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Electrochemical and FTIR Studies of PVDF-HFP/(CF3SO3)2Zn/Fe2O3 Composite Polymer Electrolytes

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Abstract--**Complex polymer electrolytes (CPE) consisting of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) as polymer host, zinc trifluoromethanesulfonate (zinc triflate) as dopant salt and iron oxide nanoparticles as fillers were prepared by solution casting technique using acetone as solvent. The various compositions of the complex polymer electrolyte films prepared are (75 wt.% PVDF-HFP + 25 wt.% zinc triflate) + x wt.% Fe_2O_3 where x = 1, 3, 5, 7, and 10. Complex impedance analysis and Fourier transform infrared spectroscopy (FTIR) were employed to study the effect of the concentration of Fe_2O_3 nanofiller on the conductivity of the complex polymer electrolytes and amorphous nature of the PVDF-HFP polymer host. The results of the FTIR study suggest that the Fe_2O_3 nanoparticles interact with the polymer-salt system to increase the amorphous nature of the PVDF-HFP polymer host and improve ionic mobility. This is supported by the conductivity values obtained for the complex polymer electrolyte samples by complex impedance analysis.**

Keywords
Composite Polymer electrolyte, Nanoparticles, Poly(vinylidene fluoride-co-hexafluoropropylene) , Zinc trifluoromethanesulfonate.

I. INTRODUCTION

Composite polymer electrolytes (CPEs) have attracted a great deal of attention in the recent years as they can serve as substitutes for liquid electrolytes in various electrochemical devices such as batteries, electrochromic display devices and sensors. Composite polymer electrolytes may be prepared by dispersing nanoscale inorganic fillers such are TiO_2, SiO_2 and Al_2O_3 nanoparticles in polymer-electrolyte systems. Studies show that nanofillers enhance physical and electrochemical properties of CPEs [1-4]. Many polymers have been studied to determine their suitability to serve the host polymer in polymer electrolytes. Poly (vinylidenefluoride-co-hexafluoropropylene) (PVDF-HFP) polymer which exhibits semi-crystalline nature and high dielectric constant ($\varepsilon = 8.4$) value is considered to be a good candidate for use as polymer host. PVDF-HDP polymer has both amorphous phase that allows ionic mobility and crystalline phase that provides mechanical stability [5]. A suitable salt is dissolved in the host polymer to furnish mobile cations for ionic conduction within the host polymer matrix. In the recent past triflate salts of Mg and Zn are being considered as more environmentally safe alternatives to Li triflate salts there are used in lithium batteries. In the present study zinc trifluoromethanesulfonate (zinc triflate) was used as the dopant salt to furnish Zn^{2+} ions for ionic conduction [6]. Studies have shown that inclusion of nanofillers in polymer electrolytes reduces the crystalline phase and increases the amorphous phase of the host polymer matrix and thereby nanofillers are reported to enhance ionic mobility and conductivity in CPEs [7,8]. In the present work various compositions of PVDF-HFP/ZnTf/Fe_2O_3 CPEs were prepared by solution casting technique and the effect of Fe_2O_3 fillers on the ionic conductivity of the CPE was studied through AC impedance spectroscopy and Fourier transform infrared spectroscopy studies.

II. EXPERIMENTAL

A. Preparation of the complex polymer electrolyte

Analar grade poly(vinylidenefluoride-co-hexafluoropropylene) (PVDF-HFP), zinc trifluoromethanesulfonate (zinc triflate) and Fe_2O_3 nanoparticles were purchased from Aldrich. Composite polymer electrolytes were prepared by solution casting technique using acetone as solvent with the following compositions (75 wt.% PVDF-HFP + 25 wt.% zinc triflate) + x wt.% of Fe_2O_3 where x = 1, 3, 5, 7, and 10 and (75 wt.% PVDF-HFP + 25 wt.% zinc triflate) is the optimized polymer-salt composition. Weighed quantity of

PVDF-HFP polymer was homogeneously dissolved in acetone by stirring for about 2 hours. Then weighed quantity of zinc triflate was then added to solution of the PVDF-HFP polymer and dissolved completely. Finally weighed quantity of Fe_2O_3 nanoparticles were dispersed in the polymer-salt solution. The suspension was poured in petri dishes and allowed to evaporate in a vacuum desiccator at room temperature. Mechanically stable, dry free standing films of 80 – 100 μm thickness were obtained by this method.

B. Methods of characterization

The ionic conductance of the CPE films of various compositions was determined by AC impedance measurement using a computer controlled Hewlett Packard model HP4284A Precision LCR meter in the frequency range of 20 Hz – 1 MHz within the temperature window of 300 – 373 K. The CPE film was sandwiched between two stainless steel electrodes and held in place by spring action. The temperature was regulated using a thermostat. Fourier transform infrared spectroscopy studies on the CPEs was carried out using Perkin Elmer RX1 IR spectrometer in the region of 4000 – 400 cm^{-1}.

