# CHAPTER SEVEN

## Discussion

Solid polymer electrolytes (SPEs) have received much attention for more than three decades due to its potential application in electrochemical devices such as batteries, fuel cells, supercapacitors, hybrid power sources, display devices, sensors etc. They are formed by dissolving salt in a macromolecule, typically polymers containing polar groups such as oxygen (O) and nitrogen (N) atoms with lone pair electrons that can form complexes with cation of the salt [Pradhan et al., 2008]. Polymer electrolytes usually contain both crystalline and amorphous phases. It has been reported that the ion conduction takes place primarily in the amorphous phase [Kuo et al., 2003]. Ionic transport in polymer electrolyte is however not completely understood and this remains an obstacle in achieving the required room temperature conductivity [Natesan et al., 2006]. Chitosan is a natural polymer derived from the deacetylation process of chitin. A monomer of chitosan consists of hydroxyl (OH) and amine ($NH_2$) functional groups which have lone pair electrons that are suitable for the preparation of polymer electrolytes [ Majid and Arof, 2007]. Thus the ability of chitosan as a host polymer is due to the OH and $NH_2$ groups in chitosan structure to dissolve inorganic salt as a result of electrostatic interaction. This work attempts to study the electrical and dielectric properties of solid and nanocomposite polymer electrolyte based on chitosan to demonstrate and interpret the dependence of DC conductivity on temperature and dielectric constant. The work also undertakes to understand the relaxation processes and to demonstrate the electrode polarization effect on AC conductivity dispersion.

It is well known that the structure of polar polymers used in polymer electrolytes is strongly influenced by the inorganic salts and filler nanoparticles. Thus understanding the structure and morphological property of these solid and nano-composite electrolytes based on chitosan will help to explain the structure-property relationship.

From the XRD results of CS:AgTf, CS:NaTf and CS:LiTf systems in Chapter Four, it can be seen that with increasing salt concentration the crystallinity of chitosan greatly reduced and the amorphous region enhanced which is important for ion conduction. There are no peaks corresponding to pure salts (AgTf, NaTf and LiTf) appearing in the complexes indicating the complete dissolution of salts in chitosan matrix and diminishing the chitosan crystallinity. The deconvolution results reveal that with increasing salt concentration the crystallite size and degree of crystallinity of chitosan based solid electrolytes (CS:AgTf, CS:NaTf and CS:LiTf) are decreased. Kumar et al., (2011), and Su’ait et al., (2009), have reported that the decrease in intensity and broadening of XRD pattern can be ascribed to the amorphous enhancement with the addition of doping salt. The amorphous nature results in greater ionic diffusivity with high ionic conductivity.

A small peak for silver nanoparticle was observed for all the CS:AgTf compositions at $2\theta°$ = 38°. The XRD result at different temperatures for CSA6 sample in chapter four indicates that the crystalline peaks due to silver nanoparticles are increased. According to Yu et al., (2007), the prominent peaks at $2\theta$ values of about 38° and 44° represented the (111) and (200) Braggs reflections of face-centered cubic of metallic silver particle, respectively. The

UV-vis analyses at different temperatures demonstrate that the surface plasmon resonances (SPR) of silver nanoparticles are increased with temperature increase. SPR can be described as the resonant photon-induced collective oscillation of valence electrons, established when the frequency of photons matches the natural frequency of surface electrons oscillating against the restoring force of positive nuclei. The resonant photon wavelength is different for different metals. For example, gold, silver and copper nanostructures exhibit resonant behaviors when interacting with ultraviolet (UV) and visible (vis) photons [Linic et al., 2011]. Thus the observed SPR in CS:AgTf SPEs in the present work reveal that the silver ions are reduced to metallic silver nanoparticle, because only metallic nanoparticles are able to show the SPR. Existence of silver nanoparticle in CS:AgTf system is also observed by TEM method. Furthermore the SEM and EDX analysis confirmed the existence of silver nanoparticles and their leakages to the surface of the sample.

It can be noticed that for CS:NaTf system some additional peaks were observed. The deconvolution results of pure chitosan reveal that these peaks exist in pure chitosan but their intensity and positions are shifted upon the addition of NaTf salt. Thus these peaks can be due to the complex formation of some long-range order between chitosan and NaTf salt especially at salt concentration greater than 2 wt.% of NaTf. It can be seen that the intensity of these new peaks are greatly decreased at 10 wt. % of NaTf salt. The morphology study of CS:NaTf system indicates that the samples are smooth.

