Role of Additives for High Performance Polymer Electrolytes

Jitender Paul Sharma\textsuperscript{1*} and Vikas Bharti\textsuperscript{2}

\textsuperscript{1} Department of Physics, Himachal Pradesh Technical University, Hamirpur, HP, India
\textsuperscript{2} Department of Chemistry, Govt. Hydro Engineering College, Bilaspur, HP, India

E-mail: sharma JP78@yahoo.co.in

Abstract. Today, the progress of polymer electrolytes with high ambient ionic conductivity, better mechanical and thermal properties, has become the main objective in the field of polymer science because of their requirements in super capacitors, rechargeable batteries, fuel cells and other electrochemical devices. Many kinds of polymer electrolytes have been developed, however main drawback is the low ionic conductivity, which is inadequate for most of the device applications. Efforts have been made to enhance the ionic conductivity of polymer electrolytes to meet the demand for different devices. Although polymer electrolytes with high value of ionic conductivity ($\sim 10^{-3}-10^{-4}$ S/cm) have been developed but these also suffer from poor mechanical properties. Incorporation of plasticizers as well as nano fillers in polymer electrolytes, is of great importance for enhancing their performance in devices. In the recent years, researchers came up with an idea to make the use of ionic liquids in polymer electrolytes to address the problem of low ionic conductivity of polymer electrolytes at room temperatures as well as to keep good electrochemical and mechanical properties. The optimized ionic conductivity value of the order of $\sim 10^{-3}$ S/cm has been observed by different workers at different concentrations of ionic liquids. Also, polymer gel electrolytes have been reported to possess high ionic conductivity (of the order of $\sim 10^{-2}$ S/cm) at ambient temperature. However, despite possessing high value of ionic conductivity these gel electrolytes have poor mechanical and thermal properties. Hence, the modified polymer /gel electrolytes having optimized properties, are described in this review paper. An attempt has also been made to highlight the work of different researchers in the form of synthesis, characterization and analysis of different modified polymer electrolytes for their use in different ionic devices.

Keywords: Polymer electrolytes, Plasticizer, Filler, Ionic Conductivity, Mechanical Properties.

1. Introduction

Solid State Ionics is an interdisciplinary branch of science and technology that deals with the study of solids having high ionic conductivity value ($10^{-1}$-$10^{-4}$ S/cm) which are generally known as superionic conductors or fast ion conductors. Polymer electrolytes occupy an important position in Solid State Ionics. Ion conducting polymer electrolytes are important and have received extensive attention because of their requirements in rechargeable batteries, super capacitors, fuel cells, sensors, smart windows and other electrochemical devices [1]. The research on polymer electrolytes and their use in batteries had begun in the year 1970 and continued up to now [2-6]. In past decades, researchers have focused on the implementation of polymer based high performance Li-ion batteries. High ionic conductivity, electrochemical, mechanical, thermal, interfacial and dimensional stability are the essential requirements for the materials to be used in the device applications. Since, polymer electrolytes have low ionic conductivity as well as poor mechanical properties at ambient temperature; therefore, many approaches have been adopted to enhance their conductivity to the required value applicable for devices. Common methods used to enhance the ionic conductivity of polymer electrolytes are the synthesis of plasticized as well as nanocomposite polymer /gel electrolytes. However, the enhancement in the ionic conductivity has been observed in the case of plasticized polymer electrolytes, yet deterioration of the mechanical properties of polymer electrolytes at the large extent of incorporation of plasticizer, is the existing problem. For nanocomposite polymer electrolytes, although the improvement in the ionic conductivity value is small as compared with the plasticized polymer electrolytes however,
it leads to a significant modification in the mechanical properties. Recently, it has also been observed that incorporation of ionic liquids into the polymer electrolytes, has become one of the best approaches to enhance the ionic conductivity and other electrochemical properties. Optimized ionic conductivity value of the order of $\sim 10^{-3}$ S/cm has been observed in the polymer electrolytes containing different concentrations of ionic liquids by different researchers [7-11] and hence, ionic liquids have been considered as good performing dopants for polymer electrolytes. In this review article, role of additives such as plasticizer, ionic liquids and nano-filler to develop the polymer /gel electrolytes having optimum properties is described. An attempt has also been made to represent the work of various researchers towards developing the high performance polymer electrolytes.

