



AC Conductivity and Thermal Characterization of PAN Doped Gel Polymer Electrolytes for Polymer Battery Applications

Narasimharao Maragani¹, K. Vijaya Kumar^{2*}

¹Solid state Ionics Research Laboratory, Dept. of Physics, K L University, Guntur-522 502, A.P, India.

²Dept. of Physics, Dayananda Sagar Academy of Technology and Management, Bangalore-560 082-India

Abstract: Thin films of poly acrylonitrile (PAN) doped with sodium Fluoride (NaF) were prepared by solution casting technique. The Gel polymer Electrolyte films have an average thickness of 142 μm . The films were prepared with different (wt%) ratios. The structural formations were analyzed by X-Ray Diffraction method (XRD). The alternating current (AC) Conductivity and thermal conductivity of the gel polymer electrolyte composites were studied as function of applied frequency, temperature and NaF concentration. The AC conductivity was determined from the impedance data and thermal conductivity was measured using the transient electric pulse method. It was found that the AC Conductivity increases with increasing temperature and NaF Concentration. The formed fluoride complexes also contribute in increasing the AC quantities. It was also found that the thermal conductivity of the gel polymer electrolyte films increases with both temperature and NaF concentration. The DSC measurements showed a decrease in the degree of crystallinity and increase of amorphous regions with increasing concentration of salt NaF. The sample containing 30 wt% of NaF exhibited the highest conductivity of $1.82 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature (303K) and $2.96 \times 10^{-3} \text{ S cm}^{-1}$ at 373K.

Keywords: Gel polymer electrolyte, AC Conductivity, Impedance, Thermal conductivity.

Introduction:

During the past two decades, solid-state polymer and polymer gel electrolytes have attracted great interest because of the possibility of their usage in lithium batteries because polymer gel electrolytes are leakage-free and have much higher ionic conductivity. The dissolution of low lattice energy salts into a solvating polymer leads to the formation of polymer electrolyte. These can conduct ions and the mobility of these ions can be improved by the addition of plasticizers¹. Recent research indicates that much effort is being envisaged in developing new energy storing devices in view of day by day increasing demand for power but depletion in naturally existing resources to meet required demand in this aspect Energy storage devices are assuming importance². Conducting polymers are considered good candidates to replace traditional metals in specific applications. Indeed, this new generation combines advantages of polymers (lighter weight, mechanical flexibility, easy-processing, biocompatibility, chemical stability) and conducting materials (electrical properties)³. The development of compact, light weight, cost effective and high energy density batteries are in great interest and demand in recent years⁴. 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 batteries⁵. Polymer electrolytes find numerous applications in everyday usage as electrochemical devices such as polymer batteries, super capacitors, sensors and electro chromic windows⁶. The gel polymer electrolytes have been reported with sufficient mechanical strength, high ionic

conductivity at room temperature, stable and well compatibility with lithium electrodes⁷. Due to the unique soft matter characteristics, gel polymer electrolytes (GPEs) have been extensively investigated in the past decades. The GPEs, however, suffer from a trade-off issue between mechanical properties and ionic conductivity. Our group has recently reported a new strategy to fabricate mechanically flexible GPEs with Satisfactory electrochemical performance⁸. Poly acrylonitrile (PAN) has ionic conductivity and mechanical strength greater than solid polymer electrolyte poly ethylene oxide based electrolytes⁹⁻¹⁰. The development of proton rechargeable batteries would be an interesting study as sodium may be considered as an alternative to lithium as negative electrode (anode) due to its low cost, natural abundance, non-toxicity, low atomic mass (23.0) and high electrochemical reduction potential¹¹. Many researchers have worked on the conductivity of gel polymer electrolyte systems formed by adding lithium salts to PAN¹²⁻¹⁴. The gel polymeric electrolytes have a unique hybrid structure, which possesses cohesive properties of solids and diffusive properties of liquids simultaneously¹⁵. 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 properties¹⁶. 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 electrolyte¹⁷. The gel polymer electrolytes have been reported with sufficient mechanical strength, high ionic conductivity at room temperature, stable and well compatibility with lithium electrodes¹⁸⁻¹⁹.

In the present work, the effect of dopant concentration on the AC conductivity and thermal stability has been investigated to optimize plasticizer concentration providing maximal conductivity and congenial mechanical stability were carried out on PAN based polymer electrolytes.

