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Spectroscopic analysis of composite polymer electrolyte PVA:NH_4PF_6:ZrO_2

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Abstract
Proton conducting composite polymer electrolytes have been prepared by using semi crystalline polymer Poly (vinyl alcohol), proton donor NH_4PF_6, and nanofiller ZrO_2 with solvent DMSO by Solution Casting Technique. The maximum Ionic conductivity of the polymer electrolyte has been found to be 2.222 x 10^{-3} Scm^{-1} for 2mol% ZrO_2 incorporated polymer electrolyte 70PVA: 30 NH_4PF_6 at ambient temperature. Magnitude Bode plot analysis shows a negative temperature Co-efficient of resistance type behavior. The Kohlrausch exponent of the best conducting composite polymer electrolyte is less than one indicating Non-Debye nature of the prepared polymer electrolytes. The loss tangent plot shows a peak at particular frequencies for different temperature due to the active component (ohmic) of current.

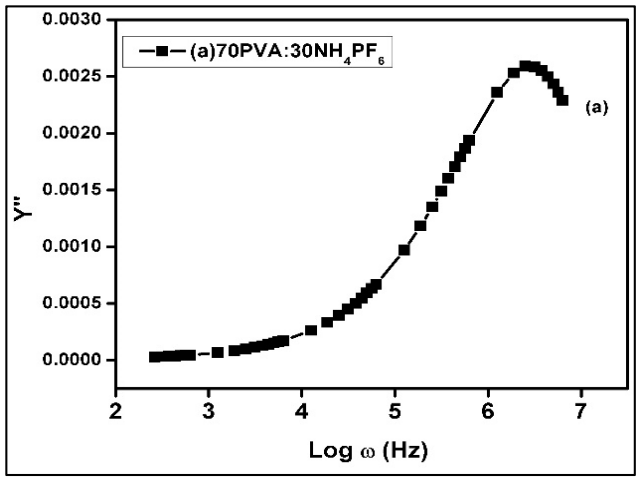
Keywords: Admittance, Bode plot, Loss tangent

1. Introduction
Solid polymer electrolytes are regarded as key components in Electro chemical devices such as Fuel cells, Batteries, Electro chromic display etc., since the ionic conduction in the polymer electrolytes has a strong influence on the performance of these devices [1]. The solid polymer electrolytes have advantages over the liquid electrolytes such as thermally stable, low volatility with easy handling, ability to eliminate corrosive solvent and harmful gas formation [2]. Poly (vinyl alcohol) PVA is used as host polymer in the present study due to its thermal and chemical stability, good storage capacity, film forming ability, dopant dependent electrical and thermal properties etc., PVA is well known to form complexes with ammonium salts. Therefore, ammonium hexafluorophosphate has been chosen as proton donor. The nanofiller Zirconium di oxide ZrO_2 acts as solid plasticiser.
In our earlier work, we have dealt with preparation of polymer electrolyte with PVA and ammonium hexafluoro phosphate (NH_4PF_6). In the present work, the optimized high conductivity polymer electrolyte 70PVA:30 NH_4PF_6 (mol %) has been further optimized to find the effect of the nanofiller ZrO_2 of 45nm size on the ionic conductivity of the proton conducting polymer electrolyte. The electrical characteristics of the prepared composite polymer electrolytes have been studied.

2 Experimental Techniques
2.1 Sample Preparation
Poly (vinyl alcohol) (PVA) with molecular weight 1,25,000 (AR grade Sd fine chem. make), ammonium hexafluoro phosphate (NH_4PF_6) purchased from Aldrich, USA and the nano filler Zirconium di Oxide (ZrO_2) from Aldrich USA of particle size 45nm and Dimethyl Sulphoxide (DMSO) as solvent are used as starting material to prepare composite polymer electrolytes by solution casting technique. From our earlier work, it has been observed the optimum concentration of PVA and NH_4PF_6 as 70mol% and 30mol%. The nano filler ZrO_2 is added to this optimum concentration (70PVA:30NH_4PF_6) as 1mol%, 2mol% and 3mol%. Appropriate weights of PVA, NH_4PF_6 are dissolved in DMSO by using magnetic stirrer. The Nano filler ZrO_2 is suspended in the 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 80^0C for 5 days. Free standing nature of the electrolyte has obtained.

2.2 Conductivity measurements
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 (θ). 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.

