

FTIR and ^1H NMR Study on PAN-NH₄SCN Based Fuel cell Applications

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Abstract : Polymer electrolytes are made up of poly (acrylonitrile) (PAN) as host polymer and ammonium thiocyanate (NH₄SCN) as dopant prepared by solvent casting method. The XRD analysis denotes the amorphous nature of prepared polymer electrolytes. The main goal of the FTIR study is to confirm the nitrile group 2245 cm⁻¹. The ^1H NMR Study is focused on identification and structural determination in the polymer electrolyte system. TG analysis show that particularly weight loss in the cast membranes.

Key words: PAN, FTIR, ^1H NMR and TG analysis.

Introduction

In the past few years, solid polymer electrolytes are of enormous interest for use in all solid state electrochemical devices namely batteries, sensors, and fuel cell¹. One of the most part objectives in polymer research is the main of the polymer system with high ionic conductivity at an ambient temperature, good mechanical strength and thermal property². The ionically conducting polymer electrolytes are mostly of alkali ions such as Li⁺, Na⁺. Recently it has been accepted that developing proton [H⁺] ion conductors have huge technological applications³. Particularly very few proton conducting polymer electrolytes for fuel cells have been reported so far⁴⁻⁸.

The ammonium salt is a good donor of proton polymer electrolytes. Literature survey denotes that the FTIR- ^1H NMR based PAN: NH₄SCN is insufficient. PAN is used commercially as plastics as well as fibers. It has High strength, abrasion resistance and good insect resistance⁹. In the Present work, PAN doped ammonium thiocyanate (NH₄SCN) membranes have been prepared and characterized by XRD, FTIR, ^1H NMR and TG methods.

Experimental Section

Materials Used

Poly (acrylonitrile) (PAN) (average molecular weight=1, 50,000) and Ammonium thiocyanate (NH₄SCN) and Dimethyl formamide (DMF) bought from Aldrich, SISCO and MERCK, were used for the Preparation of polymer electrolyte.

Purification

The materials purchased were annealed at 373K under Vacuum 10⁻³ in Technico oven, for 10 hrs before use.

Preparation

The electrolytes were prepared by solvent casting technique. This technique is easy to handle and low cost method. By adding PAN, NH_4SCN is dissolved by DMF solvent (MERCK). Aqueous solutions of PAN and NH_4SCN were stirred continuously with magnetic stirrer for 24 hrs to obtain complete homogeneous jelly solution. The solution was then cast on to a glass plate and samples were dried. The film thickness is obtained for micrometer range.

Characterization technique

The phase analysis of the proton conducting polymer at room temperature was performed with X-ray diffractometer. The Fourier transform infra red (FTIR) spectrum was recorded in the range ($4000\text{-}400\text{ cm}^{-1}$) using Jasco FTIR 460 plus (Japan). The Nuclear magnetic resonance was recorded in the DMSO- d_6 solution using Bruker spectrometer with standard TMS reference. The thermal analysis was recorded in the NETZSCH with N_2 gas with crucible alumina is a reference material.

Results and discussion

X-ray diffraction analysis

X ray diffraction has been widely used for determining crystal structure of polycrystalline materials and chemical analysis. The X-ray diffraction method is a widely used tool for structural identification through the interaction of electromagnetic radiation to give interference effects with structures comparable in size to the wave length of the radiation. It is a non-destructive method¹⁰. The X-ray diffraction pattern of pure PAN, and PAN- NH_4SCN complexes are show in fig 1 (a-g). Normally original PAN shows $2\theta=17^\circ$ which corresponds to the planar spacing $d=5.4\text{A}^\circ$ and can be indexed to (110) reflection¹¹.The X-ray pattern indicated all developed electrolytes is shown $2\theta=17^\circ$ it's indicated PAN present in all the system.

The peak $2\theta=24^\circ$ and $2\theta=26^\circ$ (JCPDS-23-0029) corresponding to pure NH_4SCN have been found to be absent in all salt-doped complexes. No new peaks have been found in the complex. It indicates complete dissociation of salt into the polymer matrix.

