



Structural design strategies of polymer binders for Silicon-based anodes in lithium-ion batteries

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Keywords:

Polymeric binder, Si anode, binder-electrode interaction, evolution

Citation: Lim, S. Y.; Kim, J. H.; Mun, J. Structural design strategies of polymer binders for Silicon-based anodes in lithium-ion batteries. *Microstructures* 2026, 6, 2026031. <https://dx.doi.org/10.20517/microstructures.2025.93>

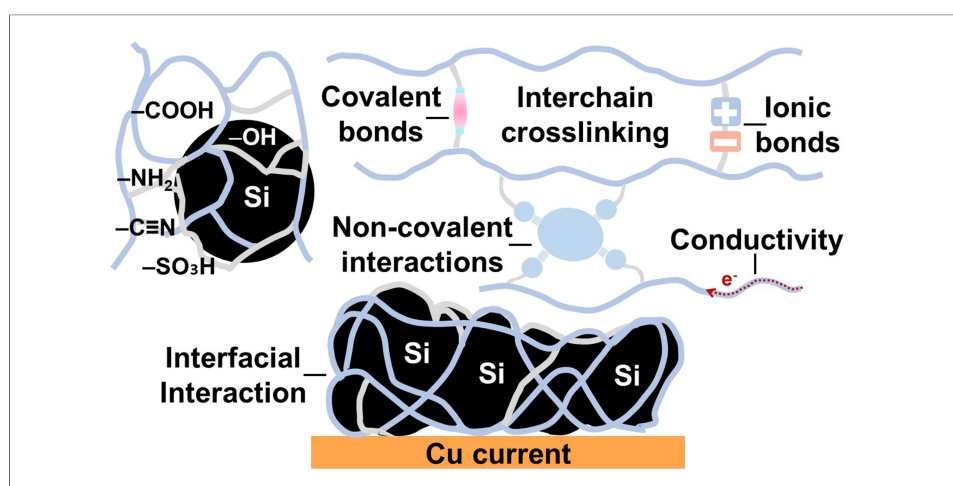
Received: 29 Jun 2025
First Decision: 12 Aug 2025

Revised: 25 Aug 2025
Accepted: 1 Sep 2025
Published: 13 Mar 2026

Academic Editor:
Zaiping Guo

Copy Editor:
Fangling Lan

Production Editor:
Fangling Lan



Abstract

Silicon (Si) anodes have emerged as promising candidates for next-generation lithium-ion batteries owing to their high theoretical capacity. However, their practical application is hindered by severe volume expansion and unstable electrode interfaces during cycling. Polymer binders play a critical role in mitigating these issues by maintaining electrode integrity and enhancing interfacial stability. This review provides a systematic classification of polymer binders for Si-based anodes according to their binding mechanisms, including covalent, hydrogen-bonding, and supramolecular interactions. The discussion emphasizes how structural configurations, such as linear, branched, and cross-linked architectures, affect mechanical resilience, adhesion strength, and compatibility with high-loading electrodes. Recent advances in multifunctional and dynamic cross-linked binders are highlighted, with particular focus on strategies to accommodate large volume changes and suppress interfacial degradation. In addition, a comparative analysis of advantages and

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limitations for various binder systems is provided, along with perspectives on future development trends. This work aims to guide the rational design of polymer binders for achieving stable, high-energy-density Si-based anodes.

INTRODUCTION

Lithium-ion batteries (LIBs), which are deeply integrated in our daily lives, are a type of secondary battery that operates based on redox electrochemical reactions involving lithium ions. Among all metals, lithium is the lightest and has a very low standard reduction potential, enabling lithium-based batteries to deliver not only high specific capacities but also high operating voltages exceeding 3 V. Owing to these advantages, LIBs have become essential for powering small electronic devices, such as mobile phones, and are also regarded as one of the most promising candidates for electric vehicles, a market expected to grow rapidly in the near future^[1-4]. The most commonly used anode material in LIBs is graphite, which is cost-effective and offers excellent cycling stability. However, its practical capacity is limited to approximately 350-370 mAh g⁻¹^[5-17], which poses a significant limitation for the development of high-energy-density LIBs. Due to this inherent capacity limitation of graphite, there has been an increasing drive to explore alternative anode materials with higher energy storage capabilities. Among them, Si is highly desirable for the next-generation anode.

Si is well known to be abundant in nature, inexpensive, and possesses a remarkably high theoretical capacity of approximately 4,200 mAh g⁻¹^[18-35], which is more than ten times that of graphite. Nevertheless, Si undergoes drastic volume expansion up to 400% during lithiation and shrinkage during delithiation^[36-41]. These extreme volume fluctuations induce mechanical failures, such as pulverization, electrode delamination, and layer separation^[42-47], ultimately leading to capacity degradation caused by electrically isolated particles and irreversible lithium consumption. To address these challenges, polymer binders have emerged as critical components in Si-based electrodes. Typically, binders serve as additives that maintain the adhesion between active material particles and between the electrode and the current collector, thereby preserving the mechanical integrity of the electrode^[48-51]. In the case of Si anodes, recent studies have emphasized that polymer binders play a far more critical role than previously considered, significantly influencing long-term cycling stability. A polymer binder is the only component in the electrode that ensures stable adhesion without inducing undesirable side reactions in organic electrolyte systems, even during repeated charge-discharge cycles. It can accommodate the extreme volume changes of Si, thereby maintaining mechanical stability and consistent electrochemical performance. Although the binder occupies only a small fraction of the total electrode mass, it plays a crucial role in maintaining cohesion among active materials, conductive additives, and the current collector, and in some cases contributes to enhanced ionic or electronic conductivity.

This review aims to systematically classify the various polymer binders reported to date based on their binding mechanisms, with particular emphasis on polymer-polymer and polymer-surface interactions, molecular structures, and mechanical properties. Through this analysis, we intend to provide a comprehensive understanding of how structural and interfacial design strategies affect the electrochemical performance of Si-based anodes. Over the past two decades, the development of polymer binders for Si anodes has progressed from the use of conventional PVDF binders to water-based CMC/SBR systems, and more recently to PAA-based formulations capable of accommodating high-Si loading. This evolution is summarized in [Figure 1](#), which presents an industrially oriented timeline of binder development, highlighting representative milestones and their technological significance. By establishing this historical and structural context, the Introduction provides a clear framework for readers to follow the detailed discussions and critical perspectives presented in the subsequent sections of this review.

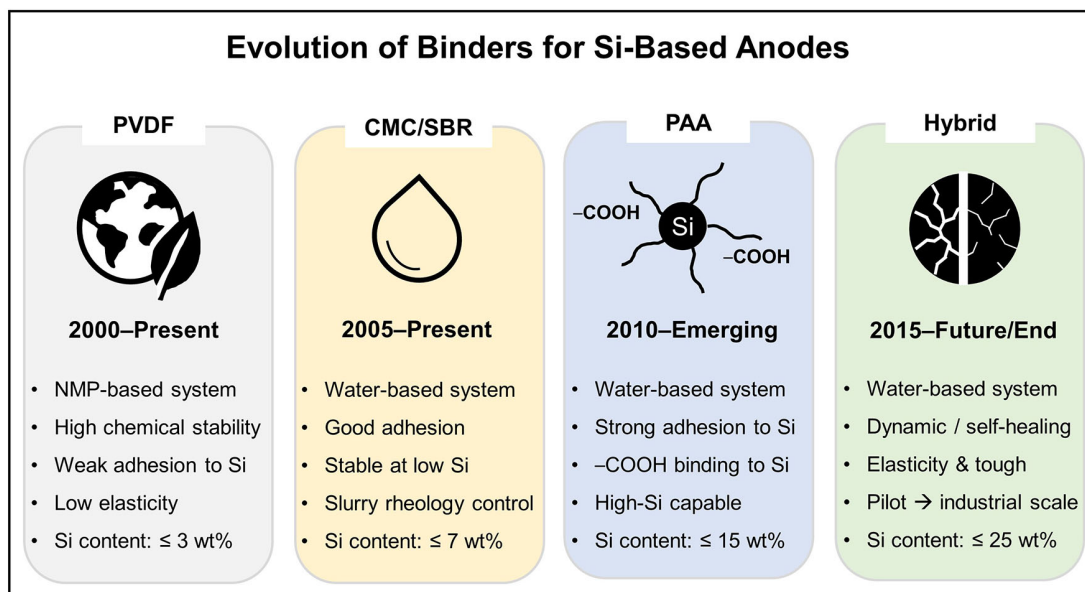


Figure 1. Roadmap of binder evolution for Si-based anodes. Conventional PVDF binders (2000–Present) exhibit high chemical stability but suffer from weak adhesion and poor elasticity. CMC/SBR systems (2005–Present) introduce water-based processing and improved adhesion, though stability is limited to low Si content. PAA binders (2010–Emerging) provide strong Si adhesion via –COOH anchoring and enable higher Si loading. Hybrid systems (2015–Future/End) feature cross-linked/branched architectures with improved toughness, self-healing behavior, and scalability toward industrial applications. The original figure was created by the authors.

WORKING FUNCTIONS OF BINDERS

This section outlines the essential roles of polymer binders in Si-based anodes, linking molecular-level interactions to macroscopic electrode behavior. We discuss how binders contribute to mechanical integrity, interfacial stability, and ion/electron transport, and identify key performance metrics that guide binder design for high-capacity applications.

Interaction mechanisms between polymer binders and electrode constituents

Polymer binders used in battery electrodes are applied in small quantities, typically below 3 wt% of the total electrode composition. Despite their limited proportion, significant research has been devoted to enhancing high-energy battery performance by engineering the chemical properties of polymeric binders. A comprehensive understanding of both the functional roles of binders in LIB electrodes and the operational mechanisms of Si anodes is essential for developing advanced binder systems that improve electrochemical performance. Various binder materials have been designed through structural tailoring and the incorporation of functional moieties to achieve high elasticity, strong interfacial adhesion, and mechanical flexibility. The following sections explore these roles in greater detail within the context of Si-based anodes. Although the adhesive mechanisms of binders are inherently complex and cannot be fully described by a single model, the most widely accepted binding mechanisms include mechanical interlocking, chemical bonding, van der Waals interactions, and electrostatic forces^[52]. When binders interact with active material and conductive additive particles, the system typically forms three distinct interfacial layers^[53,54]. First, upon dispersion in a solvent, the binder spreads uniformly across particle surfaces, forming a primary adhesion layer. Surrounding this, a secondary immobilized layer is established, where molecular-level interactions anchor adjacent polymer chains, reinforcing structural cohesion. Finally, residual free polymer chains give rise to an outer surplus layer, which contributes to the overall mechanical and chemical properties of the binder system. The specific configuration and properties of these interfacial layers are largely governed by the inherent characteristics of the polymer and the surface chemistry of the contacting materials. Variations in polymer composition, molecular weight, and functional groups can significantly influence how the binder

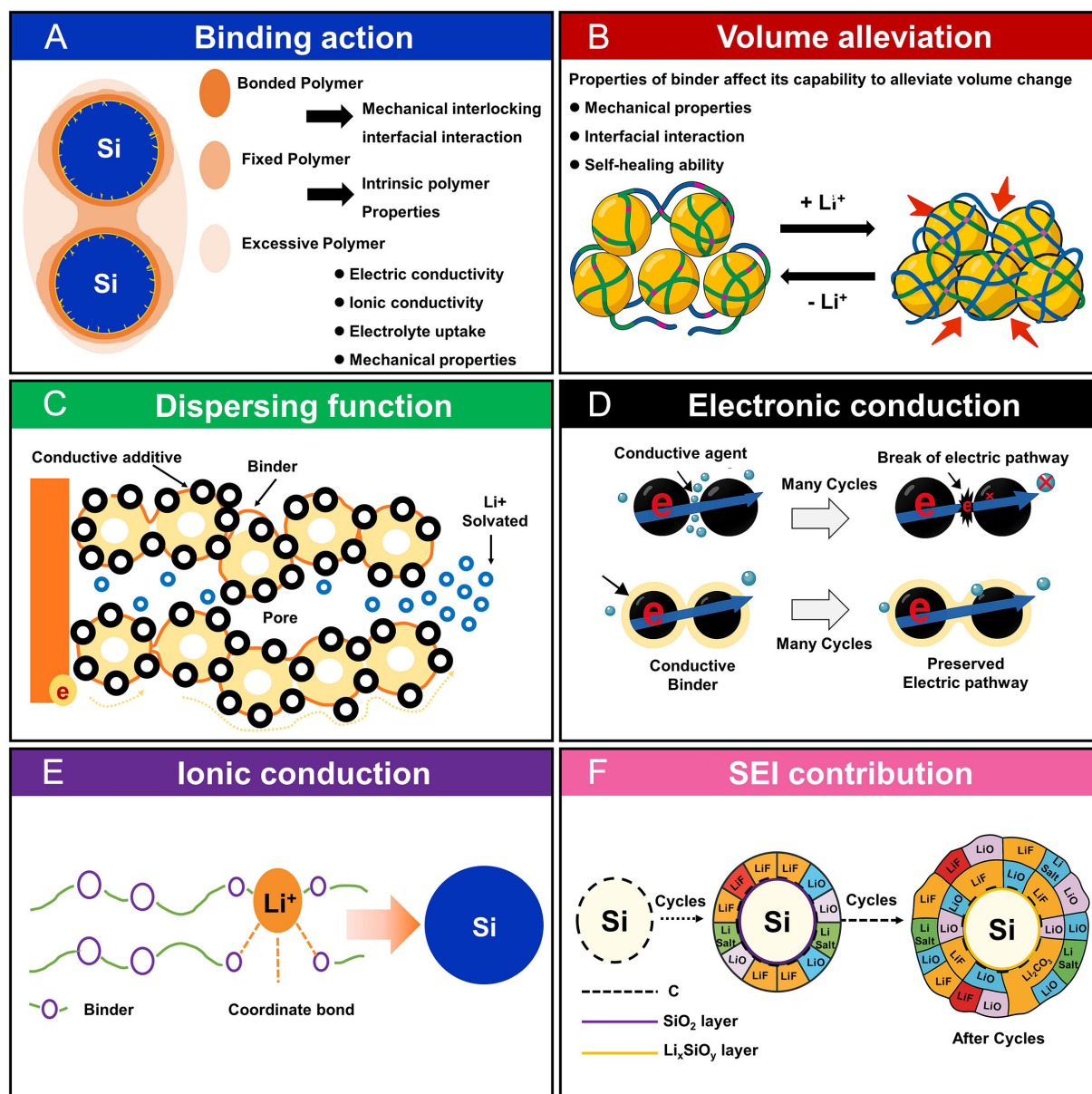


Figure 2. Schematic illustration of the functional roles of polymer binders in electrodes (A) Binding action; (B) Mitigation of volume expansion; (C) Dispersion of active materials; (D) Facilitation of ionic conductivity; (E) Enhancement of electronic conductivity; (F) Contribution to SEI formation. The original figure was created by the authors.

interacts with different particle surfaces, thereby affecting interfacial stability and electrode performance [Figure 2A]^[52]. Beyond this framework, several complementary theories such as adsorptive interactions, wetting dynamics, and acid-base interactions have also been proposed to further explain the complexity of binder adhesion mechanisms^[52]. In the case of Si anodes, this topic becomes even more critical. Si can expand by up to 300% during cycling, leading to severe mechanical disruption of the electrode and rapid capacity degradation. Understanding the precise bonding mechanisms at play is therefore essential for developing binders capable of accommodating these extreme volume fluctuations without compromising electrode integrity.

