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Review

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Interfacial Engineering with PEO-Based Ultrathin Layers for Stable All-Solid-State Lithium Batteries: From Passive Protection to Active Regulation

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Abstract: Unstable solid-solid interfaces present a major challenge for all-solid-state lithium batteries. Poly (ethylene oxide)-based electrolytes offer good processability and intrinsic compatibility with electrodes. However, their narrow electrochemical stability window and low room-temperature ionic conductivity limit practical application. Recent work reveals a transition in interfacial engineering. The field is moving from passive physical barriers to ultrathin, actively regulated multifunctional interfacial layers. This review summarizes recent advances in PEO-based ultrathin interfacial modification layers. These layers are fabricated by in situ polymerization, atomic layer deposition, and self-assembly. The discussion focuses on three core interfacial regulation mechanisms. The first mechanism is the controlled formation and compositional tuning of solid electrolyte interphase and cathode electrolyte interphase layers. The second mechanism is viscoelastic mechanical adaptation. This adaptation suppresses stress accumulation and lithium dendrite penetration. The third mechanism is homogenized lithium-ion transport. It enhances interfacial charge-transfer kinetics. The synergistic integration of these functions effectively stabilizes the lithium metal anode and high-voltage cathode interfaces. Emerging strategies involving smart-responsive interfaces and bio-inspired multilayer architectures are also discussed. This review provides a concise and mechanism-oriented framework. It guides the rational design of PEO-based interfacial layers and supports the development of high-energy-density, high-safety all-solid-state lithium batteries.

Keywords: ultrathin interfacial modification layer; *in situ* polymerization; atomic layer deposition; self-assembly

1. Introduction

Lithium-ion batteries (LIBs) have been widely commercialized and currently dominate the energy storage landscape [1–6]. However, their energy density is approaching the theoretical limit. This prompts the exploration of next-generation battery systems such as lithium metal batteries (LMBs) [7–9]. Lithium metal offers an ultrahigh theoretical specific capacity of 3860 $mAh \cdot g^{-1}$ and a low redox potential of −3.04 V. This makes it an ideal anode material for high-energy-density batteries. Consequently, LMBs are regarded as promising candidates for next-generation energy storage systems [10–12].

However, the high chemical reactivity of lithium metal makes LMBs highly susceptible to lithium dendrite growth. This growth occurs during repeated plating and stripping processes. The dendrites can penetrate the separator and cause short-circuiting [13]. In addition, low coulombic efficiency and poor cycling stability impede their practical application [14]. To address these challenges, many strategies have been explored. These include electrolyte optimization [15], the construction of artificial solid electrolyte interphases (SEI) on lithium metal anodes [16], and the replacement of conventional liquid electrolytes with solid electrolytes [17,18].

Among these approaches, the adoption of solid electrolytes is considered an effective pathway to address the intrinsic limitations of LMBs [19]. Solid electrolytes offer several advantages. These include improved interfacial compatibility, high thermal stability, flexibility, nonflammability, and resistance to electrolyte leakage. This significantly enhances battery safety [20,21]. Compared with inorganic solid electrolytes [22], solid polymer electrolytes (SPEs) exhibit superior flexibility. They also provide better interfacial contact with electrodes and excellent processability. This makes them more suitable for large-scale manufacturing and practical deployment [23,24]. Various polymer matrices have been extensively investigated for SPEs. These include poly(ethylene oxide) (PEO) [25], polyacrylonitrile (PAN) [26], poly(vinylidene fluoride) (PVDF) [27], poly(methyl methacrylate) (PMMA) [28], and polycarbonate (PC) [29]. Among them, PEO and its derivatives have attracted particular interest. This is due to their high viscoelasticity, flexible chain segments, and excellent coordination capability with lithium ions [30,31]. These characteristics enable PEO-based electrolytes to achieve intimate interfacial contact with electrodes. They also facilitate lithium-ion transport. Nevertheless, PEO-based SPEs still suffer from several intrinsic drawbacks. These include a narrow electrochemical stability window, low room-temperature ionic conductivity, and limited lithium-ion transference number. These drawbacks severely restrict their high-power-density and high-rate performance [32]. In addition, high interfacial impedance and lithium dendrite penetration remain critical challenges. They hinder the practical implementation of PEO-based LMBs [33]. In particular, chemical instability and mechanical mismatch occur at the interface between the lithium metal anode and PEO-based SPEs. They readily induce the formation of unstable interphases. They also promote dendritic lithium growth. These interfacial failures directly lead to short circuits and rapid capacity degradation. This significantly compromises cycling life and safety [34,35].

In recent years, ultrathin interfacial modification layers based on PEO have emerged as an innovative and highly effective strategy to address these challenges [36,37]. Rather than modifying the bulk electrolyte, this approach focuses on engineering a nanoscale functional layer at the critical electrode-electrolyte interface. By constructing thickness-controlled interlayers at the nanometer or sub-micrometer scale, the intrinsic coordination ability and mechanical adaptability of PEO chains can be fully exploited to enable stable lithium-ion transport while simultaneously enhancing interfacial chemical and mechanical stability. It has been demonstrated that PEO-based ultrathin modification layers can significantly improve interfacial contact, reduce interfacial resistance, and enhance ionic transport efficiency [38]. More importantly, their functional role has evolved from that of a passive physical barrier to an active interfacial regulator capable of guiding uniform lithium deposition and stabilizing interphase formation. This emerging research field integrates advances in polymer chemistry, interfacial science, and electrochemistry, leading to substantial improvements in battery performance [39,40]. For example, Wang et al. [41] reported an ultrathin blended SPEs prepared via electrospinning. By incorporating a bio-based polyamide with strong lithium-ion affinity, the electrolyte achieved an ionic conductivity of 4.26×10^{-4} $S \cdot cm^{-1}$ at 50 °C, along with enhanced mechanical strength and electrochemical stability. As a result, the assembled $LiFePO_4$‖Li all-solid-state battery retained 80.5% of its initial capacity after 580 cycles when tested at 60 °C and 0.5 C. In another study, Xie and co-workers [42] constructed a 22 μm thick ultrathin dual-solvent polymer electrolyte through cross-linking and hydrogen-bonding interactions among PEO, tetra ethylene glycol dimethyl ether, and succinonitrile. The modified NCM622‖DSPE‖Li cell exhibited excellent cycling stability, maintaining 80.0% capacity retention after 300 cycles at 30 °C and 0.1 C. Beyond pristine PEO-based SPEs, PEO-based composite solid polymer electrolytes (CSPEs) have also been actively developed. Wan et al. [43] designed an 8.6 μm thick ultrathin flexible CSPEs using a polyimide (PI) matrix with vertically aligned nanochannels as a mechanical scaffold, filled with PEO/LiTFSI as the ion conductor. This electrolyte delivered an ionic conductivity of 2.3×10^{-4} $S \cdot cm^{-1}$ at 30 °C

while exhibiting excellent mechanical strength and safety performance. The assembled $LiFePO_4$‖Li all-solid-state battery remained stable performance after 200 cycles when tested at 60 °C and 0.5 C. To meet the high-voltage requirements necessary for practical application [44], Fu's group [45] employed a dual-salt strategy combined with UV-initiated crosslinking to fabricate a 20 μm thick ultrathin PEO-based polymer electrolyte. Preferential decomposition of lithium difluoro (oxalato) borate (LiODFB) resulted in the formation of a stable cathode electrolyte interphase (CEI) rich in LiF and $Li_xBO_\gamma F_z$ species on the NCM622 surface, effectively suppressing PEO oxidation. Consequently, the NCM622‖Li cell retained 94.7% of its capacity after 100 cycles at 4.2 V under 30 °C.

Although these studies clearly demonstrate the considerable potential of ultrathin PEO-based interfacial modification layer, which can enhance the performance of solid-state lithium batteries. However, the field still lacks a systematic and unified summary from a functional perspective. In particular, a coherent framework is still missing. This framework should address design principles, fabrication strategies, structure-performance relationships, and universal applicability across different battery systems. This review presents the first comprehensive overview focused specifically on PEO-based ultrathin interfacial modification layers. It aims to clarify the technological evolution of this emerging strategy. It also seeks to elucidate the underlying interfacial regulation mechanisms. It summarizes performance-enhancement approaches (Figure 1). It outlines future research directions. This work provides an integrated and mechanism-oriented perspective. It seeks to accelerate the practical realization of high-safety and high-energy-density all-solid-state lithium batteries (ASSLBs).

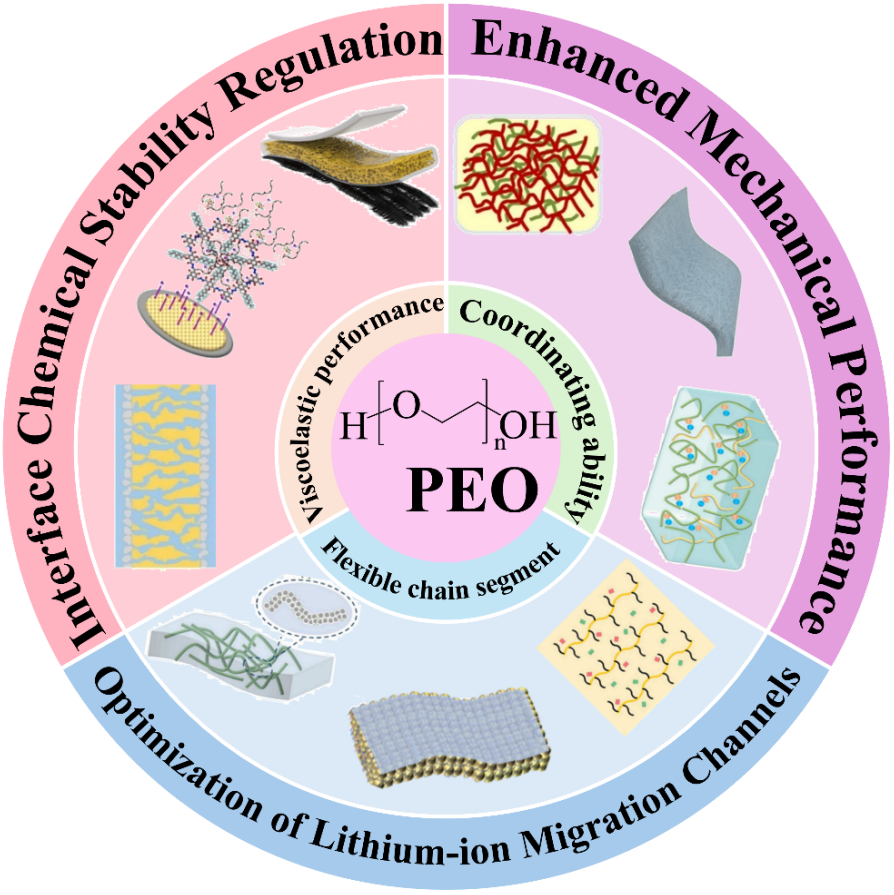

Figure 1. Schematic illustration of precise fabrication techniques and synergistic optimization strategies for three types of ultrathin interfacial modification layers in PEO-based solid-state electrolytes [18]. Copyright 2025, Wiley [46]. Copyright 2024, Wiley [47]. Copyright 2024, Springer Nature [48]. Copyright 2024, RSC [49]. Copyright 2022, ACS [50]. Copyright 2025, ACS [51]. Copyright 2025, Elsevier [52]. Copyright 2022, RSC [53]. Copyright 2023, Elsevier.

2. Design Principles of PEO-Based Ultrathin Interfacial Layers

Before discussing the design principles, it is essential to clearly define the thickness-related terminology used throughout this review, as ambiguity in this aspect may lead to conceptual confusion in literature. In this work, we define "ultrathin interfacial modification layer" refers specifically to localized functional layers constructed directly at the electrode/electrolyte interface, typically with thicknesses in the nanometer to sub-100 nm range. These layers are not intended to function as the primary ion-conducting medium; instead, their roles are to regulate

interfacial chemistry, homogenize lithium-ion flux, suppress parasitic reactions, and improve mechanical compatibility. In contrast, the term "ultrathin electrolyte" or "ultrathin solid polymer/composite electrolyte membrane" denotes continuous ion-conducting films with thicknesses generally in the micrometer scale, typically several to ten micrometers. These membranes primarily aim to reduce bulk transport distance, decrease internal resistance, and enhance energy density while maintaining sufficient ionic conductivity and mechanical integrity. Importantly, these two categories should not be considered strictly mutually exclusive. In many advanced systems, hierarchical architecture is adopted, in which a micrometer-scale ultrathin electrolyte is integrated with a nanoscale interfacial layer. Such multiscale designs enable synergistic coupling between bulk ion transport and interfacial regulation. By explicitly distinguishing these concepts, the structural roles and functional mechanisms of different "ultrathin" components can be more clearly understood, thereby improving the rigor and comparability of related studies.

With this terminology clarified, the design principles of PEO-based ultrathin interfacial layers can be discussed more systematically. PEO-based interfacial modification layers are typically designed with an ultrathin architecture, with thicknesses ranging from several nanometers to several tens of nanometers [54]. This structural characteristic enables precise interfacial regulation while minimizing additional resistance to lithium-ion transport [55]. Such fine control over layer thickness is commonly achieved through advanced fabrication techniques, including *in situ* polymerization, atomic layer deposition (ALD), and self-assembly. These approaches ensure that the modification layer conforms intimately to the electrode surface, thereby establishing a uniform and well-defined interfacial microenvironment [56]. In contrast, ultrathin PEO-based electrolyte membranes usually fall in the micrometer regime, typically from several to several tens of micrometers. Although both categories aim to minimize transport resistance and improve cell-level performance, their structural roles and design priorities are fundamentally different. For instance, even in a 7 μm thick PEO-based electrolyte, the introduction of an additional nanoscale interfacial layer can further enhance interfacial ion migration and stability without compromising mechanical integrity [57].

2.1. Interface Functional Design Based on the Properties of PEO

The intrinsic physicochemical properties of PEO constitute the fundamental basis for its role in interfacial regulation [58]. Among these properties, viscoelasticity represents a core advantage of PEO-based interfacial modification layers [59]. This viscoelastic nature enables the layer to elastically deform under localized stress, effectively buffering the mechanical pressure generated by lithium dendrite growth and providing physical protection at the interface (Figure 2a). Experimental and theoretical studies have demonstrated that such mechanical adaptability significantly mitigates stress concentration and prolongs the cycling life of solid-state lithium batteries [59,60].

In parallel, facilitating efficient lithium-ion transport is another essential function of PEO-based interfacial layers [61,62]. The ether oxygen groups along the PEO backbone can strongly coordinate with lithium-ion, thereby promoting preferential lithium-ion transport while suppressing anion migration [63]. This selective coordination reduces concentration polarization and minimizes parasitic interfacial reactions [64]. For example, after introducing a PHATN organic polymer framework, the -C=N- groups in PHATN cooperate with the ether oxygen groups of PEO to form a reinforced lithium-ion coordination environment. This synergistic interaction constructs an enhanced lithium-ion transport network and significantly increases the lithium-ion transference number of the electrolyte system [65,66].

To further improve lithium-ion transport efficiency, additional functional components are often introduced to reinforce and optimize the coordination mechanism of PEO. As a representative example, the incorporation of the DFBOP lithium salt, featuring -F and -PO_4 functional groups, enables the formation of synergistic coordination structures with both PEO chains and lithium-ion. Density functional theory (DFT) calculations further reveal that DFBOP exhibits stronger binding with lithium-ion than conventional LiTFSI, as evidenced by the optimized adsorption configurations and Mulliken charge population analysis. This result indicates enhanced lithium-ion coordination and stronger anion immobilization (Figure 2b). Such interactions not only facilitate lithium-salt dissociation but also promote the formation of a composite interfacial layer enriched with inorganic conductive phases. This interphase accelerates lithium-ion transport across the interface and enhances interfacial stability [67,68].

Moreover, the construction of a continuous and efficient ion-conduction network is crucial for reducing interfacial impedance and improving electrochemical kinetics [69]. Pristine PEO typically exhibits low ionic conductivity at room temperature due to its high crystallinity. The introduction of novel nanohybrid fillers effectively disrupts the crystalline domains of PEO, increasing the fraction of amorphous regions that favor ion transport. Simultaneously, these fillers help establish interconnected ion-conduction pathways, thereby lowering the interfacial resistance between the electrode and the electrolyte [70,71].

