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Chitosan-PEG-NaI based bio-polymer electrolytes: structural, thermal and ion dynamics studies

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Abstract

BPE films based on Chitosan (CS)-PEG)-NaI were prepared using solution cast technique. The prepared electrolyte films were subjected to thermal, structure and conductivity studies using TGA, XRD, ATR-FTIR and AC impedance spectroscopic techniques. The thermal gravimetric analysis (TGA) reveals that the CS and [CS-PEG]-NaI based films decomposes in multi step. Onset decomposition temperature ($T_{\text{d,onset}}$) also decreases with increasing NaI content in CS-PEG based films. The [CS-PEG]-NaI based films are thermally stable up to ~220.2 °C. XRD result shows that CS has semi-crystalline nature having its characteristic peak appeared at 2θ ~ 23.1°. The % degree of crystallinity ($X_c$) decreases with increasing NaI content in CS-PEG based films. ATR-FTIR study confirms the interaction between bio-polymer, CS with PEG and NaI. The sample containing 40 wt%NaI shows dc conductivity value $\sim 7.25 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C. The values of frequency exponent s for BPE films were found to be 0.68 to 0.22. Scaling of ac conductivity with respect to NaI concentration has been performed. Mobility ($\mu$) and total number density of charge carriers ($N$) were estimated from loss tangent spectra.

1. Introduction

Polymer electrolytes are the better candidates for the replacement of liquid electrolytes due to good mechanical strength, improved safety features, ease of fabrication in different shapes and size, good processability, flexibility and proper electrode-electrolyte interface [1, 2]. Polar polymer (like PEO, PVA, PVP, PMMA etc) complexed with inorganic salts like NaPO₃, LiBF₄, LiClO₄ [3–6] are widely used but their low room temperature conductivity has limited the performance of devices. Synthetic polymers are high–cost polymers compared to naturally abundant, renewable biopolymers such as Chitosan (CS), starch and cellulose [7–9]. Bio-polymers as host are very promising candidates for the preparation of electrolytes for long term device applications due to the presence of several attractive groups with side chain and their biodegradable properties [10, 11]. CS is one of the promising natural bio-polymer derived from chitin has naturally abundant, renewable, biodegradable, cost effective and eco-friendly [12]. These materials were used for food packaging materials, drug delivery applications and dietary fibers [13]. CS-based BPEs have potential applications in electrochemical devices such as batteries, dye-sensitized solar cells and double-layer capacitors [14, 15]. Due to the presence of amine (NH₂) and hydroxyl (O–H) groups on the glucosamine unit of CS, it complexes with various inorganic salts and provides free mobile ions in the system. Plasticization is a promising approach to enhance the ionic conductivity at room temperature [16, 17]. Several plasticizers having high dielectric constant and low viscosity such as low molecular weight polyethylene glycol (PEG), ethylene carbonate (EC), and propylene carbonate (PC) can be used to reduce the semi crystalline/crystalline phase of host matrix. Degree of amorphosity of plasticized polymer electrolyte is mostly depends the functional groups of plasticizers, miscibility of plasticizer with polymers and their compatibility [18]. PEG (low molecular weight) is low toxic, biocompatible and it has high population of O–H groups which interacts with polymer backbone via H–bonding and overall reduces the crystalline phase. In the present study CS is being suggested as host polymer because of its semi crystalline/amorphous nature which may permit faster ionic mobility and low molecular weight PEG-200 as plasticizer.
In the present work [CS-PEG]-NaI based BPEs were prepared using solution cast technique and structural analysis was performed using ATR-FTIR and XRD technique. Thermal and ionic transport properties were investigated using TGA and ac impedance spectroscopic techniques, respectively.

