



## Electrical and Thermal Studies of PVA Based Polymer Electrolytes

## KEYWORDS

Electrical analysis, thermal analysis

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**ABSTRACT** Poly (Vinyl alcohol) and ammonium fluoride ( $NH_4F$ ) have been used as starting material to prepare low cost proton conducting polymer electrolytes. Conductance spectra analysis reveals that ionic conductivity of salt  $NH_4F$  doped Polymer electrolyte has been found to increase with temperature which in turn suggests that the ionic conduction is temperature dependent. Spectroscopic analysis of  $Z''(\omega)$  and  $M''(\omega)$  curves indicate the presence of Non – Debye type of relaxation in the electrolyte. Thermal analysis implies that the salt doped polymer electrolyte has more thermal stability than undoped polymer electrolyte.

**Introduction:**

Polymer electrolytes have an immense application in electrochemical devices. Poly (Vinyl alcohol) is biodegradable, biocompatible and non toxic polymer. PVA is well known to form complexes with ammonium salts. It has dopant dependent optical and electrical properties, good film forming ability. These properties have led to utilize PVA as the host polymer for the present study. Ammonium salts are proton donors. The present study focuses on PVA based polymer electrolyte doped with  $NH_4F$  salt. The prepared polymer electrolytes have been subjected to electrical and thermal studies.

**Experimental**

PVA (Molecular weight = 1,25,000 AR grade sd fine chem., make) and  $NH_4F$ (AR grade make) are used as starting material with Dimethyl Sulphoxide (DMSO) as solvent. Different molar ratios of PVA:  $NH_4F$  as (100 – X) (X = 0,15) have been prepared by solution casting technique. Appropriate weight of PVA and  $NH_4F$  are dissolved in DMSO by using magnetic stirrer until a homogeneous mixture is formed. Then the mixture is poured into glass Petri dish and is allowed to evaporate the solvent in the vacuum oven at 80°C for 5 days. Free standing nature of the electrolyte has obtained.

Electrical measurements have been performed on HIO-KI make LCZ meter (model 3532) in the frequency range 42Hz – 1MHz at different temperatures ranging from 303K to 343K using stainless steel as blocking electrodes. Thermal analysis TG & DTA have been carried out using SDT Q600 V8.3 Build 101 in the atmosphere of nitrogen from 0°C to 600°C.

**Results and Discussion****Electrical analysis:**

The complex conductivity  $\sigma^*(\omega)$  yields information about the hopping rates of intramolecular and intermolecular distribution while the dc conductivity reflects the summation of all the hopping rates in the distribution. The measurement of  $\sigma^*(\omega)$  at various temperatures is useful to obtain the temperature dependence of the hopping rate. As a consequence,  $\sigma^*(\omega)$  measurements are expected to yield more detail about understanding of the conducting mechanism in the system.

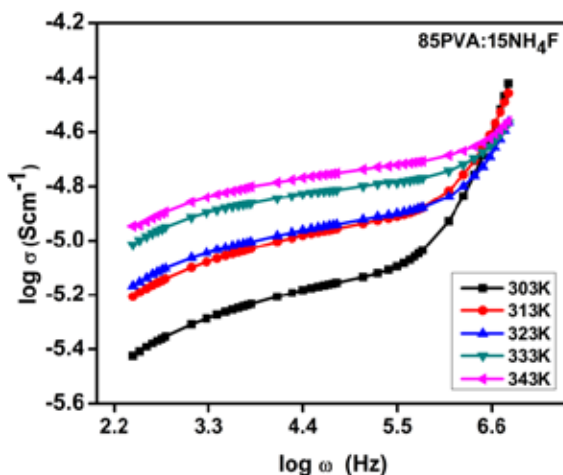


Figure 1 Conductance spectra

Conductance spectra of PVA (85):  $NH_4F$  (15) at different temperatures are shown in Figure. 1. It has two well defined regions. The low frequency plateau region corresponds to the dc conductivity of the bulk material while the high frequency dispersion region corresponds to the ac conductivity. It has been found that the dc conductivity increases with increase in temperature. It suggests that the free volume around the polymer chain causes the mobility of ions and polymer segments and hence the conductivity [1].

