Advances of polymer binders for silicon-based anodes in high energy density lithium-ion batteries

Yu-Ming Zhao | Feng-Shu Yue | Shi-Cheng Li | Yu Zhang | Zhong-Rong Tian | Quan Xu | Sen Xin | Yu-Guo Guo

1CAS Key Laboratory of Molecular Nanostructure and Nanotechnology, CAS Research/Education Center for Excellence in Molecular Sciences, Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing, China
2Shenzhen EUBO New Material Technology Co., Ltd, Shenzhen, China
3University of Chinese Academy of Sciences, Beijing, China

Correspondence
Yu-Guo Guo, CAS Key Laboratory of Molecular Nanostructure and Nanotechnology, CAS Research/Education Center for Excellence in Molecular Sciences, Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, China.
Email: ygguo@iccas.ac.cn

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Abstract
Conventional lithium-ion batteries (LIBs) with graphite anodes are approaching their theoretical limitations in energy density. Replacing the conventional graphite anodes with high-capacity Si-based anodes represents one of the most promising strategies to greatly boost the energy density of LIBs. However, the inherent huge volume expansion of Si-based materials after lithiation and the resulting series of intractable problems, such as unstable solid electrolyte interphase layer, cracking of electrode, and especially the rapid capacity degradation of cells, severely restrict the practical application of Si-based anodes. Over the past decade, numerous reports have demonstrated that polymer binders play a critical role in alleviating the volume expansion and maintaining the integrity and stable cycling of Si-based anodes. In this review, the state-of-the-art designing of polymer binders for Si-based anodes have been systematically summarized based on their structures, including the linear, branched, crosslinked, and conjugated conductive polymer binders. Especially, the comprehensive designing of multifunctional polymer binders, by a combination of multiple structures, interactions, crosslinking chemistries, ionic or electronic conductivities, soft and hard segments, and so forth, would be promising to promote the practical application of Si-based anodes. Finally, a perspective on the rational design of practical polymer binders for the large-scale application of Si-based anodes is presented.

KEYWORDS
high energy density, lithium-ion battery, multifunctional binder, polymer binder, silicon anode
1 | INTRODUCTION

Since the first commercialization of lithium-ion batteries (LIBs) in 1991, LIBs have made significant strides and become the most predominant power sources for various portable electronic devices and electric vehicles.1-4 Moreover, as an efficient energy storage technology with relatively higher energy density and longer cycle life, LIBs also play a crucial role in dealing with the global climate problems and promoting the global sustainable development.5,7 However, after nearly 30 years of development, the conventional LIBs, which are composed of a graphite anode and lithium transition metal oxide cathode (e.g., LiCoO$_2$, LiNi$_x$Co$_{y}$Mn$_{1-x-y}$O$_2$ (NCM), or LiNi$_x$Co$_y$Al$_{1-x-y}$O$_2$ (NCA)), are approaching their theoretical limitations in energy density and even the state-of-the-art commercial LIBs are insufficient to satisfy the fast-growing modern technologies and consumer demands.6,8 Developing innovative electrode materials or battery techniques to make LIBs with significantly improved energy density and lowered cost is highly demanded in both academia and industry.

