher temperature, salt ( $\text{NH}_4\text{SCN}$ ) is highly dissociated, which facilitate more free ions ( $\text{NH}_4^+$ ) in the electrolyte system.

Figure-6(c) & (d) shows the real and imaginary part of electric modulus with frequency for different composition of nanocomposite electrolyte system. Also the imaginary part of electric modulus spectra increase with increasing frequency. In this case, electrode polarization/interfacial polarization effect is seen to completely vanish in contrast to the dielectric formalism. Low values (nearly zero) of  $M'$  and  $M''$  in low frequency region is indicative of removal of electrode polarization. Increase of  $M'$  with frequency may be due to distribution of relaxation process over the frequency range. This leads to conductivity relaxation spreading over the range of frequency, which gives loss peak in  $M''$  over the frequency. This is observed around frequencies ( $<500\text{Hz}$ ). The appearance of peak in imaginary part of the dielectric modulus can be assumed to be related with the translation ionic dynamics and the conductivity relaxation of the mobile ions.

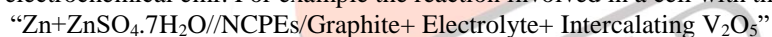
## VI. SOLID STATE BATTERY FABRICATION:

Solid State batteries are fabricated by sandwiching the solid electrolyte (NCPE in present studies) between two electrodes (cathode & anode). The solid state rechargeable batteries are assembled by two step process. In the first step, anode and cathode powdered materials are pressed in a pelletizing die to obtain pellets of electrodes. Since the focus of present work is to develop a proton conducting rechargeable all solid state battery, in order to supply protons,  $\text{Zn}+\text{ZnSO}_4.7\text{H}_2\text{O}$  with stoichiometric ratio 3:1 was chosen as anode material. The anode materials ( $\text{Zn}$  power &  $\text{ZnSO}_4.7\text{H}_2\text{O}$ ) were crushed in agate to form fine powder. Thereafter this mixture was subjected to pelletizing die at  $\sim 5\text{Kbar}$  pressure for 20-30 minutes. Similarly cathode composite material comprising of (graphite, solid electrolyte, and any intercalation material like  $\text{V}_2\text{O}_5$ ,  $\text{MnO}_2$ ,  $\text{PbO}_2$ , and  $\text{TiS}_2$  in stoichiometric ratio 2:2:5) were again crushed and mixture was pelletized following the similar procedure. Finally, the NCPE sample possessing optimum conductivity were sandwiched between anode and cathode pellets. The cells dimensions were approximately (dia-1.76cm, thickness 1cm and the so designed estimated cells weighed 2 gram).

The principle of e.m.f generation in solid state battery is identical like to liquid/ aqueous electrolyte cell. An electrochemical reaction at cathode or anode inside of the interface is responsible for the generation of electrochemical emf. Theoretically, emf can be expressed in terms of Kiukhola and Wagner's equation [30-33].

In order to drain high energy density from a battery light electrode materials and/or electrode pair with high chemical potential difference should be used. The anode should be electropositive and should supply mobile ions to the electrolyte, while cathode should be electronegative. In a good solid state battery, the key parameters of interest are: life expectancy, charge retention, ability to recharge and deliver high power/capacity with high energy efficiency over a wide temperature range. These parameters primarily depend on the open circuit voltage (OCV), polarization or departure from OCV, cycle efficiency and ampere hour efficiency under various discharge /charge conditions. Capacity of battery or the amount of energy released during discharge depends upon load conditions as well as battery design parameters.

An electrochemical reaction at the cathode or anode of the interface is essentially responsible for the generation of electrochemical emf. For example the reaction involved in a cell with the configuration



The performance of a battery is evaluated from the cell parameters [28-32]. Various related parameters on the batteries based on NCPE were estimated. The open circuit voltage (OCV) of fabricated were noted using high resolution multimeter and were found to be 1.46 V for [93PEO-7 $\text{NH}_4\text{SCN}$ ]: 1% Zn-ferrite. After OCV measurements these four cells were subjected to self discharge without any application of load for 12h. Later on these cells were charged again on the application with 3V input DC voltage. During charging process circuit  $1\text{M}\Omega$  resistance was connected in series to the input. The experiment was repeated with other resistances like  $10\text{K}\Omega$  &  $100\text{K}\Omega$ . The discharging characteristics of cells were monitored by measuring voltages in interval of 5min. for a period of 200min. The cell voltage, current and other parameters of batteries were estimated with help of discharging characteristic (plateau region of voltage versus time plot). Though cells were discharged all three resistances, parameters have been evaluated only for discharge characteristics through  $1\text{M}\Omega$ . These parameters were calculated using following relations [29].

