Structural, electrical properties and dielectric relaxations in Na\(^+\)-ion-conducting solid polymer electrolyte

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Received 26 December 2017, revised 1 March 2018
Accepted for publication 6 March 2018
Published 28 March 2018

Abstract

In this paper, we have studied the structural, microstructural, electrical, dielectric properties and ion dynamics of a sodium-ion-conducting solid polymer electrolyte film comprising PEO\(_8\)-NaPF\(_6\)+ x wt. % succinonitrile. The structural and surface morphology properties have been investigated, respectively using x-ray diffraction and field emission scanning electron microscopy. The complex formation was examined using Fourier transform infrared spectroscopy, and the fraction of free anions/ion pairs obtained via deconvolution. The complex dielectric permittivity and loss tangent has been analyzed across the whole frequency window, and enables us to estimate the DC conductivity, dielectric strength, double layer capacitance and relaxation time. The presence of relaxing dipoles was determined by the addition of succinonitrile (wt./wt.) and the peak shift towards high frequency indicates the decrease of relaxation time. Further, relations among various relaxation times (\(\tau_{\varepsilon'} > \tau_{\tan\delta} > \tau_2 > \tau_m\)) have been elucidated. The complex conductivity has been examined across the whole frequency window; it obeys the Universal Power Law, and displays strong dependency on succinonitrile content. The sigma representation (\(\sigma'' \) versus \(\sigma'\)) was introduced in order to explore the ion dynamics by highlighting the dispersion region in the Cole–Cole plot (\(\varepsilon''\) versus \(\varepsilon'\)) in the lower frequency window; increase in the semicircle radius indicates a decrease of relaxation time. This observation is accompanied by enhancement in ionic conductivity and faster ion transport. A convincing, logical scheme to justify the experimental data has been proposed.

Keywords: FTIR, ionic conductivity, dielectric properties, sigma representation, relaxation time

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

Development of suitable free-standing solid polymer electrolytes is the biggest challenge and emerging opportunity for the next generation of high energy density lithium ion batteries which can be substituted globally as an alternative source in conjunction with solar and wind energy, to address increasing consumption at both household and neighborhood levels. Polymer electrolyte research falls within the focus of most of the scientific community due to their wide range of application, including energy storage/conversion devices, electrochromic devices, supercapacitors, sensors and fuel cells. Amongst these, batteries are playing an ever more significant role in meeting the demands of humanity and industry. As the electrolyte is a key component of the battery device. The presence of polymer in the electrolyte system enables it to
take a desirable shape, with adequate size, suitable flexibility, mechanical strength, thermal stability and wide electrochemical window while remaining cost effective [1–7].

The first report (50 years ago) regarding sodium $\beta^\prime$-alumina (NaAl$_{11}$O$_{17}$) solid state ionic conductor (SSIC) motivated researchers toward sodium based devices as an alternative to lithium. Sodium ion batteries (SIB) are achieving new heights as a promising candidate in the field of energy storage, due to sodium’s high abundance, low cost and suitable redox potential ($E_{Na^+Na}^{\text{redox}} = -2.71$ V versus standard hydrogen electrode; only 0.3 V above that of lithium), and lower manufacturing costs in comparison to lithium [8–11]. In 1973, P V Right first reported ionic conductivity in a polymer matrix comprising PEO and alkali metal salts. Later, Armand first recognized their significance in such real world applications as energy storage/conversion devices [4, 5]. Most conventional energy storage/conversion devices are based on a gel/liquid polymer electrolyte system. Gel polymer electrolytes have high ionic conductivity ($10^{-3}$ S cm$^{-1}$), but their poor mechanical strength due to the presence of plasticized solvents prevents their use as an electrolyte in such applications. The issues of leakage, flammability, hazardlessness and poor chemical compatibility prevent the use of liquid electrolytes in high energy storage/conversion devices. The remarkable trend nowadays is toward miniaturization of energy storage devices, which in turn will boost the growth of the energy sector. At present, solid polymer electrolytes (SPEs) are the most auspicious possibility to replace the liquid/gel polymer electrolyte system, and so overcome the abovementioned issues. In single ion conductors bulky salts with smaller cation and the bulky anion play a dominant role in fast charge carrier ion dynamics [12].

Poly (ethylene oxide) is the most promising aspirant among all polymers in use over the last three decades, due to its low glass transition temperature and high degradation temperature. The presence of an electron donor ether group ($\sim$O–) in its polymer backbone ($\sim$CH$_2$–CH$_2$–$\sim$O–) makes it interesting for coordination with the available cations. The high dielectric constant ($\sim$4–5) support salt dissociation in order to improve the desirable properties of SSIC, due to its high polarity, dielectric constant ($\sim$55) and adequate melting point ($62$ °C) (which supports better dissociation of salt in the polymer during desolvation) [26]. The above properties have motivated us to study the effect of succinonitrile (SN) on the dielectric relaxation and ion dynamics of prepared polymer salt complex film, since dielectric parameters play a constructive role in polymer electrolytes in terms of energy storage as well as in the electrical transport of the relevant charge carriers. As stated earlier, the relaxation of one coordinating site promotes ion migration to another coordinating site via the (electron rich) ether group of the host polymer. Hence, the shorter relaxation time seems to be beneficial for rapid ion transport. It can be represented by the relationship, $\sigma \tau T = \text{constant}$, in the polymer electrolyte system under investigation. Thus, frequency dependent parameters such as complex conductivity, complex permittivity and relaxation time provide valuable information regarding the ion dynamics of the SSICs, and are important in understanding ion dynamics and relaxation [27–31]. The variation of relaxation time has been systematically evaluated by plotting relevant correlations (viz. dielectric loss, tangent loss, modulus and imaginary part of the impedance) [26, 32–35].

The present investigation was undertaken to study the role of SN in improving the ion migration in a prepared polymer electrolyte system, and to understand the ion dynamics over the whole frequency window. X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy were used to probe the complex formation, and to visualize polymer–ion–ion interactions, respectively. Impedance spectroscopy was used to study the electrical conductivity and ion transport number. As the number of free charge carriers directly influences the dielectric constant of the system, the various dielectric parameters ($\varepsilon'$, $\varepsilon''$, $\sigma_{ac}$, $\tan\delta$) of SN have been thoroughly analyzed. Also, all dielectric parameters were simulated using the relevant equation, and validate the present experimental study. The various transport parameters, such as number density of charge carriers, mobility, diffusion coefficient and relaxation time (average & molecular),
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are properly correlated with the ionic conductivity results. We have proposed a novel scheme to highlight the interaction between the constituents of the solid polymer electrolyte matrix. The molecular structures of PEO, NaPF₆ and SN are shown in figure 1.

2. Methodology

2.1. Materials preparation

PEO with a molecular weight of 1 × 10⁶ g mol⁻¹ (Sigma-Aldrich), NaPF₆ and SN from Aldrich were used as base material. Anhydrous acetonitrile from Sigma Aldrich was used as a solvent. The host polymer (PEO) and the salt NaPF₆ were vacuum dried before use. The O/Na⁺ ratio was constant 8:1 that is an optimized value for high ionic conductivity. The polymer electrolytes were synthesized via standard solution cast technique. Initially, 0.5 g of PEO and appropriate salt (O/Na⁺ = 8:1) were dissolved in the 15 ml acetonitrile (ACN) at room temperature for 6–8h. Then various wt. % of SN were added to the polymer salt solution and stirred for 18–20h. The resulting viscous solution was cast onto petri dishes and stored in a desiccator with silica gel till a dry film was obtained. Further drying was done in a vacuum oven to remove the residual solvent. The samples are designated as SPE-x, where x = 1, 2, 3, 4, 5, 6 & 7. SPE 1 designates the pure PEO and SPE 2 to SPE 7 are designated for the wt. % of SN added (0, 1, 2, 3, 4, 5 wt. %) PEO₈-NaPF₆ sample.

2.2. Characterization

XRD (Bruker D8 Advance) performed for the determination of crystallinity and recorded with Cu-Kα radiation (λ = 1.54 Å) in the Braggs angle range (2θ) from 10⁰ to 60⁰. FTIR spectra (Bruker Tensor 27, Model: NEXUS–870) were recorded in absorbance mode over the wavenumber region from 600 to 3500 cm⁻¹, to probe the presence of various interactions such as polymer–ion, ion–ion interaction and complex formation. The ionic conductivity was measured by impedance spectroscopy (CIS) over the frequency range of 1 Hz to 1 MHz, using a CHI 760 electrochemical analyzer. An AC sinusoidal signal of 10 mV was applied across the cell configuration SS|SPE|SS in which SPEs films were sandwiched between two stainless steel (SS) electrodes. The ion transference number was measured via 𝐼 − 𝑡 characteristics by applying a voltage of 10 mV. As the present report is focused on the dielectric relaxation and charge carrier dynamics, it becomes important to apply dielectric analysis. The impedance data is then transformed into the dielectric constant, dielectric loss, complex conductivity data, which is further transformed into the real and imaginary parts of the modulus. All plots were fitted with corresponding equations by Origin 8 software to evaluate the various parameters that enable us to explore the ion dynamics.

3. Results and discussion

3.1. XRD analysis

To investigate the structural changes in prepared polymer electrolyte, XRD is a crucial technique which provides details in terms of the shift in the peak position, broadening, intensity reduction. Figure 2 depicts the XRD diffractograms of the pure PEO (figure 2(a)) and polymer salt complex

![Figure 1. The structures of PEO, NaPF₆ and SN.](image1.png)

![Figure 2. XRD spectra of the (a) pure PEO, (b) PEO-NaPF₆; 0 wt. % SN), (c) 1 wt. % SN, (d) 2 wt. % SN, (e) 3 wt. % SN, (f) 4 wt. % SN and (g) 5 wt. % SN.](image2.png)
anion migration [14]. The arrangement of the polymer chain, and promotes the fast ion transport parameters, which are to be analyzed in the upcoming sections. At high SN content, there is not sufficient dissolution of the SN in the polymer salt system and the plastic nature of SN dominates, as can be seen in the micrograph (figure 3(f)). It can be concluded that the incorporation of SN into the polymer salt system enhances the amorphous content, which is desirable for fast SSIC.

3.3. Fourier transform infra-red spectroscopy (FTIR) analysis

FTIR is a powerful tool to probe possible polycation–ion–ion interaction and observed spectral changes in the functional group of the polymer host due to the addition of salt and SN. The FTIR absorbance spectra of the pure polymer and polymer salt complex with x wt. % (x = 0, 1, 2, 3, 4 and 5) SN are depicted in figure 4. The various absorption bands corresponding to modes of PEO are observed, and complexation of polymer and salt is confirmed. The peak located at 950 cm\(^{-1}\) corresponds to the C–O stretching vibration mode, and shifts towards the lower wavenumber side, suggesting the effect of salt on host polymer. The fundamental peak for PEO—corresponding to symmetric and asymmetric C–O–C stretching mode—is observed near 1100 cm\(^{-1}\), and is interesting for us since it tells us about the interaction between cations and the ether group of the polymer chain. The change in peak intensity and position of this peak indicates the interaction of the cation (Na\(^{+}\)) with an ether group (\(-\text{O}\cdot\cdot\cdot\text{O}^{+}\)) in the host polymer [37, 39]. Further addition of SN results in an asymmetrical peak, suggesting that SN plays an active role in altering the interaction present in the polymer salt complex. CH\(_2\) bending and asymmetric/symmetric twisting vibrations are observed near 1340 cm\(^{-1}\), 1282 cm\(^{-1}\) and 1230 cm\(^{-1}\) respectively. All solid polymer electrolyte films show strong absorption bands in the region 2800 cm\(^{-1}\) to 2950 cm\(^{-1}\) which correspond to the symmetric and asymmetric vibration of C–H stretching mode of the CH\(_2\) group in PEO [36]. Further addition of SN changes the stretching mode (peak position and shape) and two separate stretching modes are clearly visible now. Strong evidence of interaction is obtained, which confirms that complex formation between the polymer, salt and SN further modifies the polymer chain arrangement. Since the Na\(^{+}\) ion is IR inactive, our focus is on the evaluation of anion peak rather than that of the cation, and reflections appearing in the anion peak are transformed onto the cation peak for the analysis. The peak associated with the anion is attributed to the interaction between polymer and PF\(_6\) anion and is made evident by deconvoluting the hexafluorophosphate

| Sample | 2θ (°) | d-spacing (Å) | R (Å) |
|--------|--------|---------------|-------|
| SPE 1  | 19.03  | 4.66          | 5.82  |
| SPE 2  | 18.87  | 4.69          | 5.87  |
| SPE 3  | 18.63  | 4.75          | 5.94  |
| SPE 4  | 18.38  | 4.82          | 6.02  |
| SPE 5  | 18.16  | 4.87          | 6.09  |
| SPE 6  | 18.54  | 4.78          | 5.97  |
| SPE 7  | 18.66  | 4.74          | 5.93  |
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The anion band, confirming the presence of free ions and ion pairs. The typical vibrational mode of the $\text{PF}_6^-$ anion in SPEs films has been observed in the wavenumber region $\sim800–900\text{ cm}^{-1}$. The presence of asymmetry in the peak for all SPE systems may be attributed to loss in degeneracy from octahedral symmetry $O_h \rightarrow C_3\nu$ arising due to the simultaneous presence of more than one component—i.e. free ions and ion pairs. So, to study above degeneracy and presence of both ions, deconvolution of the $\text{PF}_6^-$ peak is undertaken, as explained somewhere [40, 41].

The number of free ions is an important parameter in polymer electrolytes, as it directly affects ionic conductivity. Hence, we evaluate the free ions and ion pair contribution here using equation (1):

$$\left\{ \begin{align*}
\text{Fraction of free anion} &= \frac{\text{Area of free ion peak}}{\text{Total peak area}} \\
\text{Fraction of ion pair} &= \frac{\text{Area of ion pair peak}}{\text{Total peak area}}
\end{align*} \right. \quad (1)$$

Figure 3. FESEM micrographs of the (a) PEO (b) PEO-NaPF$_6$ (c) PEO-NaPF$_6$-2% SN (d) PEO-NaPF$_6$-3% SN (e) PEO-NaPF$_6$-4% SN and (f) PEO-NaPF$_6$-5% SN polymer electrolytes.

The deconvoluted pattern of SPE films is shown in figure 5; the peak at lower wavenumber is attributed to free ions, and that at higher wavenumber to ion pairs. The changing profile (change in position and area) of free ion and ion pair peak on the addition of the SN illustrates the change in polymer–ion interaction due to presence of polar nitrile group in SN [42]. A relative comparison of corresponding free ion area and ion pair area is summarized in table 2 and high free ion area
Figure 4. FTIR spectra of pure PEO (SPE 1) and polymer salt (SPE 2) with SPE 3–7 with x wt. % of SN.

Figure 5. Deconvolution of the PF$_6^-$ vibration mode in the wavenumber range 800 cm$^{-1}$ to 900 cm$^{-1}$ for (a) 0 wt. % SN, (b) 1 wt. % SN, (c) 2 wt. % SN, (d) 3 wt. % SN, (e) 4 wt. % SN, (f) 5 wt. % SN.

Table 2. Position of deconvoluted free ion and ion pair peaks of SPE films.

| Sample code | Free ion Area (%) | Wavenumber (cm$^{-1}$) | Ion pair Area (%) | Wavenumber (cm$^{-1}$) | Corr. coff. ($r^2$) |
|-------------|------------------|------------------------|-------------------|------------------------|-----------------|
| SPE 2       | 54.95            | 833                    | 45.04             | 854                    | 0.99            |
| SPE 3       | 55.17            | 830                    | 44.82             | 857                    | 0.98            |
| SPE 4       | 57.15            | 833                    | 42.84             | 854                    | 0.99            |
| SPE 5       | 62.20            | 834                    | 37.79             | 856                    | 0.99            |
| SPE 6       | 63.27            | 835                    | 37.32             | 854                    | 0.99            |
| SPE 7       | 58.67            | 833                    | 41.32             | 858                    | 0.99            |
The correlation between free ion area, ionic conductivity and matrix depicts the same pattern, but with decreased bulk resistance, indicating triggering of the ion transport mechanism in the polymer electrolyte system. The ionic conductivity of the SPE film depends on the concentration of the mobile ions, ion charge and mobility (how easily an ion is moved through the solid) and expressed as \( \sigma = n e \mu \).

The conductivity of all SPEs was calculated using equation (2):

\[
\sigma = \frac{t}{R_b \times A}.
\]

Here, ‘\( t \)’ is the thickness of the polymer electrolyte (cm), ‘\( A \)’ is the area of the blocking electrode (cm²), and \( R_b \) is the bulk resistance of polymer electrolyte films.

For the sample with 4 wt. % SN, the highest ionic conductivity is due to lowest value of bulk resistance, as shown in the inset of figure 6. The pure polymer shows a lower value of ionic conductivity, and addition of salt to the polymer system shows enhancement in conductivity. The increase of ionic conductivity may be due to the release of free charge carriers via the interaction of cations with the electron rich ether group of the host polymer. The coordinating sites provided by the polymer chain support the migration of cations, which leads to the higher ionic conductivity of the system. Further, the addition of SN dissociates more salt due to the high polarity of SN (N≡C–CH2–CH2–C≡N) molecules, and makes the polymer chain flexible, leading to faster segmental motion of polymer chains. The highest ionic conductivity is obtained for SPE 6, which contains 4 wt. % SN in the polymer salt system. The low value of bulk resistance \( (R_b) \) for SPE 6 as compared to other samples provides evidence of its high ionic conductivity. The decrease of ionic conductivity at high SN content may be due to the dominance of plastic effects of SN leading to ion pair formation or blockage of ion conducting pathways. The double layer capacitance observed at low frequency side is calculated using equation (3) and given in table 3:

\[
C_{dl} = \frac{1}{\omega Z''}.
\]

Here, \( \omega \) is the angular frequency and \( Z'' \) is the imaginary part of impedance at low frequency. The high value of double layer capacitance is achieved for the highest ionic conducting sample, and is as expected from the deconvoluted FTIR results which concluded the highest free ion area for the same. The correlation between free ion area, ionic conductivity and double layer capacitance has been assessed by plotting the graph in the last section of the manuscript. Since the ions play an important role in the current system, the ionic nature of polymer electrolyte needs to be made evident, as reported in the subsequent section.

