

## Structural, Thermal and Battery Characteristic Properties of $\text{NH}_4\text{CF}_3\text{SO}_4$ Doped Pan Films for Electrochemical Cell Applications

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**Abstract :** Gel polymer electrolyte films using polyacrylonitrile (PAN) as polymer and Ammonium Trifluoro methane sulfonate ( $\text{NH}_4\text{CF}_3\text{SO}_4$ ) as dopant has been prepared at different wt% ratios by solution cast technique. The gel polymer electrolyte thick films have been characterized using analytical techniques such as X-Ray diffraction (XRD), Differential scanning calorimetry (DSC), Cell parameters like open circuit voltage (OCV), short-circuit current (SCC), energy density and power density has been calculated and compared with the data from the earlier reports. The variation of the conductivity with salt concentration ranging from 10 to 40 wt % studied. The Gel polymer Electrolyte's bulk resistance was measured by using AC conductivity at room temperature (303K). It can be revealed that conduction mechanism to be the Arrhenius-type thermally activated process. This mechanism can be calculated by Impedance spectroscopy. The sample containing 30% of  $\text{NH}_4\text{CF}_3\text{SO}_4$  exhibits the highest conductivity of  $1.68 \times 10^{-3} \text{ S cm}^{-1}$  at room temperature (303K) and  $3.46 \times 10^{-3} \text{ S cm}^{-1}$  at 378K for 70:30 wt% films. The transport numbers both electronic ( $t_e$ ) and ionic ( $t_i$ ) are evaluated using Wagner's polarization technique.

**Keywords :** Gel Polymer Electrolyte; Solution Casting Technique; Discharge Characteristics; Electrochemical Cell Applications.

### Introduction:

Most of the research is devoted to find the materials for electrochemical energy storage devices that play a tremendous role in technical applications like computers, communication devices, industrial controls, electric vehicles, space chips etc<sup>1</sup>. Consequently much attention has been focused in the development of batteries, fuel cells etc. Batteries constitute an important component in the techno-economic growth. The usage of solid polymer electrolytes (SPE) in the batteries provides an added advantage that the mechanical strength enhances and favors the gain in electrochemical properties. Research has been focusing to tailor a solid polymer electrolyte possesses high ionic conductivity as well as good mechanical strength. Polymer electrolytes are of mammoth interest for use in solid state lithium – based batteries, because of their advantage over conventional lithium ion batteries, such as safety, no-leakage of electrolyte, higher energy density and flexible geometry. This allured many researchers on the development of lithium polymer batteries<sup>2</sup>. The rapid development of new technologies such as cell phone, notebook PC, and electric vehicle (EV) has promoted research aimed at improving battery performance with special effort devoted to Lithium batteries<sup>3</sup>. Gel polymer electrolytes (GPEs) are potential candidates to be used as electrolyte membranes in high-energy density rechargeable lithium batteries, fuel cells, solar cells, and electro chromic windows. GPEs can be formed using many different

polymer systems. Lithium ion battery has been studied widely and deeply in the energy sources rapid growth time, especially the electrode material. As we all know, superior performance of lithium ion battery is determined by active electrode material and excellent electrolytes. The gel polymer electrolytes have been reported with sufficient mechanical strength, high ionic conductivity at room temperature, stable and well compatibility with lithium electrodes<sup>4</sup>. In the last few decades an effort has done for the development of gel polymer electrolytes such as polyvinyl alcohol (PVA), poly vinyl pyrrolidine (PVP), polyethylene glycol (PEG), poly acrylonitrile (PAN), poly vinylidene fluoride (PVdF). Among the above listed polymers, Polyacrylonitrile (PAN) has been intensively investigated because of its excellent characteristics and its applications. PAN is the good potential materials which are having high storage capacity, high dielectric strength, and electrical properties. PAN –based electrolytes have advantages compared to other polymer electrolytes due to their good mechanical strength and high ionic conductivity at ambient temperatures<sup>5-7</sup>. The literature survey indicates that only few attempts have been made using sodium salt doped PAN –based polymer electrolytes. Osman *et al.*<sup>8</sup> have made a comparative study of lithium and sodium triflates in PAN-based ion conducting polymer electrolytes and found higher ionic conductivity and lower activation energy for sodium triflate –doped films than for lithium triflate – doped films. A detailed literature indicates that the PAN complexes with ammonium salt have found less attention as proton conducting polymer electrolytes<sup>9</sup>

