

Li-ion transport, structural and thermal studies on lithium triflate and barium titanate incorporated poly(vinylidene fluoride-co-hexafluoropropene) based polymer electrolyte

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ABSTRACT

Solid polymer electrolytes (SPEs) are fabricated by incorporating lithium triflate (0–240 wt.%) into the PVdF-HFP (poly(vinylidene fluoride-hexafluoropropylene)) matrix. In the first phase, effects of lithium triflate content on ionic conductivity and structural properties of the SPEs are analysed and optimized. The ionic conductivity studies show that the AC and DC conductivities of SPEs increase with increasing the lithium triflate content and reach to orders of 10^{-2} and 10^{-3} S/cm, respectively. In the second phase, composite polymer electrolytes are fabricated by incorporating a ceramic filler, barium titanate (0–12 wt.%) to the optimized lithium triflate composition (15 wt.%) in PVdF-HFP matrix. The ionic conductivity of composite polymer electrolytes increases up to an order of one with the addition of filler up to 6 wt.% and decreases with further increase in the filler wt.%. Thermo-gravimetric analysis suggests that the thermal stability of the electrolytes enhances by the addition of ceramic filler. The structural studies of the electrolytes show that the crystallinity decreases on addition of lithium triflate and barium titanate.

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1. Introduction

The demands for consumer electronic products are increasing day by day and these products are so ubiquitous and firmly fixed in our lives. In view of increase in demand for these products on one hand, the resources for the power sources are not abundant on the other hand. So, finding a feasible, reliable and an economic power source for these products is of much concern. All these facts have been a driving force for the research in the field of energy sources like batteries, fuel cells, etc. Batteries are the major source of power in almost all electronic equipments used in day to day life and also in electric vehicles. These can be classified based on their size, chemistry, voltage, specific energy, specific power, shelf life, etc. A basic battery consists of negative and positive electrodes separated by an electrolyte housed inside a container, where the charge is stored and released electrochemically by conduction of ions through the electrolyte and flow of electrons in the external circuit. Among various types of batteries, Li-ion batteries have proved more fascinating owing to their high specific energy, low maintenance, good cycle life and better power density [1]. These are classified as secondary batteries having carbonaceous material as a negative

electrode, transition metal oxide containing Li-ion as a positive electrode and an electrolyte.

The main requirements of an electrolyte are to have good durability in highly reductive and oxidative environment, high ionic conductivity, mechanical stability, and to ease electrochemical reactions [2]. The electrolytes are classified into two types based on their nature: liquid electrolytes and solid electrolytes. Liquid electrolytes can afford very high ionic conductivity (up to 10^{-2} S/cm). In spite of high conductivity, liquid electrolytes also have certain disadvantages like leakage, corrosion of electrodes, gas formation during operation, and limitation in operating temperature, etc. [3]. In order to overcome these problems, a lot of focus has been given to solid electrolytes. Solid electrolytes can be classified into glass or ceramic electrolytes and polymer electrolytes. Glass electrolytes are much more suitable for high temperature applications. Recently, Singh et al. have reported ionic conductivity of 10^{-3} S/cm in AgI doped LiPO_3 glass matrix [4].

Polymer electrolytes have gained much attraction because of their potential applications. These electrolytes are mainly classified as solid polymer electrolyte (SPE), gel electrolytes and composite electrolytes [5]. Studies have been carried out using different polymers such as acrylonitrile-butadiene-styrene (ABS) [6], polyvinyl chloride (PVC) [7], polyacrylonitrile (PAN) [8], poly(methylmethacrylate) (PMMA) [9], polyvinyl acetate (PVAc) [10], polyvinylidene fluoride (PVdF) [11], poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP) [12], etc., having different combinations of lithium salts (lithium percholate

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(LiClO₄) [13], lithium hexafluorophosphate (LiPF₆) [14], lithium aluminate (LiAlO₂) [15], lithium triflate (CF₃LiO₃S) [16], etc.), loaded in the polymer matrix [17]. The major challenge is to prepare an electrolyte membrane with high ionic conductivity along with good mechanical and thermal stability. Because both the properties are diametric, so achieving an optimal balance without any compromise is of much concern.

Among all the polymers, PVdF-HFP polymer matrix is mostly preferred for the Li-ion battery electrolytes. The excellent stability, high solubility, lower crystallinity and glass transition temperature, and high dielectric constant ($\epsilon = 8.4$) make the PVdF-HFP based electrolyte systems more suitable for many applications [18]. Saika and Kumar have reported that the ionic conductivity and transport properties of PVdF-HFP based system are much better than PVdF based system [19]. In spite of various advantages, this system has some problems like poor mechanical and thermal properties, interfacial instability, etc. In order to overcome these disadvantages, inorganic fillers like silica (SiO₂), titania (TiO₂), alumina (Al₂O₃), strontium oxide (SrO) and barium titanate (BaTiO₃) are incorporated into the polymer matrix [20,21]. Rajendren et al. have reported high ionic conductivity (2.56×10^{-3} S/cm) using polyvinyl alcohol (PVAc)/PVdF-HFP matrix with 8 wt.% LiClO₄ and 8 wt.% BaTiO₃ filler [22]. Similarly, Ulaganathan et al. have also reported an ionic conductivity of 5.56×10^{-3} S/cm for PVAc/PVdF-HFP matrix filled with lithium borohydride (LiBH₄) and 8 wt.% BaTiO₃ [23]. Ragavan et al. have reported that the incorporation of BaTiO₃ in polymer matrix enhanced the mechanical strength of polymer electrolyte membranes [7]. In addition to that, BaTiO₃ has good interaction with PVdF-HFP, which in turn enhances the overall ionic conductivity. These studies have motivated to optimize the weight % of lithium triflate in PVdF-HFP matrix without blending or adding any plasticisers and also to study the synergetic effect of BaTiO₃ in the presence of lithium triflate.

