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REVIEW

Nanocomposite polymer electrolytes

S. Austin Suthanthiraraj[1] · M. Johnsi[1]

Abstract The present effort reviews the state-of-the-art trends in respect of composite polymer electrolytes (CPEs) which are nowadays revolutionizing the modern approach towards energy storage and power supply gadgets. This evaluation mainly encompasses a series of systems based on polymer hosts such as poly(ethylene oxide) (PEO), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP), poly(vinylidene fluoride) (PVDF), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), and polyvinylchloride (PVC) developed and analyzed so far apart from certain nanofiller incorporated composite polymer electrolytes being used in conjunction with well-suited electrodes owing to their practical significance in several advanced types of power sources including hybrid electric vehicles. The emerging nanoscale techniques have by now led the market to appreciate the application potential of nanostructured inorganic and organic materials so as to realize enhanced efficiencies of batteries thereby providing one of the most promising energy storage devices as well.

Keywords Polymer electrolytes · Nanofillers · Batteries

Introduction

In the realm of modern society and industry, an important requirement involves production, storage, and distribution of energy.

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The need and impact on the development of highly performing chemical energy storage devices therefore remains one of the central challenges faced by the scientific research [1–3]. In recent years, several surveys have emphasized on the development of solid state polymer electrolytes as they are considered as important materials both from fundamental as well as practical applications in high energy batteries, super capacitors, fuel cells, smart windows, sensors, and electrochemical devices, etc. [4–8]. In this context, it is worthwhile to mention the list of best candidates for such applications based on materials such as ceramics, polymers, hybrids, or gels [9].The realization of employing solid polymer electrolytes in power sources is mainly due to certain advantageous features such as feasibility of high ionic conductivity, non-volatility, no decomposition at the electrodes, no possibility of leaks, shape flexibility, wide electrochemical stability window, higher temperatures of operation, and superior structural stability and so on [2, 10, 11]. Over the past two decades, the relevant literature survey reports on numerous approaches based on solid polymer electrolytes which are solid or gel ion-conducting membranes consisting of an ionic salt dispersed in a polymer matrix forming ionically conducting solid solutions.

The most commonly studied polymer electrolyte is the high molecular weight polyethylene oxide (PEO) which qualifies as a host polymer (because of its high power of solvation for lithium salts and good compatibility with electrode) [9, 12]; however, one of the major drawbacks that obstructs its applicability in many electrochemical applications is its low conductivity [13–16]. Another ideal candidate as polymer host for solid polymer electrolytes (SPEs) is a semi-crystalline and chemically resistant copolymer, namely polyvinylidenefluoride-co-hexafluoropropylene (PVDF-CO-HFP). In recent years, high dielectric constant material PVDF-CO-HFP polymer with excellent mechanical strength has received a major attention towards realization of appreciably high charge–storage capacitors and electro-active materials [17, 18].

It was reported by Wang and coworkers [19] that an electrolyte is responsible for the ionic conduction mechanism in a PVDF-based GPE system while the PVDF matrix acts as the passive substrate that the solution holds within the porous framework of the polymer. Although reasonable conductivity is achieved by increasing the content of Li salts such as LiClO$_4$, LiPF$_6$, and LiCF$_3$SO$_3$ [20–22], appropriate mechanical properties of the PVDF-based SPE system have significantly deteriorated. Furthermore, the leakage of solvent from the above polymer electrolyte would also damage Li electrode and thereby ionic conductivity drops to a lower value. To overcome such problems and to achieve an excellent compatibility with Li electrodes, dispersion of nano or submicronsized inorganic fillers into the polymer matrix would be expected to greatly influence ion-conducting properties of the polymer electrolyte [23–26]. On the other hand, a detailed investigation by Sarnowska et al. [27] as performed through Bellcore process (preparing method of gels) in order to determine the effect of inorganic filler surface modified with acidic groups, morphology of the polymer matrix, temperature dependent ionic conductivity, and interfacial stability. However, those polymer electrolytes prepared by this technique are known to undergo poor rate capability [28]. The dispersion of fillers into polymer films not only enhances the ionic conductivity of a polymer electrolyte system but also improves the overall physical and electrochemical properties as well.

Ramesh and coworkers [29] reported that the observed maximum ionic conductivity is closely related to the formation of nanosized filler grain boundaries, i.e., ion-hopping mechanism. At this point, the effective addition of SiO$_2$ nanofiller to PMMA/PVC-based electrolyte interacts within the electrolyte matrix thereby resulting in the formation of a space charge layer. The inter-particle distance of those interfacial layers varies with the level of filler loading. As a result, such space charge layers formed by the nanofillers overlap themselves and tend to form a continuous network of a conduction pathway which promotes a faster and more favorable ionic conductivity [29]. The incorporation of electrochemically inert ceramic filler particles of α-alumina in the case of a PEO-based solid polymer electrolyte system at room temperature was first demonstrated by Weston and steele [30], and though it possess a low conductivity more recent studies have revealed the feasibility of incorporation of a number of nonconducting fillers in order to promote an enhancement of ionic conductivity in a series of PEO-based systems. In addition to lithium battery applications, these fillers are expected to promote the electrolyte system towards higher dynamics of transportation of ions, in conjunction with mechanical and interfacial stability features even in the absence of a liquid [31, 32]. Dilip et al. [33] and Tsutsumi H et al. [34] focused on various other factors that may depend on ion transport properties like dielectric constant of the polymer host, degree of dissociation and loading of salt, aggregation of ions, and mobility of a

