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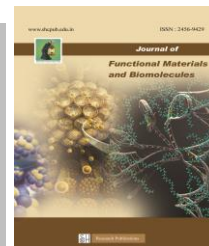
AC Impedance analysis of Solid Polymer Electrolyte based on PVP and PPA composite polymer with Ammonium Fluoride

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Abstract

A new composite solid polymer electrolyte based on polyvinylpyrrolidone (PVP) and poly p–amino benzoic acid (PPA) along with an ionic dopant ammonium had been prepared by solution casting technique using the water as a solvent. PPA was prepared from the monomer by ammonium persulphate in the acidic medium. Electro chemical characterization was carried out by AC impedance analysis and from these studies; it was observed that the composites of 90 mol % of (PVP – PPA) with 10 mol % NH_4F possess highest conductivity i.e., **1.021 X 10^{-08}**S/ cm with low relaxation time and acted as good polymer composite electrolyte compared to other ratio. The relaxation time and dielectric property of the electrolyte also proves the same. From the dielectric study, the dielectric constant was measured and listed.

1 Introduction

The field of polymer electrolysis is slightly more than a decade old. The interest for these materials parallels that for polymers in general, whose appearance in new scientific domains or applications have been steadily increasing. The research of new materials with high ionic mobility had been actively pursued, resulting in a fascination for silver halide [1] and for the so called "aluminas". It became soon evident that the high conductivity found, for instance, in silver iodide resulted more from then intrinsic properties of the Ag^+ ion (softness) than from the crystallographic architecture; chances to find equivalent properties for other, more useful, ions appeared then small, except for twin Cu^+ [2]. The thin polymers will be suitable for an all-solid-state system, as a good contact is easily achieved with soft materials. A brief historical survey of the conductive complexes formed between solvating molecules and metal salts. The elucidation of the special conducting mechanism of these materials have been a challenging emulation for the scientific community. Yet, unsettled questions remain concerning the extent of dissociation and the transport numbers. These materials have up

to now kept their promises for applications of their use are now generally accepted and also apply to the newly considered gel electrolytes which are polymer-immobilized non-protic liquids.

Conducting polymers or more precisely, intrinsically conducting polymers are organic polymers that conduct electricity [3]. Such compounds metallic conductivity or can be semiconductors. The biggest advantages of conducting polymers are their process ability, mainly by dispersion. Polymer is also referred to as a solid solvent that possesses ion transport properties similar to that of the common liquid ionic solution. It usually comprises a polymer matrix and electrolyte, wherein the electrolyte such as lithium salt dissolves in a polymer matrix, which is used in metal ion batteries, sensors, fuel cells and super capacitors.

Composite polymer electrolytes can significantly improve the performance in electrochemical devices such as lithium-ion batteries. The amorphous domains of semi crystalline polymer facilitate the ion transport, while an enhanced mobility of polymer chains contributes to high ionic conductivity [4]. The electronic and ionic conductivities of Composite polymer electrolytes depend on the characteristics of particles size, porosity, concentration, surface area and the interaction between particles and the polymer matrices. The enhanced electrochemical and mechanical properties of composite polymer electrolytes are important for their technological application in electrochemical devices [5].

Fluoride ion is more mobile in the solid state than in the oxide one because of its Mono valent nature [6]. However, the ionic radii of these two ions are almost same $(1.4A^0)$. Fluorine ion being the smallest among the halogen series provides good anionic conduction. The solid solution of PbF_2 with SnF_2 i.e., $PbSnF_4$ and CaF_2 with rare earth fluorides such as LaF_3 has exhibited conductivity of the order of 10^{-3} S/cm at ambient temperature [7, 8]. High

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ionic conductivity has been realized by generating vacancies through doping aliovalent cation fluoride.

A polymer blend, or polymer, is a member of a class of materials analogous to metal alloys, in which at least two polymers are blended together to create a new material with different physical properties [9]. In this present work the composite polymer PVP and PPA doped with ammonium fluoride salt as an ionic dopant was prepared as a thin films and electrochemical characterization of this film has been analyzed by using the AC Impedance analysis. The conductivity, relaxation time and dielectric constant was measured and presented.

