NOVEL BIOPOLYMER CRUST BASED COMPOSITE ELECTROLYTE AND THEIR ELECTRICAL PROPERTIES

E. Bemtta¹, M.A. Jothi Rajan²

Abstract-In this paper, we report a novel, biopolymer crust based composite electrolyte for electrochemical device applications. Electrical properties of the prepared biopolymer crust electrolyte (BCE) are characterized using various techniques like electrochemical impedance spectroscopy (EIS), Infrared spectroscopy (IR), X-ray diffraction (XRD), and scanning electron microscopy (SEM). To develop the electrical properties of BCE, potassium iodide (KI) has been added in chitosan biopolymer matrix. EIS shows enhancement in ionic conductivity on salt doping. Infrared spectroscopy confirms the formation of composite nature. XRD shows the reduction in crystallinity of chitosan by salt doping as well affirms the composite nature. Scanning electron microscopy (SEM) supports the result of XRD by reduction in crystallinity. To further affirm the conductivity enhancement in KI incorporated chitosan based BCE system, a theoretical hopping model is also described in details.

Keywords: Biopolymer electrolyte, FTIR, SEM, XRD, hopping mechanism.

1. INTRODUCTION

Biopolymers obtained from natural sources have attracted considerable attention in scientific and technological communities due to their abundance, and wide range of interesting properties [1]. The eco-friendly nature of biopolymers is added to their resourcefulness in modern times, since there is an increasing concern for protecting the environment. These interesting aspects of natural polymers urged the polymer crust electrolyte community to turn towards natural polymers for electrolytic applications [2]. Concurrent literature on crust based polymer electrolyte strongly reflects the increasing interest toward the use of biopolymers [3,4]. Among various natural polymers, chitosan is a subject of academic interest in terms of its structure and interesting properties [5]. It is a good crust forming substance with high mechanical strength, which is a deacetylated product of chitin, and it is obtained from the cuticle of the marine crustaceans such as crabs, and shrimps. The structure of chitosan is composed of hydroxyl and amino groups. The nitrogen atom of amino group have lone pair electrons that can behave as potential sites for ion transportation and should be able to solvates inorganic salt, and exhibit the properties adherent to biopolymer electrolyte [6]. Pure chitosan have room temperature conductivity between the orders of $10^{-10}$ to $10^{-9}$ S/cm [7]. This much conductivity is not sufficient to enhance the efficiency of electrochemical devices. Therefore, to improve the electrical properties of chitosan, researchers try to composite chitosan with different types of inorganic salts. Buraidah et al [8] reported that polymer electrolyte system prepared by mixing ammonium iodide with chitosan produce a room temperature electrical conductivity of $3.7 \times 10^{-7}$ S/cm. But Rahul Sing et al [9] reported that polymer electrolyte system prepared by mixing 50wt% KI with starch polymer produce an ambient electrical conductivity of $3.41 \times 10^{-4}$ S/cm. The structure of starch not consists of any amino group, but chitosan have number of amino groups [10]. Therefore the ionic conductivity of chitosan with KI composite is expected to high. Therefore, in this work authors took an effort to study the effect of the addition of KI in chitosan matrix.

2. EXPERIMENTAL

2.1 Materials

Chitosan ($C_{n}H_{2n+2}NO_{m}$) low molecular weight was purchased from sigma aldrich, and potassium iodide (KI) was purchased from S.d fine-chem limited, Mumbai. Double distilled water (D2) was used as solvent, throughout the preparation.

2.2 Preparation of polymer crust electrolyte

1.7 wt% of chitosan solutions were prepared. These solutions were stirred for 3h at room temperature, clear harmonized solutions were obtained. Different wt% of KI solutions (10, 20, 30, 40 and 50 wt %) were prepared separately, and it was stirred for 2h, to obtain a homogeneous solutions. The different wt% (10, 20, 30, 40 and 50 wt %) of KI solutions was poured into chitosan solutions. The overall solutions were again stirred for 3h to get an identical matrix. The samples were coined as CK1, CK2, CK3, CK4, and CK5. All the samples were poured into glass petri dishes and were kept to dry. The dried BCE was then kept in desiccators to avoid any trace of moisture.

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2.3 Characterization methods
The EIS of the BCE was measured at room temperature using princeton applied research modal Versa STAT MC instrument in the frequency range from 1 Hz to 1 MHz. In EIS a small sinusoidal potential is applied across the BCE and current through the sample was measured. From this, the impedance was obtained for every operating frequency. FTIR spectra were recorded using Perkin Elmer spectrometer in the transmission mode from 400 cm$^{-1}$ to 4000 cm$^{-1}$ at a resolution of 1 cm$^{-1}$. X-ray diffractogram were recorded using Siemens D500 x-ray diffraction meter. X-rays of 1.5406 Å wavelength were generated by a Cu K$\alpha$ source. The 2θ angle was varied from 10° to 80° at a resolution of 0.1°. The morphology of prepared samples was studied using Carl Zeiss EVO 18 Carl instrument and observed using the signal of SE1. Pictures were captured by automatic image capturing software. Magnifications are indicated at the bottom of each figure.

3. RESULTS AND DISCUSSION
3.1 Conductivity analysis
The conductivity is calculated using equation (1) stated in ref. [11]. The calculated values of ionic conductivity are listed in Table. 1, and plotted in Fig. 1.

