Preparatory And Enhancement Studies Of Eco-Friendly Polysaccharides Electrolyte Chitosan For Electrochemical Properties With Ammonium Salt

Section A-Research Paper

PREPARATORY AND ENHANCEMENT STUDIES OF ECO-FRIENDLY POLYSACCHARIDES ELECTROLYTE CHITOSAN FOR ELECTROCHEMICAL PROPERTIES WITH AMMONIUM SALT

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Abstract

In recent years, solid state technology is most challenging and it focus towards the proficient electrochemical storage system consuming high conductivity and energy power with non-toxic and reasonable cost. This research work is primarily, concerned with the study of biopolymer electrolyte membrane that exhibit a standard ionic conductivity range. Research has been done to create a environmental acceptable biopolymer electrolyte, Chitosan (CT) complex with Ammonium Nitrate (NH_4NO_3) salt by solution-casting method. Ammonium nitrate with two different compositions ranging of 0.5g and 0.7g has been added to rise the ionic conductivity of Chitosan based biopolymer film. The obtained electrolytes were characterized by XRD, FTIR, and EIS, CV, LSV study. Addition of salt enhances the amorphous nature of the membranes, as confirmed by XRD. The compositions of CT (1g) with (0.7 g) NH_4NO_3 exhibit an excellent degree of amorphous nature. FTIR analysis reveals the complex and vibrational formation between the salt and biopolymer. AC impedance investigation, the ionic conductivity value for CT (1g) with (0.7g) NH_4NO_3 has been determined to be 1.9×10^{-2} S/cm. Dielectric permittivity (ε^*) has been used to study the dielectric behavior of electrolyte. As the NH_4NO_3 content rise, the ε' and ε'' increased as well and proving that they are ionic conductors. The maximum ionic conductivity membrane's electrochemical range of 1.16V has been determined by the application of Linear Sweep Voltammetry (LSV). The final output results suggest that the highest conducting electrolyte film, function well as a proton conductor in electrochemical system.

Keywords: Biopolymer electrolyte; solid state devices; ionic conductivity; electrochemical impedance; complex formation; amorphous and crystalline nature.

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Introduction

Electrochemical energy storage devices (EES) play a vital role in research area to complete the energy requirements in devices like fuel cells, electrochemical double layer capacitors (EDLC), proton, magnesium and lithium batteries, etc (1-4). Acid based membrane such as Naflon, perflurosulphonic leads to environmental climate change and subsequently affects the economic growth, health and polluting power sources. On other hand, polymeric and biopolymeric made electrolyte membranes are most optimists and used in above mentioned energy devices. Biopolymeric based electrolytes are compact, cost-free, and performed high efficient in energy technology field. Biopolymers like Pectin, Chitosan, Cellulose, Starch, Xanthum gum are most often used in electrolytic study [5-8]. Among these, chitosan is most popular and ecological friendly product, originated from chitin. It is a copolymer of glucosamine and polysaccharides of unique cationic group [9, 10]. It is under the group of amine having rigid structure, high crystallinity in nature. Due to its polycationic nature, chitosan has a physiochemical property which leads high performance in barrier properties, proton conductivity and thermal stability [11, 12]. Currently, biopolymer based conducting battery create a huge impact in research area. Mainly development of proton battery receives the intense impact and itself has great applications like ionic mobility, conductivity, great intensity, etc.

Ochubiojo and Rodrigues (2012) reported the ammonium salts such as ammonium chloride, ammonium nitrate, ammonium bromide, ammonium thiocyanate are good proton donors and subsequently used in proton electrolyte system [13]. Blending of chitosan with ammonium salt which is proton (H$^+$) species modifies the chitosan fraction and decreases the crystallization of salt, which increases the mechanical stability and proton donor in ammonium salt rises the ionic conductivity of electrolytes [14-15]. The complex creates a coordination interlinkage between charge carriers of lone pair electrons in chitosan. This regular interaction of charge carriers makes the biopolymer more conductive [16, 17]. Moreover, the addition of plasticization is next level to magnify the conductivity of an electrolyte. The good amount of plasticizer enlarges the mobility of free ions in electrolyte [18].