The present work, thick films have been prepared by doping  $\text{NH}_4\text{CF}_3\text{SO}_4$  in PAN and the resulting films are characterized using techniques like XRD, DSC and their Discharging, conducting properties have been investigated to find their suitability in developing an efficient electrochemical cell.

## Materials and Methods

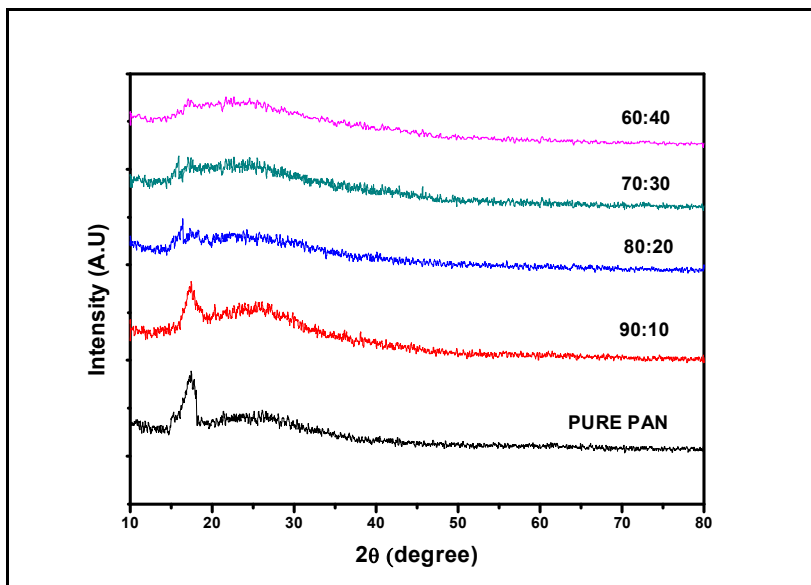
Polyacrylonitrile (PAN), with average molecular weight 1,50,000 g/mol purchased from Aldrich, Ammonium Trifluoro Methane Sulfonate ( $\text{NH}_4\text{CF}_3\text{SO}_4$ ), Ethylene Carbonate (EC) and dimethyl formamide (DMF) received from Merck were used as the raw materials in this research work. All chemicals were used as received without further purification. Appropriate quantities of PAN and  $\text{NH}_4\text{CF}_3\text{SO}_4$  in plasticizing solvents (EC and DMF) are stirred continuously for several hours at 60°C until a homogeneous solution has been obtained. There are many of techniques are available for making films such as sputtering, hot pressing method, flash evaporation method and solution casting technique<sup>10</sup>. The homogeneous viscous gel solution was then casted on Petri dishes and dried at 60°C for 10 days. The transparent, free standing and flexible films of thickness ranging from 110-160  $\mu\text{m}$  have been obtained. The prepared films characterized by using X-ray diffraction, PANalytical X'pert PRO (Philips, Netherlands). The conductivity values were measured in the temperature range from 303-373K. The transport numbers were calculated by using Wagner's polarization technique<sup>11</sup> and Watanabe technique<sup>12</sup>. In this technique a prepared gel 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. The discharge characteristics like open circuit voltage (OCV), short circuit current (SCC), power density etc. were monitored under a constant load of 100 K $\Omega$ . DSC thermograms were recorded to measure glass transition temperature and melting temperature of PAN – based electrolytes by using Auto Q20 DSC, TA instruments, at a heating rate of 10°C/min under nitrogen atmosphere in the temperature range 40-350°C.

