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Conductivity Studies in Poly Methyl Methacrylate Based Solid Polymer Electrolytes Complexed with Different Chloride Salts

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Abstract

Ionic conducting polymers are of considerable interest recently, as they have wide range of applications including electrical storage devices. The present study is aimed at designing and characterizing one such ion conducting polymer complexed with various ionic salts. Here, solid polymer electrolyte films consisting of Poly methyl methacrylate (PMMA) complexed with various chloride salts (X) (X= KCl, NaCl, MgCl2) have been prepared by the solvent casting technique. Fourier transform infrared spectroscopy (FTIR) confirmed the formation of polymer-ion complex. The ionic conductivity studies have also been carried out using AC impedance spectroscopy technique. Interestingly, the maximum value of conductivity (8.268 X 10-8 S/cm) has been observed for PMMA/NaCl complex at ambient temperature.

Keywords: Polymer electrolyte, Ac impedance, PMMA, FTIR.

Introduction

In general, most polymers are electrically non conductive. However, ion conducting polymers prepared by dissolving an inorganic salt into a polymer matrix have gained considerable attention for more than a decade [1]. The rapid increase in the use of novel group of solid polymer electrolyte (SPE) has a tremendous role in electrochemical devices such as displays, sensors, electro-chromic windows, super-capacitors and rechargeable batteries [2-4]. More recently considerable research efforts have been made in the development of secondary batteries. Today polymer batteries are valid candidates for portable devices such as cellular phones, notebook pc, computer memory backup and aerospace industries. Solid polymer electrolytes have many advantages such as good mechanical strength, high ionic conductivity, good dimensional stability and processing flexibility.

Reported gel polymer electrolytes are poly ethylene oxide (PEO) [5], poly methyl methacrylate (PMMA) [6-7], poly vinyl chloride (PVC) [8], polyvinylidene fluoride (PVdF) [9], poly vinyl alcohol (PVA) [10], poly ethyl methaacrylate (PEMA) [11] and

poly acrylonitrile (PAN) [12]. Research on PMMA based solid polymer electrolytes was carried out in 1985 by Iijima and co wokers [13]. Kushwaha et al [14] reported the preparation and characterization of magnesium ion conducting polymer composite films doped with Mg(ClO4).

The present study investigates the prepared PMMA- (X) complexes (X= KCl, NaCl, MgCl2) using Fourier transform infrared spectroscopy (FTIR) and Ac impedance spectroscopy techniques. It is found that incorporating Na+, which is a fast conducting ion, in an amorphous material results in the polymer matrix having good solubility and better conductivity.

Materials and Methods

All polymer electrolyte samples were prepared by solvent casting technique. Specific amount of polymer PMMA (30%) of average molecular weight 1.7 x 105 (Aldrich) and chloride salts (8 – 10%) were taken separately and the solutions were prepared using the solvent tetrahydrofuran (THF) (60%) from E-Merk and were allowed it dissolve for a day. The dissolved polymer solution and salt were mixed together and the solution was stirred continuously for several hours to obtain a homogeneous mixture. The solution thus obtained was cast on a glass plate and allowed to evaporate slowly at room temperature. The resulting films were dried in vacuum for 2 hrs. The bulk electrical conductivity of the complex was recorded using the Keithley LCZ meter. FTIR measurements were also carried out using Perkin –Elmer 577 IR spectrophotometer in the range 200-4500 cm-1.

Results and discussion

Fourier Transform Infrared Spectroscopy

FTIR analysis helps in identifying the nature of bonding and the presence of different functional group in the sample. FTIR spectra of pure polymers and polymer complexes have been recorded in the transmittance mode and are shown in figure 1. The frequencies at 2948 cm-1, 1245 cm-1 and 1736 cm-1 are assigned to CH2 stretching ,C-C-O bending and stretching mode of the C=O group of pure PMMA. These bands are strong in pure PMMA but their intensities are reduced considerably in the PMMA- (X) (X= KCl, NaCl, MgCl2) complexes.

Moreover, the vibrational peaks observed in pure PMMA (912, 1367, 1433, 2359 and 3616 cm-1) (988, 1151,1365, 1736 and 3616 cm-1), (365, 1366, and 3616 cm-1) are absent in the polymer complex PMMA- (X) (X= KCl, NaCl, MgCl2). In addition, few peaks observed for the complexes PMMA- KCl (3544, 2596, 1829 cm-1), PMMA- NaCl (1289 and 2420 cm-1) and PMMA- MgCl2 (1147 cm-1) are absent in pure PMMA. The appearance of new peaks along with the changes in the existing peaks indicates the concrete formation of ion-polymer complex.

