TG/DTA and Optical Studies on Nano ZrO$_2$ Incorporated Polymer Electrolytes for Rechargeable Proton Batteries

Radha KP[*]

Department of Physics, S.F.R. College for Women, Sivakasi 626123, Tamil Nadu, India

ABSTRACT

Nano composite polymer electrolytes based on poly (vinyl alcohol) PVA as host polymer, ammonium hexafluoro phosphate (NH$_4$PF$_6$) as salt and zirconium di oxide (ZrO$_2$) as nano-filler have been prepared by Solution Casting Technique. Admittance analysis shows that the addition of the nano-filler ZrO$_2$ to the polymer electrolyte 70 PVA:30NH4PF6 enhances the amorphous phases of polymer matrix which in turn increases the ionic conductivity. 0.03g ZrO$_2$ added polymer electrolyte has maximum ionic conductivity 3.029 × 10^{-3} Scm^{-1} at ambient temperature. The weight loss for ZrO$_2$ added polymer electrolyte is less compared to pure polymer electrolyte suggesting that the thermal stability of composite polymer electrolyte system has been improved due to the addition of the nano-filler ZrO$_2$. The optical band gap decreases from 3.68eV of nano-filler undoped polymer electrolyte to 3.21 eV of nano-filler incorporated polymer electrolytes.

Keywords: Admittance, Thermal, Ultraviolet

INTRODUCTION

Most of the experimental research works are carried out towards development of proton conducting solid polymer electrolyte based on poly(vinyl alcohol) (PVA) doped with various ammonium salts like NH$_4$ F, [1] NH$_4$Cl, adipic acid [2] etc. PVA is a cost effective bio degradable synthetic polymer with good charge storage capacity excellent film forming capacity, donor dependent electrical and optical Properties etc. PVA is a semi crystalline material. The author Zhang et al. [3] reported that semi crystalline materials exhibit improvement in certain physical Properties due to crystal amorphous interfacial effect. The hydrogen bond present in PVA is an instrumental to proton conductivity in polymer electrolyte. PVA is well known to form complexes with ammonium salts. The conduction mechanism of proton conducting polymer electrolyte with ammonium salts have been investigated spectroscopically in the past decades [4]. Literature studies reveal that the incorporation of nano-filler is contemporary way of enhancing the ionic conductivity of the polymer electrolytes. In the present work, the nano-filler zirconium di oxide (ZrO$_2$) is added to the polymer electrolyte PVA/NH$_4$PF$_6$. The prepared electrolytes are subjected to the electrical, thermal and optical studies.

MATERIALS AND METHODS

Synthesis of polymer electrolyte

In the present work PVA with molecular weight 1,25,000 (AR grade Sd fine chem. make), ammonium hexafluoro phosphate (NH$_4$PF$_6$) purchased from Aldrich, USA and the nano filler ZrO$_2$ from Aldrich USA of particle size 45 nm and dimethyl sulphoxide (DMSO) as solvent are used as starting material. Composite polymer electrolytes X (70PVA:30 NH$_4$PF$_6$): (1–X) ZrO$_2$ (X=0, 0.02, 0.03 and 0.04 g) have been prepared by solution casting technique. Appropriate weights of PVA, NH$_4$PF$_6$ are dissolved in DMSO by using magnetic stirrer separately. Then these two solutions are mixed together and stirred well. The nano filler ZrO$_2$ is suspended in this solution and then stirred well to get homogenous mixture. The mixture is then poured into glass petri dish and is allowed to evaporate the solvent in the vacuum oven at 80ºC for 5 days. Free standing nature of the electrolyte has obtained.

Table 1: Sample code and weight, direct band gap and ionic conductivity of all nano composite polymer electrolytes

Sample code	Weight of		Direct band gap (eV)	Ionic conductivity at 303K (Scm^{-1})
	X (70PVA:30 NH$_4$PF$_6$) (g)	(1-X)ZrO$_2$ (g)		
HFZ0	1	0	3.68	2.580 × 10^{-4}
HFZ1	0.98	0.02	3.37	1.876 × 10^{-3}
HFZ2	0.97	0.03	3.21	3.029 × 10^{-3}
HFZ3	0.96	0.04	3.48	2.145 × 10^{-3}

Characterization

Thermo gravimetric analysis (TG) has been studied using SDT Q600 V8.3 Build 101 at a heating rate of 20°C/min in the range 0°C to 800°C in the atmosphere of Nitrogen. AC conductivity measurements have been carried out on PVA: NH_4PF_6:ZrO_2 systems of uniform thickness having an area of 1 cm^2. Polymer electrolytes have been sandwiched between two stainless steel (SS) electrodes applying a potential of 1V from 42 Hz to 1 MHz using HIOKI make LCZ meter (model 3532) interfaced to a computer. The conductivity has been calculated from complex impedance plots of measured impedance (Z) and phase angle ($_\theta$). The temperature of the cell has been controlled using a thermostat and electrical measurements of the polymer electrolytes have been carried out in the temperature range 303K–343K.The absorbance spectra have been measured using UV-2400 PC Series in the Wavelength Range 200 nm to 900 nm with medium scan speed of sampling interval 0.1.

