

Characterization of Plasticized Poly (Methyl Methacrylate) Polymer Electrolyte Systems

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(Paper presented at the *7th National Conference on Solid State Ionics* held in Coimbatore, India, 6-8 June 2006)

Characterization of Plasticized Poly (methyl methacrylate) Polymer Electrolyte Systems

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Abstract

In the present study, six systems of films have been prepared by the solution casting technique; they are the pure PMMA system, the (PMMA-EC) system, the (PMMA-LiBF₄) system, the (PMMA-LiCF₃SO₃) system, the (PMMA-EC-LiBF₄) system and the (PMMA-EC-LiCF₃SO₃) system. The conductivities of the films from each system are characterized by impedance spectroscopy. The room temperature electrical conductivity for the highest conducting film in the (PMMA-EC-LiBF₄) and (PMMA-EC-LiCF₃SO₃) systems are $4.07 \times 10^{-7} \text{ S cm}^{-1}$ and $3.40 \times 10^{-5} \text{ S cm}^{-1}$ respectively. It can be deduced that plasticizer, EC has dissociated more LiCF₃SO₃ salt compared to LiBF₄ salt, thereby increasing the number of charged carriers in the (PMMA-EC-LiCF₃SO₃) sample. The conductivity-temperature studies are carried out in the range of temperature from 303 K to 373 K. The results show that the conductivity is increased when the temperature is increased. Scanning Electron Microscopy analysis show the surface of (PMMA-EC-LiCF₃SO₃) sample is smooth and homogeneous, hence lithium ions can traverse through the (PMMA-EC-LiCF₃SO₃) sample easier compared to (PMMA-EC-LiBF₄) sample. X-Ray Diffraction studies show that the conductivity is increased when the crystallinity of the samples is reduced.

Keywords: Polymer electrolytes, conductivity, plasticizer, lithium salts, SEM

1. Introduction

Solid polymer electrolytes (SPEs) have been proposed as a substitute for the liquid electrolyte in electrochemical devices and particularly in rechargeable lithium batteries [1]. Incorporating salt into polymer matrix forms a polymer electrolyte that can conduct ions. Mechanically they behave like solids but the conductivity behaviour in their internal structure is expected to be like that of the liquid state.

Various approaches have been attempted to improve the ionic conductivity and mechanical stability. These approaches include; synthesizing new polymers [2-4], blending of two polymers [5,6] and adding plasticizers to polymer electrolytes to form plasticized polymer electrolytes [7-11]. Plasticized polymer-lithium salt electrolytes have been given a lot of attention [12-16], due to their potential application in solid state batteries [16-18]. The addition of plasticizers such as propylene carbonate (PC) and ethylene carbonate (EC) to polymer electrolytes reduces the glass transition temperature, T_g [19-20] thus increasing segmental motion of the polymer resulting in conductivity enhancement.

In the present work, the plasticized polymer electrolyte systems composed of Poly(methyl methacrylate) (PMMA) as a host polymer and EC as a plasticizer containing lithium salts, i.e. lithium tetrafluoroborate (LiBF₄) and lithium triflate (LiCF₃SO₃) as the salts have been studied. The conductivity and morphology structure of the PMMA-based polymer electrolytes are investigated using the impedance spectroscopy, Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) techniques.

2. Experimental

2.1. Sample Preparation

PMMA with molecular weight of 9.96×10^5 g/mol (Aldrich) was dissolved in tetrahydrofuran (THF) solvent. The plasticizer, EC (Fluka) and the lithium salts LiBF₄ and LiCF₃SO₃ (Aldrich) were added accordingly. The mixtures were continuously stirred with a magnetic stirrer for a several hours. After complete dissolution, the solutions were cast in petri dishes and left to dry by solvent evaporation at room temperature to form films. The films were then kept in a desiccator for further drying until characterizations are to be carried out.

2.2. Impedance Spectroscopy

To measure the impedance of the films, the samples were cut into a round shape that fit the size of the electrodes. The samples were then sandwiched between the two stainless steel blocking electrodes with a diameter of 2 cm. A HIOKI 3531 LCR bridge that has been interfaced with a computer was used to perform the impedance measurement for each polymer electrolyte film in the frequency range of 50 Hz to 1 MHz. From the Cole-Cole plots obtained, the bulk resistance, R_b of each sample was determined and hence the conductivity (σ) of the samples were then calculated using $\sigma = t/R_b A$; where t is the sample thickness (cm), A the effective contact area of the electrode and the electrolyte (cm^2), and R_b is the bulk resistance (Ω). The conductivity-temperature studies were carried out in the range of temperature from 303 K to 373 K.

