Ion dynamics and dielectric relaxation behavior of PVA-PVP-NaI-SiO$_2$ based nano-composites polymer blend electrolytes

Pankaj Singh, P.N. Gupta, A.L. Saroj

Department of Physics, Institute of Science, Banaras Hindu University, Varanasi, 221005, India

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**ABSTRACT**

In this paper we have reported the loading effect of SiO$_2$ nano-particles on the electrical transport properties and dielectric relaxation behavior of the PVA-PVP-NaI based nano composite polymer blend electrolytes (NCPBEs). Solution cast technique has been used for the preparation of PVA-PVP-NaI-SiO$_2$ based NCPBE films. AC impedance spectroscopic technique is used for the study of electrical conductivity and dielectric properties. The frequency dependence of AC conductivity with different SiO$_2$ concentration for all prepared NCPBEs obeys the Jonscher power law (JPL) with exponent, n = 1. The dielectric permittivity ($\varepsilon'$&$\varepsilon''$), electric modulus (M & M$''$) vs. frequency plots at different concentrations and temperatures were reported. Mobility ($\mu$), dc conductivity ($\sigma_d$) and total number of charge carriers (N) were estimated and found that mobility varies with the SiO$_2$ concentration. Sample containing 0.6 wt% of SiO$_2$ shows optimum dc conductivity, $\sigma_d$ ~ 5.07 $\times$ 10$^{-6}$ S/cm with $\mu$ ~ 4.60 $\times$ 10$^{-7}$ and N ~ 6.98 $\times$ 10$^{21}$. Dielectric relaxation peaks have been observed for all samples and relaxation time (\tau) is minimum for 0.6 wt%SiO$_2$ based NCPBE film.

1. Introduction

Nano-composite polymer blend electrolytes (NCPBEs) have generated great interest in developing new materials because of their potential application in the fabrication of electrochemical devices such as batteries, super capacitors, fuel cell etc [1,2]. The uses of solid polymer electrolytes based on alkali metal salts have certain limitations such as low ionic conductivity at room temperature, low mechanical flexibility and poor chemical stability [3-5]. Several methods have been incorporated for improving these properties such as cross-linking, polymer blending [6, 7], use of nano-fillers [8] and plasticizers [9]. In these methods, though polymer blending is cost-effective but this method has drawn much attention for improving the matrix properties due to interactions between the functional groups of polymers via hydrogen bonding and ionic interactions [6]. Poly (vinyl) alcohol (PVA) containing hydroxyl (O–H) is a semi-crystalline polymer, studied enormously because of their many important physical and chemical properties such as high dielectric constant, water solubility, good charge storage capacity and dopant dependent electrical, dielectric and optical properties [10]. Water solvable polymer, poly(vinyl) pyrrolidone (PVP) also have a special attention among the conjugated polymers because of its good environmental stability, easy processability and amorphousness which support easy charge transportation [11–13]. The interactions between PVP-PVA were taken place via inter-chain hydrogen bonding between carbonyl group (C=O) of PVP and hydroxyl group (O–H) of PVA [14]. Addition of nano-fillers in polymer matrices has been found to be an effective method of enhancing the ionic conductivity of polymer material for higher thermal and mechanical stability which are additional requirements of solid polymer electrolytes for a wide range of electrochemical applications [15,16]. Nano-fillers provide a better ion conductive pathway by enhancing the surface area to volume ratio in the polymer matrices [17–19]. The enhancement of conductivity in the nano-composite polymer electrolytes has been described by two factors, first is the large specific surface area provided by the nano-particles (at nano scale) and second is the interactions that occur between the surface groups of the nano-particles and the polymer matrix [20–22]. The addition of nano-particles creates disorder in the polymer matrix which is directly associated with bulk ionic conductivity [23]. The nano-composite polymer films show the better electrochemical stability towards a metal anode and also enhanced cation transport number [24–26]. The ion conduction mechanism in these polymer electrolytes has not been studied so for and our interest regarding the study of ion-dynamics behavior of such systems are of the fundamental importance. A systematic study for understanding the role of nano-particles in

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* Corresponding author.
E-mail address: al.saroj@bhu.ac.in (A.L. Saroj).

