Proton Conducting Polymer Electrolyte Based on Pan

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ABSTRACT Various polymers such as PVA, PVAc, PVP and etc., doped with ammonium salts have been studied for proton conduction. But the study of proton conduction in polymer PAN is scarce. The proton conducting polymer electrolytes composed of polyacrylonitrile (PAN) with ammonium nitrate (NH_4NO_3) in different molar ratios, have been prepared by solution casting method, using DMF as solvent. The increase in amorphous nature of the polymer electrolytes has been confirmed by X-ray diffraction analysis (XRD). The complex formation between polymer and dissociated salt has been confirmed by Fourier transform infrared spectroscopy (FTIR). The ionic conductivity, dielectric permittivity (*) and electric modulus (m*) have been calculated from the ac impedance spectroscopy in the frequency range 42HZ-5MHZ. The activation energy of doped PAN polymer electrolyte is calculated using Arrhenius plot. Based on the study of relaxation spectra, it is found that the relaxation time decreases with increase in temperature.

INTRODUCTION

In recent years, proton conducting polymer electrolytes have attracted considerable attention owing to their application in fuel cells, humidity & gas senors and electrochromic displays.[1,2] The main advantages of polymer electrolytes are their good mechanical properties, the ease of fabrication of films of desirable sizes, and their ability to form good electrode – electrolyte contact. Solid polymer electrolytes (SPE), consisting of an ionic conductive polymer matrix and a supporting electrolyte salt, were firstly introduced by Fenton et al.[3] The development of polymer system with high ionic conductivity is one of the main objectives in polymer research. A variety of polymers such as Poly (acrylonitrile) (PAN), Poly (vinyl chloride) (PVC) and Poly (methyl methacrylate) (PMMA) has been used as polymer matrices.[4-5] Proton conducting polymer electrolytes can be obtained by doping the polymer either with alcohol, amine, amide or amide groups[6] or with strong acids or ammonium salts. Ammonium salts have been reported as good donors of proton to the polymer matrix. Literature survey indicates that the synthesis and characterization of ammonium salts doped proton conducting polymer electrolytes based on Poly (acrylonitrile) (PAN) is rare.

PAN is one of the most important fibers – forming polymers and has been widely used because of its high strength, abrasion resistance and good insect resistance.[7] PAN is used to produce large variety of products including ultra filtration membranes, hollow fibers for reverse osmosis, fibers for textiles, oxidized frame retardant fibers like PANOX and carbon fiber. However the conductivity of PAN is < 10^{-14} S cm^{-1} and the static problem restricts its further applications. PAN is usually synthesized using free radical polymerization. Usually they are copolymers of acrylonitrile and methyl acrylate or acrylonitrile and methyl methacrylate. PAN has a melting point of about 319[0]C, and it also decomposes at this temperature. So PAN membrane is prepared by solution casting technique. In the present work, NH_4NO_3 doped PAN polymer electrolytes have been prepared and subjected to various characterizations such as XRD, FTIR and Ac impedance spectroscopy.

EXPERIMENTAL DETAILS

The polymer PAN (Aldrich) of average molecular weight 1, 50, 000 and the salt NH_4NO_3 were used as the raw materials in this study. Dimethyl formamide (DMF) was used as the solvent. The polymer electrolytes PAN doped with NH_4NO_3 in different compositions such as 100:0; 95:05; 90:10; 85:15; 80:20 and 75:25 were prepared by solution - casting technique. The mixture of PAN and NH_4NO_3 was stirred continuously with a magnetic stirrer for several hours at temperature 60[0] C to obtain a homogenous solution. The solution was then poured into propylene petri dishes and allowed to evaporate in vacuum oven at 65[0]C. After 48 hours, free standing transparent films were obtained.

X-ray diffraction patterns of the prepared samples were recorded at room temperature on a Philips X'Pert PRO diffractometer using Cukα radiation. FTIR spectra were recorded for the polymer electrolyte films using a SHIMADZU - IR Affinity -1 Spectrometer in the range of 400 - 4000 cm^{-1} at room temperature. Conductivity measurements were carried out by using a HIOKI - 3532 LCZ meter in the frequency range of 42 Hz – 1MHz over the temperature range of 303 – 343 K.

Possible interaction between PAN and NH_4NO_3.

