**REVIEW**

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# Interface Engineering and Optimization Strategies for High-Energy-Density Batteries Based on Polymer Composite Electrolytes

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**Polymer composite electrolytes (PCEs) offer significant advantages in enhancing the safety, stability, and energy density of batteries, making them a crucial component for achieving high-energy-density energy storage systems. However, one of the primary bottlenecks in improving the performance of PCEs lies in the interface challenge, which can be exacerbated and manifested in interface instability, side reactions, and poor interface compatibility, ultimately leading to a significant decline in ion conduction efficiency and overall battery performance of high-voltage or high-energy-density systems. Therefore, systematically analyzing the critical technical narrowing and proposing targeted solutions under high-energy-density conditions is of great significance for advancing the development of next-generation energy storage systems. Although existing strategies have shown promising results, their applicability in high-energy-density batteries remains uncertain. In this work, a comprehensive analysis of the interface challenges associated with high-energy-density polymer batteries is performed, the feasibility of existing approaches is evaluated, and practical optimization strategies are proposed to address these critical issues. Moreover, the insights presented here provide valuable guidance for the industrial-scale production of PCEs, helping to bridge the gap between laboratory innovations and practical applications.**

## 1. Introduction

With the pressing concerns surrounding energy shortages and environmental degradation, the quest for efficient, safe, and durable energy storage solutions has emerged as a focal point in contemporary scientific and technological inquiry. Lithium (Li)-ion batteries (LIBs), renowned for their exceptional energy density and extended lifecycle, have found widespread application in portable electronics, electric vehicles (EVs), and renewable energy storage systems.[1–6] However, conventional liquid electrolyte LIBs are plagued by inherent shortcomings,[7,8] including the volatility and flammability of the electrolyte, thereby constraining their long-term stability and safety. Additionally, these batteries are prone to decomposition under high voltage, thus limiting enhancements in energy density. Consequently, solid-state electrolyte (SSE) batteries have emerged as a pivotal avenue in the pursuit of next-generation energy storage technologies, owing to their superior safety features and potential for heightened energy density.[9–13] The SSE stands as a cornerstone component in solid-state batteries, with its performance exerting a direct influence on overall battery efficacy and safety.[14] An ideal SSE should possess several key characteristics: high ionic conductivity, a wide electrochemical window, excellent lithium-ion transference number ($t_{\mathrm{Li}^+}$), sufficient mechanical strength, and good interface compatibility.[15] High

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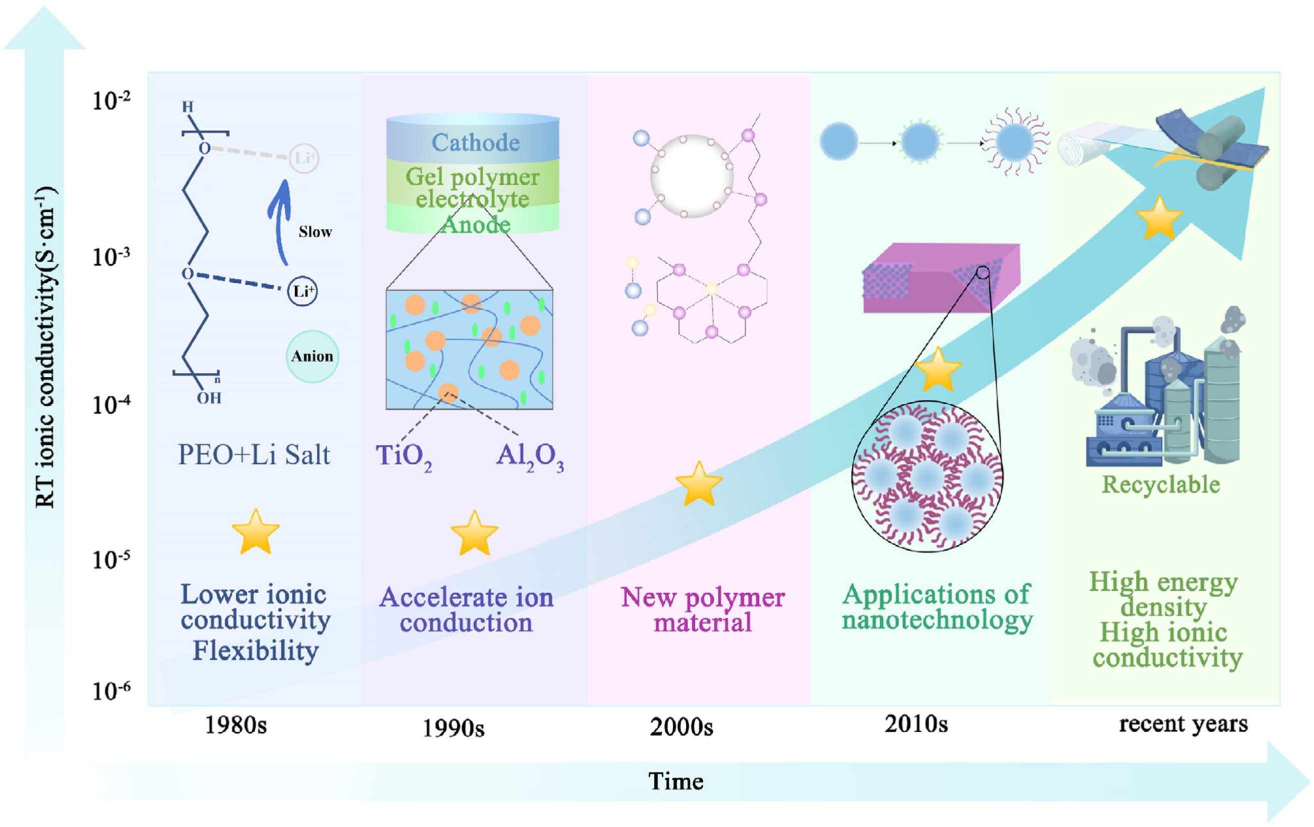

**Figure 1.** The development of PCEs in recent years.

ionic conductivity and a broad electrochemical window are essential for the electrolyte's performance under high-voltage conditions. High-voltage battery systems offer significant advantages in terms of increased energy and power densities, making them a critical direction for the future development of battery technologies.[16] Sufficient mechanical strength and good interface compatibility facilitate the integration of SSEs with high-energy-density anodes (such as lithium metal, silicon, and anode-free systems). When the electrolyte's shear modulus is sufficiently high, it can effectively suppress the growth of Li dendrites.[17] Additionally, the electrolyte should exhibit a certain degree of elasticity to accommodate the volume expansion of the electrodes.[18] In summary, an ideal SSE not only can operate reliably across a broader voltage spectrum, but it can also seamlessly integrate with high-energy-density Li-metal anodes and high-voltage cathode materials, thus markedly enhancing overall battery energy density.[19–22]

In the study of solid electrolytes, SSEs are typically classified into three categories: inorganic solid electrolytes (ISEs), solid polymer electrolytes (SPEs), and polymer composite electrolytes (PCEs).[23] ISEs include oxide electrolytes, sulfide electrolytes, and halide electrolytes. While these materials exhibit relatively high ionic conductivity at room temperature and excellent mechanical properties, they are still limited by issues such as interface contact and processing challenges, which hinder their practical applications.[24–26] In contrast, SPEs, which are composed of Li salts mixed with polymers, offer good interface compatibility and ease of processing.[27–29] However, their relatively poor ionic conductivity at room temperature and lower voltage tolerance remains significant obstacles to their widespread use. The PCEs have become the focus of research in recent years because of the advantages of both organic and inorganic materials, showing excellent ionic conductivity and mechanical strength.[30–32] Over decades of development, PCEs have achieved notable progress, as depicted in **Figure 1**. In the 1980s, as research on solid electrolytes deepened, polymer electrolytes emerged as a focal point. Early investigations centered on polyethylene oxide (PEO) and its complexation with Li salts.[33] While the PEO–Li salt system exhibited good flexibility and film-forming properties, its ionic conductivity remained subpar, particularly at room temperature, lagging significantly behind liquid electrolytes. In the 1990s, to bolster the ionic conductivity and mechanical strength of polymer electrolytes, researchers began integrating inorganic fillers into the polymer matrix.[34] The incorporation of inorganic fillers, such as alumina ($Al_2O_3$), silicon dioxide ($SiO_2$), and Li salts, into the PEO matrix, as demonstrated by Scrosati's team, has significantly enhanced the ionic conductivity, interfacial stability, and thermal stability of PCEs.[35,36] In the 21st century, propelled by advancements in nanotechnology, nanofillers have gained prominence in PCEs. Nanofillers, characterized by their high specific surface area and exceptional physical and chemical properties, have significantly augmented the performance of composite electrolytes.[37,38] Nanocomposites such as nano-oxides ($TiO_2$ and $SiO_2$) and nanosilicates (e.g., layered montmorillonite) have been employed to bolster the mechanical properties and ionic conductivity of polymer matrices. In a bid to further enhance the performance of PCEs, researchers have shifted their focus to functional fillers and surface modification technologies.[37,39,40] Surface modification facilitates the enhancement of filler dispersion and interfacial compatibility within the polymer matrix. In recent years, amidst escalating demand for high-energy-density and high-safety batteries, research into the application of PCEs in all-solid-state LIBs has surged. Novel PCEs, including high-concentration electrolytes based on Li salts, polymer–nanocomposite electrolytes, and self-healing composite electrolytes, have emerged, offering promising avenues for enhancing ionic conductivity, mechanical properties, and electrochemical stability.[37,38,41,42]

Although polymers offer a variety of advantages, they face significant challenges related to interfacial stability (electrode–electrolyte and electrolyte–electrolyte) and inherent structural stability.[43–49] These issues become particularly pronounced under high-energy-density conditions. However, the growing demand for high-energy-density solid-state lithium batteries (SSLBs) in the market is driven by the urgent need for enhanced energy storage systems in EVs and portable electronics. Meeting this demand necessitates overcoming significant technical challenges to ensure both high performance and safety. In this work, we first present a comprehensive overview of the components of PCEs, including polymer matrices and inorganic fillers, followed by an in-depth discussion on their ion transport mechanisms. Given that high-energy-density cathode materials are pivotal for enhancing the overall energy density of battery systems, we analyzed the interface challenges between PCEs and layered oxides (e.g., Nickel Cobalt Manganese Oxide, NCM), focusing on interface contact challenges and parasitic side reactions. Additionally, we discussed the critical interfacial issues between high-capacity anode materials and PCEs, including interfacial stability, dendrite growth, and volume expansion. Effectively resolving these interfacial problems is essential for achieving high-energy-density batteries. While numerous studies have explored optimization strategies from the perspective of cathode and anode materials, this work emphasizes the optimization strategies of the interface between PCEs and high-voltage cathodes and high-capacity anodes, which is different from previous reviews. Furthermore, the insights presented in this review provide valuable guidance on advanced characterization techniques, emerging applications of artificial intelligence (AI) in the PCE field, and strategies for scalable manufacturing, thereby contributing to a broader and more forward-looking perspective. Finally, we summarize the key findings and outline future research directions to facilitate the development of next-generation high-energy-density solid-state batteries.

## 2. Composite Polymer Electrolytes

Composite polymer solid electrolytes are typically formed by combining inorganic fillers with polymer-based electrolytes. Depending on the proportion of these components, PCEs can be classified into two main types: one where inorganic filler is mixed with a polymer/Li salt matrix, and another where polymer/Li salt serves as a filler within an inorganic solid electrolyte matrix. As shown in **Figure 2**, inorganic fillers can be further classified into inert fillers and active fillers. Inert fillers do not enhance the conductivity of lithium ions ($Li^+$), while active fillers do. This section will briefly introduce the content of polymer electrolyte, focus on the type of inorganic filler, and explore the ion transport mechanism of inorganic filler content.

### 2.1. Polymer Matrix

Based on the functionalized backbone units, common polymer matrices can be divided into five main categories: ether-based matrix, nitrile-based matrix, siloxane-based matrix, carbonate-based matrix, and fluorine-based matrix. Since the 1970s, ether-based polymers, including PEO, have been a focal point in research. Notably, the teams of Scrosati and Armand have made remarkable contributions in this field.[35,36,50,51] Their unique ether oxygen groups excel in coordinating and deionizing Li salts, facilitating efficient ion transport.[52] Additionally, ether-based polymers offer compatibility with Li metal and high flexibility, enhancing their practicality.[53,54] However, these polymers face challenges like a limited electrochemical stability window (ESW) and high-voltage oxidative decomposition, which constrain their performance in high-voltage Li-metal batteries.[18] Nitrile-based polymers exhibit excellent thermal stability and antioxidant properties. The strong bond of the $-C \equiv N$ group endows these polymers with significant antioxidant capabilities, especially under high-voltage conditions. Furthermore, their higher dielectric constant improves Li salt solubility, increasing free $Li^+$ concentration and enhancing ionic conductivity and battery performance. However, nitrile-based polymers exhibit high reactivity with Li-metal anodes, which can lead to severe anode corrosion and significant damage to the electrolyte–electrode interface,[55,56] ultimately resulting in suboptimal battery performance. Siloxane-based polymers possess high oxidation resistance and interfacial stability, making them theoretically suitable for high-voltage Li batteries.[57] Despite these advantages, the electrolytes prepared from these polymers often exhibit low ionic conductivity and poor mechanical properties, making them unsuitable as solid electrolytes for high-energy-density SSLBs.[58] Carbonate-based polymers feature polar groups, such as $-O-(C=O)-O-$, exhibit superior electrochemical performance and thermal stability in SSEs compared to conventional PEO-based systems. This enhancement arises from their high dielectric constant and flexible amorphous architecture, which synergistically promote ionic conductivity and $Li^+$ transport dynamics while ensuring structural integrity across wide temperature ranges.[59] However, these polymers face challenges like poor oxidation resistance and unstable Li-metal interphases, which limit their application in high-voltage Li-metal batteries.[60,61] Fluorinated polymers exploit the high electronegativity of fluorine atoms to modulate both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels. This modulation significantly bolsters the polymers' resistance to both oxidation and reduction, making them particularly advantageous in high-voltage Li-metal batteries.[62–64] Nevertheless, their unique semicrystalline properties may hinder ion transport, potentially affecting their effectiveness as solid electrolytes for Li-metal batteries.

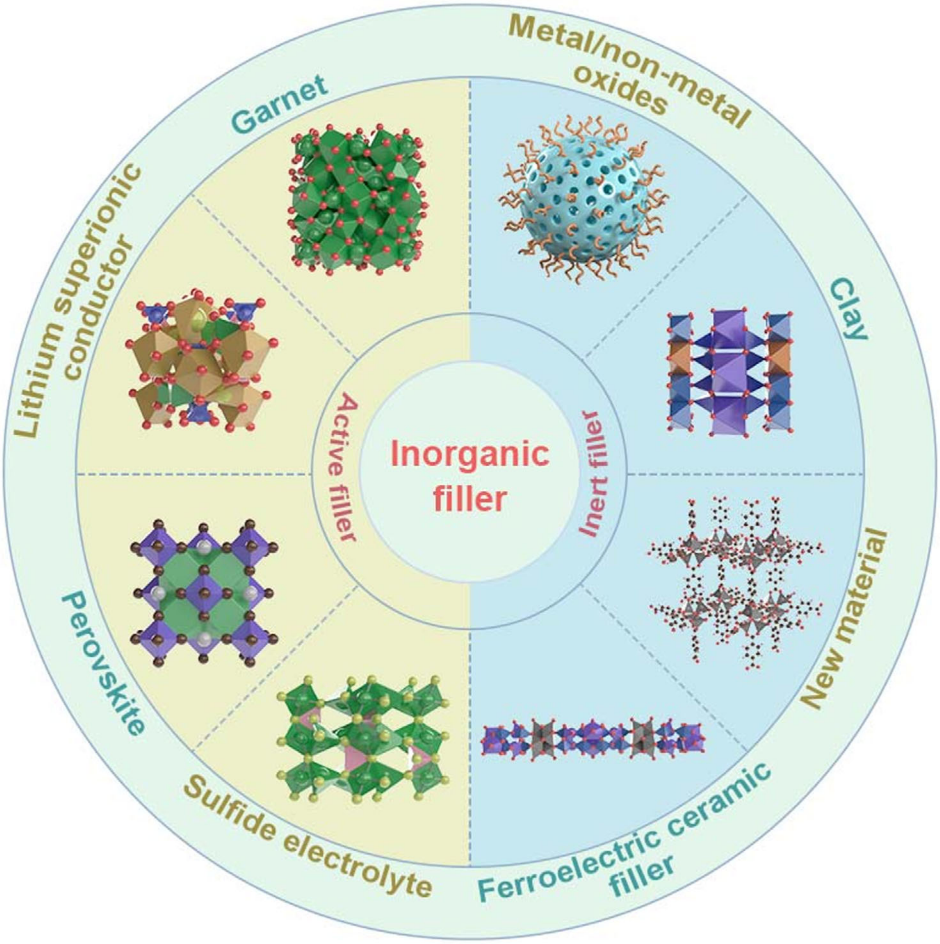

Figure 2. The main types of active and inert fillers in inorganic fillers.

In recent years, driven by the increasing demands for higher energy density, environmental friendliness, and battery safety, research on polymer electrolytes has gradually shifted toward multifunctionality and high performance. This has led to the emergence of a series of novel polymer electrolyte materials. For example, phosphazene-based polymer electrolytes, with their exceptional thermal and chemical stability, have become a prominent research focus.[65–67] Aurbach and co-workers have introduced a gelation process using a butenoxy-cyclotriphosphazene (BCPN) monomer, which has significantly enhanced the safety of lithium-metal batteries.[68] Simultaneously, bio-derived polymer electrolytes, as key materials for sustainable development, offer environmentally friendly characteristics due to their natural origin, while demonstrating excellent ionic conductivity in electrochemical devices.[69] Raj et al.[70] introduced the design of cyclic carbonates, leveraging their excellent ionic conductivity and interfacial stability to effectively address the issue of insufficient electrolyte conductivity in solid-state Li-metal batteries, thereby significantly enhancing the ionic conductivity and cycling stability of the batteries. Moreover, fully charged polymer electrolytes, such as poly(ionic liquids (ILs)) (PILs) and sulfonated polymers, take advantage of the fixed ions on the main or side chains to provide high ion selectivity and conductivity.[71,72] Supramolecular polymer electrolytes, with their self-healing capabilities and dynamic, reversible hydrogen bonding networks, have opened new pathways for flexible electronics and high-safety battery applications.[73,74] In addition, polyphosphate electrolytes, known for their high flame retardancy and environmental stability, have been widely applied in Li-metal batteries and high-voltage batteries.[75] However, polymer electrolytes exhibit several intrinsic limitations, including low ionic conductivity, inadequate mechanical strength, poor thermal stability, and a restricted electrochemical window. Their inherently low ionic mobility at room temperature impedes efficient ion transport, while insufficient mechanical robustness exacerbates the risk of Li dendrite formation, jeopardizing battery safety. Furthermore, many polymers are prone to thermal degradation under elevated temperatures, constraining their applicability in high-temperature environments. Additionally, their limited tolerance to high voltages can induce side reactions, further compromising the overall performance and longevity of the battery system.

