

Ion conducting polymer electrolytes: A Review

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Abstract:

In this paper, a brief review on ion conducting polymer electrolytes has been done. Superionic solids and their classifications on the basis of morphology, nature of mobile species, concentration of ions etc. have been discussed. Literature revealed that the polymer electrolytes are preferred due to some of their special properties like ease of preparation, good electrode-electrolyte contact, wide range of composition and hence wider control of properties, mechanical stability, flexibility, chemical inertness etc. The studied literature on polymer electrolytes reported by various authors was mainly with the following polymers: polyethylene oxide(PEO), polymethylmethacrylate(PMMA), polyacrylonitrile(PAN), polyvinylidene fluoride(PVdF), polyvinylidene fluoride-co-hexafluoropropylene(PVdF-HFP). The ionic conductivity of the order of 10^{-2} to 10^{-3} S/cm of polymer electrolytes at room temperature has been reported which is suitable for their use in device applications.

Keywords: Ionic conductivity; polymer electrolytes; gel; composite polymer electrolytes.

Introduction

The solids with high value of ionic conductivity ($> 10^{-4}$ S/cm) and negligible electronic conductivity ($< 10^{-8}$ S/cm) are generally known as superionic solids. These are also called fast ion conductors. The branch of material science and technology, which deals with the study of superionic solids, is known as solid state ionics. The scope of solid state ionics is not confined to solid electrolytes but it covers Physics, Chemistry and Material Science involving all kinds of ionic transport in solid state. These materials have gained a lot of importance because of their useful applications in many solid state ionic devices which includes solid state batteries, fuel cells, supercapacitors, sensors, electrochromic devices etc. [1]. On the basis of morphology, superionic conductors are generally classified in different categories like crystalline/polycrystalline, glasses, composites and polymer electrolytes. Out of these, polymer electrolytes are preferred due to some of their special properties like ease of preparation, good electrode-electrolyte contact, wide range of composition and hence wider control of properties, mechanical stability, flexibility, chemical inertness etc.

A solvent free system in which ion conducting phase is formed by dissolving salt in high molecular weight polar polymer matrix is called polymer electrolyte. Fenton and Wright in early seventies were the first to show the complexation of polyethylene oxide (PEO) with different metal salts (MX) in ion-conducting polymers [2-3]. Although complexation of PEO with different alkali metal salts was reported in 1973, yet their technological importance was highlighted by Armand *et al.* [4-5]. PEO based polymer electrolytes have poor mechanical properties and low ionic conductivity at room temperature, which limits their applications in devices. Many approaches have been adopted to enhance the ionic conductivity of electrolytes

to a reasonable value suitable for their device applications. The ionic conductivity of polymer electrolytes can be increased by synthesizing (i) plasticized polymer electrolytes and (ii) composite polymer electrolytes. The increase in conductivity was observed to be more in the case of plasticized polymer electrolytes, but it also deteriorates the mechanical properties of the electrolyte. In case of composite polymer electrolytes, although the increase in conductivity is small as compared to plasticized polymer electrolytes, yet it leads to a significant improvement in the mechanical properties of electrolytes. The other method to improve ionic conductivity is polymer gel electrolyte, in which the solvent is retained in the polymer matrix.

Polymer gel electrolytes belong to a salt-solvent-polymer hybrid system in which the salt solution is immobilized with the addition of a suitable polymer matrix as done by Feuillade and Perche [6]. In these electrolytes, the salt provides the mobile ions for conduction and the polymer provides the mechanical stability. The solvent is retained in these gel electrolytes and acts as the conducting medium. The solvent used should generally have high dielectric constant, which helps in better salt dissociation and low viscosity. This increases mobility and low melting and high boiling points which increases the temperature range over which these electrolytes can be used. Initial work on polymer gel electrolytes is mainly with various lithium salts, which is due to their potential applications as electrolytes in high energy density lithium batteries. In the recent years, proton conducting polymer gel electrolytes have also attracted considerable attention due to their possible use in various devices working at ambient temperature. Both polymer gel electrolytes as well as plasticized polymer electrolytes show high ionic conductivity but poor mechanical strength. To improve mechanical strength and ionic conductivity, nano-particles have been dispersed in these electrolytes and hence nano-composite polymer electrolytes are formed.

Literature Survey

Polymer Electrolytes:

In 1973, Wright *et al.* first reported the complexation of high molecular weight polymers like polyethylene oxide (PEO) and few Sodium and Potassium salts [3]. The suitability of these electrolytes for battery applications was highlighted by Armand *et al.* [4-5]. These polymer electrolytes are free from solvents and have been extensively studied for different mono-, di-, tri-valent metal salts and various ammonium salts. Different polymers complexed with different metal salts have been studied. Several hypotheses have been proposed to explain the ionic motion in PEO chains. The ionic conductivity in PEO was initially associated with its crystalline phase. In the recent years, proton conducting polymer electrolytes have attracted considerable attention due to their possible use in various electrochemical devices, like fuel cells, electrochromic displays, supercapacitors, humidity and gas sensors etc. These materials are prepared by adding appropriate salt or acid containing a proton conducting species in a suitable polymer matrix. Generally, polymers with polar groups like polyethylene oxide (PEO), polypropylene oxide (PPO), polypropylene glycol (PPG), polyethylene imine (PEI), polyvinyl pyrrolidone (PVP), polyethylene succinate (PESc), polyvinyl alcohol (PVA) etc. have been used as the host polymer matrices and different ammonium salts and acids like NH_4SCN , NH_4ClO_4 , NH_4I , NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$, H_3PO_4 , H_2SO_4 , HCl , CH_3COOH etc. as dopant materials. In 1984, Stainer *et al.* reported the complexes

