



^1H NMR Studies of Proton Conducting Polymer Blend Electrolyte Based On PVA: PVP: NH_4X ($\text{X}=\text{NO}_3^-$, CH_3COO^-)

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Abstract:

The proton salt (X) ($\text{X}=\text{NH}_4\text{NO}_3$ and $\text{CH}_3\text{COONH}_4$) doped with 50PVA: 50PVP blend polymer electrolyte has been prepared by simple solution casting technique using water as a solvent. XRD studies revealed that the crystallinity of polymer blend has been reduced due to the addition of ammonium salts. The conductivity of polymer blend electrolyte is discussed using the results of AC impedance studies. The maximum conductivity has been observed in the order of 10^{-3} S cm^{-1} and 10^{-5} S cm^{-1} for the composition of 30Wt% of NH_4NO_3 and 30Wt% of $\text{CH}_3\text{COONH}_4$ doped with 50PVA:50PVP blend. NMR spectroscopy is an important analytical method that is extensively used to study the structure and properties of macromolecules. The temperature dependent ^1H NMR study reveals the increase in proton mobility with temperature and hence confirms that proton is responsible for conduction at all temperatures. The ionic transference number of polymer electrolyte has been found from dc polarization technique.

Keywords: PVA-PVP, Proton salt, XRD, ^1H NMR, Conductivity.

I. INTRODUCTION

In the past few years there has been an increasing interest in the synthesis and characterization of solid polymer electrolyte because of its dimensional stability, processability, flexibility, electrochemical stability, safety and longer life. Among solid polymer electrolytes, proton conducting polymer electrolytes have received considerable attention in electrochemical devices [1]. In most solid polymer electrolyte, the polymer host is doped with inorganic salts in order to enhance the conductivity. The ionic conductivity is due to mobility of the conducting species contributed by the inorganic salt which dissociated into ions. Various approaches have been made to modify the structure of polymer electrolytes in order to improve their conductivity, electrochemical and mechanical properties. These approaches include, synthesizing new polymers, cross linking two polymers, blending of two polymers, adding plasticizers to polymer electrolytes and adding inorganic inert fillers to make composite polymer electrolytes. Among these approaches, polymer blending is one of the most important contemporary ways for the development of new polymeric materials and it is a useful technique for designing materials with a wide variety of properties. Polyvinyl alcohol (PVA) is a semi crystalline polymer, studied extensively because of its many interesting physical properties, which arise from the presence of OH group and the hydrogen bond formation. Polyvinyl pyrrolidone has drawn a special attention amongst the conjugated polymers because of its good environmental stability, easy processability and excellent transparency. Both polymers are having a good charge storage capacity and dopant dependent electrical and optical properties. [2]. When these two polymers are mixed, the interactions between PVA and PVP are expected to occur through interchain hydrogen

bonding between the carbonyl group of PVP and hydroxyl group of PVA. Most of the studies on PVA-PVP blend polymer electrolytes have been reported for its dielectric properties, thermal properties, pyroelectric behaviour, miscibility, viscosity and compatibility. The present work has been deals with the study of Structural, Conductivity and Vibrational behavior of PVA-PVP polymer blend electrolyte with addition of ammonium nitrate (NH_4NO_3) and ammonium acetate ($\text{CH}_3\text{COONH}_4$) salt.

II. EXPERIMENTAL TECHNIQUE

Polyvinyl alcohol (PVA) from S d fine has molecular weight 1, 25, 000 g/mol and polyvinyl pyrrolidone (PVP) from MERCK has molecular weight K90 has been used as raw materials to prepare polymer blend electrolyte. Each quantity of PVA and PVP (50/50) is added to double distilled water with stirring the solution at room temperature to complete dissolution. Required quantity (5Wt%, 10Wt%, 15Wt%, 20Wt%, 25Wt%, 30Wt% and 35Wt%) of NH_4NO_3 and (5Wt%, 15Wt%, 20Wt%, 30Wt% and 35Wt%) of $\text{CH}_3\text{COONH}_4$ also dissolved in double distilled water and added to the polymeric solution with continuous stirring. The solutions have been poured onto cleaned petri dishes and evaporate at room temperature. After drying the films were peeled from Petri dishes and kept in vacuum desiccators until use. The X-ray diffraction pattern of polymer electrolytes has been recorded using $\text{CuK}\alpha$ ($\lambda=1.54060\text{\AA}$) radiation. The ionic conductivity study of the polymer electrolytes has been carried out in the temperature range of 303-373K over a frequency range of 42Hz- 1MHz using a computer controlled HIOKI 3532 LCR meter. ^1H NMR studies have been carried out using a Bruker Spectrometer with Larmor frequency 400 MHz. The ionic transference number has been found from dc polarization

technique. The complexation of the Ammonium Nitrate and Ammonium Acetate with 50PVA-50PVP blend polymer has been shown in [Fig 1].

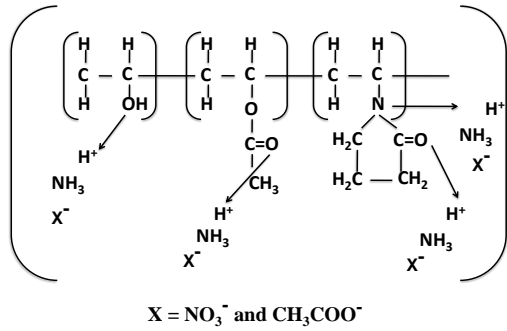


Figure.1. Possible Interaction Between The Polymer And Salt

III. RESULT AND DISCUSSION
IV. X-RAY DIFFRACTION ANALYSIS

Fig 2 and Fig 3 represents the XRD patterns for the pure PVA, PVP, 50PVA-50PVP blend and blend complexed with ammonium nitrate (NH_4NO_3) and 50PVA-50PVP blend complexed with ammonium acetate (CH_3COONH_4). The XRD pattern in the fig 2 and 3 (a) for pure PVA shows that the film is semicrystalline and a crystalline peak at 19.7° and it corresponds to orthorhombic PVA (110) reflection [3] and the pure PVP exhibits a broad peak between 12° & 15° and 19° & 24° as shown in Fig 2 and 3 (b).

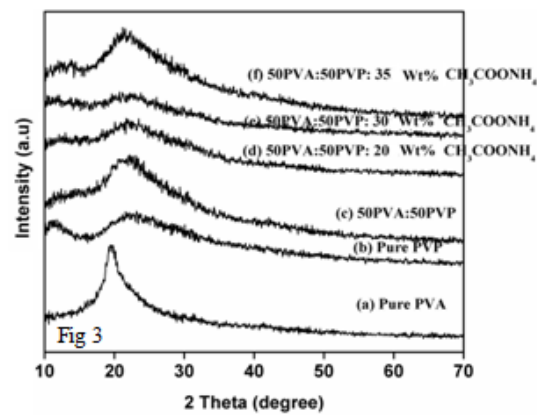
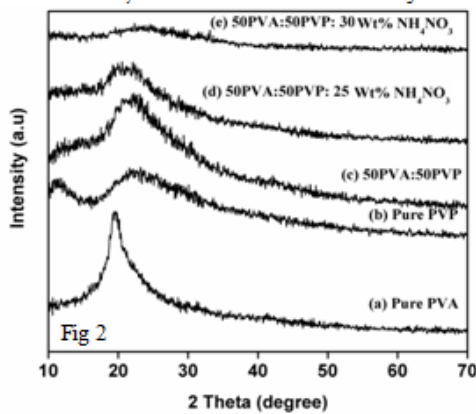


Figure .2. xrd pattern of pure pva, pvp, 50pva:50pvp blend and 50pva:50pvp blend with 25wt% and 30wt% of nh_4no_3

Figure.3. xrd pattern of pure pva, pvp, 50pva:50pvp blend and 50pva:50pvp blend with 20wt%, 30wt% and 35wt% of ch_3coonh_4

The above mentioned peaks become less intense when the concentration of NH_4NO_3 and CH_3COONH_4 is increased [Fig 2 (d and e) and 3 (d, e and f)]. This could be due to the disruption of PVA and PVP structure by ammonium salts. Hodge et al established a correlation between the intensity of the peak and the degree of crystallinity. The maximum amorphous nature has been observed for the composition of 50PVA:50PVP:30Wt% NH_4NO_3 and 50PVA:50PVP:30Wt% CH_3COONH_4 . This amorphous nature results in greater ionic diffusivity with a high ionic conductivity, which can be obtained in amorphous polymers that have flexible backbone. No peaks corresponding to ammonium salts appeared in the complexes which indicate the complete dissolution of salt in the polymer matrices. Thus, the X-ray diffraction analysis reveals complex formation the polymer matrices.

