

ELECTRICAL AND STRUCTURAL PROPERTIES OF PVC-LiCF₃SO₃ POLYMER ELECTROLYTE

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ABSTRACT

Polymer electrolyte films of poly (vinyl) chloride (PVC) as polymer host doped with lithium triflate (LiCF₃SO₃) as doping salt were prepared by solution cast technique. The conductivities of the samples were investigated by using Impedance Spectroscopy (IS). The sample containing 45 wt. % LiCF₃SO₃ showed the highest room temperature conductivity of $1.0660 \times 10^{-8} \text{ Scm}^{-1}$. The reason for the high conductivity in this sample is attributed to its low crystallinity as accounted by XRD (X-ray diffraction).

Keywords: PVC; LiCF₃SO₃; ionic conductivity; XRD; Scherrer Length;

INTRODUCTION

The major objective in solid polymer electrolyte (SPE) research is the evolution of polymeric system that has reasonable ionic conductivity [1]. SPEs are attractive materials because of their characteristics such as having good mechanical and thermal stability, free from leakage and light in weight [2,3,4]. Therefore, extensive research has been carried out on SPE in search of polymer electrolytes with acceptable conductivity which have potential application in solid state batteries [5].

In the present work, structural and electrical studies of polymer electrolyte of polyvinyl chloride (PVC) doped with lithium triflate (LiCF₃SO₃) is investigated using X-ray Diffraction (XRD) and Impedance Spectroscopy (IS) respectively. PVC has reasonable cost in comparison with other plastics that have high degree of adjustable and processing possibilities [6]. Besides, from the scientific point of view, PVC is used because of the presence of lone pair electrons at the chlorine atom where inorganic salts can be solvated, which can strengthen the polymer backbone [7].

Materials and Methods

PVC (very high molecular weight) and LiCF_3SO_3 (99% of purity) were all purchased from Sigma-Aldrich and used as received. Tetrahydrofuran (THF) was purchased from Merck Millipore, was used as solvent. PVC and LiCF_3SO_3 in various wt.% concentrations were dissolved in THF separately. Then they were mixed together and continuously stirred at room temperature until homogenous solutions were obtained. The solutions were then cast into glass dishes and subsequently dried at room temperature until polymer films were formed. The polymer films were vacuumed oven and then kept dry in a dessicator for further characterisation.

Complex impedance measurements were carried out by placing each polymer film between two stainless steel electrodes. The conductivity was measured using HIOKI 3532-50 LCR Bridge for frequencies ranging between 100 Hz to 1 MHz. The ionic conductivity of the electrolyte was calculated using:

$$\sigma = \frac{t}{R_b A} \quad (1)$$

where t is the thickness of the electrolyte film and A is the film-electrode contact area. The bulk resistance, R_b was obtained from a complex impedance plot of Z_i (imaginary impedance) versus Z_r (real impedance).

By using X'pert Pro Analytical Diffractometer system, the XRD spectra of the polymer films were obtained. The samples were scanned with a beam of monochromatic CuK_α -X-radiation of wavelength $\lambda = 1.5418 \text{ \AA}$ between Bragg angles (2θ) angles of 10° to 90° .

RESULTS AND DISCUSSION

Conductivity analysis

Figure 1 shows the room temperature ionic conductivity of PVC- LiCF_3SO_3 versus weight percent concentration of LiCF_3SO_3 salt. From this figure, it is observed that the conductivity gradually increased from $5.2343 \times 10^{-10} \text{ Scm}^{-1}$ for pure PVC system to $1.0660 \times 10^{-8} \text{ Scm}^{-1}$ for 45 wt. % LiCF_3SO_3 -55 wt. % PVC. The increase in ionic conductivity may due to the increase in the number of free ions because of increase of salt concentration in amorphous phase[6,8]. As the concentration of LiCF_3SO_3 is further increased to 50 wt. %, lower conductivity is observed which is $5.4357 \times 10^{-9} \text{ Scm}^{-1}$. At this point, the decrease in ionic conductivity after the maximum point maybe endorsed by the decrease in number of free ions due to formation of ion aggregates because of the presence of a large number of ions[6,8]. Presence of ion aggregations reduced the overall number of effective charge carriers and ion mobility, thereby reducing ionic conductivity[9].

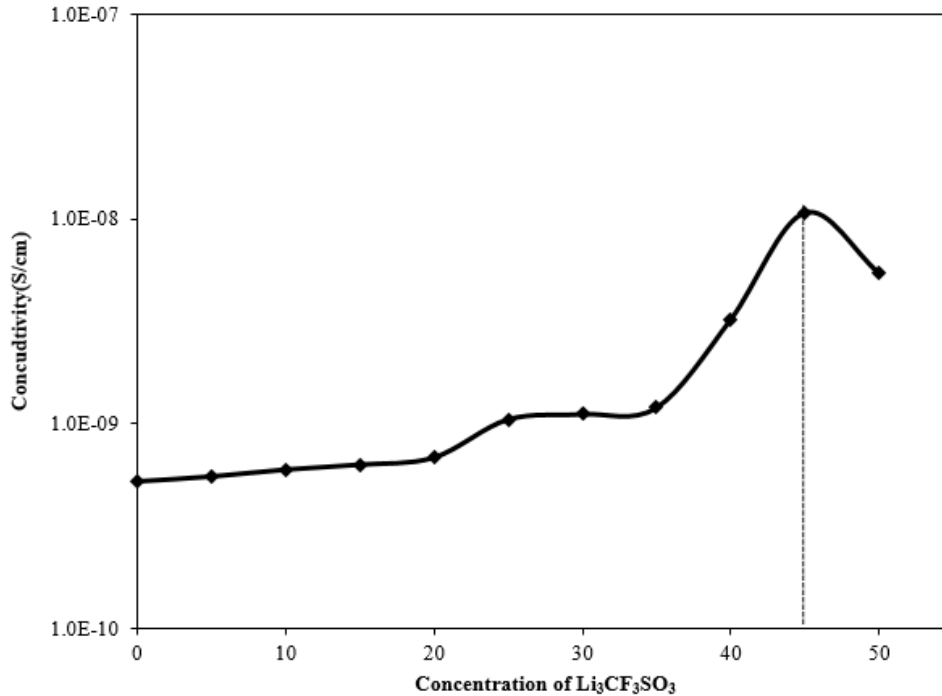


Figure 1: Variation of room temperature conductivity with concentration of LiCF_3SO_3

X-ray diffraction analysis

XRD analysis is one of the ways to study the nature of a material, whether amorphous or crystalline [5]. Figure 2 shows the XRD spectra of pure LiCF_3SO_3 , pure PVC, 80 wt. % PVC-20 wt. % LiCF_3SO_3 , 70 wt. % PVC-30 wt. % LiCF_3SO_3 , 60 wt. % PVC-40 wt. % LiCF_3SO_3 , 55 wt. % PVC-45 wt. % LiCF_3SO_3 , and 50 wt. % PVC-50 wt. % LiCF_3SO_3 systems.

It was found that pure LiCF_3SO_3 is crystalline in nature with peaks at 16.5° , 19.8° , 20.4° , 22.6° , 24.6° , and 33.0° . Meanwhile pure PVC is found to be amorphous in nature with a broad amorphous hump centered at 21.2° . The addition of LiCF_3SO_3 into PVC transformed the amorphous hump to appear broader and flatter (less intense). As concentration of LiCF_3SO_3 increased, the intensity of XRD peaks decrease which indicates an increase in amorphous phase in the PVC- LiCF_3SO_3 electrolytes[3,8]. Meanwhile, when 50% of salt is fused into PVC, the broad amorphous hump observed in the XRD spectrum disappeared reducing the spectrum of this sample to almost flat.

