

Phase-separation-driven solid polymer electrolytes for high-performance lithium-metal batteries: A comprehensive review

Yulong Liu¹, Hang Yang², Suyuan Li¹, Huanyan Xu²(✉), Zhirong Zhang¹(✉)

¹ College of Physics and Electromechanical Engineering, Hexi University, Zhangye 734000, China

² School of Materials Science and Chemical Engineering, Harbin University of Science and Technology, Harbin 150080, China

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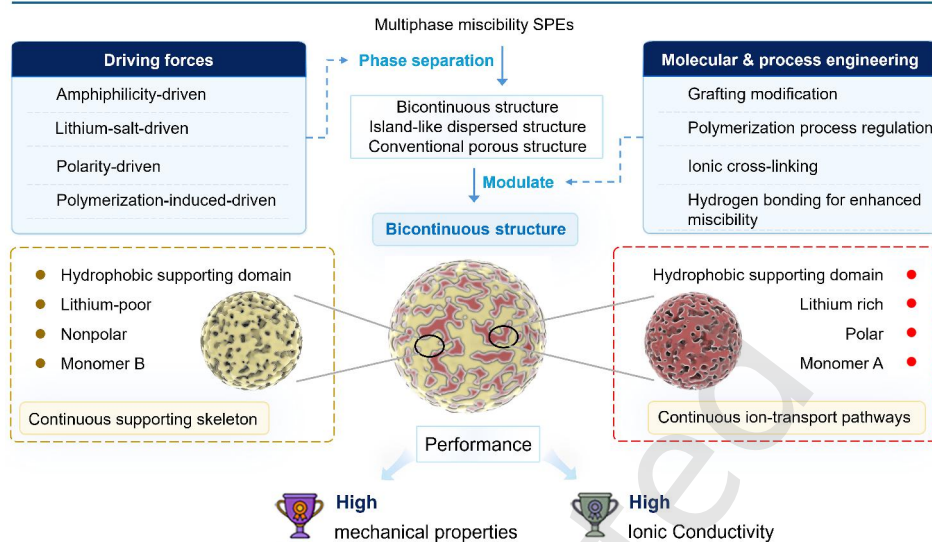
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Phase-separation-driven solid polymer electrolytes



This review systematically summarizes how multiphase-miscible solid polymer electrolytes can undergo phase separation and form two-phase structures under various driving forces. Further molecular and process engineering can construct bicontinuous morphologies that combine high ionic conductivity with excellent mechanical properties, thereby broadening the application of these electrolytes in lithium-metal batteries.

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Yulong Liu¹, Hang Yang², Suyuan Li¹, Huanyan Xu² , and Zhirong Zhang¹ 

¹ College of Physics and Electromechanical Engineering, Hexi University, Zhangye 734000, China

² School of Materials Science and Chemical Engineering, Harbin University of Science and Technology, Harbin 150080, China

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 Address correspondence to Zhirong Zhang, zhangzr@hxy.edu.cn; Huanyan Xu, xuhuanyan@hrbust.edu.cn

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ABSTRACT: Solid-state lithium metal batteries (SSLMBs) offer high energy-density potential and improved thermal safety by reducing leakage-prone and flammable liquid components, making them promising candidates for high-safety, high-specific-energy batteries. Solid polymer electrolytes (SPEs) feature low density, good flexibility, structural tunability, facile processing, and scalability; however, it remains a great challenge to co-optimize high ionic conductivity, mechanical strength, electrochemical stability, and interfacial compatibility. Current studies predominantly improve SPE performance by incorporating inorganic fillers or small-molecule plasticizers, whereas the phase evolution and structure-property relationships of multiphase systems containing a second polymer component remain insufficiently understood. Influenced by segmental interactions, component ratios, lithium-salt coordination, polymer crystallization, and processing history, uncontrolled macrophase separation can cause compositional heterogeneity, internal defects, disrupted ion-transport pathways, and deteriorated interfacial contact. In contrast, precise control over phase separation can generate bicontinuous soft-hard micro/nanostructures, in which the soft phase forms continuous ion-transport pathways and improves interfacial contact, while the hard phase provides mechanical support, thereby partially decoupling the trade-off between ionic conductivity and mechanical strength. Accordingly, this review focuses on phase-separation-driven solid polymer electrolytes, systematically elucidating their structural design principles and the relationships among phase structure, ion transport, mechanical properties, and interfacial behavior. It further summarizes the driving factors, regulation strategies, advanced characterization techniques, and theoretical simulation methods of phase separation, while discussing challenges related to morphological stability, interfacial regulation, and scalable manufacturing, thereby providing guidance for designing multiphase polymer electrolytes for high-performance SSLMBs.

KEYWORDS: lithium metal batteries; solid polymer electrolyte; phase separation; lithium-ion transport

1 Introduction

With an ultra-large theoretical specific capacity (3860 mAh g^{-1}) and a minimal electrochemical potential (-3.04 V versus the standard hydrogen electrode), lithium metal makes lithium metal batteries (LMBs) one of the most competitive technologies for future energy storage devices. These unique inherent merits render lithium metal a perfect anode material to attain extremely high energy densities. For this reason, LMBs exhibit outstanding application value in numerous areas, covering portable electronic devices and electric traffic, as well as cutting-edge airborne transport equipment represented by electric vertical takeoff and landing (eVTOL) aircraft. However, conventional liquid-based LMBs face significant safety and reliability challenges. In particular, the uncontrolled growth of lithium dendrites can puncture porous separators, leading to internal short circuits, electrolyte leakage, thermal runaway, and even fires. These issues critically undermine the operational safety and practical deployment of LMBs [1, 2].

To address these concerns, solid-state lithium metal batteries (SSLMBs) utilizing solid-state electrolytes (SSEs) have garnered increasing attention. SSEs offer the potential to physically block dendrite propagation and improve thermal and electrochemical stability, thereby enhancing overall battery safety and lifespan [3-5]. SSEs are broadly categorized into inorganic and polymer-based systems. Representative inorganic solid electrolytes include oxides and sulfides such as $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ (LLZTO), $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$ (LATP), and $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) [6-9]. Such substances commonly possess rapid ion transport capabilities together with wide electrochemical stability ranges. However, sulfide-based electrolytes are prone to chemical degradation upon exposure to moisture and air, releasing toxic gases such as H_2S . Meanwhile, while oxide-type electrolytes maintain stable chemical performance, their rigid sintered construction causes two critical drawbacks: mechanical fragility and weak interfacial bonding against electrodes. This not only raises interfacial impedance but also hinders industrial large-batch preparation. Solid polymer electrolytes (SPEs), however, overcome these

limitations via distinctive strengths like flexible mechanics, low density, straightforward processing, and intimate electrode contact, laying a solid foundation for their practical application in high-energy-density batteries. Systems based on polyethylene oxide (PEO), polyvinylidene fluoride (PVDF), and their derivatives have been extensively studied. However, SPEs still face several performance bottlenecks, including low room-temperature ionic conductivity, insufficient electrode-electrolyte interfacial contact and stability, and limited mechanical properties, which hinder their large-scale application.

To address these limitations, small-molecule plasticizers [10-12], inorganic fillers [13, 14], and ionic liquids [15-17] are commonly introduced to enhance segmental mobility, promote lithium-salt dissociation, or establish additional ion-transport pathways. The effectiveness of these modifiers depends on their content, size or molecular structure, surface chemistry, dispersion state, and interactions with the polymer matrix. Excessive incorporation, however, may cause filler agglomeration, plasticizer leakage, mechanical deterioration, or interfacial instability. By comparison, introducing a second polymer component enables material properties to be tuned over a broader compositional range. It also spatially separates ion transport and mechanical reinforcement into different polymer phases—namely, soft phase and hard phase—offering a new strategy for resolving the trade-off between ionic conductivity and mechanical strength. Typically, the soft phase consists of polymers or components with low glass-transition temperatures and high segmental mobility, such as PEO, polyethylene glycol (PEG)-based polymers, polycarbonates, and domains rich in plasticizers such as tetramethylene sulfone (TMS) [18] or ionic liquids. These phases generally facilitate lithium-ion transport by solvating lithium salts and promoting ion migration coupled with segmental motion. In contrast, polymers with high moduli, crystalline domains, rigid molecular backbones, or highly cross-linked networks—such as polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) [19], and other rigid or cross-linked polymer frameworks—primarily provide mechanical support.

Because the entropy of mixing is low for polymer blends, most dissimilar polymers exhibit limited miscibility or thermodynamic incompatibility. Their phase behavior is further governed by molecular weight, component ratio, interaction parameters, selective coordination of lithium salts, polymer crystallization, solvent evaporation, and curing history. Uncontrolled phase separation can cause excessive domain coarsening and weak interphase formation, leading to discontinuous ion-transport pathways, heterogeneous stress and ionic-flux distributions, and deteriorated electrode contact. When the composition and temperature of a system enter the spinodal region, small concentration fluctuations spontaneously grow without a nucleation barrier, resulting in spinodal decomposition and an interpenetrating co-continuous morphology at the early stage. Unless kinetically arrested through crosslinking, polymerization, crystallization, vitrification, or rapid solidification, this structure continues to coarsen and ultimately evolves toward macrophase separation. It should be noted that spinodal

decomposition in conventional polymer blends differs from microphase separation in block or graft copolymers. In the latter, covalent linkages between chemically distinct segments suppress macrophase separation, facilitating the formation of stable nanoscale domains.

When a co-continuous morphology is arrested at an appropriate length scale, a functionally differentiated soft-hard dual-phase structure can be obtained. An ideal bicontinuous structure consists of soft and hard phases that independently span three-dimensional space and interpenetrate to form two percolating networks throughout the material. The soft phase, characterized by a low glass-transition temperature and strong lithium-salt-solvation capability, can provide low-tortuosity Li-ion transport pathways while improving electrode interfacial contact. The hard phase, formed by high-glass-transition-temperature, crystalline, or crosslinked domains, can serve as a mechanical support network, improve resistance to deformation, and reduce the risk of lithium-dendrite penetration. Such spatial division of functions can partially decouple ionic conduction from mechanical reinforcement, enabling the synergistic optimization of electrochemical and mechanical properties [20-22]. Nevertheless, bicontinuous morphologies generally exist only within narrow compositional and processing windows and are highly sensitive to phase volume fractions, molecular weight, interaction parameters, viscosity ratio, the thermodynamic driving force for phase separation, and solidification rate. In practice, geometric perfection is not essential. A functionally effective quasi-bicontinuous or interpenetrating percolation structure can be achieved provided that the ion-conducting phase forms a three-dimensionally connected, low-tortuosity, and nearly isotropic transport network, while the mechanically reinforcing phase retains sufficient connectivity.

When the system deviates from the co-continuous window, or when the interconnected morphology is not arrested before domain coarsening, one phase may undergo interfacial-tension-driven network breakup and contraction into isolated domains, producing a dispersed island morphology. If a solvent-rich or extractable phase is removed after phase separation, the corresponding domains may be converted into isolated or interconnected pores, generating a conventional porous structure. Thus, bicontinuous, dispersed island, and porous structures can be regarded as distinct topological outcomes associated with network preservation, network breakup, and selective phase removal, respectively.

The properties of a dispersed island morphology are primarily determined by the continuous phase. When the ion-conducting soft phase is dispersed as isolated domains within a hard matrix, long-range ion-transport pathways are interrupted, increasing transport tortuosity and interfacial resistance. Conversely, when the hard phase forms isolated domains within a continuous soft matrix, ion transport remains relatively efficient, but mechanical loads cannot be effectively transferred between the hard domains, limiting their ability to resist localized deformation and dendrite growth. Conventional porous structures generally rely on pores filled with liquid or gel electrolytes to facilitate rapid ion transport. However,

excessive porosity, nonuniform pore distributions, or incomplete pore filling can reduce the effective modulus of the electrolyte and induce localized current concentration and dendrite penetration. In contrast, the advantage of solid-solid bicontinuous structures lies not in increasing porosity but in retaining two interconnected functional phases, thereby establishing continuous ion-transport and load-bearing networks.

Current research on polymer-blend electrolytes remains largely focused on compositional screening and macroscopic performance optimization. The mechanisms governing phase-separation pathways, topological evolution, and domain coarsening are not yet systematically understood, and quantitative structure-property relationships linking phase structure, ion transport, mechanical response, and interfacial stability remain to be established [23-25]. Therefore, design principles integrating material composition, processing history, and phase-structure evolution are urgently needed to guide the development of phase-separated polymer electrolytes that combine high ionic conductivity, structural integrity, interfacial stability, and resistance to lithium-dendrite growth. Fig. 1 summarizes current phase-separation-driven design strategies and their key structure–property relationships for polymer electrolytes in high-performance SSLMBs.

