Review

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Solid Polymer Electrolytes for Zinc Ion Batteries

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Abstract: To date, zinc ion batteries (ZIBs) have been attracting extensive attention due to their outstanding properties and the potential to be the solution for next-generation energy storage systems. However, the uncontrollable growth of zinc dendrites and water-splitting issues seriously restrict the further scalable application. Over the past few years, solid polymer electrolytes (SPEs) have been regarded as a promising alternative to address these challenges and facilitate the practical advancement of zinc batteries. In this review, we revisited the research progress of SPEs applied in zinc batteries in the past few years and focus on introducing cutting-edge polymer science and technologies that can be utilized to prepare advanced SPEs for high-performance zinc batteries. The operating mechanism of SPEs and the functions of polymers will be summarized. To highlight the polymer functions, SPEs are categorized into three types, respectively, homogenous polymer SPEs, hybrids polymer SPEs, and nanocomposites SPEs, which are expected to reveal the roles and principles of various polymers in zinc batteries. This review presents the current research progress and fundamental mechanisms of polymer-based SPEs in zinc batteries, outlines the challenging issues encountered, and meanwhile proposes potential solutions for future endeavours.

Keywords: Solid polymer electrolytes; Zinc batteries; Nanocomposites; Zinc dendrites; Ion conductivity

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1. Introduction

To date, the increased consumption of fossil fuels has led to emerging environmental issues such as climate change and air and water pollution, which have garnered significant and wide attention. Over the past few decades, there has been a growing emphasis on and development of renewable energy sources and their corresponding energy storage systems. Several energy storage systems, such as lithium-ion batteries, sodium-ion batteries, lithium-air batteries, fuel batteries, and alkaline metal batteries, have been developed with outstanding performance. Among these, the research and development of rechargeable lithium-ion batteries has been particularly feasible and practical. As a result of their exceptional energy density, high voltage, and excellent cycling performance, lithium batteries have successfully been utilized in various areas, such as electric vehicles, energy storage stations, and portable electronics. Nevertheless, lithium-ion batteries are still facing some crucial challenges, for example, high cost and fire safety issues that seriously restrict further applications. Recently, aqueous zinc ion batteries (ZIBs) have attracted extensive attention owing to the high theoretical volume capacity of Zn metal anode (5854 mAh cm^{-3}) [1,2], the low redox potential of Zn/Zn^{2+} (-0.76 V vs standard hydrogen electrode (SHE)) [3,4], nontoxicity, and rich zinc resources. However, similar to lithium batteries, when using zinc metal as the anode material, ZIBs also have safety issues induced by the uncontrollable growth of zinc dendrites [5–9]. The dendrites are usually formed on the surface of anodes where the zinc ions are reduced to zinc metal, which are like whiskers and can pierce through the separator and lead to battery short circuits and even explosion [5–7]. In addition, the formation of zinc dendrites is usually accompanied by side chemical reaction among electrolyte, zinc metal and zinc salts and cause the continuous consumption of electrolytes zinc salts which will lead to reduced capacity, low efficiency and short lifespan. Another crucial issue is induced by the water splitting process, as the ZIBs use water as the solvent, which may lead to corrosion, hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [10–12]. These side reactions may lead to continuous consumption of water and poor battery efficiency. Additionally, cathode materials of ZIBs, including MnO_2 [13,14], Prussian blue analogs [15,16], and vanadium-based oxides [17–19] could partially dissolve in aqueous electrolytes and lead to deteriorated performance. Therefore, to realise excellent prolonged cycling lifespan and stability of ZIBs, many efforts have been devoted to electrolyte improvement strategies.

Solid polymer electrolytes (SPEs) have attracted significant attention in recent years as a promising alternative to liquid electrolytes in rechargeable zinc batteries [20–26]. Normally, as per the compositions, SPEs are one type of polymer electrolytes (PEs) that could be used to realise advanced ZIBs. There are another two PEs categories that can also be applied in safe ZIBs, respectively gel polymer electrolytes (GPEs) and hybrid polymer electrolytes (HPEs) [21,27–29]. Summarily, all three types of PEs consist of long polymer chains and zinc salts/mediums. In terms of SPEs, the zinc salts may be dissolved in polymer chains [23,25,30,31]. For GPEs, it is prepared by dissolving the zinc salts in solvent and getting the gels [32–35]. As for HPEs, it is mainly realised by crosslinking or copolymerization methods to connect two or more types of polymer chains in which zinc salts are dispersed [29,36].

In this review, we will focus on the development of solid-state polymer electrolytes for zinc-ion batteries. Owing to the remarkable advantages of SPEs, including high ionic conductivity, mechanical flexibility, and improved safety, which make them ideal for use in advanced energy storage systems. There have already been some reviews introducing the electrolytes development of zinc batteries [21,22,37,38]. However, these reviews mainly introduced the electrolytes from the aspects of cathodes/electrolytes, structure design, types of zinc batteries, and polymer types. It should be noted that in this review, we focus on the SPEs with various polymer strategies that can achieve high-performance and safe ZIBs. Additionally, when it comes to summarising the SPEs for ZIBs, we mainly include the solid-state polymer electrolytes applied in ZIBs, a few SPEs that are close to gel-like state but have unique structures and outstanding properties are also categorized and introduced here. In detail, we discuss the properties and characteristics of SPEs, including their types, preparation methods, and ion transport mechanisms. Additionally, we review recent advances in the development of solid polymer electrolytes for zinc-ion batteries, highlighting their synthesis, performance, and limitations. At last, we conclude with a summary of the current status and future directions of SPEs for ZIBs.

2. Classification of SPEs

Owing to the significant research interests of ZIBs in recent decades, extensive reviews regarding ZIBs chemistry have been conducted by Wu et al. [39], Zhang et al. [40], Mo et al. [41] and Wang et al. [42]. These reviews comprehensively reviewed the materials of anode, cathode and electrolyte, also the physiochemical and thermomechanical properties of different material combinations. However, the engineering of an electrolyte can be complicated as it affects the mass transport, energy storage mechanisms, and reactions of ZIBs, the versatility of potential electrolyte materials has further increased the difficulty of reviewing ZIBs electrolytes systematically. Wu et al. [39] performed an excellent review of an extensive range of polymer-based electrolytes and categorised them into solid, hydrogel and hybrid state electrolytes. Zhang et al. [40] classified electrolytes into aqueous, aqueous gel, organic, ionic liquids and deep eutectic solvents. In this mini-review, a wide spectrum of SPEs studies will be reviewed and categorised into three groups, namely the Homogenous Polymer SPEs, Hybrid Polymer-based SPEs and Nanocomposites Polymer Electrolytes. This study aims to revisit the current state of solid-state electrolytes engineering for ZIBs, specifically on the cutting-edge technologies of SPEs utilising polymer science and technologies to realise advanced ZIBs. Different from the existing reviews, in this review, it’s anticipated to highlight the functions of polymers, polymer hybrids and polymer composites inside SPEs and how these polymer systems can enhance the performance of ZIBs. This is also the reason to categorise the SPEs into three types. The discussion of Homogenous Polymer SPEs will help to study the research mechanism of one kind of polymer on the performance of ZIBs. In terms of Hybrid Polymer-based SPEs, the illustrations will reveal the interaction between different polymer components that can promote the ion mobility and facilitate the battery property. At last, polymers can also play key functions on improving the safety and performance of ZIBs along with inorganic materials, this section will introduce how the inorganic/polymer nanocomposites can significantly impact the zinc ion transport and maintain a stable operating process for a long lifespan.

3. Literature Review

3.1. Homogenous Polymer Matrix SPEs

In the early SPE studies, organic polymer matrices such as polyethylene oxide (PEO) [43], polyvinylidene fluoride (PVDF) [44], Polyacrylamide (PAM) [45], and polyvinyl alcohol (PVA) [46] were widely adopted with low molecular weight plasticizer (i.e.) to enhance the ionic conductivity of the electrolytes. Nonetheless, these polymers were commonly reported with low ionic conductivity and poor interface compatibility. For instance, being one of the most common electrolyte materials for LIBs and ZIBs, the flexible chains of PEO have allowed Zn^{2+} ions to be transferred by segmental motion [47]. However, efficient Zn^{2+} conduction and Zinc electrochemistry have been difficult to achieve owing to the high-degree crystallization of PEO and its interfacial incompatibility with Zn metal. This leads to the poor ionic conductivity of PEO, reported approximately 1.09×10^{-6} to 2.87×10^{-5} Scm^{-1} at room temperature. To enhance the ion transfer, Zhao et al. [48] employed poly(ethylene glycol) methyl ether acrylate (PEGMEA) to build an in-situ polymerized PEO-based SPEs. This approach formulated a cross-linking structure within the amorphous regime and improved the ionic conductivity of 2.87×10^{-5} Scm^{-1}, as revealed in Figure 1(a). Except overcoming the poor interfacial ion transport common to PEO-based SPEs, the in-situ strategy also improves the reversibility of Zn electrochemistry in symmetrical cells. Except for PEO, Poly(vinylidene fluoride) (PVdF) has been one of the common electrolytes in ZIBs development owing to its porous semicrystalline structures, where the strong electron-withdrawing effect can be observed at the CF_2 functional groups. This accelerates the isolation of the metal salts, increasing the number of charges that contributes to the ionic conductivity [49]. Song et al. [50] utilised solution casting methods to synthesise PVdF-HFP (poly(vinylidene fluoride-hexafluoropropylene))-based SPE, where the ionic conductivity of 2.44×10^{-5} Scm^{-1} was achieved at room temperature, with a mass ratio of 0.4 between $Zn(Tf)_2$ and PVdF-HFP. Furthermore, the intrinsic structure of PVdF-HFP also allows the flow of charge through complexation and decomplexation within the polymer segments, as depicted in Figure 1(b). Nevertheless, PVDF possesses similar drawbacks to PEO, where low ionic conductivity, high interfacial resistance, rapid degradation and poor mechanical strength can be observed in early ZIB studies [40].

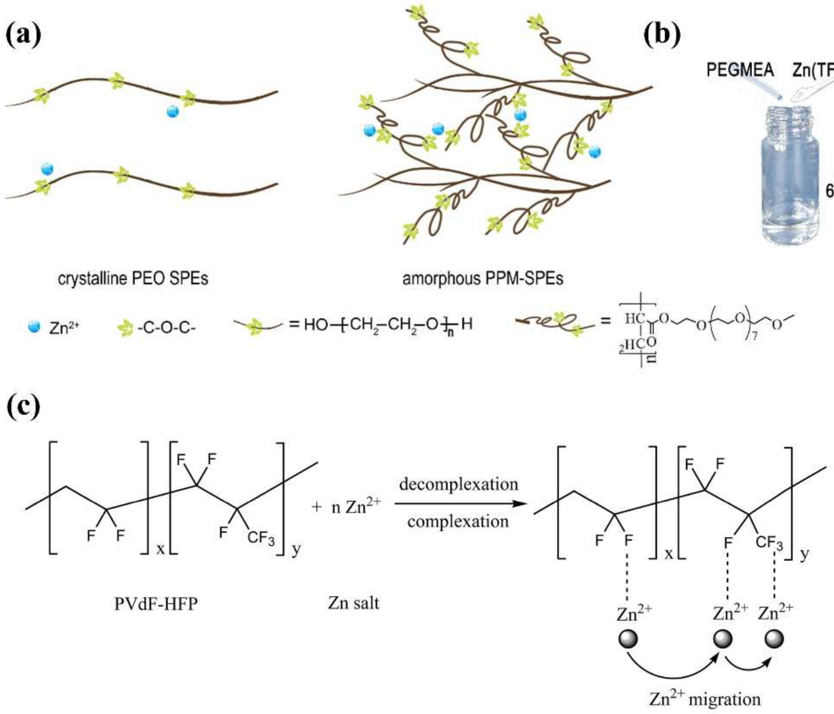


Figure 1. (a) Schematic diagrams for crystalline PEO SPEs (left) and amorphous PPM-SPEs (right). Reproduced with permission from [48]. (b) The preparation process of PPM-SPEs. (c) Schematic diagram showing the complexed Zn2+ transport mechanism in polymer electrolytes. Reproduced with permission from [50].