In a comparison, Hamsan et al [19] reported, ammonium nitrate (NH$_4$NO$_3$) blended with methylcellulose-starch has provided a good result of high ionic conductivity range. Muthuvinayagam and Sudaramahalingam [20] resulted the conductivity of 6.39×10^{-5} S/cm for NH$_4$NO$_3$ incorporated with polymer at room temperature. Aziz et al [21] fabricated the glycerolized chitosan based electrolyte of 1.37×10^{-4} S/cm ionic conductivity and it is more suitable for electrochemical energy applications. Mohamad et al [23] and Abou-Aiad, et al [24] reported on the production of solar cells and fabrication of proton cell using PVA-Chitosan complexed film. Buraidah et al [25] reported the gel polymer electrolyte of chitosan blended with NH$_4$I has resulted the ionic conductivity of 3.73×10^{-7} S/cm. Additionally, compared Chitosan with another ammonium triflate (NH$_4$CF$_3$SO$_3$) has good ionic conductivity of 8.19×10^{-7} S/cm at ambient temperature [26]. Sekhon et al. previously reported NH$_4$F and NH$_4$BF$_4$ doped polymer electrolyte using NMR technique to view the translational and rotational motion of (NH4+/H$^+$) and (F$^-$/BF4-) [27]. However, there is no detailed work has been done with Chitosan and Ammonium nitrate. Hence, we studied the proton conducting electrolyte based chitosan and analyzed the structural, vibrational and electrical properties of resultant film.

2. Materials and experimental methods

In this work, a host polymer Chitosan (CT) (CH$_2$COOH) and salt of Ammonium nitrate (NH$_3$NO$_4$) to be incorporated were purchased from Bangalore, India. The electrolyte membrane was prepared using solution casting method. 1 g of chitosan (Molecular weight, 310,000-370,000 and viscosity 800- 1900 cP) was dissolved in 50 ml of distilled water with 1% of acetic acid solution. Different concentration of ammonium nitrate salt of 0.5g and 0.7g were dissolved individually in 30 ml of distilled water. Table 1 shows the composition of prepared electrolytes. The above mentioned precursors were stirred until attaining a fine homogenous solution. After a period of time, the salt solution and polymer solution were mixed together in one beaker and get stirred until complete dissolution. Finally, the procure resultant solutions were poured into disparate polypropylene Petri dishes and placed it on hot standing film. The resultant films were subjected for different characterizations.
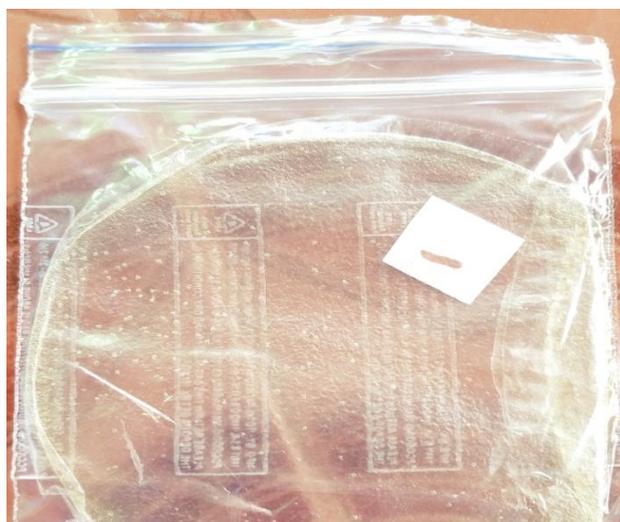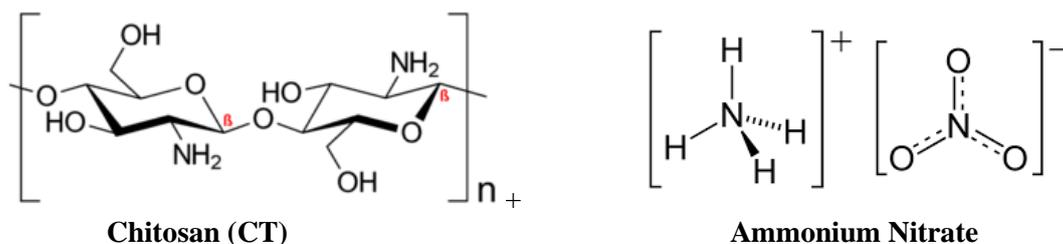
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Chitosan (CT)   **Ammonium Nitrate**

Figure 1. Resultant free standing film

Table 1: Composition of prepared electrolyte

Biopolymer and Salt	Compositions (gram)
Pure Chitosan (a)	1 g
Chitosan : NH_4NO_3 (b)	1:0.5 g
Chitosan : NH_4NO_3 (c)	1:0.7 g

Sample Characterization

Smart lab SE X-Ray was used to study XRD pattern of electrolytes. From XRD, the nature of electrolyte components could be detected. The patterns were obtained with required amount of voltage and current at room temperature. The angle in the scanning range is of $5° \leq 2\theta \leq 80°$. FTIR study was carried out using Perkin-elmer instrument in the wavelength range of 400-4000 cm$^-$1. Complexation and vibrational interaction between salt and polymer are conformed in FTIR studies. It also gives structural, bonding nature and composition of resultant electrolytes. Electrical impedance spectroscopy (EIS) analyzes ionic conductivity and electrical properties of prepared electrolyte. Resultant film has been sliced with the good thickness and sandwiching the sliced piece is placed in between of two stainless steel electrodes to capture the reading.

