Na-ion Transportation, Dielectric Relaxation and Electric Modulus Behavior of (PEO/PVDF) Based Nanocomposite Polymer Electrolyte

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Abstract. Nanocomposite Polymer Electrolyte (NCPE) films were prepared with a blend of two polymers: poly ethylene oxide (80 wt% PEO) and poly vinylidene fluoride (20 wt% PVDF) complexed with a salt, sodium perchlorate (7.5 wt% NaClO4) and a nano-filler, iron oxide (x wt% Fe2O3) (i.e., (0.8PEO/0.2PVDF) + 7.5 wt% NaClO4 + x wt% Fe2O3). The complexation and surface morphology of prepared NCPE films have been investigated using XRD and SEM techniques, respectively. Electrochemical Impedance Spectroscopy (EIS) studies were done in the frequency range from 10 Hz to 4 MHz to understand the Na-ion transportation, dielectric relaxation and electric modulus of the prepared NCPE films. The impact of Fe2O3 nano-filler concentration (Fe2O3 wt%) on the Na-ion transportation, dielectric relaxation and ionic conductivity has been studied. The AC conductivity of all the prepared NCPE films at high frequency followed the Jonscher’s power law. The DC ionic conductivity values calculated from the bulk resistance (Rb) of the NCPE films were consistent with the values calculated using Jonscher’s power law. The temperature-dependent ionic conductivity followed the Arrhenius rule between 303 and 333 K. The highest ionic conductivity of 1.13 × 10−4 S/cm was achieved at ambient temperature for the NCPE-16 film (0.8PEO/0.2PVDF) + 7.5 wt% NaClO4 + 16 wt% Fe2O3, and it is due to lowest crystallinity of NCPE-16 film. The ionic and electronic transport numbers of all the NCPE films were calculated using Wagner’s polarization technique.

KEY WORDS: Na-ion transport, Fe2O3 Nano-filler, Ionic conductivity, Electrochemical Impedance Spectroscopy.
1 Introduction

In the past two decades, tremendous research has been conducted on the synthesis and characterization of solid polymer electrolytes (SPEs) [1–5]. The primary objective of this research is to attain the technical requirements of ionic conductivity at room temperature which will in turn useful in designing and developing flexible types of advanced high-performance solid-state rechargeable batteries. The SPE material with appropriate ionic conductivity is an essential constituent in the applications of solid-state batteries. It is used as an ionic conducting medium between the electrodes in the working state and used as a separator for the electrodes in the open state. The SPE material acts as a transport pathway for ions in solid-state rechargeable batteries. Hence, the required ionic conductivity at ambient temperature should be nearby $10^{-5}$ S/cm to meet requirements for practical applications of solid-state rechargeable batteries. Generally, the SPE materials are used in the fabrication of solid-state rechargeable batteries to determine all the energy storage capacity of the battery, the operating temperature range, and safety matters. Most of the SPEs exhibit low ionic conductivity, which is nearby $10^{-5}$ S/cm at room temperature. In order to improve the ionic conductivity at room temperature, various types of approaches have been adopted in the design of SPE materials. The various approaches are (i) using a dipolar liquids with high dielectric constant as plasticizers [6–8], (ii) the addition of ionic liquids [9–11], (iii) the dispersion of inorganic nanoparticles [12–15] and (iv) the addition of plasticizers and nano-fillers simultaneously [16–18]. The main objective of adding various plasticizers and nano-fillers in a SPE is to lower the crystalline in the SPE film. So that the amorphous phase increases with the free volume in the ion-dipole complex of SPE and abridge the ion transport process easily, hence the ion conductivity increased. However, the critical comparison and analysis of the experimental results of PEO-based SPEs with plasticizers and nano-fillers trust that the requirement to lower the crystallinity of PEO to increase ionic conductivity is not a universally accepted fact because several SPEs do not increase or a slight increase in ionic conductivity, but the crystallinity of PEO is significantly reduced. Keeping this fact in mind, several researchers used a mixture (polymer blend) of PEO polymers and other polymers as a matrix when preparing various SPE materials.