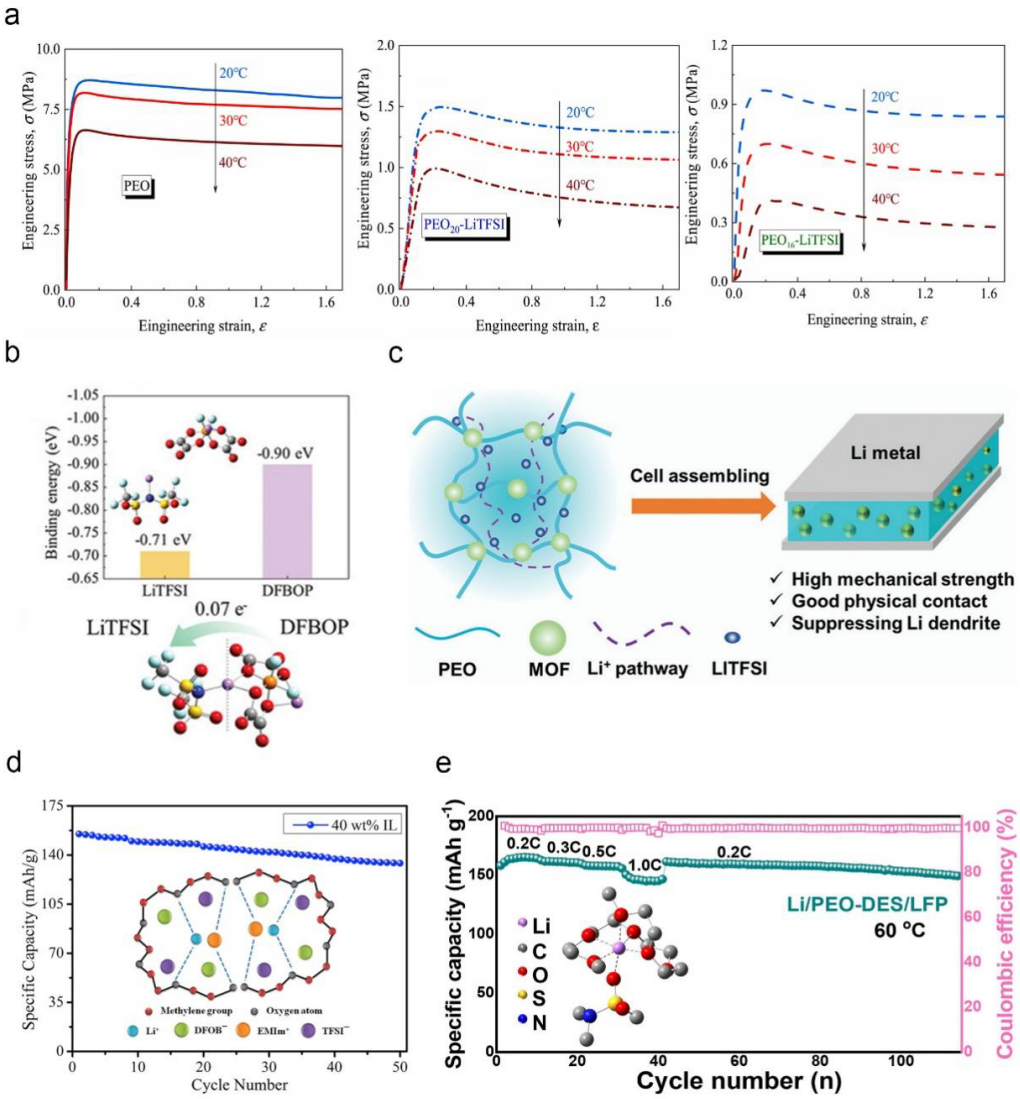

Figure 2. Schematic illustration of the structure–function relationships and key regulation mechanisms of PEO-based ultrathin interfacial layers: (**a**) Viscoelastic deformation of PEO buffering stress induced by lithium dendrite growth [59]. Copyright 2023, Elsevier. (**b**) Binding energies, optimized adsorption configurations of LiTFSI and DFBOP, and Mulliken charge population analysis [67]. Copyright 2024, Wiley. (**c**) Schematic illustration of PEO-MOF-based SSPE and its advantages for stabilizing lithium metal [72]. Copyright 2022, RSC. (**d**) Effects of ionic liquid incorporation on ionic conductivity, electrochemical stability, and flame retardancy [73]. Copyright 2017, Elsevier. (**e**) Electrochemical performance of Li‖PEO-DES‖LFP solid-state battery [68]. Copyright 2022, Elsevier.

2.2. Interface Chemistry and Structure Coupling

Beyond enhancing ion transport, PEO-based interfacial modification layers also function as effective physical barriers that substantially improve interfacial chemical stability. The ultrathin PEO layer isolates lithium metal from direct contact with the bulk electrolyte, suppresses undesired side reactions, and regulates the formation of a stable SEI. For example, Han et al. [72] induced the formation of an inorganic-rich SEI dominated by LiF on the lithium metal surface, which effectively inhibits continuous electrolyte decomposition and improves interfacial chemical stability.

PEO-based modification layers also play a critical role in stabilizing high-voltage cathode interfaces [74]. On the surfaces of high-nickel cathodes such as NCM materials, PEO segments can coordinate with transition-metal species, thereby suppressing metal dissolution while simultaneously mitigating oxidative degradation of the polymer under high-voltage conditions. As a result, structural degradation of the cathode and electrolyte decomposition are effectively alleviated, enabling stable battery operation at elevated potentials [56,66].

The choice of lithium-salt anions exerts a pronounced influence on the performance of PEO-based interfacial layers. Different anions exhibit distinct coordination affinities toward PEO segments and lithium-ion, directly affecting ionic conductivity, electrochemical stability windows, and the chemical composition of SEI/CEI layers [75].

Rational selection and design of lithium-salt anions therefore provide a powerful means to synergistically optimize both bulk transport properties and interfacial chemical stability [68].

In addition, controlling the microscopic directionality of lithium-ion transport offers a promising avenue for advanced interfacial engineering. Certain PEO-based modification layers exhibit anisotropic ion-transport behavior, which enables directional regulation of lithium-ion flux. For instance, schematic of PEO-MOF SPEs and its advantages against Li metal (Figure 2c). This ordered microstructure enhances lithium-ion conduction along preferred pathways, thereby facilitating uniform and efficient ion transport at the electrode–electrolyte interface [72].

To comprehensively enhance the multifunctional performance of PEO-based interfacial layers, the incorporation of functional additives has proven to be an effective strategy. Ionic-liquid doping has been widely employed to optimize interfacial properties (Figure 2d). Ionic liquids not only increase ionic conductivity and broaden the electrochemical stability window of PEO-based layers but also modulate the coordination strength between lithium-ion and PEO segments, thereby promoting lithium-ion dissociation and migration. Furthermore, ionic liquids improve flame retardancy and thermal stability, contributing to enhanced battery safety [73].

2.3. Design Rules and Key Metrics

PEO-based ultrathin interfacial modification layers integrate precise structural design with multifunctional performance. These layers are typically constructed with thicknesses ranging from several to tens of nanometers [76], and are fabricated via advanced techniques such as *in situ* polymerization, ALD, and self-assembly, enabling conformal, uniform, and defect-free coatings. The viscoelastic properties of the PEO-DES electrolyte effectively buffer mechanical stress induced by lithium dendrite growth, while the coordination between ether oxygen groups and lithium-ion promotes preferential lithium-ion transport, leading to a high lithium-ion transference number (Figure 2e). To further enhance interfacial performance, functional components such as coordination frameworks, tailored lithium salts, and ionic liquids are introduced to construct efficient ion-transport pathways and reduce interfacial impedance. Acting as both chemical and physical regulators, these ultrathin layers suppress parasitic reactions, regulate the formation of stable SEI/CEI structures, and improve interfacial stability at both lithium metal anodes and high-voltage cathodes. In certain systems, anisotropic ion-transport behavior further enables directional control of lithium-ion flux. Collectively, these design strategies enable PEO-based ultrathin interfacial layers to function as multifunctional regulatory platforms that simultaneously enhance ion-transport kinetics, cycling stability, and operational safety, providing a robust foundation for next-generation solid-state lithium batteries.

3. Fabrication Techniques for Ultrathin Interfacial Modification Layers

Ultrathin interfacial modification has emerged as a core technological strategy for optimizing critical interfaces in solid-state lithium batteries, including electrode–electrolyte and separator-electrolyte interfaces [77]. By suppressing parasitic interfacial reactions and regulating lithium-ion transport behavior, ultrathin interlayers can effectively enhance electrochemical stability, cycling durability, and rate capability [78]. Consequently, the development of precise and compatible fabrication techniques is essential for constructing high-performance interfacial layers [79].

State-of-the-art fabrication approaches for ultrathin interfacial layers emphasize nanoscale precision, uniformity, and strong interfacial adhesion. Among these, *in-situ* polymerization (Figure 3a) [80–83], ALD (Figure 3b) [84–86] and self-assembly (Figure 3c) [87–90] have been widely recognized as three representative and complementary techniques. Each method offers distinct advantages in terms of thickness control, interfacial conformity, and functional tunability, thereby enabling the rational design of interfacial layers tailored to specific electrochemical requirements.

To provide a clearer overview of recent advances in PEO-based ultrathin interfacial engineering, representative examples reported in the literature are summarized in Table 1. The table compares different fabrication strategies, including *in situ* polymerization, ALD, and self-assembly, together with their corresponding layer thicknesses, target electrode interfaces, functional roles, and key electrochemical performances. These representative studies demonstrate that rationally designed ultrathin interfacial layers can effectively regulate lithium-ion transport, suppress dendrite growth, stabilize high-voltage cathodes, and significantly enhance the cycling stability of ASSLBs. It should be noted that the electrochemical performances listed in Table 1 are compiled from original reports under varying testing conditions, such as temperature, current rate, voltage window, and cell configuration. Direct cross-comparison of capacity retention or cycling stability without accounting for these differences may lead to misleading conclusions. Therefore, the data are presented to illustrate representative results of each strategy rather than to serve as a direct performance ranking.

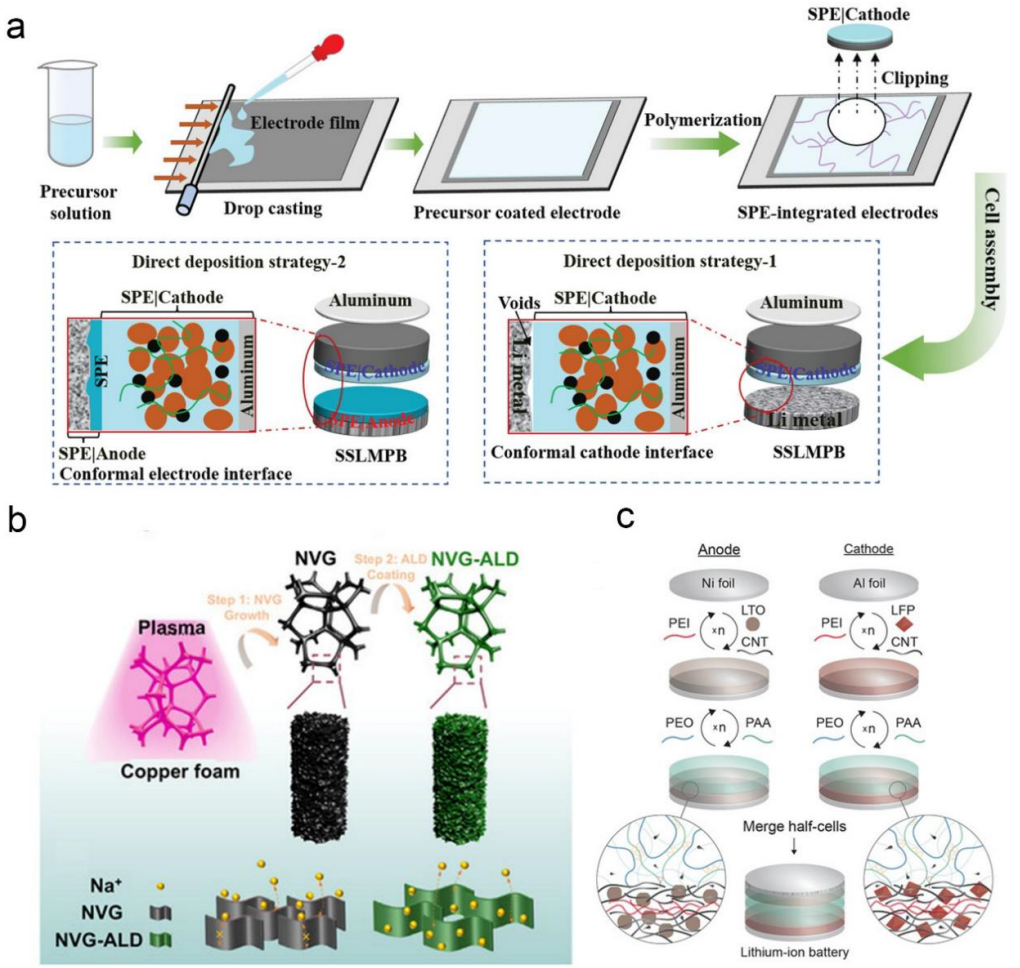

Figure 3. Schematic illustration of three core fabrication techniques for ultrathin interfacial modification layers: (**a**) *In situ* polymerization strategy for SSPLBs [83]. Copyright 2023, Wiley. (**b**) Fabrication of NVG and NVG-ALD [86]. Copyright 2025, Wiley. (**c**) Self-assembly driven by intrinsic intermolecular interactions for ordered interfacial architectures [87]. Copyright 2021, Wiley.

Table 1. Representative examples of PEO-based ultrathin interfacial engineering strategies for ASSLBs.

System	Thick	Method	Target	Function	Key Result	Ref.
PEO-DSPE	22 μm	Is	Bipolar	Dendrite suppression	80% capacity retention after 300 cycles	[42]
PEO dual-salt	20 μm	Is	NCM622	LiF-CEI	94.7% capacity retention after 100 cycles	[45]
PTFEMA/PEO	35 nm	Is	High-voltage cathode	Window expansion	Stable up to 5.1 V	[85]
EPD-PEO	40 μm	Is	Cathode	Contact improvement	Faster Li^+ transport	[91]
PEO/Li_2S_6	22 μm	Is	Anode	Reduced crystallinity	1.8×10^{-4} S·cm^{-1}	[92]
LATP coating	11 μm	Is	NCM811	Ni/Li suppression	81% capacity retention after 100 cycles	[93]
Li_3PO_4 interlayer	2.1 nm	ALD	LCO	Window expansion	Improved high-voltage cycling	[84]
ZnO-PEO	100 nm	ALD	Electrolyte	Ion channel	Increased conductivity	[94]
ZnO QD-PEO	4 nm	ALD	NCM811	Reduced crystallinity	Stable cycling	[95]
LLTO protection	10 nm	ALD	LCO	High-voltage stabilization	Stable at 4.5 V	[96]
Al_2O_3 coating	4 nm	ALD	Cr_8O_{21}	Anti-oxidation	Long-life cycling	[97]
PEO-MXene	56 μm	Sa	Li anode	Corrosion suppression	Increased conductivity	[98]
Agarose-g-PEO	32 μm	Sa	Anode	Helical transport	1.2×10^{-4} S·cm^{-1}	[48]
PEO/COF-F6	14 μm	Sa	Li anode	Flux regulation	Stable for 1000 h	[50]
PEO/LLZTO buffer	6 μm	Sa	Anode	Mechanical barrier	Stable for 1600 h	[99]
PEO-UPy	70 nm	Sa	Anode	Self-adhesive	High-current cycling	[100]

Is: *In-situ* Polymerization; Sa: Self-assembly.

3.1. In-Situ Polymerization

In situ polymerization has emerged as a highly versatile and innovative interfacial engineering strategy for advanced electrochemical systems, particularly ASSLBs [101]. The core concept of this approach lies in

constructing ultrathin interfacial modification layers directly at the target interface between the electrode and electrolyte during cell assembly or operation, without the need for external processing steps [102]. This on-site formation characteristic fundamentally circumvents common issues associated with conventional ex situ coating methods, such as interfacial delamination, secondary damage, and insufficient adhesion between the coating and the substrate [103,104]. Through *in situ* polymerization, ultrathin interfacial layers with precisely controlled composition and structure can be generated, enabling intimate molecular-level contact with the underlying electrode surface (Figure 4a) [105]. Such conformal interfaces significantly improve interfacial compatibility and electrochemical stability, particularly for solid-state lithium metal batteries, and are therefore regarded as one of the most effective strategies for addressing persistent electrode-electrolyte interfacial challenges [82,106].