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RESULTS AND DISCUSSION

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Admittance analysis

The admittance plot is a powerful method to investigate the ion conduction mechanism. The complex admittance Y* is given by the relation

$$Y^*=1/Z^*=Y' + jY'' \tag{1}$$

Where Y'and Y'' is the real and imaginary part of admittance respectively.

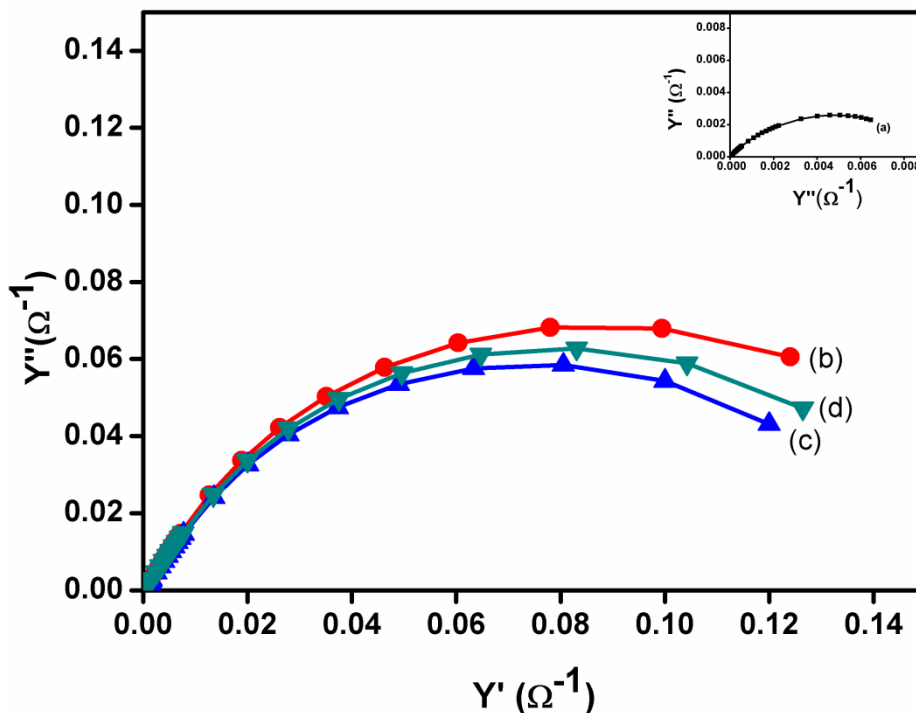

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Figure 1: Admittance plot of all nano composite polymer electrolyte

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The plot (Figure 1) shows a low frequency arc representing the series combination of the bulk resistance (R_b) and electrode capacitance C_e as shown in the equivalent circuit 1.

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Equivalent circuit-1

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The intercept of the low frequency arc on the real axis is $1/R_b$ [2]. The value of $1/R_b$ of all samples has been obtained from curve fitting method. Then the conductivity of all samples has been calculated using the relation.

$$\sigma = \ell/R_b A \tag{2}$$

Where, l is the thickness of the polymer electrolyte and A is the surface area of the electrolyte. The calculated values are presented in Table 1. The incorporation of ZrO_2 to PVA enhances the ionic conductivity from 10^{-4} to 10^{-3} Scm^{-1} at room temperature. The polymer electrolyte HFZ2 has maximum ionic conductivity 3.029×10^{-3} Scm^{-1} at ambient temperature. The addition of the nanofiller ZrO_2 to the polymer electrolyte PVA/NH_4PF_6 enhances the amorphous phases of polymer matrix which in turn increases the ionic conductivity of the nano composite polymer electrolytes.