Maintaining structural integrity of Si electrodes with binders

The mechanical properties imparted by polymer binders play a critical role in accommodating the

substantial volumetric fluctuations experienced by Si electrodes during cycling [Figure 2B]. To effectively mitigate the mechanical stress induced by expansion and contraction, binders must exhibit key characteristics, such as tensile strength, adhesive strength, flexibility, and elasticity^[55]. When the interaction between the binder and Si particles is sufficiently strong, the resulting interfacial adhesion can exceed the stress generated by volume expansion, thereby stabilizing the electrode interface and maintaining structural integrity over repeated cycles. In addition to mechanical reinforcement, another essential function of polymer binders lies in their ability to disperse electrode components uniformly throughout the slurry. The primary role of a binder is to uniformly bind the active material and conductive agents via dispersion in solvent and to facilitate the formation of a homogeneous electrode slurry that coats the current collector evenly during the drying process [Figure 2C]. One of the critical challenges during slurry preparation is the propensity of Si particles to aggregate with conductive additives, which typically exhibit high specific surface area and fine particle size. This non-uniform dispersion can disrupt the uniformity of the electrode architecture and impair electrochemical performance. Therefore, polymer binders should be designed to promote homogeneous distribution of all electrode components throughout the mixing process.

In particular, polymers containing aromatic moieties are highly effective in dispersing carbon-based conductive agents via π - π stacking interactions between the aromatic rings of the binder and the graphitic surfaces of the additives. These noncovalent interactions suppress aggregation and promote uniform dispersion, thereby enhancing the formation of a continuous electronic network. As a result, both electronic and ionic transport within the electrode are improved [Figure 2D and E]. Given the importance of these functions, a wide range of polymeric materials has been employed as binders in LIB electrodes, each offering distinct structural and chemical properties.

Moreover, the solid electrolyte interphase (SEI) formed on the surface of active material critically influences the electrochemical behavior of LIBs [Figure 2F]. In Si anodes, continuous volume changes expose new surfaces, leading to ongoing SEI formation. The composition of the SEI layer can vary depending on the electrolyte used, and the resulting surface chemistry can affect the adhesion of the binder. The addition of binders plays a key role in promoting uniform dispersion of electrode components, which contributes not only to a more homogeneous SEI but also to a more stable interfacial structure. A uniformly distributed SEI is beneficial in reducing surface resistance during electrochemical reactions. In Si anodes, the SEI is primarily composed of reduction products such as Li_2CO_3 , LiF, and Li_2O ^[54]. Among these, LiF is particularly important for maintaining the mechanical and chemical stability of the SEI^[56]. Therefore, the formation of a stable SEI of appropriate thickness on the active material surface is critical for maintaining electrode capacity and prolonging cycle life. In addition to mechanical stability and SEI formation, the chemical stability of polymer binders toward liquid electrolytes is a critical factor affecting the long-term performance of Si anodes. During extended cycling, binders may undergo swelling, partial dissolution, or degradation due to reactions with electrolyte components, such as LiPF_6 salt and carbonate solvents. Such degradation can weaken interfacial adhesion and disrupt the electronic network within the electrode. Functional groups in the binder, including -OH, -COOH, and amide moieties, can interact with electrolyte additives, such as fluoroethylene carbonate (FEC), influencing SEI composition and stability. As reported in a recent study by An *et al.*,^[57] optimizing the chemical compatibility between the binder and electrolyte is essential to suppress undesirable side reactions and maintain the mechanical integrity of the electrode. Therefore, designing binders with enhanced chemical resistance, reduced solubility in electrolyte, and the capability to maintain robust adhesion under electrochemical stress is critical for improving both cycling stability and coulombic efficiency of Si-based electrodes. Polymer binders aid in this process by providing mechanical support, preventing interfacial collapse during repeated volume changes of Si^[58]. Following the discussion on the mechanical properties and dispersibility of polymer binders, it is also essential to examine how molecular-level interactions, particularly those involving functional groups, govern the performance of Si anodes.

For Si anodes, polymers have been actively engineered not only to improve electrolyte wettability and ionic/electronic conductivity, but also to reinforce mechanical robustness and electrochemical stability, both of which are crucial for managing drastic volume changes during cycling. Therefore, the molecular architecture of the binder polymer is a key determinant of electrode performance.

CLASSIFICATION OF POLYMER BINDERS BY ORIGIN

Si tends to be oxidized in air to form a surface layer of SiO_2 (or SiO_x), which contains hydroxyl (-OH) groups that impart hydrophilic properties to the surface^[59-63]. Hydrophilic functional groups improve electrolyte wettability and dispersion, which can facilitate ion transport in the composite electrode. These polymers not only form stronger interfacial bonds with Si particles but also improve adhesion to the current collector, thereby contributing to improved structural stability of the electrode. Furthermore, the diversity and density of functional groups within the binder matrix give rise to various types of molecular interactions such as hydrogen bonding, electrostatic attraction, and van der Waals forces that collectively influence the electrode's mechanical integrity and cycling performance. As these interactions are highly dependent on the chemical functionalities present in the polymer backbone, optimizing the binder composition to tailor such interactions is a key strategy in the design of next-generation binders for high-capacity Si anodes. While the chemical functionality of polymer binders governs interfacial behavior at the molecular scale, their three-dimensional (3D) structural architecture plays an equally important role in maintaining mechanical durability. The degree of polymer chain branching, cross-linking, and network formation determines the binder's capacity to accommodate internal stress and to preserve the mechanical stability of the electrode during continuous cycling.

Polymer binders are commonly categorized into linear, branched, and cross-linked structures, each offering distinct mechanical responses to the significant volume changes associated with Si anodes [Figure 3]^[64,65]. Depending on their structural configuration, these binders exhibit varying capabilities to buffer or relieve mechanical stress during electrode expansion and contraction. To address the mechanical degradation associated with volumetric fluctuations of Si, recent research has focused on developing binders with networked polymer architectures. These systems introduce multiple interaction points through covalent bonds or combined covalent and noncovalent linkages, which limit polymer chain deformation and improve mechanical resilience^[55]. Such reinforced polymer networks enable Si anodes to better tolerate repeated volume expansion and contractions, ultimately contributing to enhanced structural stability and prolonged cycle life.

Natural polymer binders

In this subsection, we focus on naturally derived polysaccharide binders, which offer environmental benefits, aqueous processability, and abundant functional groups for Si adhesion. We discuss their advantages, performance limitations at high Si loading, and industrial considerations for large-scale implementation.

Naturally derived polysaccharides (e.g., CMC, chitosan, alginate, carrageenan) provide dense networks of -OH/-COOH^[63] groups that enable multi-point adsorption on hydroxylated Si surfaces via hydrogen bonding and, under appropriate processing, esterification. Compared with synthetic binders, their advantages are low cost, aqueous processability, and benign rheology for large-area coating^[65]. However, their molecular-weight distributions and batch variability can lead to dispersion inconsistency and viscosity drift at scale. Across the literature, three common behaviors emerge: (i) cellulose- or alginate-type binders improve early-cycle cohesion and facilitate more uniform SEI formation; (ii) performance gains diminish at higher Si fractions unless elasticity and interparticle bridging are reinforced; and (iii) slurry stability is sensitive to the degree of substitution/oxidation and to the presence of co-binders or salts. These trends indicate that polysaccharides are highly effective as industrial baselines for low-to-moderate Si loading, while

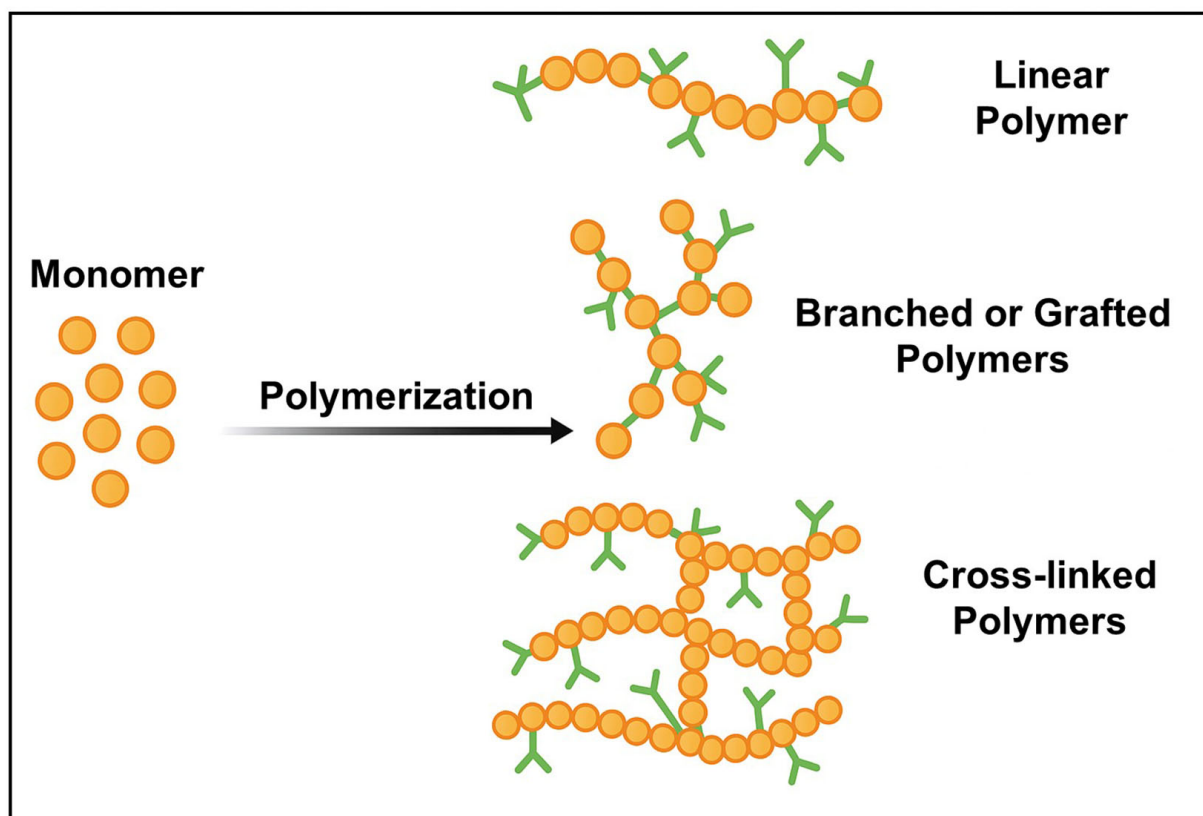


Figure 3. Representative polymer structures formed by polymerization: linear, branched/grafted, and cross-linked networks. This original figure was created by the authors.

high-loading electrodes require either compositional hybridization or architectural modification to sustain mechanical compliance and stable interfaces over long cycling.

From a manufacturing viewpoint, we find that controlling substitution/oxidation levels and ionic strength is as important as choosing the polysaccharide family itself, because these parameters dictate slurry stability and coating uniformity at line scale. Representative examples include Carboxymethyl cellulose (CMC) [Figure 4A]^[16,65,66], Chitosan (CS) [Figure 4B]^[67,68], Sodium alginate (SA) [Figure 4C]^[69], and Lambda (λ)-carrageenan (L-CGN) [Figure 4D]^[70,71]. Among them, CS is one of the most abundant natural polysaccharides, similar to CMC. To overcome its poor water solubility, Lee *et al.* developed a network binder by incorporating epoxidized natural rubber (ENR) into chitosan. When applied to Si anodes, this binder maintained a high specific capacity of approximately 2,310 mAh g⁻¹ even after 500 cycles [Figure 4E]^[72]. This performance was attributed to the synergistic effect of strong adhesion and elastic buffering in the polymer network. Polysaccharide-based binders can form not only hydrogen bonds but also covalent ester bonds through condensation reactions between the carboxyl groups in the binder and the hydroxyl groups on the Si surface. CMC, a representative linear binder, is widely used in commercial applications, typically in combination with styrene-butadiene rubber (SBR)^[16]. Owing to its excellent thickening and dispersing properties, low cost, safety, and eco-friendliness, CMC/SBR binders have been commonly adopted. Ko *et al.* demonstrated that a graphite/a-Si nanolayer composite electrode using 4 wt% CMC/SBR maintained a reversible capacity of 450–500 mAh g⁻¹ for more than 100 cycles^[73]. This performance was ascribed to the high elongation of the binder, strong adhesion, and formation of a stable SEI layer. CMC offers reliable thickening and dispersion in water, strong polar interactions with Si, and compatibility with SBR in commercial lines. Its main limitation at higher Si contents is insufficient elastic

recovery under large volume change; this can be mitigated by modest PAA blending or by tuning the degree of substitution to balance viscosity and film ductility. In recent years, the development of water-soluble cellulose-derived binders, such as CMC, has further enhanced the stability of Si anodes by reinforcing interparticle cohesion and facilitating the formation of a stable SEI layer^[31]. These improvements are primarily attributed to their strong hydrogen-bonding capability and effective bridging effects between active material particles. However, while the CMC/SBR binder may be suitable for Si contents below 5 wt%, higher Si loadings demand binders with enhanced interfacial adhesion, better dispersibility, and improved mechanical elasticity. In this context, another natural polysaccharide, SA, exhibits excellent elasticity and contains abundant carboxyl groups, contributing to strong adhesion with Si surfaces. Kovalenko *et al.* were the first to demonstrate the effectiveness of SA as a binder for Si anodes, showing its ability to mitigate large volume expansion of Si through superior mechanical support^[69]. The resulting electrode retained 85% of its initial capacity after 100 cycles [Figure 4F]. To further enhance its performance, mussel-inspired catechol groups with strong binding capability were grafted onto the alginate backbone. A catechol-grafted PAA binder improved cycling performance and slurry rheology^[64,74], and a catechol-grafted alginate binder (Alg-C) maintained $> 2,000 \text{ mAh g}^{-1}$ over 400 cycles [Figure 4G]. Overall, alginate offers high elasticity and abundant carboxylates for strong adhesion, but batch variability and slurry sensitivity to multivalent cations can complicate scale-up. Partial functionalization (e.g., catechol grafts) effectively improves adhesion and crack suppression, although it adds synthesis complexity and cost.