2. Experimental details

2.1. Materials and Preparation of polymer electrolytes films

Chitosan (CS) obtained from Merck, sodium iodide (NaI) procured from Eagal Lab. Pvt. Ltd and polyethylene glycol (PEG-200) purchased from Merck were used as the raw materials for the preparation of [80CS-20PEG]-xNaI (x = 0, 10, 20, 30, 40) based BPEs. The bio-polymeric films were prepared using conventional solution cast technique by taking different desired % wt ratio of CS, PEG and salt, NaI. The samples were prepared by first dissolving CS in hot (~70 °C) diluted acetic acid solution containing 20 wt%PEG (1 gm of CS is dissolved in 100 ml tripled deionizer distilled water containing 2% acetic acid) and later by mixing NaI in desired wt% ratio. The mixture was then stirred continuously for 48 h until homogeneous viscous slurry was obtained. The slurry was poured into polypropylene Petri dishes and dried in oven at 40 °C for 5 days to ensure the removal of solvent. After drying, the films were peeled from Petri dishes. Free standing films were obtained having thickness ~100–120 μm. The films were stored in dried silica gel containing evacuated desiccators for further measurements.

2.2. Characterization techniques

X-ray diffraction (XRD) measurement of the [CS-PEG]-NaI based bio-polymeric films was carried out using the x-ray diffractometer (Philips x-ray diffractometer (PW 1710)) where CuKα source generated x-rays having wavelengths, λ = 1.5406 Å and the glancing angle 2θ was varied from 5°–70° with a step size of 0.1°. The ATR-FTIR spectra of the prepared films were recorded in the transmittance mode using Perkin-Elmer spectrometer in the wave number range 400 to 4000 cm⁻¹ with the resolution of 1 cm⁻¹. Thermo-gravimetric analysis (TGA) technique was used to study the thermal properties of the prepared solid BPE films and their decomposition temperatures. The TGA measurements were carried out using TGA/DSC-I (Mettler Toledo) at the heating rate of 10 °C min⁻¹ in presence of nitrogen as an inert atmosphere with the accuracy of ±0.1 K. Wanye Karr impedance analyzer (6500B) was used for recording the data of conductivity measurement in the frequency range 20 Hz to 10 MHz. For the temperature dependent impedance measurement, the samples were sandwiched between two stainless steel blocking electrodes inbuilt in Wayne Kerr sample holder and the whole assembly was kept in the furnace with the accuracy of ±1°C.

3. Results and discussion

3.1. XRD analysis

Figure 1 shows the XRD patterns of (a) CS-PEG and (b)–(d) [CS-PEG]-xNaI (x = 10, 30, 40) based BPE films, respectively. Pure CS has mainly two characteristic peaks at 2θ ~ 10° (weak reflection) and 19.7° (strong reflection) associated with the crystalline regions which can be used to estimate crystallinity [19]. In the present study, the characteristic peaks of CS-PEG based film appeared at 2θ = 10.2° and 21.3° with riding over halo show the semi-crystalline nature (figure 1(a)) of bio-polymer. These characteristic peaks can be ascribed to the average intermolecular distance of the crystalline part of pure CS membrane. The characteristic peaks associated with the semi-crystalline nature of CS are appeared at 2θ ~ 10° & 21° [20, 21] and it is found that the peaks become broader and 2θ angle shifts to higher region with NaI loading due to the enhancement in amorphous phase. On the addition of salt, NaI the degree of crystallinity is suppressed more effectively due to complexation occurring between the functional groups of CS (such as NH₂ (amine) and corboxamide (C==O–NHR)) with the cations of dopant salt possibly due to weaknesses of intermolecular and intra-molecular hydrogen bonds of CS. At high salt content (40 wt%) the system is almost amorphous and only one broad halo has been observed centered at 2θ = 23.1°.