polymer chain network. A recently developed strategy in the field of polymer electrolytes deals with introducing room temperature ionic liquids consisting of bulky, asymmetric organic cations, and inorganic anions such as imidazolium, phosphonium, and quaternary ammonium which are of increasing electrochemical interest even though they are found to have some practical limitations, for instance, poor dimensional and mechanical stabilities [29]. Therefore, these problems could be avoided by suitable reinforcement of a uniform dispersion of nanosized inorganic fillers in order to improve their mechanical stability and ionic conductivity [35, 36]. Generally, in the arena of nanocomposite polymeric systems, much interest has been witnessed owing to certain peculiar characteristics of nanomaterials like size, mechanical properties, morphology, interfacial features, and low-level concentrations which may significantly influence a desirable change within a polymer matrix. Moreover, it is a fast growing area of research and, hence, these nanocomposites appear to promise new applications in many fields such as mechanically reinforced lightweight components, non-linear optics, battery cathodes, nano-wires, sensors, and systems alike. Among the various approaches available for enhancing the conductivity of solid polymer electrolytes nanocomposites based on layer-structured clays are well-known for their improved ionic conductivity, mechanical strength, thermal stability, stiffness, dimension stability, and gas barrier properties of polymer electrolytes [37]. Recently, researchers have paid considerable attention towards development of these promising new materials namely polymer electrolyte systems based on nanoclays since these clays are characterized with special features of a large interfacial contact area with the polymer host in intercalated and exfoliated forms, thereby sustaining the mechanical property of the polymer and also increases the solubility of salts due to high dielectric properties. Moreover, this class of nanocomposite has a high cation-exchange capacity, appropriate interlayer charge, and in particular the use of intercalated or exfoliated state of montmorillonite (MMT) plays an important role in enhanced ion conduction which has been widely reported in literature [38–40].

Prasanth et al. [41] also reported that incorporation of a nanoclay into a host polymer matrix is an effective method to minimize the ion pair formation and thereby explained the mechanism involving the structural modification and promotion of Li$^+$ conducting pathways increasing the lithium salt dissociation and showing that such polymer–clay nanocomposites are superior. On the other hand, dielectric relaxations and conduction mechanisms in polyether–clay composite polymer electrolytes under high carbon dioxide pressure were studied by Kitajima et al. [42]. The same group explored a comparison on PEO–clay composites, wherein PEO chains were inserted between the clay layers and compared with the conventional PEO–LiBF$_4$ system in terms of the conductivity of PEO–Li–MMT composites where the latter is found to

exhibit an improved conductivity because of the fast segmental motion of PEO chains feasible in the Li–MMT composites with a negligibly small temperature dependence. Jung et al. [43] have reported that the mechanical property of gel polymer electrolytes/octadecylamine modified montmorillonite nanoclay (OMMT) enhances their ionic conductivity. More recently, nanocomposite polymer electrolytes alone are identified to yield a promising candidate which may offer good and better electrolyte/electrode compatibilities, morphological, electrochemical stability, and safety hazards [23, 44–46].

However, relatively few investigations were performed by Fujinami and coworkers in 1997 [47] on solid polymer electrolytes derived from single-ion-conducting electrolytes, probably due to low conductivities and complicated synthesis routes where single-ion conductors are blended with high molecular weight poly(ethylene oxide) (PEO) so as to improve their conductivity, although similar studies were also made with Nafion (single-ion conductor) with a view to improve the protonic conductivity. Single-ion conductors have many advantages over typical bi-ion-based solid polymer electrolytes. During discharge in bi-ion salt-based solid polymer electrolytes, both the mobile anions and cations may migrate towards the oppositely charged electrodes, thereby polarizing the electrolyte and increasing its resistivity. Recharging the cell would therefore require more energy, time, and a greater electrochemical potential. As a result, polarization problem of the cell is unique to bi-ionic salt-based solid polymer electrolytes. This problem may be solved by using single-ion-based conductors in which the constituent anions are immobilized [48]. The immobilization of anions within the polymer is the most common approach for creating a promising single-ion conductor. To overcome all these limitations of classical polymer electrolytes, single-ion-conducting nanocomposite polymer electrolytes have recently been investigated and reported in the literature. Bertasi and coworkers [49, 50] focused their research work on doping polyethylene glycol 400 (PEG400) with different amounts of a fluorinated TiO_2-based nanofiller (LiFT) that is surface-functionalized with Li^+ cations, and these materials could provide a high ionic conductivity of about $>10^{-5}$ Scm^{-1} at room temperature. Interestingly, in this case the fluorinated TiO_2 nanoparticle (LiFT) acts like a macro-multi-anion support wherein PEG400-based polymeric matrix serves as a weak ligand for the coordination of Li^+ cations. The significant difference between the masses of Li^+ cation and multi-anion nanoparticle gives rise to a new type of Li^+ single-ion-conducting nanocomposite polymer electrolyte. Similar work featuring nanocomposite polymer electrolytes based on Li^+ functionalized surface with fluorinated Fe_2O_3 nanofiller (LiFI) was demonstrated to yield single-ion conduction in those electrolyes [51]. Usually, polymer electrolytes are characterized with low transference number and, consequently, they are more susceptible to polarization phenomena that may eventually limit the power delivery during battery discharge. To date, the development of polymer electrolytes showing both high lithium transference number (approaching unity) and high ionic conductivity at ambient temperature remains a major intriguing and challenging task. More recently, Porcarelli et al. [52] succeeded with the synthesis of single-ion-conducting polymer electrolytes (SIPEs) simultaneously exhibiting high lithium transference number, high ionic conductivities at room temperature, and good mechanical strength. Such a unique combination of properties allowed their use as thin-film separators in lithium batteries operating at room temperature.