In addition to polysaccharides, various other bio-based polymers have been explored as sustainable binder materials. Jang *et al.* designed a nature-inspired L-CGN binder derived from sulfated polysaccharides of red algae^[71]. This binder contains abundant -OH and $-\text{SO}_3^-$ functional groups, which enable strong hydrogen bonding with the -OH groups on the Si surface. As a result, even after 50 cycles, the CGN binder demonstrated superior interfacial adhesion to Si particles and internal cohesion within the electrode, as confirmed by SEM analysis, compared to conventional binders such as SA, CMC, and PAA. This case highlights the effective applicability of naturally derived functional groups in Si anode binder systems [Figure 4H]^[71]. In addition, Kim *et al.* addressed the high viscosity and solubility issues of natural polysaccharide binders by introducing oxidized λ -carrageenan (Ox-L-CGN)^[70]. Through partial oxidation using sodium periodate, aldehyde functional groups were introduced, leading to a reduction in molecular weight and an improvement in rheological properties. The optimized binder (Ox-L-CGN-5), with its appropriate solubility, achieved a high initial Coulombic efficiency of 78.6% and a reversible capacity of $2,534 \text{ mAh g}^{-1}$ after 100 cycles, while also exhibiting excellent performance under high-mass-loading and nanoscale Si conditions.

Notably, excessive oxidation (Ox-L-CGN-10) hindered effective network formation, resulting in increased electrode pulverization and unstable SEI regeneration, which significantly degraded electrochemical performance. This degradation is presumed to result from reduced solubility, which compromised the structural integrity and stability of the water-processable binder system [Figure 4I]^[70]. Sulfated polysaccharides can enhance adhesion and internal cohesion via hydrogen bonding and electrostatic interactions; controlled oxidation lowers viscosity and improves coatability, yet over-oxidation weakens network formation and accelerates pulverization at high strain. Despite their appeal in terms of sustainability and processing advantages, natural polymer binders pose challenges, such as irregular molecular weights and complex chemical structures, which can lead to inconsistent performance. Nevertheless, the environmental and functional benefits of naturally derived materials continue to drive intensive research in this area. While polysaccharides, such as guar gum (GG) and gum arabic (GA), have been employed as components in certain binder systems, they are not considered key materials for Si anode applications and are thus excluded from the scope of this study.

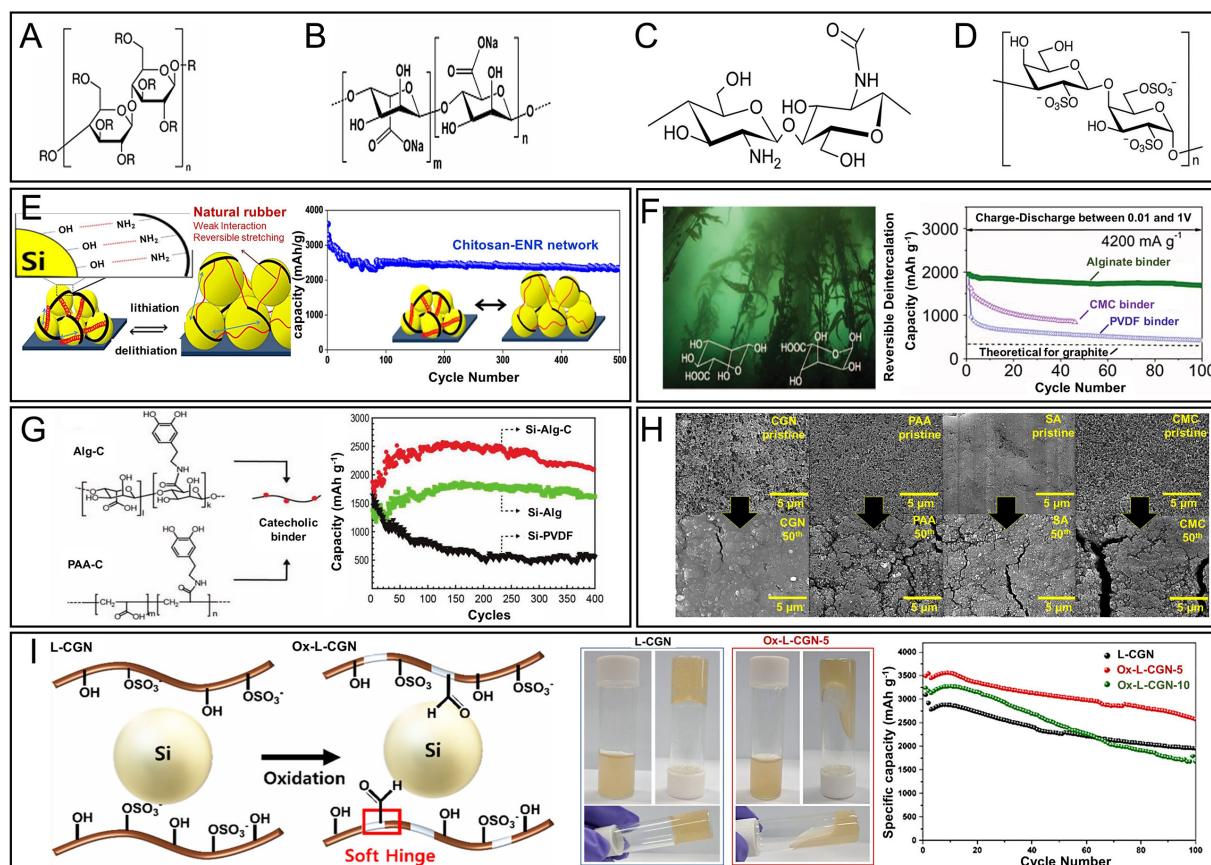


Figure 4. Chemical structures of polymer binders containing hydrophilic functional groups and their effects on Si anode performance. (A) CMC; (B) SA; (C) CS; (D) L-CGN; (E) Design of the binder material (left) and cycling stability (right) of a Si anode using a natural rubber/chitosan network binder. Adapted with permission from ref. [772]; (F) Chemical structures of the mannuronic and guluronic acid repeat units (left); cycling performance of nano-Si anodes with alginate (SA), CMC, and PVDF binders (right; 0.01–1.0 V vs. Li/Li⁺). Adapted from ref. [644]; (G) Catechol-conjugated polymer binders and cycling performance of Si electrodes using Alg-C, Alg, and PVDF binders. Adapted from ref. [644]; (H) Cycling performance of Si electrodes using different natural polymer binders (CGN, PAA, SA, CMC). The Si@CGN electrode demonstrated the highest capacity retention over 100 cycles, underscoring the superior binding and structural stabilizing effect of lambda carrageenan. Adapted with permission from ref. [771]; (I) Schematic illustration of the synthesis of Ox-L-CGN, comparison of its solubility in distilled water with that of L-CGN, and cycling performance of Si electrodes using different polymer binders. The optimized Ox L-CGN 5 binder demonstrated improved solubility and enhanced electrochemical performance, attributed to its optimized viscosity and formation of a stable polymer network. Adapted with permission from ref. [70].

Synthetic polymer binders

This subsection examines synthetic binders, highlighting their tunable architectures and ability to integrate functional groups not easily accessible in natural polymers. We outline how molecular design impacts mechanical resilience, adhesion to Si, and compatibility with high-solid-loading slurry processes.

Synthetic binders offer tunable architectures and functionalities that are difficult to achieve with natural polymers. For Si electrodes, the central design problem is to combine strong interfacial bonding with elastic stress dissipation and electrolyte compatibility while maintaining slurry processability at high solid loading. Here we synthesize cross-study evidence into three takeaways: linear fluorinated baselines are robust but adhesion-limited on Si; acrylic chemistries (e.g., PAA) add dense -COOH sites and stiffness for higher Si content; and architectural modifications (branched/cross-linked/dynamic) are required when areal loading and volumetric strain exceed the elastic window of linear binders. In the following discussion, we focus on representative synthetic binders and their performance-structure relationships, beginning with the widely used fluorinated baseline PVDF and progressing to non-fluorinated acrylic and nitrile-based systems. Notably, synthetic polymers, like polyvinylidene fluoride (PVDF) [Figure 5A] [75,76], a fluoropolymer, as well as

non-fluorinated options like polyacrylic acid (PAA) [Figure 5B]^[11,75,77-80], and Polyacrylonitrile (PAN) [Figure 5C]^[81], are being actively researched. PVDF, a fluorocarbon-based binder, has a chemical structure of $-(\text{CH}_2-\text{CF}_2)_n-$ and possesses excellent thermal and electrochemical stability, making it the most widely used binder in commercial LIBs. From an industrial standpoint, PVDF remains a commercial baseline due to thermal/chemical stability and well-established processing. However, its non-functional linear backbone interacts weakly with Si, and NMP-based processing plus gel-like swelling in certain electrolytes can impair coating uniformity and interparticle contact under large strain. Heat-treatment or copolymer strategies partially enhance mechanical integrity, but for Si-rich electrodes, the adhesion/elasticity deficit typically necessitates alternative or hybrid binders. The presence of fluorine (F) atoms in fluoropolymer materials reacts with lithium ions to form LiF in the SEI layer, which is electronically insulating but mechanically and chemically stabilizing; this contributes to interfacial stability rather than providing electronic conductivity^[56,63]. However, PVDF binders have several issues when used as binders for Si anode materials. The first issue with PVDF arises from its non-functional linear chain structure, which can lead to weak interactions with the Si surface, potentially causing a decline in cycle performance. PVDF also lacks flexibility and mechanical properties, which limits its ability to accommodate the volume changes occurring in Si anode electrodes. This can result in the breakage of adhesive bonds between particles, further impacting battery performance. Various copolymers containing the PVDF group have been applied and studied as electrode binders; however, several limitations have been reported. Despite its high polarity and good interaction with polar organic electrolytes, this fluoropolymer tends to expand and become gel-like under high-temperature conditions, reducing its physical performance. When PVDF dissolves in a solvent, it forms a high-viscosity solution, which can significantly hinder the uniform dispersion of active materials and conductive additives. This can lead to uneven electrode coatings, ultimately blocking ion channels and negatively impacting performance. To address the challenges associated with fluoropolymer materials, several approaches have been suggested. A key method involves enhancing performance through thermal treatment. For example, after 50 cycles, PVDF-based binders treated at 120 °C showed a 20.1% retention in capacity ($< 250 \text{ mAh g}^{-1}$), while heat treatment at 220 °C effectively reduced the expansion of the Si electrode [Figure 5D]. This resulted in a significant increase in capacity retention, reaching 75.4% ($> 1,000 \text{ mAh g}^{-1}$), while also improving the stability of the electrode^[82,83]. While fluorinated polymers such as PVDF have been widely employed due to their excellent electrolyte compatibility and wettability, they present several limitations. Most notably, the use of flammable and potentially explosive organic solvents raises secondary safety and environmental concerns. In response, fluorine-free polymer binders are emerging as cost-effective, safer, and more environmentally friendly alternatives, garnering increasing attention and research interest. Among these alternatives, acrylic-based polymers represent a typical class synthesized via controlled polymerization techniques. Their physical and chemical properties vary depending on the functional groups introduced into the monomers. One representative example is PAA, polymerized from acrylic acid monomers bearing $-\text{COOH}$, which has demonstrated promising performance as a binder for Si anodes^[84]. Because each monomer unit of PAA contains a $-\text{COOH}$, the polymer provides a high density of acidic sites for strong interactions with Si. Moreover, PAA exhibits robust mechanical properties that help maintain electrode integrity during the severe volume changes associated with lithiation and delithiation. The use of PAA in Si anodes was first reported in 2010, where a Si/PAA electrode achieved stable cycling performance, retaining approximately 75% of its initial capacity over 100 cycles at 0.5 C^[62]. Subsequent studies found that the addition of alkaline agents, such as NaOH, could significantly enhance the electrochemical performance of PAA-based binders, increasing their capacity from 1,300 to 2,000 mAh g^{-1} . Furthermore, PAA has emerged as a viable alternative to increase the Si content in graphite/Si composite electrodes. PAA not only exhibits strong adhesion to Si particles but also offers water-processability, eliminating the need for toxic organic solvents such as NMP, which is a key advantage for eco-friendly and scalable electrode fabrication^[85]. PAA provides dense carboxylates for strong interfacial bonding and higher matrix stiffness, supporting increased Si fractions in graphite/Si composites. Industrial interest stems from aqueous processing,

