

Review

Development on Solid Polymer Electrolytes for Electrochemical Devices

Li Ping Teo, Mohd Hamdi Buraidah  and Abdul Kariem Arof *

Centre for Ionics University of Malaya, Physics Department, Faculty of Science, University of Malaya, Kuala Lumpur 50603, Malaysia; lptheo@um.edu.my (L.P.T.); mhburaidah@um.edu.my (M.H.B.)

* Correspondence: akarof@um.edu.my; Tel.: +603-79677143

Abstract: Electrochemical devices, especially energy storage, have been around for many decades. Liquid electrolytes (LEs), which are known for their volatility and flammability, are mostly used in the fabrication of the devices. Dye-sensitized solar cells (DSSCs) and quantum dot sensitized solar cells (QDSSCs) are also using electrochemical reaction to operate. Following the demand for green and safer energy sources to replace fossil energy, this has raised the research interest in solid-state electrochemical devices. Solid polymer electrolytes (SPEs) are among the candidates to replace the LEs. Hence, understanding the mechanism of ions' transport in SPEs is crucial to achieve similar, if not better, performance to that of LEs. In this paper, the development of SPE from basic construction to electrolyte optimization, which includes polymer blending and adding various types of additives, such as plasticizers and fillers, is discussed.

Keywords: solid polymer electrolytes; ionic conductivity; ionic transport; plasticizers; fillers; electrochemical devices



Citation: Teo, L.P.; Buraidah, M.H.; Arof, A.K. Development on Solid Polymer Electrolytes for Electrochemical Devices. *Molecules* **2021**, *26*, 6499. <https://doi.org/10.3390/molecules26216499>

Academic Editor: Maria Manuela Silva

Received: 10 September 2021
Accepted: 25 October 2021
Published: 28 October 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

In any electrochemical devices, the electrolyte is viewed as the core constituent separating the cathode and anode, and it serves as the medium for charge transport. The electrolytes in electrochemical cells exist in three forms, viz liquid, gel and solid. Liquid electrolytes (LEs) are usually found to be highly conducting; thus, they are favored in all kinds of electrochemical devices, namely lithium-ion batteries, dye-sensitized solar cells (DSSCs), quantum dot sensitized solar cells (QDSSCs), fuel cells, electrochemical double layer capacitors (EDLCs), electrochromic devices (ECDs) and so on. However, LEs are sometimes volatile and vulnerable to evaporation, leakage and corrosion in the long-term. This will lead to stability and safety issues of the electrochemical devices. Moreover, LEs can also cause the formation of solid electrolyte interphase (SEI) at the anode surface not only in Li-ion batteries but also for all alkali-metal-ion batteries. This can bring adverse effects on their performance. On the other hand, gel-type electrolytes that inherit both characteristics from electrolytes in liquid and solid forms can reduce complications due to safety, but they suffer from structural instability and low mechanical property. Hence, electrolytes in the solid state are the better and more trustworthy choice to resolve the safety problems without compromising the structural and mechanical traits.

Solid polymer electrolyte (SPE), which is fundamentally made up from dissolved conducting salt within the polymer host, was first discovered by three polymer chemists from Sheffield, UK, i.e., Fenton, Parker and Wright, about 48 years ago [1]. Then, in 1978, Armand and co-workers [2] envisioned the promising implementation of SPE in solid-state batteries. Since then, research on SPE has improved tremendously. In order for SPE to be utilized in electrochemical devices, it must have reasonably good ionic conductivity, good chemical, and thermal and mechanical stabilities, as well as good interfacial contact with electrodes. SPE is considered safe, due to the absence of volatile and flammable solvents, as well as flexible, since it can accommodate volume changes in electrodes

during charging/discharging reactions of electrochemical cells (namely in Li-ion batteries). Furthermore, SPE can be prepared in various shapes and desired designs to meet the needs of electrochemical devices. It can be prepared as an ultra-thin membrane which is lightweight, thus offering promising high energy and power density. SPE is unique compared to liquid electrolyte in the sense that the polymer matrix is in charge for the solvation of ions, while the ions are located at sites which are flexible and can travel within the polymer segments. In order to be functional in electrochemical devices, the SPE must fulfil some prerequisites [3]:

- i. Good ambient ionic conductivity of the order between 10^{-4} and 10^{-2} S cm^{-1} .
- ii. Wide electrochemical stability window.
- iii. Mechanically stable in order to be safe and durable for devices operation
- iv. Thermally stable when in contact with electrode components.
- v. Chemical and electrochemical compatibility with electrodes.
- vi. Obtainability—the raw materials should be abundantly found and low-priced.

A basic SPE contains a polymer and a salt. The salt is dispersed in the polymer matrix, and the ions can conduct through the polymer chains. In order for the polymer to function as host in polymer electrolytes, the macromolecules must possess polar groups which have lone-pair electrons for dative bonding with the cation from the salt. Both synthetic and natural polymers can serve as polymer matrices in SPEs as long as they have functional group(s) to fulfil the complexation criterion. Various polymer electrolytes have been developed from polymers, such as poly(ethylene oxide) (PEO) [1,4,5], cellulose [6], polyvinylidene fluoride (PVDF) [7], poly(vinyl alcohol) (PVA) [8], polyacrylonitrile (PAN) [9], chitosan [10], poly(methyl methacrylate) (PMMA) [11], starch [12] and poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) [13], to name a few. This review presents some achievements on both the synthetic polymers and biopolymers as polymer host in SPEs used, along with working and counter electrodes in various electrochemical devices namely lithium-ion batteries, sodium-ion batteries, DSSCs, QDSSCs, fuel cells, supercapacitors, EDLCs, ECDs, proton-conducting batteries and proton-exchange membrane fuel cells (PEMFCs). Here, we pay special attention to the conductivity aspect of SPEs in these electrochemical devices. Different types of approaches taken by researchers to improve the ionic conductivity of SPEs are also discussed.

2. Ion Transport Properties and Conduction Mechanism in SPEs

Ionic conductivity is one vital characteristic in determining whether the SPE is practical and efficient for device applications. The ionic conductivity of an electrolyte is calculated by using the bulk resistance from the Nyquist impedance plot. The electrolyte is subjected to a small potential typically 10 mV to ensure a linear current–voltage relationship for impedance measurement. According to the Nernst–Einstein relationship, the ionic conductivity, σ , is directly proportional to the diffusion coefficient of ions, D , as shown in the following equation:

$$\sigma = \frac{q^2 n}{k_b T} D \quad (1)$$

where q is elementary charge, n is the number of ions, k_b is Boltzmann constant and T is temperature. Since the electrolyte consists of salts that can ionize into cations and anions, Equation (1) can be written as follows:

$$\sigma = \sigma_+ + \sigma_- = \frac{q^2}{k_b T} (n_+ D_+ + n_- D_-) \quad (2)$$

where σ_+ and σ_- are the ionic conductivity of cations and anions respectively, n_+ is the number of cations, n_- is the number of anions, D_+ is the cationic diffusion coefficient and D_- is the anionic diffusion coefficient. The movement of ions are varied in the electrolyte systems depending on the solvation environment (liquid, solid and gel).

As aforementioned, a polymer electrolyte generally consists of inorganic salts solvated in a polymer matrix that contains functional groups, such as -OH, -C=O, -NH₂ and -COC-. The functional groups help to solvate salts into ions via electrostatic interaction. It has been acknowledged for the past three decades that the motion of ions in polymer matrix is coupled with the segmental movement of the polymer chains, and this is described as the Brownian motion by many researchers [14]. Therefore, it is believed that the ion movements can only occur in amorphous polymers where the polymer chains are freely moveable to transport the ions. It is well-known that the motion and flexibility of polymer chains are higher in polymer matrix that possess low glass transition temperature, T_g . Hence, the selection of polymer is crucial in the development of polymer electrolyte. The relation between conductivity and T_g can be explained by the Vogel-Tammann-Fulcher (VTF) equation:

$$\sigma = \sigma_0 T^{1/2} \exp\left(\frac{-B}{T - (T_g - 50\text{K})}\right) \quad (3)$$

where σ_0 is the prefactor and B is related to the activation energy. T_g can also be determined from differential scanning calorimetry (DSC). Based on Equations (2) and (3), the conductivity of a polymer electrolyte can be amplified by increasing the number density of mobile ions and lowering the T_g . Another approach is by decoupling ion diffusion with the polymer chains. A simplest way to fulfil the above criteria is by adding high dielectric constant plasticizers into the polymer electrolyte. A high dielectric constant can weaken the attraction forces between the ions in the salt and thus enhances the salt dissociation and the increase in number density of mobile ions [3]. Plasticizers also facilitate the pathway of ions transportation by increasing the amorphousness of the polymer electrolyte film and providing the additional coordination sites for ions to conduct.

Whu and Wick [4] have investigated the role of propylene carbonate (PC) as plasticizer in PEO-based electrolytes having lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) via Monte Carlo and molecular dynamics simulations. They found that the conductivity showed significant improvement with the addition of PC due to the increase in mobility of TFSI⁻ ions [4]. The lithium ions' diffusion remained unchanged and showed stronger interaction with the ethylene oxide oxygen as compared to the carbonate oxygen. Radial distribution function of lithium also showed weak binding between lithium and oxygen atom of TFSI⁻ in the presence of PC [4]. Therefore, the probability of lithium ions' transportation through the oxygen atom of PEO was higher than that of carbonate and TFSI⁻ oxygen [4].

Webb and co-workers [5] calculated the diffusion of lithium ions in different types of polymers, namely PEO, poly(methylene oxide) (PMO), poly(propylene oxide) (PPO), poly(trimethylene oxide) (PTMO), poly(ethylene oxide-alt-methylene oxide) (P(EO-MO)) and poly(ethylene oxide-alt-trimethylene oxide) (P(EO-TMO)), using molecular dynamics and dynamic bond percolation models. They have assigned short molecular dynamics trajectories to identify the distribution of the solvation sites and used it in dynamic bond percolation model to calculate the ionic hopping rate. According to them, the largest number of site density belongs to the polymer with the highest oxygen atom content which is PMO (oxygen to carbon atomic ratio is 1:1). This is followed by P(EO-MO) (2:3), PEO (1:2), P(EO-TMO) (2:5), PPO (1:3) and PTMO (1:3). Even though the ratio of oxygen to carbon atoms for PPO and PTMO are the same, the site density is slightly higher in PPO which may be due to the arrangement of atoms in the PPO [5]. The rate of hopping sites, k_0 , with distance, r , can be calculated by using the following equation:

$$k_0(r) = \tau^{-1} e^{-E_{dis}(r)/k_b T} e^{-E_\lambda(r)/k_b T} \quad (4)$$

where τ^{-1} is frequency, and E_{dis} and E_λ are the dissociation and reorganization energies, respectively. Based on the calculation, the authors found that PMO exhibited the smallest value of k_0 , whereas that of PPO was the largest [5]. They have used these values to

calculate lithium-ion diffusion, using the kinetic Monte Carlo simulation. Among the polyethers studied, the diffusion of lithium ions in P(EO-TMO) was the highest [5].

Diffusion coefficient of ions, D , can also be determined from the following equation:

$$D = \frac{d^2}{4\tau_2\delta^2} \quad (5)$$

where d is the thickness of the electrolyte, $\tau_2 = 1/\omega$ and $\delta = dk^{-1}/A\varepsilon\varepsilon_0$ (where ω is the angular frequency taken at the minimum value of impedance in Bode plot; k^{-1} is double layer capacitance; ε is dielectric constant of the electrolyte; and ε_0 is the permittivity in free space). Based on Equation (5), D in PVA-based polymer electrolyte containing potassium iodide salt has been calculated [6]. The k^{-1} value was obtained by fitting the Nyquist plot of the electrolyte. Since the complex impedance plot shows only a tilted spike, the plot has been fitted based on the series connection of bulk resistance, R_b , and constant phase element, CPE.

The total impedance (real, Z' and imaginary, Z'') can be described as follows:

$$Z' = R_b + \cos(\pi p/2)/k^{-1}\omega^p \quad (6)$$

$$Z'' = \sin(\pi p/2)/k^{-1}\omega^p \quad (7)$$

where p is a fraction of a right angle. The mobility, μ , and number density, n , of ions can be obtained by using the following equations:

$$\mu = qD/k_bT \quad (8)$$

$$n = \sigma/q\mu \quad (9)$$

It is evident that Equation (1) is the combination of Equations (8) and (9). The calculated transport properties (D , n and μ) have been used to explain the conductivity behavior in PVA-based electrolyte containing different salt concentrations [8]. Relationship between σ , n and μ can be expressed as follows:

$$\sigma = qn\mu \quad (10)$$

In our earlier studies [8], it was found that the ionic mobility has contributed more in the highest conducting electrolyte, since n decreased due to the establishment of ion pairs and ionic aggregates. Noor has calculated n for lithium triflate in gellan-gum-based SPE by using the method from Fourier transform infrared (FTIR) spectroscopy [9,15]. Areas of free ions (A_f), ion pairs (A_p) and ion aggregates (A_a) have been identified via FTIR deconvolution in wavenumber region between 1030 and 1060 cm^{-1} , and their percentage can be calculated based on the following equations:

$$\text{Free ions (\%)} = \frac{A_f}{A_f + A_p + A_a} \times 100 \quad (11)$$

$$\text{Ion pairs (\%)} = \frac{A_p}{A_f + A_p + A_a} \times 100 \quad (12)$$

$$\text{Ion aggregates (\%)} = \frac{A_a}{A_f + A_p + A_a} \times 100 \quad (13)$$

From Equation (11), n can be calculated from the following:

$$n = \frac{M \times N_A}{V} \times 2 \times \text{percentage of free ions} \quad (14)$$

where N_A is the Avogadro's number, M is number of moles of lithium triflate and V is the electrolyte's volume.

The n value can also be calculated from the famous Rice and Roth model which was originally developed to describe the conductivity behavior for superionic conductors [16]. The equation is as follows:

$$\sigma = \frac{2}{3} \left[\frac{(Zq)^2}{mk_bT} \right] n E_A \tau \exp \left[-\frac{E_A}{k_bT} \right] \quad (15)$$

where E_A is the activation energy; q is the electron charge; m is the mass of ions; Z is the vacancy of conducting species; and $\tau = r/v$, where r is the distance between two coordinating sites and v is the velocity of ions, which is given as follows:

$$v = \sqrt{\frac{2E_A}{m}} \quad (16)$$

E_A is the minimum energy required for an ion to hop in between sites, and it can be obtained from the Arrhenius equation, as shown below:

$$\sigma = \sigma_0 \exp \left(\frac{E_A}{k_bT} \right) \quad (17)$$

where σ_0 is the pre-exponential factor. A low E_A value is required for high conductivity. In general, the mechanism of ion transport in polymer electrolytes is via hopping and coupled with the segmental motion of the polymer [3]. However, Grotthuss motion which is another type of hopping mechanism has been proposed to describe proton conduction in chitosan-based SPE containing ammonium iodide (NH_4I) [10]. Chitosan structure is rigid and possesses high T_g , thus resulting in minimal chain motion. This led to the proposal of the Grotthuss model as the proton-conduction mechanism in the SPEs. Grotthuss mechanism is the proton conduction process where the proton hops between the coordination sites decoupled from the polymer chain motion. This mechanism is also known as proton hopping. Besides these factors, other parameters that can influence the feasibility of polymer electrolytes in applications for electrochemical cells include ion (cationic and anionic) transference number (t_{ion}), degree of crystallinity, etc.

3. Basic Solid Polymer Electrolytes

A simple SPE consists of a polymer and a salt where both are dissolved in a solvent before the solvent is allowed to evaporate, while the ions continue to be free and mobile inside the polymer matrix [3]. The salt can be either inorganic or organic salt but when used in DSSCs application, the SPE must contain additional materials, i.e., iodine (I_2) crystals to act as redox mediator, while the salt must be iodide-based salts, since iodide/triiodide (I^-/I_3^-) redox couple is commonly used [17]. Likewise, for application in QDSSCs, the basic SPE should have sulfide/polysulfide ($\text{S}^{2-}/\text{S}_x^{2-}$) redox mediator with sulfide-based salts. Similarly, the salt should be lithium-based, sodium-based, magnesium-based and proton-based if it is going to be employed in cells of Li-ion, Na-ion and Mg-ion and proton batteries as well as PEMFCs. Besides this, the salt must meet the criterion of having low lattice energy for easy solvation in polymer matrix [3]. Tables 1 and 2 list some of the most popular polymers and salts used in polymer electrolytes, along with their special traits that enable them to be favored among others by the researchers worldwide. The T_g of polymer will affect the crystallinity of the electrolytes, and usually low T_g is preferred. Meanwhile, the lattice energy of salt will determine how easy it can dissociate in the polymer matrix. The lattice energies of the salts in Table 2 are calculated in this work, using the Kapustinskii equation [18]. All materials have both their own benefits and drawbacks. For instance, PEO, being the first polymer host used in polymer electrolytes and still remaining one of the most popular polymers until now, is favored for its talent to solvate many types of salts and exhibit good mechanical strength and thermal stability. It is a semicrystalline macromolecule, and thus, its crystalline part restricts the increment of conductivity. As for

the salts, lithium perchlorate (LiClO_4), as an example, shows good ionic conductivity, but it is a strong oxidizer, hence making it explosive, and so it must be handled with caution. As for the solvent choice, certain features, including dielectric constant, melting point, boiling point and viscosity, have to be taken into consideration for salt dissociation and solvation of polymer. Some frequently employed solvents are summarized in Table 3, along with their physical attributes.

Table 1. Typical polymers used in polymer electrolytes, along with their characteristics.

| Polymer | Functional Group(s) | Glass Transition Temperature, T_g ($^{\circ}\text{C}$) | Reference |
|--|------------------------|--|-----------|
| Poly(ethylene oxide) (PEO) | Ether | −64 | [19] |
| Polyacrylonitrile (PAN) | Nitrile | 125 | [19,20] |
| Poly(vinyl alcohol) (PVA) | Hydroxyl | 82 | [21] |
| Cellulose | Hydroxyl, Ether | 220 | [22] |
| Poly(methyl methacrylate) (PMMA) | Ester, Carbonyl | 105 | [19] |
| Polyethyl methacrylate (PEMA) | Ester, Carbonyl | 63 | [23] |
| Polyvinylidene fluoride (PVDF) | Difluoromethylene | −40 | [19] |
| Chitosan | Hydroxyl, Amine, Ether | 203 | [24] |
| Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) | Difluoromethylene | −90 | [19] |
| Starch | Hydroxy, Ether | 70 | [25] |

Table 2. Some popular salts used in polymer electrolytes, along with their properties [18,26,27].

| Salt | Cationic Radii (pm) | Anionic Radii (pm) | Lattice Energy (kJ mol^{-1}) |
|---|---------------------|--------------------|---|
| Lithium bis(trifluoromethanesulfonyl)imide (($\text{LiN}(\text{CF}_3\text{SO}_2)_2$) or (LiTFSI)) | 60 | 328 | 564 |
| Lithium trifluoromethanesulfonate or lithium triflate (LiCF_3SO_3) | 60 | 268 | 730 |
| Lithium perchlorate (LiClO_4) | 60 | 234 | 718 |
| Lithium tetrafluoroborate (LiBF_4) | 60 | 227 | 735 |
| Lithium hexafluorophosphate (LiPF_6) | 60 | 254 | 681 |
| Sodium iodide (NaI) | 102 | 216 | 674 |
| Sodium thiocyanate (NaSCN) | 102 | 213 | 680 |
| Ammonium iodide (NH_4I) | 143 | 216 | 605 |
| Lithium iodide (LiI) | 60 | 216 | 762 |

Table 3. Physical properties of some solvents [28–30].

| Solvent | Donor Number, DN | Dielectric Constant, ϵ at 25°C | Viscosity (cP) at 25°C | Melting Point, T_m ($^{\circ}\text{C}$) | Boiling Point ($^{\circ}\text{C}$) |
|------------------------------|------------------|---|--|---|--------------------------------------|
| Acetone | 17.0 | 20.6 | 0.30 | −94.7 | 56.1 |
| Acetonitrile (ACN) | 14.1 | 35.9 | 0.37 | −43.8 | 81.6 |
| N-methyl-2-pyrrolidone (NMP) | 27.3 | 32.2 | 1.67 | −24.4 | 202 |
| Tetrahydrofuran (THF) | | 7.58 | 0.46 | −108.4 | 60 |
| N,N-Dimethylacetamide (DMAc) | 27.8 | 37.8 | 0.93 | −20 | 166.1 |
| Dimethyl sulfoxide (DMSO) | 29.8 | 46.5 | 1.99 | 18.5 | 189 |
| Gamma-butyrolactone (gBL) | 18.0 | 39.0 [†] | 1.70 | −44 | 204 |
| N,N-Dimethylformamide (DMF) | 26.6 | 36.1 | 0.80 | −61 | 153 |
| Ethylene carbonate (EC) | 16.4 | 89 [*] | 1.90 [*] | 36 | 238 |
| Propylene carbonate (PC) | 15.1 | 64 | 2.50 | −49 | 241 |
| Ethanol | 19.2 | 25 | 1.08 | −114 | 78 |
| Water | 18.0 | 78 | 0.89 | 0 | 100 |

* At 40°C . † At 20°C .

3.1. Preparation Methods of SPEs

SPEs can be prepared via several methods, including solution casting [31], phase inversion [32], photopolymerization [33] and electrospinning [31] techniques, to name a few. Solution cast or solvent casting method is the most conventional and easy way to prepare electrolyte film. In this procedure, the polymer and salt are dissolved in an appropriate solvent before casting onto suitable substrates (e.g., glass plates). The solvent is then evaporated after being left to dry either at ambient condition or elevated temperature inside oven. Solution casting route can be performed at room temperature atmosphere or inside glove box, depending on its needs. After complete drying, the SPE is a free standing membrane with thickness usually in millimeter range. Solangi and co-authors [31] have compared PVA-based SPE containing potassium iodide (KI), potassium chloride (KCl) and sodium chloride (NaCl) salts prepared by using electrospinning and solution-casting techniques. Regardless of which salt was used, the electrolyte fabricated via the former method demonstrated superior ionic conductivity ($5.95 \times 10^{-6} \text{ S cm}^{-1}$ for NaCl-containing SPE) than that prepared by the latter ($1.87 \times 10^{-6} \text{ S cm}^{-1}$ for SPE having NaCl) [31]. The electrospinning approach can produce film of fibers morphology with a large surface-area-to-volume ratio. Moreover, the electrospun membranes were more thermally stable than the solution-cast prepared films. Among the three salts, electrolytes comprising NaCl exhibited the highest conductivity irrespective of the preparation method [31]. Nonetheless, there are many parameters that need to be controlled and optimized in electrospinning process such as polymer molecular weight and solution viscosity, conductivity and surface tension. Furthermore, the electrospinning setup conditions, e.g., flow rate, applied voltage and distance from tip of syringe containing solution to collector, are tedious and time-consuming. In contrast to electrospinning, the solution-casting route is a more straightforward and convenient approach for membrane preparation.

The phase inversion technique can produce porous structure which is beneficial for ionic transport. Using this method, SPE membrane consisting of PDVF-HFP, LiClO_4 and cerium oxide (CeO_2) exhibited sponge-like morphology with tiny pores and ionic conductivity of $2.50 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C [32]. In this procedure, a solution containing PVDF-HFP, CeO_2 and NMP solvent was stirred for 24 h before being coated onto a glass plate via the doctor-blade method. This was followed by immersion in deionized water (about 3 to 5 h) for solvent extraction and phase inversion, which took place before drying under vacuum-pressure condition. The last step was to soak the membrane in LiClO_4 liquid electrolyte for 6 h [32]. Liu et al. [34] have combined phase-inversion and chemical-reaction routes to obtain PVDF-PAN- SiO_2 - LiPF_6 SPE membrane that gave ambient conductivity of $3.32 \times 10^{-3} \text{ S cm}^{-1}$. For comparison, the same composition membrane has been prepared by phase-inversion method, and it was found that the ambient conductivity was $2.83 \times 10^{-3} \text{ S cm}^{-1}$ [34]. The higher conductivity obtained by the membrane prepared by the combined method was attributed to larger porosity and better homogeneous pores distribution as compared to that developed from the phase-inversion technique only [34]. The former also showed better properties in terms of heat resistance, mechanical strength and electrochemical stability than the latter [34]. An unconventional way to prepare SPE films is through dry-mixing without the use of solvent. Dry-mixing is combined with hot-pressing. Eriksson et al. [35] have obtained thin films of SPEs containing poly(3,3-dimethylpentane-2,4-dione) as the polymer matrix and LiTFSI salt after pressing the dried homogenous mixture between two polytetrafluoroethylene (PTFE) plates, under high pressure (2 MPa) and temperature (100°C) conditions, inside an argon-filled glove box for 1 h. The polymer was desiccated in vacuum state before uniformly mixing and pulverizing the polymer and salt. Although the ambient conductivity value was low, of the order of $10^{-8} \text{ S cm}^{-1}$, it gave a rather high Li^+ ion transference number ($t_{\text{Li}^+} = 0.70$) at 80°C [35]. For the sake of comparison, the LiTFSI-containing SPE but with PEO as polymer host has been prepared by the same method and it showed a higher ambient conductivity ($10^{-5} \text{ S cm}^{-1}$) with low Li^+ transference number ($t_{\text{Li}^+} = \sim 0.15$) [35]. High cationic transference number

is useful for application in Li-ion batteries. Table 4 shows some selected works of simple SPEs systems available in the literature.

Table 4. Basic SPEs films, along with their conductivity and significant properties.

| Electrolyte System | Preparation Method | Conductivity, σ (S cm ⁻¹) | Important Findings | Reference |
|--|----------------------------|--|---|-----------|
| PEO-NaSCN | Solution casting | 9.86×10^{-8} (RT) | $t_{ion} = 0.85$ $n = 1.21 \times 10^{20} \text{ m}^{-3}$; $\mu = 5.10 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ | [36] |
| PEO-NaFNFSI [EO]/[Na]=15 | Solution casting | 3.16×10^{-6} (80 °C) 3.36×10^{-4} (30 °C) | Thermal stability > 300 °C; $T_g = -36.3$ °C $t_{Na+} = 0.24$ (80 °C) Oxidation potential = 4.87 V vs Na ⁺ /Na NaCu _{1/9} Ni _{2/9} Fe _{1/3} Mn _{1/3} O ₂ /SPE/Na cell: Initial capacity = 122.4 mAh g ⁻¹ (0.1 C, 80 °C)70% capacity retention at 1 C after 150 cycles (80 °C) | [37] |
| PEO-LiCF ₃ SO ₃ | Ball-milling and hot press | 1.00×10^{-6} | $T_g = -64.4$ °C; % $\chi_C = 37.3\%$ | [38] |
| PAN-LiTFSI | Solution casting | 2.54×10^{-4} (25 °C) | % $\chi_C = 9.3\%$ ITO-WO ₃ /SPE/CeO ₂ -TiO ₂ -ITO ECD: Cathodic coloration at -1.25 V; Anodic bleaching at -0.40 V | [39] |
| CMC-(NH ₄) ₂ CO ₃ | Solution casting | 7.71×10^{-6} (30 °C) | % $\chi_C = 30.9\%$; $t_{ion} = 0.98$ CMC film without salt: $\sigma = 10^{-9} \text{ S cm}^{-1}$ | [40] |
| NaCMC-Na ₂ S-S | Solution casting | 2.79×10^{-5} (30 °C) | $E_A = 0.38 \text{ eV}$ $n = 15.24 \times 10^{18} \text{ cm}^{-3}$; $\mu = 11.44 \times 10^{-6} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$; $D = 2.94 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ TiO ₂ -CdS-ZnS/SPE/Pt QDSSC (light intensity of 100 mW cm ⁻²): OCV = 0.41 V; $J_{sc} = 4.92 \text{ mA cm}^{-2}$; $FF = 0.45$; $\eta = 0.90\%$ | [41] |
| Pectin-LiCl | Solution casting | 1.96×10^{-3} (30 °C) | $E_A = 0.23 \text{ eV}$ Tensile strength = 4.61 MPa Electrochemical stability window 3.77 V Zn/SPE/LiFePO ₄ cell: OCV = 1.25 V | [42] |
| PEO-LiCF ₃ SO ₃ [EO]/[Li] = 9:1 | Solution casting | 1.40×10^{-6} (30 °C) | $T_g = -39$ °C; $T_m = 64$ °C | [43] |
| Sago starch-KI | Solution casting | 3.41×10^{-4} (RT) | Dielectric relaxation time = $2.33 \times 10^{-7} \text{ s}$ N3/TiO ₂ /SPE/Pt DSSC (light intensity of 100 mW cm ⁻²): OCV = 0.58 V; $J_{sc} = 0.29 \text{ mA cm}^{-2}$; $FF = 0.43$; $\eta = 0.57\%$ | [44,45] |
| Corn starch-MgSO ₄ | Solution casting | 8.52×10^{-5} (30 °C) | SEM micrograph of SPE shows rough surface, while that of starch film without salt shows otherwise. | [46] |
| PEMA-NH ₄ I | Solution casting | 1.80×10^{-5} (30 °C) | $t_{ion} = 0.93$ Ru-based dye/TiO ₂ /SPE/Pt DSSC (light intensity of 100 mW cm ⁻²): OCV = 0.56 V; $J_{sc} = 1.52 \text{ mA cm}^{-2}$; $FF = 0.51$; $\eta = 0.43\%$ | [47] |

NaSCN—sodium thiocyanate; RT—room temperature; NaFNFSI—sodium (fluorosulfonyl)(n-nonafluorobutanesulfonyl)imide (Na[(FSO₂)(n-C₄F₉SO₂)N]); % χ_C —degree of crystallinity percentage; CMC—carboxymethyl cellulose; ITO—indium tin oxide; WO₃—tungsten (VI) oxide; CeO₂—cerium (IV) oxide; TiO₂—titanium dioxide; (NH₄)₂CO₃—ammonium carbonate; NaCMC—sodium-carboxymethylcellulose; Na₂S—sodium sulfide; S—sulfur; OCV—open circuit voltage; J_{sc} —short circuit current density; FF —fill factor; η —efficiency; CdS—cadmium sulfide; ZnS—zinc sulfide; Pt—platinum; LiCl—lithium chloride; LiFePO₄—lithium iron phosphate; N3—*cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II); MgSO₄—magnesium sulfate.

3.2. Strategies to Improve Ionic Conductivity of SPEs

In order to boost the ionic conductivity of SPEs, there are many approaches which have been taken by researchers, as stated in the following subsections.

3.2.1. Incorporation of More Than One Salt

One viable approach to boost the ionic conductivity of SPEs is to add another salt. The combination of two or more salts in the right proportions can give synergistic outcomes. In most cases, the sum concentration of salts is the same as the highest conducting electrolyte that contained only on one type of salt. This means that the total weight of salts remained unchanged, but an appropriate amount for salt one has been substituted by salt two. Since the amount of each salt in a mixed salt electrolytes is lower than the concentration of salt in single-salt electrolyte systems, the probability of ion recombination to form ion pairs will be reduced in former case, and thus, there are more free ions for conduction [48,49]. In addition, decrement in T_g and degree of crystallinity ($\% \chi_c$) of the electrolyte are observed in mixed salt systems [48]. Tao and Fujinami [50] reported that highest conductivity was achieved at $5 \times 10^{-5} \text{ S cm}^{-1}$ (30 °C) in PEO-based SPE containing lithium borate and lithium aluminate salts as compared to PEO electrolyte with one salt only regardless which one. Only minimal capacity fading was observed in $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2/\text{Li}$ cell with double salt-containing SPE after 30th cycle, but no results were given for that of single salt [50]. The type of cation and anion determine the electrochemical performance of devices. For Li-ion, Na-ion and Mg-ion cells, it is obvious that dissimilar anions influence the performance of the devices. For DSSCs, the variation of cations since the anion is fixed following the redox mediator used. Studies of mixed salt systems containing different cations [51,52] or dissimilar anions [49,53,54] have shown superior ionic conductivity than single salt systems. For instance, higher conductivity was obtained for an electrolyte based on PEO- CaBr_2 - CaI_2 (30:1:1) than for a PEO-based electrolyte with only one salt, i.e., either calcium iodide (CaI_2) or calcium bromide (CaBr_2) [52]. Similarly, enhanced conductivity has been detected for PEO electrolyte having dual salts of zinc bromide (ZnBr_2) and lithium bromide (LiBr) [51] and PEO-based electrolyte comprising the same compositions of binary salts of copper trifluoromethanesulfonate ($\text{Cu}(\text{CF}_3\text{SO}_3)_2$) and zinc trifluoromethanesulfonate ($\text{Zn}(\text{CF}_3\text{SO}_3)_2$) [55].

The incorporation of double salts does not always warrant higher conductivity than single salt but can still result in better performance of electrochemical devices, since conductivity is not the sole influencing factor. This has been showcased in the work of Dissanayake et al. [56], who have prepared PEO-based SPE with KI and TPAI salts via the solution-cast method. SPE containing sole salt of KI gave higher conductivity than electrolyte having double salts. Conductivity was lowest for electrolyte with lone TPAI salt since its cation is larger than K^+ and thus less mobile. Moreover, the degree of crystallinity for PEO-TPAI electrolyte was higher than that of PEO-TPAI-KI SPE [56]. DSSC employing hybrid salts displayed the best performance, with an efficiency (η) of 4.22% and short circuit current density (J_{sc}) of 8.00 mA cm^{-2} , followed by cells having single TPAI ($J_{sc} = 6.38 \text{ mA cm}^{-2}$; $\eta = 3.54\%$) and KI ($J_{sc} = 6.52 \text{ mA cm}^{-2}$; $\eta = 3.09\%$) under illumination of 100 mW cm^{-2} . Their open-circuit voltage (OCV) values were 0.69, 0.77 and 0.75 V for KI, TPAI and KI+TPAI electrolytes, respectively [56]. A large-sized cation boosted OCV value, while it reduced J_{sc} , as can be seen when comparing the two single salt-containing electrolytes. The addition of a second salt decreased the cation conduction and enhanced J_{sc} , leading to a higher η [56].

Zhao and co-workers [57] have studied the influence of primary, secondary and ternary salts on PEO-based SPEs incorporated with halloysite nanoclay (HNC) for application in Li-ion batteries. For PEO-LiTFSI-HNC SPEs, the ambient conductivity was $\sim 5.62 \times 10^{-5} \text{ S cm}^{-1}$, and there was a slight increment when a secondary salt, i.e., lithium bis(oxalate)borate (LiBOB), was added, but then there was a decrement in conductivity ($\sim 1.99 \times 10^{-5} \text{ S cm}^{-1}$) was observed with the addition of a third salt, lithium nitrate (LiNO_3) [57]. Nonetheless, T_g values were enhanced from -47.02 to -40.48 °C for single

to ternary salt-containing SPEs [57]. Mechanical strength also improved as proven from dynamic mechanical analysis (DMA). The authors have concluded that each respective salts have their own role with LiTFSI being the main contributor to ionic conduction, whereas the presence of LiBOB and LiNO₃ salts was to ensure the emergence of cathode electrolyte interphase and solid electrolyte interphase SEI on cathode and anode, respectively [57]. Each of these salts have complemented each other and yielded Li-ion-cell performance with better electrochemical stability. Cells employed one and two salts suffered failure within the first five cycles. In contrast, the lithium nickel cobalt manganese oxide (NMC)/Li cell with SPE containing trio salts exhibited the discharge capacity of ~116 mAh g⁻¹ at 60th cycle [57]

3.2.2. Modification on Polymer Host

The partial crystallinity nature of polymer host is usually the main culprit behind the low conductivity of SPEs. This issue can be resolved by making some alteration on the polymer itself. For example, biopolymers, i.e., cellulose and chitin, are highly crystalline with rigid polymer chain backbone, even though they can still serve as host in polymer electrolyte. Cellulose can be chemically modified into methyl cellulose (MC), carboxymethyl cellulose (CMC), hydroxypropyl cellulose (HPC) and sodium carboxymethyl cellulose (NaCMC), to name a few. Similarly, chitosan structure can be altered into carboxymethyl chitosan, hexanoyl chitosan (HCh), N-methylene phosphonic chitosan, chitosan-N-propyl sulfonic acid, etc. Besides reducing crystallinity, the modified polymer will have greater solubility to dissolve in various solvents, as compared to its predecessor. N-phthaloyl chitosan (PhCh) is the product obtained after the chemical adjustment of chitosan in a solution mixture of phthalic anhydride and DMF under a nitrogen gas environment. Chitosan has been successfully transformed into PhCh with the presence of peaks belonging to the phthalimido functional group at wavenumbers 1713 and 1733 cm⁻¹, as proven by FTIR analysis [58]. Dilute acids of formic, acetic, butyric, lactic, maleic and malic are some solvating agents for chitosan [59,60], but the water content may deteriorate the performance of some electrochemical devices, such as Li-ion batteries and DSSC. PhCh can dissolve in pyridine, DMAc, DMF, DMSO and *m*-cresol [61,62]. Aziz et al. [58] reported that PhCh is more amorphous and thermally stable than the antecedent, chitosan. The former requires a higher decomposition temperature (356 °C) than the latter (290 °C). PhCh-based SPE consisting of NH₄SCN prepared via solution-casting method displayed conductivity of 2.42×10^{-5} S cm⁻¹ at 25 °C and $t_{ion} = 0.91$ [58]. The PhCh film had the ambient conductivity of $\sim 1.93 \times 10^{-10}$ S cm⁻¹ [58]. O-nitrochitosan is another derivative of chitosan after reacting with sodium hydroxide and fumed nitric acid, as synthesized by Rahman et al. [63]. The appearance of new bands at wavenumbers 1355 and 1646 cm⁻¹ were attributed to nitro (-O-N=O) functional groups, as evidenced by the FTIR spectrum of o-nitrochitosan [63]. The ambient conductivity was greatly enhanced for the modified chitosan film (5.22×10^{-6} S cm⁻¹) at room temperature, while the unmodified chitosan film exhibited low conductivity of 8.88×10^{-10} S cm⁻¹ [63]. The large increment was attributed to the high electronegativity of nitro group [63]. Although no dopant salt was incorporated, the authors believed that o-nitrochitosan can be a promising polymer electrolyte membrane in PEMFC [63].

PEO is excellent to solvate Li⁺ ion, which is especially useful for application in Li-ion cells, even though its crystalline portion hampers the conductivity enhancement. Usually, the conductivity of PEO electrolyte containing lithium salts is no greater than 10⁻⁴ S cm⁻¹ under ambient condition with a low value of lithium-ion transference number ($t_{Li^+} < 0.40$) [64]. Luckily, its chemical structure can be modified and incorporated with various types of functional groups or moieties. Another strategy to improve the conduction of PEO-based electrolyte is to modify its linear chain into hyper-branched structure. Jing et al. [64] have prepared LiTFSI-containing SPE based on PEO having a hyper-branched arrangement and grafting with another PEO of linear chains to improve the ionic conductivity without sacrificing its mechanical strength. An increment by one

order of magnitude was observed when compared to SPE having PEO linear chain, which was attributed to reduction in crystallinity [64].

Besides polymer modification, the polymer can also undergo copolymerization, grafting, crosslinking and blending with a second polymer in order to lower the crystallization. Imperiyka and co-authors [65] have photo-copolymerized polyglycidyl methacrylate (P(GMA)) with PMMA as the polymer host. SPE with configuration P(GMA-co-MMA)-LiClO₄ displayed the ambient conductivity of $8.70 \times 10^{-6} \text{ S cm}^{-1}$ [65]. The bonding of one polymer chain with that of another polymer is known as a crosslinking reaction. This process can take place physically and chemically (photo-induced polymerization, curing, etc.). In 2016, Lehmann et al. [66] prepared SPE containing PEO (M_w 2000 g mol⁻¹) crosslinked with poly(ethyleneimine) (PEI) (M_w 600 g mol⁻¹) and LiTFSI salt and obtained the conductivity of $3.90 \times 10^{-5} \text{ S cm}^{-1}$ at 40 °C. The values of T_g , percentage of crystallinity, tensile strength and cationic transference number were -33 °C, 20%, 0.47 MPa and 0.76 (40 °C), respectively. Meanwhile, SPE, which comprises 600 M_w PEI, with the same salt, attained the conductivity of $1.50 \times 10^{-6} \text{ S cm}^{-1}$ at 40 °C and T_g of -65 °C [66]. In 2016, Youcef et al. [67] systematically studied the concentration effect of crosslinking agent (divinylbenzene (DVB)) on SPE based on PEO crosslinked poly(ethylene glycol) diacrylate (PEGDA) with LiTFSI salt that had been prepared via polymerization under ultraviolet (UV) irradiation, using a photo-initiator, -hydroxy-2-methylpropiophenone and acetonitrile solvent. At optimum concentration of 10%mol DVB, conductivity of $1.40 \times 10^{-4} \text{ S cm}^{-1}$, lithium-ion transference number (t_{Li^+}) of 0.21 and high electrochemical window of 4.30 V were obtained at 70 °C [67]. At the same temperature and C/10 rate, LiFePO₄/Li battery employing this electrolyte delivered the first discharge capacity of 138 mAh g⁻¹ which was sustainable even after the 20th cycle (138 mAh g⁻¹) [67]. The SPE has also been tested in Li-sulfur battery under similar conditions and acquired the capacity of 175 mAh g⁻¹ after the 50th cycle, with an initial capacity of 375 mAh g⁻¹ [67]. After cycling, there was no lithium dendrite formation, as evidenced through SEM micrograph. In addition to inhibit crystallinity percentage, the crosslinked electrolyte is said to have the ability to hamper lithium dendrite growth when being used in Li-ion cells and to improve dimensional stability at elevated temperatures [66–69].

In a separate report, PEO underwent crosslinking reaction with tetraethylene glycol dimethyl ether (TEGDME) employing 4-methyl benzophenone (MBP) as crosslinker agent, LiTFSI salt under UV radiation without solvent usage [68]. It is said that MBP can remove H⁺ from its methylene group via hydrogen abstraction to form free-radical chains [68]. Likewise, TEGDME that contained the methylene group produced free radicals. These free-radical chains have interlinked with -EO- unit of PEO chain under UV exposure to form SPE film that displayed features, such as being highly amorphous and having a uniform morphology, high mechanical strength, good flexibility, low T_g of -34 °C and compatibility with Li metal electrode. At 25 °C, the SPE showed a conductivity of $0.11 \times 10^{-3} \text{ S cm}^{-1}$, t_{Li^+} of 0.55 and diffusion coefficient of Li⁺ ion of $5.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [68]. The TiO₂/Li cell having such an electrolyte had good cyclability over 100 cycles, with a capacity of ~138 mAh g⁻¹ and almost 90% capacity retention [68]. Lim et al. [70] employed an in situ polymerization procedure to prepare SPE based on crosslinking poly(ethylene glycol) diglycidyl ether (PEGDE) and bisphenol A diglycidyl ether (BADGE) with 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIMTFSI), using PEI as crosslinker without solvent. The SPE was prepared directly on activated carbon electrode for supercapacitor application before the curing process. Such an SPE film showed a conductivity of $2.41 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C and capacitance value of 19.8 F g⁻¹ at 2 mV s⁻¹ scan rate with decent cyclability upon 10,000 cycles [70].

Chitosan in 1% acetic acid solution was subjected to a crosslinking process with methanesulfonic acid (MSA) and dodecylbenzene sulfonic acid sodium salt (DBSA-Na), using sulfuric acid as an agent to form chitosan-MSA and chitosan-DBSA membranes, respectively [71]. Such an action improved the proton conductivity and the thermal and mechanical stabilities of the chitosan-based membranes, which can be applied as solid

electrolyte membranes in PEMFCs. At the elevated temperature of 90 °C, the proton conductivity was $3.09 \times 10^{-4} \text{ S cm}^{-1}$ for chitosan-DBSA film, whereas $2.18 \times 10^{-4} \text{ S cm}^{-1}$ was the conductivity exhibited by the chitosan-MSA membrane [71]. The non-crosslinked chitosan membrane was also prepared for comparison and showed lowest conductivity of $1.04 \times 10^{-4} \text{ S cm}^{-1}$ at same temperature [71]. The grafted copolymers consisting of natural rubber and methyl methacrylate, namely 49% PMMA-grafted NR (MG49) [48,72,73] and 30% PMMA-grafted NR (MG30) [74], have been used as polymer hosts to produce polymer electrolytes. Su'ait et al. [72] reported a conductivity of $1.00 \times 10^{-12} \text{ S cm}^{-1}$ for pure MG49 at 30 °C, and this value increased to $2.30 \times 10^{-7} \text{ S cm}^{-1}$ when MG49 was incorporated with 20 wt.% LiBF_4 salt. Such an electrolyte of MG49- LiBF_4 was then added to another salt (LiI and LiCF_3SO_3) by the same group of researchers for the mixed-salt effect [48]. It was found that the ambient conductivity increased with different salts and combination of salts as follows: LiCF_3SO_3 ($2.15 \times 10^{-11} \text{ S cm}^{-1}$) < LiI ($4.73 \times 10^{-9} \text{ S cm}^{-1}$) < $\text{LiCF}_3\text{SO}_3 + \text{LiBF}_4$ ($7.71 \times 10^{-9} \text{ S cm}^{-1}$) < LiBF_4 ($1.42 \times 10^{-8} \text{ S cm}^{-1}$) < $\text{LiBF}_4 + \text{LiI}$ ($1.89 \times 10^{-6} \text{ S cm}^{-1}$) [48]. This clearly demonstrates that the ionic conductivity was enhanced significantly for the MG49-based SPE having double salts of LiBF_4 and LiI at a ratio of 30:70, while the addition of LiCF_3SO_3 into the MG49- LiBF_4 electrolyte had an adverse effect on the conductivity. The transference number of ions for the five samples was observed to increase in the same order of conductivity [48]. It can be understood that the degree of crystallinity increased in the reverse order [48]. Modified natural rubber has superior elastic features for better interfacial contact between electrolyte and electrode when applied in electrochemical devices. Another strategy to improve the properties of electrolyte is to bind the anion directly to the polymer chain to form a single-ion-conducting polymer electrolyte. Such an electrolyte consisting of poly[lithium 1-[3-(methacryloyloxy) propylsulfonyl]-1-(trifluoromethylsulfonyl) imide] (PLiMTFSI) attached to PEG-crosslinked poly(2-hydroxyethylacrylate) (PHEA) showed improved mechanical strength as compared to an electrolyte of crosslinked PEG-PHEA doped with LiTFSI, even though its conductivity is lower than the latter [75]. Nonetheless, the single-ion-conducting polymer electrolyte could minimize lithium dendrite formation and gave better results in Li-ion cells.

3.2.3. Treatment of SPEs

The polymer electrolytes can also be subjected to radiation in order to tune their properties in terms of structural, thermal, electrical and mechanical aspects. Various radiation sources, including gamma rays, X-rays, ultraviolet rays, electron, neutron and ion beams, can be employed. Solution-cast-prepared SPE based on PEO with lithium sulfate (Li_2SO_4) salt has been irradiated with low-energy electron beams of 8 MeV by Raghu et al. [76]. At 30 °C, the conductivity was enhanced to the order of $10^{-4} \text{ S cm}^{-1}$ for PEO- Li_2SO_4 electrolyte after exposure to 30 kGy dose of electron beam from $10^{-5} \text{ S cm}^{-1}$ for non-irradiated electrolyte. Analyses from DSC and X-ray diffraction (XRD) demonstrated that the former have a lower melting temperature (67.6 °C) and are more amorphous in nature, with reduced crystallinity, than the latter (69.4 °C melting temperature and more crystalline), while FTIR results indicated that the polymer chain was disrupted and degraded after irradiation [76]. Irradiating of Li^{3+} ion at high energy of 60 MeV on two different electrolytes of PEO-NaI and PVP-NaI showed increment in conductivity as compared to unirradiated electrolyte films [77]. Besides conductivity, higher values for number of mobile ions, ionic mobility and dielectric constant have been reported for the solution-cast-prepared SPE after ion-beam irradiation [77]. PAN-based SPE having LiBOB salt also exhibited enhancement in conductivity and transport properties (n , μ and D) after being radiated with a gamma-ray dose of 15 kGy [78]. Ambient conductivity was increased by 58.6 times from $1.74 \times 10^{-6} \text{ S cm}^{-1}$ to $1.02 \times 10^{-4} \text{ S cm}^{-1}$, while improvement of 12.2, 4.8 and ~4.7 times was obtained in n , μ and D , respectively [78]. Likewise, PVDF-LiBOB SPE has attained higher values of conductivity and ionic transport upon gamma-ray radiation as compared to non-irradiated electrolyte [79]. Hema et al. [80] also reported similar observation in PVA-PVDF- LiCF_3SO_3 - SiO_2 SPEs, where conductivity was boosted

to $9.40 \times 10^{-4} \text{ S cm}^{-1}$ at 30°C after gamma-ray exposure (15 Gy dose). The conductivity of such an electrolyte without radiation treatment was $1.70 \times 10^{-4} \text{ S cm}^{-1}$. Ionic transference number for the irradiated SPE also showed increment ($t_{ion} = 0.99$) as compared to that of non-gamma ray treated SPE ($t_{ion} = 0.98$) [80]. On the other hand, lower values for the percentage of crystallinity, T_g and melting point were detected in the former than in the latter [80]. In general, it is to be noted that conductivity enhancement has been observed at optimized dosage of radiation irrespective of the sources due to polymer chain scission, whereas too much radiation dose will be detrimental to the properties of SPE, and this is attributed to crosslinking and increase in crystallinity.

In another work of Raghu et al. [81], a comparison was made between gamma-ray (cobalt-60 source) and electron-beam (energy of 8 MeV) treatments on PEO-based SPEs of cadmium chloride (CdCl_2) salt. Non-irradiated electrolyte exhibited the lowest conductivity value at $8.63 \times 10^{-6} \text{ S cm}^{-1}$ at 30°C , as compared to gamma-ray-treated (0.115 S cm^{-1}) and electron-beam-irradiated (0.175 S cm^{-1}) electrolytes. Micrographs from scanning electron microscopy (SEM) showed less PEO spherulites in both irradiated SPEs as compared to that of non-irradiated SPE, indicating that a more amorphous region existed in the former case. In addition, the SEM image for electrolyte after electron-beam exposure displayed a homogenous morphology, while the formation of aggregates was seen in the micrograph of SPE irradiated with gamma radiation [81]. The SPEs were irradiated with electron beam and gamma ray separately at two different doses (50 and 150 kGy), and it was found that, at the 150 kGy dosage, both types of radiation gave a higher conductivity (of the order of $10^{-4} \text{ S cm}^{-1}$) than that irradiated at the 50 kGy dose (around $10^{-5} \text{ S cm}^{-1}$) [81]. The authors have concluded that the electron-beam treatment is an effective approach as compared to gamma-ray radiation in making the SPE more conducting due to reduction in crystallinity. Recent work illustrated contradictory results, wherein no effect was observed on the conductivity upon neutron irradiation at varied dosages (15 to 47 kGy) on PVDF–LiBOB SPEs prepared via solution-casting route [82]. Ambient conductivity was the highest at $1.27 \times 10^{-5} \text{ S cm}^{-1}$ for the non-irradiated SPE as compared to similar electrolyte after exposed to neutron radiation with lowest value at $4.30 \times 10^{-7} \text{ S cm}^{-1}$ for SPE subjected to 47 kGy dose [82]. This was attributed to decrement in μ and D , as well as higher degree of crystallinity. The authors have deduced that an improvement in mechanical integrity in the electrolyte has occurred after being irradiated with a neutron [82]. Sinha et al. [83] have observed that there was a slight decrement in conductivity at ambient temperature for the solution-cast-prepared SPE based on PEO with ammonium perchlorate (NH_4ClO_4) salt after being irradiated with gamma rays, followed by minor conductivity increment at 50°C . In the following sections, additional ingredients such as secondary polymer, plasticizers, fillers and other additives that have been integrated into various SPEs are discussed.

3.2.4. Blended Solid Polymer Electrolytes

Polymer blending can be regarded as the most convenient and simplest way to prepare SPEs that are highly conducting, flexible and thermally stable and that have good mechanical strength without additional employment of materials such as initiator, linker agent, radiation sources, etc., thus indirectly making this approach more cost-effective as compared to other techniques aforementioned. In this technique, two or more polymers which are miscible in the appropriate solvent form a homogenous solution before addition of the conducting salt. The blending of polymer approach is able to (i) reduce the glass transition temperature, (ii) decrease the degree of crystallinity, (iii) increase the ionic conductivity, (iv) improve the thermal stability, (v) enhance the mechanical strength and (vi) boost the performance of electrochemical devices. There are many studies on blended SPEs available in the literature. Table 5 lists some of the systems under this category.

Table 5. Various blended SPEs systems, along with their conductivity values and other important parameters.

| Electrolyte System | Preparation Method | Conductivity, σ (S cm ⁻¹) | Important Findings | Reference |
|---|---------------------------|--|---|-----------|
| PVA:PVP (70:30)-25 wt.% LiNO ₃ | Solution casting | 6.83×10^{-4} | $E_A = 0.27$ eV; $T_g = 80$ °C 70 PVA:30 PVP film: $\sigma = 1.58 \times 10^{-6}$ S cm ⁻¹ ; $T_g = 130$ °C Degree of swelling lower than blend SPE | [84] |
| Chitosan:PVA (1:1)-NH ₄ I | Solution casting | 1.77×10^{-6} (30 °C) | $E_A = 0.38$ eV Without PVA blend: $\sigma = 3.73 \times 10^{-7}$ S cm ⁻¹ (30 °C) $E_A = 0.46$ eV | [85] |
| Chitosan:PEO (1:1)-NH ₄ I | Solution casting | 3.66×10^{-6} (30 °C) | $E_A = 0.31$ eV; $t_{ion} = 0.85$ N3/Ag-TiO ₂ /SPE/Pt DSSC (light intensity of 100 mW cm ⁻²): OCV = 0.58 V; $J_{sc} = 2.84$ mA cm ⁻² ; $FF = 0.69$; $\eta = 1.13\%$ Without PEO blend: $\sigma = 3.73 \times 10^{-7}$ S cm ⁻¹ (30 °C); $E_A = 0.46$ eV | [86] |
| PEMA:PVDF-HFP (70:30)-LiCF ₃ SO ₃ | Reflux + Solution casting | 2.87×10^{-7} (RT) | PEMA-LiCF ₃ SO ₃ : $\sigma = 9.18 \times 10^{-8}$ S cm ⁻¹ (RT) | [87] |
| 50% (PEO+LiTFSI):50% PPC [EO]/[Li] = 18:1 | Solution casting | 2.04×10^{-5} (25 °C) 2.82×10^{-4} (60 °C) | $E_A = 0.78$ eV; $T_g = -41.3$ °C; $T_m = 49.7$ °C; %X _C = 22.10%; $t_{Li+} = 0.184$ (60 °C); Electrochemical stability window 4.90 V LiFePO ₄ /SPE/Li cell (0.5C, 60 °C): Discharge specific capacity of 112 mAh g ⁻¹ after 100th cycle Without PPC blend: $\sigma = 1.02 \times 10^{-5}$ S cm ⁻¹ (25 °C); $\sigma = 1.77 \times 10^{-4}$ S cm ⁻¹ (60 °C); $E_A = 0.80$ eV; $T_g = -35.2$ °C; $T_m = 58.1$ °C; %X _C = 48.07%; $t_{Li+} = 0.156$ (60 °C); Electrochemical stability window 4.25 V Discharge specific capacity = 93 mAh g ⁻¹ after 100th cycle (0.5 C, 60 °C) Decreased crystallinity with PPC addition Improved interface stability | [88] |
| PEO:PVP (9:1)-8 wt.% LiClO ₄ | Solution casting | 0.23×10^{-5} (30 °C) | Bandgap energy = 4.07 eV (indirect) and 4.35 eV (direct) Thermally stable till 324 °C Lowest intensity in photoluminescence results compared to that at other PEO:PVP ratios | [89,90] |

Table 5. Cont.

| Electrolyte System | Preparation Method | Conductivity, σ (S cm ⁻¹) | Important Findings | Reference |
|---|--------------------|--|--|-----------|
| CMC:PVA:NH ₄ NO ₃ (56:14:30 wt.%) | Solution casting | 1.70×10^{-3} | $T_g = 88.7 \text{ }^\circ\text{C}$; $t_{H^+} = 0.42$ Decomposition temperature = 340 °C | [91] |
| MG49:PMMA (70:30)-25 wt.% LiBF ₄ [O]/[Li] = 5:1 | Solution casting | 8.60×10^{-6} (30 °C) | MG49-PMMA film: $\sigma = 1.10 \times 10^{-12}$ S cm ⁻¹ (30 °C) | [73] |
| MG49:PMMA (70:30)-25 wt.% LiClO ₄ [O]/[Li] = 6:1 | Solution casting | 1.50×10^{-8} (30 °C) | MG49-PMMA film: $\sigma = 1.10 \times 10^{-12}$ S cm ⁻¹ (30 °C) | [73] |
| CMKC:CMC (60:40)-LiI | Solution casting | 3.89×10^{-3} (27 °C) | $T_g = -43.0 \text{ }^\circ\text{C}$ N719/TiO ₂ /SPE/Pt DSSC (light intensity of 100 mW cm ⁻²): OCV = 0.492 V; $J_{sc} = 0.40$ mA cm ⁻² ; $FF = 0.57$; $\eta = 0.11\%$ | [92] |
| HCh:PVC (90:10)-NaI | Solution casting | 1.50×10^{-5} (RT) | $\% \chi_C = 24\%$; $D = 1.10 \times 10^{-8}$ cm ² s ⁻¹ ; $\mu = 4.10 \times 10^{-7}$ cm ² V ⁻¹ s ⁻¹ ; $n = 2.30 \times 10^{20}$ cm ⁻³ N3/TiO ₂ /SPE/Pt DSSC (light intensity of 100 mW cm ⁻²): OCV = 0.58 V; $J_{sc} = 8.62$ mA cm ⁻² ; $FF = 0.59$; $\eta = 2.93\%$ | [93] |
| PEO:WPU (3:1)-LiTFSI [EO]/[Li] = 16:1 | Solution casting | 3.10×10^{-3} (80 °C) | $T_g = -45.4 \text{ }^\circ\text{C}$; thermally stable till 300 °C LiFePO ₄ /SPE/Li battery: Discharge capacity = 122 mAh g ⁻¹ after 100th cycle (1C, 80 °C), 96% capacity retention | [94] |
| PEO:TPU (3:1)-LiTFSI [EO]/[Li] = 16:1 | Solution casting | 5.30×10^{-4} (60 °C) | $t_{Li^+} = 0.31$; Tensile stress 1.38 MPa LiFePO ₄ /SPE/Li battery: Discharge capacity = 112 mAh g ⁻¹ after 100th cycle (1 C, 60 °C), 96% capacity retention | [95] |
| PEO-PVP-NaIO ₄ (65:25:10 wt.%) | Solution casting | 1.56×10^{-7} (30 °C) | $E_A = 0.22$ eV; $T_g = 50.2 \text{ }^\circ\text{C}$; $\% \chi_C = 55.0\%$ $D = 2.72 \times 10^{-8}$ cm ² s ⁻¹ ; $\mu = 1.0 \times 10^{-4}$ cm ² V ⁻¹ s ⁻¹ ; $n = 9.35 \times 10^{15}$ cm ⁻³ Direct optical bandgap = 3.60 eV Refractive index = 2.28 | [96] |
| PEO:PVP (4:1)-Mg(NO ₃) ₂ | Solution casting | 5.80×10^{-4} (25 °C) | $E_A = 0.31$ eV; $t_+ = 0.33$ Thermally stable till 220 °C MgMn ₂ O ₄ /SPE/Mg battery: OCV = 1.46 V | [97] |

Table 5. Cont.

| Electrolyte System | Preparation Method | Conductivity, σ (S cm ⁻¹) | Important Findings | Reference |
|---|--------------------|--|---|-----------|
| PVDF-HFP:PEO (4:1)-KI-TBAI-I ₂ | Solution casting | 4.53×10^{-5} (25 °C) | $T_m = 144.9$ °C; % $\chi_C = 18.1\%$ N3/TiO ₂ /SPE/Pt DSSC (light intensity of 60 mW cm ⁻²): $OCV = 0.674$ V; $J_{sc} = 4.39$ mA cm ⁻² ; $FF = 0.50$; $\eta = 2.46\%$ Without PEO blend: $\sigma = 9.99 \times 10^{-6}$ S cm ⁻¹ (25 °C) $T_m = 146.5$ °C; % $\chi_C = 23.5\%$ $OCV = 0.648$ V; $J_{sc} = 3.78$ mA cm ⁻² ; $FF = 0.46$; $\eta = 1.88\%$ | [98] |
| PVAc:PMMA (70:30)-LiCl | Solution casting | 1.03×10^{-5} (30 °C) | $E_A = 0.25$ eV; $T_g = 42.6$ °C; $t_+ = 0.97$ $D_+ = 6.93 \times 10^{-11}$ cm ² s ⁻¹ ; $\mu = 2.65 \times 10^{-9}$ cm ² V ⁻¹ s ⁻¹ ; $n = 2.35 \times 10^{22}$ cm ⁻³ | [99] |

PVP—poly(vinyl pyrrolidone); LiNO₃—lithium nitrate; PPC—propylene carbonate; CMKC—carboxymethyl κ -carrageenan; N719—di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II); PVC—poly(vinyl chloride); WPU—waterborne polyurethane; TPU—thermoplastic polyurethane; NaIO₄—sodium periodate; Mg(NO₃)₂—magnesium nitrate; TBAI—tetrabutylammonium iodide; PVAc—poly(vinyl acetate); LiCl—lithium chloride.

Sengwa et al. [100] have investigated the effect of SPE preparation method on conductivity. The SPE comprising PEO blended with PMMA at a ratio of 1:1 and LiCF₃SO₃ salt has been prepared in four ways: (i) conventional solution cast coupled with hot melt-pressing; (ii) ultrasonication followed by solution casting and hot melt press; (iii) irradiation of microwave before solution-cast and hot-melt-press techniques; and (iv) ultrasonication followed by microwave exposure, solution casting and hot melt press. The authors have observed that conductivity decrement of the similar SPE in the following order: $\sigma_{(\text{route iii})}$ (1.99×10^{-6} S cm⁻¹) > $\sigma_{(\text{route iv})}$ (1.56×10^{-6} S cm⁻¹) > $\sigma_{(\text{route i})}$ (1.36×10^{-6} S cm⁻¹) > $\sigma_{(\text{route ii})}$ (0.11×10^{-6} S cm⁻¹) [100]. They have speculated that the electrolyte made from microwave-assisted solution-cast/hot-melt-press procedure has produced more of a pathway for ionic conduction as compared to other methods [100]. Another unrelated work has compared the usefulness of the blending approach with grafting technique on LiClO₄-containing SPE system with sulfonated polyether ether ketone (SPEEK) and polyethylene glycol (PEG) as polymer hosts [101]. The SPEEK grafted with PEG electrolyte gave higher conductivity (around 10^{-5} S cm⁻¹) when compared to SPEEK-PEG blended electrolyte (10^{-6} S cm⁻¹) at 30 °C, thus implying the grafting method can suppress PEG crystallinity more than the blending technique [101].

Liu and co-workers [102] have combined both chemical (crosslinking) and physical (blending) routes together, i.e., crosslinked (3-glycidyoxypropyl)trimethoxysilane (GLYMO) with polyetheramine and also crosslinked poly(ethylene glycol) diglycidyl ether (PEGDGE) with polyetherdiamine before blending their products at 70:30 ratio in THF solvent and added with LiClO₄ salt. The [EO]/[Li] ratio was optimized at 16:1. Such a unique SPE exhibited the conductivities of 1.20×10^{-4} S cm⁻¹ and 8.30×10^{-4} S cm⁻¹ at 30 and 80 °C, respectively [102]. The T_g value was -43.6 °C, and the transference number of Li⁺ ions was 0.28 at 70 °C. This electrolyte was thermally stable up to 260 °C and gave the capacities of 110 mAh g⁻¹ (The first cycle) and 61 mAh g⁻¹ (100th cycle) when applied in LiFePO₄/Li battery at 0.2 C rate [102]. As a summary, blended SPEs show superior properties than SPEs containing single polymer matrix.

3.2.5. Plasticized Solid Polymer Electrolytes

The main idea of plasticized polymer electrolyte is to improve the elasticity by lowering the T_g . As stated in the previous section and Equation (3), the segmental movement of the polymer backbone contributes to the conductivity of SPEs. Increasing the segmental

motion will improve the ionic conductivity and can be easily achieved by adding plasticizers into the polymer matrix. There are many types of plasticizers such as EC, PC, PEG, DMSO, diethyl carbonate (DEC), dimethyl carbonate (DMC), glycerol, gBL and DMF to name a few that affect the ionic conductivity of SPEs in different ways. Note that EC, PC, DMSO, gBL and DMF can also serve as a solvent, as listed in Table 3, while PEG of low molecular weight (M_w) is usually used as a plasticizing agent. Plasticizers with high a dielectric constant, e.g., EC, as mentioned in the previous section, helps in salt dissociation, lowering the formation of ion pairs and ion aggregates leading to conductivity enhancement. Besides high dielectric constant, a good plasticizer should possess low viscosity to increase the mobility of ions. Furthermore, the incorporation of plasticizer in an electrolyte offers additional passage for ion transport. Some plasticized polymer electrolytes in the solid form that have been studied are tabulated in Table 6.