Accordingly, in this review important findings pertaining to the appropriate influence on a nano-composite polymer electrolyte matrix comprising various host polymers in conjunction with the incorporation of suitable dopant salts and an account of various nanosized inorganic fillers such as Al_2O_3, ZrO_2, TiO_2, and CeO_2 has been summarized in detail. Meanwhile, nanosized fillers are known to provide the required large surface area and maximum number of Lewis acid-base groups on their surface for a favorable migration of mobile ions to proceed in these amorphous phases. Since the impact of polymer-in-filler systems may offer an extraordinary mechanical strength along with appreciable electrical conductivities, it is really a challenge for the entire battery production technology which is expected to gain in popularity and develop rapidly in the forthcoming years.

Basic aspects of polymer electrolytes

From a practical point of view, ion-conducting polymer electrolytes suitable for a rechargeable battery should essentially satisfy the basic requirements that have evolved regarding the selection of the host polymer, salt, and polymer electrolyte as a combined matrix exhibiting an appreciably high ionic conductivity along with good electrochemical and mechanical stability features. [9, 14, 53].

- As a consequence, the host polymer also should possess an amorphous or low crystalline nature and comprise polar groups such as O, N, S, and F and so on in its chain with a high molecular weight apart from sufficient electron pair donors in order to coordinate with cations.
- The polymer is expected to exhibit a very low glass transition temperature (T_g), i.e., higher flexibility of the polymer chain which facilitates for fast ion conduction and thereby provides dissociation of salt that in turn enhances only whenever the lattice energy of the chosen salt and cohesive energy of the polymer are low enough.
- To achieve the desired performance level, the identified polymer electrolyte should possess ionic conductivities approaching or beyond 10^{-3} S cm^{-1} at ambient conditions.
- The electrolyte should have considerably high cationic transport number rather than anionic which is necessary

in order to reduce the concentration gradients set up by the mobility of both cations and anions during repeated charge-discharge steps and thus produce higher power density values too [11, 54].

- Electrochemical properties such as high decomposition potential of the polymer electrolyte and low interfacial resistance also remain as important parameters for an electrolyte to be considered suitable for high performance polymer electrolyte-based electrochemical power devices [55].
- The polymer electrolyte should possess high chemical and thermal stability in order to maintain long-time durability within the operating conditions of the specific device and in specific it ought to be electrochemically compatible with electrode materials.
- The stiffness for a polymer electrolyte material becomes a significant criterion during its fabrication in the form of a device.
- The polymer electrolytes should be cost effective in order to exploit the usage of polymer electrolytes in various electrochemical devices.

Major categories of polymer electrolytes

Solid polymer electrolytes

Dry solid polymer electrolyte is basically a single phase system and found to be a non-crystalline material encompassing the dissolved salt where both the positively (cations) and negatively (anions) charged ions of the salt are mobile [11]. And distinctly, the polymer host by itself used as a solid solvent along with lithium salt and does not contain any organic liquids [56]. On the other hand, solid polymer electrolytes are prepared by complexing with suitable ion donating salts involving ClO_4^-, $CF_3SO_3^-$, BF_4^-, or AsF_6^- species etc. into high molecular weight polymers such as poly (ethylene oxide) (PEO), poly (propylene oxide) (PPO), and poly (vinylpyrrolidone) (PVP) which carry polar groups such as -O-,-N-H-, and-C-N-.Those polymers and ionic salts would have a tendency to make these complexes and remain as a single phase. The development of lithium batteries based on poly (ethylene oxide) (PEO) was first extensively investigated by Wright et al. [57, 58]. PEO has high solvating power for lithium ions and high compatibility with the lithium electrode so as to form complexes [59]. However, it is also known that the observed high conductivity (10^{-3}–10^{-4} Scm^{-1}) of most PEO-based polymer electrolytes requires operation over the temperature range 80–100 °C below which these electrolytes suffer from low conductivity values in the range of 10^{-7}–10^{-8} Scm^{-1} because of the existence of high degrees of crystallinity of PEO [15, 60, 61]. The resulting low electrical conductivity value of polyethylene oxide (PEO) still obstructs its applicability in different types of electrochemical device applications [9, 13, 14]. Moreover, due to the presence of highly crystalline phases in systems like PEO and PPO, solvent-free polymer electrolytes suffer a major drawback. In such systems, for practical applications the ionic conductivity has been achieved up to 10^{-4} Scm^{-1} approximately below their melting temperature beyond which a polymer electrolyte predominantly exists in an amorphous phase [14, 62, 63].

The development towards realization of solid state lithium batteries based on high molecular weight polymers offers excellent and potential candidates as new polymer electrolytes and the main reason to select this type of host polymers is because of the fact that they possess the ability to form stable complexes with salt-based cations in general and yield a homogenous matrix. Moreover, the lattice energy of the dissolved salt should be low enough in order to facilitate its dissociation and hence to increase the electrochemical stability of the resultant polymer electrolyte [62].

Gel polymer electrolytes

Polymer gel electrolytes are usually formed by incorporating certain organic additives into a polymer matrix which exhibit the effect of softening of the polymer. Such gel electrolytes constitute an important class of ion-conducting polymeric materials since their improved room temperature ionic conductivity values are comparable with that of liquid electrolytes. Earlier in 1975, Feuillade and Perche [64] demonstrated this kind of concept by dissolving suitable alkali metal salts in a polar, high dielectric liquid solvent, and then by adding polymer mixtures with a view to form a mechanically stable electrolyte film of desired shape and size. At this stage, these organic solutions of the alkali metal salt remain trapped within the polymer matrix and appear like an intermediate phase of solid and liquid, i.e., gel type with a high conductivity close to the liquid electrolytes. In this case, polymer acts like a stiffener for the solvent which solvates the salt and acts as a conducting medium. Many literatures reports on the cohesive properties of solids and diffusive transport properties of liquids make the gel polymer electrolytes a promising candidate for its application in different electrochemical devices [65–67].

