

INVESTIGATION ON LITHIUM BIS TRIFLUORO METHANE SULPHONYL IMIDE SALT BASED POLYMER ELECTROLYTE FILMS

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Abstract

Solid polymer electrolyte films with different weight percent ratios of lithium bis (trifluoro methane sulphonyl) imide (LTFSI) salt were prepared using solution casting method. The conductivity and dielectric response of the solid polymer electrolyte systems were studied within the frequency range of 120Hz and 1kHz at room temperature. The conductivity of an electrolyte depends on the ability of the polymer host to solvate the (LTFSI) salt. Polymers with higher dielectric constant will serve the purpose better. The dielectric constant and electrical conductivity follow the same trend with (LTFSI) salt concentration. It was observed that the magnitude of conductivity had increased with the increase in salt concentration. FTIR and XRD techniques were used in the complexed studies. The values of dielectric constant were decreased with increasing frequency.

Keywords: Electrolyte films, LTFSI, FTIR and XRD techniques .

Introduction

Solid polymer electrolyte membranes have shown great enthusiasm in the research work due to their wide range of applications in Electrochemical devices such as Fuel cells, Cell phone batteries, Sensors, Rechargeable batteries, Capacitors, Memory devices, Electro chromic display devices etc. Solid polymer electrolytes in Lithium ion batteries is an interesting field due to numerous characteristics such as no leakage, more flexibility, high energy density, more safety, and ease to manufacture. This made researchers in the development of Lithium polymer batteries. Lithium polymer batteries consist of polymer electrolyte as separator and charge carrier of ions which have been used as power sources for portable devices due to high energy density. Chitosan is a derivative of chitin which can be obtained from crab and shrimp shells. Chitosan is produced from deacetylation of chitin to overcome the solubility limitation of chitin in common solvents. Due to the NH₂ and OH functional groups that can serve as conjunction sites, chitosan is a good sorbent with high affinity for transition metal ions. Chitosan has good film forming ability, porous scaffolds, and hydrogels. Ion-conducting polymer electrolytes based on chitosan have also been reported. From the fundamental point of view, ionic conduction in polymer electrolysis still poorly understood. Ion transport is complex and depends on factors such as salt concentration, dielectric constant of host polymer, degree of salt dissociation and ion aggregation, and mobility of polymer chains. Dielectric analysis of ion conducting polymer electrolytes can provide information on ion transport behavior and ionic/molecular interaction in solid polymer electrolytes. In the present research work; Solid polymer electrolyte films with LITFSI salt are prepared with different concentrations and characterized by XRD, FTIR. XRD reveals the semi crystalline, amorphous nature of the polymer film. FTIR analysis provides the complexation and the extent of blending between the polymer and salt. Annealing method study reveals the thermal properties of the polymer and activation energy of the polymer electrolyte system.

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Experimental Procedures

Preparation of samples

Solid polymer electrolyte films were used as host polymer electrolytes and were prepared by standard solution casting techniques. All samples were prepared at room temperature and stored under dry conditions. A 5 g of prepared chitosan flake was dissolved in 500 mL of 1 % (w/v) acetic acid solution. The solution was stirred by hotplate stirrer, for 80 hours at an ambient temperature, and then the chitosan acetate host polymer solution was kept on overnight. The solution was maintained at 80 °C in water bath for one hour. The degassed and well-mixed solutions (30 mL) were casted onto petri dish, and dried in air for 3 days at room temperature until constant weight. The dried transparent chitosan films (0% doping salt) were detached from the petri dish. A 1 g of LTFSI salt was dissolved in 100 mL with distill water to make 1 % (w/v) doping salt solution by using magnetic stirrer. A 2.4 mL of 1 % (w/v) doping salt solution was mixed with 27.6 mL of 1 % (w/v) chitosan acetate solution by using hotplate stirrer. The 30 mL of polymer salt solution was obtained as 8wt % doping salt solution. It was prepared to more 8wt % in each still to still 40wt% dopant. The degassed and well-mixed solution was cast onto petri dish, and dried in air for 3 days at room temperature until constant weight.

