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Establishing a Resilient Conductive Binding Network for Si-Based Anodes via Molecular Engineering

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Cite This: *Acc. Chem. Res.* 2022, 55, 2088−2102 Read Online

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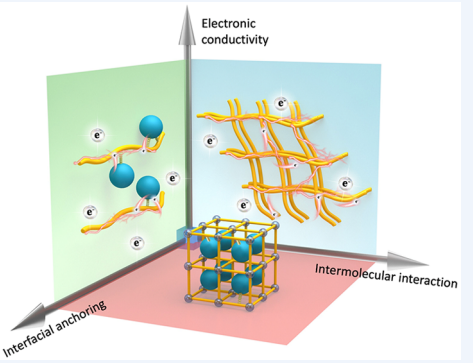
CONSPECTUS: Silicon-based anode materials have become a research hot spot as the most promising candidates for next-generation high-capacity lithium-ion batteries. However, the irreversible degradation of the conductive network in the anode and the resultant dramatic capacity loss have become two ultimate challenges that stem from inherent characteristics of the Si-based materials, including poor conductivity and massive volume changes (up to 300%) during cycling. Apart from optimization of the active materials, one effective way to stabilize high-capacity Si-based anodes is by designing polymeric binders to reinforce the conductive networks during repeated charge and discharge processes. As an inactive component in the electrode, the binder not only holds other components (e.g., active materials, conductive agents, and current collectors) together to maintain the mechanical integrity of the electrode but also serves as a thickener to facilitate the homogeneous distribution of particles. Therefore, binders play a key role in Si-based anodes by maintaining the integrity of conductive networks in the electrode.



In this Account, on the basis of the extensive binder-related work on Si-based anodes since the 2000s, efforts made on maintaining the conductive network can be categorized into two main strategies: (1) stabilization of the primary conductive network (which generally refers to conductive agents) by enhancing the binding strength and resilience of the binding between electrode components (i.e., Si particles, conducting agents, and current collectors) via various interactions (e.g., dipolar interactions and covalent bonds) and (2) construction of the secondary conductive network by employing conductive binders, which serve as a molecular-level conductive layer on active materials. In this sense, functional groups in binders can be divided into two categories: mechanical structural units and conductive structural units. On the one hand, functional groups with strong polarities (e.g., −OH, −COOH, $-NH_2$, and −CONH−) generally serve as binding structural units because of their bonding tendencies; on the other hand, exhibiting high electronic conductivity, conjugated functional groups (e.g., $-C_4H_4O_2S-$, $-C_{16}H_9$, $-C_{13}H_8-$, and $-C_{12}H_8N-$) are commonly found in conductive binders. Through establishing the correlation between structural units and their corresponding properties, we systematically summarize the optimization strategies and design principles of binders to achieve a robust conductive network in Si-based anodes. In addition, integration of desirable mechanical properties and high conductivity into the binder in order to achieve a multidimensionally stable conductive network is proposed. Through an insightful retrospective and prospective on binders, a key electrode component, we hope to provide a fresh perspective on performance optimization of Si-based anodes.

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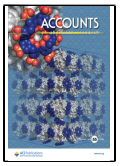
Received: April 29, 2022
Published: July 22, 2022



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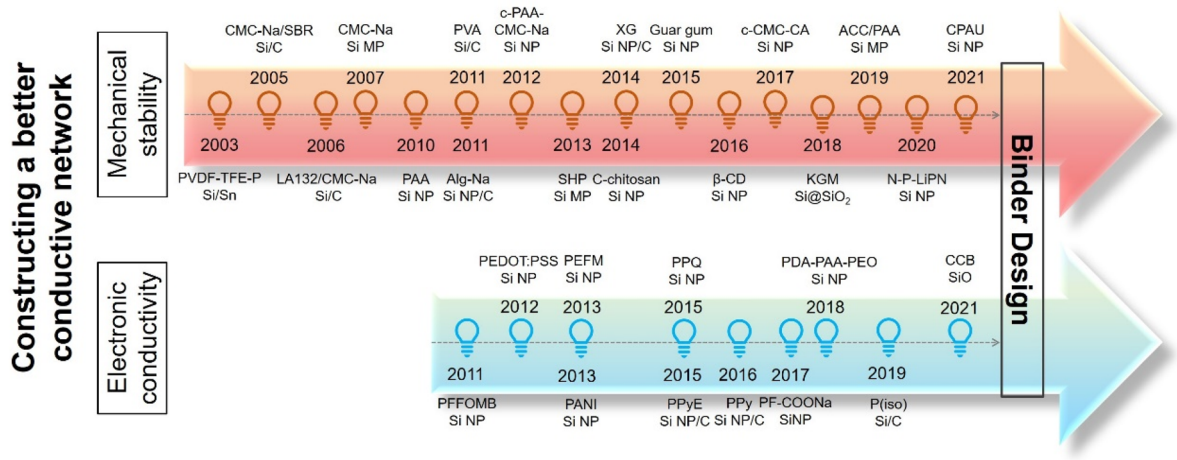

Figure 1. Timeline of major milestones in Si-based anode binder research.

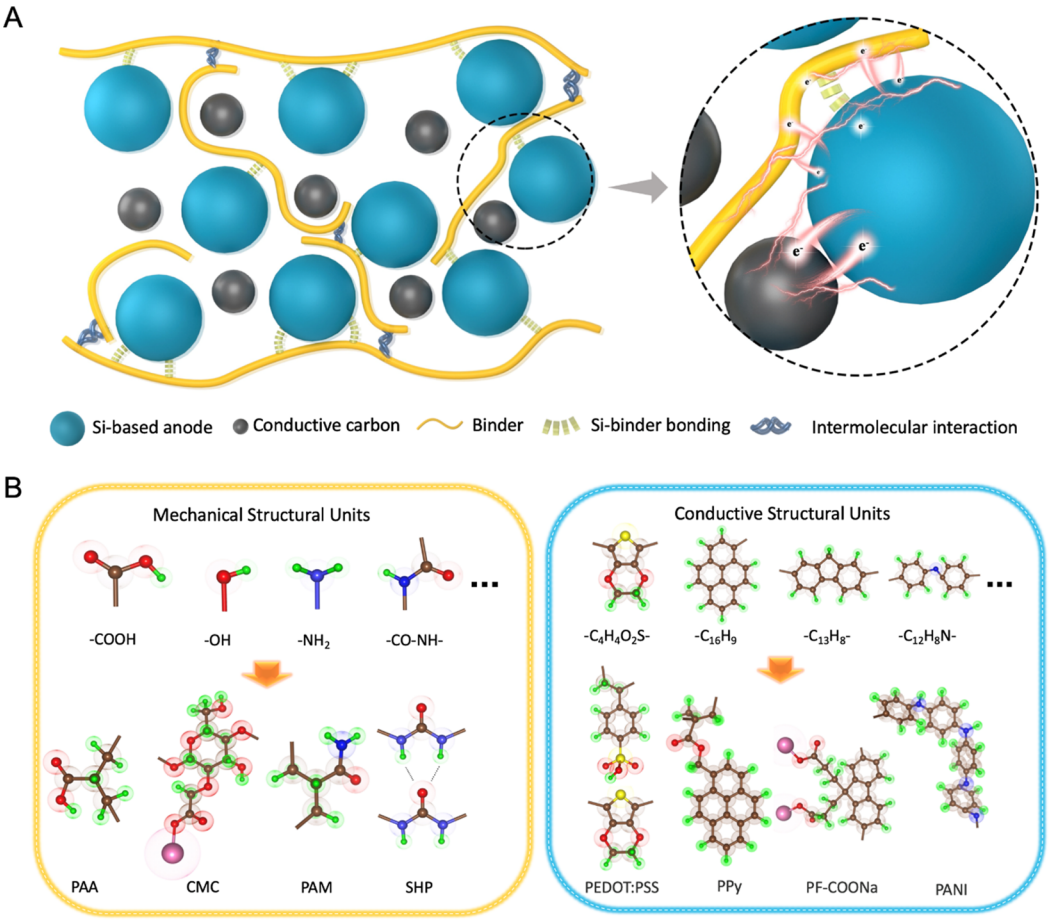

Figure 2. (A) Schematic illustration of key factors for the conductive network in a Si-based electrode. (B) Representative mechanical and conductive structural units of different binders in Si-based anodes.

intrinsic conductivity to serve as the secondary conductive network but also exhibits excellent mechanical properties to preserve the network.