Since then, polymer gel electrolytes with a number of polymer hosts, namely poly(vinylidene fluoride) (PVdF) [68, 69], polyacrylonitrile (PAN) [70, 71], poly(ethylene oxide) (PEO) [72, 73], poly(methyl methacrylate) (PMMA) [74], thermoplastic polyurethane (TPU) [74, 75], and poly(propylene carbonate) (PPC) [76–79] have been synthesized which exhibited ionic conductivity values in the range $\sim 10^{-4}$–10^{-3} Scm^{-1} at ambient temperature. The main disadvantages of polymer gel electrolyte are increased reactivity with lithium metal electrode, solvent volatility, and poor mechanical stability at high degree of plasticization due to its gel type nature [80]. To retain the desired mechanical properties of polymer gel electrolytes, these films have to be hardened either by chemical or

physical curing process (high energy radiation), which results in high processing costs [36].

Composite polymer electrolytes

Incorporating inert oxides into polymer electrolytes has recently attracted many researchers due to its appealing properties such as improved mechanical stability, enhanced ionic conductivity, and electrode-electrolyte interface stability [23, 32].One of the major problems encountered earlier was the unsuccessful operation and safety limitation with regard to lithium batteries. Accordingly, all these shortcomings of the lithium battery could be eliminated/minimized by employing nanocomposite polymer electrolytes instead of conventional/gel/plasticized polymer electrolytes. On the other hand, an innovative class of nanocomposite polymer electrolytes was also widely examined which provides many unique opportunities in producing ion-conducting materials capable of satisfying the demanding requirements of automotive and portable electronics industries. Single-ion-conducting nanocomposite polymer electrolytes are typically based on a polyether matrix used to dissolve a lithium salt and to suspend inorganic nanofiller such as SiO_2, TiO_2, Al_2O_3, ZrO_2, ZnO, and clay. It was suggested that the presence of inorganic species at the interface with the polymeric chains generates a grain boundary effect, thereby significantly increasing the observed conductivity [50]. Interestingly, single-ion-conducting nanocomposite polymer electrolytes are the only species involved in electrodic processes and such ions are mobile in the long-range charge transfer events, thereby avoiding the development of concentration gradients and polarization phenomena within the cell. Furthermore, the possibility of overcoming the low transference number and low conductivity systems from devising polymer electrolytes, wherein the Li-containing functional groups are bonded to the polymer backbone [81]. The remarkable performance of lithium polymer cells operating at room temperature suggests that these materials may represent an important step towards the development of the next generation of safe, cost-effective, and environmentally friendly lithium polymer batteries.

Composite polymer electrolytes are basically solid polymer electrolytes which act as a two-phase system in which the conventional polymer electrolyte acts as a first-phase host matrix and disperses with different types of micro, nano, conducting, zeolites, ionites, insulating etc., as a second-phase dispersoid [36, 67]. The dispersion of nano/micro-ceramic fillers particles also improves the morphological, electrochemical, and mechanical properties of solid polymer electrolytes. [23, 44, 46, 67]. The insulating ceramic fillers like Al_2O_3, ZrO_2, TiO_2, CeO_2, SiO_2 etc. have been investigated by many research groups and important composite polymer electrolyte systems developed so far are listed in Table 1.

Polymer nanocomposite system containing inert fillers

Nanocomposite polymer electrolytes containing Al_2O_3 nanofiller

To realize the enhancement of various properties of polymer electrolytes, Al_2O_3 nanopowder is found as one of the most extensively studied inert nanofillers. The occurrence of an enhancement on the observed room temperature in ionic conductivity of the typical polymer electrolyte system PEO/$LiClO_4$ was studied by Qian et al. [99]. A model was demonstrated by Croce et al. [100] attributing the role of Al_2O_3 filler in the composite polymer electrolyte and it is not only limited to prevent the crystallization of the polymer chain but also in promoting specific interactions between surface groups and both the PEO segments and electrolyte ionic species resulting in the rise of the fraction of free ions which may be transported fast at the filler surface through the conduction pathways. Lim et al. [101] reported that the impact of the nature of Al_2O_3 nanofiller surface group enhances the observed ionic conductivity of the polystyrene/$LiCF_3SO_3$ system. Research has been focused in order to increase both the mechanical strength and electrochemical performance of electrolytes dispersed with the reduced-size nanofillers. In fact, Krawiec et al. [102, 103] studied the enhancement conductivity of PEO-$LiBF_4$ system with the decreasing size of Al_2O_3 filler particle size. Besides these facts, those properties based on nanocomposites are quite often considered to provide promising electrolyte materials for the development of efficient and reliable rechargeable batteries.