### 2.2. Inorganic Filler

#### 2.2.1. Inert Filler Materials

Inert fillers can be called $Li^+$ insulators, which are essentially unable to conduct $Li^+$ and may even affect the transport of $Li^+$ in the polymer phase.[76] However, the addition of inert fillers can also increase the amorphous region in the polymer phase, thereby reducing the crystallinity and glass transition temperature ($T_g$) of the polymer phase and improving the transport efficiency of $Li^+$. And the surface groups of inert fillers will have Lewis acid–base interaction with anions to promote further dissociation of Li salt. Common inert fillers include $Al_2O_3$,[77] $ZrO_2$,[78] $SiO_2$,[79] $TiO_2$,[80] MgO, ZnO, BN, clay materials, new materials, etc., because of their simple synthesis method, size control and high stability advantages, widely used in PCEs. Li et al.[81] prepared $\gamma$-$Al_2O_3$ fiber by electrospinning technology, and mixed it with flexible polypropylene oxide (PPO)/Lithium bis (trifluoromethanesulfonyl)imide (LiTFSI) to prepare flexible PCEs, which inherently formed a continuous channel and shortened the ion migration path. Based on the Lewis acid–base action, $\gamma$-$Al_2O_3$ can react with the anion of Li salt to release more $Li^+$, which increases the number of $Li^+$ migration and effectively improves the ion migration rate. And $\gamma$-$Al_2O_3$ reacts with Li metal to form a buffer layer, which enhances the safety performance of solid-state batteries. Wu and co-workers[82] integrated $SiO_2$ nanoparticles into vinyl ethylene carbonate (VEC) monomer, and enhanced the antioxidant capacity of PCEs through the interaction of the —OH group on $SiO_2$ surface with oxygen atoms in poly(vinylethylene carbonate) (PVEC) molecular skeleton and O—S—O group in LiTFSI (that is, hydrogen bonding). The interface compatibility between PCEs and high-voltage cathode materials is improved, and the assembled PCE-based solid-state battery has good cycle stability and high energy density under high voltage. In addition to the above common inert fillers, several novel materials have been increasingly developed in recent years. Notable examples include ferroelectric ceramic fillers, metal–organic frameworks (MOFs), and 2D materials (graphene oxide, MXene, and muscovite, etc.). Among them, the pioneering work on MOFs and covalent organic framework (COFs) was conducted by Yaghi et al. Their research in 1995 led to the synthesis and crystallization of the first MOFs.[83] In 2005, he further extended their approach to the design and crystallization of the first 2D COFs.[84] As for 2D materials, the groundbreaking discovery of graphene was made by Novoselov et al. Their work in 2004 unveiled the extraordinary properties of this single-atom-thick carbon material.[85,86] These innovative materials bring unique properties to polymer electrolytes, expanding their potential for advanced energy storage applications. Compared to standard fillers, ferroelectric ceramic fillers stand out due to their high dielectric constant, which facilitates Li salt dissociation and significantly enhances ionic conductivity. Furthermore, their intrinsic spontaneous polarization, which can be reversed by an external electric field, not only optimizes ion transport pathways but also improves interfacial stability, effectively addressing critical challenges in solid-state battery technology. Kang et al.[87] introduced nanometer $Bi_4Ti_3O_{12}$ (BIT) into PEO matrix to prepare PCEs with fast $Li^+$ ion conduction network. The abundant oxygen vacancy of BIT nanofibers helps to accelerate the dissociation of LiTFSI and promote the rapid transfer of free $Li^+$. By density functional theory (DFT) calculation, it is found that the ferroelectric property of BIT and the internal electric field can promote the rapid transfer of $Li^+$ along the highly conductive layer. The piezoelectric properties of BIT can homogenize the interfacial electric field and promote uniform Li deposition, thereby inhibiting the continuous growth of Li dendrites, providing an effective strategy for achieving solid-state Li-metal batteries with high voltage and high energy density. MOFs, with their unique porous structures, high specific surface area, tunable architectures, and outstanding chemical stability, show immense potential for enhancing ionic transport pathways, interfacial stability, and flame retardancy in polymer electrolytes.[88,89] Dong et al.[90] utilized advanced characterization techniques combined with theoretical simulations to design a series of nano-MOF materials. They systematically investigated the influence of pore structures and unsaturated metal sites on the ionic transport properties and electrochemical stability of MOF-based quasi-solid-state electrolytes, providing valuable insights into their functional mechanisms. Similar to MOFs, 2D materials feature layered structures, exceptional mechanical strength, and highly tunable surface functional groups, which collectively contribute to enhancing the ionic transport pathways, mechanical stability, interfacial compatibility, and thermal resistance of polymer electrolytes.[91–95] Bao et al.[96] successfully designed an oxyethyl-poly(ionic liquid) and grafted it onto graphene oxide, resulting in the synthesis of ox-PIL@GO. This material establishes coordination interactions, electrostatic interactions, and ion–dipole interactions with PEO, effectively reducing the crystallinity of the polymer electrolyte while significantly enhancing its ionic conductivity, mechanical strength, and ion transference number. However, inert fillers inherently lack ionic conductivity and often exhibit limitations such as functional singularity, poor dispersion within the polymer matrix, and a tendency to aggregate. These drawbacks result in an absence of active contributions to ion transport, uneven performance, and increased interfacial resistance. Consequently, it is essential to strike a balance between maximizing the advantages of inert fillers and addressing their shortcomings. This can be achieved through strategies such as optimizing filler content, implementing surface modifications, and designing advanced composite materials.

#### 2.2.2. Active Filler Materials

In contrast to inert fillers, active fillers can significantly enhance the migration of $Li^+$ and improve the electrochemical performance of PCEs. These fillers possess low activation energy, high defect rates, and act as $Li^+$ donors, increasing the free $Li^+$ concentration at the interphase between fillers and the polymer matrix, thereby boosting the overall ionic conductivity of PCEs. Common active fillers include garnet, Li superionic conductors,[97] perovskites,[98] and sulfide electrolytes.[99] As shown in **Figure 3a**, fillers can also be categorized into 0D nanoparticle fillers, 1D nanofiber fillers, 2D nanosheet fillers, and 3D framework fillers.

Incorporating nanoparticle fillers into the polymer matrix is a classical strategy for preparing PCEs. Researchers have prepared PCEs by integrating $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ (LLZTO) nanoparticles into a polyvinylidene fluoride (PVDF) matrix with a polyimide (PI) film as the host. LLZTO nanoparticles are uniformly

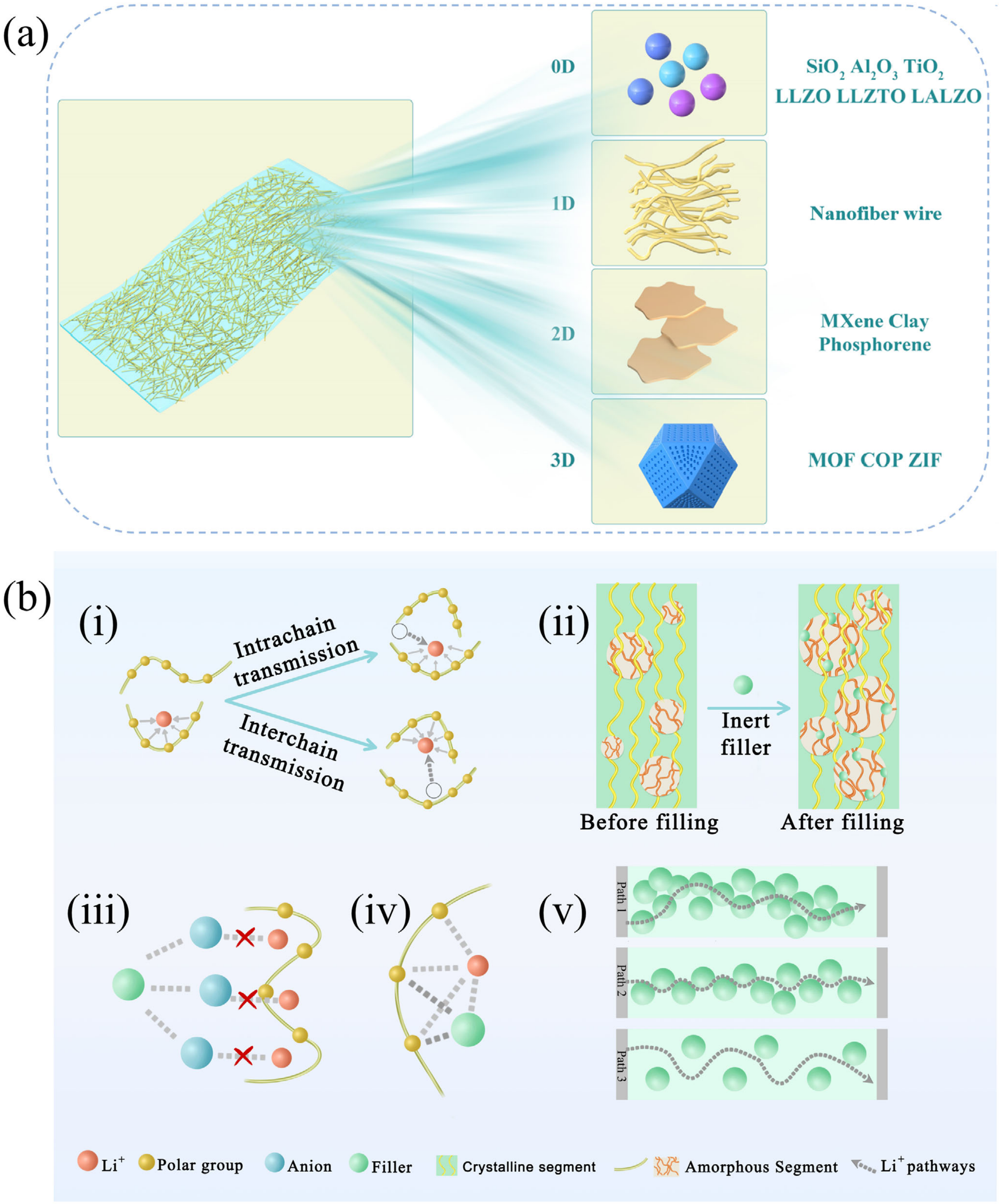

**Figure 3.** a) Four different dimensions of inorganic fillers. b(i)–(v) Schematic diagram illustrating the transmission mechanism of Li$^+$ in various conditions.

dispersed in PVDF, forming a continuous $Li^+$ transport path, thereby improving ion conductivity and reducing the formation of Li dendrites by creating a stable $Li^+$ conductive passivation layer. Additionally, the low electronic conductivity of the PCE prevents electrons from passing through the electrolyte, thus avoiding the decomposition of electrolyte at high voltages. Solid-state $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/Li pouch cells using this PCE demonstrate excellent cycle stability and high functional safety at high voltages, and can withstand harsh environments such as folding, cutting, and spiking.[100]

Beyond 0D nanoparticle active fillers, 1D nanofibrous active fillers can also be disorderedly dispersed in the polymer. The $Li_7La_3Zr_2O_{12}$ (LLZO) nanofiber membrane, prepared by a sol–gel electrospinning method and subsequent calcination, can be combined with PVDF to produce an enhanced electrolyte.[101] LLZO in nanofiber form provides more ion transport channels, reducing electrolyte resistance. The optimized electrospinning process aligns LLZO in a specific direction, minimizing the scattering and obstruction of $Li^+$ during transmission, thus enhancing battery safety and energy density. This electrolyte exhibits a stable electrochemical window against Li metal in the voltage range of 0–5.0 V, achieving excellent performance and stability in high-voltage, high-energy-density Li batteries.

Active fillers with a 2D nanosheet structure have also attracted significant attention due to their structural characteristics. Small-sized 2D nanosheets are particularly favored in practical applications as they provide continuous ion transport paths. These nanosheets, when sufficiently small, offer a larger contact area and more interfaces, resulting in higher ionic conductivity. Chen et al.[102] prepared layered Li montmorillonite (LiMNT) via ion exchange and developed a new type of PCE through solution casting and hot pressing. The interlayer structure of the polymer matrix embedded in LiMNT facilitates rapid $Li^+$ transport and inhibits space-charge layer formation.

However, high concentrations of active fillers can agglomerate in the polymer matrix, blocking ion transport paths and resulting in low ionic conductivity of PCEs. An effective solution is to construct a 3D skeleton structure of active fillers within the polymer matrix. For instance, a composite solid electrolyte (PPL, Polyphenylene) was fabricated by casting PEO–LiTFSI onto a polyacrylonitrile (PAN)/LLZTO electrospun fiber network, which serves as a structural reinforcement for improved mechanical strength and ionic conductivity.[103] The 3D interconnected network structure significantly reduces the crystallinity of the PEO polymer, forms a continuous $Li^+$ transport channel, and enhances the ionic conductivity of the electrolyte. After cycling, a stable interphase forms on the PPL surface, stabilizing the interface between the Li-metal anode and the electrolyte and reducing side reactions. The electrochemical stability window up to 4.6 V is crucial for adapting high-voltage cathode materials. When PPL is paired with high-voltage cathode materials (such as NCM and lithium–cobalt oxide (LCO)), the battery exhibits stable cycling performance and high discharge capacity, demonstrating its potential for high-energy-density batteries.

In addition to the aforementioned traditional active fillers, recent years have seen the emergence of novel active fillers, such as alloy fillers,[104,105] liquid metals (LMs),[106,107] bio-based materials, and mineral-based materials,[108] have been steadily developed. Among them, Wu et al.[109] introduced Galinstan ($Ga_{62.5}In_{21.5}Sn_{16}$), as an innovative active liquid alternative to conventional passive solid fillers, aiming to achieve self-healing protection against dendrite formation. Unlike solid inorganic fillers, LM droplets, owing to their fluidic nature—particularly at temperatures below the melting point of the polymer—can significantly reduce the polymer's crystallinity and enhance $Li^+$ conductivity. Furthermore, LMs serve as dynamic chemical traps, facilitating in situ alloying during battery operation to block and consume Li dendrites upon contact. Additionally, the formed Li–LM alloy exhibits a low deposition energy barrier, effectively inhibiting dendrite growth and providing a robust mechanism to improve both battery safety and performance. Gu et al.[110] introduced a novel soy protein-based vitrimer, an innovative polymer material characterized by its dynamic covalent network. This vitrimer leverages thermally activated bond exchange reactions to modify its topological structure, thereby significantly enhancing ionic conductivity. Moreover, the dynamic covalent bonds (imine bonds) within the electrolyte not only impart excellent mechanical properties but also enable the material to exhibit adaptive behavior under high-temperature or humid conditions, thereby forming exceptional flame-retardant properties. Nevertheless, due to the mismatch in physical and chemical properties, differences in interfacial energy, or interfacial reactions, active fillers and polymer electrolytes often face issues such as poor interface compatibility, cleavage, or chemical reactions, leading to interfacial degradation. This degradation causes a reduction in ionic conductivity, an increase in interfacial resistance, and significantly affects battery performance. Particularly in high-energy-density systems, the safety and cycling stability of the battery are also compromised. To overcome these challenges, it is crucial to optimize both the concentration and distribution of active fillers, while simultaneously improving the compatibility and stability of the filler–polymer interphase through advanced strategies, such as surface functionalization.

### 2.3. Ion Transport Mechanism of PCEs

The primary transport pathways of $Li^+$ in PCEs are illustrated in Figure 3b. In polymer electrolytes, the crystalline segments hinder $Li^+$ migration, with $Li^+$ primarily moving through the amorphous segments. The transition between these two segments is primarily influenced by the $T_g$. In the amorphous segments, $Li^+$ can be transported in two ways: intrachain transport within the polymer's polar groups and interchain transport (as shown in Figure 3b(i)). After the addition of fillers, the fillers effectively reduce the $T_g$ and crystallinity of the polymer, thereby increasing the amorphous segments (as shown in Figure 3b(ii)). Moreover, as depicted in Figure 3b(iii,iv), certain fillers can significantly enhance interactions with anion groups in the Li salts or improve coordination with active groups in the polymer chains, weakening the binding strength between the polymer chains and $Li^+$, thus releasing more free $Li^+$.

For inert filler-based PCEs, the ion transport mechanism is akin to that of SPEs, as the fillers are $Li^+$ insulators.[111] The ion transport mechanism in SPEs within a flexible matrix primarily relies on the continuous reconstruction of ether–oxygen atom binding sites in polymer units and the free volumes generated by polymer chain segment dynamics.[112] Currently, the ion transport mechanism for many types of polymer electrolytes remains unclear, but the macroscopic study of ion conductivity with temperature provides valuable insights. The temperature dependence of ionic conductivity in polymer solid electrolytes mainly follows two conduction mechanisms: the Vogel–Tamman–Fulcher (VTF) type and the Arrhenius type.[113] In polyether-based flexible polymers such as PEO and PPO, the ionic conductivity coefficient with temperature and chain relaxation time of the polymer electrolyte generally follow the VTF equation[114] as shown in Equation (1). However, the crystalline regions in SPEs, which are less affected by chain segment motion, are better described by the Arrhenius equation. According to the Arrhenius equation (as shown in Equation (2)), ion transport in SPEs is induced by a simple hopping mechanism decoupled from polymer chain breathing.[115] Additionally, under an electric field, $Li^+$ is more likely to move through nearby coordination sites rather than migrate with the polymer chain segments[116]

$$\tau = \tau_0 \exp\left[B/(T - T_0)\right] \tag{1}$$

$$k = A \exp\left(-E_a/RT\right) \tag{2}$$

where $\tau_0$, $B$, and $T_0$ are the fitting parameters; $k$ is the rate constant; $A$ is the pre-exponential factor or frequency factor, which depends on the chemical and physical properties of the battery, and $E_a$ is the activation energy. When active fillers are incorporated, the $Li^+$ transport pathways can be categorized into three types based on the filler content and type: 1) when the active filler content is noticeably lower than that of the polymer, $Li^+$ primarily transports through the polymer's amorphous segment; 2) when there is sufficient active filler and the surface of the active filler contains $Li^+$ conduction channels, $Li^+$ primarily migrates along the filler surface; 3) when the active filler content is high and its ionic conductivity in the bulk phase of the active fillers is significantly higher than that of the polymer, $Li^+$ primarily migrates within the active fillers, as shown in Figure 3b(v).[117] In general, for PCEs with a large proportion of polymer phase, $Li^+$ transport mainly occurs in the amorphous region of the organic polymer phase. Widely accepted models and derived theories, such as the free-volume model, effectively explain $Li^+$ transport in the amorphous region. For example, in common PEO-based PCEs, the combination of PEO and inorganic fillers reduces the crystallinity of PEO. With the assistance of complexation and decomplexation and PEO chain segment movement, $Li^+$ can rapidly move between complexation sites. The breaking and formation of coordination bonds (Li—O bonds) under an electric field allow $Li^+$ to achieve rapid movement within or between chains.[118]

Active fillers themselves have high ionic conductivity and can provide additional ion transport pathways in PCEs. Although the low content of active fillers in most, a certain amount of $Li^+$ can still migrate through the vacancy mechanism or interstitial mechanism of these active fillers.[119] The vacancy mechanism, based on Schottky defects, involves the formation of cationic vacancies accompanied by anionic vacancies, resulting in many vacancies for $Li^+$ migration. The interstitial mechanism, associated with Frenkel defects, involves anionic vacancies forming due to cations occupying interstitial sites. $Li^+$ can diffuse via direct interstitial diffusion or interstitial knock-off diffusion. In direct interstitial diffusion, $Li^+$ jumps directly from one interstitial position to another. In interstitial knock-off diffusion, $Li^+$ migrates indirectly, as one interstitial atom replaces a normal lattice position, pushing the original lattice atom to another interstitial position. Since the ionic conductivity of active fillers is higher than that of the polymer matrix, the overall ionic conductivity should theoretically improve with increasing active filler content. However, when the active filler content is high, ion transport paths shift from the polymer matrix to the network formed by the active filler, potentially reducing the proportion of $Li^+$ involved in conduction and interfering with ion transport.[120]

The dispersion of active fillers in the polymer matrix, typically small in size, creates numerous interface regions in the composite solid electrolyte. The surface defects of active fillers are varied and highly reactive, leading to complex interface conditions.[121] The Lewis acid–base interaction[122] between the active group on the filler surface and the Li salt increases the concentration of free $Li^+$ at the interphase and builds an ion channel between the active filler and the polymer matrix.[123] Researchers also propose that the space-charge effect explains ion transport in the inorganic–organic interphase: due to differences in $Li^+$ concentration and energy levels at the interphase and interactions between the active filler and polymer matrix, a Li-rich space-charge layer spontaneously forms, acting as a fast transport channel for $Li^+$ driven by the free energy of the interphase.[124,125]

The ionic conductivity mechanism of PCE is influenced by the dynamic behavior of the polymer, the type and dispersion of the filler, and the ionic behavior at the interphase. An in-depth understanding of the synergistic mechanism between the polymer and the inorganic filler is the key to optimizing the ionic conductivity of PCE.

## 3. Interface Challenges between PCEs and High-Capacity Cathodes

Solid-state batteries are heralded as a pivotal direction in the evolution of battery technology due to their superior safety and energy density potential. A key factor in enhancing the energy density of battery systems is the use of high-energy-density cathode materials such as nickel (Ni)-rich layered oxide (e.g., NCM), LCO, and Li-rich manganese-based oxide materials (LRMO).[126] High-capacity cathode materials offer substantially higher energy densities ($>$380 Wh kg$^{-1}$) compared to Lithium Iron Phosphate (LFP), ≈180 Wh kg$^{-1}$), making them more suitable for EV applications where extended driving range and compact battery design are critical. While LFP remains widely used due to its superior safety and thermal stability, its lower operating voltage and specific capacity constrain its adoption in premium, performance-oriented markets. These materials, with their unique chemical composition and structural advantages, are crucial to modern high-energy-density battery technology. This section focuses on the interface challenges between solid electrolytes and NCM cathode materials, including issues such as interface contact and side reactions.