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modified the electrical and dielectric properties of NCPBES will provide an opportunity to develop new ideas in this field. In the present work we have studied the loading effect of SiO$_2$, nano-particles on the ac conductivity behavior, dielectric properties, mobility and total number of charge carriers of PVA-PVP-NaI based NCPBE using AC impedance spectroscopic technique.

2. Materials and experimental details

PVA having average molecular weight $\sim$1,25,000 g/mol with purity $>98\%$ and degree of hydrolysis $\sim$89%, PVP with average molecular weight $\sim$44,000 g/mol with purity $>99\%$ and salt, sodium iodide (NaI) salt were procured from Merck, Germany. SiO$_2$ nano-particles having average particle size $\sim$14 nm with surface area 200 $\pm$ 25 m$^2$/g was purchased from Sigma Aldrich. Deionized distilled water was used as a solvent for the preparation of PVA-PVP-NaI-SiO$_2$ based polymeric films.

The NCPBES have been prepared using solution casting technique. In this technique the desired wt\% ratio of materials ([50PVA-50PVP]:30NaI): xwt\%SiO$_2$ with x 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 were mixed separately in solvent and the mixture was kept in oven at 50 C for 24 h to swell, after that the solution is stirred continuously for 5 h to obtained the viscous slurry. The viscous slurry was poured on polypropylene Petri-dishes and put into the oven at 40 C for 10 days in order to evaporation of solvent, after that free standing films having thickness of $\sim$50–90 µm were obtained. All the prepared films were kept in evacuated desiccators for further measurements. The prepared polymeric films were characterized using AC impedance spectroscopic technique in the frequency range 20Hz-1MHz by using high precision Wayne Kerr impedance analyzer 6500 B with bias voltage 100 mV.

3. Results and discussion

3.1. AC conductivity analysis

Frequency dependent ac conductivity formalism has been used to explore the ion dynamics behaviour of various polymer electrolytes [10, 13,27]. For polymer electrolytes it is expected that ac conductivity curves follows the Jonscher’s Power law (JPL) ($\sigma_{ac}$ $\propto$ $\omega^{n}$ $\propto$ $\sigma_{dc}$ $\propto$ $A^\beta$), where the exponent n is restricted to be less than one for different frequency range, A is the temperature dependent parameter, $\sigma_{dc}$ is the dc/bulk conductivity and f is the frequency. The ion motion passes from free hopping (n 0) to correlated hopping (0 < n < 1) [28] followed by caged movement of ions greater than one (n > 1), [29]. Fig. 1(A) and (B) show the ac conductivity spectra of PVA-PVP-NaI-xwt%SiO$_2$ (x 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) at ambient temperature (30 C) and for PVA-PVP-NaI-0.6 wt%SiO$_2$ at different temperatures, respectively. It is observed that the ac conductivity spectra of NCPBES mainly consists two regions (Fig. 1(A)). The first region is frequency independent plateau region assigned to the bulk conductivity of the sample. The bulk ionic conductivity ($\sigma_{dc}$) of the samples was obtained from extrapolation of plateau region to the Y-axis. The second region is high frequency region in which conductivity increases with frequency ($\sigma_{ac}$ $\propto$ $A^\beta$). It is found that 0.6 wt%SiO$_2$ sample consist of three regions indicating low, mid and high frequency region. In the low frequency region, conductivity decreases with increasing frequency due to polarization effect. The values of $\sigma_{dc}$, A and n for all NCPBE based polymeric films at 30 C were obtained from fitted ac conductivity spectra and are listed in Table 1. From Table 1 it has been found that dc conductivity, $\sigma_{dc}$, varies with SiO$_2$ concentration with n > 1 support the caged type movement of ions. Polymer blending also enhances the flexibility of polymer chains creates large free volume which facilitates the translational motion of free ions, hence an increase in the ion mobility [30]. The maximum conductivity was found to be 5.07 x 10$^6$ S/cm at 30 C for PVA-PVP-30NaI-0.6 wt% SiO$_2$ system. Fig. 1 (B) shows the fitted ac conductivity spectra of 0.6 wt % SiO$_2$ based polymer blend electrolyte at different temperatures and it is found that the value of n decreases with increasing temperature (inset Fig. 1(B)). In the low frequency region conductivity decreases with frequency and there is upward shifting of plateau region with temperature due to increase in the bulk ionic conductivity.