Our earlier investigation on the effect of blend composition on ionic conductivity of Na$^+$ ion conducting PEO + PVDF blended polymer electrolytes, the selection of a polymer to blend, the salt to add, and the nano-filler to be disperse played a vital role in obtaining improved ionic conductivity. Mahboube Mohamadi et al. reported the miscibility of the blend of polymers PEO and PVDF [19]. The PEO offers excellent performance due to its exceptional features of its high dielectric constant, highly flexible ethylene oxide segments, and the capability to dissolve various inorganic salts. Therefore, it was a good decision to use a polymer in preparing SPEs [20, 21]. And it was noticed
Na-ion Transportation, Dielectric Relaxation and Electric Modulus Behavior of ... that due to the strong electron-withdrawing functional group (–C–F), PVDF-based SPE has high anode stability [22] whereas the highest ionic conductivity $2.84 \times 10^{-6}$ S/cm was obtained for (80 wt% PEO + 20% PVDF) + 5 wt% NaClO$_4$ SPE film (Optimum conducting composition (OCC)) [23]. In the second system, we have found the effect of NaClO$_4$ concentration on the ionic conductivity of sodium ion-conducting PEO/PVDF solid polymer electrolytes. The highest ionic conductivity $5.94 \times 10^{-5}$ S/cm was obtained for (80 wt% PEO + 20% PVDF) + 7.5 wt% NaClO$_4$ SPE film [24]. In the third system, TiO$_2$ nanofiller was dispersed in (80 wt% PEO + 20 wt% PVDF) + 7.5 wt% NaClO$_4$ SPE film to prepare nanocomposite polymer electrolyte. The highest ionic conductivity $8.75 \times 10^{-5}$ S/cm was obtained for (80 wt% PEO + 20% PVDF) + 7.5 wt% NaClO$_4$ + 15 wt% TiO$_2$ NCPE film [25].

In the present study nanocomposite Polymer Electrolyte (NCPE) films based on a blend of two polymers poly ethylene oxide (PEO) and poly vinylidene fluoride (PVDF) blended with sodium perchlorate (NaClO$_4$) salt and nano-filler iron oxide (Fe$_2$O$_3$) (i.e., (0.8PEO/0.2PVDF) + 7.5 wt% NaClO$_4$ + x wt% Fe$_2$O$_3$ where $x = 4, 8, 12, 16, and 20$) were prepared using solution casting method. Various experimental methods like XRD, FTIR and SEM, have been carried out to study the complexation, functional groups and surface morphology of the prepared NCPE films, respectively. The study of Electrochemical Impedance Spectroscopy (EIS) was made in the frequencies range, 100 Hz and 4 MHz to understand the conductivity, dielectric and electrical modulus spectra of NCPE films in the temperature range, 303 and 333 K. The ionic and electronic transport numbers of the prepared NCPE films were calculated using Wagner’s polarization technique.

2 Experimental

2.1 Materials

The materials such as, polymers PEO (Avg. MW = 2, 00,000 g/mol), PVDF (Avg. MW = 2, 75,000 g/mol), nano-filler Iron oxide (Fe$_2$O$_3$, particle size < 50 nm) and salt Sodium perchlorate (NaClO$_4$, AR grade, purity $\geq 98.0\%$) were obtained from Sigma Aldrich. Common solvent N,N-Dimethylformamide, DMF (99.5%) was obtained from MERCK.

2.2 Preparation of nanocomposite polymer electrolyte (NCPE) films

Using solution casting method, the NCPE films (i.e., (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO$_4$ + x wt% Fe$_2$O$_3$ (where $x = 4, 8, 12, 16, and 20$)) were prepared. Initially, polymeric solution of the blend of polymers PEO and PVDF for weight ratio of 80:20 (80 wt% PEO/20 wt% PVDF) was prepared with the amounts of PEO (2.4 g) and PVDF (0.6 g). The blend of polymers was dis-
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solved in the common solvent DMF at 60°C for 2 h on a magnetic stirrer. Later, 7.5 wt% amount of NaClO\textsubscript{4} (0.225 g) and 4 wt% amount of Fe\textsubscript{2}O\textsubscript{3} (0.12 g) with respect to the total quantity of polymer blend (3 g) was added to polymeric blend solution. The solution was again kept on a magnetic stirrer for 36 h at room temperature for dissolution of the salt and nano-filler to obtain the homogeneous viscous solution. Finally, this polymeric electrolyte homogeneous viscous solution was casted onto a glass petri-dish. For the film formation, the casted solution was kept in a temperature-controlled vacuum oven at 60°C for 48 h and then cooled to room temperature on its own, which resulted in free-standing NCPE film. In the same way, the other NCPE films were prepared according to the taken up composition, (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO\textsubscript{4} - x wt% Fe\textsubscript{2}O\textsubscript{3} (where x = 4, 8, 12, 16, and 20). The NCPE films with their labels are listed in Table 1. Figure 1 shows the procedure of preparation of NCPE films using the solution casting technique.