A representative manifestation of *in situ* polymerization is interface-induced *in situ* segregation, which enables spatially resolved compositional tuning of polymer electrolytes at the electrode surface. By triggering microphase separation through photo or thermally induced polymerization, functional components with strong lithium-ion coordination capability can be selectively enriched at the interfacial region [107]. This localized enrichment enhances lithium-ion transport while simultaneously suppressing undesirable side reactions [108]. For high-voltage systems, *in situ* electrochemical passivation can be synergistically combined with interfacial segregation effects to stabilize cathode-electrolyte interfaces [109–111]. For example, Ye et al. demonstrated the formation of a stable CEI at the interface between a PEO-based electrolyte and an NCM811 cathode [112]. In this system, a trace amount of liquid electrolyte reacts *in situ* with the cathode surface to generate a passivation layer that isolates PEO from direct contact with the cathode, thereby preventing catalytic decomposition under high-voltage operation (Figure 4b). Similarly, in halide-based ASSLBs, rapidly crosslinked polymer interphases have been constructed via *in situ* reactions to address the intrinsic incompatibility between halide electrolytes and lithium metal. Luo et al. [113] reported a poly(butylene oxide) electrolyte interface formed through *in situ* crosslinking reactions, in which crosslinked products preferentially accumulate at the interface, effectively stabilizing lithium metal and enabling high-current-density cycling (Figure 4c). This interfacial engineering concept is readily transferable to PEO-based systems, where *in situ* crosslinking strategies can improve interfacial contact, suppress PEO crystallization, and inhibit lithium dendrite penetration.

Beyond chemically driven approaches such as segregation and crosslinking, electrochemically driven *in situ* deposition offers another powerful route for interfacial engineering. This strategy exploits applied electric fields during electrolyte fabrication or cell operation to induce the deposition of functional interfacial layers with high ionic conductivity and mechanical robustness. For instance, electrophoretic deposition (EPD) enables the *in situ* formation of ultrathin composite polymer electrolyte layers directly on cathode surfaces, effectively eliminating particle agglomeration issues associated with conventional solution-casting processes and significantly enhancing interfacial contact and ion-transport efficiency (Figure 4d) [91].

Building on this concept, Liu et al. [80] employed an *in situ* two-step synthesis strategy to construct a bilayer polymer electrolyte, consisting of a base polymer matrix formed via *in situ* polymerization and a functional surface layer subsequently deposited *in situ*. The synergistic interaction between the two layers maintains high ionic conductivity while substantially improving interfacial stability, resulting in a pronounced extension of battery cycle life. Furthermore, *in situ* polymerization has been combined with nanofiber engineering to fabricate hybrid interfacial layers with superior mechanical and electrochemical performance. *In situ* polymerized hybrid nanofiber membranes integrate reinforcing nanofibers with polymer matrices through strong intermolecular interactions, forming mechanically robust yet ion-conductive interfacial layers (Figure 4e). Such structures effectively suppress lithium dendrite growth and enhance both safety and long-term cycling stability [114]. When applied to PEO-based systems, the synergistic interaction between PEO chain segments and nanofiber networks further enhances interfacial stability while improving overall ionic conductivity. Additional physicochemical mechanisms further expand the scope of *in situ* interfacial engineering. For example, concentration-polarization-induced phase transformation enables dynamic regulation of lithium deposition behavior in polymer electrolytes, promoting uniform lithium plating and stabilizing the electrode-electrolyte interface from a kinetic perspective (Figure 4f) [115]. Meanwhile, *in situ* polymerization of highly elastic monomers allows the direct formation of ultrathin elastic interlayers that can accommodate volume changes of lithium metal anodes, alleviate interfacial stress concentration, and suppress side reactions [116]. The resulting elastic interphases homogenize interfacial pressure distribution, as illustrated by simulated stress profiles (Figure 4g), and significantly enhance cycling stability and safety [116]. In addition, in situ SEI engineering has also been shown to suppress interfacial side reactions and improve long-term cycling stability [117].

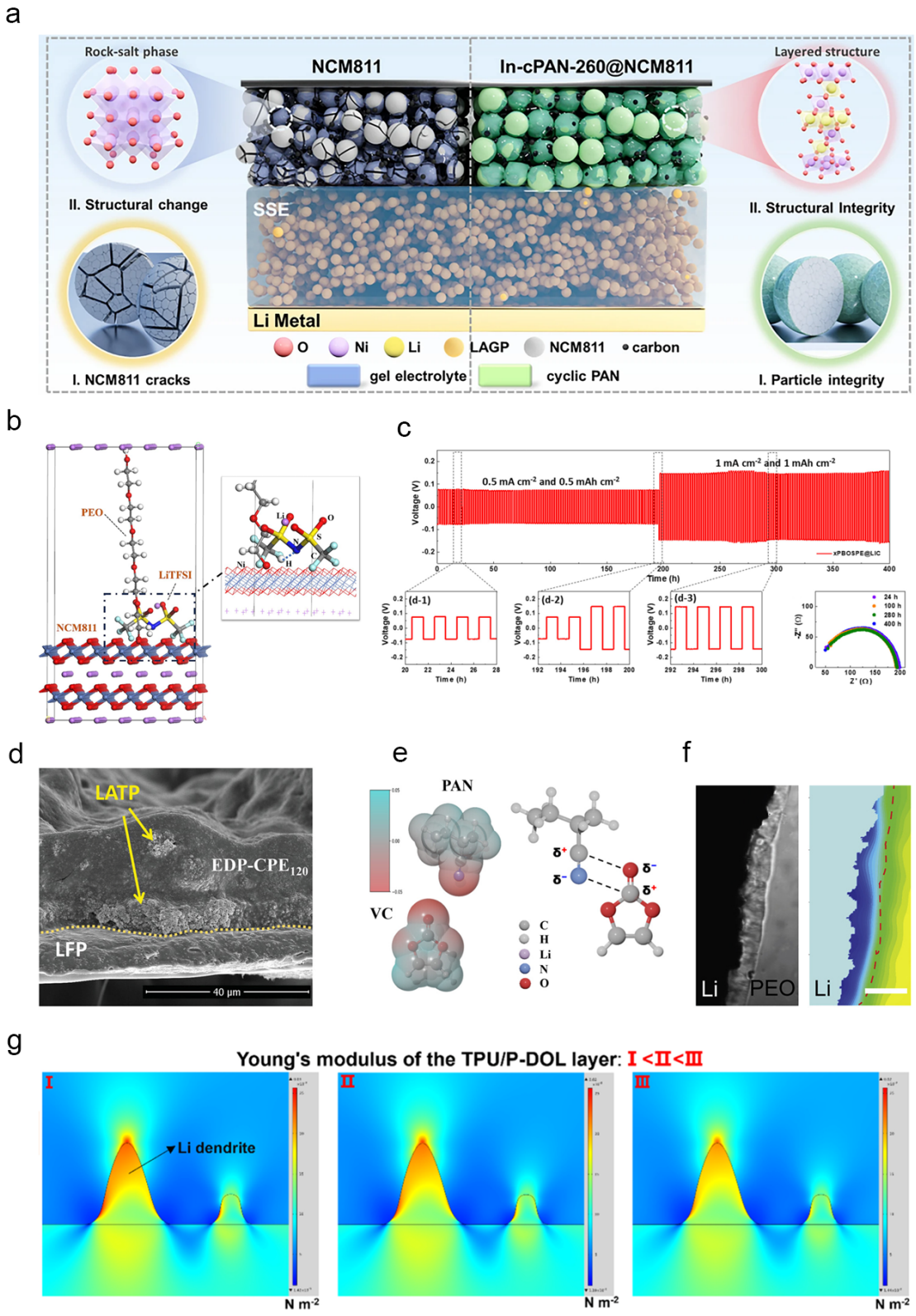

Figure 4. Representative applications and mechanistic illustrations of *in situ* polymerization strategies: (**a**) Multiscale models of solid-state batteries [105]. Copyright 2025, Springer Nature. (**b**) Degradation mechanism of PEO electrolytes on NCM cathode surfaces [112]. Copyright 2024, Elsevier. (**c**) Stabilization of lithium metal interfaces via *in situ* crosslinked polymer interphases [113]. Copyright 2023, ACS. (**d**) Cross-sectional SEM image of LFP/EPD-CPE$_{120}$ [91]. Copyright 2023, Wiley. (**e**) Electrostatic potential distribution of PAN and VC monomers [114]. Copyright 2025, ACS. (**f**) Concentration-polarization-induced phase transformation regulating lithium deposition [115]. Copyright 2022, Elsevier. (**g**) Simulated pressure distribution at Li/(TPU/PDOL) interface [116]. Copyright 2025, Elsevier.

In summary, in situ polymerization enables the on-demand construction of functional interfacial layers with excellent conformity and dynamic compatibility. Through mechanisms such as segregation, crosslinking, and electrochemically driven deposition, this approach allows precise regulation of interfacial chemistry and microstructure, thereby fundamentally improving interfacial stability. As a cornerstone strategy for solid-state battery interface engineering, in situ polymerization provides indispensable support for the development of next-generation high-performance energy-storage systems.

3.2. ALD

ALD is a thin-film fabrication technique based on self-limiting surface reactions, enabling the deposition of functional layers with atomic- or molecular-level thickness control [118–120]. In a typical ALD process, two or more gaseous precursors are alternately introduced into the reaction chamber, where they undergo sequential adsorption and surface reactions [121,122]. After each reaction step, excess precursors and byproducts are purged with an inert gas, and the cycle is repeated to achieve layer-by-layer film growth [123]. Owing to its self-limiting reaction mechanism, ALD offers unparalleled advantages in thickness precision, compositional uniformity, and conformality, even on substrates with complex geometries and high aspect ratios [124].

In solid-state lithium batteries, ALD has been widely employed for interfacial modification and structural engineering of electrodes, electrolytes, and separators [125–128]. For instance, Cai et al. [84] deposited an ultrathin Li_3PO_4 layer on $LiCoO_2$ cathodes via ALD. Under high-voltage operation, the Li_3PO_4 layer transformed *in situ* into $LiPO_3$, which exhibits a wider electrochemical stability window, thereby significantly improving interfacial stability and cycling performance in PEO-based ASSLBs (Figure 5a). By constructing dense and uniform interfacial layers, ALD effectively suppresses parasitic side reactions, mitigates lithium dendrite growth, and reduces interfacial impedance. ALD has also proven effective in improving the interfacial compatibility between lithium metal and solid electrolytes [129]. Depositing ultrathin Al_2O_3 or ZnO layers on garnet-type or sulfide-based solid electrolytes markedly enhances their wettability toward lithium metal, reducing interfacial resistance from several thousand $\Omega \cdot cm^2$ to only tens of $\Omega \cdot cm^2$ (Figure 5b) [130]. In addition, ALD enables the fabrication of composite electrolytes with ordered ion-transport pathways. By selectively depositing ZnO within block copolymer templates, well-defined ionic conduction channels can be formed, leading to simultaneous enhancement of ionic conductivity and mechanical robustness (Figure 5c) [94].

Beyond conventional surface coatings, derivative ALD-based techniques such as vapor-phase infiltration (VPI) offer innovative solutions for bulk electrolyte modification. Bao and co-workers [95] applied VPI to PEO-based solid electrolytes by alternately introducing DEZ and H_2O vapors, achieving *in situ* formation of uniformly dispersed ZnO quantum dots within the polymer matrix (Figure 5d). This approach effectively reduced PEO crystallinity lowered interfacial impedance, and enhanced electrochemical performance. The resulting NCM811‖PEO-based electrolyte‖Li cells exhibited high discharge capacity and stable cycling behavior.

Similarly, Liang's laboratory [96] employed ALD to fabricate a protective lithium lanthanum titanate interlayer on $LiCoO_2$ cathodes, which suppressed interfacial decomposition and extended the electrochemical stability window of PEO-based electrolytes to 4.5 V (Figure 5e). Zhang et al. [97] further demonstrated that an approximately 4 nm-thick Al_2O_3 coating deposited via ALD effectively inhibited oxidative degradation of PEO electrolytes on highly oxidative Cr_8O_{21} cathodes, enabling long-term cycling with high energy density (Figure 5f).

Overall, ALD represents an ideal technique for constructing ultrathin, dense, and conformal interfacial layers. Its atomic-scale precision not only enables effective suppression of interfacial degradation and impedance growth, but also allows synergistic optimization of interfacial and bulk properties through derivative strategies such as VPI. As such, ALD has become a cornerstone technology for high-performance and safe solid-state lithium batteries.

3.3. Self-Assembly

Self-assembly refers to a spontaneous process in which molecular or nanoscale building blocks organize into ordered structures through intrinsic interactions such as hydrogen bonding, coordination, van der Waals forces, and electrostatic interactions [131]. When applied to interfacial engineering in solid-state batteries, self-assembly also enables precise control over interfacial chemistry and microstructure under mild processing conditions [132].

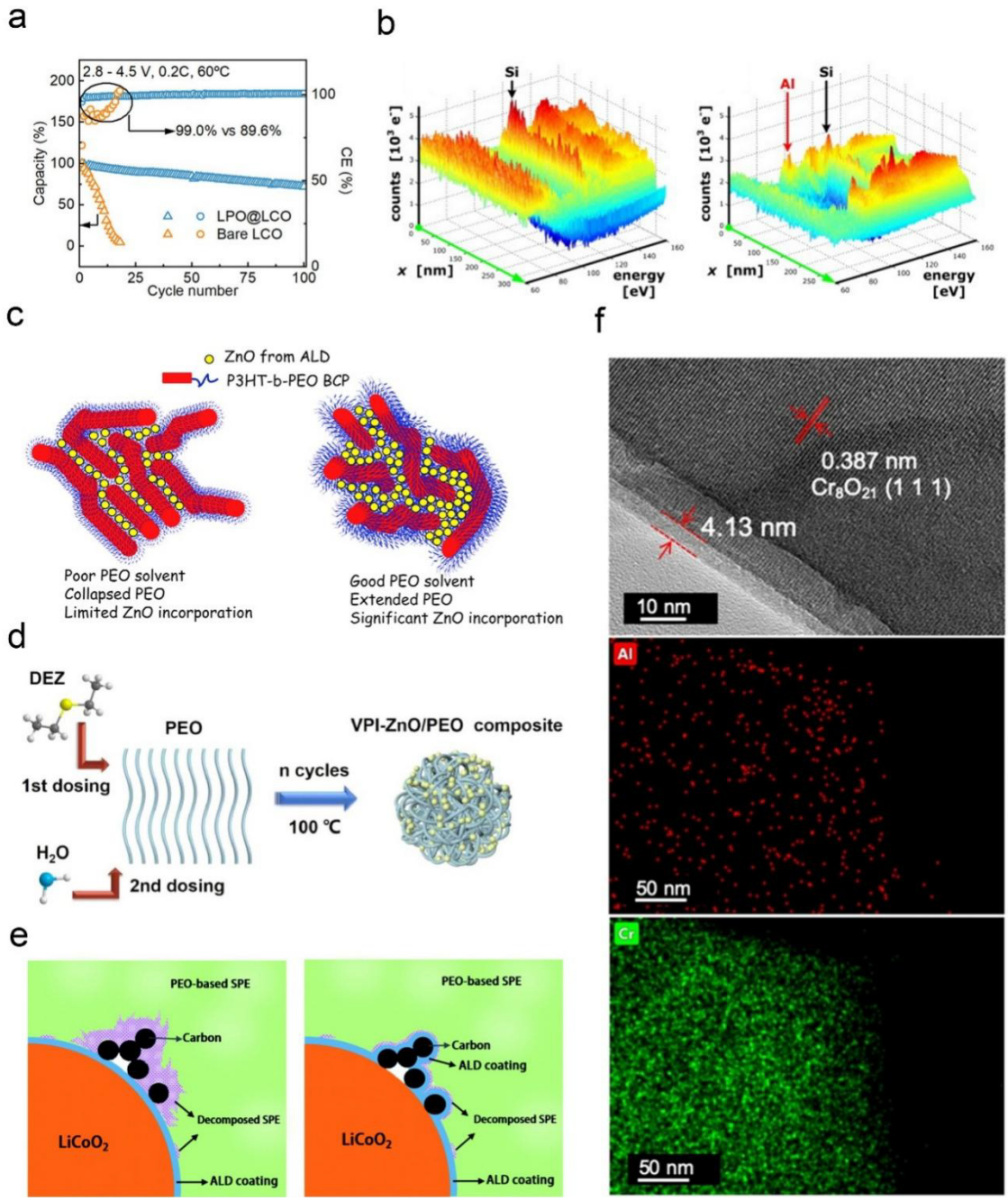

Figure 5. Examples of ALD-enabled interfacial engineering: (**a**) Cycling performance comparison of pristine and Li_3PO_4-coated $LiCoO_2$ cathodes [84]. Copyright 2023, Wiley. (**b**) Schematic illustration of incomplete pore infiltration during ALD Al_2O_3 deposition [130]. Copyright 2013, Elsevier. (**c**) Self-assembly behavior of P3HT-b-PEO block copolymers and corresponding ZnO loading [94]. Copyright 2016, Elsevier. (**d**) Schematic illustration of the vapor-phase infiltration process [95]. Copyright 2021, Elsevier. (**e**) Degradation suppression mechanism of ALD-protected $LiCoO_2$ particles [96]. Copyright 2020, RSC. (**f**) TEM image and EDS mapping of Al_2O_3-coated Cr_8O_{21} cathode [97]. Copyright 2021, MDPI.