3.2. Temperature dependent dc conductivity study

Fig. 2 shows the log $\sigma_{dc}$ vs. 1000/T plots for different wt% SiO$_2$ for PVA-PVP-NaI based NCPBE samples. It shows Arrhenius type thermally activated behaviour (ion dynamics associated with thermal activation

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_{dc}$ (S/cm)</th>
<th>n</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>X 0.0</td>
<td>5.52x10$^6$</td>
<td>1.10</td>
<td>7.31x10$^{12}$</td>
</tr>
<tr>
<td>X 0.2</td>
<td>1.29x10$^7$</td>
<td>1.20</td>
<td>9.42x10$^{12}$</td>
</tr>
<tr>
<td>X 0.4</td>
<td>3.24x10$^7$</td>
<td>1.10</td>
<td>5.07x10$^{12}$</td>
</tr>
<tr>
<td>X 0.6</td>
<td>5.07x10$^6$</td>
<td>1.14</td>
<td>4.27x10$^{12}$</td>
</tr>
<tr>
<td>X 0.8</td>
<td>6.32x10$^6$</td>
<td>1.17</td>
<td>2.04x10$^{12}$</td>
</tr>
<tr>
<td>X 1.0</td>
<td>2.05x10$^6$</td>
<td>1.15</td>
<td>3.36x10$^{12}$</td>
</tr>
</tbody>
</table>

Table 1 Values of power low exponent (n), A and dc conductivity ($\sigma_{dc}$, S/cm) for PVA-PVP-NaI-xwt%SiO$_2$ (x 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) based polymeric films at 303 K obtained from fitted ac conductivity plots.

Fig. 1. Frequency dependent AC conductivity plots for (A) PVA-PVP-NaI-xwt%SiO$_2$ at different SiO$_2$ concentrations and (B) for PVA-PVP-NaI-0.6 wt%SiO$_2$ at different temperatures.
3.3. Tangent loss (tanδ) and relaxation time (τ) analysis

Loss tangent (tanδ) is the ratio of loss factor (ε″) to dielectric constant (ε′) and can be expressed as \( \tan\delta = \frac{\varepsilon''}{\varepsilon'} \). The ε′ is related with the storage of charge carriers near the electrode-electrolyte interface and ε″ estimate the energy losses in movement of charge carriers in the presence of electric field. The real (ε′) and imaginary part (ε″) of dielectric permittivity can be expressed as:

\[
\varepsilon' = \frac{\varepsilon}{\varepsilon' + \omega\varepsilon_0} \quad \text{and} \quad \varepsilon'' = \frac{\varepsilon}{\varepsilon' + \omega\varepsilon_0}
\]

where ε′ and ε″ are the real and imaginary part of impedance, \( C_0 = \frac{\varepsilon}{\varepsilon' + \omega\varepsilon_0} \) is capacitance of free space, \( \varepsilon_0 \) is the permittivity of free space, \( l \) is the thickness of the polymeric film and \( a \) is the area of the blocking electrode and \( \omega = 2\pi f \) is the frequency. The relaxation time, \( \tau \) is described as, \( \tau = \frac{1}{\pi\varepsilon_0\varepsilon''(\omega)} \) (i.e. maximum power transfer taken place) where \( f \) is the dielectric relaxation peak frequency. Fig. 3(A) shows that the variation of tanδ with frequency, for NCPBEs at different wt% of SiO2. It is observed that tanδ peaks were shifted towards the higher frequency region with the addition of SiO2 nano-particles and it is optimum for 0.6 wt% SiO2 sample due to fast segmental motion of polymer chains of NCPBEs [36] and tanδ decreases in high frequency region. The peaks observed in tanδ vs. frequency plots reveal the matching of the relaxation frequency of polymer chains/dipole orientation with the frequency of applied external electric field. Fig. 3 (B) shows the variation of relaxation time, \( \tau \) with SiO2 concentration in prepared NCPBEs. It has been observed that the relaxation time, \( \tau \) is minimum for 0.6 wt% SiO2 sample shown in Fig. 3(B).