![Solution Casting Method](image)

Figure 1. Preparation procedure chart of NCPE films using solution casting technique.

2.3 Characterization and impedance spectroscopic studies of NCPE films

All the compositions of the complexation of salt NaClO\textsubscript{4} and nano-filler Fe\textsubscript{2}O\textsubscript{3} with the blend of polymers (PEO/PVDF) were investigated using Shimadzu XRD-7000 X-Ray Diffractometer in the range, 10° and 80°. FTIR studies were
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carried out for all the prepared NCPE films in the range of frequency, 400 cm$^{-1}$ and 4000 cm$^{-1}$ using SHIMADZU FTIR-8400S. The surface morphology of all the NCPE films was studied using Hitachi S-3700N Scanning Electron Microscope. The N4L-PSM1735 Impedance Analysis Interface was employed in the frequency range, 100 Hz to 4 MHz to record the impedance spectra of all the prepared NCPE films. Using impedance spectroscopy data, the electrical, dielectric and electrical modulus properties of prepared NCPE films were calculated. The temperature-dependent ionic conductivity of prepared NCPE films was calculated in the temperature range, 303 and 333 K. Wagner’s polarization technique was used to measure the ionic transport number using a Digital Nano Ammeter (Scientific Equipment Roorkee, Model DNM-121).

3 Results and Discussion

3.1 XRD studies

The XRD patterns of pure PEO (Polymer), pure PVDF (Polymer), NaClO$_4$ (Salt), Fe$_2$O$_3$ (Nano-filler) and (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO$_4$ - x wt% Fe$_2$O$_3$ (where x = 4, 8, 12, 16 and 20) NCPE films are shown in Figure 2. The prominent diffraction peaks at 19.24°, and 23.35° belong to

![XRD patterns of pure PEO, pure PVDF, NaClO$_4$, Fe$_2$O$_3$ and (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO$_4$ - x wt% Fe$_2$O$_3$ NCPE films.](image)

Figure 2. XRD patterns of pure PEO, pure PVDF, NaClO$_4$, Fe$_2$O$_3$ and (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO$_4$ - x wt% Fe$_2$O$_3$ NCPE films.
PEO, which have crystalline segments and represent the crystal planes (1 2 0) and (1 1 2) of the monoclinic crystal structure [26]. There are two other important low-intensity peaks at 36.32° and 20.53°, which belong to the α phase and β phase of PVDF, respectively. Thus, it confirmed the polymorphism of PVDF [27, 28]. The low intensity peaks at 33°, 35°, 43.5°, 53°, 57° and 62° correspond to (0 1 2), (1 1 0), (1 1 3), (0 2 4), (0 1 8) and (1 1 6) crystalline planes belong to pure Fe$_2$O$_3$ [29]. The crystalline peaks at 36°, 32°, 25° and 22° belonging to NaClO$_4$ were not appearing in the NCPE films, which confirms that NaClO$_4$ is completely dissolved in the blend of polymers PEO and PVDF.

3.2 FTIR studies

FTIR is an essential analysis tool that can provide evidence of the functional groups and complexity between the various components in the NCPE films. Figure 3 shows the Fourier transform infrared (FTIR) spectra of (80 wt% PEO + 20 wt% PVDF) + 7.5 wt% NaClO$_4$ – x wt% Fe$_2$O$_3$ NCPE films. Due to the C–O–C rocking bond of pure PEO polymer, a transmittance peak was observed at 1123 cm$^{-1}$. The peaks at 2928 cm$^{-1}$ and 1638 cm$^{-1}$ correspond to the C–H asymmetric stretch bond and C–C stretch bond of pure PEO, respectively. A
strong O–H group of PEO is observed at a broad peak near 3448 cm$^{-1}$. The peak observed at 842 cm$^{-1}$ was due to the C–H$_2$ bond of pure PVDF belonging to its $\beta$ phase [30]. The transmittance peaks observed at 487 cm$^{-1}$ and 512 cm$^{-1}$ were attributed to Fe–O stretching and Fe–O bending bonds, respectively. FTIR spectroscopic analysis showed that adding a small amount of PVDF to the PEO host polymer improved the interaction between the ions and the polymer which increases ion dissociation.