In PEO-based systems, the flexible polymer chains and polar ether oxygen groups provide a favorable platform for self-assembled interfacial layer formation. Solvent-free self-assembly strategies have been widely explored to eliminate solvent residues and simplify processing [133]. For example, Xu et al. [98] exploited strong hydrogen-bonding interactions between $Ti_3C_2T_x$ MXene and succinonitrile molecules, together with lithium-ion with PEO coordination, to construct a stable self-assembled interfacial layer (Figure 6a). This layer not only suppressed lithium corrosion but also optimized the lithium-ion transport environment, resulting in significantly enhanced ionic conductivity. Similarly, Ding and co-workers [134] employed polar organic molecules to form ultrathin artificial SEI layers on lithium metal via solvent-free self-assembly (Figure 6b). These interlayers exhibited high mechanical strength and favorable ionic conductivity, effectively suppressing lithium dendrite

growth and enabling ultralong cycling stability. Hong's group [135] further demonstrated that coordination-driven self-assembly between Cu^{+}, BH_4^{-}, and electrolyte components could generate ordered interfacial structures with improved ionic conductivity and rate performance (Figure 6c). Targeted self-assembly strategies have also been developed to stabilize high-nickel cathode/PEO-based electrolyte interfaces, Dai et al. [136] designed functional molecules that selectively react with residual lithium species on cathode surfaces, forming dense and uniform protective layers through solvent-free self-assembly, the number of battery cycles has significantly increased (Figure 6d). These layers effectively suppressed transition-metal dissolution and interfacial side reactions, significantly improving cycling stability.

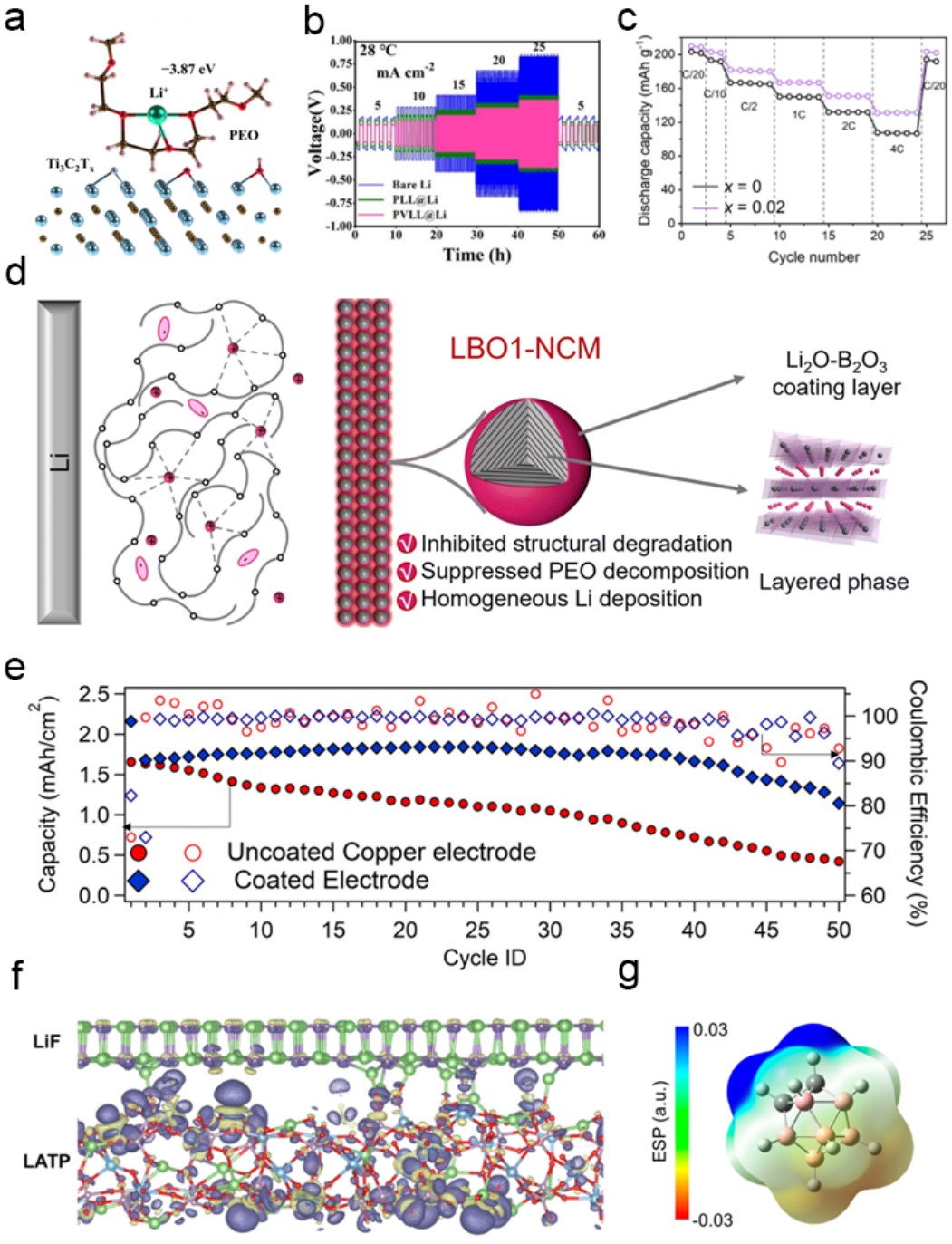

Figure 6. Self-assembly strategies for constructing functional interfacial layers: (**a**) Molecular models and binding energies of PEO/$Ti_3C_2T_x$ systems [98]. Copyright 2025, Elsevier. (**b**) Cycling stability comparison of bare and modified Li anodes [134]. Copyright 2025, Elsevier. (**c**) Rate performance of self-assembled solid electrolytes [135]. Copyright 2025, Elsevier. (**d**) Mechanism of interfacial property enhancement [136]. Copyright 2024, RSC. (**e**) Cycling performance of coated and uncoated Cu anodes [137]. Copyright 2021, Elsevier. (**f**) Charge density difference mapping [138]. Copyright 2025, Elsevier. (**g**) Simulated electrostatic potential distribution of o-carborane molecules [139]. Copyright 2025, ACS.

In addition to solvent-free approaches, initiated chemical vapor deposition (iCVD)-assisted self-assembly has emerged as a powerful tool for constructing ultrathin polymeric interphases with precise thickness control [140]. Stalin's group [137] fabricated an ultrathin zwitterionic polymer interphase on lithium metal via iCVD, which regulated lithium-ion solvation and suppressed dendrite growth (Figure 6e). Plasma-enhanced iCVD has also been employed to simultaneously achieve bulk doping and interfacial layer formation. For example, Li et al. [138] constructed a LiF-rich buffer layer on LATP electrolytes through plasma-assisted decomposition and self-assembly of F-containing species (Figure 6f), resulting in ultralong cycling stability exceeding 9000 h. Furthermore, Wang's team [139] utilized iCVD to activate o-carborane precursors, enabling self-assembly into dual-stable interfacial layers via hydrophobic–hydrophilic interactions (Figure 6g). This approach effectively inhibited dendrite growth while enhancing ion-transport kinetics, offering a versatile platform for molecular-level interfacial design.

In summary, self-assembly techniques provide a highly flexible and controllable pathway for constructing ordered interfacial layers. Whether through solvent-free or iCVD-assisted approaches, self-assembly enables precise regulation of interfacial chemistry, structure, and functionality, thereby playing a vital role in stabilizing solid-state battery interfaces.

3.4. Toward Integrated Fabrication

This section systematically reviewed three representative fabrication techniques for constructing ultrathin PEO-based interfacial modification layers: *in situ* polymerization, ALD, and self-assembly. Each technique exhibits distinct advantages and complementary characteristics, collectively enabling precise interfacial engineering at the nanoscale.

In situ polymerization offers unparalleled interfacial conformity and dynamic compatibility through on-site layer formation, making it particularly suitable for repairing and integrating complex interfaces. ALD provides atomic-level thickness control and excellent three-dimensional conformality, enabling the fabrication of dense protective layers that effectively suppress interfacial degradation and broaden electrochemical stability windows. Self-assembly relies on intrinsic intermolecular interactions to spontaneously form ordered structures, offering advantages in processing simplicity, structural tunability, and functional versatility.

Looking forward, interfacial fabrication strategies are evolving from single-technique optimization toward synergistic integration of multiple approaches. By combining the adaptability of *in situ* polymerization, the precision of ALD, and the ordering capability of self-assembly, advanced multilayered and gradient interfacial architectures can be realized. Such integration, together with advanced characterization and in-process monitoring techniques, is expected to drive the transition from empirical interface modification to precision-guided interfacial design.

4. Functional Optimization Strategies

4.1. Active vs. Passive Interfacial Engineering

PEO-based ultrathin interfacial modification layers have emerged as a class of pivotal interface-engineering materials for realizing high-performance ASSLBs [141]. Their essential role lies in stabilizing the highly reactive electrode-electrolyte interfaces while maintaining efficient ionic transport across solid-solid boundaries [142]. Specifically, the intrinsic compatibility between PEO-based interlayers and PEO electrolytes ensures continuity of lithium-ion conduction, thereby minimizing interfacial impedance [143]. In addition, the excellent film-forming capability of PEO enables the construction of dense yet ultrathin physical barriers that isolate reactive interfaces without sacrificing ionic conductivity [144]. More importantly, by deliberately regulating the local chemical and electrochemical environment, these interfacial layers can actively guide uniform lithium deposition, substantially improving kinetic stability and dendrite resistance [145].

Nevertheless, the inherent limitations of PEO-based electrolytes, including low room-temperature ionic conductivity, insufficient interfacial chemical stability, and limited dendrite suppression capability, which pose intrinsic challenges to the design of ultrathin interfacial layers. Although reducing electrolyte thickness effectively lowers internal resistance and enhances gravimetric energy density, excessive thinning may amplify interfacial instability if not properly engineered. To address this dilemma, current strategies can be broadly categorized into two synergistic paradigms: active regulation and passive protection, which together enable performance enhancement while preserving long-term interfacial stability.

In the following discussion, functional optimization is considered at two coupled structural levels: nanoscale interfacial layers and micrometer-scale ultrathin electrolyte membranes, because both can contribute to interfacial stabilization in practical ASSLB architectures.

4.2. Active Regulation

Active regulation strategies aim to modulate the interfacial chemical environment and lithium-ion transport behavior at molecular and nanoscopic scales, thereby optimizing interfacial performance from its origin. This approach represents a fundamental shift from traditional "passive shielding" toward interfacial chemistry-guided design.

4.2.1. Lithium-Ion Transport Pathway Engineering

Lithium-ion migration kinetics critically determine charge-transfer efficiency, rate capability, and cycling stability in ASSLBs [146]. Conventional solid electrolytes are simultaneously constrained by limited intrinsic ionic conductivity and large interfacial resistance. To overcome these bottlenecks, a synergistic strategy that integrates ultrathin structural design with microscopic regulation of ion-transport pathways has been widely adopted.

Ultrathin architectures serve as the physical foundation for enhancing ionic mobility by significantly shortening absolute lithium-ion diffusion distances, thereby reducing both bulk resistance and electrochemical polarization [147]. Reducing electrolyte thickness from the conventional 100-150 μm range to 10–20 μm can decrease lithium-ion diffusion time by nearly an order of magnitude. For example, Wu et al. [148] fabricated an ultrathin PEO/polyethylene composite electrolyte (PPL), which enabled stable full-cell operation at 30 °C despite a moderate room-temperature ionic conductivity. Beyond thickness reduction, structural interlocking between ultrathin electrolytes and electrodes further minimizes interfacial resistance. A representative example is a 16 μm-thick three-dimensional LLZO-PAN composite electrolyte prepared via integrated electrospinning, which reduced interfacial impedance from 154.2 Ω to 15.6 Ω [149]. These examples, obtained under different experimental configurations, illustrate distinct routes toward interfacial resistance reduction.

Simultaneously, ultrathin architectures facilitate the uniform incorporation of a high fraction of inorganic fillers. Zhang et al. [46] prepared a 14 μm-thick LZSP/PEO/PVDF composite electrolyte with a ceramic content as high as 91%, establishing continuous ion-conduction pathways and achieving a room-temperature ionic conductivity of 1.16×10^{-4} S·cm^{-1} (Figure 7a). Similarly, by comparing of tensile strengths tested at different thicknesses of the PEO electrolyte, the PEO-LAGP Particle electrolyte and the PEO-LAGP Fiber electrolyte, with the inset showing the stress-strain curves of the 100 μm thick PEO-LAGP Particle electrolyte and PEO electrolyte membrane [47] that ultrathin electrolyte reinforced by a pre-fibrillated LAGP continuous skeleton suppressed PEO crystallization and reduced transport resistance.

On this basis, microscopic regulation of lithium-ion transport channels represents a core strategy for achieving intrinsically high ionic mobility [150,151]. These strategies can be broadly divided into three categories. First, regulating the alignment and chemical structure of polymer segments to construct directional transport pathways. Conventionally, randomly entangled polymer chains lead to tortuous lithium-ion migration paths. Wan et al. [43] utilized vertical nanochannels within a PI matrix in an 8.6 μm thick PI/PEO/LiTFSI electrolyte to induce the directional alignment of PEO chains along the channels. This resulted in a lithium-ion diffusion coefficient along the channel direction of 1.3×10^{-8} cm^2·s^{-1} at 30 °C, which is 2.3 times higher than that in a system with randomly arranged PEO, and a room-temperature ionic conductivity of 2.3×10^{-4} S·cm^{-1} at the same temperature. Molecular dynamics simulations confirmed that the directional alignment of segments reduces path tortuosity and lowers the energy barrier for lithium-ion transport [43]. Further chemical modifications can optimize channel performance. For instance, in an ultra-thin electrolyte composed of agarose-grafted PEO with a single-helix structure, the helical backbone provides axial transport channels, while the PEO side chains act as radial "ionic bridges," facilitating rapid lithium-ion migration between chains. This structure achieves a room-temperature ionic conductivity of 1.2×10^{-4} S·cm^{-1} and a lithium-ion transference number of 0.34. Simultaneously, it enhances mechanical strength, with a tensile strength of 5.5 MPa, thereby mitigating the short-circuit risk associated with insufficient mechanical performance in ultra-thin electrolytes [48]. Additionally, for all-solid-state lithium-metal batteries, Fang et al. [92] integrated Li_2S_6 into a 22 μm thick PEO-based polymer electrolyte. The synergistic effect between Li_2S_6 and PEO modulates segmental mobility, reducing the energy barrier for lithium-ion transport between PEO chains and increasing the room-temperature ionic conductivity to 1.8×10^{-4} S·cm^{-1}. Thus, the introduction of Li_2S_6 can reduce PEO crystallinity and facilitate the formation of a stable interface (Figure 7b).