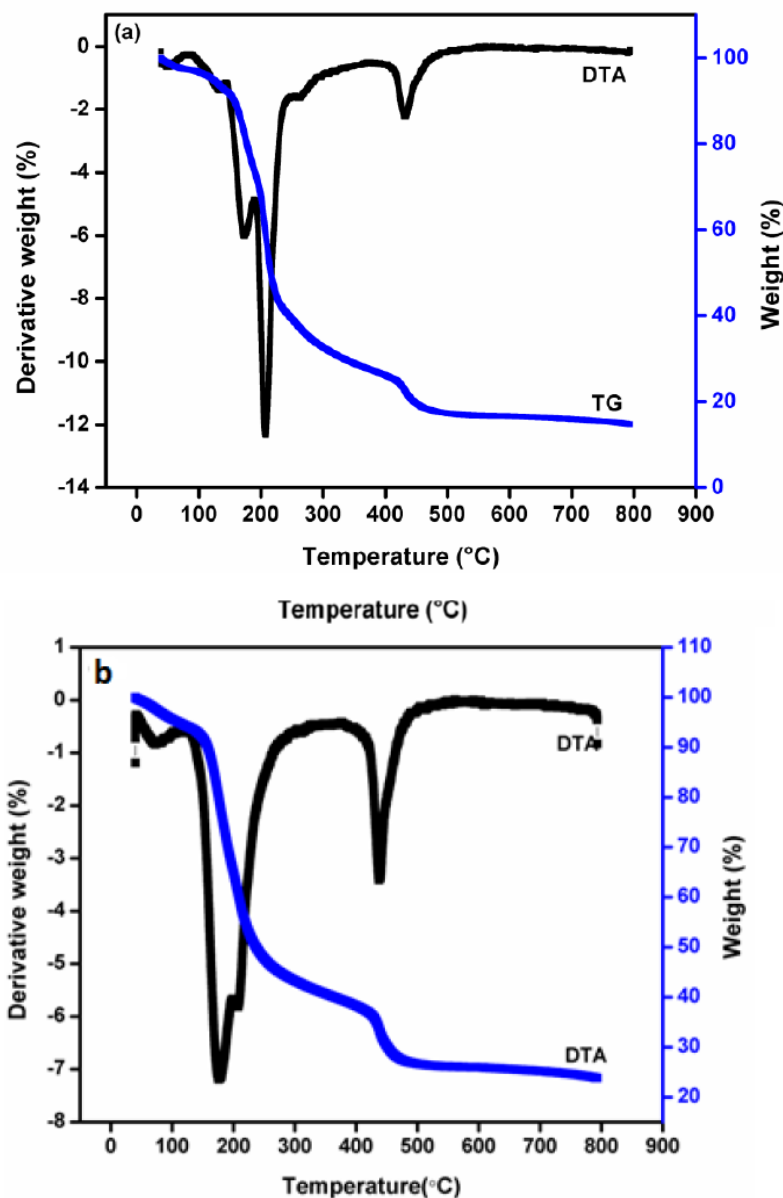<div align="center">

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TGA/DTA analysis

Figure 2: TG/DTA thermographs of composite polymer electrolytes X(70PVA:30NH₄PF₆): (1-X) ZrO₂ (X=0, 0.02, 0.03 & 0.04 g)

Figure 2 shows thermographs of all nano composite polymer electrolytes at a heating rate 10°C/min and in the temperature range of room temperature to 800°C. A derivative weight loss plot can be utilized to indicate the point at which weight loss is most apparent. The plot shows three weight loss regions of all nano composite polymer electrolytes. The initial weight loss for nano-filler free polymer electrolyte occurs in the temperature region 39.4°C to 151.4°C with sharp peak at 131.6°C in the DTA curve. It may be due to evaporation of physically weak and chemically strong bound H_2O from the polymer matrix. Similar results have been reported by the author Abdelrazek [5]. The weight loss of this polymer electrolyte is about 7.3%. It has been observed that the major weight losses have occurred in the temperature range of 151.4°C to 414.6°C accompanied by DTA peaks at 173.6°C and 210.1°C with weight loss of 67.1% in TGA thermo gram. The reason may be that the degradation of side chain (O-H) of PVA and the weight loss corresponding to this temperature range is 67.1%. Finally, the third stage of decomposition occurs in the temperature between 414.6°C and 476.1°C corresponding to the weight loss of 7.4%. It is accompanied by the DTA peak at 434.1°C. This may be attributed to the cleavage of C-C backbone of PVA polymer which is commonly called as carbonation according to the author Qiao [6]. Composite polymer electrolyte HFZ2 also shows three major processes of weight losses for all the prepared electrolytes as shown in Figure 2b. The first degradation temperature ranging from 36.6°C to 154.3°C is associated with the loss of water molecules. It is accompanied by DTA peak at 73.1°C. The weight loss corresponding to this temperature range is from 7.1%.