3.4. Complex dielectric permittivity study

Study of complex dielectric permittivity (ε*) is an important tool for understanding the electrode polarization effect and energy dissipation in terms of dielectric constant (ε′) and dielectric loss (ε″), respectively of ion conducting materials. It is given by the equation:

\[
\varepsilon^* = \varepsilon + \frac{i\omega\varepsilon_0}{\varepsilon''}
\]

Where \( \varepsilon_1 \), \( \varepsilon_0 \), and \( \varepsilon'' \) is the dielectric constant at very high frequency (\( \omega \rightarrow \infty \)), \( \varepsilon'' \) and \( \varepsilon'' \) is the relaxation time. Real and imaginary parts of the dielectric permittivity are expressed as:

\[
\varepsilon' = \frac{\varepsilon_1}{\varepsilon_0} \quad \text{and} \quad \varepsilon'' = \frac{\varepsilon_1\omega}{\varepsilon_0}
\]

Thus the value of \( \omega\tau \) changes from 0 to \( \infty \) and hence the dielectric constant varies from \( \varepsilon_0 \) to \( \varepsilon_1 \), i.e. decreases due to blockage of ion migration or ion diffusion [37, 38]. Fig. 4 (A-B) show the variation of ε′ and ε″ with frequency at different concentration of silica nano-particles for PVA-PVP-NaI-SiO2 based NCPBEs and Fig. 4 (C-D) at different temperatures for PVA-PVP-NaI-0.6 wt% SiO2, respectively. It has been observed that in Fig. 4 the values of ε′ and ε″ are high in low frequency region because of space charge polarization near the electrode electrolyte interface [39,40]. With increasing the concentration of silica nano-particles in PVA-PVP-NaI polymer matrix there is an increase of localization of charge carriers near the electrode electrolyte interfaces hence an increase in ε′ and ε″ values, respectively. Dielectric loss (ε″) spectra for 0.6 wt% SiO2 based NCPBE consists single relaxation peak associated with the dielectric relaxation of polymer blend. At the higher frequency, changing of applied field direction has been rapid periodic reversal that create a negative environment for dipole alignment, so that ion diffusion stop in the direction of field and hence ε′ and ε″ both decreases with increasing frequency for all PVA-PVP-NaI-SiO2 based NCPBEs [41].

3.5. Variation of ε′ and ε″ with temperature and SiO2 concentration

The variation of ε′ and ε″ with temperature at different frequencies for PVA-PVP-NaI-0.6 wt%SiO2 and the variation of ε′ and ε″ with silica nano-particles (SiO2) at different frequencies are shown in Fig. 5.(A-B)
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and Fig. 5 (C-D), respectively. It is observed that in Fig. 5 (A) the values of \( \varepsilon' \) increases with temperature exponentially and decreases with frequency. The values of \( \varepsilon'' \) for 0.6 wt%SiO\(_2\) containing sample increases exponentially with temperature as well as frequency (Fig. 5 (B)). This is because of re-orientation of dipoles (functional groups of PVA and PVP) attached with the chains of polymer/polymer blend [42]. The values of \( \varepsilon' \) and \( \varepsilon'' \) are optimum near 0.6 wt%SiO\(_2\) nano-particles loading in the PVA-PVA-NaI based sample and their values decreases with frequency (Fig. 5 (C-D)). With the loading of SiO\(_2\) in PVA-PVP-NaI based films, the \( \varepsilon' \) is optimum for 0.6 wt% containing sample, because of weak interactions between loan pair of electrons of oxygen of SiO\(_2\) with the functional groups of PVA-PVP polymer blend. The high values of permittivity indicates the enhancement in ionic conductivity expressed as \( \sigma_{dc} \). Nqμ where N, q and μ are the total number of charge carrier density, electric charge and mobility, respectively.

3.6. Electric modulus studies

Ion transport mechanism of prepared NCPBEs was further explored by using electric modulus formalism [43]. The complex electric modulus (\( M^* \)) is the inverse of the complex dielectric permittivity (\( \varepsilon^* \)) and can be expressed as:

\[
M^* \sim \frac{1}{\varepsilon^*} \sim \frac{1}{\varepsilon' - j\varepsilon''} = \left( \frac{\varepsilon'}{\varepsilon''} \right) \left( \frac{j\varepsilon''}{\varepsilon''} \right)
\]
where $M'$ and $M''$ are the real and imaginary parts of the complex electric modulus $M'(o)$ in terms of $\varepsilon'$ and $\varepsilon''$. The frequency dependence of $M'$ and $M''$ spectra at different wt% of SiO$_2$ for PVA-PVP-NaI-SiO$_2$ based NCPBEs is shown in Fig. 6(A-B). Similarly, frequency dependent variation of $M'$ and $M''$ at different temperatures for highest conducting NCPBEs i.e. 0.6 wt% of SiO$_2$ are shown in Fig. 6(C-D). It is observed that the electric modulus in low frequency region is approaching to zero due to negligible contribution of electrode polarization. The value of $M'$ and $M''$ as a function of frequency at ambient temperature for NCPBEs dispersed with different wt% of SiO$_2$ suggests that large capacitance is associated with the electrodes and confirms the non-Debye behavior. At high frequencies the value of $M'$ and $M''$ increases with increasing frequency. It is also observed that with increasing the temperature the value of $M'$ and $M''$ decreases due to increase in mobility of charge carriers with temperature. The value of $M'$ and $M''$ shows some relaxation peak which shifts towards higher frequency with increasing temperature because of faster ionic motion, leading to decrease in relaxation time. Thus the charge carriers are thermally activated. From Fig. 6 (A-B) it is also observed that $M'$ and $M''$ vs. frequency spectra are much broader than what is expected for the ideal Debye type and show the asymmetry and skewed towards the high frequency. Such a broad nature of peak is an indication of the non-Debye type relaxation.

3.7. Variation of $\sigma_{dc} (\text{Scm}^{-1})$, $N (\text{m}^{-3})$ and $\mu (\text{m}^2\text{V}^{-1}\text{s}^{-1})$ with silica nano-particles

The ion diffusivity ($D$), $\mu$ and $N$ can be obtained by analyzing the dielectric and ac conductivity spectra. $D$ can be estimated by using the relation: $D = \frac{2\mu_N \varepsilon_0^2}{2 \tan \delta_{max}}$ where $\tan \delta_{max}$ is the maximum value of $\tan \delta$, $f_{max}$ is the frequency at which $\tan \delta$ is maximum and $l$ is the thickness of film [44]. By knowing the value of $D$ (obtained from Fig. 3(A)) and $\sigma_{dc}$ (obtained from fitted ac conductivity spectra) $N$ could be calculated using the Einstein equation: $N = \frac{\varepsilon k T}{6 \pi \eta R}$ where $k$ is the Boltzmann’s constant, $T$ is the absolute temperature and $q$ is the elementary charge. The $\mu$ can also be calculated from the relation: $\mu = \frac{D}{\varepsilon_0}. The value of ion diffusivity varies from $5.99 \times 10^{-6}$ to $3.68 \times 10^{-7}$. The value of total number of charge carriers varies from $2.18 \times 10^{11}$ to $1.84 \times 10^{17}$. The mobility is varied from $2.29 \times 10^{-5}$ to $1.41 \times 10^{-5}$ with the increasing concentration of SiO$_2$. The value of $N$ ($\sim 6.98 \times 10^{21} \text{m}^{-3}$) and $\mu$ ($\sim 4.60 \times 10^{-7} \text{m}^2\text{V}^{-1}\text{s}^{-1}$) is optimum for PVA-PVP-NaI-0.6 wt%SiO$_2$ based NCPBE film.

4. Conclusions

The AC conductivity spectra of NCPBEs with SiO$_2$ concentrations and temperatures follow the Jonscher power law (JPL) with $n > 1$(caged type charge carriers hopping takes place). The maximum dc conductivity at room temperature has been found to be $\sim 5.07 \times 10^{-6} \text{S/cm}$ for 0.6 wt%SiO$_2$ containing NCPBE film with lowest activation energy $\sim 0.79$ eV. Mobility ($\mu$) and total number of charge carriers ($N$) were estimated for all samples and it is found that mobility varies with the concentration of SiO$_2$. Sample containing 0.6 wt% SiO$_2$ shows optimum mobility, optimum total number of charge carriers with highest relaxation frequency ($f_{max}$). Dielectric loss ($\varepsilon''$) spectra for 0.6 wt%SiO$_2$ based NCPBE consists single relaxation peak associated with the dielectric
relaxation of polymer blend. The dielectric permittivity and electric modulus studies shows the non-Debye relaxation behavior.

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