Second, introducing low-polarization inorganic fillers to construct a "ceramic-polymer" synergistic transport system. Lewis acid sites on the surface of inorganic fillers, such as LLZTO, can strongly adsorb anions, thereby increase the concentration of free lithium-ion and significantly enhance the lithium-ion transference number. Wu et al. [152] fabricated a 20 μm-thick LLZTO/PEO/PVDF composite electrolyte. The LLZTO ceramic filler forms a "ceramic-polymer" bicontinuous phase with PEO and PVDF. The Lewis acid sites on the LLZTO surface capture anions, boosting the free lithium-ion concentration, while the interaction between PEO and PVDF reduces

the system's crystallinity (Figure 7c). This results in a lithium-ion transference number of 0.78 and a room-temperature ionic conductivity of 6.49×10^{-4} S·cm^{-1}.

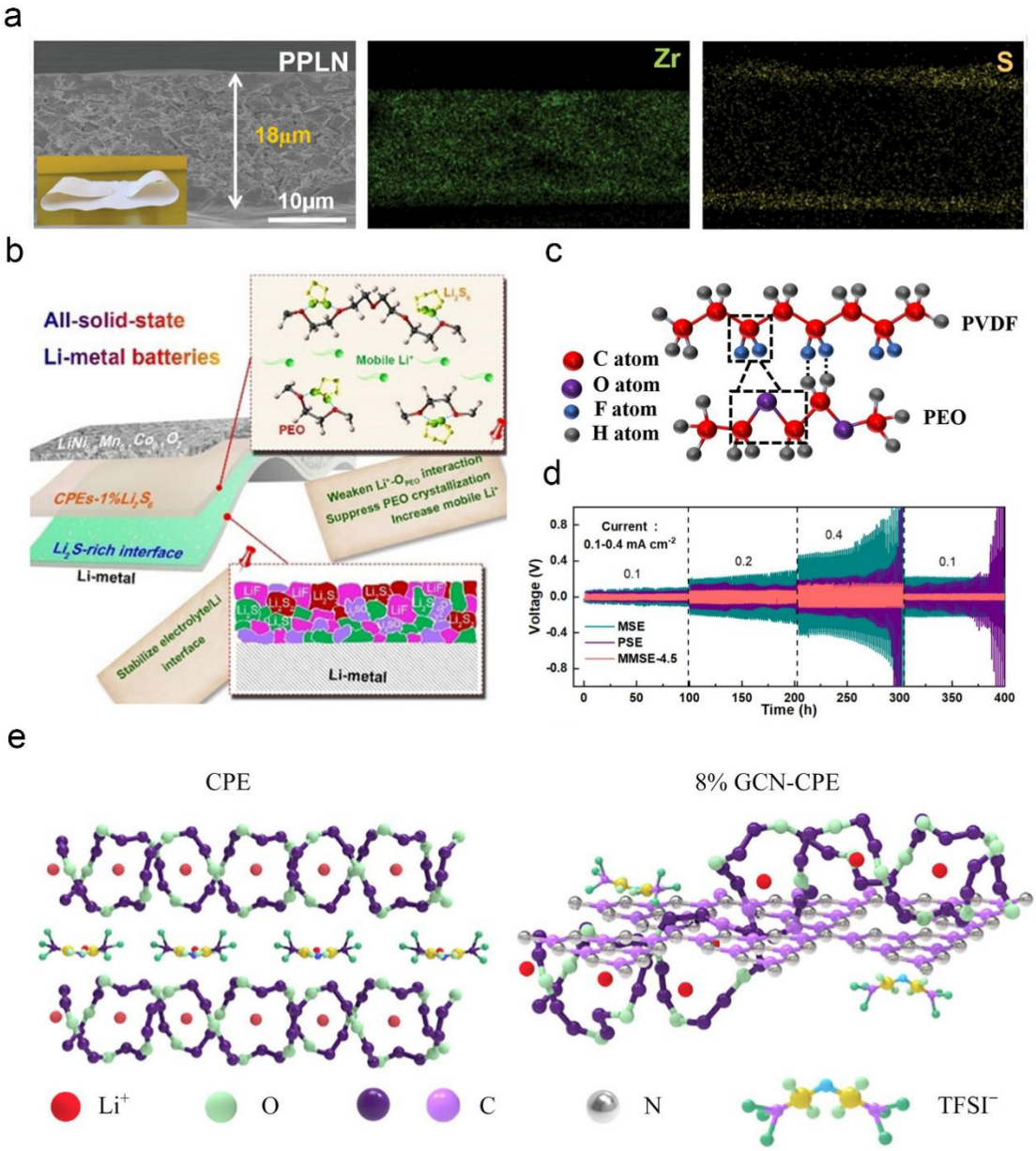

Figure 7. Strategies for ultrathin structural design and lithium-ion transport optimization: (**a**) Cross-section SEM and corresponding EDS images of PPLN [46]. Copyright 2024, Wiley. (**b**) Reduction of PEO crystallinity and interface stabilization induced by Li_2S_6 additives [92]. Copyright 2021, Wiley. (**c**) Interactions between PVDF and PEO contributing to high Li^+ transference number [152]. Copyright 2023, Springer Nature. (**d**) Voltage profiles of Li‖SPE‖Li symmetric cells at various current densities [153]. Copyright 2021, ACS. (**e**) Structural schematic of g-C_3N_4-reinforced composite electrolytes and morphology of stabilized lithium anode [154]. Copyright 2023, Elsevier.

Third, introduce ionic liquids or non-metallic two-dimensional fillers to construct multiple transport pathways and inhibit polymer crystallization. The introduction of ionic liquids provides additional transport paths for ultra-thin electrolytes. Yao's team [153] developed an MMSE electrolyte composed of UiO-66 MOF and EMIMTFSI ionic liquid. Li symmetric cells using this electrolyte exhibited stable voltage plateaus across different current densities (Figure 7d), demonstrating their capability for rapid ion transport with a wide operating temperature range and high transference number. Furthermore, Tleukenov et al. [155] studied a 20 μm-thick PEO-PVDF-co-HFP/GO composite electrolyte. GO nanosheets disrupt the PEO crystalline structure and introduce oxygen-containing functional groups to create transport sites. The smooth morphology of the electrode surface after cycling indirectly reflects the positive role of GO doping in stabilizing lithium deposition. Finally, the structural schematic of a g-C_3N_4-reinforced composite electrolyte and the corresponding morphology of the

stabilized lithium anode (Figure 7e) comprehensively illustrate the dual mechanism of two-dimensional fillers: providing hopping sites and inhibiting crystallization, thereby holistically enhancing both ionic conductivity and interfacial stability [154].

Furthermore, the construction of weakly solvating electrolytes through steric hindrance engineering of solvent molecules also represents an effective strategy for optimizing lithium-ion migration channels. For instance, Li et al. [156] designed a triethoxy orthoformate (TEOF)-based locally concentrated electrolyte, which utilizes the steric hindrance effect of ethyl groups to weaken the coordination between solvent molecules and lithium-ion, resulting in an anion (FSI^-)-dominated solvation structure. This configuration not only reduces the lithium-ion desolvation energy barrier but also promotes the preferential decomposition of anions to form a LiF-rich SEI. Consequently, Li||Cu cells achieved stable cycling over 450 cycles at 0.5 $mA \cdot cm^{-2}$, while Li||NMC811 high-voltage (4.3 V) full cells maintained 95.6% capacity retention after 150 cycles. In contrast to the polymer chain engineering approaches used in PEO-based systems, this strategy offers a novel polymer-independent pathway for optimizing lithium-ion transport channels through precise molecular design of small-molecule solvents.

4.2.2. Interfacial Chemistry Regulation

Beyond transport kinetics, the interfacial chemical microenvironment fundamentally governs interphase composition, mechanical integrity, and long-term stability [157]. Accordingly, the research paradigm has shifted from macroscopic physical blocking toward chemical microenvironment regulation [158,159].

In conventional PEO-based electrolytes, strong coordination between lithium ions and ether oxygen atoms, along with detrimental anion decomposition, often leads to the formation of heterogeneous and unstable SEI/CEI layers [143,160]. The time-dependent evolution of interfacial resistance clearly illustrates this instability (Figure 8a). To address this issue, Li et al. [49] designed a composite electrolyte in which a mixed-conducting interphase (MCI) interwoven with a LiF-rich SEI formed at the lithium interface, enabling stable cycling for over 2000 h (Figure 8b). Molecular-level chemical regulation has further advanced interfacial design. Zhang et al. [161] introduced a molecular crowding strategy using 15-crown-5 to modulate lithium-ion solvation, thereby inducing the formation of LiF-rich SEI/CEI layers and enabling ultralong cycling stability (Figure 8c). Such approaches exemplify an "inside-out" chemical design philosophy that targets the thermodynamic and kinetic origins of interfacial reactions.

Recently, bio-inspired framework materials such as COFs and MOFs have opened new avenues for precise ionic microenvironment engineering (Figure 8d) [162–164]. Liu et al. [50] modified a 14 μm PEO-based electrolyte with fluorinated COF. Utilizing the channel confinement of COF and the electrostatic interactions of fluoroalkyl chains, this strategy promotes uniform lithium-ion distribution and $TFSI^-$ decomposition. Li/Li symmetric cells showed no dendrite growth after 1000 h of cycling, and the LFP/CPPL-F6/Li cell demonstrated 97.3% capacity retention after 150 cycles at 60 °C and 0.5 C (Figure 8e). These strategies ingeniously leverage the confinement effects of framework materials and the specific interactions of functional groups. They not only extend the concept of ion environment regulation but also elevate it to the level of "nano-/micro-structure engineering," achieving synergistic optimization of ion transport, interfacial composition, and mechanical properties.

4.2.3. Process Integration and Multi-Interface Design

Building upon the core regulation strategies mentioned above, advanced fabrication techniques, innovative cell configurations, and multi-interface synergistic design further extend the dimensions of active control, achieving comprehensive optimization of interfacial performance.

First, from the perspective of constructing functional interfaces, researchers have introduced functional interlayers into electrolytes to regulate ion transport and deposition behavior. The MXene functional layer design proposed by Kou et al. [165] exploits the unique two-dimensional layered structure, excellent electronic conductivity, and abundant surface functional groups of MXene materials [166]. This functional layer creates a uniform ion-redistribution interface on the surface of an ultrathin PEO matrix. Its 2D channels guide the directional migration of lithium-ion, while the surface functional groups form weak interactions with PEO chains to suppress crystallization, simultaneously homogenizing the lithium-ion flux by modulating the interfacial electric field (Figure 8f). This strategy operates synergistically on both physical and chemical levels, effectively mitigating lithium-dendrite growth and the increase of interfacial impedance.

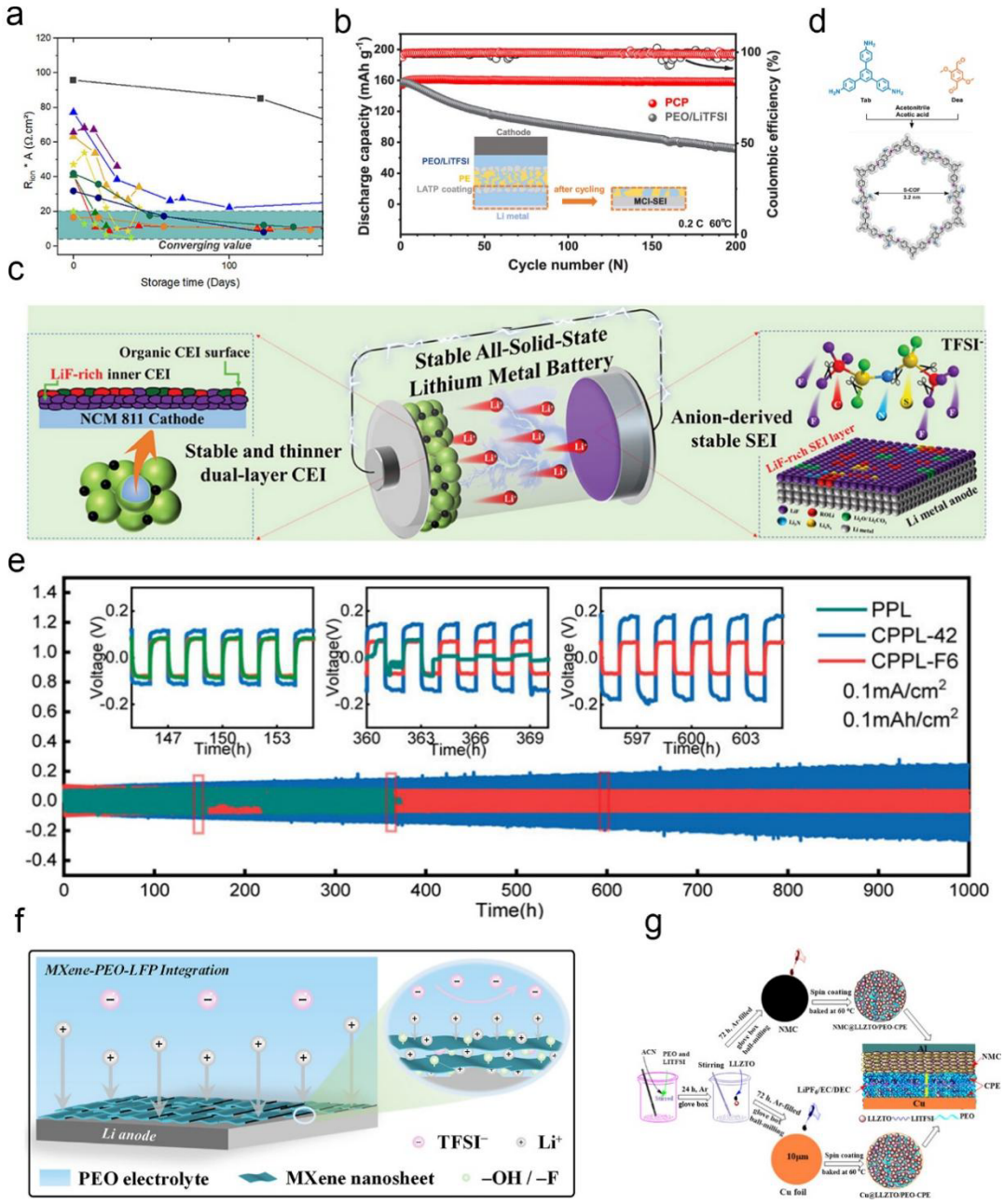

Figure 8. Mechanisms of interfacial chemistry regulation and ionic microenvironment engineering: (**a**) Evolution of interfacial resistance at PEO-based interfaces [143]. Copyright 2024, ACS. (**b**) Formation of MCI–SEI hybrid interphase [49]. Copyright 2022, ACS. (**c**) Molecule crowding strategy inducing anion-rich Li^+ solvation structure [161]. Copyright 2024, Wiley. (**d**) Schematic illustrations of S-COF synthesis [164]. Copyright 2022, Elsevier. (**e**) Long-term cycling performance of Li‖Li cells [50]. Copyright 2025, ACS. (**f**) MXene-functionalized interface regulating Li^+ flux [165]. Copyright 2024, Elsevier. (**g**) Integrated ultrathin electrolytes design for anode-free batteries [167]. Copyright 2020, ACS.

Once the functional layer is successfully constructed, ensuring robust and intimate contact with the electrode relies on innovations in fabrication processes. Conventional lamination methods are prone to introducing interfacial defects. To address this, the Liu team [80] developed an in-situ two-step synthesis process. This technique first forms an 8 μm PEO base layer on the electrode via solution casting, followed by in-situ polymerization to generate a 5 μm cross-linked polymer functional layer on top. This "bottom-up" in-situ construction achieves "seamless" molecular-level contact between the electrolyte and the electrode, avoiding interfacial voids. Meanwhile, the bilayer structure itself provides a functional gradient: the underlying layer ensures ion transport, while the upper layer enhances mechanical stability. This approach extends interfacial optimization beyond material selection toward process-enabled structural integration. As interfacial issues on the anode side are alleviated, research focus naturally extends to the stabilization of high-voltage cathode/electrolyte

interfaces. Side reactions between ultrathin electrolytes and highly reactive Ni-rich cathodes are a key factor limiting battery cycle life. To address this, Wang and colleagues [168] developed an ultrathin dry-coated Li-ion-conductive glass-ceramic conformal layer of Li_2O-B_2O_3-ZnO with thickness of 2–3 μm. This coating plays a dual role: as a physical barrier to suppress structural degradation of the cathode material under high voltage, and as an ion-conducting channel to reduce interfacial charge-transfer resistance. This strategy expands the concept of interface optimization from "preventing dendrites" to "suppressing cathode degradation," achieving simultaneous protection of two key internal interfaces in the battery.

