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A simple P(VdF-HFP)–LiTf system yielding highly ionic conducting and thermally stable solid polymer electrolytes

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ABSTRACT

In the present work, we report a simple solid polymer electrolyte (SPE) system that is solely based on poly(vinylidene fluoride-co-hexafluoropropylene) [P(VdF-HFP)] and lithium trifluoromethanesulfonate (LiTf). The SPEs produced exhibit high ionic conductivity of ~10^{-4} S cm^{-1} at ambient temperature when 40 wt.% of LiTf is incorporated. There is an anomaly when moderate amount of LiTf is added into the polymer. This can be related to formation of neutral ion pairs, and substantiated by calculation of activation energy and scanning electron micrographs. TGA thermograms also show that all the samples tested are thermally stable up to 400 °C, even with the incorporation of LiTf. The highest ionic conducting sample achieves highest onset temperature of decomposition.

1. Introduction

The development of high energy density, easily portable and safe power sources is one of the key global technological challenges, as driven by the desire of shifting away from the current heavy dependence on fossil fuels. Solid polymer electrolytes (SPEs) fulfill these requirements and overcome the limitations of conventional liquid electrolytes by addressing drawbacks such as electrolyte leakage, flammable organic solvent, and electrolytic degradation of electrolytes [1]. However, SPEs suffer from one of the important industrial aspects, which is low ionic conductivity. There have been many efforts in improving the ionic transport properties of polymer electrolytes to enhance their power application feasibility.

Poly(vinylidene fluoride-co-hexafluoropropylene) [P(VdF-HFP)] has received great attention due to its outstanding thermal and electrochemical stability [2]. This copolymer exhibits amorphous PHFP phase that aids ionic conduction, and at the same time crystalline PVdF phase acts as a mechanical support [3]. This satisfies the two contradictory properties of highly ionic conducting and good mechanical strength. Recently, P(VdF-HFP) has shown potential as polymer electrolyte material of rechargeable lithium batteries owing to its high solubility, low crystallinity and glass transition temperature [4]. Many researchers present encouraging results for P(VdF-HFP)-based polymer electrolytes with different types of dopant salts, such as lithium fluoroalkyl phosphate [5], lithium perchlorate [6] and lithium bis(trifluoromethanesulfonyl) imide [7].

Lithium trifluoromethanesulfonate salt, LiTf, is one of the most common lithium salt used in polymer electrolyte research. In this study, we utilize only P(VdF-HFP) and LiTf to study about their interaction, electrochemical and thermal properties. Without any other additives or chemicals, we can examine the basic interaction of ionic conduction in polymer and influence on thermal stability. Our studies find that even when P(VdF-HFP) is incorporated with LiTf, which is generally regarded as having lower ionic conductivity as compared to other lithium salts of its family [8], the SPEs produced exhibit exceptional ionic conductivity, thermal stability and mechanically stable with the coexistence of amorphous and crystalline phases. There are great potentials for this system to be further investigated with other additives such as plasticizers and ceramic fillers.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride-co-hexafluoropropylene), [P(VdF-HFP)] with average $M_w = 455{,}000$, was obtained from Sigma-Aldrich. Lithium trifluoromethanesulfonate salt, LiTf [$LiCF_3SO_3$], was obtained from Fluka and dried at 100 °C for 1 hour to eliminate trace amounts of water in the material, prior to the preparation of solid polymer electrolytes (SPEs). Acetone of AR grade was obtained from J.T. Baker.

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2.2. Preparation of thin films

Several polymer electrolyte complexes were prepared as in the compositions according to its weight ratio of polymer to lithium salt, ranging from 95/5 to 60/40. The thin films were prepared by solution casting technique with acetone as solvent. The mixture was cast on a Petri dish and allowed to evaporate slowly inside a fume hood. This procedure yields mechanically stable and free standing films. The thickness of the films was measured using a micrometer screw gauge.

2.3. Instrumentation

The samples were cut out resembling shape of stainless steel blocking electrodes used in this study and sandwiched between them. A HIOKI 3532-50 LCR Hi-Tester was used to perform the impedance measurements for each SPE over the frequency range of 50 Hz to 1 MHz. The same measurement was also performed for selected samples from 30 to 80 °C. Those selected SPEs were then subjected to scanning electron microscopy (SEM), with the model Leica S440. Thermogravimetric analysis (TGA) was performed with a Mettler Toledo analyzer that consists of a TGA/SDTA851^{e} main unit and STARe software with 10 °C min^{-1} heat rate between 30 and 500 °C under a nitrogen atmosphere.

3. Results and discussion

3.1. Alternating current (AC) impedance studies

Fig. 1 shows two Cole–Cole plots of samples with (a) 5 and (b) 40 wt.% of LiTf. It can be observed in Fig. 1(a) that for low concentration of lithium salt, a semi-circle with a long tail, or more commonly known as electrode spike, is clearly observed. When the salt content increases, the semicircle diminishes completely and leaves only with a sharp tail as in Fig. 1(b). This is typical for a very ionic conductive thin film sample. There are two axes in a Cole–Cole plot, namely real and imaginary part of total impedance *Z*. The lowest point of imaginary *Z* axis is extrapolated to determine the bulk resistance, R_b. The ionic conductivity of thin film sample can then be calculated using Eq. (1):

$$\sigma = l/R_bA \tag{1}$$

where σ is ionic conductivity, l is thickness of the thin film sample, R_b is bulk resistance determined from impedance spectroscopy and A is surface area of stainless steel blocking electrodes. Fig. 2 illustrates the variation of log ionic conductivity values as a function of lithium triflate (LiTf) weight percentage incorporated into P(VdF-HFP). It can be clearly observed that the ionic conductivity increases exponentially with the addition of LiTf at the beginning, then becomes relatively constant and reaches the highest ionic conductivity of 1.56×10^{-4} S cm^{-1} at 40 wt.% of LiTf.

