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A Review: Ionic Conductivity of Solid Polymer Electrolyte Based Polyethylene Oxide

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Solid state electrolyte system-based polyethylene oxide (PEO) been widely used as one of the promising polymer host that mainly used in advance material such as secondary battery. They have many benefits of PEO such as good electrochemical stability, excellent compatibility with inorganic salts, reasonable fabrication cost, good safety, and good energy density. However, due to the semicrystalline behaviour this electrolyte system poor mechanical strength and thermo-stability limit its application in solid polymer electrolyte (SPE). Worldwide research has been conducted to enhance the mechanical strength and electrochemical properties of the PEO electrolyte system such as blending, inorganic filler and plasticizer etc. Therefore, in this review the topic has been narrow down on issues of PEO polymer electrolytes system.

Keywords: Polyethylene oxide, solid polymer electrolyte, ionic conductivity, inorganic filler, secondary battery

1. INTRODUCTION

Polymer electrolyte (PE) have gotten a lot of interest due to their prospective applications in rechargeable batteries and fuel cells [1]. Flexible thin layer polymer electrolyte film possesses the ability to fabricate into desires fabrication. Moreover, the flexible polymers accommodate the shape changes during charge – discharge cycle [2]. In last two decades, many kinds of research have taken a lot of focus on lithium-ion batteries because of their advantages included virtually no electrolyte leakage, increased energy density, adjustable geometric voltages, high output voltage, cycle batteries, low pollution levels, and other aspects [3].

LIB has been widely applied today in many consumer electronics such as mobile phones, personal computers, digital cameras, electric vehicles (EV), and electric hybrids (HEV). A LIB is made up of three key parts which are the anode, cathode, and electrolyte. The electrolyte is the crucial component to allow free moving ions, particularly lithium-ion mobility from anode to cathode and vice versa for the system's transport path [4].

Therefore, SPE materials with a polymer matrix and lithium salts were introduced to solve problems especially in liquid electrolyte systems that use flammable liquid solvents and generate problems with waste disposal and management [5].

2. SOLID POLYMER ELECTROLYTES (SPE)

Generally, SPE can improve LIB safety by optimizing polymeric film materials. SPE has good stability, low interfacial resistance, flexibility, stretchability, and inexpensive fabrication cost. The mechanical and electrochemical properties are major difficulties of SPE application [3]. SPE is also flexible and can be fabricated into desired shapes during the charge-discharge cycle. The high ionic conductivity, high specific energy, no electrolyte leakage, high safety for long-term usage, good mechanical strength, large electrochemical stability windows, lightweight, and ease of processability are some of the other benefits of SPE [5].

The low ionic conductivity, σ ($<10^{-6}$ S cm^{-1}) of SPE at various temperature mainly due to the presence of crystalline phase of the polymer restricts their wide utilization [6]. Numerous studies have been conducted to achieve an optimal balance between the amorphous and crystalline phases in SPE for ionic conductivity and mechanical properties, including the synthesis of novel polymer matrix. Researchers can improve the performance of the polymer electrolyte system by reducing crystallinity, increasing the proportion of the amorphous region and the concentration of ions contained in the system, decreasing the glass transition temperature of the polymer electrolyte system, and improving the capacity of lithium – ion through blocking, grafting, crosslinking, compositing, and blending methods [3].

3. POLYETHYLENE OXIDE (PEO)

PEO is the most common polymer host among the numerous polymers that have been investigated because of its excellent thermal and mechanical stability. As indicated in Figure 1 PEO is a polyether with a chemical structure [7].

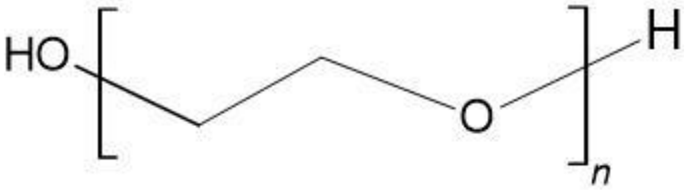

Figure 1. Chemical structure of PEO

PEO has a 70% - 85% crystallinity at room temperature and used as a polymer host for electrolyte development [8]. PEO is a non-toxic, biocompatible, water-soluble polymer that is used in various applications such as in conductive composites with carbon black, etc. [9]. In addition, it has special features such as high safety, high energy density, high electrochemical stability, and excellent compatibility with inorganic salts [10] which makes PEO a viable polymer material for use as a polymer electrolyte [11].