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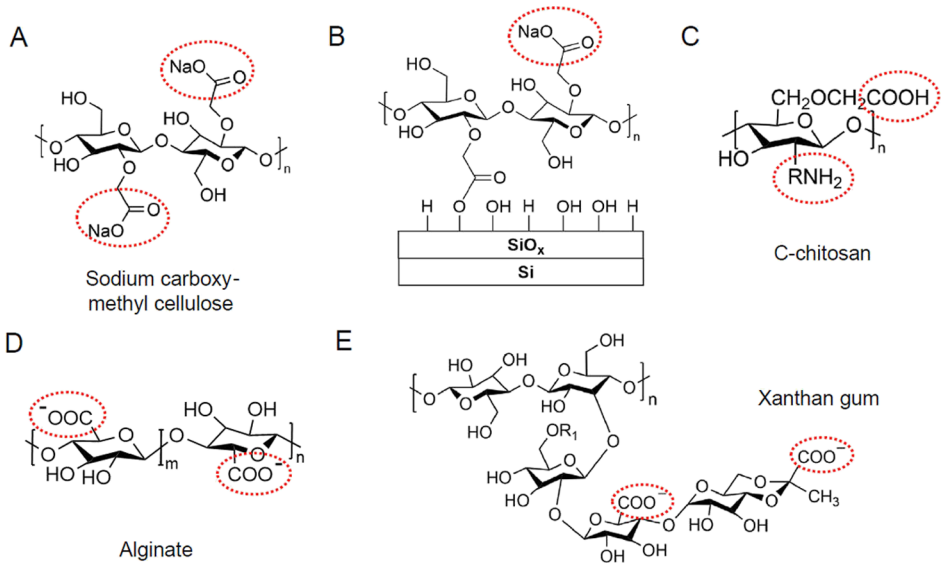

Figure 3. (A) Molecular structure of sodium carboxymethyl cellulose (CMC-Na). (B) Condensation reaction between a free carboxylate group of CMC-Na and the partially hydrolyzed SiO_2 layer on the surface of a Si particle. (C–E) Molecular structures of (C) C-chitosan, (D) alginate, and (E) xanthan gum.

produced additional robustness to balance the softness of the hydrogen-bond-containing self-healing polymer and provide a strong binding force with the Si surface.

1. INTRODUCTION

In the efforts to develop next-generation lithium-ion batteries (LIBs), high-capacity electrode materials are desirable. Among the promising candidates, silicon-based anodes stand out because of their theoretical specific capacity (1000–4200 mAh g^{-1}), low redox potential (~0.4 V vs Li/Li^+), environmental friendliness, and low cost. However, their large volume swing (100–300%) during cycling leads to pulverization of the active materials and separates them from the conductive network. Such a process also induces the generation of an unstable and thick solid–electrolyte interphase (SEI).[5] Therefore, building a robust conductive network in Si-based anodes can be considered a general strategy to realize their practical use.

As an inactive component in the electrode, a binder not only holds the other components (e.g., active materials, conductive agents, and current collectors) together to maintain the mechanical integrity of the electrode but also serves as a thickener to facilitate the homogeneous distribution of particles.[6] Nevertheless, the importance of the binder is often underestimated for intercalating-type electrode materials, which barely suffer from volume changes.[7,8] However, once drastic volume changes are taken into consideration, upgrading the binder will be necessary to maintain the integrity of conductive networks.

On the basis of the extensive binder-related work on Si-based anodes from the 2000s to nowadays (Figure 1), efforts made to maintain the conductive network can be categorized into two main strategies: (1) maintaining the primary conductive network, where electrons are transferred through limited physical contact between conductive agents (e.g., conductive carbon) and other electrode components, through boosting of the mechanical stability of the electrode on a macroscopic level and (2) construction of a secondary conductive network, where electrons are transferred through less conductive agents (e.g., the binder) but with larger contact areas by employing conductive binders, which serve as a molecular-level conductive layer on the active materials. From the perspective of electron transfer, the primary conductive network allows faster electron flow but exhibits a limited distribution. To prevent the active materials from being disconnected from the primary conductive network, the traditional strategy is either to upgrade the intermolecular interactions of binders or to enhance the interfacial anchoring between the binder and the active materials (Figure 2A). The former approach aims to reinforce the mechanical strength of the binder, whereas the latter improves the adhesive property of the binder. More recently, binders with improved electronic conductivity have been investigated to serve as the secondary conductive network in the electrode.[9] As an extension of the primary conductive network, the secondary conductive network not only ensures that the active materials remain in the conductive network in cases where they are physically separated from conductive agents but also homogeneously offloads the current flow on the surface of the active materials so that voltage polarization can be reduced (Figure 2A).

For electrode materials, their electrochemical properties are dictated by their crystalline structures, which consist of periodically arranged basic structural units with vastly different functions.[10] By the application of this fundamental understanding to binder studies, different functional groups in binders can also be divided into two categories: mechanical structural units and conductive structural units. As demonstrated in Figure 2B, on the one hand, functional groups with strong polarities (e.g., –OH, –COOH, $-NH_2$, and –CONH–) generally serve as mechanical structural units because of their bonding tendencies, whereas on the other hand, conjugated functional groups that exhibit high electronic conductivities (e.g., $-C_4H_4O_2S-$, $-C_{16}H_9$, $-C_{13}H_8-$, and $-C_{12}H_8N-$) are commonly found in conductive binders. Herein, a retrospective study on the developmental trend of binders for Si-based anodes is carried out. From the perspective of different structural units and the corresponding properties, we systematically summarize the optimization strategies and design principles of binders to provide an in-

https://doi.org/10.1021/acs.accounts.2c00259
Acc. Chem. Res. 2022, 55, 2088–2102

depth understanding of the construction of a stable conductive network in Si-based anodes.

2. ESTABLISHING MECHANICALLY ROBUST ELECTRODES

As previously discussed, a binder's ability to maintain the primary conductive network can be evaluated from two aspects: (1) the interaction between the binder and other electrode components and (2) the interaction between polymeric binders. The former interaction represents how well the active materials adhere to the electrode, and the latter determines the macroscopic mechanical properties of the electrode. On the basis of different binding units, these interactions can be divided into different categories in ascending order of bonding strength: van der Waals force (weak), dipolar interaction (medium), and covalent interaction (strong). As a commercial binder for cathode materials, polyvinylidene fluoride (PVDF) consists of a symmetrical C−F skeleton,[11] which precludes specific interactions other than the van der Waals force. Such a weak binding force cannot endure the large volume change of Si-based anodes during the lithiation and delithiation processes. Although thermal treatment and cross-linking methods have been adopted to improve the cycling performance,[12,13] the relatively poor mechanical properties of PVDF still limit its application in Si-based anodes. Therefore, instead of an isotropic force like the van der Waals force, specific directional bonding is required to construct a robust electrode. This section separately discusses specific interfacial anchoring between binders and active materials and inter/intramolecular bonding between binders. It should be noted that many binders may possess more than one type of interaction. Therefore, binders are categorized on the basis of their main interaction forces.