Silicon (Si) can release a specific capacity over 3500 mA h g$^{-1}$, which is almost 10 times of the conventional graphite anodes (~372 mA h g$^{-1}$). Meanwhile, it shows a relatively low operating voltage (below 0.5 V vs. Li$^+$/Li) and is the second most abundant element in the Earth’s crust. These advantages make Si one of the most promising anode materials for the next-generation high energy density LIBs.9-14 However, the intrinsic huge volume change (~300%) of Si particles during alloying/dealloying process with Li$^+$ will lead to pulverization of Si particles, electrode delamination, unstable solid electrolyte interphase (SEI), and finally the severe degradation of battery performance, which greatly hinders the commercial application of Si-based anodes in LIBs.12,13,15,16 To solve these problems, strategies like constructing micro-structured, nano-structured and micro-nano composite structured Si anodes have been widely explored to mitigate the volume expansion in Si anodes.17-21 Si monoxide and its suboxides (SiO$_x$) with a specific capacity around 1500–2000 mA h g$^{-1}$ have also attracted a lot of attention due to their natural buffering effect and highly improved cycling stability.22,23 However, despite the significant progress in Si or SiO$_x$ materials, the individual utilization of Si or SiO$_x$ anodes to improve the energy density of LIBs is usually quite difficult because of the massive usage (>10 wt%) of polymer binders and conductive agents as well as the severe electrode swelling. According to the calculations by Kasavajjula et al., for LIBs with a ~200 mA h g$^{-1}$ cathode material and the conventional battery components (electrolyte, separator, current collectors, case, etc.), replacing graphite anode with anode materials having a specific capacity on the order of 1000–1200 mA h g$^{-1}$ could significantly enhance the energy density of LIBs.17 Currently, the most practical and commercially viable method to achieve this goal is the co-utilization of Si-based anodes and the conventional graphite anode.14,24-26 Although numerous progress has been made on Si/graphite or SiO$_x$/graphite composite anodes, overcoming the rapid capacity fading caused by the huge volume expansion of Si component remains a major challenge for their large-scale application in the high energy density LIBs.

Except for optimizing the Si-based materials themselves, advanced design of polymer binders plays a crucial role in ensuring the stable cycling of Si-based anodes and has attracted substantial attention.27-31 Polymer binder occupies only a small proportion (<5 wt%) in the commercial LIBs electrodes, serving to glue all components (active materials, conductive agents and current collectors) together, so as to maintain the electrodes with good electrical conductivity and mechanical integrity.29,32 The most popular polymer binders, poly(vinylidene difluoride) (PVDF) or sodium carboxymethyl cellulose/styrene butadiene rubber (CMC/SBR), could work very well in graphite anode and maintain its long-term cycling stability, due to the very limited volume expansion (~10%) of graphite upon full lithiation.33 However, when in face of the huge volume expansion of Si-based anodes, PVDF or CMC/SBR binder with low binding ability will lead to severe pulverization of Si particles, large electrode expansion and unacceptable cycling performances of cells.34-36 Many studies have demonstrated that the cycling stability of Si-based anodes is strongly dependent on the type of polymer binders employed.29,37-39 For example, using the poly(acrylic acid) (PAA) binder, Si or carbon-coated Si nanoparticle (SiNP) anodes exhibited much more improved cycling stability than using the CMC or PVDF binder.40 Neutralizing PAA with sodium hydroxide (NaOH) or lithium hydroxide (LiOH) and regulating the degree of neutralization could further optimize the cycling stability and reversible capacity retention of Si-based anodes.41,42 Moreover, it is known that Si microparticles (SiMPs) are more inexpensive and suitable for massive production than the nano-structured or hierarchically structured Si materials, but at the same time SiMPs show more severe pulverization and capacity fading than the latter. Through the rational design of polymer binders, remarkably reduced volume expansion of SiMPs and greatly improved cycling stability of SiMPs anodes could be achieved.43-47 For example, Choi et al. designed a pulley-inspired and highly elastic sliding-ring polyrotaxane-polyacrylic acid (PR-PAA) binder for SiMPs anode.44 The ring sliding motion of α-cyclodextrins...
(α-CDs) along the polyethylene glycol (PEG) chains endows the PR-PAA binder with extraordinary elasticity, enabling even the pulverized Si particles coalesced without disintegration and superior cycling stability of SiMPs anodes. Later, Wang et al. developed a water-soluble poly(acrylic acid)-poly(2-hydroxyethyl acrylate-co-dopamine methacrylate) (PAA-P(HEA-co-DMA)) binder for SiMPs anode.\textsuperscript{47} The abundant carboxyl and catechol groups in (PAA-P(HEA-co-DMA)) and the multiple crosslinking networks made the binder with strong adhesive strength to alleviate the volume expansion of SiMPs and maintain the integrity of electrodes, finally leading to excellent cycling and rate performances of SiMP anodes.