Materials and methods:

Poly acrylonitrile (PAN), with average molecular weight 1,50,000 g/mol purchased from Aldrich, Sodium Fluoride (NaF), 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 NaF in plasticizing solvents (EC+DMF) are stirred continuously for nearly 36 hours at 50⁰ C until a homogeneous solution has been obtained. The homogeneous viscous gel solution was then casted on Petri dishes and dried at 50⁰ C for one week. The transparent, free standing and flexible films of thickness ranging from 100-150 μ m have been obtained.



Fig 1: PAN Complexed Gel polymer Electrolyte film with NaF salt

The prepared films were characterized by using the conductivity values were measured in the temperature range from 303– 373 K. The A.C conductivity has been measured using the conductivity set up at the room temperature range 303K by using HIOKI 3532-50 LCR HITESTER over a frequency range 42Hz - 5MHz. DSC thermo grams were recorded to measure glass transition temperature and melting temperature of PAN – based electrolytes by using Mettler-Toledo DSC 822e with a heating rate of 10⁰C/min.

Results and Discussion:

XRD studies:

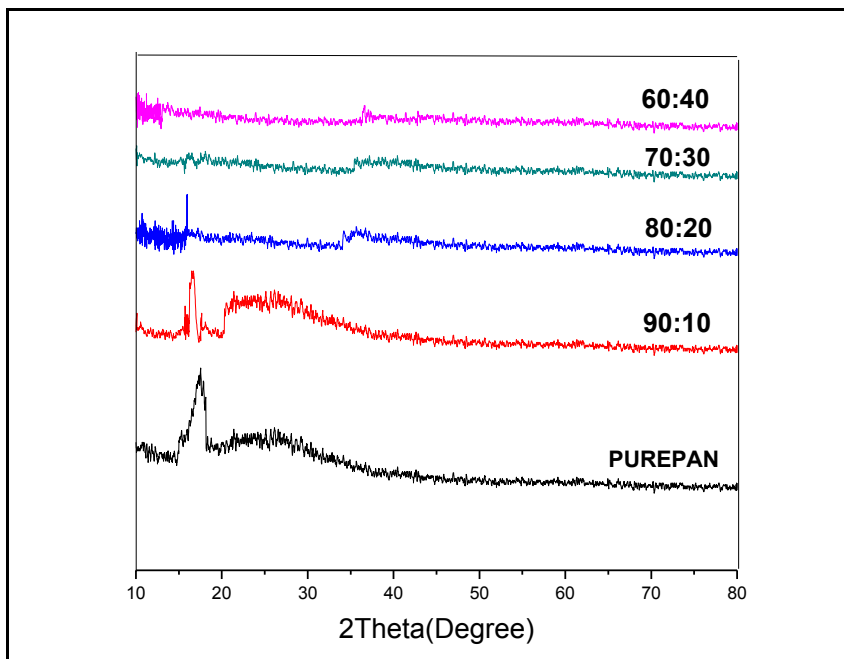
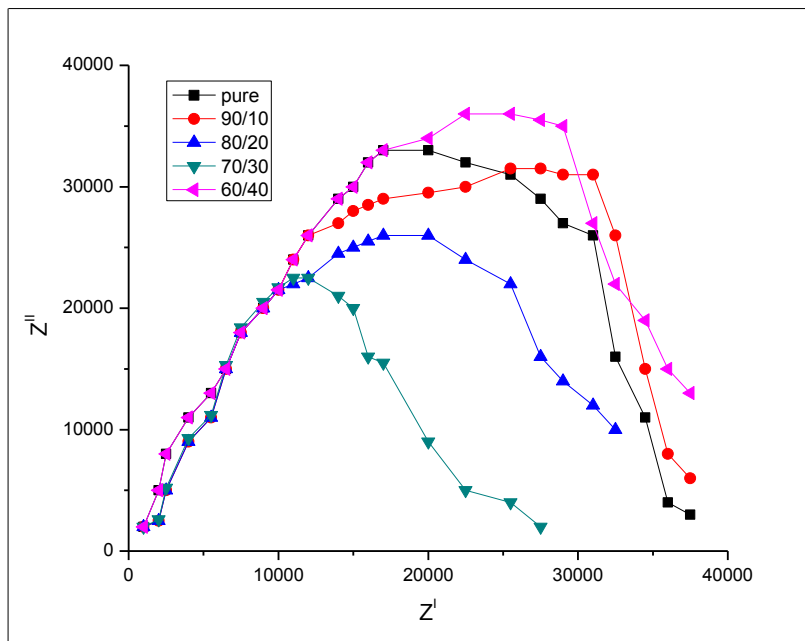
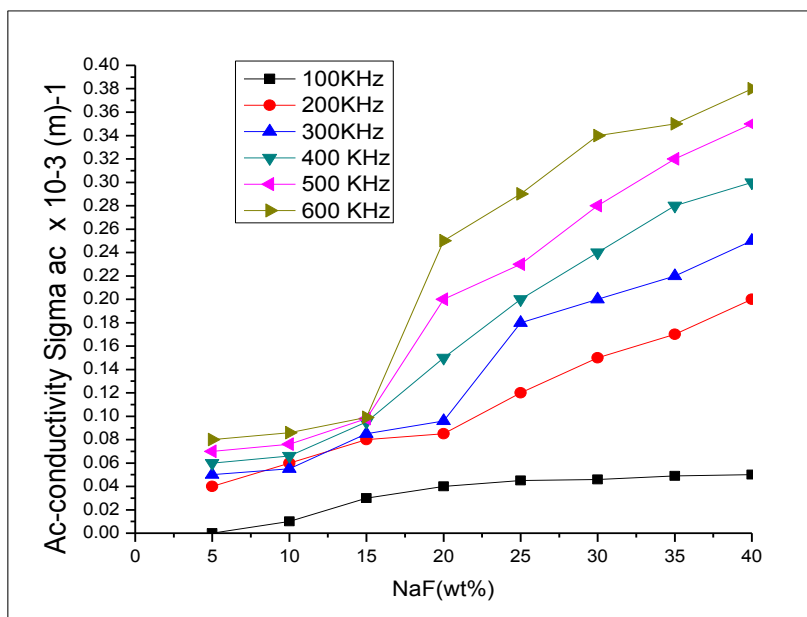