The possible interaction between PAN and NH_4NO_3 has been pictorially represented in the scheme 1 along with the structure. The proton from the salt interacts with the polar groups of the host polymer matrix.
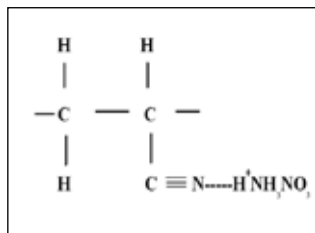
Scheme 1. Possible interactions of NH_4NO_3 with the host polymer PAN

RESULTS AND DISCUSSION
X-ray Diffraction Analysis
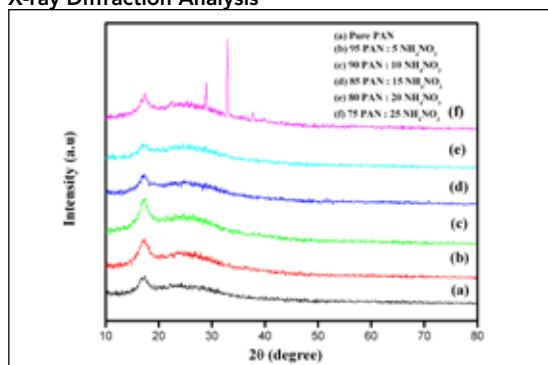

Figure 1. XRD pattern of pure PAN and PAN doped with different NH4NO3 concentrations.

X-ray diffraction (XRD) studies have been carried out to investigate the occurrence of complex formation between the polymer & the salt and amorphous nature of the polymer complex. Fig 1 shows the X-ray diffraction patterns of Pure PAN and PAN doped with different compositions of $NH_4 NO_3$. The XRD pattern in the figure 1(a) for Pure PAN film shows that the film is semicrystalline and a crystalline peak at $2\theta = 17^\circ$ and it corresponds to orthorhombic PAN (110) reflection.[8-10] These diffraction peak intensity is markedly get reduced in the complexes. It is clear from this fig that 80 PAN: 20 NH_4NO_3 polymer electrolyte has high amorphous nature which is revealed by the decrease of intensity and the increase of broadness of the diffraction peak of PAN when compared to other composition. It can be interpreted in terms of the criterion of Hodge et al[11] who has established a correlation between the height of the peak and the degree of crystallinity. Also, peaks corresponding to pure NH_4NO_3 have been found to be absent in the complexes upto 20mol% NH_4NO_3 indicating a complete dissociation of salt in the polymer matrix. However, peaks corresponding to NH_4NO_3 at 27.1°, 30.8° and 39.4° are present in the 75mol% PAN:25mol% NH_4NO_3 [JCPDS. 83- 0520].This indicates the presence of some undissociated salt in this composition which increases the crystalline nature of the polymer electrolyte at higher concentration of salt.

Fourier Transform Infrared Analysis
Fourier transform infrared analysis (FTIR) spectroscopy is important for the investigation of polymer structure. Since it provides information about the complexations and interactions between the various constituents in the polymer electrolytes. These interactions can induce changes in the vibrational modes of the molecules in the polymer electrolyte. The FTIR spectrum of pure PAN and PAN-NH_4NO_3 complexes of various compositions are shown in fig (2). The C≡N stretching band in the FTIR spectrum is by far the most characteristic feature of nitrile group which appears at 2245 cm^{-1} in pure PAN. The nitrile band is displaced to 2246.57 cm^{-1}, 2247.01 cm^{-1}, 2246.33 cm^{-1} and 2246.23 cm^{-1} for 95mol% PAN:5mol% NH_4NO_3, 90mol% PAN:10mol% NH_4NO_3, 85mol% PAN:15 mol% NH_4NO_3 and 80mol% PAN:20mol% NH_4NO_3 polymer complexes respectively.
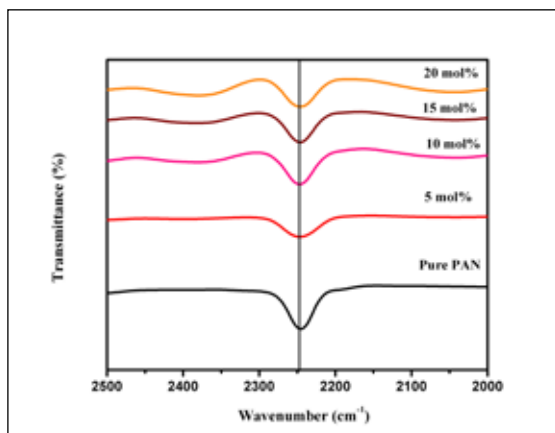

Figure 2. FTIR spectra of pure PAN, 95mol% PAN-5mol% NH_4NO_3, 90mol% PAN-10 mol% NH_4NO_3, 85 mol% PAN-15 mol% NH_4NO_3 and 80 mol% PAN-20mol% NH_4NO_3.