To overcome the addressed drawbacks of conventional SPEs, especially low ionic conductivity and high interfacial resistance. Ma et al. [51] developed an amorphous SPE containing a high concentration of Zn salts by in situ performing ring-opening polymerization of a precursor of 1,3-dioxolane (DOL) within an electrochemical cell in Figure 2(a). The in-situ formed SPEs demonstrate high ion conductivity of 1.96×10^{-2} Scm^{-1} at room temperature and non-dry properties. Owing to the well-connected pathways and lesser interfacial defects, only 10 % interfacial impedance is retained compared to a conventional battery, leading to a higher columbic efficiency. Moreover, the developed battery successfully achieved charging/discharging cycles of 1800 hours without dendrite growth. To further enhance ion conductivity and mechanical strength, Liu et al. [52] synthesised dry polymer “PHP” by introducing 2,6-bis((propylimino)methyl)-4-chlorophenol (Hbimcp) ligand into the poly(propylene oxide) (PPO) polymer chain, where the SPE film is formed after slow volatilization in a polytetrafluoroethylene mould at ambient temperature. The PHP SPE were reported with a moderate ion conductivity of 10^{-5} Scm^{-1} and significant flexibility at 1000 % elongation strain and fast self-healing capability. Also, the ZIB exhibits remarkable cycling stability (125 % capacity retention after 300 cycles) and a high coulombic efficiency (94 % after 300 cycles). These favourable properties can be attributed to the unique coordination system of PHP, where the strong coordination withstands stress during stretching while the fast ligand exchange between zinc ions and the PHP polymer chains endows ion conductivity. Moreover, the imine bonds in the polymer also enables acidic degradation of the electrolyte that improve its recyclability.

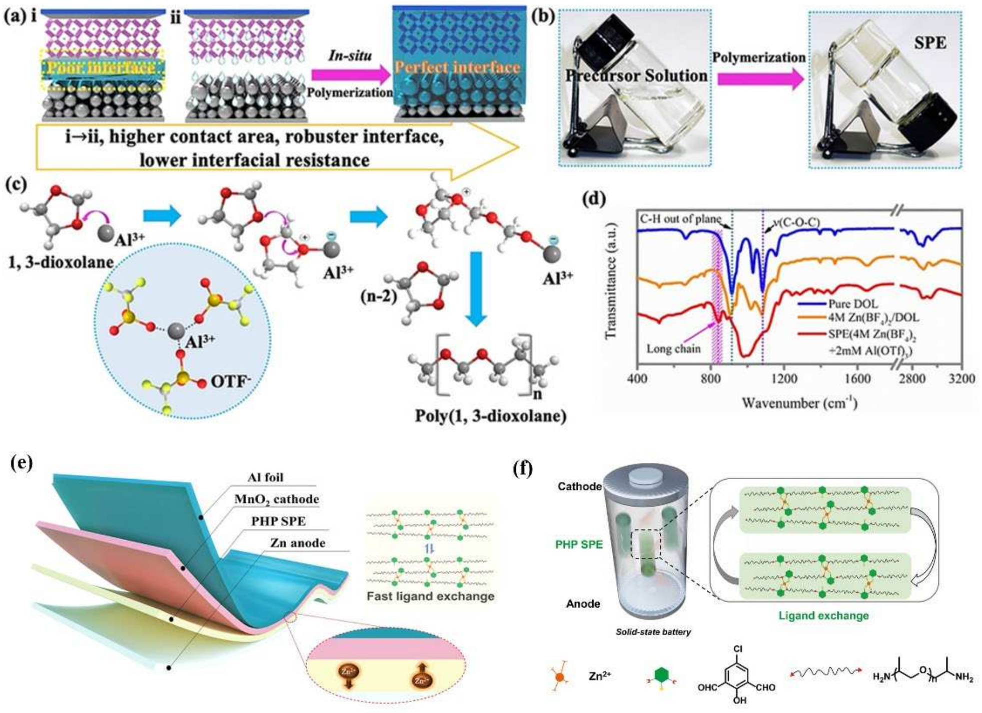


Figure 2. a) Schematic illustration of ex situ and in situ-formed SPEs for Zn batteries. b) Digital photograph depicting the liquid 4 M Zn(BF4)2/DOL solution and SPEs formed spontaneously in an electrolyte containing 2 mM Al(OTf)3 salt. c) Corresponding reaction mechanism depicting how Al(OTf)3 initiates polymerization of DOL. d) FT-IR spectrum of pure DOL, liquid 4 M Zn(BF4)2/DOL solution and SPE(4 M Zn(BF4)2+2 mM Al(OTf)3). Reproduced with permission from [51]. (e) Schematic image of solid polymer electrolyte (SPE) utilizing coordination of zinc ions is designed and then introduced into an all-solid ZIB. (f) Solid-state battery based on the PHP SPE and mechanism of the conduction of zinc ions. Reproduced with permission from [52].

Except for electromechanical and cost efficiency, environment-friendly and recyclable energy storage devices are essential for a successful transition towards sustainability. Brige et al. [2] fabricated bio-based SPE utilising hydroxyethylcellulose (HEC), an amorphous homogenous biopolymer that has side chains of ethylene oxide groups grafted on the cellulose backbone. As a result, despite the HEC possess good film-forming ability compared with PEO, the low capability of salt-dissociation of HEC has exhibited poor ion conductivity of 10^{-6} S cm^{-1}. In order to enhance the electromechanical performance of bio-based SPEs, Huang et al. [53,54] have developed bio-based SPEs introducing Kappa-Carrageenan and Guar Gum for flexible Zn-MnO2 batteries, which are eco-friendly, low-cost, and highly conductive. The Kappa-Carrageenan electrolytes have exhibited excellent ion conductivity of 3.32×10^{-2} Scm^{-1}, fast charging and discharging capability (120.0 mAh g-1 at 6.0 A g^{-1}), impressive cycling stability (80 % remained after 450 cycles) and moderate bending durability (95 % after 300 cycles). Furthermore, the mechanical stiffness of the SPE is further reinforced by employing rice paper as a scaffold. While the guar gum electrolyte-based flexible quasi-solid-state ZIB has delivered enhanced flexibility and conductivity than Kappa-Carrageenan, the eco-friendly electrolyte has astonishing ion conductivity of 1.07×10^{-2} Scm^{-1} at room temperature, which is even higher than conventional polymer electrolytes. The SPE ZIB also delivers fast charging and discharging capability (131.6 mAh g^{-1} at 6.0 A g^{-1}) and effectively suppresses the zinc dendrites formation during cycling with a remarkable cycling cyclability (100 % capacity retention after 1900 cycles, 85 % capacity retention after 2000 cycles at 6.0 A g^{-1}) and high bending durability (81.3 % capacity retention after continuously bending to 180° for 1000 cycles). The biopolymer electrolytes synthesised by Huang et al. have exhibited significant potential for a bio-based electrolyte of high-performance ZIBs and achieve outstanding ion conductivity and cycling performance for SPE-based

ZIBs. Table 1 summarises the reviewed literature and studies in this section, including their molecular structures, ionic conductivity, features and the published year.

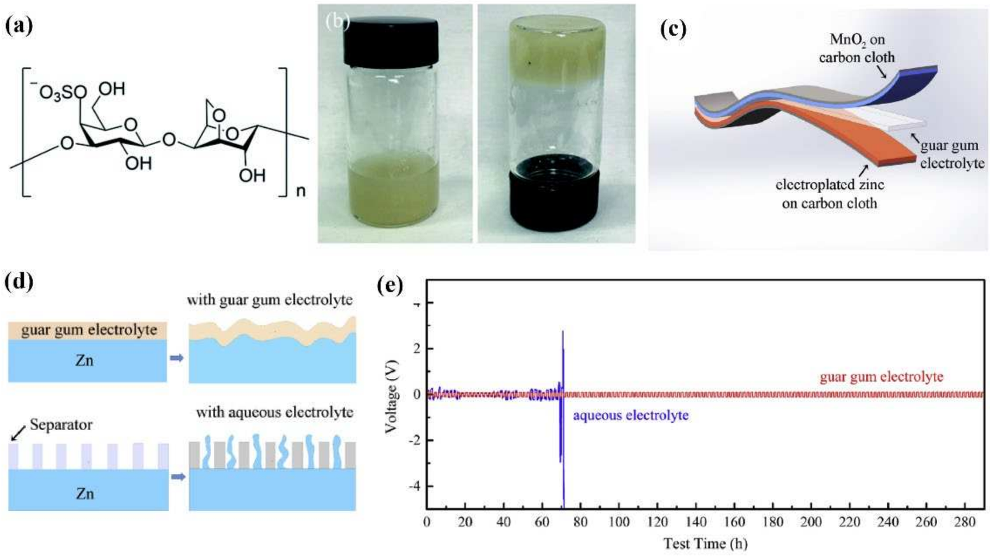
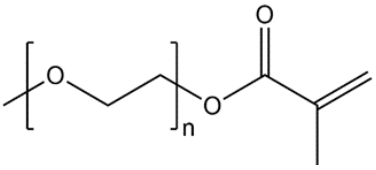
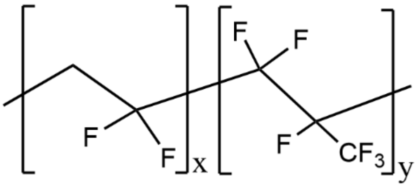
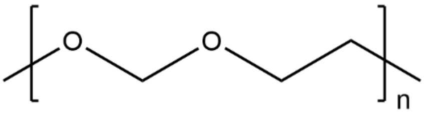
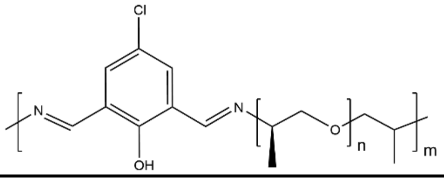


Figure 3. (a) The molecular formula of kappa-carrageenan. (b) Photograph of kappa-carrageenan electrolyte after adding 2 M ZnSO4 and 0.1 M MnSO4 aqueous solutions. Reproduced with permission from [53]. (c) Schematic illustration of the structure of the solid-state Zn–MnO2 battery. (d) Schematic diagram of the morphology change of the zinc foil in guar gum electrolyte and aqueous electrolyte after cycling. (e) Zn stripping/plating from Zn/Zn symmetrical cells at 0.24 mA cm−2 in guar gum electrolyte and aqueous electrolyte. Reproduced with permission from [54].

Table 1. The molecular structure, ionic conductivity and features of homogenous polymer matrix electrolyte.

Name	Molecule Structure	Ionic Conductivity (Scm^{-1})	Features	Year, Ref
PEO-PPM		2.87×10^{-5}	• Low interfacial resistances	2021, [48]
PVdF-HFP		2.44×10^{-5}	• Thermal stability • Electrochemical stability	2020, [50]
Poly(1,3-dioxolane)		1.96×10^{-2}	• Cycling cyclability • Stretchable	2020, [51]
PHP		6×10^{-6}	• Cycling stability • High coulombic efficiency	2021, [52]

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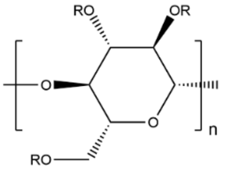
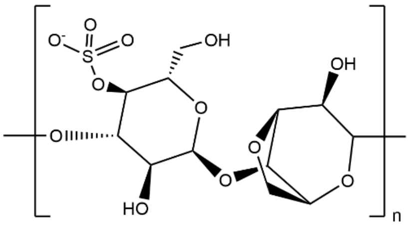
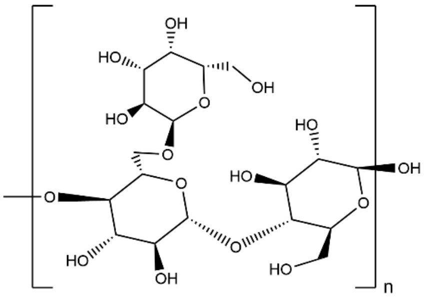
HEC	 R = H or CH_2CH_2OH	1×10^{-6}	• Solubility	2022, [2]
Kappa-Carrageenan		3.32×10^{-2}	• Eco-friendly • Fast charging	2019, [53]
Guar Gum		1.07×10^{-2}	• Eco-friendly • Fast charging • Cycling cyclability	2019, [54]

3.2 Hybrid Polymer Matrix SPEs

The engineering of high-performance SPEs is complex and challenging as the electrolyte has to be conductive with high charging/discharging capability and capacity retention, also mechanically stretchable or stiff to be flexible according to applications. However, it is rare to discover homogeneous materials with all the aforementioned properties. Hence, SPEs composed of hybrid polymer matrices have gained significant research interests, where the polymers are often synthesised through crosslinking, self-assembling, or copolymerization. With various combinations of polymer matrices, this could grant the SPE with favourable properties, such as efficient ion transportation in amorphous structures, crosslinking reinforcement in mechanical robustness and flame-retardant mechanism.

