



^1H NMR Study on PVP- NH_4Cl based- Proton conducting Polymer Electrolyte

KEYWORDS

proton conducting polymer electrolytes, FTIR, ^1H NMR, ionic conductivity**N.Vijaya**

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ABSTRACT

Proton conducting polymer electrolytes comprising poly (N-vinyl pyrrolidone) (PVP) as host polymer and ammonium chloride (NH_4Cl) as dopant have been prepared in different compositions by solution cast technique. FTIR analysis, temperature dependent conductivity, transference number and ^1H NMR measurements have been carried out to characterize the prepared polymer electrolytes. It has been observed from conductivity measurements that the polymer complex with 15 mol% NH_4Cl has the highest conductivity of $2.51 \times 10^{-5} \text{ S cm}^{-1}$ at ambient temperature with low activation energy (0.49 eV). The temperature dependence of conductivity of the polymer electrolyte is found to obey Arrhenius law. The transference number data suggests that the charge transport in this polymer electrolyte system is mainly due to ions. ^1H NMR study shows that the protonic transport in PVP: NH_4Cl system is contributed by NH_4^+ ion. The temperature dependent ^1H NMR study reveals the increase in mobility of NH_4^+ ion with temperature.

Introduction

Over the past few years, considerable attention has been focused on the solid polymer electrolytes because of their potential applications in solid state electrochemical devices such as fuel cell, battery, supercapacitor, gas sensor, electrochromic display devices, etc [1-2]. Investigations on the solid polymer electrolytes have been made to improve their electrical, mechanical and thermal properties suitable for their use in solid state devices. These properties can be modified by adding ammonium salts to suitable polymer matrix. Several ammonium salt-doped proton-conducting polymer electrolytes based on various polymers such as PVA [3], PAA [4], PEO [5], CA [6], PVP [7], etc. have been investigated by many researchers. The protonic transport in these polymer electrolytes generally involves motion of groups like H^+ , NH_4^+ , H_3O^+ , OH^- etc. The conductivity of these polymer electrolytes depends not only on the motion of protons but also on the segmental motion of the polymer chains [2] which can be related to the glass transition temperature of the polymer electrolytes. Solid state NMR spectra can be used to investigate the different environments of protons in the polymer matrix, motion of protons and the interaction between the polymer and the salt in the polymer electrolytes [8,9].

Recently, we reported the proton-conducting polymer electrolyte based on Poly (N-vinyl pyrrolidone) (PVP)-Ammonium chloride (NH_4Cl) with good thermal and electrical properties [10]. As a continuation of our previous work, in this paper, we report the conduction mechanism, ionic transference number and ^1H NMR studies of the polymer electrolyte based on PVP: NH_4Cl .

Experimental Details

Poly (vinyl pyrrolidone) (PVP) of average mol. wt. 40,000 g mol^{-1} obtained from S d Fine chemicals, India and ammonium chloride obtained from Spectrum, India have been used as the starting materials. The solution casting method has been used for the preparation of proton conducting polymer electrolytes. The solvent used in this method is distilled water. Appropriate quantities of PVP and NH_4Cl in different mole ratios are stirred continuously with magnetic stirrer for

several hours. After complete dissolution, the solutions are cast in poly propylene petri dishes and left to evaporate at room temperature for several days until the films are formed. The films are then kept in a vacuum oven for 2 days at 50°C for further drying. Transparent and flexible films of thickness ranging from 0.022 cm to 0.033 cm are obtained. The prepared films have been characterized by various experimental techniques.

FTIR spectra have been recorded for the electrolyte films in the range of $400\text{--}4000 \text{ cm}^{-1}$ at room temperature using a SHIMADZU-IR Affinity-1 Spectrometer. DSC thermograms for the prepared polymer electrolytes have been obtained using a NETZSCH DSC 204F1 at a heating rate of 2 K/min under nitrogen atmosphere in the temperature range -50 to 250°C . Conductivity measurements have been carried out on the polymer electrolyte films in the frequency range 42 Hz–1 MHz over the temperature range 303–343 K by sandwiching them between aluminum blocking electrodes using HIOKI 3532 LCZ meter interfaced with a computer. Transference number measurement has been made using Wagner's DC Polarization technique. ^1H NMR spectra have been performed on a Bruker Spectrometer with Larmor frequency 400 MHz and the chemical shift has been referenced to TMS. The commercial software "PEAKFIT" (Jandel Scientific Peakfit) has been used to fit the ^1H NMR spectra.