In fact, compared with the complicated and high-cost nanostructure or hierarchical fabrication of Si-based materials, developing high-performance polymer binders for Si-based anodes, especially the low-cost, safe, and environmentally friendly aqueous binders, also represents a cost-effective approach to improve the cycling performance of Si-based anodes.\textsuperscript{30,48,49} To date, an increasing number of polymer binders, with characteristics like high elasticity, strong adhesive, self-healing, ionic or electronic conductivity, and so forth, have been developed for various Si-based anodes. All these explorations provide a variety of very helpful instructions for designing of advanced polymer binders to promote the practical application of Si-based anodes. In this review, we have summarized the most recent advances of polymer binders for Si-based anodes according to their different structures, including the linear, branched, crosslinked, and conjugated conductive polymer binders (Figure 1). Especially, we pay special attention to the macromolecular structure and functional group design, and the structural and functional evolution of numerous polymer binders for Si-based anodes. It is expected that, through the systematic evaluation of the previous studies, this review can provide a basic understanding of designing principles of polymer binders for Si-based anodes and insightful instruction for the future practical polymer binder design.

2 | DESIGNING OF POLYMER BINDERS FOR Si-BASED ANODES

The most challenging issues for Si-based anodes are the huge volume change during lithiation/delithiation cycling and the subsequent intractable problems, such as the cracking and pulverization of active materials caused by the large mechanical stresses, delamination of electrode from the current collector, and fragile SEI layer.\textsuperscript{11} All these issues lead to the irreversible consumption of Li ions, accelerated depletion of electrolyte, sharply increased internal resistance, severe volume expansion of cells, and finally the rapid decay of cell capacity and short cycle life. Polymer binder works to bind all electrode components (including active material, conductive agent and current collector) in together through multiple interactions, including mechanical interlocking, chemical bonding, van der Waals’ forces, electrostatic forces, and so forth, which are greatly related with the backbone structure and functional groups of polymer binders.\textsuperscript{50} Rational design of polymer binders with strong adhesive strength could efficiently alleviate the volume expansion.

\textbf{FIGURE 1} An overview of various polymer binders for Si-based anodes
of Si particles, reduce the cracking or pulverization of active materials and improve the cycling stability of Si-based anodes. According to the polymer structure, polymer binders for Si-based anodes are simply divided into four categories, namely linear, branched, crosslinked, and conjugated conductive polymer binders. A summary of different polymer binders for Si-based anodes and the corresponding representative cycling performances have been shown in Table 1.

Linear polymer binders interact with Si particles or other electrode components mainly through the side functional groups. Due to the one-dimensional structure, linear polymer binders usually show limited binding strength to suppress the volume expansion and maintain the integrity of Si-based anodes. However, the linear binders are usually much cheaper and easy to be synthesized, and the binding strength and physicochemical properties can be easily regulated by means of copolymerization, blending or post-modification. Therefore, a great deal of natural derived (e.g., CMC, alginate (Alg, or sodium alginate denoted as SA), chitosan (CS)) or synthetic (e.g., PAA, poly(vinyl alcohol) (PVA)) linear polymers have been studied as binders for Si-based anodes. Compared with the one-dimensional contacts by linear polymer binders, branched polymer binders tend to form multidimensional contacts with Si particles, thus distributing or dissipating the mechanical stresses generated by Si volume change to multiple branched chains or points. Therefore, the branched polymer binders are expected to exert stronger adhesive strength and more effective suppression of volume expansion of Si-based anodes than the linear polymer binders. Particularly, many branched polymer binders are developed based on modifying the effective linear polymer binders. For example, PAA was demonstrated to be an effective linear binder for Si-based anodes due to its large amount of carboxyl groups. Grafting PAA onto CMC can further improve the binding ability of branched PAA-g-CMC binder, enabling much more improved cycling performances of Si anodes than that of PAA, CMC or physically mixed PAA/CMC binders.