The dried transparent chitosan films (8 % doping salt) were detached from the petri dish. Finally, chitosan film compound of 8wt % was obtained. The same procedure were carried out for the preparation of chitosan films compound of 8, 16, 24, 32, 40 % LTFSI were prepared.

Characterization of samples

The ionic conductivities of the samples were measured at within at room temperature using EXTECH 380193 LCR meter with a frequency range of 120 Hz and 1 kHz. The conductivity (σ) was determined using the equation below:

$$\sigma = \frac{1}{\rho(0) / 2S / W * \log(e)2} \quad (1)$$

From equation 1, $\rho(0) = 2\pi SR$, 'S' represents the distance between the two contact probe, 'W' represents the thickness of sample and R is the resistance of the sample. The dielectric constant ϵ_r can be defined as:

$$\epsilon_r = C_p t / \epsilon_0 A \quad (2)$$

From equation 2, 't' represents the thickness of sample, 'A' is the area of the surface of the sample, C_p is the capacitance of the specimen in Farad and ϵ_0 is the permittivity of free space.

X-ray diffraction (XRD): In this work, X-ray diffraction were carried out using a Rigaku x-ray powder diffractometer which employs Cu- K_α x- radiation of wavelength $\lambda = 1.54056\text{\AA}$ between a 2θ angle of 5° to 70° . X-ray diffraction was carried out to determine the nature of the materials whether a material is amorphous or crystalline.

FTIR spectrometer : Prepared chitosan films with various composition of doping salt, which were examined by IR-8400, Shimadzu, Japan (Universities' Center, University of Yangon.)

Results and Discussion

The structural, conductivity and dielectric properties of the polymer electrolytes based on LTFSI salt were investigated. The samples were prepared by solution cast method by taking different concentration of different ratio (i.e., Cs0%, Cs8%, Cs16%, Cs24%, Cs32% and Cs40%). The compatibility between the polymer matrix and the inorganic dopants has great influence on the properties electronic conductivity of the polymer electrolytes.

X-ray diffraction and FTIR studies

In order to investigate the effect of LTFSI salt on the structure of chitosan-based polymer electrolyte, x-ray diffraction of pure chitosan film, and their complexes have been performed. These crystalline structures contribute to the peaks in the XRD pattern of Cs0%, Cs8%, Cs16%, Cs24%, Cs32% and Cs40% are shown in Fig. 1. As seen in the XRD pattern of the pure chitosan Cs0%, the high intensity peak at around $2\theta = 22^\circ$. The increase in the broadness of the peak reveals the amorphous nature of the complexed system. Thus XRD analysis reveals the complex formation between the polymer and the salt.

The FTIR spectra were recorded to study the structure of polymer, polymer-salt interactions and complexation in polymer electrolytes. The interaction between polymer and salt influence vibrational modes of atoms or molecules which in turn generates change in chemical and physical properties of the polymer. The most frequently performed observations to confirm the complexation of the polymer host with salts are variation in intensity of the bands, shifting of the bands with respect to the salt content. Figure.2 represents the FTIR spectrum of chitosan and chitosan: LTFSI complexes in the wave number region between 500 cm^{-1} and 4000 cm^{-1} . Although there is possibility of overlapping between the N–H and the O–H stretching vibrations, the strong broadband at $3300\text{--}3500\text{ cm}^{-1}$ is characteristic of the N–H stretching vibration. The significant decrease of transmittance intensity and shifting in this band region indicates that the N–H vibration was affected by the attachment of the cation salt. The shifting and decrease in intensity are attributable to the fact that the attachment of cation salt to nitrogen and oxygen atoms can reduce the vibration intensity of the N–H or O=C–NHR bonds due to the molecular weight becoming greater after cation binding. The shifting and the vibrational bands at 2881, 2885, 2889, 2879 were assigned as asymmetric stretching and symmetric stretching of CH_3 and CH_2 corresponds to crystalline nature of chitosan which has been shifted to low frequencies at 2879 cm^{-1} of reducing intensity at 24wt% due to increase of LTFSI salt concentration; which shows the decrease of crystalline nature of the pure chitosan. It means amorphous nature of the polymers enhances the electrical conductivity of the sample. This indicates only certain amount of salt is able to dissolve which limits the number of Lithium ions generated which affects the electrical conductivity. The absorption band at 1633, 1637, 1629, 1641 and 1637 cm^{-1} corresponds to stretching vibration of $\text{C}=\text{O}$. The absorption band at 1402 corresponds to C-F stretching, shifted to high frequency at 1404, 1408 and 1406 cm^{-1} for increase of concentration of LTFSI salt. This happens due to weak interaction between H atoms of CH_2 groups and F atoms of CF_2 groups. The peaks at 3000 to 2900 cm^{-1} frequencies correspond to C-H stretching vibration of polymer. The observed peaks at 3650 to 3000 cm^{-1} show OH and -OOH groups. This occurs due to highly hygroscopic nature of LTFSI salt that absorbs moisture from the atmosphere. The shifting and a decrease in intensity of C–O bands are also indicative that complexation between the cation of the salt and oxygen atom has occurred.

