Electrochemical Impedance and Dielectric studies on PEO/PVA with NH$_4$Cl based proton conducting polymer electrolyte

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ABSTRACT

A proton conducting polymer electrolytes based on poly (ethylene oxide) and poly (vinyl alcohol) doped with ammonium chloride having different compositions has been organized by solution casting technique using distilled water as solvent. From the electrochemical impedance spectroscopy analysis, the ionic conductivity has been noted to increase with increasing salt concentration up to 10 wt% of NH$_4$Cl. The ionic conductivity, dielectric permittivity (ε') and dielectric loss (ε'') have been worked out from AC impedance spectroscopy in the frequency range 10 Hz-300 KHz and the temperature range from 303K-343 K. The dielectric properties of the sample 10 wt % of NH$_4$Cl were plotted.

KEY WORDS: Polymer composites, blending, Impedance spectroscopy and dielectric properties.

1. INTRODUCTION

Nowadays, ionically conducting polymers have been of considerable interest because of their possible application as a solid polymer electrolyte. The solid polymer electrolytes have attracted great scientist's interest during the final two decades because of their advantages such as high energy density batteries, solid state electrochemical cells, fuel cells, sensors and electrochemical devices. The primary advantages of polymer electrolytes are their good mechanical properties, the simplicity of assembly of films of desirable sizes and their ability to form good electrode-electrolyte contact. The evolution of polymer systems with high ionic conductivity is one of the primary objectives in polymer research. A mixture of polymers such as poly (vinyl alcohol), poly (ethylene oxide), poly (acrylonitrile), poly (vinyl chloride) and poly (methyl methacrylate) has been used as polymer matrices. Ammonium salts have been described as good donors of the proton to the polymer matrix. Granting for the best of our knowledge, there is no work related to PEO and PVA doped with ammonium chloride.

PEO is the most appropriate base material due to its ability to act as host to various metal salt systems for a wide scope of concentration. PVA is added to improve the ionic conductivity and stability of the electrolyte. Ammonium salt has been added as proton donator which is essential for proton conducting polymer electrolyte.

2. EXPERIMENTAL PROCEDURE

The host polymer poly (ethylene oxide) (PEO) of intermediate molecular weight of 6×105, poly (vinyl alcohol) with an average molecular weight of 26000 and the ammonium salt (NH$_4$Cl) were purchased from Sigma-Aldrich chemicals limited, U.S.A. Distilled water was used as solvent. The obtained PEO, PVA and NH$_4$Cl were dried at 55ºC in vacuum for 5 hours to get rid of moisture. The polymers PEO and PVA were dissolved at room temperature and 70ºC respectively. Afterwards, that polymers-salt complex was stirred well for 24 hours to get a homogeneous solution. The result was then poured into propylene petri dishes and left to evaporate in vacuum oven at 80ºC. After 24 hours free standing films were held. Flexible thin films with a thickness of about 0.1-0.4 mm were obtained. The prepared films were submitted to an AC impedance analysis, in parliamentary procedure to work out the ionic conductivity. This was carried out with the help of stainless steel blocking electrodes using a computer controlled micro autolab type III potentiostat/Galvanostat in the frequency range of 10Hz-300 KHz over the temperature range 303-353K.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Impedance Spectroscopy: The electrochemical impedance spectroscopy is an important tool to investigate the mechanism of the polymer electrolytes. Electrical characterizations of all prepared samples have been performed using impedance spectroscopy technique. Fig.3 represents the complex impedance plot of the highest conductivity sample (EA2) at different values from room temperature to 70ºC. The impedance studies were extended out from 10 Hz to 300 KHz. The semicircle gives the information close to the impedance properties of the electrolyte. The patch for all the samples shows a semicircle in the high frequency range and a spike in the low frequency range. The low frequency intercept of the semicircle on the real axis yields the bulk resistance (Rb) of the electrolyte.