Fig. 2: XRD plots of pure PAN and PAN complexed films for different wt % of NaF.

Generally polymer electrolytes are composed of amorphous phase and crystalline phase. XRD technique is widely used to study the phase compositions of polymer electrolytes. Inherent relations between the crystal structure and the diffraction pattern can be solved by analyzing the diffraction peak characteristics²⁰. X-Ray Diffraction pattern of the sample was taken using XPERT-PRO Diffractometer. X-Ray scattering has been a unique and standard characterizing tool to investigate the structural properties of materials. In these studies one basically monitors either the intensity of elastically scattered X-Ray photons as a function of the scattering angle in XRD²¹⁻²². The XRD characterizations of PURE PAN and NaF with different ratios are given in Fig.2. From the Figure reveals that the XRD pattern of Pure PAN exhibits well defined peaks are observed NaF which are indicates the crystalline nature of salt and also a broad peak is observed for Pure PAN corresponds to crystalline orthorhombic PAN(110) which is centered at around 17.50° and broad peak corresponds to amorphous content lies in between 10° - 30° which corresponds to amorphous content indicating its semi crystalline nature²³⁻²⁴. The characteristic diffraction peaks of PAN-NaF at an angle 17.50° and 16.07° are reduced upon the addition of the plasticizers and NaF salt. The diffractograms in Fig.1 reveals that the amorphous nature is predominant in the complex which is due to the addition of plasticizers. The diffraction pattern of PAN-NaF shows intense peak at an angles at $2\theta=17.50^\circ, 16.68^\circ$ and 16.07° , which reveals the crystalline nature of the ionic salt²⁵. The salt content of 30 wt % peak disappeared in the complexes, which indicates the complete dissolution of the salt in the polymer matrix, PAN base NaF salt complex shows the amorphous state. A fully amorphous structure produces a greater polymer flow and ionic diffusivity. Hodge et al²⁶ established a correlation between the intensity of the peak and degree of crystallinity. From these results the XRD studies confirmed that there exist a definite complexation between the polymer and salt.