This may be due to inductive effect created by the interaction between the nitrogen atoms in C≡N with the ions from the salt. Similar FTIR spectra for pure PAN and PAN containing the lithium and sodium salts have been observed by Zurina and his co-workers.[12] It is also observed that the intensity of this peak decreases with increase of salt concentration.
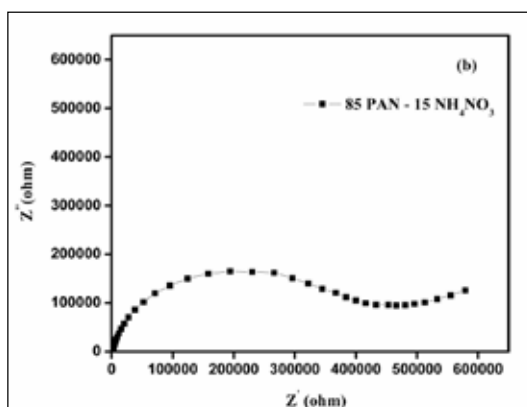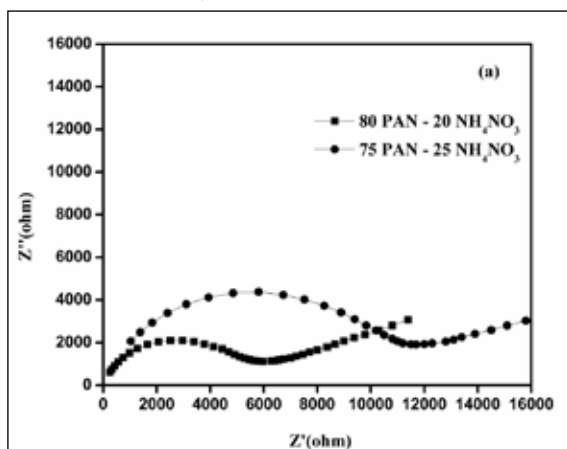
Ac Impedance Analysis

Figure 3(a,b). Shows the complex impedance plot for different ratios of PAN-NH4NO3 polymer electrolyte systems at ambient temperature (303 K).

Electrical characterization of all the prepared polymer samples has been performed using Ac impedance spectroscopy

technique. Fig 3(a & b) shows the complex impedance plot for different mole ratios of PAN-NH₄NO₃ polymer electrolyte system at ambient temperature (303 K).The complex impedance plots show two well - defined regions: the semicircle observed in high frequency region, which is due to the bulk effect of the electrolytes. The semicircle yields information about the properties of the electrolyte. The low frequency spike is non- vertical and yields information about electrode-electrolyte interface.[13] The bulk resistance (R_b) of the polymer electrolytes has been calculated from the intercept of the high frequency semicircle or the low frequency spike on the real impedance (Z') axis. The bulk capacitance (C_b) of the electrolyte has been calculated from the relation $\omega C_b R_b = 1$ at the arc maximum. It is found to be in the order of Pico Farad. It is attributed to the conduction process through the bulk of the material.[14]

From any point on the spike, the electrode capacitance has been calculated using the relation

$$C_e = 1 / z'' \omega \quad \text{-------------- (1)}$$

Where z'' – Imaginary part of the impedance and ω is its corresponding frequency. Thus the magnitude of all the fundamental electrical properties of the cell may be obtained from the impedance analysis. The presence of the semicircle in the impedance plots reveals that there is bulk polarization and ion migration which are physically in parallel.

The ionic conductivity (σ) is calculated using the equation

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

where l and A are thickness and area of the polymer electrolyte film respectively. The highest ionic conductivity at ambient temperature has been found to be 2.742x10⁻⁶ S cm⁻¹ for the 20mol % salt – doped polymer electrolyte. This conductivity value is 8 orders greater than that of pure PAN (<10⁻¹⁴ Scm⁻¹) as reported by WEI PAN.[15] The dc conductivity values for various compositions of PAN-NH₄NO₃ polymer electrolytes at room temperature are presented in Table 1.

