International Journal of Latest Research in Engineering and Technology (IJLRET)
ISSN: 2454-5031
www.ijlret.com ǁ PP.95-99

Preparation and characterization of proton conducting polymer electrolyte based on PVA, amino acid proline and NH_4SCN

R.Hemalatha[1], M.Alagar[2], S.Selvasekarapandian[3], B.Sundaresan[2]
[1]*S.F.R.College for women,Sivakasi.*
[2]*Centre for research and Post graduate studies in Physics, AyyaNadarJanakiAmmal College, Sivakasi.*
[3]*Materials Research Centre, Coimbatore.*
Corresponding author: S.Selvasekarapandian
E- mail id: sekarapandian@rediffmail.com

Abstract: Polymer electrolytes are an important component of many electrochemical devices. In the present study, an attempt has been made to prepare the proton conducting polymer electrolytes based on poly vinyl alcohol doped with amino acid proline and different molar ratios of ammonium thiocyanatethat have been prepared by Solution Casting Technique using distilled water as solvent. The maximum conductivity has been found to be **1.17×10^{-3} S/cm** at ambient temperature for 75Mwt% PVA: 25Mwt% Proline: 0.5 molar mass percentage NH_4SCN polymer membrane using AC impedance analyzer. The temperature - dependent conductivity of the polymer membrane obeys Arrhenius behavior. The highest ionic conductivity polymer electrolyte has low activation energy **0.08eV** among the prepared polymer electrolytes. The dielectric spectra exhibit the low frequency dispersion due to space charge accumulation at the electrode – electrolyte interface.

Keywords: AC Impedance analyzer, Dielectric studies.

1. Introduction:

Solid polymer electrolytes have attracted the attention of scientists, because of its good ionic conductivity, flexibility, long life time, good mechanical strength, short time period of film formation and the possibility of their application parts such as fuel cells, electro chromic display devices, gas sensors and super capacitors etc. Many people have already worked with polymer PVA (Polyvinyl alcohol) because of its good film forming nature, flexibility, low cost, semi - crystalline nature, high tensile strength and its hydroxyl group.Proline ($C_5H_9NO_2$) is one of the non- essential amino acid of molar mass 115.13 g/mol. The amino acid proline helps in the regeneration of skin and helps to reduce sagging and wrinkles. The author Bhuvaneswari et al has already reported on the conductivity studies of amino acid (25Mwt% Proline) doped with PVA (75Mwt% PVA) based polymer electrolytes and ionic conductivity value in the order of
$\sim10^{-5}$S/cm**[1]**.Literature studies reveal that ammonium salts are good proton donors **[2]**.In the present work, different molar mass percentage of salt NH_4SCN has been added with 75Mwt% PVA: 25Mwt% Proline in order to enhance its conductivity. The prepared polymer electrolytes have been subjected to AC- Impedance technique.

2. Experimental Procedure

2.1 Sample Preparation

In the present study, poly vinyl alcohol PVA (MERK) of average molecular weight of 1,25,000 and the amino acid proline of molecular weight of 115.13 g/mol (LOBA CHEMIE) are used as starting material with water as solvent. 75Mwt% of host polymer PVA and 25Mwt% of amino acid proline was dissolved using water as solvent. Then the different concentrations of NH_4SCN were dissolved individually in water and these solutions were added to the PVA: Proline solution and stirred well by using magnetic stirrer to obtain a homogeneous mixture. The obtained mixture is casted in propylene petridish and kept in hot air oven under 50°C for one day. Mechanically strong, transparent and flexible films have been obtained.

2.2 Characterization

AC impedance study

Conductivity measurements have been carried out by using a HIOKI – 3532 LCZ meter in the frequency range of 42 Hz – 1MHz over the temperature range of 303K – 343K.

3. Results and Discussion

3.1 Conductivity Analysis

Conductance spectra

The conductance spectra describe the frequency dependence of the conductivity. The typical log ωversuslog σ relation for 75 Mwt% PVA: 25Mwt%Proline, 75 Mwt% PVA: 25Mwt%Proline: 0.4 (molar mass percentage) NH_4SCN, 75Mwt% PVA: 25 Mwt%Proline: 0.5 (molar mass percentage) NH_4SCN,and 75Mwt% PVA: 25 Mwt% Proline: 0.6 (molar mass percentage) NH_4SCN at 303 K have been shown in the **Figure 1** respectively.