The ionic conductivity of the polymer electrolytes can be estimated utilizing the equation, $\sigma = \ell/RbA$, Where ℓ and A are the thickness and area of the polymer electrolyte respectively. Table. 1 shows the conductivity values of all the samples with respect to the concentration of the salt and temperature. The high ionic conductivity at ambient temperature has been found to be 6.42x10-8 Scm-1 for the 10 wt% of salt-doped polymer electrolyte is observed that as the temperature increases, the ionic conductivity of the polymer electrolyte increases for all pieces. It has been

noted that as the temperature increases, the diameter of the semicircle decreases implying the decrease in bulk resistance.
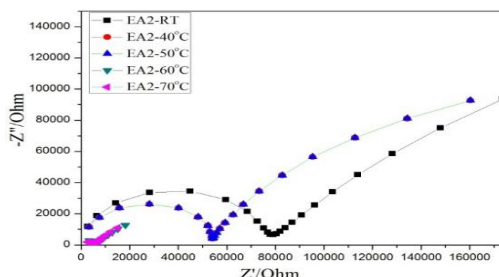

Fig.1.Nyquist plot of polymer electrolyte samples at five different temperatures

The ionic conductivity of the polymer electrolyte increases with the increase of temperature which can be easily understood on the basics of ionic transport mechanism of solid polymer electrolytes. When the temperature is increased, the ionic mobility of the polymer chain is enhanced and the fraction of free volume in a solid polymer electrolyte increases accordingly, which contributes to an increase in the ionic conductivity of the polymer electrolyte. In summation, the mobility of charge carriers increases with increase of temperature resulting in an increment in the ionic conductivity at higher temperatures. It has been set up that the conductivity increases with an increase in NH_4Cl concentration up to 10 wt%. This may be ascribed to the growth in the number of mobile charge carriers and also to the increment in the formless nature of the polymer electrolyte which reduces the energy barrier thereby facilitating the fast ion transport. It is observed that the further addition, when ammonium salts greater than 10 wt% the volume resistance of the electrolytes are increased therefore the ionic conductivity is decreased.

Table.1.Conductivity values of all samples at five different temperatures

Sample Code	303K	313K	323K	333K	343K
EA_0	7.37×10^{-11}	2.22×10^{-10}	5.90×10^{-10}	1.86×10^{-9}	3.0×10^{-7}
EA_1	3.91×10^{-11}	1.17×10^{-7}	1.94×10^{-7}	4.38×10^{-7}	9.98×10^{-7}
EA_2	6.42×10^{-8}	8.89×10^{-8}	9.78×10^{-8}	5.06×10^{-7}	1.6×10^{-6}
EA_3	3.94×10^{-8}	9.61×10^{-8}	3.70×10^{-7}	6.25×10^{-7}	2.91×10^{-6}
EA_4	2.89×10^{-8}	6.75×10^{-8}	2.53×10^{-7}	4.16×10^{-7}	1.50×10^{-6}
EA_5	8.70×10^{-9}	1.44×10^{-8}	1.62×10^{-8}	1.74×10^{-8}	1.80×10^{-7}

3.2. Dielectric Spectra Analysis: The dielectric behaviour of a material is broadly distinguished by complex permittivity as

$$\varepsilon^* = \varepsilon' - i\varepsilon''$$

Where, ε' - dielectric constant, ε'' - dielectric loss

The dielectric phenomenon is a potent instrument to understand the ion behaviour and for getting information of ionic and molecular interactions in solid polymer electrolytes. The ion transport property depends on many factors like degree of salt dissociation and its concentration, dielectric constant of host polymer, degree of ion aggregation and mobility of polymer chains.

Dielectric relaxation and frequency dependent conductivity is sensitive to the apparent movement of charge species and dipoles present in the polymer dielectric relaxation is a consequence of the reorientation process of dipoles in the polymer chains, which shows maxima in ε'' spectra. Hence the analysis of the relative permittivity of polymer electrolyte helps to see the correlation between ionic relaxation time with conductivity and the polarization effects at the electrode/electrolyte interface. The complex permittivity (ε^*) or dielectric constant of a system is determined by, $\varepsilon^* = \varepsilon' - i\varepsilon''$.

