Characterization of PVDF-HFP-LiCF$_3$SO$_3$-ZrO$_2$ Nanocomposite Polymer Electrolyte Systems

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Abstract. Nanocomposite polymer electrolytes were prepared by incorporating different amounts of zirconium oxide (ZrO$_2$) nanofiller to poly(vinylidene fluoride-*co*-hexafluoropropylene)-lithium trifluoromethane sulfonate (PVDF-HFP-LiCF$_3$SO$_3$). X-ray diffraction (XRD) study has been carried out to investigate the structural features of the electrolyte films while a.c. impedance spectroscopy has been performed to investigate their electrical properties. The conductivity of nanocomposite polymer electrolyte systems is influenced by nanofiller concentration. The increase in conductivity is attributable to the increase in the fraction of amorphous region and the number of charge carriers and vice versa. The highest conductivity obtained is in the order of 10^{-3} S cm^{-1} for the system dispersed with 5 wt% of ZrO$_2$ nanofiller.

Introduction

Polymer electrolytes are promising materials for electrochemical device applications, namely rechargeable batteries, fuel cells, supercapacitors, hybrid power sources, display devices, sensors etc [1-3]. This type of electrolytes has many advantages which include high ionic conductivity, high specific energy, wide electrochemical stability window, light and easy processibility. In general, the conductivity of a polymer electrolyte increases as the degree of crystallinity decreases or in other words, as the flexibility of the polymeric backbone increases. One of the various methods that have been employed to enhance the conductivities of polymer-salt electrolytes is to form composite electrolyte systems by using organic or inorganic filler as additives. It has been reported that the addition of fillers such as AlO$_2$O$_3$, TiO$_2$, BaTiO$_3$ and SiO$_2$ yields significant enhancements in conductivities [4-9]. In these cases, the fillers may act as solid plasticizers or salt dissociation promoters due to their high values of ferroelectricity. In this study, the authors have prepared nanocomposite polymer electrolytes using PVDF-HFP copolymer as the host, LiCF$_3$SO$_3$ as doping salt and ZrO$_2$ in nano size as the filler.

Experimental Methods

The polymer electrolyte systems studied in this work were prepared by mixing and stirring of PVDF-HFP (Mw ~ 400,000 g mol^{-1}) and LiCF$_3$SO$_3$ of a fixed polymer:salt wt% ratio in N-N Dimethyl formamide (DMF) to form solutions. The PVDF-HFP-LiCF$_3$SO$_3$ solutions were then added with different amounts (1 to 8 wt%) of ZrO$_2$ nanofiller (particle size: 29-60 nm) and further stirred to form homogeneous solutions. The homogeneous solutions were then cast into glass Petri dishes and allowed to evaporate slowly to form films. In this study, the PVDF-HFP:LiCF$_3$SO$_3$ wt% ratio was fixed at 55:45. This is based on the authors' prior study which showed that this ratio yielded polymer-salt electrolyte system with the highest conductivity.

Ionic conductivities of the polymer electrolyte systems were evaluated by impedance spectroscopy in the frequency range 42 Hz to 5 MHz using HIOKI 3532-50 LCR HiTester. In order to study the conductivity behaviour of the polymer electrolytes, the results of impedance measurements were

also presented in dielectric constant, ε_r formalism. The structural features of the electrolytes studied in this work were investigated by X-ray diffraction done in the scanning angle 2θ from 10° to 60° using D8 Advance X-Ray Diffractometer-Bruker AXS with Cu-K$_\alpha$ monocromatized radiation at room temperature.

