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FTIR and Ionic Conductivity Studies on PMMA based Gel Polymer Electrolytes

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Abstract: This article deals about the preparation and characterization of potassium, magnesium and ammonium ion conducting PMMA based gel polymer electrolytes. The gel polymer electrolytes were prepared by solution cast method. The formation polymer complex of ionic salts and PMMA were confirmed by FTIR. The ionic conductivities were measured by impedance spectroscopy at room temperature. It was found that the ionic conductivity of GPE is of the order of 10^{-7} Scm^{-1}.

Keywords: Gel Polymer Electrolytes, PMMA, FTIR, Ionic Conductivity, Magnesium Electrolytes, Potassium Electrolytes and Ammonium Electrolytes.

Introduction

In recent years, the size of the electronic devices is extremely getting reduced. In future, the research will be going to develop portable solid state batteries for such electronic and electrochemical devices. Among the several works on the solid batteries, it is the one that is the production of solid polymer electrolytes with high ionic conductivity. Poly methyl methacrylate (PMMA) is the one of the most extensively studied polymer, though its ionic conductivity is still quite low. The addition of plasticizers to PMMA system can improve the ionic conductivity of solid polymer electrolytes. The PMMA acts primarily as a 'stiffener', that fast ion transport occurs through a continuous conduction path of the gel, and that the presence of PMMA does not affect the electrochemical stability of the electrolyte. The most of the researchers are fabricating lithium ion conducing solid polymer electrolytes for solid state batteries. Due to high cost and safety reasons, attempts are going with other ions like sodium, magnesium, silver, copper, cadmium, zinc, potassium, ammonium etc.

In the present work, PMMA-NH_4Cl-DBP, PMMA-$Mg(NO_3)_2$-DBP, PMMA-KCl-DBP and PMMA-KBr-DBP gel polymer electrolytes were prepared by solution-cast method. The homogeneity of mixtures of ionic salts (Ammonium Chloride, Magnesium Nitrate, Potassium Chloride and Potassium Bromide) and PMMA were confirmed by Fourier Transform Infra Red (FTIR) spectroscopy. The conduction of ions were studied by impedance spectroscopy and the conductivities were obtained is of the order of 10^{-7} Scm^{-1}.

Experimental

Gel polymer electrolyte films based on poly methyl methacrylate (PMMA) complexed with NH_4Cl, $Mg(NO_3)_2$, KCl and KBr ionic salt have been prepared through the solution cast method. PMMA with an average molecular weight (Alrich) and ionic salts (NH_4Cl, $Mg(NO_3)_2$, KCl and KBr) from E-Merk were dried by heating them under vacuum at 70^oC for 12 hours. The polymer and ionic salts were dissolved in Dimethylformamide (DMF) followed by the addition of Dibutyl Pthlate (DBP). Using magnetic stirrer, the mixtures were stirred for 24 hours. After the evaporation of the solvent, the solutions were transferred to a cleaned glass plate. They were dried at room temperature for 36 hours. Then the solid polymer electrolytes were removed from the glass plate and were taken for characterization. FTIR spectrophotometer (Perkin-Elmer 883) measurements were made in the range 400–4000 cm^{-1}. The ionic conductivity of polymer complexes was measured at room temperature by Keithley LCZ meter.

Results and Discussion

FTIR spectroscopy is used to identify the functional groups and to confirm the complex formation. The FTIR spectra of pure PMMA and the polymer complex PMMA-NH_4Cl-DBP, PMMA-$Mg(NO_3)_2$-DBP, PMMA-KCl-DBP and PMMA-KBr-DBP are shown in figure 1. The C-H rocking vibrations are appeared at 842 cm^{-1}. The absorption peaks at 2950 cm^{-1} and 1242 cm^{-1} are obtained to CH_2 stretching and O-CH_2 deformation vibrations. The strong absorption peak observed at 1732 cm^{-1} is assigned to C=O stretching vibrations of pure PMMA [1]. A lot of peaks of pure PMMA are shifted in polymer complexes. Particularly the strong absorption peak of C=O stretching vibration observed at 1732 cm^{-1} and 1151 cm^{-1} are shifted to nearly 1655 cm^{-1} and 1144 cm^{-1} in polymer mixtures [2]. The peaks 1151, 1192 and

1244 cm^{-1} of pure PMMA are broadened in polymer complexes. This shifting and broadening of the absorption peaks may occur due to the interaction ions with polymer [3]. This is evidence for complex formation.

