Characterization of Plasticized Solid Polymer Electrolyte by AC Impedance Spectroscopy

Physics

KEYWORDS : solid polymer electrolytes, plasticizers, ionic conductivity, complex impedance

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ABSTRACT

Solid polymer electrolytes based on poly (N-vinyl pyrrolidone) (PVP) as host polymer, ammonium chloride (NH_4Cl) as complexing salt, propylene carbonate (PC) and ethylene carbonate (EC) as plasticizers have been prepared by solution casting technique and their complex formation has been confirmed by Fourier Transform Infrared Spectroscopy. AC impedance measurements have been carried out on the samples to find out the conductivity of the films. The film containing 85 mol% PVP, 15 mol% NH4Cl, 0.001 mol% of PC and EC each, has been found to have high ionic conductivity. The temperature dependent conductivity of the electrolyte with and without plasticizers appears to obey the Arrhenius Law. The activation energy of the plasticized polymer electrolyte, 85 mol% PVP:15 mol% NH_4Cl: 0.001 mol% PC:0.001 mol% EC is 0.517 eV, which is considerably lower than that of the film without the plasticizers. The dielectric behaviour of the electrolyte has been discussed.

1. Introduction

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 plasticizers such as propylene carbonate (PC) (ε' = 64.4) and ethylene carbonate (EC) (ε' = 89.6) 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 and tend to dissociate ion-pairs into free cations and anions thereby leading to an overall enhancement in conductivity. A variety of plastisized polymer electrolytes based on various host polymers **[1-3]** have been developed for solid state applications. In this work, the plasticized polymer electrolyte systems composed of poly (N-vinyl pyrrolidone) (PVP) as host polymer, ammonium chloride (NH_4Cl) as dopant salt, propylene carbonate (PC) and ethylene carbonate (EC) as plasticizers have been prepared by solution casting technique. The conductivity of the samples has been measured by ac impedance spectroscopy**.**

2. Experimental details

The polymer PVP of average molecular weight, M_w of 40,000 (S d fine chemicals), NH_4Cl (Spectrum), PC (Himedia) and EC (Himedia) have been used in the present work. It has been found from our earlier work that the polymer electrolyte with 85 mol% PVP and 15 mol% NH_4Cl (optimized sample) prepared by solution-casting technique using distilled water as solvent has the highest conductivity of 2.51×10^{-5} S cm^{-1}. In the present work, the plasticized polymer electrolytes have been prepared by adding 0.001 mol%, 0.002 mol% and 0.003 mol% of the plasticizers, PC and EC to the optimized polymer sample, 85 mol% PVP:15 mol% NH_4Cl. Aqueous solutions of PVP and NH_4Cl are stirred continuously with a magnetic stirrer. After complete dissolution of the salt, EC and PC are 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 48 hours until the films are formed. Thin films of thickness of 104-183 µm have been obtained. The FTIR spectra for pure PVP and for the plasticized polymer-salt complexes have been recorded at room temperature in the transmission mode using SHIMADZU IR Affinity-1 Spectrometer in the wavenumber range of 400 cm^{-1}- 4000 cm^{-1}. The electrical measurements have been performed on the prepared 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 – 50 LCR Hi-Tester interfaced with a computer.

3. Results and Discussion

3.1. FTIR Analysis

FTIR Spectroscopy is a versatile tool to analyze the polymeric materials since it provides information about the interaction between the polymer and the ions. **Figure-1** illustrates the FTIR spectra of pure PVP, 85 mol% PVP:15 mol% NH_4Cl, 85 mol% PVP:15 mol% NH_4Cl:0.001 mol% EC:0.001 mol% PC and 85 mol% PVP:15 mol% NH_4Cl:0.002 mol% EC:0.002 mol% PC.