## Results and Discussion:

### XRD studies:

The structural characteristics of pure PAN with doping of  $\text{NH}_4\text{CF}_3\text{SO}_4$  was evaluated using X-ray diffraction studies and is shown in Fig 1. It can be noted from the Fig 1 that diffraction peaks for pure PAN appeared at 17° and corresponds to orthorhombic PAN (110) reflection<sup>13-15</sup>. The peak observed at 2 $\theta$  values around 17° is less intense in complexed PAN films compared to those in pure PAN film. This indicates that the addition of  $\text{NH}_4\text{CF}_3\text{SO}_4$  salt causes a decrease in the degree of crystallinity of the PAN complex. Therefore, it can be confirmed that complexation has taken place in the amorphous phase. This amorphous nature is responsible for greater ionic diffusivity resulting high ionic conductivity<sup>16</sup>. The XRD pattern of pure  $\text{NH}_4\text{CF}_3\text{SO}_4$  salt with several sharp peaks present signifies the crystalline state of the salt and explains that salt is crystalline in nature. From these results we conclude that there exists a definite complexation between the polymer and salt. These observations are in tandem with the observations of Hodge *et al*<sup>17</sup> who established a

correlation between the intensity of the peak and the degree of crystallinity. XRD analysis has been done to know the crystallinity, inter planar spacing and inter chain separation of the polymer gel electrolyte samples.



**Fig. 1:** XRD plots of pure PAN and PAN complexed films for different wt % of  $\text{NH}_4\text{CF}_3\text{SO}_4$ .

Inter planar spacing is calculated from Bragg's Law is given by

$$n\lambda = 2d\sin\theta \quad (\text{i})$$

Where  $n$  = order of diffraction,

$\lambda$  = wavelength of X ray ( $1.5405 \text{ \AA}$ )

$\theta$  = angle of diffraction.

Likewise, the inter chain separation is calculated by using the formula

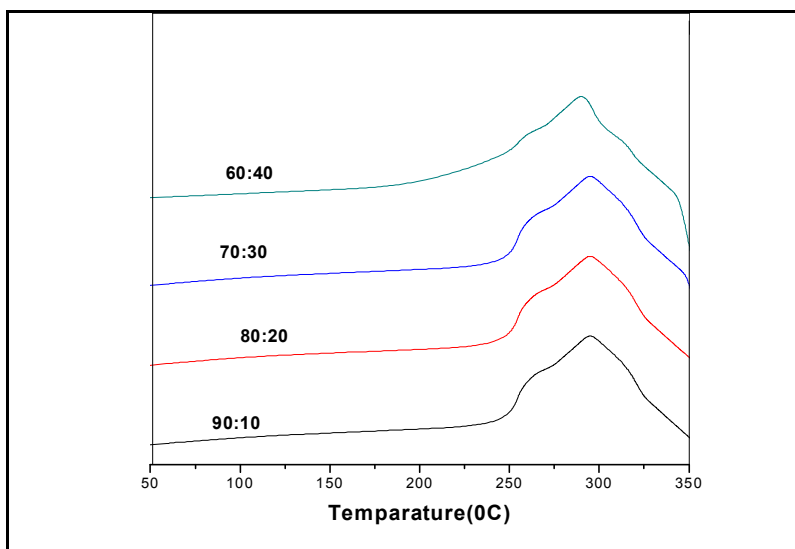
$$R = \frac{7 \times \lambda}{4\pi \sin\theta} \quad (\text{ii})$$

Where  $R$  is the inter chain length,  $\lambda$  is wavelength of X-ray,  $\theta$  is the scattering angle.