2.3. Scanning Electron Microscopy (SEM)

The cross-sectional morphology of the films was observed by SEM (Stereoscan 420, Leica). The films were vacuumed after sputtering with gold at 25 mA for 40 s.

2.4. X-Ray Diffraction (XRD)

To study the extent of crystallinity XRD was carried out with a D5000 diffractometer which employs a Cu-K α radiation.

3. Results and Discussion

3.1. Conductivity Studies

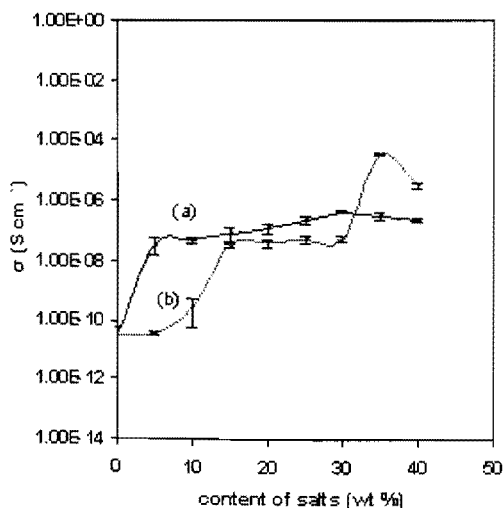


Fig. 1. Variation of conductivity versus salts content in (a) PMMA-EC-LiBF $_4$ and (b) PMMA-EC-LiCF $_3$ SO $_3$ systems.

Fig. 1(a) and (b) depict the plots of conductivity versus salts content for plasticized PMMA containing LiBF $_4$ and LiCF $_3$ SO $_3$ respectively. The highest room temperature conductivity is 4.07×10^{-7} S cm^{-1} and 3.40×10^{-5} S cm^{-1} achieved respectively from the films containing 30 wt% LiBF $_4$ in the (PMMA-EC-LiBF $_4$) system and 35 wt% LiCF $_3$ SO $_3$ in the (PMMA-EC-LiCF $_3$ SO $_3$) system. The apparent roles of a plasticizer in a host polymer are to decrease viscosity of the electrolyte and assist in the dissociation of the salts thereby increasing the number of charged carriers [21]. It can be deduced that EC has dissociated more LiCF $_3$ SO $_3$ salt compared to LiBF $_4$ salt, thereby increasing the number of charged carriers in (PMMA-EC-LiCF $_3$ SO $_3$) sample. Higher conductivity in the (PMMA-EC-LiCF $_3$ SO $_3$) sample is due to the higher number of mobile ions it contains. When the salt content is increased the free ions also increase until it was saturated when more salt was added. That makes these ions become closes to one another. Since the ions are so close to one another, thus the conductivity decreased.

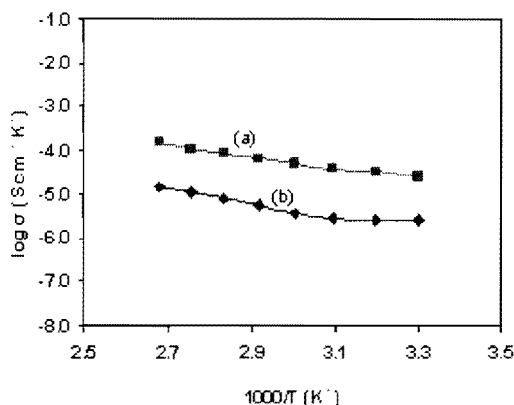


Fig. 2. Arrhenius plot for (a) PMMA-EC-LiCF $_3$ SO $_3$ and (b) PMMA-EC-LiBF $_4$ samples.

Fig. 2(a) and (b) represent the variation of ionic conductivity with the reciprocal temperature for the (PMMA-EC-LiBF $_4$) and (PMMA-EC-LiCF $_3$ SO $_3$) samples respectively. The linear variation of $\log \sigma$ versus $1000/T$ plots suggests an Arrhenius type thermally activated process [22-24]. It is observed that as temperature increases, the conductivity increases and this implies that temperature has increased the degree of salt dissociation into ions.

3.2. SEM Analysis

The porous surface is discovered in the SEM micrographs of PMMA-LiBF₄ and PMMA-EC-LiBF₄ samples as shown in Fig.3(a) and (b) respectively. It can be observed that the size of pores is decreased when the plasticizer EC was added into the PMMA-LiBF₄ sample.