### I. Electric Power (P):

This is the product of cell voltage (V) and current (I) delivered to the external load of resistance (R)

$$P = V.I = I^2R = V^2/R \text{ [W]} \quad (2)$$

### II. Electric Energy (E):

This is the product of power and the discharge time in hour

$$E = V.I.t = q. V \text{ [Wh]} \quad (3)$$

### III. Energy Density (Volume Capacity):

This is defined as the ratio of electric energy (E) and battery volume (v) in

$$E.D. = E/v \quad [\text{Wh/cc}] \quad (4)$$

#### IV. Specific Energy (Weight Capacity):

This is the ratio of electric energy (E) and battery weight (m)

$$S.E. = E/m \quad [\text{Wh/Kg}] \quad (5)$$

#### V. Specific Power (Power Density):

This is defined as the ratio of electric power (P) and battery weight (m) in

$$P.D. = P/m \quad [\text{W/Kg}] \quad (6)$$

#### VI. Current Density (J)

It is the defined as of current (I) and area of the cell

$$J = I/A \quad [\text{A/cm}^2] \quad (7)$$

The fabricated cell was found to run for more than 200h at low current drain ( $1.15\mu\text{A/cm}^2$ ). Further, the cell can withstand 10-20 cycles making it suitable low current density applications.

All these parameters were determined in the plateau region of the cell potential discharge profile by  $1\text{M}\Omega$  resistance and values have been listed in table 1.

#### VII. CONCLUSIONS:

Experimental observations of PEO based pristine electrolytes and NCPEs has been focused on the following results. XRD results shows that the doping of salt and Zn ferrite filler indicates intercalation of salt and filler in polymer mother chain and enhancement in amorphous character of NCPEs. These also support the interaction of PEO with  $\text{NH}_4\text{SCN}$  and zinc ferrite. The evaluated average crystallite sizes for different electrolytes were found to 45nm. At higher wt% of salt, NCPE (containing 8wt%  $\text{NH}_4\text{SCN}$ ) shows optimum amorphous behavior has been notice for ion conduction. The dark areas between spherulites are seen to increase in optical image which signify enhancement in amorphous behavior of NCPEs. At higher concentration of salt, spherulites grow in size along with some tiny crystals of  $\text{NH}_4\text{SCN}$  and ferrite in between the spherulites. Addition of salt in polymer matrix enhances conductivity upto 2-3 order.  $\text{NH}_4\text{SCN}$  is responsible for proton ( $\text{H}^+$ ) ion conduction in NCPEs. Dispersion of Zn-ferrite powder in electrolyte is able to change the morphology of NCPEs and enhance the ionic conductivity. CV measurement show that Zn ferrite based NCPE has good window stability between  $\pm 1.0$  Volt. The Electrode polarization or interfacial polarization is noticed in DC and DL study at low frequency regime.  $\beta$ -relaxation process is observed in tangent loss studies of NCPE. Modulus study shows removal of electrode polarization at low frequency region. The loss peak in  $M''$  graph is due to electrical relaxation at higher frequency. Open circuit voltage (OCV) of [93PEO-7 $\text{NH}_4\text{SCN}$ ]: 1% Zn-ferrite nano composite polymer electrolytes were found to be 1.46 V.