For the first time, Wright and Armand (2016) reported the findings of their research on the ionic conductivity of PEO, which measured approximately $10^{-7} S\ cm^{-1}$ at room temperature in 1973 [12]. Due to its inclination to crystallize at lower temperatures, PEO has certain disadvantages as well, one of which is a low ionic conductivity at ambient temperature. Because of the non-conductive nature of the high crystalline phase at ambient temperature, ionic conductivity is significantly lower than in pure water. An amorphous phase transition occurs at temperatures over the melting point of PEO-based PEs, resulting in an appreciable conductivity at these higher temperatures. When PEO melts, the irregularity of the crystalline phase causes the loss of its dimensional stability, resulting in a liquid with an exceptionally viscous characteristic. The quasi-liquid condition increases the flexibility of the PEO-based PE matrix while also demonstrating a low mechanical strength [13].

SPEs based on polyethylene oxide (PEO) are the most promising because of their potential to provide good solubility for lithium salts. Inorganic salts improve ionic conductivity by reducing crystallinity. This is because polymer salts are biphasic, consisting of both amorphous and crystalline phases. PEO electrolyte transports Li+ ions by local relaxation and segmental mobility. Charge transfer happens in amorphous PEO. Lithium salts' high dissociation degree is required for high ionic conductivity in polymer complexes. This is possible with low lattice energy salts and a high dielectric constant polymer host. Polymers with a Lewis base (PEO is ether oxygen) help dissolve salts by coordinating with cations [13,14,15].

Various methods have been used to increase the ionic conductivity of PEO-based electrolytes such as inorganic salts [16], nanofiller [17], plasticizer [5][18], blending [19] and crosslinking method [10,20].

4. INORGANIC SALTS

Researchers Ngai et al. (2016) reported that using an inorganic salt in a PE can improve the electrical stability and conductivity of the material in a wide range of different solvents. The interaction between polymer host and inorganic salt determines ionic conductivity, chemical stability, and mechanical strength. The low lattice energy of the complexing salt contributes to the high conductivity of CPE. Low lattice energies of polymers and inorganic salts could enhance PE stability. Solubilization of inorganic salts in polymer chains is facilitated by low salt lattice energy and high polymer dielectric constant [13].

Inorganic salts are non-metal salts and lithium salts. For non – metal salts such as ammonium acetate (CH_3COONH_4) have been chosen for its plasticizing effect. Acetate ion ($CH3COO^-$) is favoured in salt solvation via hydrogen bonding. For lithium salt like $LiPF_6$ [21], $LiCF_3SO_3$ [22], $LiClO_4$ [23], LiOX [24], and $LiBF_4$ [25] have been applied as charge carrier in the synthesis of PE. The most promising PE is PEO based on its great solubility for lithium salt [14].

S. Ibrahim et al. (2012) produced PEO-based polymer electrolyte systems with 5, 10, 15, and 20 wt.% lithium hexafluorate ($LiPF_6$). At room temperature, the system with 20 wt.% $LiPF_6$ has a maximum conductivity of 1.5 x 10^{-4} S cm^{-1}. The findings confirm that conductivity rises with temperature and salt concentration up to 20 wt.% [21].

Polymer electrolytes based on PEO and polyacrylonitrile (PAN) doped with 6, 8, and 10 wt. % $LiPF_6$. The conductivity is dependent on lower frequencies. The addition of salt reduces relaxing time and increases conductivity [26].

Solid polymer electrolyte containing 5, 10, 15, and 20 wt.% lithium trifluoromethanesulfonate ($LiCF_3SO_3$). The PEO composite with 15 wt.% $LiCF_3SO_3$ had the highest conductivity at room temperature 1.00 x 10^{-6} S cm^{-1}, while the degree of crystallinity decreased as the Li salt content increased [27].

PEO complexed with $LiClO_4$ had a conductivity of 10^{-4} S cm^{-1}, four orders higher than pure PEO. The SPE film (PEO + $LiClO_4$) with wt. % ratio (85:15) had the maximum conductivity of 3.35 x 10^{-5} S cm^{-1} at ambient temperature[23]

The highest room temperature ionic conductivity for PEO/PVA with $LiClO_4$ is 3.5 x 10^{-3} S cm^{-1}. The liquid electrolyte is quite near to that of the solid polymer blend electrolyte. It can be used in all solid-state Li-ion cells [28].

It has been demonstrated by Pradeepa et al. (2015) that a PEO blend with PVdF – HFP containing 2, 4, 6, 8, and 10 wt. % of $LiClO_4$ with propylene carbonate (PC) has been synthesized. The maximum ionic conductivity was obtained at 8 wt. % $LiClO_4$, 2.3912 x 10^{-4} S cm^{-1}[29].

PE comprised of PEO, lithium oxalate (LiOX), and borontrifluoride diethyl ether (BF_3OEt_2) have been conducted by Heishi et al. (2014). It was discovered that the absence of $BF3{\cdot}OEt_2$ resulted in an ionic conductivity of 10^{-6} S cm^{-1} at 130ºC [24].