2. Synthesis of plasticized and nanocomposite polymer/gel electrolytes

Various techniques have been implemented by the researchers to obtain free standing films of polymer electrolytes. One of the most promising techniques to obtain polymer electrolyte films, is the solution casting technique [12]. In this technique, both the salt solution and polymer solution are dissolved in a solvent and the mixture is stirred continuously with a magnetic stirrer for about couple of hours until a uniform solution is achieved. The obtained homogeneous solution is further casted in polypropylene dishes and the solvent is left to dry at room temperature for complete evaporation of solvent. The free standing films so obtained are removed from the dishes, kept in desiccator containing silica gel desiccant to dry further. Free standing and mechanically stable films are then getting ready for different experimental studies. Plasticized (polymer-salt-plasticizer or ionic liquid) and nanocomposite (polymer-salt-nano filler) polymer electrolytes are also prepared by the above method after adding stoichiometric quantities of plasticizer/ionic liquid and filler to the polymer-salt complex respectively. Polymer gel electrolytes are also prepared by the immobilizing the salt solution by adding appropriate amount of suitable polymer. Nanocomposite based polymer gel electrolytes are also developed by incorporating different concentrations of nano-filler to the obtained polymer gel electrolytes and stirring for several hours until a homogeneous and transparent solution is obtained.

3. Role of additives on the ion conducting behavior of polymer electrolytes

Complex impedance spectroscopy is often used technique to measure the electrical properties of the variety of materials. The ionic conductivity of polymer electrolytes, can be measured by sandwiching the small piece of film between two electrodes made up of stainless steel under the spring pressure. The impedance of the film, is then determined by using computer interfaced impedance analyzer in the different frequency range. Temperature dependent ionic conductivity of polymer electrolytes, can also be obtained by keeping the sample holder in temperature controlled furnace. The obtained real as well as imaginary parts of impedance ($Z'$ and $Z''$) are represented in Nyquist plot to measure bulk resistance (R). The ionic conductivity is then obtained from the relation [13]:

$$\sigma = \frac{Gl}{A} = \frac{l}{R.A}$$

where $l$ is the distance between the electrodes and $A$ is the cross-sectional area of each electrode. In this review article, the details about the electrical, structural, mechanical and thermal properties achieved by incorporating additives in the form of plasticizers or ionic liquids and fillers into the polymer electrolytes, are described as (i) plasticized polymer electrolytes and (ii) nanocomposite polymer /gel electrolytes.