In this review, we provide an in-depth look at recent progress in the development and optimization of phase- separation- driven SPEs for SSLMBs. We begin by exploring the fundamental thermodynamic principles and mechanisms underlying phase separation, which govern the morphological evolution of SPEs. Various strategies to induce and regulate phase separation are then examined, highlighting the key driving forces and their influence on electrolyte architecture through representative case studies. We also discuss experimental and theoretical approaches used to characterize phase-separated structures, shedding light on their formation and stability. This review focuses on the impacts of phase separation on key characteristics, including ionic conductivity, mechanical robustness, and interfacial compatibility, all of which jointly govern the overall electrochemical behaviors of SSLMBs. Finally, this work provides a future outlook on the existing challenges and potential opportunities of applying phase- separation- driven SPEs to develop advanced, high-efficiency SSLMBs for next-generation energy storage.



Figure 1. Current design strategies of phase- separation- driven SPEs for SSLMBs.

2 Mechanism of phase- separation- driven SPEs

Phase separation exerts a decisive influence on the fabrication of SPEs membranes, enabling the generation of complex microstructures that significantly influence material properties. In physical chemistry, phase separation refers to the transformation of a homogeneous, single-phase system into a multiphase structure. Thermodynamically, this process occurs as chemical species migrate toward regions with lower chemical potential—not merely lower concentrations—resulting in spontaneous demixing under certain conditions. In most binary polymer blends, complete miscibility is rare; mutual compatibility is typically limited to narrow compositional and thermal windows. Beyond these critical conditions, the system undergoes phase separation, yielding either homogeneous or heterogeneous morphologies depending on the temperature and composition.

These phase transitions are commonly classified into systems exhibiting a lower critical solution temperature (LCST) or upper critical solution temperature (UCST) [26, 27]. The miscibility behavior of polymer blends is often represented using phase diagrams, where the critical composition ($\phi_{TP, crit}$) at the cloud point delineates the onset of phase separation. The location of initial blend composition (ϕ_{TP}) relative to $\phi_{TP, crit}$ determines whether the system remains stable, metastable, or unstable. On the transformation rate-composition phase diagram, the cloud point curve and the metastable limit define the

regimes of phase behavior (Fig. 2a). Importantly, these interactions are not static; parameters such as temperature and solvent properties dynamically affect solubility, leading to different equilibrium and kinetic states [28]. Regardless of the underlying mechanism, the system's final morphology is primarily governed by the position of the blend composition in relation to $\phi_{TP, crit}$. This critical point is itself sensitive to factors like the transformation rate, curing temperature, polymer compatibility, molecular weight, and the blend ratio [29-31].

Of particular interest is the intersection of the glass transition temperature (T_g) and binodal curves, referred to as Bergman's point, first described by Bergman and Arnauts in 1987 [32]. This represents a unique region in the phase diagram of binary polymer-solvent systems where phase separation is interrupted or "frozen" due to vitrification (Fig. 2b). Near Bergman's point, temporary phase-separated morphologies can be trapped in nonequilibrium states, yielding polymer functional materials with fixed microstructures. However, precise control of this point is technically challenging, limiting its broad applicability [33]. Based on the region in which phase separation occurs, distinct morphologies and physical properties arise. In Region 1, the system remains fully homogeneous, exhibiting either rubbery flexibility or glassy rigidity depending on the thermal conditions. In Region 2, phase separation gives rise to bi-continuous structures composed of both dense and sparse polymer phases, with both domains retaining rubbery characteristics. Region 3 is characterized by the vitrification of the dense polymer phase before equilibrium is reached, effectively freezing the microstructure. This leads to the formation of gel-like bicontinuous domains in which solvents are immobilized within a stable polymer network—combining the softness of ionic gels with the mechanical robustness of rigid plastics. In Region 4, complete vitrification of the polymer matrix occurs, resulting in high mechanical strength; however, this process comes at the expense of losing the ionic gel functionality essential for efficient ion transport.

Phase diagrams serve as the foundation for evaluating how composition and temperature influence the microstructure, mechanical integrity, and electrochemical performance of the resulting solid electrolytes. The phase diagram of phase-separation-driven SPEs can be experimentally determined or theoretically predicted.

Alba et al. [34] illustrated the phase-separation pathway of a poly(methyl methacrylate)-polystyrene (PS-PMMA) system during atom transfer radical polymerization (ATRP) using a hypothetical phase diagram (Fig. 2c, left). The diagram indicates that the nucleation, growth, and stabilization of PMMA-rich domains depend on the initial monomer loading. Compared with free-radical polymerization (FRP), ATRP combines rapid initiation, controlled chain growth, suppressed termination, and a narrow molecular-weight distribution, producing more uniform domains with improved structural correlation. Their characteristic length scale can also be tuned through synthesis parameters to obtain robust nanostructures (Fig. 2c, right). Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), a highly polar polymer ($\epsilon_r \approx 11$), is

widely used as a matrix material in SPEs due to its favorable electrochemical and mechanical properties [35]. Jung et al. [36] combined Flory–Huggins solution theory with lattice theory to predict the binodal and spinodal curves, tie lines, and critical points of PVDF-HFP systems (Fig. 2d) [37–40]. In the ternary acetone/PVDF-HFP/lithium polymeric electrolyte (LPE) system, lithium-salt ionization and coordination with Lewis-basic sites in PVDF-HFP alter the mixing thermodynamics and phase boundaries. The phase diagram contains a central isotropic region (region I, orange) and two corner two-phase regions (Fig. 2e) [41]. The high-concentration polymer electrolyte (HCPE) lies within the single-phase isotropic region and remains stable during concentration polarization despite gradual salt depletion at the lithium-metal interface (path A). In contrast, the low-concentration polymer electrolyte (LCPE), located near the single-phase/two-phase boundary, readily undergoes phase separation under polarization (path B). The resulting rigid, PEO-rich interfacial phase suppresses dendrite growth and promotes uniform lithium deposition [42–44]. These results demonstrate that phase separation is not necessarily detrimental to SPEs. When rationally controlled through salt concentration and phase-boundary design, it can create a self-adaptive interfacial structure that combines mechanical reinforcement with stable ion transport.

Differences in molecular weight and polarity can cause severe phase separation in polymer blends, resulting in interfacial defects and voids (Fig. 2f). Compatibilizers reduce interfacial tension and improve phase dispersion, thereby stabilizing the blends and enhancing their electrochemical properties. For example, PAN-grafted MXene improved the miscibility, uniformity, and oxidation resistance of PVDF-HFP/PAN blends [45]. When coupled with an LCMO electrode, the resulting electrolyte delivered a discharge voltage of 5.1 V together with favorable capacity and cycling stability.

Thus, precise control over the thermodynamics and kinetics of phase separation is essential to engineer desirable morphologies and improve the properties of SPEs [46–49]. Phase diagrams serve as critical tools in this process, enabling prediction of single-phase or biphasic structures, phase distribution, and transitions under equilibrium and non-equilibrium conditions. Accordingly, phase-separation-driven SPEs can be rationally designed by considering key parameters such as temperature, component ratios, lithium salt concentration, and molecular interactions within the SPEs.

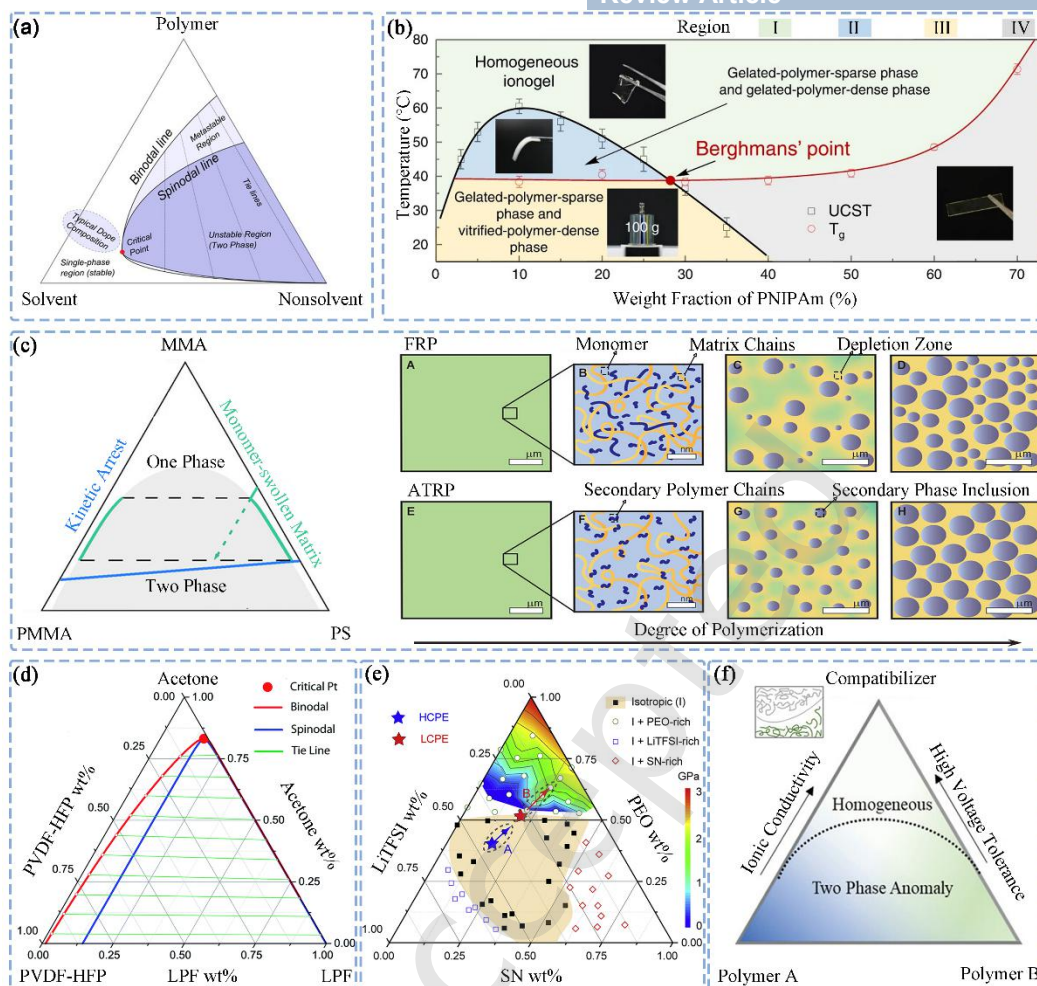


Figure 2. (a) A three-component nonsolvent-induced phase separation phase diagram [28]. © Wiley-VCH 2015. (b) A phase diagram of ionic gels composed of phase separation curves, T_g curves, and corresponding Bergmann points [35]. (c) The path of the PS-PMMA system follows during ATRP on a hypothetical phase diagram (left) and comparison of FRP- and ATRP-induced phase separation (right) [36]. (d) Phase diagram for Ace/PVDF-HFP/LPF ternary system [38]. (e) The weight percentage of the ternary PEO-LiTFSI-SN phase diagram [41]. (f) The relationship between the compatibility of two polymers and the ionic conductivity as well as high-voltage tolerance of their mixture [45]. © Wiley-VCH 2023.

3 Driving mechanisms and optimization methods for phase separation in SPEs

We summarize four major strategies for regulating phase separation [50, 51] in SPEs: amphiphilicity-driven phase separation [52, 53], lithium-salt-driven phase separation [54, 55], polarity-driven phase separation [56, 57], and polymerization-induced phase separation [58-60]. These observed phenomena in various polymer structures provide crucial insights into achieving desirable phase-separated morphologies in SPEs. Additionally, we proposed methods to optimize phase separation behavior, such as tuning the miscibility of polymer components and controlling the size and uniformity of the separated phases. Such technical breakthroughs facilitate the creation of next-generation SPE materials with improved ionic conductivity, mechanical integrity, and electrochemical stability—offering a promising route to enhance the performance and safety of LMBs. As summarized in Fig. 3, combinations that commonly lead to phase separation—owing to disparities in polarity, ion affinity, or solubility—can generally be classified into

four major categories listed below.

3.1 Driving mechanisms for phase separation in SPEs

3.1.1 Amphiphilicity-driven

Amphiphilic phase separation is typically achieved using block copolymers (BCPs), which contain both solvent-philic and solvent-phobic segments of varying lengths. These BCPs self-assemble into nanoscale structures under thermal annealing, as illustrated in Fig. 3a. The precursor solution consists of an amphiphilic BCP and a selective solvent. Due to the incompatibility between blocks, nanoscale microphase separation occurs spontaneously, forming micellar structures. These micelles are then fixed via a curing reaction, resulting in a well-defined morphology featuring soft and rigid segment domains, leading to stable phase-separation-driven SPEs [61].

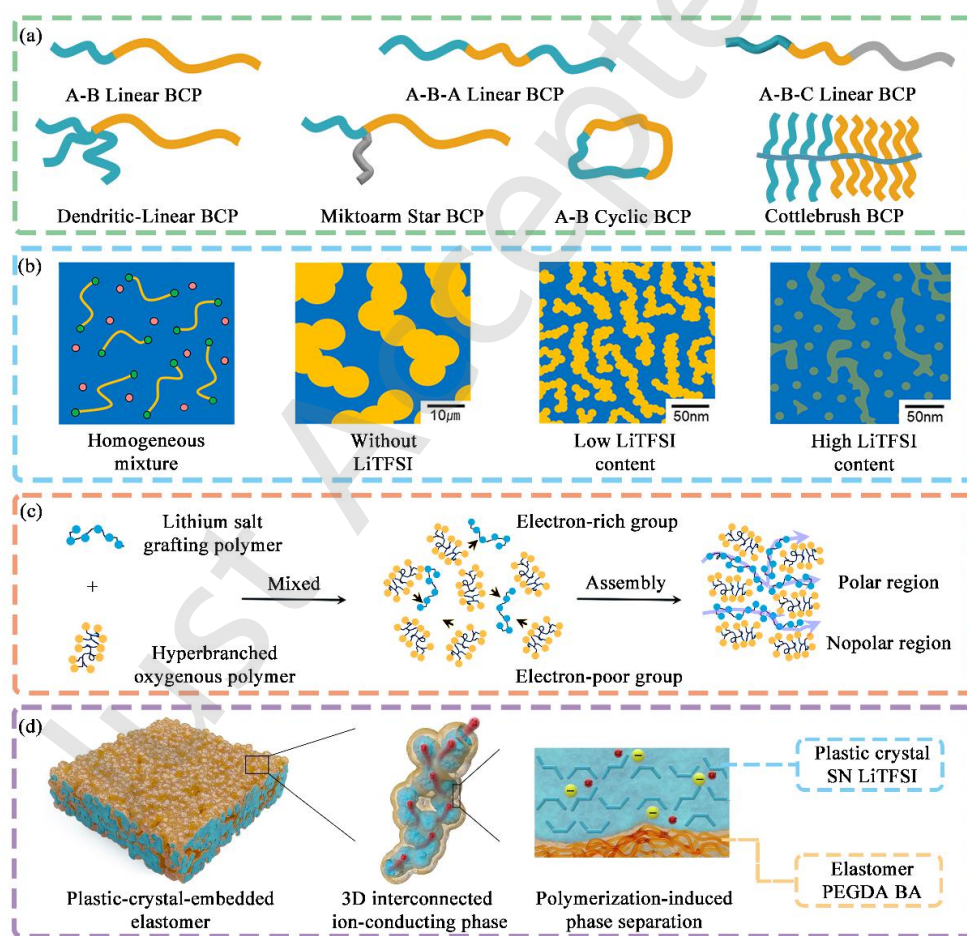


Figure 3. (a) Diagram illustrating the creation of bi-continuous network morphology through amphipathic block self-assembly [61]. © Elsevier 2020. (b) Content of phase separation can be tuned by varying the LiTFSI salt morphology [62]. © American Chemical Society 2020. (c) Phase separation is manipulated in SICPEs by the design concept of the polar and nonpolar biphasic regions [69]. © The Royal Society of Chemistry 2013. (d) Schematic illustration of the design and structure for PCEE by polymerization-induced phase separation [70]. © Springer Nature Limited 2022.

Microphase separation drives the construction of regular nano-sized domains. Owing to their low glass transition temperature (T_g), soft segments endow the system with superior ionic conduction, a favorable

Li^+ transference number, and outstanding dissolving capability for lithium salts. Meanwhile, the rigid segment, with a high thermal softening point, endows the system with outstanding mechanical rigidity and fire resistance. Importantly, the properties of BCP-derived polymer electrolytes are precisely modifiable via regulating the chemical makeup and proportion between soft and rigid blocks. This tunability allows for the preparation of nanostructured polymer SPEs with controllable morphologies and tailored multifunctional performance. Such materials offer an optimal combination of mechanical durability and ionic transport efficiency, making them highly suitable for SSLMBs.

3.1.2 Lithium-salt-driven

In liquid electrolytes, lithium salts typically dissolve in low-molecular-weight solvents, allowing for homogeneous ion distribution. In contrast, polymer electrolytes often exhibit microscale biphasic phase separation due to the significant size mismatch and limited interactions between the polymer chains and lithium salts. Unlike macroscopic delamination, this phase separation is microstructurally ordered, forming distinct lithium-rich and lithium-poor regions. The inhomogeneity in these systems arises from compatibility issues, steric hindrance, and disparities in surface activity between the polymeric host and lithium salt species. By strategically manipulating polymer-salt interactions, the spatial distribution and size of these biphasic regions can be optimized to enhance both ionic conductivity and mechanical performance. As shown in Fig. 3b, Song et al. [62] prepared an epoxy-based SPE containing polyether, an ionic liquid [1-butyl-3-methylimidazolium bis (trifluoromethyl sulfonyl) imide, BMIM-TFSI], and a lithium salt [lithium bis (trifluoromethyl sulfonyl) imide, LiTFSI]. The system underwent polymer-induced microphase separation, forming an interpenetrating bi-continuous structure comprising lithium-rich ionic domains and mechanically robust epoxy-rich phases. This morphology enabled fast ion diffusion pathways on the microscopic scale while maintaining mechanical integrity at the macroscopic level. Crucially, the degree of phase separation and resulting properties could be tuned by modulating the lithium salt concentration, allowing fine control over ionic conductivity, mechanical strength, and interfacial morphology. From a thermodynamic perspective, changes in salt content affect the interaction energies between conductive and insulating phases, leading to variations in phase size—from reduced to nanoscale domains.

3.1.3 Polarity-driven

SPEs typically exhibit slower lithium-ion transport than their liquid counterparts due to the absence of bulk solvent. In such systems, ion conduction is predominantly governed by hopping mechanisms between negatively charged sites or Lewis base groups along the polymer backbone [63-65]. To enhance ionic mobility, researchers have explored the incorporation of highly polar functional groups onto otherwise weakly polar polymer matrices. The polarity contrast between these functional groups and the host

polymer induces phase separation into polar and nonpolar regions, as illustrated in Fig. 3c. Lithium ions preferentially migrate through the polar regions, forming localized high-conductivity pathways, while nonpolar domains act as structural or mechanical support. A representative example is found in SICPEs [66-69], in which anions (e.g., from LiTFSI) are chemically bonded onto the main polymer chain. Such structural design restricts the migration of anions, yielding an elevated Li^+ transference ratio and alleviated concentration gradient polarization. Nevertheless, even with these favorable merits, single-ion-conducting polymer electrolytes commonly exhibit insufficient ionic transport capacity (10^{-4} - 10^{-1} mS cm^{-1}) due to irregular, narrow, and discontinuous conductive domains formed during phase separation. To overcome these limitations, blending strategies and functional group modifications have been employed to regulate phase morphology and promote uniformity in polar domains.

3.1.4 Polymerization-induced-driven

In contrast to thermally induced phase separation, polymerization-induced phase separation (PIPS) is driven by a chemical curing reaction that continuously alters the physicochemical properties of the blend system during polymerization. The process of reaction-induced phase separation is more complex. First, the monomers of the blend precursor dissolve to form a solution, during which phase separation does not occur. Some segments or monomers in the blend gradually precipitate from the solution when polymerization reaches a certain extent. At this point, the initial homogeneous system begins to undergo microphase separation. After curing, one type of segment in the blend phase separates, while the other type remains compatible with the matrix. This results in phase separation of the segments incompatible with the matrix resin being restricted to the nanoscale, thus producing nanoscale phase-separation-driven SPEs, which also provides a means to control different phase structures.

Beyond influencing the phase structure, the relative content and compatibility between components in a reaction-induced phase separation system also affect the viscosity evolution during curing. As the polymerization proceeds, rising viscosity limits the diffusion mobility of polymer chains, directly shaping the size and connectivity of the phase-separated domains. This mechanism enables the generation of bicontinuous nanoscale domains through PIPS; the ion-transporting components therein form an integrated 3D conductive network supported by a mechanically resilient elastomer substrate, thereby achieving synergistic mechanical strength and ionic conductivity. A common feature of these systems is the formation of cross-linked polymer networks, [70] generated via PIPS between a polymer matrix and a plastic crystal phase. The strong phase separation drives preferential lithium salt distribution into the plastic crystal-rich phase, enhancing both mechanical resilience and ion transport. As depicted in Fig. 3d, the architecture of plastic crystal-embedded elastomer (PCEE) exhibits a unique microstructure where the 3D networked SN-LiTFSI plastic crystal is partitioned into fine nanosized domains, while the surrounding PEGDA/BA (poly(ethylene glycol) diacrylate/butyl acrylate) elastomer framework alleviates the SN phase

coarsening phenomenon. This results in a continuous 3D ion-conductive SN network, enabling efficient lithium-ion transport. Consequently, SSLMBs employing such electrolytes demonstrate high energy and power density with stable operation at RT.

Based on the above statements, it can be concluded that the lithium-poor/rich biphasic strategy is the most straightforward method to induce phase separation, typically achieved by optimizing the lithium salt concentration. In contrast, other strategies require chemical modifications of polymer monomers, incorporation of functional groups to promote phase distinction, or polymerization process control to enable selective lithium salt distribution. Although these approaches are more complex, they offer the advantage of significantly enhancing polymer properties—such as through fluorine doping—by tuning the molecular structure. This study points out the potential of organic synthesis to develop a wide range of tailored polymers, offering novel strategies for boosting the performance of LMBs.

However, multiple interdependent factors influence phase separation in SPEs, which may impact both phases in a designed biphasic system. Even when the two phases are relatively compatible, merely adjusting their proportion often leads to undesirable large-scale phase separation, resulting in defects and voids that compromise electrolyte density and uniformity. This hinders the formation of continuous ion-conducting pathways, negatively affecting performance.

Therefore, it is essential to further rationally regulate the dual-phase domains by effectively improving their miscibility, minimizing excessive phase segregation, and constructing multifunctional microphase-separated structures. Such regulation enables both phases to synergistically contribute to the overall performance, resulting in phase-separation-driven SPEs with enhanced mechanical strength, ionic conductivity, and structural integrity. In the following section, we introduce several commonly used strategies to fine-tune dual-phase domain structures, as illustrated in [Fig. 4](#).

3.2 Methods for optimizing phase-separation behavior

3.2.1 Grafting modification

Graft polymers, characterized by their diverse functional groups, tunable polymerization degrees, and customizable properties, have garnered significant research attention for regulating phase separation in SPEs. These polymers are synthesized conveniently by grafting one reactive group onto another, offering a convenient and effective approach to enhancing miscibility, minimizing defects and voids caused by large-scale phase separation, and improving interfacial compatibility. As illustrated in [Fig. 4a](#), poly(ethylene glycol)-grafted polymer-like quantum dots (PPQDs) were incorporated into a PEO/LiTFSI system. Incorporating PPQDs can impede the ordered stacking of PEO chains to cut down crystallinity and expand amorphous domains favorable for fast ionic migration; meanwhile, these quantum dots disperse homogeneously across the polymer host and construct abundant PPQD/PEO phase-separated conductive

networks. These networks provide abundant complexation-decomplexation sites for lithium-ion migration, resulting in a high ionic conductivity of $5.53 \times 10^{-2} \text{ mS cm}^{-1}$ at 30°C —surpassing many previously reported PEO-based SPEs [71–74]. Therefore, the grafting of functional and designable groups onto polymer electrolytes represents an effective strategy for tuning phase separation behavior, ultimately leading to the construction of stable, high-performance SPEs with superior electrochemical properties.