3. Results and discussion
3.1 Frequency dependence of Admittance analysis



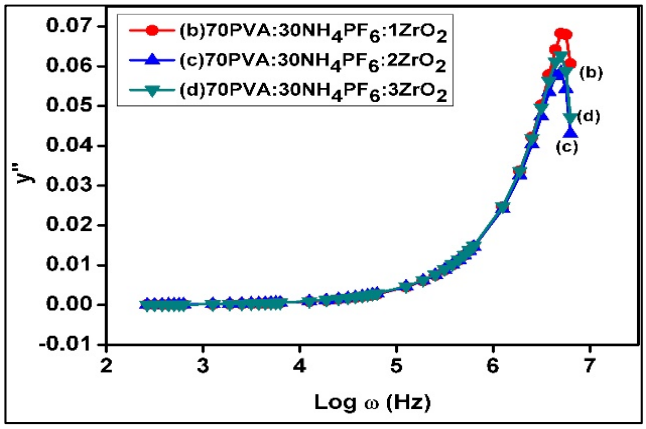


Fig 1: Imaginary part of Admittance vs frequency plot of all composite polymer electrolytes at 303K

Spectroscopic plot of imaginary part of the admittance of all samples is depicted in Fig – 1(a - d). The admittance value increases with increase in frequency and reaches maximum and then decreases. The existence of peak reveals the relaxation mechanisms [3]. The presence of the peak in the spectroscopic plot of Y" indicates that there is series combination of bulk resistance and electrode capacitor with peak maximum at $1/2R_b$. The bulk resistance (R_b) obtained from peak maximum has been used to calculate the ionic conductivity by the relation

$$\sigma = \ell / R_b A \quad (1)$$

Where l is the thickness of the polymer electrolyte and A is the surface area of the electrolyte. From the table 1, it has been observed that the composite polymer electrolyte 70 PVA:30NH_4PF_6:2ZrO_2 has maximum ionic conductivity (2.222 x 10^{-3}Scm^{-1}) at ambient temperature. The incorporation of the nanofiller ZrO_2 to the polymer electrolyte 70PVA:30NH_4PF_6 reduces the formation of ion pairs and / or ion – ion interaction which hinders the ionic conductivity in composite polymer electrolytes [4]. However the conductivity is found to decrease for 3 mol% ZrO_2added polymer electrolyte. The reason may be due to well defined crystallite regions formed by the higher concentrations of nano fillers ZrO_2 [5]. The plot between real part of the admittance and frequency is useful to diagonise the conduction mechanism (Fig 2). The frequency independent region indicates the accumulation of the charge carriers near the electrode [6].

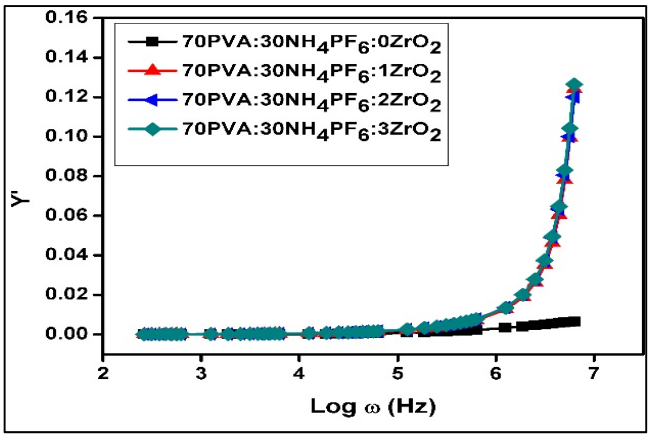


Fig 2: Real part of Admittance vs frequency plot of all composite polymer electrolytes at 303K

Table 1: Conductivity values of all polymer electrolytes

Composition (mol %)	Ionic conductivity (Scm^{-1})
70 PVA:30 NH_4PF_6:0 ZrO_2	1.45x 10^{-4}
70 PVA:30 NH_4PF_6:1 ZrO_2	1.639 x 10^{-3}
70 PVA:30 NH_4PF_6:2 ZrO_2	2.222 x 10^{-3}
70 PVA:30 NH_4PF_6:3 ZrO_2	1.636 x 10^{-3}

3.2 Magnitude Bode Plot Analysis

The complex impedance is expressed as

$$Z = |Z| e^{j\theta} \quad (2)$$

Where $|Z|$ and θ are the absolute magnitude and the phase angle of impedance.

$$|Z| = (Z'^2 + Z''^2)^{1/2} \quad (3)$$

$$\theta = \text{arc tg}\left(\frac{Z''}{Z'}\right) \quad (4)$$

Where Z' and Z'' are the real and imaginary parts of complex impedance.