PAN-NH₄NO₃ (mol %)	σ_{dc} (s cm⁻¹) at 303K	ω_m (HZ)	Relaxation time τ (s)
85 -15	2.679x10⁻⁸	6.91 x 10²	1.44 x 10⁻³
80 – 20	2.74x10⁻⁶	1.21 x 10⁴	8.22 x 10⁻⁵
75 - 25	1.43x10⁻⁶	9.20 x 10⁴	1.08 x 10⁻⁴

Table 1. Conductivity and relaxation time for various compositions of PAN-NH₄NO₃ poylmer electrolytes.
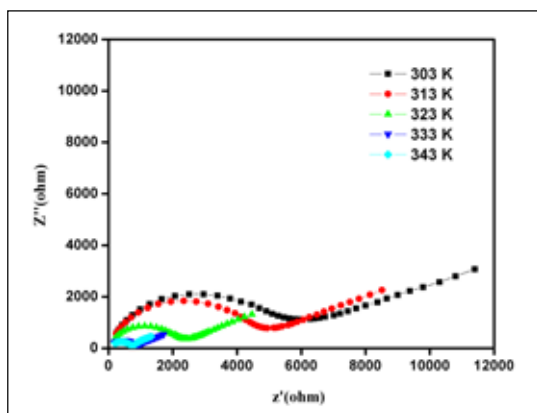

Figure 3c. Complex impedance plot for 20 mol% NH-4NO3-doped PAN polymer electrolyte at different temperatures.

Fig. 3(c) represents the complex impedance plot for the highest conductivity sample at different temperatures. It has been observed that as the temperature increases, the diameter of the semicircle decreases implying the decrease in bulk resistance. The decrease in resistance of the polymer electrolyte is due to the enhancement of the ionic mobility and the number of carrier ions with temperature. The migration of ions may occur through the free volume of polymer matrix, which can be represented by a resister. The ionic migration and bulk polarization are physically in parallel, and therefore the semicircle at high frequency can be observed.
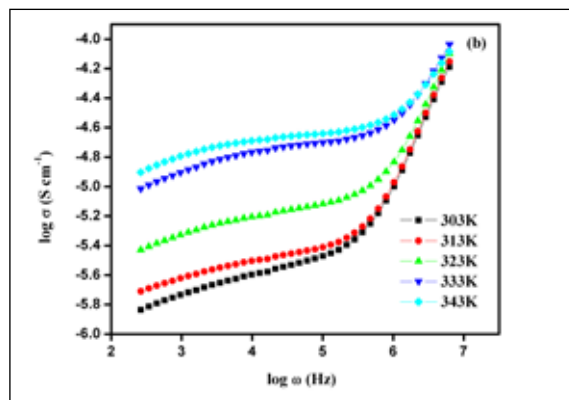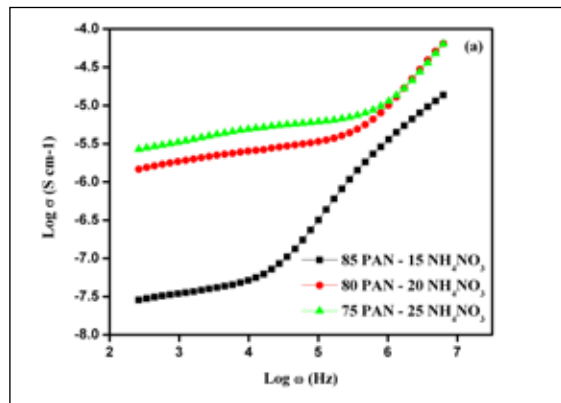
Conductance Spectra Analysis

Figure 4. Conductance spectra for [a] various compositions of PAN/NH₄NO₃ polymer electrolytes at 303 K. [b] 20 mol% NH₄NO₃-doped polymer electrolyte at various temperatures.