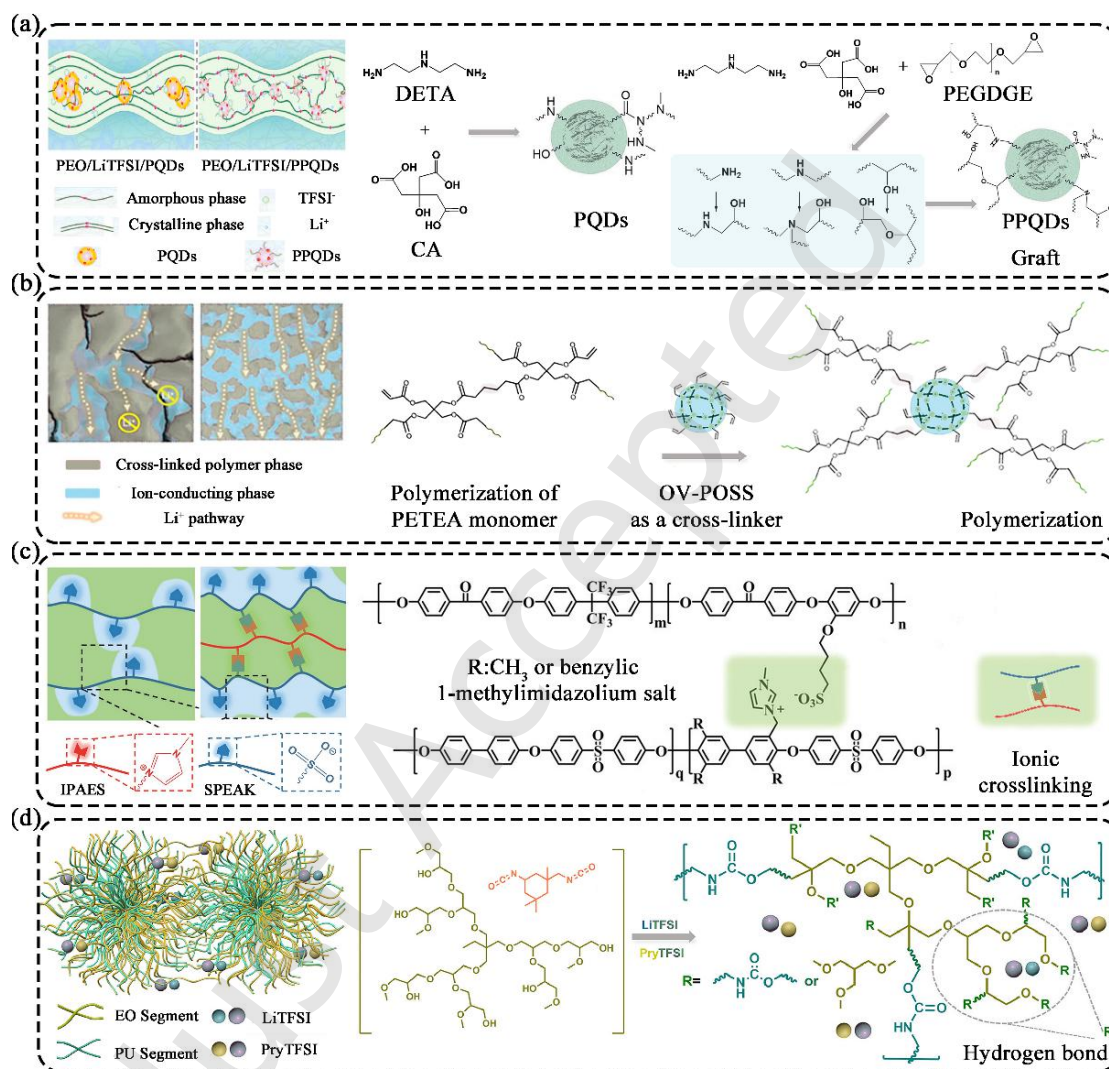


Figure 4. (a) Lithium-ion transfer schematic diagrams in graft polymer electrolytes [71]. © Elsevier 2021. (b) Controlling the Ov-POSS polymerization process enhances SPE's micro-phase structure homogeneity [75]. © Wiley-VCH 2023. (c) Ionic cross-linking membrane schematic representation with nanophase separation [78]. © Wiley-VCH 2021. (d) Schematic diagram of hydrogen bonding results in advanced miscibility with phase separation type electrolyte and assembled lithium-ion battery [81]. © Elsevier 2024.

3.2.2 Polymerization process regulation

Tuning the polymerization behavior of SPEs is an effective strategy to control phase separation and improve electrolyte performance. One promising approach involves cross-linking monomers during polymerization. For instance, introducing cross-linking agents such as octavinyl polyhedral oligomeric silsesquioxane (Ov-POSS) into the precursor solution enhances the cross-linking density of pentaerythritol tetraacrylate (PETEA) monomers (Fig. 4b) [75]. This modification allows for precise tuning of the

microstructure of the resulting polymer electrolyte, significantly improving the uniformity of its physicochemical properties [76, 77]. Moreover, cross-linking suppresses the aggregation of polymer clusters during in situ polymerization, resulting in a homogeneous, ionically conductive network.

3.2.3 Ionic cross-linking

Ionic cross-linking offers another pathway to induce nanoscale phase separation in SPEs. This approach promotes the formation of well-defined ion-conducting pathways, thereby enhancing both ionic selectivity and conductivity. Ionic cross-linked membranes (ICMs) [78] were prepared by blending sulfonated poly(aryl ether ketone) copolymer (SPAEEK) with imidazole-functionalized poly(aryl ether sulfone) (IPAES), where the two polymers have opposite charges and comparable average molecular weights (Fig. 4c) [79, 80]. Compared to non-cross-linked analogs, these ICMs exhibited significantly improved cation selectivity and demonstrated efficient charge utilization. Furthermore, the as-prepared electrolyte films deliver exceptional mechanical toughness and prolonged structural durability, making them suitable candidates for advanced SSLMB applications.

3.2.4 Hydrogen bonding for enhanced miscibility

The incorporation of hydrogen bond-rich hyperbranched polymers into SPEs can promote microphase separation and establish new ion transport channels. For example, hyperbranched polyurethane solid electrolytes [81] were synthesized through the reaction of hyperbranched polyethylene glycol with isophorone diisocyanate (IPDI), as shown in Fig. 4d. The abundant urethane-based hydrogen bonding interactions within the polymer network enhance segmental mobility and interfacial contact, thereby improving electrode-electrolyte compatibility [82, 83]. As a result, these electrolytes display excellent electrochemical performance and adaptability across a range of electrode materials at 30 °C, highlighting their strong potential for practical applications.

Such results highlight the vital function of interfacial interactions in regulating the phase separation structure of SPEs. Depending on the specific characteristics of the polymer systems and their components, various interactions—such as covalent cross-linking, ionic bonding, and hydrogen bonding—can be introduced to tailor the morphology and phase behavior. By establishing optimal microphase separation, enhancing miscibility, and suppressing large-scale defects, these strategies contribute to the development of SPEs with superior mechanical integrity and ionic conductivity. Ultimately, an in-depth insight into the intrinsic microstructural evolution of SPEs, control over crystallization and phase separation, and elucidation of the structure-morphology-performance relationships are essential for advancing SSLMBs based on phase separation-engineered SPEs.

4 Characterization and theoretical modeling of phase separation in SPEs

4.1 Characterization of phase separation in SPEs

This section outlines the experimental techniques commonly used to intuitively and quantitatively characterize the phase separation morphology in SPEs. Thorough insight into phase-separated morphological architectures is indispensable, for these microstructures exert a remarkable impact on ion transport capacity, structural durability, and electrode-electrolyte interfacial matching in solid electrolyte systems. Two primary categories of methods are employed in the structural characterization of SPEs: electron microscopy and scattering techniques.

Classic electron imaging approaches, most notably transmission electron microscopy (TEM), are widely used for their high-resolution imaging capabilities. These techniques are especially effective in systems with strong phase contrasts, such as those incorporating inorganic fillers or clearly distinct polymer segments. TEM can visualize crystallization features, phase boundaries, and nanostructured domains, thereby offering direct morphological evidence of phase separation. For instance, Timachova et al. [84] investigated ion transport behavior in PS-*b*-PEO/LiTFSI electrolytes with varying salt concentrations. As shown in Fig. 5a, TEM images demonstrated that at low salt ratios ($r = 0, 0.06, 0.18$), the bright phase shows that the PEO lamellar grains were well-ordered with few defects. However, under relatively high salt molar fractions ($r = 0.3$), the morphology became severely disrupted. To complement the morphological data, pulsed-field gradient nuclear magnetic resonance (PFG-NMR) [85, 86] was used to measure the self-diffusion coefficients of Li^+ and TFSI $^-$ ions. The anisotropic ion diffusion data revealed that the NMR morphology factor (f_{NMR}), which quantifies structural disorder, increased with salt content—shifting from $\sim 2/3$ at low concentrations to ~ 0.8 at higher ones. This indicates that defect-rich morphologies facilitate greater ion flux, thereby affecting the overall functional behaviors of nanophase-separated block copolymer electrolyte films.

In systems where phase contrast is weak—such as polymer blends with small-molecule lithium salts, plasticizers, or complex multicomponent matrices—electronic microscopy often struggles to resolve distinct phase structures. In such cases, scattering techniques aid in understanding phase separation behavior by offering detailed information on crystallization and high-quality statistics regarding phase separation sizes. For example, two-dimensional wide-angle X-ray diffraction (2D-WAXD) captures crystallinity and polymer chain ordering. Distinct diffraction patterns help identify polymeric crystalline phases and monitor their evolution during phase separation. Polarized light microscopy (PLM) allows visualization of amorphous and crystalline domains in polymer matrices. Changes in birefringence patterns can indicate microphase separation or spherulite growth and transformation. An atomic force microscope (AFM) offers topographical and phase images. Phase contrast in AFM can reveal differences in viscoelastic or compositional properties, and by comparing the phase and height images, one can deduce the degree of microphase separation with high spatial resolution [87].

He et al. [88] revealed that lithium salts play a critical role in modulating the entropy of SPEs at both the chain conformation and phase levels. The crystallinity of the fabricated electrolyte serves as a feasible indicator for evaluating its entropy variation. Reduced polymer crystallinity corresponds to a higher entropy state of polymer molecular chains. The study results indicate that, compared to low-entropy PEO (LE-PEO)/PVDF samples, the addition of lithium salts significantly suppresses large-scale phase separation of PEO and PVDF, forming high-entropy PEO (HE-PEO)/PVDF. The microphase size of PVDF is reduced dramatically, facilitating the migration of lithium ions (Li^+) in the electrolyte. Moreover, in SPEs, smaller phase sizes are achieved due to increased mixing entropy as the polymer phases strengthen, while the overall volume fraction of the blend system remains constant. By varying the interactions between components, mixing entropy can be changed. High mixing entropy is produced when strong component interactions eventually prevent phase separation. Furthermore, increasing mixing entropy can enhance blends' mechanical qualities. Next, as shown in Fig. 5b, PLM, AFM adhesion tests, and 2D-WAXD were used to examine the crystallized PEO or LE-PEO. The 2D-WAXD characterization demonstrated that the circular diffraction signals (inner and outer concentric rings) originated from crystalline PEO corresponding to the (120) and (112) lattice planes, corroborating PLM's observation of the large spherical crystalline morphology of LE-PEO. The intense coordination interaction between EO and Li^+ caused the spherical crystals to completely vanish upon adding lithium salt, along with the crystal diffraction rings. HE-PEO is the name given to the amorphous PEO- Li^+ . Additionally, the morphology and adhesion force of the membrane were revealed through the use of AFM mapping via quantitative nanomechanical testing mode. The outcome demonstrates that in comparison to LE-PEO, HE-PEO exhibits markedly elevated adhesive force, a phenomenon attributed to intense electrostatic attraction and interfacial van der Waals forces.

The structure of SPEs was prepared by using LiTFSI-doped PEO-block-poly(*n*-butyl acrylate) (PEO-*b*-PnBA) [89], with different Li:EO as the doping ratio of PEO and PnBA, and the measurements verified a disordered bicontinuous nanoscale microphase separation structure, where lithium ions are capable of forming coordination complexes with both PEO and PnBA segments. Fourier-transform infrared spectroscopy (FTIR) was adopted to quantify the real lithium salt proportion within each phase, as illustrated in Fig. 5c. When LiTFSI is incorporated into PnBA matrices, lithium salt ions coordinate with the carbonyl ($\text{C}=\text{O}$) groups of PnBA, generating a fresh shoulder absorption peak located at 1708 cm^{-1} . This identical spectral feature is also detected in the FTIR profiles of LiTFSI-blended PEO-*b*-PnBA block copolymers. The peak areas of the free and complex $\text{C}=\text{O}$ groups can be obtained by deconvolution of the FTIR peaks due to their overlapping. Furthermore, PEO has a strong complexation ability with Li^+ , which causes the PEO phase to have a relatively higher salt content. Nevertheless, variations in salt doping concentration between PEO-*b*-PnBA/LiTFSI hybrid materials decrease as the doping ratio (*r*) increases.

Based on this assumption, it can be deduced that the conductivity of SPEs is primarily affected by the grain size following phase separation by comparing the conductivity normalization coefficients of PEO-b-PnBA/LiTFSI SPEs at various r values and temperatures.

Techniques based on small-angle X-ray scattering (SAXS) facilitate examining phase separation structures within thin films, offering insights into phase separation size, aggregate morphology, interface area, and interface roughness. SAXS techniques leverage materials' scattering length density to visualize the blends' phase separation structures with comparable electron densities. Then, in SAXS, in terms of two parameters, the appearance and location of polymer peaks are shown in the Saxophone spectrogram. Equation $d = 2\pi / q$ can be used to calculate the microphase separation of an ion polymer member; the greater the value of d , the more pronounced the microphase separation in the membrane [90].

There are numerous techniques available for characterizing phase separation at different structural levels. Integrating infrared absorption peaks can assess the relative component content of phases in SPEs. Differential scanning calorimetry (DSC) verifies the compatibility of various components within SPEs. The appearance of two peaks in the glass transition temperature indicates substance incompatibility and the onset of phase separation. Additionally, DSC can evaluate polymer crystallinity and investigate the blending performance of SPE materials. X-ray diffraction (XRD) measurements are instrumental in determining the crystallinity of SPEs. Typically, amorphous polymers display a flat, broad peak, while crystalline regions or materials within polymers exhibit one or more sharp diffraction peaks. The phase behavior of hyperbranched PEO-based star-shaped polymers (hbPPEGMA-star-PS) was investigated [91], composed of a hyperbranched poly[poly(ethylene glycol) methyl ether methacrylate] (hbPPEGMA) core and PS arms, utilizing both DSC and XRD in Fig. 5d. The DSC curves of both SPEs showed an apparent T_g for PEO at about -47°C and a weak T_g for PS at approximately 101°C , with no discernible melting transition (T_m). These findings suggest that the hbPPEGMA-s-PS SPEs underwent microphase separation and effectively suppressed PEO crystallization. Two prominent characteristic peaks were observed in the XRD pattern of the PEO SPE, which contained only linear PEO chains. These peaks corresponded to the (120) and (112) lattice planes of crystalline PEO, respectively. These peaks, however, were not present in the hbPPEGMA-s-PS SPE patterns, suggesting that they are amorphous. SAXS was applied to investigate the microphase-separated morphology of hbPPEGMA-s-PS solid polymer electrolytes (SPEs). The primary scattering peak (q) and secondary higher-order reflection ($2q$) with a characteristic q ratio of 1:2 verified the formation of self-assembled lamellar nanostructures. The fundamental scattering peak located at $q = 0.21\text{ nm}^{-1}$ corresponded to the calculated d -spacings of two kinds of hbPPEGMA-s-PS SPEs, which were 29.4 and 28.6 nm, respectively. At a constant mass and volume ratio of individual components, the molecular weight of entangled polymer segments dominates the d -spacing values of the microphase-

separated structure. It showed that PS arms reorganize and entangle following phase separation, resulting in the alternating layers of self-assembled PS and PEO that form the lamellar structure.