Nanocomposite polymer electrolytes containing ZrO_2 nanofiller

To enhance the extent of ionic conductivity, nanocomposites based on several ceramic oxides have also attracted many researchers. The most serious problem involved electrolyte leakage which could be deteriorated only by the addition of inert fillers for improving the mechanical stability as well as electrode-electrolyte interfacial stability [104–108]. Though a variety of ceramic fillers have been examined and characterized over the past few years, a number of investigations were made on ZrO_2 nanoparticles in particular. Nithya et al. [109] synthesized nanosized ZrO_2 by polyacrylamide gel method. Additionally, ZrO_2 was also used for the nanocomposite polymer electrolyte based on P(ECH-EO):$LiClO_4$ system. The complexation of ZrO_2 to the polymer matrix was confirmed by XRD with an improved conductivity of the order of 10^{-4} Scm^{-1} at room temperature. On the other hand, an interesting type of composite micro-porous polymer electrolyte system based on optimized composition of P(VdF-HFP)-ZrO_2 was prepared by Kalyana et al. [110] through a preferential polymer dissolution process. The problem associated

Table 1 Polymer hosts generally studied with examples of nanocomposite polymer electrolyte [NCPE] complexes

Polymer host	Repeat unit	NCPEs	Ref
Poly(ethylene oxide)	$-(CH_2CH_2O)_n-$	$PEO-NH_4I-Al_2O_3$	[82]
		$PEO-LiBF_4-TiO_2$	[83]
		$PEO-Ag(CF_3SO_3)-Al_2O_3$	[84]
		$PEO-AgSCN-Al_2O_3$	[85]
Poly(vinylidene fluoride)	$-(CH_2-CF_2)_n-$	$PVDF-LiTf-ZrO_2$	[86]
		$PVDF-Ag CF_3SO_3)-Al_2O_3$	[87]
		$PVC-PVDF-LiBOB-ZrO_2$	[88]
		$PVDF-PVC-LiBOB-TiO2$	[89]
Poly(vinylidene fluoride-hexafluoropropylene)	$-(CH_2-CH)$	$PVDF-HFP-Nafion/AlO(OH)_n$	[90]
		$PVDF-HFP-Zn(CF_3SO_3)_2-ZrO_2$	[91]
		$PVDF-HFP-Zn(CF_3SO_3)_2-TiO_2$	[92]
		$PVDF-HFP-NH_4BF_4-SiO_2$	[93]
		$PVDF-HFP-LiPF_6-TiO_2$ hybrid	[94]
Poly(acrylonitrile)	$-(CH_2-CH(-CN))_n-$	$PAN-LiClO_4-Al_2O_3$	[95]
Poly(methyl methacrylate)	$-(CH_2C(-CH_3)-$	$PMMA-PEO-AgNO_3-TiO_2$	[96]
	$(-COOCH_3))_n$	$PMMA-LiClO_4-PANI$ nanofibers	[97]
Poly(vinylchloride)	$-(CH_2-CHCl)_n-$	$PVC-Li_2B_4O_7-DBP$	[98]

with micro-size ceramic oxide may effectively increase the larger orientation in the case of a polymer electrolyte film which in turn leads to a non-conducting plane being perpendicular to the flow of current, and thereby shows a drop in the measured ionic conductivity [111]. In order to avoid such a problem, this type of preparation process is preferred for the development of nanocomposites based on a PVDF-CO-HFP copolymer. Interestingly, it was revealed that crystallinity and viscosity are the only two factors that influence the mobility of ions as well as ionic conductivity. It is now worthwhile to mention that an improved ionic conductivity may be ascribed as due to the large amount of vacancies created by oxygen atoms that are available on the ZrO_2 surface and by this means tend to act as active Lewis acidic sites to interact with ions. Accordingly, the resulting nanocomposite polymer electrolyte system is found to be electrochemically stable up to 5.0 V vs Li/Li$^+$. Other coworkers in the same group have developed yet another nanocomposite system based on PVDF-CO-HFP-ZrO_2 as soaked in 1 M $LiClO_4$ electrolyte solution which contained ethylene carbonate (EC) and dichloro ethane (DCE) and characterized with maximum ionic conductivity of 10^{-3} Scm^{-1} at room temperature [112, 113].

Arup Dey et al. [4] reported the effect of ZrO_2 as nanoadditives on ionic conductivity of PEO-$NaClO_4$ polymer electrolyte system based on the Lewis acid-base reaction occurring between the chosen ceramic filler and polymer. This mechanism may be explained on the basis of the fact that the Lewis acid site on the surface of ZrO_2 nanoparticle interacts with base centers of ether oxygen in PEO which may lead into the complex formation. Furthermore, Ibrahim and coworkers [114] found that the dispersion of 5 wt% of ZrO_2 resulted in a

maximum ionic conductivity of 10^{-3} Scm^{-1} within the PVDF-CO-HFP-$LiCF_3SO_3$ electrolyte system. Thus, the occurrence of high conductivity may be attributed to the most probable increase in the concentration of mobile ions within the amorphous region whereas the decrease in conductivity witnessed on high concentration of ZrO_2 nanofiller may be due to the process of aggregation of filler particles which in turn results in the reduction of number of charge carriers [114].