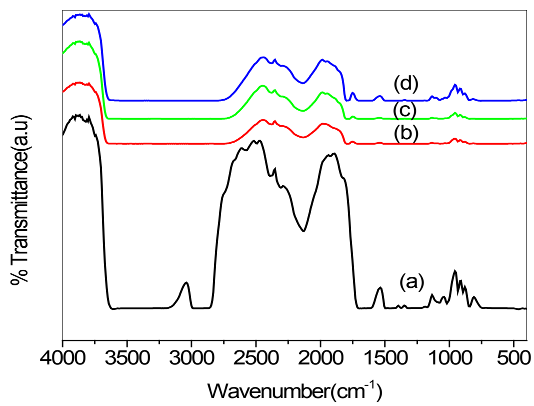


Figure-1 FTIR spectra of (a) Pure PVP (b) 85 PVP:15 NH_4Cl (c) 85 PVP:15 NH_4Cl:0.001 EC:0.001 PC and (d) 85 PVP:15 NH_4Cl:0.002 EC:0.002 PC in mol%

The positions of vibrational bands observed in the FTIR spectra of pure PVP, polymer-salt complex with 85 mol% PVP:15 mol% NH_4Cl (unplasticised) and various compositions of plasticized polymer electrolytes (PVP:NH_4Cl:EC:PC) and their assignments are listed in **Table 1.** The bands at 2129 cm^{-1}, 1697 cm^{-1}, and 844 cm^{-1} have been assigned to C-N stretching, C=O stretching and CH_2 rocking vibrations of pure PVP **[4].** The bands at 2129 cm^{-1} and 1697 cm^{-1}are found to be shifted to higher wavenumbers in the polymer-salt complex and in the plasticized polymer electrolytes as shown in the Table 1.

The vibrational peak at 844 cm^{-1} has been shifted to 840 cm^{-1} when salt is added. The peaks at 1018 cm^{-1} and 1080 cm^{-1} in the pure PVP attributed to C–C bonding effect have been shifted to lower wavenumbers in the polymer-salt complex and in the plasticized PVP system. The peak observed at 1173 cm^{-1} has been assigned to CH_2 wagging vibration of pure PVP and it has been found to be displaced to lower wavenumbers in the plasticized polymer complexes. The vibrational band at 2875 which has been assigned to CH_2 or CH Stretching in the pure PVP gets shifted to lower wavenumbers in the complexed systems with EC and PC. The shifting may be due to the interaction of the salt with the polymer matrix. The shift in the peak positions and changes in the intensity of the bands in the FTIR spectra of the salt doped samples with and without plasticizers confirm the complex formation between the polymer, the salt and the plasticizers.

Table 1 FTIR spectral assignments for various compositions of PVP:NH_4Cl:EC:PC plasticized polymer electrolytes

Absorption bands for different compositions of PVP: NH_4Cl :EC:PC in mol%				Assignment
Pure PVP	85PVP: 15NH_4Cl	85 PVP: 15 NH_4Cl :0.001 EC :0.001 PC	85PVP: 15NH_4Cl :0.002 EC :0.002 PC	
844	840	840	840	CH_2 Rocking
1018	1002	1015	1018	C-C Stretching
1080	1072	1076	1072	C-C Stretching
1173	1170	1156	1162	CH_2 Wagging
1697	1712	1704	1708	C=O Stretching
2129	2133	2137	2137	C-N Stretching
2875	2762	2774	2790	CH_2 or CH Stretching

3.2. AC impedance spectroscopy studies
3.2.1. Complex impedance analysis

AC impedance spectroscopy is a powerful experimental tool for characterizing the electrical properties of materials. The complex impedance (Cole–Cole) plots for the electrolyte system 85 mol% PVP doped with 15 mol% NH_4Cl (unplasticized) and for the systems plasticized by PC and EC each with 0.001 and 0.002 mol% concentrations are shown in **Figure 2.**