The presented XRD, SEM and EDX results of nanocomposite electrolytes of (1-x) (0.9CS:0.1AgTf)-x$Al_2O_3$($0.02 \leq x \leq 0.1$), (1-x)(0.9CS:0.1NaTf)-x$Al_2O_3$($0.02 \leq x \leq 0.1$) and (1-x) (0.9CS:0.1LiTf)-x$Al_2O_3$($0.02 \leq x \leq 0.1$) in Chapter Four reveals the effect of alumina nanoparticles (size < 50 nm) on the structural (crystallinity) and morphological properties of solid polymer electrolytes (CSA6, CSB6 and CSC6). From the XRD results of these nano-composites, it is clear that at low filler concentration (2 to 4wt.%) the amorphous region is dominant, however at high filler concentration the crystallite size and crystallinity increased and the $Al_2O_3$ crystalline peaks at 45.7 and 67.1° are appeared. According to Raghavan et al., (2010), the broadening and lowering of the intensity of diffraction peaks on incorporation of the nano-sized ceramic fillers indicated an amorphous enhancement or decrease in the crystallinity. The reduction in crystallinity results from the complex formation between the polar groups of the polymer and the surface groups of the nano-sized ceramic fillers (OH), which retards the ordering of the crystalline regions in polymer electrolyte. They further explained that the organization of polymer chains may be hindered by the cross-linking centers formed by the Lewis acid group of ceramic filler (e.g. –OH group of alumina surface) with polar group of the polymer. Thus these interactions results in a hydrogen bonding between the polar groups of the polymer and the surface groups of the filler. These interactions can stabilize the amorphous structure and enhance the ionic conductivity of the polymer electrolytes. The deconvolution of XRD results reveal the small crystallite size and crystallinity at low $Al_2O_3$ concentration (2 to 4wt. %), i.e., the amorphous domain greatly enhanced. The results of SEM and EDX analysis of these nanocomposites reveal that $Al_2O_3$ nanoparticles are finely dispersed at low concentrations (2 to 4 wt.%) while a lot of white aggregated clusters were formed and appeared on the surface of the samples at high alumina concentration (6 to 10 wt.%). These aggregates can be ascribed to the phase separation of alumina from polymer matrix because the aggregated nanoparticles are not compatible with polymer matrix [Li et al., 2005]. Thus the SEM and EDX analyses of these nanocomposites greatly supported the XRD results.

It is interesting to note that the peak of silver nanoparticles at 2θ° = 38°, in CSA6 system almost disappear in nano-composite (1-x) (0.9CS:0.1AgTf)-x$Al_2O_3$ ($0.02 \le x \le 0.1$) systems. These results indicate that $Al_2O_3$ nanoparticles prevent the silver ion reduction. The small surface plasmon resonance (SPR) peaks in UV-vis results can be ascribed to the small amount of silver nanoparticles. The SEM and EDX analysis supported the decrease in silver ion reduction in (1-x) (0.9CS:0.1AgTf)-x$Al_2O_3$ ($0.02 \le x \le 0.1$) nanocomposite systems.

The electrical and dielectric properties of solid polymer electrolytes (CS:AgTf, CS:NaTf and CS:LiTf) were investigated in order to demonstrate the dependence of bulk DC conductivity on temperature and dielectric constant. The relaxation processes in terms of loss tangent (tan δ) and electric modulus were investigated to reveal the distribution of relaxation times. To demonstrate the effect of electrode polarization on bulk AC conductivity dispersion, the impedance plots and AC conductivity spectra are studied at different temperatures.

The results of DC conductivity for CS:AgTf (CSA1 to CSA6), CS:NaTf (CSB1 to CSB6) and CS:LiTf (CSC1 to CSC6) systems are shown in chapter Five. The XRD results of these solid polymer electrolytes are in support of the DC conductivity results. The most amorphous sample of these solid polymer electrolytes exhibits the highest DC conductivity and dielectric constant. The linear increase of Log ($\sigma_{dc}$) vs 1000/T for CS:AgTf, CS:NaTf and CS:LiTf can be interpreted by a hopping mechanism between coordinates sites in these solid polymer electrolytes. As the temperature increase, the polymer chains acquire faster internal modes in which bond rotations produces backbone motion. This, in turn, favors inter-chain hopping and intra-chain ion movements that all increase the value of conductivity [Avellaneda et al., 2007, Selvasekarapandian et al., 2005]. In other words the increased vibrational motion of the polymer backbone and side chains with temperature brings the coordination sites closer to one another enabling the ions to hop from the occupied site to the unoccupied site with lesser energy required [Aziz et al., 2010a]. The drop in DC conductivity for CS:NaTf and CS:LiTf at higher temperatures for all the samples can be attributable to water desorption.

It is interesting to note that the DC conductivity vs reciprocal temperature for CS:AgTf systems decrease at a particular temperature for each sample which can be ascribed to the reduction of silver ions to silver nanoparticles. This phenomenon ($Ag^+ \rightarrow Ag^o$) in CS:AgTf samples is strongly supported by UV-vis and XRD at different temperatures. The TEM, SEM and EDX results also confirmed the formation of silver nanoparticle in CS:AgTf system.

The dielectric constant as a function of salt concentration for CS:AgTf, CS:NaTf and CS:LiTf are presented in Chapter Five. The aim of the presentation of dielectric constant as a function of salt concentration is to make a correlation between DC conductivity and dielectric constant. The dielectric constants for these solid electrolytes show two distinct regions. The low frequency regions are ascribed to electrode polarization (EP effect) and the high frequency dielectric constant region which is frequency independent and is important because these regions represent the bulk property of the samples. The high value of dielectric constant in low frequency region can be ascribed to the enhanced of charge carrier density and their accumulation at the electrode/ electrolytes interface in polymer electrolytes [Avellaneda et al., 2007, Baskaran et al., 2004]. It can be seen that the high frequency dielectric constant is also dependent on salt concentration for CS:AgTf, CS:NaTf and CS:LiTf solid electrolytes. The behavior of bulk dielectric constant (high frequency region) with salt concentration in CS:AgTf, CS:NaTf and CS:LiTf systems is similar to that observed for DC conductivity with salt concentrations for these systems. The increase in the value of dielectric constant with salt concentration indicates that there is an increase in charge carrier concentration and hence the increase in DC conductivity [Ramya et al., 2008]. Thus the room temperature study of DC conductivity and dielectric constant as a function of salt concentration reveals the correlation between these quantities ($\sigma_{dc}$ and $\varepsilon'$). These results indicated the powerful ability of dielectric property to study the conductivity behavior of solid polymer electrolytes. The smooth curve between DC conductivity and dielectric constant in CS:AgTf, CS:NaTf and CS:LiTf systems at different temperatures indicated the fact that DC conductivity in Arrhenius equation is not only temperature but also dielectric constant dependence($\sigma(\varepsilon', T) = \sigma_o \exp^{(-E_a/K_B T)}$). Thus the main goal of this work which is the demonstration of the dependence of DC conductivity on dielectric constant in solid polymer electrolytes based on chitosan (CS:AgTf, CS:NaTf and CS:LiTf) has been successfully carried out experimentally. The dependence of DC conductivity on dielectric constant in polymer electrolytes can be explained as follows. In polar polymers when the temperature is raised, dielectric constant also enhances due to the facilitation in orientation of dipoles in the polar polymer [Awadhia et al., 2006]. As the dielectric constant increases with temperature, the degree of salt dissociation and re-dissociation of ion aggregates increases which result in an increase in number of free ions or charge carrier density [Raj and Varma, 2010, Karmakar and Ghosh, 2012], and hence an increase in DC conductivity. The compensated Arrhenius results for these solid electrolytes are almost similar to Arrhenius results with no distinguishable differences. The pre-exponential factor for these solid polymer electrolytes does not show any temperature and dielectric constant dependence. Thus the compensated Arrhenius behavior and pre-exponential factor results for these solid polymer electrolytes (CS:AgTf, CS:NaTf and CS:LiTf) do not follow the Petrowsky and Frech hypothesis (2009, 2010).

The dielectric loss study at different temperatures for CS:AgTf (CSA6), CS:NaTf (CSB6) and CS:LiTf (CSC6) solid polymer electrolytes do not show any relaxation peaks. In systems with appreciable conductivity the rapid increase of dielectric loss at low frequency is due to electrode polarization and the effect of electrode polarization can completely masks the relaxation in $\varepsilon''$ spectrum [Chanmal and Jog, 2008].

The frequency dependent of loss tangent at different temperatures for these solid electrolytes indicated that with decreasing temperature the loss peaks are shifted to low frequency side. The shift of tan $\delta$ peaks to lower frequencies indicating the increase of relaxation time and the strong non-Debye relaxation [Shi et al., 2000]. The asymmetric nature of loss tangent peaks for CSA6, CSB6 and CSC6 system also indicate the non-Debye relaxation. The calculated activation energy from the relaxation frequencies (tan $\delta$ peaks) in these SPEs are very close to those obtained from the Log $\sigma_{dc}$ vs 1000/T. This suggests that the charge carriers responsible for both conductivity and relaxation are the same [Ravi et al., 2011].

To overcome the undesired electrode polarization difficulty in polymer electrolytes electric modulus formalism were used. This formalism was first used successfully for the investigation of electric relaxation phenomena in vitreous ionic conductors. It has also been used in polymers to study their conductivity relaxation. An advantage of using the electric modulus to interpret bulk relaxation properties is that variation in the large values of permittivity and loss at low frequencies are minimized. In this way the familiar difficulties of electrode nature and contact, space charge phenomena and conduction effects, which appear to obscure relaxation in permittivity representation ($\varepsilon''$), can be resolved or even ignored [Hammami et al., 2007]. The Argand plots for CSA6, CSB6 and CSC6 are incomplete half semicircle which cannot be explained by Debye model. Debye relaxation denotes a system with a single relaxation time. In Debye model, all dipoles must be identical. Thus, Debye relaxation is the dielectric relaxation response of an ideal, non-interacting population of dipoles to an alternating external electric field [Hill and Dissado, 1985]. In polymer electrolytes under an alternating external electric field different polarization mechanism such as electronic, dipolar and ionic polarization occur. Thus a distribution of relaxation times will occur in polymer electrolytes. It can be seen that with increasing temperature the Argand curves shifts towards the origin. The deviation of Argand plots from the semicircular shape can be ascribed to the increase of ion conduction and distribution of relaxation times. According to Ayesh (2010) these relaxations can be ascribed to viscoelastic relaxation.

The impedance plots and AC conductivity spectra for these solid polymer electrolytes (CSA6, CSB6 and CSC6) reveal a strong correlation between high frequency AC conductivity dispersion and high frequency semicircle of the impedance ($Z_i$-$Z_r$) plot. At low temperatures a clear and distinguishable AC conductivity dispersion can be observed for these solid electrolyte systems. The strong dependence of AC conductivity on frequency in the high frequency region is typical of highly correlated ionic motion in disordered solid electrolytes. It has been reported that dispersion in the conductivity is a direct evidence for the hopping of charge carriers. Dispersion in conductivity will occur when the carriers are not free to move throughout the sample [Potty and Khadar, 2000]. Thus the existence of these AC dispersion region in AC conductivity spectra in CS:AgTf, CS:NaTf and CS:LiTf SPEs reveal the fact the Jonschers power law can be applicable and the frequency exponent (*s*) can be used to characterize the model of ion conduction in these SPEs. At higher temperatures only a spike region (electrode polarization, EP) can be observed. These results indicate the fact that AC dispersion is a bulk property of the material. It is interesting to note that at high temperatures the EP effect diminishes the AC dispersion. At these temperatures, the ionic conductivity is high enough to produce a significant build up of charges at the electrodes (EP effect), which reduces the effective applied field across the sample and hence the apparent conductivity [Baskaran et al., 2006]. Thus the EP region can affect the ion distribution. The calculated frequency exponent from the dispersion regions were used to characterize the type of ion conduction in CSA6, CSB6 and CSC6 systems. The temperature dependent of s value for CSA6 sample showed a crossover from correlated barrier hopping (CBH) to small polaron (SP) hopping. The temperature dependent of the frequency exponent (s) indicate that the ion conduction in CSB6 and CSC6 samples obeys the OLPT model.

The results of electrical properties of nano-composite solid polymer electrolytes based on (1-x)(0.9CS:0.1AgTf)-x$Al_2O_3$ ($0.02 \le x \le 0.1$), (1-x)(0.9CS:0.1NaTf)-x$Al_2O_3$ ($0.02 \le x \le 0.1$) and (1-x)(0.9CS:0.1LiTf)-x$Al_2O_3$ ($0.02 \le x \le 0.1$), are presented in Chapter Six.

It has been observed that the bulk DC conductivity and bulk dielectric constant for these nano-composite solid polymer electrolytes increased with incorporation of alumina nanoparticles up to 4 wt.% of $Al_2O_3$ nanoparticle. However at high alumina concentration the results show a decrease of DC conductivity and dielectric constant. This can be explained by the two physical situations, namely, the space charge induced enhancement effect and the blocking effect. The space charge induced enhancement effect provides local electric fields, which accelerate the transport of conduction ions thereby increasing the conductivity. This effect has been observed and reported in numerous composite systems [Shanmukaraj et al., 2008]. The blocking effect on the other hand impedes the flow of conduction ions thereby reducing the conductivity. Tan et al. (2007), reported that at higher filler concentrations, the filler nanoparticles get close to each other that the blocking effect imposed by the more abundant alumina nanoparticles could make the long polymer chains more “immobilized,”, i.e., the reduced segmental mobility leading to the decreasing conductivity. The bulk dielectric constant and DC conductivity study as a function of $Al_2O_3$ nanoparticle concentrations and the smooth curve between DC conductivity and dielectric constant at different temperatures strongly supports the DC conductivity dependent on dielectric constant in nano-composite solid electrolytes based on chitosan. The increase in dielectric constant means an increase in carries density and hence an increase in DC conductivity. The results of DC conductivity and dielectric constant for SPEs and NCPEs in this work reveal that the frequency dependent dielectric analysis is crucial for understanding the nature of ionic transport in polymer electrolytes. Thus in chitosan based nano-composite electrolyte the objective of the present work (DC conductivity as a function of $\varepsilon'$ and T) is also successfully demonstrated. The DC conductivity and dielectric constant results at different alumina concentration are supported by XRD, SEM and EDX analysis for $(1-x)(0.9CS:0.1AgTf)-xAl_2O_3$ ($0.02 \leq x \leq 0.1$), $(1-x)(0.9CS:0.1NaTf)-xAl_2O_3$ ($0.02 \leq x \leq 0.1$) and $(1-x)(0.9CS:0.1LiTf)-xAl_2O_3$ ($0.02 \leq x \leq 0.1$) nano-composite systems. The temperature dependence of DC conductivity for all the three nanocomposite systems shows a combination of Arrhenius and VTF behavior. Arrhenius region is noticed in low temperature regime while VTF nature is exhibited at higher temperature. Similar behavior was reported for composite polymer electrolytes by other researchers [Dissanayakea et al., 2003, Kumar et al., 2002]. This can be ascribed to the increase in the fraction of free volume in the NCPEs because at higher temperatures the increased vibration of the polymer backbone and side chains can also increase in the fraction of free volume [Aziz et al., 2010a]. DC conductivity drop at a particular temperature for all the compositions of the NCPEs can be observed. Ceramic fillers exhibiting a ferroelectric to paraelectric phase transition at the characteristic temperature, which is known as Curie temperature ($T_c$). Below the Curie temperature ($T_{c)}$ the ferroelectric materials are showing spontaneous polarization. Under the influence of the electric field the dipole moments are able to follow the applied field contributing to the overall polarization of the system. However, as the temperature is approaching $T_c$, a transition takes place from order to disorder in the crystal structure of ceramic filler, and no more contribution to conductivity enhancement [Patsidis and Psarras, 2008]. Jiansirisomboon and Watcharapasorn (2008), reported the Curie temperature ($T_{c)}$ of nano-composite $BaTiO_3$:$Al_2O_3$ in the temperature range from 118 to 125°C using dielectric spectroscopy.

The results of compensated Arrhenius and pre-exponential factor in (1-x)(0.9CS:0.1AgTf)-x$Al_2O_3$ ($0.02 \leq x \leq 0.1$), (1-x)(0.9CS:0.1NaTf)-x$Al_2O_3$($0.02 \leq x \leq 0.1$) and (1-x)(0.9CS:0.1LiTf)-x$Al_2O_3$ ($0.02 \leq x \leq 0.1$) nano-composite systems shows the constant behavior of pre-exponential factor in Arrhenius equation. The relaxation peak cannot be observed in dielectric loss representation of these NCPEs (CSNA2, CSNB2 and CSNC2). This can be attributable to high electrode polarization and DC conductivity contribution to $\varepsilon''$ part which results in the obscure of relaxation peaks.

The asymmetric and broadening of loss tangent peaks indicate the distribution of relaxation times in CSNA2, CSNB2 and CSNC2 nano-composite systems. The calculated activation from the relaxation frequency is comparable with those values obtained from Log $\sigma_{dc}$ vs 1000/T. This indicates the fact that ions conduct as well as relax at the same time. An incomplete semicircle in Argand plots were observed for CSNA2, CSNB2 and CSNC2 nano-composite systems. The broadness and incomplete Argand plots demonstrates the distribution of relaxation times, i.e., non-Debye relaxation behavior in these nano-composite solid electrolytes. The shifting of Argand curves towards the origin with increasing temperature can be attributable to ion conduction enhancement as a result of decrease in resistivity.

Through the correlation between impedance ($Z_i$-$Z_r$) plots and AC conductivity spectra for CSNA2, CSNB2 and CSNC2 nano-composite electrolytes the effect of electrode polarization on the bulk AC conductivity dispersion were presented. At medium frequencies, random distribution of the ionic charge carriers via activated hopping gives rise to a frequency-independent conductivity, i.e., DC conductivity while at higher frequencies, conductivity exhibits dispersion region which increases with frequency increase and obeys the power law ($\sigma_{ac} = A\omega^s$). It can be seen that with increasing temperature the EP effect becomes prominent. The results reveal that the AC dispersion diminishes at high temperatures as a result of EP dominance. The impedance plots and AC conductivity spectra confirms that the AC dispersion region is a bulk property of the material and could be affected by the electrode polarization. The temperature dependence of s value reveals that the OLPT is the best model for the NCPE (CSNA2) system. The calculated s value from the AC dispersion region for CSNB2 and CSNC2 systems demonstrates that the CBH model is applicable to characterize the ion conduction behavior.

# CHAPTER EIGHT

## Conclusion and Future work

In this work CS:AgTf, CS:NaTf and CS:LiTf solid polymer electrolytes and (1-x)(0.9CS:0.1AgTf)-x$Al_2O_3$ ($0.02 \leq x \leq 0.1$), (1-x)(0.9CS:0.1NaTf)-x$Al_2O_3$ ($0.02 \leq x \leq 0.1$) and (1-x)(0.9CS:0.1LiTf)-x$Al_2O_3$ ($0.02 \leq x \leq 0.1$) nano-composite polymer electrolytes based on chitosan were prepared by solution cast technique.

The XRD patterns of CS:AgTf, CS:NaTf and CS:LiTf systems shows that the crystalline region decreases with increasing salt concentration. The deconvolution of XRD results reveal the small crystallite size for high salt concentration (10 wt.%) of the salts (AgTf, NaTf and LiTf).

The appearance of new crystalline peaks in the XRD pattern of CS:AgTf system is ascribed to the formation of silver nanoparticles. The UV-vis measurement confirms the existence of silver nanoparticle via the broad surface plasmon resonance (SPR) peak. The TEM analysis shows the existence of aggregated silver nanoparticles in the CS:AgTf system. The SEM shows white clusters on the CS:AgTf membranes and the EDX analysis confirms that these clusters are metallic silver particles.

The shifting of crystalline peaks of pure chitosan in CS:NaTf system can be attributed to polymer-salt complexes rather than pure NaTf salt. The deconvolution of XRD results reveal that the crystallite size and degree of crystallinity decreased in CS:NaTf SPEs.

The DC electrical studies on CS:AgTf, CS:NaTf and CS:LiTf systems shows that the ion conduction follows the Arrhenius behavior. The drop in DC conductivity in CS:AgTf system at a particular temperature for each sample is due to the reduction of silver ions to silver nanoparticles which reduces the number of silver ions participating in DC conductivity. This result is supported by UV-vis study at different temperatures. The decrease in DC conductivity at higher temperatures in CS:NaTf and CS:LiTf systems can be attributable to water desorption.

The behavior of DC conductivity and dielectric constant with salt concentration is almost the same in CS:AgTf, CS:NaTf and CS:LiTf SPEs. This result confirms that the DC conductivity and dielectric constant are strongly correlated in these solid electrolytes. The dependence of DC conductivity on dielectric constant and temperature ($\sigma_{(\varepsilon',T)} = \sigma_o \exp(-E_a / K_B T)$) were obtained through a smooth curve between DC conductivity and dielectric constant at different temperatures.

The pattern of compensated Arrhenius and normal Arrhenius behavior are the same. This indicated the non-applicability of compensated Arrhenius equation in solid electrolytes based on chitosan. The random distribution of pre-exponential factor with temperature and dielectric constant reveal the constant behavior of pre-exponential factor ($\sigma_o$) in Arrhenius equation for chitosan based solid polymer electrolytes (CS:AgTf, CS:NaTf and CS:LiTf).

The broadness of tan δ peaks reveals the distribution of relaxation times in chitosan based solid polymer electrolytes (CSA6, CSB6 and CSC6). The arc form and incomplete semicircle of Argand plots indicates that the relaxation processes in these solid electrolytes obey non-Debye behaviour.

The Nyquist plots ($Z_i$ vs $Z_r$) and AC conductivity spectra at different temperature confirms that the AC conductivity dispersion (high frequency dispersion) is a bulk material property that directly relates to the high frequency semicircle in Nyquist plots and affected by electrode polarization (EP) greatly. The temperature dependence of the frequency exponent (s) reveals the crossover from CBH to SP model in CS:AgTf (CSA6) system. The temperature dependence study of s value reveal that the ion conduction follows the CBH model in CS:NaTf (CSB6) and CS:LiTf (CSC6) systems.

In (1-x)(0.9CS:0.1AgTf)-x$Al_2O_3$ ($0.02 \leq x \leq 0.1$), (1-x)(0.9CS:0.1NaTf)-x$Al_2O_3$ ($0.02 \leq x \leq 0.1$) and (1-x)(0.9CS:0.1LiTf)-x$Al_2O_3$ ($0.02 \leq x \leq 0.1$) nano-composite polymer electrolytes the amorphous domain increased with addition of $Al_2O_3$ nanoparticles up to 4wt.%. The deconvolution of XRD results reveals that larger crystallite size is obtained for higher $Al_2O_3$ concentrations. The SEM analyses show that $Al_2O_3$ nanoparticles are well dispersed at low concentration and clusters are formed at higher alumina concentration. Thus the SEM and EDX analyses support the XRD results.

The addition of $Al_2O_3$ filler to CS:AgTf (CSA6) reduces the reduction of silver ions to silver nanoparticles. The XRD, UV-vis, SEM and EDX results strongly supports the prevention of silver ion reduction.

The behavior of DC conductivity and dielectric constant with $Al_2O_3$ concentration is almost the same in (1-x)(0.9CS:0.1AgTf)-x$Al_2O_3$ ($0.02 \leq x \leq 0.1$), (1-x)(0.9CS:0.1NaTf)-x$Al_2O_3$ ($0.02 \leq x \leq 0.1$) and (1-x)(0.9CS:0.1LiTf)-x$Al_2O_3$ ($0.02 \leq x \leq 0.1$) NCPEs. The smooth curve between DC conductivity and dielectric constant at different temperature again reveal the dependence of DC conductivity on dielectric constant in NCPEs based on chitosan.

The drop in DC conductivity at a particular temperature for all the compositions of NCPEs can be attributable to phase transition of $Al_2O_3$ filler. This reveals a good structure-properties relationship.

The asymmetric peak of loss tangent for these NCPEs reveals the distribution of relaxation times. In Argand plots the center of the circles lie below the real axis. This reveals that the relaxation processes are non-Debye behavior in chitosan based NCPEs.

The correlation between AC conductivity spectra and Nyquist plots at different temperatures reveals the electrode polarization effect on AC dispersion in these NCPEs. The temperature variation of frequency exponent (s) reveal that the ion conduction in CSNA2 sample follows the OLPT model and in CSNB2 and CSNC2 follows the CBH model.

Polymer electrolytes have attracted considerable scientific and technological importance because of their interesting physics and applications in electrochemical devices. From this work we conclude that the frequency dependent dielectric analysis is important to understand the ion transport mechanism in polymer electrolytes. Thus for future work we suggest the study of the relationship between DC conductivity-dielectric properties in, (i) Plasticized polymer electrolytes (ii) Double salt polymer electrolyte systems and (iii) Liquid polymer electrolytes.