3.1. Plasticized polymer electrolytes

In order to improve the ion conducting behavior of polymer electrolytes, incorporation of high dielectric constant as well as low dielectric constant plasticizers, such as propylene carbonate (PC), ethylene carbonate (EC), dimethyl sulphoxide (DMSO), dimethyl carbonate (DMC), diethyl carbonate (DEC), dimethyl formamide (DMF) and poly(ethylene glycol) (PEG) etc. into matrix polymer has been proposed [14-16]. The incorporation of high dielectric constant and high boiling temperature
plasticizers dissociate the ion aggregates and un-dissociated salt into free ions [17]. The low viscosity of these plasticizers also leads to high ionic mobility that enhances the ionic conductivity [18]. The plasticizers having high dielectric constant - which leads to enhanced dissociation of salt, low viscosity - which assists the motion of charge carriers by providing low resistance conduction path in the polymer matrix, low freezing and high boiling temperature - which ensures the wide temperature range workability, have been used by number of researchers for describing their role in the enhancement of ionic conductivity of various polymer electrolytes. The addition of plasticizers to polymer electrolytes, have been reported to increase the ionic conductivity of polymer electrolytes by dissociating ion aggregates along with an improvement in amorphous phase [28-38]. The addition of plasticizer reduces glass transition temperature ‘$T_g$’, increases chain mobility and lowers the percentage crystallinity of polymers and the results obtained have been reported by using different characterization techniques such as FTIR, DSC, TGA, NMR, XRD, SEM and ECS etc. [30-31]. Finally it is concluded that the increase in ionic conductivity by introducing plasticizer, having high dielectric constant may be 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. Watanabe et al. [32] have studied lithium ion conducting polymer electrolytes formed by adding ethylene carbonate (EC) and lithium perchlorate (LiClO$_4$) to polymer poly(acrylonitrile) (PAN). Abraham et al. [33] also showed that the addition of PC to PAN based polymer led to a significant enhancement in the ionic conductivity such that the conductivity was higher than that of PEO based electrolytes. Park et al. [34] have observed the increase in conductivity in PAN-LiClO$_4$ based polymer electrolytes containing EC-PC as plasticizers. It has been observed that after certain concentrations of PC-EC, the conductivity begins to decrease due to the effect on the microscopic viscosity ($\eta$). Kulkarni et al. [35] synthesized PEO based plasticized polymer electrolytes by using solvent casting technique and improvement in the ionic conductivity has been observed with the incorporation of different concentrations of plasticizer DBP to PEO-CdCl$_2$ and PEO-CdSO$_4$ polymer electrolytes. Selladurai et al. [36] reported electrical, ion transport, structural and cell performance studies of polymer electrolytes containing NaClO$_4$ with the incorporation of plasticizers such as PEG, PC and DMF. Maximum ionic conductivity of the order of $\sim 10^{-4}$ S/cm has been observed for PEG-PEO-NaClO$_4$-DMF system. Choudhary et al. [37] have reported enhancement in electrical conductivity of plasticized polymer electrolytes, due to increase in ions dissociation and amorphous behavior of the polymer electrolytes. They have also reported that the magnitude of conductivity depends upon the characteristics of plasticizer, plasticizer-salt concentration ratio and dielectric constant of plasticizer etc. Rajendran et al. [38] have studied PMMA, PEO and PVA based plasticized polymer electrolytes containing LiBF$_4$, LiClO$_4$ as salts and EC, DBP, DMP as plasticizers with ionic conductivity of $\sim 10^{-4}$-$10^{-3}$ S/cm at room temperature. Subba Rao et al. [39] reported plasticized (PEO-NaYF$_4$-DMF) polymer electrolytes and it was reported that the addition of DMF to PEO-NaYF$_4$ polymer electrolytes increases the ionic conductivity, which is due to the attractive forces between the molecules of plasticizer and polymeric chain segments. This reduces the cohesive force present between polymeric chains, an increase in segmental mobility and hence, the ion conducting behavior of polymer electrolytes. Bhat et al. [40] reported the role of incorporation of plasticizer PEG on the ionic conductivity of proton conducting PEG-NH$_4$ClO$_4$ polymer electrolytes. A maximum conductivity of $5 \times 10^{-6}$ S/cm has been observed for 40wt% plasticizer. The conductivity of PEO based polymer electrolytes, has been realized to increase with the addition of plasticizer, having dielectric constant greater than PEO, whereas, the conductivity has been observed to decrease by incorporating plasticizer, having dielectric constant lower than that of PEO [41]. Complexation of oxalic acid with PVdF-HFP and the effect of adding DMA to PVdF-HFP-oxalic acid polymer electrolyte has also been observed to improve the conductivity by three orders in magnitude by Chu et al. [42]. Maximum conductivity of 0.12x$10^{-3}$ S/cm has been observed for the polymer electrolytes containing 40wt% oxalic acid with the addition of DMA. Other researchers have also made significant contribution in the development and characterization of plasticized polymer electrolytes having high ionic conductivity values along with optimized properties [43-48]. Recently, incorporation of ionic liquids as plasticizer into the polymer electrolytes has also become one of the
leading approaches to enhance the ionic conductivity and other electrochemical properties. The optimized ionic conductivity value of the order of $10^{-3}$ S/cm has been observed at different ionic liquid concentrations by different researchers [7-11] due to which, these ionic liquids have been considered as good performing dopants for polymer electrolytes.

Since, plasticized polymer electrolytes exhibit relatively higher ionic conductivity, but a poor mechanical property is still the existing problem [28]. Therefore, an efficient and effective method is required for the improvement of mechanical properties of plasticized polymer electrolytes. On the basis of above, the authors have decided to synthesize and characterize high performance polymer electrolytes with reduced crystalline properties and enhanced amorphous properties for future perspectives.