Table 6. Examples of plasticized SPEs systems found in the literature.

| Electrolyte System | Preparation Method | Conductivity, σ ($S\ cm^{-1}$) | Important Findings | Reference |
|--|--------------------|---|--|-----------|
| PEO-LiPF ₆ -EC | Solution casting | 2.06×10^{-4} (25 °C) | Bandgap energy = 5.63 eV (indirect) and 5.80 eV (direct) Unplasticized SPE: $\sigma = 4.10 \times 10^{-5}\ S\ cm^{-1}$ (25 °C) Bandgap energy = 5.74 eV (indirect) and 5.90 eV (direct) | [103] |
| PGMA-LiClO ₄ -EC | Solution casting | 2.00×10^{-4} (RT) | PGMA was synthesized via photo-polymerization route. $E_A = 0.21\ eV$ Electrochemical stability window 3.00 V Unplasticized SPE: $\sigma = 4.20 \times 10^{-5}\ S\ cm^{-1}$ (RT); $E_A = 0.26\ eV$ Electrochemical stability window 2.50 V | [104] |
| PEO-LiClO ₄ -SN | Solution casting | $\sim 9.12 \times 10^{-5}$ (20 °C) | $E_A = 0.45\ eV$ Unplasticized SPE: $\sigma = 3.79 \times 10^{-7}\ S\ cm^{-1}$ (20 °C) $E_A = 0.89\ eV$ | [105] |
| HEC-LiCF ₃ SO ₃ -glycerol [EO]/[Li] = 6:1 | Solution casting | 1.06×10^{-5} (30 °C) | $E_A = 0.18\ eV$; $T_g = -83\ ^\circ C$ | [106] |
| Chitosan-LiClO ₄ -glycerol | Solution casting | $\sim 3.00 \times 10^{-5}$ (25 °C) | Too much glycerol, SPE easily torn off. Without glycerol: $\sigma = 1.40 \times 10^{-5}\ S\ cm^{-1}$ (25 °C) | [107] |
| Chitosan-LiClO ₄ -glycerol | Solution casting | 1.20×10^{-3} (25 °C) | $t_{ion} = 0.955$ $D = 4.19 \times 10^{-9}\ cm^2\ s^{-1}$; $\mu = 1.63 \times 10^{-7}\ cm^2\ V^{-1}\ s^{-1}$; $n = 4.57 \times 10^{22}\ cm^{-3}$ Specific capacitance = 98.99 F g ⁻¹ at scan rate 10 mV s ⁻¹ | [108] |
| PVB-LiClO ₄ -PEG ₄₀₀ | Solution casting | 2.15×10^{-6} (RT) | Unplasticized SPE: $\sigma = 5.80 \times 10^{-10}\ S\ cm^{-1}$ | [109] |

Table 6. Cont.

| Electrolyte System | Preparation Method | Conductivity, σ (S cm ⁻¹) | Important Findings | Reference |
|--|--|--|--|-----------|
| PEMA-NH ₄ I-EC | Solution casting | 1.16×10^{-5} (RT) | $t_{ion} = 0.85$ $n = 1.75 \times 10^{21}$ m ⁻³ | [110] |
| PEMA-NH ₄ CF ₃ SO ₃ -BMATSFI | Solution casting | 8.35×10^{-4} (30 °C) | $T_g = 2$ °C; $t_{ion} = 0.82$ Unplasticized SPE: $\sigma = 1.02 \times 10^{-5}$ S cm ⁻¹ ; $T_g = 68$ °C | [111] |
| PVDF-HFP-LiClO ₄ -SN | Solution casting | $\sim 1.62 \times 10^{-3}$ (20 °C) | $E_A = 0.40$ eV Unplasticized SPE: $\sigma = \sim 6.38 \times 10^{-9}$ S cm ⁻¹ (20 °C) $E_A = 0.69$ eV | [105] |
| PVDF-HFP-LiBETI-SN | Solution casting | $\sim 2.58 \times 10^{-3}$ (20 °C) | LiCoO ₂ /SPE/Li ₄ Ti ₅ O ₁₂ cell (C/10, 25 °C): Initial discharge capacity 116 mAh g ⁻¹ , 78% capacity retention after 120th cycle | [105] |
| PVDF-PEO-LiClO ₄ -SN | Solution infiltration in PVDF film + drying | 2.80×10^{-5} (25 °C) | $T_g = -75.6$ °C; $t_{Li^+} = 0.37$ (25 °C) LiFePO ₄ /SPE/Li: OCV = 3.1 V, discharge capacity 109 mAh g ⁻¹ (100th cycle), 90% capacity retention | [112] |
| PEO-LiCF ₃ SO ₃ -TiO ₂ -EC [EO]/[Li] = 9:1 | Solution casting | 1.60×10^{-4} (30 °C) | $E_A = 0.60$ eV; $T_g = -50$ °C; $T_m = 50$ °C | [43] |
| PEO-KI-PEG | Solution casting | 5.27×10^{-5} (25 °C) | Unblended PEO-KI SPE: $\sigma = 1.96 \times 10^{-5}$ S cm ⁻¹ (25 °C) Low M _w of PEG (~4000) might be trapped or crosslink in PEO-KI network | [113] |
| PEO-LiTFSI-S ₂ TFSI | Mixing, vacuum-sealed in pouch and hot press | 0.96×10^{-3} (22 °C) 4.00×10^{-3} (60 °C) | $t_{Li^+} = 0.31$ (60 °C) LiFePO ₄ /SPE/Li: Discharge capacity (1 C, 60 °C) = 160.1 mAh g ⁻¹ (500th cycle), 89.9% capacity retention | [114] |
| PEO-LiFSI-N ₁₂₂₂ FSI [EO]/[Li] = 20:1 | Solution casting | 1.78×10^{-5} (25 °C) 2.14×10^{-4} (50 °C) | $T_g = -58.1$ °C; % $\chi_C = 24.7\%$ High thermal stability with decomposition temperature above 220 °C LiFePO ₄ /SPE/Li: Discharge capacity (0.2 C, 50 °C) = 151.5 mAh g ⁻¹ (120th cycle), 95.4% capacity retention Unplasticized SPE: $\sigma = 7.24 \times 10^{-7}$ S cm ⁻¹ (25 °C) $T_g = -44.8$ °C; % $\chi_C = 33.6\%$ | [115] |
| PEO:MC (60:40)-NH ₄ I-PEG (M _w PEG 8000) | Solution casting | 3.37×10^{-3} (30 °C) | $E_A = 0.0322$ eV Unplasticized SPE: $\sigma = 7.62 \times 10^{-5}$ S cm ⁻¹ (30 °C) $E_A = 0.0465$ eV | [116,117] |

Table 6. Cont.

| Electrolyte System | Preparation Method | Conductivity, σ (S cm ⁻¹) | Important Findings | Reference |
|--|----------------------------|--|--|-----------|
| PMMA-LiClO ₄ -PC [MMA]/[Li] = 4:1 | Solution casting | 3.52×10^{-5} (30 °C) | $E_A = 0.11$ eV Conduction and relaxation via hopping mechanism | [118] |
| PVA-LiClO ₄ -DMP (30:10:60) | Solution casting | 0.15×10^{-3} (29 °C) | Conductivity-temperature relation obeys Vogel-Tamman-Fulcher (VTF) rule | [119] |
| PVA-LiCF ₃ SO ₃ -DMP (30:10:60) | Solution casting | $\sim 6.35 \times 10^{-5}$ (29 °C) | Conductivity-temperature relation obeys Vogel-Tamman-Fulcher (VTF) rule | [119] |
| PVA-LiBF ₄ -DMP (30:10:60) | Solution casting | $\sim 1.66 \times 10^{-5}$ (29 °C) | Conductivity-temperature relation obeys Vogel-Tamman-Fulcher (VTF) rule | [119] |
| PEO-LiCF ₃ SO ₃ -15 wt.% PEG (M _w PEG 6000) | Ball-milling and hot press | 1.71×10^{-5} | $T_g = -55.8$ °C; % $\chi_C = 31.6\%$ | [38] |
| PEO-LiCF ₃ SO ₃ -20 wt.% DOP | Ball-milling and hot press | 7.60×10^{-4} | $T_g = -63.9$ °C; % $\chi_C = 23.1\%$ | [38] |
| PEO-LiCF ₃ SO ₃ -20 wt.% EC | Solution casting | 8.12×10^{-5} (25 °C) | $T_g = -70.5$ °C; % $\chi_C = 31.3\%$ Without plasticizer: $\sigma = 2.89 \times 10^{-5}$ S cm ⁻¹ (25 °C) $T_g = -69.0$ °C; % $\chi_C = 31.7\%$ | [120] |
| Corn starch-LiPF ₆ -BmImTf | Solution casting | 6.00×10^{-4} (80 °C) | $E_A = 0.01$ eV; $T_g = -29$ °C Without plasticizer: $\sigma = \sim 10^{-6}$ S cm ⁻¹ (80 °C) $E_A = 0.13$ eV; $T_g = -19$ °C | [121] |
| CMC-LiBF ₄ -glycerol | Solution casting | 3.70×10^{-3} (25 °C) | $T_g = 54$ °C T_g of CMC film = 87 °C Without glycerol: $\sigma = 8.20 \times 10^{-6}$ S cm ⁻¹ (25 °C) | [122] |
| PVA-CH ₃ COONH ₄ -BmImI | Solution casting | 9.63×10^{-5} (25 °C) | $E_A = 6.68$ meV; % $\chi_C = 2\%$ $D^+ = 9.80 \times 10^{-12}$ cm ² s ⁻¹ EDLC at scan rate 10 mV s ⁻¹ , 200th cycle: Specific capacitance = 44.46 F g ⁻¹ Power density = 47.66 kW kg ⁻¹ Without BmImI: $\sigma = 1.94 \times 10^{-5}$ S cm ⁻¹ (25 °C) | [123] |
| Chitosan-NH ₄ I-BmImI | Solution casting | 3.43×10^{-5} (27 °C) | $E_A = 0.25$ eV N3/TiO ₂ /SPE/Pt DSSC (light intensity of 100 mW cm ⁻²): OCV = 0.58 V; $J_{sc} = 3.10$ mA cm ⁻² ; $FF = 0.41$; $\eta = 0.74\%$ Without BmImI: $\sigma = 3.73 \times 10^{-7}$ S cm ⁻¹ (27 °C) | [124] |
| PEO-LiTFSI-30 wt.% TCNE [EO]/[Li] = 12:1 | Solution casting | 1.11×10^{-4} (25 °C) | $T_g = -46.21$ °C Without TCNE: $\sigma = 1.21 \times 10^{-5}$ S cm ⁻¹ (25 °C) $T_g = -43.03$ °C | [125] |

Table 6. Cont.

| Electrolyte System | Preparation Method | Conductivity, σ (S cm ⁻¹) | Important Findings | Reference |
|--|--------------------|--|---|-----------|
| Chitosan-NaI-I ₂ -EMImSCN | Solution casting | 2.60×10^{-4} (RT) | N719/TiO ₂ /SPE/Pt DSSC (light intensity of 100 mW cm ⁻²): OCV = 0.53 V; J_{sc} = 2.62 mA cm ⁻² ; FF = 0.52; η = 0.73% Without EMImSCN: σ = 1.21×10^{-5} S cm ⁻¹ (25 °C) OCV = 0.35 V; J_{sc} = 1.05 mA cm ⁻² ; FF = 0.34; η = 0.13% | [126] |
| PVDF-KI-I ₂ -30 wt.% MCP | Solution casting | 4.58×10^{-5} (30 °C) | T_m = 152.8 °C; % χ_C = 51.49% N3/TiO ₂ /SPE/Pt DSSC: η = 2.65% at 60 mW cm ⁻² Without MCP: σ = 4.79×10^{-6} S cm ⁻¹ (30 °C) T_m = 170.5 °C; % χ_C = 63.80% η = 1.18% at 60 mW cm ⁻² | [127] |
| PVDF-HFP-KI-TBAI-I ₂ -4 wt.% ATDT | Solution casting | 2.82×10^{-4} (30 °C) | Porous surface morphology N3/TiO ₂ /SPE/Pt DSSC: η = 4.64% at 60 mW cm ⁻² Without ATDT: σ = 9.99×10^{-6} S cm ⁻¹ (30 °C) η = 1.88% at 60 mW cm ⁻² | [128] |
| PVDF-HFP-NaI-EMImSCN | Solution casting | 2.65×10^{-3} (30 °C) | Electrochemical stability window 3.6 V EDLC at scan rate 0.05 mV s ⁻¹ : Specific capacitance = 2.36 F g ⁻¹ | [129] |
| P(GMA-co-MMA)-LiClO ₄ -EC | Solution casting | 3.00×10^{-4} (RT) | Electrochemical stability window 3.8 V Without EC: σ = 8.70×10^{-6} S cm ⁻¹ (RT) | [65] |
| PVAc:PMMA (70:30)-LiCl-EC | Solution casting | 1.03×10^{-4} (30 °C) | T_g = 26.6 °C; t_+ = 0.98 D_+ = 7.00×10^{-11} cm ² s ⁻¹ ; μ = 2.68×10^{-9} cm ² V ⁻¹ s ⁻¹ ; n = 2.35×10^{22} cm ⁻³ Without plasticizer: σ = 1.03×10^{-5} S cm ⁻¹ (30 °C) T_g = 42.6 °C; t_+ = 0.97 D_+ = 6.93×10^{-11} cm ² s ⁻¹ ; μ = 2.65×10^{-9} cm ² V ⁻¹ s ⁻¹ ; n = 2.35×10^{22} cm ⁻³ | [99] |

PGMA—poly glycidyl methacrylate; SN—succinonitrile; HEC—hydroxyethylcellulose; PVB—polyvinyl butyral; NH₄CF₃SO₃—ammonium trifluoromethane sulfonate; BMATFSI—butyl trimethylammonium bis(trifluoromethanesulfonyl)imide; LiBETI—lithium bisperfluoroethylsulfonylimide (Li(C₂F₅SO₂)₂N); LiCoO₂—lithium cobalt oxide; S₂TFSI—triethylsulfonium bis(trifluoromethylsulfonyl)imide; LiFSI—lithium bis(fluorosulfonyl)imide; N₁₂₂₂FSI—triethylmethylammonium bis(fluorosulfonyl)imide; DMP—dimethyl phthalate; DOP—dioxy phthalate; BmImTf—1-butyl-3-methylimidazolium trifluoromethanesulfonate; CH₃COONH₄—ammonium acetate; BmImI—1-butyl-3-methylimidazolium iodide; TCNE—tetracyanoethylene; EMImSCN—1-ethyl 3-methylimidazolium thiocyanate; MCP—2-mercaptopyridine; ATDT—5-amino-1,3,4-thiadiazole-2-thiol.

It is interesting to highlight that ionic liquids can play three roles, viz as plasticizer (to enhance the flexibility of polymer backbone), conducting salt (provides cation and anion) and solvent. They are non-volatile, safe (due to non-flammability), chemically and thermally stable, and are not prone to evaporation and crystallization [130]. In addition, they exhibit low melting temperature and outstanding ionic conductivity at room temperature condition, and they also have superior solvating ability. In the work of Widstrom et al. [114], increment in conductivity has been observed after incorporating ionic liquid, S₂TFSI into

PEO-LiTFSI SPE without affecting Li^+ transference number. From Table 6, it is to be noted that $\text{N}_{1222}\text{FSI}$ is not an ionic liquid but an ionic plastic crystal that shows similar features to that of ionic liquids [115]. In contrast to conventional plasticizers, the mechanical integrity can still be retained upon addition of $\text{N}_{1222}\text{FSI}$ into the electrolyte besides reducing the polymer crystallinity and dissociating the salt. Moreover, the interfacial contact between electrolyte and electrode can be improved [115].

Another organic plastic crystal, i.e., succinonitrile (SN) is favored for its outstanding solvating capability in dissociating many salts including Li-based salts in battery application. As a result, conductivity is enhanced as can be observed in refs [105,112] from Table 6. Unfortunately, the plastic nature of SN deteriorates the mechanical strength of the electrolyte. Nonetheless, this can be easily avoided by preparing the electrolyte membrane in a different way. He et al. [131] prepared free-standing film containing PEGDA (M_w 6000 g mol^{-1}), LiTFSI and SN via photopolymerization procedure using bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (also known as Irgacure 819) as photo-initiator but without solvent. Such electrolyte which was highly amorphous with crosslinking network exhibited good ambient conductivity of $1.10 \times 10^{-3} \text{ S cm}^{-1}$, electrochemical stability window of 4.80 V with improved mechanical strength (0.24 MPa tensile strength, 84% elongation at break). $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}$ cell employing this electrolyte gave promising performance (The first discharge capacity of 140 mAh g^{-1} at 0.2 C) with 93% capacity retention for 25 cycles [131]. On the other hand, it is evident from Table 6 that PEG of low molecular weight acted as plasticizer rather than secondary polymer in PEO-KI electrolyte which showed better conductivity [113] than PEG-free SPE even though PEG might have crosslinked with PEO. Instead, conductivity improvement is attributed to extra passageways for ion migration through PEG segmental movement.

3.2.6. Composite Solid Polymer Electrolytes

Although addition of plasticizers in SPEs can easily improve the ionic conductivity, the mechanical strength of the SPEs is compromised. On the contrary, incorporating fillers in SPEs is known to improve the performance of SPEs not merely the ionic conductivity but also its mechanical strength since fillers can reduce the crystallinity of SPE films. SPE incorporated with an inorganic filler are termed as composite solid polymer electrolytes (CSPEs). In most CSPEs systems, the polymer is usually regarded as Lewis base if it donates its lone pair of electrons, while the filler is a Lewis acid in accepting the electrons. Fillers can be categorized into two types, i.e., active and inactive. Some examples of inactive fillers are titanium dioxide (TiO_2), silicon dioxide (SiO_2), alumina (Al_2O_3) and zirconia (ZrO_2). The effects of fillers are varied depending on their particles size, surface nature and amount or concentration in the CSPEs.

Tan et al. [132] investigated the effect of SiO_2 and Al_2O_3 on the PMMA-based SPEs containing LiCF_3SO_3 salt. Addition of Al_2O_3 has improved the ionic conductivity by one order of magnitude from $1.36 \times 10^{-5} \text{ S cm}^{-1}$ to $2.05 \times 10^{-4} \text{ S cm}^{-1}$. However, this effect cannot be seen for CSPE containing SiO_2 [132]. The reason behind Al_2O_3 showed significant improvement in conductivity may be because of the OH surface nature in alumina that provided additional coordination sites to oxygen atom in PMMA for ionic conduction. Moreover, the presence of H^+ on the alumina surface also help in salt dissociation thus increasing the number density of ions leading to ionic conductivity improvement of the CSPE [132]. In the same work, they also reported that the amount of Al_2O_3 influenced the conductivity of CSPE [132]. The presence of high amount of alumina grains in CSPE may cause the polymer chain to be less mobile thus affecting the transport of ions that resulted in conductivity decrement. Nonetheless, it has been reported that the mechanical strength of CSPE was enhanced at high concentrations of filler [133]. Too much or too low content of fillers would not bring positive effect on the ionic conductivity [134]. Only at optimized concentration can lead to its improvement in the CSPE [134]. The findings on acidic surface nature of alumina that enhanced the conductivity of SPE [132] are also supported by Croce et al. [135]. Following Reference [135], it can be understood that extra pathway for ion

transport was formed via hydrogen bonding when the surface of Al₂O₃ nanofiller (particle size 5.8 nm) was acidic. The SPE system that comprised PEO, LiCF₃SO₃ and acidic Al₂O₃ exhibited ionic conductivity of $2.10 \times 10^{-5} \text{ S cm}^{-1}$ at 30 °C. Slight reduction in conductivity ($1.20 \times 10^{-5} \text{ S cm}^{-1}$ at 30 °C) was observed for Al₂O₃ neutral surface which may be due to weaker interactions as compared to that in acidic form [135]. On the contrary, there was no interaction between filler, anion of salt and polymer in the case of basic Al₂O₃ surface thus subsequently causing detrimental outcome to conductivity ($7.30 \times 10^{-6} \text{ S cm}^{-1}$ at 30 °C) [135].

In another work, it was also observed that the addition of SiO₂ successfully boosted the ionic conductivity for PVA-PVP-PEG-NaI electrolyte [136]. An improvement in amorphous region of the electrolyte film via the interaction of functional groups of the polymer with the Si-O-Si of the filler may be the reason for the conductivity increase. Li and Lian [137] studied the effect of SiO₂ particle sizes (4 μm and 7 nm) in hydroxide conducting poly(acrylamide) (PAM) based SPE for alkaline batteries. The hydroxide conductivity of the SPE was amplified with the incorporation of 7 nm SiO₂ but not for SPE containing 4 μm SiO₂. Based on the micrographs and Raman studies, smaller size of SiO₂ significantly helped to delay polymer crystallization [137]. Similar observation has been reported for Al₂O₃ where the smaller particle size prevented the formation of dendrites [138]. Other than size, the morphology of filler will also give different outcome to the CSPE. Lithium dendrites formation was minimized in the case of electrolyte containing PEO, lithium (bis trifluoromethyl)sulfate, SCN and SiO₂ nanofibers as compared to similar electrolyte but with SiO₂ nanoparticles [139]. It was observed that SiO₂ aggregates was found in the latter, while the SiO₂ nanofibers were homogeneously distributed in the electrospun CSPE as evidenced from SEM images. The CSPE of SiO₂ nanofibers that had a 3D structure demonstrated better mechanical strength and flexibility with improved performance in lithium battery [139]. Incorporation of filler in electrolyte also yielded better interfacial contact with lithium metal electrode [140]. At 30 °C, SiO₂ nanofibers CSPE exhibited the conductivity of $9.32 \times 10^{-5} \text{ S cm}^{-1}$ which was highest when comparing to CSPE with SiO₂ nanoparticles ($5.28 \times 10^{-5} \text{ S cm}^{-1}$) and SPE without SiO₂ ($4.72 \times 10^{-5} \text{ S cm}^{-1}$) [139]. Occasionally, an increment in cationic transference number was observed upon the addition of fillers in SPEs [3].

As discussed earlier, the contribution of inactive or passive fillers in ionic conductivity of SPEs is clear, i.e., improving the mobility of charge carriers either through the mobility of polymer chain (amorphousness) or by providing the additional transportation sites. Active fillers, such as Li_{1+x}Al_xGe_{2-x}(PO₄)₃ [141], Li_{1+x}Al_xTi_{2-x}(PO₄)₃ [142], Li₇La₃Zr₂O₁₂ [143], Li_{0.33}La_{0.557}TiO₃ [144] and Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ [145] on the other hand, contribute directly to the lithium-ion conductivity apart from impeding crystallization and improving the mechanical integrity of the SPEs. These materials by their own serve as solid electrolytes [146–150]. Nonetheless, the fabrication processes of these ceramics are usually complicated and costly [139]. In addition, the thickness of these solid electrolytes have to be large (around 100 μm in pellet form), since they are fragile and brittle [139] thus resulting in high interfacial resistance. These drawbacks lead to introducing them in SPEs as fillers instead. Filler-added SPEs are flexible, more stable and have better interfacial compatibility with Li metal electrodes [141,151]. Furthermore, the SPEs possess better processability and higher ionic conductivity than the solid electrolytes [151,152]. Similar to inactive fillers, the size, concentration and morphology of active fillers impose different impact on the CSPEs.

Among the inorganic active fillers, Li₇La₃Zr₂O₁₂ (LLZO) having garnet structure is favored due to its chemical stability against lithium metal and large electrochemical window (>5 V) [143]. LLZO nanofibers prepared via the electrospinning method have been introduced to an electrolyte comprising PVDF-HFP as a polymer host, LiTFSI salt and ionic liquid plasticizer [153]. The CSPE delivered high ambient conductivity ($6.50 \times 10^{-3} \text{ S cm}^{-1}$), reduced crystallinity and wide electrochemical window (5.3 V) than plasticized SPE without LLZO as filler [153]. Comparison was made with basic SPE configuration of PVDF-HFP-LiTFSI in electrochemical performance of Li-ion battery. The LLZO CSPE cell displayed

good cyclability over 1000 cycles with specific capacity of 149 mAh g^{-1} , whereas the capacity decreased sharply after 50th cycle for the Li-ion cell with basic SPE [153]. Synergistic effect of LLZO filler and poly(ethylene glycol) dimethyl ether (PEGDME) plasticizer was also studied in PEO–LiTFSI SPEs system [154]. Again, improvements in conductivity, Li-ion transference number and electrochemical performance were reported [154]. In the work of Keller et al. [155], LLZO-added CSPE containing PEO and LiTFSI did not contribute to ionic conductivity but exhibited improved electrolyte-electrode interfacial contact and higher electrochemical performance in lithium battery. It was found that the addition of LLZO in SPEs suppressed lithium dendrites growth [152–156]. The lithium and zirconium sites of LLZO can be doped with other elements to boost its properties. Zhang and co-authors [157] employed tantalum (Ta) as dopant in LLZO to form $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ (LLZTO). The PAN– LiClO_4 –LLZTO CSPE showed conductivity increment by 12 times ($2.20 \times 10^{-4} \text{ S cm}^{-1}$ at $40 \text{ }^\circ\text{C}$) and higher Li^+ transference number of 0.30 than filler-free SPE [157]. In addition, the CSPE was thermally and electrochemically stable with enhanced mechanical strength [157]. It is worthy to mention that Li^+ transference number as high as 0.75 was obtained in CSPE containing LLZTO, poly(propylene carbonate) and LiTFSI with conductivity of $5.20 \times 10^{-4} \text{ S cm}^{-1}$ at $20 \text{ }^\circ\text{C}$ [158]. It is understood that the addition of nano-sized LLZTO promoted salt dissociation due to the interactions between polymer, cation and filler and subsequently impeded the diffusion of anions [158].

LLZO is preferred over NASICON-type $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) due to their inexpensive elements [155]. In contrast, germanium in the latter is costly [155]. Nevertheless, LLZO has shortcomings; for example, it has an unstable at room-temperature condition, and thus, it is reactive towards moisture and humidity [155]. Similar to LLZO, LAGP is also unreactive towards lithium metal electrodes and has been used as a filler in polymer electrolytes. PEO, LiTFSI and LAGP were mixed and ground without solvent before heating and hot-pressing to form CSPE as reported by Piana et al. [159]. The CSPE showed improvements in term of conductivity, mechanical integrity and specific capacity as compared to electrolyte without filler [159]. On the other hand, the prepared CSPE in Reference [159] showed superior interfacial contact than pelletized LAGP solid electrolyte in lithium-ion cells. However, no significant change in lithium-ion transference number was observed with the introduction of LAGP in PEO-based electrolyte. On the contrary, LAGP added in poly(propylene carbonate)-based electrolyte increased lithium-ion transference number to 0.77 with conductivity of $0.56 \times 10^{-3} \text{ S cm}^{-1}$ and improved cyclability and stability in Li-ion battery [160].

Li et al. [13] employed electrospinning technique to synthesize $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ nanorods before adding in PVDF–HFP electrolyte containing LiTFSI salt. The CSPE was more thermally stable and showed decreased crystallinity with higher ambient ionic conductivity ($1.21 \times 10^{-4} \text{ S cm}^{-1}$) and tensile strength (39.77 MPa) than filler-free electrolyte ($\sigma = 4.72 \times 10^{-5} \text{ S cm}^{-1}$; tensile strength = 38.41 MPa) [13]. Ionic conductivity of PAN-based SPE has been shown to increase with the help of an active filler namely lithium titanate nanotubes (LiTNT) [161]. From the vibrational studies, Pignanelli and co-workers observed that the presence of LiTNT in SPE helped in the increment of lithium perchlorate dissociation, whereas the impedance spectroscopy showed two semicircles that are related to lithium-ion conductivity [161]. The semicircle in the higher frequency region is accredited to the bulk resistance of lithium transport across the polymer matrix, whereas the second is ascribed to lithium transport through the interaction with the LiTNT [161]. Some authors have proposed that lithium transport can take place via three possible routes, i.e., polymer–salt matrix, polymer–filler interface and inside filler grain [162,163]. Zheng et al. [163] showed that Li-ion movement took place mainly via ceramic filler LLZO grain for PEO– LiClO_4 –LLZO system, using NMR results. On the other hand, for PEO– LiClO_4 –TEGDME–LLZO electrolyte, it was found that Li-ion motion via TEGDME-related phase was preferred over filler or polymer matrix or polymer–filler interface [164]. In our opinion, a complete understanding on the conduction mechanism of such SPEs remain challenging as there are many influential factors behind it. Other than the abovementioned

ceramic fillers, $\text{Li}_{6.4}\text{La}_3\text{Zr}_2\text{Al}_{0.2}\text{O}_{12}$ and $\text{LiSnZr}(\text{PO}_4)_3$ have also been incorporated into PEO-LiTFSI [165] and PVDF-LiTFSI [166] electrolytes, respectively.

Another category of active fillers in CSPEs are the metal organic frameworks (MOFs) which display excellent properties such as microporous structures with high surface area, good mechanical and thermal properties, and controllable pore structure. MOFs have been credited to an increased lithium-ion transference number, ionic conductivity and improve the cycling stability of batteries [167]. Several examples of MOFs as active fillers in CSPEs for battery application include aluminum(III)-1,3,5-benzenetricarboxylate (Al-BTC) [168], D-UiO-66-NH₂ [169], copper-1,4-benzenedicarboxylate (Cu-BDC) [170], HKUST-1(Cu) [171] and magnesium-benzene tricarboxylate (Mg-BTC) [172] to name a few. Overall, MOFs having 3D framework and controllable pore structures improve the interfacial contact between electrode and electrolyte. This is reflected with the addition of $\text{Zn}_4\text{O}(1,4\text{-benzenedicarboxylate})$ in PEO-LiTFSI electrolyte which stabilized the interfacial resistance and improved the cyclability up to 100 cycles [173]. As usual, its ionic conductivity was enhanced too [173]. CSPE having Cu-BDC showed enhanced thermal stability which led to safer battery at high temperatures as compared to filler-free SPE [170]. More detailed reviews on CSPEs are available elsewhere [151,174–176]. Some other CSPEs systems that have been reported by many researchers are tabulated in Table 7.

Table 7. Various SPEs systems with fillers added.

| Electrolyte System | Preparation Method | Conductivity, σ (S cm ⁻¹) | Important Findings | Reference |
|---|--------------------|--|---|-----------|
| PEO-LiCF ₃ SO ₃ -TiO ₂ [EO]/[Li] = 9:1 | Solution casting | 4.90×10^{-5} (30 °C) | $E_A = 0.82$ eV; $T_g = -46$ °C; $T_m = 60$ °C | [43] |
| PEO-LiN(CF ₃ SO ₂) ₂ -SiO ₂ [EO]/[Li] = 8:1 | Solution casting | 1.40×10^{-4} | $E_A = 0.54$ eV; $T_g = -43$ °C Without filler: $\sigma = 1.50 \times 10^{-5}$ S cm ⁻¹ (27 °C); $E_A = 0.60$ eV; $T_g = -49$ °C | [177] |
| PEO-LiClO ₄ -SiO ₂ [EO]/[Li] = 8:1 | Solution casting | 2.50×10^{-5} | $E_A = 0.55$ eV; $T_g = -44$ °C Without filler: $\sigma = 9.70 \times 10^{-7}$ S cm ⁻¹ ; $T_g = -46$ °C | [177] |
| PEO-LiClO ₄ -LLTO | Solution casting | 7.99×10^{-4} (70 °C) | LLTO nanoparticles was synthesized via Pechini precursor method. PCTB/SPE/Li cell (60 mA g ⁻¹ ; 70 °C): Discharge capacity = 104 mAh g ⁻¹ 90% capacity retention after 300th cycle | [178] |
| PEO-LiPF ₆ -EC- α CNT | Solution casting | 1.30×10^{-3} (25 °C) | α CNT was synthesized via chemical route Bandgap energy = 4.42 eV (indirect) and 4.60 eV (direct) | [103] |
| Chitosan-LiClO ₄ -glycerol-Ag nanowires | Solution casting | $\sim 2.07 \times 10^{-5}$ (25 °C) | Diameter of Ag nanowires = 20 nm Elastic modulus = ~ 3.5 MPa | [107] |
| Chitosan-LiClO ₄ -glycerol-Ag nanospheres | Solution casting | $\sim 1.00 \times 10^{-4}$ (25 °C) | Diameter of Ag nanospheres = 100 nm Elastic modulus = ~ 1.0 MPa | [107] |

Table 7. Cont.

| Electrolyte System | Preparation Method | Conductivity, σ (S cm ⁻¹) | Important Findings | Reference |
|--|---|---|---|-----------|
| PVA: PVP (1:1)-MgCl ₂ -CuS | Solution casting | 3.32×10^{-7} (RT) 1.85×10^{-3} (protonic σ at RT) | CuS nanoparticles (particle size 20 nm) was synthesized via microwave irradiation method More amorphous after CuS addition Suitable for solid state magnesium batteries, supercapacitors and PEMFC | [179] |
| PEO-PMMA (1:1)-LiClO ₄ -3 wt.% SiO ₂ [EO + C=O]/[Li] = 9:1 | Solution casting + melt press | 0.51×10^{-5} (27 °C) | SiO ₂ particle size < 15 nm $E_A = 0.32$ eV; $t_{Li^+} = 0.9894$ Electrochemical stability window 6.18 V Without filler: $\sigma = 1.72 \times 10^{-5}$ S cm ⁻¹ (27 °C); $E_A = 0.37$ eV | [180,181] |
| PEO-PMMA (1:1)-LiClO ₄ -3 wt.% Al ₂ O ₃ [EO + C=O]/[Li] = 9:1 | Solution casting + melt press | 0.38×10^{-5} (27 °C) | Al ₂ O ₃ particle size < 50 nm $E_A = 0.30$ eV; $t_{Li^+} = 0.9836$ Electrochemical stability window 6.00 V | [180,181] |
| PEO-PMMA (1:1)-LiClO ₄ -3 wt.% ZnO [EO + C=O]/[Li] = 9:1 | Solution casting + melt press | 1.67×10^{-5} (27 °C) | ZnO particle size < 100 nm $E_A = 0.27$ eV; $t_{Li^+} = 0.9857$ Electrochemical stability window 6.06 V | [180,181] |
| PEO-PMMA (1:1)-LiClO ₄ -3 wt.% SnO ₂ [EO + C=O]/[Li] = 9:1 | Solution casting + melt press | 1.00×10^{-5} (27 °C) | SnO ₂ particle size = 100 nm $E_A = 0.38$ eV; $t_{Li^+} = 0.9881$ Electrochemical stability window 6.10 V | [180,181] |
| PEO-PMMA (1:1)-LiClO ₄ -10 wt.% MMT [EO + C=O]/[Li] = 12:1 | Microwave irradiation + Solution casting and melt press | 3.79×10^{-6} (27 °C) | MMT is layered nanosheet which is compatible with PEO polymer chain Without filler: $\sigma = 1.99 \times 10^{-6}$ S cm ⁻¹ (27 °C) | [100] |
| PVDF-CA-LiTFSI-OMMT | | 3.40×10^{-4} (25 °C) | $E_A = 0.45$ eV; $t_{Li^+} = 0.315$ Tensile strength = 44.89 MPa Electrochemical stability window 4.20 V LiFePO ₄ /SPE/Li: Discharge capacity = 112.9 mAh g ⁻¹ (0.5 C; 100th cycle) Without filler: $E_A = 0.53$ eV; $t_{Li^+} = 0.120$ Tensile strength = 34.93 MPa | [182] |
| PEO-PMMA (1:1)-LiBF ₄ -EC-MMT PEO-PMMA (1:1)-LiBF ₄ -EC-MMT | Solution cast method ultrasonic-microwave irradiation solution cast method | 9.17×10^{-6} (27 °C) 6.43×10^{-6} (27 °C) | Ion-dipolar complexes intercalated in MMT network in SPE prepared via solution cast method. Exfoliated MMT structure in SPE by ultrasonic-microwave irradiation solution cast method | [183] |
| PEO-LiCF ₃ SO ₃ -20 wt.% Al ₂ O ₃ | Ball-milling and hot press | 8.64×10^{-5} (RT) | $T_g = -65.3$ °C; % $\chi_C = 18.6\%$ | [38] |

Table 7. Cont.

| Electrolyte System | Preparation Method | Conductivity, σ (S cm ⁻¹) | Important Findings | Reference |
|---|--------------------|--|---|-----------|
| PEO-LiCF ₃ SO ₃ -EC-15 wt.% Al ₂ O ₃ | Solution casting | 5.07×10^{-4} (25 °C) | $T_g = -72.0$ °C; % $\chi_C = 31.1\%$ Without filler: $\sigma = 8.12 \times 10^{-5}$ S cm ⁻¹ (25 °C) $T_g = -70.5$ °C; % $\chi_C = 31.3\%$ | [120] |
| PMA:PEG (65:35)-NaClO ₄ -nano α -Al ₂ O ₃ | Solution casting | 1.76×10^{-4} (70 °C) | $E_A = 0.38$ eV Tensile strength = 50.79 MPa Electrochemical stability window 4.50 V Na ₃ V ₂ (PO ₄) ₃ /SPE/Na cell (0.5 C, 70 °C): Discharge capacity = 85 mAh g ⁻¹ 94.1% capacity retention after 350th cycle Without filler: σ around 10^{-5} S cm ⁻¹ (70 °C) | [184] |
| PEO-PVP-NaIO ₄ -GO | Solution casting | 1.00×10^{-6} (30 °C) | Without filler: $\sigma = 1.57 \times 10^{-7}$ S cm ⁻¹ (30 °C) | [185] |
| PEO-LiTFSI-g-C ₃ N ₄ [EO]/[Li] = 20:1 | Solution casting | 3.06×10^{-5} (25 °C) 2.50×10^{-4} (60 °C) | g-C ₃ N ₄ was synthesized via thermal polycondensation route $t_{Li^+} = 0.69$; $T_g = -41.1$ °C Tensile strength = 3.97 MPa Electrochemical stability window 5.12 V at 60 °C FeF ₃ /SPE/Li cell (1 C, 60 °C): Capacity 300 mAh g ⁻¹ after 200th cycle Without g-C ₃ N ₄ : $\sigma = 2.32 \times 10^{-6}$ S cm ⁻¹ (25 °C) $t_{Li^+} = 0.25$; $T_g = -40.7$ °C Tensile strength = 0.92 MPa Electrochemical stability window 4.60 V at 60 °C | [186] |
| PEO-LiTFSI-Li ₁₀ GeP ₂ S ₁₂ [EO]/[Li] = 18:1 | Solution casting | 1.18×10^{-5} (25 °C) 1.21×10^{-3} (80 °C) | Li ₁₀ GeP ₂ S ₁₂ (particle size 2–3 μ m) was synthesized via solid state reaction method $T_g = -41.6$ °C; % $\chi_C = 42.14\%$ $t_{Li^+} = 0.26$ (80 °C) Electrochemical stability window 5.70 V LiFePO ₄ /SPE/Li cell (0.5 C, 60 °C): Discharge capacity = 137.4 mAh g ⁻¹ 92.5% capacity retention after 50th cycle Without filler: $\sigma = 6.16 \times 10^{-6}$ S cm ⁻¹ (25 °C); $= 7.98 \times 10^{-4}$ S cm ⁻¹ (80 °C); $T_g = -39.6$ °C; % $\chi_C = 67.07\%$ $t_{Li^+} = 0.22$ (80 °C) Electrochemical stability window 4.80 V Discharge capacity = ~50 mAh g ⁻¹ 50.4% capacity retention after 50th cycle | [187] |

Table 7. Cont.

| Electrolyte System | Preparation Method | Conductivity, σ (S cm ⁻¹) | Important Findings | Reference |
|--|--------------------|--|--|-----------|
| PVAc:PMMA (70:30)-LiCl-TiO ₂ | Solution casting | 4.45 × 10 ⁻⁴ (30 °C) | $T_g = 28.1$ °C; $t_+ = 0.99$ $D_+ = 7.07 \times 10^{-11}$ cm ² s ⁻¹ ; $\mu = 2.71 \times 10^{-9}$ cm ² V ⁻¹ s ⁻¹ ; $n = 2.35 \times 10^{22}$ cm ⁻³ Electrochemical stability window 2.69 V Without filler: $\sigma = 1.03 \times 10^{-5}$ S cm ⁻¹ (30 °C) $T_g = 42.6$ °C; $t_+ = 0.97$ $D_+ = 6.93 \times 10^{-11}$ cm ² s ⁻¹ ; $\mu = 2.65 \times 10^{-9}$ cm ² V ⁻¹ s ⁻¹ ; $n = 2.35 \times 10^{22}$ cm ⁻³ Electrochemical stability window 1.69 V | [99] |
| PEO-LiTFSI-Ni ₃ -(BTC) ₂ | Hot pressing | 1.40 × 10 ⁻¹ (30 °C) | LiFePO ₄ /SPE/Li cell (1 C); Discharge capacity = 75 mAh g ⁻¹ | [188] |

LLTO—Li_{0.3}La_{0.566}TiO₃; PCTB—poly(2-chloro-3,5,6-trisulfide-1,4-benzoquinone); α CNT—amorphous carbon nanotubes; CuS—copper sulfate; CA—cellulose acetate; OMMT—organic modified montmorillonite; MMT—montmorillonite; Al₂O₃—nano alumina; NaIO₄—sodium periodate; GO—graphene oxide; PMA—poly(methacrylate); g-C₃N₄—polymeric graphitic carbon nitride; Ni₃-(BTC)₂—nickel-1,3,5-benzene tricarboxylate metal organic framework.

3.2.7. SPEs Containing Other Kind of Additives

It is an undeniable fact that ionic conductivity plays a crucial role in ensuring the performance of electrochemical cells, but the cationic transference number also influences the efficacy of devices in particular batteries. Enhancement in lithium-ion transference number has been observed in PEO-LiI SPEs upon the addition of calix [4] arene with values around 0.8 to 1 at elevated temperatures between 55 and 90 °C [189]. In most cases, the cationic transference number values are found to be below 0.4 without supramolecular additives in PEO-salt SPE systems as mentioned earlier. Based on ab initio computational work, Johansson [190] predicted that the cryptands, i.e., organic compounds having large 3D molecular structure, can trap anions, such as Cl⁻, ClO₄⁻, BF₄⁻ and F⁻, and form coordination complexes, thereby reducing their tendency to re-associate with Li⁺ cation and consequently increasing the cationic transference number. However, the supramolecular compounds are unable to confine large PF₆⁻, TFSI⁻ or [(CF₃SO₂)₂N]⁻ anions within a 3D network and cannot form complexes [190].

Mazor et al. [191] investigated the influence of calix[6]pyrrole on PEO-LiCF₃SO₃ SPEs. Although the ambient conductivity was found to decrease with the addition of calix, the conductivity at 60 °C was higher than that without calix. Nevertheless, the t_{Li+} of the calix-added SPE enhanced by 185% to 0.74 from 0.26 of the calix-free SPE at 60 °C [191]. Ambient conductivity decrement is said to be attributed to the increased rigidity of polymer network, whereas an improvement in lithium-ion transference number is due to increased amount of free ions from dissociated ion aggregates. The SPE has been employed in Li/MoO_xS_y cells that exhibited a power level of 2.1 mW cm⁻² at 90 °C and a discharge capacity of ~24 μ Ah on the 60th cycle [191]. It is said that calix[6]arene can minimize the growth of lithium dendrites and subsequently improves cell performance [192]. A similar observation wherein an increased lithium-ion transference number ($t_{Li+} = 0.95$ at 70 °C) was accompanied by conductivity decrement has been reported in PEO-LiBF₄-calix[6]pyrrole system [193]. In addition, the lithium diffusion-coefficient values were 2.0 × 10⁻⁷ cm² s⁻¹ and 2.5 × 10⁻⁷ cm² s⁻¹ for calix-free and calix-incorporated PEO-based electrolytes, respectively [193].

As aforementioned, the incorporation of supramolecular additives, such as calix-based compounds, is used to increase cationic transference number by trapping/immobilizing

anion of the salt [194]. Usually, this will lead to reduce the anionic mobility and unwittingly decrease the ionic conductivity, as stated in preceding paragraph. Nevertheless, there are some controversial reports that showed otherwise. Won and co-workers [195] observed that the SPE containing PVC doped with lithium chloride (LiCl) salt and calix[4]pyrrole exhibited higher ionic conductivity, at around $10^{-3} \text{ S cm}^{-1}$ at 25°C , compared to that calix-free SPE ($10^{-5} \text{ S cm}^{-1}$). Using density functional theory, they obtained that the dissociation energies for LiCl-calix and PVC-LiCl-calix complexes were 110.8 and $-18.1 \text{ kcal mol}^{-1}$, whereas, for LiCl salt, the dissociation energy value was $145.6 \text{ kcal mol}^{-1}$ [195]. A lower dissociation energy value implies that the cation of salt is more free to move, while its anion has complexed with calix [195].

Plastic crystal SN has also been employed as a polymer matrix in electrolyte, besides serving as a plasticizer and ionizer for both Li- and Na-based salts [131,196]. In order to improve the transference number of Na^+ , Chen et al. [196] synthesized boron-containing 2-hydroxyethyl methacrylate (B-HEMA) before incorporating it into SN-based polymer electrolyte that had non-woven polypropylene-cellulose composite framework and NaClO_4 salt. This electrolyte having B^- (boron anion) acceptor was prepared via a UV-assisted curing method, using 2-hydroxy-2-methyl-1-phenyl-1-propanone as photoinitiator. This electrolyte demonstrated superior properties in terms of ambient conductivity ($3.60 \times 10^{-4} \text{ S cm}^{-1}$), tensile strength (28.2 MPa) and Na^+ transference number of ($t_{\text{Na}^+} = 0.62$) [196]. Promising results were also obtained after applying the electrolyte in Na-ion batteries (initial capacity of $\sim 105 \text{ mAh g}^{-1}$ at 0.1 C and retaining 80% capacity after 120 cycles) [196]. The boron moiety is said to complex with ClO_4^- ion of the salt, thus lowering the anionic mobility and subsequently enhancing the Na^+ ion transference number. Meanwhile, the authors have stated that the polypropylene-cellulose structure did not contribute in ionic conduction, but instead improved the mechanical property of the plastic crystal polymer electrolyte [196].

Polyaniline (PANI), which is a conducting polymer that is usually used as counter electrode in DSSCs [197,198], has been incorporated in SPE containing PEO, tetrapropylammonium iodide (TPAI) and I_2 to trap the large cations ($(\text{C}_3\text{H}_7)_4\text{N}^+$ or simply TPA^+) so that the anions can contribute more to conduction, which is beneficial in DSSC [199]. The authors also believed that PANI has performed the role of plasticizing agent in decreasing crystallinity of PEO and its melting point based on DSC analysis. Upon PANI addition, the degrees of crystallinity and T_m were reduced to 3.37% and 66.2°C from 8.93% and 66.5°C [199]. The PANI-added SPE attained higher values of room temperature conductivity ($8.61 \times 10^{-5} \text{ S cm}^{-1}$) and ionic transference number (0.99) than PANI-free SPE ($\sigma = 6.81 \times 10^{-5} \text{ S cm}^{-1}$; $t_{\text{ion}} = 0.96$). The former also gave better DSSC performance (5.01% efficiency) than the latter (efficiency 3.5%) [199].

A special additive, i.e., hydroxypropyl trimethylammonium bis(trifluoromethane) sulfonamide chitosan salt (HACC-TFSI), was synthesized via ion-exchange route, using hydroxypropyl trimethylammonium chloride chitosan salt and LiTFSI before HACC-TFSI, PEO and LiTFSI were mixed in DMF solvent to form SPE via the solution-casting technique [200]. Ionic conductivity values for HACC-TFSI-added PEO electrolyte at 30 and 60°C were $1.77 \times 10^{-5} \text{ S cm}^{-1}$ and $5.01 \times 10^{-4} \text{ S cm}^{-1}$, respectively [200]. In contrast, conductivities of $3.80 \times 10^{-6} \text{ S cm}^{-1}$ and $1.90 \times 10^{-4} \text{ S cm}^{-1}$ were recorded at the same temperature by PEO SPE without HACC-TFSI [200]. Besides better conductivity, Li^+ ion transference number and tensile strength increased by 1.7 and 3.6 times. Moreover, the SPE with HACC-TFSI was found to be resistant against elevated temperature (150°C) by retaining its shape after exposure at high temperature for one hour [200]. On the contrary, the electrolyte without HACC-TFSI has melted under similar conditions. $\text{LiFePO}_4/\text{Li}$ cell with HACC-TFSI added SPE demonstrated good cyclability and stability over 100 cycles maintaining 73% capacity of its initial capacity of $\sim 108 \text{ mAh g}^{-1}$ [200]. It is worthy to mention that this is considered quite an achievement, since there are not many cells with SPEs that can withstand and operate under such a high temperature.

4. Summary and Outlook

Solid-state electrochemical devices are the focus for the next-generation energy sources, especially for large power-consumption machines, such as electric vehicles. SPEs in electrochemical devices offer flexibility, low cost, harmless and cell cycling improvement. Basic SPEs which contain polymer and salt typically exhibit the ambient ionic conductivity of $\sim 10^{-5} \text{ S cm}^{-1}$. The conductivity must be improved at least to $10^{-3} \text{ S cm}^{-1}$ for application in devices. Additives such as plasticizers and fillers are able to improve the conductivity of the SPEs. Plasticizers are able to reduce the crystallinity of the SPEs and enhance the elasticity and the segmental motion of the polymer chain, leading to an increase the overall ionic conductivity. Fillers, on the other hand, contribute either directly (active) or indirectly (inactive) towards conductivity enhancement. In contrast to SPEs with the plasticizers, fillers are able to improve the mechanical strength of the SPEs. Blending polymers is another approach that is used specially to improve the mechanical strength, apart from conductivity enhancement. Although ionic conductivity is one significant factor determining the feasibility of SPEs in electrochemical devices, other factors, such as ionic transport and transference number of ions, also influence the performance. It is appreciable that various efforts have been undertaken in developing suitable SPEs for practical use in electrochemical devices. In our opinion, there is a promising future for SPEs to compete and substitute liquid electrolytes in electrochemical devices. Among the abovementioned approaches, we think that there is much room for developments and improvements on SPEs having active fillers, in particular, MOFs, since research on this is relatively new and less than the others. Moreover, so far, the research only focuses on MOF-containing SPEs in application for Li-ion batteries. We believe that SPEs containing MOFs as fillers have the potential to be applied in other electrochemical devices, including Li-air batteries, DSSCs, PEMFCs and supercapacitors.

Author Contributions: Conceptualization, L.P.T. and M.H.B.; validation, A.K.A.; formal analysis, L.P.T. and M.H.B.; writing—original draft preparation, L.P.T. and M.H.B.; writing—review and editing, A.K.A.; supervision, A.K.A.; funding acquisition, M.H.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: M.H. Buraidah would like to thank Malaysia Ministry of Higher Education for the FRGS grant (No. FRGS/1/2019/STG07/UM/02/3).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Fenton, D.E.; Parker, J.M.; Wright, P.V. Complexes of alkali metal ions with poly (ethylene oxide). *Polymer* **1973**, *14*, 589. [[CrossRef](#)]
2. Armand, M.B.; Gabano, J.M.; Duclot, M. *Second International Meeting on Solid Electrolytes, St. Andrews, Scotland, UK, 20–22 September 1978*; Extended Abstract No. 6.5 in *Fast Ion Transport in Solids*; Vashista, P., Mundy, J.N., Shenoy, G.K., Eds.; Elsevier: Amsterdam, North Holland, The Netherlands, 1979; p. 131.
3. Voropaeva, D.Y.; Novikova, S.A.; Yaroslavtsev, A.B. Polymer electrolytes for metal-ion batteries. *Russ. Chem. Rev.* **2020**, *89*, 1132–1155. [[CrossRef](#)]
4. Wu, H.; Wick, C.D. Computational Investigation on the Role of Plasticizers on Ion Conductivity in Poly(ethylene Oxide) LiTFSI Electrolytes. *Macromolecules* **2010**, *43*, 3502–3510. [[CrossRef](#)]
5. Webb, M.A.; Savoie, B.M.; Wang, Z.-G.; Miller III, T.F. Chemically Specific Dynamic Bond Percolation Model for Ion Transport in Polymer Electrolytes. *Macromolecules* **2015**, *48*, 7346–7358. [[CrossRef](#)]
6. Duarte, P.; Pereira, S.; Cunha, I.; Pimentel, A.; Dionísio, M.; Fortunato, E.; Martins, R.; Pereira, L. Cellulose-based solid electrolyte membranes through microwave assisted regeneration and application in electrochromic displays. *Front. Mater.* **2020**, *7*, 269. [[CrossRef](#)]

7. Wu, Y.; Li, Y.; Wang, Y.; Liu, Q.; Chen, Q.; Chen, M. Advances and prospects of PVDF based polymer electrolytes. *J. Energy Chem.* **2022**, *64*, 62–84. [[CrossRef](#)]
8. Arof, A.K.; Naeem, M.; Hameed, F.; Jayasundara, W.J.M.J.S.R.; Careem, M.A.; Teo, L.P.; Buraidah, M.H. Quasi solid state dye-sensitized solar cells based on polyvinyl alcohol (PVA) electrolytes containing I^-/I_3^- redox couple. *Opt. Quant. Electron.* **2014**, *46*, 143–154. [[CrossRef](#)]
9. Arof, A.K.; Amirudin, S.; Yusof, S.Z.; Noor, I.M. A method based on impedance spectroscopy to determine transport properties of polymer electrolytes. *Phys. Chem. Chem. Phys.* **2014**, *16*, 1856–1867. [[CrossRef](#)]
10. Buraidah, M.H.; Teo, L.P.; Majid, S.R.; Arof, A.K. Ionic conductivity by correlated barrier hopping in NH_4I doped chitosan solid electrolyte. *Phys. B* **2009**, *404*, 1373–1379. [[CrossRef](#)]
11. Kurapati, S.; Gunturi, S.S.; Nadella, K.J.; Erothu, H. Novel solid polymer electrolyte based on PMMA:CH₃COOLi effect of salt concentration on optical and conductivity studies. *Polym. Bull.* **2019**, *76*, 5463–5481. [[CrossRef](#)]
12. Teoh, K.H.; Lim, C.-S.; Ramesh, S. Lithium ion conduction in corn starch based solid polymer electrolytes. *Measurement* **2014**, *48*, 87–95. [[CrossRef](#)]
13. Li, J.; Zhu, L.; Zhang, J.; Jing, M.; Yao, S.; Shen, X.; Li, S.; Tu, F. Approaching high performance PVDF-HFP based solid composite electrolytes with LLTO nanorods for solid-state lithium-ion batteries. *Int. J. Energy Res.* **2021**, *45*, 7663–7674. [[CrossRef](#)]
14. Golodnitsky, D.; Strauss, E.; Peled, E.; Greenbaum, S. Review-On order and disorder in polymer electrolytes. *J. Electrochem. Soc.* **2015**, *162*, A2551–A2566. [[CrossRef](#)]
15. Noor, I.M. Determination of charge carrier transport properties of gellan gum–lithium triflate solid polymer electrolyte from vibrational spectroscopy. *High Perform. Polym.* **2020**, *32*, 168–174. [[CrossRef](#)]
16. Ahmed, H.T.; Abdullah, O.G. Impedance and ionic transport properties of proton-conducting electrolytes based on polyethylene oxide/methylcellulose blend polymers. *J. Sci.-Adv. Mater. Dev.* **2020**, *5*, 125–133. [[CrossRef](#)]
17. Iftikhar, H.; Sonai, G.G.; Hashmi, S.G.; Nogueira, A.F.; Lund, P.D. Progress on electrolytes development in dye-sensitized solar cells. *Materials* **2019**, *12*, 1998. [[CrossRef](#)] [[PubMed](#)]
18. Aziz, S.B.; Brza, M.A.; Brevik, I.; Hafiz, M.H.; Asnawi, A.S.F.M.; Yusof, Y.M.; Abdulwahid, R.T.; Kadir, M.F.Z. Blending and Characteristics of Electrochemical Double-Layer Capacitor Device Assembled from Plasticized Proton Ion Conducting Chitosan:Dextran:NH₄PF₆ Polymer Electrolytes. *Polymers* **2020**, *12*, 2103. [[CrossRef](#)] [[PubMed](#)]
19. Stephan, A.M. Review on gel polymer electrolytes for lithium batteries. *Eur. Polym. J.* **2006**, *42*, 21–42. [[CrossRef](#)]
20. Stallworth, P.E.; Li, J.; Greenbaum, S.G.; Croce, F.; Slane, S.; Salomon, M. Sodium-23 NMR and complex impedance studies of gel electrolytes based on poly(acrylonitrile). *Solid State Ion.* **1994**, *73*, 119–126. [[CrossRef](#)]
21. Lewandowska, K. Miscibility and thermal stability of poly(vinyl alcohol)/chitosan mixtures. *Thermochim. Acta* **2009**, *493*, 42–48. [[CrossRef](#)]
22. Gómez-Carracedo, A.; Alvarez-Lorenzo, C.; Gómez-Amoza, J.L.; Concheiro, A. Chemical structure and glass transition temperature of non-ionic cellulose ethers. *J. Therm. Anal. Calorim.* **2003**, *73*, 587–596. [[CrossRef](#)]
23. Sivakumar, M.; Subadevi, R.; Rajendran, S.; Wu, H.-C.; Wu, N.-L. Compositional effect of PVdF-PEMA blend gel polymer electrolytes for lithium polymer batteries. *Eur. Polym. J.* **2007**, *43*, 4466–4473. [[CrossRef](#)]
24. Sakurai, K.; Maegawa, T.; Takahashi, T. Glass transition temperature of chitosan and miscibility of chitosan/poly(N-vinyl pyrrolidone) blends. *Polymer* **2000**, *41*, 7051–7056. [[CrossRef](#)]
25. Lu, D.R.; Xiao, C.M.; Xu, S.J. Starch-based completely biodegradable polymer materials. *EXPRESS Polym. Lett.* **2009**, *3*, 366–375. [[CrossRef](#)]
26. Ue, M. Secondary batteries—Lithium rechargeable systems. Electrolytes: Nonaqueous. *Encyclopedia Electrochem. Power Sources* **2009**, 71–84.
27. Arof, A.K.; Teo, L.P.; Yahya, R. Ionic conductivity in some chitosan-based polymer electrolytes. *Curr. Trends Polym. Sci.* **2010**, *14*, 29–44.
28. Izutsu, K. *Electrochemistry in Nonaqueous Solutions*; Wiley-VCH: Weinheim, Germany, 2002; pp. 3–24.
29. Yu, Z.; Vlachopoulos, N.; Gorlov, M.; Kloo, L. Liquid electrolytes for dye-sensitized solar cells. *Dalton Trans.* **2011**, *40*, 10289–10303. [[CrossRef](#)]
30. Fawcett, W.R. Acidity and Basicity Scales for Polar Solvents. *J. Phys. Chem.* **1993**, *97*, 9540–9546. [[CrossRef](#)]
31. Solangi, M.Y.; Aftab, U.; Ishaque, M.; Bhutto, A.; Nafady, A.; Ibupoto, Z.H. Polyvinyl fibers as outperform candidature in the solid polymer electrolytes. *J. Ind. Text.* **2020**, 1–13. [[CrossRef](#)]
32. Vijayakumar, G.; Karthick, S.N.; Subramania, A. A new class of P(VdF-HFP)-CeO₂-LiClO₄ based composite microporous membrane electrolytes for Li-ion batteries. *Int. J. Electrochem.* **2011**, *2011*, 926383. [[CrossRef](#)]
33. Röchow, E.T.; Coeler, M.; Pospiech, D.; Kobsch, O.; Mechtaeva, E.; Vogel, R.; Voit, B.; Nikolowski, K.; Wolter, M. In situ preparation of crosslinked polymer electrolytes for lithium ion batteries: A comparison of monomer systems. *Polymers* **2020**, *12*, 1707. [[CrossRef](#)]
34. Liu, L.; Wang, Z.; Zhao, Z.; Zhao, Y.; Li, F.; Yang, L. PVDF/PAN/SiO₂ polymer electrolyte membrane prepared by combination of phase inversion and chemical reaction method for lithium ion batteries. *J. Solid State Electrochem.* **2016**, *20*, 699–712. [[CrossRef](#)]
35. Eriksson, T.; Mace, A.; Manabe, Y.; Yoshizawa-Fujita, M.; Inokuma, Y.; Brandell, D.; Jonas, M. Polyketones as Host Materials for Solid Polymer Electrolytes. *J. Electrochem. Soc.* **2020**, *167*, 070537. [[CrossRef](#)]

36. Gupta, S.; Singh, P.K.; Bhattacharya, B. Charge carriers dynamics in PEO + NaSCN polymer electrolytes. *Ionics* **2018**, *24*, 163–167. [[CrossRef](#)]
37. Ma, Q.; Liu, J.; Qi, X.; Rong, X.; Shao, Y.; Feng, W.; Nie, J.; Hu, Y.; Li, H.; Huang, X.; et al. New Na[(FSO₂)(n-C₄F₉SO₂)N]-Based Polymer Electrolyte for Solid-State Sodium Batteries. *J. Mater. Chem. A* **2017**, *5*, 7738–7743. [[CrossRef](#)]
38. Klongkan, S.; Pumchusak, J. Effects of Nano Alumina and Plasticizers on Morphology, Ionic Conductivity, Thermal and Mechanical Properties of PEO-LiCF₃SO₃ Solid Polymer Electrolyte. *Electrochim. Acta* **2015**, *161*, 171–176. [[CrossRef](#)]
39. Sim, L.N.; Sentanin, F.C.; Pawlicka, A.; Yahya, R.; Arof, A.K. Development of polyacrylonitrile-based polymer electrolytes incorporated with lithium bis(trifluoromethane)sulfonimide for application in electrochromic device. *Electrochim. Acta* **2017**, *229*, 22–30. [[CrossRef](#)]
40. Sohaimy, M.I.H.A.; Isa, M.I.N. Natural Inspired Carboxymethyl Cellulose (CMC) Doped with Ammonium Carbonate (AC) as Biopolymer Electrolyte. *Polymers* **2020**, *12*, 2487. [[CrossRef](#)]
41. Baharun, N.N.S.; Mingsukang, M.A.; Buraidah, M.H.; Woo, H.J.; Teo, L.P.; Arof, A.K. Development of solid polymer electrolytes based on sodium-carboxymethylcellulose (NaCMC)-polysulphide for quantum dot-sensitized solar cells (QDSSCs). *Ionics* **2020**, *26*, 1365–1378. [[CrossRef](#)]
42. Perumal, P.; Selvasekarapandian, S.; Abhilash, K.P.; Sivaraj, P.; Hemalatha, R.; Selvin, P.C. Impact of lithium chlorate salts on structural and electrical properties of natural polymer electrolytes for all solid state lithium polymer batteries. *Vacuum* **2018**, *159*, 277–281. [[CrossRef](#)]
43. Vignarooban, K.; Dissanayake, M.A.K.L.; Albinsson, I.; Mellander, B.-E. Effect of TiO₂ nano-filler and EC plasticizer on electrical and thermal properties of poly(ethylene oxide) (PEO) based solid polymer electrolytes. *Solid State Ion.* **2014**, *266*, 25–28. [[CrossRef](#)]
44. Singh, R.; Baghel, J.; Shukla, S.; Bhattacharya, B.; Rhee, H.-W.; Singh, P.K. Detailed electrical measurements on sago starch biopolymer solid electrolyte. *Phase Transit.* **2014**, *87*, 1237–1245. [[CrossRef](#)]
45. Singh, R.; Singh, P.K.; Tomar, S.K.; Bhattacharya, B. Synthesis, characterization, and dye-sensitized solar cell fabrication using solid biopolymer electrolyte membranes. *High Perform. Polym.* **2016**, *28*, 47–54. [[CrossRef](#)]
46. Hassan, M.F.; Azimi, N.S.N.; Kamarudin, K.H.; Sheng, C.K. Solid Polymer Electrolytes Based on Starch-Magnesium Sulphate: Study on Morphology and Electrical Conductivity. *ASM Sci. J.* **2018**, *1*, 17–28.
47. Singh, V.K.; Bhattacharya, B.; Shukla, S.; Singh, P.K. Dye-sensitized solar cell comprising polyethyl methacrylate doped with ammonium iodide solid polymer electrolyte. *Appl. Phys. A* **2015**, *118*, 877–883. [[CrossRef](#)]
48. Whba, R.A.G.; TianKhoun, L.; Su'ait, M.S.; Rahman, M.Y.A.; Ahmad, A. Influence of binary lithium salts on 49% poly (methyl methacrylate) grafted natural rubber based solid polymer electrolytes. *Arab. J. Chem.* **2020**, *13*, 3351–3361. [[CrossRef](#)]
49. Ramesh, S.; Arof, A.K. Electrical conductivity studies of polyvinyl chloride-based electrolytes with double salt system. *Solid State Ion.* **2000**, *136–137*, 1197–1200. [[CrossRef](#)]
50. Tao, R.; Fujinami, T. Application of mix-salts composed of lithium borate and lithium aluminate in PEO-based polymer electrolytes. *J. Power Sources* **2005**, *146*, 407–411. [[CrossRef](#)]
51. Yang, H.; Farrington, G.C. Poly(ethylene oxide) electrolytes containing mixed salts. *J. Polym. Sci. B Polym. Phys.* **1993**, *31*, 157–163. [[CrossRef](#)]
52. Moryoussef, A.; Bonat, M.; Fouletier, M.; Hicter, P. *Proceedings, 6th Riso International Symposium on Metallurgy and Materials Science*; Poulsen, F.W., Andersen, N.H., Clausen, K., Skaarup, S., Sorensen, O.T., Eds.; Riso National Lab.: Roskilde, Denmark, 1985; p. 335.
53. Henderson, W.A.; Passerini, S.; Smyrl, W.H. *Lithium Batteries: Proceedings of the International Symposium* (Eds. S. Surampudi, R.A. Marsh, Z. Ogumi, J. Prakash), *Mixed Salt Polymer Electrolytes—PEO_n (x) LiCF₃SO₃ (1-x) LiClO₄ (n = 12)*, Electrochemical Society Proceedings; The Electrochemical Society: Pennington, NJ, USA, 2000; Volume 99–25, pp. 515–523.
54. Deepa, M.; Sharma, N.; Agnihotry, S.A.; Chandra, R.; Sekhon, S.S. Effect of mixed salts on the properties of gel polymeric electrolytes. *Solid State Ion.* **2002**, *148*, 451–455. [[CrossRef](#)]
55. Giua, M.; Panero, S.; Scrosati, B.; Cao, X.; Greenbaum, S.G. Investigation of mixed cation effects in PEO₉Zn_{1-x}Cu_x(CF₃SO₃)₂ polymer electrolytes. *Solid State Ion.* **1996**, *83*, 73–78. [[CrossRef](#)]
56. Dissanayake, M.A.K.L.; Jaseetharan, T.; Senadeera, G.K.R.; Mellander, B.-E.; Albinsson, I.; Furlani, M.; Kumari, J.M.K.W. Solid-state solar cells co-sensitized with PbS/CdS quantum dots and N719 dye and based on solid polymer electrolyte with binary cations and nanofillers. *J. Photochem. Photobiol. A Chem.* **2021**, *405*, 112915. [[CrossRef](#)]
57. Zhao, Q.; Chen, P.; Li, S.; Liu, X.; Archer, L.A. Solid-state Polymer Electrolytes Stabilized by Task-specific Salt Additives. *J. Mater. Chem. A* **2019**, *7*, 7823–7830. [[CrossRef](#)]
58. Aziz, N.A.; Majid, S.R.; Arof, A.K. Synthesis and characterizations of phthaloyl chitosan-based polymer electrolytes. *J. Non. Cryst. Solids* **2012**, *358*, 1581–1590. [[CrossRef](#)]
59. Romanazzi, G.; Gabler, F.M.; Margosan, D.; Mackey, B.E.; Smilanick, J.L. Effect of chitosan dissolved in different acids on its ability to control postharvest gray mold of table grape. *Phytopathology* **2009**, *99*, 1028–1036. [[CrossRef](#)] [[PubMed](#)]
60. Demarger-Andre, S.; Domard, A. Chitosan carboxylic acid salts in solution and in the solid state. *Carbohydr. Polym.* **1994**, *23*, 211–219. [[CrossRef](#)]
61. Kurita, K.; Ikeda, H.; Shimojoh, M.; Yang, J. N-Phthaloylated chitosan as an essential precursor for controlled chemical modifications of chitosan: Synthesis and evaluation. *Polym. J.* **2007**, *39*, 945–952. [[CrossRef](#)]
62. Yoksan, R.; Akashi, M.; Biramontri, S.; Chirachanchai, S. Hydrophobic chain conjugation at hydroxyl group onto γ -ray irradiated chitosan. *Biomacromolecules* **2001**, *2*, 1038–1044. [[CrossRef](#)]