Table-1 Power law exponent (n) & Regression values for different compositions of PVA:  $NH_4F$

Temperature (K)	Power law exponent (n)	Regression	Conductivity ( $Scm^{-1}$ ) $10^{-5}$
303	0.573	0.99	0.69
313	0.522	0.98	1.00
323	0.396	0.96	1.10
333	0.254	0.95	1.50
343	0.180	0.95	1.70

The a.c conductivity obeys Jonscher's Power law [2] and it is found to vary with angular frequency ( $\omega$ )

$$\sigma(\omega)_{ac} = \sigma_{dc} + A\omega^n$$

Where n is the power law exponent,  $\sigma_{dc}$  and A are temperature dependent parameters. According to Funke's jump relaxation model [3], the power law exponent n is the ratio of back hop rate to the site relaxation time. If the power law exponent n is less than one, the backward hopping is slower than the site relaxation time as a result there is a translational motion of charge carriers. Otherwise, the backward hopping is faster than the site relaxation time.

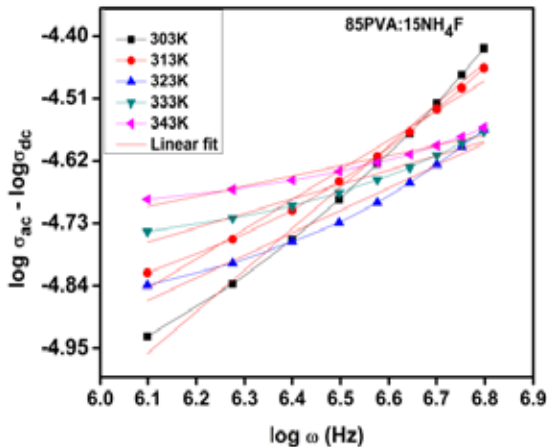


Figure- 2 Jonscher's power law plot

Figure 2 shows Jonscher's power law plot for 85PVA:15NH<sub>4</sub>F polymer electrolytes at various temperatures. The experimental data of the conductance spectra are fitted to the Jonscher's power law equation by using non-linear least square fitting procedure to extract the value of n (table - 1). It is obvious that the power law exponent n for 15mol% NH<sub>4</sub>F ammonium fluoride doped electrolyte at different temperatures is less than one. It implies that the formation of good site and less columbic interaction between the ions favors the hopping of ions thereby enhances the ionic conductivity.

**Spectroscopic analysis:**

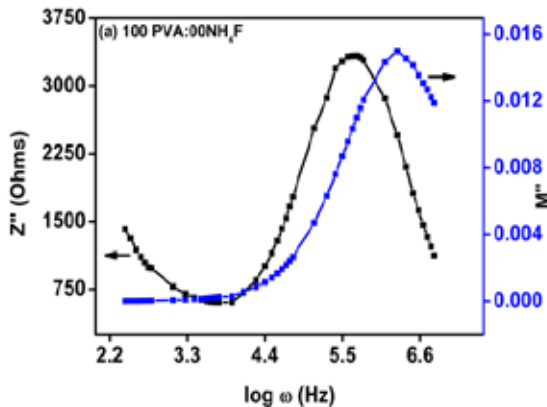


Figure 3a Variation of Z''( $\omega$ ) & M''( $\omega$ ) as a function of frequency of undoped polymer electrolyte

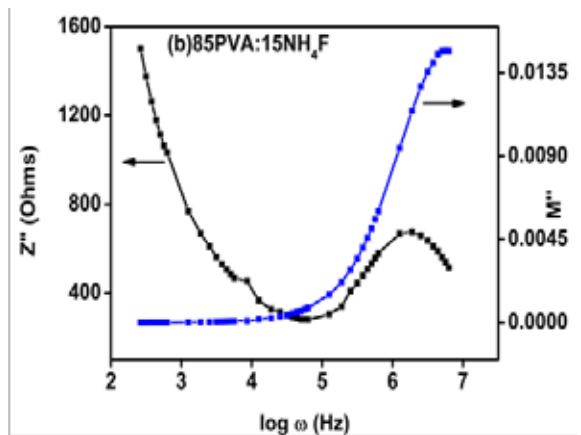


Figure 3a & Figure 3b show the combined spectroscopic plots of Z''( $\omega$ ) & M''( $\omega$ ) for PVA and 85PVA:15NH<sub>4</sub>F polymer electrolytes.