Some of the pioneer works can be found in the SPE study conducted by Ye and Xu [55], where PVDF-HFP were combined with poly(ethylene glycol) dimethyl ethers (PEGDMEs) via a solution casting method. The polymer/polymer matrix has revealed that PEGDME possesses significant salt solvation, while the blending of PVDF-HFP provides mechanical support, resulting in an ionic conductivity at 1.7×10^{-2} Scm^{-1} in ZIB composed of 0.5 M $Zn(TFSI)_2$/PEGDME/PVDF-HFP. However, drawbacks such as cyclability and large weight loss leading to ion conductivity decrement were yet to be investigated in the early work. Rathika et al. [56] employed a similar blending approach to synthesize 90 wt% PEO/10 wt% PVdF blended polymer electrolyte with 15 wt% Zinc triflate salt ($Zn(CF_3SO_3)_2$), as illustrated in Figure 4(a). This leads to the formation of an amorphous phase obtained by reducing the crystallinity of the host polymer blend matrix. Also, the blending of the polymer/polymer interface could also induce the formation of ion-polymer interactions between the polymer matrix and zinc triflate salt is depicted in Figure 4(b). This unique amorphous structure is able to reduce the cohesive force of polymer blend chains and provide a favourable segmental mobility, which improves charge mobility within the polymer blend electrolyte system.

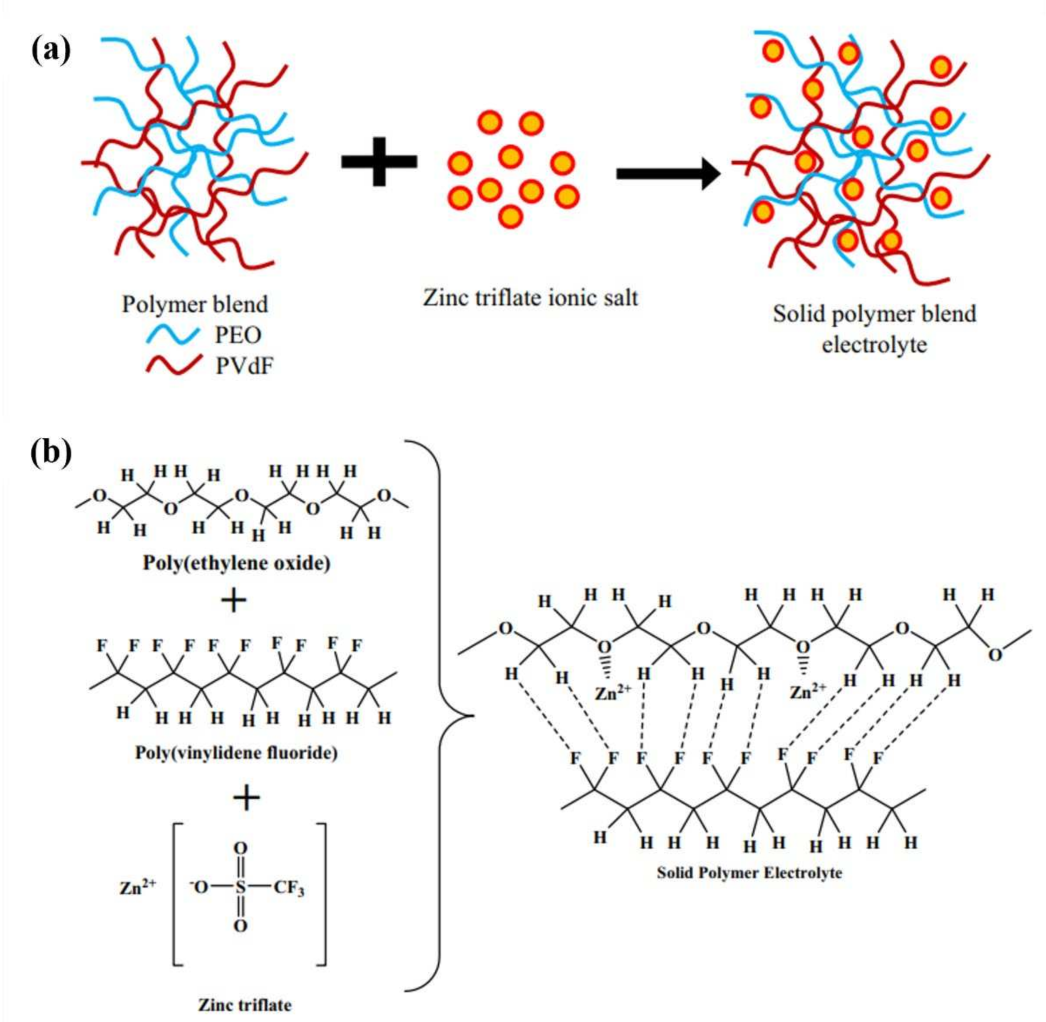


Figure 4. Schematic diagrams of the complete mechanism for the formation of solid polymer blend electrolyte systems. Reproduced with permission from [56].

Except for polymers blending, Lu et al. [57] proposed the synthesis approach of manipulating heteroleptic coordination that integrates polyacrylamide (PAAM) ligands with acetamide coligands for Zinc ion centres. As illustrated in Figure 5, the in-situ catalytic polymerization initiated by Lewis-acidic Deep eutectic solvents (DESs) has significantly enhanced the mobility of Zn^{2+} and polymer by enabling the formation of eutectic ion channels with both labile Zn^{2+}–polymer bonding. The heteroleptic coordination polymer electrolytes (HCPEs) have exhibited an ionic conductivity of 4.7×10^{-3} Scm^{-1} and a Zn^{2+} transference number of 0.44 at room temperature, attributing to the ligand exchange process to accelerate long-range Zn^{2+} transport. The increment of available distinct ligands in the limited metal coordination sphere not only established a well-lubricated ion channel to reduce the ionic migration barrier, but it also produced a flexible coordination sphere to enable fast ligand exchange. The solid-state ZIB also performed reversibility of the Zn plating/stripping process (1200 h), the cyclability of 350 cycles with Mo_6S_8 cathodes and Coulombic efficiency at ~99%. Furthermore, the HCPEs are also flexible and highly stretchable elastomers rather than mechanically rigid bodies. Impressively, the HCPEs possess a maximum stretchability of more than 800% at a stretching speed of 20 mm/min, attributed to the enhanced ligand exchange dynamics.

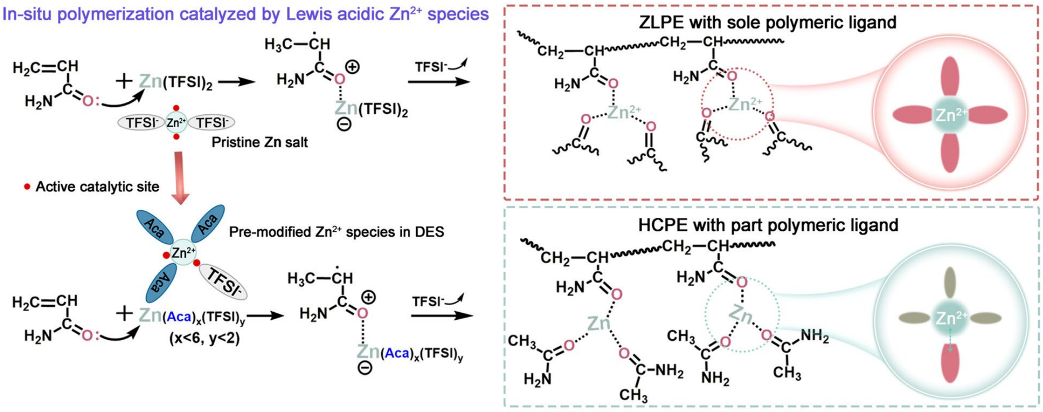


Figure 5. Schematic illustration of the concept of HCPEs. The eutectic intermolecular interactions guarantee charge separation; the regulation of the Zn2+-ion coordination environment minimizes coordinatively structural locking. Reproduced with permission from [57].

Other than hybrid polymer composition, the inclusion of bio-based polymer into hybrid polymer matrix was often adopted in SPEs research, as biopolymer offers mechanical supports, biocompatibility and environmental friendliness. Li et al. [58] introduced a gelatin and polyacrylamide (PAM)-based hierarchical polymer electrolyte (HPE) with an a-MnO2 nanorod and carbon nanotube (CNT) cathode. Figure 6 illustrates the synthesis route of the HPE, which was synthesized by grafting PAM onto gelatin chains that are filled in the network of a polyacrylonitrile (PAN) electrospun fibre membrane through a facile free radical polymerization approach. The porous hierarchical structure and a high level of water retention in the polymeric network have offered significant ionic conductivity of 1.76 × 10^{-2} Scm^{-1} at room temperature, while the superior interfacial contact between the electrodes and HPE endows enhanced ion diffusion and higher reaction kinetics for long-term cycling (capacity retention of 97 % after 1000 cycles at 2772 mA g^{-1}). Moreover, the grafting of PAM onto a gelatin hydrogel (gelatin-g-PAM) has offered favourable mechanical strength and excellent capacity retention (averaging above 90%) after under several destructive conditions, including being cut, bent, hammered, punctured, burnt, sewed using commercial sewing machine and even rinsed without any packaging.

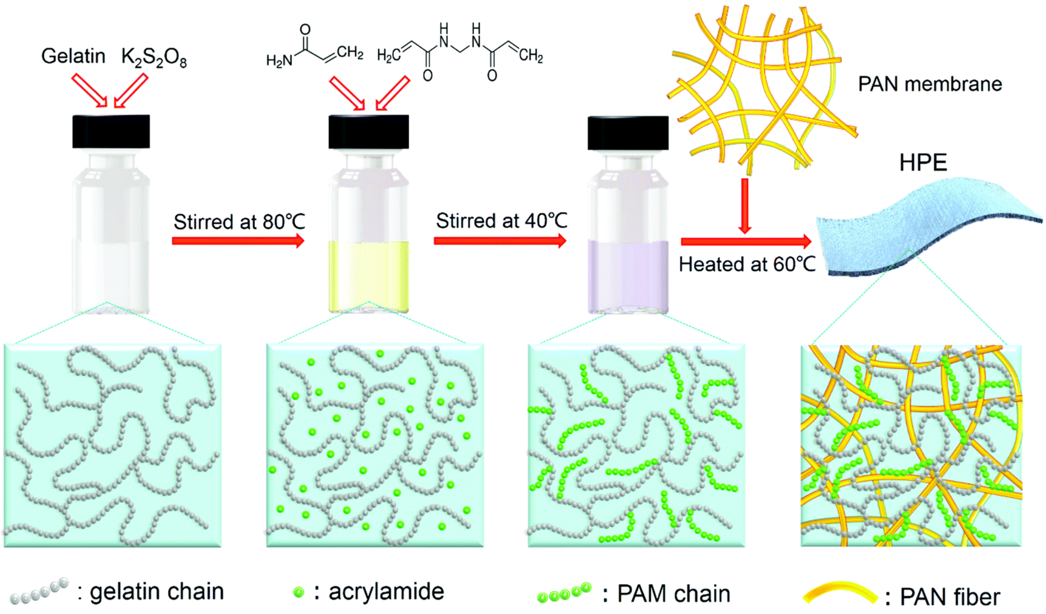


Figure 6. Schematic of the synthesis route to the HPE. The hierarchically structured HPE was synthesized by grafting PAM on gelatin chains that are filled in the network of PAN electrospun fiber membrane through a facile free radical polymerization approach. Reproduced with permission from [58].

The polymeric architecture of SPE is essential to be engineered as it constructs the pathway of ion transportation and also polymer mobility that provides mechanical stability. Qiu et al. [59] fabricated a novel zwitterionic triple-network structure hydrogel electrolyte incorporating PAM, gelatin and [(2-methylacryloxy)ethyl]dimethyl-(3-sulfonic acid propyl)ammonium hydroxide (DMAPS) for a flexible ZIB. The SPE was synthesized using a facile method, as revealed in Figure 7. (a), where the mixture was polymerized at 60°C and refrigerated. In terms of electromechanical efficiency, the addition of DMAPS on PAM/gelatin ZIBs has exhibited an ionic conductivity of 3.51× 10^{-2} Scm^{-1}. This can be attributed to the intrinsic zwitterionic groups on polymer chains, which paves separate ion migration channels for cations and anions, thus effectively accelerating the rate of ion transport. The PAM/gelatin/DMAPS electrolyte has also revealed its self-healing ability owing to the hydrogen bond interaction and delivered an excellent coulombic efficiency of over 99%. Additionally, the mechanical tests in Figure 7(c-d) has suggested that the inclusion of gelatin improves the elasticity and the toughness of the electrolyte, while DMAPS reduces the elasticity and toughness owing to its poly-zwitterion character.