Result and Discussion

X-Ray Diffraction (XRD)

The XRD patterns of polymer electrolytes are shown in figure 2. XRD is used to identify the differences in both crystalline and amorphous region in polymer electrolyte phase. Generally, amorphous region is ability to witness the ionic motion which consequently increase the conductivity range of material. The Chitosan is the evident of semicrystalline polymer and shows the broad centered peak around 20° which is associated to amorphous region [28]. A visible changes occurred in XRD pattern after addition of NH_4NO_3 salt. As the effect of composition of ammonium salt, crystallinity peak is appeared in sample (b) at the range of $2\theta = 50.1°$ and 55.3° is well compared with previously reported team of Yusof et al [29]. Subsequently, in second case absence of peak or increase in broadness in sample (c) results the thorough dissociation of biopolymer matrix and salt. Increase in broadness is testify the amorphousness of electrolyte material. The crystalline size of electrolytes displayed in Table 2 Crystalline size has been calculated by Debye Schere's equation $D = K\lambda / \beta\cos\theta$. Crystalline peak in sample (b) is due to the reunite of ions which leads the lower conductivity [30]. Where, λ is the wavelength of X-ray

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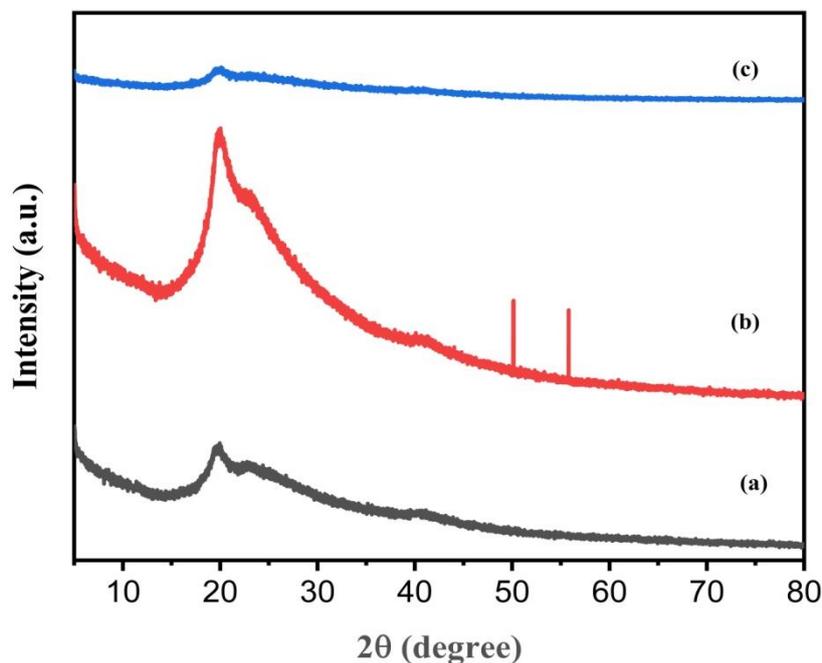
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radiation, K constant (0.89)

Figure 2. XRD patterns of (a) Pure Chitosan (b) CT: 0.5g NH₄NO₃ (c) CT: 0.7g NH₄NO₃

Table 2 Crystalline size (D) of prepared electrolytes

Composition	Diffraction Peak	Crystalline size
1g CT : 0.5 g NH₄NO₃	20.12	1.357
1g CT : 0.7 g NH₄NO₃	20.20	0.296

From Table 2 it is observed that the greatest amorphous region has less crystalline size compared to other sample. Increase in amorphousness which results the decrease in crystallinity range. It clearly shows the well incorporation of salt and polymer matrix in case of sample b. Due to complete mixture, the movement of ions is free which enhances the ionic conductivity range [31].

Fourier Transform Infrared Spectroscopy (FTIR)
The Complexation and molecular interactions of salt-Chitosan are studied from FTIR spectroscopy. Figure 3 shows the FTIR spectra of prepared electrolytes. Presence/absence of peak provide the supreme structural feature of the polymer-salt composition. The pure Chitosan attributes a high vibration band at 3283 cm⁻¹ assigned to O-H stretching [32]. This peak is slightly shifted to 3279 cm⁻¹, 3269 cm⁻¹ in the blended Chitosan-ammonium electrolyte system.