The % degree of crystallinity (X_c) were estimated from the XRD patterns using the expression:

$$X_c = \frac{A_c}{A_T} \times 100$$

(1)

where $A_c$ is the area under the crystalline peaks and $A_T$ is the total area under the XRD patterns. The area under the crystalline peaks in terms of amorphyity (semi circle has been drawn) / crystallinity (area above the semi circle) were estimated and % degree of crystallinity (equation (1)) is calculated using partial area technique. Figure 2 shows the variation of $X_c$ with the NaI content in CS-PEG based films. From figure 2, it is observed that
$X_c$ decreases with NaI content and the reduction in $X_c$ may be due to complexation/interaction between functional groups of bio-polymer CS with dissociated salt, NaI.

### 3.2. ATR-FTIR analysis

Scheme 1 shows the possible interactions between the functional groups attached with the side chains of CS backbone with Na$^+$ and PEG-200. For identifying the nature of bonding and interactions between functional
groups of bio-polymers with the dopants by knowing the vibrational energy level of the species, infrared spectroscopic analysis was performed. In present work Fourier transform infrared (FTIR) spectroscopy in total attenuated reflectance (ATR) mode was used to study the interactions/complexation between the constituents of the bio-polymer, CS with the dopant salt. Figures 3(a)–(g) shows the ATR-FTIR spectra of (a) NaI, (b) PEG-200 and (c)–(g) [CS-PEG]-xNaI with x = 0, 10, 20, 30, 40 based bio-polymeric films, respectively.

Figures 3(a), (b) shows the ATR-FTIR spectra of salt, NaI and plasticizer PEG-200. The characteristic band frequencies of NaI are appeared at 1655 cm\(^{-1}\) and 3456 cm\(^{-1}\) (figure 3(a)) and in PEG-200 1056–1114 cm\(^{-1}\), 2914 cm\(^{-1}\) and 3385 cm\(^{-1}\) are associated with C-O and C-C stretching, C-H stretching and O–H stretching, respectively (figure 3(b)). It has been found that characteristic peak of NaI appeared at 1655 cm\(^{-1}\) is disappeared in CS-PEG-NaI based films due to dissociation of salt, NaI (NaI → Na\(^+\) + I\(^-\)) and 3385 cm\(^{-1}\) (O–H stretching) of PEG-200 shifted to 3361–3420 cm\(^{-1}\) due to interaction of PEG with functional groups of CS via H-bonding.

From figure 3(c) it is observed that the vibrational bands frequencies associated with CS are appeared at 890 cm\(^{-1}\) (N–H stretching), 1107 cm\(^{-1}\) (C–O stretching), 1345 cm\(^{-1}\) (C–N stretching), 1563 cm\(^{-1}\) (NH\(_2\) (amine), 1600cm\(^{-1}\) (amide (C=O–NHR)) and 3423 cm\(^{-1}\) (O–H stretching)\(^{[22, 23]}\). From table 1 it has been observed that with the loading of NaI in CS-PEG system these vibrational bands have been found to change/shifted at 889 cm\(^{-1}\) (N–H stretching), 1056 cm\(^{-1}\) (C–O stretching), 1352 cm\(^{-1}\) (C=N stretching), 1549 cm\(^{-1}\) (NH\(_2\) (amine), 1651 cm\(^{-1}\) (amide (C=O–NHR)) and 3393 cm\(^{-1}\) (O–H stretching) due to the complexation/interaction between the CS-PEG-NaI.

3.3. TGA analysis
Thermo-gravimetric analysis (TGA) has been carried out to study the thermal properties of bio-polymer based electrolytes. Figures 4(a)–(e) shows the TGA (supported by first derivative of TGA) thermograms of [80 CS-20PEG]-xwt\%NaI with x = 0, 10, 20, 30, 40 based BPE films, respectively. From figure 4 it has been observed that CS-PEG and [CS-PEG]-NaI based films decomposes in multi steps (data are listed in table 2). From figures 4(a) and (b) it is evident that first step of TGA thermograms (weight loss ~17\% and ~16\%) is observed at ~58.2 \(^\circ\)C, associated with the evaporation of to absorbed water/moisture in CS-PEG\(^{[24]}\) and [CS-PEG]-NaI based films, respectively. The second decomposition peak (T\(_{d, peak}\)) observed at ~282.3 \(^\circ\)C is associated with the decomposition of the basic unit of polysaccharides. With the loading of NaI in CS-PEG based films, the T\(_{d, peak}\) associated with CS-PEG-NaI complexed decreased (282.3 \(^\circ\)C to 242.2 \(^\circ\)C). Onset decomposition temperature (T\(_{d, on set}\)) also decreases with increasing NaI content in CS-PEG based films. The CS-PEG-NaI based films are thermally stable upto ~190.2 \(^\circ\)C.