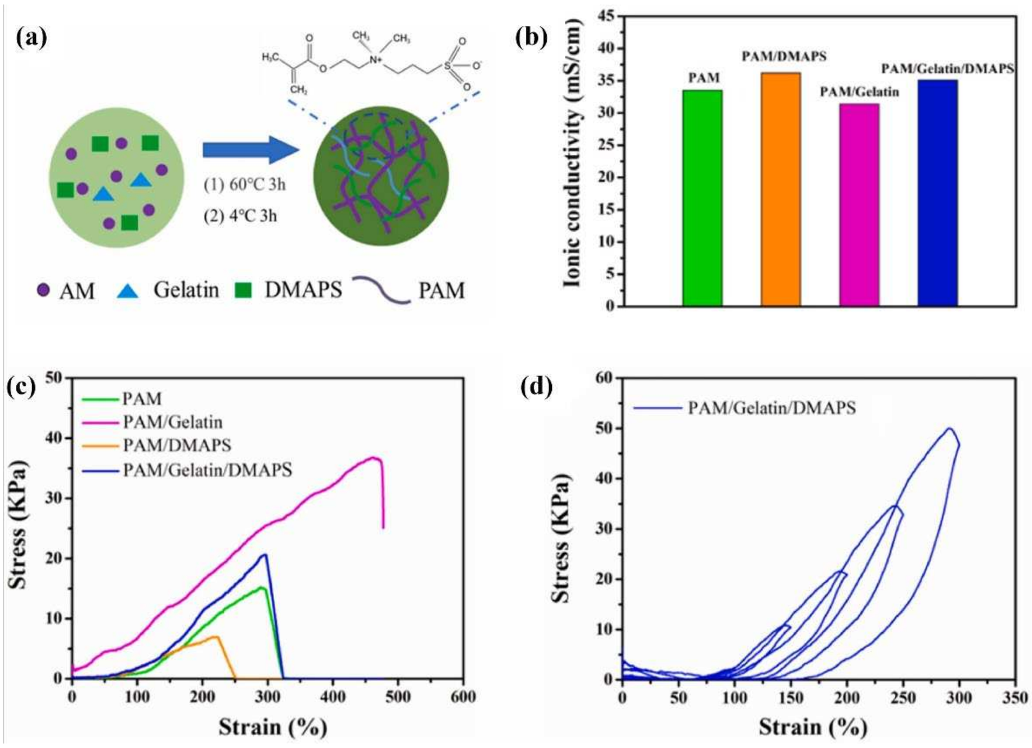


Figure 7. (a) Schematic illustration of the synthesis of PAM/Gelatin/DMAPS hydrogel with triple-network structure. (b) The ionic conductivity of different hydrogel. (c) Tensile stress-strain curves of different hydrogels. (d) Cyclic loading-unloading curves of PAM/Gelatin/DMAPS hydrogel with stretch ranges of 50–300%. Reproduced with permission from [59].

Dueramae et al. [60] have proposed a novel polymer host from carboxymethyl cellulose (CMC) and poly(N-isopropylacrylamide) (PNiPAM) as an SPE for ZIBs, which was synthesized via solution casting method. As a result, the blended CMC/PNiPAM SPEs have revealed magnificent tensile strength and modulus at 37.9 MPa and 2.1 GPa, which can be attributed to the increased stiffness of the films following the addition of PNiPAM, which contains both –NH and –OH groups that participate in strong intermolecular bonding and electrostatic interactions with the carboxyl and hydroxyl groups of CMC. These interactions may include H-bonds, dipole-dipole, and charge effects. Moreover, the thermal stability of the CMC/PNiPAM was also investigated, and the blended SPE was thermally more stable with a higher decomposition temperature compared to the pure CMC. The enhancement in thermal stability was suggested to be offered by the restricted chain motion between the respective functional groups of the CMC and PNiPAM molecules. The SPEs have exhibited moderate ionic conductivity of 1.68×10^{-4} S cm^{-1} and a high Zn^{2+} ion transference number of 0.56, owing to the porous structure that likely supported Zn- movement in the SPEs containing zinc trifate.

Among the reviews, bio-based polymers such as gelatin, cellulose and gums have generally exhibited favourable electromechanical properties due to their intrinsic polymer structure. For instance, the linear chains with carboxymethyl substitution of CMC not only provide high mechanical flexibility and stability, but also create aligned charge transport paths. To further increase the biocompatibility of SPEs, Zhou et al. [61] developed a cellulose aerogel-gelatin (CAG) solid electrolyte for implantable, biodegradable transient zinc ion battery (TZIB). As shown in Figure 8, the gelatin electrolyte was grafted into a cellulose aerogel (CA) 3D porous framework through a super-assembly strategy to obtain a CAG film as an SPE membrane. Subsequently, the 3D CA architecture was obtained via freeze-drying and pristine gelatin chain injection. The TZIB was then super-assembled from a flexible silk protein film, in situ evaporated Au film, screen printed Zn film, and MnO2/rGO hybrid materials as the encapsulation layer, collector, cathode and anode materials, respectively.

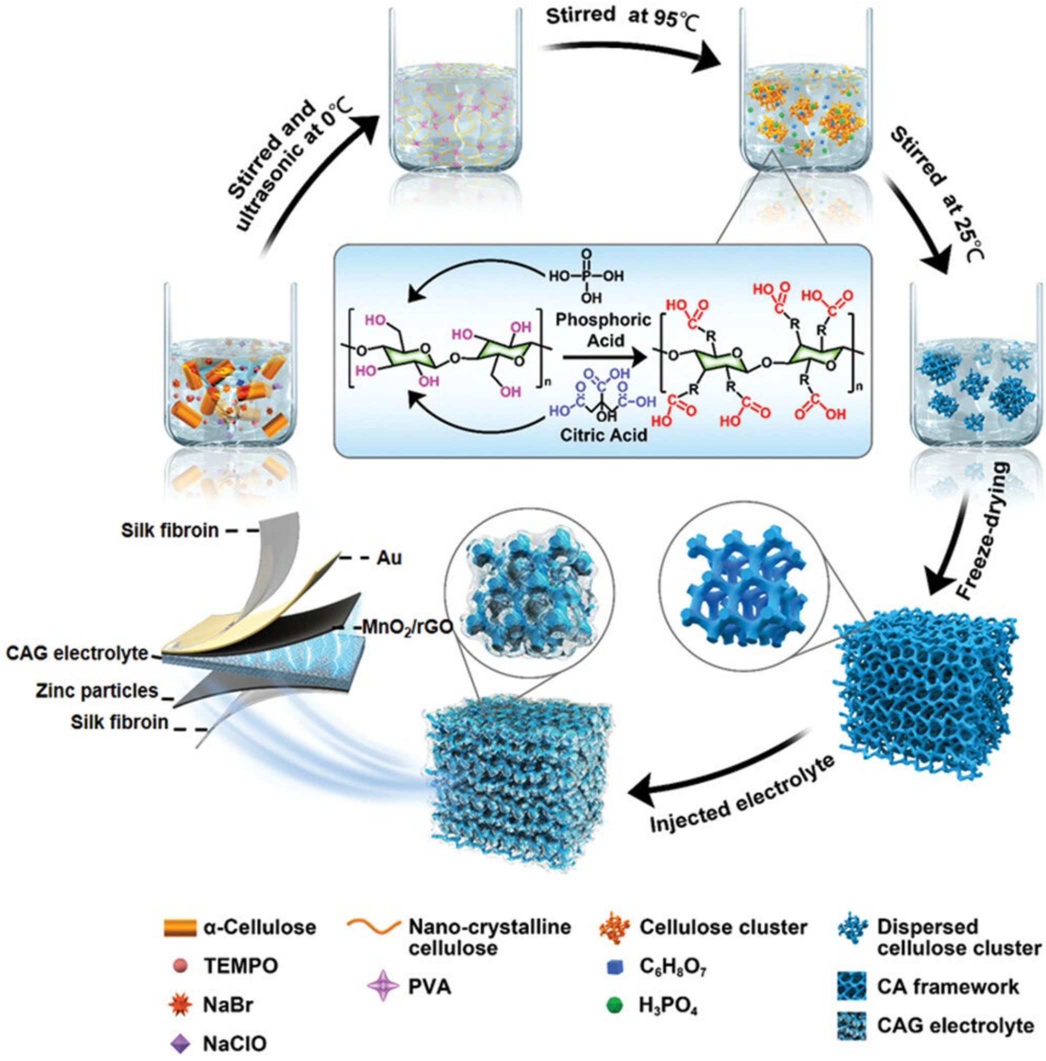


Figure 8. Schematic depicting the super-assembly synthesis route of the cellulose aerogel framework. Reproduced with permission from [61].

The CAG film has obtained a highly porous 3D structure, as illustrated in Figure 9(a), with high liquid storage capacity. This unique structure has endowed ultra-high ionic conductivity of 1.23×10^{-2} Scm^{-1} at room temperature, while maintaining great mechanical strength (i.e. bending angle >120°) and biodegradability. The porous 3D framework structure is suggested to increase the absorption of electrolytes and the strength of the TZIB body, whereas the micropores can be used for the migration

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of electrolyte ions. The CAG-based TZIB has also achieved good cyclability performance while ensuring implantability and biodegradability, the capacity retention can still reach 96.4 % after 15 cycles and 95.4% after being bent or folded. Furthermore, the TZIB can also be biodegraded by phosphate-buffered saline (PBS) solution after 30 days, as revealed in Figure 9(f). Importantly, TZIB's degradation materials do not contain any heavy metal ions, toxic polymers, or electrolytes that affect health, which can be potential self-powered transient electronics or conventional self-powered implantable medical devices in the future.

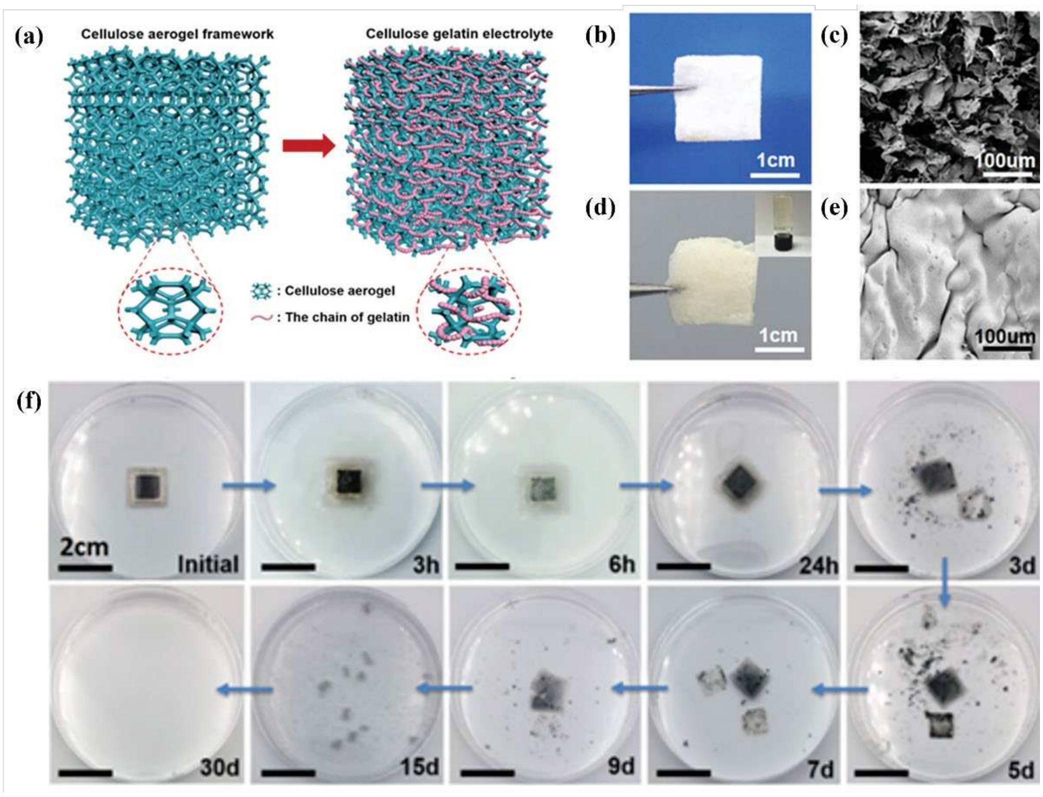


Figure 9. (a) Structure and assembly of cellulose gelatin electrolyte. (b, c) Optical image and SEM image of the CA framework. (d, e) Optical and SEM images of the CAG electrolyte film. (f) Optical images demonstrating the biodegradation profile of an encapsulated battery (device size of 1.5 × 1.5 × 0.3 cm^{-3}) in buffered protease solution at 37 °C. Reproduced with permission from [61].