The interaction between Chitosan and ammonium salt, granted valuable understanding over ionic conductivity enhancement of biopolymer electrolyte. The band observed in 2800-3600 cm⁻¹ region is assigned to C-H and O-H groups. The vibration band at 2922 cm⁻¹ of chitosan is moved to 2882 cm⁻¹, 2873 cm⁻¹ for doped electrolytes [33]. The carboxamide and amine bands are appeared within the range of 1480 cm⁻¹ – 1680 cm⁻¹, where the amine band of pure chitosan assigned at 1647 cm⁻¹ is slightly shifted to 1553 cm⁻¹ and 1558 cm⁻¹ for blended electrolytes [34]. The C-O band stretching is assigned at 1029 cm⁻¹ in chitosan is shifted to 1062 cm⁻¹, 1064 cm⁻¹ respectively of blended one [35]. From the spectrum a symmetric band of NO₃- is assigned at 828 cm⁻¹ [36] and their result is comparable with present work. Hence from FTIR spectroscopy, the interlinkage between chitosan and NH₄NO₃ is confirmed. Table 3 shows the presence of different functional group in the polymer electrolytes.
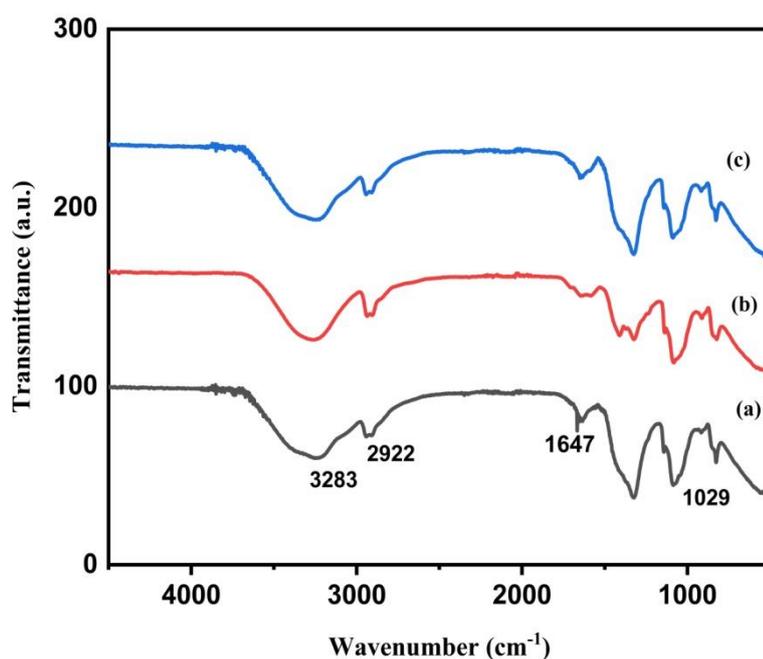
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Figure 3 FTIR spectra (a) pure Chitosan (b) CT:0.5g NH$_4$NO$_3$ (c) CT:0.7g NH$_4$NO$_3$

Table 3 Vibrational peaks and assignment of Pure Chitosan, CT:0.5g NH$_4$NO$_3$ and CT:0.7g NH$_4$NO$_3$

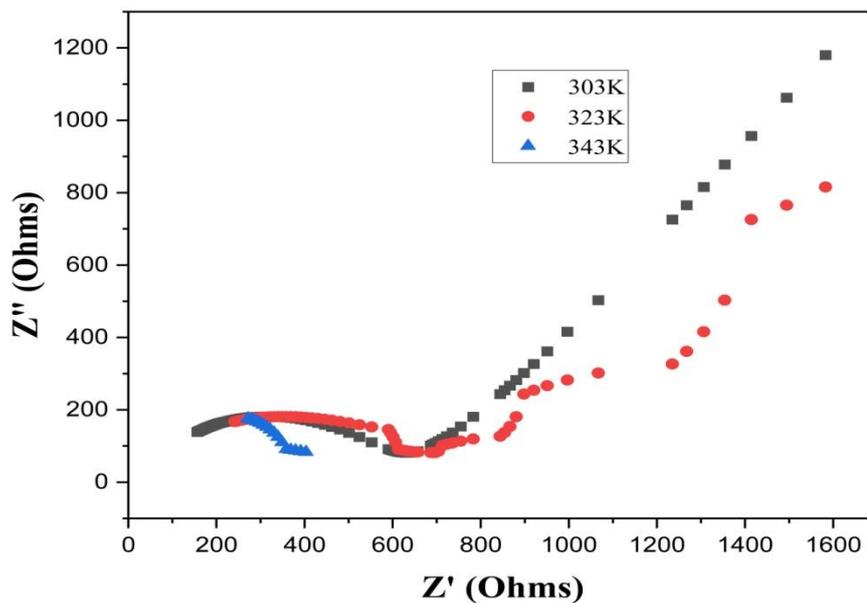| CT	CT:0.5 g	CT:0.7g	Assignments
3283	3279	3269	O-H Stretching
2922	2882	2873	C-H Stretching
1647	1553	1558	Amine group
1029	1062	1064	C=O Stretching
-	823	820	NO$_3$