**Table 1:** Different Compounds,  $2\theta$ ,  $\theta$ ,  $d$  and  $R$  values where  $2\theta$  = scattering angle,  $d$  = inter - planar spacing,  $R$  = inter – chain length

Compound PAN: $\text{NH}_4\text{CF}_3\text{SO}_4$	$2\theta$ (in degree)	$\theta$ (in degree)	$d$ ( $\text{\AA}$ )	$R$ ( $\text{\AA}$ )
100:0	17.24	8.62	3.29518	3.67280
90:10	17.23	8.61	5.09756	5.68174
80:20	16.98	8.39	5.09761	5.68179
70:30	16.17	8.08	5.09627	5.68030
60:40	16.88	8.44	5.09290	5.67654

The values of ' $d$ ' and ' $R$ ' have been calculated and shown in Table 1. It is seen that for the first composition i.e. Pure PAN the  $2\theta$  value is  $17.24^\circ$ , inter planar spacing is  $3.29518 \text{ \AA}$  and inter chain length is  $3.67280 \text{ \AA}$ . Similarly for the compound film 90:10 the values of  $2\theta$ ,  $d$  and  $R$  are  $17.23^\circ$ ,  $5.09756 \text{ \AA}$ ,  $5.68174 \text{ \AA}$  respectively. From these results, it is concluded that while increasing the amount of ammonium triflate salt the inter planar spacing is decreasing and inter chain length is increasing.

**Differential Scanning Calorimetric Studies:**

**Fig.2: DSC thermograms for PAN –complexed films for different wt% of  $\text{NH}_4\text{CF}_3\text{SO}_4$  from 40 to 350°C**

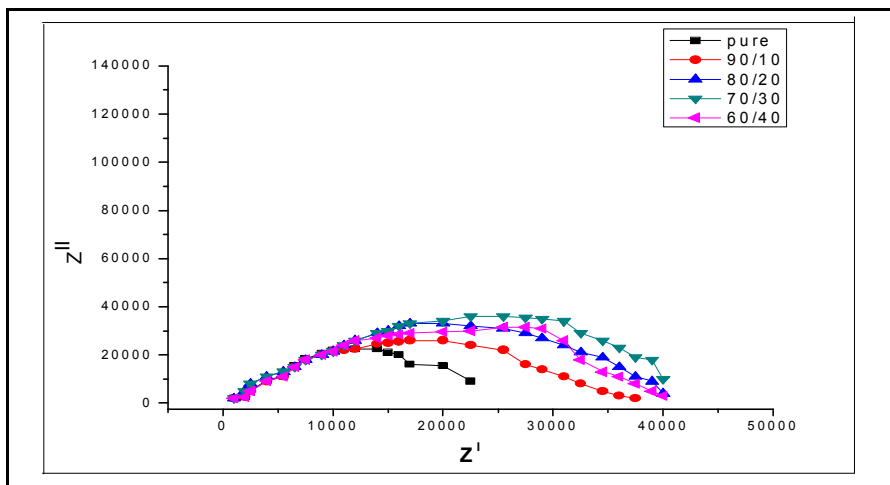
The overall thermal properties of polymer electrolyte systems can be investigated by the Differential Scanning Calorimetric (DSC) technique. The microstructure and morphology of the system is accountable for the important parameters of polymer electrolyte membrane such as the glass temperature ( $T_g$ ), melting temperature ( $T_m$ ) and thermal stability. These parameters will affect the overall separator properties of the electrolyte material when operating in a battery<sup>18</sup>. For potential applications, the gel polymer electrolytes must have not only high ionic conductivity, high transport number and wide electrochemical stability, but also thermal stability to guarantee an acceptable performance when it is operated at elevated Temperatures<sup>19</sup>. Fig 2 shows differential scanning calorimetric (DSC) thermo grams of different compositions of gel polymer electrolytes in the temperature range of 40-350°C. The melting temperature ( $T_m$ ) of pure PAN is 317°C and glass transition temperature is 107°C<sup>20</sup>. The films were subjected to Differential Scanning Calorimetric studies using Mettler-Toledo DSC 822e with a heating rate of 10°C/min. This technique is used to determine thermal properties of a polymer electrolyte system of a temperature range 10-350°C. Endothermic and exothermic peaks are observed for glass transition temperature and melting temperature.