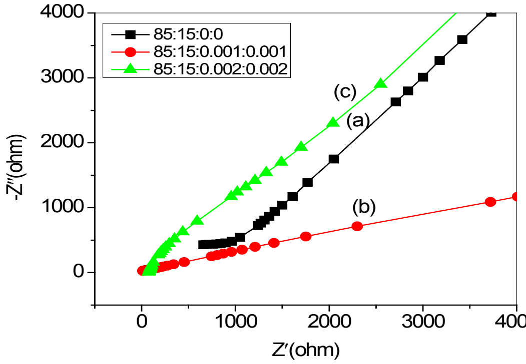


Figure 2 Complex impedance plots for (a) 85 PVP:15 NH_4Cl (b) 85 PVP:15 NH_4Cl:0.001 EC:0.001 PC and (c) 85 PVP:15 NH_4Cl:0.002 EC:0.002 PC in mol% at 303 K

The plot consists of a high frequency semicircle and a low-frequency spike. 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 intercept of the semicircle or spike with the real impedance (Z') axis gives the bulk electrical resistance (R_b) of the polymer electrolytes.

The ionic conductivity (σ) of the polymer electrolytes has been calculated using the equation,

$$\sigma = l/AR_b$$

where l and A are the thickness and area of the polymer electrolyte, respectively. The highest ionic conductivity at ambient temperature has been found to be 2.78×10^{-4} S cm^{-1} for 85 PVP:15 NH_4Cl:0.001 EC:0.001 PC polymer electrolyte. **Figure 3** represents the complex impedance plot of the highest conductivity sample at different temperatures. The ionic conductivity values for the unplasticized polymer film (85 mol% PVP:15 mol% NH_4Cl) and for the plasticized systems with different concentrations of EC and PC at different temperatures are presented in

Table 2.

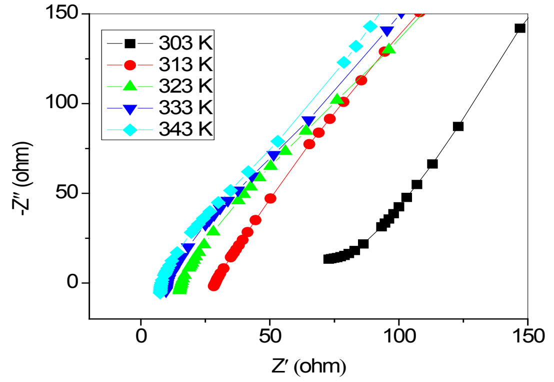
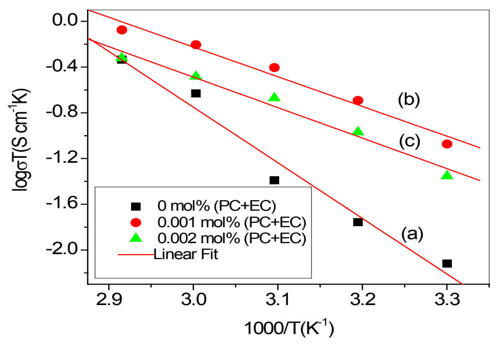


Figure 3 Complex impedance plots for 85 PVP:15 NH_4Cl:0.001 EC:0.001 PC in mol% at different temperatures

On addition of 0.001 mol% of PC and 0.001 mol% of EC, the conductivity value of 85 PVP: 15 NH_4Cl film increases from 2.51×10^{-5} to 2.78×10^{-4}. The higher dielectric constant of PC and EC may allow greater dissolution of the electrolyte salt resulting in increased number of charge carriers and hence conductivity. The apparent roles of a plasticizer in a host polymer are to decrease viscosity of the electrolyte and assist in the dissociation of the salt thereby increasing the number of charge carriers **[5]**. The decrease in conductivity at higher concentration of EC and PC may be due to the formation of ion aggregates.

3.2.2. Temperature dependent conductivity

The temperature dependence of conductivity for the electrolytes with (85 PVP:15 NH_4Cl), (85 PVP:15 NH_4Cl:0.001 EC:0.001 PC) and (85 PVP:15 NH_4Cl:0.002 EC:0.002 PC) is shown in **Figure 4**.