formed between PEO and NH_4SCN , $\text{NH}_4\text{CF}_3\text{SO}_3$ [7]. Daniel et al. have studied complexation of NH_4HSO_4 , HCl , H_2SO_4 , H_3PO_4 with polyethylene oxide (PEO), polyacrylic acid (PAA) and polyethylene imine (PEI) [8]. Some proton conducting polymer electrolytes have also been reported, viz. PEO- NH_4ClO_4 by Chandra et al. [9], PEO- NH_4ClO_4 , PEO- NH_4I by Hashmi et al. [10-11], PEO- $(\text{NH}_4)_2\text{SO}_4$, PEO- NH_4I by Maurya et al. [12-13]. Kumar et al. [14-15] studied the conductivity behaviour of PEO based proton conducting polymer electrolytes containing NH_4F and NH_4BF_4 . Chandra et al. [16] fabricated rechargeable proton conducting polymeric solid-state battery containing ammonium salt. Proton conducting polymer electrolytes containing ammonium salts viz. $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 with the highest conductivity of 10^{-6} - 10^{-5} S/cm have been studied and used in fabricating electrochemical cells by Arof et al. [14]. Proton conducting polymer electrolytes viz. PVAc- NH_4SCN , PVA- $\text{CH}_3\text{COONH}_4$ and PVP- NH_4SCN have been studied by Selvasekarapandian et al. with the highest room temperature conductivity of $\sim 10^{-4}$ - 10^{-6} S/cm [18]. Most of the polymer electrolytes have low ionic conductivity along with poor mechanical and chemical stability. Number of attempts have been made to improve the ionic conductivity of polymer electrolytes. In next sections, some of the most important polymer electrolytes viz. (i) plasticized polymer electrolytes, (ii) polymer gel electrolytes and (iii) composite polymer electrolytes (iv) plasticized composite polymer electrolytes have been discussed.

Plasticized Polymer Electrolytes:

In order to improve the ionic conductivity of polymer electrolytes, addition of low molecular weight non-aqueous organic solvents, such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), dimethyl sulphoxide (DMSO), dimethyl formamide (DMF), polyethylene glycol (PEG) etc. into matrix polymer as plasticizers has been proposed. The plasticizer should have high dielectric constant, low viscosity, low freezing point and high boiling point. The addition of plasticizer to polymer electrolytes has been reported to increase the ionic conductivity of polymer electrolytes by dissociating the ion aggregates alongwith an increase in amorphous content. PEO based polymer electrolytes are multiphase materials with amorphous phase responsible for high ionic conductivity. Berthier et al. have reported that ionic conductivity of polymer electrolytes has a specific dependence on the amorphous nature of the samples [19]. The addition of plasticizer reduces glass transition temperature ' T_g ', increases chain mobility and lowers the crystallinity of semi-crystalline polymers. Forsyth *et al.* have studied plasticized polymer electrolytes in details and results have been reported by using different techniques such as FTIR, NMR, XRD etc. [20]. They have reported that the increase in ionic conductivity with the addition of high dielectric constant plasticizer is due to (i) increased fraction of dissociated ions, (ii) increased chain flexibility, (iii) decrease in cation-anion association (iv) cation-polymer interaction and (v) increased mobility of host polymer chains etc. Bohnke et al. studied PMMA based plasticized polymer electrolytes with high conductivity of $\sim 10^{-4}$ S/cm at 25°C [21]. The most important advantage of plasticized polymer electrolytes is the relatively higher ionic conductivity but the major drawback is poor mechanical properties. Therefore, an improvement in the mechanical properties of plasticized polymer electrolyte is required.

Polymer Gel Electrolytes:

