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FTIR, XRD and DC Conductivity Studies of Proton Conducting Gel Polymer Electrolytes based on Polyacrylonitrile (PAN)

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Abstract: The present study focuses on characterizing PAN+NH$_4$I proton conducting polymer electrolyte films prepared by solution casting technique.Two plasticizers, ethylene carbonate (EC) and dimethyl formamide (DMF) were used as solvents in this system. These prepared films can be characterized by using FTIR, XRD and DC conductivity studies. The FTIR spectroscopic study illustrates the detailed interaction of PAN with NH$_4$I salt. The XRD spectroscopic patterns of all the prepared polymer electrolyte films disclose the amorphous nature of the films and it also clearly establishes the complexation of the NH$_4$I salt with the polymer PAN. The variation of conductivity with salt concentrations of 10 wt% to 40 wt% was studied. The sample containing 30 wt% of NH$_4$I exhibited the highest conductivity of 1.49×10^{-4} S cm^{-1} at room temperature (303K) and 2.46×10^{-4} S cm^{-1} at 373K.The conductivity-temperature dependence of polymer electrolyte films obeys Arrhenius behaviour with activation energy in the range of 0.07 eV to 0.25 eV. Very low value of E$_a$ suggests that proton (H$^+$) conduction is superficial in this gel polymer electrolyte of optimum composition.

Key words: Gel Polymer electrolyte, Solution Casting Technique, XRD, DC conductivity, Activation energy.

Introduction:

Solid polymer electrolytes that show high ionic conductivity and good mechanical strength is one of the targets that scientists in the polymer electrolyte field have been pursuing for decades[1]. In recent years polymer gel electrolytes are prepared well, which are formed by incorporating plasticizers into the polymer salt complex[2]. The advantages of gel polymer electrolytes are good in ionic conductivity i.e. comparable with that of liquid electrolytes and ease in processing batteries owing to their self supporting properties. Poly acrylonitrile (PAN) has ionic conductivity and mechanical strength greater than solid polymer electrolyte poly ethylene oxide based electrolytes[3,4]. Many researchers have worked on the conductivity of gel polymer electrolyte systems formed by adding lithium salts to PAN[5-7]. Ethylene carbonate (EC) is a familiar candidate for plasticizer in the gel polymer electrolytes because of its high dielectric constant (95.3) and other attractive properties[8]. The effect of plasticizer in the polymer electrolyte system is to decrease the glass transition temperature and making the polymer become more amorphous and then allowing the ionic carriers to travel freely inside the electrolyte consequently as to raise the ionic conductivity of the electrolyte[9].

In the last two decades, proton conducting polymer electrolytes has attracted a great deal of attention and have been extensively studied for advanced electrochemical devices such as high energy density batteries,

electrochromic displays, catalysts, chemical sensors, actuators, and fuel cells etc[10]. The ammonium salts have been received as excellent proton donors for host polymer[11]. The protonic transport in these polymer electrolytes, mainly, has been due to motion of groups such as H^+, NH_4^+, H_3O^+, OH^-, etc. Apart from the motion of protons, the conductivity has also been associated with the segmental motions of the polymer chain[12]. A detailed literature survey indicates that the PAN complexes with ammonium salt have found less attention as proton conducting polymer electrolytes.

In the present investigations, DC conductivity, transport properties and structural studies namely FTIR and XRD studies were carried out on PAN based polymer electrolytes. Ammonium iodide (NH_4I) has been used as a source of protons whereas the mixture of EC and DMF act as plasticizing solvents. XRD and FTIR studies have been conducted in order to investigate the structural and complexation studies of the polymer electrolytes.

Experimental:

Poly acrylonitrile (PAN), with average molecular weight 1,50,000 g/mol purchased from Aldrich, Ammonium iodide (NH_4I), ethylene carbonate (EC) and dimethyl formamide (DMF) received from Merck, were used as the raw materials in this investigation. All chemicals were used as received without further purification. Appropriate quantities of PAN and NH4I in plasticizing solvents (EC+DMF) are stirred continuously for several hours at 60° C until a homogeneous solution has been obtained. The homogeneous viscous gel solution was then casted on petri dishes and dried at 60° C for one week. The transparent, free standing and flexible films of thickness ranging from 100-150 µm have been obtained. The prepared films were characterized by using X-ray diffraction, PANalytical X'pert PRO (Philips, Netherlands). The Fourier transform infrared spectra were recorded in the range 450-4000 cm^{-1} at room temperature using the Perkin Elmer FTIR spectrometer, Spectrum II USA. The DC conductivity of polymer electrolyte films was measured using Keithley 6514 electrometer connected to lab made conductivity setup[13]. The conductivity values were measured in the temperature range from 303– 373 K. The transport numbers were calculated by using Wagner's Polarization technique[14]. In this technique a freshly prepared polymer electrolyte film was polarized in the configuration Ag/polymer electrolyte/Ag under a DC bias of 1.5 V. The resulting current was monitored as a function of time with a Keithley 6514 electrometer.