3.2. Nanocomposite polymer /gel electrolytes

(i) Nanocomposite Polymer Electrolytes (in film form)

One of the steps to improve room temperature ionic conductivity as well as mechanical properties of polymer electrolytes is the addition of fillers. Use of fillers such as silica, zeolites, oxides as additives in polymer electrolytes have shown an enhancement in ionic conductivity along with better mechanical stability [27, 49-61]. These nanocomposite polymer electrolytes have certain advantages over organic solvent based polymer electrolytes in the form of mechanical properties, ionic conductivity and electrode-electrolyte interfacial stability [62-63]. The enhancement in Li⁺ ion conductivity by three orders of magnitude was because of the dispersion of filler Al₂O₃ in Lithium Iodide as firstly noted by Liang [64] in 1973. In 1982, Weston and Steele [65] reported the enhancement in the mechanical stability of PEO-LiClO₄ electrolytes using α-Al₂O₃ particles with grain size 40 μm. In earlier studies on mixed-phase poly electrolytes consisting of NASICON [66], β-alumina [67], it has been shown that fillers do not show any enhancing effect to the ion conducting behavior of mixed phase systems. However, Skaarup et al. [68] reported the decrease in conductivity for composite polymer electrolytes containing high amounts of conducting fillers. Similar results have also been investigated by Stevens and Mellander [69] on the conductivity enhancement of mixed-phase electrolytes by introducing conducting fillers. Scrosati et al. [70] have reported the effect of dispersion of γ-LiAlO₂ to PEO based polymer electrolytes. No significant improvement in the ionic conductivity as well as electrochemical properties has been observed. Morales et al. [71] have also recorded that the ionic conductivity of the system decreases by dispersing γ-LiAlO₂ at low concentrations. An improvement in the ionic conductivity was recorded at higher concentrations of γ-LiAlO₂. In composite polymer electrolytes, surface interactions have been assumed to be answerable for enhancement in ionic conductivity as reported by Maier et al. [72]. Researchers have proposed different models to depict the variations in the electrical and mechanical properties of composite polymer electrolytes with polymer, salt and filler [73]. Croce et al. [74] have proposed a model for the effect of filler in polymer matrix to reduce the crystallization as well as to promote the specific interaction between surface groups and PEO segments. Greenbaum et al. [75] have studied PEO based composite polymer electrolytes in terms of electrochemical and solid state NMR characterizations. It has also been recorded that the Li⁺ ion diffusivity can be enhanced without any modification in segmental mobility of polymeric chains. Walls et al. [62] have reported high conductivity at room temperature by dispersing fumed silica to poly(ethylene glycol) dimethyl ether (PEGDME) containing lithium salt. However, the conductivity showed a tendency to decrease above 20wt% fumed silica. Dissanayake et al. [76] have reported that the presence of nanoporous Al₂O₃ particles having four different surface groups in PEO-LiTFSI polymer electrolytes enhances the ionic conductivity depending upon the nature of the filler surface group. Forsyth et al. [77] have studied the phase change in PEO based polymer electrolytes with the addition of TiO₂. They found that the polymer segmental motion was enhanced at low filler concentration but the enhancement diminishes at high filler concentration. Capuano et al. [70] have reported an enhancement in the ionic conductivity with the dispersion of 10wt% Al₂O₃ to PEO-LiClO₄. A significant enhancement in the interfacial stability has also been recorded due to the reduced crystallinity of polymer electrolytes. Kumar et al. [78] reported that nano fillers are more compatible to
reduce the interfacial resistance than fillers with micron size. Generally smaller the particle size, larger the conductivity enhancement [84]. Bhat et al. [79] have noted the significant improvement in Li⁺ ion conductivity in PEO based polymer electrolytes containing LiClO₄ after dispersing different concentrations of δ-Al₂O₃ nanoparticles. It was concluded that the decrease in percentage crystallinity and activation energy may be due to increase in mobility in lithium ions. The maximum conductivity of 4.5x10⁻⁸ S/cm has been observed with the addition of filler. Morita et al. [80] have investigated the role of addition of ceramic fillers on the ion transport properties of poly(ethylene oxide)-poly(methacrylate) (PEO-PMA) based polymer electrolytes, containing magnesium salt Mg[(CF₃SO₂)₂N]. The addition of ceramic filler has also been observed to improve the ionic conductivity due to the enhancement in ionic mobility. Maximum conductivity of ~10⁻³ S/cm at 60°C has been observed for composite polymer electrolytes. The dispersion of ceramic filler has also been observed to influence the thermal properties of polymer electrolytes. Khan et al. [81] have reported PEG based composite polymer electrolytes developed by dispersing hydrophobic fumed silica in PEG-Li salt solution. Along with an improvement in mechanical stability of polymer electrolytes, the ionic conductivity of the order of 10⁻³ S/cm has also been recorded. From the literature, two conductivity maxima at two different filler concentrations have been observed in case of composite polymer electrolytes due to the mobility of both the mobile ions [82-83]. Fan et al. [84] have also reported two conductivity maxima for composite PEO based polymer electrolytes containing LiClO₄ and silane modified SiO₂. The enhancement in the ionic conductivity observed due to the dispersion of ceramic filler, has been described by an effective medium theory (EMT) and existence of high conducting layer at electrolyte/filler interface. Composite solid polymer electrolytes with improved mechanical properties and electrochemical stability have been developed by incorporating MnO₂ nano-sheets for lithium metal batteries by Shujiang et al. [3]. PEO/MnO₂ composite solid polymer electrolyte exhibited higher ionic conductivity along with better tensile strength than PEO solid electrolytes. Ion transport properties of novel blended PEO-PVP based polymer electrolytes for the sodium ion rechargeable batteries have been prepared via standard solution cast technique by Sharma et al. [4]. To obtain more information about the morphology and structural changes in films, these polymer electrolytes have also been studied by using different characterization techniques. Still the main challenges in the commercialization of Li-ion battery are the low ionic conductivity and poor mechanical properties. In order to improve the overall performance of polymer-based composite electrolytes, Liu et al. [5] have obtained the ionic conductivity of the order of 10⁻⁴ S/cm along with electrochemical window of 0–5.0 V. Saito et al. [6] have fabricated cross-linked polymer electrolytic membranes containing branched poly (ethyleneimine), (PEI) and poly(ethylene oxide), (PEO). The optimized polymeric membranes have shown excellent ionic conductivity value of the order of 10⁻³ S/cm along with many potential applications in electrochemical storage devices. From the above overview of literature, it has been observed that no doubt, many studies have been recorded in case of nanocomposite polymer electrolytes, yet several issues are still unresolved. The purpose of this review is to provide an idea which will help to access the influence of dispersion of fillers as well as to guide the readers towards their best efforts in future research work. Therefore, authors have made attention to obtain polymer electrolytes having optimized ionic conductivity as well as improved mechanical and thermal properties over a wide temperature range.