#### VIII. ACKNOWLEDGMENT:

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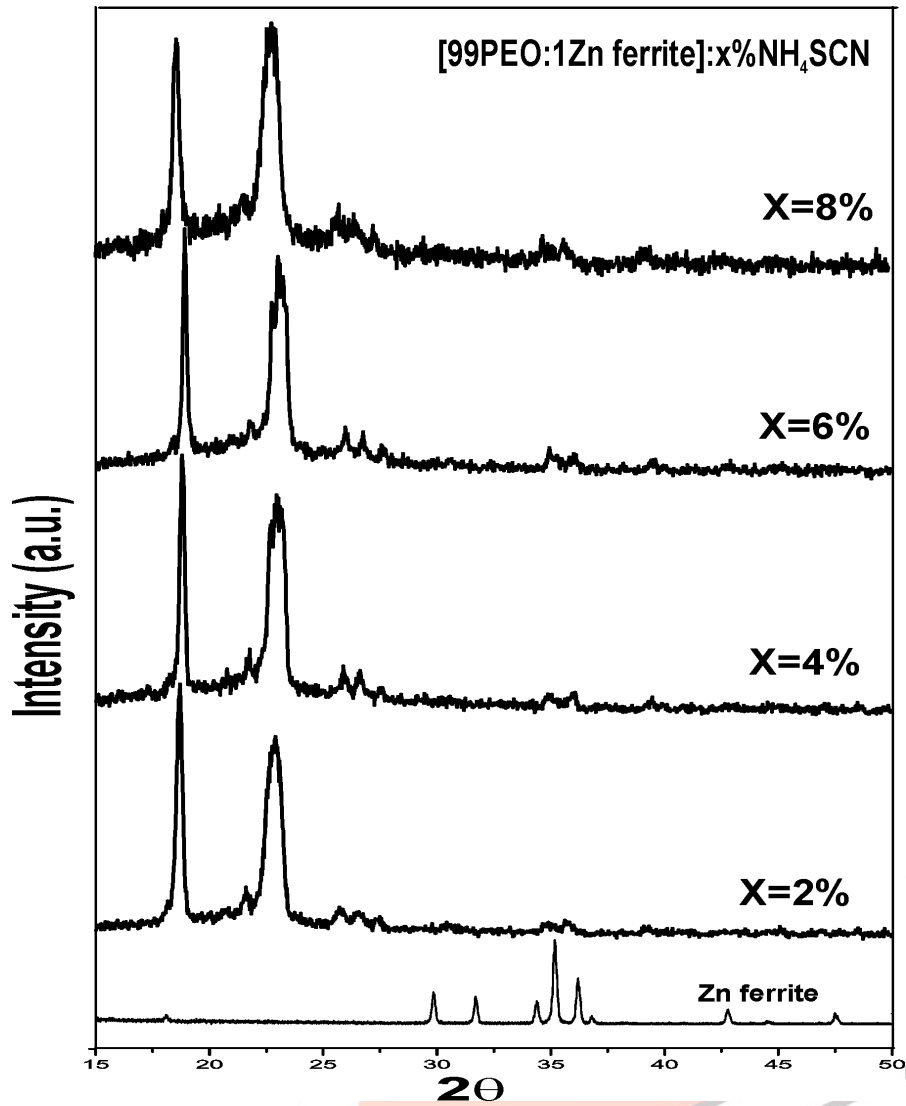
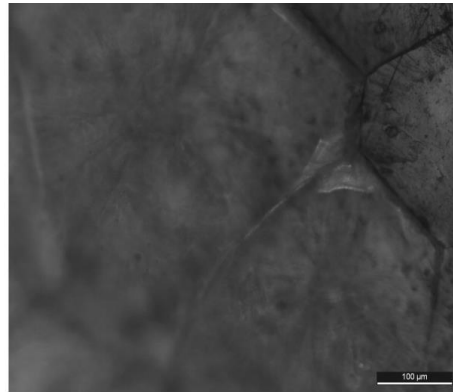


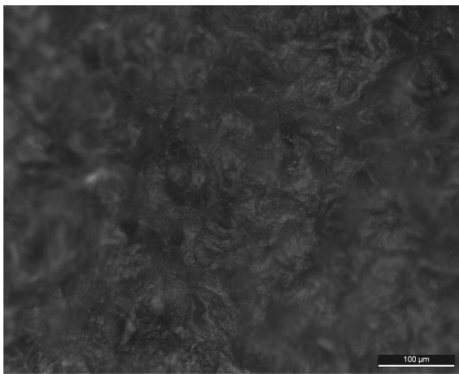
Figure-1 XRD pattern of Zn ferrite and [99PEO: 1Zn ferrite]: xNH<sub>4</sub>SCN system where (x = 2, 4, 6 & 8) nanocomposite polymer electrolyte system.