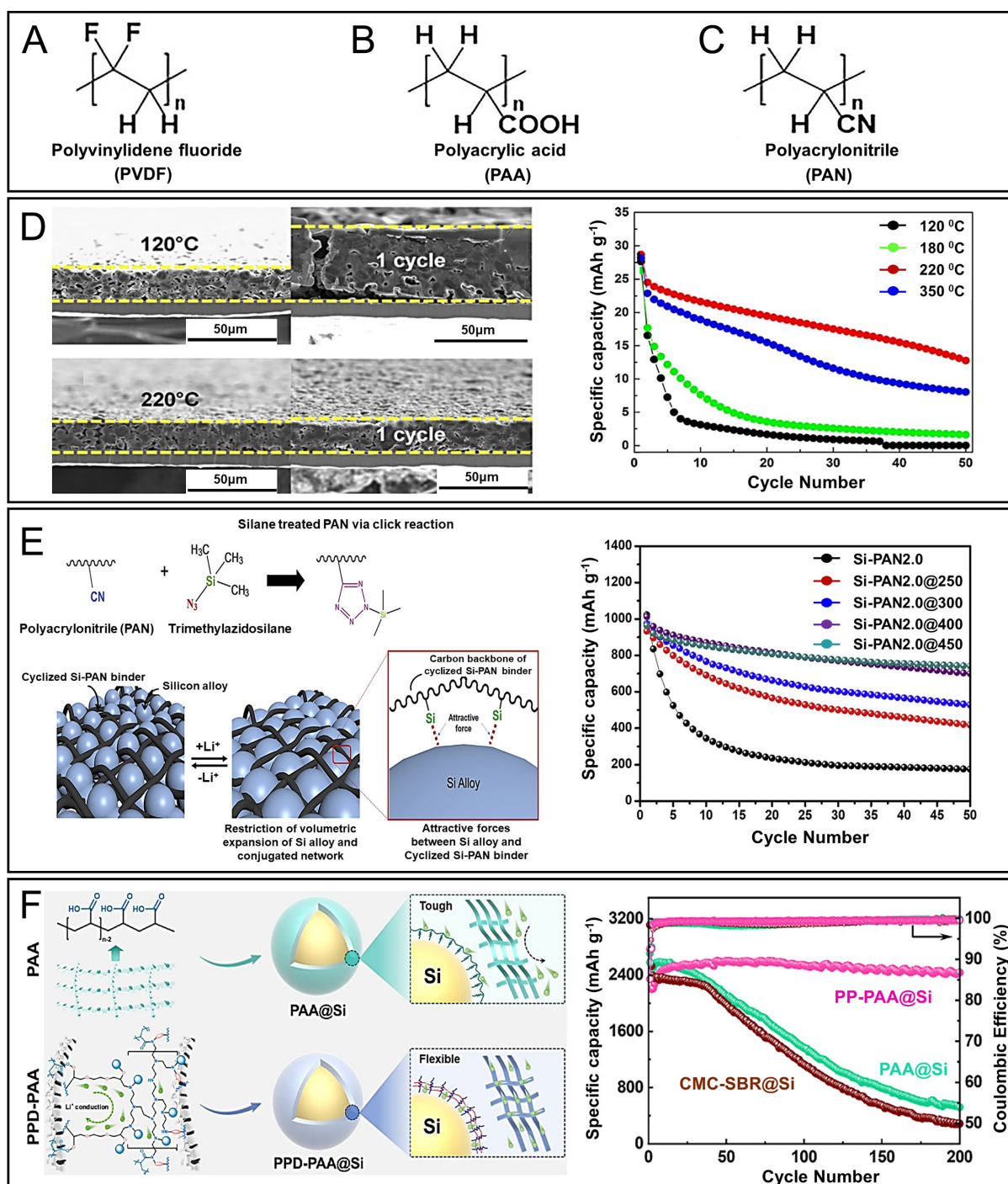


Figure 5. Chemical structures of synthetic polymer-based binders and their effects on Si anode performance. (A) PVDF; (B) PAA; (C) PVA. PVDF-based binder strategies; (D) Cross-sectional SEM images of Si-graphite/PVDF composite electrodes before and after the first cycle at various temperatures, along with the corresponding cycling performance of the Si anode. Adapted with permission from ref.^[82]; (E) Introduction of Si-functional groups via an azide-nitrile click reaction on a PAN-based polymer and the resulting electrochemical performance. Adapted with permission from ref.^[87]; (F) Schematic illustration of ion transport pathways and structural evolution in PAA@Si and PPD PAA@Si electrodes during cycling. The long-term cycling performance of Si electrodes using PAA, CMC SBR, and PPD PAA binders at a current density of 1.2 A g⁻¹ is also presented. Adapted with permission from ref.^[39].

formulation flexibility with CMC/SBR/CNT, and tunability via molecular weight/viscosity ($\approx 20\text{--}40$ kcps) to balance dispersion and coating quality. The main trade-offs are brittleness at very high stiffness and potential electrolyte interactions; recent practice emphasizes MW control and limited co-binders to preserve elastic recovery while maintaining line stability.

In our view, PVDF is an excellent baseline for graphite but structurally mismatched to high-strain Si. PAA-centered formulations currently offer the most pragmatic route to scale, provided viscosity and elasticity are co-optimized to avoid cracking at high Si loading. In addition to PAA, PAN has also been investigated as a binder, owing to the polar nature of its nitrile groups (-CN)^[81]. PAN's nitrile (-C≡N) groups confer high polarity, improving interfacial adhesion to Si and enhancing slurry rheology and electrolyte wettability rather than creating intrinsic ion-conducting pathways within the binder phase. High-molecular-weight PAN forms entangled chains that wrap and bridge Si particles, increasing mechanical integrity and adhesion; however, its intrinsic electronic conductivity remains low, and neat PAN binders may exhibit brittleness under large strains. In practice, PAN is less widely adopted than PVDF or PAA owing to higher cost and more complex processing, although targeted functionalization (e.g., silane coupling, click chemistry) has yielded hybrid organic-inorganic networks with improved durability. These modifications, while effective, must be balanced against synthesis complexity and solvent compatibility to ensure feasibility for large-scale manufacturing. The strong polarity of the nitrogen atom in the nitrile group improves both ionic conductivity and interfacial adhesion with the Si surface. One key advantage of high molecular weight PAN is its ability to form entangled polymer networks around Si particles, thereby improving mechanical integrity and adhesion. This structural advantage results in a notable improvement in capacity retention -37.95% for high-molecular-weight PAN compared with 17.5% for PVDF^[86]. While the nitrile group imparts beneficial characteristics, the intrinsic conductivity of PAN remains limited. Consequently, further improvements can be achieved by compositing PAN with conductive additives or applying doping strategies. For example, a study utilizing an azide nitrile click reaction to enhance adhesion of PAN to Si showed a significant improvement in capacity retention, achieving 522 mAh g⁻¹ after 50 cycles compared to just 152 mAh g⁻¹ for unmodified PAN [Figure 5E]^[87]. This work highlights a promising approach wherein silane-treated PAN (Si-PAN) was integrated into Si alloy electrodes. The Si-PAN binder forms a hybrid organic-inorganic structure through silane functionalization, enhancing both electrode durability and electrochemical performance. Notably, Si alloy electrodes fabricated with the optimized Si-PAN binder and thermally annealed at 450 °C delivered an initial discharge capacity of approximately 760 mAh g⁻¹ and maintained stable performance over 50 cycles^[87]. From an industrial standpoint, PAN's strong polarity and film-forming ability make it attractive for niche applications requiring high adhesion, but its relatively high cost and limited stretchability under large Si expansion mean it is more viable as a component in hybrid systems rather than as a sole binder in high-loading Si electrodes. More recently, Sun *et al.* developed a neural-network-inspired binder system by integrating an ion-conductive polymer synthesized from poly(ethylene glycol) diglycidyl ether (PEGDGE) and polyethylenimine (PEI) with a PAA backbone through noncovalent interactions [Figure 5F]^[39]. This hybrid binder (PPD-PAA) forms a flexible physical network that avoids chemical cross-linking, while enabling efficient Li-ion transport and effectively buffering the large volume fluctuations of Si via hydrogen bonding and electrostatic interactions. Impressively, the resulting electrode demonstrated superior rate capability and high capacity retention over 200 cycles, outperforming both CMC-SBR@Si and conventional PAA@Si systems^[39].

Table 1 summarizes representative linear binders used for Si anodes, including their structural features and functional groups. These binders offer good processability and enable polar interactions with Si particles; however, their limited mechanical reversibility often restricts long-term cycling stability.

Linear binders, such as PVDF, PAA, and PAN, offer well-defined molecular structures, high processability, and strong polar interactions with Si surfaces, making them compatible with scalable electrode fabrication. However, their limited mechanical reversibility and susceptibility to structural degradation during repeated cycling remain critical challenges, often restricting long-term stability. In particular, PAA, while not delivering the highest electrochemical performance, has attracted significant attention in the domestic cell industry due to its low cost and compatibility with aqueous processing.

Table 1. Summary of representative linear binders and their characteristics for Si anodes

Binder	Feature	Structure	Interaction	Ref.
CMC	High dispersion High viscosity	Linear	Hydroxyl group Carboxylate	[110]
SA	High viscosity	Linear	Hydroxyl group Carboxylate	[69]
CS	Strong hydrogen bonding	Linear	Hydroxyl group Amino group	[111]
GA	High mechanical property	Linear	Hydroxyl group	[112]
GG	High viscosity	Linear	Hydroxyl group	[113]
PVDF	Poor elasticity	Linear	Fluorine atom	[114]
PAN	High polarity/intrinsically low electronic conductivity	Linear	Nitrile group	[86]
PVA	High adhesion	Linear	Hydroxyl group	[115]
PI	High mechanical characteristics	Linear	Carbonyl group	[17,116]
PAA	High mechanical characteristics High viscosity	Linear	Carboxyl group	[117]

Current R&D efforts focus on optimizing slurry viscosity and improving adhesion to enhance electrode integrity without compromising manufacturability. Future developments are expected to focus on controlling molecular weight, diversifying functional groups, and developing hybridization strategies to balance mechanical resilience with ionic/electronic conductivity in next-generation Si-based anodes. Recent studies have also explored advanced linear synthetic binder architectures, including copolymer systems with zwitterionic functional groups and supramolecular host-guest assemblies, which have demonstrated improved Li⁺ transport, enhanced interfacial adhesion, and superior cycling stability under high-Si-loading and industrially relevant conditions^[88]

STRUCTURALLY ENGINEERED BINDERS

This section compares binders engineered with branched, covalently cross-linked, and dynamically cross-linked architectures. We identify how each structural motif contributes to stress buffering, crack suppression, and cycling stability, and we assess the trade-offs between mechanical robustness and processing feasibility.

The molecular structure of the polymer plays a crucial role in determining the effectiveness of the binder. The binders discussed above consist of linear polymer chains, where interactions primarily arise from noncovalent bonding between functional groups. As an alternative design strategy, the incorporation of covalent bonds or dynamic physical interactions between polymer chains, often associated with self-healing capabilities, can markedly improve the electrochemical performance of Si anodes.

Branched or grafted polymer binders

Here, we examine branched and grafted binder architectures, which introduce multiple interaction sites for enhanced adhesion and stress dispersion. We assess their performance benefits, synthesis challenges, and potential as an intermediate strategy between linear and fully cross-linked systems.

Branched or grafted architectures increase the density and spatial distribution of interaction sites relative to linear analogs, improving multi-point anchoring and stress dispersion around Si particles. Across reported systems, elasticity and capacity retention benefit from side-chain mediated hydrogen bonding/ionic interactions, yet synthesis complexity and viscosity management remain practical bottlenecks. We therefore view branched motifs as effective intermediates especially when used to tune chain mobility and solvent

uptake between simple linear baselines and fully cross-linked networks^[32,89,90]. Recent studies have demonstrated that compared to linear binders, branched architectures or grafted systems composed of functional moieties can better withstand the mechanical stress associated with Si expansion. Among these approaches, grafting functional groups onto a polymer backbone to generate side chains has been shown to improve both mechanical strength and interfacial adhesion in binder systems. For instance, He *et al.* developed a branched-type water-soluble binder, poly(vinyl alcohol)-grafted poly(acrylic acid) (PVA-g-PAA), synthesized via esterification between the hydroxyl groups of PVA and the carboxyl groups of PAA [Figure 6A]^[89]. Although the synthesis involves covalent ester bonding, it does not result in a cross-linked network but rather introduces functional branches onto the PVA backbone. This architecture offers abundant -COOH and -OH groups that form hydrogen bonds with Si particles, thereby improving interfacial adhesion and structural elasticity. While branched structures offer enhanced solubility and functional tunability, they often lack the robust network cohesion required to fully suppress Si volume fluctuation. Nevertheless, PVA-g-PAA exhibited promising electrochemical performance, retaining a capacity of approximately 1,000 mAh g⁻¹ after 1,000 cycles at a current density of 2.0 A g⁻¹, significantly outperforming conventional PAA binders^[89]. Building on this strategy, Shen *et al.* introduced a multidimensional branched composite binder (CA-g-PAA) by covalently grafting PAA onto a hyperbranched polyamide framework [Figure 6B]^[32]. The resulting three-dimensional network provided both mechanical resilience and strong interfacial adhesion with Si particles. Electrochemical tests revealed a high reversible capacity of ~2,500 mAh g⁻¹ over 200 cycles at 0.5 A g⁻¹, markedly superior to traditional binders^[32]. Furthermore, SEM analysis confirmed that CA-g-PAA maintained a dense, crack-free electrode morphology after prolonged cycling, unlike the heavily degraded control samples. This improved performance is attributed to the multidimensional grafted structure, which effectively buffers volumetric stress and maintains electrode integrity. Similarly, He *et al.* developed a GA-grafted poly(acrylic acid) (GA-g-PAA) binder by grafting GA onto PAA via a free radical polymerization process. The resulting binder exhibited enhanced cycle stability, higher Coulombic efficiency, and improved rate capability compared to pure PAA^[91]. In another notable example, Jolley *et al.* proposed a branched-type binder by grafting PAA onto a SBR backbone, forming PAA-g-SBR [Figure 6C]^[90]. This design combines the strong adhesion of PAA with the elasticity of SBR, resulting in improved cycling stability of Si/graphite composite anodes when tested at a charge and discharge rate of 1 C. The improved performance is primarily due to the branched configuration, in which grafted PAA chains establish hydrogen bonds and acid-base interactions with Si surfaces. Unlike physically blended PAA/SBR systems, this covalently grafted network offers superior homogeneity and interfacial bonding strength^[90]. Despite their promising attributes, branched-type polymer binders are still relatively underexplored for Si anodes. Their limited mechanical durability and weak internal cohesion often hinder their ability to fully accommodate the extreme volume fluctuations of Si. Furthermore, the loosely packed architecture can result in poor slurry dispersibility and restricted ionic conductivity. Consequently, recent research has increasingly focused on multifunctional hybrid systems that combine covalent bonding, hydrogen bonding, and ion-conductive components to enhance both mechanical stability and electrochemical performance. Recent developments have also reported highly elastic hyperbranched polymer binders that provide exceptional mechanical compliance and strong interfacial adhesion, effectively accommodating large Si volume changes and maintaining electrode integrity over extended cycling^[92].