3.4. Electrical conductivity studies
The electrical conductivity of BPE depends on the total number density of charge carriers (N) and mobility (\(\mu\)) of conducting species. Electrochemical impedance spectroscopy (EIS) has been used to study electrical transport properties of prepared BPEs. The Cole-Cole impedance plots of CS-PEG-NaI based bio-polymeric films obtained from EIS are shown in figure 5. From figure 5 it is observed that Cole-Cole plots consist of semicircular region (in high frequency region) associated with relaxation process of bulk and a long tail (in low frequency region) due to the accumulation of free charge carriers near the electrode-electrolyte interface. Cole-Cole plots were used to calculate the bulk ionic conductivity of BPEs by using the following expression: \(\sigma_b = \frac{1}{l R_b}\) where \(l\) is the thickness of the sample in cm, \(B\) is area of the sample in contact with the electrodes in cm\(^2\) and \(R_b\) is the bulk resistance of the film obtained from Cole-Cole plot (imaginary part of impedance, \(Z'\) versus the real part of impedance, \(Z''\) as shown in figure 5). The bulk/dc conductivity of [CS-PEG]-xwt\%NaI with x = 10, 20, 30, 40 based BPE films at 30\(^\circ\)C increases monotonically with increasing the NaI content (table 3) possibly due to

\[
\text{Scheme 1. Possible interaction between the functional group CS with Na}^+\text{ (cation of the salt, NaI) and PEG-200 via H-bonding.}
\]
enhanced plasticized phase. It is evident that the cations and anions of dissociated salt, NaI are responsible for conductivity in CS-PEG based plasticized films. In this system CS-PEG based plasticized phase provides mechanical support and also free volume which enhances the chains flexibility through which ions can easily transport via BPEs. The BP film containing 40 wt% NaI shows bulk/dc conductivity $\sim 1.2 \times 10^{-4}$ S cm$^{-1}$.

### 3.5. AC conductivity study

The ac conductivity spectra for [80CS-20PEG]-xwt%NaI with $x = 10, 20, 30, 40$ based BPE films at 30°C are shown in figure 6. From figure 6 it has been observed that frequency dependent ac conductivity plots are consisted of three regions: low frequency region, frequency independent plateau region and high frequency dispersion region and obeys Jonscher’s power law (JPL) defined as $\sigma_\omega = \sigma_{dc} + A\omega^s$ where $A$ is a constant, $\omega (=2\pi f)$ is angular frequency, $\sigma_{dc}$ is the bulk/or dc conductivity and $s$ is the power law exponent ($s \leq 1$ for
polymer electrolytes [25]. The long tail in ac conductivity spectra in low frequency region is attributed to the accumulation of free charge carriers near the electrode electrolyte interface [26]. The dc conductivity ($\sigma_{dc}$) was estimated by extrapolating the plateau region to the $y$-axis of the ac conductivity spectra. In the high frequency region the capacitive reactance, $X_C (= \frac{1}{j\omega C})$ becomes small and thus ac conductivity, $\sigma_{ac} (=A')$ increases with increasing frequency. The values of $\sigma_{ac}$ obtained from fitted ac conductivity spectra using $\sigma_{ac} = \sigma_{dc} + A\omega'$ are found to be in good agreement with the bulk conductivity values calculated from impedance plots (figure 5) and