3.3 SEM studies

A scanning electron microscope (SEM) is methodically used to analyze the surface morphology of all the prepared NCPE films. The 1.00 kX magnification SEM images of (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO$_4$ - $x$ wt% Fe$_2$O$_3$ NCPE films are presented in Figure 4 (a-e). From the figure, it can be observed...
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clearly that the NCPE-16 film shows a smooth surface morphology which can be attributed to the lowest crystallinity and it is exhibited the highest ionic conductivity at 303 K. Therefore, the increase in ionic conductivity can be attributed to the decrease in the crystallinity and the increase in the amorphous nature, which helped the transport of ions in the polymer electrolyte, thus increasing the ionic conductivity [31, 32].

3.4 Conductivity studies

The influence of the concentration of Fe$_2$O$_3$ nano-filler (Fe$_2$O$_3$ wt%) on the AC conductivity in the temperature range, 303 and 333 K has been studied. In the shorter frequency region, the conductivity is independent of frequency and in the high-frequency region, the conductivity increases with frequency. The change in conductivity in the high-frequency region can be attributed to the accumulation of charge at the electrode-electrolyte interface, which will produce a polarization effect. According to Jonscher AC power law, the variation of conductivity with frequency, as shown in the following formula:

$$\sigma'(\omega) = \sigma_0 + A\omega^n.$$ 

Here $\sigma'(\omega)$ is the conductivity at a particular frequency, $\sigma_0$ is the conductivity in the low-frequency region, which is independent of the frequency and called DC conductivity, $A$ is a constant, and $n$ is the frequency-exponent (its value varies from 0 to 1). The value of DC ionic conductivity was calculated by fitting the AC conductivity spectra to the best fit of Jonscher’s power law. The calculated values are designated as $\sigma_{dc\ (power\ law)}$ and they are furnished in Table 1. Figure 5 depicts AC conductivity ($\sigma'$) spectra of various NCPE films at ambient temperature. Dotted lines denote the Jonscher’s AC power-law fit using origin 8.5 program of the experimental data.

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>$\sigma_{dc\ (power\ law)}$ (S/cm)</th>
<th>$\sigma_{dc\ (R_b)}$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCPE-4</td>
<td>$3.16 \times 10^{-5}$</td>
<td>$3.27 \times 10^{-5}$</td>
</tr>
<tr>
<td>NCPE-8</td>
<td>$3.95 \times 10^{-5}$</td>
<td>$3.99 \times 10^{-5}$</td>
</tr>
<tr>
<td>NCPE-12</td>
<td>$5.38 \times 10^{-5}$</td>
<td>$5.84 \times 10^{-5}$</td>
</tr>
<tr>
<td>NCPE-16</td>
<td>$1.13 \times 10^{-4}$</td>
<td>$1.16 \times 10^{-4}$</td>
</tr>
<tr>
<td>NCPE-20</td>
<td>$6.14 \times 10^{-5}$</td>
<td>$6.28 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

The values of DC ionic conductivity were also calculated from bulk resistance ($R_b$) of the NCPE films. Figure 6(a) presents the complex impedance spectra of prepared NCPE films at room temperature. Figure 6(b) presents the complex
impedance spectra of NCPE-16 film at various temperatures. From Figure 6(a), it can be noticed that NCPE-16 film has the lowermost value of bulk resistance ($R_b$). Thus, NCPE-16 film has the highest ionic conductivity value at room temperature. The complex impedance spectra of the NCPE-16 film show the semicircle at various temperatures, which indicates that the sample is partially resistive and capacitive. Similar behavior was observed for the prepared NCPE films. The obtained complex impedance spectra were fitted in circles using the origin 8.5 program. The intercept of the fitted circle on $Z'$-axis can be used to get the bulk resistance ($R_b$) [33,34]. The DC ionic conductivity values of prepared NCPE films were determined using the relationship, $\sigma_{dc} = t/(AR_b)$ where $t$ is the thickness; $A$ is the area of cross-section and $R_b$ is the bulk resistance. The