III. RESULTS AND DISCUSSION

A. Electrochemical characterization

The AC impedance spectroscopy data was used to determine the bulk resistance (R_b) of the CPEs from the high-frequency intercept of the impedance plot on the real axis. The conductivity (σ) of the CPE was determined using the relation,

$$\sigma = l / R_b A$$

where l is the thickness of the CPE films and A is the area of CPE in contact with the stainless steel electrodes [9].

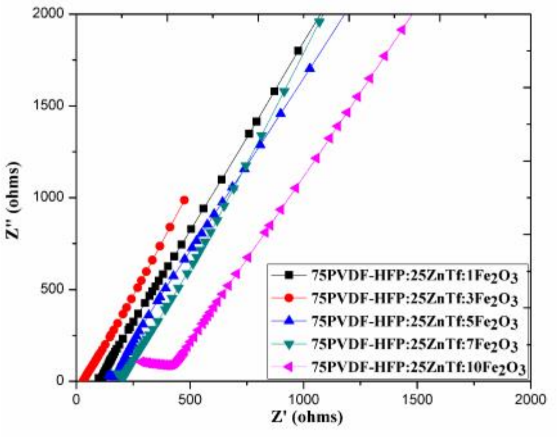

Figure 1. Typical complex impedance plots for various compositions of PVDF-HFP/(ZnTf)/Fe_3O_3 CPEs at room temperature (300 K)

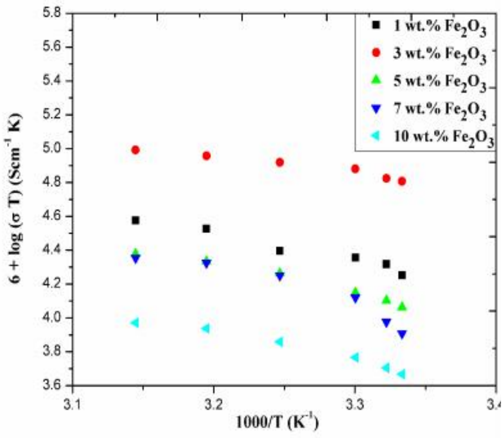

Figure 2. Temperature dependence of conductivity for various compositions of PVDF-HFP/(ZnTf)/Fe_2O_3 CPEs at room temperature (300 K)

Fig. 1 shows the AC impedance spectrum of the various compositions of 75PVDF-HFP/25ZnTf/xFe_2O_3 CPEs where x = 1,3,5,7 and 10 at room temperature (300 K). From the impedance spectra it is seen that the bulk resistance decreases for the CPEs with 1 and 3 wt.% Fe_2O_3 and then increases with further increase in Fe_2O_3 concentration.

TABLE 1. ELECTRICAL CONDUCTIVITY VALUES OF CPEs OF COMPOSITIONS (75wt.% PVDF-HFP + 25wt.% ZnTf) + x wt.% Fe_2O_3 WHERE x = 1, 3, 5, 7 and 10 AT ROOM TEMPERATURE (300 K)

Amount of Fe_3O_3 nanofiller (wt. %)	**Room temperature conductivity (±) Scm^{-1}**
1	**5.9×10^{-5}**
3	**2.1×10^{-4}**
5	**3.8×10^{-5}**
7	**2.6×10^{-5}**
10	**1.5×10^{-5}**

Table 1. shows the variation in ionic conductivity with concentration of Fe_2O_3 in the various compositions of PVDF-HFP/ZnTf/Fe_2O_3 CPEs at room temperature (300 K). It is seen that addition of Fe_2O_3 nanofillers increases the ionic conductance of the CPEs containing 1 and 3 wt. % of Fe_2O_3. The best conducting composition of the present system is the CPE with 3 wt. % of Fe_2O_3 with a conductance value 2.1×10^{-4} Scm^{-1} at room temperature (300 K). Fig. 2 shows the variation of ionic conductance with temperature. The plots appear curved for all the compositions suggesting a non-Arrhenius behavior [10].

B. *Fourier transform infrared spectroscopy*

Fig. 3 gives the FTIR spectra of various compositions of PVDF-HFP/ZnTf/Fe_2O_3 CPEs and fig. 4 gives the FTIR spectra of pure PVDF-HFP polymer and zinc triflate salt. On comparing the spectra of pure PVDF-HFP polymer, the zinc triflate salt and the CPEs the extent of interaction and complexation between the polymer, salt and the filler can the inferred. Further FTIR spectra can be used to study the effect of the filler and salt on the volume of the amorphous phase of the polymer host in the CPEs [11].