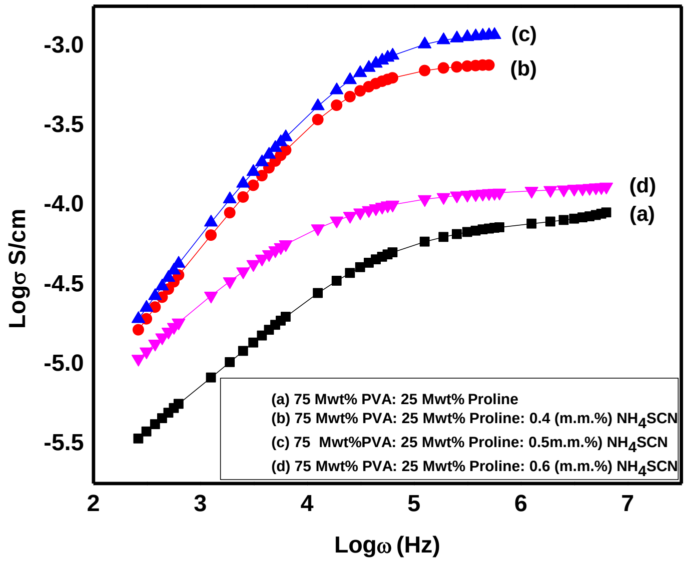

Fig.1. Conductance spectra of (a) 75 Mwt% PVA:25Mwt%Proline (b) 75 Mwt% PVA: 25 Mwt% Proline: 0.4 (m.m.%) NH_4SCN (c) 75 Mwt% PVA: 25 Mwt% Proline: 0.5 (m.m.%) NH_4SCN (d) 75Mwt% PVA: 25 Mwt% Proline: 0.6 (m.m.%) NH_4SCN at 303K

Table 1: Ionic conductivity values of PVA: Proline: NH_4SCNpolymer electrolytes at ambient temperature

Composition PVA:Proline: NH_4SCN (mol %)	**Ionic conductivity(σ_{dc}) for different compositions of PVA:Proline: NH_4SCN at 303K ($S\ cm^{-1}$)**
75:25	7.41×10^{-5}
75:25: 0.4	7.58×10^{-4}
75:25: 0.5	**1.17×10^{-3}**
75:25: 0.6	1.31×10^{-4}

From **Figure 1**the conductance spectra of complexes have low frequency region due to the space charge polarization at the blocking electrodes and plateau region corresponding to dc conductivity **[3]**. The maximum conductivity is observed for 75Mwt% PVA: 25Mwt% Proline: 0.5 molar mass percentage of NH_4SCN polymer electrolyte.

3.2 Temperature dependent conductivity

The temperature dependent conductivity of all polymer electrolytes is shown in **Figure 2.**From the figure, the conductivity increases linearly with increase in temperature for all the composition of polymer electrolytes. Arrhenius equation is given by,

$$\sigma = \sigma_0 \exp\left(-{E_a}/{KT}\right)$$

whereσ_o is pre-exponential factor and E_a is the activation energy of the polymer electrolytes.