**(ii) Nano-dispersed polymer gel electrolytes**

Polymer gel electrolytes are generally obtained by immobilizing ionic salt solution with suitable polymer matrix to get a hybrid mixture [85]. In polymer gel electrolytes, free ions are mainly provided by doping ionic salt. The solvent used acts as a conducting medium and helps to solvate the ionic salt whereas; polymer provides the mechanical stability by modifying the viscosity of polymer electrolytes [86]. Different polymers used in the preparation of polymer gel electrolytes are poly(vinylidene fluoride) PVdF [87-88], poly(methylmethacrylate) (PMMA) [89-90], poly(acrylonitrile) (PAN) [91], poly(vinylesterefluoride-hexafluoropropylene) (PVdF-HFP) [92] etc. Singh et al. [93] have reported transport properties of different PMMA based polymer gel electrolytes containing LiCF₃SO₃ salt having ionic conductivity of ~10⁻³ S/cm at room temperature. Scrosati et al. [94] have studied lithium ion
conducting and proton conducting polymer gel electrolytes and found their suitability in Li$^+$ ion batteries and fuel cells respectively. No doubt, initially the work was concentrated on gel electrolytes containing various lithium salts mainly, however, proton conducting polymer gel electrolytes have also been described due to their suitability in many devices [95]. Protons conducting polymer gel electrolytes containing H$_3$PO$_4$, H$_2$SO$_4$, HCl [96], hydroxy benzoic and aliphatic dicarboxylic acids [97] have been recorded with conductivity higher than the corresponding liquid electrolytes. Arora et al. [98] have described PMMA based polymer gel electrolytes containing different acids with PC, EC and DMF as solvents. The modification in ionic conductivity with the addition of PMMA has been described on the basis of “Breathing polymer chain model”. In accordance with this model, folding and unfolding of the polymer chain occurs due to the breathing which implies the pressure fluctuations at microscopic level [98]. This also helps to dissociate ion aggregates as well as un-dissociated salt which results in an enhancement in ionic conductivity value. Some of the recent publications by different workers on the polymer gel electrolytes have also been identified [98-101]. From the above discussion, it has been concluded that polymer gel electrolytes have been observed to possess high ionic conductivity, but their mechanical and thermal stability still need further improvement. Data of some available patents on different polymer electrolytes has also been shown in Table 1.