2 Experimental Sections

The solution containing 0.1 mol/L of 4-amino benzoic acid, 0.15mol/L of $(NH_4)_2SO_8$, and 0.2mol/L of HNO_3 have been mixed thoroughly at 40^0 C with constant stirring for 24Hrs. After 24Hrs the brown mass of poly p - amino benzoic acid (PPA) precipitation has been formed. The brown mass has been filtered, washed and dried.

Polymer thin films act as a polymer electrolyte membrane based on composite polymer (PVP - PPA) with an ionic dopant Ammonium fluoride has been prepared. The solution cast technique has been used to prepare by adding composites of 80 mol % and 20 mol% of PVP – PPA with different salt ratio of NH_4F concentration (90:10, 93:7, 95:5, and 97:3).

The nomenclature of the prepared polymer electrolyte systems are:

Table 1. Nomenclature of PVP – PPA with an ionic dopant NH_4F

S. No	Ratio	Composition	Nomenclature
1	90:10	(90% PVP+ 10%PPA) +10%NH_4F	F1
2	93:7	(90%PVP+10% PPA) +7%NH_4F	F2
3	95:5	(90%PVP+10% PPA) +5%NH_4F	F3
4	97:3	(90%PVP+10% PPA) +3%NH_4F	F4

AC impedance spectroscopy is used to measure the electrochemical property of the solid polymer electrolytes. In this study PSM – 1735 impedance analyzer has been used to perform the electrochemical characterization. From this technique, the conductivity of thin film of composite polymer has been observed and also the mechanism of conduction has been determined. The impedance has been measured by the use of silver as a blocking electrode with different frequency in the range of 1μz - 5MHz.

3 Result and Discussion

AC-impedance spectroscopy is useful to identification of electrochemical properties of polymer electrolyte membrane. Apart from the conductivity this study gives the following valuable information by using the various formulas [10]. Dielectric constant, Dielectric loss, Modulus

analysis, Dissipation factor analysis which gives the relaxation time of charge carrier during the hopping mechanism, Capacitance character i.e., electrode electrolyte interface phenomenon.

The conductivity analysis of PVP - PPA with NH_4F based polymer electrolyte membrane in water system is given below,

3.1 Impedance spectra analysis

The Fig 1. shows that the composite polymer impedance spectrum of (PVP - PPA)-NH_4F with various salt ratios (90:10, 93:7, 95:5, 97:3).
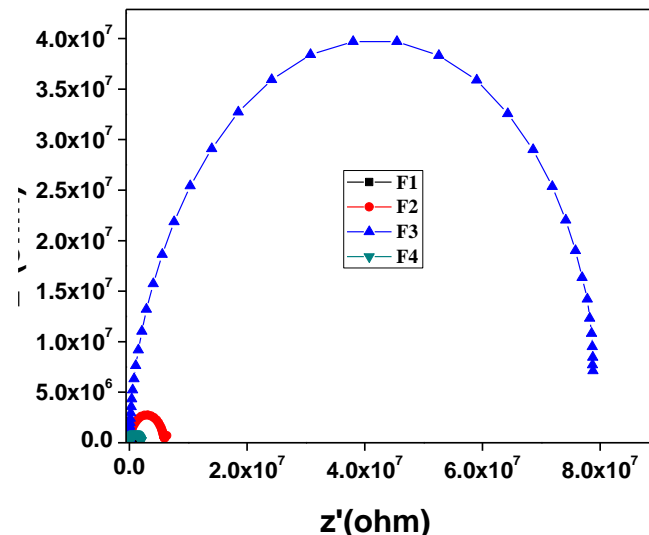

Fig. 1 The Cole-Cole plot of PVP - PPA composite polymer with Ammonium fluoride

From these spectra, the resistance of the bulk polymer electrolyte membrane is calculated by using the relation,

$$\sigma = (t/Rb*A)$$

Where,

Rb – bulk electrolyte resistance
t- Thickness of the thin film
a- Area of the sample

The semi-circle of cole – cole plot indicates the effect of bulk electrolyte and spike has been attributed to capacitance character of the electrolyte. In this spectrum, it shows that there is a spike in F2 system not others. This indicates the fluoride system doesn't having any capacitance character or there is no effect due to blocking electrodes.

Table 2. Conductivity of PVP – PPA with ammonium fluoride system from Cole – Cole plot.