2.1. Interfacial Anchoring between Binders and Active Materials

Si particles are generally covered with a native and partially hydrolyzed SiO_2 layer, and the resultant superficial free silicic acid tends to undergo a chemical reaction (condensation) with the −COOH groups of the binder. In the past decades, polysaccharides have been proposed in binder formulation, with CMC-Na as the most prominent example. As a polymeric derivative of cellulose, sodium carboxymethyl cellulose (CMC-Na) consists of carboxymethyl-substituted β-glucopyranose with abundant −OH and $-COO^-$ groups (Figure 3A).[14] The ester bonds between CMC-Na chains and silicon particles were detected by Winter et al. (Figure 3B),[15] and they can be regulated through optimization of the pH[16] and the degree of substitution (DS), that is, the ratio of −OH groups substituted by $-OCH_2COONa$. Liu et al. found that the electrochemical performance of a Si-based anode using CMC-Na with DS = 0.55 was superior to those using CMC-Na with lower or higher DS values.[17] It should be noted that CMC-Na with an excessive DS tends to result in self-bonding and coiling of CMC-Na inside particles, which may have a negative impact on the binding performance between anode materials.[18]

Apart from CMC-Na, other polysaccharides with structures similar to that of CMC-Na have also been investigated. Zhang et al. used carboxymethyl chitosan (C-chitosan), a chitosan derivative with improved solubility in water, as a new binder for Si anodes (Figure 3C).[19] It was implied that the −OH, $-NH_2$, and −COOH groups in C-chitosan were bound to the hydroxylated Si surface, and C-chitosan exhibited superior electrochemical performance compared with CMC-Na. Alginic acid is a copolymer of 1→4-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues. Sodium alginate (SA), a high-modulus natural polysaccharide extracted from brown algae that contains $-COO^-$ groups in each of the polymer's monomeric units, was also used for Si-based anodes (Figure 3D).[20] Better performance was realized by the use of SA as the binder of Si anodes compared with CMC-Na because of the formation of strong R−C(=O)−O−Si bonds between SA and Si. Moreover, another polysaccharide, xanthan gum (XG),[1,21] which also contains −COO− groups in each of the polymer's monomeric units, was used as the binder for Si-based anodes by Wang and co-workers (Figure 3E).

Apart from polysaccharides, polyacrylic-based polymers containing a higher ratio of carboxylate groups in the molecules among the most promising candidates for binders of Si-based electrodes. Poly(acrylic acid) (PAA) with a high concentration of −COOH groups could potentially form strong covalent bonds on the surface of Si-based materials, leading to improved electrochemical performance. The first report on the use of PAA as the binder for Si anodes was by Yushin et al. in 2010.[22] Apart from nano-Si anodes, PAA was applied to SiO anodes by Komaba et al. and showed superior performance compared with PVDF, CMC-Na, and poly(vinyl alcohol) (PVA) binders.[23] Besides, such binding ability can be enhanced by modifying PAA with natural organics (glycinamide, catechol, and rosin) containing other functional groups (Figure 4A).[24,25] To achieve more efficient ester bonding, Hong et al. chemically etched Si particles to produce abundant −OH groups on the surface (Figure 4B). The abundant ester bonds formed on the Si−PAA interfaces led to a sufficiently high mechanical stability of the electrode for long-term

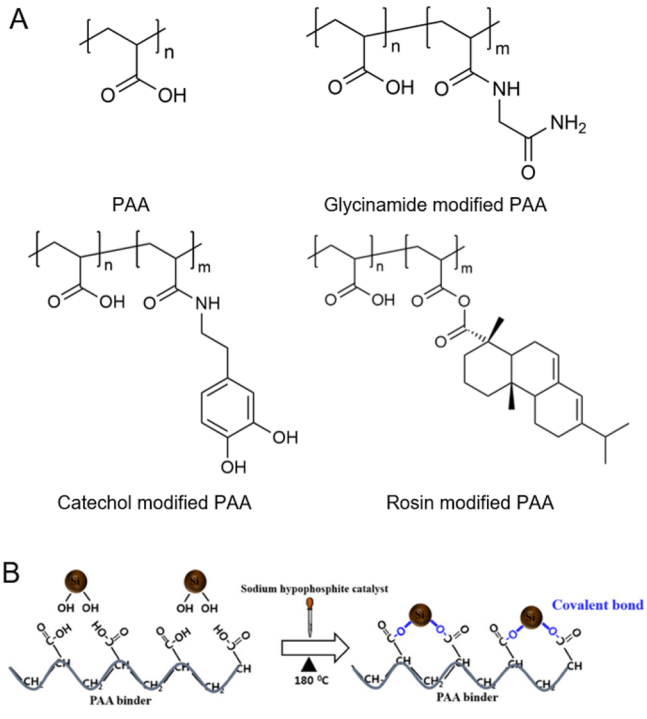

Figure 4. (A) Chemical structures of PAA and PAA-based copolymers. (B) Graphical representation of the chemical interactions between Si nanoparticles treated with piranha solution and PAA binder. Adapted from ref 26. Copyright 2019 American Chemical Society.

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Acc. Chem. Res. 2022, 55, 2088−2102

cycling.[26] As a copolymer that possesses a main polymer chain containing polyacrylonitrile (PAN) and PAA, LA132 was investigated by Xie et al. to fabricate SiO_x anodes.[27] Similarly, the presence of the carboxyl groups was proved to play an important role in alleviating the volume expansion of the Si-based materials.

2.2. Improving Intermolecular Interactions of Binders

2.2.1. Hydrogen-Bond-Derived Dynamic Networks. A hydrogen bond is the attraction between a hydrogen atom bonded on one molecule or molecular fragment X−H (the donor) and another atom or atomic group (the receptor), which is denoted as "X−H···Y", as shown in Table 1.

Table 1. Typical Hydrogen Bonds

X−H···Y	X−H group	Y group
F−H···F	F−H	−F
O−H···N	−COOH, −OH	$-NH_2$, −NH−, R_3N, −CN, −C═N−
O−H···O	−COOH, −OH	−COOH(R), −OH, −C═O, −C−O−C−
N−H···N	$-NH_2$, −NH−	$-NH_2$, −NH−, R_3N, −CN, −C═N−
N−H···O	$-NH_2$, −NH−	−COOH(R), −OH, −C═O, −C−O−C−

As a stronger intermolecular or intramolecular interaction compared with van der Waals forces, hydrogen bonding often dominates the bonding properties of such polymers. Hydrogen bonds can be dissociated and restored repeatedly, which endows binders with self-healing properties. In general, typical binders that are rich in hydrogen bonds are traditional homopolymers such as PAA, PVA, and some polysaccharides and glycoproteins such as crystalline β-cyclodextrin (β-CD),[28,29] agarose (AG),[30] guar gum (GG),[31] konjac glucomannan (KGM),[32] gum arabic (GA),[33] and so on, because of the abundant X−H and Y groups on the main chain.

Because of the presence of polar groups, it is well-demonstrated that cellulose-based polymers undergo many inter- and intrachain hydrogen-bonding interactions.[34,35] Larcher et al. suggested that hydrogen bonding enables a self-healing effect, which consequently preserves the electronic conductive path within the Si-based electrodes.[36] This result manifests the importance of robust polymer chain networks constructed within the electrode. To reconstruct the inter/intrachain hydrogen-bonding interactions of CMC-Na, Pan et al. applied nanosized Si particles to a SiO_x electrode slurry, which served as "nano-combs" to stretch CMC-Na chains from aggregated states.[37] As a result, an integrated and reinforced electrode structure can be constructed by the uniform and strong CMC-Na binding network.

PAA tends to possess a higher intensity of inter/intrachain interactions because of the higher density of polar groups. However, the higher crystallinity originating from the relatively ordered chain segment structure makes the PAA matrix brittle. To address this issue, Lin et al. constructed N-P-LiPN, a hard/soft modulated network binder that includes partially lithiated hard PAA as a framework and partially lithiated soft Nafion as a buffer via the hydrogen-bonding effect (Figure 5A).[38] N-P-LiPN has strong adhesion and mechanical properties to accommodate huge volume changes of Si anodes. To improve the self-healing capability of PAA, it was copolymerized with ureidopyrimidinone (UPy) moieties, which can undergo strong quadruple hydrogen bonding to endow the polymer networks with satisfactory mechanical properties.[39] Furthermore, Choi et al. introduced a polyrotaxane into PAA binder to make it have extraordinary elasticity, which is derived from the ring-sliding motion of the polyrotaxane.[40] The outstanding mechanical properties obtained by artificially increasing the polymer chain winding make the electrode remain intact in the repeated volume change process of silicon particles.

Bao et al. applied hydrogen-bond-directed self-healing polymers (SHPs) to a silicon microparticle (SiMP) anode to overcome the short cycle life (Figure 5B). SHPs have both mechanical and electrical healing capabilities, which allow cracks and damage to heal repeatedly during battery cycling.[4,41] Inspired by the composition of adhesive proteins in mussels, Yang et al. reported a PAA-based copolymer binder, poly(acrylic acid)−poly(2-hydroxyethyl acrylate-*co*-dopamine methacrylate) (PAA−P(HEA-*co*-DMA)), which can form a covalently cross-linked network with abundant hydrogen bonds in the local area, providing special self-healing capability (Figure 5C).[42]

2.2.2. Ionic-Bond-Derived Dynamic Networks. Polymers with charged groups can form an interconnected structure with metal ions or polymers carrying opposite charges through Coulombic attraction. The nondirectional and unsaturated interaction between ions allows polymer segments to form three-dimensional (3D) configurations in space. Similar to hydrogen bonding, moderate ion interaction is potentially associated with dynamic self-healing properties, which can adapt to the constant volume changes of Si-based anodes.