Preparation of CPE including PEO and Nickel oxide (NiO) with 10, 20, and 30 wt.% $LiBF_4$. At room temperature, the ionic conductivity of the electrolytes is determined, and it is discovered that the addition of salt wt.% increased the ionic conductivity of the electrolytes. The greatest ionic conductivity of 8.75 x 10^{-4} S cm^{-1} is reached for a polymer complex containing 30 wt.% of $LiBF_4$ [25]. Table 1 contains a summary of the inorganic salts found in polymer electrolytes.

Table 1. Typical inorganic salts in PEO SPE with their conductivity at room temperature

Salt	Solvent	Ionic conductivity, σ	Reference
15 wt.% $LiClO_4$	Methanol	3.35 x 10^{-5} S cm^{-1}	[23]
20 wt.% $LiPF_6$	Acetonitrile	1.5 x 10^{-4} S cm^{-1}	[21]
30 wt.% $LiBF_4$	tetrahydrofuran	8.75 x 10^{-4} S cm^{-1}	[25]
15 wt.% $LiCF_3SO_3$	-	1.00 x 10^{-6} S cm^{-1}	[27]

5. NANOFILLER

The addition of nanofillers is one of the promising methods for improving the morphological and electrochemical properties of PEO. CPEs are formed by mixing nanofiller into a polymer salt matrix, as mentioned by K. Naveen Kumar et al. (2016) [30]. Organic and inorganic molecular nanofillers were introduced into polymer electrolyte systems, and it was determined that inorganic nanofillers were more suitable additives than organic nanofillers for commercial reasons. Inorganic nanofillers such as Al_2O_3, SiO_2, TiO_2, $LiAlO_2$ have been shown to improve the ionic conductivity of polymer hosts and their interfacial characteristics in interaction with lithium cathodes.

Inorganic nanofillers can improve ionic conductivity and thermal characteristics. It has increased cation transport numbers and electrochemical stability towards a metal anode. Most researchers believe that the addition of nanofiller results in the disruption of crystallization of the polymer host matrix, which is the main reason for the increase in ionic conductivity [30].

M. R. Johan and his team (2011) discovered that filler impacts PEO dipole orientation by aligning dipole moments, whereas thermal history determines polymer chain flexibility for ion migration. Fillers generally increase transport properties, crystallization resistance, and interface stability. Conduction improvement depends on filler type and particle size. The conductivity enhancement increases with filler particle surface area [18]. Filler doped SPE has a lower crystallinity due to the potential to reorganize PEO via Lewis acid-based interactions between PEO oxygen and filler surface. Comparing nano-sized fillers to conventional particles, the higher surface area of nano-sized fillers shows preferred impacts on SPE performance increases [31].

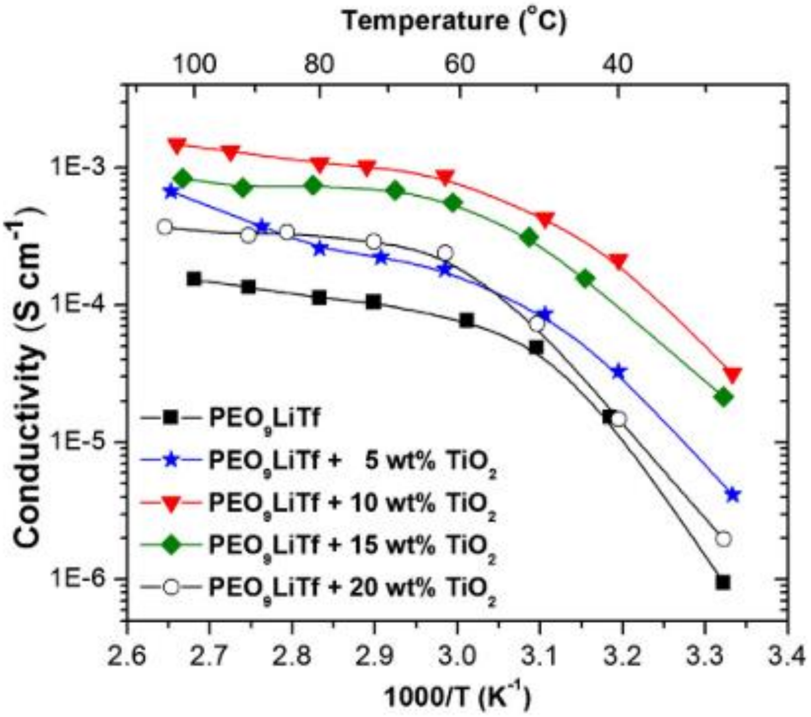

Figure 2. Variation of conductivity with inverse temperature for composite polymer electrolytes incorporating TiO_2 ceramic powder; $(PEO)_9LiTf + \chi$ wt.% TiO_2 ($\chi = 0,5,10,15$ and 20) (reprinted with permission from [34], copyright Elsevier 2014)

M. R. Johan et al. (2011) discovered that adding aluminium oxide (Al_2O_3) fillers to SPE increased the ionic conductivity to 5.07 x 10^{-4} S cm^{-1} at 15 wt.% of Al_2O_3. Transient hydrogen bonding of migrating ionic species with O-OH groups at the filler particle surface improves conductivity[18].