Sample code	Sample Ratio	Conductivity S/cm
F1	90:10	9.937 X 10^{-09}
F2	93:7	6.537 X 10^{-09}
F3	95:5	2.226 X 10^{-10}
F4	97:3	4.263 X 10^{-09}

From the table 2, the F1 (90:10) system possesses highest conductivity 9.937 X 10^{-09}S/ cm. Then F4, F2 and finally the F3 system possesses lowest conductivity 2.226 X 10^{-10} S/cm.

3.2 Conductance Spectra Analysis

By using the power law, the dc conductivity of composite has been measured and listed in the table 3. This was measured by extrapolation the low frequency plateau region on the y – axis [11].

The AC impedance conductivity of composite polymer is obtained by the relation,

$$\sigma_{ac} = \omega\varepsilon_r\varepsilon_0\tan\delta$$

Where,

ω- Angular frequency (ω= $2\pi f$)

Table 3. Conductivity of PVP – PPA with ammonium fluoride system Jonscher Power Law

Sample code	Sample Ratio	Conductivity S/cm
F1	90:10	1.021 X 10^{-08}
F2	93:7	6.767 X 10^{-09}
F3	95:5	2.334 X 10^{-10}
F4	97:3	4.183 X 10^{-09}

Conductance spectra shows that the conductivity increases as frequency also increases (log ω). The conductivity is depending upon concentration of the salt ratio, the increase in concentration the conductivity initially decreases and then increases with increase in salt concentration.
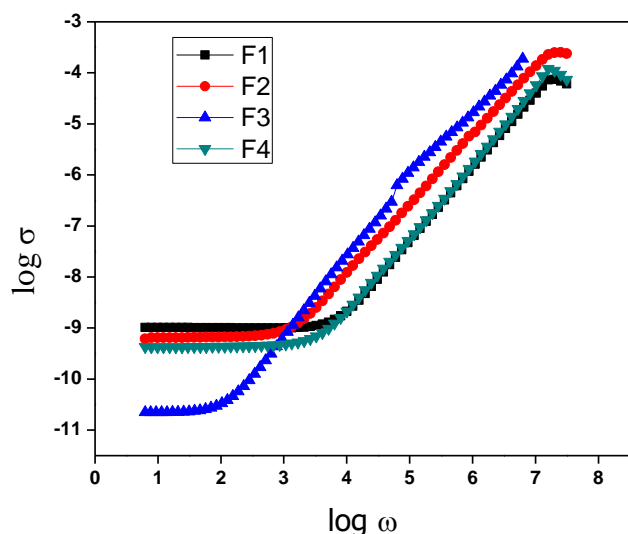

Fig.2 The conductance spectra of PVP - PPA composite polymer with Ammonium fluoride

The decrease in dc conductivity is because of the formation of ion clusters and also leads to the decrease in segmental motion in the polymer. Further increase in dc conductivity is due to the availability of charge carriers of fluoride ion and it leads to ionic mobility in the polymer

electrolyte. From the conductance spectra, the dc conductivity values are calculated [12].

3.3 Dielectric Spectra

Highest conducting system possesses highest value of dielectric constant value. Dielectric property is responsible for the storing of charge carrier present in the system. If the dielectric property increases the conductivity will also increases, which attributed to the increase in the number of charge carrier of free ions in the composites [12].

The above Fig. 3 shows the variation of dielectric constant of composites with frequency at different salt ratio (90:10, 93:7, 95:5, 97:3). From the above spectrum high dielectric constant has been observed for F1 system because of this system possesses highest conductivity. This is due to the increased charge carrier at the electrode-electrolyte interface space region. But in F2 the dielectric constant has a constant value for all frequency, which donates this complex is frequency independent at room temperature. The dielectric constants for the prepared films are 12.59, 9.37, 2.21 and 4.74 respectively.
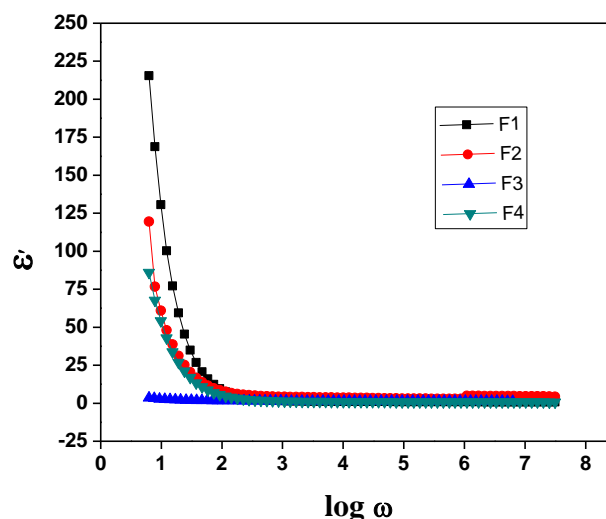