Impedance analysis

Figure 4 implies the impedance spectra of pure CT and blended polymer electrolytes of different temperatures at 303K, 323K, and 343K. Generally, the Nyquist plot is penned between the real and imaginary part of complex permittivity. In other word, the combination of high frequency semicircle followed by low frequency residual tail. The Chitosan is incorporated with various concentration of ammonium nitrate. The magnitude of basic electrical properties of a cell is also studied using impedance analysis [36.37]. In the present work, the pure Chitosan sample, shows a residual tail with spike, while complexation of salt with polymer plot shows only inclined straight line. The impedance plots of pure Chitosan Figure 4.(i) shows the half semicircular curve at high frequencies and straight line at least frequency area. Addition of salt concentration, leads the vanished of semicircle of polymer electrolyte which exists as shown in Figure 4.(ii) (iii) [38,39]. Conductance of ions has been calculated by using formula,
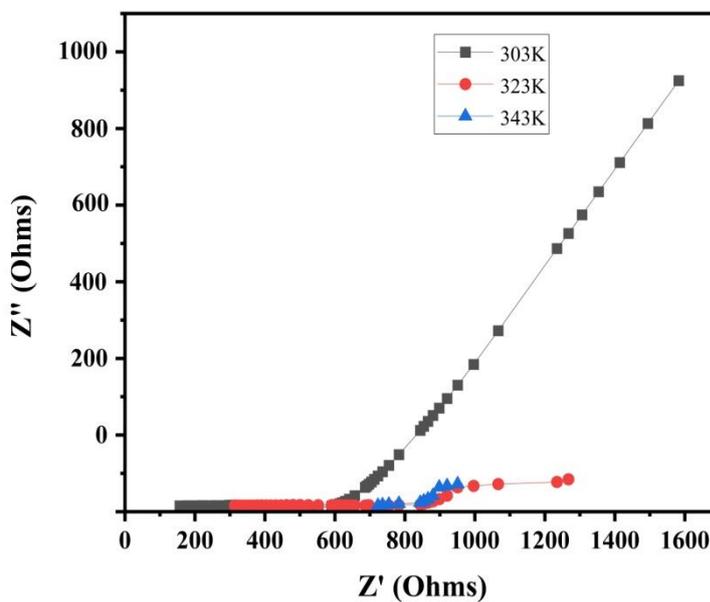
$$\sigma = l/R_bA$$

where R_b is the bulk resistance, A is area of electrolyte and l is the thickness of electrolyte. Table 4 shows the ionic conductivity value of prepared electrolytes. In all the three plots, a point is to be noted that the resistance of electrolyte is decreased as raised in temperature. This is due to transport of ions and dispersed movement of polymer while temperature increases [40]. The highest ionic conductivity increases for CT:0.7g NH$_4$NO$_3$ is 1.98×10^{-2} S/cm is barely matched with previous reported work [41]. From table 4, it is evident that the increases of ammonium nitrate salt increases the conductivity range of electrolyte, which consequently increase the charge carrier concentration. Further addition of NH$_4$NO$_3$ in Figure 4.(i) results the slightly increases in conductivity is due to recombination and neutral pairs of ions [42]. Figure 4.(ii) shows the blending of highest conductivity electrolyte, has an excellent conductivity range due to rises in amorphous nature which confirmed in XRD result. Greatest conductivity results, the flexibility, migration and exchange of ions in polymer matrix [43].

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Table 4. Ionic conductivity range of prepared electrolytes.
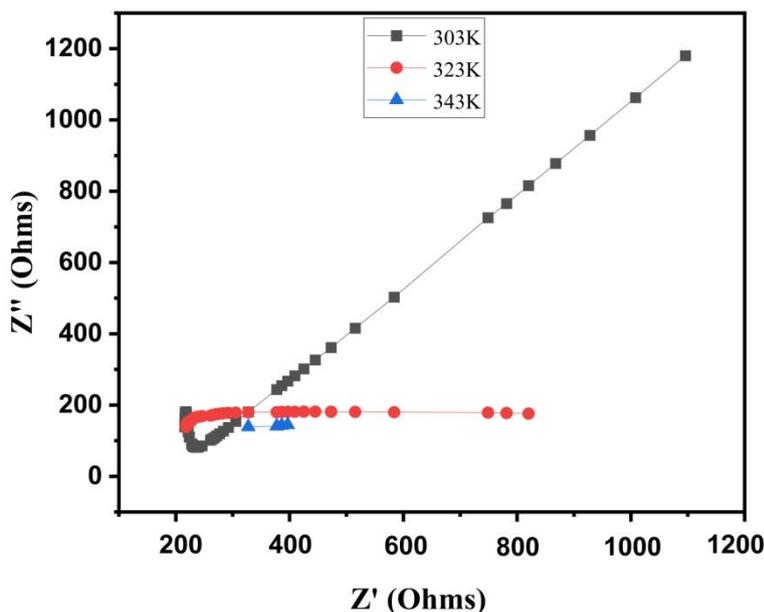
Electrolytes	Conductivity (S/cm)
CT	5.87×10^{-6} S/cm
CT:0.5 g	3.01×10^{-4} S/cm
CT:0.7 g	1.98×10^{-2} S/cm

(i)

(ii)

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(iii)

Figure 4. Impedance spectra of electrolytes, i) CT, ii) CT:0.5g NH₄NO₃, iii) CT:0.7g NH₄N O₃.