Ultimately, the stability of both the internal component interfaces within composite electrolytes and the macroscopic interfaces between electrodes and electrolytes depends on microscopic interfacial chemical compatibility. For example, in the commonly used PEO-LLZTO-PVDF composite system, the alkaline Li_2O on the LLZTO surface can induce PVDF degradation. The solution proposed by Chen et al. [169] is particularly ingenious: introducing a trace amount of acidic OX additive. This additive neutralizes alkaline byproducts, forming stable lithium salts, thereby "passivating" the reactive sites that trigger degradation at the molecular level. At the same time, OX molecules can form hydrogen bonds with PEO chains, providing an additional crystallization-suppression effect. This work demonstrates that precise interfacial chemical regulation can simultaneously address multiple interfacial challenges, elevating interface optimization to the height of molecular engineering. The SEM image shows an Al_2O_3-coated NCM composite cathode framework surface, serving as an example of constructing stable interfacial structures.

While optimizing the interfaces themselves, the design of ultrathin electrolytes must also be integrated with advanced battery configurations to maximize their effectiveness. For instance, targeting the frontier system of anode-free batteries, Zegeye et al. [167] proposed an integrated structural design. They pre-laminated a 10 μm ultrathin LLZTO composite electrolyte onto the current collector via a lamination process, forming an integrated "cathode-electrolyte-anode" electrode (Figure 8g). This design physically redefines the deposition interface, strictly confining the lithium-metal deposition space within a pre-defined, protected interface, thereby addressing the fundamental challenge of uncertain lithium-deposition space in anode-free batteries at the system-architecture level.

4.3. Passive Protection

Passive protection strategies focus on structural design and material hybridization to establish physical barrier layers and enhance mechanical robustness, thereby externally suppressing interface failure mechanisms and providing a solid foundation for active regulation approaches.

4.3.1. Mechanical Reinforcement

Mechanical performance is a critical determinant for the practical application of PEO-based ultrathin interfacial modification layers [170,171]. It directly governs the structural integrity of the interface, the effectiveness in blocking lithium dendrites, and the long-term cycling stability of batteries [172]. Given that neat PEO exhibits high crystallinity, low mechanical strength, and susceptibility to penetration by lithium dendrites at room temperature [173], enhancing its mechanical properties through material design and structural regulation is essential [174].

The formation of a three-dimensional continuous polymer network effectively restricts the sliding of PEO chains, thereby significantly improving the tensile strength, fracture toughness, and resistance to deformation of the modification layer, and preventing crack formation due to interfacial stress concentration during cycling [175]. Common approaches include the introduction of cross-linkers or the formation of chemically cross-linked structures via in-situ polymerization [176]. For example, the Liu team [51] prepared an ANF/PEO-LiTFSI composite electrolyte via vacuum filtration, utilizing hydrogen bonding between ANF to construct a 3D cross-linked network (Figure 9a). This structure endowed a mere 16 μm thick ultrathin modification layer with mechanical strength 13 times higher than that of neat PEO-LiTFSI, while fast ion transport channels were established along the PEO/ANF interfaces. Consequently, Li‖Li symmetric cells demonstrated stable cycling for 2200 h, and Li‖$LiFePO_4$ full cells achieved 95% capacity retention after 150 cycles. Wang et al. [177] fabricated a 38 μm thick nylon@PEO/LiTFSI composite electrolyte via coaxial electrospinning at 45 °C, in which physically entangled nylon nanofibers formed a 3D cross-linked network. The electrolyte exhibited mechanical strengths of 3.32 MPa at 25 °C and 2.44 MPa at 60 °C, significantly higher than those of pure PEO membranes and enabled intimate interfacial contact with $LiFePO_4$ cathodes, resulting in stable cycling for 100 cycles at 0.2 C and 60 °C (Figure 9b). Importantly, cross-linked PEO networks can maintain stable mechanical strength over a wide temperature range, avoiding chain sliding and interfacial failure caused by temperature fluctuations (Figure 9c) [178].

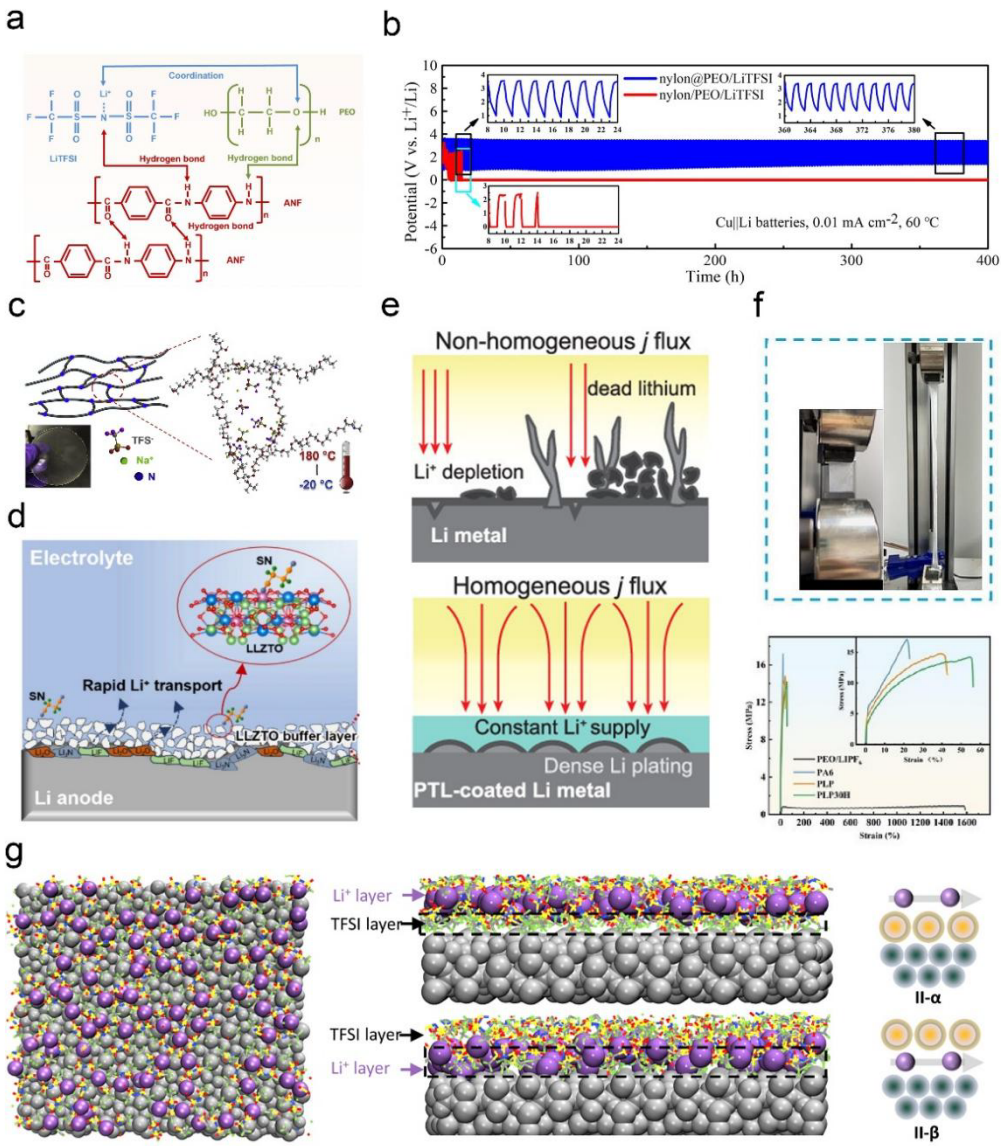

Figure 9. Mechanical reinforcement strategies for ultrathin PEO-based interfacial layers: (**a**) Hydrogen-bonding interactions among PEO, LiTFSI, and aramid nanofibers [51]. Copyright 2025, Elsevier. (**b**) Lithium plating/stripping behavior of nylon-reinforced electrolytes [177]. Copyright 2022, Springer Nature. (**c**) Temperature-dependent mechanical stability of crosslinked PEO networks [178]. Copyright 2019, Elsevier. (**d**) LLZTO buffer-layer modification mechanism [99]. Copyright 2025, Elsevier. (**e**) Suppression of lithium dendrite growth by cellulose-based coatings [179]. Copyright 2024, Elsevier. (**f**) Tensile behavior of fiber-reinforced membranes [53]. Copyright 2023, Elsevier. (**g**) Dual lithium-ion transport pathways [180]. Copyright 2024, Elsevier.

Introducing nano-reinforcements with high intrinsic modulus into PEO-based modification layers enhances overall mechanical strength while constructing continuous ion-conduction pathways, enabling synergistic optimization of mechanical properties and ionic conductivity. For instance, Yang et al. [99] employed spin-coating transfer to directionally embed LLZTO nanoparticles onto the surface of a PEO/SN-based electrolyte, creating an ultrathin buffer layer only 6 μm thick with a Young's modulus as high as 13,843.2 MPa. This structure could adsorb free SN molecules to avoid corrosion of the lithium anode and effectively suppress lithium-dendrite growth. The modification of the PEO/SN electrolyte with an LLZTO buffer layer (Figure 9d) enabled stable cycling of Li symmetric cells for 1600 h at room temperature, and $LiFePO_4$‖Li full cells retained 98.4% capacity after 200 cycles at 0.5C. In addition, aligned one-dimensional PTFE nanofibers can form a mechanical support skeleton that significantly improves the tensile and puncture resistance of the modification layer.

Improving the rigidity of PEO chains through chemical modification or compositional adjustment is an effective strategy to suppress chain sliding, optimize the lithium-ion conduction environment, and balance mechanical properties with ionic transport [181]. Common methods include introducing rigid groups such as aromatic rings or siloxane segments into PEO chains to reduce chain flexibility. For example, Feng et al. [52]

induced orderly alignment of PEO segments by incorporating PTFE, forming a rigid-flexible alternating structure that endowed the modification layer with a tensile strength of 350 MPa and an ionic conductivity of 2.91×10^{-5} S·cm^{-1} at 30 °C. This ordered chain structure reduced defects in amorphous regions, enabling Li symmetric cells to cycle stably for 3500 h at 30 °C. Wang et al. [177] compounded PEO-LiTFSI with PTFE via hot-pressing; the rigid PTFE segments induced directional alignment of PEO chains, increasing the crystallinity of the modification layer from 35.16% to 62.91% and achieving a mechanical strength of 3.32 MPa at 25 °C.

Beyond the three mainstream approaches described above, mechanical optimization of PEO-based ultrathin solid electrolytes can also be achieved through fiber reinforcement, porous skeleton support, multi-component compositing, and other routes, significantly improving mechanical strength and structural stability while maintaining ultrathin dimensions. For example, Yang et al. [170] modulated quenching rate and electrolyte thickness to enable a 10 μm thick PEO_{16}-LiTFSI electrolyte to maintain structural integrity during service, with interfacial adhesion strength meeting long-cycle requirements. The Ordaz group [179] modified the lithium metal surface with a 1.4–1.6 μm thick cellulose-based composite coating; the high Young's modulus of cellulose effectively suppressed lithium-dendrite growth (Figure 9e). Liu et al. [53] used an electrospun PA6 fiber membrane as a skeleton to prepare an ultrathin composite electrolyte <10 μm thick. The tensile strength was significantly enhanced by the fiber-network support, and the electrolyte exhibited self-extinguishing flame-retardant properties. Optical images and stress-strain curves of PLP-series membranes before and after tensile testing visually demonstrate the fiber-reinforcement effect (Figure 9f). Zhao et al. [180] constructed a 23 μm thick ultrathin composite electrolyte using an ePTFE porous skeleton, raising the tensile strength to 9.65 MPa while ensuring ion conduction through interface-orientation-induced effects (Figure 9g). Zhang et al. [182] employed PAN fiber reinforcement combined with an in-situ thermal curing process; the SEM image shows the cross-sectional structure of the PAN-fiber-reinforced composite electrolyte. The electrolyte exhibited a tensile strength of 5.62 MPa, a modulus exceeding 100 MPa, and formed an Li_3N-rich layer at the interface that effectively resisted lithium-dendrite penetration. This work provides a mechanically robust ultrathin-electrolyte solution for high-energy-density ASSLBs.

4.3.2. Physical Barriers and Composite Architectures

PEO-based electrolytes, owing to their excellent flexibility, favorable processability, and fundamental compatibility with electrode materials, are regarded as a highly promising choice for constructing ASSLBs. However, their inherent shortcomings, such as relatively low room-temperature ionic conductivity, insufficient interfacial chemical stability, and limited capability to suppress lithium dendrites, severely hinder their practical application [158]. While an ultrathin design can effectively reduce internal resistance and increase energy density, it may further exacerbate these interfacial issues. Therefore, researchers are actively exploring sophisticated interface engineering approaches to regulate the interfacial chemistry of ultrathin PEO-based electrolytes, thereby endowing them with more balanced overall performance [183]. These systematic advances in interface modification strategies are laying a critical foundation for the development of high-performance all-solid-state batteries.

The core scientific concept behind interface modification lies in breaking the traditional "trade-off" dilemma between mechanical and electrochemical properties of single-component materials [184]. Inspiration for overcoming this dilemma can be drawn from nature, for instance, the hierarchical structure of tooth enamel has been mimicked in composite solid-state electrolyte design to achieve outstanding impact resistance and mechanical compatibility (Figure 10a). For ultrathin PEO-based electrolytes, weak mechanical strength and poor interfacial compatibility form a mutually reinforcing, coupled problem: insufficient mechanical strength allows dendrites to penetrate easily, while interfacial side reactions continuously corrode the electrolyte and generate gas, further degrading interfacial contact and mechanical integrity. Hence, advanced interface modification strategies are not merely about physical blocking; rather, they aim to actively construct a "composite interlayer" between the electrode and the electrolyte by introducing functional components. This interlayer simultaneously provides mechanical reinforcement, optimized ion transport, and enhanced electrochemical stability [185].

For example, Chen et al. [93] coated NCM811 cathodes with 1 wt% LATP and paired them with an ultrathin, PVDF-reinforced PEO-LLZTO composite electrolyte. Through an in-situ polymerization process that optimized interfacial contact, the LATP coating formed a stable interface with the electrolyte, suppressing oxidative decomposition and Li^+/Ni^{2+} cation mixing in NCM811. As a result, coin cells delivered a capacity retention of 81% after 100 cycles at 60 °C and 0.5 C. Computational analysis revealed the LLZO structure and the Ni-Li exchange energy at the NCM811/LLZO interface, providing a theoretical explanation for the improved interfacial stability (Figure 10b). Zhang et al. [186] proposed a cathode-engineering strategy using NASICON-type ion conductors surface-coated with a PEO-based polymer, constructing a three-dimensional ion-conductive network.

This enabled a 3 μm ultrathin SPEs layer to achieve excellent compatibility with the Li electrode. LFP/Li cells exhibited 96.6% capacity retention after 1000 cycles at 60 °C and 1 C, along with superior fire-resistance and nail-penetration safety.