V. AC IMPEDANCE ANALYSIS
VI. CONDUCTANCE SPECTRA

Fig 4 and 5 shows that the frequency dependence conductance spectra of 25Wt%, 30Wt% and 35Wt% of ammonium nitrate doped with 50PVA:50PVP polymer blend electrolyte and 20Wt%, 30Wt% and 35Wt% of ammonium acetate doped with 50PVA:50PVP polymer blend electrolyte at room temperature. The curve consists of three distinct regions with in the measured frequency range. The low frequency spike describing electrode-electrolyte interfacial phenomena which is ascribed to the space charge polarization at the blocking electrodes, followed by the frequency independent plateau region and the extrapolation of the plateau to zero frequency gives the value of dc ionic conductivity. The dc conductivity values for all the composition of PVA: PVP with ammonium nitrate and ammonium acetate polymer blend electrolytes at room temperatures have been presented in table 1. In the high frequency region the conductivity increases with frequency. The ac conductivity $\sigma(\omega)$, obeys the jonscher's power law [4], and it is found to vary with angular frequency ω ,

$$\sigma(\omega) = \sigma_{dc} + A \omega^\alpha$$

where

σ_{dc} is the dc conductivity, A and α are temperature dependent parameters.

The maximum conductivity has been found to be $1.41 \times 10^{-3} S cm^{-1}$ and $8.12 \times 10^{-5} S cm^{-1}$ at 303K for 50PVA:50PVP:30Wt% NH_4NO_3 and 50PVA:50PVP:30Wt% CH_3COONH_4 blend polymer electrolyte. High values of ionic conductivity obtained for these blend polymer electrolytes might be due to the very high amorphous nature of the blended polymer matrix.

Table .1. Conductivity for 50pva:50pvp polymer blend with different weight percentage of nh_4no_3 and ch_3coonh_4 at room temperature

Polyme r	Composition		Composition	
	Salt NH_4N O_3	σ ($S cm^{-1}$)	Salt CH_3COON H_4	σ ($S cm^{-1}$)
50PV A:50P VP	25Wt%	1.07×10^{-5}	20Wt%	3.98×10^{-6}
	30Wt%	1.41×10^{-3}	30Wt%	8.12×10^{-5}
	35Wt%	8.70×10^{-5}	35Wt%	9.12×10^{-6}

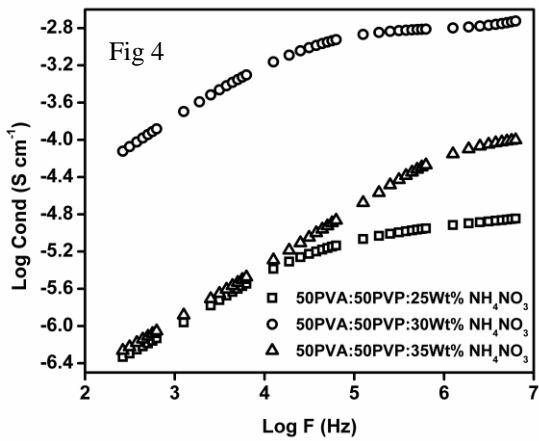


Figure.4. conductance spectra of different wt% of ammonium nitrate doped with 50pva:50pvp blend

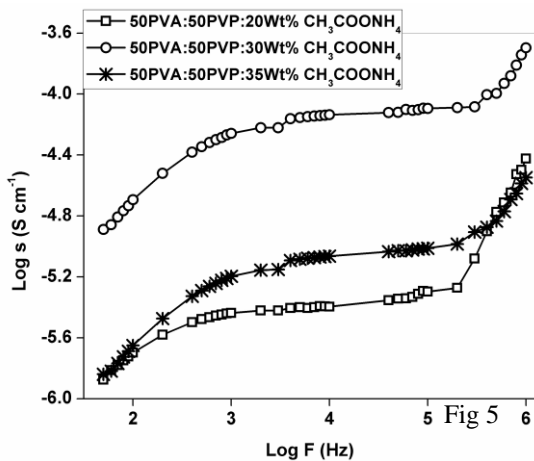


Figure.5. conductance spectra of different wt% of ammonium acetate doped with 50pva:50pvp blend