### 3.1. Challenges of Interface Contact

The quality of the interface contact between the electrolyte and the electrode has a crucial impact on the performance of

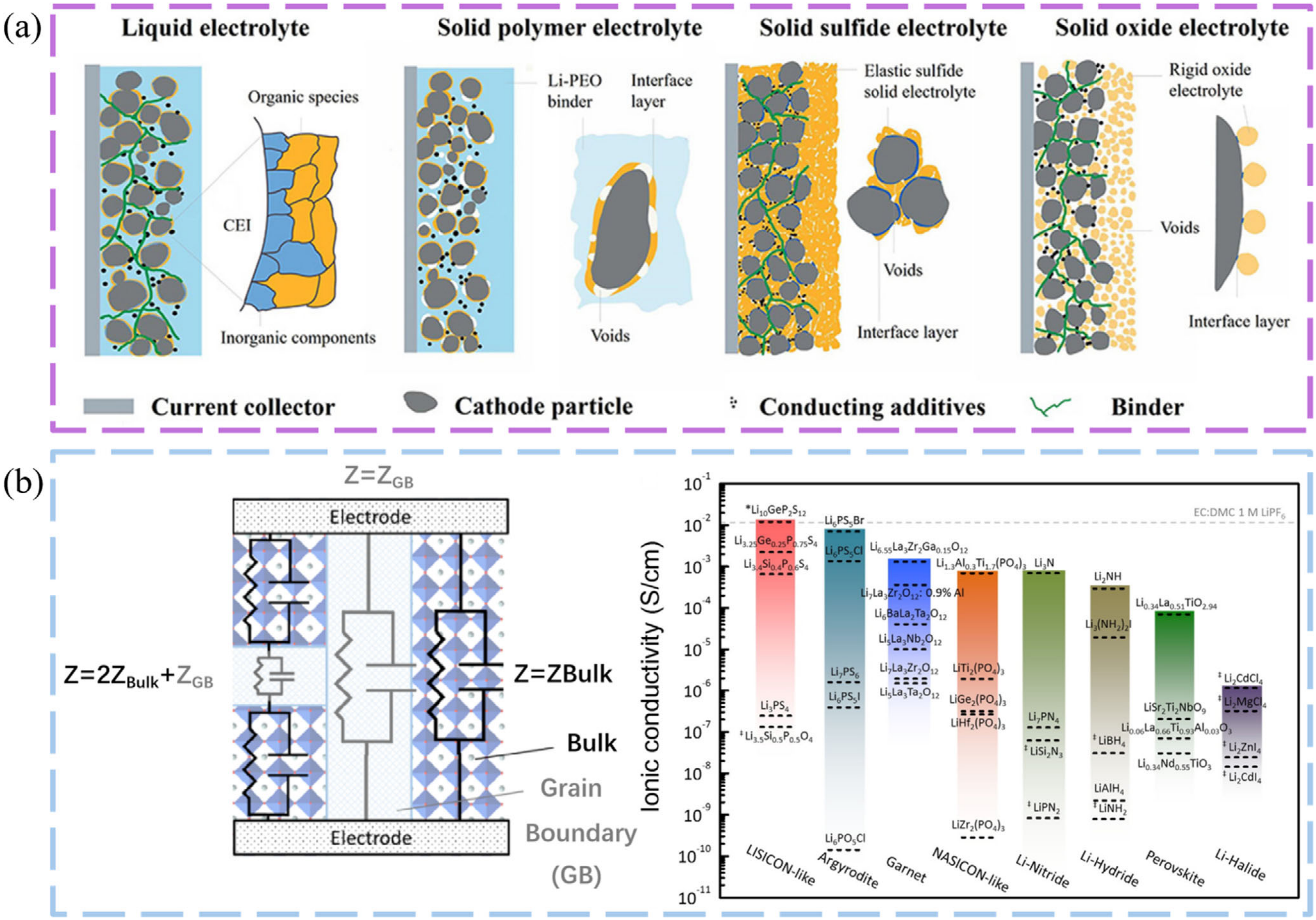

**Figure 4.** a) Schematic diagram of different models' morphology at the interphase between cathode and electrolyte. Reproduced with permission.[138] Copyright 2018, Frontiers Media SA. b) Schematic diagram of conduction pathways in polycrystalline material and summary diagram of room temperature $Li^+$ conductivity with known structure and composition. Reproduced with permission.[139] Copyright 2016, American Chemical Society.

solid-state batteries. In PCEs, the inherent softness of the polymer matrix contrasted with the rigidity of the electrode materials often makes it challenging to achieve a tight and uniform physical contact between them. This poor interface contact leads to high interface impedance at the boundary, hindering the efficient transport of ions between the electrolyte and the electrode, which significantly affects the battery's capacity utilization and cycling stability.

### 3.1.1. Interface Impedance

Interface impedance is categorized into two primary types:[127] the impedance at the interphase between the solid electrolyte and the active material, and the impedance within the solid electrolyte itself. **Figure** 4a illustrates a typical cathode–electrolyte interphase (CEI) topography model, highlighting the different types of interface impedance generated by the contact between various electrolytes and cathodes. Polymer molecules with highly polar groups often lead to increased rigidity of SSEs.[38] This rigidity, when combined with the solid contact at the electrode interface, results in high contact resistance, a significant contributor to the internal resistance of solid-state LIBs. This high contact resistance negatively impacts the battery's charge–discharge performance, energy density, and cycle stability. Another source of impedance at the electrolyte-active material interface is the nanoionics effect. The introduction of a secondary conductive phase in the polymer electrolyte alters the conductive path, and the discontinuous interphase between the main body and the dispersed phase promotes the formation of a narrow charge region. Enhancing the ionic conductivity of PCEs is closely related to this charge region.[128] A space-charge layer is generated at the interphase between PCEs with different chemical potentials and the cathode.[129] For example, when a sulfide solid electrolyte contacts the cathode, a high-impedance Li defect layer (essentially a space-charge layer) forms at the cathode–electrolyte interphase during $Li^+$ diffusion, significantly affecting the battery's power density and high-rate charge–discharge capability.[130] One method to mitigate the nanoionics effect is to shield the sulfide with a thin oxide buffer layer, preventing direct contact with the cathode.[131] Unlike conventional liquid electrolyte batteries, polymer electrolytes and electrodes tend to form voids at the interface after repeated cycling due to interfacial reactions with the electrolytes and cracking of the cathode. As the number of cycles increases, the effective contact area between the two gradually decreases, leading to a significant rise in interfacial resistance.[132,133] This issue can be effectively mitigated by introducing ionic additives to enhance interfacial stability and maintain consistent contact.[18,134,135] In solid-state oxide electrolytes, the poor point contact between the oxide electrolyte and the cathode results in insufficient $Li^+$ transport pathways, leading to uneven current distribution, increased polarization, and nonuniform strain. To address these issues, strategies such as in situ synthesized electrolytes, the introduction of buffer layers, and the development of gel-based systems have proven to be effective solutions.[126,136,137]

The internal impedance of the solid electrolyte can also be divided into two types: grain boundary impedance between fillers and the impedance between the filler and the polymer matrix. As shown in the left image of Figure 4b, the presence of grain boundaries in the polycrystalline samples was confirmed through impedance spectroscopy. The right image shows the room-temperature ionic conductivity of different solid electrolytes based on computational analysis. Grain boundary impedance can significantly affect the properties of the solid electrolyte. For example, the grain boundary resistance of an oxide solid electrolyte reduces its $Li^+$ conductivity.[139] The Schottky barrier model attributes this reduction to severe $Li^+$ loss in the space-charge layer, making grain boundary impedance significantly higher than the internal resistance of the solid electrolyte. Ohta et al.[140] attributed the low conductivity of solid electrolytes to high grain boundary impedance resulting from low carrier concentration in the space-charge layer and the formation of different resistive interphases. Moreover, the presence of different intrinsic structures or impurity accumulation at grain boundaries can obstruct ion conduction pathways, significantly increasing grain boundary resistivity and decreasing ionic conductivity. In addition to grain boundary issues, internal impedance can also arise from the interphase between the filler and the polymer matrix. Ion conduction in polymer-based electrolytes primarily occurs in the amorphous region. While adding fillers to PCEs can reduce the polymer's crystallinity and potentially enhance ionic conductivity, poor interface compatibility between the filler, and the polymer phase can lead to filler particle aggregation. This aggregation increases impedance and hinders $Li^+$ transport within the electrolyte.[141]

### *3.1.2. Ionic Conductivity*

Low ionic conductivity arises not only from the intrinsic properties of the electrolyte itself but also significantly from poor interface contact. Inadequate interface contact leads to the formation of voids, which are typically caused by mismatches in thermal expansion coefficients or mechanical properties between the electrolyte and electrode materials. These voids disrupt the continuous pathways essential for efficient $Li^+$ transport, resulting in a severe reduction in ionic conductivity. Another scenario involves the formation of nonconductive interfacial layers due to chemical incompatibility; reactions between the electrolyte and the electrode can produce passivation layers or interphase compounds that impede ion migration. Additionally, insufficient wettability between the polymer matrix and the electrode surface can hinder intimate contact, further obstructing ion transfer. To address the issue of low ionic conductivity at the interphase, several strategies can be employed. These include enhancing the interface contact through the application of coatings[31,142] or adhesives,[143,144] improving interfacial property by surface functionalization,[145–147] and preventing the formation of nonconductive interfacial layers by buffer layers,[148–150] which can effectively solve interface problems between the electrolyte and electrode materials.

### 3.2. Interfacial Side Reactions

Interface side reactions pose a significant challenge that adversely impacts battery stability and safety. These side reactions can lead to structural alterations in materials, gas evolution, polymer decomposition, and heat generation. This cascade of effects increases the kinetics of undesirable reactions, accelerating material degradation and loss of functionality, thereby further exacerbating these issues. Addressing these problems is crucial for the development of reliable and efficient PCEs.

### *3.2.1. Structural Alterations*

Under high-voltage conditions, inorganic fillers in PCEs undergo various adverse structural changes that affect battery performance. For example, studies have shown that copper oxide fillers experience morphological changes under high voltage, which in turn impact ionic conductivity and electrochemical stability within the polymer electrolyte.[151] Additionally, LLZO fillers with bimodal particle sizes can enhance the mechanical strength of PCEs; however, the interaction between the fillers and the polymer matrix may lead to structural changes that disrupt ionic conduction pathways.[152] In the case of sulfide electrolytes, such as $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ (LGPS), high voltage can cause the decomposition of sulfide groups, forming sulfur or other nonconductive byproducts, thereby hindering $Li^+$ transport.[153] As shown in **Figure 5a**, sulfide electrolytes with different effective bulk modulus ($K_{\mathrm{eff}}$) undergo different decomposition pathways under different voltage, such as transitioning from a highly conductive phase to a less conductive one, which further degrades the electrochemical properties of the material.[154]

### *3.2.2. Gas Evolution*

Even with the addition of a small amount of organic electrolyte in solid-state batteries, chemical reactions between the cathode and electrolyte remain a primary source of gas production. The chemical oxidation of the electrolyte, catalyzed by active substances like singlet oxygen,[157] can lead to violent reactions and gas production. Figure 5b shows that interfacial side reactions involving the polymer can produce HF.[155] This HF further corrodes the cathode material, leading to transition metal dissolution, capacity decay, increased internal resistance, and reduced cycle stability. Ni-rich cathodes are also prone to forming $Li_2CO_3$ on their surfaces, which can decompose electrochemically, increasing $Li^+/Ni^{2+}$ mixing and interfacial polarization resistance.[158] At potentials exceeding 4.3 V (vs $Li^+/Li$), significant amounts of $CO_2$ and $O_2$ may be released, indicating the formation of a reconfigurable layer several nanometers thick after the first charge.[159]

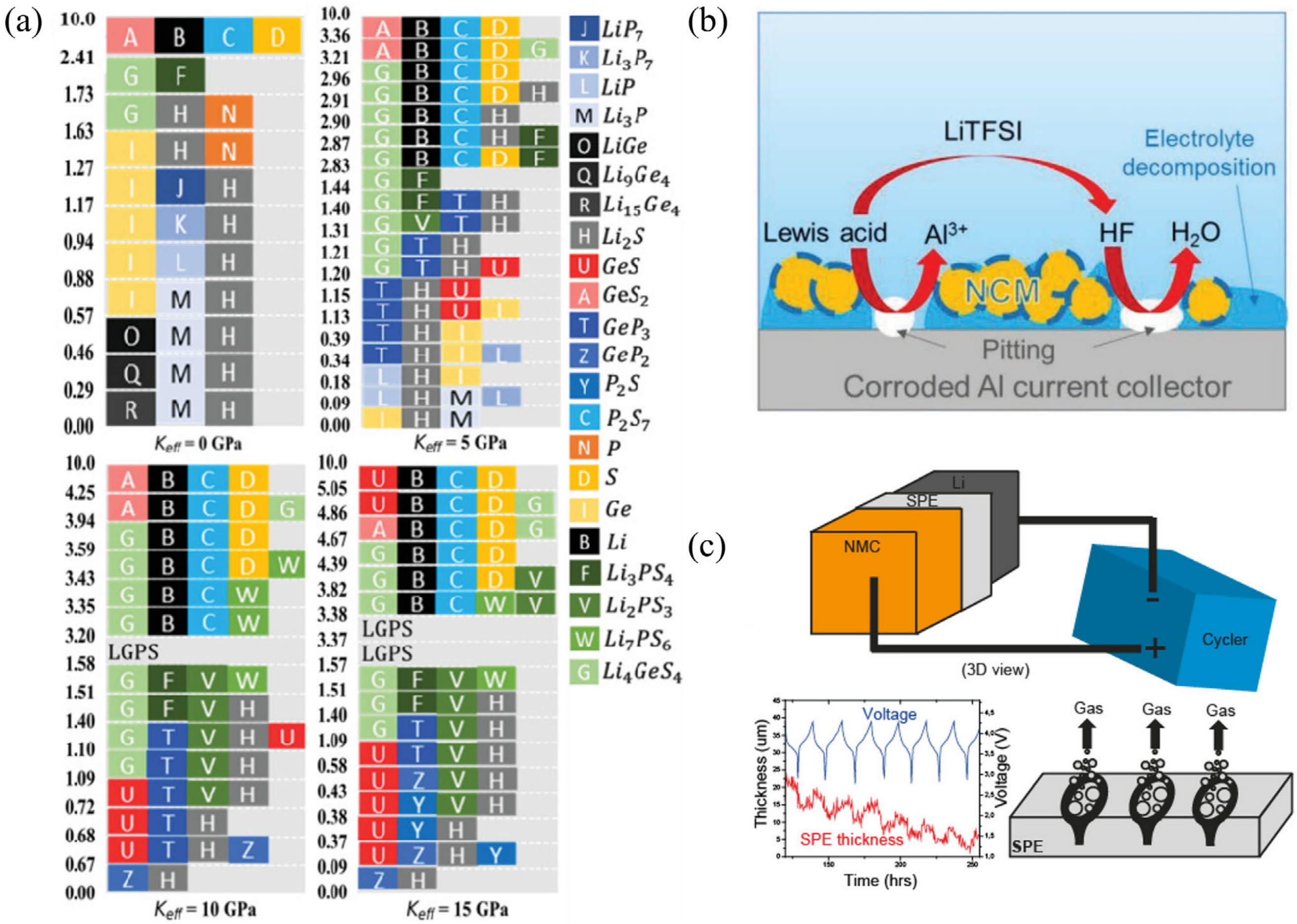

**Figure 5.** a) Decomposition reaction pathways at different $K_{eff}$ and the products induced by different phase equilibriums in different voltage ranges. Reproduced with permission.[154] Copyright 2020, Wiley-VCH. b) The side reaction at the surface of Ni-rich cathode materials. Reproduced with permission.[155] Copyright 2020, Wiley-VCH. c) Schematic diagram of the reactions producing gases. Reproduced with permission.[156] Copyright 2020, American Chemical Society.

The decomposition of the polymer matrix is significantly influenced by these surface reconfiguration phenomena.

### *3.2.3. Polymer Decomposition*

Achieving high energy density often necessitates operating over a wider voltage range. The stability of the interphase between PCEs and high-energy-density cathode materials becomes increasingly critical under high-voltage conditions.[160] At elevated voltages, the polymer in PCEs can become thermodynamically unstable, leading to oxidation and triggering undesirable electrochemical reactions.[161] The electrochemical instability of functional groups such as C—O, C═O, and C—H in the organic phase of composite electrolytes can deteriorate the cathode–electrolyte interfacial stability, causing voltage polarization and capacity fading. This not only compromises battery performance but also raises safety concerns. Furthermore, under such high-voltage stress, the ESW, determined by the HOMO and LUMO levels of the polymer, plays a pivotal role in maintaining interfacial stability. A narrow ESW increases the likelihood of reactions between the NCM cathode and the PCE, accelerating degradation and further reducing battery lifespan.

### *3.2.4. Heat Generation*

Whether in solid-state or liquid batteries, undesirable exothermic side reactions at the interface can trigger complex electrochemical and mechanical interactions. During battery cycling, side reactions between the electrolyte components and electrodes, combined with the high resistance to $Li^+$ transport and the electrochemical decomposition of solvents and additives at elevated voltages, result in the generation of substantial heat.[162–165] Elevated temperatures exacerbate instability by increasing oxygen species at the interface, thereby reducing the electrolyte's stability. Additionally, temperature fluctuations can induce mechanical stress and thermal expansion mismatches at the interface; stress-induced microcracks and delamination create additional pathways for side reactions. At high temperatures, as the mobility of $Li^+$ and degradation products increases, these problems become more complex, leading to accelerated interfacial reactions.[166]

Under thermal exposure, solid electrolyte demonstrates complex thermal behaviors.[167] These processes are crucial for the safety of polymer-based solid-state batteries.[168] Gas production (Figure 5c),[156] such as $CO_2$ and $O_2$, during cycling can block parts of the electrode surface, hindering $Li^+$ transport and causing uneven current distribution, which is a critical challenge in developing advanced LIBs. Jo et al.[169] through various in situ analyses, discovered the multidirectional crosstalk of intermediate reaction gases within closed full cells. By-products from the anode–electrolyte interaction produce $C_2H_4$ gas, which then migrates to the cathode, accelerating the release of $O_2$. The $O_2$ produced at the cathode returns to the anode, further promoting the formation of additional $C_2H_4$ at the anode. This creates a self-amplifying loop. It shows for the first time that intermediate products can continuously interact to form a redox cycle, which worsens thermal runaway.

## 4. Interface Challenges between PCEs and High-Capacity Anode Materials

The transport of $Li^+$ at the electrode–electrolyte interphase has garnered significant attention in the context of solid-state LIBs. The stability of this interphase remains a critical bottleneck, impeding the broader adoption and performance of these batteries. Previously, we discussed the challenges associated with the cathode–electrolyte interface. In this section, we shift focus to the interface issues between PCEs and the anode. Although high-capacity anode materials can significantly reduce electrode thickness, critical challenges persist—including inadequate electrolyte–electrode contact at the anode interface, the growth of Li dendrites, and decomposition under high voltage. Effectively resolving these interfacial issues can greatly facilitate the realization of high-energy-density batteries.