AC Impedance analysis

The electrical properties of the polymer electrolytes are characterized by the complex impedance method using Keithley LCZ meter. The bulk resistance (Rb) is obtained from the intercept on real impedance axis at the high frequency end of the Nyquist plot of complex impedance. The ionic conductivity (σ) is evaluated using the the equation $\sigma = l/(RbA)$ where (Rb), (l) and (A), are the bulk resistance, the film thickness and contact area of the film, respectively. The typical impedance plot for the composition PMMA/NaCl is shown in figure 2. The conductivity value for solid polymer electrolytes containing different chloride salts are given in table 1. It is observed that PMMA/NaCl shows a higher conductivity of 8.268 X 10-8 S/cm compared with other electrolytes. The increased conductivity may be due to the migration of free NaCl ions through the polymer PMMA compared to KCl and MgCl2. Figure 3 depicts the variation in conductivity of the prepared polymer electrolytes. Na+ is a fast conducting ion in a number of crystalline and

amorphous materials, its incorporation in the polymer system may have enhanced the conductivity [15]. However, it is found that the conductivity of all samples in our study is 1000 times lower than the value obtained for PVdF-PEMA-LiX (X = ClO4, CF3SO3) – EC + PC based electrolytes at 301 K as reported by Subadevi et al [16]. This may be due to the lower size of Li+ ion used by them. Further studies in this direction have to be made including the use of plasticizers and nano particles to develop the mechanical and electrical properties of the polymer electrolytes in electrochemical cells.

Conclusion

Solid polymer electrolyte based on PMMA doped with different chloride salts have been successfully prepared by solvent casting technique. The maximum value of ionic conductivity is observed to be 8.268 X 10-8 S/cm for the PMMA/NaCl system at room temperature. Interestingly, this sample also found to have good mechanical stability. The complex formation in polymer electrolyte system has been confirmed using FTIR studies.

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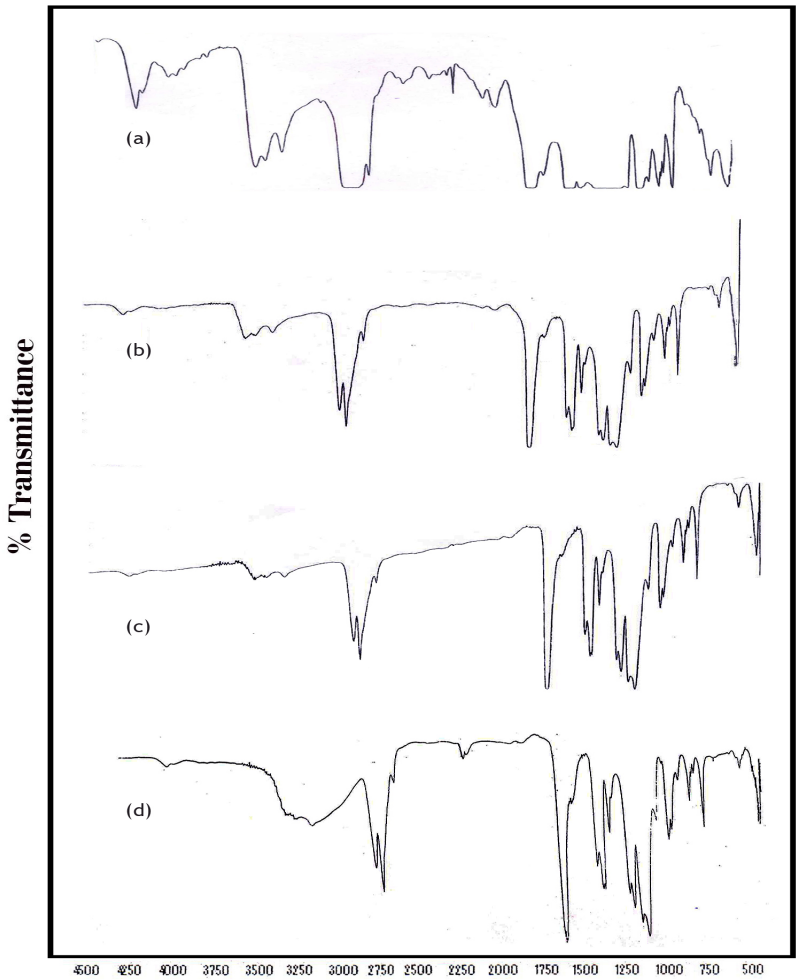
Table 1 Conductivity of the polymer electrolytes at 303 K

S.No	Complex (PMMA – X)	Conductivity value σ X 10-8 S/cm
1	X = NaCl	8.268
2	X =KCl	5.697
3	X = MgCl2	5.548

Figure 1



FTIR plots for a) pure PMMA b) PMMA-KCl c) PMMA-NaCl d) PMMA-$MgCl_2$

Figure 2

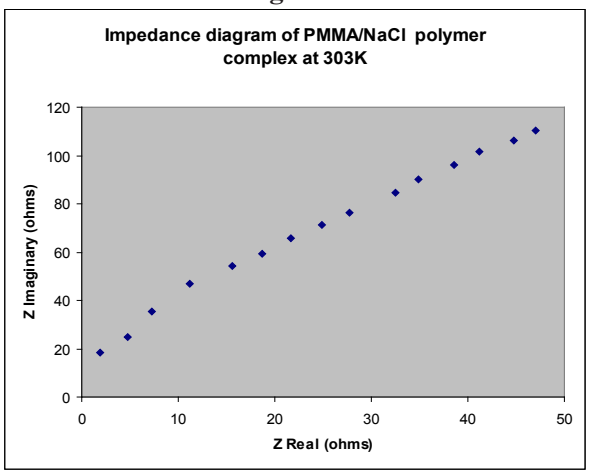


Figure 3 Variation in conductivity of prepared polymer electrolytes