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Research Paper Physics

Effect of PC on Solid Polymer Electrolyte Based on PVA

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ABSTRACT

Solid polymer electrolytes based on Poly(vinyl alcohol) (PVA) as host polymer, ammonium chloride (NH4Cl) as salt and propylene carbonate (PC) as plasticizer have been prepared by solution casting technique. The prepared polymer electrolytes have been characterized by impedance spectroscopy and FTIR spectroscopy. The FTIR analysis reveals complex formation among the polymer, salt and plasticizer of the electrolytes. From ac impedance spectroscopic studies, it has been found that 85PVA:15NH4Cl:20 PC has high ionic conductivity of 2.16×10-5 Scm-1 at ambient temperature. The temperature dependent conductivity of the electrolyte obeys the Arrhenius equation. The activation energy of the high conductivity sample 85 PVA:15 NH4Cl: 20 PC is 0.138 eV, which is considerably lower than that of the electrolyte without the plasticizer.

KEYWORDS : Arrhenius plot, Conductance spectra, FTIR

1.Introduction

A Proton-conducting polymer electrolytes are an important class of materials due to its application for the development of fuel cells, solid state batteries, sensors and electrochemical devices **[1]**. The main advantages of polymeric electrolytes are their mechanical properties, ease of fabrication of thin films of desired sizes and their ability to form proper electrode–electrolyte contact **[2]**. An intense research has been focused on the development of solid polymer electrolytes with high ionic conductivity at ambient temperature and good chemical and mechanical stability for their applications in electrochemical devices. Several approaches have been made to improve the conductivity of polymer electrolytes. Adding plasticizer such as propylene carbonate (PC) to polymer electrolytes is a useful technique to enhance the conductivity of polymer system. These plasticizers impart salt-solvating power and high mobility to the ions in the polymer electrolytes and also increase the amorphous content of the polymer matrix.

A variety of plastisized polymer electrolytes based on various host polymers **[3]** have been developed for solid state applications. Hydroxyl containing poly (vinyl alcohol) (PVA) is a semi crystalline polymer, studied extensively because of its many interesting physical properties, having high dielectric strength (1,000 kV/mm), good charge storage capacity and dopant dependent electrical and optical properties which arise from the presence of OH groups and the hydrogen bond formation.

It has been found from our earlier work that the polymer electrolyte with 85 PVA and 15 NH_4Cl (optimized sample) has the highest conductivity of 1.12×10^{-5} S cm^{-1} at ambient temperature. Now an attempt has been made to enhance the ionic conductivity of 85 PVA and 15 NH_4Cl by incorporating the plasticizer propylene carbonate in different molar ratios. The prepared polymer electrolytes have been subjected to different analysis.

2.Experimental details

The polymer PVA of average molecular weight of 1,25,000 (AR grade SD fine chemicals) , NH_4Cl (AR grade, Merck) and PC (AR grade, Merck) are used in the present work. DMSO solutions of PVA and NH_4Cl are stirred continuously with a magnetic stirrer. After complete dissolution of the salt, PC is added accordingly and the mixtures are stirred well for several hours to obtain homogeneous solutions. The solutions are then cast in poly propylene Petri dishes, and the samples are vacuum dried at 70°C for 5 days in a vacuum oven until the films are formed. Mechanically strong and flexible films have been obtained.

3. Results and Discussion

3.1. FTIR Analysis

On addition of the salt into the polymer host, the cation of the metal is expected to coordinate with the polar groups in the host polymer matrix resulting in the complexation.

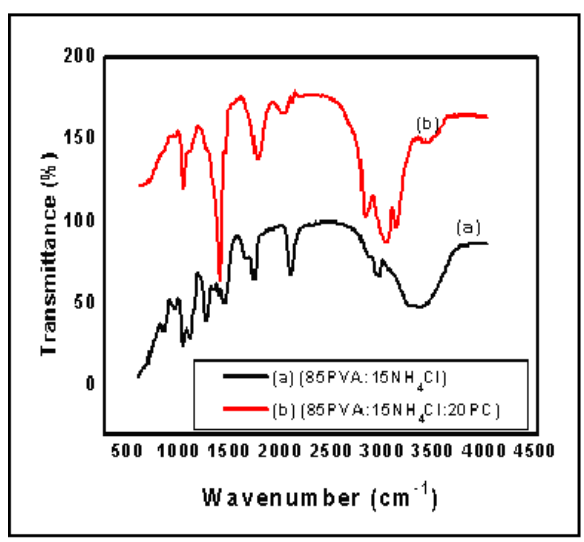

Fig.1.FTIR spectra of (a) 85 PVA:15 NH_4Cl and (b) 85 PVA:15 NH_4Cl:20PC

This type of interaction will influence the local structure of the polymer backbone and certain infrared active modes of vibration will be affected. In this context, the infrared spectroscopic studies will give the evidence of the complexation. The FTIR spectrum of optimized systems of 85 PVA:15 NH_4Cl and 85 PVA:15 NH_4Cl:20 PC are shown in **Figure.1.**

Table 1 Absorption bands & assignments of all plasticized polymer electrolytes.

Absorption bands for 85PVA:15NH_4Cl:XPC (mol%)		Assignment
X = 0	X = 20	
945	947	O-H Out of plane (b)
1020	1024	C-C (S)
1373	1388	O-H In plane (b)
1431	1436	C-O (S)
1720	1753	C=O (S)
2073	2094	C-N (S)
2939	2808	CH_2 or CH (asymmetric)

The positions of vibrational bands observed in the FTIR spectra of 85 PVA:15 NH_4Cl (unplasticised) and 85 PVA:15 NH_4Cl:20 PC and their assignments are listed in Table 1. The bands at 945 cm^{-1}, 1373 cm^{-1}, 1431 cm^{-1} and 1720 cm^{-1} have been assigned to O-H out of plane bending, O-H in plane bending, C-O stretching (coupled) (or) O-H in plane bending and C=O stretching vibrations of 85PVA :15NH_4Cl get shifted in 85 PVA:15 NH4Cl:20 PC[4]. The shift in the peak positions and changes in the intensity of the bands in the FTIR spectra of the samples with and without plasticizers confirm the complex formation between the polymer, the salt and the plasticizers**.**

3.2. AC impedance analysis

3.2.1. Conductance spectra analysis

The frequency dependent of the conductivity for two polymer electrolytes at 303K is depicted in **Figure.2.**

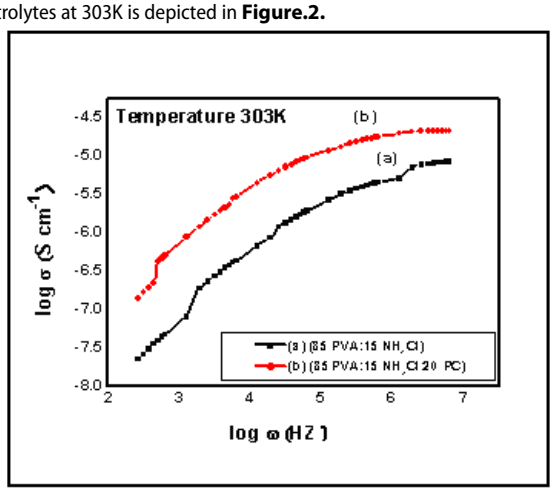

Fig.2. Conductance spectra of (a) 85 PVA:15 NH_4Cl and (b) 85 PVA:15 NH_4Cl:20PC at 303K.

On addition of 20 mol% PC, the conductivity value of 85 PVA: 15 NH_4Cl film increases from 1.12×10^{-5} to 2.16×10^{-5}. The high dielectric constant of PC may allow greater dissolution of the electrolyte salt resulting in an increased number of charge carriers and hence conductivity. The ionic conductivity values of 85 PVA: 15 NH_4Cl:XPC (X=0,20mol%) polymer electrolytes at different temperatures are presented in table 2.

Table.2. Ionic conductivity of all plasticized polymer electrolytes

Composition of 85PVA:15NH_4Cl : XPC (mol%)	Ionic conductivity (Scm^{-1})		
	303K $\times10^{-5}$	**333K** $\times10^{-5}$	**343K** $\times10^{-5}$
X=0	1.12	1.25	1.87
X=20	2.16	3.13	4.88

3.2.2.Temperature dependence of ionic conductivity

The temperature dependence of conductivity for (85PVA:15NH_4Cl) and (85 PVA:15 NH_4Cl: 20 PC) polymer electrolytes over a temperature range 303-345 K is shown in **Figure.3.**

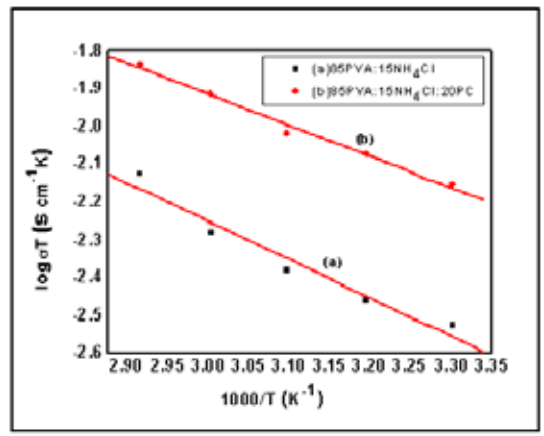

Fig.3. Conductivity Vs Temperature plot of (a) 85 PVA:15 NH_4Cl and (b) 85 PVA:15 NH_4Cl:20PC

The plot shows that the conductivity increases with increase of temperature. The apparent role of a plasticizer in a host polymer is to decrease viscosity of the electrolyte thereby enhances the chain flexibility.

From the Table 3, it has been observed that the calculated regression values of all the electrolytes are close to unity. It suggests that the prepared polymer electrolytes follow Arrhenius equation,

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

where σ_0 is the conductivity pre-exponential factor and E_a is the activation energy for conduction. The nature of cation transport is quite similar to that occurring in ionic crystal, where ions jump in to neighboring vacant sites and hence, increase conductivity to higher value.

Table 3 Ionic conductivity and activation energy values for polymer electrolytes

Composition of 85PVA : 15NH_4Cl : XPC (mol%)	Activation energy, E_a (eV)	Regression	Standard value
X=0	0.141	0.9683	0.0322
X=20	0.138	0.9942	0.0157

The activation energy E_a calculated from the slope of the plots has been presented in the Table 3. The low activation energy of the plasticized electrolyte is suitable for electrochemical devices.

4.Conclusion

PVA:NH_4Cl and PVA:NH_4Cl:PC proton conducting polymer electrolyte have been prepared by solution casting technique.. The complexation behavior among the polymer, the salt and the plasticizers has been confirmed by FTIR studies. Ionic conductivity of the electrolyte increases by the addition of 20mol% PC to 85PVA:15 NH_4Cl polymer electrolyte. This may be due to the lowering of viscosity with the addition of plasticizer. The prepared electrolytes follow Arrhenius equa-

tion in the temperature range of 303 to 343 K.

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