

Structural and conducting properties of proton conducting tri-blend polymer electrolytes

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Abstract - Variety of blend polymer such as PVA: PAN, PEO: PVP, PVdF:PVA and etc doped with NH_4NO_3 have been studied for proton conduction. But the study of proton conducting tri-blend polymer electrolyte is rare. Inventive Solid polymer electrolytes based on Polyvinylalcohol (PVA), Polyacrylonitrile (PAN), Polyvinylidene fluoride (PVdF) doped with ammonium nitrate (NH_4NO_3) have been prepared by solution casting technique using Dimethylformamide (DMF) as solvent. To analyse the structural and conducting property, the prepared films are characterized by XRD and AC impedance techniques respectively. X-ray diffraction revealed the amorphous nature of the prepared polymer electrolytes. From the AC impedance technique, it has been found that the highest ionic conductivity is 9.12×10^{-4} (S/cm) for 80% (PVA: PAN: PVdF) : 20% NH_4NO_3 polymer electrolyte at 303K.

Keywords - Ionic conductivity, Tri-blend, Solid polymer, XRD, AC impedance and Modulus.

I. INTRODUCTION:

In our recent years solid polymer electrolyte is expected to replace the conventional liquid electrolytes due to its better durability, flexibility and long life time. Liquid electrolytes have been known as better candidates for various applications due to their considerable ionic conductivities. At the onset of introducing batteries, liquid electrolytes had shown good performance. Due to some disadvantages such as leakage and corrosion, attention has been diverted towards solid electrolytes [1]. Various research groups have developed polymer electrolytes and investigated the ways of improving their ionic conductivity [2]. Some of the methods employed for the enhancement of conductivity are cross linking of two polymers, blending of two or more polymers, addition of plasticizer to the polymer electrolyte, usage of inorganic inert fillers etc..

Currently, the research work is focused on the development of blend polymer with better conductivity for fuel cell and batteries related application. As the physical and chemical properties of both the polymer chain are different, the resulting blend is entirely unique with the possibility to improve the conducting nature. Many blend polymer electrolyte system have been studied and reported in the literature [3-5]. It is seen from the literature that blending of two polymers improved the conductivity of the polymer electrolytes. When the electrical nature of a single polymer doped with salt is compared with a blend polymer doped with the salt it is found that the conductivity is increased [6-7]. So, the present study is aimed at analyzing proton conducting tri-blend polymer electrolytes. Lithium ionic conducting tri-blend polymer electrolytes has been studied by Tamilvathana et.al [8]. To the best of author's knowledge, there is no report on "tri-blend polymer based on Polyvinylalcohol [PVA], Polyacrylonitrile [PAN], Polyvinylidene fluoride [PVdF] dispersed with ammonium nitrate [NH_4NO_3]. PVA has excellent film forming ability, high tensile strength and flexibility. PAN is a resinous, fibrous, rubbery organic polymer which possesses good mechanical strength. PVdF has low weight, low chemical corrosion resistance and heat resistance. In literature survey, the NH_4NO_3 is a good proton donor.

II. Experimental Techniques:

Synthesis of Electrolytes

The present work details with the preparation of tri-blend polymer electrolyte dispersed with ammonium nitrate by using solution casting method. Blend polymer electrolytes are prepared with PVA (M.wt.1,25,000), PAN (M.wt.1,25,000), PVdF (M.wt.5,30,000) of various composition and ammonium nitrate using di-methylformamide (DMF) as solvent. PVA is stirred in DMF at 80°C for 2 hours and after its complete dissolution, PAN is added and stirred for 1 hour after its complete dissolution, PVdF which is separately dissolved in DMF at 80°C is then added and stirred. Then ammonium nitrate is added. The mixture is stirred till it becomes homogeneous. Then it is poured in the petri dish and kept in vacuum oven for solvent evaporation at 70°C for 2 days. After the complete evaporation of the solvent the stand alone films were carefully removed from the petri dishes and sealed in an air tight cover. Polymer blend (0.9PVA: 0.08PAN: 0.02PVdF by weight) is denoted by PPP. The following weight compositions of proton conducting polymer electrolyte have been prepared.

100% PPP – 0 % NH_4NO_3

95 % PPP – 5 % NH_4NO_3

90 % PPP – 10 % NH_4NO_3

85 % PPP – 15 % NH_4NO_3

80 % PPP – 20 % NH_4NO_3

75% PPP – 25% NH_4NO_3

are synthesized and are characterized by different experimental technique.