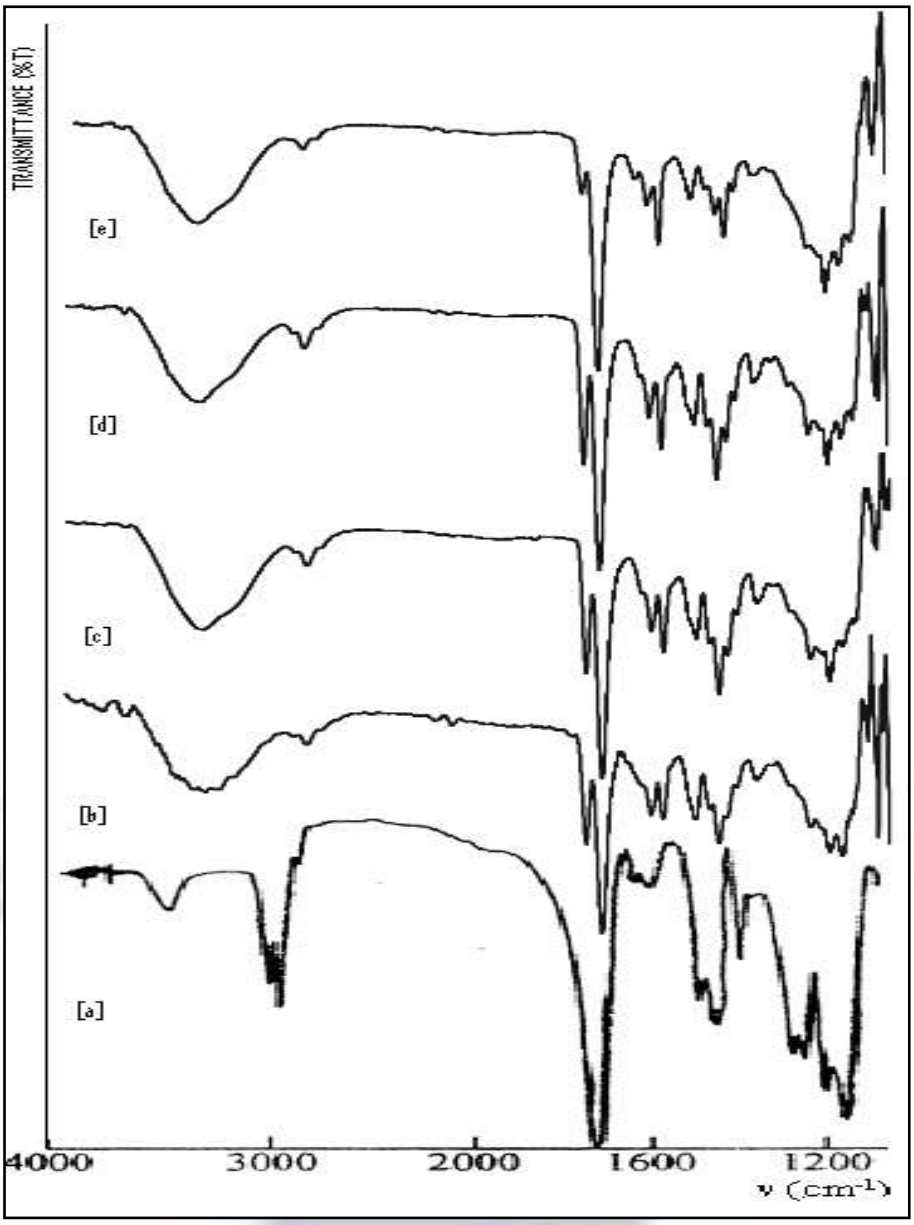

Fig. 1: FTIR Spectrum of [a] Pure PMMA [b] PMMA-NH_4Cl-DBP [c] PMMA-$Mg(NO_3)_2$-DBP [d] PMMA-KCl-DBP and [e] PMMA-KBr-DBP