Branched-like polymer architectures offer enhanced multi-point anchoring and network connectivity compared to their linear counterparts, enabling improved adhesion to Si surfaces and better stress distribution during cycling. The incorporation of multiple functional side chains can facilitate both mechanical stability and Li-ion transport pathways, thereby enhancing long-term capacity retention. However, the synthesis of branched polymers often requires more complex monomer feed ratios and reaction controls, which can lead to batch-to-batch variability. Additionally, higher viscosity in aqueous processing may limit slurry uniformity at a large scale. To advance industrial applicability, future work

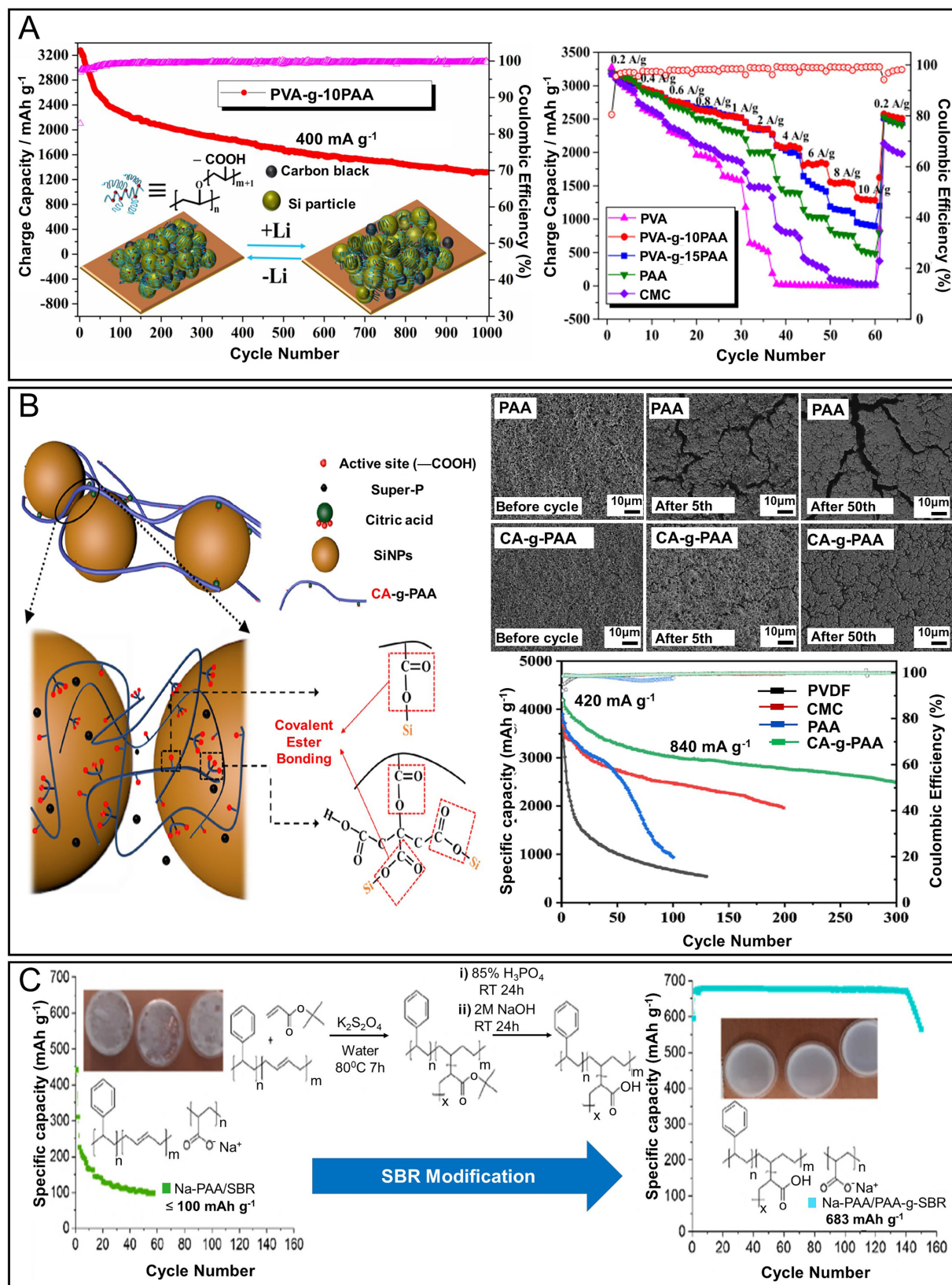


Figure 6. Electrochemical performance and structural stability of Si anodes employing polymeric branched binders. (A) Cycling performance of a Si electrode using the Si@PVA-g-10PAA binder over 1,000 cycles at a current density of 400 mA g⁻¹, accompanied by rate performance comparisons with various binders including PVA, PVA-g-10PAA, PVA-g-15PAA, PAA, and CMC. Adapted with permission from ref.^[89]; (B) Schematic illustration of the interaction between Si particles and the CA-g-PAA binder. Cross-sectional SEM images of Si electrodes with PAA and CA-g-PAA binders before cycling and after 5 and 50 cycles, along with corresponding cycling performance using different binders. Adapted with permission from ref.^[32]; (C) Schematic illustration and long-term cycling performance of Si/graphite composite anodes using Na-PAA/SBR and Na-PAA-g-SBR binders, demonstrating the superior stability and capacity retention imparted by the grafted binder system. Adapted with permission from ref.^[90].

should prioritize scalable synthetic strategies, optimized branching density, and cost-efficient monomers that balance mechanical robustness with manufacturability.

Cross-linked polymer binders

In this section, the term “cross-linked” encompasses both covalent and physical network formations. While covalent cross-links (e.g., esterification, amidation) provide permanent structural reinforcement, physical cross-links (e.g., hydrogen bonding, ionic interactions, supramolecular assemblies) can also deliver significant mechanical and interfacial benefits. Both types are considered here due to their relevance in suppressing Si anode pulverization and delamination. To overcome the limitations of conventional linear polymer binders, cross-linked polymer systems have been extensively explored. These systems form strong covalent bonds between polymer chains, thereby achieving high mechanical strength, an essential property for preserving the structural integrity of Si anodes during repeated cycling. On a molecular level, covalent bonding between the binder and hydroxyl-terminated Si surfaces (Si-OH) helps mitigate stress from volumetric expansion. Covalently cross-linked binders form robust three-dimensional networks that effectively suppress active material pulverization and electrode delamination, but their structural irreversibility can limit long-term adaptability under extreme cycling. Hybrid designs incorporating partially dynamic cross-links have recently been explored to mitigate this trade-off. However, since these covalent bonds are typically irreversible, they cannot reform once broken, which may lead to a gradual deterioration in adhesion between the binder and Si particles. Despite this limitation, chemically cross-linked binders built on well-chosen polymer backbones have demonstrated excellent long-term cycling performance. Their interconnected polymer networks effectively accommodate the repeated volume changes of Si while maintaining mechanical cohesion and interfacial adhesion over extended cycles^[93,94]. A notable challenge is that highly cross-linked binders are often insoluble in common solvents, necessitating thermal activation or specialized processing to form stable networks. A representative example is the thermally cross-linked PAA-PVA binder system, where esterification occurs between the hydroxyl groups of PVA and the carboxyl groups of PAA under elevated temperatures^[69,89]. The resulting interpenetrating polymer network (IPN) significantly enhances mechanical robustness and provides abundant functional groups for strong interactions with Si surfaces. This architecture effectively stabilizes the electrode against Si expansion/contraction during lithiation and delithiation, while outperforming linear alternatives in both adhesion and elasticity. Notably, the PAA-PVA binder delivered a stable capacity of $\sim 2,283 \text{ mAh g}^{-1}$ over 100 cycles, surpassing PVDF and NaCMC systems [Figure 7A]^[95]. Cross-linked binders also excel in suppressing electrode thickness changes during cycling. For instance, electrodes using linear binders such as SA experienced irreversible thickness growth of $\sim 16.5\%$ after just five cycles. In contrast, PAA-PVA cross-linked binders limited this change to $\sim 4.5\%$, owing to the rigidity of their IPN structure^[95]. In another study, a cross-linked binder synthesized via esterification between PAA and CMC retained over 60% of its initial capacity after 100 cycles at 0.5 C, even under high mechanical stress^[84], highlighting the structural resilience of the covalent network.

Zhang *et al.* also introduced a chemically cross-linked binder system comprising PAA, CMC, and CNT-NH₂ to improve mechanical and electrical properties [Figure 7B]^[34]. Spontaneous esterification and amidation reactions, which involve the formation of ester bonds between -COOH and -OH groups and amide bonds between -COOH and -NH₂ groups, occurred during electrode fabrication and resulted in a stable three-dimensional polymer network. This structure buffered Si expansion while preserving electronic pathways, resulting in improved cycling stability and overall performance. Recent studies have further demonstrated the potential of multifunctional cross-linked networks for Si anodes^[96]. For example, a CA@CMC binder system formed via esterification between the -COOH groups of citric acid and the -OH groups of CMC created a mechanically robust, three-dimensional covalent network that not only mitigated Si pulverization but also in situ regulated the SEI composition, enriching LiF content and enhancing

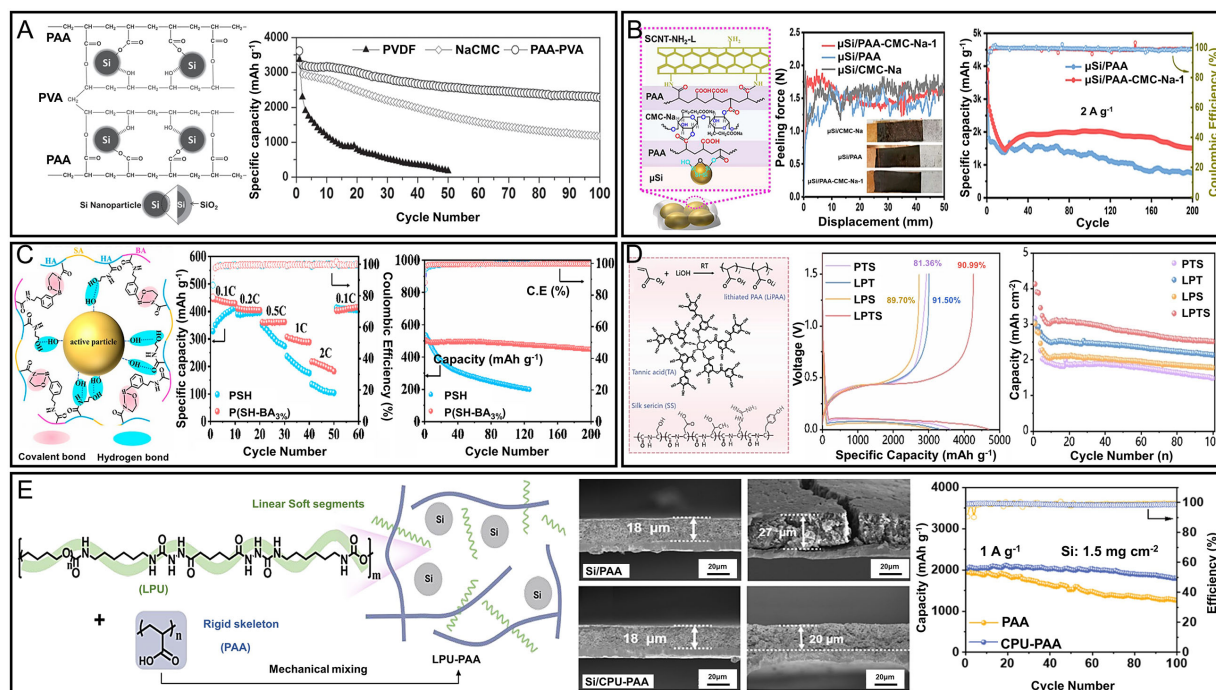


Figure 7. (A) Schematic illustration of the interaction between cross-linked PAA-PVA and the Si anode, and the cycling performance of Si electrodes using PAA-PVA, NaCMC, and PAA binders. Adapted from ref.^[64]; (B) Schematic illustration of polymer interaction among PAA, NaCMC, and functionalized SCNT, enhancing mechanical integrity, and peeling test results and cycle performance comparison among μ Si electrodes using PAA-NaCMC 1, PAA, and NaCMC binders. Adapted with permission from ref.^[134]; (C) Schematic illustration of Si/C composite anodes incorporating the cross-linked binder P(SH-BA). Rate capability comparison of Si/C₄₅₀ electrodes with various binder systems. Long-term cycling performance and Coulombic efficiency of coin-type Si/C₆₀₀/Li half cells employing P(SH-BA3%) and PSH binders (tested at 0.2 C). Adapted with permission from ref.^[131]; (D) Schematic representations of LiPAA, TA, and SS, followed by a depiction of the physicochemically cross-linked LPTS composite polymer binder and its functional integration into Si-based anodes during lithiation/delithiation. Initial galvanostatic charge-discharge profiles of Si/PTS, Si/LPT, Si/LPS, and Si/LPTS electrodes at 0.1 C are shown, along with their cycling stability at 0.5 C, highlighting the improved electrochemical performance enabled by the LPTS binder system. Adapted with permission from ref.^[138]; (E) Schematic illustration of the Si/CPU-PAA anode architecture and hierarchical stress-dissipating polymeric network. Cycling performance of Si anodes in half cells at 1 A g⁻¹ with a high Si mass loading of 1.5 mg cm⁻². Morphological comparison between Si/PAA and Si/CPU-PAA anodes before and after 50 cycles in Si/Li half cells, demonstrating the structural reinforcement provided by the CPU-PAA binder. Adapted with permission from ref.^[22].

interfacial stability over 500 cycles. In another approach, Sun *et al.* synthesized a covalently cross-linked 3D binder, P(SH-BA), via RAFT polymerization of hydroxyethyl acrylamide, sodium acrylate, and phenylboronic acid^[13]. Boronic acid moieties form dynamic covalent B-O and B-N linkages with -OH and -CONH₂ groups, constructing a resilient network [Figure 7C]. Remarkably, at a binder dosage of just 3 wt%, the optimized P(SH-BA3%) retained 83.56% of its capacity after 600 cycles at 0.5 C, with high Coulombic efficiency. This confirms that boron-mediated dynamic linkages offer an effective balance between mechanical strength and ion transport, making them suitable for high-energy LIBs.

Xiao *et al.* developed a multifunctional composite binder composed of LiPAA, tannic acid (TA), and silk sericin (SS), forming a physically cross-linked network via hydrogen bonding [Figure 7D]^[38]. TA acts as a molecular bridge between the carboxyl groups of LiPAA and the amino/hydroxyl groups of SS, forming an interpenetrating supramolecular network. This structure provided superior elasticity, cohesion, and adhesion. The Si/LPTS electrode showed excellent rate capability, delivering over 1,500 mAh g⁻¹ even at 2 C, and nearly full capacity recovery at 0.1 C. The use of silk sericin, a biodegradable protein, enhances structural stability and environmental compatibility, offering a practical and sustainable solution for Si anodes. He *et al.* developed a dual cross-linked binder system composed of cross-linked polyurethane (CPU) and PAA, where covalent and hydrogen bonds synergistically construct a physicochemical network [Figure 7E]^[22]. The

resulting CPU-PAA binder exhibited high toughness, superior tensile strength, and hierarchical stress dissipation, thereby maintaining the structural integrity of the Si anode and reducing thickness swelling. Finite element analysis revealed that this binder effectively mitigates internal stress during cycling. As a result, the Si/CPU-PAA anode achieved a capacity retention of 82.3% after 150 cycles at a high current density of 5 A g⁻¹[22]. This physicochemical dual-network(Si/CPU-PAA) preserved electrode integrity during prolonged cycling, as confirmed by scanning electron microscopy (SEM) images showing dense, crack-free structures compared to Si/PAA after 50 cycles.