Ac Conductivity of PAN+ Sodium Fluoride (NaF):**Fig.3. Impedance plot for the conductivity of polymer electrolyte PAN: NaF at Room temperature****Figure 4. Variation in AC conductivity with NaF concentration.**

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 concentration²⁷.Conductivities of the film at room temperatures were calculated using the formula $\sigma=L/R_b A$, where L is the thickness of the sample and A is the electrode area. 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. Figure 4 shows the variation in the AC conductivity (σ_{AC}) with the NaF concentration, measured at different frequencies. The σ_{AC} is nearly constant up to 10wt%, after that, it increases rapidly with increasing NaF concentration. The value of about 10wt% dopant content can be considered a critical one and called a percolation threshold for the thin films composites²⁸⁻²⁹. It is a general thought that the AC conductivity is related to frequency as reported in the empirical Jonschers universal law model²⁷ which is given by the equation ($\sigma_{AC}(f) = \sigma_{DC} + Bf^m$). Where B and m are coefficients, f is the frequency of the applied field (Hz), σ_{DC} is the DC conductivity of the material, and σ_{AC} is the AC conductivity in $(\Omega m)^{-1}$. At higher frequencies, the conductivity increases as a power of frequency with exponent $0 < m < 1$. In this case, B and m are temperature dependents. 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 NaF content from 10 wt% to 40wt%. 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 conductivity³⁰.

Table1: The activation energy values for all samples at (f = 600 KHz)

Polymer Electrolyte	Activation energy (E_a) (eV)	Mobility (μ) in (m^2/Vs)
PAN: NaF(90:10)	0.47	$1.24 \times 10^{-4} m^2/Vs$
PAN: NaF (80:20)	0.32	$1.86 \times 10^{-4} m^2/Vs$
PAN: NaF (70:30)	0.25	$2.35 \times 10^{-4} m^2/Vs$
PAN: NaF (60:40)	0.28	$3.24 \times 10^{-4} m^2/Vs$

Initially by adding the salt concentration the conductivity also increasing, because of the charge carriers increasing but at high concentration the conductivity of the compositions decreases due to an effect of ion segregations and higher ion pairs which decreases the mobility and charge carriers. The data reveals that the Mobility of charge carriers also increased with increasing of salt ratios. In general as the conductivity for 70:30 increases the sharp peaks of the salt crystallinity decreases. The crystallinity in the salt the moment of ions obstructs by blocking its path, but there is an increasing of amorphous region due to its free volume this is due to the motion of an ionic charge, migration of ions through the amorphous region.

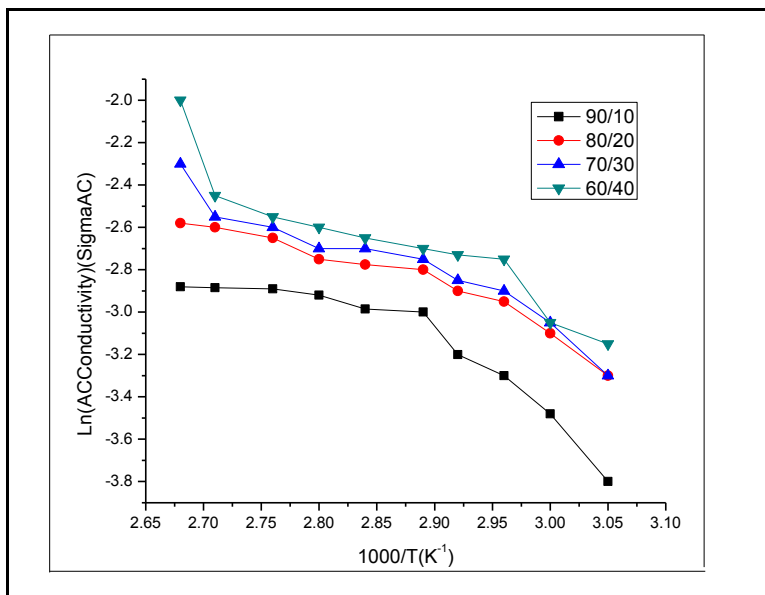


Figure 5. Ln(AC) versus 1000/T for PAN/NaF composites at frequency 600 kHz. AC: alternating current; PAN: poly(acrylonitrile); NaF: sodium Fluoride.