The combined spectroscopic plot of Z''( $\omega$ ) & M''( $\omega$ ) becomes important since impedance plot highlights the most resistive element of the sample and modulus plot highlights the capacitive element which explains conduction mechanism within the grain interior. The shift in the polarization peaks of Z''( $\omega$ ) & M''( $\omega$ ) again confirms the distribution of relaxation time in the present sample [4]. This small difference in the peak frequency is common phenomena associated with dispersion in bulk ac conductivity and dielectric permittivity of a non-ideal dispersive conductor. The width of the peaks of both Z''( $\omega$ ) & M''( $\omega$ ) are greater than Debye peak (1.14 decades) suggesting the non-Debye type relaxation for all the temperatures.

**Thermal analysis:**

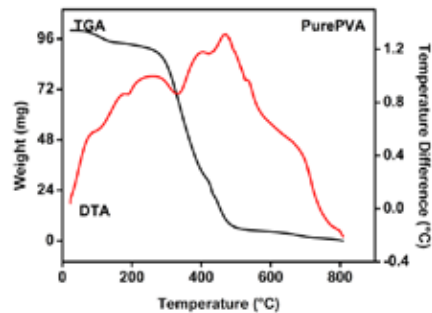


Figure 4 TG/DTA curve of undoped polymer electrolyte

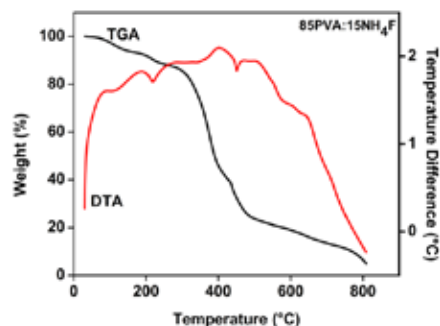


Figure 5 TG/DTA curve of salt doped polymer electrolyte

TG/DTA analysis has been used to investigate the thermal degradation, phase transitions and crystallization of the polymers. Figure 4 and 5 show the TG/DTA thermogram of pure PVA and 85PVA:15NH<sub>4</sub>F polymer electrolyte. Mishra and Rao reported that Pure PVA has thermal stability of decomposition [5] and it has thermal stability up to 265°C. The gradual weight loss up to 69°C in Pure PVA and 77°C in salt doped polymer electrolyte is due to the result of loss of solvent from the electrolyte. The first decomposition has been found to occur at 259°C with weight loss of 9.1% followed by an endothermic curve at 336°C in the DTA curve of Pure PVA and at 294°C with weight loss of 14% followed by an endothermic curve at 344°C in the DTA curve of 15 mol% NH<sub>4</sub>F doped polymer electrolyte. It is due to decomposition of the acetate and side – chain of PVA. The second decomposition occurs at 402°C with weight loss of 67% in pure PVA and at 431°C with weight loss of 61% in salt doped electrolyte. These weight losses are accompanied by endothermic curves at 428°C and 451°C in Pure PVA and salt doped electrolyte respectively. The second degradation is due to oxidation combustion of the PVA main chain [6]. The complete decomposition takes place in the temperature range 480°C to 721°C in Pure PVA and 485°C to 752°C in 15 mol % NH<sub>4</sub>F doped polymer electrolyte. It has 586°C in the DTA curve of Pure PVA and at 573°C in the DTA curve of salt doped polymer electrolyte is concurrent with weight losses.

**Table – 2 TG Degradation temperature & DTA Curve peak Temperature of polymer electrolytes**

Sample	TG Degradation Temperature (°C)		DTA Curve Peak Temperature(°C)	
	I	II		
Pure PVA	259	402	336	428
85 PVA:15NH <sub>4</sub> F	294	431	344	451

From the table2, it has been observed that I & II degradation temperature of salt doped polymer electrolyte is higher when compared with Pure PVA. The thermal stability of 15 mol% NH<sub>4</sub>F doped polymer electrolyte is up to 294°C. It concludes that NH<sub>4</sub>F doped polymer electrolyte has more thermal stability, heat resistant than Pure PVA .

#### Conclusion:

The Polymer electrolyte PVA – NH<sub>4</sub>F have been prepared by solution casting technique.

Impedance analysis implies that NH<sub>4</sub>F doped polymer electrolyte is a very good proton conductor.

From the spectroscopic spectra, it has been observed that there is a shift in the peak frequency for Z''(ω) & M''(ω) curve reveals that there is more than one type of relaxation behavior exist in the polymer electrolyte.

Thermal analysis concretes that the thermal stability of the undoped polymer electrolyte has been found to increase for the salt NH<sub>4</sub>F doped polymer electrolyte.

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