| Sr. No. | Inventor | Polymer Electrolyte (Title) | Conductivity order (S/cm) | Patent Number (Year) |
|-------|----------|-----------------------------|---------------------------|---------------------|
| 1     | K. M. Abraham M. Alamgir | Mixed polymer electrolyte and mixed polymer electrolyte battery | 10$^{-5}$ | US5166009A (1992) |
| 2     | B. Kumar L. G. Scanlon Jr. J.D. Schaffer | Polymer-ceramic composite electrolytes | 10$^{-5}$ - 10$^{-3}$ | US5695873A (1997) |
| 3     | M. Zafar A. Munshi | Solid polymer electrolytes | 10$^{-1}$ - 10$^{-4}$ | CA2382118A1 (2001) |
| 4     | W. Smith J. McCloskey | Polycarbonate oligomers and polymers for use in electrolytes | 10$^{-5}$ | US20020168575A1 (2002) |
| 5     | Y. Kang C. Lee S. K. Kim | Polyalkylene oxide polymer composition for solid polymer electrolytes | 10$^{-4}$ | US20030044688A1 (2003) |
| 6     | M. Singh I. Gur H. B. Eitouni N. P. Balsara | Multiple electrolyte electrochemical cells Images | 10$^{-7}$ | US20110281173A1 (2011) |
| 7     | M. Singh I. Gur H. B. Eitouni N. P. Balsara | Solid electrolyte material manufacturable by polymer processing methods | 10$^{-5}$ | 8268197 (2012) |
| 8     | Y. S. Kim D. S. Kim K. S. Lee | Anion exchange polymer electrolytes | 10$^{-7}$ | US8492049B2 (2013) |
| 9     | B. Hsieh H. B. Eitouni M. Singh | Polymer electrolyte materials based on block copolymers | 10$^{-5}$ | US20120029099A1 (2014) |
| 10    | M.A. Zimmerman | Solid ionically conducting polymer material | 10$^{-4}$ | WO2016182884A1 (2016) |
| 11    | P. Kofinas A. Ghosh | Polymer Solid Electrolyte for Flexible Batteries | 10$^{-7}$ | US20100255383A1 (2016) |
In order to overcome limitations attained by polymer gel electrolytes, the effect of dispersion of filler to polymer gel electrolytes will also be one promising line of investigation to develop nano-dispersed polymer gel electrolytes, having high ionic conductivity values, good mechanical as well as thermal properties. Still little work has been done on the addition of nanoparticles to the gel electrolytes. Therefore, authors would also like to develop and study nano dispersed polymer gel electrolytes, especially by making the use of biodegradable polymer, in order to replace traditional polymer electrolytes to optimize their properties as earlier as possible.

### 4. Summary

Generally, polymer electrolytes have been observed to possess low ionic conductivity, poor mechanical as well as thermal property due to which there is a need to synthesize high performing polymer electrolytes. Although, incorporation of plasticizer has increased the ionic conductivity value as discussed yet improper concentration may deteriorate the mechanical properties of polymer electrolytes. Nanocomposite polymer electrolytes have shown the significant improvement in mechanical as well as thermal properties of polymer electrolytes; however ion transport properties still need further improvement. To address the problem of low ionic conductivity of polymer electrolytes, the addition of...
ionic liquids as plasticizer in polymer electrolytes has also been considered as one of the promising approaches. Therefore, in order to overcome the limitations of polymer electrolytes having low ionic conductivity values, the addition of additives in the combined form such as plasticizer/ionic liquid and nano filler will be one of the leading approaches. Since, polymer gel electrolytes have been reported to possess high ionic conductivity at room temperature. However, despite possessing high ionic conductivity values, the addition of additives in the combined form such as plasticizer/ionic liquid and ionic liquids as plasticizer in polymer electrolytes has also been considered as one of the promising perspectives.

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