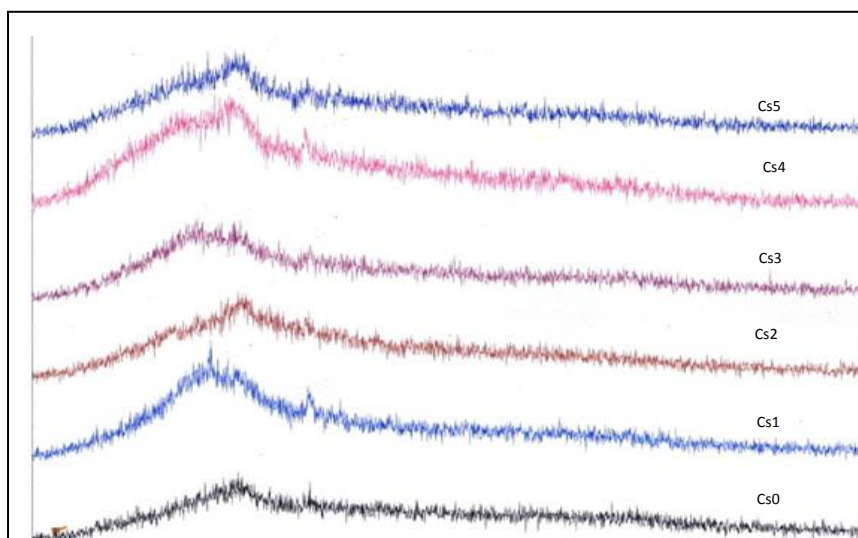


Figure 1 XRD spectra of LTFSI Salt -Chitosan polymer electrolyte films

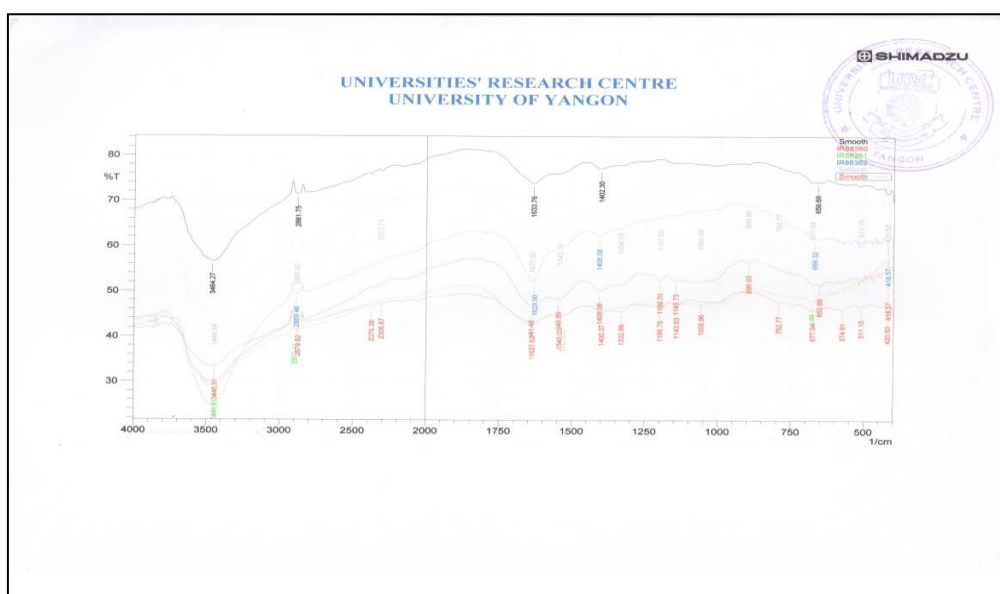


Figure 2 FTIR spectra with various concentrations of LTFSI salt

Electrical conductivity dielectric studies of solid polymer electrolytes

The electrical properties of the polymer electrolyte were studied using EXTECH 380193 LCR meter. Table.1 shows the various composition of (LTFSI) salt and chitosan solution. The value of electrical conductivity for solid polymer electrolytes samples with different weight percentages of (LTFSI) salt is plotted in Figure.3 and shown in Table.2. The conductivity was increased due to enrichment of (LTFSI) salt content reaching a highest value with 24wt% thereafter it decreases with further increase in amount of (LTFSI) salt content. The value of dielectric value for solid polymer electrolytes samples with different weight percentages of (LTFSI) salt is plotted in Figure.4 and shown in Table.3. The dielectric constant was found to increase upon the addition of (LTFSI) salt and these parameters are significantly influenced by the frequency. A dielectric medium has been assumed which is made up of well conducting grains and poorly conducting grain boundaries respectively. The grain are highly conductive and