### 4.1. Lithium-Metal Anode

#### *4.1.1. Interface Contact Challenge*

In solid-state batteries utilizing Li metal as the negative electrode, repeated volume changes of Li during charge and discharge cycles progressively degrade the interface contact, leading to increased interfacial impedance between the Li metal and the polymer electrolyte.[170] Over time, the solid electrolyte interphase (SEI) at the interface becomes uneven and thickened, significantly deteriorating the interfacial compatibility between the electrolyte and the electrode, thereby raising the kinetic barriers for electrochemical reactions, as shown in **Figure 6**a.[171,172] The effective strategies to solve the challenge of Li-metal anode contact with PCE are mainly to improve the wetness of the interface[173–176] and introduce buffer layer.[175,177,178] For instance, the solid–solid interface between inorganic solid-state electrolytes and Li anode typically exhibits high interfacial resistance. In contrast, polymer electrolytes improve interface contact, enhancing ionic conductivity and electrochemical stability, which mitigates issues like dendrite formation and performance degradation.[179] PCEs based on polymer electrolytes not only achieve good interface contact but also offer wider electrochemical windows, enhancing interfacial stability. However, the volume changes during cycling can disrupt this contact, leading to increased interfacial resistance. To mitigate this issue, researchers have focused on improving interfacial wettability. Through liquid-phase treatment[180,181] and in situ polymerization techniques,[182,183] which involve introducing a controlled amount of liquid into PCEs, the interfacial compatibility between the Li-metal anode and the electrolyte is significantly enhanced. This approach not only increases energy density and extends cycling life but also reduces interfacial resistance, ultimately leading to improved overall electrochemical performance in solid-state batteries.[184] Moreover, polymerized phases are susceptible to severe side reactions after prolonged exposure to Li metal.[185,186] Primarily, low reduction stability of PCEs may lead to reduction reactions at the anode, generating unstable byproducts that form an uneven, resistive interfacial layer, thereby impairing the electrochemical performance of batteries.[187] Additionally, inadequate chemical compatibility between PCEs and the anode exacerbates side reactions, while poor mechanical and electrochemical compatibility can lead to interfacial delamination or microcracking under cycling-induced stress, further obstructing ion transport pathways.[188] Lastly, insufficient wettability at the interface disrupts uniform electrolyte distribution, resulting in localized high current densities that promote dendritic growth.[189]

#### *4.1.2. Lithium Dendrite Challenge*

Li dendrite formation in Li-metal batteries arises from several interconnected factors, with the primary driver being the uneven deposition of $Li^+$ during charging. As $Li^+$ migrate toward the anode, regions of high current density cause localized ion flux, leading to the nucleation of dendritic structures. It is worth noting that two pivotal mechanisms influencing dendrite growth are space-charge effects and ionic conductivity. Space-charge effects occur when ions accumulate near the electrode interface, creating a non-uniform ion flux that fosters dendrite formation. Additionally, poor ionic conductivity within the electrolyte results in uneven ion distribution, creating high current zones that facilitate dendritic growth. This phenomenon is further aggravated by mechanical stress from volume changes during cycling and electrochemical instability at the electrode–electrolyte interphase. While elevated temperatures enhance ion mobility, they also exacerbate dendrite formation by allowing ions to accumulate more rapidly in localized regions. As depicted in Figure 6b, Chen and co-workers[190] proposed a comprehensive framework for the interface reactions and evolution between Li metal and the solid electrolyte, which can be categorized into three distinct stages: 1) the transport of $Li^+$ from the anode to the interface via the SSE; 2) the electrochemical reduction of $Li^+$ at the interface, accompanied by parasitic side reactions that lead to the development of the SEI layer; and 3) the nucleation and subsequent growth of Li deposits. Recently, building on the SEI model proposed by Peled and Yamin last century,[191,192] Wang and co-workers[193] proposed a novel mechanism for Li dendrite growth, known as the electrochemical–mechanical model.[194–196] When Li and the solid electrolyte form an SEI, the Li dendrites either penetrate the SEI or nucleate within the solid electrolyte, depending on the variation between the applied interfacial

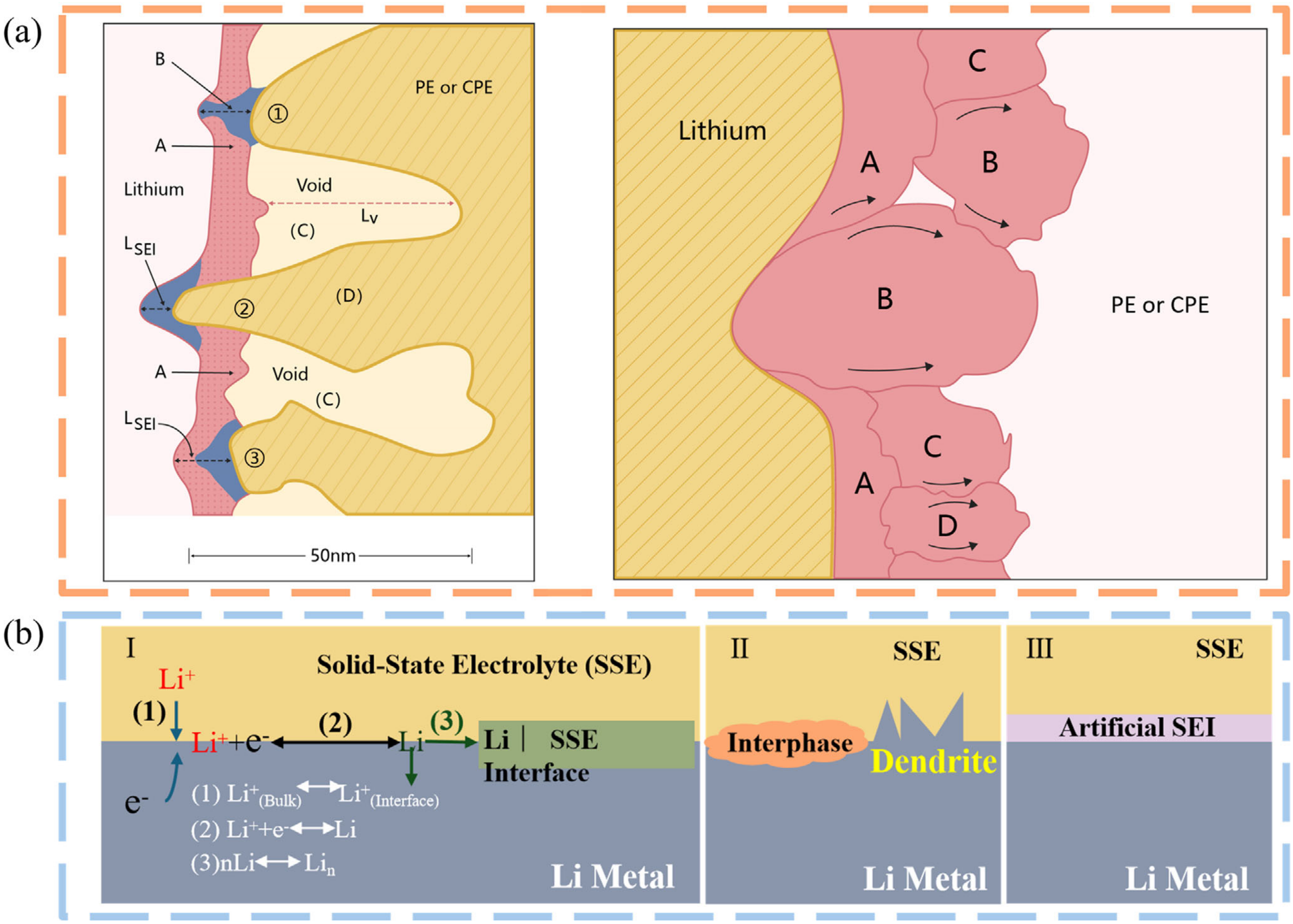

**Figure 6.** a) Schematic diagram of the Li | polymer electrolyte interphase and a small segment of the SEI. Reproduced with permission.[171] Copyright 1995, Elsevier. b) Schematic diagram of interfacial reaction and the evolution of the Li | solid-state electrolyte interface. Reproduced with permission.[190] Copyright 2018, Elsevier.

overpotential (AIOP) on the Li side of the SEI and the critical interfacial overpotential (CIOP) of the SEI. The magnitude of the CIOP is primarily determined by the intrinsic properties of the SEI, with higher CIOP values effectively suppressing dendrite growth. Consequently, the electronic conductivity of both the SEI and the solid electrolyte plays a pivotal role in determining whether Li dendrites can form. Halogen atom doping[197,198] has been shown to reduce the electronic conductivity of the solid electrolyte and SEI, thereby increasing the CIOP and enhancing the SEI layer's ability to suppress dendrite formation. Additionally, inserting an artificial SEI layer with high CIOP directly at the Li–solid electrolyte interface through physical[199] or chemical[200] methods can also inhibit dendrite growth without limiting the Li plating capacity. The presence of Li dendrites significantly degrades battery performance by compromising safety (due to the risk of internal short circuits and thermal runaway), deteriorating interface contact (increasing interfacial resistance and reducing ion transport efficiency), and diminishing cycling stability (through irreversible Li loss and rapid capacity fade). Strategies to suppress dendrite growth include enhancing the mechanical strength of the electrolyte, designing stable interfacial modification layers, and optimizing ionic conductivity. These approaches help to mitigate dendrite formation, thereby improving the overall performance of Li-metal batteries.[201–203]

The integration of Li-metal anodes in solid-state batteries faces two critical challenges: deteriorating interface contact and the growth of Li dendrites. Repeated volume changes and interfacial reactions lead to increased resistance and poor compatibility, while dendrite formation—driven by uneven $Li^+$ flux, space-charge effects, and insufficient mechanical/electrochemical stability—poses serious safety and performance risks. Improving interfacial wettability, constructing artificial SEI layers, and optimizing electrolyte properties such as ionic and electronic conductivity are essential strategies to enhance interfacial integrity and suppress dendrite growth.

### 4.2. Silicon Anode

#### *4.2.1. Volume Expansion Challenge*

In high-energy-density PCE batteries, silicon anodes are of particular interest not only due to their remarkable potential to significantly enhance the energy density of the entire system, but also

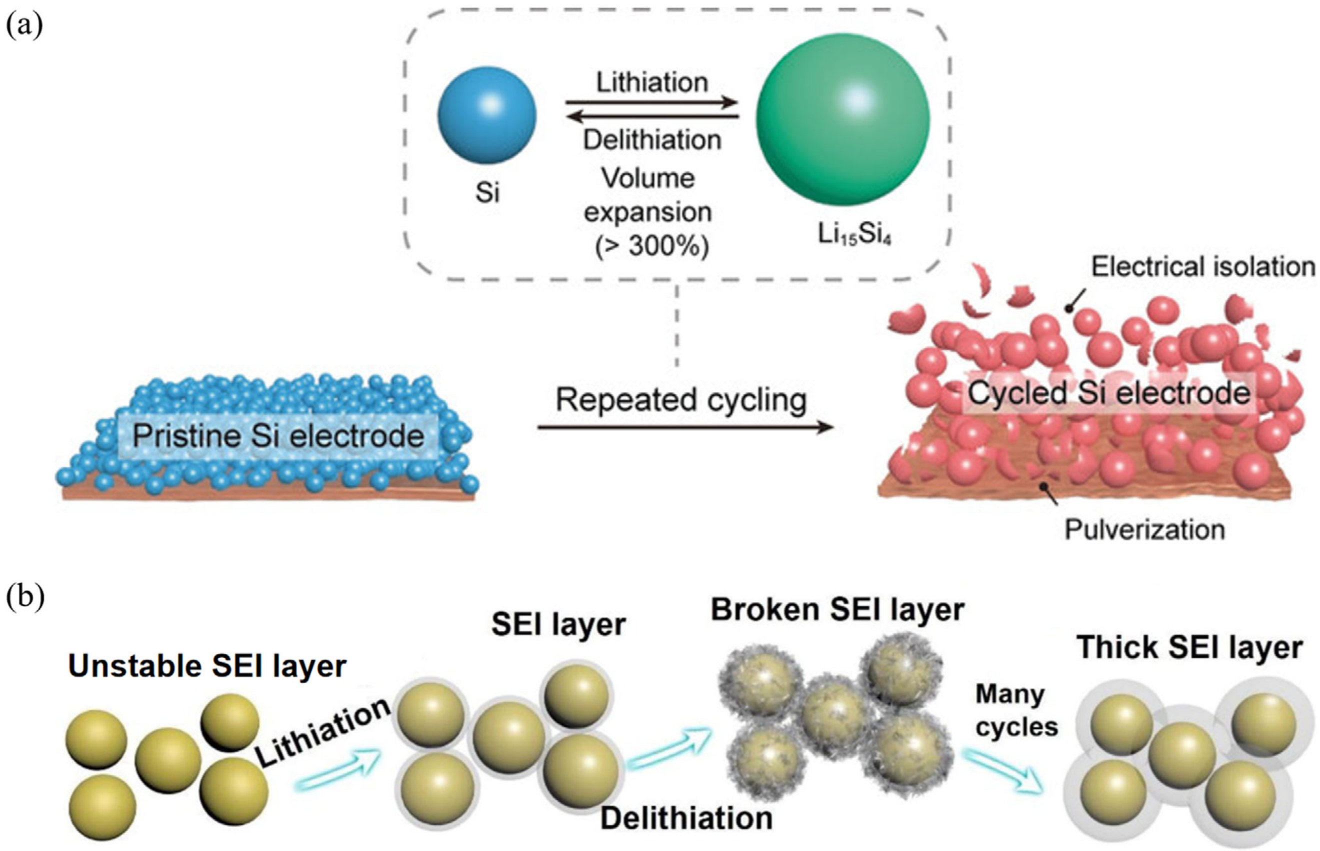

**Figure 7.** a) Schematic diagram of the failure mechanism of Si anodes. Reproduced with permission.[204] Copyright 2020, Wiley-VCH. b) Schematic diagram of SEI problems for Silicon anodes. Reproduced with permission.[205] Copyright 2021, Elsevier.

the soft polymer matrix can accommodate the substantial expansion stress of silicon. However, the reversibility of this system remains a critical concern. As shown in **Figure** 7a, in the PCE-based LIBs, the silicon anode undergoes substantial volume expansion during full lithiation.[204] This dramatic volume change causes deformation of the SEI layer, leading to its rupture and subsequent reconstruction (Figure 7b),[205] significantly increasing irreversible Li consumption and shortening battery life. The SEI layer plays a pivotal critical role in passivating the surface to prevent further electrolyte decomposition and irreversible Li consumption. Fortunately, PCEs, with their excellent flexibility, can sustain good interface contact with silicon under external pressure. Nevertheless, the interphase between PCEs and the anode still exhibits significant porosity (10–40%), which is further exacerbated by the continuous pulverization of silicon particles during repeated lithiation and delithiation, leading to severe interfacial degradation and loss of cycling stability.[206] Volume expansion of silicon anodes causes interface contact issues with PCEs. Main solutions include using composite silicon materials,[206–208] forming SEI layers,[209] applying coatings,[210–212] and modifying polymers.[213–215] In recent years, the use of in situ polymerization of gel polymer electrolytes has become increasingly popular in silicon anode batteries, effectively limiting the expansion of silicon and suppressing the reduction of contact area.[216–218] Ma and co-workers[219] proposed a strategy using in situ polymerized gel polymer electrolyte, poly(vinylene carbonate) matrix-gel polymer electrolyte (PVCMGPE), which balances ion conductivity, $Li^+$ transference number, mechanical strength, electrochemical stability with high-voltage cathodes, and flame retardancy. A 2.7 Ah pouch cell (Si/C@C-Gr|GPE|NMC) was assembled, where the synergistic effects of innovative electrode design and enhanced interfacial stability enable efficient $Li^+$ utilization, thus extending both the cycle life and energy density of the battery.

### *4.2.2. Interface Reaction Challenge*

Another major challenge between silicon anodes and PCEs is chemical reactivity, which can negatively impact the overall electrochemical performance and longevity of the battery. The interfacial reactivity initiates a series of side reactions that degrade both the silicon surface and the PCEs, resulting in the continuous formation of an unstable SEI layer (Figure 7b), which degrade the electrochemical performance of the battery and cause capacity fade over prolonged cycling.[206,220] Additionally, the high interfacial reactivity is further exacerbated by the formation of Li silicates or polysiloxanes at the interface, which are electrically and ionically insulating species that lead to an increase in interfacial resistance.[221] The continuous formation and decomposition of these insulating species not only reduce the mechanical integrity of the PCEs but also accelerate the degradation of the SEI, leading to irreversible capacity loss and poor cycling stability.[222] Furthermore, the presence of reactive functional groups in the PCEs, such as carbonyl or ester groups, can lead to complex degradation pathways when interacting with silicon surfaces.[223] These reactions can result in the breaking of covalent bonds within the polymer backbone, leading to the release of volatile by-products and a breakdown of the polymer structure.[224] Overall, the interfacial reactivity between silicon anodes and PCE poses a significant barrier to achieving high-capacity PCE batteries. Therefore, developing more stable interfacial chemistries and mechanically robust PCEs is crucial for ensuring long-term high-performance operation in solid-state battery applications. Zhang and co-workers[225] designed an innovative PCE structure consisting of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ (LATP) and poly(vinylidene fluoride)-*co*-hexafluoropropylene (PVDF-HFP), which forms a stable SEI layer at the interface of the modified silicon anode. This layer is composed of highly ordered inorganic LiF domains integrated with the main components of PVDF-HFP. The SEI layer effectively facilitates the transport of $Li^+$ across the interface while preventing undesirable side reactions.

Silicon anodes in PCE batteries offer great potential for high energy density but face two major challenges: severe volume expansion during cycling and high interfacial reactivity. These issues lead to unstable SEI layers, poor interfacial contact, and continuous capacity fade. To address them, strategies such as composite silicon structures, interfacial coatings, SEI regulation, polymer matrix modification, and in situ gel polymerization have been developed. Future efforts must focus on designing PCEs with enhanced mechanical resilience and interfacial chemical stability to ensure long-term cycling performance and reliability.

### 4.3. Other High-Energy-Density Anode Materials

**Figure** 8a summarizes the materials of several high-energy-density batteries.[226] Significant progress has also been made in the development of other high-energy-density anode materials, including anode-free material, aluminum metal material, and various alloy materials. These materials demonstrate the potential to maintain high specific capacities while overcoming the interfacial and stability challenges associated with conventional anodes through tailored material design and structural optimization, thereby meeting the application requirements of next-generation high-energy-density energy storage devices. However, their practical implementation still faces several critical challenges, including poor long-term cycling stability, interphase reactivity, and scalability issues that must be addressed to fully realize their potential.

#### *4.3.1. Anode-Free Material*

In recent years, anode-free batteries attracted great attention due to the absence of a $Li^+$ insertion host on the anode side, which significantly reduces the weight and thickness of the battery while providing higher energy density.[229] As shown in Figure 8a, the energy density of anode-free SSBs (AFSSBs) can reach 408 Wh $kg^{-1}$ (1514 Wh $L^{-1}$).[226] Additionally, due to the high safety and energy density of SSEs, AFSSBs are considered a promising strategy for next-generation high-energy batteries.[230] AFSSBs use current collectors such as Ag, Au, Cu, or Si as substrates for $Li^+$ deposition. However, they still face the same dendrite growth issues as solid-state Li-metal batteries. This is because the more rigid current collectors struggle to maintain good contact with solid electrolytes, leading to localized high current density at the interface, hindering uniform Li deposition.[231,232] Another major issue is the high interfacial resistance between the anode-free current collector and the polymer electrolyte, which hinders efficient $Li^+$ transport across the interphase, thereby limiting the overall electrochemical performance. This high interfacial resistance is often exacerbated by the formation of unstable interphases during the repeated Li plating and stripping processes, leading to rapid capacity decay and shortened cycle life.[233,234] Additionally, the high reactivity of the anode-free surface can induce polymer degradation, resulting in the formation of an unstable SEI, which further increases interfacial resistance and accelerates electrolyte decomposition. Moreover, the mechanical properties of PCEs are typically insufficient to withstand the volumetric changes associated with Li deposition and stripping, leading to the formation of cracks and delamination at the interface. These dendrite problems, coupled with interfacial resistance and high reactivity, pose significant obstacles to the development of high-performance AFSSBs.

#### *4.3.2. Aluminum-Metal Material*

In addition to anode-free batteries, aluminum, with its exceptionally high energy density (2250 Wh $L^{-1}$), has recently been considered a viable alternative to Li metal (2060 Wh $L^{-1}$).[235] The redox potential of aluminum metal is +1.66 V, which creates a significant voltage difference in the battery's reactions. During discharge, aluminum metal is oxidized to form aluminum hydroxide, releasing heat and thereby generating electrical energy, which contributes to a high energy output. Due to the abundance and low cost of aluminum, aluminum-metal batteries present a promising alternative energy solution, particularly for applications requiring high energy density. When integrating aluminum-metal anodes with polymer-based electrolytes in solid-state batteries, several challenges arise, primarily due to the electrochemical and mechanical instability at the interface. Aluminum exhibits high reactivity with many common polymer electrolytes, which can lead to the formation of passivating layers and degradation products at the aluminum/electrolyte interface. This issue is further compounded by the low room temperature ionic conductivity of polymer electrolytes, which limits efficient charge transport and results in poor overall battery performance. Moreover, the poor coordination between the polar groups in the polymer matrix and the active species further restricts the ionic conductivity of the solid electrolyte, thereby hindering efficient ion transport.[236] Additionally, aluminum dendrites may form during plating and stripping processes, potentially leading to mechanical failure of the polymer matrix, which in turn causes short circuits and significantly reduces the cycle life of the battery.[237]

#### *4.3.3. Alloy Anode Material*

In addition to the aforementioned anode materials, alloy anodes (e.g., Sn, Sb, P, and Bi) are gaining widespread attention due to

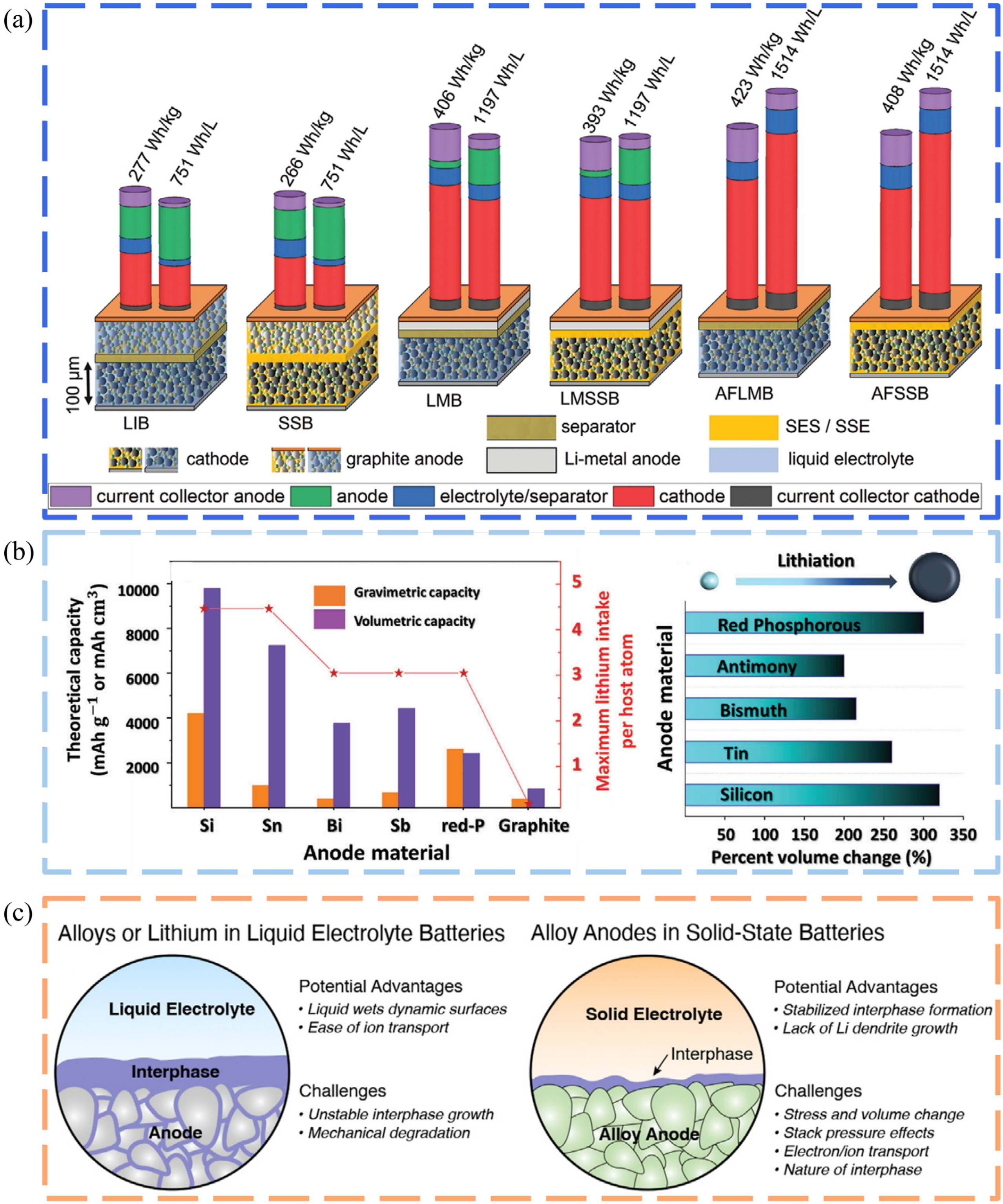

**Figure 8.** a) Schematic diagram of cell configurations, stack weight and volume distribution, and estimated energy density for conventional Li$^+$ batteries and solid-state batteries with intercalation type electrodes, Li-metal anode, and anode-free configuration. Reproduced with permission.[226] Copyright 2021, Wiley-VCH. b) Theoretical gravimetric and volumetric capacities of typical alloy anodes in comparison to graphite, along with maximum possible Li intake per host atom for each and corresponding volume expansion of alloy anodes upon lithiation. Reproduced with permission.[227] Copyright 2023, Wiley-VCH. c) Schematic diagram of an alloy anode or Li-metal anode in a liquid electrolyte environment, along with potential advantages and challenges and alloy anode used in a solid-state battery. Reproduced with permission.[228] Copyright 2022, Elsevier.