Characterization of Electrolytes

In order to study the Structural, Conductivity properties of the blend polymer electrolytes, they are characterized by XRD and AC impedance techniques respectively.

- XRD- To determine the amorphous nature of the polymer electrolytes. (Using XPERT- PRO diffractometer)
- AC Impedance – To study the electrical properties of the polymer electrolytes. (Using HIOKI-3532 LCZ meter)

III. RESULT AND DISCUSSION

X-ray Diffraction Analysis:

XRD analysis is used to determine the amorphous nature of the prepared polymer electrolytes. The amorphous nature of the polymer complex can be easily confirmed by the broad peak observed in the X-Ray Diffraction patterns.

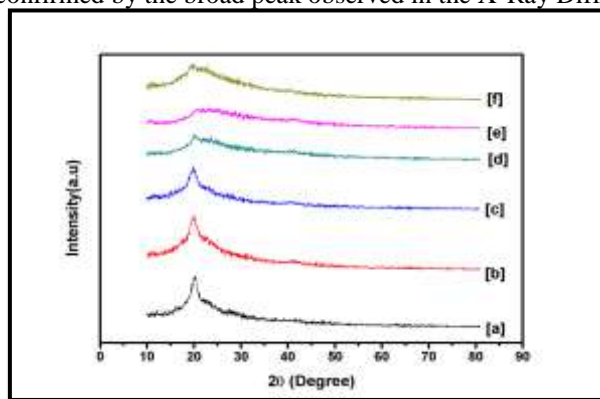


Fig. 1 XRD pattern of blend polymer electrolytes of composition (a) 100% (PPP): 0% NH_4NO_3 (b) 95% (PPP): 5% NH_4NO_3 (c) 90% (PPP): 10% NH_4NO_3 (d) 85% (PPP): 15% NH_4NO_3 (e) 80% (PPP): 20% NH_4NO_3 (f) 75% (PPP): 25% NH_4NO_3

When a polymer is complexed with a salt or an acid, the crystallinity of polymeric host could be disrupted by the addition of impurities [9,10]. Fig. 1 represents the XRD patterns of blend polymer electrolyte (PPP) and blend polymer electrolyte dispersed with different composition of NH_4NO_3 . A broad peak around 20.16° which is attributed to the blend (PPP) has been found to be slightly shifted in the complexed system. The amorphous nature of the blend system can be interpreted in terms of the Hodge et.al [11] criterion, which has been established a correlation between the height of the peak and degree of crystallinity. The crystallite size (D) of prepared electrolytes has been calculated by Debye – Scherer's formula [12].

$$D = K\lambda / \beta \cos\theta \text{-----(1)}$$

Where K is the dimensionless shape factor, with a value close to unity; λ is the wavelength of X-ray radiation (1.54 \AA), β is the full width half maximum calculated by using Origin software and θ is the diffraction angle and these values are taken from the dataset (XPERT- PRO diffractometer). The crystallite size (using equation1) and relative intensities are taken from the dataset (XPERT- PRO diffractometer) of the prepared samples are shown in Table 1.

Table 1. Crystallite size and relative intensities of the dispersed blend polymer electrolytes

Composition	2θ (deg)	FWHM (deg)	Crystallite size(\AA)	Height (Relative intensity)
100% PPP: 0% NH_4NO_3	20.17	1.273	0.634	270.5
95% PPP: 5% NH_4NO_3	20.09	1.533	0.526	257.8
90% PPP: 10% NH_4NO_3	19.87	2.038	0.395	204.6
85% PPP: 15% NH_4NO_3	19.38	2.426	0.332	110.3
80% PPP: 20% NH_4NO_3	20.57	2.801	0.288	59.8
75% PPP: 25% NH_4NO_3	20.06	2.202	0.435	95.8

From Table 1, it can be seen that 80% (PPP): 20% NH_4NO_3 has the lowest crystallite size, low intensity and high full width half maximum (FWHM) of the peak around 20° . So this electrolyte is more amorphous compared to other polymer electrolytes. The decrease in intensity and increase in the broadness of the peak reveal the increase in amorphous nature of the complexed system. The result obtained from the XRD measurements strongly suggests that there is interaction between the polymer matrix and the salt NH_4NO_3 .