Covalently cross-linked binders provide robust, permanent networks that effectively suppress Si pulverization and electrode delamination, delivering high mechanical strength and stable cycling even under high areal loadings. Their dense network structure minimizes irreversible deformation, maintaining electrical and ionic pathways over prolonged operation. Nonetheless, the irreversible nature of covalent bonds can limit adaptability to extreme volumetric changes, and the multi-step synthesis or thermal curing requirements may increase production cost and energy consumption. Future research should focus on hybrid cross-linking approaches that integrate partial reversibility, reduce curing temperatures, and employ eco-friendly, water-based processing routes to bridge the gap between laboratory performance and industrial-scale electrode fabrication.

Dynamically cross-linked polymer binders

Here, we review binders that employ reversible cross-links to enable autonomous healing and stress relaxation. We analyze their potential to combine mechanical adaptability with ionic conductivity, while addressing the challenges of bond lifetime control, rheology management, and scalability.

Self-healing polymers refer to materials in which physically separated chains can recombine through the formation of new bonds at reactive sites on adjacent chains via dynamic cross-linking mechanisms^[97]. Unlike conventional cross-linking, in which broken bonds are irreversible, dynamic cross-linking enables the formation of new interactions at alternative active sites even after bond dissociation. This mechanism is driven by a multitude of noncovalent interactions, such as hydrogen bonding, ionic interactions, and π - π stacking, acting collectively like microscopic Velcro. These reversible bonds allow the material to adapt to mechanical deformation by temporarily dissociating and reassembling, thereby enabling flexible and self-healing behavior. In the context of Si anodes, the use of self-healing binders helps mitigate the mechanical stress induced by large volume expansion. Upon expansion, the cross-linked polymer network stretches to dissipate mechanical stress, while upon contraction, it reverts to its original configuration by re-establishing bonds and healing microcracks. One representative example is the dynamic host-guest system utilizing cyclodextrin (β -cyclodextrin polymer, β -CD) and adamantane groups by Kwon *et al.* [Figure 8A]^[97]. The hydrophobic interior and hydrophilic exterior of β -CD enable specific supramolecular binding with adamantane, and when combined with a multifunctional adamantine (AD) linker, the resulting network achieved ~90% capacity retention after 150 cycles. Another notable approach is the hydrogen-bond-based dynamic binder developed by Chen *et al.*, which involves the reaction of TA and PAA^[79]. The branched TA structure, rich in hydrogen bonding sites, forms a dynamic network that accommodates Si volume fluctuations and improves electrode integrity. Additionally, a PAA-free strategy combining CMC and cationic polyacrylamide (CPAM) was introduced to form an ionically cross-linked network through electrostatic interactions^[98]. This dynamic yet physical network showed excellent adaptability to volume changes without relying on covalent bonding, leading to improved structural resilience. In a more recent study, Kang *et al.* proposed a dynamic covalently cross-linked network (xPAA-B-DA), in which boronic ester linkages undergo reversible exchange reactions [Figure 8B]^[28]. This imparts self-healing functionality, preserves ionic transport pathways, and alleviates structural disintegration under cycling stress. Importantly, the residual dopamine moieties enhance adhesion via catechol metal and hydrogen bonding, stabilizing SEI

formation and reducing charge transfer resistance over time. In another advanced system, Kang *et al.* designed a multifunctional binder integrating multiple dynamic interactions - boronic ester (B-N) bonds, Al^{3+} carboxylate coordination, and hydrogen bonding - within a semi-interpenetrating polymer network of PAA and CMC [Figure 8C]^[99]. This design imparted robust mechanical strength, elasticity, and rapid autonomous healing under ambient conditions. The inclusion of Al^{3+} ions enhanced compressive resistance and interfacial adhesion. A particularly notable feature was the visible healing of separated hydrogel segments within 3 h without external stimuli. The binder (CMC-AAc-3) retained over 1,000 mAh g⁻¹ after 300 cycles, exhibited a high initial Coulombic efficiency of 84.7%, suppressed swelling in electrolyte, and facilitated stable SEI formation. These results underscore the versatility of dynamic hydrogel binders for Si anode applications. Building on such multifunctional dynamic architectures, recent work has reported a supramolecular polymer binder featuring hard/soft phase interactions^[100]. In this design, the hard domain integrates reversible disulfide exchange (dynamic covalent bonds), cooperative hydrogen bonding, and π - π interactions, imparting self-healing capability and robust mechanical strength. Meanwhile, the soft polyether domain establishes Li^+ ion-hopping pathways, enhancing stretchability and ionic conductivity. When applied to Si electrodes, this binder effectively suppressed volumetric expansion, promoted the formation of a dense and homogeneous SEI, and achieved a high initial coulombic efficiency of 85.2%, along with superior rate capability and cycling stability in both half-cell and NCM523||Si/C full-cell configurations. This synergy between dynamic covalent bonding and supramolecular interactions exemplifies a promising pathway for enhancing both mechanical adaptability and electrochemical performance in next-generation Si anode binders. Lastly, Xu *et al.* developed a fast self-healing and highly adhesive aqueous binder (PAA-LS) by incorporating lignosulfonate into PAA, utilizing dynamic Fe^{3+} catechol coordination^[29]. This system enables efficient healing of microcracks and stress redistribution during lithiation/delithiation, while providing mechanical robustness and strong interfacial adhesion. The SiO_x @PAA-LS electrode demonstrated an impressive capacity of 997.3 mAh g⁻¹ after 450 cycles at 0.5 A g⁻¹, outperforming conventional binders such as PAA and CMC [Figure 8D]. In full-cell tests (SiO_x ||NCM622), the binder achieved 82.72% capacity retention after 100 cycles. The superior performance stems from the synergy of dynamic coordination bonding, polar functional groups enhancing Li-ion transport, and the optimized LS content (0.5 wt%) ensuring network integrity. This work validates the practical potential of dynamic cross-linked binders for next-generation high-capacity Si oxide anodes^[29].

Table 2 categorizes various polymeric binders according to their structural architectures and bonding mechanisms, including linear, branched, covalently cross-linked, and dynamically cross-linked systems. These binders employ diverse interactions, such as hydrogen bonding, ionic interactions, covalent ester linkages, and coordination bonding to improve mechanical resilience and interfacial stability in Si anodes. Table 3 provides a concise overview of the representative binder types covered in Sections "Branched or grafted polymer binders"-"Dynamically cross-linked polymer binders", including linear, branched, covalently cross-linked, and dynamically cross-linked systems, highlighting their respective advantages and limitations. This comparative summary offers a basis for the subsequent discussion in Section "MECHANICAL PROPERTIES AND THEIR IMPACT ON SI ANODE PERFORMANCE", which focuses on the mechanical properties of these binder systems.

Dynamic cross-linked architectures combine adaptive mechanical buffering with autonomous healing, making them particularly well-suited for mitigating the extreme volume changes of high-capacity Si-based anodes. Dynamic networks leverage reversible bonds to enable autonomous crack healing and stress relaxation, though industrial deployment requires careful control of bond lifetime, mechanical stability, and slurry rheology under high-solid-loading conditions.

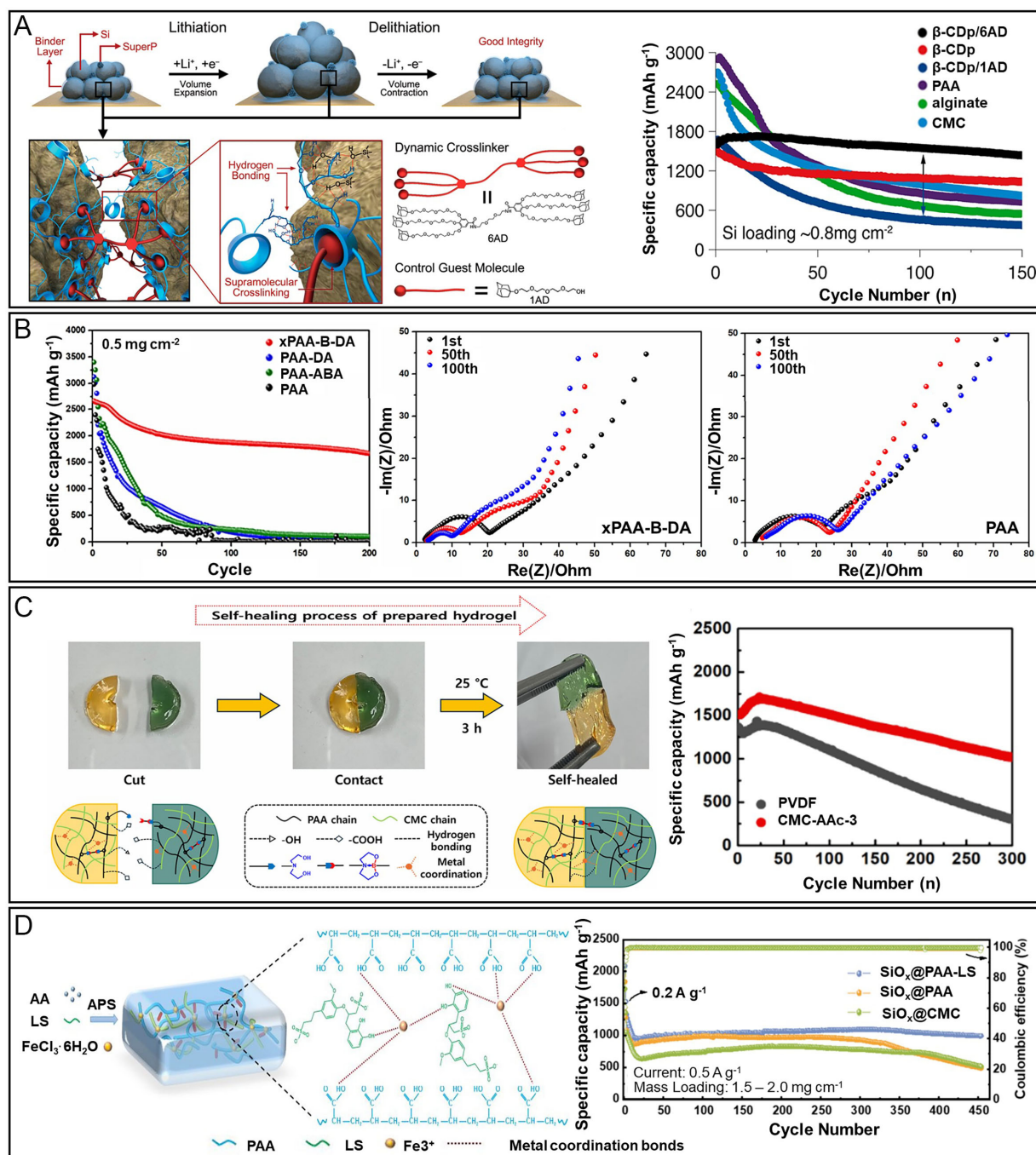


Figure 8. Electrochemical performance and structural stability of Si anodes incorporating polymeric dynamically cross-linked binders. (A) Schematic illustration of the self-healing mechanism in a polymer binder and the cycling performance of Si electrodes using dynamically cross-linked polymer binders based on CD and AD host-guest interactions. Adapted with permission from ref.^[197]; (B) Schematic illustration of the self-healing 3D polymeric binder (xPAA-B-DA), constructed via boronic ester and dopamine-based cross-linking chemistry, demonstrating its integration within Si anodes during lithiation/delithiation. Also shown are the electrochemical impedance spectra of Si@xPAA-B-DA and Si@PAA electrodes measured at the 1st, 50th, and 100th cycles under a current density of 1 C. Adapted with permission from ref.^[28]; (C) Schematic illustration of the self-healing mechanism in the CMC-AAc3 binder, along with extended cycling performance data. The CMC-AAc3 binder retained 67.2% of its initial capacity after 300 cycles at a rate of 0.2 C, demonstrating its enhanced durability under long-term operation. Adapted with permission from ref.^[99]; (D) Schematic representation of the PAA-LS binder architecture, followed by long-term cycling performance of SiO_x anodes using PAA-LS, PAA, and CMC binders at a current density of 0.5 A g⁻¹, demonstrating the improved capacity retention and enhanced electrode stability provided by the lignosulfonate-modified binder. Adapted with permission from ref.^[29].