Nano Al_2O_3 could minimize crystallinity, enhance mobility, and improve lithium-ion transport capacity in polymer matrix. Thus, it can increase to 1.62 x 10^{-4} S cm^{-1} the ionic conductivity of PEO-PMMA-LiTFSI-Al_2O_3 electrolyte [3].

To improve ionic conductivity, K. K. Wimalaweera et al. (2017) added an inert Al_2O_3 ceramic filler. As a cross-linking centre for PEO segments, filler has increased the amorphous aspect of the systems, minimizing chain aggregation, and improving ionic conductivity [32].

The highest ionic conductivity of the PEO+polyvinyl pyrrolidone (PVP)/ $LiClO_4$ polymer electrolyte system is 1.14 x 10^{-4} S cm^{-1} with 4 wt% iron (Fe) nanofiller [30].

PEO, $LiClO_4$ and NiO were used as inorganic nanofillers in solution cast CPE films. At room temperature, 7.4 x 10^{-4} S cm^{-1} ionic conductivity with 10 wt.% NiO [33].

Ionic conductivity of PEO-$LiCF_3SO_3$ with various percentages of TiO_2 nanofiller. The ionic conductivity of 10 wt.% TiO_2 was determined to be 4.9 x 10^{-5} S cm^{-1} at ambient temperature. It was because TiO_2 is more Lewis-acid than Al_2O_3, SiO_2 and ZrO_2 [34]. Figure 2 shows the ionic conductivity with varying wt.% of TiO_2.

SPE films made of PEO/EC/PC and NaNO3 were synthesized. The polymer blend was improved in ionic conductivity by adding Al_2O_3 nanofiller. The ionic conductivity was 1.86 x 10^{-4} S cm^{-1} with 8 wt.% of Al_2O_3 [35].

PEO-silver triflate ($AgCF_3SO_3$) with 1, 3, 5, 7, and 10 wt.% MgO nanofiller. Adding 5 wt.% MgO to the polymer electrolyte resulted in an ionic conductivity of 2 x 10^{-6} S cm^{-1} at ambient temperature [36].

The blends were made using a PEO/PVA/PEG/$AgNO_3$ electrolyte and Al_2O_3 as a nanofiller. It was discovered that the blend specimen containing 6 wt.% Al_2O_3 exhibits the optimal conductivity value [37].

Incorporation of nanofiller Al_2O_3 has resulted in a large increase in ionic conduction, as evidenced by the ionic transference number measurements to high ionic conductivity that have been investigated by P. Sharma et al. (2012). The improved ionic conductivity of polymer films containing Al_2O_3 nanoparticles is owing to the formation of additional conducting routes, which results in greater chain flexibility, carrier concentration, and amorphous structure. Additionally, it increases with temperature, reaching a maximum at T_m [38].

S. Ketabi et al. (2013) found that an electrolyte containing 10 wt.% SiO_2 has an ionic conductivity of 2.15 mS cm^{-1} at ambient temperature [39].

Cerium dioxide (CeO_2) was used as a nanofiller in the PEO/PEG/LiClO4/EC. With 1 wt.% CeO_2, the highest ionic conductivity of CPE is 1.18 x 10^{-4} S cm^{-1}. The nanofiller prevents polymer recrystallization, increases amorphous phase, and interacts with filler, Li^+ ions, and polymer chain. It increased conductivity by increasing ion mobility on the surface of CeO_2 nanoparticles [40].

Synthesis PEO with LiTDI and TiO_2 nanofiller. Adding nano sized TiO_2 ceramic fillers increases the SPE amorphous phase, thermal stability, mechanical strength, and ionic conductivity. The SPE has an ionic conductivity of 2.11 x 10^{-5} S cm^{-1} with 8 wt.% TiO_2 nanofillers [41].

PEO with varying $LiCF_3SO_3$ concentration and zirconia content (ZrO_2). The ionic conductivity increased from 7.39 x 10^{-4} S cm^{-1} to 5.24 x 10^{-3} S cm^{-1} by adding 3 wt.% ZrO_2 nanofiller [42].

Synthesis of nanocomposite polymer electrolytes by heating and stirring substances. The addition of ZnO nanoparticles to a nano composite polymer electrolyte (NCPE) system increased ionic conductivity from 6.38 mS cm^{-1} to 8.36 mS cm^{-1}. By expanding the amorphous phase of the NCPE system, ZnO nanoparticles create three-dimensional pathways for greater ion movement [17].