Similar research work also conducted by Zhou et al. [62] have fabricated TZIB devices, including plasticized gelatin-silk fibroin electrolyte film and a dual-yarn electrode structure. The gelatin-based electrolyte was synthesized as illustrated in Figure 10, where the gelatin solution was mixed with dissolved silk fibre. After ultrasonic treatment, the gelatin-based electrolyte was placed on the surface of the plasticized gelatin-silk protein film and obtained solidified film via rapid cooling to room temperature. During the synthesis process, the polypeptide backbone of silk protein would break into molecular conformations and be dispersed with doped gelatin chains in the formic acid. The plasticized silk protein film is formed after the volatilization of acid. Eventually, the gelatin molecule gradually recovers from the randomly coiled state to an ordered triple helix structure. This structure offers the β-sheets with strong mechanical properties evenly embedded in the gelatin-protein composite network, forming a uniform biomass composite framework. As a result, the TZIB exhibits a high specific capacity (311.7 mA h g^{-1}) and excellent cycle stability (94.6 % capacity retention after 100 cycles) due to the high ionic conductivity of 5.68×10^{-3} Scm^{-1} at room temperature. In the aspect of mechanical stability, the device also demonstrates significant shape plasticity (high capacity retention of 82.5% after 80 bends) and good biodegradability (fully degraded in 45 days under enzyme digestion).

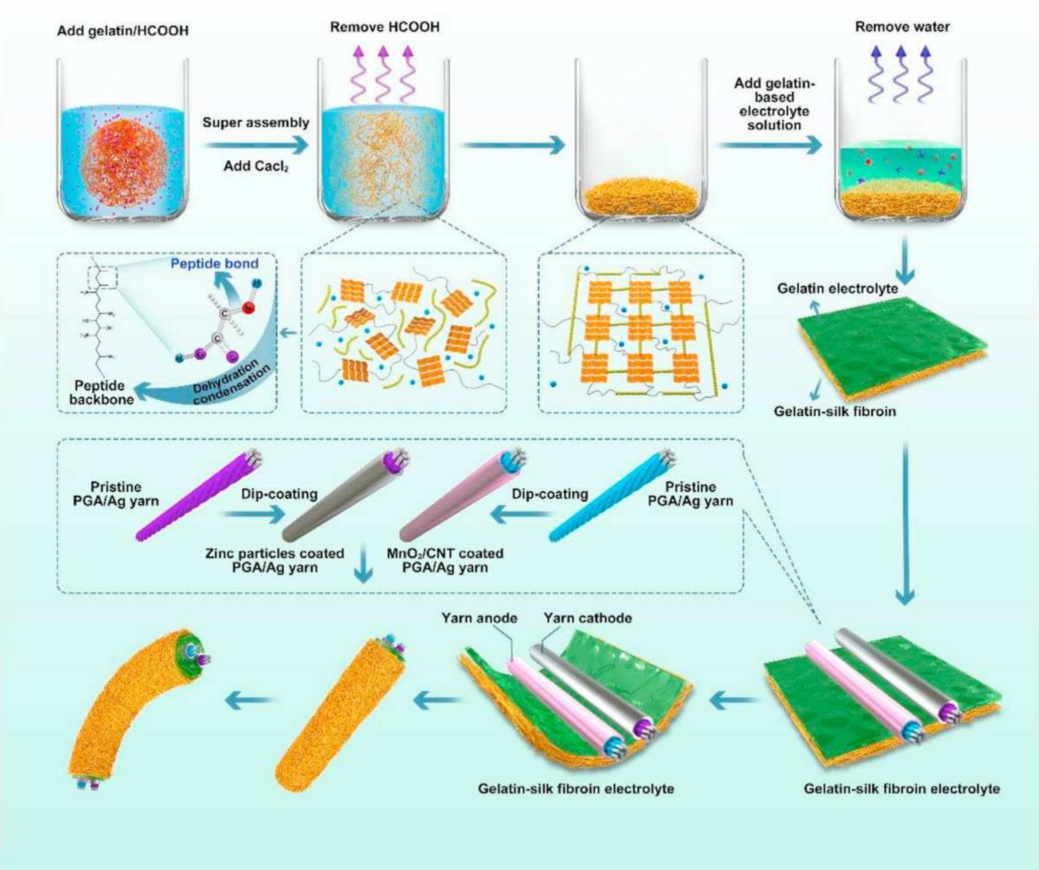
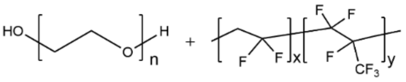
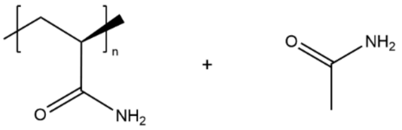
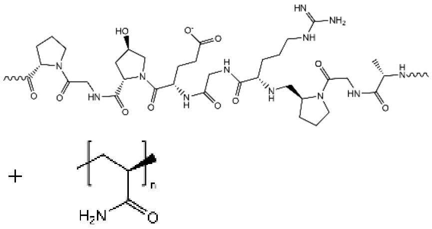
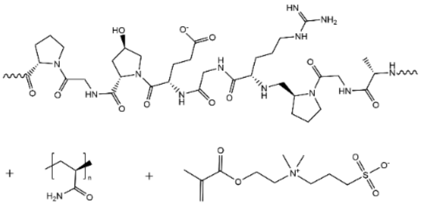
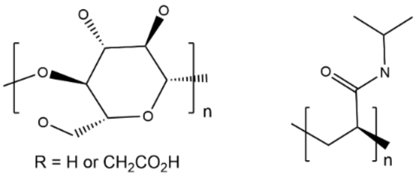
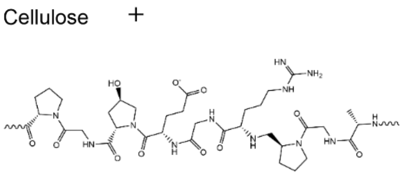
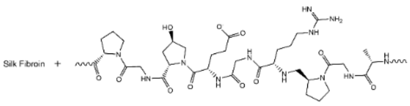
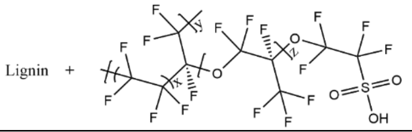


Figure 10. Schematic diagram of fabrication and encapsulation of the fiber-shaped TZIB. TZIB, transient zinc-ion battery. Reproduced with permission from [62].

Table 2 summarizes the reviewed literature and studies in this section, including their molecular structures, ionic conductivity, features and the published year. In general, the incorporation of hybrid polymer system has exhibited enhancement in ionic conductivity, capacity retention and mechanical flexibility, especially with the inclusion of biopolymer (i.e. Gelatin, Cellulose). The intrinsic structure of these biopolymers can form unique 3D architectures with various polymer matrix via crosslinking and polymerization, such as heteroleptic [57], hierarchical [58], zwitterionic [59] and super-assembled porous structures [61]. These structures possess high porosity that increase the absorption of electrolytes, provide extra channels for the migration of electrolyte ions and reinforce the integrity of the SPE by offering additional support in mechanical robustness. The engineered structures were even suggested to offer fast ligand exchanging and self-healing capacity owing to the hydrogen bond interaction. However, compared the wide investigation in electromechanical efficiency, the improvement in mechanical modulus seems relatively impoverished, specifically against the uncontrollable growth of dendritic Zn during the cycling process were rarely discussed, as the dendrites may pierce through polymer separator and induce safety concerns extremely restricting the further application [63,64].

Table 2. The molecular structure, ionic conductivity and features of hybrid polymer matrix electrolyte.

Name	Molecule Structure	Ionic Conductivity (Scm^{-1})	Features	Year, Ref
PEO/PVDF		2.5×10^{-5}	- Segmental mobility	2017, [56]
PAAM/Acetamide		4.7×10^{-3}	- Reversibility - Cyclability	2022, [57]
Gelatin/PAM		1.76×10^{-2}	- High areal energy density - Capacity retention of 97% after 1000 cycles - Wearability	2018, [58]
PAM/DMAPS/Gelatin		3.51×10^{-2}	- Mechanical stability - Flexible - Excellent coulombic efficiency	2022, [59]
CMC/PNiPAM		1.68×10^{-4}	- Great tensile strength and modulus - Flame retarded	2020, [60]
Cellulose/Gelatin		1.23×10^{-2}	- Biodegradable	2022, [61]
Gelatin-silk fibroin		5.68×10^{-3}	- Biodegradable - Excellent cycle stability - Shape plasticity	2022, [62]
Lignin/Nafion		9.1×10^{-3}	- Long cycle life	2019, [65]

3.3 Nanocomposite Polymer Electrolytes

Except for incorporating various polymer matrices via cross-linking or polymerisation, including a small quantity of nanocomposites has also attracted research interests in enhancing the mechanical, thermal, electrical and electrochemical properties of polymer electrolytes. This is due to the unique microstructure with huge lateral dimensions and thin thickness of the two-dimensional(2D) materials that endows significant specific surface area and thermal/electrical conductivities. Sownthari and Austin Suthanthiraraj [66] have employed organically modified montmorillonite (MMT) as an additive to enhance the electromechanical properties of poly(ϵ-caprolactone) (PCL) – based electrolyte via solution casting method. With 15 wt% of MMT, the modified MMT-PCL electrolyte has acquired moderate ionic conductivity of 9.5×10^{-5} Scm^{-1}. This can be attributed to the enhanced dissociation of ion pairs and higher aggregates of dopant salt facilitated by the high dielectric constant of the nanoclay, where the number of free triflate ions increases the number of free Zn^{2+} for conduction. However, the MMT-PCL showed unsatisfied thermal stability, where an earlier decomposition temperature was observed due to the decrease in the electron density caused by the interaction of Zn^{2+} ions with the carbonyl oxygen. To investigate the feasibility of applying nanofillers into a hybrid polymer matrix, Sai Prasanna and Austin Suthanthiraraj [67] have incorporated zirconia (ZrO_2) nanofillers into poly(vinyl chloride)(PVC)/poly(ethyl methacrylate) (PEMA)-based GPE also via solution casting method. As a result, the 3 wt% of ZrO_2 dispersed in PVC (30 wt%)/PEMA (70 wt%) GPE has achieved enhanced room temperature ionic conductivity of 3.63×10^{-4} $Scm{-1}$. This is due to the Lewis acid-base interaction between the electrolytic species and OH/O sites of the filler surface, which provides additional hopping sites and conducting pathways for the migrating charged species. Also, the addition of ZrO_2 to the electrolyte can strengthen the flexibility of the polymer chains by hindering its re-organization and stabilizes the amorphous phase of the composite GPE. Nonetheless, the thermal stability was not comprehensively discussed while the degradation initiated after the sample reached 100˚C.

To further strengthen the electromechanical performance of nanofiller-infused electrolyte, Chen et al. [68] have fabricated an SPE based on the poly(vinylidene fluoride-*co*-hexafluoropropylene) filled by the poly(methyl acrylate) grafted MXenes (denoted as PVHF/MXene-*g*-PMA via blade casting method, for an actual all-solid-state ZIBs with superior stability and reliability. Being a relatively new member of 2D materials, MXene (denoted as $M_{n+1}X_nT_x$, M: transition metal, X: carbon or nitrogen, T: terminating group (O, OH or F)) possesses enormous potential to be an advanced inorganic filler due to its large specific surface area and abundant surface functional groups. As shown in Figure 11(a), LiF/HCL solution was used to obtain 2D MXene first, and the PMA-grafted MXene (MXene-*g*-PMA) was prepared via in-situ surface polymerization based on the Ce(iv)/HNO_3 redox system, where the hydroxyl groups on the surface of MXene will provide active grafting sites for the PMA, while the PMA has abundant H atoms to form F–H hydrogen bonds with PVHF. The resulting SPE with PMA content of 0.05 has exhibited an excellent ion conductivity of 2.69×10^{-4} S cm^{-1} at room temperature, which is three orders of magnitude larger ionic conductivity than the PVHF matrix owing to the high electrical conductivity of MXene. Importantly, the SPE is able to maintain significant ionic conductivities at different temperatures ranging from −25 °C to 85 °C, as revealed in Figure 11(b). Mechanical-wise, Figure 11(c) suggests that the PVHF/MXene-*g*-PMA offers a significant enhancement in the elongation (60.1%), where the stress was mostly maintained at 13.2 MPa compared with the neat PVHF. Moreover, a significant coulombic efficiency of 98.9% was maintained for 350 cycles based on the long-term cyclic stability test of the Zn/Cu cell. The dendrite-free Zn plating/stripping with high reversibility was achieved over 1000 h cycles at room temperature and 200 h at high temperature, where remarkable capacity retention was maintained above 90% after 10000 cycles at room temperature for more than 90 days.