Nanocomposite polymer electrolytes containing TiO$_2$ nanofiller

Since TiO_2 is also a feasible candidate with interesting characteristics as a reinforcing nanofiller in the design of polymer nanocomposites, over a hundred research papers have been exclusively reported based on TiO_2 nanostructures embedded with polymer matrices [115, 116]. Nanocomposite polymer electrolytes involving TiO_2 nanoparticles are known to be capable of enhancing the extent of ionic conductivity, cation transference number, and eventually tend to offer improvement of mechanical strength as well. The feasibility of arriving at remarkable ionic conductivity is achieved by the occurrence of dipole interaction of TiO_2 within the polymer matrix as reported by Kim et al. [117]. The dipole property influences the extent of ion migration occurring within those nanopores because of their high dielectric constant, and Li et al. [118] also related the role of TiO_2 with dielectric constant where the TiO_2 nanoparticles may diminish the aggregation of ions within the electrolyte medium which might originate from their dielectric nature or chemical interactions existing between TiO_2 and PVDF-CO-HFP. According to Kim and coworkers

[119], research efforts under the condition of subsequent ball milling could not be carried out for TiO$_2$ nanoparticles since these nanoparticles may give rise to certain drawbacks such as very low ionic conductivity and serious issues at higher charge-discharge current densities. In order to improve the dispersibility of inorganic nanoparticles into the polymer matrix and ensure interface compatibility between polymers and inorganic nanoparticles, a new type of TiO$_2$-PMMA material by in situ sol–gel method was performed by Cao et al. [120] with a view to overcome the possible aggregation of TiO$_2$ nanoparticles in the PVDF-CO-HFP-based polymer electrolyte system for Li battery applications. Wang et al. [19] prepared TiO$_2$ nanoparticles by a similar sol–gel process in order to obtain the nanocomposite polymer electrolyte system PVDF/LiClO$_4$/TiO$_2$. A clear understanding regarding the interaction existing between TiO$_2$, LiClO$_4$, and PVDF has been elucidated and the effect of TiO$_2$ content was found to decrease the amount of crystalline phase. The maximum ionic conductivity achieved for 10 wt% TiO$_2$ loading was found to be 1.8×10^{-3} Scm^{-1} beyond which the aggregation phenomenon occurring with low surface area inhibits the mechanism of ionic conduction on the surface of TiO$_2$ nanoparticles.

Nanocomposite polymer electrolytes containing CeO$_2$ nanofiller

Cerium oxide has been under extensive research on account of its specific properties such as good electrical conductivity and high diffusivity at room temperature [121]; also because of its promising potential, it acts as a promoter or supporter in catalytic processes due to its oxygen storage capacity in industries [122, 123]. In general, ceria is one of the most reactive rare earth metal oxides [124] with a strong Lewis acid character [125]. This superior character of CeO$_2$ tends to affect the release of conducting ions by interacting with bases of the host polymer network. The electrical properties of CeO$_2$ based on PEO with potassium and ammonium salts have been reported by Arup Dey et al. [4, 125]. Moreover, Minakshia and co-workers [124] reported that the addition of CeO$_2$ nanofiller influences the overall discharge-charge performance of MnO$_2$ battery by raising the oxygen evolution potential during charging since CeO$_2$ is an excellent material to release and absorb oxygen reversibly during redox reactions. Room temperature ionic conductivities of the order of 10^{-4} Scm^{-1} were reported for PEO/PEG blends/LiClO$_4$ [126] and for the complex PVDF-CO-HFP/Zn(CF$_3$SO$_3$)$_2$ [55] with CeO$_2$ as nanofiller. As an effective means for increasing ionic conductivity, ceramic fillers play a vital role in polymer electrolytes. In the case of gel polymer systems such as PVDF-CO-HFP/LiPF$_4$/EC/DMC/EMC [127] and PVDF-CO-HFP/LiClO$_4$/EC/DMC [128], the measured ionic conductivity attained a maximum value of the order of 10^{-3} Scm^{-1} for each of these systems with CeO$_2$ as nanofiller which are widely used in lithium batteries. The increase in the observed ionic conductivity by the incorporation of the nanofiller is mainly ascribable as due to the Lewis acid character of the nanofiller which competes with cations of the salt for possible interactions occurring between the polymer matrix and nanofiller that may be expected to result in a more favorable environment for the fast ionic conduction process to proceed.

Conduction mechanisms in polymer electrolyte systems

It is pertinent to discuss the nature and origin of the conduction process in various configurations of polymer electrolyte systems that already developed so far as well their characteristics, as these electrolytes are quite suitable for practical applications as solid state devices. When compared to liquid electrolytes, polymer electrolytes are treated as materials having high energy density values with lesser chance of electrolyte leakage in a flexible light weight form and a characteristic feature of forming a solvent-free transparent thin film with high ionic conductivity. Even though the use of polymer electrolytes tends to offer a number of suitable features, certain issues such as internal shorting, use of corrosive solvent, production of harmful gases, wettability of electrodes, and presence of noncombustible reaction products on the electrode surface need to be addressed to [129, 130]. Improvement in the ionic conductivity is the most important property of polymer electrolytes desirable at ambient temperatures in the context of their technological applications.

In general, the ionic conductivity of a polymer electrolyte depends on the molecular mobility and charge transport, based on which many recent studies have been carried to investigate the nature of ion transport process [131]. The mechanism of ionic conduction in polymer electrolytes is generally a property based on the presence of the amorphous elastomeric phase. The ionic mobility is strongly influenced by the ionic association, ion-polymer interactions, and local relaxations that are prevalent within the polymer. Therefore, the concentration of ionic charge carriers of metal salts within the electrolyte depends mainly on the dielectric constant and lattice energy of the salt. Thus, higher the dielectric constant or lower the lattice energy, the charge carrier concentration is more.

