



# Modification of chitosan-based biodegradable polymer by irradiation with MeV ions for electrolyte applications



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## ARTICLE INFO

### Keywords:

Chitosan  
Solid polymer electrolytes  
SHI irradiation  
Optical properties  
Dielectric properties

## ABSTRACT

Effect of swift heavy ion irradiation on electrical and optical properties of chitosan-based solid polymer electrolyte system, prepared by the solution casting technique, was investigated. The solid polymer electrolyte films were irradiated with  $C^{+5}$  and  $Ni^{+7}$  ions of energy 60 and 100 MeV, respectively, at different fluences. X-ray diffraction (XRD) analysis revealed the transformation of chitosan structure to the amorphous phase due to the addition of salt. FTIR spectra showed diverse vibrational modes and scissioning of bonds due to ion beam irradiations. Ions produce volatile low-molecular-weight species and results in the evolution of gas during irradiation processes. The polymer electrolyte became carbon rich with more conjugated bonds and diminished the band gap, as found by the UV–Vis analysis. The variable parameters obtained by the Bergman fitting specify that the relaxation process in the polymeric matrix is non-Debye, and the conductivity of electrolyte enhanced as a function of beam parameters.

## 1. Introduction

Climate change is a global challenge and one of the major issues for human beings. It is necessary to control the recent and imminent activities of indigenous people that affect the environment worldwide. Eco-friendly natural polymers are used as solid polymer electrolytes (SPEs) because of their low toxicity, biodegradability, and less polluting nature. Presently, SPEs are widely used in the applications of electrical and optical devices as solid state batteries, gas sensors, electrochromic display devices, supercapacitors, and fuel cells [1–8]. Biodegradable polymers such as polyethylene oxide [6], polyvinyl alcohol [7], methyl cellulose [8], and chitosan [1–4] have been studied widely, and further research studies using SPE system are in progress. The advantages of SPEs are their compactness and reliability without leakage of liquid constituents.

Chitosan is a biopolymer used as a host for SPE and is derived from chitin by deacetylation [4]. After cellulose, chitosan is the second most abundant natural amino polysaccharide with distinctive structures, multidimensional properties, and wide-ranging applications in biomedical and other industrial areas [9]. Chitosan has attracted considerable attention because of its ease of processability and customization of properties to achieve the desired functionalities [10,11]. The chitosan structure contains oxygen and nitrogen atoms with a lone pair of electrons, which help to form complexes with the salt. In the SPE

system, doped inorganic salts are dissociated in the polymeric matrix, which is responsible for the ionic conductivity. At room temperature, the ionic conductivity is about  $10^{-8}$ – $10^{-7}$  S/cm [12]. The SPEs may have crystalline and amorphous phases, but the conductivity is significant in the amorphous state. Numerous attempts have been made to reduce the crystalline structure of biopolymer-based SPEs, including blending with conducting biopolymer and addition of nano fillers, ceramic fillers, and plasticizers. All these fillers improve various properties of the host polymer up to a certain extent. Hence, further modifications in the physical property of SPE matrix can be performed by irradiation with swift heavy ions (SHIs). This technique provides a unique process to modify the microstructures of materials by electronic excitation and ionization processes in a controlled manner [13,14]. We particularly preferred the silver nitrate salt as it has been rarely investigated in the SPE system with chitosan as a host. Morni et al. [4] studied the electrochemical cell performance of chitosan-doped silver nitrate salt and concluded that it can be used as an electrolyte for the fabrication of solid-state batteries. Yulianti et al. [15] used the ion implantation technique for polymer electrolyte synthesis by employing a low-energy ion (Li, Cu, or Ag) beam. In addition, the electrical properties of ion implanted-chitosan-based polymer electrolytes are enhanced by using a low energy beam. The low-energy beam cannot penetrate deep into the materials and is primarily responsible for surface modifications. Despite the vast applications of biodegradable

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chitosan-based polymer, few studies have studied the SHI irradiation-induced effects on chitosan-based SPE as a function of additive level, ion beam species, and ion fluences. A comparative study of ion beam effects on the electrical and optical properties of SPE was also conducted.