![Fig.1. Effect of KI content on KI incorporated chitosan crust electrolyte at room temperature.](image)

From Table 1 and Fig.1, it is clear that addition of KI in chitosan matrix enhances the ionic conductivity, and a conductivity maximum is obtained at 1.7 wt% of chitosan, incorporated with 40 wt% of KI compositions. The addition of KI beyond 40 wt% shows saturation in ionic conductivity. The enhancement in ionic conductivity at 1.7 wt% of chitosan incorporated with 10 wt% of KI composition to 1.7 wt% of chitosan incorporated with 40 wt% of KI compositions are attributed to the fact that adding KI provides more mobile charge species (K$^+$ ion and I$^-$ anion) to chitosan matrix. These mobile ions enhance the overall ionic conductivity. While the reduction in ionic conductivity at 1.7 wt% of chitosan incorporated with 50 wt% of KI is due to the formation of dipoles by ion agglomeration$^{[12]}$.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Chitosan wt %</th>
<th>Salt wt %</th>
<th>Conductivity $\sigma$ S/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>1.7</td>
<td>10</td>
<td>6.4120 x 10$^{-4}$</td>
</tr>
<tr>
<td>K2</td>
<td>1.7</td>
<td>20</td>
<td>9.9893 x 10$^{-4}$</td>
</tr>
<tr>
<td>K3</td>
<td>1.7</td>
<td>30</td>
<td>1.8956 x 10$^{-3}$</td>
</tr>
<tr>
<td>K4</td>
<td>1.7</td>
<td>40</td>
<td>4.2842 x 10$^{-3}$</td>
</tr>
<tr>
<td>K5</td>
<td>1.7</td>
<td>50</td>
<td>4.1745 x 10$^{-3}$</td>
</tr>
</tbody>
</table>

![Scheme.1. hopping model for conductivity enhancement in KI incorporated chitosan matrix.](image)
The conductivity enhancement, according to the primed theoretical hoping model in scheme I, is due to the oxygen in chitosan can easily get associated with cation (K+). Under the influence of applied potential, the weakly bound K⁺ ions can hope together with I⁻ consistently transferred to the coordinating side of the chitosan. As a result, charge carrier ions can roam freely because of less resistance, this less resistivity will enhance the ionic conductivity.

3.2 Dielectric analysis

The values of real dielectric constant ε' and imaginary dielectric constant ε” are calculated by using the equation (2) and (3) reported in ref. [11], and plotted in Fig. 2(a) and 2(b). Fig 2(a) and 2(b) shows a plateau in the higher frequency region, physically means that the charge carriers are moving with the rate of polarity change of the applied field. The higher value of dielectric constant in low frequency is due to the polarization. This is due to, at low frequencies, electronic, ionic and interfacial polarizations respond easily to the time varying electric field, but as the frequency of the electric field increases different polarization contributions filters out due to the presence of mobile ion movements, as a result, the net polarization of the material decreases which leads to the decrease in the value of ε’ and ε” at higher frequency.

3.3 Dielectric loss analysis

The tan loss is calculated using equation (4) stated in ref. [11], and plotted in Fig. 3. Fig. 3, shows a big hump towards the higher frequency side, and the tangent loss peaks shift toward the high-frequency side on increased KI concentration. This is mainly happened because of the motion of mobile ions. The reduction in peak height on increased concentration is the proof for amorphous phase. This is further assisted by our XRD and SEM results.

3.4 Dielectric modulus analysis

The values of real dielectric modulus M’ and imaginary dielectric modulus M” are calculated by using the equation (5) and (6) reported in ref. [11]. In Fig 4(a) and 4(b), it is clear that both M’ and M” show an increase at the higher frequency end and exhibit a long tail feature at low frequency end is probably due to the large capacitance associated with the electrodes.
3.5 FTIR analysis

The composite nature of crust polymer electrolyte is studied by Infrared spectroscopy. Fig. 5 shows the recorded IR spectrum of pure chitosan crust along with the spectrum of chitosan incorporated with KI crust. The Fig. 5 shows that almost all the peaks related to host materials of chitosan is present in chitosan incorporated KI sample. Disappearance of any new peaks other than host materials clearly affirms the composite nature of the samples [18]. The increase in intensity of KI incorporated chitosan crust proves the complete dissolution of KI in chitosan matrix [19].

3.6 XRD analysis

To further affirm the composite nature as well as effect of salt concentration, we have recorded the X-ray diffraction. The recorded X-ray diffraction patterns of pure chitosan crust as well as chitosan incorporated with KI salt are shown in Fig. 6. Pure chitosan shows a broad hump at 20°. XRD spectrum of KI shows well defined crystalline peaks [20], but chitosan incorporated with KI based BCE XRD spectrum is free from the peaks related to KI, it suggests complete dissolution of KI salt [21]. It is noted that XRD pattern of KI incorporated chitosan crust do not contain any additional peaks which clearly affirm the composite nature of crust electrolyte system, and additionally, the intensity of the hump decreases by incorporating KI salt concentration and hump seems to flat. All these information’s clearly affirm that incorporated salt enhances the amorphous region which is well known favorable condition for conductivity enhancement [22].
3.7 SEM analysis
SEM is used to further clarify the role of incorporation of KI salt in chitosan matrix. We have recorded SEM micrographs and the micrographs are shown in Fig. 7(a) and 7(b). In Fig. 7(a), it is clear that pure chitosan crust shows well known rough matrix with interconnected gel grains \(^{[23]}\). In Fig. 7(b), incorporation of KI salt enhances amorphous matrix and large size pores are clearly viewed in SEM micrograph \(^{[24]}\). This result is already observed in our XRD data and tan loss results.

CONCLUSION
Chitosan incorporated with KI based crust electrolyte was prepared successfully. Complex impedance spectroscopic analysis shows that addition of increasing wt% of KI provides the extra charge carries, and enhanced the overall conductivity. The decrease in conductivity is due to ion agglomeration. IR as well as XRD confirms composite nature of crust electrolyte. SEM reveals the enhancement in amorphous region of crust electrolyte by KI incorporation which is further assisted by our XRD data and tan loss results.

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REFERENCES


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