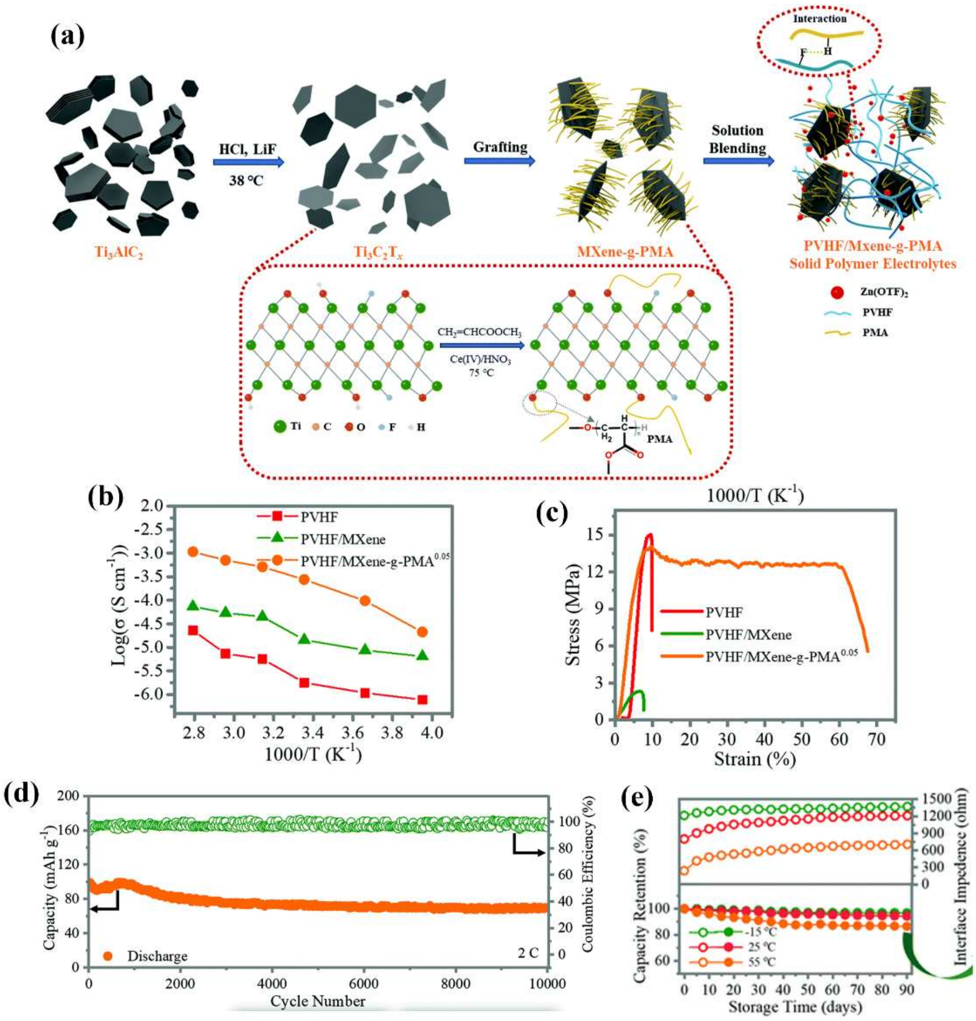


Figure 11. (a) Schematic illustration of the overall preparation process of the SPEs. (b) Temperature scan of the ionic conductivities. (c) strain-stress curves. (d) Cycling performance and coulombic efficiency. (e) Capacity retention and interface impedance after being stored for 90 days at different temperatures. Reproduced with permission from [68].

Liu et al. [69] reported a GPE for high-performance ZIBs employing MXene-derived TiO_2 nanosheets as an additive, which was obtained via hydrothermal reaction. The nanosheet was mixed with Polyvinyl alcohol (PVA) and $Zn(CF_3SO_3)_2$ in dissolved solution and frozen via the solution casting method, as revealed in Figure 12(a). With the 3 wt% of TiO_2 additives, the resulting GPE (PZ3T) performed a moderate ionic conductivity of 1.243×10^{-5} Scm^{-1} and excellent mechanical reinforcement, where the tensile strength and elongation at break were significantly improved, as illustrated in Figure 12(b). Importantly, the GPE has also exhibited self-healing behaviour owing to the hydroxyl groups and hydrogen bonds between PVA chains and TiO_2 nanoparticles. Moreover, excellent Coulombic efficiency of 99.8% and stable and reversible Zn plating/stripping for over 3000 hours were observed, attributing to the dendrite suppression effect in the PVA-Zn(CF3SO3)2–3% TiO2 (PZ3T) GPE.

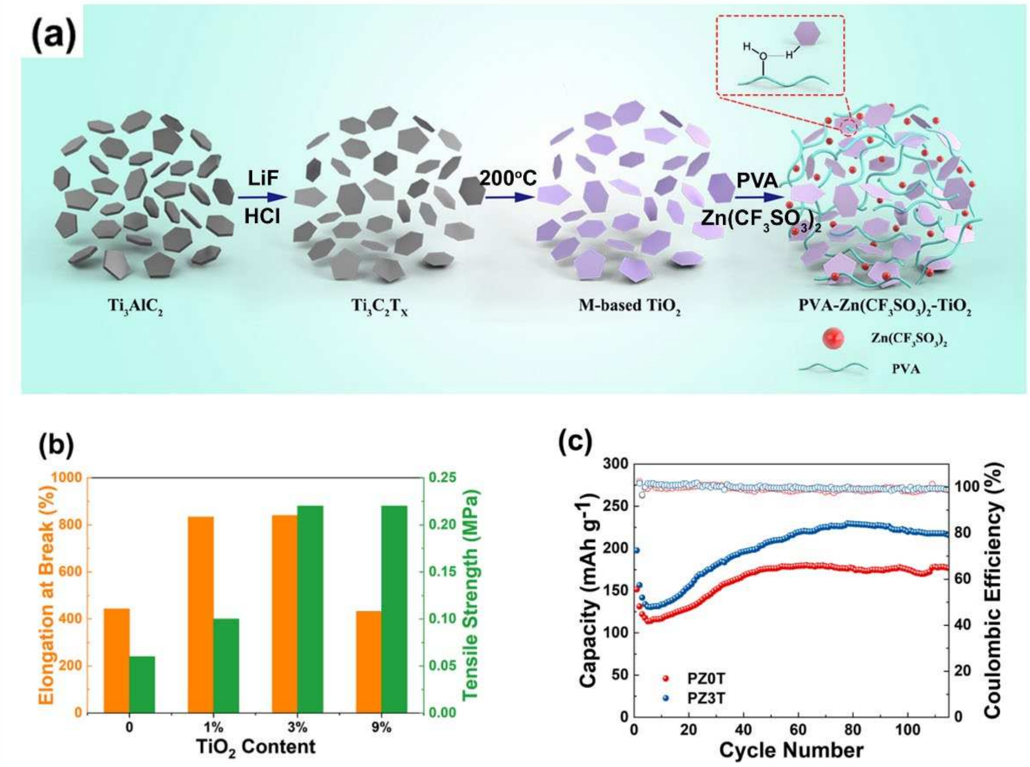
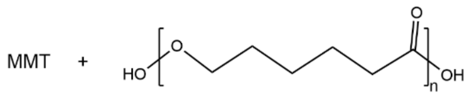
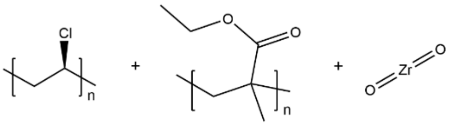
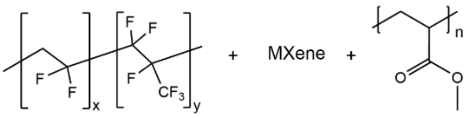
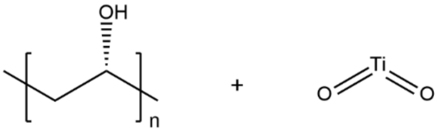


Figure 12. (a) Schematic diagrams for the fabrication of gel polymer electrolyte with TiO2 from Ti3C2Tx MXene; (b) elongation at break and tensile strength of the as-prepared GPEs with different amounts of TiO2 added; (c) Cycling performance and Coulombic efficiency of PZ0T and PZ3T GPEs at 200 mA g− 1 between 0.2 and 1.6 V. Reproduced with permission from [69].

Table 3 summarizes this section's reviewed literature and studies, including their molecular structures, ionic conductivity, features and the published year. Compared to homogenous polymer and hybrid polymer matrix designs, the inclusion of nanoparticles into electrolytes for ZIBs is relatively rare and remains unexplored. In general, the addition of nanomaterials would offer advancement to ionic conductivity and mechanical robustness of the SPEs, where the fillers are able to form ion migration paths on the filler surface and decrease the polymer crystallinity [70]. MXene has exhibited astonishing electromechanical performance throughout the review, including capacity retention, long-life cycling, and self-healing mechanisms. Furthermore, it significantly reinforces the structural integrity of the polymer in elongation and tensile strength, enabling MXene as an anti-corrosion elastic constraint (AEC) against the corrosion of zinc dendrites by inducing uniform zinc deposition on the smooth surface of the TiO_2-based SPE.

Table 3. The molecular structure, ionic conductivity and features of nanocomposite electrolytes.

Name	Molecule Structure	Ionic Conductivity (Scm^{-1})	Feature	Year, Ref
MMT/PCL		9.5 × 10^{-5}	- Biodegradable - Weakened thermal stability	2015, [66]
PVC/PEMA/ ZrO2		3.63 × 10^{-4}	- Moderate thermal stability	2019, [67]

PVHF/Mxene /PMA		2.69×10^{-4}	- Excellent capacity retention - Wide range of operational temperature - Long-life cycling	2021, [68]
PVA/TiO2		1.243×10^{-5}	- Reinforcement in mechanical stability - Self-healing	2022, [69]

4. Summary and Perspectives

In this review, we have discussed the state-of-the-art development of solid polymer electrolytes for zinc-ion batteries. We have highlighted the cutting-edge technologies of using SPEs in zinc-ion batteries, including their high safety, low cost, and potential for high energy density applications. Different routes employing polymer and polymer composites as SPEs to realise high-performance and safe zinc-ion batteries are also introduced and discussed, including homogenous polymer SPEs, hybrids polymer SPEs, and nanocomposites polymer SPEs.

In terms of the homogenous polymer SPEs, polymers like PEO, PVdF, PAM, and PVA can improve ionic conductivity and may be used to be part of the SPEs and applied in ZIBs. Unfortunately, the relatively low ionic conductivity seriously restricts further practical applications. Among them, SPEs containing bio-based polymers show good mechanical properties and promising electrical chemical properties when applied in ZIBs, which are attracting abroad attention.

On top of homogenous polymer SPEs, the addition of other functional polymers can obviously improve the ionic conductivity and tensile strength and can endow ZIBs with excellent electrochemical performance. The combination of various polymers can integrate different functions from each component and impart the SPEs' outstanding compatibility with electrolytes. Usually, various polymers may form crosslinking, self-assembly structures that can significantly enhance the mechanical strength of SPEs, improve the ionic conductivity of ZIBs, and realise promising electrochemical properties and safety. Specifically, the mixing of polymer interfaces can induce the formation of ion/polymer interactions that would facilitate the movement of zinc ions and achieve great ion conductivity. In addition, the unique amorphous structure can also reduce the cohesive force of polymer blend chains and offer favourable segmental mobility that can improve ion mobility within the polymer blend electrolyte system. Surprisingly, biopolymers such as gelatin, gums, and cellulose play critical roles in hybrid polymer SPEs and can provide mechanical support, biocompatibility and environmental friendliness. These SPEs with biopolymers exhibit favourable electrochemical properties due to their intrinsic features, e.g., the linear chains with carboxymethyl substitution of CMC may provide high mechanical flexibility and stability and meanwhile create aligned charge transport paths.