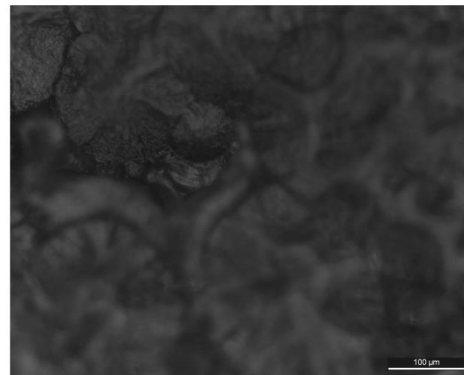
Pure PEO



93PEO-7NH<sub>4</sub>SCN



PEO-Zn ferrite-NH<sub>4</sub>SCN(99:1:2)



PEO-Zn ferrite-NH<sub>4</sub>SCN(99:1:4)

**Figure-2 optical image of pure PEO, pristine electrolyte and [99PEO:1Zn ferrite]: xNH<sub>4</sub>SCN system where (x = 2 & 4) nanocomposite polymer electrolyte system.**

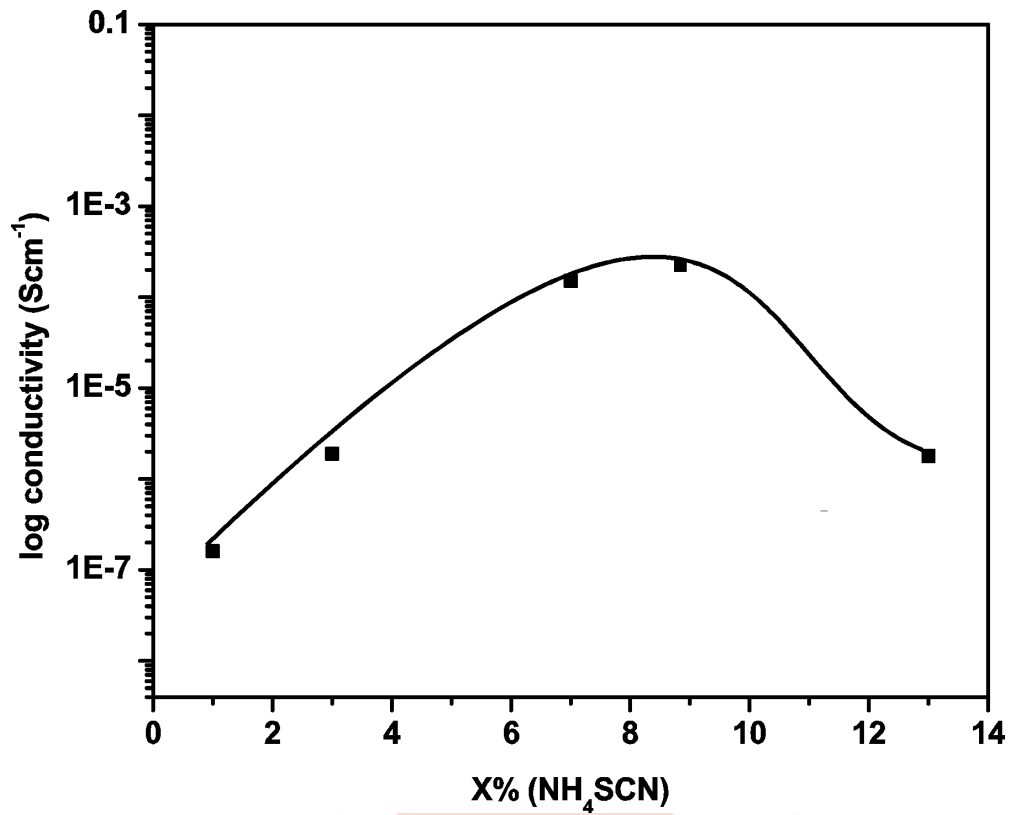


Figure-3(a) Variation of conductivity with composition of NH<sub>4</sub>SCN salt.



