

AC Conductivity Studies on PVDF-co-HFP Based Nano Composite Polymer Electrolytes In Presence of Al₂O₃

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Abstract— Composite polymer electrolytes (CPEs) comprising poly(vinylidene fluoride-hexafluoro propylene), PVDF-co-HFP and zinc triflate, Zn(CF₃SO₃)₂ with varying concentrations of Al₂O₃ nanofiller have been prepared by solution casting technique by consuming N,N-dimethyl formamide, DMF as the common solvent. The freshly-prepared free standing, translucent thin films were characterized using AC impedance spectroscopic analysis. The polymer electrolyte specimen with the particular composition 75wt% PVDF-co-HFP: 25wt% ZnTr + 5wt% Al₂O₃ showed the highest conductivity of 10⁻⁴ S cm⁻¹ at 298 K among such CPEs as confirmed from impedance measurements. The variation of relative dielectric constant and that of electric modulus with respect to frequency have been discussed by the effective dispersion of Al₂O₃ nanofiller into the polymer electrolyte system. The electrical conductivity relaxation time have been evaluated from the electric modulus M⁻¹ which showed the occurrence of non-Debye type of relaxation phenomenon. Correlation of frequency-dependent conductivity results has enabled an understanding of the role played by these fillers in ion conduction characteristics of the chosen CPEs.

Keywords - Polymer Electrolytes; Conductivity; Dielectric Properties, Electric Modulus

I. INTRODUCTION

Polymer electrolytes are materials of great importance in different electrochemical devices due to their unique characteristics such as easy mouldability, good electrode-electrolyte contact [1,2]. These polymer electrolytes form a bridge between liquid electrolyte and solvent-free ceramics [3]. Because of their high ionic conductivity, polymer electrolytes have attained precedence over conventional polymer electrolytes. In recent years, polymethylmethacrylate (PMMA), polyacrylonitrile (PAN), polyvinylidene fluoride (PVdF) and polyethylene oxide (PEO) [4] have been reported as suitable polymer host material for the preparation of polymer gel electrolytes. Among the above mentioned polymers pure polyvinylidene fluoride hexa fluoropropylene (PVDF-co-HFP) having an average molecular weight 400,000 has been selected, wherein PVDF serves as a polymer host owing to the presence of a strong electron withdrawing group (-C-F) and when PVDF is combined with HFP as a copolymer the crystalline nature gets reduced and improves the amorphous state, thereby providing an appreciably good mechanical strength to the polymer matrix [5]. The mixture containing polymer and salt was stirred magnetically for 4 h. Zinc is a non-toxic and inexpensive stable material which is more abundantly available than lithium, and hence could be an equally good option for safer batteries [6,7]. A careful analysis of the literature reveals that nano-fillers like Al₂O₃, ZrO₂, CeO₂ and TiO₂ when incorporated into the polymeric host formed nanocomposite polymer electrolytes with improved physical and chemical properties. It has been established that the addition of nano-size filler into polymer-salt complexes would give rise to better mechanical strength, elevated ionic conductivities, good electrode-electrolyte interfacial stability and reduced degree of crystallinity in the case of nanocomposite polymer electrolytes. Hence, the present investigation having the various concentrations of nano-size particles such as, 1,3,5,7 and 10 wt% of Al₂O₃ has been chosen as nanofiller.

II. EXPERIMENTAL

The host polymer, namely PVDF-co-HFP (M_w -400000, Sigma Aldrich) and ionic dopant, ZnTr (M_w-363.53 g/mol, Sigma Aldrich), nanofiller Al₂O₃ (>100 nm, Sigma Aldrich) and N,N dimethyl formamide (Sigma Aldrich) were used as procured. Composite polymer electrolytes of various compositions were prepared by employing simple solution casting technique. Based on the observed electrical conductivity values and stability of freshly-prepared thin film specimens, the optimized molar ratio of salt and polymer host in the case of the polymer electrolyte system, PVDF-co-HFP: ZnTr was 75:25. The homogenous solution of 75PVDF-co-HFP: 25ZnTr was thus prepared using N,N-dimethyl formamide as the common solvent to which appropriate amounts of Al₂O₃ nano particles were also subsequently dispersed. The solution thus obtained was cast into glass petri dishes and dried in a vacuum oven at 60° C for 12 h in order to remove any traces of DMF. Samples of thin film

polymer electrolytes derived after the removal of DMF were stored inside a vacuum desiccator for 24 h with a view to avoid absorption of any moisture by these specimens meant for further characterization.