Fig. 4 (a&b) shows the frequency dependence of the conductivity for different compositions of PAN/NH₄NO₃ polymer electrolytes at room temperatures and for 20mol% NH₄NO₃–doped polymer electrolyte at different temperatures. The plot shows three regions: low frequency dispersion region due to the space – charge polarization at the blocking electrodes, frequency independent plateau region corresponding to dc conductivity and the high frequency dispersion region corresponding to bulk relaxation phenomenon. The extrapolation of the plateau to zero frequency gives the value of dc conductivity. It is also seen that the dc conductivity increases with increase of temperature suggesting that the free volume around the polymer chain causes the mobility of ions and polymer segments.[16]

The ac conductivity obeys Jonscher's power law represented by

$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^{\alpha} \quad \text{-------------- (3)}$$

where α is the power law exponent, A is the temperature dependent parameter, and σ_{dc} is the dc conductivity. According to jump relaxation model, α is given by

$$\alpha = \frac{back \quad hop \quad rate}{Site \quad relaxation \quad time} \text{------------ (4)}$$

If $\alpha<1$, i.e., the backward hopping is slower than the site relaxation time, then the charge carriers have translational motion. If $\alpha>1$, the backward hopping is faster than the site relaxation time. The α values have been calculated by fitting the conductivity spectra with Jonscher's power law equation using non-linear least squares fitting procedure.The α values have been found to be less than 1 for 20 mol% salt doped sample which may be due to the presence of free site for next hop and the backward motion is slower due to less columbic interaction between the ions.

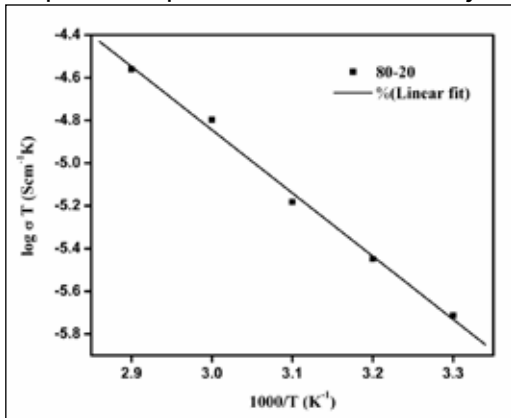### Temperature Dependence of Ionic Conductivity

Figure 5. Temperature dependence of proton conductivity of the PAN/NH$_4$NO$_3$ polymer electrolytes.

The temperature dependence of proton conductivity for the prepared PAN/NH$_4$NO$_3$ polymer electrolytes over the temperature range 303K-343K is shown in the fig(5). It is observed from the fig that the conductivity increases linearly with increase of temperature, for the optimized (80PAN:20NH$_4$NO$_3$) polymer electrolyte. This composition exhibits the highest ionic conductivity. The dc conductivity values obey the Arrhenius type thermally activated process given by the relation,

$$\sigma = (\sigma_0 / T) \exp[-E_a / kT] \text{-------------- (5)}$$

Where σ_0 is the pre-exponential factor, E_a is the activation energy, k is the Boltzmann constant and T is the absolute temperature. The activation energy for the highest conductivity sample has been found to be 0.58 eV. The increase in conductivity with temperature can be linked to the decrease in viscosity and hence increased chain flexibility.[17]
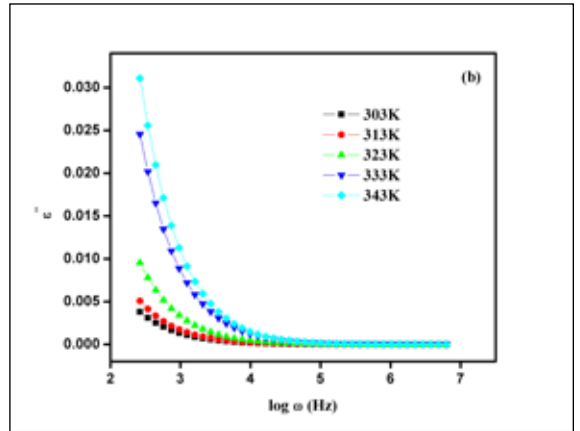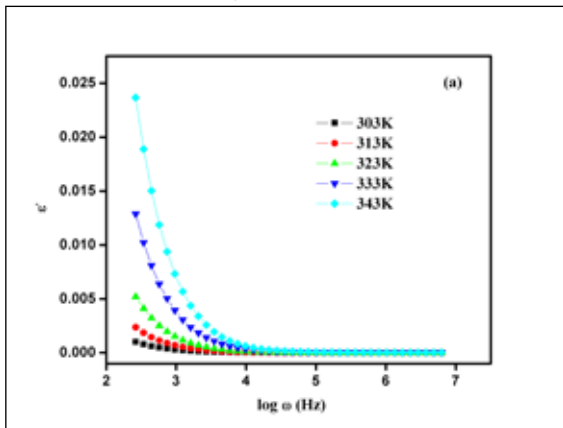
Dielectric Spectra Analysis

Figure 6(a&b). Frequency dependence of ε' (ω) and ε'' (ω) for 20 mol% NH$_4$NO$_3$ - doped PAN at different temperatures.