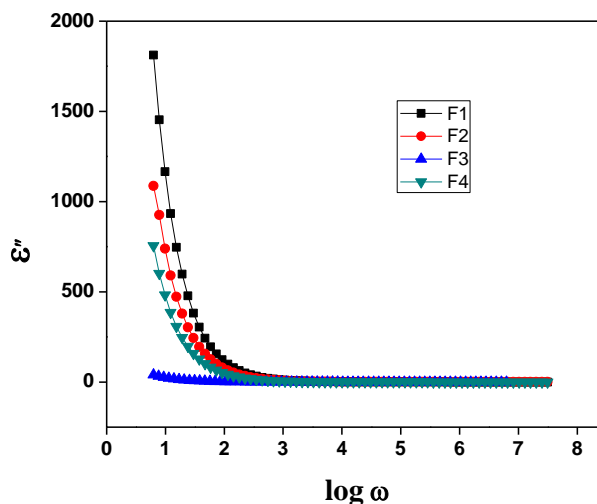**Fig.3 The dielectric constant spectrum of PVP - PPA composite polymer with Ammonium fluoride**

Fig. 4. The dielectric loss spectrum of PVP - PPA blend polymer with Ammonium fluoride

In low frequency region, the accumulation of charge at the interface has been observed [13]. The dielectric loss spectrum of log ω vs ε'' plots for F1, F2, F3, F4 with different frequency are given in Fig. 4. At low frequency for F1 system having the large dielectric loss is due to the mobility of free charge carrier with in the composite polymeric electrolyte material.

3.4 Modulus Spectra Analysis

Elecrical response of the polyemr electrolyte has also been measured by modulus analysis. The ablove Fig. 5 gives the variation of M' values with different frenquency for this polymer electrolyte system. The value of M' approaches zero in low frequency region, where as at high frequency region the M' value increasses with increasing the conductivity, which reveals that the conduction is due to the mobility of ions.
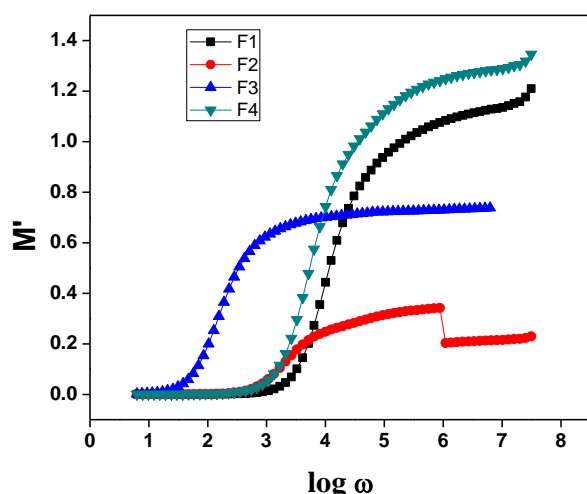

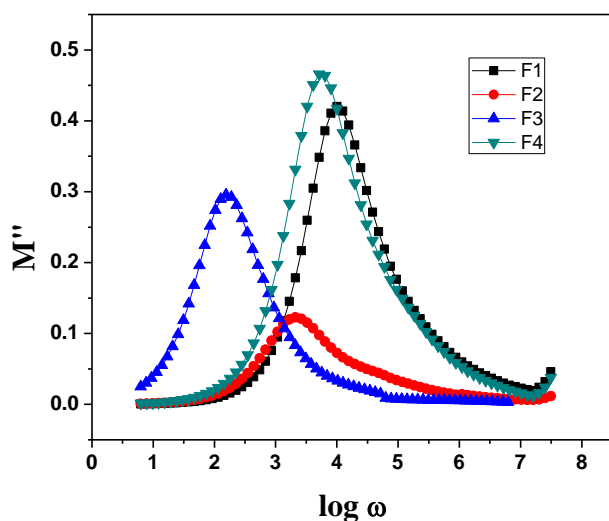**Fig.5 log ω vs M' of PVP - PPA composite polymer with different concentration of Ammonium fluoride**