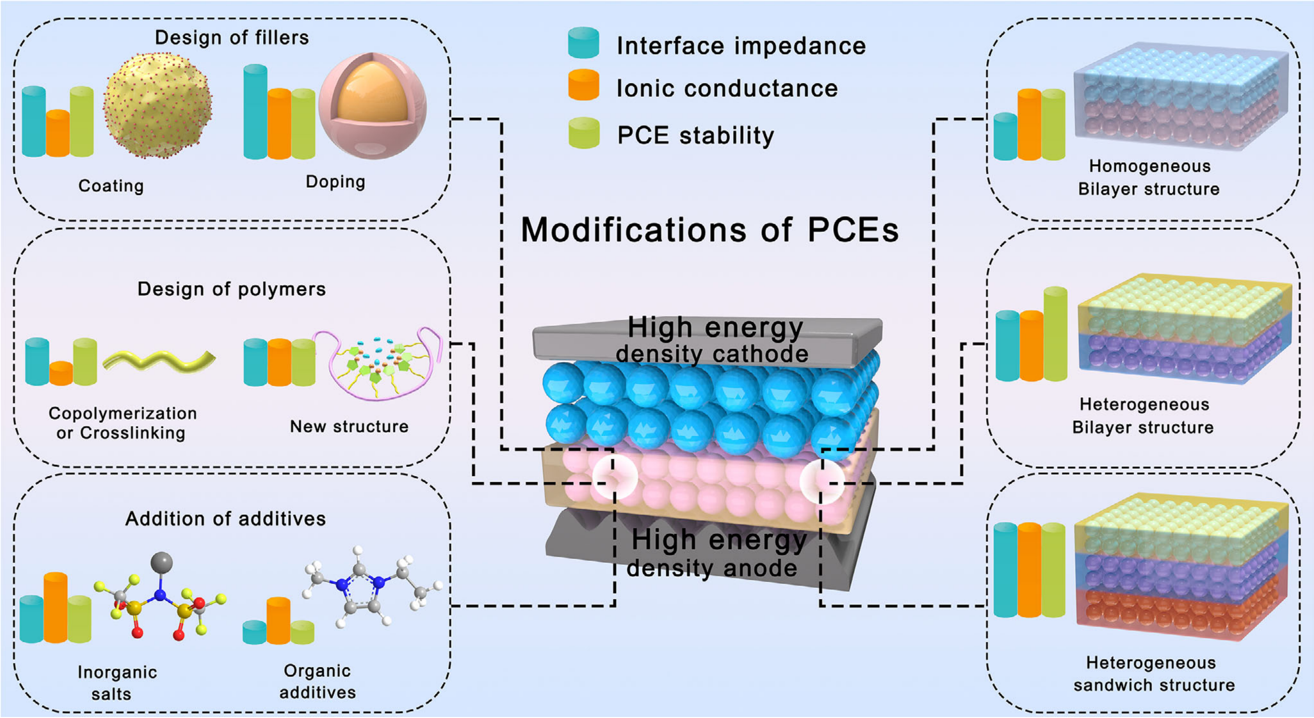

**Figure 9.** Summary diagram of PCEs' modification methods.

their ability to form solid solutions that can accommodate large amounts of Li$^+$, limiting dendrite formation while offering excellent energy density (as shown in Figure 8b).[238–241] For example, the specific capacity of silicon–graphite composites can reach 1500–2000 mAh g$^{-1}$, while silicon–tin alloy anodes can achieve a specific capacity of 2000–3000 mAh g$^{-1}$, and tin alloys have a specific capacity ranging from 600 to1000 mAh g$^{-1}$. However, in liquid electrolytes (Figure 8c), the rigid SEI layer is disrupted by the volumetric expansion and contraction of alloy particles during Li insertion/extraction. This leads to repeated consumption of Li$^+$ and electrolyte solvents to reform the SEI layer, ultimately resulting in high interface impedance and cell failure.[242–244] In contrast, polymer-based SSEs do not flow during the volume changes of alloy materials, which maintains consistent wetting of the alloy surface and reduces interface impedance. Moreover, the SEI layer formed is relatively thin.[245–247] However, the substantial volumetric changes induce significant mechanical stress at the anode–electrolyte interface (Figure 8b), leading to severe delamination, cracking, and eventual loss of electronic contact, which results in poor cycling stability and reduced battery lifespan.[228,248] By employing strategies such as composite material design, nanomization, and surface coatings, these issues can be effectively mitigated, thereby enhancing the performance of alloy anode materials in LIBs.

## 5. Modification Strategies

High-energy-density SSLBs, which consist of three key components (i.e., cathode, anode, and electrolyte), represent a complex system engineering challenge. However, severe interfacial issues between these components significantly undermine the cycling stability and safety of the batteries, posing major obstacles to their large-scale commercialization. Unlike conventional reviews that list the effects of each strategy, we focus on key parameters of solid-state batteries. These include interface impedance, ionic conductivity, and PCE stability. As illustrated in **Figure 9**, we provide a comprehensive summary and analysis aimed at guiding researchers in making informed decisions when selecting modification strategies. While numerous studies have explored optimization strategies for both cathode and anode materials, the focus of this section is on the modification and optimization strategies for solid electrolytes, including design of filler, design of polymers, addition of additives, and structural engineering of PCEs.

### 5.1. Design of Basic Materials

#### *5.1.1. Filler Modification*

For PCEs, although the incorporation of inorganic fillers into the polymer matrix significantly enhances ionic conductivity—thanks to the fast ion conduction at the filler–polymer interphase or through the fillers themselves—a high filler content can lead to particle agglomeration, disrupting the percolation network within the electrolyte.[249] Additionally, some inorganic fillers may inevitably react with the electrodes after being introduced, resulting in slower Li$^+$ transport and reduced cycling performance. To fully leverage the advantages of inorganic fillers while mitigating agglomeration effects, it is possible to design a percolation network with maximum interphase volume. As shown in **Figure 10a**, a polydopamine (PDA) coating was formed on the

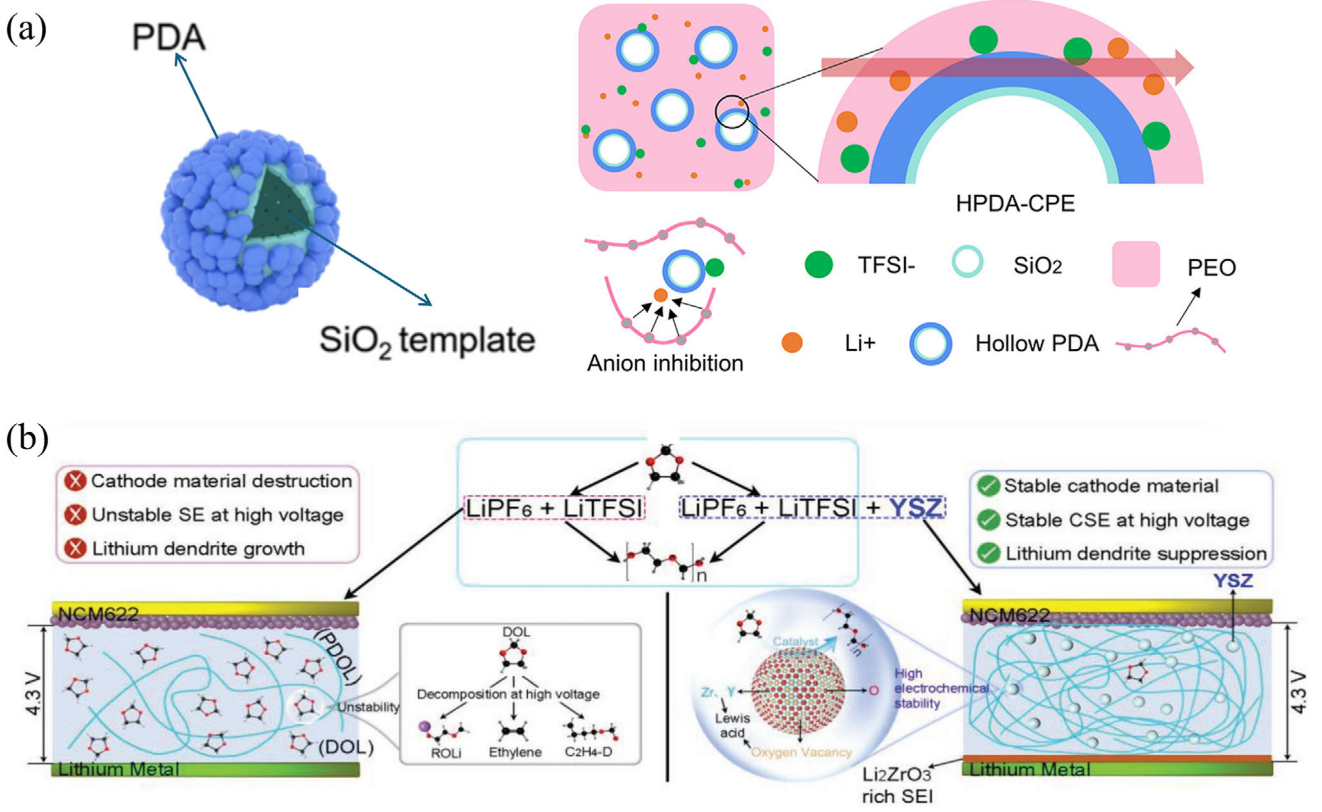

**Figure 10.** a) Schematic diagram of the working mechanism of the all-solid-state Li-metal battery with HPDA–PCE (hollow polydopamine-PCE). Reproduced with permission.[250] Copyright 2022, American Chemical Society. b) Schematic diagram for YSZ enhancing the performance of PDOL-based (Poly(1,3-Dioxolane)-based) solid-state batteries. Reproduced with permission.[251] Copyright 2022, Wiley-VCH.

surface of hollow silica nanospheres by self-polymerization, and then introduced into the PEO-based electrolyte system, which improved the compatibility between the electrolyte and the high-voltage cathode material and improved the ionic conductivity.[250]

Furthermore, researchers have fabricated PCEs by incorporating yttria-stabilized zirconia (YSZ) nanoparticles containing abundant Lewis acid sites into a 1,3-dioxolane (DOL) matrix through in situ catalytic polymerization.[251] As illustrated in Figure 10b, the Lewis acid sites on YSZ nanoparticles can adsorb Li-salt anions, releasing more free Li$^+$, increasing carrier concentration, and thus improving ionic conductivity. A robust, $Li_2ZrO_3$-rich ionic conductive layer is formed in situ at the anode interface, enhancing adhesion between the electrolyte and electrode, reducing interfacial resistance, and promoting uniform Li deposition, thereby effectively suppressing dendrite growth. The incorporation of YSZ broadens the electrochemical stability window of the PCE, reduces damage to the cathode materials caused by DOL monomers at high voltage, and enables high-voltage, high-energy-density SSLBs. Recently, a computational study conducted by Liu et al. using DFT has effectively confirmed the ability of anion vacancies in fillers to anchor the anions of Li salts, thereby significantly enhancing the migration of Li$^+$ within the electrolyte. Through the clever modulation of functionalized carbon dots (CDs), they successfully synthesized flower-like $SnS_2$-based fillers rich in sulfur vacancies. Notably, these CDs, resembling gems decorating the surface of $SnS_2$, not only carry abundant organic functional groups but also serve as a bridge connecting the fillers with the polymer, greatly improving the compatibility between the two. This, in turn, imparts excellent mechanical properties to the material while establishing rapid ion transport channels. Additionally, a $Li_2S/Li_3N$ layer spontaneously forms at the interphase between the Li metal and the electrolyte, providing favorable conditions for the rapid diffusion of Li$^+$ and uniform Li deposition, effectively suppressing the formation of Li dendrites.[252] However, within the polymer matrix, the haphazard distribution of fillers precipitates bending in ion channels, subsequently elongating the ion transmission pathway and diminishing ion conductivity. Deng et al.[253] have innovatively harnessed ultraviolet-induced polymerization technology, coupled with a magnetic-field-assisted approach, to meticulously craft PCE materials that boast vertically oriented channels. Through meticulous control over the magnetic field orientation, they have achieved precise vertical alignment of the rod-like structures. This meticulously engineered arrangement of ion channels drastically curtails the migration distance of Li$^+$ within the electrolyte system. Additionally, the hollow and mesoporous silicon rods, which function as pivotal components of the electrolyte, offer ample adsorption space, thereby augmenting electrochemical kinetic properties.

Through the strategic modulation of the surface chemical characteristics and spatial arrangement of fillers, a multiscale ionic transport network can be established, thereby synergistically improving the uniformity of interfacial ionic flux and enhancing mechanical buffering capacity. The cornerstone of industrializing resides in the creation of economically viable surface modification techniques and precision dispersion equipment, which together ensure optimal compatibility at the filler–polymer interphase and promote long-term cycling stability.

### *5.1.2. Polymer Modification*

Polymer inherent limitations, including a narrow ESW, poor mechanical properties, and limited chemical stability, hinder their application in high-energy-density SSLBs. Thus, modifications are required to improve their overall performance and meet the demands of next-generation energy storage systems. The modification of polymers typically involves crosslinking existing polymers and the development of novel polymer structures. The Armand team's work in the 1990s was an early exploration in this field.[254] As depicted in **Figure 11a**, a fluorinated bifunctional solid polymer electrolyte (FB-SPE) was synthesized through visible-light-initiated radical polymerization of fluorinated and polyether-based segments. The introduction of fluorinated chains facilitates the formation of robust Li—F interactions, which stabilize the SEI by generating a uniform and densely packed LiF-rich layer. This stabilized SEI effectively reduces interface impedance and inhibits the growth of Li dendrites. By promoting uniform $Li^+$ transport and minimizing parasitic reactions at the interphase, the FB-SPE significantly enhances interface contact, thereby ensuring stable cycling performance and prolonging the battery's operational lifespan.[255] Similarly, Shen and co-workers[256] recently introduced an innovative design concept for an anion-modulated polymer electrolyte (AMPE) tailored for high-voltage Li-metal batteries. By incorporating high-voltage-tolerant and high-charge-density units, namely 1-allyl-1-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide (IL) and 3-sulfolene (SE), along with an anion receptor unit, boranetriyltris(oxy)tris(ethane-2,1-diyl)tris(2-methylacrylate) (B-HEMA), the AMPE achieves exceptional ionic conductivity and boasts an oxidation stability window of up to 5.55 V. The inclusion of B-HEMA effectively regulates the dissociation of anion–cation pairs, thereby enhancing both ionic conductivity and interfacial stability. Furthermore, the decomposition of $TFSI^-$, facilitated by the anion receptor, drives the formation of a mosaic-like SEI on the Li-metal anode. This SEI, characterized by an outer layer comprising $Li_2S$ and $LiSO_2F$ and an inner layer enriched with LiF, plays a pivotal role in reducing interface impedance and suppressing Li dendrite growth. In recent years, advancements in polymer synthesis techniques have established various controlled polymerization methods, such as reversible addition–fragmentation chain transfer (RAFT) polymerization and organocatalyzed ring-opening polymerization (ROP), as effective strategies for constructing polymers with diverse topologies. As shown in Figure 11b, Xue and co-workers[257] synthesized copolymers with tailored architectures using a one-pot approach that integrates RAFT polymerization and ROP. This innovative strategy provides precise control over molecular weight and topology, enabling the formation of both linear and grafted copolymers. When employed as polymer matrices in SPEs, these copolymers exhibit exceptional interfacial properties, including improved interface contact and significantly reduced impedance. These advancements are attributed to the uniform distribution of functional groups, which ensures stable ion transport across the interface. Furthermore, the tailored polymer structures effectively mitigate side reactions at the interface, thereby stabilizing the SEI, enhancing cycling stability, and prolonging battery lifespan.

Crosslinking innovations and novel topological polymer architectures effectively expand the electrochemical window and mechanical robustness of PCEs. Future advancements must prioritize overcoming the challenges associated with the large-scale synthesis of functional monomers. Additionally, employing in situ polymerization techniques to minimize the density of interfacial defects will be essential for achieving continuous production with high yield.

### *5.1.3. Introducing Additives*

Additives, which can be divided into organic additives and inorganic additives, play a key role in optimizing the performance of high-energy-density PCEs by improving ionic conductivity, stabilizing interphases, and enhancing mechanical properties.[258]

Organic additives are typically based on polymers or small organic molecules that enhance electrolyte performance by regulating the microstructure of the electrolyte, improving ion conductivity, and extending the electrochemical window, thereby increasing the energy density of battery systems. Common organic additives include macromolecular polymers, polymer plasticizers, and ILs. Macromolecular polymers, such as PVDF-HFP, enhance the ionic conductivity and impedance characteristics of electrolytes by improving structural stability and interfacial electrochemical stability.[259] Polymer plasticizers, such as polyethylene glycol (PEG) and plasticized polymers, effectively reduce the $T_g$ of the electrolyte, enhance its mechanical flexibility, and improve the interface contact between the electrolyte and the electrode, thereby addressing issues related to interface contact and impedance.[260] ILs, composed of organic cations paired with inorganic or organic anions—such as 1-ethyl-3-methylimidazolium tetrafluoroborate ($[Emim]BF_4$)—exhibit excellent electrochemical stability and high ionic conductivity (**Figure 12a**),[261] particularly at lower temperatures, while also broadening the electrochemical window, making them ideal for improving both the stability and energy density of advanced battery systems.[258,262] Yao et al.[263] proposed a novel dual-polymer@inorganic network composite solid electrolyte (DNSE@IN), which is formed through a continuous nonhydrolytic sol–gel reaction of tetraethyl orthosilicate (TEOS) and the semi-interpenetration of PVDF-HFP with PILs. The resulting DNSE@IN structure features a robust dual-polymer@inorganic network, exhibiting high ionic conductivity and demonstrating superior safety performance, as it showed no signs of combustion in flammability tests.

Inorganic salts, such as LiTFSI, Lithium Bis(fluorosulfonyl)imide (LiFSI), $LiPF_6$, $LiBF_4$, $LiClO_4$, and LiBOB, provide mobile $Li^+$, thereby enhancing the ionic conductivity of the electrolyte. These salts can be applied in various forms within PCEs, including single, double, or triple salt systems. In a single Li-salt system, electrochemical properties

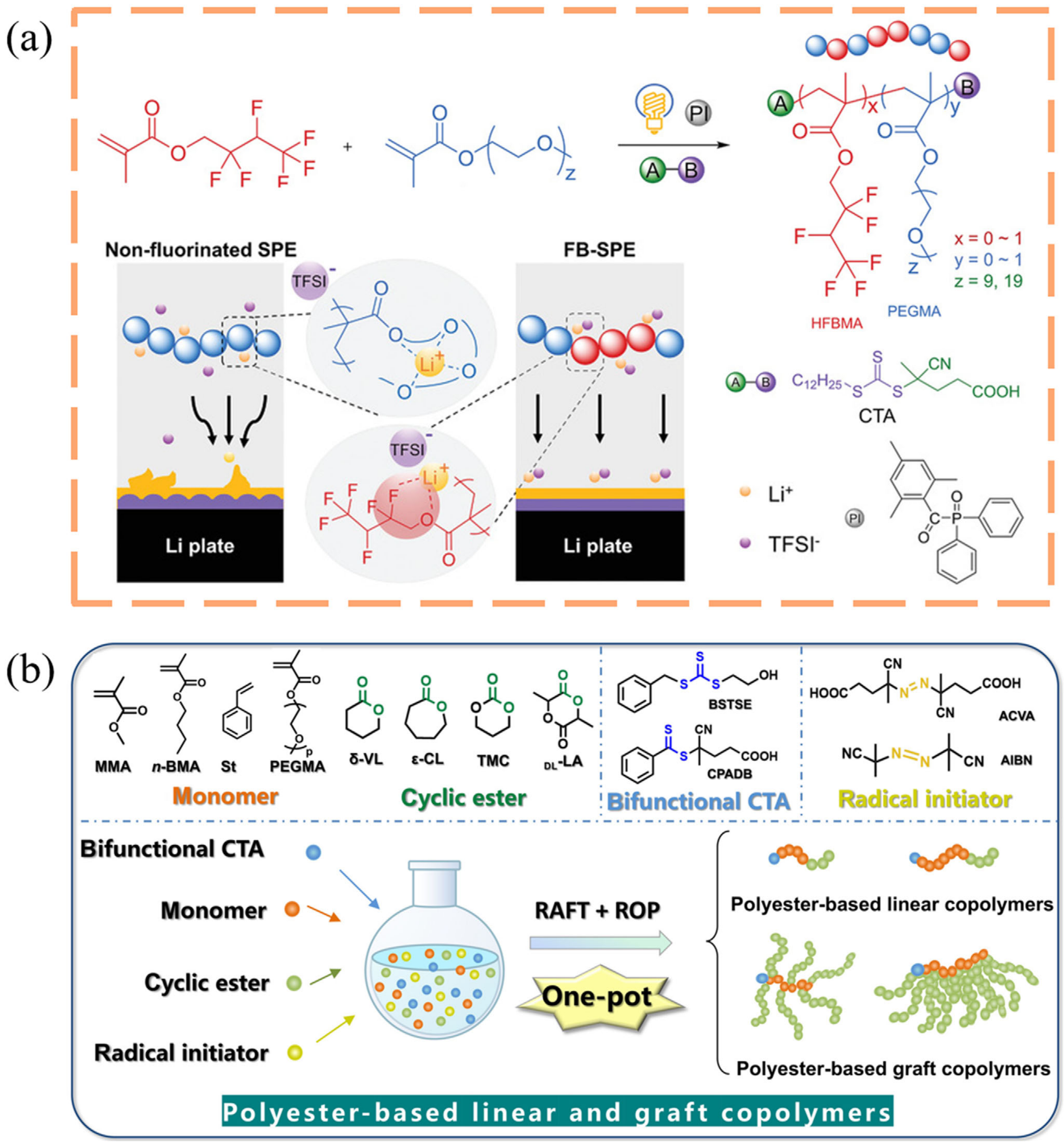

**Figure 11.** a) Schematic diagram of synthesizing FB-SPE by visible-light-driven photo-controlled radical polymerization and different interfacial phenomena at the surface of Li anode influenced by different $Li^+$ coordination behavior with conventional SPE and FB-SPE, respectively. Reproduced with permission.[255] Copyright 2021, Wiley-VCH. b) Schematic diagram of synthesizing different structural copolymers. Reproduced with permission.[257] Copyright 2021, Chinese Chemical Society.

may be constrained due to the limited $Li^+$ migration number and the degree of salt dissociation (Figure 12b). However, by incorporating different types of anions into a multisalt system, the $Li^+$ migration number can be increased, interfacial stability can be improved, thermal stability can be enhanced, and the electrochemical window can be broadened.[264,266,267] For instance, as depicted in Figure 12c, the combination of $LiClO_4$ and $LiPF_6$ significantly contributes to modulating the SEI chemistry, rendering it highly suitable for high-voltage battery applications. This dual-salt system facilitates the

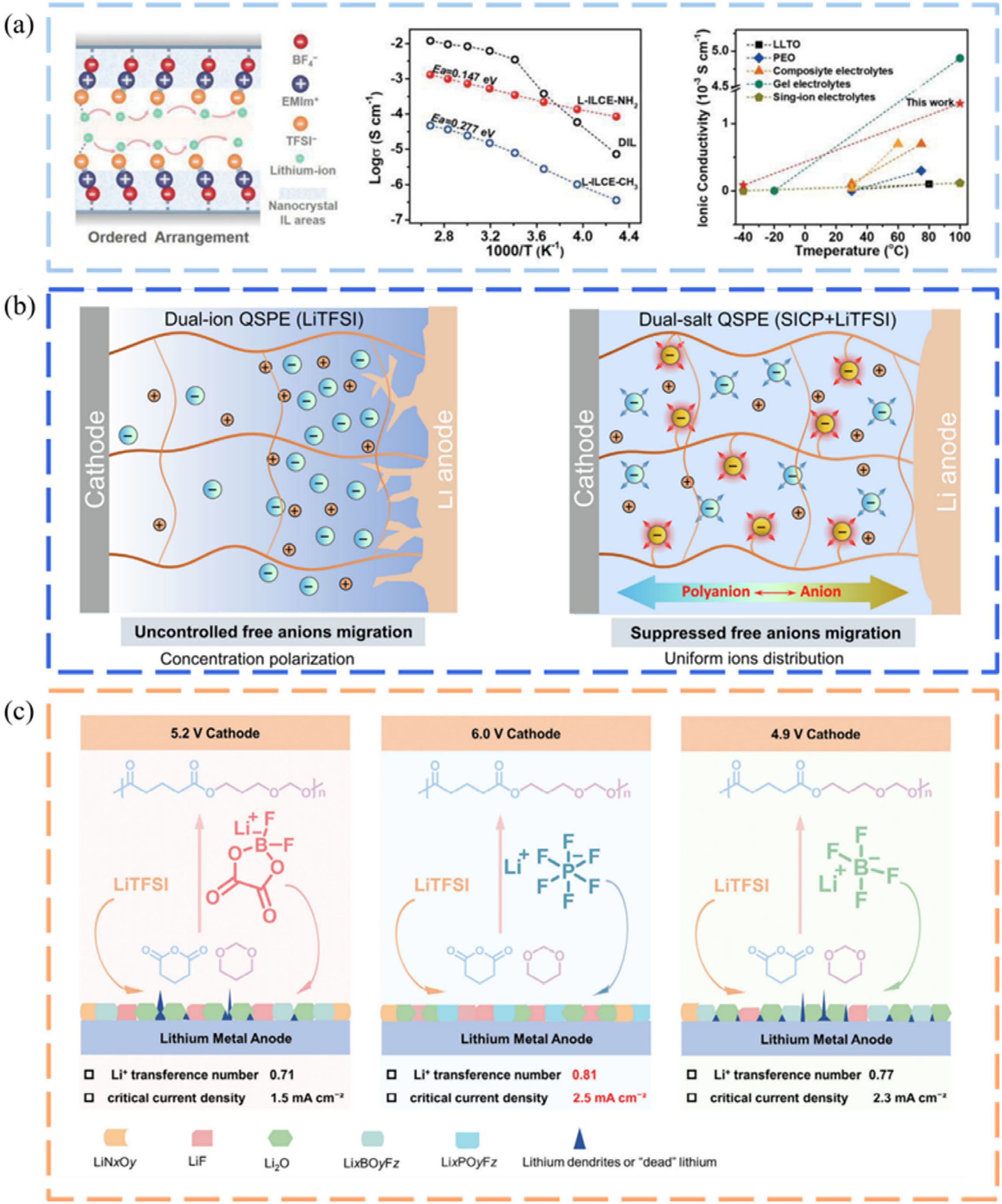

**Figure 12.** a) Schematic diagram of proposed model for the Li$^+$ transport mechanism in interlayer. The temperature-dependent conductivity of different electrolytes and comparison of ionic conductivity with other SSEs and gel electrolytes. Reproduced with permission.[261] Copyright 2023, Wiley-VCH. b) Schematic diagram of concentration polarization in traditional dual-ion quasi-solid polymer electrolyte (QSPE) system after cycling and alleviated concentration polarization and uniform ion distribution in dual-salt QSPE system after cycling. Reproduced with permission.[264] Copyright 2024, Elsevier. c) Schematic diagram of the fabrication of polymer electrolytes and the effect of salts on the compositions of SEI layers. Reproduced with permission.[265] Copyright 2024, Wiley-VCH.

formation of a dense and robust SEI layer, enriched with LiF and other inorganic components, which effectively reduces interface impedance and mitigates continuous electrolyte decomposition at the electrode interface. Moreover, the enhanced interfacial stability ensures uniform ion transport while suppressing side reactions, thereby substantially improving the cycling performance and energy density of the battery. This underscores the pivotal role of electrolyte composition in optimizing interfacial properties to advance the performance of high-voltage solid-state batteries.[265,268] Recently, Fu et al.[269] introduced an innovative triple-salt composite electrolyte with temperature-responsive properties, designed for smart temperature-controlled Li batteries. The system incorporates the halide $Li_3YBr_6$, along with LiTFSI and $LiNO_3$, as active fillers within a low-melting-point polymer matrix composed of PEG dimethyl ether (PEGDME) and PEO, all embedded in a pretreated alumina fiber scaffold. When the temperature exceeds 60 °C, the electrolyte transitions into a liquid state, optimizing the liquid–solid interface contact, significantly lowering interfacial resistance, and enhancing the battery's discharge capacity. Conversely, when the temperature falls below 30 °C, the electrolyte solidifies, leading to a substantial increase in ionic conductivity and solid–solid interface resistance, thereby activating the battery's temperature control "switch" function. This innovation provides new insights for the development of smart temperature-controlled Li batteries.

Strategic deployment of multifunctional additives (ionic liquids and multisalt systems) offers transformative solutions for stabilizing high-voltage electrode/PCE interfaces. Comprehensive evaluation of additive-electrode compatibility and dynamic evolution during cycling remains critical for performance optimization.

### 5.2. Design of PCEs' Structure

An ideal SSE should not only offer sufficient safety, stability, and energy density but also possess a wide enough electrochemical window to match high-voltage cathode materials, along with sufficient mechanical strength to resist dendrite penetration. However, it is challenging for a single-layer SSE to meet all these requirements. In this section, various design strategies for PCE structures are introduced to address these challenges.

#### *5.2.1. Bilayer Structure Design*

*Homogeneous Bilayer Structure*: A popular strategy is the multilayer electrolyte design, which involves stacking two or more electrolyte films with different functions. This allows the selection of appropriate films to accommodate the different requirements of the anode and cathode, thereby enhancing the compatibility with high-voltage and high-energy-density Li solid-state batteries. For example, as illustrated in **Figure 13a**, a bilayer PCE structure was fabricated by coating LLTO particles and combining them with PVDF. The ultrathin PDA coating (≈4 nm) on the anode side prevents direct contact between LLTO and Li metal, reducing interfacial resistance and suppressing possible side reactions under high voltage. Additionally, the chelation of $Li^+$ with catechol groups enhances the ionic conductivity of the electrolyte. On the cathode side, the PCE can withstand high voltage, improving both the voltage stability and energy density of the battery while maintaining performance under extreme conditions, which is significant for the development of safe, high-energy-density SSLBs.[270]

*Heterogeneous Bilayer Structure*: Researchers proposed a bilayer heterogeneous electrolyte structure that combines a soft, wet composite gel with an ion-conducting matrix designed for high voltage stability.[272] The composite gel, composed of a metal-organic framework (Cu-HKUST-1) and PEO/PVDF-HFP, helps form a stable electrode/electrolyte interphase, suppressing Li dendrite growth, reducing interfacial resistance, and enhancing the electrochemical stability of the battery. The matrix, consisting of PVDF-HFP, LiTFSI, and garnet-type $Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$ nanowires, provides the necessary flexibility and high-voltage tolerance, ensuring stable battery performance under high-voltage conditions. In another design, a bilayer structured ultrathin (4.2 µm) PCE was prepared by incorporating PEO and PAN into a 3D porous film (UFF, ultrathin fireproof framework) made via electrospinning (Figure 13b). This bilayer structure not only addresses the degradation issue of PEO under high voltage but also prevents side reactions caused by direct contact between PAN and Li metal, achieving stable compatibility with both the Li-metal anode and high-voltage cathode, thereby aiding long-term cycling stability at high energy density. Moreover, DFT calculations of adsorption energy confirm that ceramics and polymers exhibit excellent contact and adhesion, which reduces polymer crystallinity, promotes Li salt dissociation, and enhances ionic conductivity.[271]

Bilayer electrolytes transcend the performance limitations inherent in single materials by integrating functional capabilities across partitioned zones. Their primary value resides in the synergistic optimization of flexible adaptation at the anode interface coupled with high voltage stability at the cathode interface. However, the key challenge for industrialization lies in the advancement of ultrathin interlayer bonding technologies, which are essential for minimizing interfacial resistance and enhancing mechanical robustness.

#### *5.2.2. Sandwich Structure Design*

In recent years, several studies have pointed to sandwich-structured novel PCEs composed of homogeneous polymer layers. For instance, Xin and co-workers[273] proposed a versatile design paradigm for SSEs, which involves sandwiching a ceramic lithium-ion conductor (LIC) between two electronically insulating layers. This innovative configuration effectively addresses key interfacial challenges in SSLBs. As depicted in **Figure 14a**, the researchers developed a UV-curable ethylene acrylate (UVEA) polymer film to serve as a separator, significantly enhancing interface contact by conforming seamlessly to the ceramic surface. This improved contact minimizes interface impedance and facilitates efficient ion transport across the interphase. Moreover, the UVEA layer supports the formation of a robust SEI, enriched with LiF and other inorganic components, which mitigates side reactions and suppresses Li dendrite growth. By resolving these critical interfacial issues, the proposed design markedly enhances cycling stability and overall battery performance, highlighting

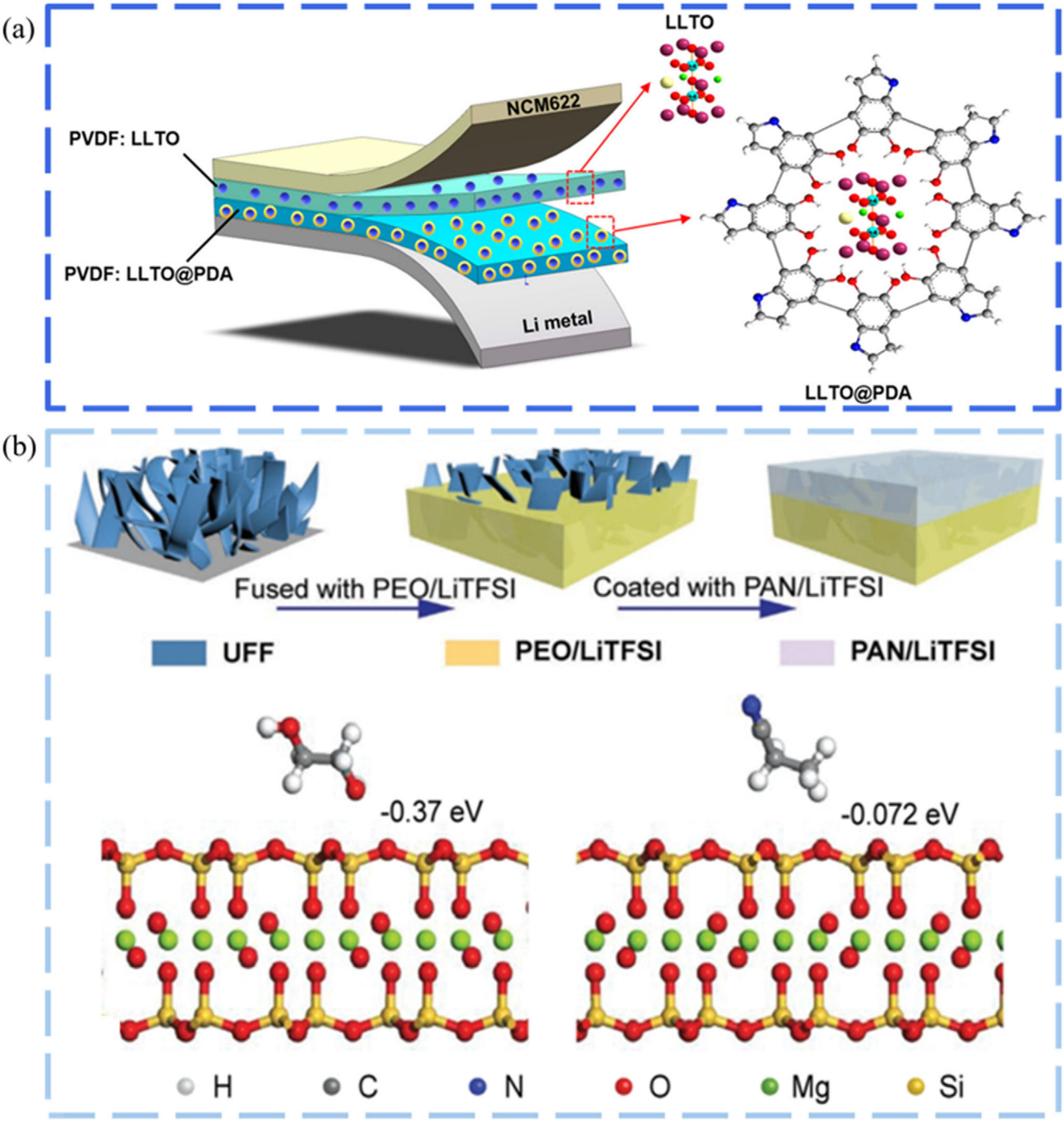

**Figure 13.** a) Schematic diagram of the bilayer membrane electrolyte with PVDF:LLTO on one side and PVDF:LLTO@PDA on another side. Reproduced with permission.[270] Copyright 2020, American Chemical Society. b) The preparation diagram of the double-layer UFF/PEO/PAN/LiTFSI PCEs and DFT calculated adsorption energy of PEO and PAN monomers on the UFF. Reproduced with permission.[271] Copyright 2021, Wiley-VCH.

the pivotal role of interfacial engineering in advancing solid-state battery technologies. Building on this design concept, researchers proposed a novel sandwich-structured PCE composed of heterogeneous polymer layers. As depicted in Figure 14b, the significant interfacial mismatch between ISEs and electrode materials presents a critical challenge to their practical application. To address this issue, researchers designed a compatible sandwich-structured composite polymer electrolyte (DPCE) by coating LATP with oxidation-resistant PAN and reduction-inhibiting PEO. The PAN layer establishes a soft and stable contact with high-voltage cathodes, effectively reducing interface impedance and enhancing ionic transport at the cathode interface. Simultaneously, the PEO layer protects LATP from reduction reactions at the Li-metal anode, suppressing side reactions

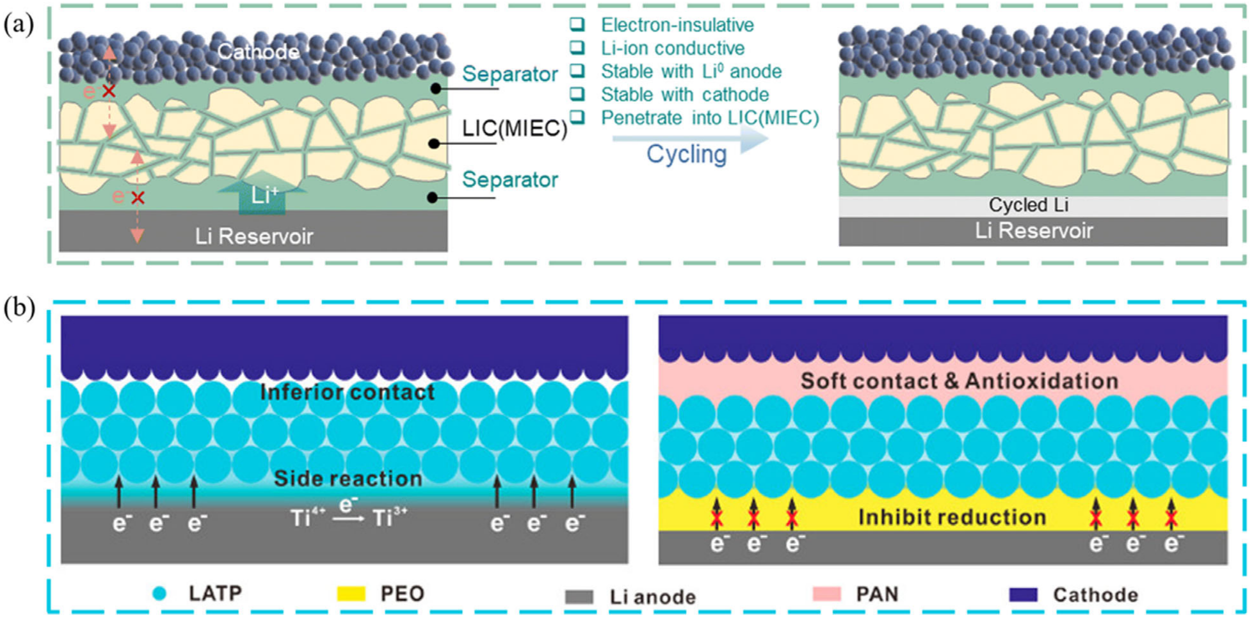

**Figure 14.** a) Schematic diagram of electrochemical performance of the sandwich SSE. Reproduced with permission.[273] Copyright 2023, Royal Society of Chemistry. b)Schematic diagram of illustrations of the solid full battery with pristine LATP and DPCE. Reproduced with permission.[274] Copyright 2019, American Chemical Society.

and stabilizing the interface. Furthermore, the ionic regulation capabilities of LATP ensure a uniform distribution of $Li^+$ and anions, mitigating the formation of space-charge layers. This regulation minimizes polarization, prevents dendrite growth, and significantly improves the electrochemical stability and safety of the battery system.[274] Compared to single layer or bilayer designs, this heterogeneous sandwich structure integrates the advantages of multiple materials, leading to a comprehensive improvement in battery performance. Triphasic sandwich architectures with functional interlayers effectively mitigate space-charge effects and dendrite propagation. Industrial viability hinges on developing mechanically robust, sub-micrometer-scale interlayer materials and resolving interfacial fusion challenges in multilayer integration processes.

### 5.3. Optimization of Fabrication Processes

The fabrication process plays a pivotal role in determining the interfacial properties of PCEs in solid-state batteries. Precise control over fabrication parameters, such as the integration of components, film uniformity, and curing conditions, directly impacts interface contact, impedance, and the overall electrochemical performance of the system. This section explores various fabrication strategies and their optimization, highlighting their contributions to improving interfacial stability, suppressing dendrite growth, and advancing the performance of solid-state batteries.

#### *5.3.1. Filler Blending Method*

The filler blending method is one of the most widely used techniques for fabricating PCEs. This approach involves uniformly dispersing fillers, such as ceramic particles or clay nanosheets, within a polymer matrix, resulting in macroscopically homogeneous internal structures. The polymer matrix serves as the foundation of the PCEs, while the fillers play a critical role in enhancing its electrochemical performance. For instance, PCEs prepared via UV-initiated polymerization incorporating 2D inert fillers demonstrate improved interface contact with electrodes, significantly reducing interface impedance. Additionally, the fillers facilitate the formation of a robust SEI, characterized by a dense and stable LiF-enriched structure. This optimized SEI effectively suppresses side reactions and inhibits Li dendrite growth, ensuring enhanced cycling stability and safety.[275] Additionally, functionalizing the filler surface can further optimize the compatibility between the fillers and the polymer matrix. For instance, surface-modified fillers like ethoxylated alumina (F-$Al_2O_3$) achieve uniform dispersion within the matrix, significantly improving the interfacial properties of PCEs.[276] This uniformity reduces ion transport heterogeneity caused by filler aggregation, enhances $Li^+$ conduction at the interface, and lowers interface impedance. Additionally, functionalized fillers promote the formation of a stable SEI enriched with dense LiF layers, effectively suppressing Li dendrite growth and mitigating side reactions. These results highlight the importance of filler blending in not only improving bulk properties but also resolving interfacial issues, making it a pivotal strategy for advancing solid-state battery performance.

The fundamental advantages of filler-matrix blending technology, which relies on simple mechanical mixing, include its straightforward and efficient processing, substantial cost–effectiveness, and strong material compatibility. Looking ahead, its potential can be further unlocked through advancements in process automation and the meticulous design of filler microstructures.

### *5.3.2. Framework-Embedding Method*

When fabricating PCEs using the filler blending method, an excessively high or low filler ratio can adversely affect the performance of both the PCEs and the overall battery system. The framework-embedding method effectively addresses the issue of filler aggregation while providing a continuous and stable pathway for Li$^+$ transport within the electrolyte. By ensuring uniform filler distribution, this method significantly enhances ionic conductivity while maintaining the electrochemical stability and safety of the battery. Additionally, the macroscopic morphology and chemical composition of the framework play a crucial role in determining the interfacial properties of the electrolyte. For instance, the framework-embedding method utilizing nanofibrous PAN membranes exemplifies an effective strategy for overcoming interfacial challenges in solid-state batteries.[277] Through electrospinning followed by precise calendaring, the PAN framework achieves enhanced mechanical robustness and uniformity, which ensures intimate and conformal contact with electrode surfaces. This improved interface contact significantly reduces impedance, facilitating efficient ion transport across the interface. Furthermore, the PAN framework promotes the formation of a dense and stable SEI enriched with LiF and $Li_3N$, effectively suppressing side reactions and inhibiting the growth of Li dendrites. These interfacial improvements lead to markedly enhanced cycling stability and safety. Additionally, the exceptional thermal stability of the PAN framework ensures reliable electrolyte performance under elevated temperatures, further advancing the long-term operational reliability of solid-state battery systems. Moreover, the framework-embedding method markedly enhances the integration of solid electrolytes with cathodes, effectively addressing critical interfacial challenges. By incorporating a mechanically robust and thermally stable nanofibrous framework, this strategy ensures improved adhesion and conformal contact with the cathode surface.[278] This seamless integration minimizes interfacial gaps, mitigates impedance, and facilitates efficient ion transport across the cathode–electrolyte interphase. Additionally, the optimized framework design promotes uniform Li$^+$ flux at the interface, reducing the risks of localized polarization and space-charge layer formation. These improvements collectively enhance cycling stability and mitigate capacity fading during prolonged operation. Furthermore, the integration process employs scalable fabrication techniques, such as electrospinning followed by precise calendaring, ensuring uniformity and reproducibility for large-scale production. This scalable methodology not only underscores the practical feasibility of solid-state batteries but also sets the stage for more reliable and efficient solid electrolyte–cathode integration in next-generation energy storage systems.

The 3D interpenetrating network skeleton significantly enhances interface bonding strength through the mechanical interlocking effect. The key innovation resides in the realization of a synergistic distribution of stress and electric field between the electrolyte and the electrode. To facilitate practical production, it is imperative to develop low-temperature curing processes aimed at minimizing energy consumption, alongside leveraging digital twin technology to optimize the alignment of skeleton porosity and permeability.

### *5.3.3. Multilayer Bonding Method*

PCEs fabricated using 3D frameworks inherently exhibit heterogeneous species randomly distributed at the electrode–electrolyte interface, leading to localized charge accumulation around these species. This uneven charge distribution can facilitate uncontrolled dendrite growth, posing significant safety risks to the battery. Additionally, a single-layer solid electrolyte is often insufficient to meet the ideal requirements of an SSE. Consequently, researchers have advocated for the use of multilayer electrolytes to address the distinct needs of the anode and cathode. For instance, stacking two or more electrolyte membranes with different functionalities enables the creation of multilayer PCEs, as discussed in Section 5.2. Moreover, a promising approach has been proposed to enhance the electrolyte–electrode interface by constructing ultrathin protective layers. These protective layers serve to precisely regulate the interface characteristics, thereby mitigating issues such as dendrite formation and side reactions due to nonuniform charge distribution. The key advantage of this intermediate protective layer strategy is its ability to efficiently modulate the interface contact between the electrolyte and the electrode, reduce interfacial reactions, and substantially decrease interface impedance. For example, Yang and co-workers[279] modified trilayer hybrid solid electrolytes (Tri-HSE) by incorporating Li Nafion (LiNf)-functionalized multiwalled carbon nanotubes (f-MWCNTs), which improved the adhesion between the electrolyte and the electrode. This modification enhanced interface contact, suppressed dendrite growth, and reduced side reactions. The optimized interface contact significantly lowered interface impedance, enhanced Li$^+$ conductivity, and substantially improved the electrochemical stability and cycling performance of the battery. Similarly, Wang and co-workers[280] developed a thin PEO/Lithium Difluoro(oxalato)borate (LiDFOB) protective layer (1 μm) on the surface of LCO, which markedly improved the interface contact between the cathode and the electrolyte. The bilayer PEO electrolyte design effectively reduced interface impedance and enhanced Li$^+$ transport efficiency. During electrochemical cycling, the PEO/LiDFOB protective layer in situ formed a stable cathode–electrolyte interphase, which efficiently suppressed side reactions between LCO and PEO at elevated voltages. This method not only holds great potential in enhancing battery safety and cycling performance but also exhibits strong scalability and application prospects, owing to its minimal impact on electrolyte thickness and internal impedance.

Ultrathin functional interlayers (<100 nm) utilizing chemical bonding mechanisms dramatically reduce electrode/PCE contact resistance. Industrial translation requires synchronized development of precision thickness-controlled systems and high-speed continuous coating technologies. Furthermore, a failure threshold model should be developed to correlate the interfacial bonding strength with the cycle life.

### *5.3.4. In Situ Polymerization*

In situ polymerization has emerged as a powerful and versatile strategy for constructing conformal polymer electrolyte layers directly within the electrode architecture post cell assembly. Initially introduced by Sun et al.[281] in 1997, this technique has been extensively employed to mitigate interfacial challenges in PCEs. By initiating polymerization in situ, the resulting polymer matrix intimately conforms to the electrode surface, effectively eliminating interfacial voids, suppressing undesirable side reactions, and facilitating the formation of uniform and robust SEI and CEI. Depending on the polymerization mechanism, several approaches have been developed, including thermally initiated, photoinitiated, and ion-induced in situ polymerization.[61,282–284] For instance, Luo et al.[285] demonstrated an anionic polymerization of catechol acrylate additives on Li metal, forming a self-adaptive poly(catechol–Li) SEI layer that enabled dendrite-free lithium cycling for over 8500 h at 10 mA cm$^{-2}$. Likewise, Ma and co-workers[219] proposed a strategy of using gel polymer electrolytes to enhance the mechanical stability of silicon anodes and stabilize interfacial performance by chelating transition metal ions, thereby improving the utilization rate, stress dispersion, and extreme temperature tolerance of LIBs. More recently, Aniagbaoso et al.[286] proposed a photopolymerization-induced microphase separation (Photo-PIMS) strategy to generate nanostructured quasi-solid electrolytes featuring continuous ion-conducting pathways and enhanced mechanical robustness. Collectively, these advances underscore the potential of in situ polymerization as a scalable and interface-tailored solution for next-generation SSLBs, delivering enhanced safety, efficiency, and long-term cycling stability.

In situ polymerization significantly enhances the electrode/PCE interface by forming conformal layers that eliminate voids and suppress side reactions. To advance this strategy for practical batteries, it is crucial to select appropriate polymerization methods, ensure material compatibility, and optimize conditions for uniform and nanostructured electrolytes. This approach holds great promise for improving the safety, efficiency, and cycling stability of next-generation SSLBs.

## 6. Industrialized Preparation

Polymer-based solid-state batteries are gaining significant momentum due to their suitability for scalable manufacturing, which includes ease of mechanical processing and consistent product quality. This technology has undergone preliminary industrial validation, with several companies successfully integrating polymer-based solid electrolytes into their EVs.[287] Numerous studies have shown that SSLBs using polymer-based PCEs instead of organic liquid electrolytes and separators offer unparalleled safety, superior energy density, and immense potential for practical applications.[288] Therefore, it is imperative to develop feasible methods for large-scale production of PCE films, as they could significantly accelerate the practical implementation of high energy density Li batteries based on PCEs.

### 6.1. Advanced Characterization

To gain a comprehensive understanding of the performance and behavior of PCEs, it is essential to investigate the interfaces both within the PCE material itself and between the PCEs and the electrodes. These interfaces are critical to ionic transport, charge distribution, and overall electrochemical behavior. Consequently, thorough characterization of these interfacial regions is vital for elucidating the mechanisms that govern the functionality of PCEs in solid-state batteries. In the following section, we present a sectional exploration of the various advanced characterization techniques used to probe the interfaces of PCEs. We will also delve into the underlying mechanisms of ionic transport and interfacial stability, which are pivotal for optimizing the performance and long-term reliability of PCE-based systems.

Given the importance of interface characterization, several relatively straightforward techniques are typically employed to examine the microstructure and surface properties of PCEs. These include scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning tunneling microscopy (STM), and atomic force microscopy (AFM), which provide detailed insights into the material's microstructure and surface morphology. Additionally, surface-sensitive techniques such as X-ray photoelectron spectroscopy (XPS), electron spectroscopy for chemical analysis (ESCA), secondary ion mass spectroscopy (SIMS), Auger electron spectrometry (AES), and low-energy ion scattering spectroscopy (LEIS) are used to analyze surface composition and probe depths ranging from a few nanometers to the outer atomic monolayer, offering valuable information on the interfacial structure and stability.[289,290]

While the aforementioned characterization techniques provide valuable static insights into the microstructure and surface properties of PCEs, they fall short in capturing the dynamic behaviors and electrochemical processes, particularly under metastable or unstable conditions. This limitation shows the need for in situ or operando methods. These techniques monitor structures and reactions in real time, helping us better understand PCEs under working conditions.[291] To address these challenges, a variety of advanced in situ characterization techniques have been developed, allowing researchers to observe the intricate, dynamic interactions at play within PCEs. To provide a clearer understanding of the commonly used in situ techniques for characterizing PCEs, a comparative summary is presented in **Table 1**.

In addition to these in situ characterization techniques, other advanced methods, such as in situ Auger electron spectrometry (AES),[327] in situ X-ray absorption spectroscopy (XAS),[328] and high-resolution time-of-flight secondary ion mass spectrometry (ToF-SIMS),[329,330] are also rapidly evolving. With the advancement of technology, the composition of PCEs and their chemical processes with electrodes have become increasingly complex, making them difficult to accurately reveal. This complexity poses significant challenges to the characterization of PCEs and their interfaces with electrodes, while also presenting both urgent demands and abundant research opportunities. Therefore, the development of more advanced in situ characterization techniques will become an indispensable key tool in energy materials research, driving a deeper understanding of the behavior and mechanisms of these materials. Furthermore, with the rapid advancement of computational simulations and AI technologies, their application in the characterization of PCEs' internal structures and interfaces is increasingly demonstrating immense potential.[331–333] Through machine learning (ML) and deep learning (DL) algorithms, these technologies can rapidly extract complex structural and dynamic behavioral patterns from large datasets, offering new insights into the characterization of PCEs.[334,335] Computational simulations, on the other hand,

**Table 1.** Summary of common in situ characterization techniques for PCEs.

| Technique | Function | Observable objects | Advantages | Limitations | Refs. |
|---|---|---|---|---|---|
| In situ X-ray diffraction (XRD) | Monitor crystal structure evolution and phase transitions | Crystal structure, phase transformation | High sensitivity, quantitative structural analysis, real-time tracking | Not suitable for amorphous phases; low spatial resolution | [289, 292, 293, 294, 295] |
| In situ XPS | Analyze elemental valence changes and interfacial reactions | Elemental oxidation states, chemical composition, interface products | High surface sensitivity, strong chemical state analysis | Requires vacuum; limited probing depth (a few nanometers) | [296, 297, 298, 299] |
| In situ neutron depth profiling (NDP) | Visualize $Li^+$ concentration distribution and migration pathways | $Li^+$ distribution and transport dynamics | High sensitivity to Li; nondestructive and bulk penetrating | Expensive equipment; limited spatial resolution; only for Li | [300, 301, 302, 303] |
| In situ nuclear magnetic resonance (NMR) | Investigate ion dynamics and local structural evolution | Local chemical environments and diffusion of nuclei ($Li^+$, $F^-$, $H^+$, etc.) | Differentiates chemical environments; quantifies ion mobility | Weak signals; long acquisition time; requires strong magnetic field | [304, 305, 306, 307, 308, 309, 310] |
| In situ imaging | Visualize morphological and structural evolution | Electrode surface morphology, deposition, cracking, dendrites | Direct visualization; easy operation | Low resolution; limited chemical information | [311, 312, 313, 314, 315, 316, 317, 318] |
| In situ Optical Microscopy (OM) | Track volume expansion and crack formation | Surface morphology, particle size, expansion behavior | Low cost; real-time optical observation | Limited spatial resolution and depth; lacks structural/chemical info | [319, 320] |
| In situ Raman | Detect chemical bond and molecular structure changes | Chemical bonds, functional groups, polymer chains | High specificity; applicable to solids/liquids; non-destructive | Fluorescence interference; low sensitivity to aqueous systems | [321, 322, 323] |
| In situ Fourier Transform Infrared Spectroscopy (FTIR) | Identify functional group evolution and interfacial reactions | Functional groups, intermediates, polymer structure | Real-time monitoring of chemical changes; broad applicability | Low spatial resolution; water interference | [324, 325, 326] |

provide precise quantitative methods to predict and optimize the performance of PCEs in various electrochemical environments, further assisting in the validation and supplementation of experimental results.[336–338] The integration of these technologies not only accelerates the design and optimization of PCEs but also significantly enhances our understanding of their internal mechanisms and interfacial reactions, providing essential theoretical support and technical foundations for the development of next-generation high-efficiency batteries.

### 6.2. Application of AI in PCEs

AI has become a transformative force across various fields, not only driving revolutionary advances in technology but also playing a pivotal role in scientific research and industrial applications. In materials science, the value of AI is particularly evident, especially in fields such as biomedicine, nanotechnology, and energy storage. AI's ability to process vast amounts of data, recognize hidden patterns, and predict material behaviors allows for accelerated material design, thus improving the efficiency and success rate of discovering materials with superior properties. In particular, AI-driven methods have found crucial applications in the development of PCEs, which are integral to the advancement of solid-state batteries. By combining polymers with inorganic materials, PCEs offer promising solutions for next-generation energy storage systems, where AI plays a pivotal role in optimizing both the electrochemical and mechanical properties of these materials. In the future, AI is poised to play a key role in several aspects of PCEs research.

#### *6.2.1. AI for the Design and Optimization of PCEs*

The design and optimization of PCEs involve complex interactions between polymer matrices and inorganic fillers. Traditional methods for optimizing these materials are often time-consuming and resource intensive. However, AI has revolutionized this process by enabling efficient material discovery and optimization through data-driven approaches. For instance, ML[339] techniques are widely used to analyze vast datasets of material properties, while DL[340,341] models can identify correlations between molecular structures and performance metrics, such as ionic conductivity and mechanical strength. By leveraging reinforcement learning (RL), AI can autonomously explore new combinations of polymer and inorganic materials, optimizing the properties of PCEs without human intervention. Additionally, generative adversarial networks (GANs)[342,343] can be employed to design new composite materials by generating potential candidates based on existing data and performance requirements. These AI-driven methods not only speed up material discovery but also reduce the risk of trial-and-error approaches, making the development of high-performance PCEs more efficient and cost effective.

#### *6.2.2. Modeling and Analysis of Interfacial Phenomena*

The interface between electrolytes–electrolytes and electrolyte–electrodes is a critical region that determines the overall performance of solid-state batteries. A poor interface can lead to issues like dendrite formation, high interfacial resistance, and low cycling stability, significantly impacting battery efficiency and longevity. AI has become a powerful tool for modeling and analyzing these interfacial phenomena. By utilizing molecular dynamics (MD)[344] simulations in conjunction with ML[345] models, it is possible to predict how different electrode materials interact with the electrolyte interface at the atomic level. For instance, AI-driven clustering techniques can classify the different atomic configurations at the interface, enabling the identification of stable, conductive, and dendrite-resistant structures. Furthermore, graph neural networks (GNNs)[346,347] have been employed to model complex interactions in the electrode–electrolyte interface, providing insights into how structural modifications can enhance the stability and conductivity of the interface. The synergy between MD simulations, ML, and GNNs allows researchers to study interfacial behavior under a wide range of conditions, facilitating the design of more stable and efficient solid-state batteries.