Dielectric studies

Dielectric analysis is used to analysis the conductivity behavior of prepared incorporated electrolytes and also reveals the polarization effect in electrolyte interface [44]. Figure 5(i) & 5(ii), shows the frequency dependence of real part (ε') and imaginary part (ε'') of dielectric constant and dielectric loss, ω is the angular frequency. The real and imaginary part is used to calculate from impedance data by the formula is,

$$\varepsilon^* = 1 / j\omega C_o Z$$

where $C_o = \varepsilon_\circ A / t$, $\varepsilon_\circ$ is permittivity of free space, A is area and t is thickness of electrolyte [45]. $\omega = 2\pi f$. Real part explains the dipole alignment related with ionic, space charge polarization. Figure 5 shows the variation of ε' and ε'' of pure Chitosan and complexation of polymer with salt. In this interpretation, the spectra are divided into high and low frequency region. From Figure 5(i) at low frequency, dielectric loss is due to polarization of electrode and the materials energy

barrier may become invariant as a result of applied electric filed. The greatest dielectric constant at low frequency is obtained by ions leap in energy barrier [46]. Movement of charge carrier only in high frequency range, they do not jump and not come into contact with electrode surface. So, dielectric constant is low at high frequency [47]. The value of dielectric constant is increases for 0.7g salt concentration polymer matrix.

From Figure 5 (ii) Imaginary part (ε'') provides the information of increases or decreases of ions transport by applied electric field. In other words the high charge accumulate at boundary interface, which provide the constant movement of ions/dipoles in the field [48]. From dielectric loss plot showed that the transport of ions in the polymer matrix has decreased at high frequency. At low frequency, charge accumulation may cause a rise in dielectric loss [49]. Dielectric loss is maximum for 0.7 g polymer-salt complex, when compared to other polymer matrix.
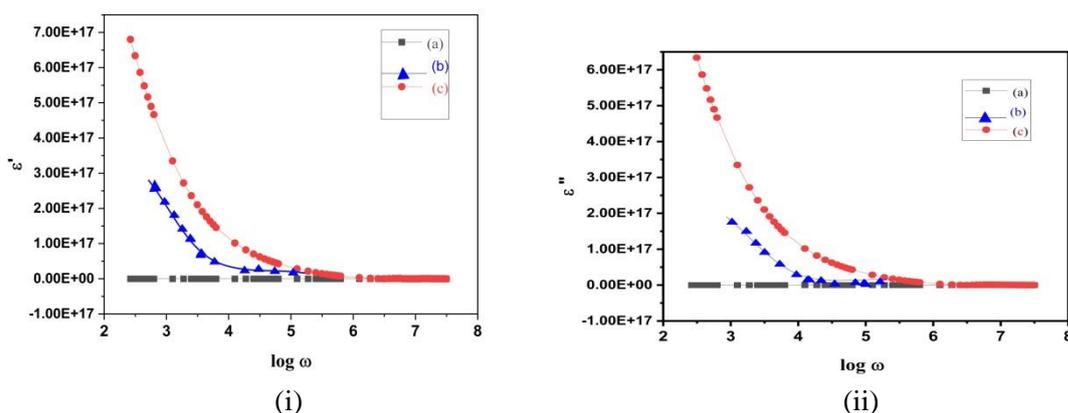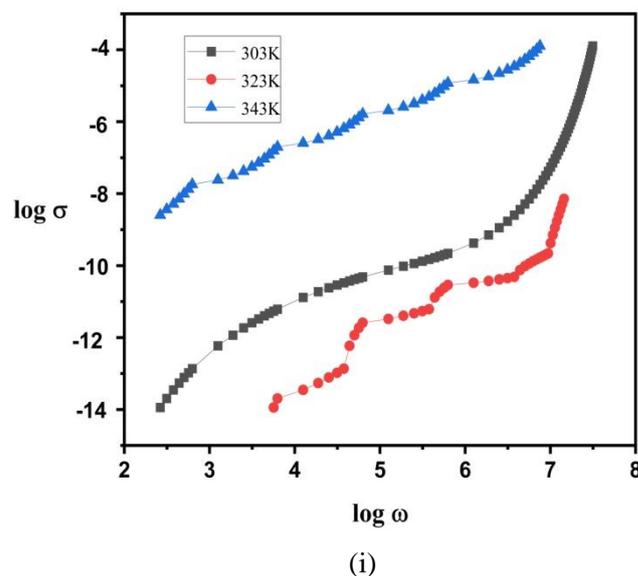
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| (i) | (ii) |