Table 2. Onset temperature ($T_{d,\text{onset}}$) and decomposition temperature peaks ($T_{d,\text{peak}}$) for [CS-PEG]-xNaI based BPE films.

| [CS-PEG]-xwt%NaI | $T_{d,\text{onset}}$ | $T_{d1,\text{peak}}$ | $T_{d2,\text{peak}}$ | $T_{d3,\text{peak}}$ | $T_{d4,\text{peak}}$ |
|------------------|---------------------|----------------------|----------------------|----------------------|----------------------|
| $x = 0$          | 232.2               | 281.3                | 363.4                | —                    | —                    |
| $x = 10$         | 224.1               | 188.2                | 272.1                | —                    | 406.2                |
| $x = 20$         | 229.3               | 195.4                | 264.2                | 296.2                | 406.1                |
| $x = 30$         | 196.2               | 222.3                | 260.2                | —                    | 403.1                |
| $x = 40$         | 201.2               | 246.3                | —                    | —                    | —                    |

Figure 4. (a)–(e) TGA (supported by first derivative of TGA) thermograms of [80CS-20PEG]-xwt%NaI with $x = 0, 10, 20, 30, 40$ based BPEs.
the values of power law exponent, s for prepared BPEs are less than 1. It is observed that the $\sigma_{dc}$ increases and s is decreased with increasing NaI content in CS-PEG based system which support the correlated barrier hopping (CBH) type conduction mechanism. The values of $\sigma_{dc}$ conductivity were found to be in good agreement with the bulk conductivity values calculated from Cole-Cole plots (table 3).

### 3.6. Dielectric permittivity and electric modulus study

Chitosan (CS) is a linear amino polysaccharide having different functional groups such as amine (NH$_2$), carboxamide (C=O-NHR) and hydroxyl group (OH) with the CS backbone. Due to the presence of dissociated salt, NaI in CS-PEG based films, the dielectric permittivity and electric modulus studies will play a significant role to understand the ion transport mechanism. The dielectric permittivity is defined as: $\varepsilon'' = \varepsilon' - j\varepsilon''$ where $\varepsilon'$ is the real (or dielectric constant) and $\varepsilon''$ is the imaginary (or dielectric loss) parts of frequency dependent dielectric permittivity. Both $\varepsilon'$ and $\varepsilon''$ are estimated from impedance spectroscopy data obtained from Wayne Karr impedance analyzer (6500B) in the frequency range 20 Hz to 10 MHz. Figures 7(A) and (B) show the $\varepsilon'$ and $\varepsilon''$ spectra at different NaI concentrations in CS-PEG based BPE films. It has been observed that the values of $\varepsilon'$ & $\varepsilon''$ both are increased with increasing NaI content in low frequency region and have decreased exponentially with frequency (figures 7(A) and (B)) while for higher wt%NaI (30 and 40 wt%) containing samples, $\varepsilon''$ spectra showed a non-exponential behaviour (figure 7(B)) with single relaxation peak. Dielectric relaxation (peak in $\varepsilon''$ spectra) is observed due to segmental motion of polymer chains/or reorientation of dipoles attached with the backbone of bio-polymer, CS chains. Higher loaded NaI based sample has large number of free charge carriers (N is optimum for CS-PEG-40 wt%NaI based film) hence the movement of ions from one site to another will perturb the electric potential of the surroundings. The relaxation peak in $\varepsilon''$ spectra shifted towards higher frequency with increasing NaI.

