Blend polymer electrolyte films based on poly(ethyl methacrylate)/poly(vinylidenefluoride-*co*-hexafluoropropylene) incorporated with 1-butyl-3-methyl imidazolium iodide ionic liquid

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ABSTRACT

Poly(ethyl methacrylate) (PEMA) and poly(vinylidenefluoride-*co*-hexafluoropropylene) (PVdF-HFP) in the weight ratio of 70:30 are chosen as hosts for the development of a polymer blend electrolyte system containing lithium trifluoromethanesulfonate (LiTf) salt as ion provider and 1-butyl-3-methyl imidazolium iodide (BMII) as ionic liquid. The best ambient conductivity is achieved at 4.86×10^{-5} S cm^{-1} in the polymer blend-salt sample incorporated with 12.5 wt.% BMII. The imidazolium (BMI$^+$) cations of BMII have interacted with the oxygen atoms in the ethoxy (O–C$_2$H$_5$) groups of PEMA as well as the fluorine atoms in the CF$_2$ groups of PVdF-HFP. Competition between the Li$^+$ ions and BMI$^+$ ions for the coordination sites at the polar atoms of the polymer blend host exists and plays a role in determining the number density and mobility of the free ions. Thermal gravimetric analysis (TGA) has shown that the BMII-based polymer electrolytes are thermally stable up to about 200 °C.

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1. Introduction

Many researchers are currently working on polymer electrolytes as alternatives to commercial liquid electrolytes used in electrochemical devices such as lithium ion batteries, fuel cells, solar cells, supercapacitors and electrochromic devices [1–5]. Ionic conductivities at room temperature of solid polymer electrolytes are often insufficient for practical application in electrochemical devices. Hence, numerous methods have been utilized by researchers to enhance the ionic conductivities by incorporation of plasticizers with low viscosity and high dielectric constant ionic liquids (ILs) and fillers [6–7].

As molten salts which consist of dissociated cations and anions at room temperature, ILs exhibit attractive properties such as good ionic conductivity, high thermal stability between 200 and 300 °C hence wide temperature range of operation, wide electrochemical window and low vapor pressure. In recent years, 1-butyl-3-methyl imidazolium iodide (BMII) is gaining the interest of researchers not only as an additive to enhance the ionic conductivity of polymer electrolytes but also as a source of iodide ions for dye sensitized solar cell application [8,9].

Numerous reports on IL-based polymer electrolytes employing single polymer have been reported [10–14]. However, there are limited reports on polymer blend electrolyte system incorporated with IL [1, 15–17]. Ramesh et al. [15] studied poly(methyl methacrylate)/poly(vinyl chloride)-lithium bis(trifluoromethyl)sulfonimide-1-butyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide gel polymer electrolytes (GPEs) and obtained a maximum conductivity of around 0.16 mS cm^{-1} upon loading of 60 wt.% IL at ambient condition. Dimensionally stable membranes were produced by Thayumanasundaram and co-workers [16] based on poly(vinyl alcohol) (PVA)/poly(acrylic acid) (PAA) blend incorporated with LiTFSI and 70 mol% of 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR$_{14}$TFSI) which exhibited conductivity of 0.2 mS cm^{-1} at room temperature [16]. Zhai and co-workers [17] reported a maximum conductivity of 1.4 mS cm^{-1} at 30 °C for PMMA/PVdF-HFP-lithium perchlorate (LiClO$_4$)-BMIBF$_4$ GPEs which were prepared by immersing microporous PMMA/PVdF-HFP films into LiClO$_4$ salt-BMIBF$_4$ IL mixture.

Fluoropolymers such as poly(vinylidenefluoride-*co*-hexafluoropropylene) (PVdF-HFP) and polymethacrylates such as poly(ethyl methacrylate) (PEMA) have gained attention as potential polymer hosts to produce good polymer electrolytes [18]. With high dielectric constant ~8.4, PVdF-HFP contains predominantly crystalline PVdF phase and amorphous VdF phase which provides necessary mechanical strength and good ion transport matrix. PVdF-HFP incorporated with ILs have been reported to exhibit high ionic conductivity close to 10 mS cm^{-1}, high thermal stability (up to 310 °C) [19], wide electrochemical window up to 4–5 V [20] and form free-standing films [21]. PEMA on the other hand is an amorphous polymer which produces transparent polymer electrolyte films that are versatile to be used in both non-optical and optical devices [22]. Blending both PVdF-HFP and PEMA is expected to produce a polymer blend which has the strengths, if not improved properties, of the individual polymers. To

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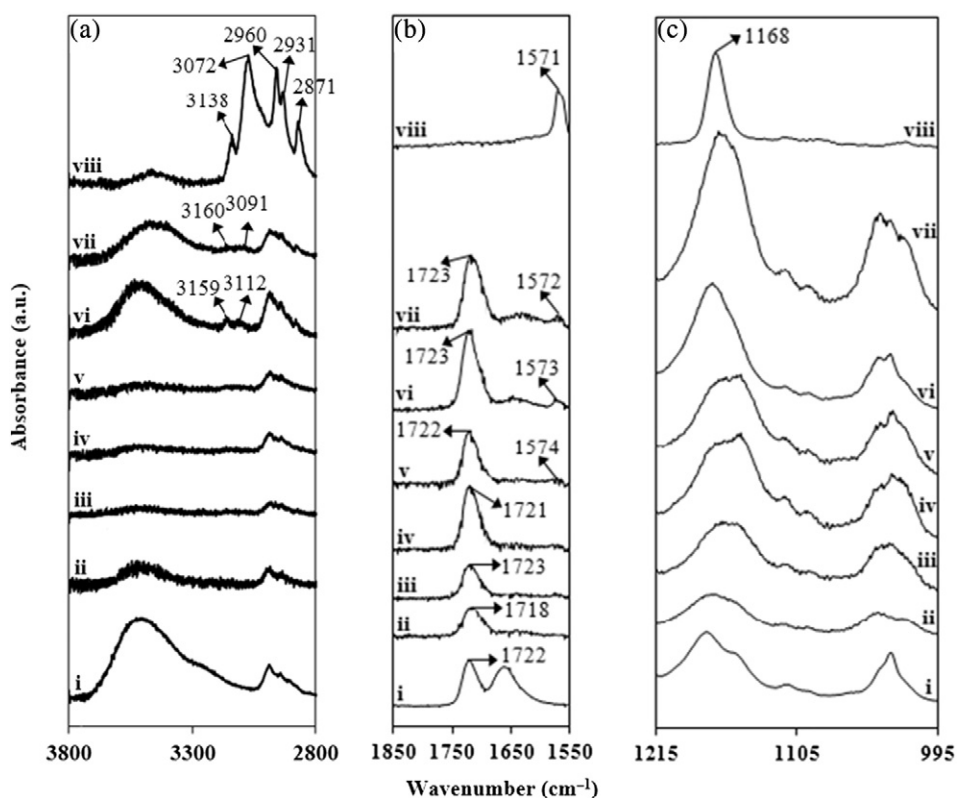**Fig. 1.** FTIR spectra between (a) 2800–3800 cm^{-1}, (b) 1550–1850 cm^{-1} and (c) 995–1215 cm^{-1} of i. BI–0, ii. BI–5, iii. BI–10, iv. BI–12.5, v. BI–15, vi. BI–17.5, vii. BI–20 and viii. BMII.

the best of our knowledge, there is no report on polymer blend based on PEMA and PVdF-HFP which employs LiTf as salt and BMII as ionic liquid. Hence, this paper will shed some light on the effect of BMII on the conductivity, molecular interactions and thermal properties of the polymer electrolyte system.

2. Experimental

2.1. Materials

Poly(ethyl methacrylate) (PEMA) (M$_w$ = 515,000, CAS = 9003-42-3, density = 1.11 g cm^{-1}) in powder form, poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-HFP) (CAS = 9011-17-0, density = 1.78 g cm^{-1}) in pellet form, lithium trifluoromethanesulfonate (LiTf) (density = 1.90 g cm^{-1}), 1-butyl-3-methyl imidazolium iodide (BMII) (density = 1.49 g cm^{-1}) in liquid form were purchased from Aldrich and acetone was obtained from J.T. Baker. Prior to use, LiTf salt was dried at 130 °C for 3 h to eliminate moisture.

2.2. Preparation of polymer electrolyte films

Solid polymer electrolytes with varied amounts of BMII were prepared by solution casting technique. 0.7 g PEMA, 0.3 g PVdF-HFP and a fixed amount of LiTf were dissolved in acetone to form PEMA/PVdF-HFP:LiTf (70:30; wt.%:wt.%). Prior to use, LiTf salt was dried at 130 °C for 3 h to eliminate moisture. Varied amounts (5, 10, 12.5, 15, 17.5 and 20 wt.%) of BMII were then added into the solution. The mixtures were stirred vigorously for 2 h under reflux between 55 and 65 °C to allow complete dissolution of the materials, and complexation to occur. The homogeneous mixtures with different amounts of BMII were cast onto different glass petri dish and left to dry at 45 °C in oven to form PEMA/PVdF-HFP-LiTf-BMII polymer electrolyte films. The samples were stored in a desiccator for several days before characterization to remove residual solvent. The samples were designated as BI–*x*

where the prefix BI represents BMII ionic liquid and *x* refers to the wt.% of BMII added.

2.3. Characterization techniques

2.3.1. Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy was carried out on the polymer electrolyte films using the Thermo Scientific Nicolet iS1O Smart iTR* ATR in the absorbance mode over the wavenumber region from 650 to 4000 cm^{-1} with resolution of 1 cm^{-1}. As such only shifts larger than 2 cm^{-1} were considered. Deconvolutions of IR bands were performed using the OMNIC software. The deconvolutions were carried out by fixing the number of IR peaks and line shape, and allowing band parameters such as full width at half height, area, intensity and band shape to vary without constraints during the iteration [23]. The Gaussian/Lorentzian function was employed to fit the selected bands of the polymer electrolyte samples [24–26] and all the deconvoluted spectra were best fitted using a constant baseline. All resultant peaks created through curve-fitting matches the original spectrum when added together. The area percentage of free ions (%FI) is calculated according to the equation below:

$$\%\mathrm{FI} = \frac{A_{FI}}{A_{FI} + A_{IP}} \times 100\% \tag{1}$$

where A_{FI} and A_{IP} refer to areas of free ions and ion pairs respectively. The values were obtained directly from OMNIC software.

2.3.2. 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 Hz to 1 MHz at 298 K. The impedance studies were carried out by sandwiching the polymer electrolyte film between two stainless steel electrodes under spring pressure. The thickness of each sample was