$$Z = Z' - jZ'' \quad (5)$$

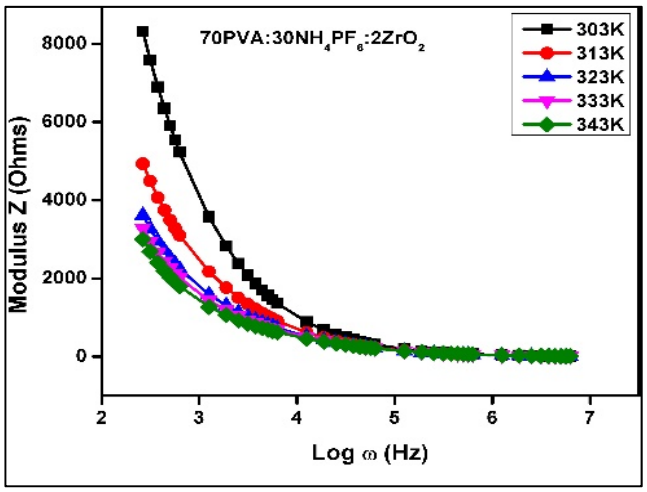


Fig 3: Magnitude Bode Plot

Fig 3 shows the variation of modulus of the impedance as a function of frequency of the best conducting sample at several temperatures. It has been observed that the magnitude of Z decreases with increasing temperature in the low frequency region and shows a negative temperature coefficient of resistance type behavior. In the high frequency region, the plots show a plateau region i.e., Frequency – independent values of Z. The values of Z coincide at higher frequencies at all temperatures indicates a possible release of space charge. As a consequence there is reduction in the resistive behavior of the polymer with rise in temperature.

3.3 Phase Bode Plot Analysis

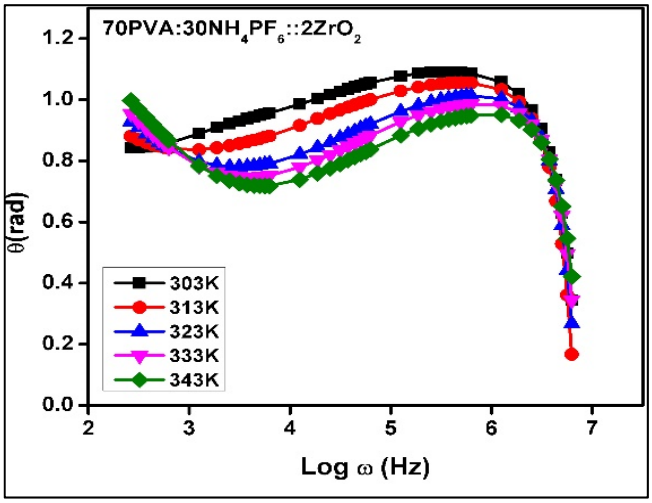


Fig 4: Phase Bode Plot of the electrolyte

The angular frequency dependence of the phase angle (θ) of the best conducting electrolyte at various temperatures is depicted in Figure 4. The phase angle is characterized by broad peak appearing at unique frequency within the temperature range studied. The position of theses peaks shifts to higher frequency with rise in temperature. In the high frequency region the magnitude of maxima decreases gradually with rise in temperature. Finally it merges to 0.16278 radians because the ohmic current (active component) is independent of frequency and the capacitive reactance increases in proportion to the frequency [7].

3.4 Modulus analysis

The complex electrical modulus formalism has been used to analyze the electrical properties because it gives main response of the bulk of the sample. It is a suitable formalism to extract phenomena such as electrode polarization and conductivity relaxation times. Fig 5 (a,b) depicts real and imaginary parts of electric modulus of all composite polymer electrolytes at different temperatures. Both M' and M'' values decreases with increasing temperature. It is an indicative of the increased mobility of the charge carriers with temperature. The appearance of peak in M' indicates that prepared composite polymer electrolytes are ionic conductor. The peak value of M' decreases with increasing temperature is due to a plurality of relaxation mechanism. The appearance of long tail in M" spectra provide an evidence of the long range ionic hopping predominant in the composite polymer electrolyte material. Kohlrausch – Williams – Watts's law describes the distribution of relaxation time as

$$\varphi\langle t\rangle = \exp\left[-\left(t/\tau\right)^{\beta}\right] \qquad (6)$$

Where φ (t) describes the time evolution of the electric field within a material, τ is the conductivity relaxation time and β is the Kohlrausch exponent. In the present work, the values of for the composite polymer electrolyte containing 2 mol% ZrO_2 at selected temperature are determined from the full width at half maximum (FWHM) of asymmetric modulus M' (Fig. 5a) using the equation

$$\beta = \frac{1.14}{\text{FWHM}} \qquad (7)$$

The value of FWHM is 1.14 decades for a typical Debye peak which gives β = 1 for Debye relaxation [8]. The value of β for a practical solid polymer electrolyte is less than 1[9]. It has been found that the value of β for composite polymer electrolyte containing 2 mol% ZrO_2 in the temperature range 303K – 343K is from 0.507 to 0.628 (table 2). The small values of β indicate the deviation of relaxation time with respect to Debye relaxation time.