A new series of nanocomposite polymer electrolyte (NCPE) systems consisting of PEO blend with PPG, zinc trifluoromethanesulfonate [$Zn(CF_3SO_3)_2$] as dopant salt and Al_2O_3 filler has been created. The ionic conductivity of 3 wt.% Al_2O_3 was found 2.1 x 10^{-4} S cm^{-1} to be higher than pure polymer electrolyte at ambient temperature [43].

It was discovered that the dispersion of Al_2O_3 nanoparticles in the PEO/PMMA blend significantly alters the size and shape of PEO spherulites in the polymer nanocomposite (PNC) films, which is due to the formation of polymer-nanoparticle interactions and the simultaneous alteration of PEO/PMMA blend polymer-polymer interactions in the PNC films. The PEO spherulites provide the crystalline phase, whereas the Al_2O_3 decreases the degree of crystallinity [44].

The ionic conductivity of polymer blend complexes varied with salt and filler particle concentrations. The best ambient temperature conductivity for PEO/PEG/$LiCF_3SO_3$/EC/3 wt.% TiO_2 was 2.66 x 10^{-4} S cm^{-1}. Because of the Lewis acid-base interaction and amorphous phase, the energy barrier is lower, allowing for maximum segmental mobility of lithium ions [45].

The ionic conductivity of CPE films can be improved by adding ferroelectric $BaTiO_3$. With the addition of 6 wt.% $BaTiO_3$ filler, the ionic conductivity improved to 6 x 10^{-3} S cm^{-1} [46].

The ionic conductivity of optimized PNC films with 15 wt.% TiO_2 nanofiller is estimated at 10^{-4} S cm^{-1}. The polymer with TiO_2 nanofiller reduced the driving force for phase separation, produced homogeneous films at 15 wt.% TiO_2 nanofiller and improving the electrical and mechanical properties of polymer films [47].

The addition of 0.175 wt.% TiO_2 filler into the plasticized nanofibrous electrolyte that has been synthesized resulted in the maximum room temperature ionic conductivity of 0.085 mS cm^{-1} [48].

The maximum ionic conductivity was found with 5 wt.% Al_2O_3, 4.2 x 10^{-4} S cm^{-1} at 24°C. The use of nanofillers changed the conductivity of electrolyte samples [49]. Table 2 summarizes the most used nanofillers.

Table 2. Typical nanofiller of PEO SPE with ionic conductivity in room temperature

Nanofiller	**Solvent**	**Ionic conductivity, σ**	**Reference**
0.175 wt.% TiO_2	Acetonitrile	8.5 x 10^{-5} S cm^{-1}	[48]
8 wt.% TiO_2	Acetonitrile	2.11 x 10^{-5} S cm^{-1}	[41]
5 wt.% MgO	Acetonitrile	2 x 10^{-6} S cm^{-1}	[36]
8 wt.% Al_2O_3	Methanol	1.86 x 10^{-4} S cm^{-1}	[35]
10 wt.% TiO_2	Acetonitrile	4.9 x 10^{-5} S cm^{-1}	[34]
10 wt.% NiO	Tetrahydrofuran	7.4 x 10^{-4} S cm^{-1}	[33]
15 wt.% Al_2O_3	Acetonitrile	5.07 x 10^{-4} S cm^{-1}	[18]
3 wt.% ZrO_2	Acetonitrile	5.24 x 10^{-3} S cm^{-1}	[42]

6. PLASTICIZER

Plasticization is one method of enhancing amorphous phase content in PEO-LiX electrolytes [14]. It has also been utilized to change PEO morphology. Plasticizers are additives that attempt to enhance plasticity and mobility of ions, thus improving ionic conductivity at room temperature. It has been usually applied in the preparation of PEs. Low molecular weight plasticizers include dimethyl carbonate (DMC), diocthyl adipate (DOA), DBP, DEC, PC, and EC. Plasticizers dissolve more charge carriers and increasing ion mobility. Plasticizers in PEs improve the ionic conductivity, thermal and mechanical stability [13].

The plasticizer DOP was applied to increase the ionic conductivity of the PEO – $LiCF_3SO_3$ solid polymer electrolyte, and it was shown to be the most effective. The maximum ionic conductivity was 7.60 x 10^{-4} S cm^{-1} with 20 wt.% DOP. This might be attributed to the addition of DOP to the PEO – $LiCF_3SO_3$ solid polymer electrolyte caused increased mobility of polymer chains by the replacement of polymer-polymer interactions with polymer plasticizer interactions [5].