Polymer gel electrolytes also known as (polymer-salt-solvent) hybrid system have been reported, in which the solvent is retained in the electrolytes and show high value of conductivity. These are prepared by first dissolving the salt in the solvent and then, a suitable polymer is added slowly to immobilize the liquid electrolyte which results in gel formation. The solvents should have high boiling point and low freezing point, high dielectric constant and low viscosity. The polymers generally used in gel electrolytes, are polyethylene oxide (PEO), polymethyl methacrylate (PMMA), polyacrylonitrile (PAN), polyvinylidene fluoride (PVdF), polyvinylidene fluoride-co-hexafluoropropylene (PVdF-HFP) etc. [22-25]. Most of the initial work on polymer gel electrolytes has been mainly based on gels containing different lithium salts viz. lithium perchlorate (LiClO_4), lithium trifluoromethane sulfonic acid (LiCF_3SO_3) and lithium hexafluoro phosphide (LiPF_6) etc. An interest in these salts is due to their potential use as electrolyte in high energy density lithium batteries [24]. Proton conducting polymer gel electrolytes is another category of polymer electrolytes in which solvent is retained in the electrolytes and show high value of conductivity at ambient temperatures. A new type of proton conducting systems based on non-aqueous polymeric gels has been reported mainly with polymers like polymethylmethacrylate (PMMA), polyethylene oxide (PEO), polyvinylidene fluoride (PVdF), polyvinylidene fluoride-co-hexafluoropropylene (PVdF-HFP) and acids such as phosphoric acid (H_3PO_4), predeuterated phosphoric acid (D_3PO_4), benzoic acid (BA), salicylic acid (SA), paratoluene sulfonic acid monohydrate (TOS) as dopant materials and solvents like ethylene carbonate (EC), propylene carbonate (PC), dimethylformamide (DMF), dimethylacetamide (DMA), methylformamide (MF) etc. as well as binary/ternary solvent mixtures. Gum acacia (GA) - natural gum having high molecular weight polysaccharide acidic material that is acidic in nature and the least viscous among hydrocolloids. The ion-conducting behaviour of water-soluble gum acacia (GA) based gel electrolytes have also been studied with salt ammonium chloride (NH_4Cl) concentration at different GA content and temperature [26].

Composite/nano-composite plasticized polymer electrolytes:

Numerous research efforts to improve conductivity, while retaining the mechanical stability of polymer electrolytes at room temperature have been made towards the incorporation of nano-sized particles into polymer electrolytes. In 1973, Liang reported that the addition of the insulating particles (Al_2O_3) to a poor ionic conductor (LiI) resulted in an increase in conductivity [27]. Later on, in polymer electrolytes obtained by the complexation of polyethylene oxide (PEO) with different metal salts, the addition of insulating particles (like as Al_2O_3 , SiO_2 , TiO_2 and $\gamma\text{-LiAlO}_2$) with particle size in the micro and nano range were also reported to result in an increase in conductivity along with an improvement in the mechanical and thermal properties of the electrolytes. The increase in conductivity was also reported to depend upon the particle size and concentration of the insulating matrix particles. Plasticized composite polymer electrolytes have been synthesized by dispersing insulating matrix to plasticized polymer electrolytes. Michael et al. have reported the enhancement in ionic conductivity by one order of magnitude (4.29×10^{-4} S/cm) upon the dispersion of $\gamma\text{-Al}_2\text{O}_3$ in plasticized (PEO- LiClO_4 -DOP) polymer electrolytes along with the good mechanical stability [28]. Lee et al. have studied the ionic conductivity behaviour of sulfonated-SEBS/ SiO_2 /DBP composite polymer electrolytes for their use in polymer batteries using LiClO_4 , LiCF_3SO_3 as

salts and DBP as plasticizer. The ionic conductivity has been found to increase with an increase in content of silica for the polymer electrolytes containing plasticizer and maximum conductivity of 2.6×10^{-3} S/cm and 1.4×10^{-3} S/cm have been observed for polymer electrolytes containing LiClO_4 and LiCF_3SO_3 respectively. The addition of both plasticizer and insulating matrix to the polymer electrolytes has been reported to result in an increase in conductivity, which is higher than that observed for composite and plasticized polymer electrolytes. Dissanayake et al. have studied the combined effect of Al_2O_3 nanofiller and plasticizer (EC) on the conductivity enhancement in polymer electrolyte (PEO- LiCF_3SO_3) [29]. Maximum conductivity of 1.5×10^{-4} S/cm has been observed for electrolytes containing 50wt% EC and 15wt% Al_2O_3 . Therefore, simultaneous addition of plasticizer and insulating matrix in polymer electrolytes may be the better option to obtain plasticized composite polymer electrolytes with high conductivity along with better mechanical properties. Kumar and co-authors studied various nano-dispersed polymer gel electrolytes and nano-composite plasticized polymer electrolytes containing different acids and salts [30-44]. The conductivity shows an enhancement in mechanical as well as electrical properties of gel electrolytes. PVdF-HFP based nano-composite plasticized polymer electrolytes with different ammonium salts and acid have been reported by Sharma et al. [45-48]. PMMA based nano-dispersed polymer electrolytes containing LiBF_4 salt have been studied by Arora et al. & Singh et al. in which ionic conductivity, SEM, TGA and rheological studies of these electrolytes have been reported [49-50].

Conclusions

Different ion conducting polymer electrolytes like polymer electrolytes, plasticized polymer electrolytes, polymer gel electrolytes, composite polymer electrolytes have been reviewed in this paper. The polymer electrolytes show poor mechanical properties and low ionic conductivity at room temperature, which limits their use in device applications. Different methods have been reported by different authors to enhance the ionic conductivity of polymer electrolytes like addition of plasticizers, dispersion of fillers of different size to polymer electrolytes.

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