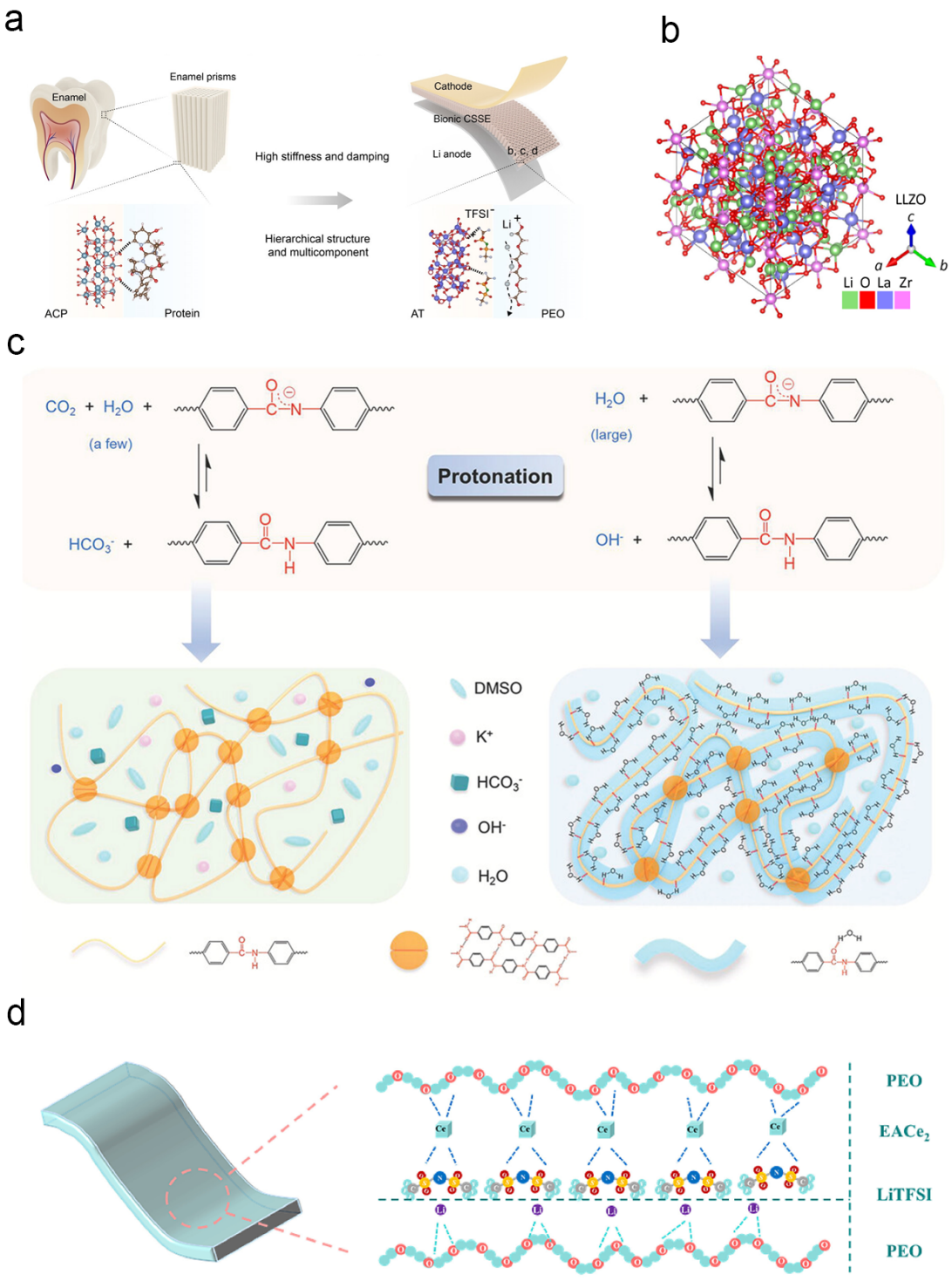

Figure 10. Composite architectures and physical barrier design for ultrathin PEO-based electrolytes: (**a**) Bio-inspired hierarchical electrolyte structure [184]. Copyright 2025, Wiley. (**b**) Crystal structure of LLZO and Ni-Li exchange energy at NCM811/LLZO interface [93]. Copyright 2024, Elsevier. (**c**) Self-assembly mechanism of aramid nanofiber aerogels [187]. Copyright 2024, Wiley. (**d**) Ion-transport pathways incoordination network based composite electrolytes [188]. Copyright 2021, Elsevier.

A broader range of reinforcement strategies collectively enriches the landscape of interfacial optimization for ultrathin PEO electrolytes. For example, Da et al. [187] induced the formation of an aramid nanofiber aerogel three-dimensional skeleton (Figure 10c), enhancing the stability of both the electrolyte bulk and the interface from

the perspectives of mechanical reinforcement and ion-conductive network construction. Meanwhile, Wu's and Li's group [188,189] introduced an infinite coordination polymer nanonetwork and a hydrolysis-resistant additive, respectively, functionalizing the interface through different dimensions such as nanostructure engineering and interfacial chemical protection (Figure 10d). These studies complement each other, indicating that the future development of ultrathin polymer electrolytes will inevitably be a comprehensive systems engineering endeavor that integrates functional material design, advanced fabrication processes, interfacial chemistry regulation, and innovative battery architectures.

4.4. Summary

Overall, optimization of PEO-based ultrathin interfacial layers relies on the synergistic integration of active regulation and passive protection strategies. Active regulation addresses the root causes of interfacial instability through precise control of ion-transport pathways and chemical microenvironments, while passive protection provides external mechanical and physical barriers to suppress dendrite penetration and structural failure. Together, these approaches transform the interface from a passive boundary into a multifunctional regulatory zone, laying a robust foundation for high-energy-density, long-life, and safe ASSLBs.

5. Electrode-Level Applications

In the pursuit of high-energy-density LMBs, both lithium metal anodes and high-voltage cathodes, serving as the core electrochemical components, encounter fundamental challenges that critically limit device-level performance [190]. Ultrathin PEO-based interlayers, owing to their unique physicochemical properties and structural versatility, have emerged as an effective and scalable solution to address these challenges. When judiciously integrated via surface modification or *in situ* construction strategies, such interlayers enable simultaneous regulation of interfacial chemistry, ion transport, and mechanical stability. As a result, they represent a pivotal technological pathway toward the practical realization of high-performance solid-state lithium batteries. This section systematically summarizes the application principles and device-level outcomes of ultrathin PEO-based interlayers at both lithium metal anodes and high-voltage cathodes, supported by representative research advances.

5.1. Lithium Metal Anodes

Lithium metal is widely regarded as the ideal anode material for next-generation batteries due to its ultrahigh theoretical specific capacity and lowest electrochemical potential. However, its practical implementation is severely hindered by uncontrolled lithium dendrite growth and persistent interfacial side reactions, which lead to poor cycling stability and serious safety concerns [191,192]. Engineering the lithium metal surface with an ultrathin PEO-based interlayer offers a targeted and effective strategy to overcome these obstacles [193].

The dendrite-suppressing capability of such interlayers originates from the synergistic combination of mechanical reinforcement and directional lithium-ion transport regulation. High mechanical strength resists dendrite penetration, while regulated ion-transport pathways homogenize the local lithium-ion flux, thereby mitigating dendritic nucleation [100]. For example, Xie et al. [42] fabricated a 22 μm ultrathin DSPE, in which TEGDME and SN were anchored within the PEO matrix through polymer–plasticizer interactions. This architecture formed a mechanically robust and ionically uniform interfacial layer that effectively suppressed lithium dendrite growth and stabilized long-term cycling.

Beyond dendrite suppression, ultrathin PEO-based interlayers also serve as effective chemical shields that physically isolate lithium metal from direct contact with reactive electrolyte components, thereby mitigating parasitic interfacial reactions. Chen's group [145] developed a PCN-PEO composite interlayer that integrates lithium-ion-selective transport channels from protonated carbon nitride PCN nanosheets with the excellent film-forming ability of PEO (Figure 11a). This design enabled an LFP full cell to operate stably for over 500 cycles at 2.0 C. Supramolecular engineering further enhances interfacial stability. Wang et al. [100] constructed a Li-PEO-UPy supramolecular polymer interlayer (Figure 11b), in which UPy motifs spontaneously react with lithium metal to form a self-stabilizing and strongly adhesive interface, enabling prolonged stable cycling under high current densities. These representative studies, conducted under varying experimental conditions, illustrate the broad applicability of PEO-based interlayers for lithium metal anode stabilization.

Importantly, precise thickness control is critical for optimal performance. Studies indicate that an interlayer thickness of 5–20 nm achieves the best balance between ionic conductivity, mechanical strength, and energy density, enabling capacity retention exceeding 90% [194]. The synergistic regulation of interfacial chemistry through rational cation-anion combinations further enhances cycling stability in all-solid-state lithium metal batteries (Figure 11c).

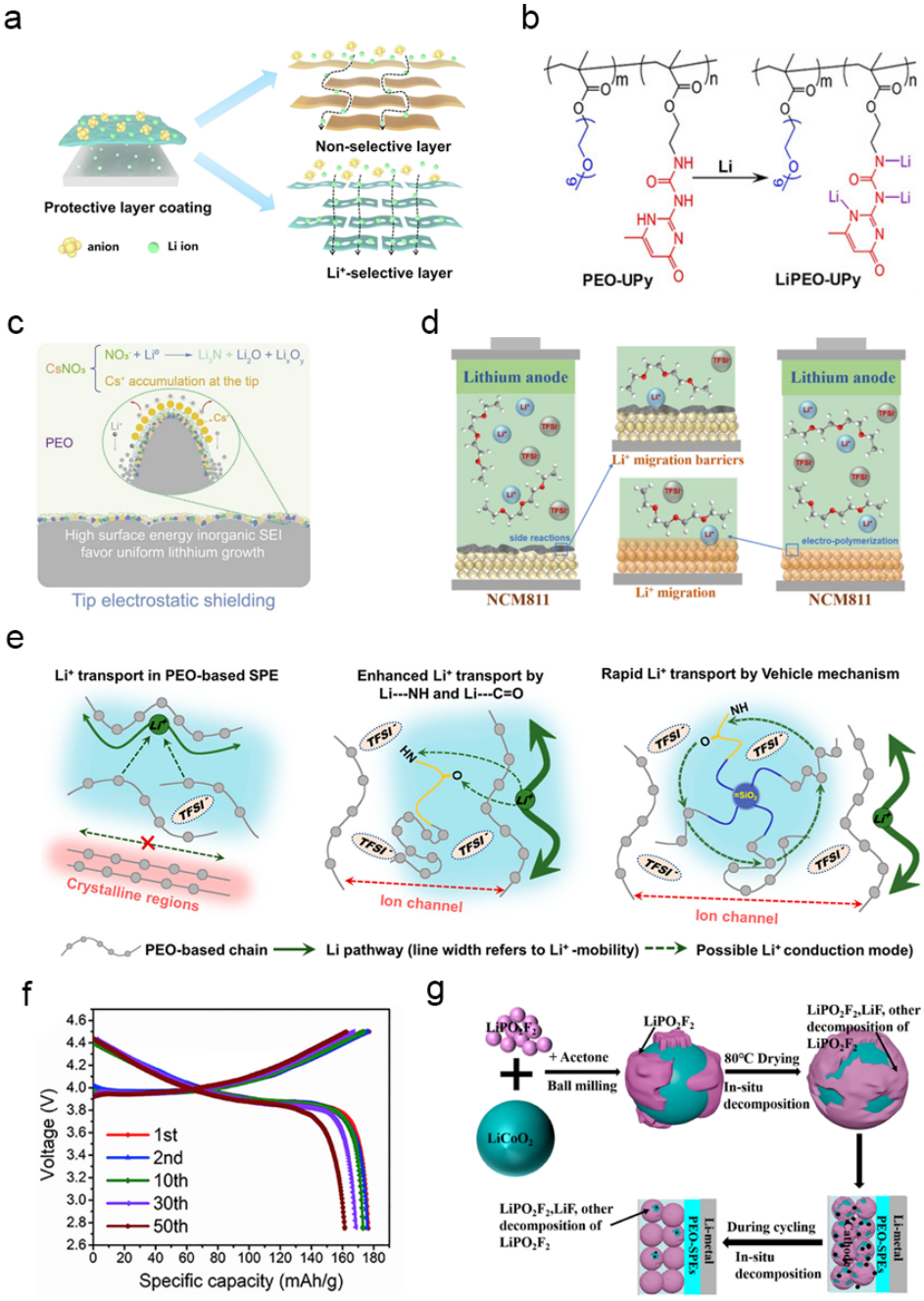

Figure 11. Applications of ultrathin PEO-based interlayers at electrodes: (**a**) Artificial SEI with fast Li^+ transport and uniform flux [145]. Copyright 2024, Springer Nature. (**b**) Structures and lithium-binding behavior of supramolecular PEO-UPy polymers [100]. Copyright 2019, Wiley. (**c**) Synergistic effects of cation-anion regulation on cycling stability [194]. Copyright 2025, Elsevier. (**d**) *In situ* formation of PTFEMA/PEO interfacial layer [85]. Copyright 2022, ACS. (**e**) Composite electrolyte architecture based on AM-SiO_2 [195]. Copyright 2021, ACS. (**f**) Rate performance of LATP-modified $LiCoO_2$ cathodes [196]. Copyright 2018, Elsevier. (**g**) Interface stabilization mechanism at $LiCoO_2$/PEO interface [197]. Copyright 2022, Elsevier.

5.2. High-Voltage Cathodes

High-voltage cathode materials, including NCM-series oxides and $LiCoO_2$, are essential for achieving elevated energy densities. However, under high-voltage operation, these materials suffer from electrolyte oxidation, sluggish interparticle ion transport, and interfacial delamination [198]. To address these challenges, *in situ* construction of ultrathin PEO-based interlayers on cathode surfaces has been widely explored [199–201].

In terms of interfacial oxidative stability, *in situ* formed PEO-based interlayers physically isolate the cathode surface from the electrolyte, suppressing catalytic decomposition and extending the electrochemical stability window beyond 4.5 V. Huang et al. [202] employed molecular vapor synthesis to construct a sulfone-containing

polymer interlayer on $LiCoO_2$, achieving 83% capacity retention after 500 cycles at 4.6 V. Li et al. [85] further extended the oxidation stability of PEO-based electrolytes to 5.1 V by *in situ* electropolymerization of trifluoroethyl methacrylate (TFEMA), forming a PTFEMA/PEO interlayer (Figure 11d). Cai's team [195] fabricated a P-P-A@SiO_2 electrolyte through the composite of acrylamide (AM) and vinyl-modified nano-SiO_2 (Figure 11e), achieving an electrochemical stability window of 5.1 V with no PEO decomposition under high-voltage conditions.

Ultrathin PEO-based interlayers also enhance interparticle lithium-ion transport by forming continuous ion-conduction networks on cathode surfaces. Yang et al. [196] deposited a <20 nm LATP interlayer via an *in situ* method, enabling $LiCoO_2$ to deliver 120 $mAh \cdot g^{-1}$ at 5 C under 4.5 V operation (Figure 11f). Feng et al. [197] reported a uniform 3 nm $LiPO_2F_2$ coating formed via in situ decomposition, which significantly improved the cycling stability of high-voltage $LiCoO_2$ cathodes (Figure 11g).

In addition, the intrinsic flexibility and strong adhesion of PEO-based interlayers effectively mitigate interfacial delamination caused by repeated volume changes of cathode particles. Ye et al. [112] demonstrated that an in situ derived CEI layer on NCM811 remained tightly adhered after 200 cycles, significantly outperforming unmodified counterparts. Similar structural integrity was observed in PTFEMA/PEO-modified NCM811 cathodes, confirming the mechanical compliance of PEO-based interlayers [85].

5.3. Summary

In summary, ultrathin PEO-based interlayers demonstrate broad applicability at both lithium metal anodes and high-voltage cathodes. At lithium metal anodes, they homogenize lithium-ion flux, suppress dendrite growth, regulate SEI formation, and markedly extend cycling life. At high-voltage cathodes, *in situ* constructed PEO-based interlayers isolate reactive surfaces, expand electrochemical stability windows, enhance interparticle ion transport, and alleviate interfacial delamination. Through rational material design and thickness optimization, these interlayers systematically mitigate dominant interfacial failure mechanisms, providing a robust and scalable pathway toward high-performance and high-safety lithium battery devices.

6. Future Perspectives

PEO-based interfacial engineering has demonstrated remarkable promise in stabilizing lithium metal interfaces and enabling high-performance ASSLBs. Nevertheless, substantial challenges persist in simultaneously achieving long-term cycling stability, high-rate capability, and robust operability under extreme electrochemical and mechanical conditions. Future research is therefore expected to transcend single-parameter optimization and evolve toward intelligent, multilevel, and mechanism-guided interfacial design paradigms. In this context, several emerging directions are anticipated to define the next frontiers of PEO-based interfacial engineering (Figure 12), with increasing emphasis on practical feasibility and scalable implementation.