In theory, linear or branched polymer chains are prone to slide upon a continuous volume change of Si particles, which is unfavorable for polymer chains or Si particles to recover to their original state, especially after many cycles. If all the polymer chains are interconnected to form a three-dimensional (3D) network, irreversible polymer chain sliding would be largely reduced. Meanwhile, the large deformation stresses by Si particles could be distributed to numerous crosslinking points. Thus, developing 3D interconnected polymer binders would be an ideal way to alleviate the huge volume change of Si particles. According to the crosslinking chemistries, the interconnected polymer binders can be divided into the covalently and dynamically crosslinked polymer binders. Especially, the dynamic crosslinking bonds can be recovered spontaneously after breaking, enabling the crosslinked binders with self-healing property, which is potentially more favorable for accommodating the repeated volume change of Si particles.

Another very important category of binder is the electronic conductive polymer binders, which contain a highly π-conjugated structure showing tunable metal-like electronic conductivity. The repeated volume change may lead to pulverization of Si particles and especially the isolated Si particles or fragments losing electrical contacts with current collector or conductive agent, thereby the accelerated capacity loss. Replacing the conventional insulating polymer binder with electronic conductive polymer binder is expected to maintain the electric conductivity of Si particles and overall electrode. In addition, it is known that the electrodes are made up of active material, conductive additive, and polymer binder. Using electronic conductive polymer as both conductive agent and binder is hopeful to reduce the proportion of inactive material in electrode, and therefore enhance the specific energy density of battery.

Finally, though polymer binders for Si-based anodes can be roughly divided into linear, branched, crosslinked, and conjugated conductive polymer binders according to their structures. For practical applications, multiple requirements need to be considered during the designing of polymer binders for Si-based anodes, such as low cost, high adhesive strength, mechanical stability, electrochemical stability, slurry stability, low usage, high initial Coulombic efficiency (CE), stable cycling of Si-based anodes at commercial level areal loading, and so forth. Polymer binders with single structure or function often cannot meet the requirements. Therefore, a comprehensive designing of polymer binders with multiple functions, such as the combination of different structures, interactions, crosslinking chemistries, ionic or electronic conductivities, soft and hard segments, and so forth, has received much more attention, showing great promise for the stable cycling of Si-based anodes.

### 2.1 Linear polymer binders for Si-based anodes

For linear polymer binders, the binding ability is largely decided by their molecular weight ($M_w$) and side groups. By means of copolymerization, blending or post-modification, the binding ability can be further improved. Natural derived polymers including CMC, Alg, CS, and so forth, and synthetic polymers including PAA,
| Type of binder | Solvent | Si-based anodes | Binder ratio | Areal loading (mg cm\(^{-2}\)) | Initial CE | Cycling performance | Current density (mA g\(^{-1}\)) | Year | Ref. |
|---------------|---------|----------------|-------------|-------------------------------|-----------|--------------------|-------------------------------|------|------|
| Alginate (Alg) | Water   | SiNPs (~37 nm) | 15%         | —                             | —         | 1700 mA h g\(^{-1}\) after 100 cycles | 4200                          | 2011 | 62  |
| Renatured DNA/Alg | Water   | SiNPs (~50 nm) | 20%         | 0.7                           | 84.6%     | ~2000 mA h g\(^{-1}\) after 160 cycles | 1750/0.5C                      | 2018 | 63  |
| Alg-catechol | Water   | SiNPs          | 20%         | 0.2–0.3                       | 60.1%     | ~2100 mA h g\(^{-1}\) after 400 cycles | 2100/0.5C                      | 2013 | 64  |
| PAA-catechol | Water   | SiNPs          | 20%         | 0.2–0.3                       | 71.2%     | ~1800 mA h g\(^{-1}\) after 400 cycles | 2100/0.5C                      | 2013 | 64  |
| Carboxymethyl chitosan | Water | SiNPs (150 nm) | 8%          | 1.4                           | 89%       | 766 mA h g\(^{-1}\) after 100 cycles | 200                           | 2014 | 66  |
| Guar gum | Water   | SiNPs          | 20%         | 0.2–0.3                       | 88.3%     | 2222 mA h g\(^{-1}\) after 100 cycles | 2100                          | 2015 | 67  |
| Guar gum | Water   | SiNPs (≤50 nm) | 5%          | 0.75                          | —         | 1000 mA h g\(^{-1}\) after 100 cycles | 3600/1C                       | 2015 | 69  |
| Agarose | