



Review on the Physicl Properties of Polyethylene Oxide

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HIGHLIGHTS

- This work uncovers crucial techniques for doped polymer.
- Doped Polymers offer more unique properties than pure polymers and their advanced applications.
- This work provides insights into recent advances in doped polymer technology.

ABSTRACT

Solid polymeric electrolytes have become crucial today due to their stability and high conductivity. Recently, lithium ion-doped polymeric electrolytes have gained intense attention for their superior ability to create highly conductive electrolytes for batteries and energy storage. This innovative electrolyte type has displaced many traditional systems due to their flammability and bulkiness. Traditional liquid organic electrolytes pose risks due to their flammable and unstable nature. Solid-state composite electrolytes offer both mechanical stability and electrical conductivity by using solid polymeric matrices like polyethylene oxide and polyurethane reinforced with inert fillers like alumina and titanium dioxide. Polyethylene oxide (PEO)-based materials show promise as polymer hosts for high-energy-density lithium batteries due to their safety, cost-effectiveness, and compatibility with lithium salt. However, the linear PEO's insufficient ionic conductivity, stemming from high crystallinity in ethylene oxide chains, limits production at low temperatures. This review delves into lithium salt effects, matrix types, plasticizer and filler impact, and composite electrolyte mechanisms.

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1. Introduction

Solid-state composite electrolytes synthesized using lithium salts are extensively used for the fabrication of high-performance batteries [1], computer systems [2], and other mobile devices [3]; due to their high capacity and their eco-friendly competencies [1]. For example, conventional electrolytes aren't desired in modern technology because they comprise organic solvents in liquid form. This type of electrolyte is extremely dangerous because it can result in catastrophic outcomes, including unexpected ignition and leakage [4]. Therefore, solid-state composite electrolytes are preferred. It was reported that the first solid electrolytes traced back to the 60s of the 20th century, while Takahashi indicated that the ionic conductivity of the Ag_3Si compound has extraordinarily excessive conductivity of 10-2 S/cm [5]. The first varieties of stable electrolytes were of ceramic origin. Because of their ceramic properties, they have low fracture sturdiness. They are very brittle; therefore, the point of interest turned into diverting from the inorganic and brittle electrolytes to the natural and bendy electrolytes [6].

Since the 70s, electrolytes made the usage of polymeric matrices require complexation with the salts of lithium, and it was mentioned that the ionic conductivity ought to attain up to 10-5 S/cm at temperatures higher than 40°C [7]. Solid-state electrolytes provide high mechanical stability, but this type of electrolyte leads to the growth of lithium dendrite, which can be undesired because it decreases conductivity [8,9]. The SPEs ionic conductivity can be improved and extended by the addition of liquid plasticizers, like ethylene carbonate (EC), propylene carbonate (PC), and dimethyl carbonate (DMC), into the electrolyte [10,11], or lithium salts consisting of $(LiClO_4)$ [12-15], lithium hexafluoroarsenate $(LiAsF_6)$ [13,16-19] and lithium tetrafluoroborate $(LiBF_4)$ [20-23], or the usage of inert fillers, consisting of alumina, silica, TiO_2 and ZnO [24,25-28]. The types of polymeric electrolytes are shown in Figure 1. This article reviews the most utilized polymer matrices, and the effect of lithium salts and fillers on the electrolyte properties will be reviewed in detail. It is worth mentioning that the number of published articles has been increasing recently due to the advances in polymer science and technology, as seen in Figure 2.

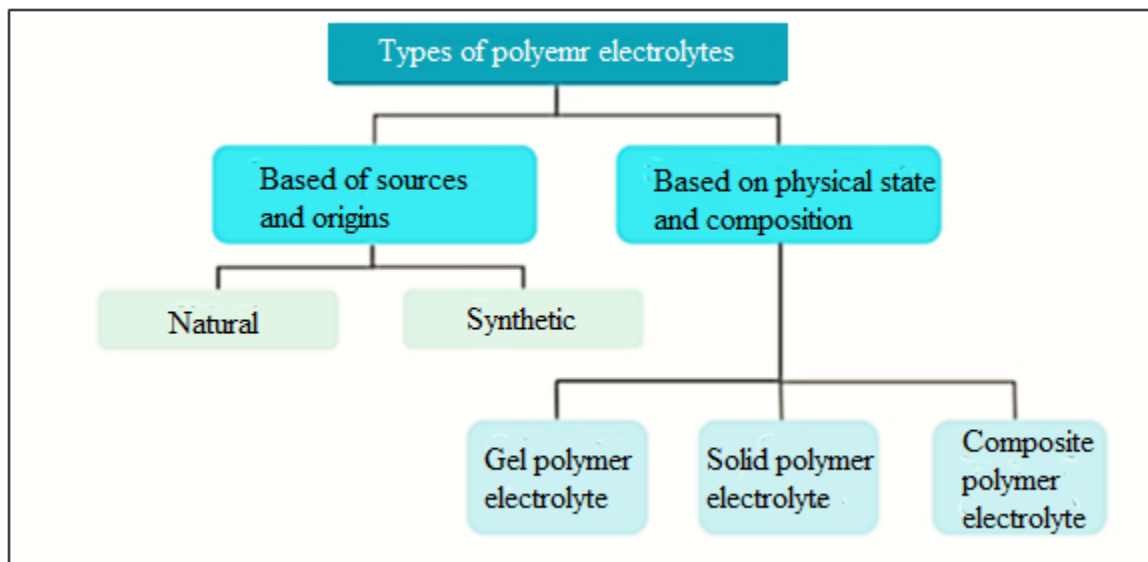


Figure 1: Types of polymer electrolytes

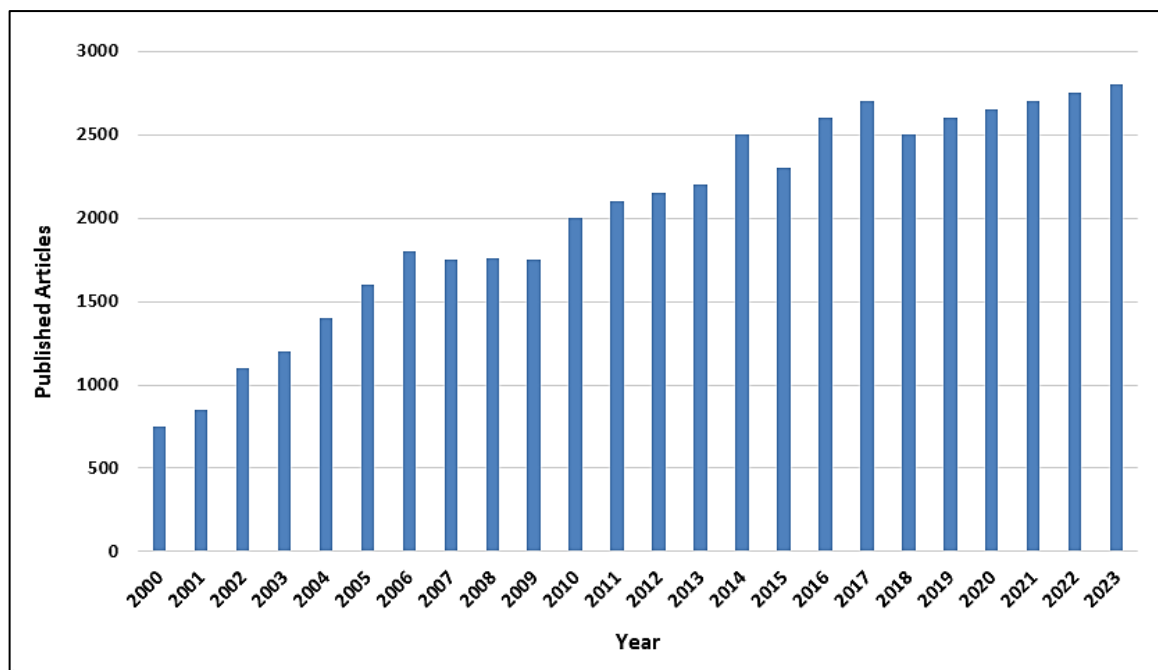


Figure 2: Number of published articles on the polymer-based solid electrolyte from 2000 to 2023

2. Polymer Matrices for Solid State Electrolytes

There is a huge range of polymeric matrices for the solid-state composite electrolytes, as depicted in Figure 3; these are polyacrylonitrile (PAN) [29], polystyrene (PS) [30,31], polymethyl methacrylate (PMMA) [32], polyvinylidene fluoride (PVF) [33], polyvinyl pyrrolidone (PVP) [34]. One of the excellent matrices that might be widely utilized in SPEs is polyethylene oxide (PEO); this is attributed to the high electro-donating ether-oxygen (EO) groups of PEO, smooth macro-molecular backbone, higher thermal balance, and appropriate mechanical residences, therefor it has become the maximum frequently studied polymer base for SPEs. The ionic conductivity for the mentioned polymers can be seen in Figure 4 and Table 1. The chemical composition of polyethylene oxide is $H(OCH_2CH_2)_nOH$; PEO is water-soluble and has a semi-crystalline kingdom at room temperature. Generally, PEO is the name for the polymer with a molecular weight (M_n) higher than 20,000. When the molecular weight is lower than 20,000, the polyethylene glycol (PEG) PEO crystalline structure can be revealed in Figure 5 [35].

Both anions and cations are essential in solid-state polymeric electrolytes during the conduction process. Still, due to the oxidation and reduction of the process, only positive ions of Li^{+1} are desired [36]. It is recommended to explore the usage of PVF and PVP polymers to prepare high-conductivity electrolytes.

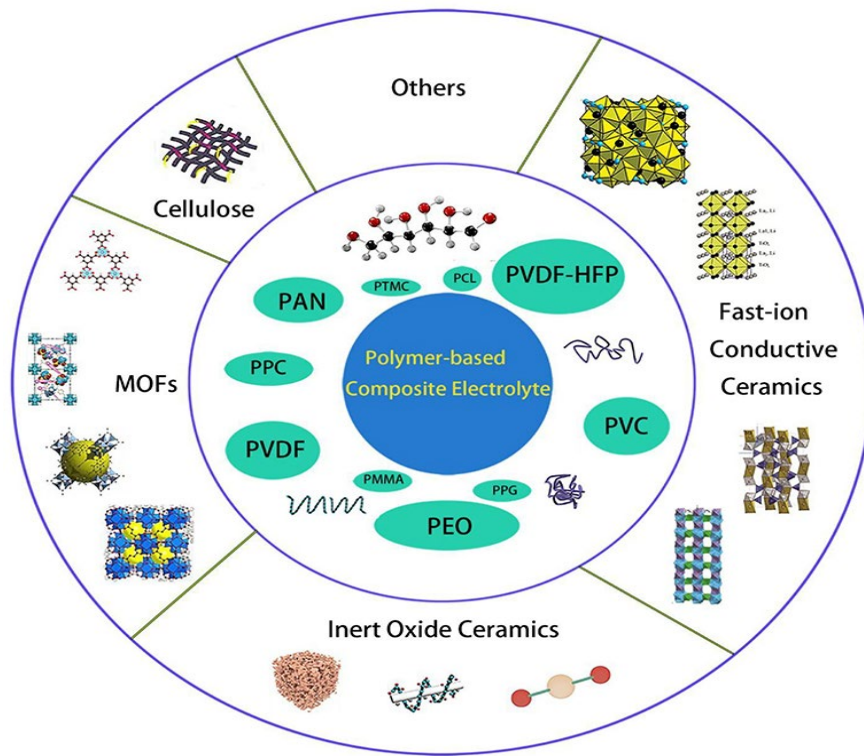


Figure 3: Different types of electrolyte polymer matrices

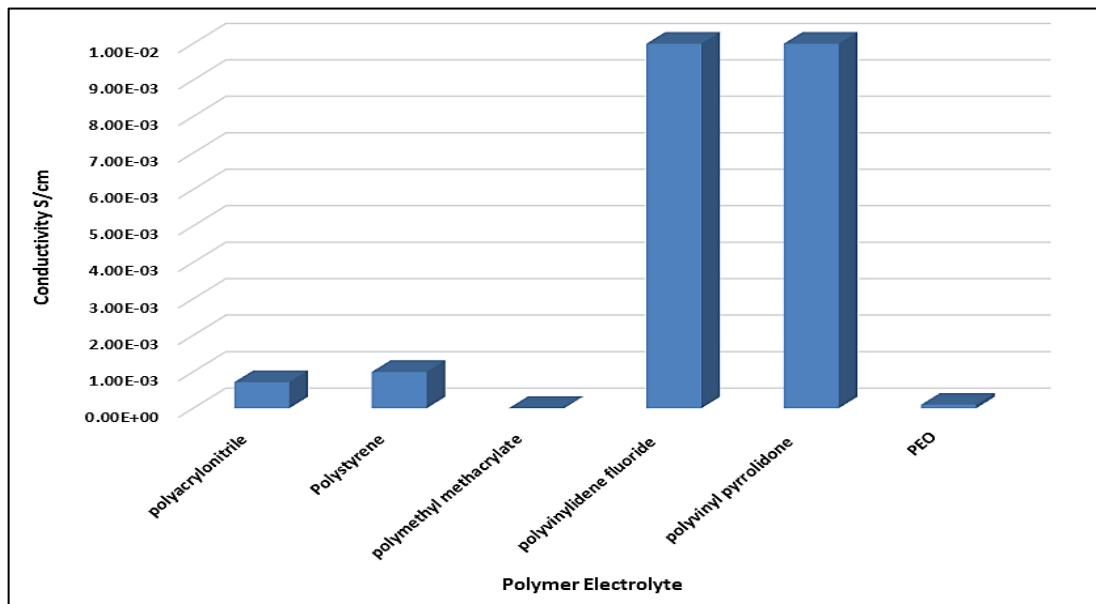


Figure 4: Ionic conductivity for various polymer electrolytes

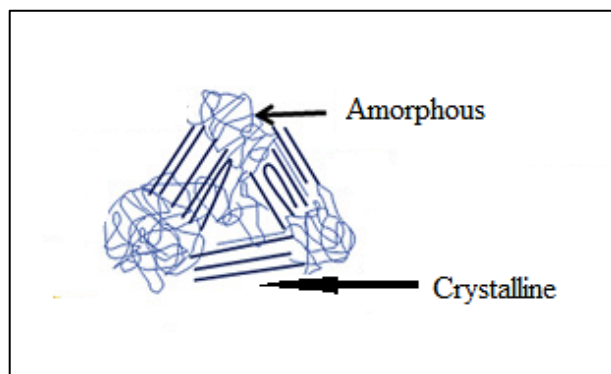


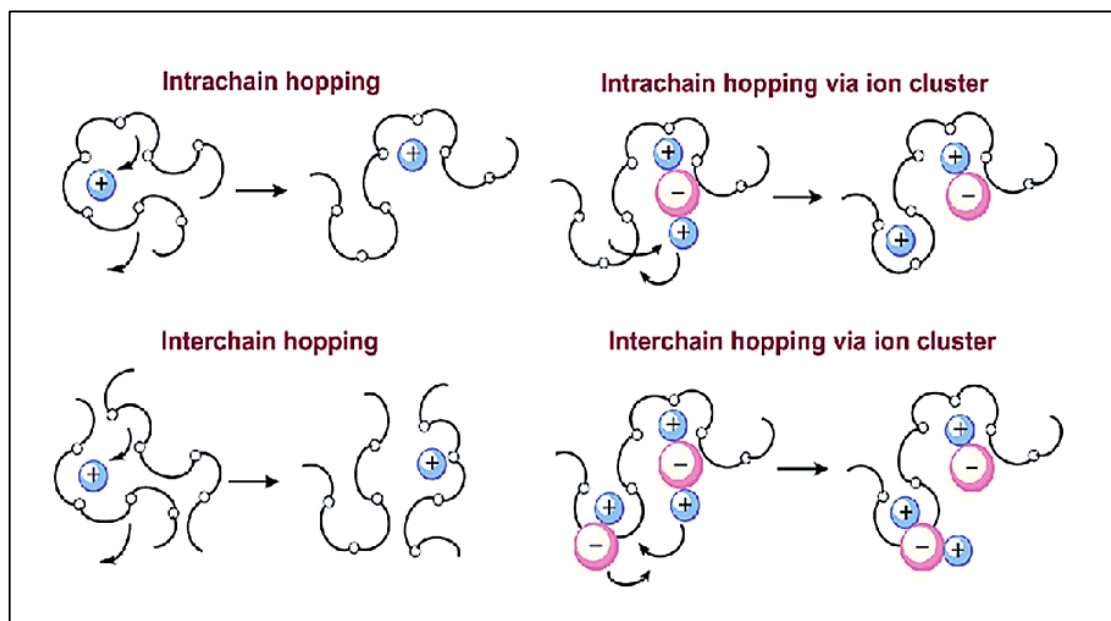
Figure 5: PEO structure

Table 1: Ionic conductivity for various polymer electrolytes

Polymer	S/cm
Polyacrylonitrile	7.20E-04
Polystyrene	1.00E-03
Polymethyl methacrylate	1.00E-05
Polyvinylidene fluoride	1.00E-02
Polyvinyl pyrrolidone	1.00E-02
PEO	1.00E-04

3. Mechanisms of Solid-State Electrolyte Conduction

The mechanism of SPEs electrolytes can be defined as interchain and intrachain hopping of ions, and a typical polymer electrolyte is usually composed of two components, the polymer matrix and lithium salt, which are the key factors that affect ionic conductivity. Not all lithium salts can dissociate and act as free ions in the polymer matrix when the lithium salts dissolve. Therefore, lithium salts' first and most important requirement is their solubility in the polymer matrix, the combination, and the breakage of ethylene oxide and Lithium bonds. Firstly, the electro-donating group of ethylene oxide will complex itself with the ions of Li^+ . Within the lithium-ethylene electrolytes, there are the most effective 5 ethylene oxide groups to match with one Li^+ . Afterward, the segmental movement of the polymer is accountable for the lithium ions conduction, and this motion is limited to non-crystalline areas only. Consequently, the conductivity of those electrolytes depends on the provision of non-crystalline regions. Another important element that governs the conductivity is the glass transition temperature (T_g) because the lower the glass transition temperature, the better the conductivity of polyethylene oxide electrolyte at room temperature. Because of that, a great PEO material must gain two conditions: Excessive amorphous percentage and low glass transition temperature. Low molecular weight PEO is fantastic for electrolytes because of the excessive conductivity, but this has changed into trade with the reduction in the mechanical properties. As a consequence, such electrolytes aren't sensible. Better molecular weight PEO is more potent in mechanical properties, but the excessive crystalline portion of this polymer form will reduce the conductivity. One approach to booming the amorphous region is using grafting or crosslinking methods. Those approaches comprise amorphous polymers with the PEO polymer to reduce the crystalline regions [37]; the entire mechanism is shown in Figure 6.

**Figure 6:** Mechanism of conductivity in PEO SPE

4. Influence of Lithium Salts

Lithium salts have a powerful role in the electrical properties of the synthesized electrolytes, and there are a variety of salts, such as lithium perchlorate (LiClO_4), Lithium tetrafluoroborate (LiTf), and Lithium hexafluoroarsenate (LiFA) [38]. These days, a brand new generation of lithium salts, which is the Lithium bis (trifluoromethane sulfonyl) imide (LiTFSI), has attracted excessive attention amongst clinical research due to its advanced conductivity and solubility, and that is owing to the weak anion bonds with the advantageous lithium cations. Consequently, the dissolving of LiTFSI salt in polymeric matrices is enough for Li^+ to emerge as unfastened from the linkage of anions. Afterward, this loose- Li^+ will bond with EO to comprehend the delivery in bulk PEO [39,40].

Lee et al. [37], investigated the impact of lithium salts on the conductivity of PEO electrolytes; they discovered that lithium perchlorate became the satisfactory salt to be utilized due to the better ionic conductivity of the electrolyte (9.88×10^{-5} S/cm). It was attributed to the lowest lattice energy of lithium salt. It was speculated that the low lattice energy of lithium salt increased the number of carrier ions in the composite electrolyte, allowing higher ionic conductivity.

Michael et al. [41] fabricated an SPE using LiClO_4 as a salt. The conductivity that was carried out became $(9.76 \times 10^{-5} \text{ S/cm})$ at room temperature, and the higher concavity at low temperature was attributed to the application of polymeric plasticizers. The authors also studied the effect of filler content on the conductivity. They found that the conductivity was increased to $(4.29 \times 10^{-4} \text{ S/cm})$. This increase in conductivity was attributed to the decrease in the electrolyte's crystallinity and the increase in the amorphous phase. The conductivity was measured from the room temperature up to 100°C . It was found that the conductivity increased with the temperature increase due to the increase in the hopping process of ions and the increase in the amorphous phase; it is worth mentioning that the researchers only used steel electrodes in the form of discs.

Niedzicki et al. [42] fabricated stable country electrolytes using PEO as a matrix, PEG as a plasticizer, and LiTf as a salt; they observed that the ionic conductivity was very high (10^{-4} S/cm) at 40°C , and this achievement was attributed to the massive anion and the application of PEG plasticizer. Prasanth et al. [43] synthesized a strong country electrolyte using a mix of PEO, PVDF, and LiTFSI as salt. They discovered that the low-temperature conductivity became very high within the order of $(4.9 \times 10^{-3} \text{ S/cm})$. The conductivity for various electrolyte salts is displayed in Figure 7 and Table 2. It is recommended to prepare polymeric electrolytes using LiBF_4 and LiPF_6 as salts due to the high conductivity of these salts.

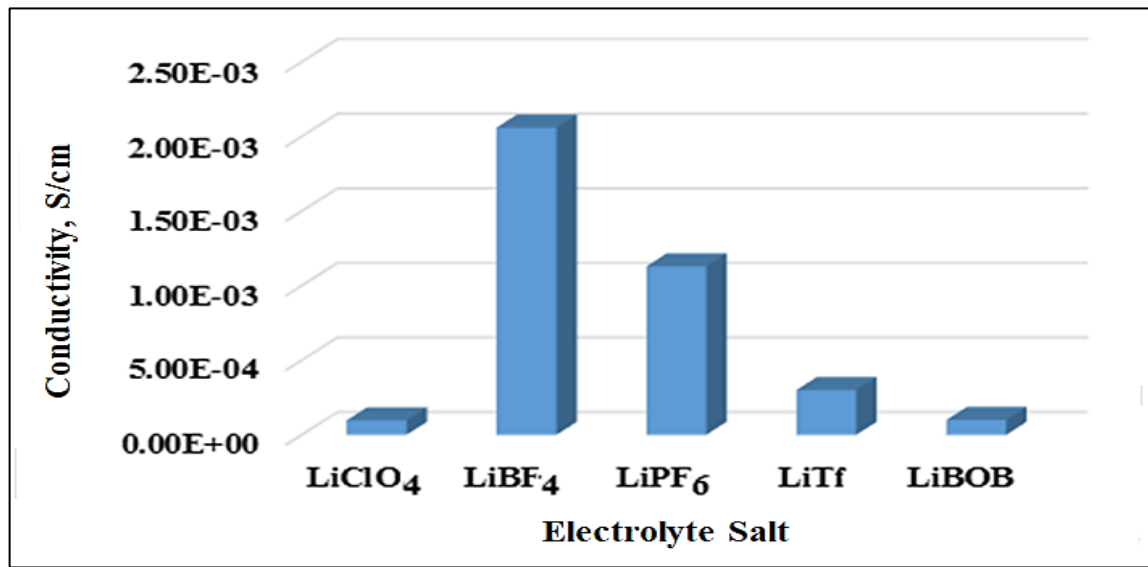


Figure 7: Ionic conductivity for various electrolyte salts, LiClO_4 [44], LiBF_4 [45], LiPF_6 [45], LiTf [46], LiBOB [47]

Table 2: Ionic conductivity for various types of lithium salts

Salt	Conductivity S/cm	REF
LiClO_4	$9.76\text{E-}05$	44
LiBF_4	$2.06\text{E-}03$	45
LiPF_6	$1.13\text{E-}03$	45
LiTf	$3.00\text{E-}04$	46
LiBOB	$1.00\text{E-}04$	47

5. Influence of Plasticizers

Most polymeric matrices suffer from low ionic conductivity; the widely used PEO is among these matrices. The material suffers from the crystalline phase at room temperature. Therefore, the segmental motion is restricted, so the ionic conductivity is very low. One of the most innovative approaches to decrease the crystallinity is the introduction of plasticizers in the matrix phase; these polymeric plasticizers decrease the crystallinity. Hence, the segmental motion is increased; consequently, the ionic conductivity is dramatically increased. There are numerous types of plasticizers, such as the liquid low molecular weight PEG and other organic plasticizers, like Polyethylene glycol dimethyl ether (PEGDME), Tetraethylene glycol dimethyl ether (TEGDME), Ethylene Carbonate (EC), Propylene carbonate (PC), and Dimethyl phthalate (DMP) [48].

Yamamoto et al. [48] observed that the polyethylene oxide polymer was doped with LiTFSI electrolytes and mixed with PEGDME as a plasticizer. It was found that the ionic conductivity was increased from $(1.3 \times 10^{-4} \text{ S/cm})$ to $(3.8 \times 10^{-4} \text{ S/cm})$ at 60°C for PEO- LiTFSI electrolyte within the presence of 18 wt.% of PEGDME, and an excessive diffusion coefficient of $(8.38 \times 10^{-8} \text{ S/cm})$ was acquired at 60°C .

Frech et al. [49] synthesized polymeric electrolytes with the use of tetramethylene glycol (TEG) and tetramethylene glycol dimethyl ether (TEGDME) in PEO- LiTf with the systematic ratio of 9:1. The conductivity of this electrolyte $[(\text{PEO})(\text{TEG})_3]_9\text{LiTf}$ ($6.5 \times 10^{-5} \text{ S/cm}$) turned into three instances better than that of polyethylene oxide - LiTf at 30°C (6.5×10^{-5}). Furthermore, the $[(\text{PEO})_{1-x}(\text{TEG})_x]_9\text{LiTf}$ complexes manifested better conductivities than the corresponding $[(\text{PEO})_{1-x}(\text{TEGDME})_x]_9\text{LiTf}$ complexes. Figure 8 displays the ionic conductivity of various plasticizers. PC and EC as plasticizers can be highly recommended for the preparation of electrolytes due to the high conductivity that will be achieved as tabulated in Table 3.

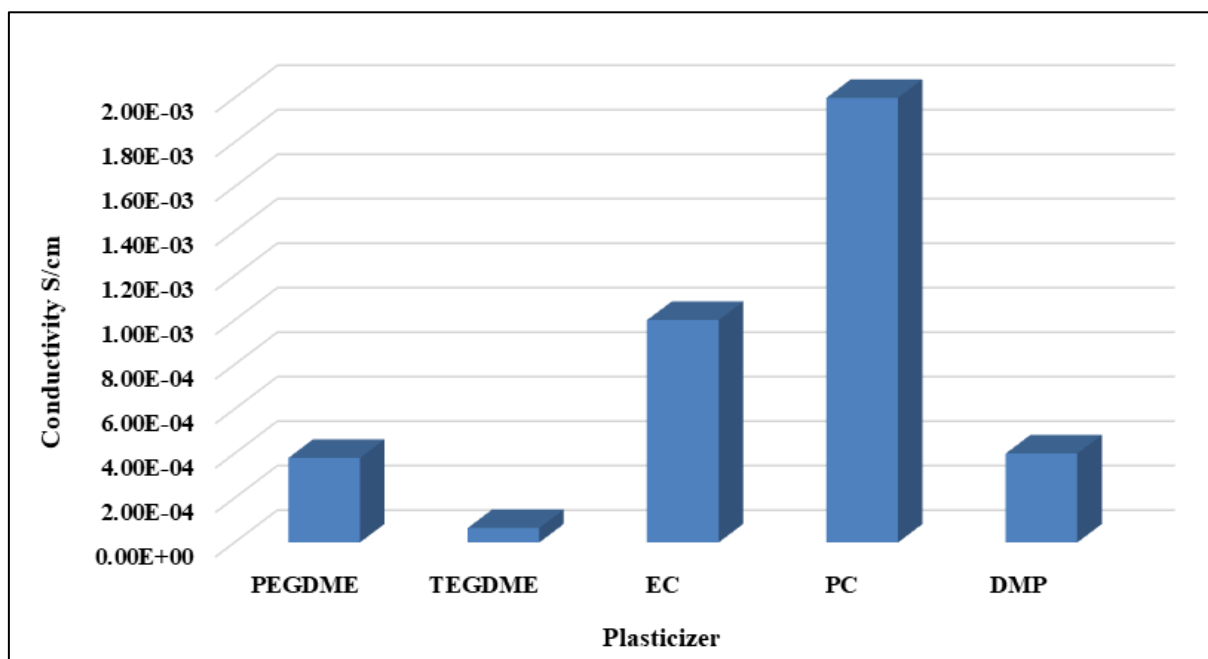


Figure 8: Ionic conductivity for various plasticizers, PEGDME [48], TEGDME [49], EC [50], PC [51], and DMP [52]

Table 3: Ionic conductivity for various plasticizers

Plasticizer	Conductivity S/cm	REF
PEGDME	3.80E-04	48
TEGDME	6.50E-05	49
EC	1.00E-03	50
PC	2.00E-03	51
DMP	4.00E-04	52

6. Influence of Inert Fillers

Inert fillers are extensively researched for solid-state polymeric electrolytes due to the SPEs' low mechanical strength and high crystallinity. One approach to solve this is the utility of inert fillers such as Alpha Alumina (α -Alumina) in the form of small particle size powders; these fillers will reinforce the electrolyte's polymeric matrix and decrease the polymer matrix's crystallinity. One of the first efforts was for Weston and Steele in 1982; they synthesized PEO electrolytes doped with LiClO_4 and reinforced by Alpha Alumina (α -Alumina) and found that the addition of inert fillers of Alumina led to a high ionic conductivity [53]. Since then, numerous researchers have tried to develop new SPEs using other inert fillers, such as Zinc Oxide (ZnO), titanium dioxide (TiO_2), silica (SiO_2), and zirconium dioxide (ZrO_2) [54-57].

Scrosati et al. [55] used metallic oxide fillers, which included Alumina and Titanium dioxide, with the PEO-primarily based electrolytes; this caused an increase in the ionic conductivity via 1-2 orders of importance. Later, they discovered that the active groups inside the nanoparticle have an essential position on the conductivity. Satisfactory conductivities were acquired using acidic Al_2O_3 nanoparticles. The hydrogen bonds between the filler surface and the anion and PEO chain improved ionic dissociation. An improved ionic conductivity changed into located with the addition of nanoporous Al_2O_3 to the PEO-LiTFSI system. The quality conductivity of (2×10^{-3} S/cm) was obtained at 90°C in the PEO-based CPE with the acidic Al_2O_3 [54,58].

Different non-metallic oxide fillers can be additionally utilized; these are Lithium aluminate (LiAlO_2) montmorillonite clay (MMT), silicon carbide (SiC), silicon nitride (Si_3N_4), boron nitride (BN), and even amorphous carbon nanotubes (CN) [59-62].

Hu et al. [63] synthesized the polyethylene oxide composite SPE using mesoporous lithium aluminate nano-sheets as the reinforcing phase. The conductivity of the composite SPE with 15 wt.% filler reached a maximum of (2.24×10^{-5} S/cm) at 25°C , which changed into more than orders higher than that without the filler, and the CPE exhibited correct electrochemical stability as much as 5.0 V.

Alloin et al. [64] investigated the incorporation of cellulose nanocrystals to enhance the mechanical residences of PEO-LiTFSI electrolytes without compromising the conductivity. It was speculated that those promising reinforced polymer electrolytes may be utilized in numerous electrochemical power sources. From Figure 9 and as tabulated in Table 4, it can be easily recommended ZnO and TiO_2 for future work to explore conductivity enhancement.

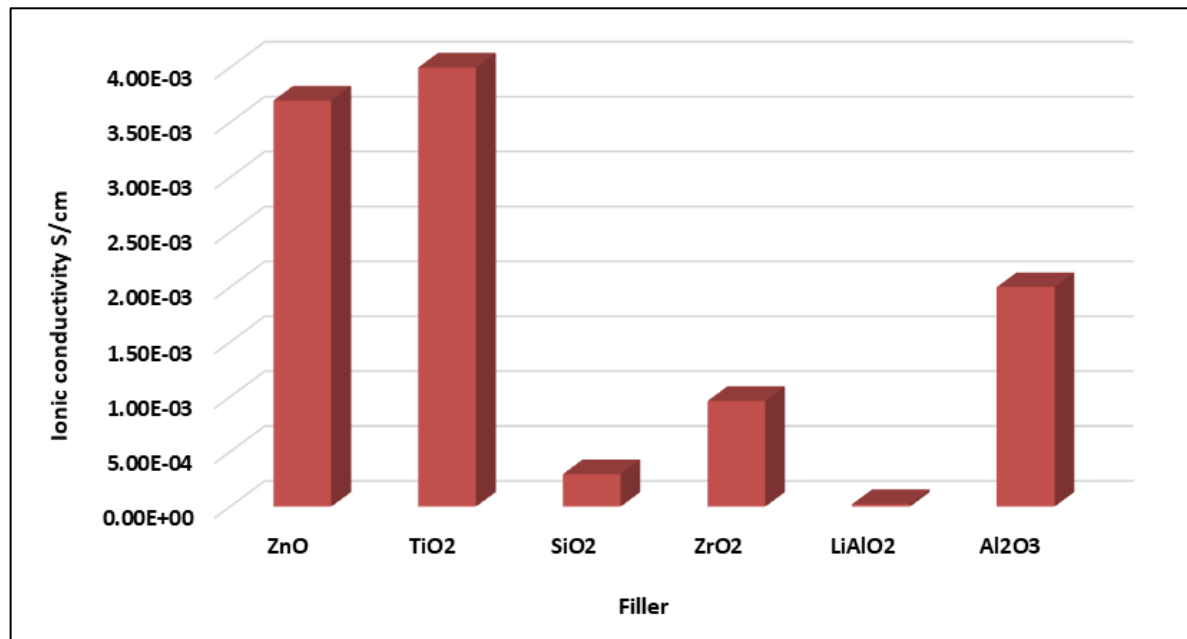


Figure 9: Ionic conductivity of several fillers, ZnO [65], TiO₂ [66], SiO₂ [67], ZrO₂ [68], LiAlO₂ [54], Al₂O₃ [63]

Table 4: Ionic conductivity of inert fillers

Filler	Conductivity S/cm	Ref.
ZnO	3.70E-03	[65]
TiO ₂	4.00E-03	[66]
SiO ₂	2.96E-04	[67]
ZrO ₂	9.62E-04	[68]
LiAlO ₂	2.24E-05	[63]
Al ₂ O ₃	2.00E-03	[54]

7. Influence of Active fillers

The active fillers can be added to the solid polymer matrix and refer to the ceramic fillers which contain Li⁺ ions in their composition; these fillers can be Lithium nitride (Li₃N), Lithium aluminite (LiAlO₂), Lithium aluminum germanium phosphate (Li_{1+x}Al_xGe_{2-x}(PO₄)₃) (LAGP), Lithium aluminum titanium phosphate Li_{1+x}Al_xTi_{2-x}(PO₄)₃ (LATP), Lithium lanthanum titanate (Li_{1.3}xLa_{2/3-x}TiO₃) (LLTO), Lithium lanthanum zirconium oxide (Li₇La₃Zr₂O₁₂) (LLZO), etc. These ceramic materials have high conductivity, good chemical stability, and wide electrochemical windows and can directly participate in Li⁺ transport. Active fillers have a stronger enhancement effect on the ionic conductivity of SPEs than passive fillers. This is mainly due to active ceramics' intrinsic high bulk ionic conductivity. There are several theories to explain this phenomenon [69]:

- 1) These structures have numerous continuous defects, and the activation energy is low.
- 2) The ionic conductivity is achieved by the concerted hopping of multiple ions instead of a single ion.
- 3) The sub-lattice is highly disordered, and thus, the hopping between the lattices won't be disturbed.

LATP is a highly recommended active filler for future work due to its high conductivity, these fillers are shown in Table 5.

Table 5: Ionic conductivity of Active fillers

Fillers	Systems	Concentration of fillers	Maximum ionic conductivity, S/cm
LiAlO ₂	PEO-LiTFSI-15 wt.% SN	10 wt.%	1.36×10 ⁻⁵ at 30°C
LATP	PEO-LiClO ₄	15 wt.%	1.378×10 ⁻³ at 100°C
LLTO	PEO-LiN (SO ₂ CF ₂ CF ₃) ₂	20 wt.%	5.0×10 ⁻⁴ at room temperature
LAZO	PEO-LiClO ₄	15 wt.%	9.5×10 ⁻⁶ at 20°C

8. Solid-State Electrolytes Fabrication Techniques

Fabrication methods for composite SPEs are difficult; the most widely used techniques are the solution casting method (SCM) [70] and thermo-compression [71]. Every technique has its blessings and disadvantages. For instance, membranes produced with the aid of answer casting have top flexibility and ductility. Inert fillers can be blended and brought uniformly by utilizing the stirring technique using a magnetic stirrer, for instance. For the thermo-compression approach, the solvent can be excluded from the entire procedure; consequently, there's no need for the evaporation process that's time-consuming. So, selecting the right technique in line with exceptional needs is vital. The best solubility of lithium salts within the organic solvents has brought about the utility of the solution casting technique.

The solution casting method is as follows: The polymer is dissolved in an appropriate solvent using a magnetic stirrer, after which salts are introduced and blended. Afterward, the solution is cast onto Petri dishes to acquire the membranes after the evaporation of the solvent [71].

In the thermo-compression method, solvents aren't used, which could be a super distinction from solvent casting. The starting materials are mixed by a ball mill, and the movie is immediately shaped by using a hot press. The steps of thermo-compression are as follows: The starting substances are first filtered and sieved, then ball milled to reap small particle length. Then, the powders are warm-pressed between two steel plates. Hence, membranes are accomplished [71]. Those techniques are shown in Figure 10 (a,b). It is highly recommended to use the solution casting method for electrolyte preparation due to the ease of the process and low cost.

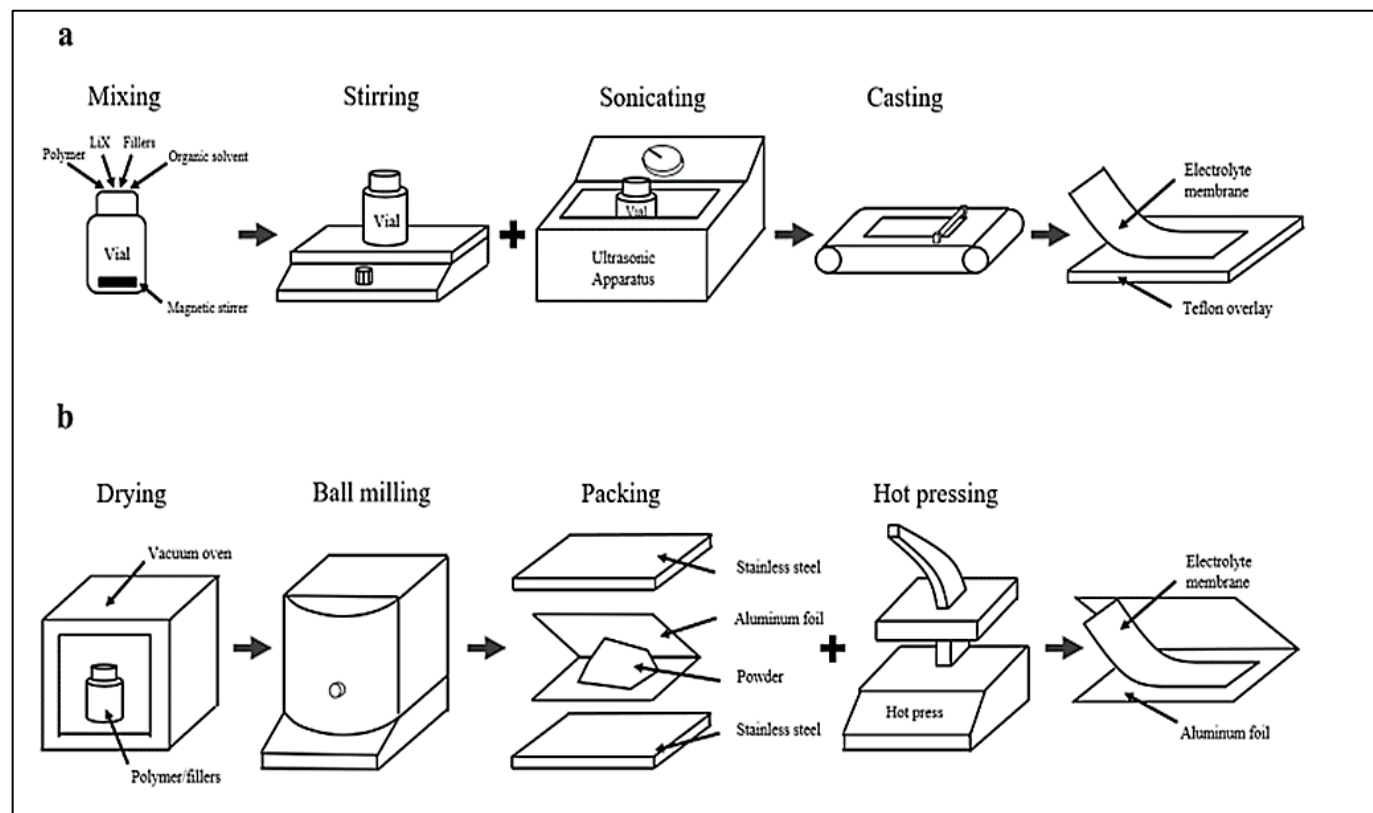


Figure 10: Fabrication techniques of SPE; (a) Solution casting method and (b) Thermo-compression method. [71]

9. Conclusion

Polymeric electrolyte membranes fabricated using polyethylene oxide as a matrix are widely studied in Li-Ion batteries. PEO electrolytes synthesized using different salts and fillers have been reviewed in this article. It was concluded that the salt type plays a vital role in the overall ionic conductivity of the electrolyte. The highest conductivity achieved was by using LiBF_4 salt. Also, it was inferred that the plasticizers' presence in the vicinity of the matrix promotes the conductivity by enhancing the segmental motion of the polymer. Fillers play an important role in the conductivity enhancement process by decreasing the electrolyte's crystalline phase. The type of polymer also plays a vital role in the ionic conductivity, and the higher the molecular weight of the polymer, the lower the ionic conductivity of the electrolyte will result.

Author contributions

Conceptualization, F. Kamal, N. Hameed, E. Salim and S. Gopinath; methodology, F. Kamal, N. Hameed, E. Salim, and S. Gopinath; software, F. Kamal, N. Hameed, E. Salim, and S. Gopinath; validation, F. Kamal, N. Hameed, E. Salim, and S. Gopinath; formal analysis, F. Kamal, N. Hameed, E. Salim, and S. Gopinath; investigation, F. Kamal, N. Hameed, E. Salim, and S. Gopinath; resources, F. Kamal, N. Hameed, E. Salim, and S. Gopinath; data curation, F. Kamal, N. Hameed, E. Salim, and S. Gopinath; writing—original draft preparation, F. Kamal, N. Hameed, E. Salim, and S. Gopinath; writing—review and editing, F. Kamal, N. Hameed, E. Salim, and S. Gopinath; visualization, F. Kamal, N. Hameed, E. Salim, and S. Gopinath; supervision, N. Hameed; project administration, F. Kamal, N. Hameed, E. Salim, and S. Gopinath. All authors have read and agreed to the published version of the manuscript.

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Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

Conflicts of interest

The authors declare that there is no conflict of interest.

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