

FTIR studies of PEMA/PVdF-HFP blend polymer electrolyte system incorporated with LiCF_3SO_3 salt

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ABSTRACT

Poly(ethyl methacrylate), PEMA and poly(vinylidene fluoride-co-hexafluoropropylene), PVdF-HFP have been chosen as hosts for the development of a polymer blend electrolyte system. Lithium trifluoromethanesulfonate (triflate), LiCF_3SO_3 is the lithium ion, Li^+ provider. The ratio of PEMA:PVdF-HFP in the blend is fixed at 70:30 in order to obtain transparent films with good mechanical stability. The polymers and LiCF_3SO_3 salt have been refluxed for 2 h at temperatures between 55 and 65 °C. The concentration of LiCF_3SO_3 salt has been varied from 0 to 40 wt.%. Fourier transform infrared (FTIR) spectroscopy has shown that blending between PEMA and PVdF-HFP has occurred from the changes in the CH_2 scissoring [$\delta(\text{CH}_2)$], asymmetrical $\text{O}-\text{C}_2\text{H}_5$ bending [$\gamma(\text{OC}_2\text{H}_5)$], CH_2 twisting [$\tau(\text{CH}_2)$], C–O stretching of –COO– group [$\nu(\text{CO})$], asymmetrical C–O–C stretching [$\nu_2(\text{COC})$] and C–O stretching of – OC_2H_5 [$\nu(\text{C}-\text{O})$] from PEMA as well as the symmetrical CF_2 stretching [$\nu_s(\text{CF}_2)$], α -phase and the amorphous region of PVdF-HFP. Complexation occurs via the coordination of Li^+ ions with the oxygen atom in the carbonyl (C=O) and ester (–COC–) groups of PEMA as well as with the fluorine atom in – CF_2 and – CF_3 groups in PVdF-HFP. Curve fitting of spectral bands in the symmetrical $\nu_s(\text{SO}_3)$ stretching region in the polymer blend–salt complexes has shown that free ions (1031–1032 cm^{-1}) and ion pairs (1040–1042 cm^{-1}) are present in samples incorporated with 10 wt.% LiCF_3SO_3 and above, while ion aggregates at 1049 cm^{-1} are formed when 40 wt.% LiCF_3SO_3 is added into the polymer blend. The increase in the ionic conductivity at high salt contents could be explained by the greater amount of free ions as compared to ion pairs and ion aggregates.

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1. Introduction

Polymer electrolytes are potential candidates as a medium for charge transport in electrical double layer capacitors, rechargeable batteries, fuel cells and electrochromic devices. Polymer electrolytes are safe, flexible, mechanically stable and can offer higher energy density as compared to commercial liquid electrolytes. Polymer electrolytes consist of salts dissolved in solid polymers, and the polymer must contain a Lewis base which serves to coordinate the cations, thus promoting dissolution of the salt [1]. However, the cation–Lewis base bonding must be labile to allow ion mobility [2].

Poly(methyl methacrylate), PMMA and poly(ethyl methacrylate), PEMA are methacrylic ester polymers. PEMA has excellent chemical resistance, high surface resistance and offers high optical transparency [3]. PMMA electrolytes have been widely investigated by researchers due to its high ambient temperature ionic conductivity, which resembled that of liquid electrolytes. PEMA is reported [4] to exhibit higher mechanical strength than

PMMA. PVC/PEMA– LiPF_6 –EC–PC displayed higher elastic modulus and elongation as compared to PVC/PMMA– LiPF_6 –EC–PC polymer electrolyte. High transparency, sufficient mechanical strength, elasticity and good adhesion onto substrates [3] make PEMA suitable for use as a host for ionic conduction in electrochromic devices. On the other hand, poly(vinylidene fluoride–hexafluoropropylene), PVdF-HFP consisting of crystalline VdF and amorphous HFP units allows ionic conductivity to occur with ease [5]. PVdF-HFP has high dielectric constant $\epsilon \approx 8.4$, and thus can accommodate high concentration of charge carriers.

PEMA contains electron pairs at the oxygen atoms of C=O and C–O– C_2H_5 groups [6] while fluorine (F) atoms in PVdF-HFP have electron pairs that can coordinate with the cation of a salt [7] to form polymer–salt complexes. From the change in the position, shape and intensity of the bands representing the polar group, complexation between an inorganic salt and polymer host can be confirmed. Lithium trifluoromethanesulfonate (LiCF_3SO_3) or lithium triflate is widely used as a doping salt to provide lithium ions (Li^+) for ionic conduction in polymer electrolytes. Fig. 1 shows the chemical structure of PEMA, PVdF-HFP and lithium triflate.

In this study, PEMA and PVdF-HFP were chosen so as to develop a polymer blend electrolyte system with LiCF_3SO_3 as salt. Acetone

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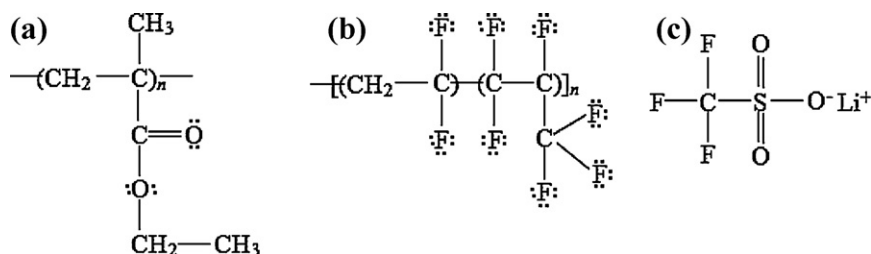


Fig. 1. Chemical structure of (a) PEMA, (b) PVdF-HFP and (c) lithium triflate. (The pair of dots represent lone pair of electrons.)

was used as solvent. The objectives of this study are (i) to show miscibility between PEMA and PVdF-HFP, (ii) to investigate the complexation sites where Li^+ ions bind to the polymers and (iii) to study the effect of ionic association on the ionic conductivity of the polymer blend–salt complexes by FTIR analyses.