Figure 5(i) dielectric constant of prepared electrolytes (a) CT, (b) CT:0.5g NH₄NO₃ (c) CS:0.5g NH₄NO₃

(ii) dielectric loss of prepared electrolytes. (a) CT, (b) CS:0.5g NH₄NO₃ (c) CS:0.7g NH₄NO₃

Conductance spectra analysis

Figure 6 shows the conductivity logarithmic graphs for each prepared sample at different temperature as function of frequency. The ionic conductivity increases with enhance the temperature from 303 K to 343K. This results the expansion in polymer chain plasticity and decrease of viscosity range [50]. Increase in frequency with respect to temperature, results in the enhancement of conductivity. The mid frequency plateau region attributed to faster ionic movement and increase of bond rotations [51,52]. The appearance of the plateau region is the signature of establishment of ionic conductivity. The increase of frequency greater the charge mobility and increase in enhancement of conductivity of NH₄NO₃ system.

(i)

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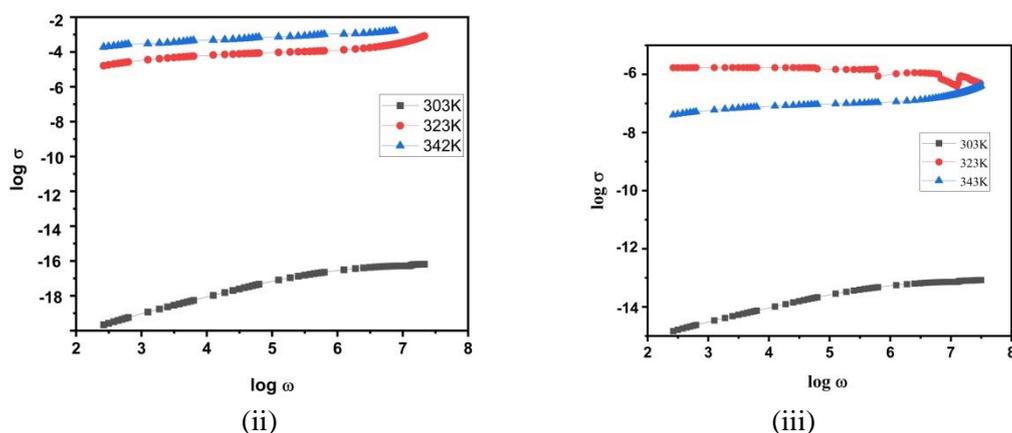*Section A-Research Paper*

(ii)

(iii)

Figure 6. Conductance spectra of prepared blended electrolytes at different temperature range (i)Pure Chitosan CT, (ii) CT:0.5g NH₄NO₃ (iii) CT:0.7g NH₄NO

Cyclic Voltammeter (CV)

Cyclic Voltammeter, reveals the storage behavior of charge at the electrode-electrolyte interface of an battery assembly**.** One popular method for assessing the electrochemical behaviour of electrolytes is cyclic voltammetry. One pivotal factor in determining the highest potential limits achievable for device applications is electrolyte stability [53]. The cell has been sweeping at scan rates of 100 mV/s within the potential range of -2 to 2 V. The CV performed in the electrolyte is shown in Figure 7. The reduction peak transitions to a lower voltage, whereas the oxidation peak exhibits the reverse behaviour. In the voltage range under investigation, the voltammogram displays oxidation and reduction peaks. This implies that at the electrode–electrolyte interface, anodic oxidation and cathodic reduction occur.

The rate of electron transfer at the electrode surface is sufficiently quick in reversible processes. In the case of the thin electrolyte condition, surface of the electrolyte are homogeneous and have a uniform potential [55]. The entire electrolyte is also electrochemically active. The peak in the CV curve are caused by the interaction of the electrode and electrolyte. The anionic oxidation seems to be accountable for the charge compensation above 1 V. At reductions of less than -1V, the anionic redox process is plainly evident. It demonstrates the voltage hysteresis caused by the anionic redox reaction manifests asymmetrically. This results the ion accumulation between electrode and electrolyte [54]. As a result, the developed films are appropriate for battery use, according to CV analysis.
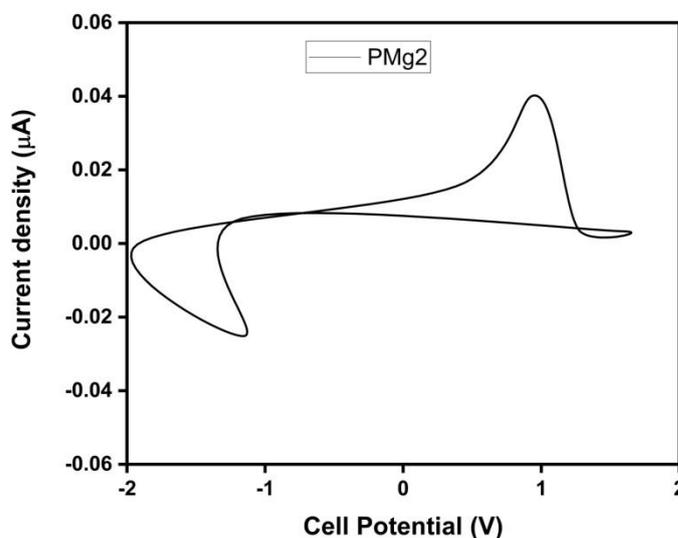

