

CONDUCTIVITY STUDIES OF BIOPOLYMER ELECTROLYTE BASED ON POTATO STARCH/CHITOSAN BLEND DOPED WITH LiCF_3SO_3

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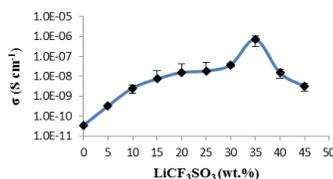
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Graphical abstract



Abstract

Biopolymer electrolytes are currently attracting a great deal of attention as substitute for synthetic polymers in electrochemical devices, as they are cost effective and eco-friendly. In this research, the biopolymer potato starch/chitosan blend polymer electrolyte film doped with LiCF_3SO_3 was prepared by solution casting method. Sample with 35wt. % LiCF_3SO_3 showed the highest ionic conductivity at room temperature. The dielectric studies reveal the non-Debye nature of the electrolyte. The Rice and Roth model was used quantitatively to explain the conductivity trends of the prepared electrolyte systems. The complexation of salt with the polymer host was studied using Fourier transform infrared (FTIR) spectroscopy.

Keywords: Starch, conductivity, FTIR, polymer electrolyte

Abstrak

Kebelakangan ini elektrolit biopolimer menarik banyak perhatian sebagai pengganti polimer sintetik dalam peranti elektrokimia, kerana sifatnya yang kos efektif dan mesra alam. Dalam kajian ini, biopolimer kanji kentang/kitosan campuran polimer filem elektrolit didopkan dengan LiCF_3SO_3 telah dihasilkan dengan menggunakan kaedah penyelesaian pemutus. Sampel dengan 35 peratusan berat LiCF_3SO_3 menunjukkan kekonduksian ionik tertinggi pada suhu bilik. Kajian mendedahkan sifat elektrolit adalah bukan-Debye. Model Rice dan Roth telah digunakan secara kuantitatif untuk menerangkan trend kekonduksian sistem elektrolit polimer yang disediakan. Interaksi antara garam dan hos polimer dan garam telah dikenal pasti dengan menggunakan Fourier mengubah inframerah (FTIR) spektroskopi.

Kata kunci: Kanji, kekonduksian, FTIR, elektrolit polimer

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1.0 INTRODUCTION

Polymer electrolytes (PE) have been extensively studied because of their potential application in electrochemical devices. PE is defined as a solvent-free system whereby the ionically conducting pathway is generated by dissolving the low lattice energy metal salts in a high molecular weight polar polymer matrix with aprotic solvent [1]. A lot of polymers have been used as a host in solid polymer electrolyte such as polyethylene oxide (PEO), polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA) and polyvinylidene fluoride (PVDF). Scientists are currently actively looking for alternative polymer host with improved conductivity and mechanical properties as well as being cost effective and environmentally friendly. Starch is a polysaccharide composed of amylose and amylopectin. It is a natural polymer that is non-toxic, available in abundance, biodegradable and renewable. Starch dissolves readily in hot water and forms film easily. Amongst the various starches available such as arrowroot, corn and potato starches, the morphology of potato starch is found to be better in comparison to other starches and it forms a more flexible film with high conductivity in comparison to others [2]. It has been suggested that by modification of starch through blending with other polymers can improve its physical properties [3]. Starch-chitosan blends are known to exhibit good film forming property due to the presence of high density of amino groups and hydroxyl groups and they can form inter and intramolecular hydrogen bonds [4,5]. Xu *et al.* [6] prepared chitosan-starch composite film and found the film properties have improved.

In the present work, a solid biopolymer electrolyte based on potato starch/chitosan blend and doped with various amount of LiCF_3SO_3 salt was investigated. LiCF_3SO_3 is the charge carriers' provider. The prepared samples will then be characterized by electrochemical impedance spectroscopy (EIS) and Fourier transform infrared (FTIR) spectroscopy. The effect of amount of salt on the ionic conductivity trend was studied using EIS and FTIR was employed to study the interactions between the potato starch-chitosan and lithium ions.

2.0 EXPERIMENTAL

Potato starch and chitosan (Fluka) were used to prepare the samples using solution casting method. Potato starch solution was prepared by dispersing 0.25 g of potato starch in 50ml distilled water solution, which then was heated on hotplate and maintained at the temperature of 90°C for 30 minutes under gentle stirring. Chitosan solution was prepared by dissolving 0.75 g of chitosan in 50 ml 1% ethanoic acid solution. The ratio of starch to chitosan (25:75) was used since it shows the least crystalline structure [5]. The various weight percentage of lithium triflate

(LiCF_3SO_3) was added to the potato starch-chitosan (PSC) mixture and was continuously stirred for 24 hours in order to achieve a homogeneous mixture. The homogenous mixture was cast on a plastic petri dish and was allowed to evaporate completely at room temperature. Finally, free standing polymer electrolyte films (thickness 400 to 450 μm) were obtained. These electrolyte films were then kept in a vacuum oven at room temperature for a week before being characterized.