With respect to ionic conductivity, dielectric properties constitute a specific significance in the characteristics of ionic and molecular interactions. Dielectric constant is a measure of reduction of columbic interaction which facilitates the polymer to dissolve the appropriate salt. The mechanism involved in the movement of charged species and dipole orientation of the polymer electrolyte may be analyzed by means of frequency-dependent conductivity and dielectric relaxation and all these studies provide the necessary details pertaining to complete ionic transport mechanism in the case of fast ion conductors [132, 133]. Using PEO as a polymer, a great deal of research has been performed on polymer electrolytes

though the polymer viz., PEO limits its applicability due to its crystalline behavior which results in low conductivity. Another important parameter which may determine the ionic conductivity of a polymer electrolyte matrix is its crystallinity in view of the fact that crystalline polymers and crystalline regions in semi-crystalline polymers do not allow ions to move freely. The transport of ion carriers is thus restricted in the case of crystalline phase so that the segmental motion and conductivity are very low. However, in the case of an amorphous phase, there is a segmental motion of polymer chain which facilitates the displacement of ions. As a result, the transport of ions is relatively easy and therefore yields an enhanced conductivity as well. Nevertheless, it is also understood that in the case of polymer electrolytes, the battery performance is limited by the rapid diffusion by the cations. These cations are coiled by the chain segments of the polymer while leaving their anions to occupy separate positions. At this point, if there is a relaxation of polymer segments, the transport of cations would take place so that the cations are released from a segment and then occupy another segment. Thus, segmental relaxation requires the presence of free volume within the polymer matrix which is a condition that could be achieved if the polymer is in an amorphous state [54].

It is important to mention that several investigators have suggested that the electrical conductivity mechanism in polymer electrolyte systems generally takes place through two distinct events. The first aspect is associated with the charge migration of ions between coordination sites available within the polymer host material, whereas the second step may be attributed to an increase in the observed conductivity produced by the segmental motion of polymeric chain itself [134, 135].

Therefore, attempts have been made to enhance the ionic conductivity of polymer electrolytes to a reasonable value suitable for their use in practical applications, by forming co-polymers [136], blending with inert ceramic filler [137] and soon. Blending with ceramic filler showed high conductivity since the role of filler is to influence the recrystallization kinetics of the polymer chains and thereby to promote the amorphous regions for the transport of cations [54].Earlier in 1998, Croce et al. [23] reported the enhancement in conductivity up to three orders of magnitude at low temperature and about one order of magnitude at high temperature for the system PEO-LiClO$_4$-containing ceramic fillers. The mechanism through which the incorporation of inorganic fillers to the polymer electrolyte complex was explained in terms of Lewis acid-base type of interactions. The degree of dissociation of the salt in the complex would be greater because of those interactions between the polar surface groups of the inorganic solid oxide filler and the ionic species of the electrolyte. As the solid oxide filler is arranged in a long connecting channel manner within the polymer electrolyte host, the transport of ions is achieved through the sequential replacement of ion to adjacent hole.

This probable conducting mechanism could be achieved simultaneously and work synergistically to yield favorable ionic conductivity [138]. On the other hand, volume fraction of the filler particles depends on the conductivity of a composite. In other words, the conductivity increases with an increase in the volume fraction of filler particles so that the total amount of amorphous phase around the fillers also increases. It is clear from the above fact since the surface area of the filler particles increases, the conductivity also increases. However, in the case of high filler content, the particles get agglomerates so that surface area would be compact, and this would probably reduce the fraction of amorphous state around the filler. At a specified content of filler, the continuous network of amorphous state disappears so that the cationic transport is blocked [54]. Therefore, the enhancement of conductivity in polymer electrolyte composites may be effectively estimated with the conductivity of filler particles [139].

Important application areas of polymer electrolytes

In 1970s, the beginning of research in the field of polymer electrolytes had been widely accepted for various applications in electrochemical power devices. The use of polymer electrolytes offers the possibility of thin films formation which enables the device miniaturization. Good adhesive nature of polymer electrolytes promotes better electrode-electrolyte contact in some of the following devices discussed below.

Fuel cells are considered to be the most promising candidates as zero-emission power sources in the application point of view, which are environmental friendly devices for energy conversion and power generation [140]. The development of fuel cells has been worldwide over 150 years, ever since their invention in 1839 by William Robert Grove. The fuel cell became a real option in 1980s due to an increase in the awareness of energy and environment concerns. At present, less pollution for the betterment of human life has become a matter of great concern; however the extensive use of fossil fuels has resulted in severe pollutant emissions, including SOx (sulfur oxides), NOx (nitric oxides), CO (carbon monoxide), and particulates which poses severe threat to the health of human beings [141]. Since fuel cells possess higher electrical energy conversion efficiencies compared to heat engines, fuel cells may be expected to reduce dependence on fossils fuels and diminish poisonous and toxic emissions into the atmosphere. As fuels cells are essentially zero-emission power sources, they have been identified as the most efficient, sustainable, and potent technology to meet the energy security features. Over the past decades, though the technology in the case of fuel cell has significantly developed, there are some technological barriers still which delay the commercialization in many applications such as insufficient durability, cell life time, and fuel cell component costs [142]. Nevertheless, the high cost involved with commercialization of fuel cells may be

addressed by the development of new materials and fabrication processes [143]. Generally, there are different types of fuel cells which are classified based on electrolyte materials. Among various electrolyte materials, the category of solid polymer-based electrolytes constitutes the one which offers more advantages due to characteristic superior features such as high efficiency and high energy density.