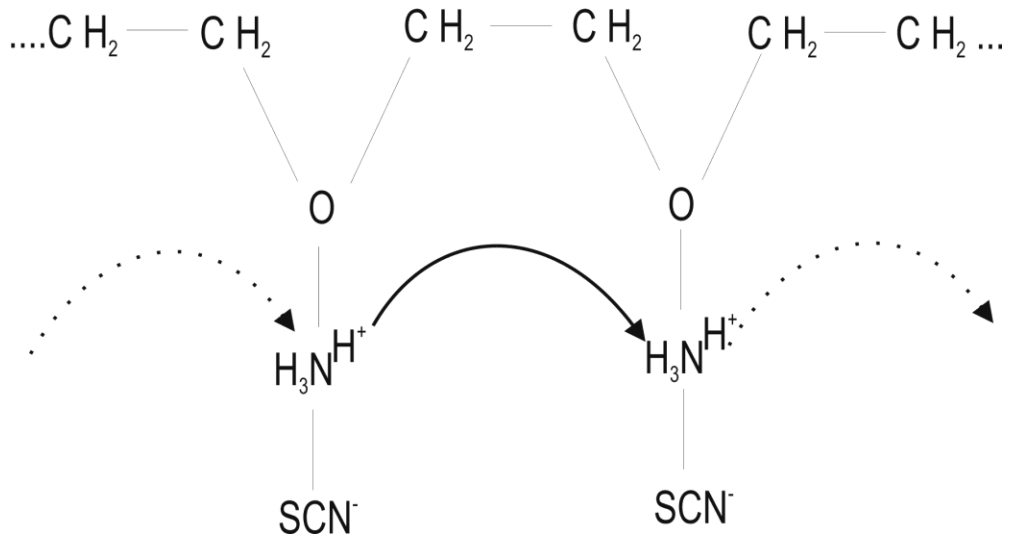


Figure-3(b) Scheme of ion conduction mechanism in PEO: NH<sub>4</sub>SCN electrolyte system

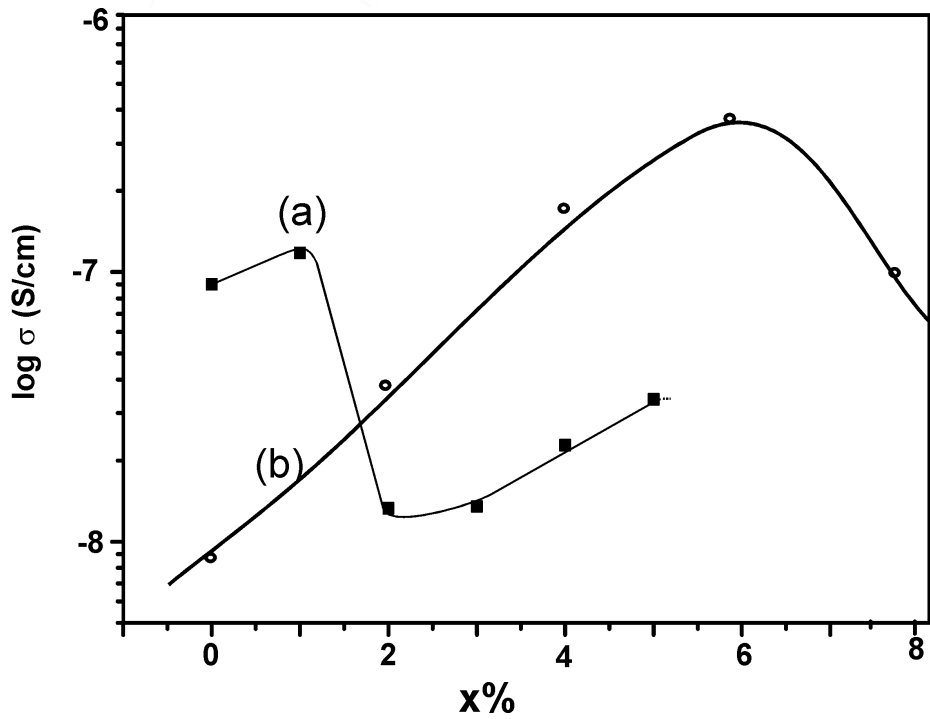


Figure-3(c) Variation of conductivity with variation of salt (NH<sub>4</sub>SCN) in 1wt% fixed Zn-ferrite and for [93PEO-7NH<sub>4</sub>SCN]: x% Zn-ferrite nanocomposite polymer electrolyte system.