The samples were characterized using HIOKI 3531-01 LCR Hi-Tester between the frequency ranges of 50 Hz to 1 MHz. Infrared studies were carried out using FTIR Spectrometer Spectrum (Perkin Elmer) between the range 4000 cm^{-1} and 440 cm^{-1} with resolution of 4 cm^{-1} .

3.0 RESULTS AND DISCUSSION

3.1 Conductivity Studies

The electrochemical impedance spectroscopy is an excellent tool to characterize many of the electrical properties of the material and their interfaces with the electrode materials. In the present study the ionic conductivities of PSC blend polymer electrolyte film with various weight percent of LiCF_3SO_3 was investigated. The variation of conductivity with salt content is shown in Figure 1. It is observed that the ionic conductivity of PSC system increases with the addition of LiCF_3SO_3 and reaches an optimum value of $7.11 \times 10^{-7}\text{ S cm}^{-1}$. The increase in conductivity could be attributed to the increase in the number of charge carriers. From the graph, it was observed with the addition of more than 35 wt. % LiCF_3SO_3 , the conductivity starts to decrease. The decline in conductivity can be explained by the formation of ions pairs producing neutral species which reduces the number of free ions.

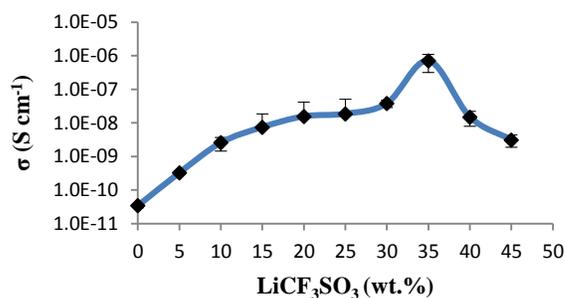


Figure 1 Ionic conductivity of PSC blends with various amount of LiCF_3SO_3 at room temperature

3.2 Temperature Dependence–Ionic Conductivity Studies

Figure 2 illustrates the ionic conductivity of the prepared PSC blends with various amount of LiCF₃SO₃ against the reciprocal absolute temperature. From this Figure it can be clearly seen that the polymer electrolytes exhibit Arrhenius behavior as their regression values are close to unity. This linear relationship shows that the ionic conductivity is thermally activated.

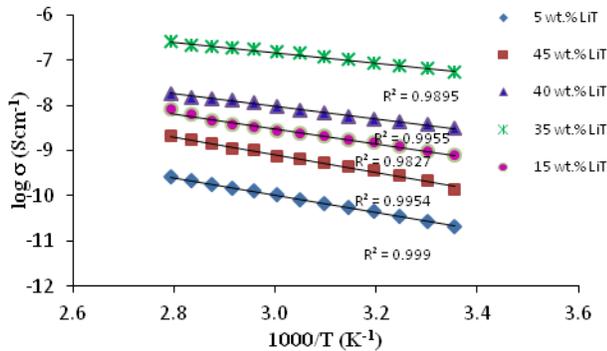


Figure 2 Arrhenius plots for the conductivity of PSC-LiCF₃SO₃ complexes

3.3 Dielectric Behavior Studies

Dielectric studies provide an important insight regarding the trend of ionic conductivity in polymer electrolytes. Dielectric constant is a measurement of charge stored in a material while dielectric loss represents the energy losses due to movement of ions when the polarity of electric field reverses rapidly [7]. The relationship between impedance data and dielectric constant and loss values are given by the following formula

$$\epsilon_r = \frac{Z_i}{\omega C_0(Z_r^2 + Z_i^2)} \quad (1)$$

$$\epsilon_i = \frac{Z_r}{\omega C_0(Z_r^2 + Z_i^2)} \quad (2)$$

where Z_i is an imaginary part of impedance, Z_r is a real part of impedance, C₀ is vacuum capacitance and ω is angular frequency.