## 2. Experimental

### 2.1. Materials

Chitosan powder (deacetylation 75–85%, molecular weight 50,000–190,000 Da) and acetic acid were purchased from Sigma-Aldrich. Silver nitrate with a molecular weight of 169.87 g/mol was supplied by Suvidhinath Laboratories, India. Double-distilled water was used during the synthesis procedure.

### 2.2. Preparation of SPE

The solution casting method was used for the synthesis of chitosan-based SPE. The chitosan powder was dissolved in 1.0% acetic acid. To this chitosan suspension, different amounts of silver nitrate were added separately. The mixture was stirred continuously with heating until it became completely homogeneous. Furthermore, it was sonicated for half an hour. The sonicated solution was poured into a Teflon petri dish at room temperature to get free-standing SPE thin films (thickness ~60  $\mu\text{m}$ ). For simplicity, the SPE films were labeled as CS, CSA, CSB, CSC, and CSD for 0, 5, 10, 15, and 20 wt% of silver ions in the respective chitosan acetate solution. In addition, we restrict our discussions up to 15 wt% concentration because, recrystallization of salt occurred beyond 15% concentration, as observed in many literatures [1–3,5,6,12,16]. The obtained films were kept in desiccators with silica gel for further desiccation.

### 2.3. SHI irradiation of SPE

The SPE films of area  $1.5 \times 1.5 \text{ cm}^2$  were fixed on a vertical sliding copper ladder. After achieving vacuum around  $10^{-6}$  Torr, these films were irradiated with 60-MeV  $\text{C}^{+5}$  and 100-MeV  $\text{Ni}^{+7}$  ions in the materials science beam line scattering chamber at IUAC, New Delhi, India. The ion beam current was 0.5 pA. The irradiation was performed at room temperature by scanning  $1 \times 1 \text{ cm}^2$  area of the SPE film in the x-y plane at fluences of  $1 \times 10^{11}$  and  $1 \times 10^{12}$  ions/ $\text{cm}^2$ .

### 2.4. Energy loss and range of carbon and nickel ions in SPE

The SRIM 2013 code [17] was used to obtain the electronic energy loss ( $S_e$ ), nuclear energy loss ( $S_n$ ), and projected range of 60-MeV  $\text{C}^{+5}$  and 100-MeV  $\text{Ni}^{+7}$  ions in chitosan ( $\text{C}_6\text{H}_{11}\text{O}_4\text{N}$ ) polymer matrix having an approximate mass density of  $0.25 \text{ g/cm}^3$ . The simulated values of  $S_e$  and  $S_n$  and the projected range for  $\text{C}^{+5}$  ion were 69.29 keV per micron,  $3.88 \times 10^{-2}$  keV per micron, and 554  $\mu\text{m}$ , respectively. In the case of  $\text{Ni}^{+7}$  ions, the obtained values of  $S_e$  and  $S_n$  and the projected range were  $11.1 \times 10^2$  keV per micron, 1.81 keV per micron, and 126  $\mu\text{m}$ , respectively. This implies that the nuclear energy loss during SHI irradiation is almost negligible for both ions, while the electronic energy loss seems to be dominant. In addition, the value of  $S_e$  for  $\text{Ni}^{+7}$  ions is hundred times higher than that for  $\text{C}^{+5}$  ions.