![Complex impedance plot](image)

**Figure 6.** (a) Complex impedance plot of (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO$_4$ - x wt% Fe$_2$O$_3$ NCPE films at room temperature. (b) Complex impedance plot of NCPE-16 film at various temperatures.
Figure 7. Temperature-dependent ionic conductivity of (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO$_4$ + x wt% Fe$_2$O$_3$ NCPE films between the temperatures 303 and 333 K.

DC ionic conductivity values calculated using power-law are good in agreement with the values calculated from the bulk resistance. The DC ionic conductivity values calculated from the bulk resistance and designated, as $\sigma_{dc}(R_b)$ and they are listed in Table 1.

Figure 7 shows the temperature-dependent ionic conductivities of various prepared NCPE films. The temperature-dependent ionic conductivity of all NCPE films follow the Arrhenius rule, i.e. $\sigma = \sigma_0 \exp \left( -\frac{E_a}{kT} \right)$ in the temperature range from 303 to 333 K, where $\sigma_0$ is the exponential pre-factor, $k$ is the Boltzmann constant, and $E_a$ is the activation energy. It can be observed from Figure 7 that the NCPE-16 film shows good ionic conductivity results. Hence, (80 wt% PEO + 20 wt% PVDF) + 7.5 wt% NaClO$_4$ + 16 wt% Fe$_2$O$_3$ (NCPE-16) is the optimization ratio for the current study. The maximum room temperature ionic conductivity of $1.13 \times 10^{-4}$ S/cm was attained for the NCPE-16 film.

3.5 Ionic and electronic transport number measurements

The Wagner polarization technique was employed to calculate the ionic and electronic transport numbers of all the prepared NCPE films. The NCPE film was polarized at a constant DC voltage of 2 V, and the current value was measured over time. The initial current ($I_i$) was the total current, which was generated by electrons and ions. As the polarization increases, the current was blocked by the ions and the final current ($I_f$) was triggered by the electrons. The initial current decreases and remains constant as the ionic species decrease. At this stage, the final current was due to electrons only. The electronic and ionic transport
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numbers were measured with the following formulae:

\[ t_{\text{ion}} = 1 - \frac{I_f}{I_i} \quad [35, 36] \]
\[ t_{\text{el}} = 1 - t_{\text{ion}} \quad [37] \]

The measured values of electronic and ionic transport numbers are furnished in Table 2. From Table 2, it can be observed that the ionic transport numbers of the prepared NCPE films is almost equal to 1, which confirms the domination of ionic conductivity. This result will benefit the shelf life of the battery. Therefore, solid-state rechargeable batteries made of these NCPE films which can store sufficient energy during charging and provide maximum power during discharge [38].

<table>
<thead>
<tr>
<th>NCPE film</th>
<th>Ionic transport number</th>
<th>Electronic transport number</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCPE-4</td>
<td>0.91</td>
<td>0.09</td>
</tr>
<tr>
<td>NCPE-8</td>
<td>0.93</td>
<td>0.07</td>
</tr>
<tr>
<td>NCPE-12</td>
<td>0.95</td>
<td>0.05</td>
</tr>
<tr>
<td>NCPE-16</td>
<td>0.98</td>
<td>0.02</td>
</tr>
<tr>
<td>NCPE-20</td>
<td>0.89</td>
<td>0.11</td>
</tr>
</tbody>
</table>

3.6 Dielectric studies

The dielectric constant of a material is a measure of the energy stored in the material. The following expression gives the relation between frequency-dependent complex dielectric function \( (\varepsilon^*) \) and complex impedance \( (Z^*) \):

\[ \varepsilon^* = \varepsilon'(\omega) - i\varepsilon''(\omega) = \frac{1}{i\omega C_0 Z^*}, \]

where \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary parts of the complex dielectric permittivity respectively, \( \omega \) is the angular frequency and \( C_0 \) is the capacitance of the NCPE film in a vacuum.