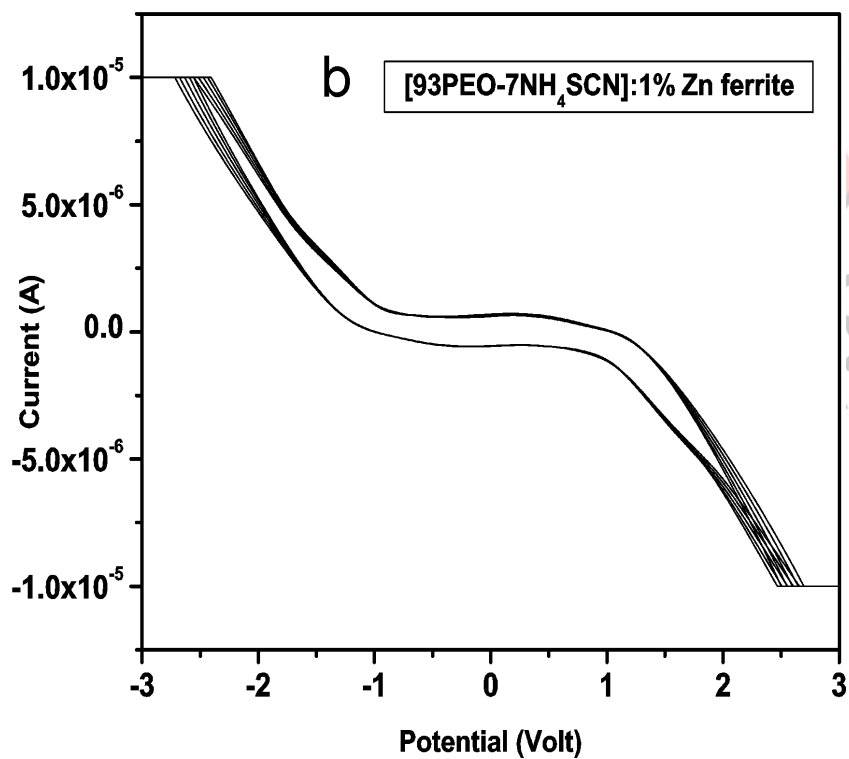
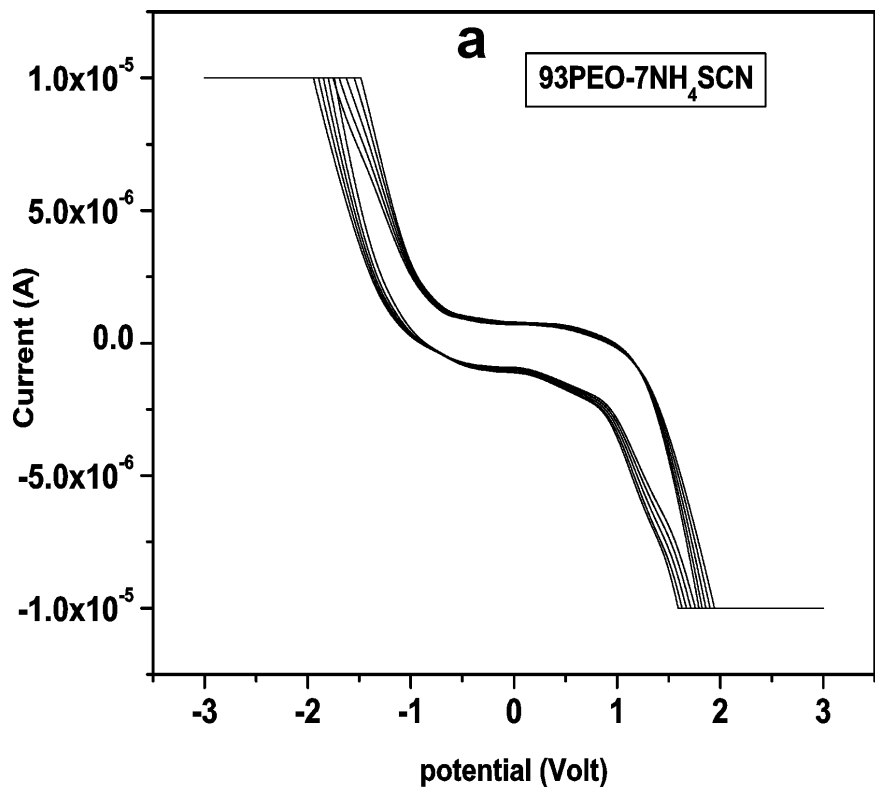