Succinonitrile (SN) is a widely used additive to improve CPE Li^+ conductivity. A membrane made of PEO-SN-25 wt.% $LiCF_3SO_3$ had an ionic conductivity of 7.0 x 10^{-4} S cm^{-1} at room temperature (293K) [50].

Chitosan with PEO doped with ammonium nitrate (NH_4NO_3) electrolyte films with varying EC plasticizer concentrations. The ionic conductivity obtained is 2.06 x 10^{-3} S cm^{-1} 70 wt.% EC [51].

With the use of a typical solution casting approach, we created the PEO-Lithium conductor $Li_7La_3Zr_2O_{12}$- succinonitrile (PEO-LiTFSI-SN). Its maximal conductivity is 1.19 x 10^{-4} S cm^{-1} at room temperature [52].

The host polymer was PEO, the salt was ammonium bifluoride (NH_4HF_2), and the plasticizers were propylene carbonate (PC), dimethyl acetamide (DMA), dimethyl chloride (DMC), and diethyl carbonate (DEC). It was shown that polymer electrolytes comprising PC and DMA have a greater increase in ionic conductivity than electrolytes including DMC and DEC, which is owing to an increase in both the amorphous phase and dielectric constant of PEO. Maximum ionic conductivity of PC 1.40 x 10^{-4} S cm^{-1} at room temperature while retaining mechanical stability and flexibility [53].

The maximum ionic conductivity was found by S. Suthanthiraraj et al. (2012) with $(PEO)_{50}AgCF_3SO_3$:2 wt.% SnO_2 + 30 wt.% of PC which is 5.9 x 10^{-5} S cm^{-1} at room temperature [54].

High dielectric constant of EC – based complex, the greatest conductivity value achieved was 3.26 x 10^{-4} S cm^{-1} when compared to other plasticized materials such as propylene carbonate (PC), ethylene carbonate (EC), γ-butyrolactone (GBL), diethyl carbonate (DEC), and dimethyl carbonate (DMC) [55].

The development of a film that is composed of a PEO and PMMA blend-based matrix with $LiBF_4$ as a dopant salt and varying wt.% PEG as a plasticizer. The ionic conductivity of films increases non-linearly, whereas that of solution cast films increases asymmetrically with PEG content. Its conductivity varies due to the strength of the polymer-ion, plasticizer-ion, and polymer-plasticizer interactions as well as polymer chain segmental motion in the solid ion – dipolar complex. To prepare all solid-state ion conducting devices, the PEG concentrations and sample preparation methods of SPE at low temperature are discovered in the range of 1.79 to 4.22 μS cm-1 [56].

The increase in ionic conductivity with PSPE plasticizer concentration varies with film preparation. The maximal ionic conductivity of 15 wt% EC prepared by US-MW technique is 1.86 x 10^{-5} S cm^{-1} at ambient temperature, whereas low concentration EC films have conductivity of 10^{-6} S cm^{-1} [57].

The increased conductivity with HPF_6 (10 wt%) compared to NH_4PF_6 (10 wt%), both with 32 wt% PC. The breakdown of ion aggregates in higher acid concentrations caused HPF_6 to enhance free ion concentration [58].

At all temperatures, the only larger variation in conductivity that is greater than 10 wt.% EC plasticizer is observed with the PEG system in the PEO – PMMA blend matrix. Because PEG has a lower dielectric constant than PEO, it organizes polymer chains. Compared to PEG-based systems, EC-based systems have higher dielectric constants and greater dissociation of dopant salts [59].

Polymer electrolyte films based on PEO doped with NH_4I and glycerol. The unplasticized system had 3.96 x 10^{-5} S cm^{-1} ionic conductivity with 70 wt.% PEO and 30wt.% NH_4I. Adding 10 wt.% glycerol to the electrolyte films increased conductivity to 1.77 x 10^{-4} S cm^{-1}, the most conducting unplasticized film at room temperature. The glycerol plasticizer causes more ammonium iodide dissociation to mobile ions by lowering columbic contacts between the ions [60].

The plasticizer PC in the electrolyte system reduced the crystallinity of the PEO polymer matrix. The contribution of free ions up to 40 wt.% of PC enhances ionic conductivity, while contributions of ion pairs and ion aggregates decrease conductivity. The polymer electrolyte dielectric constants rise with PC [61]. Table 3 shows the most common plasticizer for PEO polymer electrolytes.