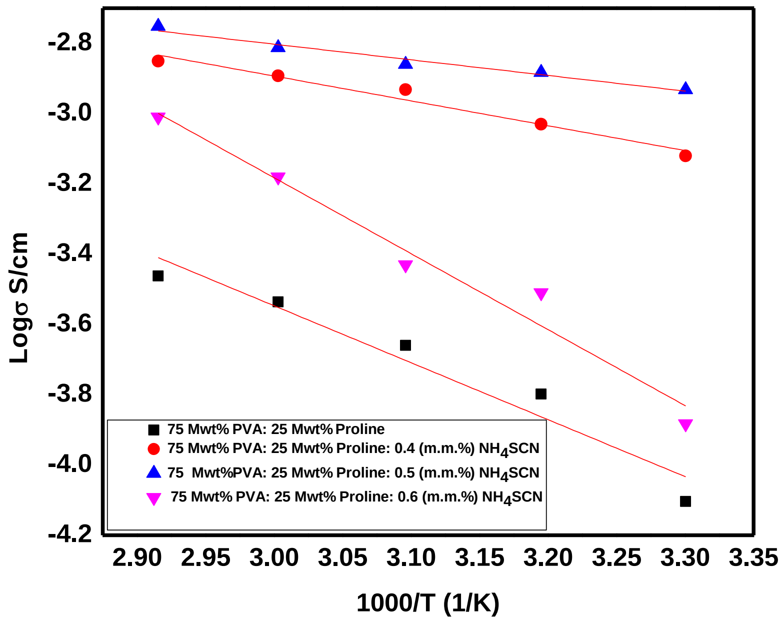

Fig.2. Arrhenius plot of (a) (a) 75 Mwt% PVA:25Mwt%Proline (b) 75 Mwt% PVA: 25 Mwt% Proline: 0.4 (m.m.%) NH_4SCN (c) 75 Mwt% PVA: 25 Mwt% Proline: 0.5 (m.m.%) NH_4SCN (d) 75Mwt% PVA: 25 Mwt% Proline: 0.6 (m.m.%) NH_4SCN.

Table 2 Activation Energy Values of PVA:Proline: NH_4SCN polymer Electrolytes

Composition of PVA:Proline: NH_4SCN (mol %)	**E_a (eV)**	**Regression values**
75:25	0.32	0.92
75:25: 0.4	0.14	0.96
75:25: 0.5	**0.08**	**0.96**
75:25: 0.6	0.42	0.96

It is also understood that the increase in conductivity with increase in temperature is related to the decrease in viscosity which in turn increases chain flexibility **[4]**. The activation energy E_a, evaluated from the slope of the plots.The 75 Mwt% PVA: 25 Mwt% Proline: 0.5 (m.m.%) NH_4SCN polymer matrix shows low activation energy of **0.08eV** leading to high ionic conductivity of **1.17×10^{-3} S/cm** at **303 K**.The regression values are very close to unity suggesting that it obeys the Arrhenius equation (**Table 2)**.The low activation energy for the ion transport is due to the increase in amorphous nature of the polymer electrolytes that facilitates the fast proton ion motion in the polymer network.

3.3 Dielectric Analysis

The dielectric response is generally described by the complex permittivity,

$$\varepsilon^* = \varepsilon'(\omega) - i\varepsilon''(\omega)$$

where real ε'(ω) and imaginary ε"(ω) components are the storage and the loss of energy in each cycle of the applied electric field.The log ω vsε' and ε" plots for 75 Mwt% PVA: 25 Mwt% Proline: 0.5 (m.m.%) NH_4SCN of four different temperatures are shown in Figure 3 and 4 respectively.

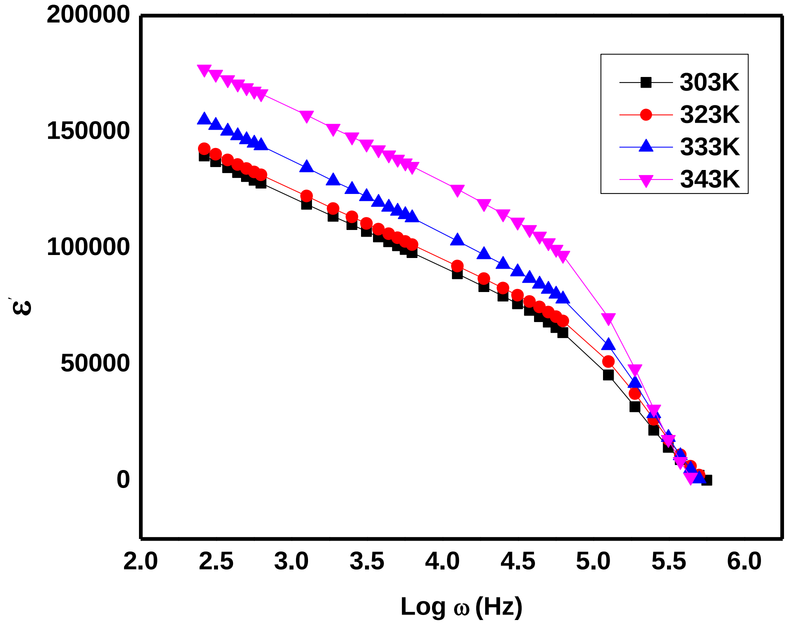

Fig.3. Variation of ε′ as a function of frequency for 75 Mwt% PVA: 25 Mwt% Proline: 0.5 (m.m.%) NH_4SCN atdifferent temperatures