Figure 7. CV of CT:0.7 NH₄NO₃

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Linear Sweep Voltammetry (LSV)

The polymer electrolyte with high conductivity's electrochemical stability window is determined using the LSV technique. LSV is often a type of voltammetric technique where the working electrode is subjected to an applied potential, and time is adjusted linearly in response to that potential. Two blocking electrodes made of stainless steel surround the polymer electrode, and the scan rate of 100 mV/s voltage is applied within the potential window of 0 to 2V. As the voltage increase, the current progressively increases. There is a little current flow on below 1.0V. The stability window observed at approximately 1.16 V and this value is applicable potential for application in solid state batteries and the stability range is approximately equal to the previously reported work by Shukura et,al [56]. Consequently, the voltage value makes electrolyte stable and capable for battery application.
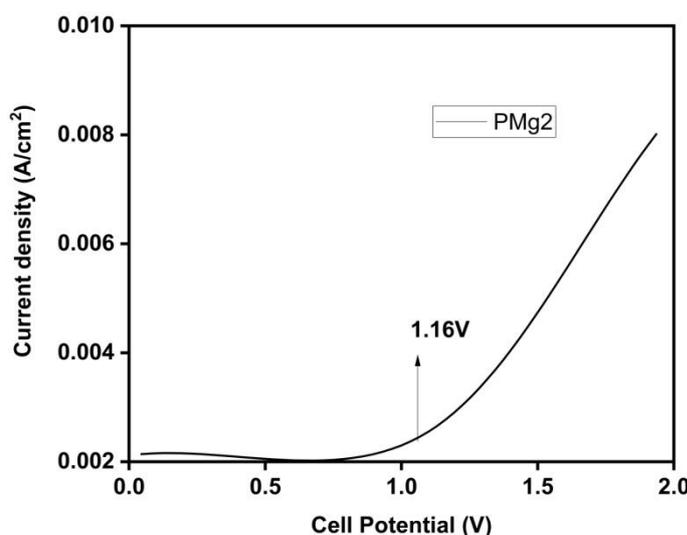

Figure 8. LSV of CT:0.7 NH₄NO₃

Conclusions

Chitosan based biopolymer electrolyte with two various concentrations of ammonium nitrate has been prepared using solution casting method. XRD confirms the increase in amorphous nature of electrolyte with inclusion of concentration of salt with Chitosan. High amorphous region results the increase of ionic conductivity of electrolyte system. FTIR confirms the vibrational and complex formation between the salt (NH_4NO_3) and biopolymer blended (CH_3COOH). Using impedance data, Nyquist plot has been plotted and found the highest ionic conductivity of polymer electrolyte CT:0.7g NH_4NO_3 is 1.98×10^{-2} S/cm. When salt is added, the diameter of the semicircle is depressed. It displays the rise in ionic conductivity at 0.7g salt concentration. Concentration of salt raises the amorphous nature and homogenous quality of electrolyte which in turn increases ion mobility and diffusion in polymer matrix. From the dielectric studies, conductivity behavior and polarization effect of prepared electrolyte reveals the dominant of charge carriers ions in conduction process. From the dielectric analysis, interpret the electrode polarization and ionic movement of charge in electric field. The polarization of the electrode and ion energy barrier leap causes dielectric loss at low frequencies. The charge carrier only moves in the high frequency band; it does not jump or make contact with the electrode surface. Thus, at high frequencies, the dielectric constant is low. The dielectric loss plot revealed a decrease in ion transport in the polymer matrix at high frequencies. Conductance study is used to analysis the logarithmic conductivity of electrolyte as function of frequency. The plateau are and subsequent spike at high frequency are consistent. For different temperature the area is subsequently change. More plateau observed in 0.7 g salt concentration polymer matrix when compared to pure Chitosan. By measuring the current in response to a change in voltage, cyclic voltammetry (CV), a commonly used electrochemical analysis technique, allows for the examination of electrochemical redox and oxides processes involving active materials. The electrode and the solid polymer electrolyte

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interface appear to be easily capable of cathodic deposition and anodic oxidation of ammonium, according to the CV measurement. LSV, verifies the greatest conductance electrolyte has a electrochemical stability upto 1.16 V. These results indicates the highest conducting electrolyte membrane has a potential to act as good conductor for proton developing battery system.

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