Figure-4 Cyclic voltametric response of (a) pristine electrolyte (b) [93PEO-7NH<sub>4</sub>SCN]: 1%Zn-ferrite nanocomposite polymer electrolyte system

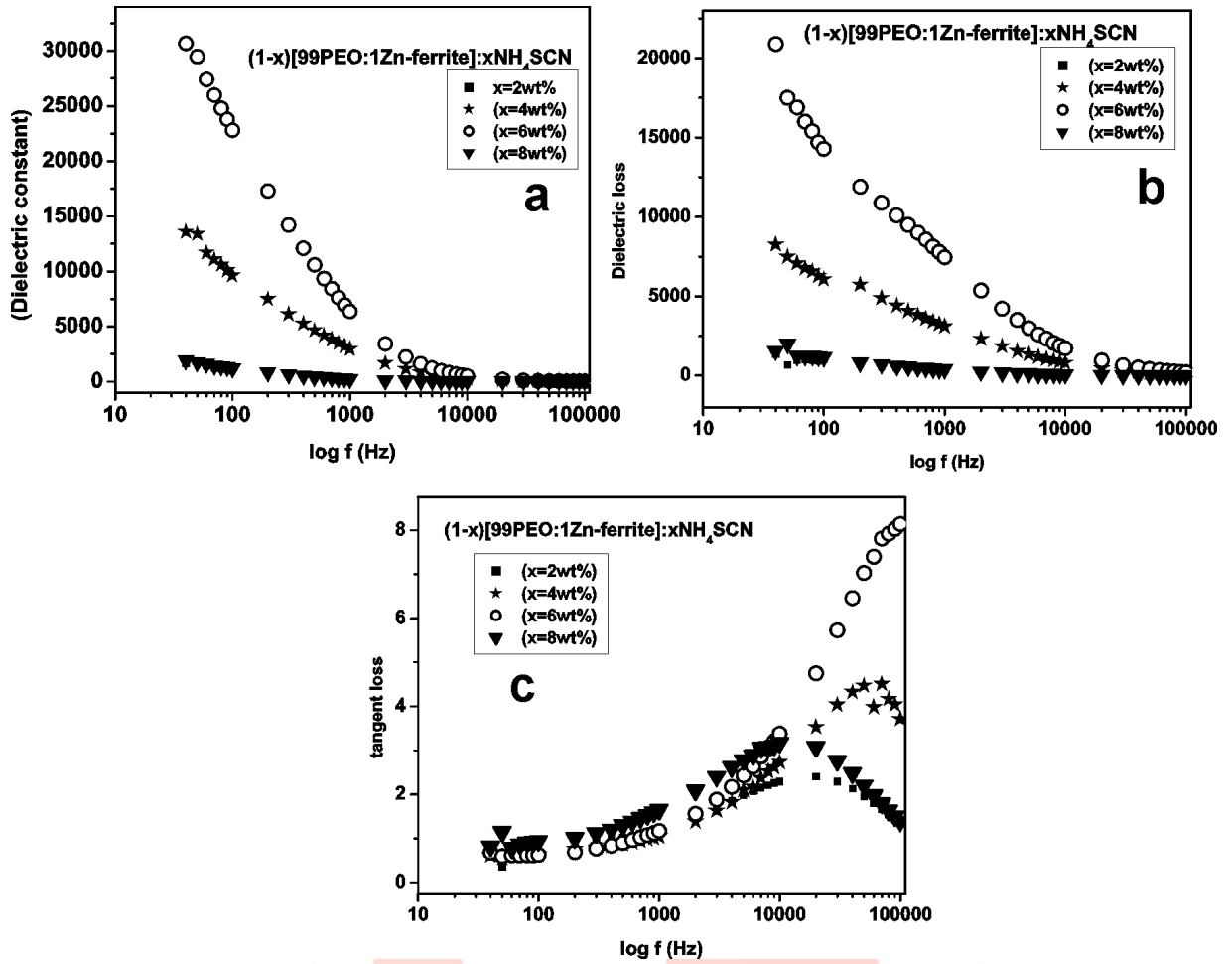


Figure-5 Variation of (a) real part of dielectric relaxation (b) imaginary part of dielectric relaxation and (c) tangent loss with frequency for  $[99\text{PEO}:1\% \text{Zn-ferrite}]: x\text{NH}_4\text{SCN}$  nanocomposite polymer electrolyte system.