Table 2. Polymeric binders with diverse structures and interactions for Si anodes

Binder	Feature	Structure	Ref.
Ox-L-CGN	Hydrogen bonding,	Linear	[70]
LGN	Electrostatic interaction	Linear	[71]
POWPU	Multiple Hydrogen bonding	Linear	[12]
API	Multiple Hydrogen bonding	Linear	[17]
PA2X1	Multiple Hydrogen bonding	Linear	[10]
PEaMAc	Hydrogen bonding, Ionic interactions	Linear	[78]
MW PAA	Hydrogen bonding, Ionic interactions	Linear	[11]
PIBDA	Noncovalent interactions	Linear	[118]
β -CDp	Multi-hydrogen-bonding interactions	Branched	[119]
PAA-NH ₃	Ionic bonding, Strong adhesion	Branched	[120]
GA-g-PAA	Covalent interaction	Branched	[121]
CA-g-PAA	Covalent interaction	Branched	[32]
PVA-g-PAA	Hydrogen bonding	Branched	[89]
PAA-g-SBR	Covalent-Noncovalent bonding,	Branched	[90]
PAA/PVA	Ester bonding, Strong adhesion	Cross-linked	[95]
PAA-CMC	Ester bonding, Strong adhesion	Cross-linked	[117]
b-Li0.5PAA@SA	Ester bonding, Mechanical Strength	Cross-linked	[122]
SBR/CMC-PEG Im-Zn ²⁺	Ester bonding, Zinc ion	Cross-linked	[123]
SA/Ca ²⁺	Ester bonding, Calcium ion	Cross-linked	[124]
cxPAA-PEI(x)	Condensation reaction	Cross-linked	[93]
PAA-CMC-Na	Covalent-Noncovalent bonding	Cross-linked	[34]
AGE binder	Covalent bonding	Cross-linked	[9]
CPU-PAA	Covalent-Noncovalent bonding	Cross-linked	[22]
LPTS	Covalent-Noncovalent bonding	Cross-linked	[38]
Alg(Ni)-PAM-TA	Covalent, Coordination bonding, Hydrogen bonding	Cross-linked	[40]
SiO ₂ -P(SH-BA)	Covalent bonding	Cross-linked	[13]
PPD-PAA	Covalent-Noncovalent bonding	Cross-linked	[39]
PVA-Malonic Acid	Covalent ester bonding	Cross-linked	[14]
PEI-PVA	Covalent ester bonding Multi noncovalent interactions	Cross-linked	[43]
HM	Covalent ester bonding, Noncovalent interactions	Cross-linked	[27]
FP2SA	Ionic bonding, Covalent interactions	Dynamic cross-linked	[63]
β -CDp-6AD	Multi Noncovalent interactions	Dynamic cross-linked	[97]
TA-c-PAA	Multi Noncovalent interactions	Dynamic cross-linked	[79]
CMC-CPAM	Ionic bonding	Dynamic cross-linked	[98]
xPAA-B-DA	Dynamic covalent bonding Multi Noncovalent interactions	Dynamic cross-linked	[28]
PEI@PAA@CMC	Dynamic covalent bonding, Multi Noncovalent interactions	Dynamic cross-linked	[15]
PAA-LS	Coordination bonding Multi Noncovalent interactions	Dynamic cross-linked	[29]
CMC-AAc-Al ³⁺	Coordination bonding Multi Noncovalent interactions	Dynamic cross-linked	[99]
SA@Borax	Dynamic covalent bonding Multi Noncovalent interactions	Dynamic cross-linked	[26]

Table 3. Comparative advantages and disadvantages of representative polymer binder types for Si-based anodes

Binder type	Advantages	Limitations
Linear polymer binders	<ul style="list-style-type: none"> - Film-forming; uniform coating - Simple synthesis; water-processable - Interfacial bonding (H-bonding/polar) - Low cost; commodity-grade 	<ul style="list-style-type: none"> - Limited mechanical strength - Irreversible fracture; electrical contact loss
Branched or grafted polymer binders	<ul style="list-style-type: none"> - Multifunctional groups; multi-point adhesion - Improved toughness, crack suppression - Tunable modulus, branch/graft density control - Interface stabilization; SEI stability 	<ul style="list-style-type: none"> - Synthesis complexity, batch variability - Higher slurry viscosity, solids cap - Cost ↑ (functional monomers/initiators) - Adhesion-elasticity trade-off
Covalently cross-linked polymer binders	<ul style="list-style-type: none"> - Robust 3D network; high mechanical strength - Suppress particle pulverization; crack control - Maintain structural integrity (Long-term) 	<ul style="list-style-type: none"> - Irreversible network; limited self-healing - Harsh synthesis/curing (temperature/time) - Curing shrinkage; residual stress
Dynamically cross-linked polymer binders	<ul style="list-style-type: none"> - Reversible bonding; self-healing - Expansion-contraction tolerance - Mechanical resilience; interfacial stability - Extended cycle life 	<ul style="list-style-type: none"> - Electrolyte-sensitive; bond weakening - Narrow processing window - Healing-rate mismatch

Their versatility in incorporating multiple reversible interactions ranging from hydrogen bonding and π - π stacking to metal-ligand coordination enables simultaneous improvement of structural resilience, interfacial adhesion, and ionic conductivity. Nevertheless, the complexity of multi-component synthesis, the inherently high cost of functionalized precursors, potential variability in dynamic bond lifetimes, and uncertainties in long-term stability under industrial processing conditions remain barriers to commercialization. Future efforts will need to focus on cost-effective precursor selection, large-scale aqueous synthesis routes, and rheological optimization to fully leverage the advantages of dynamic cross-linked binders in mass-produced next-generation LIB electrodes. While these dynamic cross-linked architectures have been primarily investigated in conventional liquid electrolyte systems, similar design principles can be extended to solid-state battery (SSB) configurations. In SSBs, the absence of liquid electrolyte eliminates swelling and dissolution issues, but introduces challenges related to maintaining intimate solid-solid interfacial contact and ensuring sufficient ionic conductivity across the electrode-electrolyte interface^[101-103]. Binders in this context must combine strong adhesion to both the Si anode and solid electrolyte with mechanical compliance to accommodate substantial volume changes during cycling. Incorporating ion-conductive polymer segments, such as polyethylene oxide (PEO) or polycarbonate-based backbones, can facilitate Li⁺ transport through the binder phase and reduce interfacial resistance^[104-106]. Furthermore, hybrid binder systems containing ceramic fillers, such as Li₇La₃Zr₂O₁₂ (LLZO), have been explored to enhance both mechanical robustness and ionic conductivity in SSB environments^[107] (Boaretto *et al.*, 2022^[107]). Developing binders that integrate high interfacial adhesion, appropriate mechanical flexibility, and Li⁺ conduction pathways is therefore essential for achieving stable cycling performance of Si anodes in solid-state battery systems.

MECHANICAL PROPERTIES AND THEIR IMPACT ON SI ANODE PERFORMANCE

This section links the structural and chemical design of binders to measurable mechanical parameters such as tensile strength, elongation, and modulus. We explore how these properties influence Si anode cycling stability, and outline testing methods relevant for both laboratory studies and industrial qualification.

Building on the comparative analysis in Table 3, which outlined the structural architectures and bonding mechanisms of various polymer binder systems, this section focuses on how these design differences translate into mechanical behavior. In particular, we discuss why the ability to accommodate substantial volume changes and maintain electrode integrity is a decisive factor for the practical deployment of Si-based anodes, especially in the context of high-loading and micrometer-sized Si particles.

Previous research on Si anode binders has predominantly focused on the functional groups and structural configurations of polymers. However, relatively few studies have comprehensively examined how the intrinsic material properties, particularly the mechanical characteristics of polymeric binders, influence their overall performance. Moreover, most investigations on Si anodes have utilized nanoparticles or engineered nanostructures. While these approaches are effective in mitigating volume change issues, they remain impractical for large-scale commercial implementation due to cost-related limitations. In this context, Si microparticles (SiMPs) have emerged as a more economically viable alternative. Yet, the use of micrometer-sized Si presents significant challenges. During cycling, these particles undergo severe volume expansion, leading to particle fracture, loss of contact with the binder, electrical isolation, and eventual failure of the conductive network. As particle size increases, these issues become more pronounced, underscoring the urgent need to develop binder systems capable of maintaining electrode integrity in SiMP-based electrodes. To address this challenge, recent research has explored elastic cross-linked polymers as promising binder candidates. Elastic binders are designed to encase SiMPs and buffer the mechanical stress induced by their repeated expansion and contraction, thereby preserving electrical pathways and structural coherence. For such systems to be effective, the binder must possess sufficient elasticity and mechanical resilience to withstand the internal stresses imposed by SiMP deformation. Inspired by the mechanical principle of a pulley system, a novel binder architecture known as the molecular pulley binder (PR-PAA) was developed^[47,108]. In this design, polyrotaxane (PR) molecules are covalently bonded to a PAA backbone, forming a cross-linked polymer network where PR acts as a dynamic “cord”. The PR consists of polyethylene glycol (PEG) chains threaded through cyclodextrin (α -CD) rings, which serve as movable pulleys. This design enables the distribution of mechanical stress across the network and allows for reversible deformation under volumetric changes. The repulsive interactions between the α -CD rings provide additional restorative force, contributing to the elasticity required to return to the original conformation during Si contraction. This unique architecture enables the PR-PAA binder to maintain electrode integrity even when using SiMPs, which are inherently difficult to stabilize due to their large volume fluctuations [Figure 9A]^[47,108]. Remarkably, with just 10 wt% binder content relative to the total electrode mass, the PR-PAA-SiMP electrode achieved an initial Coulombic efficiency exceeding 90%, and retained 91% of its capacity after 150 cycles [Figure 9B and C]^[47,109]. This indicates that the stability of SiMPs is influenced not only by the adhesive properties or structural features of the polymer but also by its physical characteristics, such as elasticity. As such, the mechanical properties of the polymer are crucial in determining the effectiveness of binders for Si anodes. Key attributes, such as elasticity, are vital to how well the binder maintains its structure under the stresses caused by the expansion and contraction of Si during cycling. These findings demonstrate that the mechanical properties of the polymer, particularly elasticity, are just as critical as chemical adhesion or structural design in determining the effectiveness of the binder. Attributes such as flexibility, resilience, and stress dissipation directly influence electrochemical stability, long-term durability, and capacity retention of Si-based anodes in LIBs. Therefore, future binder development must integrate mechanical considerations alongside chemical functionalities to meet the demands of practical high-energy-density battery systems. Among the various binder systems exhibiting comparable electrochemical performance, the PR-PAA binder stands out due to its uniquely engineered mechanical adaptability. Compared to conventional cross-linked polymers, the molecular pulley architecture of PR-PAA incorporates mechanically sliding polyrotaxane units that enable dynamic stress redistribution throughout the binder matrix. This design not only buffers the internal strain induced by the volumetric expansion of SiMPs but also allows the network to reversibly recover its structure during contraction. Such a mechanically adaptive response is critical for maintaining long-term electrode integrity under practical conditions. Therefore, the distinction of PR-PAA lies not merely in its cycle life metrics, but in its rational structural design that integrates elasticity, reversibility, and stress tolerance, essential qualities for scalable and durable Si anode systems.

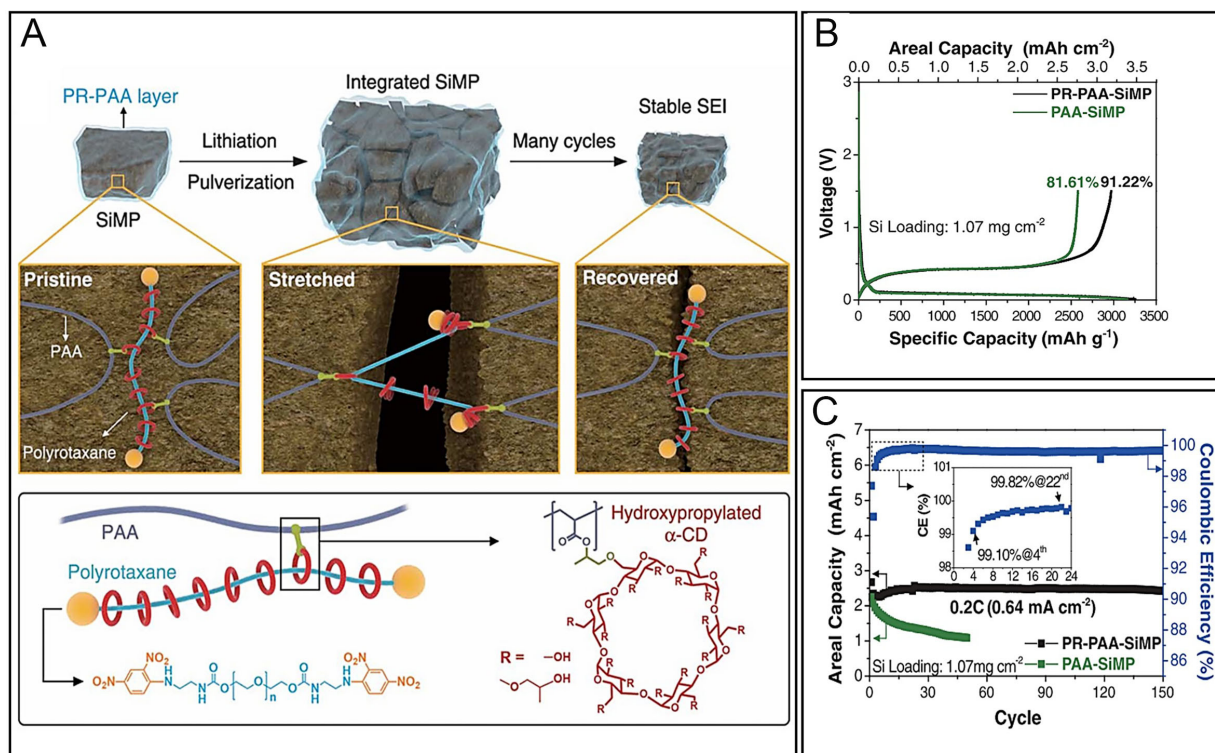


Figure 9. Self-healing polymer binders based on PR-grafted PAA (PRPAA) structures and their application to Si anodes, highlighting enhanced mechanical reversibility and interfacial stability during repeated lithiation/delithiation. (A) Chemical structure and schematic illustration of a molecular pulley-type binder using a polyrotaxane backbone. Adapted with permission from ref.^[108]; (B and C) Initial charge-discharge profiles of Si electrodes with the molecular pulley binder and cycling performance of the Si anode using the PR-based binder. Adapted with permission from ref.^[109].

Table 4 provides a comparative overview of various polymeric binders for Si anodes in terms of specific capacity, cycle life, and binder content. Conventional binders such as PVDF exhibit limited cycling performance, whereas advanced systems incorporating functional groups, grafted architectures, or dynamic cross-linking mechanisms demonstrate significantly improved capacity retention over extended cycling. These results highlight the importance of binder design in achieving stable electrochemical performance in high-capacity Si-based electrodes.

From our perspective, the next stage of mechanical binder design should focus on scalable synthesis routes that preserve elasticity and stress-dissipating features, while balancing cost and process compatibility to enable widespread adoption in industrial SiMP-based anodes.