Sun et al. developed an alginate hydrogel binder for Si/C anodes utilizing the cross-linking effect between SA molecules via Ca^{2+} ions.[43] It was shown that the SA chains could be rearranged as a result of the ionic bonding between Ca^{2+} ions and $-COO^-$ groups of SA. The improved electrochemical performance is attributed to the enhanced mechanical properties of the cross-linked SA network. Additionally, Lee et al. studied the origin of the improved performance of Ca^{2+} added SA as a binder for Si anodes.[44] Their results revealed that the high unzipping energy, spontaneous rezipping, and electrolyte desolation of the cross-links contribute to the significant improvement in stiffness, toughness, and resilience of the electrolyte-solvated alginate binder compared with SA and other commercial binders. Moreover, other multivalent cations, such as Al^{3+}, Ba^{2+}, Mn^{2+}, and Zn^{2+}, were also applied to prepare alginate hydrogel binders for Si anodes (Figure 6A).[45] Al-alg and Ba-alg outperformed the other binders by showing good peeling test performance as well as the ability to maintain the electrode integrity during the charge and discharge processes. Furthermore, a polyacrylate binder that was ionically cross-linked by Fe^{3+} ions was successfully applied to the SiMP anodes (Figure 6B). The degradation of the SiMP electrode was effectively alleviated by tuning the monovalent (Na^+) and multivalent (Fe^{3+}) cations in the polyacrylate-based binder.[46]

Apart from the ionic interactions between the polymer and metal ions, those between polymers carrying opposite charges can also form 3D network structures. As shown in Figure 6C, Mun et al. reported a binder with electrostatic cross-links induced by a reversible interaction between acidic PAA and basic poly(benzimidazole) (PBI).[47] The physically cross-linked binder (PAA−PBI) was shown to endow Si composite electrodes with high mechanical strength, resulting in markedly enhanced battery performance compared with those based on PAA as the binder. Similarly, a self-healing porous scaffold structure formed by the electrostatic interaction between

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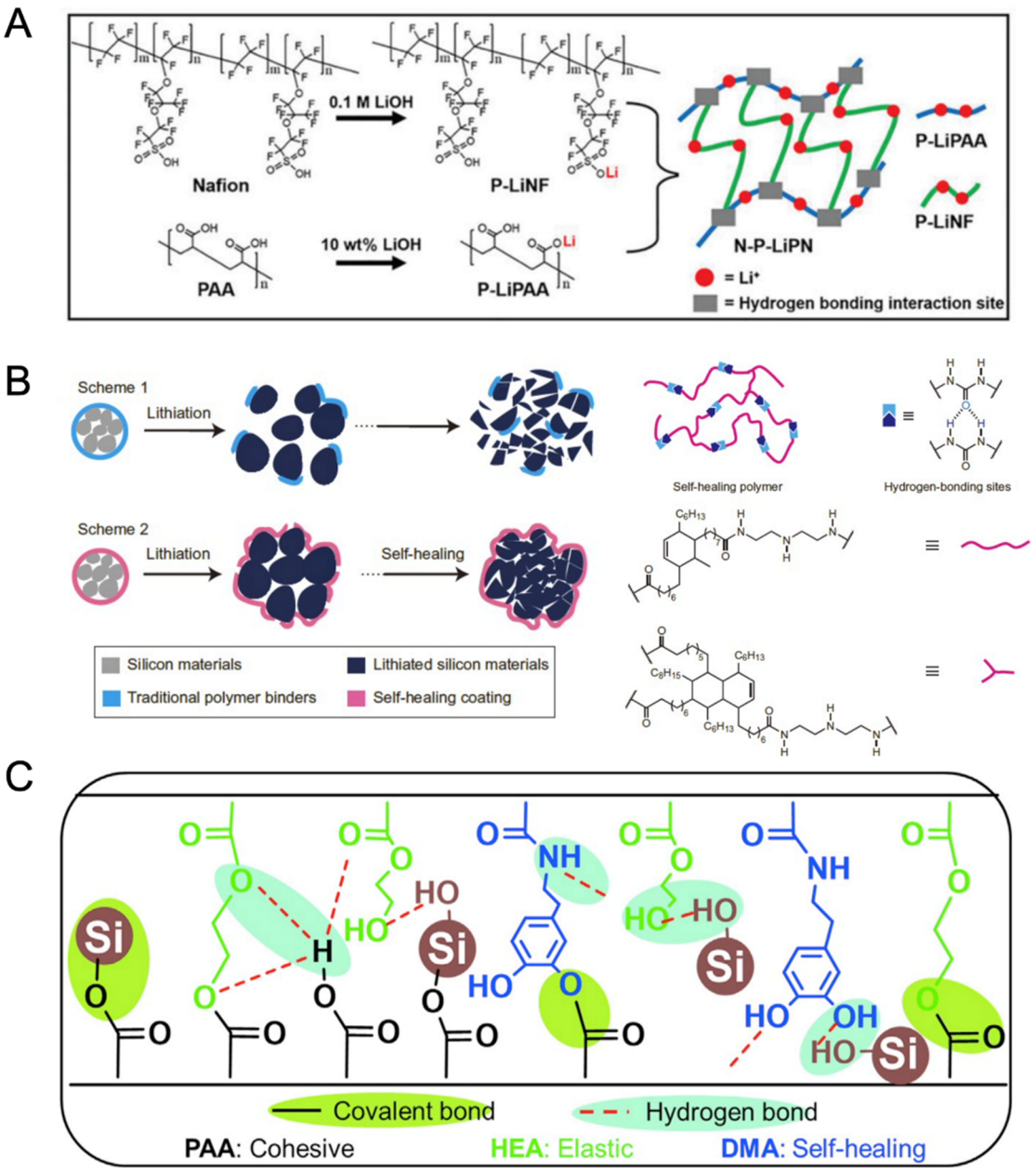

Figure 5. (A) Schematic of the preparation of the N-P-LiPN binder. Adapted with permission from ref 38. Copyright 2020 Wiley-VCH. (B) Schematic illustration of the design and behavior of the stretchable self-healing electrode and the chemical structure of the SHP. Adapted with permission from ref 41. Copyright 2013 Nature Publishing Group. (C) Structural formulas of PAA-P(HEA-*co*-DMA) copolymers and their interaction with Si. Adapted with permission from ref 42. Copyright 2018 Elsevier.

carboxylates ($-COO^-$) of Alg and protonated amines ($-NH_3^+$) of C-chitosan was found to effectively tolerate the tremendous volume changes of Si and preserve the electrode structure during cycling processes.[48]

2.2.3. Covalent-Bond-Derived Cross-Linking Networks. Because of the wide existence of carboxyl and hydroxy groups in the linear polymeric binders, the esterification reaction is the most commonly studied method to synthesize covalently cross-linked binders. Choi et al. first demonstrated that a cross-linked binder (c-PAA-CMC) comprising a cyclic polymer (CMC-Na) and a linear polymer (PAA) could be utilized to mitigate the large volume expansion of silicon anodes upon lithiation.[49] On the basis of the higher density of hydroxyl groups in PVA chains, Wang et al. developed an interpenetrated gel polymer binder for high-performance Si anodes by using a facile in situ thermal cross-linking technique based on linear polymers (PVA and PAA).[50] Instead of direct esterification reactions between polymers, micromolecules are also used as the cross-linkers to form cross-linked binder networks. Guo et al. developed a cross-linked carboxymethylcellulose and citric acid polymer binder (c-CMC-CA) by thermally induced condensation of −OH groups of CMC-Na and −COOH groups of citric acid (Figure 7A). It is suggested that c-CMC-CA possesses a high mechanical capability to tolerate the stress induced by the volume changes in Si-based anodes during electrochemical charge−discharge cycling.[51]