VII. CONCENTRATION DEPENDENT CONDUCTIVITY

The variation of room temperature ionic conductivity of 50PVA:50PVP blend with different weight Percentage of ammonium salts polymer electrolyte as a function of NH_4NO_3 and $\text{CH}_3\text{COONH}_4$ concentration is shown in Fig 6. It has been found that the conductivity increase with increase in ammonium nitrate and ammonium acetate concentration upto 30 weight percentage of salt concentration. The conductivity reaches maximum of $1.41 \times 10^{-3} \text{ S cm}^{-1}$ and $8.12 \times 10^{-5} \text{ S cm}^{-1}$ at 303K in the PVA/PVP blend polymer electrolytes having 30 Wt% NH_4NO_3 and 30 Wt% $\text{CH}_3\text{COONH}_4$.

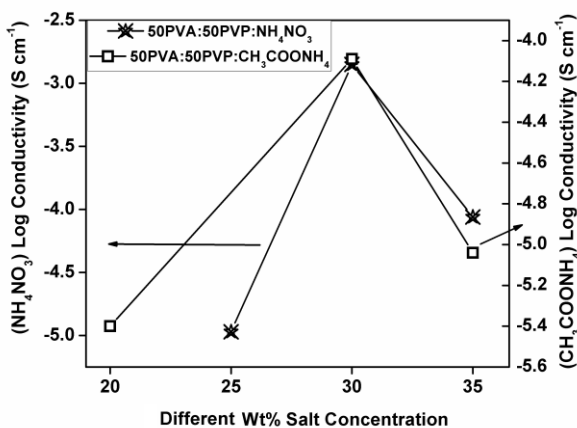


Figure.6. Log Σ Vs Salt Concentration Of NH_4NO_3 And $\text{CH}_3\text{COONH}_4$ At Room Temperature

This may be due to the increase in the number of mobile charge carriers and also to the increase in the amorphous nature of the

polymer electrolyte, which reduces the energy barrier thereby facilitating the fast ion transport. However, a decrease in conductivity is observed for 35 weight percentage concentration of NH_4NO_3 and $\text{CH}_3\text{COONH}_4$ doped with Poly (Vinyl alcohol) and Poly (Vinyl pyrrolidone). This is may be due to the aggregation of ions, leading to the formation of ion clusters, thus decreasing the number of mobile charge carriers.

VIII. ^1H NMR SPECTROSCOPIC ANALYSIS

The Solid State NMR has been used to provide information on the polymer complexes, such as various local environments of proton in the polymer matrix, mobility of the charge carriers and also gives information about the interaction between the polymer and the salt in the polymer electrolytes. The solid state ^1H NMR spectra of Pure 50PVA-50PVP blend and blend doped with different wt% of NH_4NO_3 and $\text{CH}_3\text{COONH}_4$ polymer electrolyte at room temperature are shown in figure7. The peak centered at 4.67ppm is attributed to the alcoholic proton of the host polymer. It is clear from the figure that addition of NH_4NO_3 into PVA-PVP introduces a new peak 7.33ppm attributed to ammonium proton. The intensity of ammonium peak has been found to be higher while its linewidth has been found to be least for 50PVA: 50PVP:30 Wt% NH_4NO_3 polymer blend electrolyte. The alcoholic proton peak appears with higher intensity and its linewidth decreases for 50PVA:50PVP:30Wt% NH_4NO_3 than other composition. This reveals the more interactions taking place between the alcoholic oxygen atom and the ammonium ion of the salt thereby increasing the conduction of proton ion in the 50PVA:50PVP:30Wt% NH_4NO_3 polymer electrolyte system than in other compositions of 50PVA:50PVP: X NH_4NO_3 (X = 5Wt%, 10Wt%, 15Wt%, 20Wt%, 25Wt%, and 35Wt %). Fig 8 represents the ^1H NMR spectra for 50PVA:50PVP: 30Wt% NH_4NO_3 polymer electrolytes at different temperatures. Two peaks at 4.95ppm and 7.95 ppm are more prominent in the fig 8. Deconvoluted ^1H NMR spectra 50PVA: 50PVP: 30Wt% NH_4NO_3 polymer blend electrolytes at different temperatures have been shown in fig 9. Six resonance peaks at 3.7ppm, 4.42ppm, 4.81ppm, 5.46ppm, 5.96ppm and 7.78ppm have been observed. The peak at 3.7ppm can be attributed to the signal of NCH_2 of PVP. The peak centered at 4.42ppm ascribed to the proton of the hydroxyl group in the polymer is observed to be broad which may be related to intermolecular hydrogen bonding. This peak persists at all temperatures with small change in chemical shift. The peak at 4.81ppm corresponds to the water protons associated with $\text{C}=\text{O}$ groups in hydrophilic cavities of the polymer [5].