Miscibility of polymer plasticizers and salt are determined by giving single ( $T_g$ ) and single ( $T_m$ ). ( $T_g$ ) is used to determine amorphous and flexibility nature of polymer. when plasticizers are added to PAN ( $T_m$ ) decreases from 317-296°C and ( $T_g$ ) decreases from 107-70°C. When salt is added to PAN ( $T_g$ ) increases from 70-95°C and ( $T_m$ ) increases from 296-305°C. With the increase in the concentration of salt from 10 to 40 wt % due to the interaction between PAN and salt. This increase causes the stiffening of polymer back bone. Finally concluded that plasticizers addition decreases ( $T_g$ ) and ( $T_m$ ) values and salt increases the ( $T_g$ ) and ( $T_m$ ) respectively.

**Ac Conductivity of PAN+  $\text{NH}_4\text{CF}_3\text{SO}_4$ :**

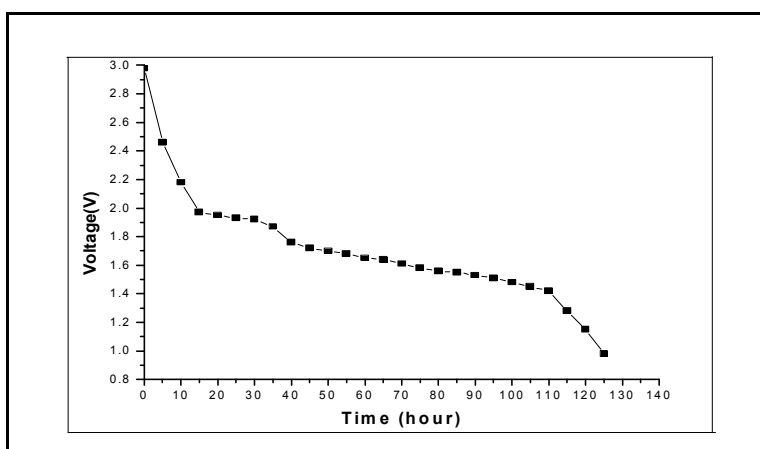
The A.C conductivity has been measured using the conductivity setup at room temperature range 303K by using HIOKO 3532-50 LCR Hitester over a frequency range 42Hz to 5MHz, The Gel polymer Electrolyte's bulk resistance was measured by using AC conductivity at room temperature (303K). It can be revealed that conduction mechanism to be the Arrhenius-type thermally activated process. This mechanism can be calculated by Impedance spectroscopy. The conductivity mechanism greatly depends upon the ions mobility concentration<sup>21</sup>. The Fig.3 representing Impedance plot for the conductivity of polymer electrolyte PAN: $\text{NH}_4\text{CF}_3\text{SO}_3$  at Room temperature, Complex impedance plots consists of high frequency semicircle which is related to the conduction process in the bulk of the complex i.e. parallel combination of bulk resistance (due to the drifting of ions), bulk capacitance (due to polymer chain) and a low frequency range, indicates the bulk effect of blocking electrodes i.e. the interface between the electrode and electrolyte is due to the migrations of ions<sup>22</sup>. The bulk resistance ( $R_b$ ) of polymer electrolyte for all samples was calculated from the interception of

the semicircular arc on the real impedance ( $Z'$ ) axis. With the increase of salt concentration the bulk resistance decreases. This may be due to the increase in the mobile charge carriers by the addition of salt. The ionic conductivity increases with increasing  $\text{NH}_4\text{CF}_3\text{SO}_3$  O content from 10 wt% to 40wt% Conductivities of the film at Room temperatures were calculated using the formula  $\sigma = L/RbA$ , where  $L$  is the thickness of the sample and  $A$  is the electrode area



**Fig.3. Impedance plot for the conductivity of polymer electrolyte PAN:  $\text{NH}_4\text{CF}_3\text{SO}_3$  at Room temperature**

#### Discharge Studies:



**Fig.4. Discharge characteristics of PAN:  $\text{NH}_4\text{CF}_3\text{SO}_4$  (70:30) polymer electrolyte electrochemical cell (load =100K $\Omega$ )**