### Table 3. Bulk/dc conductivity data and power law exponent (s) for CS-PEG-NaI based films.

| Sample [CS-PEG]-x wt%NaI | $\sigma_{dc}$ (S/cm) from ac conductivity spectra | Power law exponent (s) | $\sigma_{dc}$ (S/cm) from Cole-Cole plots |
|--------------------------|-----------------------------------------------|------------------------|------------------------------------------|
| x = 10                   | $7.8 \times 10^{-6}$                          | 0.68                   | $3.2 \times 10^{-5}$                      |
| x = 20                   | $3.5 \times 10^{-5}$                          | 0.65                   | $1.5 \times 10^{-5}$                      |
| x = 30                   | $1.1 \times 10^{-4}$                          | 0.54                   | $7.8 \times 10^{-3}$                      |
| x = 40                   | $1.9 \times 10^{-4}$                          | 0.22                   | $1.2 \times 10^{-4}$                      |

Figure 5. Complex impedance plots of (a)–(d) [80CS-20PEG]-x wt%NaI with x = 10, 20, 30, 40 based BPE films.
content reveals that the segmental motion of bio-polymer chains/reorientation of dipoles and ionic motion are strongly coupled [27].

To realize the conductivity relaxation associated with ionic conduction process, the complex electric modulus ($M^*$) study has been performed. The $M^*$ can be expressed as:

$$M^* = \frac{1}{\epsilon''} = M' + jM'' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} + j\frac{\epsilon''}{\epsilon'^2 + \epsilon''^2}$$

where $M'$ and $M''$ are the real and imaginary parts of the complex electric modulus. Figures 9(A) and (B) show $M'$ and $M''$ spectra of CS-PEG-NaI based BPE films at 30 °C. Both the $M'$ & $M''$ spectra has long tail up to some MHz.
frequencies and their values approaches to zero in low frequency region clearly indicates that the electrode polarization makes negligible contribution \[28, 29\]. In figure 8(B), it has been observed that the $M''$ spectra consists conductivity relaxation peaks and these peaks were shifted towards higher frequency side with increasing NaI content in CS-PEG based BP films. The movement of charge carriers and segmental motion of bio-polymer chains are being affected by NaI concentration.

3.7. Scaling of AC conductivity spectra
To get deeper insights about the effect of NaI concentration on ion dynamics behavior of CS-PEG based BP films, the scaling of AC conductivity spectra has been performed using following law \[30\]:

$$\frac{f}{f_0} = s \frac{\omega_c}{\omega}$$

where $f$ is the scaling function independent of concentration and temperature, and $\omega_c$ is angular characteristic frequency. The details of scaling procedure are given in our previous publication \[31\]. The scaling of ac conductivity spectra at different NaI concentrations for CS-PEG based films are shown in figure 9. The successful scaling of data sets; collapse in to single spectra shows that the ion conduction process can be explained by same physical mechanism. In low frequency region a noticeable disparity has been observed (figure 9) because of the conduction mechanism is more sensitive to NaI concentration. In higher frequency region conductivity spectra merges into a single master curve which indicates that the loading of NaI in CS-PEG has no effect on conductivity relaxation.

3.8. Total number density of charge carriers (N), diffusivity constant (D) and mobility (μ) study
Bulk Ionic conductivity ($\sigma_{dc}$) is the most important property of an electrolyte, expressed as $\sigma_{dc} = NqT$ where $N (=\frac{a_{29}K_B}{\alpha^0})$, where $K_B$ is Boltzmann’s constant, $q$ is the elementary charge, $T$ is the absolute temperature, $\sigma_{dc}$ is the dc conductivity and $D$ is the ion diffusivity) is the total charge carrier density and $\mu \left(=\frac{\sigma_{dc}}{q\bar{\epsilon}}\right)$ is the mobility. $D$ can be estimated from $\tan\delta$ versus $f$ plot by using the relation \[31\]:

$$D = \frac{f_{\text{max}}^2}{\frac{32}{5} \pi \tan\delta_{\text{max}} \mu}$$

where $l$ the thickness of the sample, $f_{\text{max}}$ is the frequency at which $\tan\delta$ is maximum and $\tan\delta_{\text{max}}$ is the maximum value of loss tangent \[31\]. The values of $f_{\text{max}}$ and $\tan\delta_{\text{max}}$ were estimated from figure 10. The calculated value of $N$ and $\mu$ for CS-PEG-40wt%NaI based film were found to be $\sim 0.8 \times 10^{22}$ m$^{-3}$ and $\sim 1.4 \times 10^{-7}$ m$^2$ V$^{-1}$ s$^{-1}$ at 30 °C, respectively.

