Synthesis, characterization and application of biopolymer-ionic liquid composite membranes

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**A B S T R A C T**

Biopolymer composite membranes based on chitosan doped with an ionic liquid (IL) 1-ethyl 3-methylimidazolium thiocyanate (EMImSCN) have been developed and characterized. The doped ionic liquid films show remarkable enhancement in ionic conductivity ($\sigma$). The Fourier transform infrared (FTIR) spectroscopy, atomic force microscopy (AFM) and X-ray diffraction studies (XRD) affirmed the composite nature, good incorporation of ionic liquid and reduction in crystallinity of films, respectively. The interaction between ionic liquid, chitosan and iodide polymer electrolyte matrix was evaluated by cyclic voltammetry. The fabricated dye sensitized solar cell (DSSC) using this new biopolymer electrolyte membranes shows promising performance.

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1. Introduction

Biological polymers (biopolymers) received recent attention from academia and industry because they offer a degree of functionality which is not available in most of the reported synthetic polymers\cite{1,2}. Chitosan is the N-deacetylated form of chitin with a repeat unit of $\beta$(1,4)-linked 2-acetamido-2-deoxy-$\alpha$-glucose. Due to many advantageous properties like good complexity with ionic salts, high ionic conductivity ($\sigma$) ($10^{-4}$ S cm$^{-1}$ in hydrated condition), nontoxicity and biodegradability it is frequently used in fuel cell, battery, sensor, photovoltaic and medical applications\cite{3–6}. In photovoltaic area dye sensitized solar cells (DSSC) are now proposed as alternative renewable energy source since it fulfills the requirements like low cost and high efficiency\cite{7,8}. Among all popular electrolytes for DSSC, gel and polyethylene oxide (PEO) based polymer electrolytes are proposed as suitable solid electrolytes because they show high ionic conductivity ($\sigma$) as well as efficiency\cite{9–11}. Ionic liquid (IL) based electrolytes are also good competitor albeit the liquid nature of most of the IL is known as barrier\cite{8,12}. Keeping this in mind we have already proposed IL doped PEO solid polymer electrolyte showing efficient DSSC performance\cite{13–16}.

Here we report the development of solid polymer electrolyte films of chitosan doped with low viscosity IL 1-ethyl 3-methylimidazolium thiocyanate (EMImSCN) and utilized it in DSSC application. To our knowledge no previous report has been published on chitosan doped IL polymer electrolyte and its photovoltaic application.

2. Experimental section

Chitosan (84% deacetylated), sodium iodide (NaI) and iodine were received from Sigma–Aldrich Chemical Co., USA while ionic liquid IL (EMImSCN) was purchased from Fluka. Chitosan solutions were prepared by dissolving 250 mg of chitosan in 25 ml of 1% acetic acid solution and stirring overnight. The IL doped chitosan films were obtained by adding different concentrations of IL (10, 20, 40, 60, 80, 100, 120, 150 and 200 wt%) in chitosan solution and mixed thoroughly. The solution was then casted on polypropylene petridishes. After drying the films at 50°C for overnight, these films were taken off and finally dried under vacuum. The $\sigma$ of these films were measured using stainless steel dye connected with Solartron (SI 1287 coupled with FRA model no. 1252A). The Fourier transform infrared spectroscopy (FTIR) were recorded using an IR spectrometer (Thermo Electron Corp./Nicolet 380). Atomic force microscopy images (AFM) of these films were obtained using multimode nanoscope IV (Digital Instruments, Canada) operated in tapping mode. A CHI 600 electrochemical measurement was used.
for cyclic voltammetry (CV) in 0.1 phosphate buffer solution at pH 7. Voltammograms were recorded using conventional three electrode system with Ag/AgCl as reference, platinum wire as counter and printed carbon with drop coated polymer electrolyte solution as working electrode. For redox couple formation ($I_1/I_3^-$) in DSSC, 1.5 g of NaI and iodine ($I_2$) were added in chitosan and chitosan:IL polymer electrolyte solutions since this composition shows highest $\sigma$ [5]. We have finally fabricated DSSC with an active area of 0.16 cm$^2$ [13]. The photovoltaic performance ($J$–$V$ curve) of the DSSC were measured with the help of Keithley 2400 source meter unit at 1 sun light intensity condition (100 mW cm$^{-2}$).