In addition to esterification reactions, other reaction types were also applied to the cross-linking of polymers with hydroxy groups, such as aldol condensation, Schiff base formation, copolymerization, etc. Yan et al. reported a cross-linked binder

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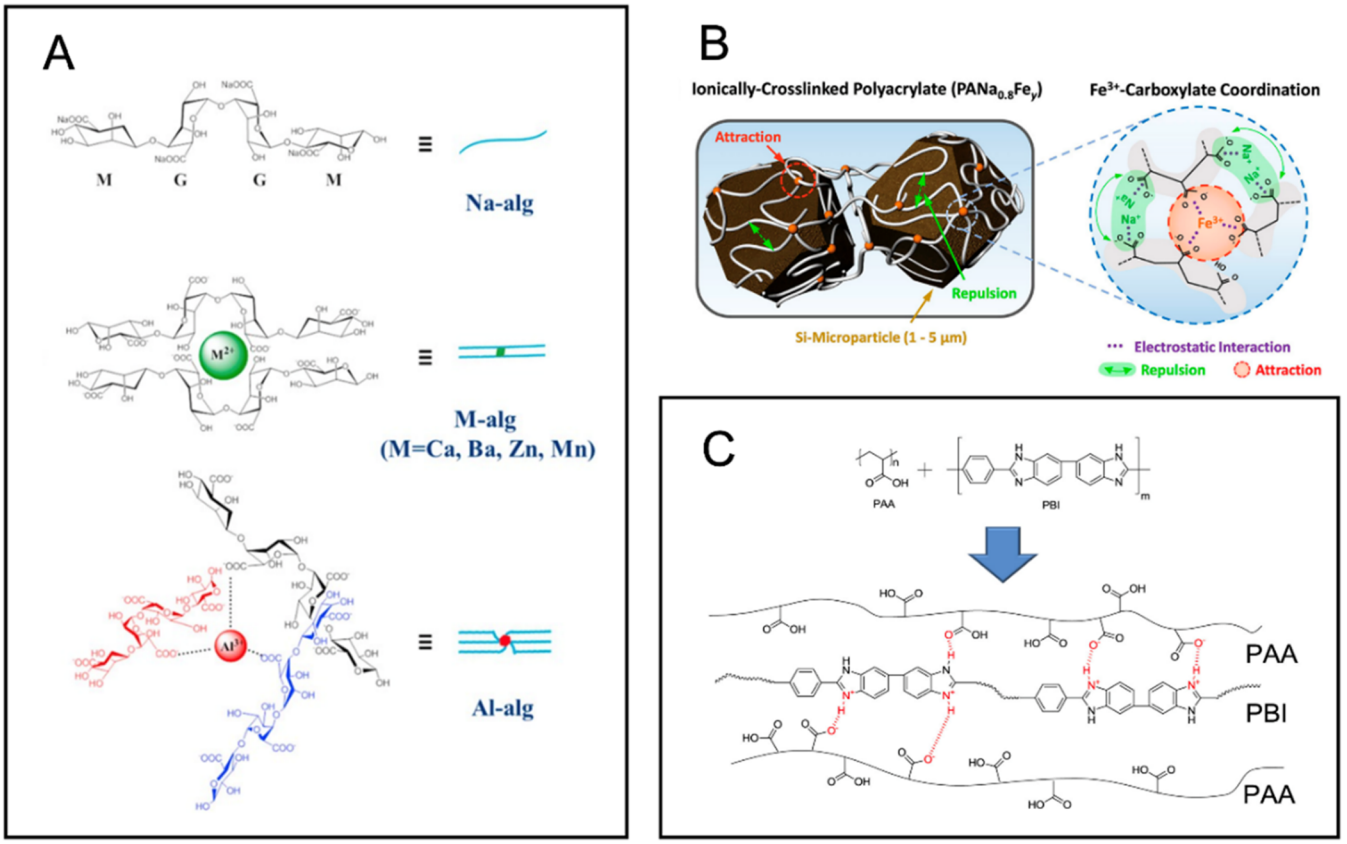

Figure 6. (A) Schematic of the molecular structures of Na-alg, M-alg, and Al-alg. Adapted with permission from ref 45. Copyright 2017 Elsevier. (B) Sodium polyacrylate chains chelated by monovalent cations ($(C_3H_{3.2}O_2Na_{0.8})_n$) repel each other, and the multivalent Fe^{3+} cations act as cross-linkers, contracting the nearby polymer chains. Adapted with permission from ref 46. Copyright 2020 Wiley-VCH. (C) Molecular interactions of the physically cross-linked polymeric binder through reversible interactions between PAA and PBI. Adapted from ref 47. Copyright 2015 American Chemical Society.

obtained by aldolization between −OH groups in dextrin and −CHO groups in glutaraldehyde that delivered improved electrochemical performance in Si anodes compared with PVDF, CMC, and pristine dextrin.[52] By cross-linking catechol-functionalized chitosan with glutaraldehyde via the Schiff mechanism,[79] Cao et al. developed a 3D cross-linked binder (CS-CG+GA) that exhibited improved stability of the conductive network (Figure 7B).[53] Liu et al. used a room-temperature fabrication process in which *N*,*N*-methylenebis-(acrylamide) (MBAA) acted as the cross-linker for PAM to synthesize a covalently cross-linked PAM (c-PAM) hydrogel.[54] The robust 3D c-PAM binder network not only significantly enhances the strain resistance of the electrode but also shows a strong affinity for bonding with the nano-Si surface.

Despite the strong binding effect exhibited by covalent bonds, it should be noted that cross-linking could lower the solubility of binders in solvents (e.g., H_2O, NMP) and eventually result in inhomogeneity of the electrodes. To circumvent this issue, Liu et al. reported a polymer binder with a highly stretchable and elastic network structure that was realized by in situ cross-linking of PAA with isocyanate-terminated polyurethane oligomers consisting of poly(ethylene glycol) (PEG) chains and UPy moieties through the reaction between isocyanate and carboxyl groups during the electrode preparation process (Figure 7C).[55] This binder not only sufficiently accommodates the volume change of Si but also provides strong mechanical support to effectively sustain the integrity of the Si anodes.

3. EXTENDING CONDUCTIVE NETWORKS AT THE MICROSCOPIC LEVEL

3.1. Applications of Conductive Polymers in Si-Based Anodes

Exhibiting inherent flexibility, the conductive binder could serve as an additional electron migration path to tackle the limiting features of the solely primary conductive network, helping to construct a hierarchical conductive network (Figure 8A). Despite the difference in the conductivity levels of the primary and secondary conductive paths, the polarization of alloy-based anodes would decrease because of the molecular-level contact with the conductive binder (Figure 8B).

The development of conductive binders is mainly based on π-conjugated conducting polymers possessing delocalized π-electronic conductive units, which have been extensively studied in many fields such as light-emitting diodes, biosensors, organic electrodes, etc.[56−58] In general, conducting polymers possess a typical electronic band gap (E_g) of 1.5−3.0 eV, which can be regulated by adjusting the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the π system.[59] Some representative π-conjugated conductive units for conductive polymers are listed in Figure 8C. The charge transport occurs via mobility of charge carriers along the conjugated polymer chains and by hopping of these charges from chain to chain.[60] However, many conductive polymers are not natural for the application of binders. First, the relatively rigid chain structures of these

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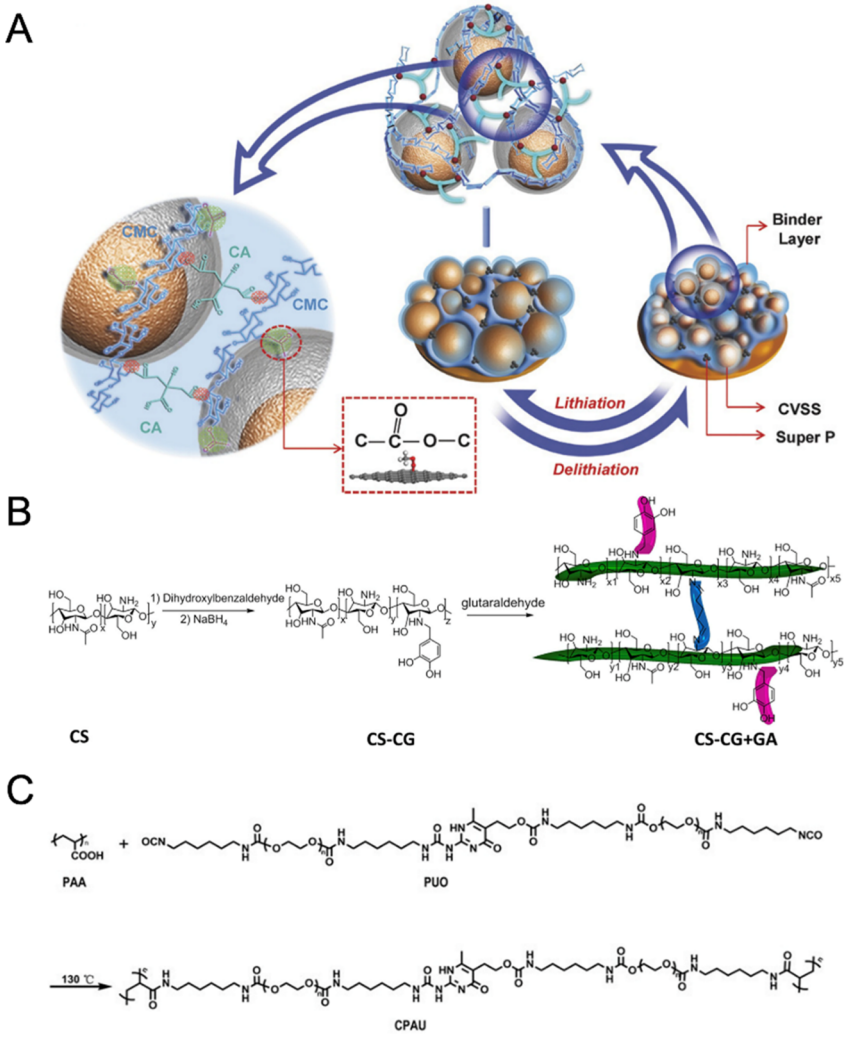

Figure 7. (A) Schematic illustration of chemical bonding between CVSS and the binder and cross-linking between CMC and CA. Adapted with permission from ref 51. Copyright 2017 Wiley-VCH. (B) Illustration of the synthesis of cross-linked catechol-rich CS network. Adapted from ref 53. Copyright 2019 American Chemical Society. (C) Synthetic scheme of the cross-linking of PAA with isocyanate-terminated polyurethane oligomers. Adapted from ref 55. Copyright 2021 American Chemical Society.

polymers result in low solubility in many solvents, which inhibits their applicability in conventional paste-casting electrode preparation protocols. Although they could be electrochemically deposited onto the anodes or even mixed with Si particles by mechanical ball milling,[61,62] those strategies are not suitable for constructing an effective secondary conducting network because of the lack of dispersion and the poor physical contact with the active materials.

Apart from processability, their conducting mechanism and chemical/electrochemical stability are also essential factors to be considered when they serve as conductive agents in anodes. For instance, although some widely used conductive polymers (e.g., polyaniline (PANI)) are suitable for use as cathode binders, it is difficult to maintain their doping states in reducing environments. As a result, their conductivity is compromised when they are used in anodes.[63] Therefore, conductive polymers that can be cathodically doped are potentially more suitable for anodes. For example, poly(phenanthraquinone) (PPQ) can be cathodically doped through electrochemical reduction in the voltage range of 0.1−0.15 V vs Li/Li^+ during the first lithiation process. Because of the enhanced electronic conductivity, PPQ significantly boosted the rate performance of Si anodes.[64] Nevertheless, the lack of mechanical structural units might hinder their large-scale applications. Since the most critical aspects of conductive binders are their capabilities to conduct and bind, the key to constructing a stable secondary conductive network can be regarded as following two main strategies: (1) tuning the conductivity of conductive binders through electrochemical or chemical doping and (2) enhancing the robustness of the secondary conductive network by introducing mechanical structural units.

3.2. Doping Chemistry of Conductive Binders for Better Conductivity

The conductivity exhibited by the primary conducting agent (i.e., acetylene black) could be as high as 10^2−10^3 S cm^{-1}. In comparison, most conjugated polymers are semiconductors with electronic conductivities less than 10^{-6} S cm^{-1} in their neutral states, which could hardly serve as a secondary conductive network. To boost the charge mobilities within the Si-based electrodes, tuning the conductivity of conjugated polymers is a key strategy for developing conductive binders. Similar to inorganic semiconductors, the conductive polymer chains could generate positive/negative charges via oxidation/

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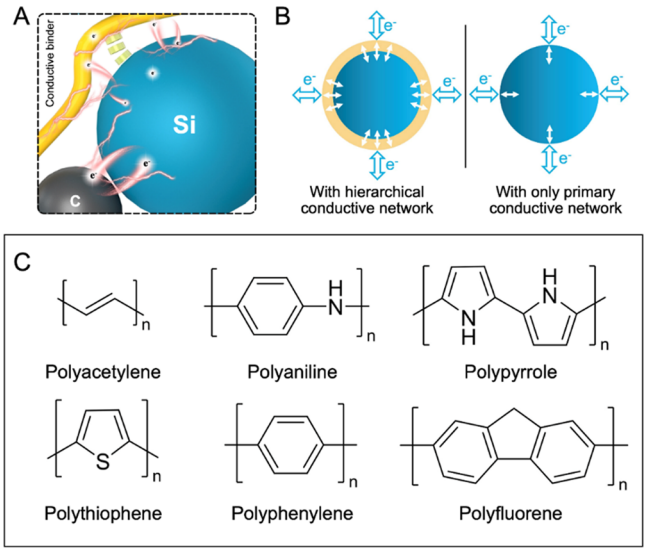

Figure 8. (A) Scheme of the hierarchical conductive network consisting of primary (i.e., conductive carbon) and secondary (i.e., conductive binder) conductive agents. (B) Scheme of the depolarization effect on active materials enabled by the hierarchical conductive network. (C) Molecular structures of typical conductive polymers.

reduction and stay electrically neutral by counterion doping. As a result, conductivities as high as 10^0–10^3 S cm^{-1} could be achieved for these polymers after cathodic (n-type)/anodic (p-type) doping through chemical or electrochemical methods.[65−68]

Tailoring the HOMO/LUMO energy levels of the π system is effective for enhancing the conductivity of conductive binders for Si-based anodes. Polyfluorene (PF) derivatives are well-known as highly fluorescent compounds and blue-light-emitting materials. They contain a rigidly planar biphenyl structure in the monomer unit with facile functionalization at C9, providing access to regulation of the solubility and other physical properties.[69] To optimize the LUMO energy level of PF-based polymers, Liu et al. employed synchrotron-based soft X-ray absorption spectroscopy (XAS) to monitor their unoccupied conduction states (Figure 9A).[63] It was found that compared with poly(9,9-dioctylfluorene) (PFO), poly(9,9-dioctylfluorene-*co*-9-fluorenone) (PFFO) exhibited a new LUMO state at 287.7 eV (much lower than those of PFO and PANI) due to the addition of carbonyl groups. This finding was further confirmed by ab initio density functional theory (DFT) simulation results. Thereafter, Pan and co-workers proposed a similar strategy by synthesizing a phenanthraquinone (PQ)-doped PF-based copolymer (PFPQ-COONa) (Figure 9B).[70] The enhanced n-type doping enabled by the PQ units yielded an improvement of the rate capability of Si nanoparticle electrodes without compromising the cycling stability. Computational simulations of the HOMO and LUMO distributions for both the initial state and the reduced state of the segment strongly indicated increased chemical activity located in the reduced PQ group.

