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Dielectric and FTIR studies on blending of [xPMMA–(1 − x)PVC] with LiTFSI

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ABSTRACT

Poly(methyl methacrylate) (PMMA)/poly(vinyl chloride) (PVC) polymer blend electrolytes with lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) as a dopant salt were prepared by solution casting technique. Various blend ratio of PMMA/PVC was studied in this present work. Based on the results obtained from AC-impedance spectra, the weight ratio of PMMA/PVC that is 70:30 exhibited the highest ionic conductivity at room temperature. The ionic conductivity and dielectric relaxation studies of the blended polymer electrolyte have been determined by AC-impedance spectroscopy over a wide frequency regime. In addition, Fourier Transform Infrared (FTIR) studies revealed the complexation between PMMA, PVC and LiTFSI.

1. Introduction

The development of polymer electrolytes has received an upsurge of interest as it is a prospective candidate for advanced electrochemical devices such as batteries, electrochromic devices, fuel cells and sensors. Solid polymer electrolytes (SPEs) have intrinsic advantages over conventional liquid electrolytes. These include features such as eliminating leakage of hazardous liquid or gas, high ionic conductivity, wider operating temperature and superior structural stability. Besides, it possesses good chemical and electrochemical stabilities as well as low volatility with excellent photochemical stability [1,2].

In the initial study of poly(ethylene oxide) (PEO) with various inorganic lithium salts, PEO failed to exhibit high ionic conductivity at ambient temperature due to higher degree of crystallization. In order to attain high ionic conductivity at ambient temperature, an amorphous polymer, poly(methyl methacrylate) (PMMA) was used in this work. The attempt of using PMMA is due to its flexible polymer backbone. Although the conductivity can be enhanced by introducing PMMA, the mechanical strength is reduced. Hence, it exhibits brittle property especially under a loaded force. Polymer blending is an attempt to improve ionic conductivity and mechanical strength. PVC was thus introduced into this polymer system as mechanical stiffener. It is an inexpensive polymer, exhibits easy processability and is well compatible with a large number of plasticizers making it as a promising candidate [3]. In this study, PVC and PMMA have been blended to complement each other. To further improve the ionic conductivity, attempt was made using lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) because it has large and highly flexible anions. Additives such as plasticizers or inorganic fillers are absent in this present work. The compatible ratio of PMMA and PVC was investigated in this LiTFSI-based polymer electrolyte. In this present work, the weight ratio of polymer blend to lithium salt is 90:10.

2. Experimental procedure

PMMA with an average molecular weight of 35,0000 g mol^{-1} (Aldrich), high molecular weight of PVC (Fluka), inorganic dopant salt, LiTFSI (Fluka) and solvent, THF (J.T. Baker) were used without further purification in

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Table 1
Designations and compositions of PMMA–PVC–LiTFSI based polymer electrolytes.

Designation	Composition of PMMA: PVC: LiTFSI				
	PMMA		PVC		LiTFSI
	Weight (g)	Weight percentage (wt.%)	Weight (g)	Weight percentage (wt.%)	Weight (g)
PE 1	0.81	90	0.09	10	0.10
PE 2	0.72	80	0.18	20	0.10
PE 3	0.63	70	0.27	30	0.10
PE 4	0.54	60	0.36	40	0.10
PE 5	0.45	50	0.45	50	0.10
PE 6	0.36	40	0.54	60	0.10
PE 7	0.27	30	0.63	70	0.10
PE 8	0.18	20	0.72	80	0.10
PE 9	0.09	10	0.81	90	0.10

this study. All the polymer electrolytes were prepared by means of solution casting method. Prior to the preparation of the polymer electrolytes, LiTFSI was dried at 100 °C for 1 h to eliminate trace amounts of water in the material. The compositions prepared were [xPMMA–$(1-x)$PVC] where x is between 0.1 and 0.9 with an increment of 0.1, and the weight ratio of polymer blend to lithium salt is 90:10. Table 1 shows the composition of particular polymer blend electrolytes with its designation. Appropriate amounts of PMMA, PVC and LiTFSI were dissolved in THF. The solution was stirred continuously for 24 h to obtain a homogenous mixture at room temperature. After that, the solution was cast on a glass Petri dish and allowed to evaporate slowly inside a fume hood. Eventually, a free standing thin film is produced.

The freshly prepared samples were subjected to AC-impedance spectroscopy and Fourier Transform Infrared spectroscopy (FTIR). For impedance spectroscopy, the thicknesses of the thin films were measured by micrometer screw gauge. The ionic conductivity of the samples was determined by using HIOKI 3532-50 LCR HiTESTER connected to a computer for data acquisition over a frequency range between 50 Hz and 1 MHz. The thin films were sandwiched between two stainless disk electrodes. In contrast, FTIR analysis was carried out by using FTIR Spectrometer Spectrum RX1 (Perkin–Elmer) in the wave region between 4000 and 400 cm^{-1}. The resolution of the spectra obtained at room temperature was 4 cm^{-1}. The FTIR data obtained were recorded in the transmittance mode.

3. Results and discussion

3.1. AC-impedance studies

AC-impedance spectroscopy is used to measure the ionic conductivity of polymer electrolytes by placing the thin electrolyte film between two blocking electrodes. Fig. 1 shows the typical impedance plot for PE 3 at room temperature. The ionic conductivity of polymer electrolyte is determined by using the equation as shown below.

$$\sigma = \frac{\ell}{R_b A}$$

where ℓ is the thickness (cm), R_b is bulk resistance (Ω) and A is the known surface area (cm^2) of polymer electrolyte.

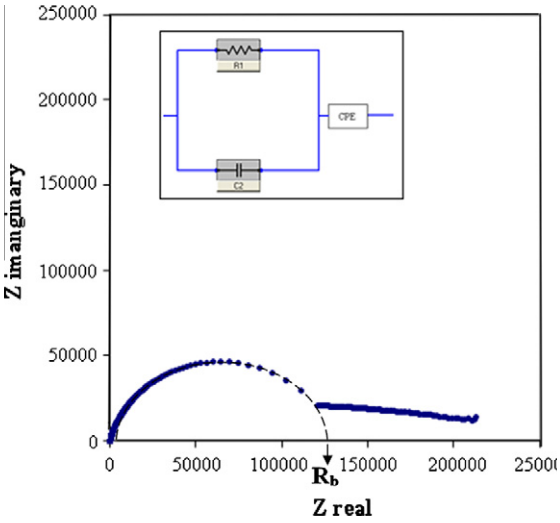

Fig. 1. Typical Cole–Cole plot of PE 3 at ambient temperature.

The R_b of the thin electrolyte film is calculated by extrapolation of the semicircular region to its highest frequency as shown in Fig. 1. Fig. 1 depicts the typical Cole–Cole impedance plot of PE 3 at room temperature and its equivalent circuit (inset of the figure). In general, this impedance plot has been divided into two well defined regions: a slanted spike at low frequency and a semicircle portion which reveals the characteristic of a parallel combination of R_b and bulk capacitance of the polymer matrix at high frequency [4]. This parallel combination of resistance and capacitance can be represented by the inset of the figure. However, the spike is slanted at an angle less than 90°. This phenomenon indicates the non-idealism of capacitance and induces to an establishment of double layer at the blocking electrodes or also known as non-Debye effect. It implies that a constant phase element is appeared at the electrode and polymer electrolyte interface and leads to a formation of double layer at the electrodes, as shown in inset of Fig. 1. In addition, the angle and the amount of inclination is attributed to the distribution of conductivity relaxation time which defined as the time required to build up charges at the electrode and electrolyte interface before