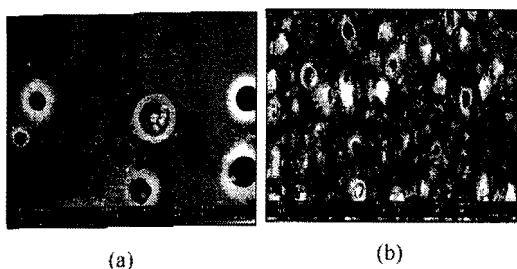


Fig. 3. SEM images of (a) PMMA-LiBF₄ and (b) PMMA-EC-LiBF₄ samples.

Fig. 4(a) and (b) depict the SEM micrographs of PMMA-LiCF₃SO₃ and PMMA-EC-LiCF₃SO₃ samples respectively. The surface of these samples is smooth and homogenous and is expected to continue in the bulk. Hence, lithium ions can traverse through the triflate sample easier compared to hexafluoroborate sample resulting in the triflate sample being more conductive.

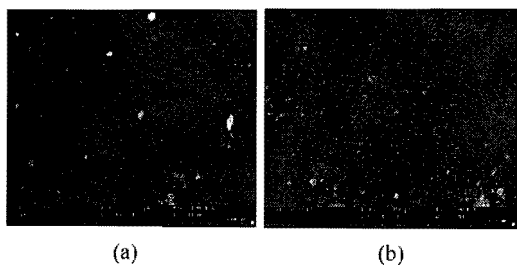


Fig. 4. SEM images of (a) PMMA-LiCF₃SO₃ and (b) PMMA-EC-LiCF₃SO₃ samples.

3.3. XRD Studies

Fig. 4 shows the x-ray diffraction patterns of pure PMMA, LiBF₄, LiCF₃SO₃, PMMA-EC-LiBF₄ and PMMA-EC-LiCF₃SO₃. The amorphous and crystalline phase of the polymer and salts are observed. Most of the peaks pertaining to LiBF₄ disappeared in the PMMA-EC-LiBF₄ film and indicates the complete dissolution of the salt in the plasticized polymer matrix. The sharp peaks at $2\theta = 16.6^\circ$, 19.8° and 22.5° of LiCF₃SO₃ are absent in PMMA-EC-LiCF₃SO₃ film.

These results reveal that the complexation has occurred and the complexes formed are amorphous. Berhier et al. [25] established that ionic conductivity in polymer electrolytes is associated with the amorphous phase of the studied samples.

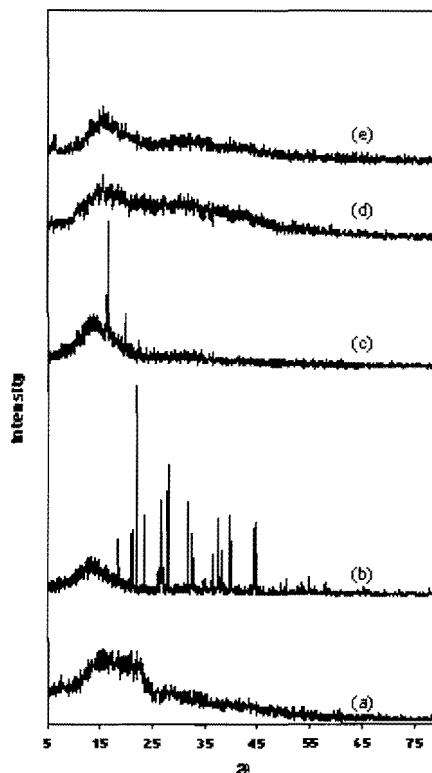


Fig. 5. XRD patterns of (a) pure PMMA, (b) LiBF₄, (c) LiCF₃SO₃, (d) PMMA-EC-LiBF₄ and (e) PMMA-EC-LiCF₃SO₃ samples.

4. Conclusions

The ionic behaviour of plasticized PMMA systems containing the LiBF₄ and LiCF₃SO₃ salts has been studied. The room temperature conductivity for the highest conducting film in the (PMMA-EC-LiBF₄) and (PMMA-EC-LiCF₃SO₃) systems are $4.07 \times 10^{-7} \text{ S cm}^{-1}$ and $3.40 \times 10^{-5} \text{ S cm}^{-1}$ respectively. LiCF₃SO₃ is easily dissociated by EC compared to LiBF₄. The porosity of LiBF₄ sample probably hinders lithium ion movement on the surface and in the bulk resulting in its lower conductivity. XRD studies show that the conductivity is increased when the crystallinity of the samples is reduced.

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