have high values of permittivity. At low frequency region grain boundaries are more effective than the grains in electrical conduction. Thinner the grain boundary results the higher value of dielectric constant. Higher values of the dielectric constant observed at lower frequencies have been also explained on the basis of interfacial/space polarization due to nonhomogeneous dielectric structure.

Table 1 Various composition of LTFSI salt and chitosan Solution

Sample	Volume of 1 % (w/v) LTFSI (mL)	Volume of 1 % (w/v) Chitosan (mL)	Weight percent of LTFSI Salt (%)
Cs0	0	30	0
Cs1	2.4	27.6	8
Cs2	4.8	25.2	16
Cs3	7.2	22.8	24
Cs4	9.6	20.4	32
Cs5	12.0	18.0	40

Table 2 Conductivity measurement for various composition of lithium bis (trifluoro methane sulphonyl) imide salt and solid polymer electrolyte film at R.T

Name of Sample	Weight percent of Salt (%)	Conductivity (x 10 ⁻¹¹ S m ⁻¹)
Cs0	0	1.44
Cs1	8	1.79
Cs2	16	2.15
Cs3	24	3.11
Cs4	32	1.78
Cs5	40	1.58

Table 3 Dielectric measurement for Various Composition of Lithium bis (tri fluoro ethane sulphonyl) imide Salt and Solid Polymer Electrolyte Film at R.T

Name of Sample	Weight percent of Salt (%)	Dielectric Constant (120Hz)	Dielectric Constant (1kHz)
Cs0	0	9.04E-09	5.51E-09
Cs1	8	1.04E-07	5.39E-08
Cs2	16	1.12E-07	5.50E-08
Cs3	24	2.51E-07	6.35E-08
Cs4	32	1.98E-07	5.69E-08
Cs5	40	1.00E-07	5.60E-08