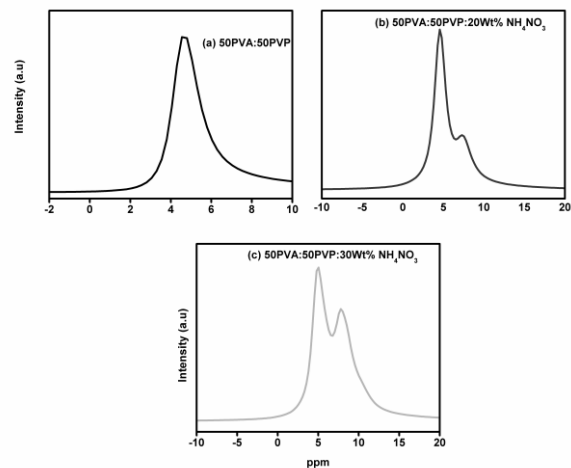


Figure.7. ^1h nmr spectra of 50pva:50pvp blend and 50pva:50pvp:x nh_4no_3 (x=20wt% and 30wt%) polymer electrolyte at 303k

The peaks at 5.46ppm, 5.96ppm and 7.78ppm correspond to ammonium protons in different chemical environments. The appearance of the ammonium proton peaks is due to the dissociation of salt into NH_4^+ and NO_3^- ions in the host polymer matrix. With increasing temperature, changes in the chemical shift have also been observed in the ammonium peaks which strongly prove the interaction between the NH_4^+ and the host polymer matrix. It is to be noted that the lineshape and width of the solid state NMR spectra are strongly temperature dependent due to the motion-dependent anisotropic nuclear spin interactions. As the temperature rises, the molecular motion is accelerated and narrowing of line shape occurs [6]. From the fig 10 a new peaks at 2.8ppm and 5.6ppm (small hump) for 50PVA:50PVP:20Wt% $\text{CH}_3\text{COONH}_4$ polymer blend electrolyte has been observed. These peaks have found to be shifted at higher salt concentrations (50PVA:50PVP:X $\text{CH}_3\text{COONH}_4$ (X = 30Wt% and 35Wt%)) indicating the interaction between the host polymers matrix and the salt. Fig 10 represents the Deconvoluted spectra of 50PVA: 50PVP: 30Wt% $\text{CH}_3\text{COONH}_4$ polymer blend electrolyte at different temperatures. Four resonance peaks have been observed at 2.8ppm, 4.3ppm, 4.5ppm and 5.3ppm in the ^1H NMR spectrum of the polymer blend electrolyte at 303K. The broad peak with a chemical shift 2.8ppm has been associated with $-\text{CH}_2\text{C}=\text{O}$ of the host polymer PVP. The peak centered at 4.3 ppm ascribed to the proton of the hydroxyl group in the host polymer is observed to be narrow which may be related to intermolecular hydrogen bonding. This peak persists at all temperatures with small change in chemical shift. A new peak with a chemical shift of 4.5 ppm has been observed at all temperatures. This may be due to the interaction of protons from the salt with the host polymer because of which alcoholic proton persists in two different environments. The peak at 5.3ppm corresponds to ammonium protons. The appearance of the ammonium proton peak is due to the dissociation of salt into NH_4^+ and CH_3COO^- ions in the host polymers matrix. The changes in the chemical shift have been observed in all the peaks with increasing temperature which strongly prove the interaction between the salt and the host polymer matrix. The temperature dependent ^1H NMR linewidth measurements have been found to be consistent with the temperature dependent conductivity analysis. The narrowing of the proton signals with increase of temperature indicates the raised proton mobility and hence the conductivity.