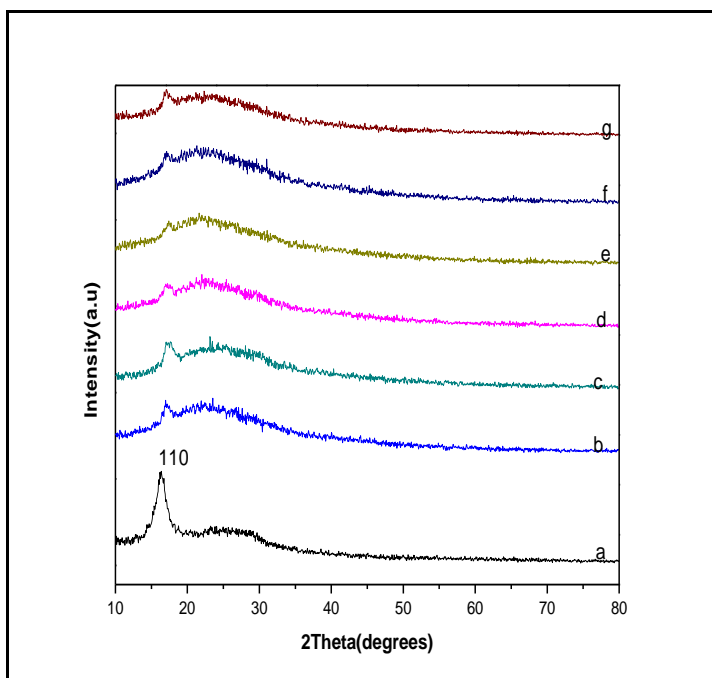


Fig 1. XRD Pattern of (a) Pure PAN, (b) 100PAN:0 NH_4SCN , (c) 95PAN:5 NH_4SCN , (d) 90PAN:10 NH_4SCN , (e) 85PAN:15 NH_4SCN , (f) 80PAN:20 NH_4SCN , (g) 75PAN:25 NH_4SCN .

Fourier Trans form infrared analysis

Infrared spectroscopy is to characterize the structural properties of polymers, including tacticity, branching, crystallinity, hydrogen bonding and orientation¹². To use infrared spectroscopy to carry out

quantitative analysis of additives in polymers. FTIR spectra of original PAN, NH_4SCN and complexes are shown in fig 2& 3. The vibrational band 2245cm^{-1} $\text{C}\equiv\text{N}$ Stretching band is shown in the original PAN¹³.

The vibrational band 1250cm^{-1} C-N Stretching is shown in Pure PAN. The vibrational bands 3110cm^{-1} and 2362cm^{-1} are attributed to γ N-H stretching and γ CN stretching. The vibrational bands at 1622cm^{-1} and 1400cm^{-1} are attributed to $\gamma\text{C}\equiv\text{N}$ asymmetric vibration and combined effect of C-S symmetric stretching. The vibrational band 943cm^{-1} and 820cm^{-1} are attributed to $\gamma\text{C-S}$ Symmetric bending vibrations and SCN^{-1} Polar groups. These bands can be observed in the spectrum of pure NH_4SCN ¹⁴.

The complex FTIR fig shows that 2245cm^{-1} is shifted in the positions 2240cm^{-1} , 2244cm^{-1} . This results corresponds to pure PAN present in the system. 2065cm^{-1} this peak is shifted to that 2058cm^{-1} , 2069cm^{-1} , 2094cm^{-1} . The vibrational band 1400cm^{-1} combined effect of C-S symmetric vibration is shifted in the positions 1442cm^{-1} , 1483cm^{-1} . The peak observed at 820cm^{-1} in the NH_4SCN is slightly shifted to the peaks 815cm^{-1} , 810cm^{-1} . This corresponds to SCN^{-1} ion present in the system. This result confirms proton interaction in the system.