INDUSTRIAL PERSPECTIVES AND FUTURE RESEARCH DIRECTIONS

This section discusses binder development from an industrial perspective, focusing on scalability, cost efficiency, and process compatibility. Despite numerous reports of effective binders for Si-based electrodes, their utilization has remained largely limited to the SBR/CMC binder system for negative electrodes, reflecting the persistence of unresolved technical approaches in alternative approaches. For high-volume production lines, the most impactful binder strategy is one that supports incremental Si loading increases from low percentages (≤ 5 wt%) for initial validation, toward mid-to-high fractions (> 15 wt%) without requiring disruptive changes to coating, drying, or calendaring processes. Industrial practice shows that stable scale-up is more often achieved through evolutionary integration (e.g., gradual Si ratio increase) rather than step-change adoption of high-Si electrodes. Binder technology must also align with particle size

Table 4. Electrochemical performance of reported polymer binders for Si anodes

Binder	Capacity/Cycles (mAh g ⁻¹ /cycles)	Binder mass (wt%)	Ref.
PVDF	600/50	8	[114]
CMC	2,733/55	15	[125]
GG (Gellan Gum)	2,222/100	15	[125]
SA (Na-Alg)	1,700/50	15	[69]
CS	950/50	8	[126]
CS/rubber	1,350/50	15	[72]
PAA	2,500/100	25	[80]
PAN	1,639/50	10	[86]
PAA/PVA	2,283/100	20	[95]
PAA-UPy	2,638/110	20	[111]
b-Li0.5PAA@SA	1,584/150	20	[122]
PAA-NH ₃	711/100	10	[120]
Alg-C	1,700/400	20	[74]
AA(xx)UR(yy)	2,334/100	15	[33]
PI-BIDA	1,350/150	10	[118]
Si@API	1,444/200	20	[17]
Ox-L-CGN-5	2,534/100	20	[70]
Si/POWPU	1,204/400	20	[12]
HAMN-based Si/C	1,386/600	10	[127]
C-Alg-g-PAAm	836/100	15	[94]
β-CDp	1,471/200	20	[119]
β-CDp-6AD	1,542/100	10	[119]
c-PAA-CMC	2,100/100	20	[117]
cxPAA-PEI(x)	2,606/100	20	[93]
CS-grafted-PANI	1,091/200	20	[67]
PAA-CMC-Na	950/400	20	[34]
PR-PAA	2,971/100	10	[47]
CMC-CPAM	1,906/100	20	[98]
PVA-g-PAA	2,001/150	10	[89]
Na-PAA-g-SBR	673/130	10	[90]
AGE binder	2,000/100	20	[9]
CPU-PAA	1,500/400	10	[22]
LPTS	2,082/400	5	[38]
Alg(Ni)-PAM-TA	1,863/200	10	[40]
SiO-P(SH-BA)	500/600	3	[13]
PPD-PAA	2,400/200	-	[39]
PVA-Malonic Acid	2,267/100	20	[14]
PEI-PVA	2,126/200	20	[43]
Si-HM	1,426/100	10	[27]
SiOx-PAA-Dex ₉	1,200/100	10	[41]
xPAA-B-DA	1,674/200	20	[28]
PEI@PAA@CMC	1,310/400	6.5	[15]
SiOx-PAA-LS	997/450	10	[29]
CMC-AAc-Al ³⁺	1,028/300	15	[99]
SA@Borax	1,655/500	10	[26]

strategy. Micrometer-scale Si, despite higher volumetric expansion than nanoscale Si, offers advantages in raw material cost, supplier diversity, and easier quality control during slurry preparation. This shifts binder requirements toward stronger elastic recovery and fracture suppression, ensuring mechanical stability under high strain while maintaining slurry compatibility at industrial speeds. From a cost perspective, the binder is a minor mass fraction but a critical cost-control lever. Reducing binder content from typical research levels (≥ 10 wt%) to commercial targets (≈ 2 -3 wt%) not only improves energy density but also cuts raw material expenses and reduces solvent usage, thereby lowering overall electrode manufacturing cost per kWh. Cost modeling by several manufacturers indicates that binder-related savings can directly offset the higher cost of Si powders, especially in early high-Si pilot lines. Commercial LIB manufacturing lines still rely heavily on the CMC/SBR system for graphite-rich electrodes. However, PAA-based systems are increasingly favored for Si-rich blends due to their superior interfacial adhesion and mechanical stiffness. Challenges such as brittleness at high modulus, electrolyte sensitivity, and functionalized monomer cost must be addressed through molecular weight tuning, controlled branching, or hybridization. Hybrid binder architectures that combine adhesive and elastic domains, while maintaining aqueous processability, are emerging as the most viable pathway to bridge lab-scale performance with mass-production reliability. In the industrial context, the binder that succeeds will not necessarily be the one delivering the highest lab-measured capacity, but the one that integrates seamlessly into high-throughput coating lines, demonstrates reproducible performance across batches, and enables cost reductions through simplified formulations, reduced loading, and compatibility with existing equipment.

For manufacturers, the most competitive binders will be those that align with key industrial goals:

- (i) Cost per kWh reduction through minimized binder loading and inexpensive feedstocks;
- (ii) Robust process compatibility and yield stability, ensuring reliable performance during slurry preparation, coating, drying, and calendaring at industrial scales;
- (iii) Scalability across multiple anode chemistries, from graphite-Si blends to full Si and emerging solid-state formats;
- (iv) Environmentally responsible processing, supported by water-based formulations and sustainable manufacturing practices.

By framing binder development in terms of these manufacturing and economic imperatives, research directions can be better aligned with the realities of commercial cell production, ensuring a smoother transition from promising laboratory concepts to profitable mass-market solutions. By embedding these industrial considerations into the binder selection and design framework, this review aims to bridge the gap between academic insights and manufacturable, cost-effective solutions, an aspect often missing in conventional literature but essential for successful Si anode commercialization.

CONCLUSION

The concluding section synthesizes key insights from the review, summarizing the trade-offs, design principles, and industrial considerations for Si anode binders. We provide a consolidated outlook on the most promising directions for future development, integrating both scientific and manufacturing perspectives.

Polymer binders play a crucial role in maintaining the structural integrity and electrochemical stability of Si

anodes. They not only mitigate the detrimental effects of volume expansion, such as pulverization and electrode delamination, but also stabilize the interface between the active material and the electrolyte. In particular, the incorporation of functional groups capable of forming secondary interactions with Si surfaces enhances adhesion, while supramolecular and mechanical characteristics of the binder directly influence cycling performance. This review has outlined key considerations in the rational design of polymer binders for Si anodes, emphasizing the importance of both chemical and physical interactions. First, the formation of strong interfacial adhesion through hydrophilic functional groups is essential to anchor the binder to both the active material and the current collector. Second, an optimal balance between bonding strength and flexibility achieved through covalent cross-linking or hydrogen bonding helps the binder accommodate the mechanical strain of Si during cycling. Notably, recent studies suggest that the inclusion of elastic properties in the binder design correlates positively with long-term cycling stability, especially in systems using micrometer-sized Si. Moreover, from a practical application standpoint, minimizing the binder content within the electrode is imperative for achieving higher energy densities. While many existing studies have used binder contents exceeding 10 wt%, commercial viability typically requires ≤ 3 wt%. Therefore, future research must continue to explore binder systems that maintain high performance even at significantly reduced loading levels. A particular focus should be placed on enhancing mechanical adaptability and reducing binder content, while preserving strong interfacial and cohesive properties, which are key aspects for the development of scalable, high-performance binder systems for next-generation Si anodes in LIBs.

In conclusion, we outline the key future directions for the rational design of polymer binders for Si anodes. These perspectives are schematically summarized in [Figure 10](#). The figure illustrates future strategies for commercial Si-based binders, highlighting three core directions: (i) adhesion engineering to enhance interfacial binding and mechanical cohesion; (ii) electrolyte optimization to improve interfacial compatibility and suppress undesirable side reactions; and (iii) binder engineering to reduce binder content, accommodate volume fluctuations, facilitate ionic transport, and ensure an aqueous slurry process. These approaches collectively aim to enhance mechanical durability and electrochemical performance, while also supporting cost-effectiveness and environmentally sustainable processing. As Si continues to gain traction as a high-capacity anode material, the development of multifunctional, structurally robust, and scalable binder systems will remain a critical component in realizing practical next-generation LIBs.

From an industrial perspective, manufacturing strategies for Si anode binders can largely be divided into two approaches: replacing CMC with PAA in the conventional CMC/SBR dual binder system, or substituting SBR with PAA altogether. The adoption of PAA is driven by the need to increase Si content for high-energy and high-power batteries, while mitigating volumetric expansion through its high rigidity. Current development efforts focus on optimizing PAA binders with a viscosity range of 20,000–40,000 cps and tailoring molecular weight to balance slurry rheology, particle dispersion, coating uniformity, electrode density, and mechanical strength. PAA also offers notable formulation flexibility, being compatible with other binders and conductive additives such as CMC, SBR, and CNT.

In industrial practice, the preferred binder is not necessarily the one with the highest laboratory performance, but the one that consistently operates reliably on a production line. In this regard, PAA meets key requirements including cost-effectiveness, process stability, reproducibility, and established performance data. It also offers potential for cost reduction through simplified formulations, reduced binder content, and compatibility with existing aqueous processing lines. Looking ahead, the development of single-component binder systems that can simultaneously provide mechanical robustness, strong adhesion, and ionic conductivity is an emerging yet technically challenging research direction. Such systems often face difficulties in achieving optimal coating quality and sufficient adhesion under high Si-loading conditions, due to the challenge of balancing multiple functional requirements within a single polymer matrix. Overcoming these

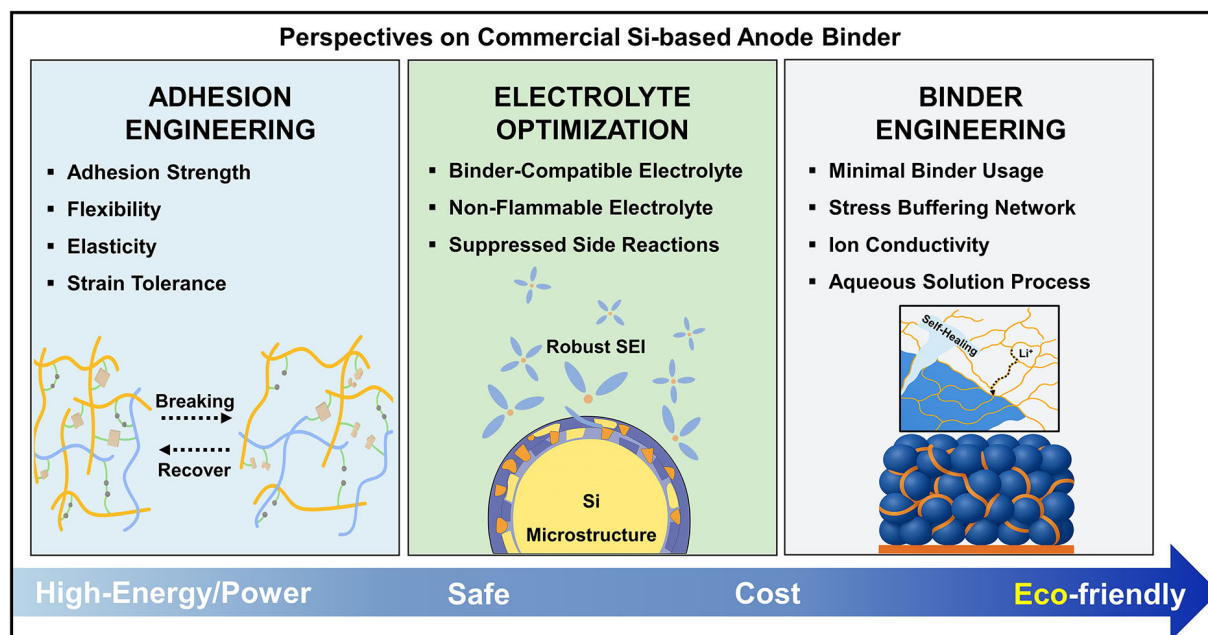


Figure 10. Schematic representation of future design strategies for commercial Si anode binders. Key directions include: (i) adhesion engineering to enhance interfacial binding and mechanical cohesion; (ii) electrolyte optimization to improve compatibility and suppress undesirable side reactions; and (iii) binder engineering to reduce binder content, accommodate volume fluctuations, facilitate ionic transport, and ensure water solubility. These strategies collectively aim to enhance mechanical durability and electrochemical performance, while supporting cost-effectiveness and environmentally sustainable processing. The original figure was created by the authors.

limitations will require advanced molecular design to improve slurry wettability, enhance interfacial bonding with active materials and current collectors, and maintain uniform particle dispersion. If successfully realized, these systems could simplify electrode formulations, reduce processing complexity, and improve production efficiency. They also hold the potential to significantly lower manufacturing costs for both lithium-ion and solid-state batteries, representing a transformative pathway toward the commercialization of high-capacity Si anode technologies across multiple battery platforms. Looking across the evolution of binder technologies, it is clear that progress has followed a stepwise trajectory from PVDF toward water-based CMC/SBR systems, then to PAA-centered formulations, and most recently to dynamic cross-linked and multifunctional architectures. This pathway, summarized in the industrially oriented roadmap of [Figure 1](#), highlights how binder design has continuously adapted to balance adhesion, mechanical robustness, ionic conductivity, and processing feasibility. Importantly, the “Future” stage in the roadmap underscores the shift from academic demonstrations toward scalable solutions such as multifunctional and solid-state binders. By situating these perspectives at the conclusion of the review, we aim to emphasize not only the scientific advances achieved so far but also the practical milestones and challenges that lie ahead for commercialization. Looking ahead, the development of single-component multifunctional binder systems that can combine mechanical robustness, strong adhesion, and ionic conductivity represents a particularly promising yet technically demanding research direction. If realized, such systems could greatly simplify electrode formulations and accelerate the commercialization of high-capacity Si anode technologies.

In summary, this review has synthesized recent advances in natural, synthetic, branched, covalently cross-linked, and dynamically cross-linked binders for Si-based anodes, with an emphasis on linking molecular design strategies to electrochemical performance and manufacturability. By integrating cross-study analysis and author perspectives, we have identified key trade-offs between adhesion, elasticity, ionic conductivity, and processing compatibility. Industrially, while PAA-centered systems currently offer a

pragmatic path for higher Si loadings, hybrid and multifunctional binders hold promise for long-term scalability. Continued innovation in binder chemistry, coupled with environmentally responsible manufacturing, will be essential for realizing the full potential of Si-based anodes in both liquid electrolyte and solid-state battery systems. Beyond material-level advances, the next phase of binder research will benefit from system-level integration, where binder design is coupled with conductive additives, electrode architecture, and electrolyte formulations. Such holistic approaches are expected to maximize the practical impact of binder innovation, ensuring that progress in molecular design translates effectively to full-cell stability, scalability, and cost competitiveness.

DECLARATIONS

Authors' contributions

Characterization, original draft writing: Lim, S. Y.; Kim, J. H.
Review, editing, and supervision: Mun, J.

Availability of data and materials

Not applicable.

AI and AI-assisted tools statement

Not applicable.

Financial support and sponsorship

This work was supported by the Ministry of Trade, Industry & Energy/Korea Evaluation Institute of Industrial Technology (MOTIE/KEIT) (20022514 & RS-2024-00449747).

Conflicts of interest

Kim, J. H. is a Senior Editorial Board member of the journal *Microstructures*. Kim, J. H. was not involved in any steps of editorial processing, notably including reviewer selection, manuscript handling, or decision making, while the other authors have declared that they have no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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