The initial increase is simply due to the increased availability of Li^{+} ions in the system. However, from 15 wt.% onwards, the ionic conductivity decreases gradually until 30 wt.%. This may be due to neutral ion pair formation from Li^{+} and Tf^{-} ions, or more commonly known as ion-pair effect. High concentration of salt has higher tendency towards this type of formation. This reduces the availability of free mobile ions and possibly obstructs the conducting path, which subsequently contribute to the slight decrease of ionic conductivity. It can also be related to the formation of linkages between the salt itself, causing it to crystallize, thus resulting in the decrease of ionic conductivity [9]. This proposition can be substantiated by activation energy calculation and scanning electron microscopy (SEM) images in latter sections. When the concentration of LiTf exceeds 30 wt.%, the presence of excessive Li^{+} and Tf^{-} ions starts to disrupt and convert the crystalline phase of P(VdF-HFP) to amorphous, thus changing the morphology of polymer and further enhances the ionic conductivity.

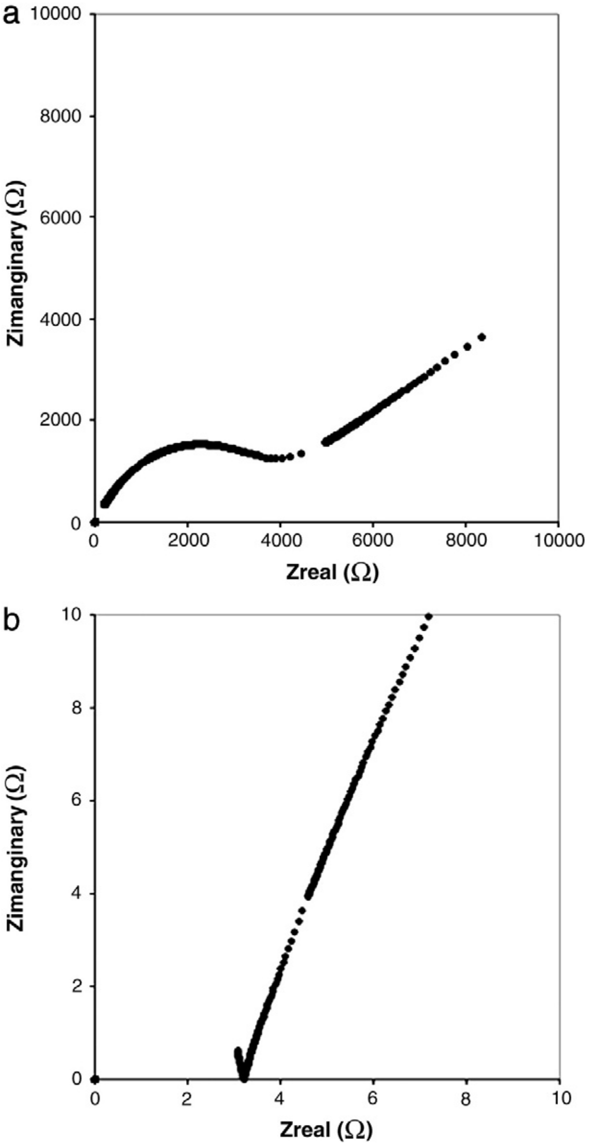

Fig. 1. Cole–Cole plots of samples with (a) 5 and (b) 40 wt.% of LiTf.

The ionic conductivity is also measured at different temperatures, from 30 to 80 °C, in order to evaluate the ionic conduction mechanism in the SPEs. The variation of log ionic conductivity as a function of inverse absolute temperature for selected samples, with 10, 25 and 40 wt.% LiTf respectively, coded as LT10, LT25 and LT40 respectively,

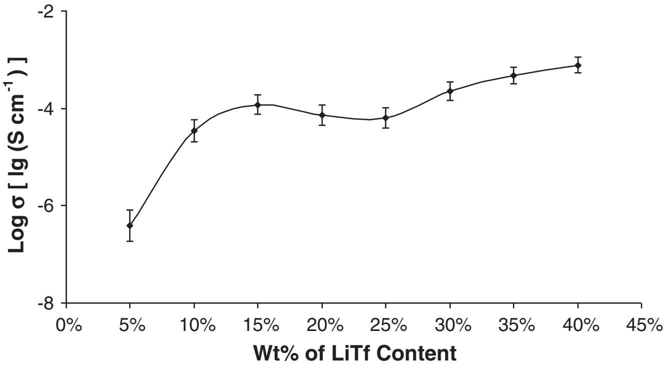

Fig. 2. Variation of log ionic conductivity as a function of lithium triflate (LiTf) weight percentage incorporated into P(VdF-HFP).