The plots show that the conductivity increases with increase of temperature. The calculated regression values for all the films are close to unity. This indicates that the plots obey Arrhenius law,

Table 2 Ionic conductivity and activation energy values for polymer electrolytes

PVP:NH_4Cl: EC:PC (mol%)	Ionic conductivity, σ (S cm^{-1})			Activation Energy, E_a (eV)	Regression
	303 K	323 K	343 K		
85:15: 0:0	2.51×10^{-5}	1.26×10^{-4}	1.35×10^{-3}	0.967	0.986
85:15: 0.001:0.001	2.78×10^{-4}	1.22×10^{-3}	2.46×10^{-3}	0.517	0.987

PVP:NH_4Cl: EC:PC (mol%)	Ionic conductivity, σ (S cm^{-1})			Activation Energy, E_a (eV)	Regression
	303 K	323 K	343 K		
85:15: 0.002:0.002	1.46×10^{-4}	6.61×10^{-4}	1.33×10^{-3}	0.522	0.987

Figure 4 Variation of conductivity with inverse temperature for (a) 85 PVP:15 NH_4Cl (b) 85 PVP:15 NH_4Cl:0.001 EC:0.001 PC and (c) 85 PVP:15 NH_4Cl:0.002 EC:0.002 PC in mol%

$\sigma T = \sigma_0 \exp(-E_a/kT)$ 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 into neighboring vacant sites and hence, increase conductivity to higher value **[6].** It is also understood that the increase in conductivity with temperature can be linked to the decrease in viscosity and hence increased chain flexibility **[7]** The activation energy, E_a, evaluated from the slope of the plots for the films with (85 mol% PVP:15 mol% NH_4Cl), (85 mol% PVP:15 mol% NH_4Cl:0.001 mol% EC:0.001 mol% PC) and (85 mol% PVP:15 mol% NH_4Cl:0.001 mol% EC:0.001 mol% PC) have been presented in the **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 ion motion in the polymer network. The increase in amorphous nature also provides a bigger free volume in the polymer electrolyte system upon increasing the temperature **[8]**.

3.2.3. Dielectric spectra analysis

The dielectric response is generally described by the complex permittivity ε*=ε′−iε″, where real ε′ and imaginary ε″ components are the storage and loss of energy in each cycle of applied electric field. F**igure 5** shows the variation of ε› as a function of frequency for different compositions of PVP:NH_4Cl:EC:PC polymer electrolytes at 303 K. **Figure 6** shows the variation of ε" with frequency for the highest conducting system with 0.001 mol% of EC and PC each, at different temperatures. The values of ε' and ε" are very high at low frequencies and relatively constant at higher frequencies. Such high value of ε′ may be due to the interfacial effects within the bulk

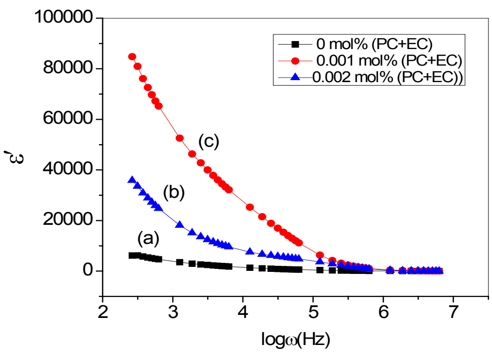


Figure 5 Variation of ε′ with frequency for (a) 85 PVP:15 NH_4Cl (b) 85 PVP:15 NH_4Cl:0.001 EC:0.001 PC and (c) 85 PVP:15 NH_4Cl:0.002 EC:0.002 PC in mol% at 303 K

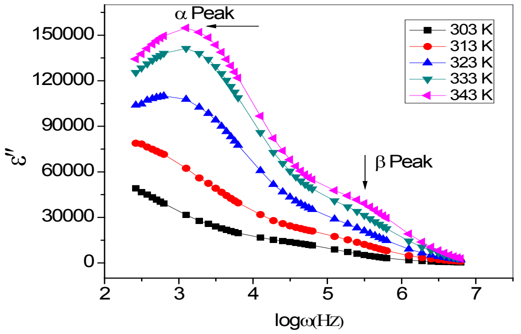


Figure 6 Variation of ε» with frequency for 85 PVP:15 NH_4Cl:0.001 PC:0.001 EC in mol% at different temperatures

of the sample and electrode effects **[9]**. At higher frequencies, the periodic reversal of the electric field is in such a way that there is no excess ion diffusion in the field direction resulting in the decrease in dielectric constant **[10].**