### 2.5. Characterizations of SPE

XRD measurement was performed using a Bruker D8-Advance diffractometer to study the amorphous or crystalline structure of SPE. The wavelength of monochromatic Cu-K $\alpha$  radiation is 1.5418  $\text{\AA}$ , and the diffraction patterns were recorded at angles of  $5^\circ \leq 2\theta \leq 65^\circ$ . FTIR analysis was performed using a JASCO-4100 spectrometer to confirm the complexation between polymer and salt and the radiation-induced

modifications in the structural properties of the electrolyte. The FTIR spectra were recorded in the transmission mode from 400 to  $4000 \text{ cm}^{-1}$ , with a resolution of  $1 \text{ cm}^{-1}$  after 100 accumulated scans. UV-visible spectroscopy was performed to study the optical properties of the electrolyte using a Hitachi Model U-3300 spectrometer. The absorption spectra were recorded in 200–800 nm wavelength range. Complex impedance spectroscopy was performed using a Solartron SI-1260 impedance gain/phase analyzer to investigate the electrical properties of the SPE. The SPE films were sandwiched between two silver electrodes under spring tension. The impedance was measured in the frequency range of 10 Hz–10 MHz at ambient temperature with 1-V AC signal amplitude. The data were collected using a fully automated interfaced with a computer. The Z-View2 software was used to further analyze the AC electrical data. The highest conductivity was obtained for the CSC sample (similar observations on the conductivity were reported by Morni et al. [4]). The surface morphology of the electrolyte samples was studied in the tapping mode using AFM Nanoscope digital Instruments, Canberra, USA, in air at ambient temperature. The electronic digital caliper (Forbes) was used to measure the thickness of the electrolytes.

## 3. Results and discussion

### 3.1. XRD analysis

To investigate the effect of silver nitrate salt with chitosan-based polymer, the XRD study of pure chitosan and chitosan–silver nitrate salt complexes was conducted. Fig. 1 shows the X-ray diffraction patterns of pure chitosan and silver nitrate-doped chitosan-based electrolytes. Different peaks observed at  $8.2^\circ$ ,  $11.6^\circ$ ,  $15^\circ$ ,  $18^\circ$ , and  $21.7^\circ$  were identified as the characteristic peaks of pure chitosan. The two peaks that appeared at  $8.2^\circ$  and  $11.6^\circ$  indicate a hydrated crystalline structure, while the peak at  $15^\circ$  may be attributed to the anhydrous crystalline structure. In addition, the broader peaks that appear at  $18^\circ$  and  $21.7^\circ$  show the existence of an amorphous phase of chitosan [18]. A comparison of the X-ray diffraction patterns of pure chitosan and silver nitrate-doped chitosan-based electrolytes revealed that the different peaks corresponding to chitosan disappeared and a broader peak evolved upon the addition of salt. This confirms the interaction between the silver nitrate salt and chitosan matrix. The broadening of peak can be attributed to the increased separation of the polymeric chain of the SPE incorporated with salt. In addition, the synthesis temperature of SPE system (about  $60 \pm 2^\circ\text{C}$ ) helped to achieve the amorphous phase. In addition, the peak that corresponds to silver nitrate salt was not observed in the XRD pattern. This suggests the structural rearrangement of host polymer and salt with no surplus salt present in the SPE, but the crystalline peaks with very small intensity that appeared at  $\sim 38^\circ$  and  $\sim 44^\circ$  correspond to the (1 1 1) and (2 0 0) planes of silver nanoparticles, respectively. During the synthesis, chitosan acts both as reducing and capping agents in a lightly heated system, yielding silver nanoparticles [19]. In addition, the pattern of irradiated SPE system did not reveal any considerable change.

### 3.2. FTIR analysis

To understand the interaction of chitosan with silver nitrate salt and the effect of SHI irradiation on existing chemical bonds/functional groups within the compound, IR transmittance measurements were made. Fig. 2 represents the IR spectra of CS and highest conducting electrolyte system CSC. First of all, no peak was observed at  $1590 \text{ cm}^{-1}$  attributed to the  $-\text{NH}_2$ , but a band appeared at  $1540 \text{ cm}^{-1}$  conforming  $\text{NH}_3^+$  [20]. This implies that the SPE is basically in the acetate form. The strong characteristic vibration band center at  $3426 \text{ cm}^{-1}$  corresponds to the overlapping of O–H stretching vibrations with the N–H stretching. The bands that appeared at  $1639 \text{ cm}^{-1}$  (amide I group) and  $1329 \text{ cm}^{-1}$  (amide III group) correspond to the mode of amino group

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