Characterization And Ionic Conductivity Of Polymeric Electrolytes Based On Chitosan-Ammonium Thiocyanate-TiO₂ Ceramic Materials

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Abstract

Various amounts of TiO₂ particles are used as filler in preparation of chitosan-ammonium thiocyanate-composite polymer electrolytes. The role of filler in this present work is as agent to improve the conductivity of the films. Films of chitosan and its complexes were prepared using solution casting technique. Different amounts of TiO₂ 3 wt. %, 6 wt. %, 9 wt. %, 12 wt. %, 15 wt. % and 18 wt. % were added to the highest room temperature conductivity sample in chitosan-salt system i.e sample containing 40 wt. % NH₄SCN. The impedance of the composite films has been measured in the temperature and the frequency range 298 K-373 K and 50 Hz to 1 MHz, respectively. The conductivity value of this sample is 1.29 x 10⁻² S cm⁻¹. With addition of 3 wt. % TiO₂ filler the ionic conductivity increased to 2.75 x 10⁻² S cm⁻¹. XRD and FTIR results are also discussed.

Keywords: ionic conductivity, ceramic fillers, polymer-nanocomposite, chitosan

1. INTRODUCTION

Solid polymer electrolytes have been the subject of numerous studies. Their technological importance can be seen in the fabrication of lithium-ion polymer batteries [1], capacitors [2], and electrochromic devices [3]. Most research on electrolytes focused on increasing their conductivity while at the same time maintains good thermal and mechanical stability. The addition of inert oxides to the polymer electrolytes has recently become an attractive approach, due to improved mechanical stability and enhanced ionic conductivity [4-6]. The increase in conductivity of the composite electrolytes depends upon the concentration and the sizes particle fillers. In general, the smaller the inert particle, the larger the conductivity enhancement [7-8].

The disadvantage of organic fillers such as propylene carbonate (PC) and ethylene carbonate (EC) is that they are more expensive compared with inorganic fillers [9]. Fillers can promote more free ions and produce more amorphous regions in the electrolyte for transport of charge carriers [10].

In this work chitosan-NH₄SCN-TiO₂ composite polymer electrolyte has been developed, in which the titanium dioxide (TiO₂) as the filler has increase the conductivity. The effects of TiO₂ in chitosan-NH₄SCN are also studied by XRD, FTIR and SEM.

2. EXPERIMENTAL

2.1 Materials and Preparation

Chitosan (highly viscous) was procured from Fluka as the polymer host. Acetic acid was procured from Univar Chemicals. Ammonium thiocyanate (R&M) was used.
the doping salt and TiO₂ (titanium (IV) oxide) from Aldrich was used as filler.

The chitosan was dissolved in 1 % acetic acid and the mixture was stirred at room temperature for 3 h to obtain a homogeneous solution. 40 wt. % of ammonium thiocyanate was added to the solution and stirred until the salt has dissolved completely. TiO₂ was added accordingly at the required concentrations. The homogenous solution was then cast into several plastic petri dishes to get the films.

2.2 Characterizations

2.2.1 Conductivity Measurements.

The dried films were cut into a suitable size and mounted on the conductivity holder with stainless steel electrodes of 1 cm diameter under spring pressure. The impedance of all samples was measured using the HIOKI 3531-01 LCR Hi-Tester interfaced to a computer with frequency ranging from 50 Hz to 1 MHz and also at temperatures from 298 K to 393 K. The electrical conductivity was then calculated using the equation:

\[
\sigma = \frac{t}{R_b A}
\] (1)

Here \( t \) is thickness of the sample, \( A \) is the surface area of contact and \( R_b \) is the bulk resistance of the sample.

2.2.2 X-Ray Diffractometer (XRD)

X-ray diffraction was performed using Shimadzu D5000 to examine the crystalline nature of the prepared polymer composite samples.

2.2.3 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectroscopy patterns were recorded using Thermo Scientific/Nicolet iS10. Infrared absorption spectra were collected in the range from 4000 to 400 cm⁻¹ at room temperature with a resolution of 1 cm⁻¹.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of some prepared samples obtained at room temperature.

The XRD pattern of pure chitosan shows two halos at 20° = 15.5° and 21.6°. It was reported that pure chitosan film exhibit peaks at 20 angles of 21°, between 16° to 24° and 29° [11]. When 40 wt. % NH₄SCN was added to pure chitosan acetate, the intensity of both peaks has decreased and gives a completely amorphous film. The broad peaks indicate that the films are amorphous [12]. The conductivity will increase when the material becomes more amorphous or less crystalline. Based on the diffractograms, the sample with 3 wt. % of...
filler exhibits the most amorphous diffractogram. Thus it may have higher conductivity compared to the other samples. Fig. 2 shows the effect of filler on the conductivity of chitosan-NH$_4$SCN-TiO$_2$ system at room temperature.