#### *6.2.3. AI for Characterization of PCEs and Battery Life Prediction*

Advanced characterization techniques, such as X-ray diffraction (XRD), high angle ring dark field image (HAADF), and X-ray absorption fine structure (XAFS), generate vast amounts of data that require advanced analysis. AI, particularly deep convolutional neural networks (CNNs),[348,349] could integrated with these techniques to automate the interpretation of microstructural images, enabling the identification of material defects, grain boundaries, and phase transitions with high accuracy. By training CNNs on large datasets of material images, AI can detect subtle changes in material structures that might otherwise go unnoticed. Additionally, AI models are now capable of predicting the long-term performance of solid-state batteries by analyzing patterns in experimental data. For example, recurrent neural networks (RNNs)[350] and long short-term memory (LSTM)[351,352] networks are being used to predict the degradation and cycle life of PCEs, based on data collected during cycling tests. This predictive capability enables researchers to foresee potential failures before they occur, guiding the design of more durable and efficient materials. Moreover, AI-driven feedback loops that integrate data-driven performance predictions with material optimization create a comprehensive, closed-loop system for enhancing both the structure and the performance of PCEs.

### 6.3. Developments in Industrialization

As PCE technology transitions from the research phase to practical applications, the focus shifts to overcoming the challenges associated with large-scale industrialization. Numerous enterprises and research institutions are making significant strides in scaling up the production of PCEs, addressing both the technical complexities and market demands necessary for commercialization. These efforts span across various sectors, particularly in the automotive and energy industries, and are focused not only on enhancing the performance and cost-effectiveness of PCEs but also on tackling the obstacles related to mass manufacturing, regulatory compliance, and economic feasibility. In this section, we highlight key organizations—both corporate leaders and academic institutions—that are at the forefront of advancing PCE technologies toward industrialization, and explore their contributions to bringing these innovations to the market.

### *6.3.1. Welion New Energy*

Welion, a leading Chinese company, has made significant advancements in the industrialization of PCEs, utilizing hybrid oxide solid–liquid technology developed by the Institute of Physics (IOP) at the Chinese Academy of Sciences (CAS). This innovative technology enables batteries with longer cycle life and higher energy density, positioning Welion at the forefront of the solid-state battery sector. In 2018, the company achieved a breakthrough by developing SSLBs with an energy density exceeding 300 Wh $kg^{-1}$ using in situ solidification technology . By the end of 2022, Welion had successfully mass-produced a hybrid solid–liquid battery with an energy density of 360 Wh $kg^{-1}$, capable of powering an EV for 1000 km on a single charge . Welion has also laid the foundation for large-scale production with a new facility in Jiangsu, China, aiming to reach an annual production capacity of 100 MWh. By leveraging existing manufacturing technologies, the company is working to reduce production costs and enhance efficiency, making the transition from pilot scale to mass production more feasible. Looking ahead, Welion is targeting an energy density of 400 Wh $kg^{-1}$ by 2025 and 600 Wh $kg^{-1}$ by 2030 for its SSLBs, further enhancing the commercial viability of these batteries for mass-market applications . While challenges remain—particularly in optimizing production processes and securing a stable supply chain—Welion's efforts highlight the growing potential for PCEs in the energy storage industry, signaling a promising future for the widespread adoption of solid-state technology.

### *6.3.2. ProLogium*

ProLogium has made notable strides in the industrialization of PCEs through its advanced research in SSLBs. ProLogium's "MAB" bipolar solid-state battery architecture, featuring LLTO nanowire-reinforced PEO electrolytes, enhances volumetric energy density by 50% and supports 12 min fast charging (80% State of Charge (SOC) on 400 V platforms). Its Dunkirk plant, under construction, aims for 48 GWh capacity by 2027, with partnerships including Mercedes–Benz and VinFast. The company's development of a high-energy SSLB, featuring a $SiO_x$/graphene anode, has resulted in a battery capable of delivering an energy density of 440–485 Wh $L^{-1}$ while maintaining an impressive cycle life of over 1000 charge–discharge cycles. More recently, ProLogium has innovated further by incorporating a 100% silicon oxide anode, which significantly enhances energy density to 695–770 Wh $L^{-1}$, providing an even greater performance potential. The company's achievements extend to the fabrication of prototype Li-metal SSLBs, reaching an energy density of 1025 Wh $L^{-1}$ for 500 cycles. These advancements not only demonstrate ProLogium's technical prowess but also underscore the company's commitment to scaling PCEs for broader industrial applications. With plans to commence trial production of all-solid-state Li batteries (ASSLBs) in 2023 and transition to full-scale manufacturing by 2024, ProLogium's progress offers a compelling example of how research and development are being seamlessly integrated into the commercialization of PCEs, setting the stage for transformative changes in the energy storage sector.

### *6.3.3. Qingtao Energy*

Qingtao energy exemplifies significant progress toward industrialization in the realm of PCEs. The company established its first production line for SSLBs in 2018, marking an important milestone in the commercialization of this technology. By September 2021, their SSLB products had successfully passed national inspection certification, achieving an impressive energy density of 368 Wh $kg^{-1}$ and a discharge capacity exceeding 116 Ah at a 1/3 C rate. The IM L6 model, equipped with Qingtao energy's first-generation "Lightyear" semi-solid-state battery (oxide–polymer composite electrolyte), delivers an energy density of 368 Wh $kg^{-1}$ and a 1002 km China light-duty vehicle test cycle (CLTC) range. This battery leverages dry-process solid electrolyte layer integration and nanocoating technology, enabling 400 kW ultrafast charging (12 min for 400 km) while passing stringent safety tests. Mass production began in April 2024, marking a critical step toward semi-solid-state battery adoption in passenger vehicles. To further scale up production, QingTao has invested 5.5 billion yuan to develop a 10 GWh power SSLB production base, underscoring their commitment to expanding capacity and advancing the industrialization of solid-state battery technology. This initiative is not only pivotal for meeting the growing demand for high-performance energy storage but also highlights the potential of PCEs in commercial applications, offering valuable insight into the future viability of PCEs in large-scale production.

### *6.3.4. Factorial Energy*

An example of significant progress in the industrialization of PCEs can be seen in the work of Factorial Energy, which has made notable strides in the development of SSLBs. The company demonstrated that its 40 Ah SSLBs achieved an impressive 97.3% capacity retention rate after 675 cycles. With an energy density of 770 Wh $L^{-1}$ or 350 Wh $kg^{-1}$, the SSLB showcases the potential for high-performance energy storage solutions. Factorial Energy has since entered into deep collaborations with major automotive companies, including Hyundai, Kia, and Mercedes–Benz, to further advance the commercial application of solid-state batteries in EVs. This partnership reflects growing confidence in PCE-based technologies and highlights the ongoing efforts to scale up production and improve the viability of solid-state batteries for mass-market adoption.

### *6.3.5. SSB Technology Innovation Center*

SSB Technology Innovation Center (SSB-TIC), in collaboration with major automotive manufacturers such as Toyota and Honda, has made significant advancements in the development of solid-state batteries utilizing PCEs. The center's research focuses on optimizing the electrochemical performance, interface compatibility, and cycle stability of PCEs, aiming to make them suitable for large-scale production. Through these collaborations, SSB-TIC has successfully moved from laboratory-scale development to pilot production, overcoming critical challenges related to material cost and manufacturing scalability. These efforts highlight the increasing momentum toward the commercialization of PCE-based solid-state batteries, with the automotive sector playing a pivotal role in driving this transition toward industrial-scale application.

#### *6.3.6. Massachusetts Institute of Technology*

Massachusetts Institute of Technology (MIT) has made significant strides in advancing the commercialization of PCEs, particularly in the field of solid-state batteries. Through extensive research, MIT has developed high-performance PCEs that exhibit enhanced ion conductivity, mechanical stability, and safety compared to traditional liquid electrolytes. Their collaboration with companies like Solid Energy Systems has been pivotal in bridging the gap between laboratory-scale innovation and industrial-scale production. MIT's recent developments have focused on enhancing the performance and scalability of PCEs, particularly through the integration of ceramic and polymer materials to create hybrid electrolytes that combine high ionic conductivity with mechanical flexibility. The team has made significant strides in reducing the processing temperatures of ceramic electrolytes, a critical step for their industrial-scale production. By lowering the temperature required for processing Li garnet-based electrolytes, MIT's research has the potential to make these materials more commercially viable, reducing costs associated with high-temperature sintering processes traditionally required for ceramic electrolytes. Additionally, MIT has identified a key factor in preventing dendrite formation—a challenge that has hindered the development of solid-state batteries. Their findings emphasize the importance of achieving smooth, defect-free surfaces in the electrolyte materials, an insight that could streamline the production process and improve battery reliability. This work, along with ongoing efforts to improve manufacturing techniques for PCEs, highlights MIT's contribution to bridging the gap between research and large-scale commercialization, offering valuable insights into the future of solid-state battery technologies.

### 6.4. Challenges in Industrialization

PCEs present immense potential for applications in EVs, renewable energy storage, and portable electronics. However, translating laboratory-scale breakthroughs into industrial-scale production remains fraught with significant challenges. The primary obstacles lie in the complexity of manufacturing processes, the high cost of materials, and the need for enhanced long-term performance reliability. Addressing these challenges is paramount to unlocking the full potential of PCEs and fostering their widespread adoption in next-generation energy storage systems. One of the most pressing challenges is the intricacy of manufacturing processes. Conventional fabrication methods, such as sol–gel processing, chemical vapor deposition (CVD), and physical vapor deposition (PVD), offer precise material control but are labor-intensive, time-consuming, and costly, making them unsuitable for large-scale production. The transition to more scalable techniques, such as melt casting and hot press sintering, introduces new complexities, including challenges in maintaining material homogeneity, electrolyte–electrode interface stability, and ionic conductivity across large production batches. These limitations underscore the urgent need for innovative, high-throughput, and cost-efficient manufacturing solutions that can bridge the gap between laboratory research and industrial deployment. Beyond process scalability, the high cost of materials remains a formidable barrier to commercialization. The widespread use of ceramic fillers (e.g., LLZO) and specialized lithium salts (e.g., LiTFSI and LiFSI) significantly drives up production expenses due to their complex synthesis routes, stringent purity requirements, and limited availability. Moreover, the demand for these high-performance materials in other energy-related applications further exacerbates cost pressures, creating economic constraints that hinder PCEs from achieving market competitiveness. Developing cost-effective, abundant, and environmentally sustainable alternatives is crucial to mitigating these financial burdens and ensuring the long-term economic viability of PCE-based energy storage technologies. Lastly, long-term performance reliability remains a critical concern that must be addressed before large-scale deployment can be realized. PCEs must exhibit exceptional electrochemical and mechanical stability to ensure sustained performance under real-world operating conditions. However, issues such as interfacial instability, lithium dendrite growth, and degradation over extended charge–discharge cycles pose significant challenges. The development of advanced interface engineering strategies, dendrite-suppressing architectures, and novel hybrid electrolyte compositions is essential to enhance the durability and safety of PCEs in practical applications.

### 6.5. Future Potential and Solutions

#### *6.5.1. Applications of AM and Automation Technologies*

Additive manufacturing (AM) technologies presents one of the most promising solutions for the production of PCEs. By allowing precise control over electrolyte structure and design, AM minimizes material waste and facilitates the fabrication of complex shapes. This technology offers high flexibility and can be tailored for specific requirements, making it a strong candidate for future large-scale production. However, further optimization is needed to enhance material compatibility and production speed to meet industrial-scale demands.

#### *6.5.2. Pathways to Reduce Material Costs*

Reducing production costs is crucial for the commercialization of PCEs. The key strategies include developing low-cost alternative materials, such as replacing expensive Li salts (e.g., LiTFSI) with more affordable options like $LiClO_4$ or $LiBF_4$, and optimizing production processes to enhance efficiency. AM, for instance, allows precise material deposition, which minimizes waste and improves production efficiency. Additionally, adopting circular economy principles, such as recycling materials and fillers, can further reduce raw material costs and environmental impact. Scaling up production also contributes to cost reduction through economies of scale achieved by bulk material procurement and automated production lines. Collectively, these approaches offer a promising pathway to making PCEs economically viable for large-scale applications, particularly in energy storage systems like EVs.

#### *6.5.3. Process Consistency in Scale Production*

One major challenge is achieving uniform material distribution, as inconsistent mixing of polymer matrices and fillers leads to performance variations. Advanced mixing techniques and AM offer precise control over material distribution. Thickness control is equally important, as uneven electrolyte thickness affects ion transport, which can be mitigated using techniques like CVD and real-time thickness monitoring. Interface quality between the electrolyte and electrodes is also vital; as poor contact increases impedance and degrades performance. This can be improved through functional coatings and surface treatments. Automation and smart manufacturing systems enhance process consistency by reducing human error and enabling real-time adjustments, while advanced characterization methods, such as XRD and SEM, ensure the microstructural and surface quality of materials during production. By addressing these challenges, PCEs' production can achieve the consistency needed for commercial applications.

#### *6.5.4. Green Manufacturing and Sustainable Development*

Green manufacturing aims to reduce energy consumption through low-temperature processes, minimize material waste via additive manufacturing, and recycle materials like Li salts and polymers. Sustainable development focuses on using eco-friendly, biodegradable, or recyclable materials and incorporating a circular economy model to maximize resource efficiency. Additionally, adopting solvent-free or green-solvent processes and utilizing renewable energy sources helps lower emissions and pollution during production. These strategies collectively reduce the environmental impact of PCE manufacturing while offering cost-effective and high-performance solutions for industries such as EVs and energy storage systems.

## 7. Conclusion and Perspective

This paper provides a comprehensive review of the use of PCEs in Li batteries, focusing on the critical interface issues that impact their performance. Unlike traditional polymer electrolytes, PCEs, composed of inorganic fillers and polymer matrices, offer enhanced mechanical properties and ionic conductivity, making them integral to the development of next-generation SSLBs. However, interface issues, particularly at the electrolyte–electrode interface, significantly affect PCE performance.

The review begins with a classification of various types of PCEs, emphasizing the importance of fillers in enhancing mechanical strength and ionic conductivity. The differences between inert and active fillers in influencing ion transport mechanisms are highlighted. The paper then addresses the interface problems between solid electrolytes and electrodes, crucial for efficient battery operation. Specific attention is given to the challenges posed by interfaces between PCEs and ternary cathode materials, which impact battery performance and energy density. Additionally, the interface issues between PCEs and high-energy-density anodes like Li metal and silicon are explored, along with strategies for optimization. The discussion concludes with an examination of modification strategies for both ternary cathode materials and PCEs to facilitate higher energy density battery designs. The industrialization of PCEs primarily relies on scalable preparation methods such as casting, solvent-free dry processes, and hot/cold pressing to enhance mechanical strength and ionic conductivity. Interface improvement strategies, including surface coating, interlayer design, and optimized external pressure application, are crucial for reducing interfacial resistance and improving battery performance. Proper optimization of these methods is key to enabling large-scale production of high energy density SSLBs.

In summary, the paper highlights the current challenges in PCE research, particularly at the interfaces, and proposes potential solutions through advanced materials and innovative design strategies. The combination of these approaches shows promise for enhancing the performance and stability of PCEs in Li batteries.

As shown in **Figure 15**, future research should prioritize several key areas to address existing challenges and advance toward commercial viability.

### 7.1. Understanding the Electrolyte–Electrode Interface

Gaining a deeper understanding of the fundamental mechanisms at the electrolyte–electrode interface is crucial. Advanced characterization techniques, such as in situ TEM,[360] in situ nuclear magnetic resonance (NMR),[361] neutron depth profiling (NDP),[362] and in situ neutron imaging,[363] provide real-time insights into the formation and evolution of SEI and Li dendrites. These methods are instrumental in deepening our understanding of interfacial phenomena at the nanoscale, thereby guiding the development of more effective strategies for enhancing battery performance. This knowledge is invaluable for designing more effective strategies. Furthermore, collaboration between theoretical and experimental research is essential for the advancement of PCEs. Computational models can elucidate ion transport mechanisms and interactions among electrolyte components, guiding the synthesis of new materials and the optimization of electrolyte composition.

### 7.2. Development of Superior Materials

The exploration and development of new materials with enhanced properties are vital. Research should focus on novel polymer substrates and inorganic fillers that offer higher ionic conductivity, improved mechanical strength, and chemical stability. For instance, incorporating 2D materials like graphene or MXenes as fillers in PCEs can create continuous pathways for ion transport and bolster the mechanical properties of the electrolyte. Furthermore, the structure of custom polymer matrices

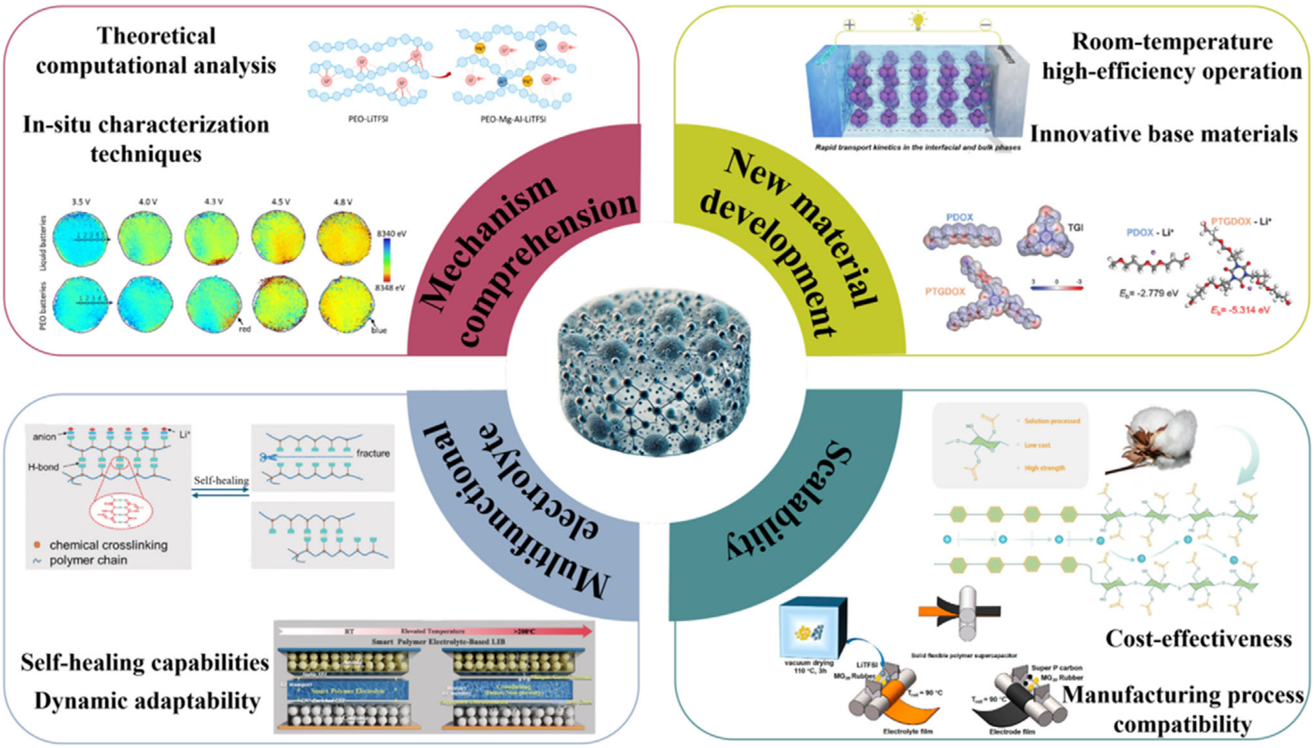

**Figure 15.** Mind mapping of the strategies related to polymer electrolytes and interface in PCEs. Reproduced with permission.[353–359]

can be predicted using AI,[364,365] enabling the selection of high-performance polymers for crosslinking, thereby significantly enhancing the flexibility, thermal stability, and compatibility of PCEs with various electrode materials. Additionally, the development of solid electrolytes that can operate efficiently at room temperature is crucial for expanding the applicability of PCEs in advanced energy storage systems.

### 7.3. Designing Multifunctional Electrolytes

There is a need for designing multifunctional electrolytes that can self-repair or adapt to changes during the battery cycle. Self-healing materials can mend cracks and maintain optimal contact between the electrolyte and electrode, thereby extending the battery's lifespan. Furthermore, developing electrolytes that dynamically adapt to the volume changes of electrodes during cycling will help maintain interfacial stability and overall battery performance.

### 7.4. Scalability and Cost–Effectiveness

Consideration of scalability and cost–effectiveness is essential to transition from laboratory research to commercial applications. Developing manufacturing processes compatible with existing battery production lines is critical for the successful commercialization of advanced PCEs. By addressing current challenges and leveraging interdisciplinary research, it is possible to develop high-performance, stable, and commercially viable solid-state batteries, meeting the growing demand for energy storage in various applications.

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## Conflict of Interest

The authors declare no conflict of interest.

## Author Contributions

Z.H. and Z.W. contributed equally to this work. Z.H. contributed to conceptualization, formal analysis, and writing of the original draft. Z.W. contributed to conceptualization, formal analysis, and writing of the original draft. X.C. contributed to literature review and data collection. L.Y. contributed to literature review and data collection. T.H. contributed to figures and writing. X.H. contributed to figures and writing. W.H. contributed to

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composite polymer electrolytes, high energy density, industrialized preparation, interface challenge, modification strategy

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