Results and Discussions**FTIR Analysis**

Fig.1 depicts the FTIR spectra of pure PVP and PVP doped with different concentrations of NH_4Cl . The vibration bands at 2135, 1703, 1429, 933, and 844 cm^{-1} have been assigned to C–N stretching, C=O stretching, CH_2 wagging, C–C bonding, and CH_2 bending vibrations of pure PVP, respectively [7]. The bands observed at 2135 and 1703 cm^{-1} in pure PVP have been shifted to 2137 and 1701 cm^{-1} , respectively, in 95 mol% PVP-5 mol% NH_4Cl polymer electrolyte. The band at 1429 cm^{-1} has been shifted to 1425 cm^{-1} in 95 mol% PVP:5 mol% NH_4Cl polymer electrolyte and 1433 cm^{-1} in 85 mol% PVP-15 mol% NH_4Cl polymer electrolyte. The bands at 933 and 844 cm^{-1} have been shifted to 935 and 848 cm^{-1} in the 85 mol%

PVP:15 mol% NH₄Cl.

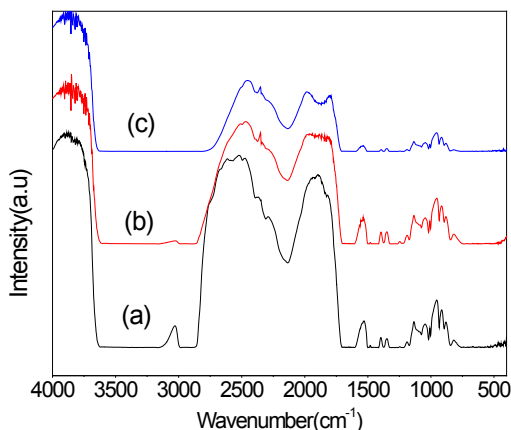
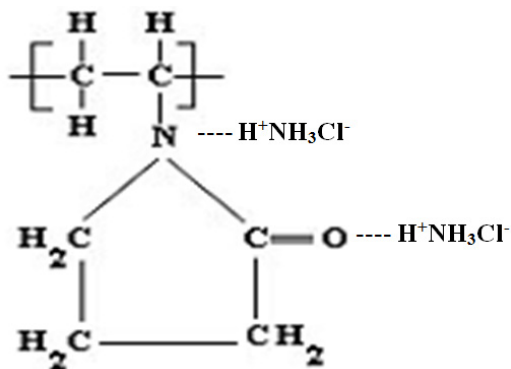


Fig. 1 FTIR spectra of (a) Pure PVP and PVP doped with (b) 5 mol% NH₄Cl and (c) 15 mol% NH₄Cl

The broad peak around 2925 cm⁻¹ corresponds to the symmetric CH₂ stretching of pure PVP. This peak is found to be shifted to lower wavenumber in the salt-doped system. Furthermore, change in the intensity of these peaks is observed. A new peak is also seen at 1869 cm⁻¹ in the 15 mol% salt doped system. These results indicate the interaction of the salt with the polymer matrix. The possible interaction between the host polymer (PVP) and the salt (NH₄Cl) is shown in Scheme 1.

The shift in the peak positions and change in the intensity of the peaks, alteration in the band shapes and appearance and disappearance of some bands in the FTIR spectra of doped samples confirm the complex formation between the polymer and the salt.



Scheme 1 Possible interaction of NH₄Cl with the host polymer PVP

DIFFERENTIAL SCANNING CALORIMETRY ANALYSIS

DSC analysis has been carried out to determine the glass transition temperature (T_g) of the polymer electrolytes. Fig.2 shows the DSC curves for two different compositions of PVP-NH₄Cl polymer electrolytes. It is already reported that the glass transition temperature, T_g of the pure PVP is 359 K [11]. A step-like change with slight shifts has been observed in the DSC curves of polymer electrolytes which correspond to their respective glass transition temperature. The T_g has been determined at the midpoint of this step change. It is observed that the T_g of polymer electrolyte decreases with the increase of concentration of NH₄Cl salt. This decrease in the glass transition temperature can be due to the plasticization of the electrolyte with the addition of salt. The incorporation of the salt into the PVP matrix results in weakening of the dipole-dipole interaction between the PVP chains which makes the

ions move freely through the polymer chain network when an electric field is applied. The glass transition temperature of the PVP doped with 15 mol% NH₄Cl is found to be 332 K. The low glass transition temperature causes faster segmental motion of the polymer electrolyte resulting in an increase in conductivity.

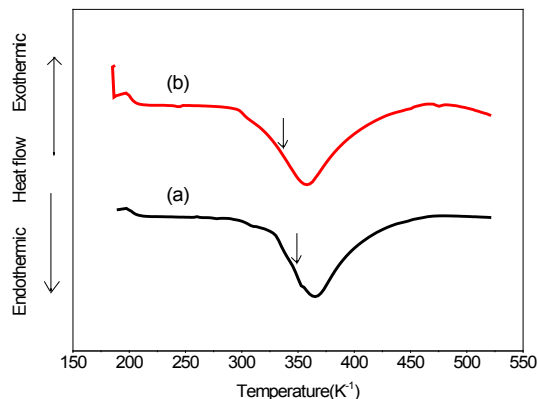


Fig.2 DSC curves of PVP-NH₄Cl polymer electrolyte with (a) 5 mol% and (b) 15 mol% of NH₄Cl

Conductivity Analysis

Fig.3 shows the Cole-Cole plot for 85 mol% PVP:15 mol% NH₄Cl (highest conducting sample) at different temperatures.. The plot consists of a depressed semicircle at high frequencies and a spike at low frequencies. The semicircle may be due to the bulk effect of the electrolyte and the spike may be due to the effect of the blocking electrodes. The bulk resistance (R_b) of the electrolyte is obtained from the intercept of the high-frequency semicircle or the low-frequency spike on the Z' - axis. The ionic conductivity of the film is then calculated using the equation,

$$\sigma = l/(R_b A), \text{ where}$$

l is the thickness of the electrolyte film, R_b is the bulk resistance and A is the area of the film. The highest ambient temperature conductivity value is found to be 2.51 × 10⁻⁵ S cm⁻¹ for the sample with 85 mol% PVP-15 mol% NH₄Cl.

The conductivity values for the electrolyte film with 85 mol% PVP:15 mol% NH₄Cl at different temperatures are given in Table 1. The ionic conductivity has been found to be 3.17 × 10⁻⁴ S cm⁻¹ at 343 K for this composition.

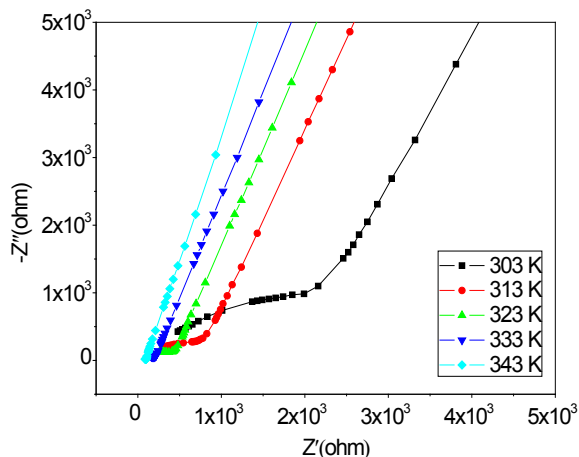


Fig.3 Cole-Cole plot for 85 mol% PVP-15 mol% NH₄Cl polymer electrolyte at different temperatures

Table 1 Ionic conductivity (σ) and activation energy (E_a) values for 85 mol% PVP:15 mol% NH_4Cl polymer electrolyte at different temperatures

Composi- tion of PVP: NH_4Cl (mol%)	Ionic conductivity, σ (S cm^{-1}) at different tempera- tures					E_a (eV)
	303 K	313 K	323 K	333 K	343 K	
85:15	2.51×10^{-5}	5.21×10^{-5}	9.38×10^{-5}	1.59×10^{-4}	3.17×10^{-4}	0.49

Fig.4 represents the variation of ionic conductivity with inverse temperature for 85 mol% PVP-15 mol% NH_4Cl over the temperature range from 303 to 343 K.