![Graph](image1)

**Fig. 2** Room temperature conductivity of polymer composite samples with different filler content.

The polymeric composite shows maximum in conductivity at 3 wt. % of TiO$_2$. The conductivity value is 2.75 x $10^{-4}$ S cm$^{-1}$. At this filler content, the addition of filler may have created additional pathways for the ion to transport and could have also resulted in a greater number of mobile ions due to dissociation of the salt [13-14]. The conductivity decreases for the sample containing 6 wt. %, 9 wt. %, 12 wt. %, 15 wt. % and 18 wt. %. This results are in good agreement with the XRD results where the crystallinity of the samples have increased with increasing amount of filler thus decreasing the conductivity. The conductivity ($\sigma$)-temperature ($T$) plots of the chitosan based electrolyte is shown in Fig. 3.

![Graph](image2)

**Fig. 3** Arrhenius plot of conductivity for (a) chitosan acetate-40 wt. % NH$_4$SCN and (b) chitosan acetate-40 wt. % NH$_4$SCN-3 wt. % TiO$_2$.

The plot shows that as the temperature increases, the conductivity also increases. Ng and Mohamed [15] have also observed the same trend. The conductivity-temperature relationship of chitosan-based polymer electrolyte can be characterized by an Arrhenius behavior, suggesting that the conductivity is thermally stable. The activation energy, $E_a$ of the sample can be calculated using the modified Arrhenius equation below:

$$\sigma = \sigma_0 \exp \left( \frac{E_a}{K_B T} \right)$$
Here $T$ is the experimental temperature in Kelvin, $\sigma$ is conductivity, $\sigma_0$ is pre-exponential factor, $E_a$ is the activation energy and $K_B$ is the Boltzmann constant. From the slope of the graph in Fig. 3, the calculated activation energy for conduction is $0.19$ eV and $0.08$ eV for salted and composite samples, respectively. The decrease in activation energy is consistent with an increase in conductivity as reported in many reports on conductivity studies of polymer electrolytes [16-17].

The increase in ion dissociation and reduction of ion pairing in the electrolyte can be discussed further based on the FTIR spectrum as shown in Fig. 4.

![FTIR spectrum of film containing (a) chitosan acetate, (b) chitosan acetate-NH4SCN, and (c) chitosan acetate-NH4SCN-TiO2 in the region from 700 to 2300 cm\(^{-1}\).](image)

**Fig. 4** IR spectrum of film containing (a) chitosan acetate, (b) chitosan acetate-NH4SCN, and (c) chitosan acetate-NH4SCN-TiO2 in the region from 700 to 2300 cm\(^{-1}\).

The carbonyl band of the chitosan acetate spectrum can be observed at $1634$ cm\(^{-1}\) and the amine band at $1544$ cm\(^{-1}\). The carbonyl band has shift to lower wavelength at $1612$ cm\(^{-1}\) and the amine band at $1513$ cm\(^{-1}\). The shift in the chitosan-salt spectrum indicates some interactions have occurred between the salt and the nitrogen donors of the chitosan. SCN\(^-\) belongs to point group symmetry and has three vibrational modes associated with C\(-\)N\(=\)C stretching, C\(\equiv\)C stretching and doubly degenerate SCN bending, respectively. C\(-\)N\(=\)C stretching in most PEO-based polymer electrolytes appears as one envelope in the region between $2150$ and $2000$ cm\(^{-1}\) [21-22].

In this work CN stretching can be observed at $2043$ cm\(^{-1}\) in the spectrum of chitosan with salt and shift to $2045$ cm\(^{-1}\) in the spectrum of chitosan with salt and filler. The intensity of this band also increases due to the addition of filler. The polymer-salt complex formation and the proton interaction have been confirmed from the above analysis.

### 4. CONCLUSIONS

It can be inferred that the presence of the ceramic filler can help to improve the conductivity of the prepared samples. XRD and FTIR results clearly showed interaction between TiO2 filler and the completely amorphous chitosan-based polymer electrolyte. The conductivity value of the order $~10^{-4}$ S cm\(^{-1}\) that has been obtained by adding the TiO2 filler to chitosan-salt polymer electrolyte can make the composite polymer electrolyte as a potential material for some electrochemical devices.
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