With regard to typical p-type conductive polymers, chemical doping is a common approach to achieve high conductivity. For example, protonated copper(II) phthalocyanine tetrasulfonate salts can act as dopants to provide electronic conductivity of polypyrrole.[71] Protonic acid dopants can protonate the nitrogen groups on PANI, leading to the

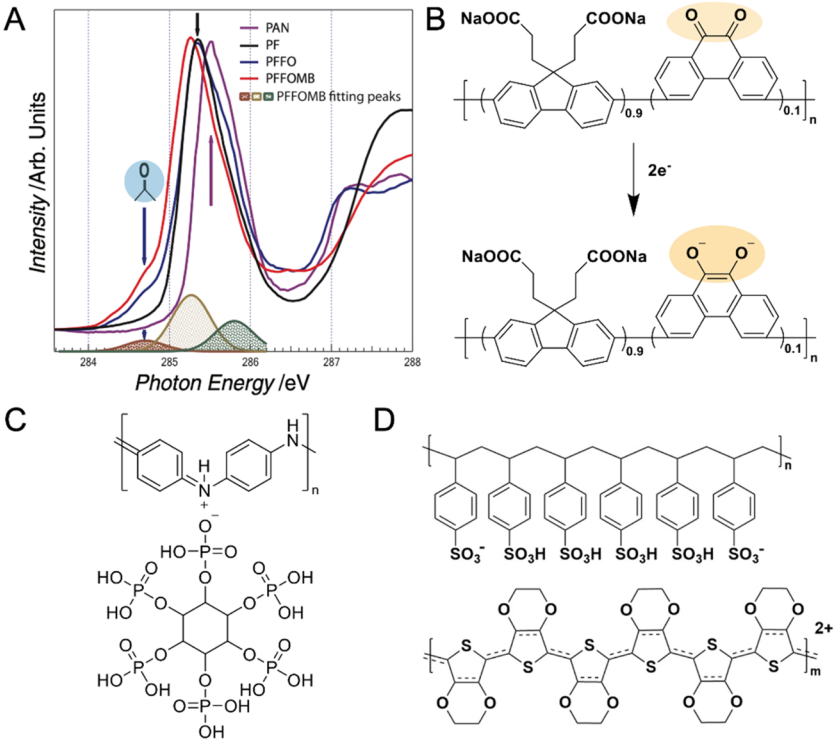

Figure 9. (A) Carbon 1s XAS spectra collected on a series of polymers. Adapted with permission from ref 63. Copyright 2011 Wiley-VCH; (B) Scheme of the proposed reduction reaction of PFPQ-COONa. (C) Chemical formula of phytic acid-doped PANI. (D) Molecular structure of PEDOT:PSS.

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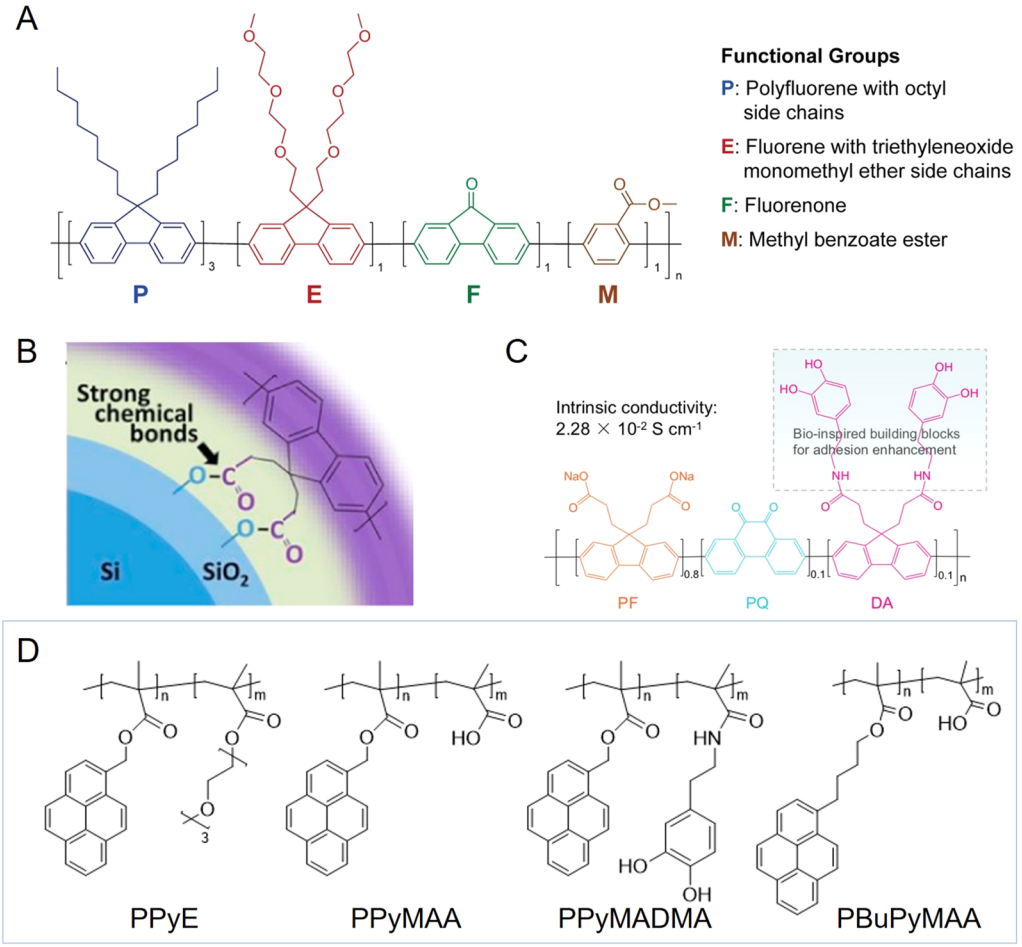

Figure 10. (A) Chemical structure and functional groups of PEFM. Adapted from ref 78. Copyright 2013 American Chemical Society. (B) Schematic of the formation of chemical bonds between PF-COONa and Si. Adapted with permission from ref 3. Copyright 2017 Elsevier. (C) Chemical structure of PFPQDA with bioinspired building blocks. Adapted with permission from ref 79. Copyright 2022 Wiley-VCH. (D) Chemical structures of PPy-derived copolymers: PPyE, PPyMAA, PPyMADMA, and PBuPyMAA.

delocalization of positive charge on polymer chains, which not only improves the conductivity but also promotes the processability of PANI. Cui et al. used phytic acid as both the gelator and dopant for a PANI binder to improve the mechanical strength and conductivity of the electron-conducting framework via in situ polymerization (Figure 9C).[72] Processable poly(3,4-ethylene dioxythiophene) (PEDOT) binders were developed by the use of poly-(styrenesulfonate) (PSS) as a dopant,[73] and the mixture (PEDOT:PSS) has been widely employed as the conductive binder for both anodes and cathodes in LIBs (Figure 9D).[74] Zhang et al. prepared a Si/PEDOT:PSS composite electrode by in situ polymerization, and that electrode showed improved cycling performance compared with a Si electrode without the polymer matrix, especially for the initial cycles.[75] Additionally, the electronic conductivity of PEDOT:PSS composites can be further enhanced by introducing additional dopants such as formic acid (FA)[76] or sulfuric acid.[66] For example, PEDOT:PSS with 20 wt % FA was found to promote the Si electrodes' electronic conductivity up to 4.2 S cm^{-1}, which was over 100 times that of the Si/PEDOT:PSS electrode before FA treatment.[77]

3.3. Improving the Mechanical Properties of Conductive Binders

To overcome the inherently weak binder−binder and binder−Si interactions for conductive binders, one effective strategy is to introduce binding units into the chemical structure of the conductive binder to improve the interaction anchoring the binder to the other electrode components as well as intermolecular interactions. In 2013, Liu et al. introduced methyl benzoate ester units as the source of polar groups to improve the adhesion of a PF-based binder, which adheres to the SiO_2 surface of the Si particle and the CuO surface of the Cu current collector more effectively (Figure 10A).[78] At the same time, incorporating a short ether moiety increased the ductility of the polymers to accommodate the volume change of Si electrodes. Thereafter, a high content of carboxylate groups was introduced into PF-COONa by Pan and co-workers,[3] resulting in strong adhesion to Si particles and hence the superior cycle stability of Si electrodes (Figure 10B). Afterward, apart from the presence of covalent bonds originating from carboxyl groups within the electrodes, abundant hydroxyl and acylamino groups were further brought into the polymer chains to generate multiple dynamic hydrogen-bonding interactions (Figure 10C).[79] For better adhesion and swelling properties of pyrene-based conductive polymers, a series of copolymers were prepared by introducing