The frequency dependence of ε″ for (85 PVP:15 NH_4Cl:.001 EC:.001 PC) at different temperatures clearly shows the low frequency α relaxation peak and high frequency β relaxation peak which are pronounced at higher temperatures. This may be caused by the movement of main segments and side group dipoles **[4],** respectively of the polymer electrolyte. It is also observed that the dielectric constant and dielectric loss increase with increase of temperature. This is because as temperature increases, the degree of salt dissociation and redissociation of ion aggregates increases, resulting in the increase in the number of free ions or charge carrier density. High values of ε› and ε″ have been obtained for the plasticized electrolytes than the unplasticized one. This is due to the enhanced charge carrier density in the space charge region.

4. Conclusion

The PVP- based ion conducting polymer electrolytes containing EC, PC and NH_4Cl have been prepared and studied by AC impedance spectroscopy. The complexation behaviour between the polymer, the salt and the plasticizers has been confirmed by FTIR studies. Ionic conductivity of the electrolyte increases by one order of magnitude with the addition of 0.001 mol% of EC and PC each. This may be due to the lowering of viscosity with the addition of plasticizer. The conductivity-temperature studies follow Arrhenius equation in the temperature range of 303 to 343 K. The dielectric loss spectrum of the polymer electrolyte plasticized with 0.001 mol% of EC and 0.001 mol% of PC exhibits α and β relaxations.

REFERENCE

[1] Forsyth, M., Meakin, P. M., & MacFarlane, D. R. (1995). A 13C NMR study of the role of plasticizers in the conduction mechanism of solid polymer electrolytes. Electrochimica Acta, 40(13-14), 2339-2342. | [2] Akashi, H., Tanaka, K., & Sekai, K. (1998). An Ionic Conductivity and Spectroscopic Study of Ionic Transport Mechanism in Fire-Retardant Polyacrylonitrile-Based Gel Electrolytes for Li Polymer Batteries. Journal of Electrochemical Society. 145(3), 881-887. | [3] Lee, Y. M., Ko, D. H., Lee, J. Y., & Park, J. K. (2006). Highly Ion-Conductive Solid Polymer Electrolytes Based on Polyethylene Non-Woven Matrix. Electrochimica Acta, (52), 1582-1587. | [4] Ramya, C. S., Selvasekarapandian, S., Hirankumar, G., Savitha, T., & Angelo P. C. (2008). Investigation on dielectric relaxations of PVP–NH4SCN polymer electrolyte. Journal of Non-Crystalline Solids, (354), 1494–1502. | [5] MacFarlane, D. R., Sun, J., Meakin, P., Fasoulopoulos, P., Hey, J., & Forsyth, M. (1995). Structure-property relationships in plasticized solid polymer electrolytes. Electrochimica Acta, 40(13-14), 2131-2136. | [6] Souquet, J. L., Levy, M., & Duclot, M. (1994). A single microscopic approach for ionic transport in glassy and polymer electrolytes. Solid State Ionics 70-71: 337-345. | [7] Rajendran, S., Sivakumar, M. & Subadevi, R. (2004). Investigations on the effect of various plasticizers in PVA-PMMA solid polymer blend electrolytes. Materials Letters, 58, 641-649. | [8] Michael, M. S., Jacob, M. M. E., Prabaharan, S. R. S., & Radhakrishna. S. (1997). Enhanced lithium ion transport in PEO-based solid polymer electrolytes employing a novel class of plasticizers. Solid State Ionics, 98(3-4) 167-174. | [9] Ramesh, S., Yahya, A. H., Arof, A. K., (2002). Dielectric behavior of PVC based polymer electrolytes. Solid State Ionics, 152–153, 291–294. | [10] Adachi, K., Urakawa, O., (2002). Dielectric study of concentration fluctuations in concentrated polymer solutions. Journal of Non-Crystalline Solids. 307–310, 667-670.