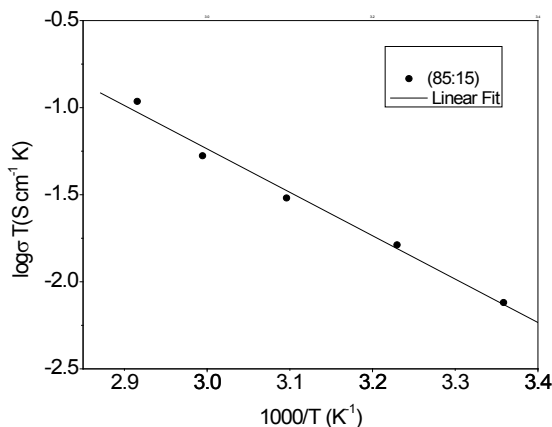


Fig.4 variation of ionic conductivity with inverse temperature for 85 mol% PVP-15 mol% NH_4Cl

The ionic conductivity of the electrolyte film increases with increasing temperature, indicating Arrhenius type thermally activated process given by the relation,

$$\sigma T = \sigma_0 \exp(-E_a/kT)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy for ion conduction and k is the Boltzmann constant. The activation energy value for the polymer electrolyte is calculated by linear fit of the Arrhenius plot and is given in **Table 1**. Low activation energy of 0.49 eV is obtained for the highest conducting sample (15 mol% NH_4Cl -doped sample). This may be due to the increase in amorphous nature of the polymer electrolyte with addition of salt that facilitates the ionic motion in the polymer network.

Transference Number Measurement

The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) transport number have been determined in PVP- NH_4Cl electrolyte systems using Wagner's dc polarization technique. In this technique, the dc current is monitored as a function of time on the application of fixed dc voltage of 1.02 V across the sample using aluminium blocking electrodes. **Fig.5** shows the variation of polarization current as a function of time for the polymer electrolyte, 85 mol% PVP-15 mol% NH_4Cl , possessing the highest conductivity at 303 K. The dc current decreases slowly and attains saturation.

The ionic transference number has been calculated from the polarization current versus time plot using the equations,

$$t_{\text{ion}} = (I_i - I_f) / I_i \quad \text{----- (3.8)}$$

$$t_{\text{ele}} = I_f / I_i \quad \text{----- (3.9)}$$

where I_i is the initial current and I_f is the final residual current.

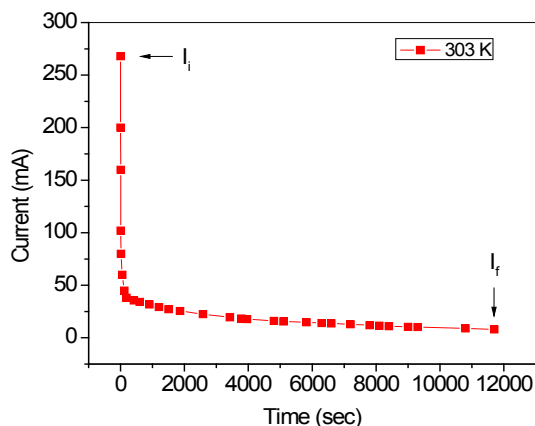


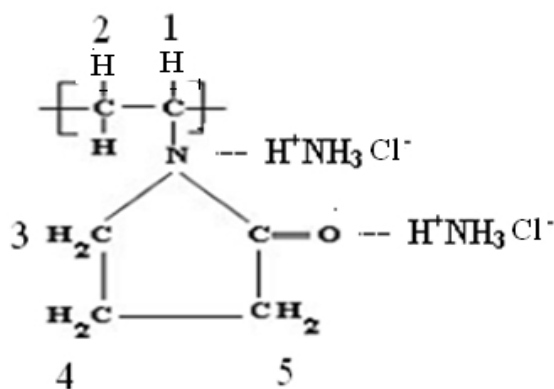
Fig.5 Variation of polarization current as a function of time for the polymer electrolyte, 85 mol% PVP-15 mol% NH_4Cl at 303 K

The ionic transference number (t_{ion}) for all PVP- NH_4Cl electrolyte systems has been found to be in the range of 0.93-0.97. This suggests that the charge transport in these electrolyte films is predominantly due to ions [12].

^1H NMR SPECTROSCOPIC ANALYSIS

The ^1H NMR measurements have been taken as a function of temperature for the pure PVP and the optimized polymer electrolyte (85 mol% PVP:15 mol% NH_4Cl).

The chemical structure of PVP has been shown in **Scheme 2** with the indication of different protons to make the discussion easier. The ^1H NMR spectrum of pure PVP at 298 K is shown in **Fig.6**. The broad peak observed at 3.59 ppm for pure PVP in the fig.6 can be attributed to the signals of NCH - position 1 in scheme 1 and NCH_2 - position 3 in scheme 1 fragments of PVP. Addition of NH_4Cl to the PVP matrix (sample with 85 mol% PVP and 15 mol% NH_4Cl) introduces some new peaks in the ^1H NMR spectrum of the sample. This may be due to the interaction of the salt with the host polymer PVP. The recorded ^1H NMR spectra for the highest conductivity sample (85 mol% PVP-15 mol% NH_4Cl) at different temperatures have been shown in **Fig.7**. Two peaks at ~ 3.3 ppm and ~ 6.8 ppm are more prominent in the spectra of the sample at 298 K.



Scheme 2 Chemical structure of PVP with the indication of different protons

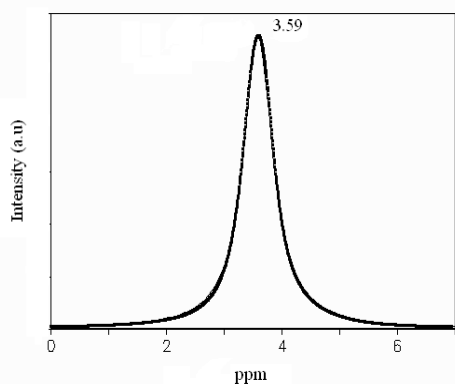


Fig. 6 ^1H NMR spectrum of pure PVP at 298 K

For better understanding, the resonance peaks observed in the ^1H NMR spectra of the sample have been deconvoluted using commercially available peak fit software. Fig.8 (a, b, c & d) represent the deconvoluted spectra of 15 mol% NH_4Cl doped polymer electrolyte at different temperatures. The resonance peaks have been fitted by Lorentzian lineshapes at all temperatures. Three resonance peaks at 6.83 ppm, 3.43 ppm and 3.27 ppm have been fitted for the ^1H NMR spectrum of the electrolyte at 298 K.

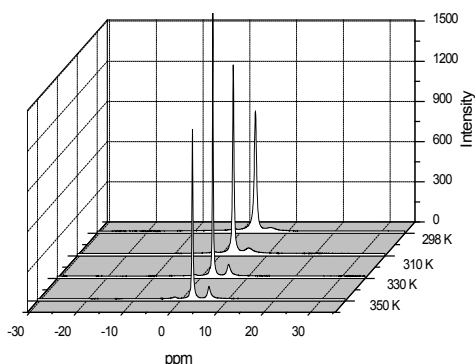


Fig.7 ^1H NMR spectra of 85 mol% PVP-15 mol% NH_4Cl polymer electrolyte at different temperatures

The peaks at 3.43 ppm and 3.27 ppm have been attributed to the signals of NCH and $-\text{NCH}_2$ of the fragments of PVP [13]. The peak centered at 6.83 ppm can be attributed to NH_4^+ proton [14,15]. The appearance of the peak at 6.83 ppm may be due to dissociation of salt into cation (NH_4^+) and anion (Cl^-) and that of the peaks at 3.43 ppm and 3.27 ppm may be due to the interaction of NH_4^+ ion with N atom of NCH and $-\text{NCH}_2$. In general, the N atom in NCH and $-\text{NCH}_2$ group has more electronegativity which can interact with electropositive NH_4^+ ion. With increasing temperature, changes in the chemical shifts have been observed in the ammonium peaks which strongly prove the interaction between the NH_4^+ and the host polymer matrix. At higher temperatures (330 K and 350 K), a new peak with chemical shift of ~ 2 ppm attributed to $-\text{CH}_2\text{C}=\text{O}$ of fragment of PVP has been observed. This may be due to the interaction of NH_4^+ with O atom of $-\text{CH}_2\text{C}=\text{O}$ at higher temperatures which confirms the segmental motion of the host polymer. It is seen that the lineshape and the width of solid state NMR spectra are strongly temperature-dependent anisotropic nuclear spin interactions. As the temperature rises, the molecular motion is accelerated and narrowing of lineshape will occur [16].