The present study is focused to prepare a SPE and to optimize the lithium triflate wt.% in PVdF-HFP matrix for high ionic conductivity and high thermal stability. The study also aims to prepare a composite polymer electrolyte (lithium triflate/PVdF-HFP/BaTiO₃) and analyses the synergetic effect of BaTiO₃ on the properties of the optimized lithium triflate composition.

2. Materials and methods

2.1. Materials

Poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP, Sigma Aldrich-USA) and Lithium triflate (CF₃LiO₃S, Sigma Aldrich-USA) were chosen as the base polymer and the salt dopant in the polymer matrix, respectively. Again, to prepare lithium triflate/PVdF-HFP/BaTiO₃ composite polymer electrolytes, barium titanate (BaTiO₃, Sigma Aldrich) was used as the filler material, while acetonitrile (Ranbaxy) was taken as a solvent. All the materials were used without further purifications.

2.2. Preparation of polymer electrolyte films

Solution casting method was employed to prepare both the lithium triflate/PVdF-HFP SPEs and the lithium triflate/PVdF-HFP/BaTiO₃ composite polymer electrolyte films. In the first phase, SPEs were prepared by dissolving PVdF-HFP polymer in the solvent and then lithium triflate salt was added. The composition of the salt was varied from 0 to 240 wt.%. In the second phase, composite polymer electrolyte membranes were prepared by adding BaTiO₃ to the optimized salt composition obtained from the first phase.

The weighed amount of PVdF-HFP polymer was dissolved in 10 ml of acetonitrile by magnetic stirring for 2 h at 60 °C to form solution A. Similarly, another solution (solution B) was prepared by dissolving the required amount of lithium triflate in 5 ml of acetonitrile by magnetic stirring for 2 h at 60 °C. After complete dissolution of the polymer and

salt, solutions A and B were mixed together and stirred for 1 h at 60 °C. The solution was then poured on a cleaned glass plate kept horizontally flat to form a thin film. Similarly, to prepare the composite polymer electrolyte films, BaTiO₃ was dispersed in solution B by magnetic stirring and then added to solution A. The films were then dried for 24 h at room temperature and preserved in the desiccator. Finally, the films were cut into required sizes for different characterizations. The thicknesses of the prepared films were in the range of 0.15–0.3 mm.

3. Characterizations

The surface morphology of the electrolyte membranes was studied using scanning electron microscope (SEM; Zeiss EVO MA-15). Since the membranes are made up of polymers, which have low electronic conductivity, gold coating was used to prevent the charging. The images were taken at an accelerating voltage of 10 kV. The elemental composition of the films was analysed using energy dispersive X-ray (EDX) analysis on a Zeiss EVO 50 SEM. The analysis was performed at five different places on each film and the average atomic percent and weight percent were calculated. The phase evolution of the prepared films was studied using X-ray diffraction (XRD; Bruker D8 focus) patterns using Cu K- α radiation having a wavelength (λ) of 1.5418 Å. The 2θ values were varied from 10 to 80°, with a scan rate of 3°/min, step size of 0.02 and slit size of 0.6 mm. Again, the thermal stability of the optimized electrolyte films was analysed by thermogravimetric analysis (TGA) using PerkinElmer TG/DTA instrument in nitrogen atmosphere from ambient temperature to 700 °C with a heating rate of 10 °C/min. Finally, the ionic conductivity was calculated from the impedance data obtained using the electrochemical analyser (Model no: 608D, CHI Instruments) over a frequency range of 20 kHz–2 MHz at room temperature (295 K). Samples of 1×1 cm² were used for the impedance measurement.

4. Results and discussion

4.1. Ionic conductivity

The AC and DC ionic conductivities of pure polymer, SPEs and composite polymer electrolytes are calculated from the impedance data obtained using electrochemical analyser. The maximum AC conductivity of the pure polymer is 10^{-8} S/cm. Upon addition of lithium triflate, the AC conductivity increases by several orders of magnitude and reaches to as high as 1.2×10^{-2} S/cm at 0.06 MHz for 240 wt.% lithium triflate loaded

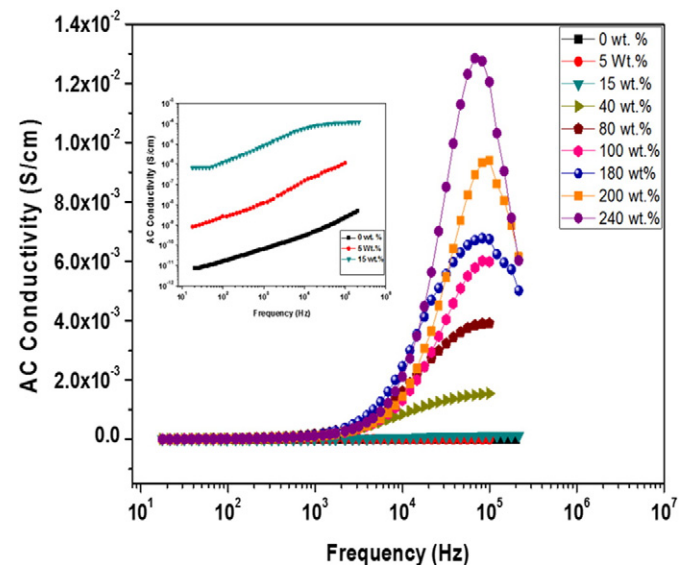


Fig. 1. AC conductivity vs. frequency of pure polymer and SPEs with different lithium triflate loadings (inset: exponential nature of 0, 5 and 15 wt.% salt loaded SPEs).

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