Fuel cell is an electrochemical cell which converts the fuel source into an electric current by an electrochemical process involving essentially electrode-electrolyte system with a continuous supply of fuel like hydrogen (H_2), natural gas, or methanol (CH_3OH) at anode and an oxidant like oxygen (O_2) or peroxide (H_2O_2) at cathode. In other words, by a simple electrolysis mechanism the fuel cell could directly convert chemical energy into electrical energy [144]. The main component of the fuel cell setup is composed of anode, cathode, and an electrolyte. The working principle of a hydrogen fuel cell is of two steps: (i) at the anode region, hydrogen directly penetrates through the porous anode and ionizes to release electrons and protons, (ii) at the cathode region, oxygen reacts with the electrons and protons from the electrolyte to form water. At this stage, the electrical energy is produced and flows from the anode to the cathode through an electrical circuit. There are different types of fuel cells which have been designed and developed into a variety of applications. On the basis of the electrolyte, fuel, and oxidants, the fuel cells have been categorized into different groups which include alkaline fuel cell (AFC), direct methanol fuel cell (DMFC), proton exchange membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC) [145]. The various fuel cells could be distinguished by the type of electrolytes used. Polymer electrolyte fuel cell (PEFC) eliminates the corrosion problems [146]; factors such as durability and cost still remain as the major barriers to fuel cell commercialization [147].The conversion of biological compounds from domestic waste water into electrical energy may be analyzed by microbial fuel cell (MFC) [148]. Perfluorinated polymer electrolyte membranes such as Nafion and Flemion have been extensively used as polymer electrolytes for fuel cells. These polymer electrolytes have sufficient electrochemical properties, mechanical properties, and chemical and thermal stabilities [149]. Fuel cells possess the distinct advantage with high efficiency, low production cost, and low emissions of pollutants and act as the clean alternatives with novel renewable energy storing mechanisms [150]. As mentioned above, the principle advantage is of great importance as there is a need to decrease and eliminate vehicle emmisions within cities and these fuel cells are the possible alternative to conventional energy conversion systems.

Battery is a self-contained unit that converts the chemical energy stored in its active materials into electrical energy by means of electrochemical redox (reduction-oxidation) reactions. Solid state batteries exhibit various advantages over conventional liquid electrolyte-based batteries like, prevention of electrolyte leakage into the electrodes, miniaturization, durability, and safety concerns. A battery is constructed with one or more electrochemical cells which are electrically connected at their terminals. There are two types of battery: (a) a primary battery consists of one or more cells in the charged state and it discharges during the operation until the energy is exhausted. (b) A secondary battery is composed of one or more cells and usually is assembled in the discharged state. The electrical energy may be restored to the charged state even after being discharged in operation [144].The basic configuration of a typical solid state polymer battery include two electrodes namely positive electrode (cathode) and negative electrode (anode) which are immersed into an electrolyte solution. The cathode is a good electron acceptor that receives electrons from the external circuit (reduction), e.g., lithium cobalt oxide, manganese dioxide, lead oxide etc. The anode is a good electron donor that releases electrons into the external circuit, e.g., lithium, zinc, lead etc. The electrolyte is a pure ionic conductor that provides the conduction pathway and separates the anode from the cathode for the electrochemical operation [145]. Electrolytes used in batteries are usually found in liquid form, which may be subdivided as aqueous solution, non-aqueous solvent, and solid electrolytes. Whereas, liquid electrolytes were commonly employed in various types of batteries like nickel-cadmium, mercury cell, and lead-acid accumulator configurations, non-aqueous, or organic solvent-based electrolytes find their applications in lithium batteries [145].

Due to a promising feature of lithium ion-based batteries, tremendous attention was made towards small devices, such as portable computers, cellular phones, and mobile electro-optic equipment [151]. For useful applications in lithium batteries, some crucial properties of solid polymer electrolytes like ionic conductivity, dimensional stability, cyclability, safety, high energy density, light weight, solvent free, leak proof, wide electrochemical window, good compatibility with lithium electrode, and good thermal and mechanical strength are taken into consideration [152–155]. Though lithium battery is a popular and potential gadget available in market, it suffers from certain serious drawbacks due to the highly reactive nature of lithium metal, and it would lead to the formation of a passivation layer at electrode-electrolyte interface, thereby increasing the internal resistance of batteries and result in handling problems like highly corrosive and risk of explosion. In view of the above-mentioned limitations, many researchers have realized the need for a better alternative with low-cost and environment-friendly battery systems like sodium-, magnesium- and zinc-based all-solid state rechargeable batteries involving new polymer electrolytes [156–161].

Conclusions

In this review, stable and high conducting polymer electrolytes have been highlighted for fabricating flexible and environment-friendly fuel cells and batteries. Based on the literature available, some important parameters related to these polymer electrolytes have been discussed in order to bring out the technological aspects of these materials into industries. At the global level, researchers have made many efforts to improve the ionic conductivity of polymer electrolytes. In this context, one of the most popular approaches with interesting features involves addition of nanosized ceramic filler due to its unique structures and tunable properties and making itself suitable for real-world applications. This type of addition of filler particles not only improves the overall electrical conductivity of polymer electrolytes but also their mechanical properties as well. Moreover, the filler effectively acts as a solid plasticizer which is capable of enhancing ion transport properties and ensuring good interfacial property between electrodes. A lot of attention has been focused on polymer electrolyte nanocomposites because of simplicity in their processing and the fact that nanoparticles have a wide range of applications from energy, catalytic, magnetic and electronic to biomedical, pharmaceutical, and cosmetic industries. Various kinds of host polymer with different ionic salt and inorganic nanofillers have been discussed in this overview. High power applications of lithium cells seem to be indispensable for low scale even though other cells also have been explored in battery technology. Though the mechanism of ionic conductivity enhancement in various electrolyte systems has been discussed, still the role played by nanosized ceramic fillers is not well understood. However, the fact that a polymer in a composite system offers extraordinary mechanical stability coupled with remarkable ionic conductivity, it is an interesting challenge for the expansion of battery production technology. This new approach is therefore expected to gain much attention and develop itself very rapidly in the upcoming years.

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