Hence, this paper offers a comprehensive overview of characterization techniques such as SEM, TEM, PLM, AFM, 2D-WAXD, PFG-NMR, FT-IR, XRD, DSC, and SAXS, employed for analyzing the morphology and structure of phase separation. Firstly, DSC can directly assess the occurrence of phase separation by measuring the amount of T_g . Since the amorphous composition and molecular arrangement determine T_g , samples undergoing phase separation will exhibit more than one T_g . However, DSC methods have limitations in identifying phase separation; test results can be influenced by various thermal events occurring during heating, and sensitivity to different systems can vary. Secondly, SAXS characterization delivers structural insights into the dimension, morphology, and spatial distribution of crystalline domains and nanostructured phases embedded in the materials, thus offering precise scale information on phase separation. It also offers fast response times and enables in situ or dynamic characterization of samples.

Furthermore, combining multiple tests can complement each other's advantages. For example, combining DSC and SAXS tests can integrate samples' thermodynamic and morphological changes more accurately, facilitating the study of phase transitions and the creation of representative phase diagrams. Thirdly, SEM, TEM, AFM, and PLM typically offer a straightforward and intuitive view of phase separation morphology with clearly defined phase boundaries. However, preparing some samples for these tests can be challenging, particularly those sensitive to air and moisture, elastic materials prone to curling or wrinkling, or electrolytes susceptible to degradation and aging under high temperatures or high-energy electron beams, increasing testing difficulty and introducing errors. Lastly, 2D-WAXD determines the occurrence or extent of phase separation through the intensity of scattering patterns or diffraction rings in reciprocal space. XRD, FT-IR, and PFG-NMR assess the degree of phase separation in SPEs or interactions between different phases based on peak intensities and shifts in spectra.

By harnessing the complementary advantages of these diverse testing methods, precise characterization of phase separation structures is attained. Timely adjustments in the regulation strategies of biphasic domains allow for the controlled modulation of SPEs' morphology, further elucidating the dependency relationship between phase separation and electrolyte performance. Establishing the double enhancement between electrolytes' mechanical and electrical properties is the key to optimizing the morphology of SPE films and improving the device's performance.

4.2 DFT study of phase-separation mechanisms in SPEs

Phase separation in polymer solutions leads to complex morphologies involving intricate physical mechanisms. Ordinary characterization methods vary significantly in their operational length scales. Additionally, the preparation process for SPEs testing samples is complex, making it challenging to observe the phase-separation-driven SPEs or employ in situ imaging techniques, thus making it

inconvenient to capture the complete formation process of SPEs phase separation. The material's behavior appears more like a "black box". To gain more profound insights into the hidden mechanisms, besides developing effective characterization techniques for thoroughly examining phase separation behavior, computational materials science can effectively observe PEM phase separation behavior over time scales, which will investigate the physics principles underlying the phase separation process, advancing research on phase separation behavior.

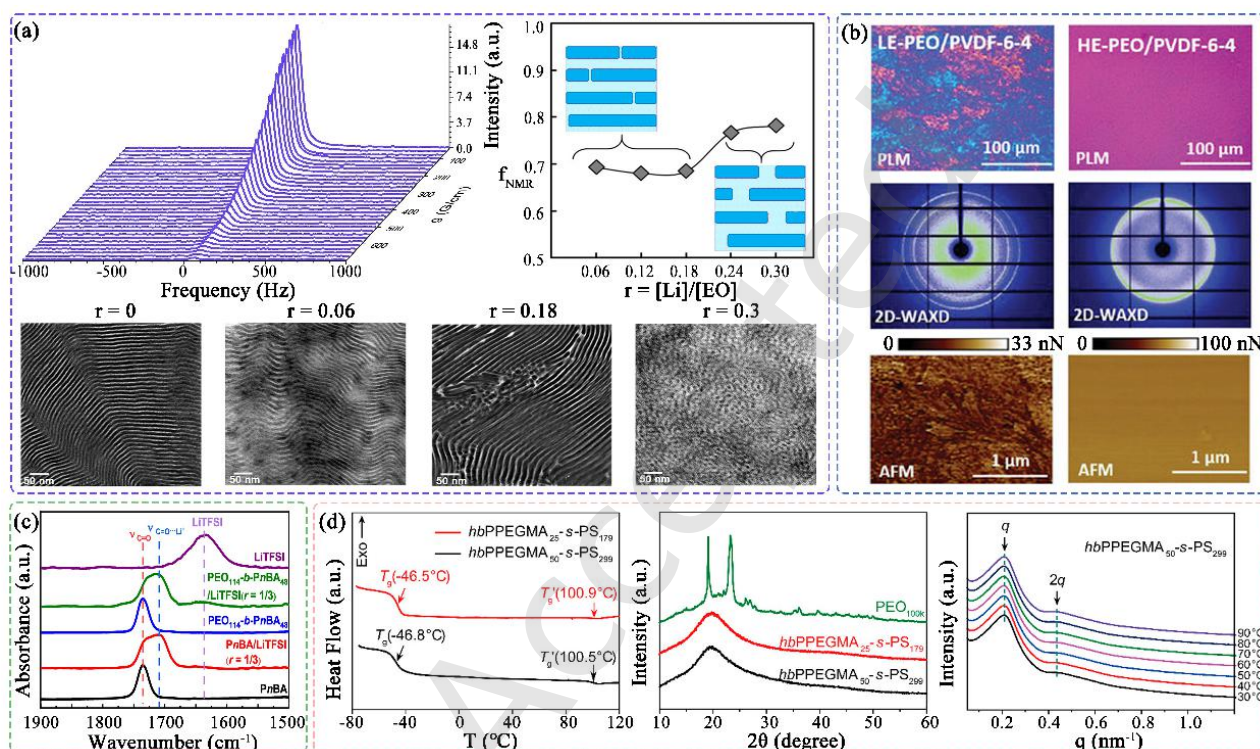


Figure 5. (a) NMR morphology factor, f_{NMR} , and dark-field TEM images of PS-b-PEO/LiTFSI electrolytes [84]. © American Chemical Society 2018. (b) PLM captures, 2D-WAXD patterns, and AFM force mapping of LE-PEO and HE-PEO electrolytes [88]. © Wiley-VCH 2023. (c) FTIR spectra of PEO-b-NBA/LiTFSI hybrids [89]. © American Chemical Society 2023. (d) DSC curves, XRD patterns, and SAXS diffractograms of hbPPEGMA-s-PS SPEs [91]. © American Chemical Society 2019.

Using molecular dynamics (MD) simulations [92, 93], the phase behavior of ternary mixtures [94] with lithium salt, organic solvent, and ionic liquid (IL) was studied in Fig. 6a. According to the study, the system experiences phase separation at RT, yielding two separate microdomains: an ion-concentrated zone accommodating all ionic species and a tiny proportion of organic solvent moieties. In contrast, the other domain is mainly made up of organic solvent molecules. It also investigated how temperature, IL volume fraction, and salt concentration related to this mixture's phase behavior. Our observations indicate that this procedure performs more favorably under elevated temperatures and is governed by entropic effects, regardless of lithium salt loading. The diffusion kinetics of lithium cations within the electrolyte are largely controlled by microphase segregation behavior, which results in slower kinetics in the ion-rich

region. High-concentration domains may affect lithium battery performance, particularly under low ionic liquid volume loadings.

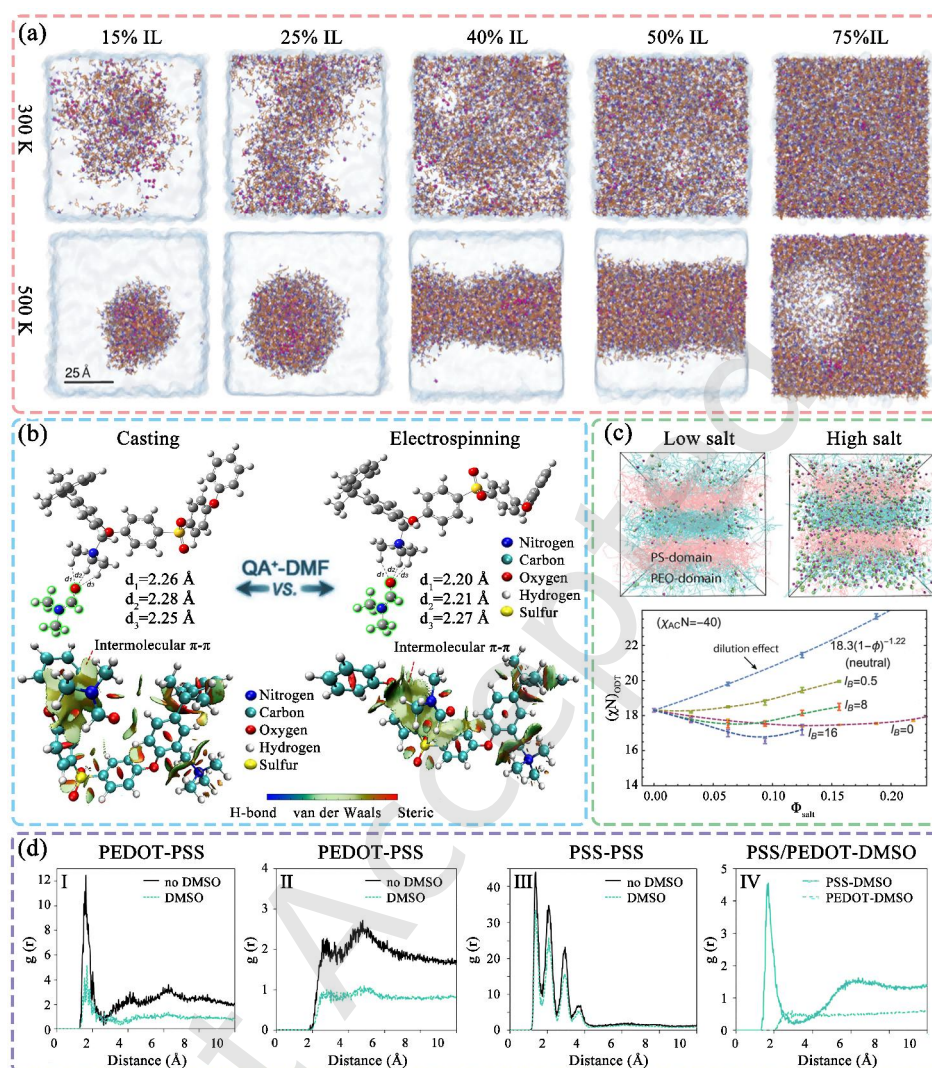


Figure 6. (a) Phase separation in the ternary mixtures with lithium salt, organic solvent, and ionic liquid at 300 and 500 K [94]. © American Chemical Society 2021. (b) Potential mechanisms of microphase separation in the QAPSF-DMF system during the electrospinning and casting processes, and the color images represent RDG isosurfaces [95]. © Elsevier 2022. (c) Shift in $(\chi N)_{ODT}$ as a function of salt concentration and representative lamellar morphologies from simulations at low or high salt concentrations [96]. (d) RDFs of PEDOT-PSS hydrogen bond interactions with and without DMSO [99]. © The Royal Society of Chemistry 2013.

To precisely and reliably investigate phase segregation originating from intermolecular forces, density functional theory (DFT) simulations were carried out. Geometrically optimized dimethylformamide (DMF) and imidazolium (Im^+)-functionalized polysulfone (PSF) repeating units were first subjected to electrostatic potential (ESP) analysis to locate sites prone to intermolecular interactions, probing the mechanism underlying the promotion of microphase separation during the electrospinning of alkaline polymer electrolytes.

Figure 6b [95] shows the non-covalent interactions between Im^+ and PSF or quaternary ammonium (QA^+) and the common solvent DMF; the color images represent reduced density gradient (RDG)

isosurfaces. The results indicate that the electrostatic field-augmented Im^+ -DMF interactions attenuated chain-chain interactions originating from Im^+ - Cl^- electrostatic interactions, promoting the outward migration of Im^+ toward the nanofiber surface. The resulting microphase separation creates continuous, long-range ion-conduction pathways.