The solid state electrochemical cell was fabricated with the configuration of anode Na/PAN:  $\text{NH}_4\text{CF}_3\text{SO}_4$ (70:30)/Cathode( $\text{I}_2+\text{C}+\text{Electrolyte}$ ).The thickness of both the electrodes is 1mm.The surface area and thickness of PAN+  $\text{NH}_4\text{CF}_3\text{SO}_4$  Gel polymer electrolyte were 1.42cm<sup>2</sup> and 142  $\mu\text{m}$  respectively. The discharge characteristics of the cell for a constant load of 100K $\Omega$  were evaluated at room temperature and were shown in Fig 4.

The initial sharp decrease in the voltage in these cells may be due to polarization and the formation of layer of Sodium salt at the electrode-electrolyte interface. Cell parameters like open circuit voltage (OCV),short circuit current(SCC),current density, power density, energy density and discharge capacity ,have been evaluated to the highest conducting gel polymer electrolyte system PAN:  $\text{NH}_4\text{CF}_3\text{SO}_4$ (70:30) in said electrochemical cell and the obtaining data are given table 2 .The current density is calculated using SCC value and area of the cell. Power density value is obtained by taking OCV and weight of the cell into consideration. Energy density value is calculated by evaluating the time taken for the plateau region .From table 2 ,it is obvious that the cell with the

composition PAN:  $\text{NH}_4\text{CF}_3\text{SO}_4$ (70:30) exhibits better performance and stability than PEO:NaYF<sub>4</sub> and PEO:NaI complexed polymer electrolyte systems<sup>23-25</sup> and almost compatible with the existing reports of PVA:Na Br and PVP:NaI complexed polymer electrolytes<sup>26-28</sup>. Hence, the cell developed in this work offers interesting alternatives for temperature solid state batteries. The cell parameters acquired on this polymer electrolyte system are given in table. It is confirmed that gel state cell parameters are better than the earlier reported sodium based polymer electrolyte cell system<sup>29-31</sup>.

**Table 2: Cell parameters of PAN:  $\text{NH}_4\text{CF}_3\text{SO}_4$  / (I<sub>2</sub>+C+Electrolyte) polymer electrolyte battery**

Cell parameters	Na/PAN: $\text{NH}_4\text{CF}_3\text{SO}_4$ (70:30)/(I <sub>2</sub> +C+Electrolyte).
Open circuit voltage (V)	2.92
Short circuit current ( $\mu\text{A}$ )	1.26
Effective area of the cell ( $\text{cm}^2$ )	1.33
Weight of the cell (gm)	1.5
Discharge time (h)	110
Current density ( $\mu\text{A cm}^{-2}$ )	0.992
Power density ( $\text{W Kg}^{-1}$ )	2.985
Energy density ( $\text{Wh Kg}^{-1}$ )	272.3
Discharge capacity ( $\mu\text{A h}^{-1}$ )	155.3

## Conclusions

A Gel polymer electrolyte has been developed by blending varying concentration of  $\text{NH}_4\text{CF}_3\text{SO}_4$  with pure PAN using solution casting method. The Gel polymer electrolyte has been characterized by techniques like XRD, DSC and XRD studies indicated the decrease of crystalline nature with the increase the wt % of the dopant ( $\text{NH}_4\text{CF}_3\text{SO}_4$ ) further it proved the homogeneous distribution of the dopant in the polymer. Thus semi crystalline nature of the polymeric blends has been revealed. Further, the doping has been found to enhance ionic conductivity as is being generally found in amorphous polymers having flexible backbone. Using PAN:  $\text{NH}_4\text{CF}_3\text{SO}_4$  (70:30) gel polymer electrolyte system solid-state battery (Na/PAN:  $\text{NH}_4\text{CF}_3\text{SO}_4$  (70:30) +EC+DMF/ (I<sub>2</sub>+C+Electrolyte)) has been fabricated and their discharge characteristics are studied and these results are found to be compared with existing results.

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