To the authors' knowledge, there are no reports on the literature about transparent blended polymer electrolytes based on PEMA/PVdF-HFP. From this investigation, the authors hope to shed some light on understanding the conduction mechanism in such electrolytes.

2. Experimental

2.1. Materials

Poly(ethyl methacrylate) (PEMA, MW = 515,000, CAS = 9003-42-3, Aldrich) in powder form, poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP, CAS = 9011-17-0, Aldrich) in pellet form, and acetone (J.T. Baker) were used as received. Lithium trifluoromethanesulfonate (or triflate) (LiCF_3SO_3 , Aldrich) was heated at 130°C for 3 h to eliminate any moisture prior to use.

2.1.1. Preparation of PEMA/PVdF-HFP blend polymer electrolyte films

PEMA/PVdF-HFP blend polymer electrolyte films were prepared using the reflux method. The PEMA:PVdF-HFP ratio is 70:30. Different amounts (10, 20, 30 and 40 wt.%) of LiCF_3SO_3 salt were added to the polymer solution in acetone. The mixtures were magnetically stirred vigorously at $55\text{--}65^\circ\text{C}$ for 2 h to form PEMA/PVdF-HFP polymer blend electrolytes. The transparent resultant solutions consisting of salt and the two polymers were cast onto glass plates and dried at 45°C in an oven for several hours to allow the complete evaporation of the acetone until solvent-free films were formed adhered onto the glass plates. Upon cooling at room temperature, the mechanically stable transparent films were carefully peeled from the glass plates and stored in the desiccator for several days for further drying before characterization. The thickness of the films is in the range from 25 to $30\ \mu\text{m}$. Table 1 shows the composition of polymer blend samples and their respective designation.

2.2. Characterization techniques

2.2.1. Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy was carried out on all polymer electrolyte films with thickness ranging from 25 to $30\ \mu\text{m}$ using the Thermo

Scientific Nicolet iSIO Smart ITR in the transmission mode over the wavenumber range from 4000 to $650\ \text{cm}^{-1}$ at a resolution of $1\ \text{cm}^{-1}$.

2.2.2. Curve-fitting procedures

Several wavenumber regions of the IR spectra contained overlapping of IR bands due to several closely placed bands which are contributed by different components (*i.e.* PEMA, PVdF-HFP, LiCF_3SO_3) present in a sample. In order to resolve overlapping bands within the IR region of interest, all peaks present in PEMA, PVdF-HFP, LiCF_3SO_3 and PEMA/PVdF-HFP blend had been identified. This allowed us to know the number of IR bands and their respective wavenumbers within an IR region.

In our work, a series of deconvolution of IR bands were performed using OMNIC software. The deconvolution was carried out by fixing the number and line shape, and allowing band parameters such as full width at half maximum (FWHM), area, intensity and band shape to vary without constraints during the iteration [8]. The Gaussian/Lorentzian function was employed to fit the selected bands of the polymer blend and polymer blend–salt samples [9–11] and all the deconvoluted spectra were best fitted using a constant baseline. All resultant peaks created through curve-fitting match the original spectrum when added together.

If PEMA and PVdF-HFP have interacted with each other to form a blend, the infrared spectrum of PEMA/PVdF-HFP blend film will show changes in the position, intensity and shape of the IR bands from the original characteristic bands of both polymers. New bands may form and some original bands may disappear. If PEMA and PVdF-HFP are not suitable to form a blend with each other, the IR spectrum of PEMA/PVdF-HFP blend film will show the original vibrational bands of both PEMA and PVdF-HFP. Complexation between polymer blend and salt can be investigated through changes in IR bands of polar functional groups which belong to PEMA and PVdF-HFP, and also changes in the vibrational frequencies of LiCF_3SO_3 .

2.2.3. Electrochemical impedance spectroscopy (EIS)

Impedance of the samples was determined using the Hioki 3531 Z HiTester. The measurements were done in the frequency range from 50 to 1 MHz at ambient temperature. The impedance studies were carried out by sandwiching the polymer electrolyte film between two stainless steel (SS) electrodes under spring pressure. The thickness of each sample was measured using a micrometer screw gauge. The imaginary impedance (Z'') was plotted against the real impedance (Z') and the bulk resistance was obtained from the intercept with the real-axis. The ionic conductivity, σ in S cm^{-1} of each sample was calculated using the following equation:

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

where l is the thickness of the film, R_b is the bulk resistance and A is the area of electrolyte–electrode contact.

Table 1
Designations and compositions of PEMA/PVdF-HFP (70:30)– LiCF_3SO_3 films.

Sample	(PEMA/PVdF-HFP): LiCF_3SO_3 (w/w)
S0	100:0
S10	90:10
S20	80:20
S30	70:30
S40	60:40

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