The order–disorder transition temperature (T_{ODT}) serves as a key parameter governing the microphase segregation behavior of polymeric materials. Relevant experiments have shown that it is extremely sensitive to salt content—adding a small amount of salt can increase T_{ODT} by dozens of degrees. Additionally, a coarse-grained model that explicitly accounts for Coulomb interactions has been established, which can predict T_{ODT} with high accuracy and clarify the mechanism underlying the effect of salt addition on phase behavior (the competition between ion association and solvent dilution).

In the model (Fig. 6c) [96], $(\chi N)_{\text{ODT}}$, the characteristic parameter corresponding to the T_{ODT} , where χ_{AB} or χ_{AC} is the Flory-Huggins parameter between blocks A (PEO, polyethylene oxide) and B (PS, polystyrene) or C (cations), a parameter used to measure block incompatibility, and N is the number of beads in each copolymer chain (a representation of chain length in simulations). A negative χ_{AC} indicates the affinity of PEO for cations. As $(\chi_{\text{AC}}N)_{\text{ODT}}$ increases, $(\chi_{\text{AB}}N)_{\text{ODT}}$ decreases because the selective enrichment of ions in PEO-rich microdomains lowers the system free energy. In subsequent simulations, $\chi_{\text{AC}}N$ was fixed at -40 to investigate the effects of Bjerrum length l_{B} and salt content. For diblock copolymers in a neutral solvent, $(\chi_{\text{AB}}N)_{\text{ODT}}$ varies with polymer concentration according to a power-law relationship. After salt addition, ion association and solvent dilution jointly regulate the phase behavior. At a small l_{B} , weak Coulomb interactions cannot confine all anions within the PEO-rich domains. Increasing l_{B} strengthens ion pairing and promotes ion enrichment in these domains. At high salt loading or dilution, entropic effects drive some ions into the PS-rich domains, weakening the effective PEO-PS interactions and altering $(\chi_{\text{AB}}N)_{\text{ODT}}$. These simulations demonstrate that salt content and ionic interaction strength jointly govern the order–disorder transition by regulating ion partitioning between the two domains.

Using MD simulations and DFT [97, 98], monomer-monomer and monomer-solvent interactions were analyzed through RDFs to understand the microscopic effects behind phase separation behavior. The computational results indicate hydrogen bonds are the primary interactions between the polymer and solvent. When a selective solvent is added, the differing interactions between the monomers and the solvent lead to phase separation between the two types of monomers. This phase separation occurs more rapidly as the solvent content increases.

Figure 6d displays RDFs characterizing hydrogen-bonding contacts between PEDOT and PSS. These interactions originate from sulfonate S-OH moieties on PSS and ether -O- sites within PEDOT's dioxo rings, and data are extracted from the final 200 simulation trajectories (equivalent to 100 ps) both with and without the DMSO additive [99]. In pristine PEDOT-PSS, hydrogen bonds form between the S-OH groups

of PSS and the ether oxygen sites of PEDOT Fig. 6d (I), accompanied by weaker noncovalent interactions Figure 6d (II). PSS chains also interact through inter- and intrachain hydrogen bonds, as reflected by three characteristic RDF peaks Fig. 6d (III). After DMSO treatment, the strong PSS-DMSO affinity suppresses PEDOT-PSS and PSS-PSS interactions, while PEDOT-DMSO interactions remain relatively weak Figure 6d (IV). These results demonstrate that selective solvents can regulate phase separation by redistributing intermolecular interactions, thereby modifying blend structures and potentially improving electrolyte performance.

According to these computational results, adding selective solvents with strong interactions can regulate phase separation in the system, thereby altering the structure of the blend and enhancing electrolyte performance, such as introducing highly conductive solvated lithium-ion structures with solid interactions with the polar phase.

5 Roles of phase separation in SPEs for LMBs

Excellent SPEs should possess effective lithium salt dissolution, high ion conductivity, and high ion transference number. Developing phase- separation- driven SPEs is an essential approach to achieving high-performance polymer electrolytes, attributed to two critical abilities of microphase separation-based SPE: optimizing lithium salt and electrolyte interactions and optimizing ion transport behavior in electrolyte systems.

5.1 Optimization of lithium salt and electrolyte interactions

The lithium salt is a fundamental parameter that must be considered in polymer electrolytes' final structure and conductivity. The solubility, dissociation degree, and distribution state of lithium salts within polymers directly impact the ion conductivity of the electrolyte. The thermodynamic state of polymer blends may be influenced by the electrostatic interactions of dissociated ions when polymer solvents dissolve lithium salts with a high dielectric constant. Furthermore, it is thought that the thermodynamics of ion-solvated polymer blends are very different from those of salt-free polymers. The addition of lithium salts is believed to have two opposing effects on polymer blends: electrostatic interactions motivate incompatibility, while elevated mixing entropy of minute ions facilitates better phase miscibility.

Therefore, Fig. 7(a, b) first discusses the influence of different lithium salt concentrations on SPEs' phase separation and SPEs' performance. Small-angle neutron scattering (SANS) and small-angle light scattering were adopted to characterize phase segregation within ternary PEO/PS/LiTFSI mixtures. [100].

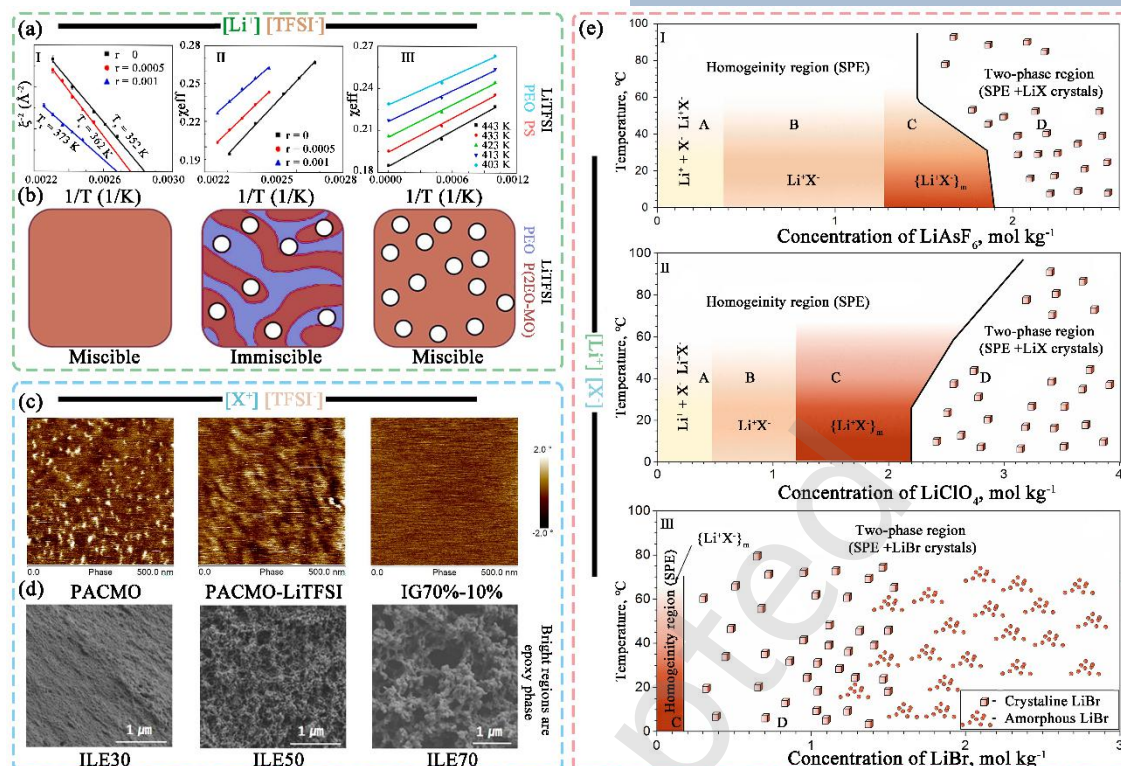


Figure 7. (a) The PEO/PS phase separation diagram at various r values and LiTFSI concentrations [100]. © Elsevier 2022. (b) Correlation between the miscibility of PEO/P(2EO-MO) blend polymer electrolytes and LiTFSI loading [101]. © American Chemical Society 2020. (c) AFM phase images of a series of P(UA-co-ACMO) [105]. © Wiley-VCH 2022. (d) FE-SEM micrographs following the extraction of the conducting electrolyte phase from epoxy with ILEs [106]. © American Chemical Society 2018. (e) Solubility temperature curves and dominant ionic species of PBAN complexed with lithium salts bearing distinct anions (PBAN-LiAsF₆, PBAN-LiClO₄, and PBAN-LiBr) [107]. © Elsevier 2019.

Firstly, as the temperature decreases, the value of ξ gradually increases, which characterizes the UCST phase behavior of PEO/PS/LiTFSI systems. Accordingly, a linear correlation emerges when plotting ξ^{-2} against $1/T$, and the spinodal temperature T_s can be solved at the condition of $\xi^{-2} = 0$. As illustrated in Fig. 7a (I), for salt loadings $r = 0, 0.0005$, and 0.001 , the spinodal temperature T_s of each sample rises along with growing LiTFSI content. Furthermore, the effective Flory-Huggins interaction parameter (χ_{eff}), a key thermodynamic descriptor, was extracted by fitting SANS data collected from homogeneous single-phase regions. The χ_{eff} value provides a microscopic measure of the interaction energy between monomers under electrostatic interactions and significant phase separation. As shown in Fig. 7a (II), χ_{eff} rises upon elevating LiTFSI loading, which implies that trace lithium salt can remarkably promote microphase segregation within PEO/PS binary mixtures. Furthermore, Fig. 7a (III) shows that χ_{eff} also increases with temperature, suggesting a temperature-dependent amplification of monomer interactions.

Studies [101] have also shown a correlation between salt concentration and polymer phase separation, which is not always a simple proportional relationship. This correlation is observed by mixing lithium salts with polymers with similar chemical structures (see Fig. 7b) but with different properties. At first, the PEO/P(2EO-MO) blend was homogeneous in the absence of salt and exhibited attractive interactions characterized by a negative χ_{eff} . Adding a small amount of salt resulted in a positive χ_{eff} . Surprisingly,

once salt loading surpasses a critical threshold, the blends undergo microphase separation and feature negative effective Flory-Huggins interaction parameters χ_{eff} . At a designated salt molar fraction, PEO/P(2EO-MO)/LiTFSI composite electrolytes deliver electrochemical performances comparable to neat PEO/LiTFSI systems prepared with identical salt content. This study demonstrates the correlation between salt concentration and polymer phase separation, which is not a simple proportional relationship. By adjusting the constituents, uniform blends consisting of polymers with dissimilar polarities can be successfully fabricated, enabling the design of innovative phase-separation-driven SPEs for LMB applications.

In addition, there is a type of low-melting-point molten salt known as ionic liquids (ILs), which are substances entirely composed of ions and remain in a liquid state at or near room temperature. Under an applied electric field, ions in ILs can achieve rapid directional movement, exhibiting high ionic conductivity, which can enhance the ionic conductivity of SPEs. Moreover, regulating ionic radii and spatial distribution can facilitate the formation of continuous ion-conducting domains in solid polymer electrolytes, further improving ion transport efficiency—such as the designed $[X^+][TFSI^-]$ structure—is an effective strategy to decouple ion motion from polymer segmental relaxation, which substantially improves the ionic conductivity of polymer electrolyte materials. Hence, Fig. 7(c, d) investigates the effects of adding ionic liquids (significantly changing the type of cations in lithium salts) on the phase separation structure and performance of SPEs. In Fig. 7c [EMIM][TFSI] was incorporated into a cross-linked P(UA-co-ACMO) network to regulate its microphase-separated structure [102-105]. AFM images show that LiTFSI enlarges the dispersed domains by introducing Li-mediated interactions with polar groups in the polymer network. Further addition of the ionic liquid produces IG70%-10% ionogels containing 70 wt% IL and 10 wt% LiTFSI, in which IL dilution reduces the degree of phase separation. AFM and TEM analyses reveal rigid nanodomains dispersed within a continuous soft phase. The rigid domains enhance strength and toughness, while the soft phase provides extensibility and continuous ion-transport pathways, enabling high mechanical strength, elongation, and ionic conductivity.

In Fig. 7d, ionic liquid/lithium-salt electrolytes (ILEs) were combined with a mechanically robust cross-linked epoxy matrix through a one-pot curing process [106]. Epoxy-rich domains provide high Young's modulus and T_g , whereas ILE-rich domains promote ion transport. ILE30 forms isolated pores within a nonconductive epoxy matrix and consequently exhibits the lowest ionic conductivity. By contrast, ILE50 and ILE70 develop interconnected, bicontinuous networks, leading to higher conductivity and distinct glass transitions for the two phases. Thus, varying the epoxy/ILE ratio enables morphology to evolve from isolated domains to a bicontinuous structure, balancing mechanical strength and ionic conductivity for multifunctional energy-storage applications.