Figure 3(a) and (b) represents the variation of ε_r and ε_i with frequency for PSC systems with 30 wt.%, 35 wt.% and 40 wt.% LiCF₃SO₃ salt, which clearly show both dielectric constant and dielectric loss values rise sharply towards lower frequency side indicating the presence of electrode polarization and space charge polarization of charges by the accumulation of charges at electrode-electrolyte interface and

confirming non-Debye behaviour of the polymer electrolytes. Whereas, ε_r and ε_i decrease with increasing frequency as the periodic reversal of the electric field occurs so fast that there is no time for accumulation of charge at the interface. The higher value of ε_r and ε_i in the PSC system with 35 wt.% LiCF₃SO₃ salt is attributed to the higher charge carrier. With more than 35 wt% LiCF₃SO₃ salt, ε_r and ε_i values are observed to decrease which can be explained due to re association of ions, leading to a decrease in conductivity [8].

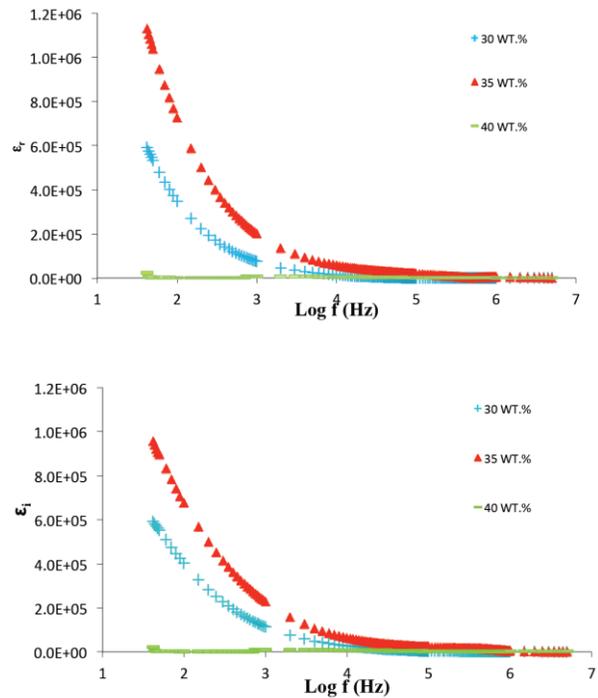


Figure 3 Frequency dependence of (a) ε_r and (b) ε_i at room temperature

3.4 Transport Parameters

The trend in conductivity can be analyzed quantitatively using Rice and Roth model from which conductivity determining parameters can be calculated. The Rice and Roth model is based on the hypothesis that an energy gap above which the conducting ion mass M can be thermally excited free ion-like states throughout the solid with velocity v [9]. According to this model, the conductivity is given by

$$\sigma = \frac{2}{3} \left[\frac{(Ze^2)}{kTM} \right] n E_a \tau \exp \left(\frac{-E_a}{kT} \right) \quad (3)$$

where Z is the valency of conducting species, e is the electron charge, m is the mass of the charge carrier and t is the traveling times of the ions. τ is obtained using

$$\tau = \frac{l}{v} \quad (4)$$

Shukur *et al.* [8] and Yusof *et al.* [10] in their study of starch–chitosan blend-based electrolytes doped with ammonium salt took l to be 10.40A, which was used in the present study.

The velocity, v of mobile ions can be calculated using

$$v = \sqrt{\frac{2E_A}{m}} \quad (5)$$

The value of n was obtained using equation (3). The ionic mobility μ is calculated using the value of n .

$$\mu = \frac{\sigma}{ne} \quad (6)$$

Table 1, list the transport parameters for the PSC systems with various wt. % LiCF_3SO_3 at room temperature. It is apparent from table, that the sample with 35 wt. % LiCF_3SO_3 has the highest number density of mobile ions, mobility and diffusion values. The values of μ and D seem to have direct relationship to the conductivity values. Rozali *et al.* [11] also reported a poor salt concentration dependence of n for their polymer electrolyte system. The authors concluded that the increase in conductivity with increasing salt concentration is due primarily to the increase in the mobility of free ions and diffusion coefficient [11].

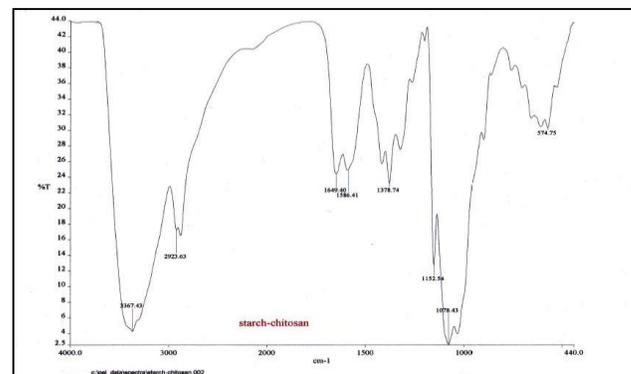
Table 1 Transport parameters of SPC systems with various wt% LiCF_3SO_3