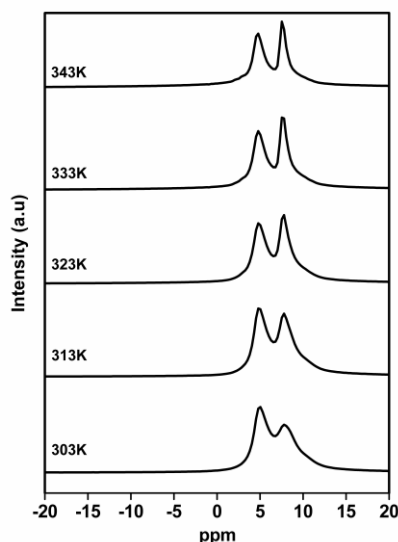


Figure .8. ^1H Nmr Spectra Of 50pva:50pvp:30wt% NH_4NO_3 At Different Temperatures

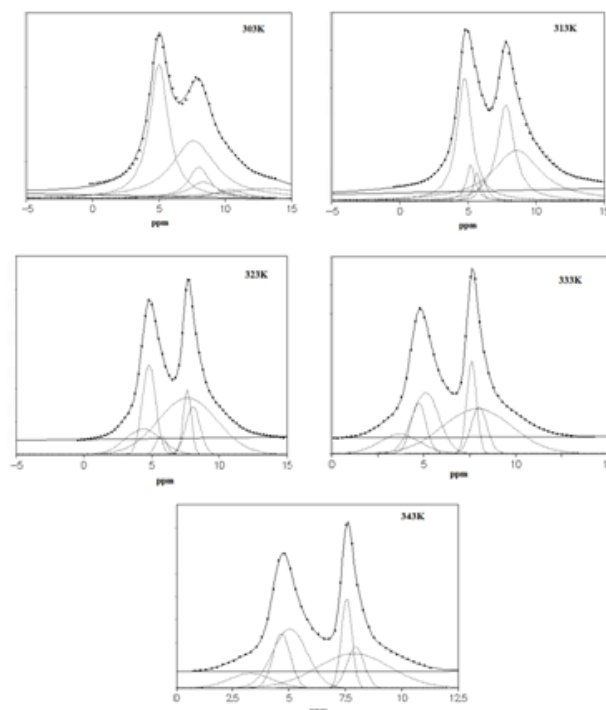


Figure.9.Deconvoluted ^1H Nmr Spectra Of 50pva: 50pvp: 30wt% NH_4NO_3 Polymer Blend Electrolytes At Different Temperatures

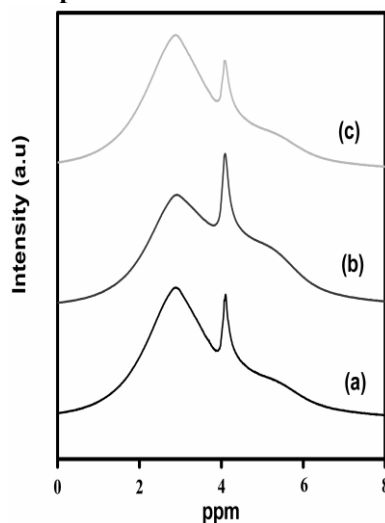


Figure.10. ^1H Nmr Spectra Of (A) 50pva: 50pvp: 20wt% $\text{CH}_3\text{COONH}_4$ (B) 50pva: 50pvp: 30wt% $\text{CH}_3\text{COONH}_4$ (C) 50pva: 50pvp: 35wt% $\text{CH}_3\text{COONH}_4$