Finally, the interactions between lithium salts with different anions and the polymer were discussed. Common lithium salts include LiAsF_6 , LiClO_4 , LiBr , LiTFSI , and LiBOB . These various lithium salts have varying dissociation constants and molecular weights, which directly affect the formation of aggregates and the results of phase separation. For example, Bushkova et al. [107] analyzed high-ion aggregates' formation and phase separation resulting from blending poly(butadiene-co-acrylonitrile) (PBAN) copolymer with various lithium salts. They employed theoretical quantum chemical calculations using GAMESS (US) and Firefly software to analyze the results. They found that salt solubility is governed by the growth of high-order ionic aggregates, $\{\text{Li}^+\text{X}^-\}_m$, and their solvation interactions with polar nitrile groups. Fig. 7e (I, II, and III) presents the concentration–temperature phase diagrams of PBAN- LiAsF_6 , PBAN- LiClO_4 , and PBAN- LiBr . The black lines separate the homogeneous aggregate-solution regions (A-C) from the phase-separated region (D), where the homogeneous electrolyte coexists with crystalline or amorphous LiX . PBAN- LiClO_4 exhibits the broadest homogeneous region, which expands with increasing temperature. Region A contains free ions and solvated ion pairs and shows VTF-type conductivity, whereas region B is dominated by ion pairs and higher aggregates, leading to Arrhenius-type behavior. Region C mainly contains solvated LiClO_4 and LiAsF_6 , while LiBr remains poorly dissolved. PBAN- LiBr lacks regions A and B, and its homogeneous region is dominated by high-order aggregates; increasing LiBr content also promotes the transformation from crystalline to amorphous LiBr . These findings clarify how salt anions regulate ionic aggregation, phase separation, and ion transport in nitrile-containing polymer electrolytes.

In this section, the interactions between lithium salt concentration, type, ionic liquid, and polymer are discussed. By selecting appropriate lithium salts, the phase separation morphology, ionic conductivity, and electrochemical stability of SPEs can be optimized, establishing the correlation between lithium salts and electrolyte phase separation. The resulting bi-continuous structure enables SPEs to achieve superior electrochemical performance without compromising their mechanical properties, thus obtaining SPEs with excellent overall performance.

5.2 Optimization of ion transport behavior in SPEs

Lithium-ion transport behavior primarily involves diffusion and migration within the ion conductor. Firstly, optimizing the design and performance of the ion conductor, such as adjusting the structure of the polymer electrolyte or directly modifying the soft phase in the polymer electrolyte that transports lithium-ions, aims to enhance lithium-ions' transport rate and efficiency. Due to the significant incompatibility between the different segment lengths of amphiphilic block copolymers (as shown in Fig. 8a), adjusting the volume fractions of the two blocks can construct microphase-separated ion-conducting structures, facilitating the design of ion transport channels. The microphase separation in SPEs suppresses the crystallization of the PEO polymer or releases the polymer chains from interfacial constraints, thereby

increasing the chain mobility in the conductive PEO phase and optimizing conductivity. The absence of mixed PEO chains also effectively enhances lithium-ion transport across a wide range of mixed fractions. Furthermore, the mechanical strength of SPEs remains largely unaffected. Similarly, gradient copolymers composed of two blocks with different gradient ratios have also been extensively studied [108]; a gradient copolymer displayed a morphology featuring diffusion domain interfaces between neighboring polar and nonpolar domains, characterized by gradual composition changes. While disordered copolymers are widely favored as polymer gel electrolytes, their lack of continuous pathways restricts conductivity. In the case of block copolymers, the sharp transition between polar and nonpolar segments impedes the formation of highly continuous morphologies. Additionally, nonpolar domains tend to bend at grain boundaries, resulting in dead ends within the conductive path. In contrast to the first two blends, gradient copolymers mitigate or minimize the presence of sharp boundaries between block copolymer regions. The smooth variation of copolymer monomer sequences, coupled with repulsive interactions between copolymer monomers, facilitates the formation of ordered microphases, thereby enabling smooth ion transport pathways. The synthesized electrolyte exhibited the highest ion conductivity, reaching 1 mS cm^{-1} .

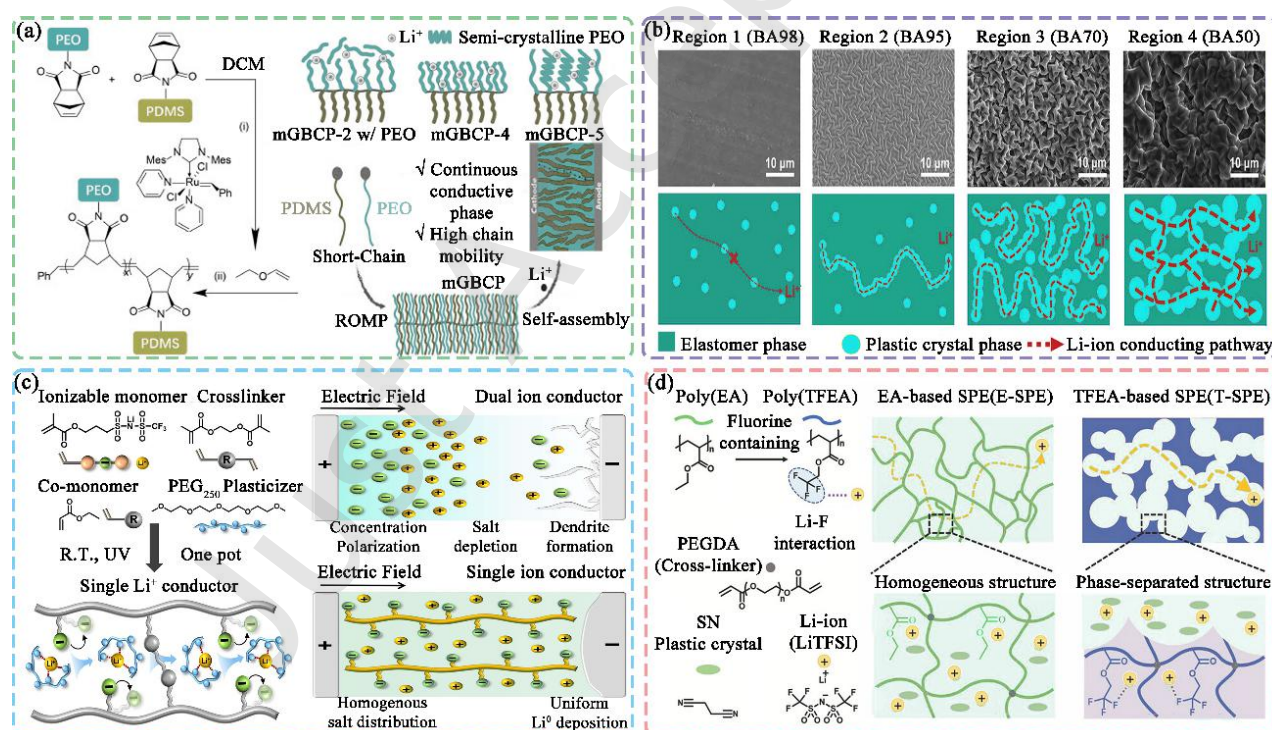


Figure 8. (a) Diagrammatic representations of how mGBCP-based Li^+ conductors self-assemble [108]. © Elsevier 2020. (b) SEM micrographs and structural schematics of PCEEs with varied BA/SN volume ratios [110]. © Wiley-VCH 2022. (c) The diagram illustrates SICPE preparation and uniform polar/non-polar region distribution in the electrolyte with PEG250 [112]. © Wiley-VCH 2023. (d) Design strategies for bicontinuous architectures, raw materials for preparing E-SPE and T-SPE, and schematic diagrams displaying their microstructural morphologies [116]. © Wiley-VCH 2024.

Secondly, it is essential to regulate the diffusion and migration behavior of lithium ions during their transport [109]. Ion migration is the directional motion of charge carriers under an electric field, and its rate depends on ionic mobility, field strength, conductive-phase conductivity, domain size, and phase connectivity in SPEs.

Elastomer electrolytes containing plastic crystals (PCEEs) were prepared from butyl acrylate (BA) and succinonitrile (SN); for example, BA98 denotes 98% BA [110]. As the SN volume fraction (f_{SN}) increased, ionic conductivity revealed four regions corresponding to distinct conductive morphologies. Region 1 (BA98) exhibited isolated SN domains and low conductivity. Region 2 (BA95) formed narrow, twisted channels. Region 3 (BA70) showed increased pathways and improved connectivity. Region 4 (BA50) developed large, interconnected worm-like channels with low curvature and the highest conductivity. Thus, the BA/SN ratio governs conductive-phase morphology, domain size, connectivity, and lithium-ion migration. Phase compatibility can be further improved using a four-arm miktoarm copolymer, PS-(PEO)₃, in which the stretched PEO arms reduce phase-domain size and enhance both ionic conductivity and mechanical strength compared with PS-PEO diblock copolymers [111].

Diffusion, in contrast, is stochastic ion transport driven by concentration gradients and governed by the gradient, temperature, and ionic diffusion coefficient. Conventional dual-ion conductors generally exhibit low lithium-ion transference numbers because Li^+ strongly interacts with Lewis-base sites in the polymer, causing anions to move faster. Anion accumulation near electrodes then produces concentration polarization, hindering Li^+ transport and promoting dendrite growth.

In contrast, diffusion describes the stochastic transport of ionic species inside conductive matrices driven by concentration differences. The diffusion kinetics are governed by three key factors: the ionic concentration gradient, ambient temperature, and the intrinsic diffusion coefficient of ions. Homogeneous electrolytes usually have no significant lithium concentration gradient. Still, under the electric field force, due to the strong coupling between lithium ions and the Lewis base sites of the polymer in a conventional dual-ion conductor (DIC), the Li^+ transport rate is usually slower than that of the corresponding anions, resulting in a low lithium-ion transference number (LTN). Additionally, inactive anions can form a concentration gradient near the electrodes, inevitably leading to concentration polarization, which affects lithium-ion transport and leads to dendrite formation issues.

Accordingly, designing and synthesizing single-ion conducting polymer electrolytes (SICPEs) constitutes a core research direction for solid-state lithium electrolyte systems. These systems are typically constructed by grafting polar functional groups (ionizable monomers) onto polymers or formed by polymerization of ionized monomers, other monomers, crosslinkers, and polyethylene glycol plasticizer (PEG 250). In Fig. 8c, SICPEs exhibited a uniform, dense, and interconnected morphology [112], which demonstrates a capability to effectively mitigate electrolyte concentration polarization, thereby substantially enhancing lithium-ion migration rates. Constructing SICPEs can provide polyanions that reduce the mobility of free anions through repulsion, promoting uniform ion distribution in the electrolyte, especially conjugated structure anions with a relatively low energy barrier to dissociate ion pairs, such as TFSI⁻, which exhibit weak pairing affinity with Li^+ ions, thereby facilitating the delocalization of negative

charges within ion pairs. Furthermore, the PEG250 plasticizer notably facilitated segmental mobility, even distributing polarized and non-polarized regions within the electrolyte. In turn, it facilitated lithium-ion transport, suppressed lithium-ion dendrite formation, and concurrently enhanced the conductivity, lithium-ion migration rates, and overall durability of batteries.

Apart from the design of single-ion polymers, there has been little research on the monomer molecules in SPEs. However, monomer chemistry plays a significant role in PIPS [113-115]. By designing monomers, ion-conductive domains (plastic crystals) can be captured in the in situ grown cross-linked polymers through PIPS, creating a bicontinuous structure composed of ionic-conductive phases and mechanical compositions. For instance, fluorinated monomers boost the hydrophobic character of polymer domains and facilitate phase segregation against hydrophilic components. Therefore, hydrophobic fluorine-bearing monomers are adopted for this purpose; the PIPS process can more easily produce phase-separation-driven SPEs with plastic crystals. For example, in Fig. 8d, different from E-SPE—a kind of ethyl acrylate-based SPE free of fluorinated monomer modification and phase separation structure—the PIPS-mediated in situ polymerization of TFEA and plastic crystals effectively enhances the mechanical characteristics, electrochemical properties, and interfacial stability of the electrolyte system [116]. While E-SPE possesses a homogeneous single-phase structure, T-SPE develops a distinct bicontinuous morphology with continuous ion-conductive plastic crystal pathways. Such structural differences stem from the thermodynamic immiscibility between in-situ formed poly(TFEA) matrices and plastic crystal phases. The fluorinated polymer T-SPE demonstrates remarkable interfacial stability with lithium metal anodes and high-voltage cathodes. LiF-abundant SEI and CEI layers deliver improved lithium redox reversibility and dense interfacial films, realizing stable Li metal deposition and well-preserved cathode structures. This result strongly validates the rational construction of phase-segregated SPEs via fluorine chemical engineering, which endows LMBs with ultralong cycling durability and high coulombic efficiency (CE).