The ionic conductivity of solid polymer electrolytes is, at a given temperature, normally 100 or 1000 times less than in liquid or ceramic electrolytes. But higher ionic conductivity is preferable for applications of solid state batteries [4]. The impedance spectra of PMMA-NH_4Cl-DBP, PMMA-$Mg(NO_3)_2$-DBP, PMMA-KCl-DBP and PMMA-KBr-DBP gel polymer electrolytes are shown in figure 2, 3, 4 and 5 respectively. The ionic conductivity of PMMA based polymer electrolytes calculated at room temperature from $\sigma = d / (RA)$ where d is thickness of the film, A is the surface area of the film and R is the bulk electrical resistance of the material which is obtained from the intercept on the real axis at the high frequency end of Nyquist plot of complex impedance. The value of ionic conductivity is found 7.14×10^{-7} Scm^{-1}, 4×10^{-7} Scm^{-1}, 3.33×10^{-7} $Scm^{-1}$and 0.91×10^{-7} Scm^{-1} PMMA-NH_4Cl-DBP, PMMA-$Mg(NO_3)_2$-DBP, PMMA-KCl-DBP and PMMA-KBr-DBP respectively. The conductivities of prepared electrolytes are quiet low as compared with existing electrolytes. It may be due the high degree of crystalline structure of polymer complexes. As the mass and degree of crystalline is more in ionic salts, the mobility of the cations (Ammonium, Magnesium and Potassium) decreases. There is a high interaction of cations with polymer may causes the low conductivity. By increasing temperature the amorphicity will increase and hence thereby the conductivity can be increased.