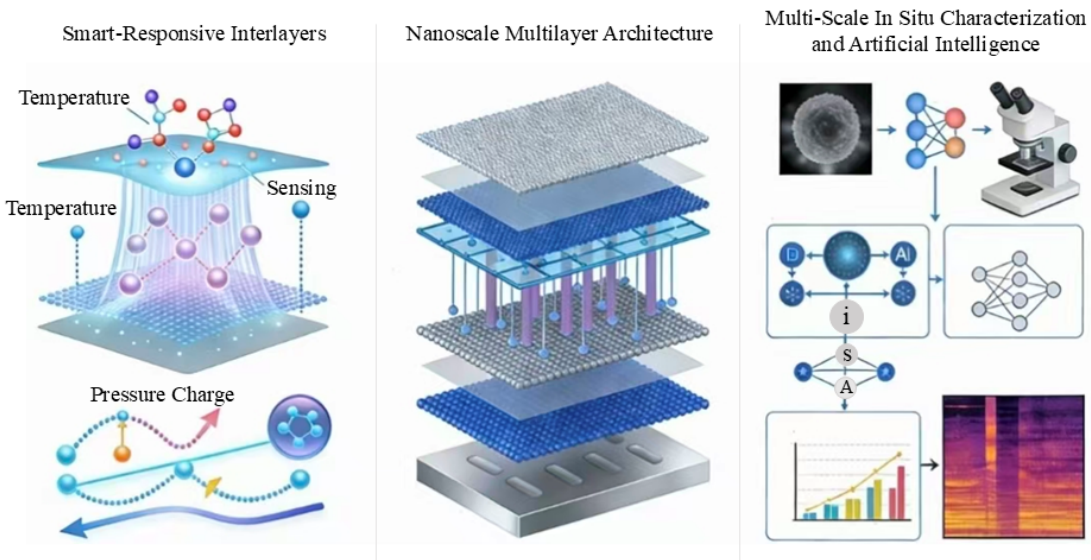

Figure 12. Future perspectives of PEO-based interfacial engineering, highlighting the development of smart-responsive interlayers, bio-inspired nanoscale multilayer architectures, and multiscale *in situ*/operando characterization techniques toward next-generation high-energy-density and high-safety ASSLBs.

6.1. Smart-Responsive Interlayers

Conventional PEO-based interlayers are predominantly static in nature and thus inherently limited in their ability to accommodate the dynamically evolving interfacial environment during repeated lithium plating/stripping. A critical breakthrough in future research lies in the development of smart, stimulus-responsive PEO-based interlayers capable of autonomously adapting to external perturbations such as temperature fluctuations, mechanical stress, and electric-field variations, thereby enabling real-time interfacial regulation and self-repair.

One promising avenue involves the design of thermos-responsive and self-healing PEO-based systems, for example through incorporation of polymers such as poly(N-isopropylacrylamide) (PNIPAM) or related phase-transition materials. In such systems, localized heat accumulation induced by dendritic lithium growth can trigger a reversible phase transition, temporarily enhancing interlayer fluidity to heal microcracks and defects while simultaneously facilitating ion transport at damaged regions. Upon thermal relaxation, the interlayer reverts to a mechanically robust state, restoring its structural integrity and dendrite-blocking capability. Beyond thermal responsiveness, the integration of piezoelectric nanomaterials offers a pathway to convert localized mechanical stress into internal electric fields that actively counteract dendrite-induced pressure gradients and redistribute lithium-ion flux. These multifunctional designs, while still at an early stage, point toward interlayers that not only passively protect but also actively participate in stabilizing the interface.

Another attractive strategy is the construction of pressure-responsive adaptive interfaces through the integration of piezoelectric or piezoresistive nanomaterials. Localized stress concentration arising from uneven lithium deposition can induce the generation of internal electric fields, which actively redistribute lithium-ion flux toward low-stress regions and suppress the dendritic "tip effect". Beyond dendrite mitigation, such mechano-electrical coupling may also enable *in situ* sensing of interfacial stress evolution, offering a new pathway for real-time interface diagnostics.

In addition, electric-field-driven interfacial reconstruction represents an emerging direction with significant potential. By incorporating components with tailored dielectric properties or anisotropic ionic conductivity into the PEO matrix, the local electric-field distribution can be dynamically modulated under high current densities, enabling directional steering of lithium-ion transport and controlled lithium nucleation. Collectively, these approaches aim to transform PEO interlayers from passive protective coatings into self-regulating and adaptive interfacial systems, reminiscent of biological interfaces with autonomous healing and feedback functions. From a practical perspective, the successful deployment of such smart interlayers will require systematic evaluation of their long-term stability, switching reliability, and compatibility with existing battery manufacturing workflows.

6.2. Nanoscale Multilayer Architecture

Single-component or simple composite interlayers often struggle to concurrently satisfy the stringent and sometimes competing requirements of high ionic conductivity, mechanical robustness, chemical stability, and electronic insulation. Inspired by the hierarchical "brick-and-mortar" architecture of natural nacre, nanoscale multilayer interfacial architectures have emerged as a compelling strategy to achieve synergistic multifunctionality.

The core concept of this approach lies in functional stratification. Through precision fabrication techniques such as ALD, molecular layer deposition, or layer-by-layer self-assembly, alternating stacks of ultrathin PEO layers and inorganic functional layers can be constructed with nanometer-level control. Within such architectures, PEO layers primarily serve as fast lithium-ion transport channels, while the inorganic layers function as mechanical reinforcement units and physical barriers against dendrite penetration. By spatially decoupling ion transport and mechanical protection, each layer can be independently optimized to perform its designated role with maximum efficiency. For instance, inorganic layers such as Al_2O_3, Li_3PO_4, or LLZTO can be tailored to provide both high modulus and electrochemical stability, while the intervening PEO layers maintain continuous ionic pathways.

Nanoscale multilayer architecture also offers pronounced advantages in terms of interfacial chemical stability. Dense outer inorganic layers can effectively shield the inner PEO matrix and lithium metal from corrosive species, while intermediate layers may scavenge residual impurities or stabilize reactive intermediates, thereby delaying parasitic interfacial reactions. Mechanically, the presence of multiple interfaces within the multilayer structure facilitates stress redistribution and crack deflection, significantly reducing the likelihood of catastrophic interlayer failure. Even if localized damage occurs, crack propagation is effectively arrested, enhancing resistance to dendrite-induced mechanical penetration.

Moreover, these architectures enable precise modulation of lithium-ion flux at the nanoscale. Subtle differences in electrochemical potential and ionic conductivity between adjacent layers can be leveraged to homogenize vertical lithium-ion transport, promoting planar lithium growth and fundamentally suppressing three-dimensional dendrite nucleation at its earliest stages. In this regard, nanoscale multilayer designs represent a

paradigm shift from homogeneous composite materials toward spatially ordered, functionally integrated interfacial systems. Looking ahead, research efforts should focus on developing scalable fabrication routes, such as roll-to-roll compatible layer-by-layer assembly and establishing design rules that correlate multilayer architecture with key performance metrics including ionic conductivity, interfacial toughness, and cycle life.

6.3. Multi-Scale In Situ Characterization and Mechanistic Understanding

Despite extensive progress, a comprehensive understanding of the dynamic evolution and failure mechanisms of PEO-based interlayers under realistic operating conditions remains elusive. Bridging this knowledge gap requires the integration of advanced *in situ*/operando characterization techniques with data-driven modeling and multiscale simulations, enabling real-time observation and mechanistic interpretation of interfacial processes.

Synchrotron-based X-ray techniques provide powerful tools for probing mesoscale interfacial evolution. *In situ* X-ray tomography can capture three-dimensional lithium dendrite nucleation, growth, fracture, and "dead lithium" formation beneath PEO interlayers in real time. Concurrently, X-ray absorption spectroscopy and diffraction techniques allow continuous tracking of PEO chain conformational changes, interfacial phase evolution, and crystallographic transformations of lithium metal during cycling.

At the nanoscale, high-resolution electron microscopy offers unparalleled insight into interfacial structure and chemistry. Cryogenic transmission electron microscopy (cryo-TEM) enables preservation of highly reactive PEO/Li interfaces in their native states, allowing atomic-scale visualization of interphase morphology and precise identification of SEI/CEI components. Furthermore, *in situ* TEM under applied electric fields provides direct visualization of lithium–interlayer interactions, offering definitive evidence for dendrite suppression mechanisms and guided lithium growth pathways.

To fully exploit the rich, multidimensional datasets generated by these techniques, artificial intelligence and data-driven approaches will play an increasingly central role. By constructing specialized databases derived from *in situ* experiments and coupling them with machine-learning algorithms, key microscopic descriptors governing interfacial stability can be identified. These descriptors can then be correlated with macroscopic electrochemical performance through multiscale modeling frameworks spanning quantum chemistry, molecular dynamics, and phase-field simulations. Ultimately, such integrated approaches will enable a transition from empirical optimization toward predictive and mechanism-driven interfacial design. Practically, establishing standardized *in situ* testing protocols and open-access data repositories will be critical to accelerating progress across the research community.

6.4. Current Challenges and Controversies

Despite the rapid progress summarized above, several critical challenges and unresolved controversies remain in the field of PEO-based ultrathin interfacial engineering. First, although thickness reduction is widely recognized as an effective strategy to shorten lithium-ion transport distance and lower internal resistance, the electrochemical benefits of ultrathin design are still fundamentally constrained by the insufficient room-temperature ionic conductivity of PEO-based systems. In many cases, improved cell performance arises from operation at elevated temperature, incorporation of plasticizers, or ceramic-assisted transport pathways, rather than from thickness reduction alone. Therefore, whether "ultrathin" design itself can deliver practical room-temperature performance remains an open question.

Second, there is a persistent trade-off between thickness minimization and mechanical robustness. Reducing the thickness of electrolytes or interlayers may enhance energy density and transport kinetics, but excessively thin architectures often become more vulnerable to mechanical failure, interfacial defect amplification, and dendrite penetration. As a result, the optimal thickness window is not universal, but strongly depends on modulus, interfacial adhesion, and the degree of structural heterogeneity. Future studies should systematically map these interdependencies to establish thickness-performance design guidelines.

Third, the literature sometimes blurs the distinction between nanoscale interfacial layers and micrometer-scale ultrathin electrolyte membranes, making cross-study comparison difficult. In some reports, the observed performance improvement originates mainly from bulk electrolyte optimization, whereas in others it arises from genuine interfacial regulation. A clearer separation of these contributions is still needed through standardized terminology and more rigorous control experiments. such as comparing systems with and without the interfacial layer under identical bulk electrolyte conditions.

Finally, from the perspective of practical deployment, the scalable and reproducible fabrication of defect-free ultrathin interfacial layers remains highly challenging. Techniques such as ALD, *in situ* polymerization, and self-assembly offer excellent precision, but their compatibility with large-area manufacturing, cost control, thickness uniformity, and long-term reproducibility under industrial conditions is not yet fully established. Addressing these

issues will be essential for translating laboratory-level interfacial engineering into commercially viable ASSLBs. Addressing these issues will require concerted efforts in process engineering, quality control, and techno-economic analysis to translate laboratory-level interfacial engineering into commercially viable ASSLBs.

In summary, the future of PEO-based interfacial engineering lies in the convergence of adaptive material design, hierarchical structural engineering, and advanced mechanistic characterization. By endowing interlayers with stimulus-responsive behavior, constructing nanoscale multilayer architectures, and leveraging multi-scale *in situ* insights, PEO-based systems are poised to overcome their current limitations and unlock new performance regimes. These advances will not only accelerate the practical deployment of high-energy-density and high-safety ASSLBs but also establish a generalizable framework for interface design across a broad range of solid-state electrochemical systems.

7. Summary and Outlook

ASSLBs are widely regarded as a key technology for next-generation energy storage systems. They offer high energy density and enhanced safety. However, their practical deployment has long been hindered by persistent challenges at solid-solid interfaces. These challenges include high interfacial resistance, lithium dendrite growth, interfacial side reactions, and mechanical instability. Among various solid electrolyte systems, PEO-based polymer electrolytes have attracted sustained interest. This interest arises from their excellent flexibility, processability, and intrinsic compatibility with electrode materials. Nevertheless, they suffer from inherently low room-temperature ionic conductivity and a limited electrochemical stability window. These factors significantly restrict practical application. The emergence of ultrathin PEO-based interfacial modification layers offers an effective and conceptually distinct solution to these challenges. This strategy does not fundamentally redesign bulk electrolytes. Instead, it focuses on constructing a nanoscale functional interlayer at the critical electrode-electrolyte interface. This approach transforms the interface from a passive contact region into an active and multifunctional regulatory zone. This review systematically summarizes recent progress in the design, fabrication, and functional mechanisms of PEO-based ultrathin interfacial layers. It highlights their role in stabilizing both lithium metal anodes and high-voltage cathodes.

This review systematically delineates the core design logic and technical trajectory in the field. The underlying principle is rooted in two intrinsic attributes of PEO: its viscoelasticity buffers dendrite-induced stress, while its ether oxygen groups facilitate selective lithium-ion coordination and transport. Through precise fabrication techniques such as *in-situ* polymerization, ALD, and self-assembly, uniform and dense protective layers with thicknesses ranging from nanometers to sub-micrometers can be engineered, thereby precluding interfacial defects at their origin. Performance optimization revolves around two complementary strategic frameworks. The first is an active modulation strategy, focusing on tailoring the interfacial microenvironment at the molecular and chemical level. This involves precise ion-coordination design, solvation structure regulation, and the introduction of functional additives to induce stable SEI and CEI formation, construct efficient lithium-ion transport channels, and fundamentally suppress side reactions, reduce impedance, and guide uniform Li deposition. The second entails a passive protection strategy, which emphasizes establishing external barriers from physical and mechanical perspectives. Methods such as constructing cross-linked networks, incorporating nano-reinforcements, or compounding high-modulus fillers are employed to substantially enhance the mechanical strength and toughness of the modification layer. This effectively resists physical penetration by Li dendrites while providing stable structural support at the interface. These two paradigms operate in concert, fostering a concurrent optimization of ionic transport, electrochemical stability, and mechanical integrity within an ultra-thin dimension.

Extensive experimental studies demonstrate that PEO-based ultrathin interfacial layers are highly effective at both electrodes. At lithium metal anodes, they homogenize lithium-ion flux, suppress dendrite growth, and isolate lithium from direct contact with reactive electrolyte components, thereby significantly extending cycle life. At high-voltage cathodes, *in situ* constructed PEO-based interlayers physically separate the cathode surface from the electrolyte, suppress catalytic decomposition and transition-metal dissolution, and extend the stable operating voltage beyond 4.5 V. Meanwhile, their continuous ion-conductive pathways reduce interfacial impedance and improve interparticle lithium-ion transport, while their mechanical compliance accommodates volume changes during cycling.

Looking forward, PEO-based interfacial engineering is expected to evolve from static optimization toward more adaptive and mechanism-guided design paradigms. Smart-responsive interlayers capable of dynamically responding to temperature, pressure, or electric-field variations may enable self-adjusting interfacial regulation and self-healing behavior. Bio-inspired nanoscale multilayer architectures, assembled through precise layer-by-layer strategies, offer promising opportunities to spatially decouple and synergistically integrate ion transport,

mechanical reinforcement, and chemical protection. In parallel, the integration of advanced *in situ* and operando characterization techniques with multiscale modeling and data-driven approaches will be crucial for elucidating dynamic interfacial evolution and establishing predictive structure–property relationships.

In conclusion, research on ultrathin PEO-based interfacial modification layers highlights a central principle. In ASSLBs, interfacial design critically governs overall device performance. This strategy shifts the focus from bulk material optimization to precise micro- and nanoscale engineering of heterogeneous interfaces. It provides a powerful pathway toward simultaneously achieving high energy density, long cycle life, and enhanced safety. Continued advances in interfacial chemistry, structural design, and characterization methodology are expected to further accelerate this progress. They will help realize high-performance solid-state lithium batteries in practical applications.

Author Contributions

L.L.: conceptualization, writing—original draft preparation; Z.C.: investigation, writing—original draft preparation; S.G.: supervision, writing—reviewing and editing; A.Z.: investigation, writing—original draft preparation; R.C.K.R.: investigation, writing—original draft preparation; Y.W.: investigation, writing—original draft preparation; D.W.: supervision, writing—reviewing and editing; X.L.: supervision, writing—reviewing and editing. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

During the preparation of this work, the authors used DeepSeek to improve the language expression of the work. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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