3.5. Ion transport study

The transference number of an ion in a polymer electrolyte system is basically the fraction of the total current carried by that ion across a given medium. Figures 7(a)–(f) shows the variation of polarization current as a function of time for the pure polymer and polymer electrolyte with SN content at room temperature [46]. An almost identical pattern is observed for

![Figure 6. Log–log plots of the complex impedance (Z’’ versus Z’) for the pure PEO and polymer salt complex with x wt. % SN (x = 1, 2, 3, 4, 5). The inset shows the graph of the highest conducting sample.](image-url)
all SPEs, which shows a very high initial total current ($I_t$) followed by a sharp drop in its value with the passage of time. After some time, the current becomes saturated; the initial high current is attributed to the contribution from both the ions and the electrons ($I_t = I_e + I_i$), while the final saturation/residual current after polarization is attributed to the contribution of electrons only due to ion blocking electrodes (SS) at the interface. For all SPE system ionic transference number was about ~0.99 and it reveals the ionic conducting nature of polymer electrolyte [47]. The ionic and electronic conductivity were evaluated and recorded in table 3 using the equation (4):

\[
\begin{align*}
I_t &= I_e + I_i \\
\sigma_{\text{ionic}} &= \sigma_{\text{electrical}} \times I_i \\
\sigma_{\text{electronic}} &= \sigma_{\text{electrical}} \times I_e.
\end{align*}
\]

The ionic conductivity and electronic conductivity are also in correlation with electrical conductivity value. The negligible value of electronic conductivity justifies the use of prepared electrolyte as a separator-cum-electrolyte in the energy conversion devices.

3.6. Dielectric spectroscopy analysis

3.6.1. Cole–Cole plot. The Cole–Cole plot ($\varepsilon\prime\prime$ versus $\varepsilon\prime$) is a powerful tool for materials retaining one or more well separated relaxation processes with comparable magnitudes and obeying the Cole–Cole formalism. The plot comprises variation of dielectric loss with dielectric storage component at constant temperature; formation of a perfect semicircle indicates the presence of a single relaxation time. Figure 8 shows a depressed semicircular arc due to broad relaxation region; maximum loss occurs at the midpoint of the semicircle (solid red lines depict the fitted plot), while the dielectric values are read from right to left with an increase of frequency. One interesting conclusion observed from the figure is that at a dielectric constant of infinite frequency ($\varepsilon_\infty$) and static dielectric constant ($\varepsilon_s$) there is no loss [48]. All SPEs shows a semicircular arc but the SPE system with 4 wt. % SN shows a tail at low frequency, which may be due to high loss. Here, charge carriers act slowly under the applied electric field, and dispersion is observed, while at high frequency, dielectric loss decreases continuously and approaches zero.

| Sample code | Transference number | Electrical conductivity ($S \text{ cm}^{-1}$) | Electronic conductivity ($S \text{ cm}^{-1}$) | Ionic conductivity ($S \text{ cm}^{-1}$) |
|-------------|---------------------|---------------------------------------------|---------------------------------------------|----------------------------------------|
| SPE 1       | —                   | $4.95 \times 10^{-8}$                       | —                                          | —                                      |
| SPE 2       | 0.90                | $1.95 \times 10^{-7}$                       | $1.95 \times 10^{-8}$                       | $1.75 \times 10^{-7}$                  |
| SPE 3       | 0.99                | $2.97 \times 10^{-7}$                       | $2.97 \times 10^{-8}$                       | $2.94 \times 10^{-7}$                  |
| SPE 4       | 0.99                | $3.22 \times 10^{-7}$                       | $3.22 \times 10^{-8}$                       | $3.18 \times 10^{-7}$                  |
| SPE 5       | 0.95                | $1.15 \times 10^{-6}$                       | $9.75 \times 10^{-8}$                       | $1.09 \times 10^{-6}$                  |
| SPE 6       | 0.96                | $0.75 \times 10^{-5}$                       | $4.52 \times 10^{-7}$                       | $0.72 \times 10^{-5}$                  |
| SPE 7       | 0.96                | $0.65 \times 10^{-6}$                       | $3.9 \times 10^{-8}$                        | $0.62 \times 10^{-6}$                  |

Figure 7. Variation of polarization current as a function of time for prepared solid polymer electrolyte, (a) 0 wt. % SN, (b) 1 wt. % SN, (c) 2 wt. % SN, (d) 3 wt.% SN, (e) 4 wt. % SN, (f) 5 wt. % SN at RT.
3.6.2. Dielectric spectrum analysis. The dielectric storage and dielectric loss are two important parameters in determining the suitability of polymer electrolytes for energy storage applications. Careful analysis of the relative permittivity in polymer electrolyte films helps to develop understanding of the polarization effect at the electrode/electrolyte interface and the correlation of relaxation time with ionic conductivity. Dielectric analysis of solid polymer electrolyte materials is desirable, to attain better insight into ion dynamics, and is analyzed, in brief, in terms of the real and imaginary parts of complex permittivity ($\varepsilon^*$). The dielectric permittivity describes the polarizing ability of a material in the presence of a functional external electric field, and how much interionic coulombic interaction energy is reduced as compared to vacuum [49–51]. The dielectric constant of a system is a dimensionless ratio of permittivity to the permittivity of free space. As permittivity is a function of frequency, it is a complex quantity expressed by equation (5):
\[ \varepsilon^* = \varepsilon' - j\varepsilon''; \varepsilon' = \frac{-Z''}{\omega C_0(Z^2 + Z''^2)} \quad \text{and} \quad \varepsilon'' = \frac{Z'}{\omega C_0(Z^2 + Z''^2)}. \quad (5) \]

Here \( \varepsilon' \) and \( \varepsilon'' \) represent the real and imaginary parts of the dielectric permittivity and \( j \) imaginary unity (\( j^2 = -1 \)). The real part of dielectric permittivity (\( \varepsilon' \)) is proportional to the capacitance, and measures the alignment of dipoles or polarization, whereas the imaginary part of dielectric permittivity (\( \varepsilon'' \)) measures dielectric loss, proportional to conductance, and represents the energy required to align the dipoles. Cole and Cole proposed the distribution of relaxation time for Debye processes [52], given by equation (6):

\[ \varepsilon_\alpha = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + (j\tau_\alpha)^{\alpha}} 0 \leq \alpha < 1. \quad (6) \]

Here, \( \alpha \) is the distribution parameter, and \( x = \omega \tau \) (\( \omega \) being the angular frequency of applied field, \( \tau \) Debye relaxation time, i.e. reciprocal of jump frequency in the absence of external electric field). The real and imaginary parts of the dielectric constant can be obtained by separating the above equation, and can be given as [53]

\[ \varepsilon' = \varepsilon_\infty + \frac{\Delta \varepsilon (1 + x^{1-\alpha} \sin \pi / 2\alpha)}{1 + 2x^{1-\alpha} \sin \pi / 2\alpha + x^{2(1-\alpha)}}, \quad (7a) \]

\[ \varepsilon'' = \frac{\Delta \varepsilon x^{1-\alpha} \cos \pi / 2\alpha}{1 + 2x^{1-\alpha} \sin \pi / 2\alpha + x^{2(1-\alpha)}}, \quad (7b) \]

The above equations can be written in another form by replacing \( \alpha \) with \( 1 - \alpha \) in equation (7), and, we obtain equation (8) [54]:

\[ \varepsilon' = \varepsilon_\infty + \frac{\Delta \varepsilon (1 + x^\alpha \cos \frac{\pi}{\alpha})}{1 + 2x^\alpha \cos \frac{\pi}{\alpha} + x^{2\alpha}}, \quad (8a) \]

\[ \varepsilon'' = \frac{\Delta \varepsilon x^\alpha \sin \frac{\pi}{\alpha}}{1 + 2x^\alpha \cos \frac{\pi}{\alpha} + x^{2\alpha}}. \quad (8b) \]

Here, \( \varepsilon_4 \) is the static dielectric constant (\( x \to 0 \)), \( \varepsilon_\infty \) is the dielectric constant (\( x \to \infty \)), \( x = \omega \tau \) as in equation (6) and \( \alpha \) is the distribution (power law) exponent of the material sample. The fitted parameters are shown in table 4 at RT. From table 4 it is observed that decrease in value of \( \alpha \) is a direct indication of more distributed relaxation time. The value of \( \varepsilon_\infty \) is maximum for the SPE 6 system, and corresponds to 4 wt. % of SN content, as shown in table 4.

Figure 9 shows the plot of frequency dependence of dielectric constant (\( \varepsilon' \)) for different SN content at RT and an absolute agreement is obtained between the experimental and fitted data over the measured frequency range. All SPEs shows strong frequency dispersion at a lower frequency, followed by a frequency independent region above 1 kHz. The addition of SN to the polymer salt system provides suitable evidence of the effective role played by SN in a polymer salt matrix. The high value of dielectric constant at a lower frequency in the graph indicates dielectric polarization, and the same trend is observed in all polymer electrolytes. Generally, there are two sources of dipoles present in polymer electrolytes. One is due to dissociation of salt (cations and anions) and the other to the ether group of PEO. The former provides a free number of charge carriers for transport. When an electric field is applied, these charges migrate along the field appropriately, but the blocking electrodes present in the circuit prevent transport of ions via an external circuit. The ions accumulated here form a polarization region due to an increase of charge species. The second dipole source deals with the significant contribution of the electron rich ether group (\( -\mathrm{O} - \)) of host polymer chain (PEO). When an electric field is applied, there may be conformational changes in the polymer chain, and this may lead to a nonzero contribution to polarization. Both of these contributions simultaneously lead to the high value of the dielectric constant [55–57].