At last, for the polymer nanocomposites SPEs, the incorporation of nanomaterials will usually significantly improve the ionic conductivity and mechanical performance. Nanomaterials may interact with polymers and form interfaces inside the polymer/inorganic composites system that can act as pathways for the zinc ions and facilitate ionic transportation efficiency. Additionally, considering the intrinsic property of inorganic materials, the addition of inorganic materials can usually obviously improve the surface modulus of SPEs which may improve the operating stability and battery safety. Also, the improved modulus of SPEs induced by inorganic materials will also benefit the suppression of zinc dendrites.

In summary, SPEs hold great promise for the development of safe, low-cost, and high-performance zinc-ion batteries. Polymer engineering plays key roles in resolving current issues encountered in the synthesis and design of SPEs applied in ZIBs. While there are still some issues remaining, below are some challenges and perspectives raised for reference.

1. In terms of SPEs, one of the major challenges is the low ionic conductivity at room temperature, which limits the performance of zinc-ion batteries. Normally, a high ionic conductivity will improve the efficiency of ion transportation that can help achieve great electrochemical performance and meanwhile can alleviate the reduction of zinc metal on the surface of anode. To address this challenge, several strategies can be employed, including the incorporation of high-conductivity salts, the functional polymers, and the use of nanocomposites.
2. Another challenge is the mechanical stability of SPEs. Most polymers used as SPEs are soft and easily deformable, which can result in the formation of dendrites and short-circuits in the battery. To address this challenge, several strategies can be employed, including the incorporation of rigid segments into the polymer backbone, the use of crosslinked polymers, and the use of ceramic fillers. According to the methods used for lithium metal batteries, the addition of inorganic materials can improve the Young's modulus of SPEs, and efficiently suppress the growth of metal dendrites. Therefore, in terms of ZIBs, the principle can also be utilised to address the safety issue induced by zinc dendrites. To date, the related studies are very limited, so this strategy might be a promising method to improve the electrochemical property and safety of ZIBs in future study.
3. Furthermore, the long-term stability of SPEs needs to be further improved. Many SPEs undergo degradation over time due to the presence of the electrochemical active species, which can lead to the deterioration of ionic conductivity and capacity. Crosslinking and in-situ polymerization methods would be reasonable methods to improve the chemical and thermal stability of the SPEs. Additionally, the incorporation of inorganic nanomaterials would also help enhance the stability of SPEs attributed to the stability of the crystalline structures.
4. At last, biomass based SPEs show promising potential in improving the ionic conductivity, biocompatibility and stability of the ZIBs. Biomass polymers or macromolecules usually contain plenty of functional groups, which can provide lots of active sites that can interact with zinc salts and electrolytes. Therefore, biomass based SPEs can show great compatibility with zinc salts and electrolytes and thus have very stable crosslinking structures and ion channels. These advantages enable biomass based SPEs as a research hotpot for high-performance and safe ZIBs.

Author Contributions: Conceptualization, I.M.D.C.C and W.W.; methodology, W.W.; software, W.W.; formal analysis, A.L. and B.L.; investigation, I.M.D.C.C.; resources, W.W., D.X.M. and L.X.; writing—original draft preparation, I.M.D.C.C. and W.W..; writing—review and editing, I.M.D.C.C. and W.W.; visualization, B.L.; supervision, W.W., A.L.-S.E.; project administration, A.L.-S.E. All authors have read and agreed to the published version of the manuscript.

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References

1. Ma, L.; Schroeder, M.A.; Pollard, T.P.; Borodin, O.; Ding, M.S.; Sun, R.; Cao, L.; Ho, J.; Baker, D.R.; Wang, C. Critical factors dictating reversibility of the zinc metal anode. *Energy & Environmental Materials* **2020**, *3*, 516-521.
2. Brige, A.; Olsson, M.; Xiong, S.; Matic, A. A comparative study of hydroxyethylcellulose-based solid polymer electrolytes for solid state Zn batteries. *Nano Select* **2022**, *4*, 102-111, doi:10.1002/nano.202200221.
3. Chuai, M.; Yang, J.; Tan, R.; Liu, Z.; Yuan, Y.; Xu, Y.; Sun, J.; Wang, M.; Zheng, X.; Chen, N. Theory-Driven Design of a Cationic Accelerator for High-Performance Electrolytic MnO2–Zn Batteries. *Advanced Materials* **2022**, *34*, 2203249.
4. Wang, G.; Kohn, B.; Scheler, U.; Wang, F.; Oswald, S.; Löffler, M.; Tan, D.; Zhang, P.; Zhang, J.; Feng, X. A High-Voltage, Dendrite-Free, and Durable Zn–Graphite Battery. *Advanced Materials* **2020**, *32*, 1905681.
5. Zuo, Y.; Wang, K.; Pei, P.; Wei, M.; Liu, X.; Xiao, Y.; Zhang, P. Zinc dendrite growth and inhibition strategies. *Materials Today Energy* **2021**, *20*, 100692.
6. Yang, Q.; Li, Q.; Liu, Z.; Wang, D.; Guo, Y.; Li, X.; Tang, Y.; Li, H.; Dong, B.; Zhi, C. Dendrites in Zn-based batteries. *Advanced Materials* **2020**, *32*, 2001854.

7. Lu, W.; Xie, C.; Zhang, H.; Li, X. Inhibition of zinc dendrite growth in zinc-based batteries. *ChemSusChem* **2018**, *11*, 3996-4006.
8. Cao, Z.; Zhu, X.; Xu, D.; Dong, P.; Chee, M.O.L.; Li, X.; Zhu, K.; Ye, M.; Shen, J. Eliminating Zn dendrites by commercial cyanoacrylate adhesive for zinc ion battery. *Energy Storage Materials* **2021**, *36*, 132-138.
9. Yang, Z.; Lv, C.; Li, W.; Wu, T.; Zhang, Q.; Tang, Y.; Shao, M.; Wang, H. Revealing the Two-Dimensional Surface Diffusion Mechanism for Zinc Dendrite Formation on Zinc Anode. *Small* **2022**, *18*, 2104148.
10. Ruan, P.; Liang, S.; Lu, B.; Fan, H.J.; Zhou, J. Design strategies for high-energy-density aqueous zinc batteries. *Angewandte Chemie* **2022**, *134*, e202200598.
11. Dang, J.; Yin, M.; Pan, D.; Tian, Z.; Chen, G.; Zou, J.; Miao, H.; Wang, Q.; Yuan, J. Four-functional iron/copper sulfide heterostructure for alkaline hybrid zinc batteries and water splitting. *Chemical Engineering Journal* **2023**, 141357.
12. Li, Y.; Wang, Z.; Cai, Y.; Pam, M.E.; Yang, Y.; Zhang, D.; Wang, Y.; Huang, S. Designing Advanced Aqueous Zinc-Ion Batteries: Principles, Strategies, and Perspectives. *Energy & Environmental Materials* **2022**, *5*, 823-851.
13. Song, M.; Tan, H.; Chao, D.; Fan, H.J. Recent advances in Zn-ion batteries. *Advanced Functional Materials* **2018**, *28*, 1802564.
14. Huang, J.; Wang, Z.; Hou, M.; Dong, X.; Liu, Y.; Wang, Y.; Xia, Y. Polyaniline-intercalated manganese dioxide nanolayers as a high-performance cathode material for an aqueous zinc-ion battery. *Nature communications* **2018**, *9*, 2906.
15. Wang, L.-P.; Wang, P.-F.; Wang, T.-S.; Yin, Y.-X.; Guo, Y.-G.; Wang, C.-R. Prussian blue nanocubes as cathode materials for aqueous Na-Zn hybrid batteries. *Journal of Power Sources* **2017**, *355*, 18-22.
16. Fang, G.; Zhou, J.; Pan, A.; Liang, S. Recent advances in aqueous zinc-ion batteries. *ACS Energy Letters* **2018**, *3*, 2480-2501.
17. Ding, J.; Du, Z.; Gu, L.; Li, B.; Wang, L.; Wang, S.; Gong, Y.; Yang, S. Ultrafast Zn2+ intercalation and deintercalation in vanadium dioxide. *Advanced Materials* **2018**, *30*, 1800762.
18. Cai, Y.; Liu, F.; Luo, Z.; Fang, G.; Zhou, J.; Pan, A.; Liang, S. Pilotaxitic Na1. 1V3O7. 9 nanoribbons/graphene as high-performance sodium ion battery and aqueous zinc ion battery cathode. *Energy Storage Materials* **2018**, *13*, 168-174.
19. Wan, F.; Niu, Z. Design strategies for vanadium-based aqueous zinc-ion batteries. *Angewandte Chemie* **2019**, *131*, 16508-16517.
20. Bósquez-Cáceres, M.F.; Hidalgo-Bonilla, S.; Morera Córdova, V.; Michell, R.M.; Tafur, J.P. Nanocomposite Polymer Electrolytes for Zinc and Magnesium Batteries: From Synthetic to Biopolymers. *Polymers* **2021**, *13*, 4284.
21. Wu, K.; Huang, J.; Yi, J.; Liu, X.; Liu, Y.; Wang, Y.; Zhang, J.; Xia, Y. Recent advances in polymer electrolytes for zinc ion batteries: mechanisms, properties, and perspectives. *Advanced Energy Materials* **2020**, *10*, 1903977.
22. Mo, F.; Guo, B.; Ling, W.; Wei, J.; Chen, L.; Yu, S.; Liang, G. Recent Progress and Challenges of Flexible Zn-Based Batteries with Polymer Electrolyte. *Batteries* **2022**, *8*, 59.
23. Liu, D.; Tang, Z.; Luo, L.; Yang, W.; Liu, Y.; Shen, Z.; Fan, X.-H. Self-healing solid polymer electrolyte with high ion conductivity and super stretchability for all-solid zinc-ion batteries. *ACS Applied Materials & Interfaces* **2021**, *13*, 36320-36329.
24. Ma, T.; MacKenzie, J.D. Fully printed, high energy density flexible zinc-air batteries based on solid polymer electrolytes and a hierarchical catalyst current collector. *Flexible and Printed Electronics* **2019**, *4*, 015010.
25. Lu, J.; Jaumaux, P.; Wang, T.; Wang, C.; Wang, G. Recent progress in quasi-solid and solid polymer electrolytes for multivalent metal-ion batteries. *Journal of Materials Chemistry A* **2021**, *9*, 24175-24194.
26. Ma, L.; Chen, S.; Li, X.; Chen, A.; Dong, B.; Zhi, C. Liquid-Free All-Solid-State Zinc Batteries and Encapsulation-Free Flexible Batteries Enabled by In Situ Constructed Polymer Electrolyte. *Angewandte Chemie* **2020**, *132*, 24044-24052.
27. Zhu, J.; Yao, M.; Huang, S.; Tian, J.; Niu, Z. Thermal-Gated Polymer Electrolytes for Smart Zinc-Ion Batteries. *Angewandte Chemie International Edition* **2020**, *59*, 16480-16484.
28. Fu, J.; Lee, D.U.; Hassan, F.M.; Yang, L.; Bai, Z.; Park, M.G.; Chen, Z. Flexible high-energy polymer-electrolyte-based rechargeable zinc–air batteries. *Advanced materials* **2015**, *27*, 5617-5622.
29. Vijayakumar, V.; Ghosh, M.; Kurian, M.; Torris, A.; Dilwale, S.; Badiger, M.V.; Winter, M.; Nair, J.R.; Kurungot, S. An In Situ Cross-Linked Nonaqueous Polymer Electrolyte for Zinc-Metal Polymer Batteries and Hybrid Supercapacitors. *Small* **2020**, *16*, 2002528.
30. Lin, C.; Shinde, S.S.; Li, X.; Kim, D.H.; Li, N.; Sun, Y.; Song, X.; Zhang, H.; Lee, C.H.; Lee, S.U. Solid-State Rechargeable Zinc–Air Battery with Long Shelf Life Based on Nanoengineered Polymer Electrolyte. *ChemSusChem* **2018**, *11*, 3215-3224.
31. Liu, J.; Khanam, Z.; Muchakayala, R.; Song, S. Fabrication and characterization of Zn-ion-conducting solid polymer electrolyte films based on PVdF-HFP/Zn (Tf) 2 complex system. *Journal of Materials Science: Materials in Electronics* **2020**, *31*, 6160-6173.