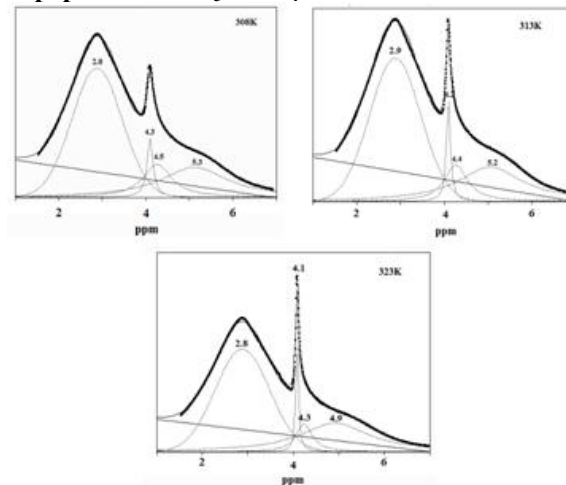


Figure.11. Deconvoluted ^1H NMR spectra of 50PVA: 50PVP: 30Wt% $\text{CH}_3\text{COONH}_4$ polymer blend electrolyte at different temperatures

IX. TRANSFERENCE NUMBER MEASUREMENT

Transference number is a dimensionless parameter which informs about the contribution of the particular charged species present in the electrolyte (ions and electrons) to the overall charge transport across the cell. The transference number corresponding to ionic (t_{ion}) and electronic (t_{ele}) transport number have been evaluated in PVA:PVP: NH_4NO_3 polymer blend electrolyte systems using DC polarization techniques. In this technique, the dc current is monitored as a function of time on the application of fixed dc voltage across the sample using stainless steel blocking electrodes. The result of dc polarization measurement on 50PVA:50PVP:30Wt% NH_4NO_3 (possessing highest conductivity) polymer electrolytes taken with stainless steel electrodes by applying 1.5V dc bias voltage (at 303K) is shown in Figure 11. The transference numbers are calculated from the polarization current versus time plot using the equations,

$$t_{ion} = (I_i - I_f) / I_i$$
$$t_{ele} = I_f / I_i$$

Where I_i is the initial current and I_f is the final residual current. The ionic transference number (t_{ion}) for all PVA: PVP: NH_4NO_3 electrolyte system has been found to be in the range of 0.94-0.98 [not shown in fig]. This suggests that the charge transport in these electrolyte films is predominantly due to ions [7].

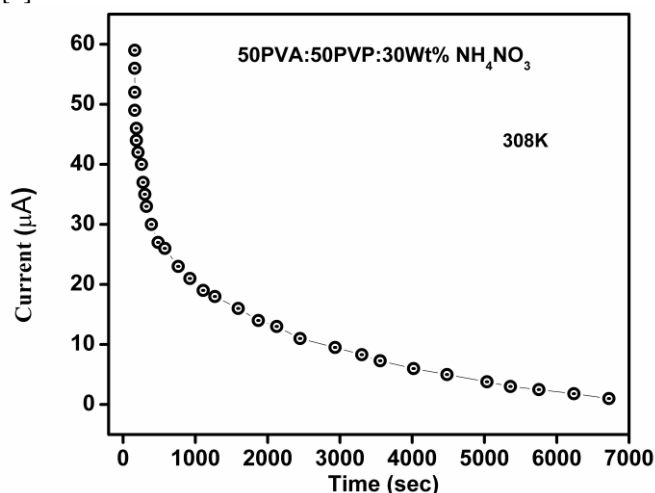


Figure.12. Current Vs Time Plot of 50pva:50pvp:30wt% Nh_4no_3 Polymer Blend Electrolyte

X. CONCLUSION

Perfluorinated polymer electrolyte membranes have been extensively used as polymer electrolytes for fuel cells. These polymer electrolytes have sufficient electrochemical properties, mechanical properties, and chemical and thermal stabilities. However, PEFCs constructed with these Perfluorinated polymer electrolyte membranes tend to be expensive and have several problems especially for use in motor vehicles. To overcome these problems and their high costs, the development of new proton-conducting polymer electrolytes is necessary for extensive applications. In this work, proton conducting polymer blend electrolyte has been prepared by solution casting technique. Prepared polymer blend electrolyte are characterized by XRD, AC Impedance, Proton NMR and dc polarization techniques.

XI. REFERENCES

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