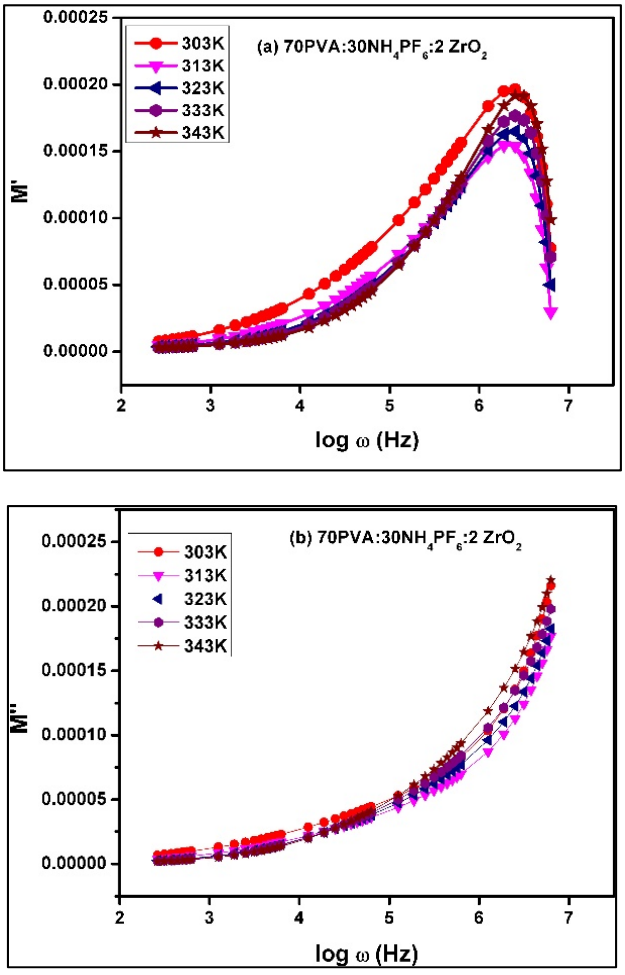


Fig 5(a, b): Real & imaginary parts of Modulus spectra of the electrolyte at different temperatures

Table 2: Kohlrausch exponent (**β**) of Composite Polymer Electrolytes at 303K

Temperature (K)	β
303	0.507
313	0.602
323	0.620
333	0.626
343	0.628

3.5 Dissipation factor analysis

The dielectric relaxation parameters of the polymer electrolytes can be obtained from dielectric loss tangent (tan δ) spectrum analysis. The dielectric loss tangent can be defined by the relation

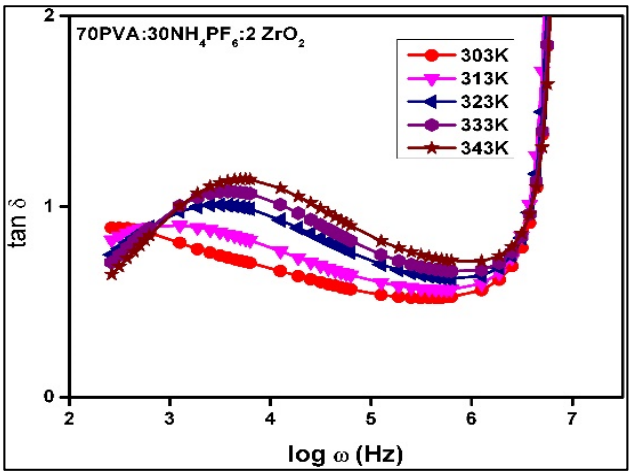


Fig 6: Loss tangent spectra for all compositions at room temperature

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \qquad (8)$$

Where ε″ is the dielectric Loss factor and ε′ is the dielectric constant of the dielectric permittivity. Figure 6 displays the variation of tangent loss at various temperatures for the best conducting electrolyte 70PVA: $30NH_4PF_6$: 2 ZrO_2.

The tangent loss peak shows a continuous trend of shifting towards high frequencies with rise in temperature. The loss tangent shows a peak at particular frequencies for different temperature due to the active component (ohmic) of current which increases more rapidly than its reactive component (capacitative). At higher frequencies loss tangent decreases with increasing frequency. The reason may be that the active component of the current is practically independent of frequency and the reactive component increases in proportion to the frequency.

4. Conclusion

Composite polymer electrolytes have been prepared using PVA, NH_4PF_6 and ZrO_2 by Solution casting technique.

- Admittance analysis shows that the composite polymer electrolyte 70PVA:$30NH_4PF_6$:$2ZrO_2$ has maximum ionic conductivity (2.222 x 10^{-3}Scm^{-1}) at ambient temperature.
- From Magnitude Bode plot analysis, it has been observed that the values of Z coincide at higher frequencies at all temperatures indicates a possible release of space charge.
- The appearance of peak in M' indicates that prepared composite polymer electrolytes are ionic conductor.
- The small values of β indicate the deviation of relaxation time with respect to Debye relaxation time.

5. Acknowledgment

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