LiCF_3SO_3 wt.%	τ (s)	n (cm^3)	μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	D (cm^2s^{-1})
5	3.16E-13	1.82E+16	1.12E-07	2.88E-09
10	3.48E-13	1.04E+16	1.55E-06	3.98E-08
15	3.79E-13	4.67E+15	9.99E-06	2.57E-07
20	3.94E-13	4.67E+15	2.10E-05	5.38E-07
25	4.02E-13	3.85E+15	3.03E-05	7.78E-07
30	4.11E-13	5.46E+15	4.38E-05	1.12E-06
35	4.11E-13	1.01E+17	4.38E-05	1.12E-06
40	3.43E-13	8.81E+16	1.07E-06	2.74E-08

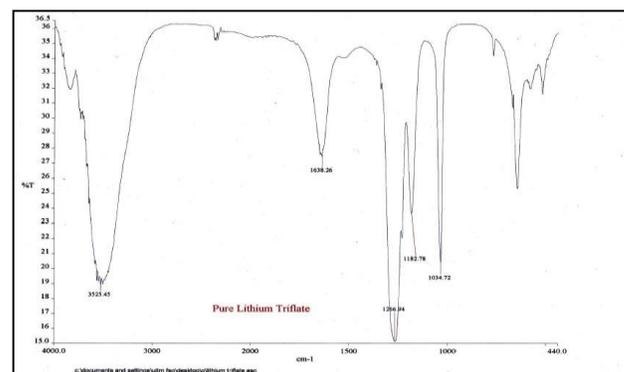
3.4 FTIR Analysis

FTIR is an efficient tool to study the local structural changes in polymer. The infrared spectra of these materials vary according to their composition and assist in confirming the complex formation among polymer matrices [12]. The complexation is essential as the movement of charges in/through polymer matrix is facilitated by association of charge carriers with polymer chains [13].

(a)



(b)



(c)

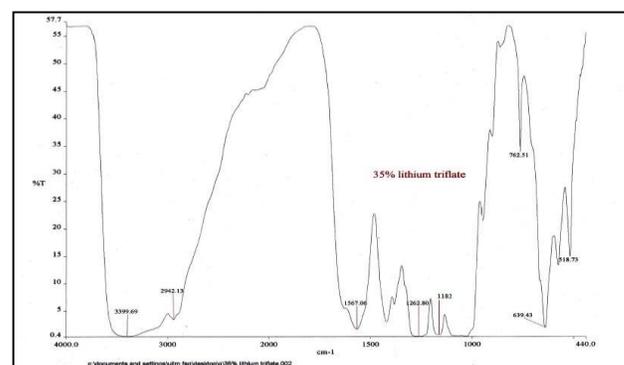


Figure 4 FTIR spectrum of (a) PSC film (b) pure LiCF_3SO_3 and (c) PSC film with 35wt.% LiCF_3SO_3

Figure 4(a) and (b) depicts the spectrum of potato starch-chitosan and pure LiCF_3SO_3 respectively. Ramesh and Chai [14] assigned 1266 and 1033 cm^{-1} bands to an asymmetric SO_3 and symmetric SO_3 vibrations. The bands at 3525, 1638 and 1182 cm^{-1} are also characteristic frequencies of LiCF_3SO_3 . The characteristic peak of pure LiCF_3SO_3 at 3525 cm^{-1} becomes broader in the starch-chitosan with 35wt.% of LiCF_3SO_3 complexes as shown in Figure 4(c). Besides, the peak of pure LiCF_3SO_3 at 1638 cm^{-1} is shifted to form a small shoulder at higher wavenumber in the broad peak at 1567 cm^{-1} in PSC with 35wt.% of LiCF_3SO_3 . Furthermore, it was observed that the relative intensity of the peak of pure LiCF_3SO_3 at 1182 cm^{-1} in Figure 4(b) drops from a moderate peak to a small and broad peak in the PSC with 35 wt.% of LiCF_3SO_3 in Figure 4(c). The change in intensity, shapes and position confirmed the complexation occur between PSC and LiCF_3SO_3 . This phenomenon of shifting and broadening of peaks are indications of acceptance of salt in the polymer host and formation of polymer-salt complexes.

4.0 CONCLUSION

The amount of LiCF_3SO_3 salt on solid biopolymer electrolytes of potato starch-chitosan was found to have a significance influence on the ionic conductivity. The maximum ionic conductivity was obtained with the sample containing of 35 wt.% LiCF_3SO_3 . The temperature dependence of ionic conductivity of PSC electrolytes films obeys the Arrhenius relationship. The FTIR spectrum spectral analysis confirmed the interactions existing between the PSC and lithium salt [13].

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