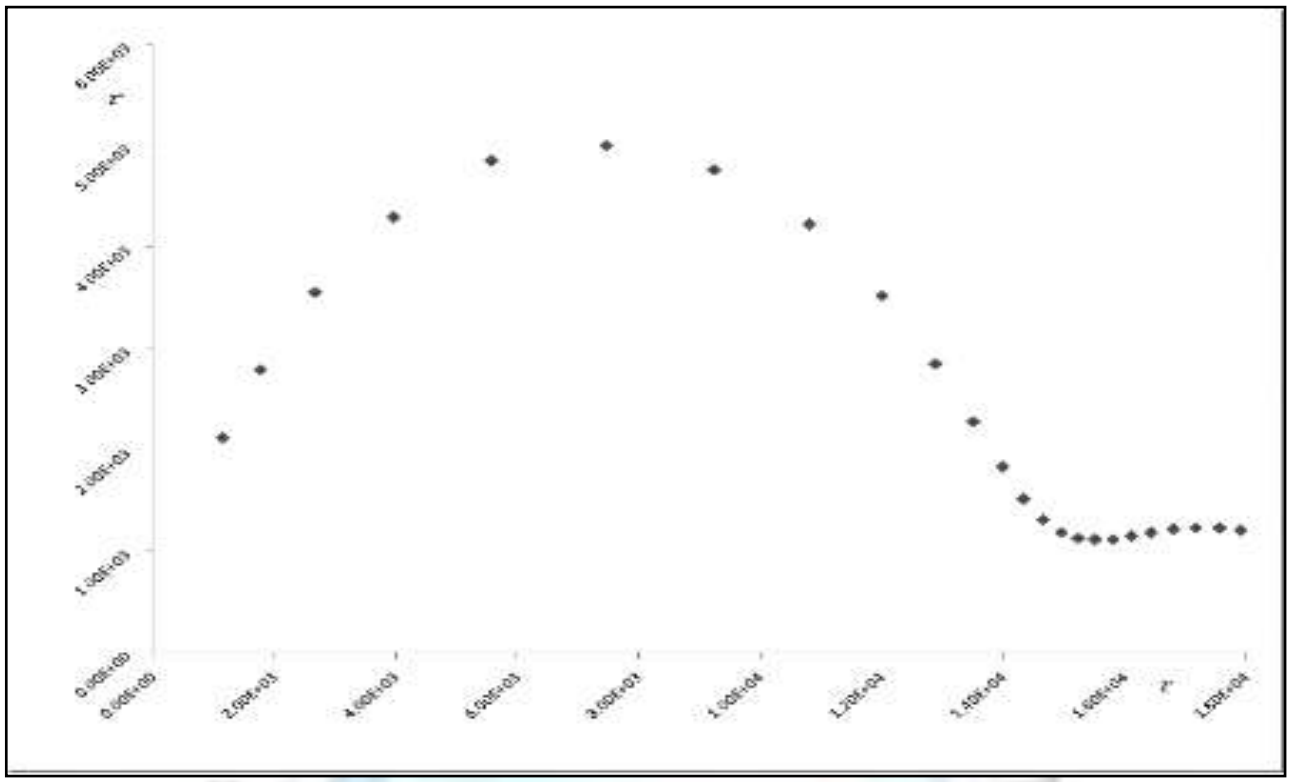

Fig. 2: Impedance Spectrum of PMMA-NH_4Cl-DBP

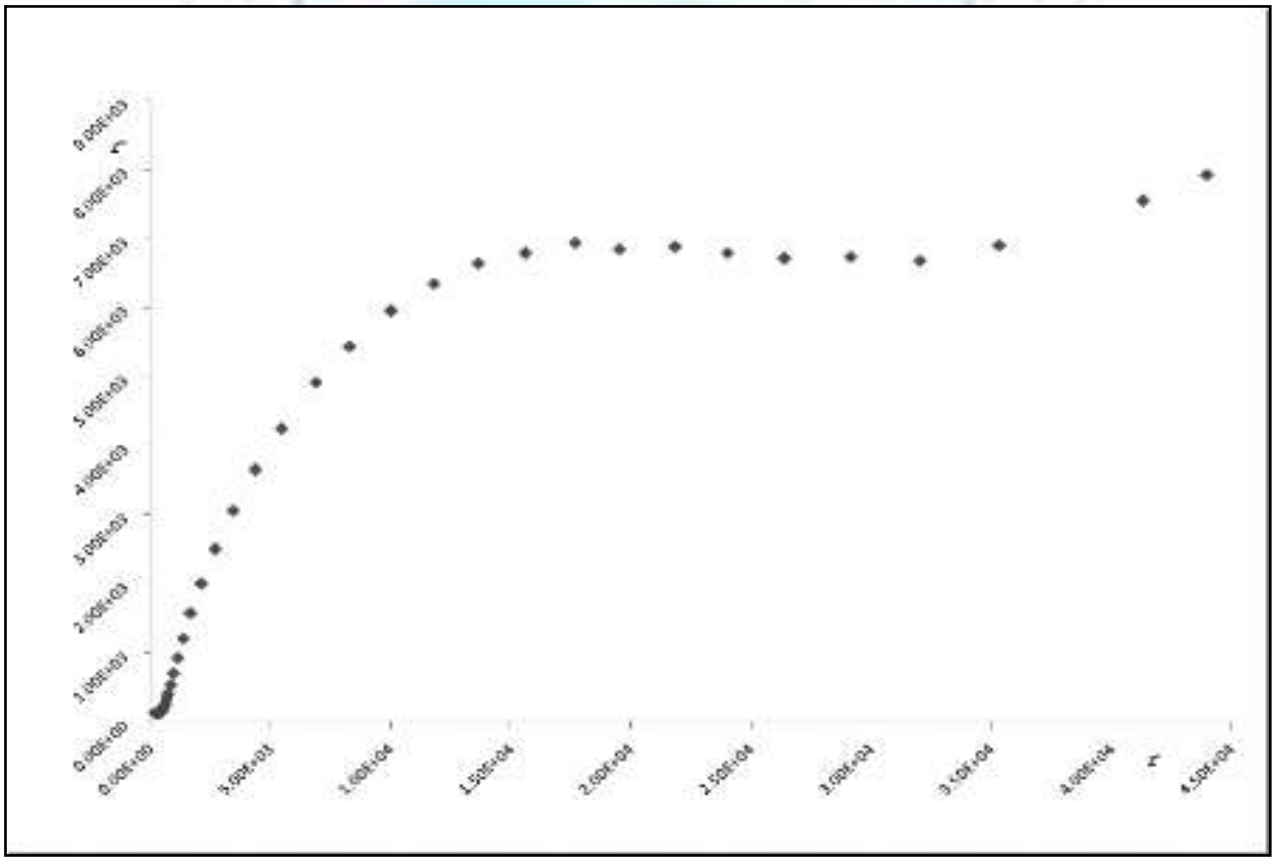

Fig. 3: Impedance Spectrum of PMMA-$Mg(NO_3)_2$-DBP

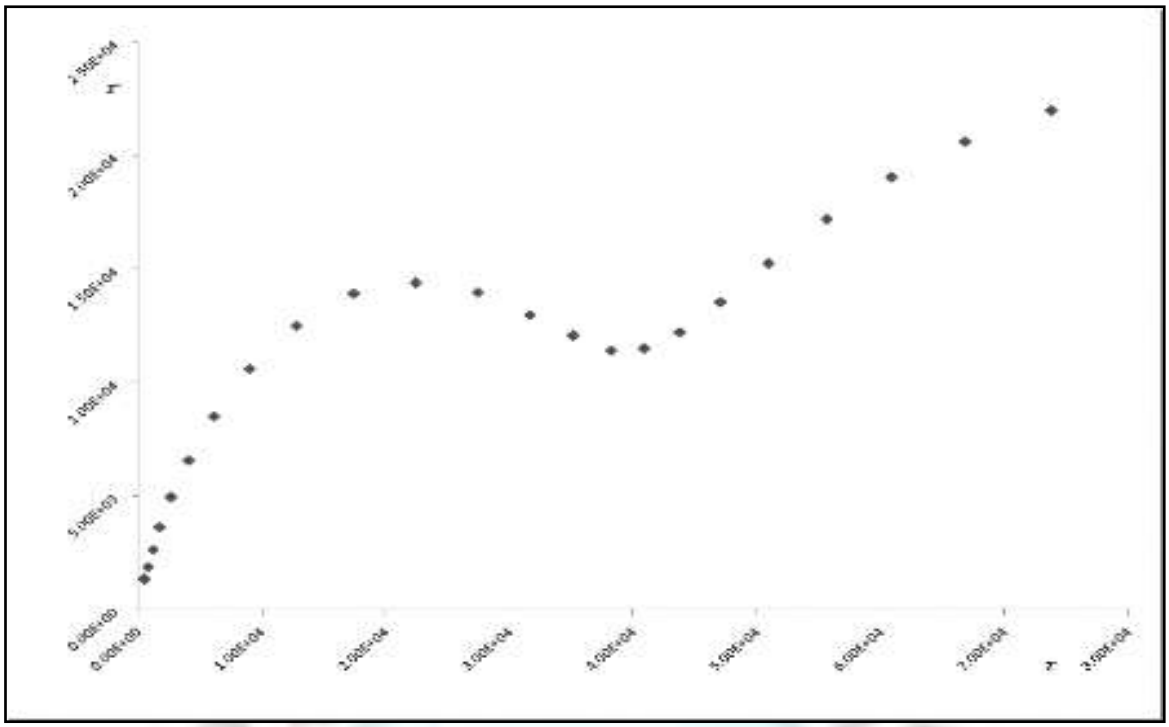

Fig. 4: Impedance Spectrum of PMMA-KCl-DBP

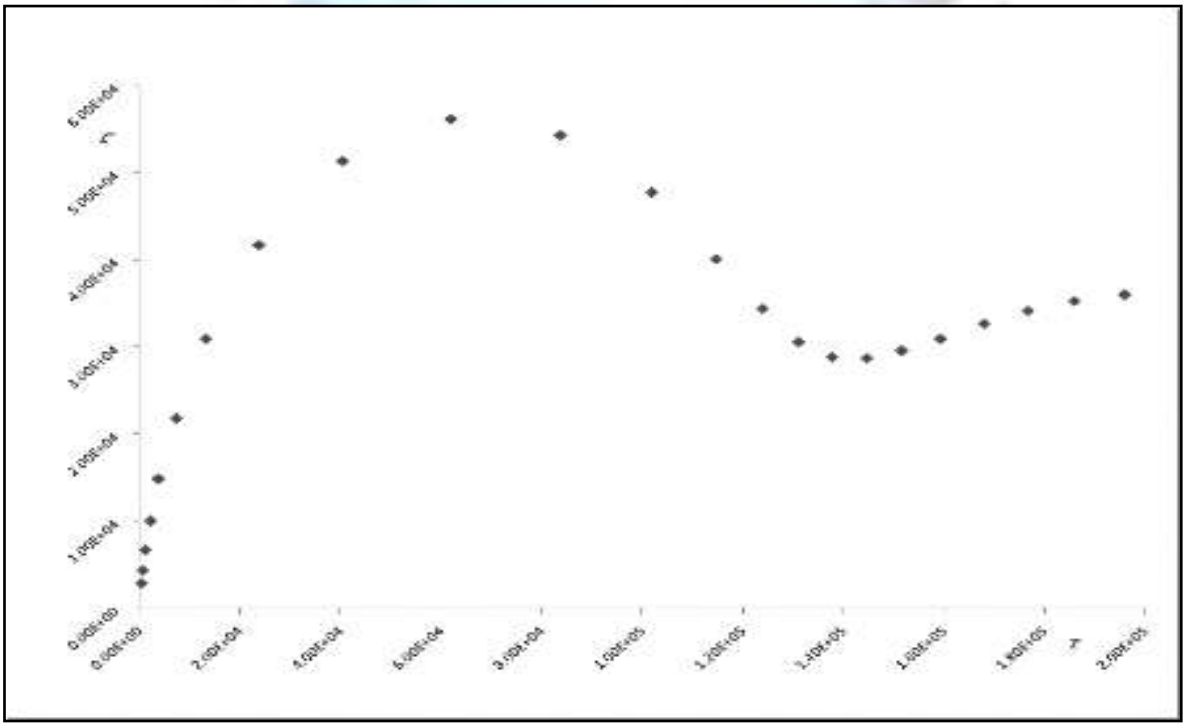

Fig. 5: Impedance Spectrum of PMMA-KBr-DBP

Conclusion

Gel polymer electrolyte films based on poly methyl methacrylate (PMMA) complexed with NH_4Cl, $Mg(NO_3)_2$, KCl and KBr ionic salt have been prepared through the solution cast method. The formation polymer complex of ionic salts and PMMA were confirmed by Fourier Transform Infra Red Spectroscopy. And their ionic conductivities were measured by impedance spectroscopy at room temperature. It was found that the ionic conductivity of gel polymer electrolytes is of the order of 10^{-7} Scm^{-1}. Even though the ionic conductivities of prepared electrolytes are low, in future, they may have a lot application in electrochemical science.

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