Results and Discussion

The XRD patterns of PVDF-HFP and PVDF-HFP-LiCF$_3$SO$_3$ dispersed with different wt% of ZrO$_2$ studied in this work are shown in Fig. 1. The XRD spectrum of PVDF-HFP-LiCF$_3$SO$_3$ exhibits a broad peak at 2θ of 20.2° corresponding to the PVDF crystalline peak [10]. The intensity of this peak decreases with the increase in ZrO$_2$ nanofiller concentration up to 5 wt%. This indicates that the fraction of crystalline phase in the polymer matrix decreases with increasing nanofiller concentration. However, further increase in filler concentration resulted in an increase in the intensity of the peak indicating an increase in the crystalline phase fraction in the polymer matrix. The peaks at 28.5°, 31.7° and 34.5°, which can be clearly seen in the XRD spectra of nanocomposite electrolyte containing 7 wt% of nanofiller, correspond to ZrO$_2$ peaks. Peaks corresponding to the LiCF$_3$SO$_3$ are not observed in all of the XRD spectra indicating that LiCF$_3$SO$_3$ is completely complexed in the polymer matrix.
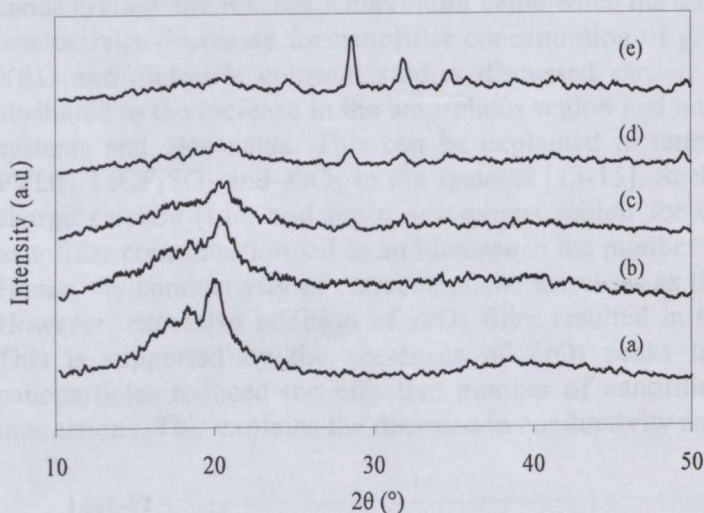

Fig. 1: XRD patterns of (a) PVDF-HFP and PVDF-HFP-LiCF$_3$SO$_3$ containing (b) 0, (c) 1, (d) 5 and (e) 7 wt% of ZrO$_2$.

Fig. 2 depicts the variation of ε_r with frequency for PVDF-HFP-LiCF$_3$SO$_3$-ZrO$_2$ nanocomposite electrolytes. The value of ε_i was obtained using the equation

$$\varepsilon_r = \frac{Z_i}{\omega C_o (Z_i^2 + Z_r^2)} \tag{1}$$

where $C_o = \varepsilon_o A/t$, ε_o is the permittivity of free space, ω is the angular frequency, Z_r and Z_i are the real and imaginary parts of complex impedance obtained from impedance measurements. According to Bhide and Hariharan [11] and Mishra and Rao [12], the high values of dielectric constant in the low frequency range as observed in Fig. 2 are assigned to the accumulation of charges at the electrode-electrolyte interfaces during the impedance measurements. As can be seen from this figure, the ε_r undergoes a gradual increase with increasing ZrO$_2$ nanofiller concentration up to 5 wt% after which it decreases with further increase of nanofiller concentration. Since the conductivity in the electrolyte systems is attributable to the migration of Li$^+$ ions, the increase in ε_r reflects the increase in the charge carrier concentration in the polymer matrix and vice versa.
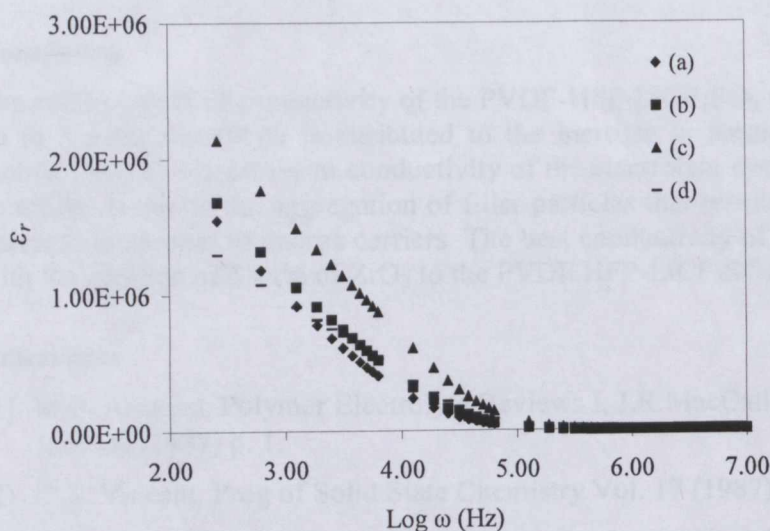
Fig. 2: Frequency dependence of dielectric constant for PVDF-HFP-LiCF$_3$SO$_3$ containing (a) 1, (b) 3, (c) 5 and (d) 7 wt% of ZrO$_2$.