Figure 8(a & b) shows the real parts of complex permittivity of \((80 \text{ wt\% PEO/20 wt\% PVDF} + 7.5 \text{ wt\% NaClO}_4 - x \text{ wt\% Fe}_2\text{O}_3)\) NCPE films at room temperature and NCPE-16 film at different temperatures, respectively. Figure 9(a & b) shows the imaginary parts of complex permittivity of \((80 \text{ wt\% PEO/20 wt\% PVDF} + 7.5 \text{ wt\% NaClO}_4 + x \text{ wt\% Fe}_2\text{O}_3)\) NCPE films at room temperature and NCPE-16 film at different temperatures, respectively. From Figure 8(a) and Figure 9(a), it can be observed that among all the prepared NCPE films, the NCPE-16 film possesses highest values of \( \varepsilon' \) and \( \varepsilon'' \). Also,
both $\varepsilon'$ and $\varepsilon''$ show the analogous behavior with frequency at various temperatures. As frequency increases $\varepsilon'$ decreases and reaches saturation and $\varepsilon'$ is higher at lower frequencies, which is due to the polar groups, the orientation of the ions and space charge polarization near the electrodes. Dielectric constant value is lower at high frequencies because of dielectric relaxation [39–41]. Both the real permittivity ($\varepsilon'$) and imaginary permittivity ($\varepsilon''$) have not found maximum relaxation which indicates the increase in ionic conductivity is mainly due to the increase in mobile ions.

Dielectric loss deals with the inherent dissipation of electromagnetic energy in dielectric materials. It is decided by the loss angle ($\delta$) which is equal to tangent of loss angle ($\tan \delta$). Figure 10(a) shows dielectric loss of (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO$_4$ - $x$ wt% Fe$_2$O$_3$ NCPE films at ambient temperature, and Figure 10(b) shows the dielectric loss of NCPE-16 film at different temperatures. The energy loss during the polarization is due to electrode polarization effects and charge transfer which can be calculated from the dielectric loss.

Figure 8. (a) The real parts of complex permittivity of (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO$_4$ - $x$ wt% Fe$_2$O$_3$ NCPE films at room temperature; (b) The real parts of complex permittivity of NCPE-16 film at different temperatures.

Figure 9. (a) The imaginary parts of complex permittivity of (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO$_4$ - $x$ wt% Fe$_2$O$_3$ NCPE films at room temperature; (b) The imaginary parts of complex permittivity of NCPE-16 film at different temperatures.

Both $\varepsilon'$ and $\varepsilon''$ show the analogous behavior with frequency at various temperatures. As frequency increases $\varepsilon'$ decreases and reaches saturation and $\varepsilon'$ is higher at lower frequencies, which is due to the polar groups, the orientation of the ions and space charge polarization near the electrodes. Dielectric constant value is lower at high frequencies because of dielectric relaxation [39–41]. Both the real permittivity ($\varepsilon'$) and imaginary permittivity ($\varepsilon''$) have not found maximum relaxation which indicates the increase in ionic conductivity is mainly due to the increase in mobile ions.

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Figure 10. (a) Tangent loss of (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO₄ + x wt% Fe₂O₃ NCPE films at room temperature; (b) Tangent loss of NCPE-16 film at different temperatures.

Figure 10(a & b) shows that the dielectric loss (\(\tan \delta = \varepsilon''/\varepsilon'\)) is proportional to the frequency for lower frequencies and reaches a maximum value at a particular characteristic frequency, later the dielectric loss (\(\tan \delta\)) decreases with increasing frequency. As the temperature increases, the peak shifts towards the higher frequencies (right shift) [42]. The peaks obtained at specific characteristic frequencies are due to the polarization of the electrodes. If \(f\) is the frequency associated with the relaxation characteristic peak, then the relaxation time (\(\tau\)) is given by \(\tau = 1/2\pi f\). Therefore, the ionic conductivity increases with decreasing relaxation time [43]. From Figure 10(a), it is clearly observed that NCPE-16 film has the highest relaxation peak highest ionic conductivity among all the NCPE films. At high temperatures, the relaxation time was reduced due to heat generated defects of the NCPE films which results higher conductivity. This is consistent with the behavior of Arrhenius.