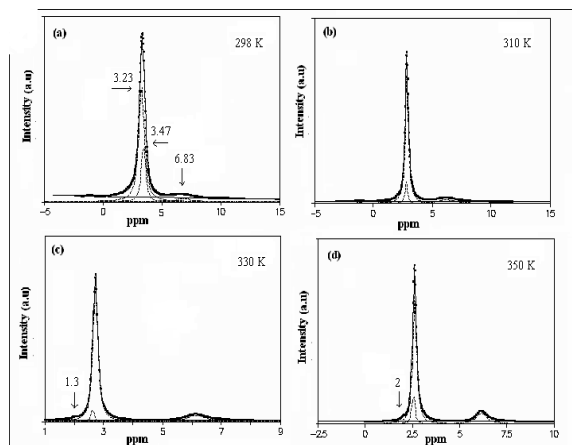


Fig.8 Deconvoluted ^1H NMR spectra of 85 mol% PVP-15 mol% NH_4Cl polymer electrolyte at different temperatures (a) 298 K (b) 310 K (c) 330 K (d) 350 K

It is observed that the linewidth of the NH_4^+ ion peak decreases with increasing temperature indicating an increase in the mobility of NH_4^+ proton in the polymer electrolyte. Similar results have been reported by Nader Binesh et al. [17], S. Selvasekarapandian et al. [8] and Muthusamy HEMA et al. [18] for PEG: NH_4ClO_4 , PVA: $\text{CH}_3\text{COONH}_4$ and PVA: NH_4X ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) polymer electrolyte systems, respectively.

From DSC analysis, the T_g of the polymer complex with 15 mol% salt has been found to be 332 K. Hence the appearance of the peak at 1.3 ppm at 330 K is found to be consistent with DSC results which explain the segmental motion of the polymer electrolyte.

The proton NMR line width of ammonium proton peak and conductivity as a function of temperature for the polymer electrolyte with 85 mol% PVP-15 mol% NH_4Cl has been shown in Fig.9.

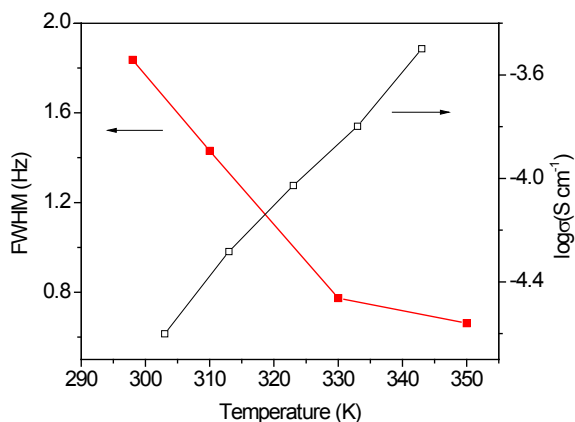


Fig.9 Proton NMR line width of ammonium proton peak and conductivity as a function of temperature for the polymer electrolyte with 85 mol% PVP-15 mol% NH_4Cl

The FWHM of the ammonium proton signal decreases with increase of temperature. The decrease in line width of the peak with increase of temperature indicates the increase in proton mobility and hence the conductivity. Hence the conductivity results are found to be consistent with the NMR results.

CONCLUSION

Proton conducting polymer electrolyte based on PVP- NH_4Cl complex of various compositions has been prepared by solu-

tion casting technique. The complex formation between the polymer and the salt has been confirmed by FT-IR analysis. The DSC analysis shows that the glass transition temperature (T_g) decreases with the addition of salt and the sample with 15 mol% NH_4Cl has T_g of 332 K. The highest ionic conductivity has been found to be $2.51 \times 10^{-5} \text{ S cm}^{-1}$ at 303 K for 85 mol% PVP-15 mol% NH_4Cl which has low activation energy

of 0.49 eV. The ionic transference number measurements suggest that the charge transport in these electrolyte films is predominantly due to ions. The temperature dependent ^1H NMR study reveals the increase in mobility of ammonium proton in the polymer electrolytes with increasing temperature. By combining the NMR results, the ionic transport in these polymer electrolytes is mainly due to protons.

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