Fig. 6. log ω vs M'' of PVP - PPA composite polymer with different concentration of Ammonium fluoride

The imaginary modulus analysis is ascribed the coupling of ionic conduction with segmental mobility. The peak maxima shifted to high frequency region as increase

in salt concentration and also maximum conducting system [14].

For F4 the maximum M'' values at lower frequency. As increasing the log ω, the modulus value tent to decreasing. Similarly, for F1, F2, F3 the M'' value is increasing as increase the frequency.

3.5 Dissipation Factor Analysis

The dielectric power loss is referred to the dissipation factor or loss tangent and is given as
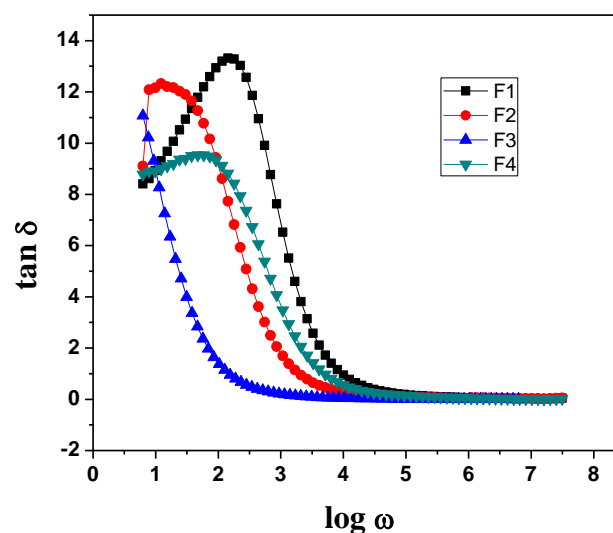
$$D_e = ε''/ε' = \tan δ$$

where, δ is the loss angle

Fig. 7 log ω vs tan δ of PVP - PPA composite polymer with different concentration of Ammonium fluoride

At low frequency, the dipoles in the composite polymers are able to keep in phase with respect to electric field and hence the power losses are low. The dipole orientation of the material could not be completed at high frequency and also the dipole become out of phase angle with electric field has been observed. Hence the maximum dielectric power loss has been also observed [15].

Table 4. Relaxation time for PVP – PPA with ammonium fluoride system

Sample code	$ω_p$	Relaxation time ($τ$) in sec
F1	160.4139	0.006234
F2	12.28584	0.081395
F3	6.289919	0.158985
F4	65.50944	0.015265

This spectrum suggests presence of relaxing dipoles in the composite polymer electrolyte. Thus, F1 complex shows higher dielectric loss than F4, which has been very much related to the conductivity behaviour of the polymer electrolyte. The highest conducting system F1

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possess low relaxation time, which was shown in table 4. The hopping mechanism has been increased with low relaxation time, so that that F1 system having the highest conductivity.

4 Summary and conclusion

The PPA has been prepared by using the ammonium persulphate and nitric acid. A solid composite polymer electrolyte system based on the blend polymer PVP and PPA complexed with different concentration of ammonium fluoride had been prepared by solvent casting method. The dc conductivity measurements are carried out for these films with respect to frequency at room temperature by using the AC impedance spectroscopy.

From the impedance spectra the depressed semicircle at high frequency is due to the bulk effect of the composite material. The conductivity is enhanced to the order of 10^{-8} -10^{-9} S/cm upon increase in salt concentration at room temperature, which is due to the mobility of charge carrier. The F1 (90:10) system possesses highest conductivity (1.021×10^{-08} S/cm), which has been observed in conductance spectra analysis. The dielectric constant (12.59) and dielectric loss spectra also prove that the conducting behaviour in the F1 system. This system has a low relaxation time 0.006234 sec, it leads to fast mobility of ions in the polymer electrolyte.

Conflict of Interest

The content, experimental data and the findings in this paper are original. It had no conflict of interest.

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