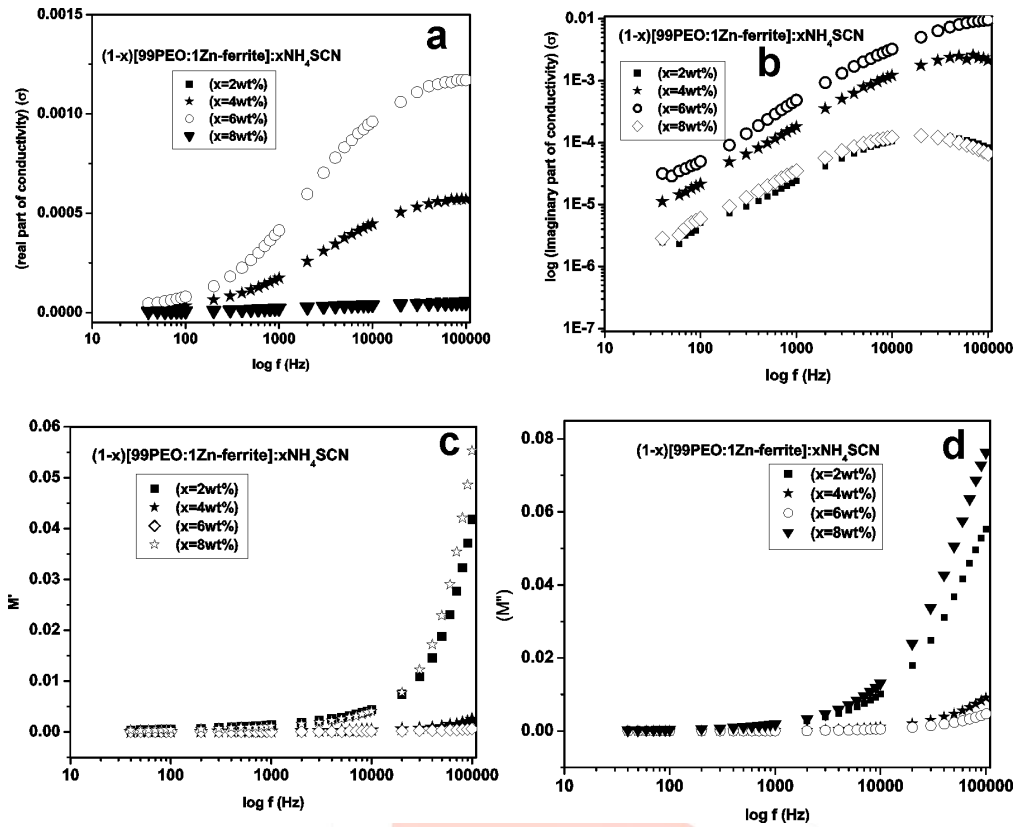


Figure-6 (a) & (b) Variation of real and imaginary part of a.c. conductivity with frequency. (c) & (d) Variation of real and imaginary part of modulus of electrolyte with frequency at different temperature for [99PEO:1%Zn-ferrite]: xNH<sub>4</sub>SCN nanocomposite polymer electrolyte system.

**Table -1 Solid state battery performance of fabricated cell for 93PEO:7NH<sub>4</sub>SCN:1% Zn-ferrite**

S.N.	Solid State rechargeable battery parameter						
	OCV (Volt)	Current (I) ( $\mu$ A)	Electric Power(P) ( $\mu$ W)	Electric energy (E) ( $\mu$ Wh)	Current density (J) ( $\mu$ Acm <sup>-2</sup> )	Power density ( $\mu$ W/Kg)	Energy density ( $\mu$ Wh/Kg)
1	1.46	1.15	1.32	1.45	0.58	278	403