This section provides a comprehensive discussion on the formation of continuous and high-speed ion transport channels within SPEs via various types of biphasic phase separation. The primary objective is to regulate lithium-ion diffusion and migration behaviors by leveraging phase separation to improve ion transport efficiency within the electrolyte matrix. Through systematic electrolyte design and theoretical analysis, we aim to establish a causal relationship between the phase-separated structure and lithium-ion transport behavior, thereby providing useful advice for the development of advanced SPEs with optimized electrochemical properties.

Ion transport behavior in SPEs is governed by several interrelated factors, including the ionic interactions of lithium salts, potential energy barriers to ion migration, and microstructural features such as voids and pores within the polymer matrix. First, modulating the ionic interactions of lithium salts presents

an effective strategy to enhance lithium-ion mobility. Electrostatic interactions with surrounding anions and polymer chains influence lithium ions under an applied electric field or concentration gradient. These interactions significantly affect the ionic conductivity and lithium-ion diffusion coefficient, particularly under near-equilibrium conditions. Second, inherent potential energy barriers impede lithium ion migration during ionic transportation. For SPEs, such energy barriers are primarily governed by the crystallinity of the polymeric matrix. Reduced crystallinity alleviates the movement restrictions of polymer chain segments, which diminishes interfacial energy barriers and enables efficient ion conduction. Finally, various microscale architectures, including cavities and pores, dominate the configuration of ionic migration routes. These intrinsic structural flaws function as continuous transport pathways to accommodate moving lithium ion complexes. Moreover, the size, morphology, and spatial distribution of these voids and pores can significantly influence the diffusion rate and directionality of lithium-ion transport, introducing both opportunities and challenges for performance optimization.

5.3 Progress of phase-separation-driven SPEs in LMBs

The critical parameters of phase-separation-driven SPEs for LMBs are listed in Table 1. These electrolytes have demonstrated impressive compatibility not only with conventional cathode materials such as LiFePO_4 (LFP), but also with high-voltage ternary cathodes. Impressively, multiple electrolyte systems retain outstanding specific discharge capacities even when subjected to high-current charge/discharge cycling, which demonstrates their great promise for deployment in advanced high-energy LMBs. In addition, lithium-lithium symmetric cells assembled with these phase-separation-based SPEs exhibit exceptional long-cycle stability, which highlights their effectiveness in suppressing lithium dendrite growth. This behavior also indirectly reflects the high mechanical strength imparted by the microphase-separated structure of the electrolytes. Collectively, these findings confirm that phase-separation-based SPEs offer a promising pathway toward stable, high-performance SSLMBs.

Table 1. Critical parameters of phase-separation-driven SPEs for LMBs

Phase-separation-based SPEs	σ (mS cm^{-1})	ESW (V)	Electrode	Li plating/ stripping	Discharge capacity (mAh g^{-1})	Testing temper- ature ($^{\circ}\text{C}$)	Ref.
$\text{LiTf}_2\text{N/TG/BT/MTA/DMBA/BEDA}$	1.00	3.00	-	-	-	25 $^{\circ}\text{C}$	[62]
$\text{LiTSPEEK/P(PEGMMA)/PC}$	0.17	5.19	$\text{Li} \text{LFP}$	-	121.7 (0.2C)	25 $^{\circ}\text{C}$	[66]
$\text{BA/PEGDA/SN/LiTFSI}$	1.10	4.50	$\text{Li} \text{NCM}$	1 mA cm^{-2} , 500 h	130.0 (1 mA $\cdot$ cm^{-2})	20 $^{\circ}\text{C}$	[70]

SEO (16-16)/LiTFSI	0.30	-	-	-	-	90 °C	[84]
HE-PEO/PVDF/LiTFSI	0.40	4.80	Li LFP	1 mA cm ⁻² , 1100 h	132.0 (1C)	25 °C	[88]
PEO- <i>b</i> -PnBA/LiTFSI	0.10	-	-	-	-	~70 °C	[89]
hbPPEGMAm-s-PSn/LiTFSI	0.09	4.34	Li LFP	0.05 mA cm ⁻² , 1400 h	142.0 (0.2C)	60 °C	[91]
P(UA-co-ACMO)-LiTFSI	2.18	-	-	-	-	25 °C	[105]
BA/PEGDA/SN/LiTFSI	1.00	4.50	Li NCM	5 mA cm ⁻² , 1000 h	3.3 mAh cm ⁻² (0.1 mA cm ⁻²)	20 °C	[110]
PEG ₂₅₀ /PEGMA/EDA/LiTFSI/FEC	0.24	> 4.20	Li LFP	0.2 mA cm ⁻² , 1000 h	135.5 (0.5C)	22 °C	[112]
TFEA/PEGDA/SN/LiTFSI	1.00	> 4.50	Li LFP	-	162.5 (0.5C)	30 °C	[116]
PPaB-MT/PVDF-HFP/LiTFSI	0.01	4.70	-	-	-	25 °C	[117]
PDADMA-FSI-LiFSI	0.07	>5.00	Li LFP	0.1 mA cm ⁻² , 400 h	158.0 (C/15)	80 °C	[118]
PEO@BPIL-3	0.22	5.00	Li LFP	0.1 mA cm ⁻² , 400 h	163.0 (0.2C)	60 °C	[119]
PHU-SN/LiTFSI/LiDFOB	0.58	4.60	Li LFP	0.05 mA cm ⁻² , 700 h	150.0 (1C)	60 °C	[120]
UHMWPEO/PVDF/DES	1.27	4.00	Li LFP	0.5 mA cm ⁻² , 400 h	150.7 (0.5C)	30 °C	[121]
CA-PEGMEA-SN-LiTFSI	1.90	4.90	Li NCM	0.2 mA cm ⁻² , 400 h	126.0 (2C)	25 °C	[122]
PVDF-LPPOSPE	0.48	4.80	Li NCM	1 mA cm ⁻² , 1200 h	150.0 (1C)	25 °C	[123]
eEP (pD5T1-M4-Z)/LiTFSI/PC	0.43	4.40	Li LFP	1 mA cm ⁻² , 1800 h	150.0 (0.5C)	60 °C	[124]
PVDF/MoS ₂ /LiFSI	0.65	4.70	Li NCM	1 mA cm ⁻² , 500 h	140.0 (3C)	25 °C	[125]

6 Perspectives and conclusions

Polymer electrolytes offer outstanding flexibility and ease of processing, making them attractive candidates for the development of high-energy SSLMBs. However, inherent drawbacks, including insufficient ionic conductivity and unfavorable electrode-electrolyte interfacial compatibility, still restrict SSLMBs in terms of cycling durability and rate capability. This review summarizes the various forms, optimization strategies, and potential applications of phase separation techniques in the development of SPEs for LMBs. The optimization approaches primarily focus on the rational selection and modification of the polymer matrix, as well as the incorporation of a secondary phase that promotes favorable interactions. As illustrated in Fig. 9, the enhancement of SPE performance can be systematically achieved through tailored material synthesis, controlled phase separation, and comprehensive characterization techniques.

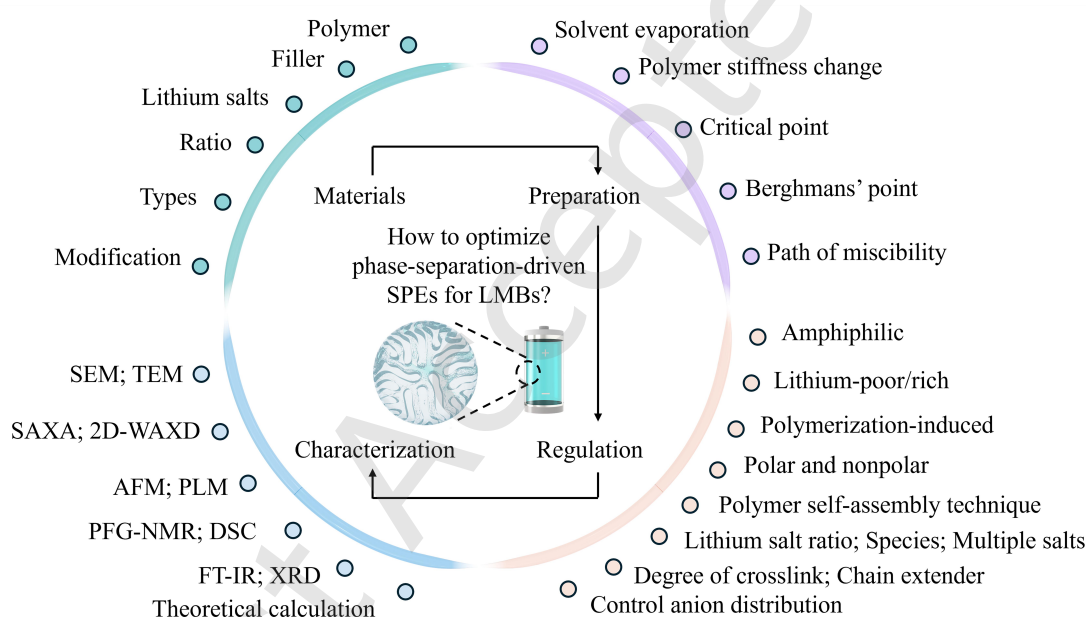


Figure 9. Summary of strategies toward optimizing phase-separation-based SPEs.

Systematically addressing performance and application bottlenecks of phase-separation-based SPEs can lead to breakthroughs from the following five perspectives:

(1) Deepen the understanding of SPEs

The interplay between components in SPEs, their structural dynamics, and resulting electrochemical behaviors is inherently complex. This review begins by exploring the phase diagram of SPEs and examines interactions between polymer phases as well as ion-polymer interactions within the matrix. Key factors — such as polymer structure, type, molecular weight, lithium salt selection, functional fillers, and processing solvents — are highlighted for their influence on electrolyte structure and function. Elaborating the underlying mechanisms behind these correlations is indispensable to rationally engineering advanced SPEs with customizable electrochemical properties.

(2) Synergistic optimization of ionic conductivity and mechanical properties of SPEs

Relatively weak ionic conductivity stands as a primary bottleneck restricting the practical application of polymer electrolytes. Approaches such as increasing lithium salt content, incorporating plasticizers (e.g., small organic molecules or ionic liquids), or introducing solvents to expand polymer free volume can improve ion transport. However, these often compromise mechanical integrity and electrochemical stability. SPEs offer a promising solution by leveraging phase separation to combine rigid and flexible polymer segments. This synergy can lead to high ionic conductivity and enhanced shear modulus, effectively suppressing lithium dendrite formation and improving battery performance.

(3) Addressing cathode-electrolyte interface challenges

The contact interphase formed between SPEs and cathode materials exerts a dominant influence on the long-cycle performance of SSLMBs. Mechanical strain at the solid-solid interface during cycling can cause delamination, interfacial cracking, and increased impedance, leading to capacity degradation or battery failure. Incorporating a flexible phase within SPEs helps maintain stable interfacial contact throughout cycling. Moreover, in situ casting of the SPE directly onto the cathode can create an integrated electrode-electrolyte composite, substantially lower interfacial resistance and enhancing electrochemical performance.

(4) Exploring low-enthalpy, high-entropy SPEs without phase separation

SPEs incorporate the advantages of polymer solid electrolytes, most doped with inorganic fillers, combining the benefits of mixed phases. This composite solid electrolyte is particularly suitable for large-scale production of SSLMBs. Furthermore, choosing various electrolyte components can significantly broaden the preparation of SPEs, enabling compatibility with a wider range of electrode materials. However, there are cases where SPEs do not undergo phase separation. For example, low-enthalpy, high-entropy SPEs [126-128] are also a research hotspot in lithium-ion batteries. Through various modifications, these electrolytes can significantly disrupt polymer chains, suppress polymer crystallinity, adjust polymer molecular orientation, and increase the disorder of the polymer, which can generate substantial free ions and high mobility, effectively driving lithium-ion storage and offering novel insights into developing phase-separation-based SPEs in lithium-ion batteries.

(5) Accelerate large-scale production and application of SPEs

Encouraging results from single-cell SSLMBs based on SPEs suggest their suitability for practical applications. SPEs are compatible with continuous roll-to-roll manufacturing processes, offering advantages such as reduced short-circuit risk in stacked configurations. Nevertheless, substantial challenges remain when translating laboratory-scale systems to roll-to-roll industrial-scale production. Limited residence time on production lines drives phase separation into a far-from-equilibrium kinetic regime, where shear-field, temperature-field and solvent-evaporation rates exhibit spatial inhomogeneity across wide-format films. Beyond reproducing laboratory-scale

molecular formulations, industrial manufacturing requires precise control over the shear history of slurries and step-wise gradient drying-quenching procedures, to accomplish nucleation and growth of nanophases within a short time and rapidly arrest the target morphology. Meanwhile, chemical or physical cross-linking must be adopted to suppress phase coarsening during material storage and cell hot-pressing. Restricted by characterization costs, nanoscale phase structures are mostly evaluated via offline sampling, and real-time in-line monitoring for full-roll films is difficult to achieve. Consequently, closed-loop control linking processing conditions, microstructures and electrochemical performance constitutes the major bottleneck for mass production.

Data availability

Not applicable.

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Declaration of competing interest

The authors declare that they have no competing interests.

Author contribution statement

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Use of AI statement

None.

Reference

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