AC Impedance analysis:

AC impedance technique is a comparatively new, but powerful method of characterizing the electrical properties of polymer electrolytes and their interfaces with electronically conducting electrodes. The complex impedance plot for blend polymer electrolytes dispersed with 0, 5, 10, 15, 20, 25% weight ratios of NH_4NO_3 at ambient temperature is shown in the Fig.2.

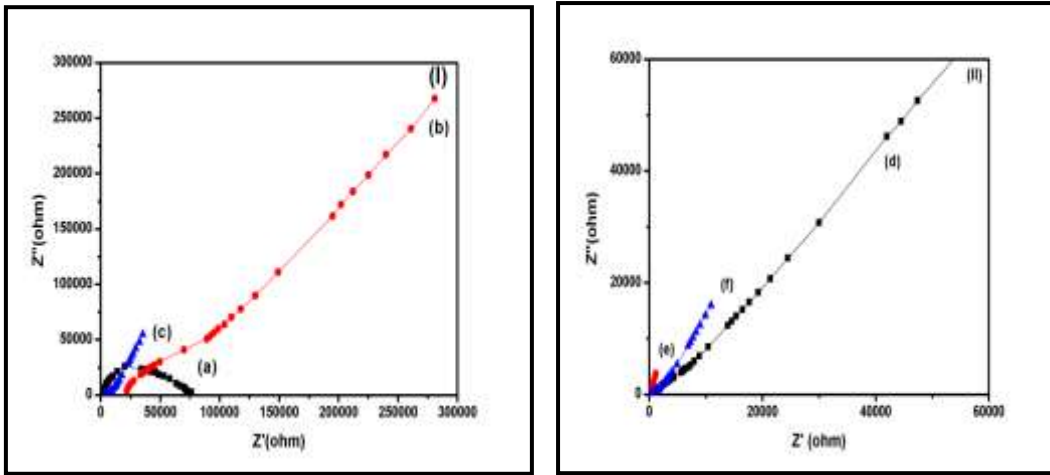


Fig. 2 Complex impedance plots for (I) (a) 100%PPP: 0%NH₄NO₃ (b) 95%PPP: 5%NH₄NO₃ (c)90% PPP: 10% NH₄NO₃ (II) (d) 85%PPP:15% NH₄NO₃ (e)80%PPP:20%NH₄NO₃ (f) 75% PPP: 15% NH₄NO₃ polymer electrolytes at 303K.

In the complex impedance plot, a high frequency semicircle only occurs for undispersed blend polymer electrolyte and it is related to the parallel combination of bulk resistor and capacitor behavior of the electrolyte. A semicircle with a spike appears for (b) and (c). The intercept of the spike and the semicircle with the real impedance (Z') axis gives the bulk electrical resistance (R_b) of the polymer electrolyte [13]. A low frequency spike occurs for (d), (e) and (f) which represent the formation of double layer capacitance of the electrode – electrolyte interface. The ionic conductivity of the polymer electrolytes has been calculated using the equation,

$$\sigma = l / A R_b \text{----- (2)}$$

where l is the thickness of the polymer electrolyte film, A is the surface area of the film and R_b is the bulk resistance of the electrolyte film. The highest ionic conductivity at ambient temperature has been found to be $9.12 \times 10^{-4} \text{ (S/cm)}$ for 80% PPP: 20% NH₄NO₃. So the conductivity of the polymer matrix increases with the addition of proton donor NH₄NO₃.

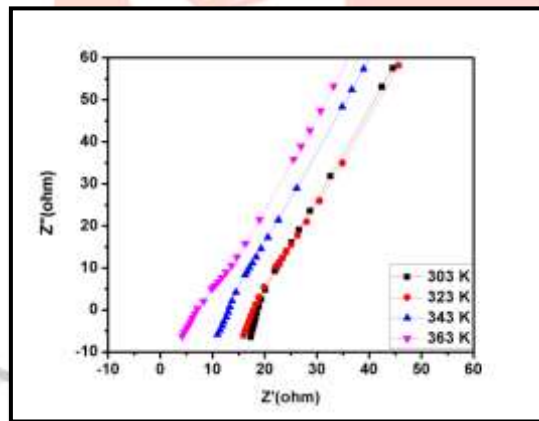


Fig. 3 Complex impedance plots for 80% PPP: 20% NH₄NO₃ polymer electrolyte at different temperatures.

Figure.3 shows that the complex impedance plots for 80% PPP: 20% NH₄NO₃ at different temperatures. The decrease in resistance of the polymer electrolyte with temperature is due to the enhancement of the ionic mobility and the number of charge carriers.

Table 2: Ionic conductivity values of the polymer electrolytes at different temperatures.

It is that, the conductivity to (80%)	Composition (Weight %)	Ionic conductivity (S/cm) at different temperatures				observed ionic increases up PPP:
		303K	323K	343K	363K	
	95:5	2.19×10^{-6}	3.78×10^{-6}	6.06×10^{-6}	7.81×10^{-6}	
	90:10	4.05×10^{-6}	5.39×10^{-6}	6.27×10^{-6}	8.29×10^{-6}	
	85:15	1.04×10^{-5}	2.38×10^{-5}	6.56×10^{-5}	1.24×10^{-4}	
	80:20	9.12×10^{-4}	9.87×10^{-4}	1.44×10^{-3}	3.76×10^{-3}	
	75:25	5.24×10^{-5}	8.86×10^{-5}	1.78×10^{-4}	4.58×10^{-4}	

20%NH₄NO₃) system which may be due to increase in the number of charge carriers and increase in the amorphous nature of the polymer electrolytes which is consistent with the XRD result. For 75% PPP:25%NH₄NO₃ electrolyte, the ionic conductivity

decreases which may be due to recombination of dissociated ions to form neutral molecules and thereby decreasing the number of mobile ions.

Modulus spectral analysis:

Another approach to investigate the electrical response of polymeric materials is the electrical modulus analysis because it effectively suppresses the electrode effect. The variation of real part and imaginary part for the electrical modulus with frequency for 80% PPP: 20% NH_4NO_3 , at various temperatures, are shown in Fig.4 (I) (II). Modulus M^* was evaluated using the following relations,

$$M^* = \varepsilon' / \varepsilon'^2 + \varepsilon''^2 \text{ and } M'' = \varepsilon'' / \varepsilon'^2 + \varepsilon''^2 \quad (3)$$

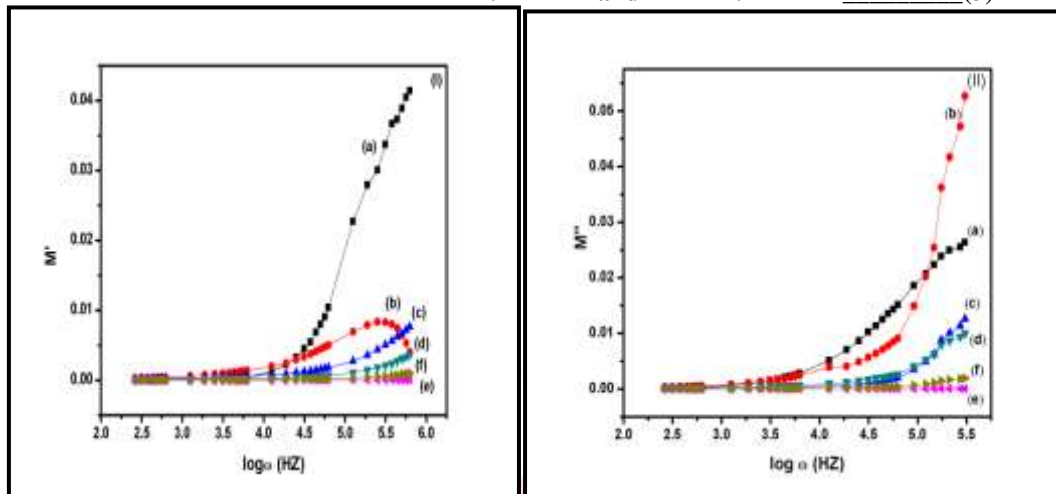


Fig.4 (I) (II) Frequency dependence of real and imaginary part M' & M'' for (a) 100% PPP: 0% NH_4NO_3 (b) 95% PPP: 5% NH_4NO_3 (c) 90% PPP: 10% NH_4NO_3 (d) 85% PPP: 15% NH_4NO_3 (e) 80% PPP: 20% NH_4NO_3 (f) 75% PPP: 25% NH_4NO_3 polymer electrolytes at 303K.

The spectrum of M' shows an asymmetric peak approximately centered in the dispersion region of M' . The modulus peak maximum shifts to lower frequencies and the peak maxima decrease with increase of temperature, suggesting the presence of more than one type of relaxation mechanism [14, 15]. The almost zero values of M'' at low frequency indicate the removal of electrode polarization. The observed long tail at low frequencies is due to the large capacitance associated with the electrodes [16].