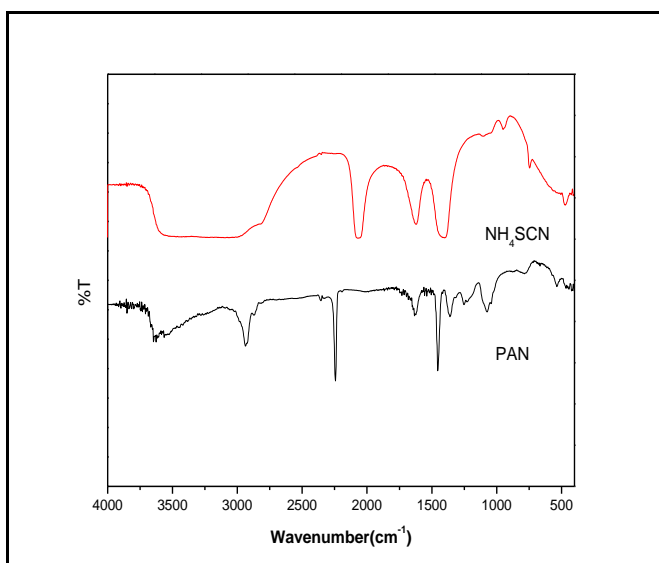


Fig2a shows that original PAN, NH_4SCN

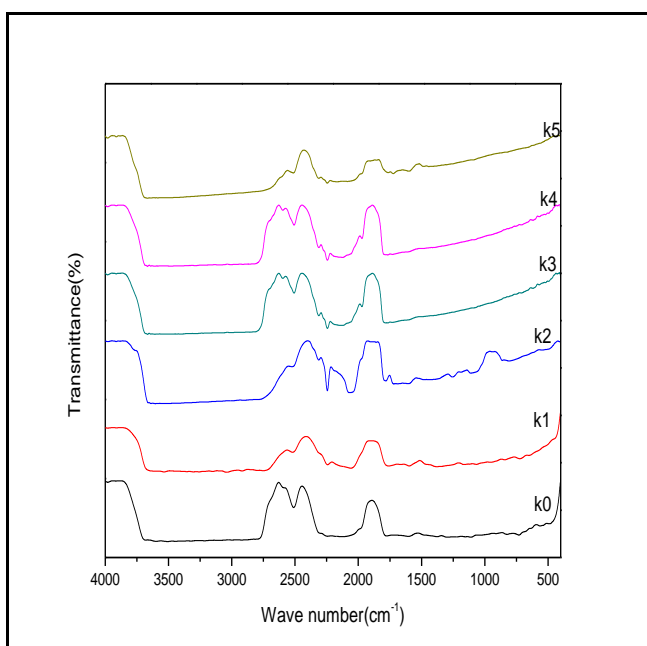


Fig 2b shows that FTIR spectra of complex polymer electrolytes

^1H NMR Spectroscopic Analysis

The ^1H NMR was recorded on a Bruker 300 MHz NMR instrument using TMS as internal standard reference and DMSO d_6 solvent. Chemical shifts are given in parts per million scales and the couplings are given in hertz. The chemical shift δ 2.73 (singlet, 1H, CH), δ 2.89 (singlet, 1H, CH), δ 3.14 (Triplet, 1H, CH, $J=7.5\text{Hz}$), δ 2.70 (singlet, 1H, CH), δ 2.89 (singlet, 1H, CH), δ 3.12 (singlet, 1H, CH), δ 7.12 (singlet, 1H, CH), δ 2.0 (singlet, 3H) are in the spectrum.

The appearance of above mentioned peaks is due to dissociation of salt into NH_4^+ and SCN^- ions in the host polymer matrix. Is also related to intermolecular hydrogen bonding in the system.