The dielectric behaviour of the polymer electrolyte system is described by using the dielectric function ε and is defined by,

$$\varepsilon^* = \varepsilon'(\omega) - i\varepsilon''(\omega) \text{-------------- (6)}$$

Where real ε' (ω) and imaginary $\varepsilon''(\omega)$ components are the storage and the loss of energy in each cycle of the applied electric field. Fig 6 (a&b) shows the frequency dependence of ε' (ω) and ε'' (ω) for 20 mol% NH$_4$NO$_3$ - doped PAN at different temperatures. It is clear from the fig (6a), that the values of ε' (ω) are very high at low frequency and decrease with increase of frequency and become constant at higher frequencies. Such high value of dielectric permittivity at low frequencies has been explained by the presence of space charge effects, which is contributed by the accumulation of charge carriers near the electrodes. At higher frequencies, periodic reversal of the field takes place so rapidly that the charge carriers will hardly be able to orient themselves in the direction of the applied field which results in the decrease of dielectric constant.[18] The large value of $\varepsilon''(\omega)$ is also due to the motion of free charge carries within the material.

Modulus Spectra Analysis

The main advantage of M* formalism is that the electrode effect can be suppressed.[19] Electric modulus M has been evaluated using the following relations

$$M' = \varepsilon' / \varepsilon'^2 + \varepsilon''^2 \text{-------------- (7)}$$

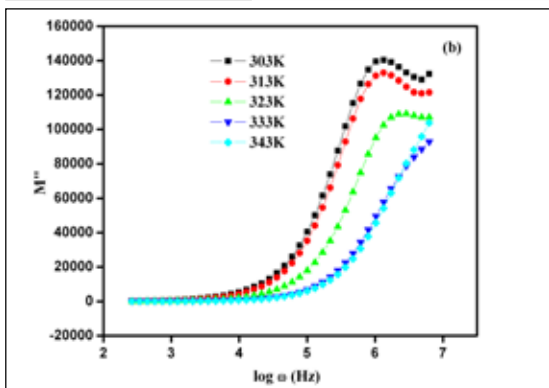$$M'' = \varepsilon'' / \varepsilon'^2 + \varepsilon''^2 \text{-------------- (8)}$$
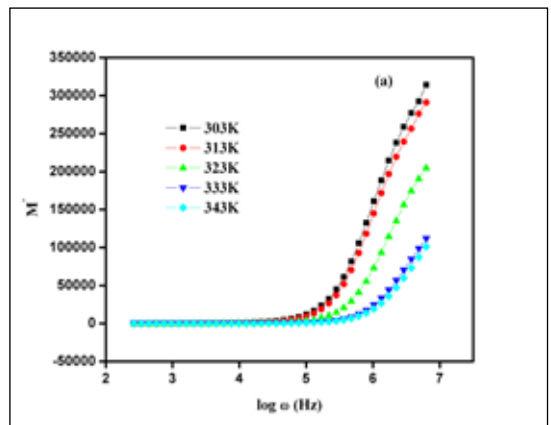
Figure 7(a&b). Frequency dependence of M ′ (ω) and M ″ (ω) for 20 mol% NH4NO3 - doped PAN at different temperatures.

Fig 7 (a, b) shows that the modulus spectra have an asymmetrical peak. The almost zero values of M ′ at low frequency indicate the removal of electrode polarization. The presence of long tail at low frequency - region also provides evidences of the large capacitance associated with the electrodes.[20] The spectrum of M ″ shows an asymmetric peak in the dispersion region of M ″. The modulus peak maximum shifts to higher frequencies and the peak maximum value decreases with increase of temperature suggesting the presence of more than one type of relaxation mechanisms.