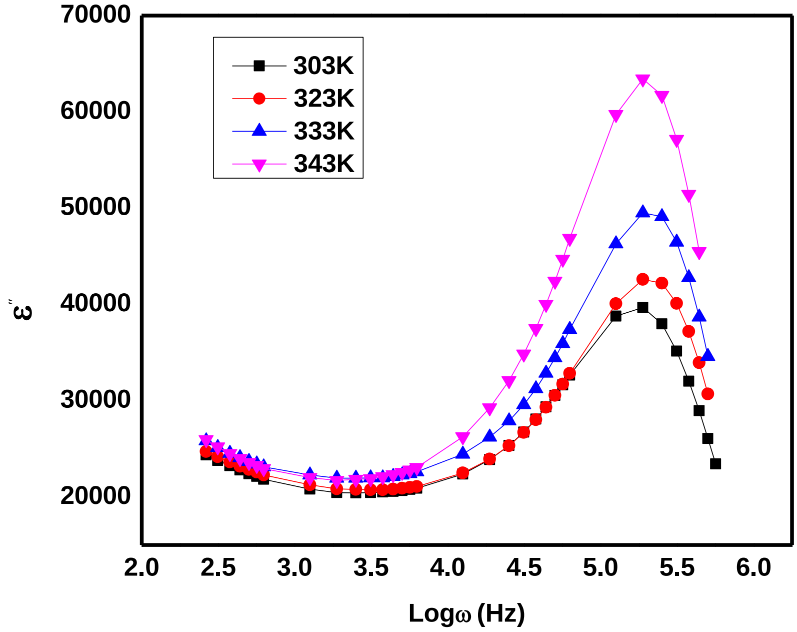

Fig.4. Variation of ε″ as a function of frequency for 75 Mwt% PVA: 25 Mwt% Proline: 0.5 (m.m.%) NH_4SCN at different temperatures

If the dielectric loss and dielectric constant of the material increases, the amount of charge stored by the material will also increase. The log ω vs ε' and ε'' plots for 75Mwt% PVA: 25Mwt% proline: 0.5(m.m.%) NH_4SCN of different temperatures are shown in respectively. From the **Figure 3**, the values of dielectric constant ε' is very high at lower frequencies due to free charge motion and presence of charge effects within the polymer membrane. From the **Figure 4**, the value of ε" is very high due to the higher charge carrier density. At the high frequency side, the curve consists of a relaxation peak. At the low frequency side β relaxation is also observed and the relaxation time has been calculated by using the following equation,

$$\tau = 1/\omega_p \, (s)$$

The hopping frequency (ω_p) and relaxation time (τ) obtained from dielectric loss spectra of 75 Mwt% PVA: 25Mwt% proline: 0.5(m.m.%) of NH_4SCN for different temperatures. Relaxation time (τ) is nearly found to be constant (5.3703E-06 s) for different temperatures. The intensity of peak increases with increase in temperature due to the movement of the side chain increases with respect to temperature**[4]**.

Conclusion

PVA and amino acid Proline based polymer electrolytes with different concentrations of ammonium thiocyanate have been prepared by solution casting technique using distilled water as solvent.

- The highest ionic conductivity has been found to be **1.17×10^{-3} Scm^{-1}** for 75 Mwt% PVA: 25Mwt% proline: 0.5(m.m.%) of NH_4SCN polymer electrolyte from the conductance spectra.
- Temperature – dependent conductivity of polymer electrolytes obeys the Arrhenius equation.
- The dielectric loss spectra of the polymer doped proline and NH_4SCN exhibits β relaxation.

References

[1]. Bhuvaneswari R, Karthikeyan S, Selvasekarapandian S, VinothPandi D, Vijaya N, ArunAraichimani, Sanjeeviraja C. Preparation and characterization of PVA complexed with amino acid proline, Ionics.2014; 21: 387.

[2]. Ramya C S, Selvasekarapandian S, Savitha T, Hirankumar G Baskaran R, BhuvaneswariM S, Angelo P C. Conductivity and thermal behavior of proton conducting polymer electrolyte based on poly (N-vinyl pyrrolidone), Eur. Polym.J. 2006; 42: 2672- 2677.

[3]. Radha KP, Selvasekarapandian S, Characterization of PVA: NH_4F: ZrO_2 Composite Polymer Electrolytes,IJSR. 2012; 1:119.

[4]. VinothPandi D, Selvasekarapandian S, Bhuvaneswari R, Premalatha M, Monisha S, Arunkumar D, Kawamura Junichi. Development and characterization of proton conducting polymer electrolyte based on PVA, amino acid glycine and NH_4SCN, Solid state ionics. 2016; 298: 15- 22.