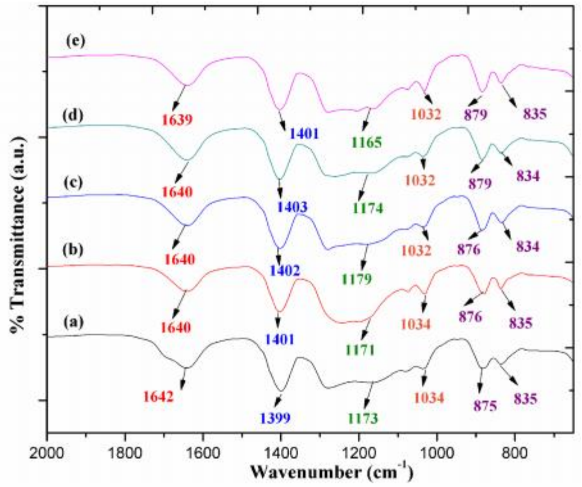

Fig. 3 FTIR spectra of various compositions of PVDF-HFP/(ZnTf)/Fe_2O_3 CPEs in the spectral range 2000-800 cm^{-1}

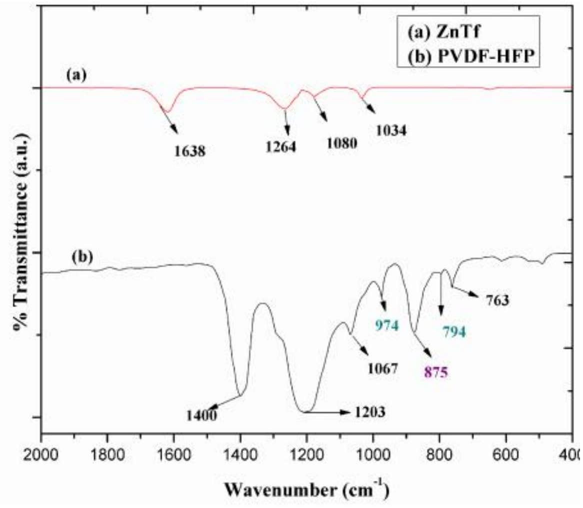

Fig. 4 FTIR spectra of of PVDF-HFP polymer and Zinc triflate salt in the spectral range 2000-400 cm^{-1}

The FTIR spectra of the pure PVDF-HFP polymer shows bands in the region of 764 and 974 cm^{-1} which correspond to the crystalline α-phase of PVDF, a band in the region of 794 cm^{-1} corresponding to the $-CF_3$ stretching, a band in the region of 875 cm^{-1} corresponding to the C-C skeletal vibration, a band in the region of 1179 cm^{-1} corresponding to $-CF_3$ symmetrical stretching and a band in the region of 1401 cm^{-1} corresponding to –C-F- stretching. The FTIR spectra of the zinc triflate salt give bands in the region of 1034 cm^{-1} corresponding to SO_3 symmetrical stretching, a band in the region of 1638 cm^{-1} which corresponds to the characteristic peak of triflate anion and bands in the region of 1264 cm^{-1} and 1180 cm^{-1} which corresponds to $–CF_3$ symmetrical vibration [12-15].

The intensity of the bands in the region of 764, 794 and 974 cm^{-1} corresponding to the α-phase of PVDF which is the crystalline region of the PVDF-HFP polymer decreases and becomes almost unnoticeable in the CPEs suggesting a decrease in the crystalline phase of the host polymer matrix. Further a new FTIR band appears in the amorphous region of the host polymer at 834 cm^{-1} with significant intensity in various compositions of the CPEs. The increase in intensity of the band in the region of 875 cm^{-1} which also corresponds to the amorphous phase of the host polymer indicates an increase in the volume of the amorphous phase of the CPEs. The increase in ionic conductivity of CPEs with 1 and 3 wt.% Fe_2O_3 can be attributed to an increase in the volume of amorphous phase of the host polymer which facilitates enhanced ionic mobility [16]. The changes in the intensities of various FTIR bands, the shifting of some bands and the appearance of new peaks in the FTIR spectra of the CPEs indicate that complexation and co-ordination has taken place between the constituents of the CPEs [17].

IV. CONCLUSION

The FTIR spectral data obtained for the various compositions of CPEs of the present system show disappearance of some bands, appearance of new peaks and shifting of bands. This suggests that there is a good complexation between the PVDF-HFP host polymer, zinc triflate dopant salt and the Fe_2O_3 nanofiller. The FTIR spectra also indicated that there is an increase in the volume of the amorphous phase of the host polymer which could be responsible for the observed increase in ionic mobility in certain compositions of the CPEs. The CPE composition with 3 wt.% Fe_2O_3 was found to be the best conducting composition for the present system.

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