Table 3. Typical plasticizer of PEO SPE with ionic conductivity at room temperature

Plasticizer	Solvent	Ionic conductivity, σ	Reference
10 wt.% glycerol	Acetonitrile	1.77 x 10^{-4} S cm^{-1}	[60]
30 wt.% PC	Acetonitrile	5.9 x 10^{-5} S cm^{-1}	[54]
0.3 ml PC	Methanol	1.40 x 10^{-4} S cm^{-1}	[53]
50 wt.% EC	Acetonitrile	1.6 x 10^{-4} S cm^{-1}	[34]
10 wt.% SN	Acetonitrile	1.19 x 10^{-4} S cm^{-1}	[52]

7. CROSS – LINKED NETWORK

Cross-linked polymers have several desirable features. Cross-linking fixes the structure of a polymer solution. The resulting polymer network is elastic and has good mechanical characteristics. They can take up water or chemical solvents to expand. Cross connections are made up of covalent chemical bonds or physical interactions [62]. Near ambient temperature, the low ionic conductivity of PEO-based dry polymer electrolyte is a significant disadvantage for applications, and useful ionic conductivity of about 10-4 S cm-1 can be achieved only above this temperature. Crosslinking with a well-developed polymer network structure can stabilize the amorphous form of linear PEO. Crosslinking between polymer chains makes it difficult to move into the crystallization state. Crosslinking is commonly done with heat or UV light, an initiator, and radiation [14].

Solid electrolyte composed of poly (ionic liquid) and polyethylene oxide (PIL-PEO) containing lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and a crosslinking monomer. The CPE is synthesized by polymerizing the monomer 1-vinyl-3-methylimidazolium bis(trifluoromethylsufonyl)imide ([VMIM]TFSI) in a PEO system. PIL-crystallinity PEO's and ionic conductivity were decreased, while its electrochemical stability was increased to 0.42 x 10^{-4} S cm^{-1} and 6.12 x 10^{-4} S cm^{-1} at 25°C and 55°C, respectively [11].

UV irradiation crosslinks poly (ethylene glycol) diacrylate PEGDA and thiosiloxane to impact high ion conduction via higher segmental mobility of the co-network. It increased thermal stability and extensibility, but also decreased T_g, resulting in increased ionic conductivity [20].

The flexible PEO with high ionic conductivity 2.7 x 10^{-4} S cm^{-1} at 24°C and increased mechanical strength was developed by crosslinking tetraethylene glycol dimethacrylate (TEGDMA) and tetraethylene glycol dimethyl ether (TEGDME) into the matrix [7].

Poly (diethylene glycol carbonate) (PDEC) and poly (triethylene glycol carbonate) (PTEC) are carbonate linked PEO. At 25°C, the optimum ionic conductivity of PTEC-based electrolyte was 1.12 x 10^{-5} S cm^{-1} [12].

With the addition of IBN, the yield stress and tensile modulus of the electrolyte membranes were increased. At 30oC, the ionic conductivity reaches a maximum of 6.77 x 10-5 S cm-1 [10]. The linkage of PEO polymer electrolytes is seen in table 4.

Table 4. Typical cross – linking of PEO SPE with ionic conductivity at room temperature

Cross – linking	Ionic conductivity, σ	Reference
PIL – PEO	6.12 x 10^{-4} S cm^{-1}	[11]
PEO – TEGDME – TEGDMA	2.7 x 10^{-4} S cm^{-1}	[7]
PEO – PEGMA – PEGDA	6.77 x 10^{-5} S cm^{-1}	[10]
PDEC – PTEC	1.12 x 10^{-5} S cm^{-1}	[12]

8. BLEND POLYMER

Combining PEO with other polymers is another method of increasing the percentage of amorphous phase [14]. Polymer blending is the process of combining polymers with or without chemical bonding. A polymer blend is a physical mixing of two or more polymers [13]. Polymer blending has been widely applied in creating new polymeric materials with various applications [63]. Preparing electrolyte with nontrivial synthetic processes that are not practicable can be overcome by using blend-based polymer. However, polymer blends are attractive goods due to their superior characteristics [14]. Blending is a major strategy to increase polymer electrolyte ionic conductivities and dimensional stability [13]. The main benefits of combining polymer electrolytes are simplicity of preparation and control of physical properties [14].

The maximum ionic conductivity of 8.84 mS cm^{-1} was achieved with 13% fumed silica (SiO_2). Even though PEO based polymer electrolyte has excellent ionic conductivity, blending with PVdF-HFP can improve the system's ionic conductivity by lowering the electrolyte's crystallinity [64].

The cPTFBC polymer improves the Li$^+$ transfer number, mechanical strength, and oxidative stability of the PEO-cPTFBC-LiDFOB electrolyte [19].

At 303 K, PEO (67 wt%)/PVP (27 wt%)/$NaNO_3$ had an ionic conductivity of 6.157 x 10^{-7} S cm^{-1} with 6 wt.% [65].

Preparation of PEO/PVP SPEs with LiBr. At 303 K, PEO (30 wt%)/PVP (70 wt%)/LiBr (4 wt%) had maximal ionic conductivity of 1.59 x 10^{-6} S cm^{-1} [8].