63. Rahman, N.A.; Hanifah, S.A.; Mobarak, N.N.; Su'ait, M.S.; Ahmad, A.; Loh, K.S.; Lee, T.K. Synthesis and characterizations of o-nitrochitosan based biopolymer electrolyte for electrochemical devices. *PLoS ONE* **2019**, *14*, e0212066. [[CrossRef](#)]
64. Jing, B.; Wang, X.; Shi, Y.; Zhu, Y.; Gao, H.; Fullerton-Shirey, S.K. Combining Hyperbranched and Linear Structures in Solid Polymer Electrolytes to Enhance Mechanical Properties and Room-Temperature Ion Transport. *Front. Chem.* **2021**, *9*, 563864. [[CrossRef](#)]
65. Imperiyka, M.; Ahmad, A.; Hanifah, S.A.; Rahman, M.Y.A. Preparation and Characterization of Polymer Electrolyte of Glycidyl Methacrylate-Methyl Methacrylate-LiClO₄ Plasticized with Ethylene Carbonate. *Int. J. Polym. Sci.* **2014**, *2014*, 63879. [[CrossRef](#)]
66. Lehmann, M.L.; Yang, G.; Nanda, J.; Saito, T. Well-designed Crosslinked Polymer Electrolyte Enables High Ionic Conductivity and Enhanced Salt Solvation. *J. Electrochem. Soc.* **2020**, *167*, 070539. [[CrossRef](#)]
67. Youcef, H.B.; Garcia-Calvo, O.; Lago, N.; Shanmukaraj, D.; Armand, M. Cross-Linked Solid Polymer Electrolyte for All-Solid-State Rechargeable Lithium Batteries. *Electrochim. Acta* **2016**, *220*, 587–594. [[CrossRef](#)]
68. Porcarelli, L.; Gerbaldi, C.; Bella, F.; Nair, J.R. Super Soft All-Ethylene Oxide Polymer Electrolyte for Safe All Solid Lithium Batteries. *Sci. Rep.* **2016**, *6*, 19892. [[CrossRef](#)]
69. Li, S.; Zuo, C.; Jo, Y.H.; Li, S.; Jiang, K.; Yu, L.; Zhang, Y.; Wang, J.; Li, L.; Xue, Z. Enhanced ionic conductivity and mechanical properties via dynamic-covalent boroxine bonds in solid polymer electrolytes. *J. Membr. Sci.* **2020**, *608*, 118218. [[CrossRef](#)]
70. Lim, J.Y.; Kang, D.A.; Kim, N.U.; Lee, J.M.; Kim, J.H. Bicontinuously crosslinked polymer electrolyte membranes with high ion conductivity and mechanical strength. *J. Membr. Sci.* **2019**, *589*, 117250. [[CrossRef](#)]
71. Vijayalekshmi, V.; Khastgir, D. Eco-friendly methanesulfonic acid and sodium salt of dodecylbenzene sulfonic acid doped cross-linked chitosan based green polymer electrolyte membranes for fuel cell applications. *J. Membr. Sci.* **2017**, *523*, 45–59. [[CrossRef](#)]
72. Su'ait, M.S.; Ahmad, A.; Hamzah, H.; Rahman, M.Y.A. Preparation and characterization of PMMA-MG49-LiClO₄ solid polymer electrolyte. *J. Phys. D Appl. Phys.* **2009**, *42*, 055410. [[CrossRef](#)]
73. Su'ait, M.S.; Ahmad, A.; Hamzah, H.; Rahman, M.Y.A. Effect of lithium salt concentrations on blended 49% poly(methyl methacrylate) grafted natural rubber and poly(methyl methacrylate) based solid polymer electrolyte. *Electrochim. Acta* **2011**, *57*, 123–131. [[CrossRef](#)]
74. Ali, A.M.M.; Subban, R.H.Y.; Bahron, H.; Yahya, M.Z.A.; Kamisan, A.S. Investigation on modified natural rubber gel polymer electrolytes for lithium polymer battery. *J. Power Sources* **2013**, *244*, 636–640. [[CrossRef](#)]
75. Sutton, P.; Airoidi, M.; Porcarelli, L.; Olmedo-Martínez, J.L.; Mugesana, C.; Bruns, N.; Mecerreyes, D.; Ullrich, S.; Gunkel, I. Tuning the Properties of a UV-Polymerized, Cross-Linked Solid Polymer Electrolyte for Lithium Batteries. *Polymers* **2020**, *12*, 595. [[CrossRef](#)]
76. Raghu, S.; Kilarkaje, S.; Sanjeev, G.; Nagaraja, G.K.; Devendrappa, H. Effect of electron beam irradiation on polymer electrolytes: Change in morphology, crystallinity, dielectric constant and AC conductivity with dose. *Radiat. Phys. Chem.* **2014**, *98*, 124–131. [[CrossRef](#)]
77. Singh, D.; Singh, P.K.; Bhattacharya, B. Ion irradiation on polymer electrolyte films: Comparative study on conductivity. *High Perform. Polym.* **2016**, *28*, 1059–1063. [[CrossRef](#)]
78. Chowdhury, F.I.; Khandaker, M.U.; Amin, Y.M.; Arof, A.K. Effect of gamma radiation on the transport and structural properties of polyacrylonitrile-lithium bis(oxalato)borate films. *Solid State Ion.* **2017**, *304*, 27–39. [[CrossRef](#)]
79. Rahaman, M.H.A.; Khandaker, M.U.; Khan, Z.R.; Kufian, M.Z.; Noor, I.S.M.; Arof, A.K. Effect of gamma irradiation on poly(vinylidene difluoride)-lithium bis(oxalato)borate electrolyte. *Phys. Chem. Chem. Phys.* **2014**, *16*, 11527–11537. [[CrossRef](#)]
80. Hema, M.; Tamilselvi, P.; Pandaram, P. Conductivity enhancement in SiO₂ doped PVA:PVDF nanocomposite polymer electrolyte by gamma ray irradiation. *Nucl. Instrum. Methods Phys. Res. B* **2017**, *403*, 13–20. [[CrossRef](#)]
81. Raghu, S.; Archana, K.; Sharanappa, C.; Ganesh, S.; Devendrappa, H. Electron beam and gamma ray irradiated polymer electrolyte films: Dielectric properties. *J. Radiat. Res. Appl. Sci.* **2016**, *9*, 117–124. [[CrossRef](#)]
82. Heffny, N.A.; Khandaker, M.U.; Osman, Z.; Woo, H.J.; Rabir, M.H.; Arof, A.K. Effect of kGy neutron doses on polymer composite consists of poly(vinylidene difluoride)-lithium bis(oxalato)borate. *Radiat. Phys. Chem.* **2021**, *189*, 109747. [[CrossRef](#)]
83. Sinha, M.; Goswami, M.M.; Mal, D.; Middya, T.R.; Tarafdar, S.; De, U.; Chaudhuri, S.K.; Das, D. Effect of gamma irradiation on the polymer electrolyte PEO-NH₄ClO₄. *Ionics* **2008**, *14*, 323–327. [[CrossRef](#)]
84. Rajeswari, N.; Selvasekarapandian, S.; Prabu, M.; Karthikeyan, S.; Sanjeeviraja, C. Lithium ion conducting solid polymer blend electrolyte based on bio-degradable polymers. *Bull. Mater. Sci.* **2013**, *36*, 333–339. [[CrossRef](#)]
85. Buraidah, M.H.; Arof, A.K. Characterization of chitosan/PVA blended electrolyte doped with NH₄I. *J. Non-Cryst. Solids* **2011**, *357*, 3261–3266. [[CrossRef](#)]
86. Buraidah, M.H.; Teo, L.P.; Au Yong, C.M.; Shah, S.; Arof, A.K. Performance of polymer electrolyte based on chitosan blended with poly(ethylene oxide) for plasmonic dye-sensitized solar cell. *Opt. Mater.* **2016**, *57*, 202–211. [[CrossRef](#)]
87. Sim, L.N.; Majid, S.R.; Arof, A.K. FTIR studies of PEMA/PVDF-HFP blend polymer electrolyte system incorporated with LiCF₃SO₃ salt. *Vib. Spectrosc.* **2012**, *58*, 57–66. [[CrossRef](#)]
88. Zhu, L.; Li, J.; Jia, Y.; Zhu, P.; Jing, M.; Yao, S.; Shen, X.; Li, S.; Tu, F. Toward high performance solid-state lithium-ion battery with a promising PEO/PPC blend solid polymer electrolyte. *Int. J. Energy Res.* **2020**, *25*, 10168–10178. [[CrossRef](#)]
89. Kesavan, K.; Mathew, C.M.; Rajendran, S.; Subbu, C.; Ulaganathan, M. Solid Polymer Blend Electrolyte Based on Poly(ethylene oxide) and Poly(vinyl pyrrolidone) for Lithium Secondary Batteries. *Braz. J. Phys.* **2014**, *45*, 19–27. [[CrossRef](#)]

90. Kesavan, K.; Mathew, C.M.; Rajendran, S.; Ulaganathan, M. Preparation and characterization of novel solid polymer blend electrolytes based on poly (vinyl pyrrolidone) with various concentrations of lithium perchlorate. *Mater. Sci. Eng. B* **2014**, *184*, 26–33. [[CrossRef](#)]
91. Saadiah, M.A.; Nagao, Y.; Samsudin, A.S. Proton (H⁺) transport properties of CMC-PVA blended polymer solid electrolyte doped with NH₄NO₃. *Inter. J. Hydrog. Energy* **2020**, *45*, 14880–14896. [[CrossRef](#)]
92. Balian, S.R.C.; Ahmad, A.; Mohamed, N.S. The Effect of Lithium Iodide to the Properties of Carboxymethyl κ -Carrageenan/Carboxymethyl Cellulose Polymer Electrolyte and Dye-Sensitized Solar Cell Performance. *Polymers* **2016**, *8*, 163. [[CrossRef](#)]
93. Muhammad, F.H.; Subban, R.H.Y.; Winie, T. Solid solutions of hexanoyl chitosan/poly(vinyl chloride) blends and NaI for all-solid-state dye-sensitized solar cells. *Ionics* **2009**, *25*, 3373–3386. [[CrossRef](#)]
94. Bao, J.; Qu, X.; Qi, G.; Huang, Q.; Wu, S.; Tao, C.; Gao, M.; Chen, C. Solid electrolyte based on waterborne polyurethane and poly(ethylene oxide) blend polymer for all-solid-state lithium ion batteries. *Solid State Ion.* **2018**, *320*, 55–63. [[CrossRef](#)]
95. Tao, C.; Gao, M.-H.; Yin, B.-H.; Lia, B.; Huang, Y.-P.; Xua, G.; Bao, J.-J. A promising TPU/PEO blend polymer electrolyte for all-solid-state lithium ion batteries. *Electrochim. Acta* **2017**, *257*, 31–39. [[CrossRef](#)]
96. Koduru, H.K.; Marino, L.; Scarpelli, F.; Petrov, A.G.; Marinov, Y.G.; Hadjichristov, G.B.; Iliev, M.T.; Scaramuzza, N. Structural and dielectric properties of NaIO₄ e Complexed PEO/PVP blended solid polymer electrolytes. *Curr. Appl. Phys.* **2017**, *17*, 1518–1531. [[CrossRef](#)]
97. Anilkumar, K.M.; Jinisha, B.; Manoj, M.; Jayalekshmi, S. Poly(ethylene oxide) (PEO)—Poly(vinyl pyrrolidone) (PVP) blend polymer based solid electrolyte membranes for developing solid state magnesium ion cells. *Eur. Polym. J.* **2017**, *89*, 249–262. [[CrossRef](#)]
98. Senthil, R.A.; Theerthagiri, J.; Madhavan, J.; Arof, A.K. Performance characteristics of guanine incorporated PVDF-HFP/PEO polymer blend electrolytes with binary iodide salts for dye-sensitized solar cells. *Opt. Mater.* **2016**, *58*, 357–364. [[CrossRef](#)]
99. Chandra, M.V.L.; Karthikeyan, S.; Selvasekarapandian, S.; Premalatha, M.; Monisha, S. Study of PVAc-PMMA-LiCl polymer blend electrolyte and the effect of plasticizer ethylene carbonate and nanofiller titania on PVAc-PMMA-LiCl polymer blend electrolyte. *J. Polym. Eng.* **2017**, *37*, 617–631. [[CrossRef](#)]
100. Sengwa, R.J.; Choudhary, S.; Dhatarwal, P. Influences of ultrasonic- and microwave-irradiated preparation methods on the structural and dielectric properties of (PEO-PMMA)-LiCF₃SO₃-x wt% MMT nanocomposite electrolytes. *Ionics* **2014**, *21*, 95–109. [[CrossRef](#)]
101. Guo, M.; Zhang, M.; He, D.; Hua, J.; Wang, X.; Gong, C.; Xie, X.; Xue, Z. Comb-like solid polymer electrolyte based on polyethylene glycol-grafted sulfonated polyether ether ketone. *Electrochim. Acta* **2017**, *255*, 396–404. [[CrossRef](#)]
102. Liu, T.-M.; Saikia, D.; Ho, S.-Y.; Chen, M.-C.; Kao, H.-M. High ion-conducting solid polymer electrolytes based on blending hybrids derived from monoamine and diamine polyethers for lithium solid-state batteries. *RSC Adv.* **2017**, *7*, 20373–20383. [[CrossRef](#)]
103. Ibrahim, S.; Ahmad, R.; Johan, M.R. Conductivity and optical studies of plasticized solid polymer electrolytes doped with carbon nanotube. *J. Lumin.* **2012**, *132*, 147–152. [[CrossRef](#)]
104. Imperiyka, M.; Ahmad, A.; Hanifah, S.A.; Mohamed, N.S.; Rahman, M.Y.A. Investigation of plasticized UV-curable glycidyl methacrylate based solid polymer electrolyte for photoelectrochemical cell (PEC) application. *Int. J. Hydrog. Energy* **2014**, *39*, 3018–3024. [[CrossRef](#)]
105. Fan, L.-Z.; Wang, X.-L.; Long, F. All-solid-state polymer electrolyte with plastic crystal materials for rechargeable lithium-ion battery. *J. Power Sources* **2009**, *189*, 775–778. [[CrossRef](#)]
106. Machado, G.O.; Ferreira, H.C.A.; Pawlicka, A. Influence of plasticizer contents on the properties of HEC-based solid polymeric electrolytes. *Electrochim. Acta* **2005**, *50*, 3827–3831.
107. Kim, J.S.; Lim, J.K.; Park, J.S. Enhancement of Mechanical Stability and Ionic Conductivity of Chitosan-based Solid Polymer Electrolytes Using Silver Nanowires as Fillers. *Bull. Korean Chem. Soc.* **2019**, *40*, 898–905. [[CrossRef](#)]
108. Aziz, S.B.; Asnawi, A.S.F.M.; Mohammed, P.A.; Abdulwahid, R.T.; Yuhanees, M.; Yusof, Y.M.; Abdullah, R.M.; Kadir, M.F.Z. Impedance, circuit simulation, transport properties and energy storage behavior of plasticized lithium ion conducting chitosan based polymer electrolytes. *Polym. Test.* **2021**, *101*, 107286. [[CrossRef](#)]
109. Li, Y.; Wang, J.; Tang, J.; Liu, Y.; He, Y. Conductive performances of solid polymer electrolyte films based on PVB/LiClO₄ plasticized by PEG200, PEG400 and PEG600. *J. Power Sources* **2009**, *187*, 305–311. [[CrossRef](#)]
110. Jibreel, U.M.; Bhattacharya, B.; Singh, P.K. Synthesis, Characterization, and Detailed Studies on Plasticized Poly(ethyl methacrylate): NH₄I Polymer Electrolyte. *Adv. Polym. Technol.* **2018**, *37*, 542–546. [[CrossRef](#)]
111. Anuar, N.K.; Subban, R.H.Y.; Mohamed, N.S. Properties of PEMA-NH₄CF₃SO₃ added to BMATSFI ionic liquid. *Materials* **2012**, *5*, 2609–2620. [[CrossRef](#)]
112. Wang, H.; Lin, C.; Yan, X.; Wu, A.; Shen, S.; Wei, G.; Zhang, J. Mechanical property-reinforced PEO/PVDF/LiClO₄/SN blend all solid polymer electrolyte for lithium ion batteries. *J. Electroanal. Chem.* **2020**, *869*, 114156. [[CrossRef](#)]
113. Reddy, M.J.; Kumar, J.S.; Rao, U.V.S.; Chu, P.P. Structural and ionic conductivity of PEO blend PEG solid polymer electrolyte. *Solid State Ion.* **2006**, *177*, 253–256. [[CrossRef](#)]
114. Widstrom, M.D.; Ludwig, K.B.; Matthews, J.E.; Jarry, A.; Erdi, M.; Cresce, A.V.; Rubloff, G.; Kofinas, P. Enabling high performance all-solid-state lithium metal batteries using solid polymer electrolytes plasticized with ionic liquid. *Electrochim. Acta* **2020**, *345*, 136–156. [[CrossRef](#)]

115. Wang, W.; Fang, Z.; Zhao, M.; Peng, Y.; Zhang, J.; Guan, S. Solid polymer electrolytes based on the composite of PEO–LiFSI and organic ionic plastic crystal. *Chem. Phys. Lett.* **2020**, *747*, 137335. [[CrossRef](#)]
116. Abdullah, O.G.; Ahmed, H.T.; Tahir, D.A.; Jamal, G.M.; Mohamad, A.H. Influence of PEG plasticizer content on the proton-conducting PEO:MC-NH₄I blend polymer electrolytes based films. *Results Phys.* **2021**, *23*, 104073. [[CrossRef](#)]
117. Ahmed, H.T.; Abdullah, O.G. Structural and ionic conductivity characterization of PEO:MC-NH₄I proton-conducting polymer blend electrolytes based films. *Results Phys.* **2020**, *16*, 102861. [[CrossRef](#)]
118. Pal, P.; Ghosh, A. Investigation of ionic conductivity and relaxation in plasticized PMMA-LiClO₄ solid polymer electrolytes. *Solid State Ion.* **2018**, *319*, 117–124. [[CrossRef](#)]
119. Rajendran, S.; Sivakumar, M.; Subadevi, R. Li-ion conduction of plasticized PVA solid polymer electrolytes complexed with various lithium salts. *Solid State Ion.* **2004**, *167*, 335–339. [[CrossRef](#)]
120. Johan, M.R.; Oon, H.S.; Ibrahim, S.; Yassin, S.M.M.; Tay, Y.H. Effects of Al₂O₃ nanofiller and EC plasticizer on the ionic conductivity enhancement of solid PEO–LiCF₃SO₃ solid polymer electrolyte. *Solid State Ion.* **2011**, *196*, 41–47. [[CrossRef](#)]
121. Liew, C.-W.; Ramesh, S.; Ramesh, K.; Arof, A.K. Preparation and characterization of lithium ion conducting ionic liquid-based biodegradable corn starch polymer electrolytes. *J. Solid State Electrochem.* **2012**, *16*, 1869–1875. [[CrossRef](#)]
122. Gupta, S.; Varshney, P.K. Effect of plasticizer on the conductivity of carboxymethyl cellulose-based solid polymer electrolyte. *Polym. Bull.* **2019**, *76*, 6169–6178. [[CrossRef](#)]
123. Liew, C.-W.; Arifin, K.H.; Kawamura, J.; Iwai, Y.; Ramesh, S.; Arof, A.K. Effects of halide anions in ionic liquid added poly(vinyl alcohol)-based ion conductors for electrical double layer capacitors. *J. Non-Cryst. Solids* **2017**, *458*, 97–106. [[CrossRef](#)]
124. Buraidah, M.H.; Teo, L.P.; Arof, A.K. Determining the potential of 55 wt.% chitosan-45 wt.% NH₄I biopolymer electrolyte for application in dye-sensitized solar cells. *Mol. Cryst. Liq. Cryst.* **2019**, *695*, 97–106. [[CrossRef](#)]
125. Polu, A.R.; Singh, P.K. Improved ion dissociation and amorphous region of PEO based solid polymer electrolyte by incorporating tetracyanoethylene. *Mat. Today Proc.* **2020**. [[CrossRef](#)]
126. Singh, P.K.; Bhattacharya, B.; Nagarale, R.K.; Kim, K.-W.; Rhee, H.-W. Synthesis, characterization and application of biopolymer-ionic liquid composite membranes. *Synth. Met.* **2010**, *160*, 139–142. [[CrossRef](#)]
127. Senthil, R.A.; Theerthagiri, J.; Madhavan, J. Optimization of performance characteristics of 2-mercaptopyridine-doped polyvinylidene fluoride (PVDF) polymer electrolytes for dye-sensitized solar cells. *J. Non-Cryst. Solids* **2014**, *406*, 133–138. [[CrossRef](#)]
128. Senthil, R.A.; Theerthagiri, J.; Madhavan, J.; Ganesan, S.; Arof, A.K. Influence of organic additive to PVDF-HFP mixed iodide electrolytes on the photovoltaic performance of dye-sensitized solar cells. *J. Phys. Chem. Solids* **2017**, *101*, 18–24. [[CrossRef](#)]
129. Tuhania, P.; Singh, P.K.; Bhattacharya, B.; Dhapola, P.S.; Yadav, S.; Shukla, P.K.; Gupta, M. PVDF-HFP and 1-ethyl-3-methylimidazolium thiocyanate-doped polymer electrolyte for efficient supercapacitors. *High Perform. Polym.* **2018**, *30*, 911–917. [[CrossRef](#)]
130. Xue, Z.; He, D.; Xie, X. Poly(ethylene oxide)-based electrolytes for lithium-ion batteries. *J. Mater. Chem. A* **2015**, *3*, 19218–19253. [[CrossRef](#)]
131. He, R.; Echeverri, M.; Ward, D.; Zhu, Y.; Kyu, T. Highly conductive solvent-free polymer electrolyte membrane for lithium-ion batteries: Effect of prepolymer molecular weight. *J. Membr. Sci.* **2016**, *498*, 208–217. [[CrossRef](#)]
132. Tan, C.G.; Siew, W.O.; Pang, W.L.; Osman, Z.; Chew, K.W. The effects of ceramic fillers on the PMMA-based polymer electrolyte systems. *Ionics* **2007**, *13*, 361–364. [[CrossRef](#)]
133. Ahmad, S.; Bohidar, H.B.; Ahmad, S.; Agnihotry, S.A. Role of fumed silica on ion conduction and rheology in nanocomposite polymeric electrolytes. *Polymer* **2006**, *47*, 3583–3590. [[CrossRef](#)]
134. Wimalaweera, K.K.; Seneviratne, V.A.; Dissanayake, M.A.K.L. Effect of Al₂O₃ ceramic filler on thermal and transport properties of poly(ethylene oxide)-lithium perchlorate solid polymer electrolyte. *Procedia Eng.* **2017**, *215*, 109–114. [[CrossRef](#)]
135. Croce, F.; Persi, L.; Scrosati, B.; Serraino-Fiory, F.; Plichta, E.; Hendrickson, M.A. Role of the ceramic fillers in enhancing the transport properties of composite polymer electrolytes. *Electrochim. Acta* **2001**, *46*, 2457–2461. [[CrossRef](#)]
136. Singh, P.; Saroj, A.L. Effect of SiO₂ Nano-particles on Plasticized Polymer Blend Electrolytes: Vibrational, Thermal, and Ionic Conductivity Study. *Polym. Plast. Technol. Mater.* **2021**, *6*, 298–305.
137. Li, J.; Lian, K. The effect of SiO₂ additives on solid hydroxide ion-conducting polymer electrolytes: A Raman microscopy study. *Phys. Chem. Chem. Phys.* **2018**, *20*, 7148–7155. [[CrossRef](#)]
138. Kim, S.-H.; Choi, K.-H.; Cho, S.-J.; Kil, E.-H.; Lee, S.-Y. Mechanically compliant and lithium dendrite growth-suppressing composite polymer electrolytes for flexible lithium-ion batteries. *J. Mater. Chem. A* **2013**, *1*, 4949–4955. [[CrossRef](#)]
139. Cui, J.; Zhou, Z.; Jia, M.; Chen, X.; Shi, C.; Zhao, N.; Guo, X. Solid polymer electrolytes with flexible framework of SiO₂ nanofibers for highly safe solid lithium batteries. *Polymers* **2020**, *12*, 1324. [[CrossRef](#)] [[PubMed](#)]
140. Jiang, Y.; Yan, X.; Ma, Z.; Mei, P.; Xiao, W.; You, Q.; Zhang, Y. Development of the PEO based solid polymer electrolytes for all-solid state lithium ion batteries. *Polymers* **2018**, *10*, 1237. [[CrossRef](#)]
141. Jung, Y.-C.; Lee, S.-M.; Choi, J.-H.; Jang, S.S.; Kim, D.-W. All solid-state lithium batteries assembled with hybrid solid electrolytes. *J. Electrochim. Soc.* **2015**, *162*, A704–A710. [[CrossRef](#)]
142. Wang, W.; Yi, F.; Fici, A.J.; Laine, R.M.; Kieffer, J. Lithium ion conducting poly(ethylene oxide)-based solid electrolytes containing active or passive ceramic nanoparticles. *J. Phys. Chem. C* **2017**, *121*, 2563–2573. [[CrossRef](#)]

143. Choi, J.-H.; Lee, C.-H.; Yu, J.-H.; Doh, C.-H.; Lee, S.-M. Enhancement of ionic conductivity of composite membranes for all-solid-state lithium rechargeable batteries incorporating tetragonal $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ into a polyethylene oxide matrix. *J. Power Sources* **2015**, *274*, 458–463. [[CrossRef](#)]
144. Liu, W.; Liu, N.; Sun, J.; Hsu, P.-C.; Li, Y.; Lee, H.-W.; Cui, Y. Ionic conductivity enhancement of polymer electrolytes with ceramic nanowire fillers. *Nano Lett.* **2015**, *15*, 2740–2745. [[CrossRef](#)] [[PubMed](#)]
145. Zhang, Q.; Liu, K.; Li, J.; Ma, C.; Zhou, L.; Du, Y. Study of a composite solid electrolyte made from a new pyrrolidone-containing polymer and LLZTO. *J. Colloid Interface Sci.* **2020**, *580*, 389–398. [[CrossRef](#)]
146. Wang, H.; Zhao, N.; Bi, Z.; Gao, S.; Dai, Q.; Yang, T.; Wang, J.; Jia, Z.; Peng, Z.; Huang, J.; et al. Clear representation of surface pathway reactions at Ag nanowire cathodes in all-solid $\text{Li}-\text{O}_2$ batteries. *ACS Appl. Mater. Interfaces* **2021**, *13*, 39157–39164. [[CrossRef](#)] [[PubMed](#)]
147. Shen, L.; Wang, L.; Wang, Z.; Jin, C.; Peng, L.; Pan, X.; Sun, J.; Yang, R. Preparation and characterization of Ga and Sr co-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ garnet-type solid electrolyte. *Solid State Ion.* **2019**, *339*, 114992. [[CrossRef](#)]
148. Huang, W.L.; Zhao, N.; Bi, Z.J.; Shi, C.; Guo, X.X.; Fan, L.-Z.; Nan, C.-W. Can we find solution to eliminate Li penetration through solid garnet electrolytes? *Mater. Today Nano* **2020**, *10*, 100075. [[CrossRef](#)]
149. Ren, Y.; Shen, Y.; Lin, Y.; Nan, C.-W. Direct observation of lithium dendrites inside garnet-type lithium-ion solid electrolyte. *Electrochem. Commun.* **2015**, *57*, 27–30. [[CrossRef](#)]
150. Shen, F.; Guo, W.; Zeng, D.; Sun, Z.; Gao, J.; Li, J.; He, B.; Han, X. A simple and highly efficient method toward high-density garnet-type LLZTO solid-state electrolyte. *ACS Appl. Mater. Interfaces* **2020**, *12*, 30313–30319. [[CrossRef](#)] [[PubMed](#)]
151. Karabelli, D.; Birke, K.P.; Weeber, M. A performance and cost overview of selected solid-state electrolytes: Race between polymer electrolytes and inorganic sulfide electrolytes. *Batteries* **2021**, *7*, 18. [[CrossRef](#)]
152. Nguyen, Q.H.; Luu, V.T.; Nguyen, H.L.; Lee, Y.-W.; Cho, Y.; Kim, S.Y.; Jun, Y.-S.; Ahn, W. $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ garnet solid polymer electrolyte for highly stable all-solid-state batteries. *Front. Chem.* **2021**, *8*, 619832. [[CrossRef](#)]
153. Zhang, W.; Wang, X.; Zhang, Q.; Wang, L.; Xu, Z.; Li, Y.; Huang, S. $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ceramic nanofiber-incorporated solid polymer electrolytes for flexible lithium batteries. *ACS Appl. Energy Mater.* **2020**, *3*, 5238–5246. [[CrossRef](#)]
154. Cha, J.H.; Didwal, P.N.; Kim, J.M.; Chang, D.R.; Park, C.-J. Poly(ethylene oxide)-based composite solid polymer electrolyte containing $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ and poly(ethylene glycol) dimethyl ether. *J. Membr. Sci.* **2020**, *595*, 117538. [[CrossRef](#)]
155. Keller, M.; Appetecchi, G.B.; Kim, G.-T.; Sharova, V.; Schneider, M.; Schuhmacher, J.; Roters, A.; Passerini, S. Electrochemical performance of a solvent-free hybrid ceramic polymer electrolyte based on $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ in $\text{P}(\text{EO})_{15}\text{LiTFSI}$. *J. Power Sources* **2017**, *353*, 287–297. [[CrossRef](#)]
156. Zhou, D.; Zhang, M.; Su, F.; Arlt, T.; Frerichs, J.E.; Dong, K.; Wang, J.; Hilger, A.; Wilde, F.; Kolek, M.; et al. Performance and behavior of LLZO-based composite polymer electrolyte for lithium metal electrode with high capacity utilization. *Nano Energy* **2020**, *77*, 105196. [[CrossRef](#)]
157. Zhang, X.; Xu, B.-Q.; Lin, Y.-H.; Shen, Y.; Li, L.; Nan, C.-W. Effects of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ on chemical and electrochemical properties of polyacrylonitrile-based solid electrolytes. *Solid State Ion.* **2018**, *327*, 32–38. [[CrossRef](#)]
158. Zhang, J.; Zang, X.; Wen, H.; Dong, T.; Chai, J.; Li, Y.; Chen, B.; Zhao, J.; Dong, S.; Ma, J.; et al. High-voltage and free-standing poly(propylene carbonate)/ $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ composite solid electrolyte for wide temperature range and flexible solid lithium ion battery. *J. Mater. Chem. A* **2017**, *5*, 4940–4948. [[CrossRef](#)]
159. Piana, G.; Bella, F.; Geobaldo, F.; Meligrana, G.; Gerbaldi, C. PEO/LAGP hybrid solid polymer electrolytes for ambient temperature lithium batteries by solvent-free, “one-pot” preparation. *J. Energy Storage* **2019**, *26*, 100947. [[CrossRef](#)]
160. Sung, B.-J.; Didwal, P.N.; Verma, R.; Nguyen, A.-G.; Chang, D.R.; Park, C.-J. Composite solid electrolyte comprising poly(propylene carbonate) and $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ for long-life all-solid-state Li-ion batteries. *Electrochim. Acta* **2021**, *392*, 139007. [[CrossRef](#)]
161. Pignanelli, F.; Romero, M.; Esteves, M.; Luciana, F.-W.; Faccio, R.; Mombrú, A.W. Lithium titanate nanotubes as active fillers for lithium-ion polyacrylonitrile solid polymer electrolytes. *Ionics* **2019**, *25*, 2607–2614. [[CrossRef](#)]
162. Boaretto, N.; Meabe, L.; Martinez-Ibanez, M.; Armand, M.; Zhang, H. Polymer electrolytes for rechargeable batteries: From nanocomposite to nanohybrid. *J. Electrochem. Soc.* **2020**, *167*, 070524. [[CrossRef](#)]
163. Zheng, J.; Tang, M.; Hu, Y.-Y. Lithium ion pathway within $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ -polyethylene oxide composite electrolytes. *Angew. Chem.* **2016**, *55*, 12538–12542. [[CrossRef](#)] [[PubMed](#)]
164. Zheng, J.; Dang, H.; Feng, X.; Chien, P.-H.; Hu, Y.-Y. Li-ion transport in a representative ceramic-polymer-plasticizer composite electrolyte: $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ -polyethylene oxide-tetraethylene glycol dimethyl ether. *J. Mater. Chem. A* **2017**, *5*, 18457–18463. [[CrossRef](#)]
165. Cai, D.; Wang, D.; Chen, Y.; Zhang, S.; Wang, X.; Xia, X.; Tu, J. A highly ion-conductive three-dimensional LLZAO-PEO/LiTFSI solid electrolyte for high-performance solid-state batteries. *Chem. Eng. J.* **2020**, *394*, 124993. [[CrossRef](#)]
166. Pareek, T.; Dwivedi, S.; Ahmad, S.A.; Badole, M.; Kumar, S. Effect of NASICON-type $\text{LiSnZr}(\text{PO}_4)_3$ ceramic filler on the ionic conductivity and electrochemical behavior of PVDF based composite electrolyte. *J. Alloys Compd.* **2020**, *824*, 153991. [[CrossRef](#)]
167. Zhao, R.; Wu, Y.; Liang, Z.; Gao, L.; Xia, W.; Zhao, Y.; Zou, R. Metal-organic frameworks for solid-state electrolytes. *Energy Environ. Sci.* **2020**, *13*, 2386–2403. [[CrossRef](#)]

168. Gerbaldi, C.; Nair, J.R.; Kulandainathan, M.A.; Kumar, R.S.; Ferrara, C.; Mustarellic, P.; Stephan, A.M. Innovative high performing metal organic framework (MOF)-laden nanocomposite polymer electrolytes for all-solid-state lithium batteries. *J. Mater. Chem. A* **2014**, *2*, 9948–9954. [[CrossRef](#)]
169. Angulakshmi, N.; Zhou, Y.; Suriyakumar, S.; Dhanalakshmi, R.B.; Satishrajan, M.; Alwarappan, S.; Alkordi, M.H.; Stephan, A.M. Microporous metal-organic framework (MOF)-based composite polymer electrolyte (CPE) mitigating lithium dendrite formation in all-solid-state-lithium batteries. *ACS Omega* **2020**, *5*, 7885–7894. [[CrossRef](#)] [[PubMed](#)]
170. Kumar, R.S.; Raja, M.; Kulandainathan, M.A.; Stephan, A.M. Metal organic framework-laden composite polymer electrolytes for efficient and durable all-solid-state-lithium batteries. *RSC Adv.* **2014**, *4*, 26171–26175. [[CrossRef](#)]
171. Wang, Z.; Zhou, H.; Meng, C.; Xiong, W.; Cai, Y.; Hu, P.; Pang, H.; Yuan, A. Enhancing ion transport: Function of ionic liquid decorated MOFs in polymer electrolytes for all solid-state lithium batteries. *ACS Appl. Energy Mater.* **2020**, *3*, 4265–4274. [[CrossRef](#)]
172. Angulakshmi, N.; Kumar, R.S.; Kulandainathan, M.A.; Stephan, A.M. Composite polymer electrolytes encompassing metal organic frameworks: A new strategy for all solid-state lithium batteries. *J. Phys. Chem. C* **2014**, *118*, 24240–24247. [[CrossRef](#)]
173. Yuan, C.; Li, J.; Han, P.; Lai, Y.; Zhang, Z.; Liu, J. Enhanced electrochemical performance of poly(ethylene oxide) based composite polymer electrolyte by incorporation of nano-sized metal-organic framework. *J. Power Sources* **2013**, *240*, 653–658. [[CrossRef](#)]
174. Zhao, Y.; Wang, L.; Zhou, Y.; Liang, Z.; Tavajohi, N.; Li, B.; Li, T. Solid polymer electrolytes with high conductivity and transference number of Li ions for Li-based rechargeable batteries. *Adv. Sci.* **2021**, *8*, 2003675. [[CrossRef](#)] [[PubMed](#)]
175. Li, L.; Deng, Y.; Chen, G. Status and prospect of garnet/polymer solid composite electrolytes for all-solid-state lithium batteries. *J. Energy Chem.* **2020**, *50*, 154–177. [[CrossRef](#)]
176. Barbosa, J.C.; Goncalves, R.; Costa, C.M.; Bermudez, V.d.Z.; Fidalgo-Marijuan, A.; Zhang, Q.; Lanceros-Mendez, S. Metal-organic frameworks and zeolite materials as active fillers for lithium-ion battery solid polymer electrolytes. *Mater. Adv.* **2021**, *2*, 3790–3805. [[CrossRef](#)]
177. Capiglia, C.; Mustarelli, P.; Quartarone, E.; Tomasi, C.; Magistris, A. Effects of nanoscale SiO on the thermal and transport properties of solvent-free, poly(ethylene oxide) (PEO)-based polymer electrolytes. *Solid State Ion.* **1999**, *118*, 73–79. [[CrossRef](#)]
178. Wei, W.; Li, L.; Zhang, L.; Hong, L.; He, G. An all-solid-state Li-organic battery with quinone-based polymer cathode and composite polymer electrolyte. *Electrochim. Commun.* **2018**, *90*, 21–25. [[CrossRef](#)]
179. Jeyabanua, K.; Sundaramahalingam, K.; Devendran, P.; Manikandan, A.; Nallamuthu, N. Effect of electrical conductivity studies for CuS nanofillers mixed magnesium ion based PVA-PVP blend polymer solid electrolyte. *Phys. B Condens. Matter.* **2019**, *572*, 129–138. [[CrossRef](#)]
180. Dhatarwala, P.; Choudhary, S.; Sengwa, R.J. Electrochemical performance of Li⁺-ion conducting solid polymer electrolytes based on PEO-PMMA blend matrix incorporated with various inorganic nanoparticles for the lithium ion batteries. *Compos. Commun.* **2018**, *10*, 11–17. [[CrossRef](#)]
181. Choudhary, S.; Sengwa, R.J. Effects of different inorganic nanoparticles on the structural, dielectric and ion transportation properties of polymers blend based nanocomposite solid polymer electrolytes. *Electrochim. Acta* **2017**, *247*, 924–941. [[CrossRef](#)]
182. Li, L.; Shan, Y.; Yang, X. New insights for constructing solid polymer electrolytes with ideal lithium-ion transfer channels by using inorganic filler. *Mater. Today Commun.* **2020**, *26*, 101910. [[CrossRef](#)]
183. Dhatarwala, P.; Sengwa, R.J.; Choudhary, S. Effect of intercalated and exfoliated montmorillonite clay on the structural, dielectric and electrical properties of plasticized nanocomposite solid polymer electrolytes. *Compos. Commun.* **2017**, *5*, 1–7. [[CrossRef](#)]
184. Zhang, X.; Wang, X.; Liu, S.; Tao, Z.; Chen, J. A novel PMA/PEG-based composite polymer electrolyte for all-solid-state sodium ion batteries. *Nano Res.* **2018**, *11*, 62244–66251. [[CrossRef](#)]
185. Koduru, H.K.; Iliev, M.T.; Kondamareddy, K.K.; Karashanova, D.; Vlachov, T.; Zhao, X.Z.; Scaramuzza, N. Investigations on Poly(ethylene oxide) (PEO)—blend based solid polymer electrolytes for sodium ion batteries. *J. Phys. Conf. Ser.* **2016**, *764*, 012006. [[CrossRef](#)]
186. Hu, J.; Chen, K.; Zhenguo Yao, Z.; Li, C. Unlocking solid-state conversion batteries reinforced by hierarchical microsphere stacked polymer electrolyte. *Sci. Bull.* **2021**, *66*, 694–707. [[CrossRef](#)]
187. Zhao, Y.; Wu, C.; Peng, G.; Chen, X.; Yao, X.; Bai, Y.; Wu, F.; Chen, S.; Xu, X. A new solid polymer electrolyte incorporating Li₁₀GeP₂S₁₂ into a polyethylene oxide matrix for all-solid-state lithium batteries. *J. Power Sources* **2016**, *301*, 47–53. [[CrossRef](#)]
188. Suriyakumar, S.; Kanagaraj, M.; Angulakshmi, N.; Kathiresan, M.; Nahm, K.S.; Walkowiak, M.; Wasinski, K.; Poltrolniczak, P.; Stephan, A.M. Charge-discharge studies of all-solid-state Li/LiFePO₄ cells with PEO-based composite electrolytes encompassing metal organic frameworks. *RSC Adv.* **2016**, *6*, 97180–97186. [[CrossRef](#)]
189. Blazejczyk, A.; Wiczorek, W.; Kovarsky, R.; Golodnitsky, D.; Peled, E.; Scanlon, L.G.; Appetecchi, G.B.; Scrosati, B. Novel Solid Polymer Electrolytes with Single Lithium-Ion Transport. *J. Electrochem. Soc.* **2004**, *151*, A1762–A1766. [[CrossRef](#)]
190. Johansson, P. Anion cryptands: A way to increased cation transport in polymer electrolytes. *Electrochim. Acta* **2003**, *48*, 2291–2294. [[CrossRef](#)]
191. Mazor, H.; Golodnitsky, D.; Peled, E.; Wiczorek, W.; Scrosati, B. A search for a single-ion-conducting polymer electrolyte: Combined effect of anion trap and inorganic filler. *J. Power Sources* **2008**, *178*, 736–743. [[CrossRef](#)]
192. Kufian, M.Z.; Arof, A.K. Effect of calix[6]arene on charge discharge behaviour of lithium air cell based on PAN-LiBOB gel polymer electrolyte. *Mater. Technol.* **2014**, *29*, A114–A117. [[CrossRef](#)]
193. Kalita, M.; Bukat, M.; Ciosek, M.; Siekierski, M.; Chung, S.H.; Rodr'iguez, T.; Greenbaum, S.G.; Kovarsky, R.; Golodnitsky, D.; Peled, E.; et al. Effect of calixpyrrole in PEO–LiBF₄ polymer electrolytes. *Electrochim. Acta* **2005**, *50*, 3942–3948. [[CrossRef](#)]

194. Panero, S.; Scrosati, B.; Sumathipala, H.H.; Wieczorek, W. Dual-composite polymer electrolytes with enhanced transport properties. *J. Power Sources* **2007**, *167*, 510–514. [[CrossRef](#)]
195. Won, J.; Lee, K.M.; Kang, Y.S.; Chang, S.-K.; Kim, C.K.; Kim, C.K. Anion complexation by calix[4]pyrrole in solid polymer electrolytes. *Macromol. Res.* **2006**, *14*, 404–407. [[CrossRef](#)]
196. Chen, S.; Feng, F.; Yin, Y.; Lizo, X.; Ma, Z. Plastic crystal polymer electrolytes containing boron based anion acceptors for room temperature all-solid-state sodium-ion batteries. *Energy Storage Mater.* **2019**, *22*, 57–65. [[CrossRef](#)]
197. Eslah, S.; Nouri, M. Synthesis and Characterization of tungsten trioxide/polyaniline/polyacrylonitrile composite nanofibers for application as a counter electrode of DSSCs. *Russ. J. Electrochem.* **2019**, *55*, 291–304. [[CrossRef](#)]
198. Li, Q.; Wu, J.; Tang, Q.; Lan, Z.; Li, L.; Lin, J.; Fan, L. Application of microporous polyaniline counter electrode for dye-sensitized solar cells. *Electrochem. Commun.* **2008**, *10*, 1299–1302. [[CrossRef](#)]
199. Dissanayake, M.A.K.L.; Kumari, J.M.K.W.; Senadeera, G.K.R.; Jaseetharan, T.; Mellander, B.-E.; Albinson, I.; Furlani, M. Polyaniline (PANI) mediated cation trapping effect on ionic conductivity enhancement in poly(ethylene oxide) based solid polymer electrolytes with application in solid state dye sensitized solar cells. *React. Funct. Polym.* **2020**, *155*, 104683. [[CrossRef](#)]
200. Tan, J.; Ao, X.; Dai, A.; Yuan, Y.; Zhuo, H.; Lu, H.; Zhuang, L.; Ke, Y.; Su, C.; Peng, X.; et al. Polycation ionic liquid tailored PEO-based solid polymer electrolytes for high temperature lithium metal batteries. *Energy Storage Mater.* **2020**, *33*, 173–180. [[CrossRef](#)]