CONCLUSION:

Proton conducting polymer electrolytes based on blend polymer (PVA, PAN and PVdF) with ammonium nitrate (NH_4NO_3) have been prepared by solution casting techniques using DMF as solvent. The X-ray diffraction pattern of the polymer electrolytes reveals the increase in amorphous nature of the polymer electrolytes. AC impedance techniques reveal that among all composition 80% PPP: 20% NH_4NO_3 has achieved highest ionic conductivity of 9.12×10^{-4} (S/cm) at room temperature. The modulus analysis suggests the presence of relaxation mechanism present in the polymer electrolytes. The highest ionic conducting sample can be used for electrochemical devices.

REFERENCES:

- [1] Kumudu Perera and M. A. K. L. Dissanayake, "Conductivity variation of the liquid electrolyte, EC: PC: LiCF_3SO_3 with salt concentration", Sri Lankan Journal of Physics, Vol.7, pp.1-5, 2006.
- [2] S.Sivadevi, S.Selvasekarapandian, S.Karthikeyan, N.Vijaya, F.Kingslin Mary Genova, C.Sanjeeviraja, H.Nithya, Iwai, Junichi Kawamura, "Proton conducting polymer electrolyte based on PVA-PAN blend doped with Ammonium thiocyanate," Int.J.Electroact. Mater.1, pp. 64-70, 2013.
- [3] X.Lu, R.A.Weiss, "Development of miscible blends of polyamide and manganese sulfonated polystyrene using specific interaction," Macromolecules 24, 4381, 1991.
- [4] J.L.Acosta, E.Morales, "Synthesis and characterization polymethylalkoxysiloxanes solid polymer electrolytes," Solid State Ionics 85, pp. 85-90, 1996.
- [5] Sandoval, C.Castro, L.Gargallo, D.Radic, J.Freire, "Specific interaction in blends containing Chitosan and functionalized polymers," Polymer 46, 10437, 2005.
- [6] S.Nithya, S.Selvasekarapandian, S.Karthikeyan, D.Vinothpandi, C.Sanjeeviraja, "Proton Conducting polymer electrolyte based on PAN," Indian Journal of Applied Research 3, 2249, 2013.
- [7] A.Jayalakshmi, A.Annapooranam, S.Sivadevi, "Effect of ammonium salt on structural, conductivity and optical properties of pvdf thin film electrolytes," International Journal of Technochem Research, vol.2, ISSN 2395-4248, pp.239-243, 2016.
- [8] A.K.Tamil Vathana, S.Sivadevi, "Investigation of Lithium Ion Conducting Blend polymer electrolytes based on PVA, PAN and PVdF," International Journal of Latest Research in Engineering and Technology, vol. 3, Issue 4, pp.66-73, April (2017).
- [9] M.Armand, "Bioinspired intelligent materials and devices," Solid State Ionics 9, pp.745-754, 1983.
- [10] G.G.Kumar, P.Kim, K.S.Nahm, R.N.Elizabeth, "Structural characterization of PVdF -HFP/PEG/ Al_2O_3 proton conducting membrane for fuelcell," J.Membrane Sci.303 pp.126-131, 2007.
- [11] R.M.Hodge, G.H Edward, G.P.Simon, "Water absorption and states of water in semicrystalline polyvinylalcohol films," Polymer 37, pp.1371-1376, 1996.

- [12] Xu M, Eyring EM, Petrucci S, "Molecular dynamics and Infrared spectra of NaSCN dissolved in the solvent macrocycle 15-crown- 5 and Polyethylene oxide dimethyl ether – 250," JPhys chem.99 ,14589, 1995.
- [13] BA. Boukamp, "A nonlinear least squares fit procedure for analysis of admittance data of electrochemical system," Solid State Ionics 20, pp.301, 1986.
- [14] S.R.Majid, A.K.Arof, "FTIR studies of chitosan-orthophosphoric acid Ammonium nitrate-Aluminiumsilicate polymer electrolyte," Mol.Cryst.liq.Cryst.484, pp.117, 2008.
- [15] Simmons JG, Nadkarni GS, Lancaster MC.J.Appl.Phys. vol.41, pp.538-544, 1970.
- [16] Mishra R, Baskaran N, Ramakrishnan PA, Rao KJ .Solid State Ionics 112, pp.261-273, 1998.