SPE based on PEO/PVA polymer complexed with $LiClO_4$ has been created. The highest ionic conductivity of PEO/PVA blend with $LiClO_4$ is 3.5 x 10^{-3} S cm^{-1}. As a free-standing film, the solid polymer mix electrolyte has a value close to that of liquid electrolytes. All solid-state Li-ion cells can use SPE with high Li-ion conductivity [28] .

The sample containing 30 wt.% NH_4I had an ionic conductivity of 7.62 x 10^{-5} S cm^{-1} at 273 K. The addition of NH_4I increases ionic mobility and diffusion coefficient [66].

The addition of TPU to the blend polymer reduces PEO crystallinity and improves lithium salt solubility into the SPE matrix. TPU can enhance mechanical and electrochemical performance. 5.3 x 10^{-4} S cm^{-1} ionic conductivity, 5 V electrochemical stability at 60°C [67].

Adding LiOH to PEO/PVA SPE composite raised its ionic conductivity to 2.18 x 10^{-5} S cm^{-1} at room temperature [4].

Porous $Li_7P_3S_{11}$ (LPS) thin films are deposited on electrodes using the doctor blade method using LPS slurry. LPS-scaffolded porous PEG-Ti composite polymer electrolyte achieves 1.6 x 10^{-4} S cm^{-1} Li ion conductivity at 25°C [68].

Its ionic conductivity at room temperature is 10-5 S cm-1, confirming its suitability to be used in the design and development of all solid-state devices, including rechargeable lithium-ion batteries [69].

PEO and PVP complexed with lithium nitrate ($LiNO_3$) were used to make flexible and freestanding SPE films. The ionic conductivity of these films is 1.13 x 10^{-3} S cm^{-1} at room temperature, which is equivalent to liquid electrolytes [63].

A novel type of PEO polymer blending with various poly (propylene carbonate) (PPC). Blending PEO with amorphous PPC increases amorphous regions and hinders PEO crystallization. The results indicate that PEO/50% PPC has the maximum ionic conductivities at 25°C and 60°C, respectively, of 2.04 x 10^{-5} S cm^{-1} and 2.82 x 10^{-4} S cm^{-1}[70]

The maximum ionic conductivity is 6.9 x 10^{-5} S cm^{-1} at 87.5 wt% PEO:PPG and 12.5 wt% $Zn(CF_3SO_3)_2$ at ambient temperature [71].

The greatest ionic conductivity 9.334 x 10^{-5} S cm^{-1} was obtained for PEO:PVdF:$NaNO_3$ (80:20:5) at ambient temperature, which is related to the formation of the amorphous phase [72].

PE-PM-PVH GPE has an ionic conductivity of 0.81 mS cm^{-1}. The increased amorphous region in the PE-PM-PVH polymer matrix could promote Li$^+$ ion transport. Second, the PE-PM-PVH polymer absorbs liquid electrolyte better, facilitating Li$^+$ ion transport. Both characteristics contribute to the enhancement of ionic transport in the solid electrolyte [73].

More ion dissociation occurs when a tiny quantity of PVdF is added to the PEO host polymer. The highest ionic conductivity of these blends is 1.01 x 10^{-3} S cm^{-1} at room temperature with 80% PEO, 20% PVdF, and 35% NH_4I [74].

The addition of $LiPF_6$, EC, and α-CNTs increases the polymer's conductivity and dielectric response, and these characteristics are modified by temperature and frequency [75].

PMHS 40 wt% has outstanding ionic conductivity of 2.0 x 10^{-2} S cm^{-1} at 80°C [76]. Table 5 shows typical PEO polymer electrolyte mixtures.

Table 5. Typical blends of PEO SPE with ionic conductivity at room temperature

Blend	Solvent	Ionic conductivity, σ	Reference
80 wt.% PEO: 20 wt.% PVdF	dimethylformamide	9.334 x 10^{-4} S cm^{-1}	[72]
90 wt.% PEO: 10 wt. % PPG	Acetonitrile	7.5 x 10^{-5} S cm^{-1}	[71]
PEO: 50 wt.% PPC	Acetonitrile	2.04 x 10^{-5} S cm^{-1}	[70]

9. CONCLUSION

PEO is a common polymer host for polymer electrolytes in lithium-ion batteries. To improve the electrolyte characteristics, PEO polymer electrolytes have been identified. Ionic conductivity of PE can be improved by increasing the amorphous fraction. Several physical/chemical procedures or doping with specific compounds can reduce crystallinity. Several methods have been used to synthesis PEO polymer electrolytes, including blending, cross-linking, plasticizers, and fillers. PE important in the development of electrochemical capacitors, batteries, fuel cells, and dye-sensitized solar cells. Numerous studies have demonstrated that the PEO polymer electrolytes are better in terms of conductivity, flexibility, and safety.

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