Figure 5 shows the dependence of the AC conductivity on temperature and NaF concentration. The σ_{AC} increases with both temperature and dopant content. Using Arrhenius type equation, the activation energy (E_a) of the thermally conduction process can be estimated from the linear fit of the slopes in Figure 5. Table 1 include s values of E_a obtained from the variation in σ_{AC} with frequency measured in temperature range between

30°C and 60°C. It can be seen that E_a value decreases with increasing NaF content from 0.47 eV for 90:10(PAN: NAF) to 0.28 eV for the 60:40(PAN: NAF) wt% doped composite. This observed decrease in E_a value implies that the energy of the prepared PAN/NaF thin films becomes narrower due to the creation of localized energy states by heating, which enhances the ion mobility and ability of the electrons to tunnel or hop easily from the valence band to conduction energy band. Similar observations were reported by Mohan et al.¹² on a study of the DC conductivity of PEO complexes with fluorides, and attributed the observed increase in the conductivity to some structural transitions from crystalline phase of the polymer to amorphous phase. These events increase the amorphous region in the polymer electrolyte and produce more active segmental motion, which stimulates the hopping mechanism and thus the conductivity becomes higher. In our study, the observed increase in conductivity and decrease in the activation energy with increasing NaF dopant content or temperature can be dominated by the mobility in the localized states bridged by the doped NaF molecules in the amorphous regions existing in the solid polymer electrolyte. With the used NaF concentration range, there is no optimum values observed under measuring conditions of applied field frequency, temperature, and NaF dopant content.

$$\sigma_{AC}\sigma = \sigma_0 \exp [-E_a / K_B T]$$

3.1. DSC Characteristics:

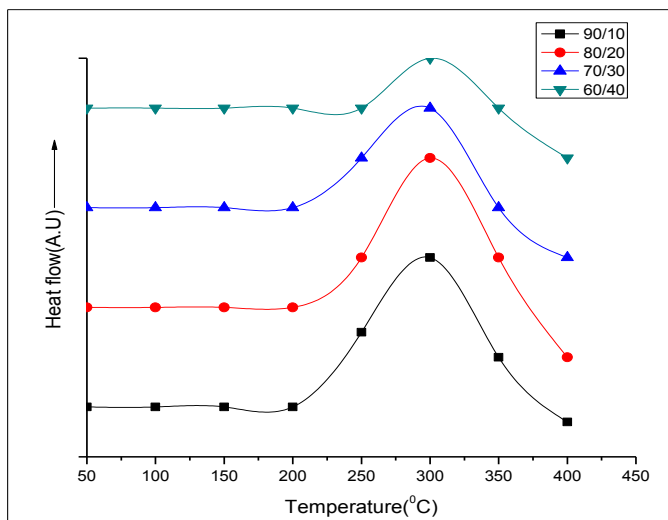


Fig.6: DSC thermograms for PAN –complexed films for different wt% of NaF from 40 to 400°C

The differential scanning calorimetry (DSC) curves of PAN:NaF films are given in Fig 6. From DSC curves, the glass transition temperature (T_g) of PAN is 107°C and the melting temperature (T_m) is 317°C³¹. 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 10-400°C. Endothermic and exothermic peaks are observed for glass transition temperature and melting temperature. 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 battery³². The increase of NaF salt concentration into the host polymer (PAN) decreases the (T_g) of the polymer. The calculated T_g values are listed in Table 2. The decrease in T_g can be due to the plasticization effect of the gel polymer electrolyte with the addition of salt. The plasticization effect is related to a decreasing of the dipole-dipole interactions between the PAN chains due to the presence of the salt. In other words, the lowering of T_g of PAN is related to the lowering of degree of crystallinity. The lowering of T_g is expected to make the ions move easily in the prepared polymer electrolyte systems. Similar results have been reported by Hiran Kumar et al. for the PVA: CH₃COONH₄ polymer electrolyte system³³. The low glass transition temperature has been found for 20 wt% of NaF doped PAN. This is in good agreement with conductivity and XRD results.

Table 2:Tg values of PAN:NaF Gel polymer electrolyte films

S.NO	Sample	T _g (⁰ C)
1	PURE PAN	107
2	90:10	97.8
3	80:20	88.26
4	70:30	83.5
5	60:40	72.8

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 Temperatures³⁴. when plasticizers are added to PAN (T_m) decreases from 317-294⁰C and (T_g) decreases from 107-72⁰C. When salt is added to PAN (T_g) increases from 72-98⁰C and (T_m) increases from 294-312⁰C. 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.

Conclusions

A Gel polymer electrolyte has been developed by blending varying concentration of NaF with pure PAN using solution casting method. The Gel polymer electrolyte has been characterized by techniques like XRD, AC Conductivity and DSC. The DSC measurements showed a decrease in the degree of crystallinity and increase of amorphous regions with increasing concentration of salt. The sample containing 30 wt% of NaF exhibited the highest conductivity of $1.82 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature (303K) and $2.96 \times 10^{-3} \text{ S cm}^{-1}$ at 373K respectively.

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