### 3. Results and Discussion

#### 3.1. Ionic conductivity measurement

Fig. 1 shows the variation of ionic liquid concentrations with room temperature ionic conductivity. The calculated values of ionic conductivity using complex impedance spectroscopy are listed in Table 1. It is noted that the ionic conductivity ($\sigma$) increases with increasing ionic liquid (IL) concentration attained maxima then decreased. The maximum $\sigma$ was $2.60 \times 10^{-4}$ S cm$^{-1}$ at 150 wt% ionic liquid concentration. This value of $\sigma$ is quite high if we compare it with pristine chitosan film where reported ionic liquid concentration. This value of $\sigma$ was $2.60 \times 10^{-3}$ S cm$^{-1}$ [1]. This enhancement in ionic conductivity value is attributed to the doping of ionic liquid. It is reported that the ionic liquids are composed of solid ions [6] and hence doping of ionic liquid in chitosan matrix provides more free ions (imidazolium cation and thiocyanate anions in present case) which increases $\sigma$ while decreasing $\sigma$, in the later part, was attributed to the aggregation of charge carriers [6,13].

#### 3.2. FTIR analysis

Fig. 2 shows the FTIR spectra of pure chitosan, ionic liquid and ionic liquid doped chitosan polymer electrolyte films. The IR spectra of chitosan films (Fig. 2a) showed peaks at 3400, 2925, 1633, 1314, and 1076 cm$^{-1}$ indicating stretching of O–H and N–H bonds, vibrations of C–H, amide I, symmetrical deformation mode of C–H, amide II formation, and stretching of C–H, respectively [4].

In case of ionic liquid (EMImSCN) spectra (Fig. 2c) we have observed both type of peaks related to imidazolium cation as well as thiocyanate anion. The peaks at 3166 and 2892 cm$^{-1}$ have been reported as stretching of C–H and antisymmetric CH$_3$ stretching, respectively. The other peaks at 1462, 1432, 1172, and 912 cm$^{-1}$ correspond to antisymmetric bending of CH$_3$, symmetric bending of CH$_3$, stretching of CH$_3$ and out of plane stretching of H–C bond [17]. The peaks at 2058, 1600, 620, and 600 cm$^{-1}$ are ascribed to the absorption of thiocyanate (SCN$^-$), stretching of CN, stretching vibration of C–S and stretching vibration bond of S–CN, respectively. It is observed that ionic liquid doped chitosan film spectra (Fig. 2b) contain almost all the peaks either related with chitosan or ionic liquid (IL) which essentially confirmed its “composite” nature.

#### 3.3. Surface morphology by AFM

Tapping mode AFM images gives information related to surface features of the films. Fig. 3 shows the surface profile of pure chitosan and ionic liquid doped chitosan polymer electrolyte films. Pure chitosan film (Fig. 3a) shows loose and uneven surface with many small crater-valley type structures with surface roughness (RMS) = 14.346 nm. The film containing 150 wt% ionic liquid concentration (maximum $\sigma$) shows almost smooth and less intense crater and valley (Fig. 3b) with reduced surface roughness of 6.823 nm. This reduction in roughness of film with IL doping clearly affirmed that ionic liquid incorporated well with chitosan matrix and also matches with our ionic conductivity ($\sigma$) data.