Results and Discussion:

XRD studies:

X-ray diffraction studies are used for finding the structure of polymer PAN and NH_4I doped PAN polymer electrolytes. Fig.1 shows the X-ray diffraction patterns of pure PAN film, pure NH_4I salt and various salt compositions of the polymer electrolyte complexes. The XRD pattern of the pure PAN film exhibits semi crystalline structure and a crystalline peak at $2\theta = 17^o$ and it corresponds to orthorhombic PAN (110) reflection[15-17]. The XRD pattern of pure NH_4I salt with several sharp peaks present signifies the crystalline state of the salt. This reveals that NH_4I salt is crystalline in nature. It is evident that the intensity of the crystalline peak of pure PAN becomes decreases with increase of salt concentration. This indicates a decrease in the degree of crystallinity of the PAN with increasing concentration of the salt.
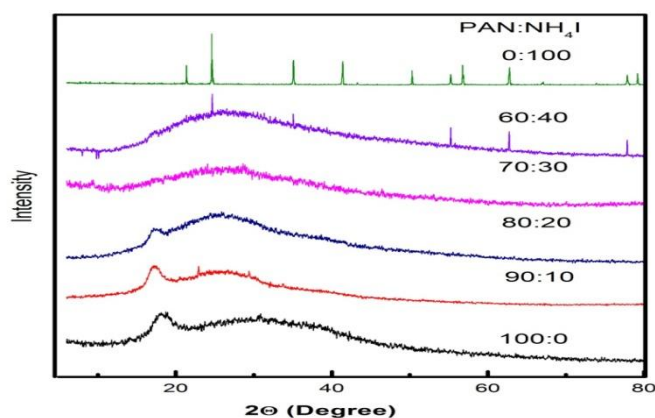

Fig. 1: XRD plots of pure PAN, NH₄I and NH₄I doped PAN polymer electrolyte films

The peak of $2\theta = 17°$ disappears at the salt content of 30 wt%. It can be seen that salt is dissociated well within the polymer matrix, and the PAN based NH_4I salt complex shows the amorphous state. A fully amorphous structure produces a greater polymer flow and ionic diffusivity. Hodge et al[18] established a correlation between the intensity of the peak and the degree of crystallinity. But, when salt is added above 30 wt.% the peak at $2\theta = 17°$ appears and also some crystalline peaks of NH_4I salt appeared. From these explanations the XRD studies confirmed that there exist a definite complexation between the polymer and salt.

FTIR studies:

The complexation of NH_4I in PAN has also been observed in FTIR spectral studies. The FTIR spectra of pure PAN and its NH_4I doped PAN complexes of different weight percent ratios are shown in fig 2. In addition, of the salt NH_4I into the polymer PAN, the cation of the metal is expected to coordinate with the polar groups in the polymer matrix resulting in the complexation.This type of interaction will influence the local structure of the polymer backbone and certain infrared active modes of vibration will be affected. The FTIR spectrum in the wave number range between 500 and 3500 cm^{-1} of pure PAN and various polymer electrolyte complexes are shown in Fig.2.

The C≡N stretching band in the infrared spectrum is certainly the characteristic feature of nitrile group which appears at 2244 cm^{-1} for the pure PAN film. The nitrile band is displaced to 2246cm^{-1} in complexed films. This might be due to the inductive effect produced by the interaction between the nitrogen atoms in C≡N and protons of salt[19]. It is also observed that the intensity of this peak decreases with increase of salt concentration and also the peak is shifted towards the higher wave number side. C-H stretching vibration of PAN appearing at 2937 cm^{-1} gets shifted to higher frequency 2944 cm^{-1}, 2950 cm^{-1}, 2952 cm^{-1}, 2961 cm^{-1} for 90PAN:10NH_4I, 80PAN:20NH_4I, 70PAN:30NH_4I and 60PAN:40NH_4I polymer complexed systems respectively. The C=O group symmetric stretch mode of EC appeared at 1779 cm^{-1}. Also the appearance of new peaks along with changes in existing peaks and/or their disappearance in the infrared spectra directly indicates the complexation of PAN and NH_4I salt.
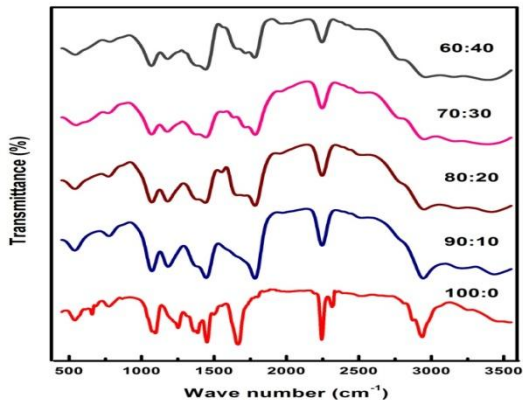

Fig. 2: FTIR spectra of pure PAN and PAN complexed films for different wt.% of NH_4I

Conductivity studies:

The ionic (H^+) conductivity versus salt concentration of polymer electrolyte PAN:NH_4I system with varying weight percentage of salt in the temperature range 303 K to 373 K is shown in Fig. 3, whereas the conductivity data at room temperature and at 373 K is presented in Table 1. It can be observed that the conductivity is increased as the salt content increases up to 30 wt%. This is due to the high amorphousness of the polymer electrolyte films which provides more free mobile protons thus giving rise to higher conductivity. Generally the conductivity of ion conducting polymer electrolytes is directly proportional to the mobility and number of charge carriers. The increase in the conductivity with increasing salt concentration can be related to the increase in the number of mobile charge carriers in the polymer electrolytes. The enhancement in conductivity is not only due to the increment of salt, but also due to EC. EC allows greater dissolution of the electrolyte salt resulting in increased number of charge carriers hence conductivity. Maximum value of conductivity obtained from this system at room temperature is 1.49×10^{-4} S cm^{-1}. This conductivity value is 10 orders greater than that of pure PAN ($<10^{-14}$S cm^{-1}) as reported[20]. However, when more than 30 wt% of NH_4I has been added, the conductivity decreases and this might be due to ion pair or ion aggregates formation[21]. Higher amount of salt incorporated in the polymer electrolytes leads to increase the viscosity of the polymer

electrolyte films. As a result, free space for proton transportation is reduced and then impedes the mobility of charge carriers. Hence, the proton conductivity is decreased.
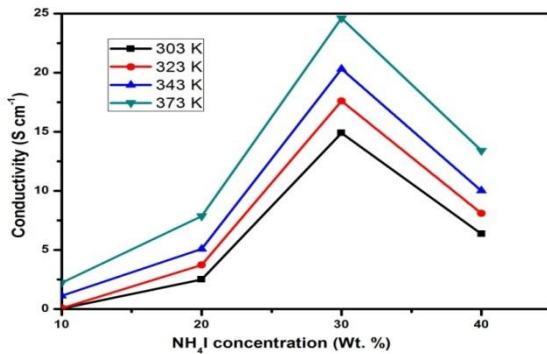

Fig.3: Proton conductivity (σ) of polymer electrolyte films as a function of NH₄I concentration

The variation of log conductivity as a function of reciprocal absolute temperature for various concentrations of NH₄I in PAN over a temperature range 303 K - 373 K is shown in Fig. 4. It is observed from the figure that the conductivity increases linearly with increase of temperature for all the complexes irrespective of salt concentration. The calculated regression values for all the films are close to unity signifying that all points lie on a straight line. The increase in conductivity with temperature can be explained as a hopping mechanism between coordinating sites, local structural relaxations and segmental motions of the polymer electrolytes. As the temperature increases the polymer chain needs faster internal modes in which segmental motion can be produced. This result favours hopping inter and intra chain proton movements and increases the conductivity of polymer electrolytes[22].

Table 1: Conductivity, activation energies and transference numbers of PAN:NH₄I films.

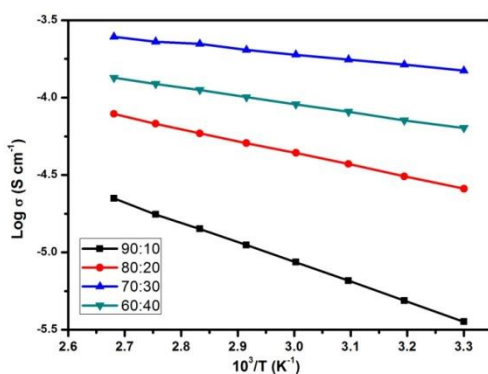| Polymer Electrolyte	DC Conductivity (S cm^{-1})		Activation energy (eV)	Transference Number	
	at 303K	at 373K		t_{ion}	t_{ele}
PAN:NH₄I (90:10)	3.55×10^{-6}	2.23×10^{-5}	0.25	0.96	0.04
PAN:NH₄I (80:20)	2.57×10^{-5}	7.85×10^{-5}	0.14	0.971	0.028
PAN:NH₄I (70:30)	1.49×10^{-4}	2.46×10^{-4}	0.07	0.98	0.02
PAN:NH₄I (60:40)	6.36×10^{-5}	1.34×10^{-4}	0.1	0.969	0.03

Fig.4: Plots of log σ versus 1000/T for PAN based polymer electrolyte films at different weight percent ratios The plots of log σ versus 1000/T obey Arrhenius rule,

$\sigma = \sigma_o \exp(-E_a/kT)$

where σ_o, the pre-exponential factor, E_a, the activation energy, k, the Boltzmann constant and T, the absolute temperature. The activation energies were calculated from the slope of these plots and the values are shown in Table 1. The calculated activation energy values were found to be in the range of 0.07 to 0.25 eV. The activation energy values obtained in this work are within the range between 0.03 and 0.36 eV as reported by

Girish Kumar et al[23]. These values are found to decrease with increasing concentration of NH_4I. This could be due to the fact that the addition of small amounts of dopant forms charge transfer complexes in the host lattice[24]. These charge transfer complexes increase the electrical conductivity by providing additional charges in the lattice, resulting in a decrease of activation energy.
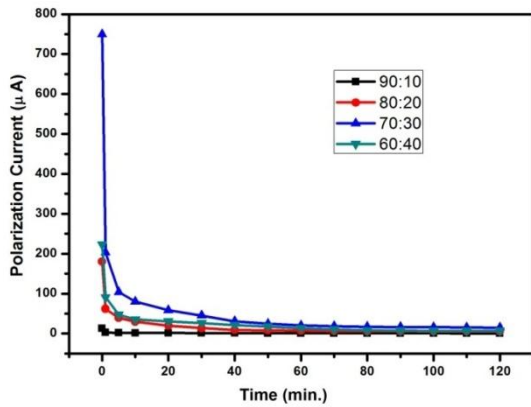

Fig. 5: Transference number measurements of PAN: NH₄I polymer electrolyte films with different wt. % ratios at room temperature

Transport number measurements

The ionic transport number (t_{ion}) has been evaluated using Wagner's polarization technique. In this technique, the DC current is monitored as a function of time on the application of a fixed DC voltage across the Ag/PAN:NH₄I/Ag cell. After polarization of the cell with 1.5V DC, the polarization current versus time plot at room temperature is obtained, which is shown in Fig. 5. The transference numbers (t_{ion}, t_{ele}) were calculated using the equations

$$t_{ion} = 1-I_f/I_i$$

$$t_{ele} = I_f/I_i$$

Where I_i is the initial current and I_f is the final current.

The calculated transference values are given in Table 1. For all compositions of polymer electrolyte films, the values of ionic transference number t_{ion} are in the range 0.96 to 0.98. The current decreases with time show that the total conductivity of the polymer electrolytes is predominantly due to ions. Hence, it proved that NH₄I salt has provided protons as mobile species in the polymer electrolyte systems.

Conclusions

The proton conducting gel polymer electrolytes consisting of ammonium iodide salt dissolved in a plasticizing solvent, EC and DMF, immobilized in a host polymer PAN have been synthesized and characterized. The complexation of the salt with the polymer is confirmed by XRD and FTIR studies. The increase in conductivity with increasing concentration of NH₄I and temperature is attributed to decrease in the degree of crystallinity and increase in the amorphisity and hopping mechanism of protons. The activation energy values obtained from conductivity data decreases with increasing proton conductivity and dopant concentration. The transference number data indicate that the conduction in these polymer electrolytes is predominantly due to proton rather than electrons.

Acknowledgements

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