Loss Tangent Spectra
The dielectric loss tangent (tan δ) can be defined by the equation

$$Tan\delta = \varepsilon'' / \varepsilon' \text{ ------------- (9)}$$

The relaxation parameters of the polymer electrolytes can be obtained from the study of tan δ as a function of frequency. The variation of tan δ with frequency for the various PAN/NH$_4$NO$_3$ polymer complexes at 303 K is shown in fig (8a). It has been observed that tan δ increases with increasing frequency and reaches a maximum. Then it decreases for further increase of frequency. For maximum dielectric loss at a particular temperature, the absorption peak is described by the relation ωτ = 1 where τ is the relaxation time and ω is the angular frequency of the applied signal. The relaxation paramaters tabulated in Table1, indicates the low relaxation time, 8.22 x 10^{-5} s for 80 mol% NH$_4$NO$_3$ polymer electrolyte which is consistent with the conductivity analysis which shows higher conductivity for 20 mol% salt doped polymer electrolyte.

Fig (8b) shows the variation of tan δ as a function of frequency for 20 mol% NH$_4$NO$_3$ doped PAN polymer electrolyte for different temperatures. The values of relaxation time for 20 mol% NH$_4$NO$_3$ -doped polymer electrolyte are tabulated in Table 2. It is seen that the relaxation time τ decreases with increase of temperature which results in an increase in the ionic conductivity. The tan δ is found to increase with frequency at different temperatures, pass through a maximum value (tan δ$_{max}$), and thereafter decreases. As the temperature is increased, the frequency at which tan (δ$_{max}$) occurred shifted to higher frequencies. This behavior suggests that the system can be represented by a parallel RC element.[21]

Temperature	Relaxation frequency log ω$_m$ (Hz)	ω$_m$ (Hz)	Relaxation time τ (s)
303 K	4.09	1.21 x 10^4	8.22 x 10^{-5}
323 K	4.21	1.62 x 10^4	6.17 x 10^{-5}
343 K	4.67	4.67 x 10^4	2.14 x 10^{-5}

Table 2. Dielectric relaxation parameters for 80 mol% PAN

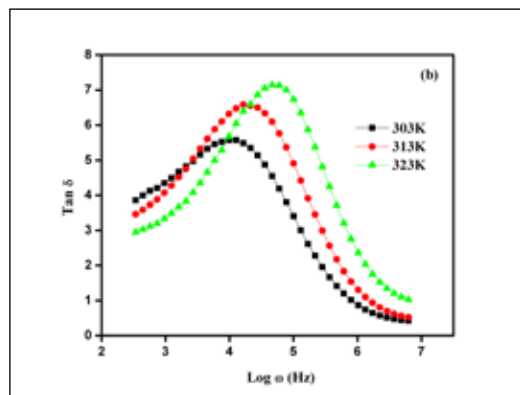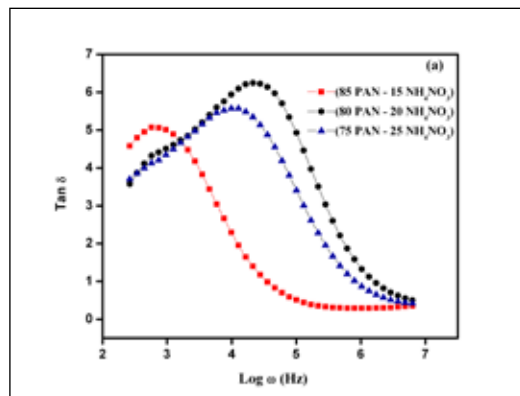– 20 mol%NH$_4$NO$_3$ polymer electrolytes at various temperatures.

Figure 8. Variation of Tan δ as a function of log ω for [a] different compositions of polymer electrolytes. [b] 20 mol% NH$_4$NO$_3$ doped polymer electrolyte for various temperatures.

CONCLUSIONS
PAN- based polymer electrolyte with different concentrations of ammonium nitrate have been prepared using the solution-casting technique. XRD analysis reveals the increase in amorphous nature of the polymer electrolyte. FTIR spectrum confirms the complex formation between polymer and the salt. From the conductivity analysis, it has been observed that the system polyacrylonitrile doped with 20 mol% ammonium nitrate has the highest ionic conductivity at room temperature and is found to be 2.742x10^{-6} S cm^{-1}. The activation energy calculated from the Arrhenius plot has been found to be low (0.58 eV) for 20 mol% salt doped PAN polymer electrolyte. The calculated relaxation parameters indicate that the low relaxation time has been obtained for 80 mol% PAN-20 mol % NH$_4$NO$_3$ ploymer electrolyte that has the highest conductivity. The temperature dependent loss spectra indicate that the charge carrier is thermally activated.

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