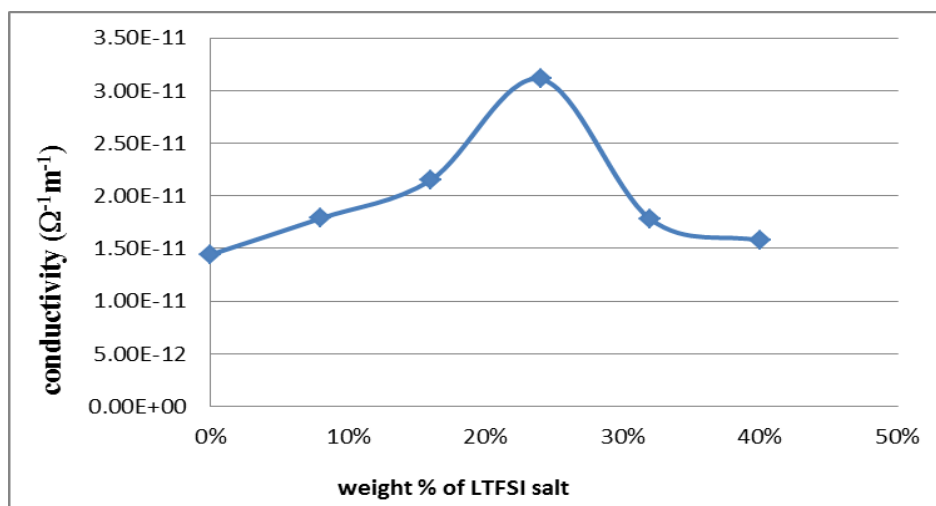


Figure 3 Conductivity measurement for various weight ratio Lithium salt polymer electrolyte films

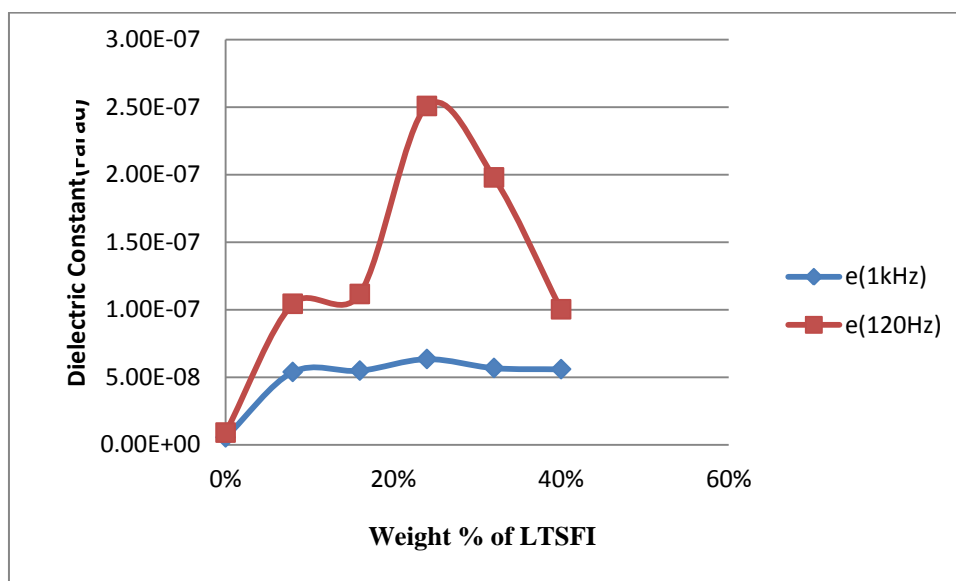


Figure 4 Dielectric measurement for various weight ratio Lithium salt polymer electrolyte films at 120Hz and 1kHz

Conclusion

Polymer electrolyte films were prepared using various composition of host polymer and LTFSI salt. X-ray diffraction shows that the amorphous phase greatly enhanced as a result of doping salt polymer. Samples with lower crystallinity exhibits higher electrical conductivity. Thus the decrease in intensity and broadening of the peaks indicates the increase in amorphous region as a result of disruption of the crystalline domain of the chitosan by the salt. According to the FTIR analyses, electrolyte film as the existence of interaction confirms that the electrolyte film was successfully prepared. The analysis of functional groups and the interaction between the constituents was observed by FTIR studies. Also the complex formation between polymer and salt was confirmed by FTIR and XRD studies. The shifting of the FTIR bands confirm the chitosan polar groups (CH_3 - and CH_2 -). Conductivity measurements were carried out on various

compositions of LTFSI polymer electrolyte film. The values of dielectric constant were decreased with increasing frequency. The conductivity and dielectric response of the solid polymer electrolyte systems were studied within the frequency range of 120Hz and 1kHz. It was observed that the magnitude of conductivity has increased with the increase in salt concentration. The sample containing 24 wt.% exhibited the highest room temperature conductivity of $3.11 \times 10^{-11} \text{ Sm}^{-1}$. The high dielectric constant at low frequency is attributable to electrode polarization. The increase of dielectric constant is responsible for the increase of DC conductivity.

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