The high value of the dielectric constant at low frequencies may be due to the presence of ion pairs, which are unable to migrate over long ranges, and behave like localized dipoles in the immobilized state. These localized dipoles are supposed to respond to the application of an externally applied electric field because of sufficient time, which increases the dielectric constant and the bulk capacitance [58]. Also, it is evident that dielectric constant increases with the addition of SN, which may be due to better dissociation of salt due to the presence of the polar nitrile group in SN. The highest value of dielectric constant at all frequencies provides direct evidence for the highest conducting sample, and is also in agreement with FTIR data. The decrease of dielectric constant at high SN content may be due to the formation of ion pairs via increased coulombic interaction or insufficient active SN content. The decrease of free charge carriers decreases the accumulation

| Sample code | \( \varepsilon_\infty \) | \( \Delta \varepsilon \) \((\times 10^3)\) | \( \tau_\alpha \) (s) | \( \alpha \) | \( \Delta \varepsilon \) \((\times 10^3)\) | \( \tau_\alpha \) (s) | \( \alpha \) |
|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| SPE 1       | −28.46          | 40.04           | 1.32            | 0.78            | 110.91          | 0.55            | 0.78            |
| SPE 2       | −199.18         | 83.91           | 1.20            | 0.69            | 161.81          | 0.49            | 0.67            |
| SPE 3       | −223.29         | 100.48          | 1.20            | 0.62            | 193.41          | 0.34            | 0.63            |
| SPE 4       | −346.09         | 93.12           | 0.63            | 0.70            | 261.00          | 0.84            | 0.63            |
| SPE 5       | −604.04         | 181.69          | 0.58            | 0.69            | 356.82          | 0.29            | 0.63            |
| SPE 6       | −7094.61        | 976.84          | 0.03            | 0.70            | 1814.38         | 0.14            | 0.58            |
| SPE 7       | −532.23         | 75.99           | 1.03            | 0.53            | 349.45          | 0.41            | 0.47            |

Table 4. Fitted \( \varepsilon' (\varepsilon_\infty, \Delta \varepsilon, \tau_\alpha, \alpha) \) and \( \varepsilon'' (\Delta \varepsilon, \tau_\alpha, \alpha) \) parameters at room temperature.
of polarization charges, and hence, the dielectric constant. Now, when we approach the high frequency window the decrease in dielectric constant is observed for all samples, due to relaxation processes as well as electrode polarization (EP). This decrease may be due to the inability of heavy positive and negative charge carriers to rotate/translate along the field direction, and directly affects the dielectric constant value. Now, the field changes direction before the dipoles become aligned along the field. The dielectric constant is now frequency independent, as the fast periodic reversal of the electric field prevents the ion diffusion in the direction of the field. The constant region is achieved due to the failure of molecular dipoles to follow the field, and contribution to dielectric constant due to orientation processes ceases. Also, the increase of dielectric relaxation strength ($\Delta \varepsilon = \varepsilon_s - \varepsilon_\infty$) with SN is a measure of increased ionic polarization. From table 4, it is clear that value of $\Delta \varepsilon$ is higher for the SPE 6 system, and its relaxation time lower, which reveals the better

![Figure 9](image_url)
dissociation of salt as compared to other SN content. We have also calculated the molecular relaxation time, and this is also in one-to-one agreement with the impedance and FTIR study [59]. The lowest value of molecular relaxation time is for the 4 wt. % SN, and supports evidence of the enhancement in ionic conductivity as obtained from electrical conductivity analysis (see supplementary discussion and figure S1 (available online at stacks.iop.org/JPhysCM/30/165402/mmedia)) and impedance study—which shows the highest ionic conductivity for the same concentration, and provides direct evidence of the increased number of free charge carriers [36].

As dielectric constant varies with the frequency of applied field, so a comparison of dielectric constant at different frequencies is depicted in figure 10: the dielectric constant is higher at lower frequencies and decreases with the increase of frequency. One fascinating point to be noted is that the dielectric constant is higher for the highest conducting sample, as expected from FTIR and impedance results. The high value of dielectric constant indicates better dissociation of salt, which directly implies free charge migration owing to the formation of a conductive network inside the polymer matrix [60].

The fitted plot of dielectric loss (\(e''\)) versus frequency (using equation (8)) is shown in figure 11; it shows the same trend as the real part of permittivity. A close agreement is observed between the experimental data and the fitted curve. The ions present in the system show the effect of inertia on the application of the field. But with the periodic field reversal field, a three-step process occurs. First, the deceleration of ions occurs; ions then stop for a negligible time; and in the final stage, ions are accelerated in the reverse direction. This generates some internal heat in dielectric, called dielectric energy loss (\(e'' = 0\) for \(\omega \tau = 0\)). The dielectric loss at low frequency is mainly due to DC resistivity, while at high frequencies it is due to dipole rotations from low to high energy states. The addition of SN helps in dissociation of salt, and releases large numbers of charge carriers, leading in turn to large heat generation or large dielectric loss [61]. The absence of any relaxation peak in the graph may be due to the large EP effect which masks the relaxation behavior of polymer electrolytes. Therefore, electric modulus and AC conductivity are attempted as alternatives to study ionic dynamics in the next sections.

3.6.3. Tangent delta analysis. Another important parameter in analyzing the relaxation behavior of polymer electrolytes is the plot of loss tangent versus frequency. The loss tangent (\(\tan \delta\)) is defined as the ratio of energy loss to energy stored in a periodical field, and is also known as the dissipation factor. The component in phase with applied voltage results in loss and \(\delta\) is the loss angle. A maximum in loss tangent versus frequency plot is obtained for a particular combination of frequencies which satisfy the equation \(\omega \tau = 1\), where \(\omega\) is the angular frequency of applied field and \(\tau\) is Debye relaxation time (reciprocal of jump frequency in the absence of external electric field). The loss is maximal for this particular frequency, as explained below. A molecule of a dielectric possesses free translational, vibrational and rotational/orientational motion in the absence of any field (\(E = 0\)). When an alternating electric field is applied (\(E \neq 0\)), a constraint is felt by the molecules or dipoles in changing their directions along the field only when the frequencies of applied external electric field and frequency of molecule rotation match closely. This matching results in maximum power transfer to the molecular dipoles from the applied field, and heating is produced in the system [62].

Figure 12 shows the variation of loss tangent with frequency for various wt. % of SN based polymer electrolyte; and signature single relaxation peaks are a fingerprint of ionic conduction via polymer chain segmental motion. The process of loss tangent can also be correlated with the glass transition temperature and amorphous content of polymers [63]. Initially, in the lower frequency region, an increase of loss tangent may be attributed to the dominance of the Ohmic (active) component over the capacitive (reactive) component. But the inverse trend is observed with the increase in frequency; this decrease of loss tangent is due to the independent nature of Ohmic part and growth of reactive component with frequency. The presence of a resonance peak is also in good agreement with the theoretical approach proposed by Debye and corresponds to the maximum transfer of energy on the application of field [64].

Now, the addition of salt in the pure polymer host shifts the relaxation peak towards the high frequency side which indicates the decrease of Debye relaxation time. The change in the loss peak and a shift in position evidences the presence of dielectric relaxation processes and a decrease of relaxation time [65]. The decrease of relaxation time provides evidence of the increase of ionic conductivity, and is in agreement with the FTIR data. Further addition of SN shifts the peak towards the high frequency side, supporting the impedance data which reciprocated high ionic conductivity. It may be concluded that the amorphous phase is enhanced after incorporation of SN into the polymer salt.
matrix, leading to fast ion migration. To obtain the relaxation time, the tan $\delta$ versus frequency is fitted generally with equation (9):

$$\tan \delta = \left( \frac{r - 1}{r + x^2} \right)^{\alpha},$$  \hspace{1cm} (9)

Here, $r$ is the relaxation ratio ($\varepsilon_s / \varepsilon_\infty$), $\varepsilon_s$ is static dielectric constant ($x \to 0$), $\varepsilon_\infty$ is dielectric constant ($x \to \infty$), $x$ is defined as in equation (6). This equation, proposed by Debye, provides satisfactory fitting for single particle and non-interacting systems (null interaction between dipoles). However, when we approach the low frequency window, the Debye model is not followed properly; this may be due to the presence of multiple type dipole polarization or the complex, heterogeneous nature of the material. In the present material system, a broad loss peak is observed which motivates us to modify the ideal Debye equation for better simulation of experimental results, as in the present case the polymer matrix is an interacting system as determined by FTIR, and this many-body interaction needs to be studied deeply via satisfactory loss plot fitting. Therefore, in order to meet experimental needs, it becomes essential to make certain empirical modifications by adding some parameter, as one parameter is used in Cole–Cole, Davidson–Cole, Williams–Watts, and two parameters in Havriliak–Negami fluctuations [66]. So, in this ideal Debye equation, shape parameter $\alpha$ is added as a power law exponent with value, $0 \leq \alpha \leq 1$, to fit the broad tangent delta plot (equation (10)). This proposed empirical equation and presence of this factor confirms the presence of more strong interaction in our system. The modified equation is expressed as equation (10):

$$\tan \delta = \left( \frac{(r - 1)}{r + x^2} \right)^{\alpha}. \hspace{1cm} (10)$$

This equation was used to calculate the fitting parameters in tangent delta plot and the fitted parameters are recorded in table 5. This equation provides the empirical confirmation of our results; the fitting observed in figure 12 also shows a close agreement of measured and fitted results. The fitted curve, represented by the solid red lines, describes the observed results accurately. The negligible slight deviation on the low frequency side is probably due to EP or the diffusion of ions towards the electrodes [67]. We can return to the Debye model for $\alpha = 1$ in equation (10). The physical significance of $\alpha$ has not yet been worked out, but this is to be done in future and will provide us crucial aspects which will justify the proposed equation.

The decrease of relaxation time with the addition of SN is due to increase of chain flexibility by interaction between cation and polymer chain. This leads to increase in amorphous content and more free volume being available for ion migration; hence, reduction in the relaxation time is observed. The lowest value of relaxation time is observed for the SPE 6 (4 wt. % SN), and the same system shows the highest value of free ion area and ionic conductivity value. So, the overall effect of SN is a reduction of relaxation time and enhanced ionic conductivity, while at very high SN content, the insulating nature of plasticizer SN increases the relaxation time in the system. The lowest value of relaxation time for SPE6 provides direct evidence for the faster ion dynamics in plasticized polymer electrolyte, and supports the FTIR and impedance data. Therefore, it is concluded that the modified equation may be useful in describing the highly interacting systems, so that the issue of fitting at a lower frequency can be resolved. In order to investigate the dielectric analysis fully, the suppressed features of Cole–Cole plot at high frequencies are explored with a new approach for the first time in the case of SSICs in the upcoming section.
Figure 12. Frequency dependence of the tangent delta loss ($\tan \delta$) for the (a) PEO, polymer salt + $x$ wt. % SN (b) 0 wt. % SN, (c) 1 wt. % SN, (d) 2 wt. % SN, (e) 3 wt. % SN, (f) 4 wt. % SN, (g) 5 wt. % SN) and (h) comparison of frequency shift with SN concentration. Solid lines are the best fit to the experimental data (a)–(g).
Table 5. Fitted tangent delta loss parameters ($r$, $\tau$, $\alpha$, $\tau_{\text{tan}}$, $\tau_{m}$) at room temperature.

| Sample code | $r$ ($\times 10^3$) | $\tau$ ($\times 10^{-9}$) | $\alpha$ | $\tau_{\text{tan}}$ ($\times 10^{-4}$ s) | $\tau_{m}$ ($\times 10^{-6}$ s) |
|-------------|----------------------|-------------------------|--------|-------------------------------|-----------------------------|
| SPE 1       | 9.01                 | 0.44                    | 0.31   | 14.83                         | 4.94                        |
| SPE 2       | 2.04                 | 0.03                    | 0.42   | 2.41                          | 1.68                        |
| SPE 3       | 3.06                 | 0.02                    | 0.42   | 1.48                          | 0.84                        |
| SPE 4       | 17.45                | 0.07                    | 0.24   | 1.73                          | 0.41                        |
| SPE 5       | 32.85                | 0.04                    | 0.26   | 0.73                          | 0.11                        |
| SPE 6       | 56.38                | 0.01                    | 0.54   | 0.17                          | 0.02                        |
| SPE 7       | 1.89                 | 0.00                    | 0.38   | 0.33                          | 0.24                        |

3.7 Sigma representation ($\sigma''$ versus $\sigma'$)

The Cole–Cole plot ($\varepsilon''$ versus $\varepsilon'$) is a very useful tool when a material possesses relaxation processes which obey the Debye equations. However, when the material possesses high ionic conductivity, the Cole–Cole representation becomes less useful, because the presence of DC conductivity leads to a divergence of $\varepsilon''$ at lower frequencies. Therefore, a new approach ($\sigma$-representation; $\sigma''$ versus $\sigma'$) has been attempted to describe the divergence in the Cole–Cole plot and is a crucial finding in the case of SSICs, as this new approach leads to the formation of a semicircle, whereas the Cole–Cole plot ($\varepsilon''$ versus $\varepsilon'$) leads to a divergence [68]. This new representation is the best alternative for getting insights of the high frequency data, being capable of eliminating the issue of high frequency data in the Cole-Cole plot. One extremely crucial point is that since both $\sigma''$ and $\sigma'$ involve the multiplication of frequency with real and imaginary dielectric parameters, high frequency features turn out to be visible in the $\sigma''$ versus $\sigma'$ plot which seem to be suppressed in the Cole-Cole plot.

The complex electrical conductivity can be written using the following expression (equation (11))

$$
\sigma(\omega) = \sigma' + i\sigma'' = \sigma_0 + \sigma_c \tan(\omega\tau) = \sigma_0 + \sigma_c \tan(\omega\tau),
$$

where $\sigma''$ is the real part of conductivity, $\sigma'$ is the imaginary part of conductivity, $\omega$ is the angular frequency, $\tau$ is the radius of the semicircle. It is very clear that when $\sigma'' = 0$, the low frequency x-intercept gives DC conductivity ($\sigma_0$), and the high frequency x-intercept gives $\sigma_c$. The radius of the semicircle ($\tau$) is inversely proportional to the relaxation time ($\tau$).

Figure 13 shows the plot of $\sigma''$ versus $\sigma'$; all SPEs show a clear semicircle, which confirms that the material obeys the Debye conduction rule. The low and high frequency intercepts provide $\sigma_0$ and $\sigma_c$, respectively. Table 6 shows the various parameters obtained from the above plot; the increase of DC conductivity with the addition of SN is evident, with a maximum for SPE 6.

Also, inset of figure 13 shows the increase of radius of a semicircle with the addition of SN in polymer salt system which indicates the decrease of relaxation time and provides evidence of faster ion dynamics. As $\tau$ is inversely proportional to $\tau$, so the highest value of $r$ for SPE 6 provides strong evidence for fast ion migration, in good agreement with the impedance, FTIR and dielectric studies. At frequencies much higher than the characteristic frequency, the $\sigma''$ versus $\sigma'$ plot shows a straight line, which is due to the $\omega^{-\alpha}$ type asymptotic behavior of $\varepsilon''$ and $\varepsilon'$. A simulated plot of the sigma representation is shown with explanation in the supplementary file (figure S2).

3.7.1 AC conductivity analysis. The AC electrical measurements (AC conductivity) of all plasticized polymer electrolytes have been obtained using equation (12):

$$
\sigma' = \sigma_{\text{ac}} = \omega\varepsilon_0\varepsilon'' = \omega\varepsilon_0\varepsilon'\tan\delta.
$$

Here, $\omega$ is the angular frequency, $\varepsilon_0$ is the dielectric permittivity of free space, and $\varepsilon''$ represents the dielectric loss. Figure 13 shows a variation of AC conductivity with frequency for different wt. % of SN in polymer salt matrix. The frequency dependent real part of electrical conductivity depicts three distinct regions: (i) low frequency dispersive region; (ii) frequency independent plateau region; and (iii) high frequency dispersive region.

The low-conductivity value at the low frequency dispersion region provides evidence of the accumulation of ions (EP) due to the slow periodic reversal of the electric field and disappears with an increase in frequency. The intermediate constant region at slightly higher frequency is the result of long range diffusion of ions; DC conductivity can be obtained corresponding to it. Region (iii) is due to short range ion transport associated with AC conductivity (hopping of charge carriers). Pure polymer and polymer salt systems show all three regions. All SPE systems show a shift in both intermediate frequency region and high frequency region towards high frequency. For highly conductive systems, a small high frequency dispersion region corresponds to hopping based conduction.

The conductivity of pure polymer is very low due to EP effects, and addition of salt increases the ionic conductivity. Two types of phenomena—long-range conduction due to the migration of free cations and anions in polymer electrolytes, and preferred site hopping conduction through the polymer hetero sites—are responsible for AC conductivity in SPEs [69]. The high frequency region is visible in pure polymer and polymer salt systems, while for another sample it falls outside the measured frequency range. The high frequency region in both systems follows Jonscher’s well known universal power law (JPL) which is a general characteristic of an SSIC expressed by equation (13):

$$
\begin{align*}
\sigma_{\text{ac}} = \sigma_{\text{dc}} (1 + (\omega/\omega_h)^n) & \quad (13a) \\
\sigma_{\text{ac}} = 2\sigma_{\text{dc}} & \quad \text{when } \omega = \omega_h. \quad (13b)
\end{align*}
$$

Here, $\sigma_{\text{ac}}$ and $\sigma_{\text{dc}}$ are the AC and DC conductivities of electrolyte, while $A$ and $n$ are the frequency independent Arrhenius constant and the power law exponent (dimensionless frequency exponent representing the degree of interaction between mobile ions and their surroundings, where
\[
\sigma'' = \sigma' + \frac{1}{1 + i\omega C_{dl}} + i\omega C_b.
\] (14)

Now, considering the equation (14) the real and imaginary part of the conductivity can be written as

\[
\sigma' = \frac{\sigma^2}{\sigma^2 + 2\sigma_b C_{dl} \omega^2 \cos \left( \frac{\alpha \pi}{2} \right) + \sigma_b (C_{dl} \omega^2)^2}
\] (14a)
\[ \sigma''(\omega) = \frac{\sigma^2_0 C_{dl} \omega^n \sin \left( \frac{\alpha \pi}{2} \right)}{\sigma^2_0 + 2\sigma_0 C_{dl} \omega^n \cos \left( \frac{\alpha \pi}{2} \right) + (C_{dl} \omega)^2} + \omega \tau_h. \]  

(14b)

However, we also have to consider the high frequency response, where both real and imaginary parts of the conductivity increase with frequency. Therefore, the real and imaginary parts of conductivity have been expressed as equations (15a) and (15b);

\[ \begin{align*}
\sigma'(\omega) &= \sigma_0 \left[ 1 + \left( \frac{\omega}{\omega_n} \right)^n \right] \quad (15a) \\
\sigma''(\omega) &= A \omega^s. \quad (15b)
\end{align*} \]

Here, all parameters have the same meaning as earlier, and both \( n \) and \( s \) have a value less than unity. Now, to investigate the complete frequency response we replace the \( \sigma_0 \) in equation (14a) by equation (15a) and equation (14b) by equation (15b). This leads us to the final relations which will

![Figure 14.](image-url)  

Figure 14. (a) Frequency dependence of real part of complex conductivity (\( \sigma' \)). Solid lines are absolute fit to the equation (16a), (b) frequency dependence of imaginary part of complex conductivity (\( \sigma'' \)) at RT. Solid lines are absolute fit to the equation (16b). The dotted line shows the change in onset frequency \( (\omega_{on}) \) with SN content.

![Figure 15.](image-url)  

Figure 15. (a) Imaginary part of complex conductivity and, (b) loss tangent plot against frequency for PEO-NaPF\(_6\) with 4 wt. % SN.

Table 7. Comparison of fitted parameters from real part and imaginary part of the complex conductivity for different SPEs at RT.

| Sample code | \( \sigma_0 \) \((\times 10^{-6} \text{ S cm}^{-1})\) | \( \omega_h \) \((\times 10^5)\) | \( \alpha \) | \( n \) | \( C_{dl} \) \((\mu\text{F})\) | \( \tau_h \) \((\mu\text{s})\) |
|-------------|---------------------------------|-----------------|-----|-----|--------|--------|
| SPE 1       | 0.05                            | 0.52            | 0.48| 0.48| 0.02   | 19.1   |
| SPE 2       | 0.22                            | 3.71            | 0.47| 0.47| 0.03   | 2.69   |
| SPE 3       | 0.39                            | 4.10            | 0.50| 0.50| 0.04   | 2.43   |
| SPE 4       | 0.52                            | 7.13            | 0.36| 0.36| 0.07   | 1.40   |
| SPE 5       | 1.02                            | 17.18           | 0.43| 0.43| 0.13   | 0.58   |
| SPE 6       | 91.4                            | 186.04          | 0.41| 0.41| 33.1   | 53.5   |
| SPE 7       | 0.97                            | 17.99           | 0.43| 0.43| 0.58   | 0.55   |

The real part of complex conductivity (\( \sigma' \)) (equation (16a))

\[ \begin{align*}
\text{Sample code} & \quad \sigma_0 \quad (\times 10^{-6} \text{ S cm}^{-1}) & \quad \omega_h \quad (\times 10^5) & \quad \alpha & \quad n & \quad C_{dl} \quad (\mu\text{F}) & \quad \tau_h \quad (\mu\text{s}) \\
SPE 3    & 0.01 & 0.10 & 0.006 & 0.97 & 1.08 \\
SPE 4    & 0.05 & 0.12 & 0.395 & 0.77 & 1.30 \\
SPE 5    & 0.10 & 0.04 & 0.014 & 0.88 & 1.52 \\
SPE 6    & 59.8 & 0.51 & 0.151 & 0.67 & 1.14 \\
SPE 7    & 2.28 & 0.28 & 0.005 & 0.69 & 1.00 \\
\end{align*} \]

The imaginary part of complex conductivity (\( \sigma'' \)) (equation (16b))

\[ \begin{align*}
\text{Sample code} & \quad A \quad (\times 10^{-6} \text{ S cm}^{-1}) & \quad C_{dl} \quad (\mu\text{F}) & \quad \alpha & \quad C_{dl} \quad (pF) \\
SPE 3    & 0.01 & 0.10 & 0.006 & 0.97 & 1.08 \\
SPE 4    & 0.05 & 0.12 & 0.395 & 0.77 & 1.30 \\
SPE 5    & 0.10 & 0.04 & 0.014 & 0.88 & 1.52 \\
SPE 6    & 59.8 & 0.51 & 0.151 & 0.67 & 1.14 \\
SPE 7    & 2.28 & 0.28 & 0.005 & 0.69 & 1.00 \\
\end{align*} \]
be used further for simulating the experimental data and are expressed as equations (16a) and (16b):

\[
\sigma' (\omega) = \frac{\left( \varepsilon_0 [1 + (\frac{\alpha}{\omega})^n] \right)^2 C_{dl} \alpha^2 \cos \left( \frac{\alpha \pi}{2} \right) + \varepsilon_0 \left[ 1 + \left( \frac{\alpha}{\omega} \right)^n \right] \left( C_{dl} \alpha^2 \right)^2 \cos \left( \frac{\alpha \pi}{2} \right)}{(\varepsilon_0 \omega^2) + 2 \varepsilon_0 \alpha^2 \cos \left( \frac{\alpha \pi}{2} \right) + \left( C_{dl} \alpha^2 \right)^2} + \omega C_b.
\]

and

\[
\sigma'' (\omega) = \frac{\left( A \omega^2 \right)^2 C_{dl} \alpha^2 \sin \left( \frac{\alpha \pi}{2} \right)}{(A \omega^2)^2 + 2 A \omega \alpha^2 \cos \left( \frac{\alpha \pi}{2} \right) + \left( C_{dl} \alpha^2 \right)^2} + \omega C_b.
\]

Here, \(C_{dl}\) is frequency independent double layer capacitance, \(\omega\) is the angular frequency, \(s\) and \(\alpha\) are exponent terms with value \(< 1\), and \(C_b\) is the bulk capacitance of solid polymer electrolyte [68].

Figure 14 a shows the profile of the real part of conductivity; solid red lines are corresponding fits. At low frequency (\(\omega \rightarrow 0\)) ion jump at faster rate from one coordinating site (\(\vec{O} \rightarrow \vec{O}\)) to another for \(\omega < \omega_h\); this increases the relaxation time. However, at high frequency (\(\omega \rightarrow \infty\)) two competing hopping mechanisms are known: one is unsuccessful hopping, in which an ion jumps back to its initial position (correlated forward–backward–forward) and another is successful hopping, in which the neighborhood ions become relaxed with respect to the ion’s position (the ions stay at the new site). For, \(\omega > \omega_h\) the number of successful hoppings is greater, indicating a more dispersive AC conductivity [74, 75]. When the frequency exceeds \(\omega_h\), \(\sigma''\) increases proportionally on, where \(n < 1\). A low chi-squared value, of order 10^{-13}, suggests best fit for the experimental results; fitted plots are shown by solid lines in figure 14(a). The frequency-dependent region fitting provides an estimate of the DC conductivity, double layer capacitance, bulk capacitance and fractional exponent \(n\) and \(s\), as shown in table 7. The values of \(n\) and \(s\) are less than unity, which suggests that the SPE system is a pure ionic conductor. The addition of SN increases the DC conductivity and reduces the hopping time which indicates the fast ion migration. The addition of SN may alter the polymer chain arrangement; increase in disorder of the polymer chain provides more space for ion transport. The polymer chain becomes flexible due to increased entropy/disorder, which results in faster segmental motion, in agreement with the impedance, FTIR study and dielectric analysis as discussed in previous sections.

Now, the frequency dependence of the imaginary part of the conductivity, along with the contribution of EP, can be written as in equation (14b). The signature of frequency dependent imaginary part of AC conductivity (\(\sigma''\)) for PEO-NaPF_s- x wt. SN (0, 1, 2, 3, 4, 5) is shown in figure 14(b); solid lines depict the best fit to the graph. The complete agreement between the experimental and fitted data in the measured frequency range strengthens the consistency of data.

The most interesting feature observed in all graphs is the presence of EP region along with intermediate frequency DC conductivity region followed by high frequency dispersion region. The growth of the polarization region is not found in all frequency windows, but starts at a particular frequency called the onset frequency (\(\omega_{on}\)), and a minimum in \(\sigma''\) is noted in all polymer electrolyte systems. This decrease of \(\sigma''\) is indication of the increase in the real part of permittivity (\(\varepsilon''\)) as in figure 8. Also, above \(\omega_{on}\), the \(\sigma''\)’s shows the frequency independent region observed in the previous section. Further, with the decrease of frequency a peak in \(\sigma''\) is growing up corresponding to a frequency \(\omega_{max}\), where maximum EP is achieved. Again, the decrease in \(\sigma''\) is evident [76, 77]. The \(\omega_{max}\) can also be correlated with the frequency corresponding to decreasing in the \(\sigma''\) value. It is observed from the figure that with the addition of salt in the pure polymer matrix \(\omega_{on}\) shifts toward the high frequency side window and indicates an increase in the frequency range of EP. Further addition of

---

**Figure 16.** Argand plot of \(M'\) versus \(M''\) for different SN content, a. 0 wt. % SN, b. 1 wt. % SN, c. 2 wt. % SN, d. 3 wt. % SN, e. 4 wt. % SN, f. 5 wt. % SN in PS matrix at room temperature. The inset in Figure 16 a) shows the graph of the pure polymer.
SN in the polymer salt matrix shifts the $\omega_{on}$ toward the high frequency side, and the frequency range of EP is enhanced. Also, the onset of EP corresponds to minima in the plot of the complex conductivity ($\sigma''$) associated with the maxima in the tangent delta plot analysis, as depicted in figures 15(a) and (b). Then, after crossing the peak towards lower frequency, the imaginary part of conductivity $\sigma''$ again shows a decreasing trend [78]. Thus, both the $\sigma'$ and $\sigma''$ variation are in good correlation with each other in terms of the onset frequency ($\omega_{on}$) and $\omega_{max}$.

3.8. Modulus study

Electric modulus study is extensively used for getting better insight into the dielectric behavior of polymer electrolytes; it can be used to investigate conductivity relaxation, by suppressing the EP effect at low frequency. So, the dielectric data is transformed in the modulus data which suppresses the electrode polarization contribution. The electric modulus can be related to the permittivity as follows (equation (17)):

$$M^* = M' + jM'' = \frac{1}{\varepsilon}$$

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \text{ and } M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \quad (17a)$$

$$M^* = j\omega C_0 Z^* = \omega C_0 Z'' + j\omega C_0 Z' \quad (17b)$$

Figure 16 shows the plot of $M''$ versus $M'$ for various SN content; all show a deformed semicircle, which indicates the presence of heterogeneous or broad relaxation processes. The presence of single semicircle is an indication of single relaxation in polymer electrolyte system. Although no complete semi-circle was observed, extrapolation may be done for better visibility. The smallest semi-circle diameter (for SPE 6 in figure 16(e)) is associated with the highest capacitance.

Figures 17(a) and (b) depict the real and imaginary parts, respectively, of electric modulus versus frequency; dispersion is seen in the high frequency region. From the graph, it is observed that $M' \to 0$ at low frequency and large capacitance, as indicated by the long tail; this is attributed to EP effects. The lower value is an indication of ion transport. When we approach the high frequency region, an increase in $M'$ is seen, with a maximum at high frequency; this corresponds to the dispersion part of the polymer electrolyte system. This type of behavior is observed when there is less restoring force for mobile charges on the application of field and indicates the long-range mobility of charge carriers [79]. The value of both real and imaginary parts of the modulus is independent of frequency, indicating the null effect of the electric field in dipole orientation.

The lower value in modulus spectrum ($M''$) in figure 17(b) is an indication of ion transport. From the figure it is observed that $M''$ spectrum approaches relaxation at the high frequency side, which is not within the experimental frequency range. Similar data have been reported previously [36]. The modulus relaxation time ($\tau_m$) has been obtained as explained earlier in the above section and shows a decrease with the addition of SN in the polymer salt system. The low value of relaxation time indicates fast cation migration from one coordinating site (ether group) of PEO to another site, resulting in an increase in ionic conductivity of solid polymer electrolyte. Finally, after the detailed electrical and dielectric analysis, it becomes important to explore the transport parameters, to strengthen the suitability of polymer electrolyte for the desired application in energy storage/conversion devices. Hence, in the next section, transport parameters are evaluated and correlated with the analysis discussed in the previous sections.

3.9. Transport parameters study

The fundamental transport parameters such as number density ($n$), ion mobility ($\mu$) and diffusion coefficient ($D$) are very crucial for completing the dielectric analysis of polymer.
electrolyte systems. The ionic conductivity is a desirable property for polymer electrolytes; it depends directly on the mobility and number of charge carriers. As in earlier results, it was observed that the ionic conductivity increases with the addition of SN in the polymer salt system. This increase may be due to an increased number of free charge carriers owing to the high polarity of SN, which supports the complete dissociation of salt, and enhances the mobility ($\mu$) and diffusion coefficient ($D$) of transport charge carriers (ions). The former of these measures ease of ion transport, and the latter the passage of ions (due to the concentration gradient) through the medium on the application of an external electrical field. Since all three parameters are dependent on each other and all together depends on the number of free ions which is obtained by the deconvolution of the FTIR pattern (as calculated above [21, 80]). The following equations (18a)–(18c) are used to obtain all parameters:

$$\begin{align*}
n &= \frac{M \times N_A}{V_{\text{total}}} \times \text{free ion area (\%)} \quad (18a) \\
\mu &= \frac{\sigma}{n} \quad (18b) \\
D &= \frac{n \mu k_B T}{e^2} \quad (18c).
\end{align*}$$

In equation (18a), $M$ is the number of moles of salt used in each electrolyte, $N_A$ is Avogadro’s number ($6.02 \times 10^{23}$ mol$^{-1}$), $V_{\text{total}}$ is the total volume of the solid polymer electrolyte, and $\sigma$ is DC conductivity. In equation (18b), $e$ is the electric charge ($1.602 \times 10^{-19}$ C), $k_B$ is the Boltzmann constant ($1.38 \times 10^{-23}$ J K$^{-1}$), and $T$ is the absolute temperature in equation (18c).

Table 8 lists the values of $V_{\text{total}}$, free ions (%), $n$, $\mu$, $D$ obtained using the FTIR method [81]. From the table it is clearly observed that the number of free charge carriers increases with the addition of SN to the polymer salt system. This increase in the number of charge carriers is due to the complete dissociation of salt in the polymer salt matrix. Further, mobility also follows the same behavior—the highest mobility value (for SPE 6) system indicates the highest ionic conductivity and also confirms our results obtained from the impedance study (figure 18). As the diffusion coefficient is inversely proportional to the viscosity, it may be said in another way that the viscosity of polymer chains decreases with the addition of SN, which enhances the migration of ions from one coordinating site to another. In the next section it is correlated with the various relaxation times.

This increase in the mobility of an ion in the plasticized polymer electrolyte may be due to the enhancement of free volume or amorphous content, which is a critical requirement for faster ion dynamics. Also, the high dielectric constant of SN results in the release of more charge carriers up to an optimum concentration (4 wt. % SN), followed by a decrease at high SN content. This decrease at high SN content may be due to the insulating or plastic effect of SN, which lowers the number of charge carriers available for conduction. This result is also in absolute agreement with the associated FTIR–ion interaction and conductivity studies, various relaxation times and dielectric analysis which strongly fulfills the criteria of polymer electrolyte material for application in energy storage/conversion devices. As such, we have confirmed the enhancement of ionic conductivity and its correlation with the dielectric analysis as well as transport parameters. Thus, it would be more interesting for us to further correlate the various relaxation times which were obtained from different plots for the same relaxation peak with the ionic conductivity, as analyzed in the following section.

3.10. Correlation of ionic conductivity ($\sigma$) with double layer capacitance ($C_{dl}$) and dielectric strength ($\Delta \varepsilon$) for various relaxation times ($\tau_c, \tau_2, \tau_{\text{tan}}, \tau_m, \tau_\delta$)

After exploring the crucial investigations in brief now, it becomes important to build a correlation between the various parameters that underpin our idea of fast ionic transport in the solid polymer electrolyte. These parameters are free ion carriers, dielectric strength, double layer capacitance, high ionic transference number; the fundamental one is relaxation time ($\tau_c, \tau_2, \tau_{\text{tan}}, \tau_m, \tau_\delta$). This report provides a detailed examination of dielectric parameters over various concentrations of SN at room temperature, and correlation is examined between all of them for a better insight into the ion dynamics of polymer electrolytes.

Figures 19(a)–(h) shows the variation of different relaxation times ($\tau_c, \tau_{\text{tan}}, \tau_m, \tau_\delta$), double layer capacitance and ionic conductivity with the varying concentration of SN. We obtain here a one-to-one correspondence between ionic conductivity with the relaxation time obtained from different processes of the present system. Figures 19(a)–(c) show that the ionic conductivity increases with the addition of SN to the polymer salt matrix; this may be due to release of more free charge carriers, which increases the double layer capacitance or polarization. Also, the increase in dielectric relaxation strength or ionic polarization ($\Delta \varepsilon$) for the same SN content indicates complete dissociation of salt (figure 19(c)). Figures 19(d)–(h), depicting the relaxation times, show a decrease for the highly ionic conducting sample. Basically, relaxation time governs

### Table 8. Values of $V_{\text{total}}$, free ions (%), $n$, $\mu$, $D$ obtained using the FTIR method.

| Sample code | $V_{\text{total}}$ ($\times 10^{-1}$ cm$^3$) | Free ions area (%) | $n$ ($\times 10^{24}$ cm$^{-3}$) | $\mu$ ($\times 10^{-12}$ cm$^2$ V$^{-1}$ s) | $D$ ($\times 10^{-14}$ cm$^2$ s$^{-1}$) |
|-------------|----------------------------------------|-------------------|-----------------|-----------------|-----------------|
| SPE 2       | 0.2                                    | 54.95             | 4.65            | 0.26            | 0.67            |
| SPE 3       | 0.2                                    | 55.17             | 4.67            | 0.39            | 1.02            |
| SPE 4       | 0.2                                    | 57.15             | 4.84            | 0.41            | 1.07            |
| SPE 5       | 0.2                                    | 62.20             | 5.27            | 1.36            | 3.51            |
| SPE 6       | 0.2                                    | 63.27             | 5.36            | 8.73            | 22.5            |
| SPE 7       | 0.2                                    | 58.67             | 4.97            | 0.81            | 2.10            |
the segmental motion of polymer chains—lower values being desirable for better performance of the electrolyte. It can be concluded that the decrease of relaxation time is accountable for the enhanced diffusion coefficient, since diffusion coefficient is in inverse relation to relaxation time. The decrease of relaxation time reveals that the ion dynamics is strongly governed by the segmental motion of the polymer chain and increase of the rate of segmental dynamics enhances the ion mobility [82]. The hopping of ions is a crucial finding here, providing evidence of ion migration in the polymer electrolyte system, and is supported by the decreased hopping time ($\tau_h$) as shown in figure 19(h). This reduction in the hopping time of the ion enables faster jumping of ions from one coordinating site to another, and hence higher ionic conductivity. Also, the increase of relaxation time at a high content of SN indicates the decrease of ionic conductivity due to plasticization effects played by SN.

Finally, we conclude that the above analysis of variation of relaxation times is in absolute agreement with the ionic conductivity value and follows the same trend. This exploration of relaxation times and their correlation is sufficient to briefly explore the ion dynamics, using dielectric analysis. Also, one remarkable point to be noted here is that all relaxation times of same relaxation process follow the order $\tau_{\varepsilon^\prime} > \tau_{\tan\delta} > \tau_z > \tau_m$ as reported by W Cao [53]. This means that the dielectric constant and loss tangent peak lie at a lower frequency, while the impedance and modulus peak are located at high frequency. So, due to their different relaxation peak position, a relaxation peak may be seen in one process and absent in another, as in the modulus spectra shown in figure 17. This agreement suggests the validity of the proposed new loss tangent equation and sigma representation, which agree well with traditional methods. Thus, the detailed investigation of the various relaxation times and their correlation with the ionic conductivity value validate the genuineness of the polymer electrolyte system under investigation.

3.11. Correlation of hopping frequency with the polymer segmental motion

The DC conductivity of a polymer electrolyte system depends on the number density of charge carriers, ion mobility and ion charge: $\sigma_{dc} = \sum q_n n_i \mu_i$. Along with these, the diffusion coefficient ($D$) plays an active role in the ion transport that varies with the hopping frequency. The ion transport in the investigated system is achieved via the coordinating sites provided by the host polymer having an electron rich ether group ($\sim O\sim$). As salt is added to the host polymer, it interacts with the polymer chain and disrupts the polymer chain arrangement, improving polymer flexibility. Also, the number of free charges for migration increases due to better dissociation of the salt and is further improved by the addition of highly polar SN. This results in the hopping of ions via the coordinating sites, and successful hopping of ions favors high ionic conductivity. The hopping contribution is achieved only at a particular frequency, called the hopping frequency. The SN in the investigated system also has a nitrile group, which plays a crucial role in the increase of polymer–ion, polymer–SN and polymer–SN interaction. The overall effect in the polymer matrix is to make the hopping of ions faster than that...
attained by the faster segmental motion of the polymer chain and is in direct correlation with the ionic conductivity and the diffusion coefficient.

The plot of figure 20(a) and (b) explores the strong correlation of the DC conductivity and the diffusion coefficient with the hopping frequency. As the hopping frequency increases with the addition of salt and SN in the polymer matrix, the same effect is evident in the conductivity and the diffusion coefficient. Since the average hopping length is inversely proportional to the hopping frequency ($\langle \lambda^2 \rangle \propto (1/\omega_h)$), a decrease of average hopping length indicates rapid ion migration [65]. This may be due to the disruption of the crystalline phase and enhanced amorphous content which is a principal requirement for the ion dynamics in the study of the polymer.
electrolytes. Thus, it can be concluded that the polymer segmental motion plays an active role in enhancing the ion transport and supports the approach of fast SSIC.

3.12. Self-proposed scheme

During the rigorous analysis of the dielectric study and ion dynamics of SN doped polymer electrolyte systems, the encouraging results inspired the proposal of a logical and convincing model to justify the findings. Figure 21, comprising three stages, describes the ion movement after salt doping in the host polymer and role of SN in such polymer electrolyte systems to complete the mechanism.

**Stage 1**: In stage 1, several polymer chains having an ether group (shown in red color) are shown close to each other due to the crystalline nature of the polymer. Now, the salt is dispersed in the polymer matrix; the salt dissociates into the cation (Na$^{+}$) and anion (PF$_6^-$), owing to the presence of coordinating interaction between the electron rich ether group and the cation (blue circle) while the anion attaches to the methyl group (CH$_2$) of the polymer chain. This separates the ion pair into cation and anion; an individual role is played now by each in the polymer matrix, as sodium has Lewis acid character while the ether group has Lewis base character and this leads to the strong tendency of the cation coordination due to the Lewis acid–base interaction. Thus, the host polymer chain provides a path for ion migration via the coordinating sites. A polymer salt complex is obtained, and interchain separation is noticeably increased in stage 1 (also evident from XRD results).

**Stage 2**: This shows the general interaction between the cation coordinated polymer chain and nitrile group associated SN. The addition of SN in the polymer salt matrix modifies the chain arrangement. One important alteration which is noticed from the experimental results, is an increase in the number of free charge carriers, which is a desirable requirement for fast SSIC. The SN, having a nitrile group (brown color circle) in its structure, helps in the salt dissociation. Now, the cation has two available sites for coordination: the ether group ($\text{C} = \text{O}$) and the nitrile group ($\text{C} \equiv \text{N}$). Also, the SN may penetrate inbetween the polymer chains, diminishing the covalent binding between the chains so that chain sliding becomes smoother, which leads to faster ion transport. The increase of the free volume due to SN penetration indicates the enhancement of the amorphous content that is desirable for the fast ion dynamics system. This increase in free volume is directly linked with the increased interchain separation that increases with the addition of SN in polymer salt complex as in XRD analysis. When there is a variation of SN content in the polymer salt matrix, SN plays a different role in the matrix; this is explained in stage, 3 below.

**Stage 3 (a)**: When the SN content is low, the covalent bonding is diminished as only partial salt dissociation is observed there, as also indicated by the FTIR deconvolution.
Some ion pair is still in the polymer matrix (dotted red circle) and this makes fewer free charge carriers available for transport.

Stage 3 (b): When the SN content is increased, an optimum content is reached at which the salt is completely dissociated and the SN plays an active role in enhancing the ion transport due to chain modification. Here, the nitrile group of the SN and the ether group of the polymer chain compete for interaction with the cation. As oxygen has more electronegativity than nitrogen, the cation has more chance of coordination with the ether group. Also, the Guttmann number (GN) plays a beneficial role, since the GN is higher for oxygen than nitrogen, so the cation has more probability to form a coordination bond with the ether group. Thus, the nitrile group helps in the release of cations from coordinating sites and makes the flow of ions inside the polymer matrix easier by increasing the interchain separation ($R$) in the polymer matrix.

Stage 3 (c): When the SN content is higher than optimal, a negative role is played by the SN, as it has inherent plastic or insulating nature and this behavior dominates at a high content. Two possible reasons may be behind the reduction of ionic conductivity or increase of the relaxation time. One fundamental reason that may exist here is the blockage of a cation by the SN (indicated by a dotted red ellipse) or destruction of conductive paths. Another reason may be the decreased tendency of the chains to slide. In other words, we can say that the viscosity of the polymer chain increases, and it becomes tougher for the cation to move due to the poor chain segmental motion. This was indicated by the increase of relaxation time, owing to slow segmental motion, that directly indicates a reduction in ionic conductivity or slower ion dynamics. Overall, the proposed scheme is in one-to-one correspondence with the electrical and dielectric parameters (such as dielectric constant and relaxation time), which validates the experimental findings.

4. Conclusions

In summary, structural, electric and dielectric analysis has been applied to a polymer electrolyte system consisting of PEO-NaPF$_6$ + SN prepared by solution cast technique. XRD
analysis confirms the decrease of crystallinity with the addition of SN. FTIR spectrum analysis confirms the presence of polymer–ion, ion–ion, interaction and complex phase formation. Impedance spectroscopy provides evidence of enhancement in ionic conductivity, with a maximum at 4 wt. % SN. The transference number has been evaluated about ~0.99 invariably for all polymer electrolyte systems, which confirms the system is purely ionic in nature. The Cole–Cole plot shows dispersion in the low frequency region, and loss tends to zero at high frequency. A decrease in dielectric permittivity and dielectric loss is observed with an increase in frequency, and the high value of dielectric constant for the system having 4 wt. % SN is in good agreement with the impedance study. The loss tangent was plotted against frequency; maximum loss occurring at a particular frequency confirms relaxation in polymer electrolytes, and the peaks shift toward the high frequency side, suggesting faster ion dynamics. The fitting of the real/imaginary dielectric parameters, dielectric loss, tangent delta and real/imaginary part of conductivity confirm the experimental validity; various fitted parameters including dielectric strength, relaxation times etc were evaluated and tabulated. The sigma representation ($\sigma'$ versus $\sigma''$) approach clearly explains the suppressed region of the Cole–Cole plot ($\varepsilon''$ versus $\varepsilon'$) at lower frequencies. The increase in semicircle radius indicates a decrease of relaxation time, hence favoring high ionic conductivity, and is also in one-to-one correspondence with the above results. The frequency dependent real and imaginary conductivity were fitted across the whole frequency window with corresponding equations. Various transport parameters, such as number density ($n$), ion mobility ($\mu$) and diffusion coefficient ($D$) were evaluated to explore the ion dynamics study and are in good agreement with the other experimental data. Finally, the various relaxation times were plotted together; all are in close agreement with the ionic conductivity data, satisfying the order $\tau_c > \tau_m > \tau_i > \tau_h$. Significant correlation was observed between the ionic conductivity, transport parameters and relaxation times in the SN doped polymer salt complex system. A scheme has been proposed which explores the various possible interactions between the constituents of the polymer composite matrix. It may thus be anticipated that the reported study will allow us to apply this polymer electrolyte in the energy storage/conversion device sector.

Acknowledgments

One of the authors (AA) thankfully acknowledges the Central University of Punjab, Bathinda for providing the fellowship and partial support from UGC start-up grant (GP-41). AA is thankful to the Gaurav Joshi and Sourav Kalra Research Scholar at the Central University of Punjab, Bathinda for support in the scheme presentation.

Supporting information

Supplementary discussion on molecular relaxation time and simulated results of Sigma representation. Supplementary figures S1 and S2 (PDF).

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