Table 2: TG and DTA data of all composite polymer electrolytes

Sample code	Region	Temperature (°C)		Weight loss (%)		DTA (°C)
		Initial	Final	Partial	Total	
HFZ0	I	39.4	151.4	7.3		131.6
	II	151.4	414.6	67.1	81.9	173.6, 210.1
	III	414.6	476.1	7.4		434.1
HFZ2	I	36.6	154.3	7.1		73.1
	II	154.3	420.3	55.5	69.3	179.5
	III	420.3	479.3	9.9		442.7

The major weight loss has been observed to be in the temperature range 154.3ºC to 420.3ºC. It may be due to the structural decomposition of the polymer electrolytes and their complexes. The weight loss corresponding to this stage is 55.5%. These are accompanied by DTA peaks at 179.5ºC in Figure 2b. The third stage of decomposition in the range 420.3ºC to 479.3ºC accompanied by DTG peaks at 442.7ºC. This is because of the cleavage of C-C backbone of PVA polymer and the weight loss is about 7.1% to 9.9%. The decomposition temperature and their weight losses of all electrolytes are shown in the Table 2. The weight loss for ZrO_2 added polymer electrolyte HFZ2 is less compared to Pure Polymer electrolyte. It concludes that the thermal stability of composite Polymer electrolyte system has been improved due to the addition of the nanofiller ZrO_2.
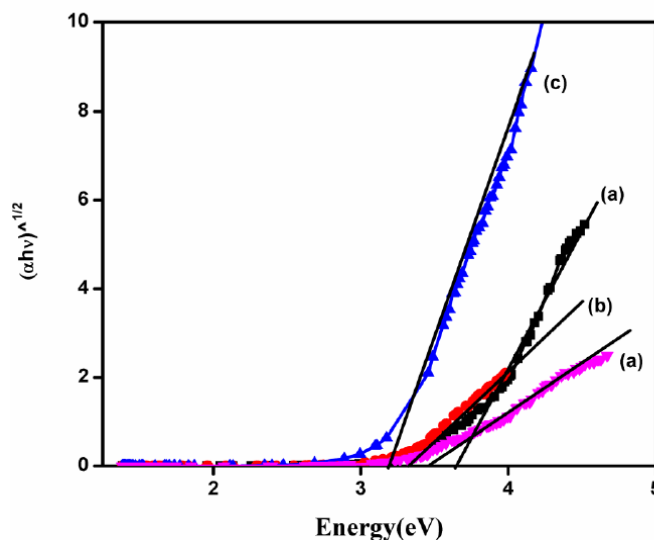
Optical band gap

Figure 3: Energy vs. (αhv)$^{1/2}$ of composite polymer electrolytes X(70PVA:30NH$_4$PF$_6$): (1-X) ZrO$_2$ (a) X=0 (b) X=0.02 (c) X=0.03 (d) X=0.04 in g

The optical energy gap (E_g) can be calculated from Mott, Davis [7] and Tauc [8] formula:

$$\alpha h\gamma = B[h\gamma - E_g]^m \tag{3}$$

Where B is a constant, hv is the photon energy, m is the power factor. The power factor (m) can take values 1/2, 3/2, 2 and 3 for allowed direct, forbidden. Indirect, allowed indirect and forbidden indirect transitions respectively [9]. A plot of $(\alpha h v)^2$ versus photon energy (hv) for PVA–NH_4PF_6-ZrO_2 composite polymer electrolytes is shown in Figure 3. The direct band gap energies are obtained from the intercept of the straight lines with the energy axis at $(\alpha h v)^2$=0. The optical band gap decreases from 3.675eV for nano-filler undoped polymer electrolyte PVA/NH$_4$ PF$_6$ to 3.21 eV for nano-filler incorporated polymer electrolytes. It is interpreted as the width of the mobility edge depends on the degree of disorder and defects present in the amorphous nature. These defects produce localized states in the forbidden gap. Similar results have been reported by the author Sharma [10].

CONCLUSION

Composite polymer electrolytes X (70PVA:30 NH$_4$PF$_6$): (1–X) ZrO$_2$ (X=0, 0.02, 0.03 & 0.04 g) have been prepared by solution casting technique. The admittance plot shows a low frequency arc representing the series combination of the bulk resistance (R$_b$) and electrode capacitance C$_e$ as shown in the equivalent circuit. TG/DTA analysis suggests that the thermal stability of composite Polymer electrolyte system has been improved due to the addition of the nano-filler ZrO$_2$. The optical band gap decreases from 3.68eV for nano-filler undoped polymer electrolyte to 3.21 eV for 0.03 g of nano-filler incorporated polymer electrolytes.

ACKNOWLEDGEMENTS

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