III RESULTS AND DISCUSSIONS

A Complex Impedance Measurements

Fig. 1 depicts that maximum conductivity attained by the addition of Al_2O_3 nano filler at 5wt% to the polymer-salt complex. The sequential other conductivity values have already shown by Austin and coworkers [8]. The improved and optimized conductivity (\uparrow_{RT}) of $1.7 \times 10^{-4} \text{ Scm}^{-1}$ at ambient temperature (298K) was obtained for the composite polymer electrolyte containing 5 wt% Al_2O_3 filler.

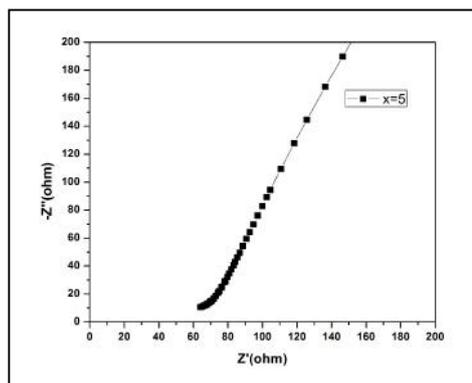


Figure 1. The impedance spectra in the case of the best conducting thin film sample with 5wt% loading of Al_2O_3 nanofiller.

B Dielectric Studies

Dielectric constant is a measure of stored charge. The variation of dielectric constant ϵ' and dielectric loss ϵ'' of frequency dependence has been studied for the present system. Fig. 2 shows the plot of real part of dielectric constant ϵ' as a function of frequency at different wt % of nano composite polymer electrolytes. For all the samples, a strong frequency dispersion is observed in the low frequency region followed by a nearly frequency independent behavior. The decrease of ϵ' with increase in frequency is ascribed to the relaxation process [9], but the material electrode polarization cannot be ignored as the samples are ionic conductors.

The electrode interface polarizations of the nanocomposites mask the other relaxation process which are at low frequencies. The nanofillers results in more localization of charge carriers along with mobile ions causing higher ionic conductivity and this may be the reason for higher ϵ' at low frequency dispersion [10]. Since dielectric loss ϵ'' is a measure of energy dissipated the observed variation of ϵ'' in the case of five different samples with frequency is presented in Fig 3. At higher frequencies, as the periodic reversal of the electric field is fast, there is no excess of ions to be diffused in the direction of the field. Therefore the polarization due to charge accumulation losses and result in a decrease in both the dielectric constant and dielectric loss [11].

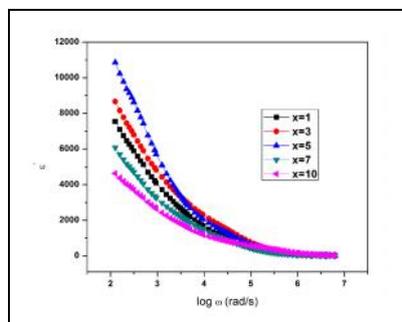


Figure 2. Variation of ϵ' as a function of frequency at room temperature (298 K)

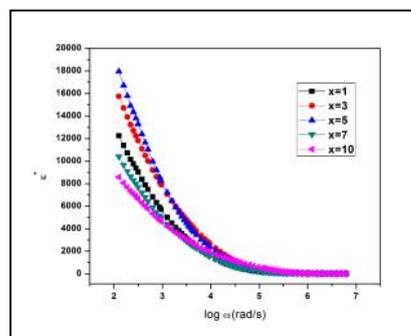


Figure 3. Variation of ϵ'' as a function of frequency at room temperature (298 K)

C Electric Modulus Analysis

Figures 4 and 5 show the real part M' and imaginary part M'' of electrical modulus as a function of frequency for various polymer electrolytes. Both M' and M'' increases at high frequency region and provides a long tail at lower frequencies. The peak in the modulus spectra show that the polymer electrolytes are ionic conductors and the peak curves at high frequencies may be due to bulk effect. The plots that M' and M'' decrease towards low frequencies are due to the electrode polarization phenomenon which makes a negligible contribution. The plots that show long tail at lower frequency are probably due to their large storage of charges at the electrodes [11].