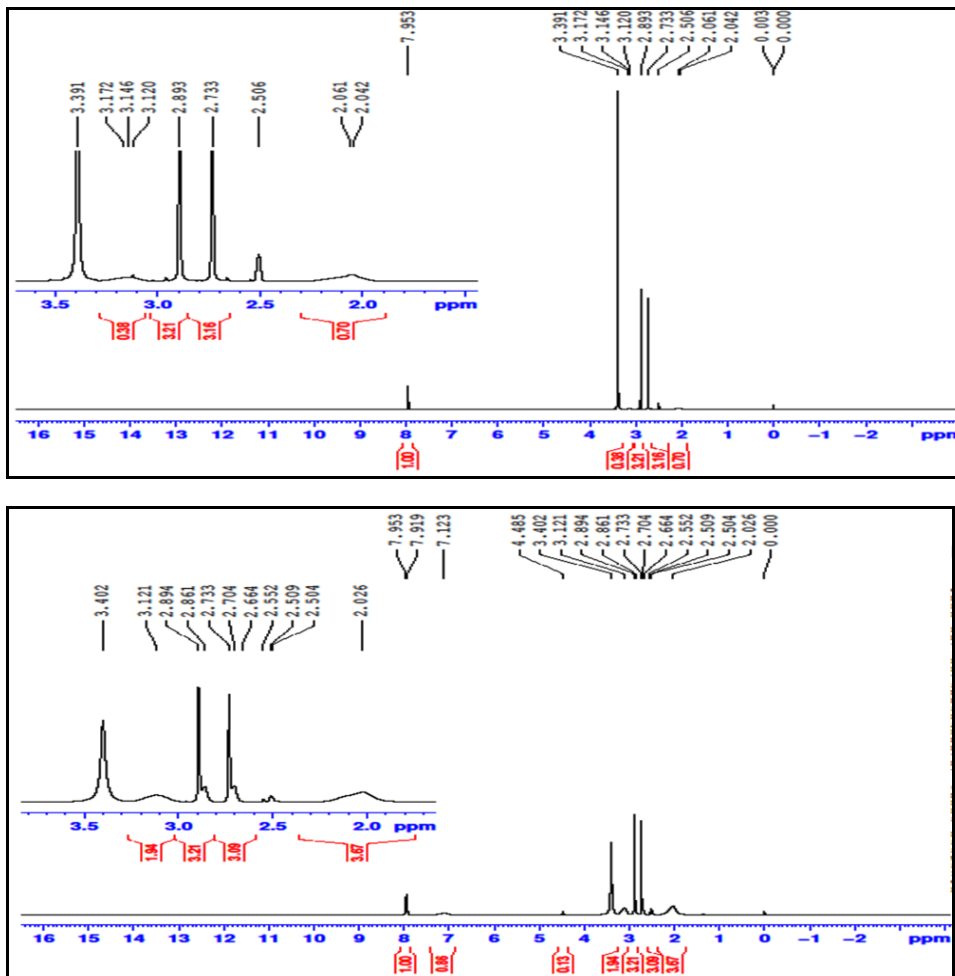


Fig 3 shows that ^1H NMR spectra of PAN, PAN Ammonium salt complexes in the System.

TG Analysis

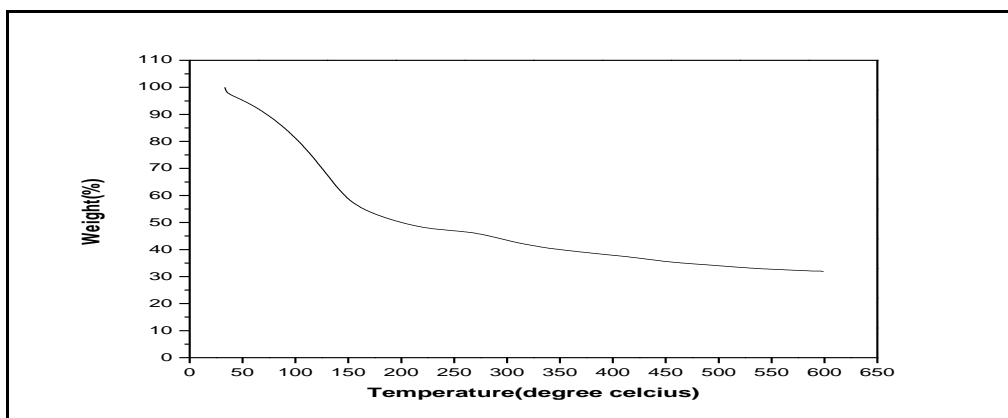


Fig 4 shows that TG analysis of PAN, PAN: NH_4SCN in the system.

The thermo gravimetric analysis of PAN (75):NH₄SCN (25) are depicted in fig. The TG curve shows a gradual weight loss of about (50 wt %) around 170⁰C which may be due to the decomposition of the polymer electrolyte. This result indicates that the electrolytes is stable over 170⁰C and are preferred in fuel cell applications.

Conclusion

PAN-NH₄SCN based proton-conducting polymer electrolytes in different weight ratios have been prepared by solution casting technique using DMF as solvent. The amorphous nature of polymer electrolyte has been confirmed by XRD analysis. FTIR spectrum confirms the complex formation between polymer and the ammonium salt. The ¹H NMR results shows migration is mainly due to proton. The estimation of TG analysis is shows that weight loss and decomposition .This system is applicable electrochemical system such as fuel cells and other device.

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