The variation of room temperature conductivity, σ as a function of ZrO$_2$ concentration is shown in Fig. 3. The figure reveals that the ionic conductivity increases with the increase in filler concentration and reaches a maximum value when the concentration of the nanofiller is 5 wt%. The conductivity decreases for nanofiller concentration of greater than 5 wt%. Based on the results of XRD and dielectric constant studies discussed earlier, the enhancement of conductivity can be attributed to the increase in the amorphous region and number of mobile ions in the nanocomposite systems and vice versa. This can be explained in terms of Lewis acid-base interactions among PVDF, LiCF$_3$SO$_3$ and ZrO$_2$ in the systems [13-15]. Such interactions produced greater number of charge carriers (Li$^+$) and more amorphous region for charge carriers to transfer. Increasing the nanofiller concentration led to an increase in the number of charge carriers and amorphous fraction. Hence, the conductivity of nanocomposite increases as the concentration of nanofiller is increased. However, excessive addition of ZrO$_2$ filler resulted in the aggregation of the nanofiller particles. This is supported by the presences of ZrO$_2$ peaks in the XRD spectra. The aggregation of nanoparticles reduced the effective number of nanofiller particles available for Lewis acid-base interactions. This explains the decrease in conductivity as shown in Fig.3.
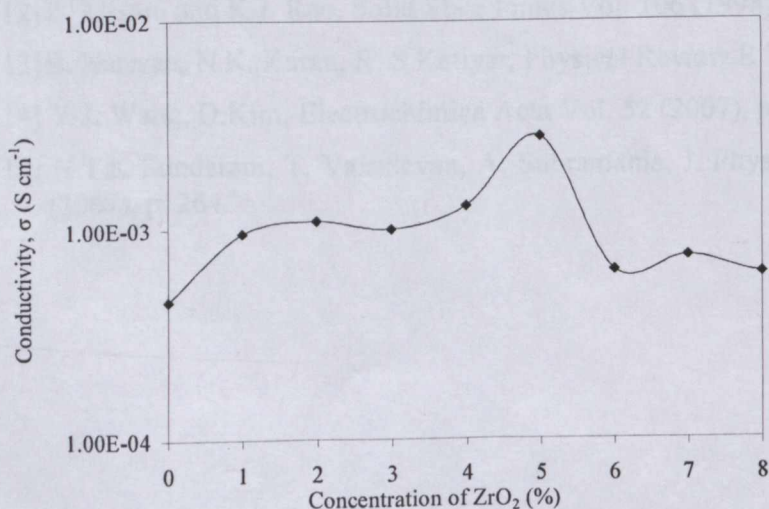

Fig. 3: Variation of room temperature conductivity, as a function of ZrO$_2$ concentration.

Conclusion

The enhancement of conductivity of the PVDF-HFP-LiCF$_3$SO$_3$ upon addition of the ZrO$_2$ nanofiller up to 5 wt% electrolyte is attributed to the increase in amorphous region and concentration of mobile ions. The decrease in conductivity of the electrolyte systems with high concentration of the nanofiller is due to the aggregation of filler particles that results in the increase in crystallinity and decrease in number of charge carriers. The best conductivity of the order of 10^{-3} S cm^{-1} is achieved with the addition of 5 wt% of ZrO$_2$ to the PVDF HFP-LiCF$_3$SO$_3$ system.

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