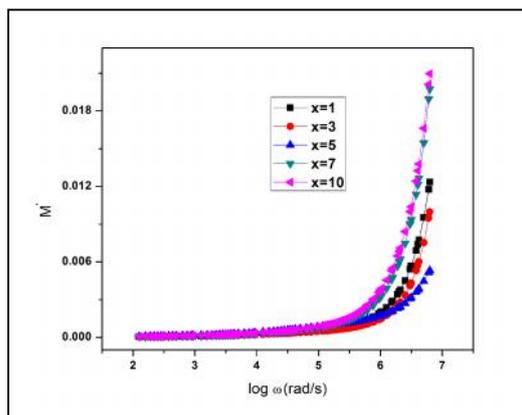


Figure 4. Variation of M' as a function of frequency at room temperature (298 K)

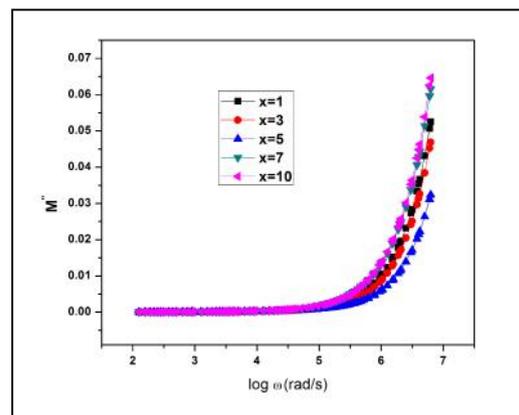


Figure 5. Variation of M'' as a function of frequency at room temperature (298 K)

IV CONCLUSIONS

The composite polymer electrolyte based on PVDF-co-HFP has been prepared by the simple solution casting technique. The composite polymer electrolyte membrane having 5 wt% Al_2O_3 exhibits a maximum conductivity of $10^{-4} Scm^{-1}$ at 298 K. The dielectric spectra reveal the dielectric relaxation process in the polymer electrolyte.

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REFERENCES

- [1] J. R. MacCallum and C. A. Vincent, "Polymer electrolyte reviews", Else. Appl. Sci. London, pp. 1–2, 1989.
- [2] F. M. Gray, "Solid polymer electrolytes fundamental and technological applications", New York, 1991.
- [3] B. Scrosati and C. A. Vincent, "Polymer electrolytes: the key to lithium polymer batteries", M R S Bull., vol.25, pp 28-30, 2000.
- [4] S. S. Sekhon, "Conductivity behaviour of polymer gel electrolytes: Role of polymer", Bull. Mater. Sci., vol. 26, pp. 321–328, April 2003.
- [5] G. Li, Z. Li, P. Zhang, H. Zhang, and Y. Wu, "Research on a gel polymer electrolyte for Li-ion batteries", Pure Appl. Chem., vol. 80, pp. 2553–2563, 2008.

- [6] G. G. Kumar, and S. Sampath, "Electrochemical and spectroscopic investigations of a gel polymer electrolyte of Poly(Methylmethacrylate) and zinc triflate", *Solid State Ionics.*, vol.176, pp. 773–780, 2005.
- [7] J. J. Xu, H. Ye, and J. Huang, "Novel zinc ion conducting polymer gel electrolytes based on ionic liquids", *Electrochem. Commun.*, vol.7, pp. 1309–1317, 2005.
- [8] M. Johnsi, and S. Austin, "Synthesis and characterization of a new composite polymer electrolyte based on Al₂O₃ nanofiller", *Int. J. Chem. Environ. & Tech.*, vol.1, pp. 12-21, April 2013.
- [9] N. Gondaliya, D.K. Kanchan, P. Sharma, M. Pant, and M. Jayswal, *AIP Confer. Proc.*, vol. 112, pp. 1313, 2010.
- [10] N. Gondaliya, D.K. Kanchan, P. Sharma, and M. S. Jayswal, "Dielectric and electric properties of plasticized PEO-AgCF₃SO₃-SiO₂ nanocomposite polymer electrolyte system", *Polym. Compos.*, vol. 33, pp. 2195–2200, 2012.
- [11] S K Tripathi, A. Gupta and M. Kumari, "Studies on electrical conductivity and dielectric behavior of PVdF–HFP–PMMA–NaI polymer blend electrolyte", *Bull. Mater. Sci.*, Vol. 35, pp. 969–975, 2012.