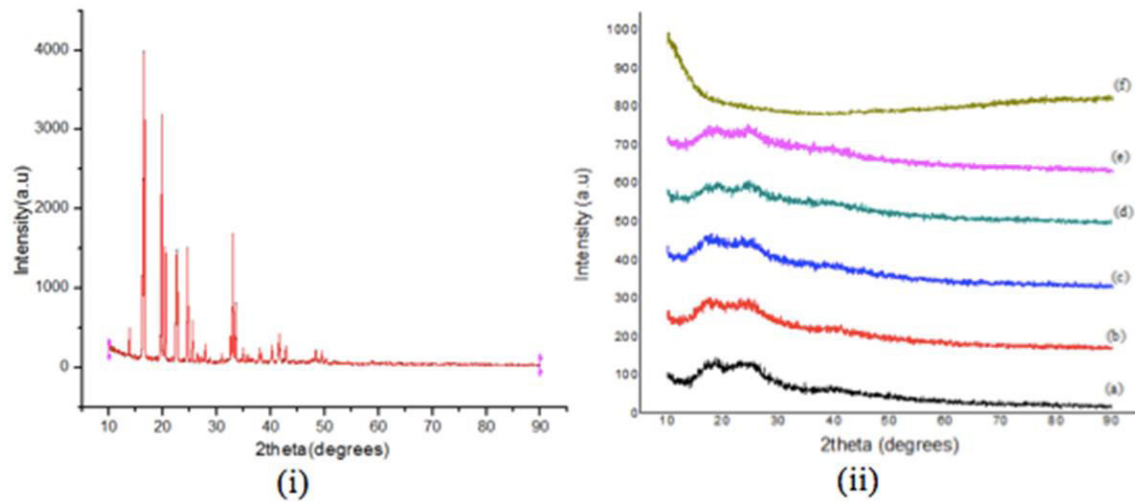


Figure 2: XRD spectra of (i) pure LiCF_3SO_3 , (ii) a) pure PVC, b) 80 wt. % PVC-20 wt. % LiCF_3SO_3 , c) 70 wt. % PVC-30 wt. % LiCF_3SO_3 , d) 60 wt. % PVC-40 wt. % LiCF_3SO_3 , e) 55 wt. % PVC-45 wt. % LiCF_3SO_3 f) 50 wt. % PVC-50 wt. % LiCF_3SO_3

The increase in amorphous phase is verified by calculation of the crystallite size using Scherrer's Length formula, given as follows:

$$L = \frac{0.94\lambda}{d \cos \theta} \quad (2)$$

Where,

$\lambda = 1.54056 \text{ \AA}$ for Cu $K\alpha$ line

d = the full width at half maximum of an X-ray diffraction peak and

θ = the corresponding Bragg angle

Table 1 lists the conductivity and the crystallite size of some of the samples studied in this work. The listed Scherrer lengths were calculated using the peak at 21.2° . The results indicate that the crystallite size reduced as concentration of LiCF_3SO_3 increased with the smallest crystallite size being 0.1166\AA for 55 wt. % PVC-45 wt. % LiCF_3SO_3 . The smaller the crystalline size, the more amorphous the sample[10,11]. Hence the sample with 55 wt. % PVC-45 wt. % LiCF_3SO_3 has the smallest crystallite size, signifying that this system is most amorphous compared to other systems and hence the reason for its high ionic conductivity.

Table 1: Variation of crystallite size with different concentrations of LiCF₃SO₃

Wt% LiCF ₃ SO ₃ [%]	FWHM	Crystallite size [D _s in Å]	Conductivity [Scm ⁻¹]
0	10.2	0.1445	5.2343x10 ⁻¹⁰
20	11.94	0.1235	6.8376x10 ⁻¹⁰
30	12.04	0.1225	1.1108x10 ⁻⁹
40	12.29	0.1200	3.2067x10 ⁻⁹
45	12.65	0.1166	1.0660x10 ⁻⁸

CONCLUSION

PVC- LiCF₃SO₃ polymer electrolyte were prepared by solution cast technique. The addition of salt increased the ionic conductivity of PVC- LiCF₃SO₃ polymer electrolytes. The highest conductivity attained in this work is 1.066x10⁻⁸ Scm⁻¹ at 55 wt. % PVC-45 wt. % LiCF₃SO₃. The increase in conductivity is because of reduction in crystallite size upon addition of salt as verified by XRD analysis. There are still opportunities to increase the ionic conductivity by integration of the existing sample with ionic liquid or plasticiser.

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