#### 3.4. X-ray diffraction measurement

The XRD patterns of pure chitosan and ionic liquid doped chitosan polymer electrolyte films are shown in Fig. 4. Pure chitosan film shows (Fig. 4a) well-known partly crystalline peak at 20$^\circ$ ∼20$^\circ$. In case of ionic liquid doped chitosan film the intensity of the hydrated peak of chitosan at 20$^\circ$ ∼20$^\circ$ reduced (Fig. 4b). Addition of ionic liquid into chitosan matrix (chitosan + 150 wt% IL) the peak intensity further decreases drastically (Fig. 4c) which clearly indicates that doping of ionic liquid reduces crystallinity of chitosan matrix which is known favourable condition for $\sigma$ enhancement.
3.5. Cyclic voltammetry

The electrochemical reaction of ionic liquid, chitosan and iodide/iodine polymer electrolyte films was carried out by cyclic voltammograms as shown in Fig. 5. It is clear that chitosan:NaI/I₂ films with and without ionic liquid shows good redox behaviour with two redox peaks at slow scan rate, while at higher scan rate it exhibited only one peak (inset Fig. 5). Chitosan film containing ionic liquid shows $\Delta E = 0.45$ and $0.58$, while without IL exhibit at $\Delta E = 0.45$ and 0.67, respectively. This was attributed by the presence of iodide redox couple [18]. It is observed that in the absence of ionic liquid (solid line) there is quite good interaction between negatively charged iodide ion and chitosan matrix, which suppresses or hinders the iodide to triiodide redox behaviour. In the presence of ionic liquid (IL) there is a competition for the interaction with chitosan between ionic liquid and iodide redox couple which results in free iodide from interaction and behaves like perfect redox couple (Fig. 5 dashed line). It may be noted that we observed no voltammetric signal for pure chitosan film and ionic liquid as they are electrochemically inactive in scanned electrochemical window.

3.6. Photovoltaic performance

The recorded photocurrent density–voltage curves ($J-V$) for the DSSC using chitosan and ionic liquid doped chitosan films (maximum $\eta$) are shown in Fig. 6. Chitosan film without ionic liquid (chitosan:NaI/I₂) shows open circuit voltage ($V_{oc}$) of 0.349 V, short-circuit current density ($J_{sc}$) of 1.05 mA cm$^{-2}$, fill factor (FF) of 0.34 and conversion efficiency ($\eta$) of 0.13% (Fig. 6a) while chitosan film with ionic liquid (chitosan:NaI/I₂ + 150 wt% IL) shows overall improvement in solar cell performance with $V_{oc}$ of 0.53 V, $J_{sc}$ of 2.65 mA cm$^{-2}$ and conversion efficiency of 0.36% (Fig. 6b).

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Fig. 3. Three-dimensional AFM topographic images of (a) pure chitosan and (b) chitosan + 150 wt% IL polymer electrolyte films.

Fig. 4. X-ray diffractograms of (a) pure chitosan (b) chitosan + 120 wt% IL and (c) chitosan + 150 wt% IL films at scan rate of 1° min$^{-1}$.

Fig. 5. Cyclic voltammograms of chitosan:NaI/I₂ (solid black line) and chitosan:NaI/I₂ + 150 wt% IL (dashed red line) at 5 mV/S scan rate.

Fig. 6. The recorded $J-V$ curve of the DSSC for (a) chitosan:NaI/I₂ and (b) chitosan:NaI/I₂ + 150 wt% IL polymer electrolyte films at 100 mW cm$^{-2}$. 
2.62 mA cm\(^{-2}\), FF of 0.52 and overall improved efficiency (\(\eta\)) of 0.73\% (Fig. 6b).

4. Conclusions

This work presents the development and characterization of a biopolymer (chitosan) doped ionic liquid films as promising candidate for photovoltaic application. The ionic liquid doped chitosan films shows improvement in ionic conductivity than pure chitosan film, which is due to enhancement in number of charge carriers provided by ionic liquid. AFM, FTIR and XRD suggest the good incorporation of ionic liquid with chitosan matrix, composite nature and reduced crystallinity of the films. Cyclic voltammogram study suggests the possible interaction between ionic liquid, chitosan and iodide/triiodide characterised by presence of two well-resolved redox peaks. Additionally we found that this new ionic liquid doped chitosan films could be a novel material to fabricate efficient DSSC. The conversion efficiency of the DSSCs were found to improve by six times showing enhancement in all the photovoltaic parameters (\(J_{sc}, V_{oc}\) and FF).

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