3.9. Ionic transference number measurement
To detect the nature of charge carriers i.e. ionic or electronic, the transference number measurements have been carried out using Wagner’s dc polarisation method \[32\]. Stainless steel electrodes were used as blocking electrodes to determine ionic transference number of [CS-PEG]-NaI based BP films. A typical polarization current versus time...
plot of [80CS-20PEG]−40 wt%NaI film is shown in figure 11. It is observed that initial current (10.5 μA) falls rapidly from its initial value with time and gets saturated at 0.6 μA. The saturation in current has been achieved when the ions movement is balanced by diffusion process. The total ionic transference number was calculated from the polarization current versus time plot (figure 11) using the following standard equation:

\[ t_{\text{ion}} = \frac{I_{\text{sat}} - I_{\text{polarization}}}{I_{\text{polarization}}} \]

where \( I_{\text{polarization}} \) is the

**Figure 9.** (a)–(d) Scaling of ac conductivity spectra at different NaI concentration for [CS-PEG]-xwt%NaI with \( x = 10, 20, 30, 40 \) based BPE films at 30°C.

**Figure 10.** (a)–(d) Loss tangent (tanδ) versus log ω plot for [CS-PEG]-xNaI with \( x = 10, 20, 30, 40 \) based BPE films.
total current i.e. the sum of ionic and electronic currents and \( I_e \) is the residual current i.e. the electronic current. The total ionic transference number was found to be \( \sim 0.94 \) for 40 wt\% NaI containing sample and for other samples its value lies in the range of 0.84 to 0.91. Ionic transference number measurement reveals that the charge species in these prepared BPEs are predominately ions only.

### 3.10. Electrochemical stability window (ESW) measurement

For the determination of maximum operational voltage of an electrolyte for its application in electrochemical devices linear sweep voltammetry (LSV) has been performed using Kithley power source meter 2450 at the scan rate 1 mVs\(^{-1}\). Figure 12 shows the LSV plot of 40 wt\% NaI containing BPE film in the voltage range \( \pm 6 \) V. From
figure 12 it has been observed that the ESW of 40 wt%NaI containing sample is −4.7 to +1.1 V. In present investigation the iodine ion \( (I^-) \) in the BPE can supply the electrons at high negative decomposition voltage. Thus this film can be used as solid electrolyte for the fabrication of dye sensitized solar cells (DSSCs).

4. Conclusions

BPEs based on [Chitosan(CS)-PEG]-NaI were prepared using solution cast technique. XRD results show the semi-crystalline nature of CS. On the addition of NaI, the % degree of crystallinity is suppressed more effectively due to complexation occurring between the functional groups of CS with the cations of dopant salt, NaI. ATR-FTIR analysis also supports the XRD results. The TG analysis reveals that the CS and [CS-PEG]-NaI based films decompose in multi steps and it also confirms the complexation of CS with NaI. Sample containing 40 wt%NaI has optimum dc conductivity at 303 K \( \times 1.2 \times 10^{-4} \, \text{S cm}^{-1} \) with ionic transference number \( \sim 0.94 \). Total number density of charge carriers \( (N) \), mobility \( (\mu) \) and dc conductivity are optimum for 40 wt%NaI containing film. AC conductivity curves follow the Jonscher’s Power law with the exponent \( s < 1 \). The scaled conductivity spectra with respect to salt concentration collapsed into a single master curve (mid and high frequency region) suggesting that all the BPEs have common ion transport mechanism.

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