Fig.2.Dielectric constant (ε') and dielectric loss (ε'') versus log (ω) for PEO/PVA doped with 10 wt% of NH_4Cl at different temperatures

Where ε', ε'' are real and imaginary components represent storage and loss of energy in each cycle of applied electric field. Fig.2 shows the variation of dielectric permittivity (ε') with frequency (logω) for PEO/PVA with 10 wt% of NH_4Cl at five different temperatures and the frequency dependence of imaginary part dielectric loss (ε''). The increased value of ε' and ε'' at the low frequency part is due to dielectric polarization. The reduction of dielectric permittivity (ε') with increasing frequency is due to the electrical relaxation process. Under the inference of an electric

field, ions tend to defuse and migrate along the orbit. But the ions are unable to cut across the electrode-electrolyte interface due to the stainless steel electrode.

The charge density increases rapidly when the thickness of the electrolyte is greater than that of the hetero charge layer which results in electrode of the subject at the interface. The dielectric constant result is in agreement with increments of the conductivity of the electrolyte system. The observed decrease in the value of ε' and ε'' above 100 KHz can be ascribed by the decrease in the in the charge accumulation at high frequencies, which is already observed in the impedance plot.

3.3. Dielectric Modulus Analysis: A further analysis of electric behaviour would be more successfully achieved by dielectric modulus (M′ and M″), which inhibited the effect of electrode polarization to give a clear indication of electrical property of the polymer electrolyte.

The dielectric modulus was analysed using the pattern

$$M' = \varepsilon'/(\varepsilon'^2 + \varepsilon''^2)$$
$$M'' = \varepsilon''/(\varepsilon'^2 + \varepsilon''^2)$$

Where calculated values of real part M′ and imaginary part M″ versus log(ω) for PEO/PVA doped with 10% of NH_4Cl at five different temperatures are shown in fig.3. From spectra it is noted that both M′ and M″ increase at higher frequencies and decreases with increasing temperature.
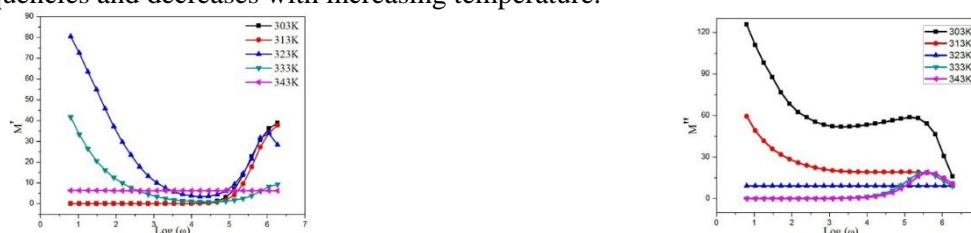

Fig.3.Real part (M′) and imaginary part (M″) versus log (ω) for PEO/PVA doped with 10% of NH_4Cl at different temperatures

Increasing moduli (M′ and M″) values at higher frequencies might be assigned to the bulk effect with the wage increase of temperature, height decreases suggesting a multitude of relaxation mechanism, lower frequencies, it is observed that modules values are vicinity of zero indicating that the issue of polarization is small, which is the main advantage of M′ and M″ modules studies.

4. CONCLUSION

Blending of polymer electrolytes were prepared by solution casting technique with different weight ratio of NH_4Cl (0, 5, 10, 15, 20, 25 wt %). Poly (ethylene oxide) (CH_2-CH_2-O) and poly (vinyl alcohol) (C_2H_4O)$_n$ were taken as polymer host matrix and ammonium chloride (NH_4Cl) as salt. The decrements of both crystalline of electrolytes were observed for 10wt% of NH_4Cl. The ionic conductivity of these six systems (EA0, EA1, EA2, EA3, EA4 and EA5) at different temperatures was calculated by using electrochemical impedance spectroscopy. The ionic conductivity increases with an increase in salt concentration was also studied. Among the various systems studied, 10wt% of NH_4Cl showed good conductivity than other salt based system. Frequency dependence of dielectric property and modulus analysis of polymer electrolytes were studied within the frequency range of 10 KHz to 300 KHz using the complex impedance analysis technique.

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