32. Wu, J.; Wang, Y.; Deng, D.; Bai, Y.; Liu, M.; Zhao, X.; Xiong, X.; Lei, Y. Low-temperature resistant gel polymer electrolytes for zinc–air batteries. *Journal of Materials Chemistry A* **2022**, *10*, 19304-19319.
33. Zhang, Y.; Wu, D.; Huang, F.; Cai, Y.; Li, Y.; Ke, H.; Lv, P.; Wei, Q. “Water-in-Salt” Nonalkaline Gel Polymer Electrolytes Enable Flexible Zinc-Air Batteries with Ultra-Long Operating Time. *Advanced Functional Materials* **2022**, *32*, 2203204.
34. Fan, X.; Liu, J.; Song, Z.; Han, X.; Deng, Y.; Zhong, C.; Hu, W. Porous nanocomposite gel polymer electrolyte with high ionic conductivity and superior electrolyte retention capability for long-cycle-life flexible zinc–air batteries. *Nano Energy* **2019**, *56*, 454-462.
35. Fan, X.; Wang, H.; Liu, X.; Liu, J.; Zhao, N.; Zhong, C.; Hu, W.; Lu, J. Functionalized Nanocomposite Gel Polymer Electrolyte with Strong Alkaline-Tolerance and High Zinc Anode Stability for Ultralong-Life Flexible Zinc–Air Batteries. *Advanced Materials* **2023**, *35*, 2209290.
36. Hong, Z.; Ahmad, Z.; Viswanathan, V. Design principles for dendrite suppression with porous polymer/aqueous solution hybrid electrolyte for Zn metal anodes. *ACS Energy Letters* **2020**, *5*, 2466-2474.
37. Wang, Y.; Wang, Z.; Yang, F.; Liu, S.; Zhang, S.; Mao, J.; Guo, Z. Electrolyte Engineering Enables High Performance Zinc-Ion Batteries. *Small* **2022**, *18*, 2107033.
38. Hansen, E.J.; Liu, J. Materials and structure design for solid-state zinc-ion batteries: a mini-review. *Frontiers in Energy Research* **2021**, *8*, 616665.
39. Wu, K.; Huang, J.; Yi, J.; Liu, X.; Liu, Y.; Wang, Y.; Zhang, J.; Xia, Y. Recent Advances in Polymer Electrolytes for Zinc Ion Batteries: Mechanisms, Properties, and Perspectives. *Advanced Energy Materials* **2020**, *10*, doi:10.1002/aenm.201903977.
40. Zhang, N.; Chen, X.; Yu, M.; Niu, Z.; Cheng, F.; Chen, J. Materials chemistry for rechargeable zinc-ion batteries. *Chem Soc Rev* **2020**, *49*, 4203-4219, doi:10.1039/c9cs00349e.
41. Mo, F.; Guo, B.; Ling, W.; Wei, J.; Chen, L.; Yu, S.; Liang, G. Recent Progress and Challenges of Flexible Zn-Based Batteries with Polymer Electrolyte. *Batteries* **2022**, *8*, doi:10.3390/batteries8060059.
42. Wang, Y.; Wang, Z.; Yang, F.; Liu, S.; Zhang, S.; Mao, J.; Guo, Z. Electrolyte Engineering Enables High Performance Zinc-Ion Batteries. *Small* **2022**, *18*, e2107033, doi:10.1002/smll.202107033.
43. Hiralal, P.; Imaizumi, S.; Unalan, H.E.; Matsumoto, H.; Minagawa, M.; Rouvala, M.; Tanioka, A.; Amaratunga, G.A.J.A.n. Nanomaterial-enhanced all-solid flexible zinc− carbon batteries. **2010**, *4*, 2730-2734.
44. Tafur, J.P.; Abad, J.; Román, E.; Romero, A.J.F.J.E.C. Charge storage mechanism of MnO2 cathodes in Zn/MnO2 batteries using ionic liquid-based gel polymer electrolytes. **2015**, *60*, 190-194.
45. Li, H.; Liu, Z.; Liang, G.; Huang, Y.; Huang, Y.; Zhu, M.; Pei, Z.; Xue, Q.; Tang, Z.; Wang, Y.J.A.n. Waterproof and tailorable elastic rechargeable yarn zinc ion batteries by a cross-linked polyacrylamide electrolyte. **2018**, *12*, 3140-3148.
46. Kaltenbrunner, M.; Kettlgruber, G.; Siket, C.; Schwödiauer, R.; Bauer, S.J.A.m. Stretchable batteries: Arrays of ultracompliant electrochemical dry gel cells for stretchable electronics (Adv. Mater. 18/2010). **2010**, *22*.
47. Yi, J.; Guo, S.; He, P.; Zhou, H.J.E.; Science, E. Status and prospects of polymer electrolytes for solid-state Li–O 2 (air) batteries. **2017**, *10*, 860-884.
48. Zhao, Z.; Wang, J.; Lv, Z.; Wang, Q.; Zhang, Y.; Lu, G.; Zhao, J.; Cui, G. In-situ formed all-amorphous poly (ethylene oxide)-based electrolytes enabling solid-state Zn electrochemistry. *Chemical Engineering Journal* **2021**, *417*, doi:10.1016/j.cej.2020.128096.
49. Kumar, G. Electrochemical characterization of poly(vinylidenefluoride)-zinc triflate gel polymer electrolyte and its application in solid-state zinc batteries. *Solid State Ionics* **2003**, *160*, 289-300, doi:10.1016/s0167-2738(03)00209-1.
50. Liu, J.; Khanam, Z.; Muchakayala, R.; Song, S. Fabrication and characterization of Zn-ion-conducting solid polymer electrolyte films based on PVdF-HFP/Zn(Tf)2 complex system. *Journal of Materials Science: Materials in Electronics* **2020**, *31*, 6160-6173, doi:10.1007/s10854-020-03169-1.
51. Ma, L.; Chen, S.; Li, X.; Chen, A.; Dong, B.; Zhi, C. Liquid-Free All-Solid-State Zinc Batteries and Encapsulation-Free Flexible Batteries Enabled by In Situ Constructed Polymer Electrolyte. *Angew Chem Int Ed Engl* **2020**, *59*, 23836-23844, doi:10.1002/anie.202011788.
52. Liu, D.; Tang, Z.; Luo, L.; Yang, W.; Liu, Y.; Shen, Z.; Fan, X.H. Self-Healing Solid Polymer Electrolyte with High Ion Conductivity and Super Stretchability for All-Solid Zinc-Ion Batteries. *ACS Appl Mater Interfaces* **2021**, *13*, 36320-36329, doi:10.1021/acsami.1c09200.
53. Huang, Y.; Liu, J.; Zhang, J.; Jin, S.; Jiang, Y.; Zhang, S.; Li, Z.; Zhi, C.; Du, G.; Zhou, H. Flexible quasi-solid-state zinc ion batteries enabled by highly conductive carrageenan bio-polymer electrolyte. *RSC Adv* **2019**, *9*, 16313-16319, doi:10.1039/c9ra01120j.
54. Huang, Y.; Zhang, J.; Liu, J.; Li, Z.; Jin, S.; Li, Z.; Zhang, S.; Zhou, H. Flexible and stable quasi-solid-state zinc ion battery with conductive guar gum electrolyte. *Materials Today Energy* **2019**, *14*, doi:10.1016/j.mtener.2019.100349.
55. Ye, H.; Xu, J.J. Zinc ion conducting polymer electrolytes based on oligomeric polyether/PVDF-HFP blends. *Journal of Power Sources* **2007**, *165*, 500-508, doi:10.1016/j.jpowsour.2006.10.042.

56. Rathika, R.; Padmaraj, O.; Suthanthiraraj, S.A. Electrical conductivity and dielectric relaxation behaviour of PEO/PVdF-based solid polymer blend electrolytes for zinc battery applications. *Ionics* **2017**, *24*, 243-255, doi:10.1007/s11581-017-2175-x.
57. Lu, G.; Qiu, H.; Du, X.; Sonigara, K.K.; Wang, J.; Zhang, Y.; Chen, Z.; Chen, L.; Ren, Y.; Zhao, Z.; et al. Heteroleptic Coordination Polymer Electrolytes Initiated by Lewis-Acidic Eutectics for Solid Zinc–Metal Batteries. *Chemistry of Materials* **2022**, *34*, 8975-8986, doi:10.1021/acs.chemmater.2c02417.
58. Li, H.; Han, C.; Huang, Y.; Huang, Y.; Zhu, M.; Pei, Z.; Xue, Q.; Wang, Z.; Liu, Z.; Tang, Z.; et al. An extremely safe and wearable solid-state zinc ion battery based on a hierarchical structured polymer electrolyte. *Energy & Environmental Science* **2018**, *11*, 941-951, doi:10.1039/c7ee03232c.
59. Qiu, M.; Liu, H.; Tawiah, B.; Jia, H.; Fu, S. Zwitterionic triple-network hydrogel electrolyte for advanced flexible zinc ion batteries. *Composites Communications* **2021**, *28*, doi:10.1016/j.coco.2021.100942.
60. Dueramae, I.; Okhawilai, M.; Kasemsiri, P.; Uyama, H.; Kita, R. Properties enhancement of carboxymethyl cellulose with thermo-responsive polymer as solid polymer electrolyte for zinc ion battery. *Sci Rep* **2020**, *10*, 12587, doi:10.1038/s41598-020-69521-x.
61. Zhou, J.; Zhang, R.; Xu, R.; Li, Y.; Tian, W.; Gao, M.; Wang, M.; Li, D.; Liang, X.; Xie, L.; et al. Super-Assembled Hierarchical Cellulose Aerogel-Gelatin Solid Electrolyte for Implantable and Biodegradable Zinc Ion Battery. *Advanced Functional Materials* **2022**, *32*, doi:10.1002/adfm.202111406.
62. Zhou, J.; Li, Y.; Xie, L.; Xu, R.; Zhang, R.; Gao, M.; Tian, W.; Li, D.; Qiao, L.; Wang, T.; et al. Humidity-sensitive, shape-controllable, and transient zinc-ion batteries based on plasticizing gelatin-silk protein electrolytes. *Materials Today Energy* **2021**, *21*, doi:10.1016/j.mtener.2021.100712.
63. Wang, W.; Liao, C.; Liew, K.M.; Chen, Z.; Song, L.; Kan, Y.; Hu, Y.J.J.o.M.C.A. A 3D flexible and robust HAPs/PVA separator prepared by a freezing-drying method for safe lithium metal batteries. **2019**, *7*, 6859-6868.
64. Wang, W.; Yuen, A.C.Y.; Yuan, Y.; Liao, C.; Li, A.; Kabir, I.I.; Kan, Y.; Hu, Y.; Yeoh, G.H.J.C.E.J. Nano architectured halloysite nanotubes enable advanced composite separator for safe lithium metal batteries. **2023**, *451*, 138496.
65. Yuan, D.; Manalastas, W., Jr.; Zhang, L.; Chan, J.J.; Meng, S.; Chen, Y.; Srinivasan, M. Lignin@Nafion Membranes Forming Zn Solid-Electrolyte Interfaces Enhance the Cycle Life for Rechargeable Zinc-Ion Batteries. *ChemSusChem* **2019**, *12*, 4889-4900, doi:10.1002/cssc.201901409.
66. Sownthari, K.; Suthanthiraraj, S.A. Preparation and properties of biodegradable polymer-layered silicate nanocomposite electrolytes for zinc based batteries. *Electrochimica Acta* **2015**, *174*, 885-892, doi:10.1016/j.electacta.2015.06.049.
67. Sai Prasanna, C.M.; Austin Suthanthiraraj, S. PVC/PEMA-based blended nanocomposite gel polymer electrolytes plasticized with room temperature ionic liquid and dispersed with nano-ZrO2 for zinc ion batteries. *Polymer Composites* **2019**, *40*, 3402-3411, doi:10.1002/pc.25201.
68. Chen, Z.; Li, X.; Wang, D.; Yang, Q.; Ma, L.; Huang, Z.; Liang, G.; Chen, A.; Guo, Y.; Dong, B.; et al. Grafted MXene/polymer electrolyte for high performance solid zinc batteries with enhanced shelf life at low/high temperatures. *Energy & Environmental Science* **2021**, *14*, 3492-3501, doi:10.1039/d1ee00409c.
69. Liu, C.; Tian, Y.; An, Y.; Yang, Q.; Xiong, S.; Feng, J.; Qian, Y. Robust and flexible polymer/MXene-derived two dimensional TiO2 hybrid gel electrolyte for dendrite-free solid-state zinc-ion batteries. *Chemical Engineering Journal* **2022**, *430*, doi:10.1016/j.cej.2021.132748.
70. Lin, D.; Liu, W.; Liu, Y.; Lee, H.R.; Hsu, P.-C.; Liu, K.; Cui, Y. High ionic conductivity of composite solid polymer electrolyte via in situ synthesis of monodispersed SiO2 nanospheres in poly (ethylene oxide). *Nano letters* **2016**, *16*, 459-465.