3.7 Electric modulus studies

Electric modulus formalism (\(M^*(\omega)\)) is often used to confirm the influence of electrode polarization (EP) effect on the complex dielectric permittivity (\(\varepsilon^*(\omega)\)) of NCPE films at low frequencies. For the frequency range dominated by the electrode polarization effect of the complex permittivity (\(\varepsilon^*(\omega)\)) the spectrum of NCPE films, the value of the \(M^*(\omega)\) spectrum remains close to zero in the same frequency range. This is due to the following fact that the product of the complex electric modulus and complex dielectric permittivity is unity. Complex electric modulus formalism explains the charge transport process, including ion dynamics and the relaxation mechanism of conductivity with frequency and temperature [44, 45].
The complex dielectric permittivity ($\varepsilon^*(\omega)$) and complex electric modulus ($M^*(\omega)$) in the electric modulus, formalism are related as

$$M^* = \frac{1}{\varepsilon^*} = \frac{\varepsilon' - j\varepsilon''}{|\varepsilon^*|} = M' + jM'' = \frac{\varepsilon'}{\varepsilon^*} + j\frac{\varepsilon''}{\varepsilon^*},$$

where $M'$ and $M''$ are the real and imaginary parts of the complex modulus ($M^*(\omega)$) respectively. Figure 11(a) shows the real parts of electric modulus spectra ($M^*(\omega)$) of (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO$_4$ - x wt% Fe$_2$O$_3$ NCPE films at ambient temperature and Figure 11(b) shows the real parts of electric modulus spectra of (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO$_4$ - x wt% Fe$_2$O$_3$ NCPE films at room temperature; (b) shows the real parts of electric modulus spectra of NCPE-16 film at different temperatures.

Figure 12(a) shows the imaginary parts of electric modulus spectra ($M^*(\omega)$) of NCPE-16 film at different temperatures. The imaginary parts of electric modulus spectra of (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO$_4$ - x wt% Fe$_2$O$_3$ NCPE films at room temperature and Figure 11(b) shows the real parts of electric modulus spectra of (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO$_4$ - x wt% Fe$_2$O$_3$ NCPE films at room temperature; Figure 12(b) shows the imaginary parts of electric modulus spectra ($M^*(\omega)$) of NCPE-16 film at different temperatures. Figure 11(a) shows that $M'$ exhibits excellent dispersion with increasing frequency and tends to reach a saturation value at high frequencies. Figure 12(a) shows that $M''$ has...
a relaxation peak. The lower value of $M'$ in the low-frequency region allows ionic conduction movement, while $M''$ shows a relaxation peak, which confirms the ionic nature of the NCPE film. The peak indicates the relaxation of the sodium ions' conductivity. The low-frequency side of the maximum value shows the long-range movement of charge carriers, and the high-frequency side of the maximum value shows the cage movement of moving ions. The movement of charge carriers receives gain as the temperature rises. This shortens the relaxation time and shifts the peak value of $M''$ to a higher frequency [46].

4 Conclusions

Structural properties, ion transportation, dielectric relaxation and electric modulii properties of (80 wt% PEO/20 wt% PVDF) + 7.5 wt% NaClO$_4$ + $x$ wt% Fe$_2$O$_3$, where $x = 4, 8, 12, 16, \text{and } 20$) are studied. The XRD patterns confirmed that all the NCPE films exhibited the amorphas nature. Also confirmed that the NaClO$_4$ salt and Fe$_2$O$_3$ nano-filler are completely dissolved in the NCPE films. The FTIR provide evidence of the functional groups and complexity between the various components in the NCPE films. The SEM studies confirm that the NCPE-16 film has smooth surface morphology and represented the lowest crystallinity among all NCPE films. The values of DC ionic conductivity follow the Arrhenius rule in the the temperature range, 303 and 333 K. The NCPE-16 film has the highest ionic conductivity of $1.13 \times 10^{-4}$ S/cm at ambient temperature, and it is attributed to the decrease in crystallinity. The ionic and electronic transport numbers of NCPE films are almost equal to 1, which confirms dominance of ionic conductivity, which will benefit the battery’s shelf life. Thus, solid-state rechargeable batteries can be made of these NCPE films which can store sufficient energy during charging and provide maximum power during discharge.

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