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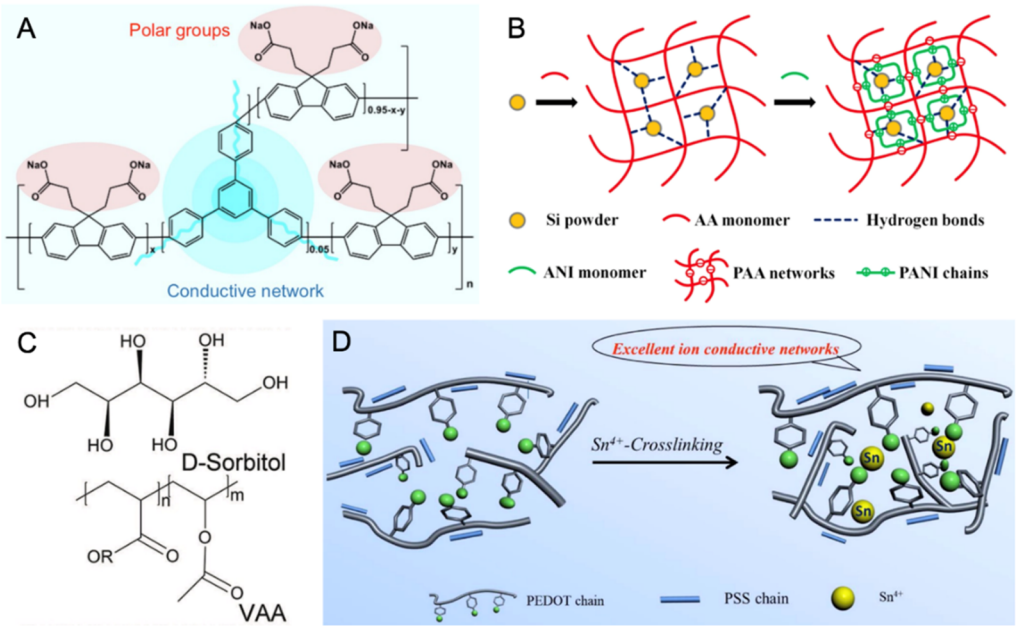

Figure 11. (A) Structure of the cross-linked conductive binder abbreviated as CCB. Adapted with permission from ref 2. Copyright 2021 Wiley-VCH. (B) Schematic illustration of the formation process for the 3D conductive PAA/PANI IPN binder for Si anodes. Adapted from ref 85. Copyright 2015 American Chemical Society. (C) Chemical structures of the cross-linking agent D-sorbitol and VAA. Adapted with permission from ref 87. Copyright 2017 Wiley-VCH. (D) Schematic representation of the Sn^{4+}-PEDOT:PSS binder structure. Adapted from ref 88. Copyright 2020 American Chemical Society.

functional groups into the PPy chains, such as ethylene oxide functional groups,[80] carboxyl groups,[81] dopamine methacrylamide (DMA) groups,[82] and butyl segments[83] (Figure 10D). Zheng et al. proposed that the inserted butyl segments act like a "spring" to maintain the mechanical integrity of the electrode.[83] Moreover, Cui et al. used phytic acid as both the gelator and dopant to improve the mechanical strength of the electron transfer framework via in situ polymerization.[84] The phosphoric acid groups in phytic acid molecules can bind to the Si surface through hydrogen bonding, hence prolonging the cycle lifetime. In a word, interweaved interactions can greatly boost the mechanical strength (i.e., intersegmental bonding) as well as the adhesion property (i.e., polymer−Si bonding) of electrodes, resulting in improved cycle stability.

Alternatively, 3D cross-linked networks could better adapt to the drastic volume changes. The cross-linked structure of conductive binders shows resilient mechanical properties, enabling the electrode to endure deformation after prolonged cycling. Pan et al. designed a polyfluorene-type cross-linked conductive binder (CCB) by connecting linear conductive binder (LCB) chains to the conjugated anchor points (i.e., triphenylbenzene) through covalent bonds to serve as a resilient secondary conductive network for SiO_x anodes that effectively maintains the integrity of the whole conductive network by preventing deformation during cycling (Figure 11A).[2] To improve the mechanical properties of PANI, Xu et al. developed a facile route to prepare a 3D conductive interpenetrated gel network for Si anodes through chemical cross-linking of acrylic acid monomer followed by in situ polymerization of aniline (Figure 11B).[85] Besides, Senftle et al. found that pyrolyzed polyacrylonitrile (PPAN) chains exhibit dense and highly ordered stacking behavior at the anode interface due to repeated pyridine structures, leading to stronger adhesion and higher Li^+ conductivity.[86] In a subsequent study, Huo et al. reported a stretchable conductive glue (CG) binder formed by cross-linking of D-sorbitol and vinyl acetate−acrylic (VAA) onto PEDOT:PSS chains. This binder can be stretched up to 400% in volume without losing conductivity (Figure 11C).[87] Qian et al. proposed a multivalent ion (Sn^{4+}) cross-linked PEDOT:PSS to enhance the strength by the formation of 3D structured polymers (Figure 11D).[88] Besides, their group also used glycerol as a cross-linker for a PEDOT:PSS binder, which significantly boosted the peeling force of Si electrodes and subsequently improved the electrochemical performance.[89]

4. CONCLUSIONS AND OUTLOOK

As demonstrated by various examples in the previous literature, the polymeric binder plays a key role in Si-based anodes by maintaining the integrity of conductive networks in the electrode. On the basis of their different roles in maintaining the conductive network of Si-based anodes, current design and improvement strategies for polymeric binders can be categorized into maintaining mechanical stability and pursuing higher electronic conductivity.

A robust macroscopic conductive network can be achieved by tuning the mechanical structural units to promote intermolecular interactions of binders or to enhance the interfacial anchoring between the binder and the active materials. Dipolar interactions essentially have reversible bonding properties, and the efficiency of bond recovery depends on the strength of dipolar interactions, which facilitates self-healing properties in the electrodes. With the highest bond energies, covalent bonds are critical for improving the binder−particle interactions, especially for active materials with large volume swings.

Alternatively, conductive binders with extended π conjugation throughout the polymer backbone serve as a conducting bridge (secondary conductive network) between Si particles via molecular-level contacts, keeping Si electro-

https://doi.org/10.1021/acs.accounts.2c00259
Acc. Chem. Res. 2022, 55, 2088−2102

chemically active during the repeated volume changes. Hence, from this perspective, their optimization approach includes promoting electronic conductivity through chemical/electrochemical doping as well as reinforcing their binding capability by introducing mechanical structural units in the molecular structures.

Finally, we offer some critical perspectives on binder research that may provide solutions for improving not only Si-based anodes but also, in broader terms, all electrode materials:

(1) In the future design of binders, mechanical properties and conductive properties should be considered simultaneously to construct a robust hierarchical conductive network. This goal might be achieved by introducing mechanical structural units (e.g., as branched chains) into a conductive polymer chain so that both binding and conducting properties can be integrated in one binder. Additionally, the interplay between binding units and conductive units is also worthy of in-depth study.

(2) Simulation techniques are also powerful tools for material screening and theoretical analysis. For instance, density functional theory (DFT) calculations could be used to estimate both properties of the binder. The prediction of electrochemical behavior and stress conditions of Si-based anodes at the macroscopic level can be achieved by finite-element simulations.

(3) Advanced characterization techniques should be developed for accurate evaluation of binders. For instance, quantitative measurement systems should be established to determine the effect of modification (e.g., doping and grafting) on the conductivity and binding properties of binders. Extra efforts also need to be dedicated to understanding various dynamic physicochemical processes of the electrode components via in situ characterization techniques (e.g., in situ Raman spectroscopy, in situ infrared spectroscopy, and in situ NMR spectroscopy).

(4) Apart from binding and conducting properties, other properties such as solubility, processability, and dispersity should be taken into account during binder design. Accordingly, relevant characterization techniques (e.g., computed tomography, rheological measurement, and zeta potential measurement) can be developed to evaluate these properties.

With this Account, we hope to stimulate research in these directions to further advance Si-based anodes for large-scale commercial applications.

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Notes

The authors declare no competing financial interest.

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https://doi.org/10.1021/acs.accounts.2c00259
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■ ACKNOWLEDGMENTS

We acknowledge financial support from The Shenzhen Science and Technology Research Grant (JCYJ20200109140416788) and the Soft Science Research Project of Guangdong Province (2017B030301013).

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https://doi.org/10.1021/acs.accounts.2c00259
Acc. Chem. Res. 2022, 55, 2088−2102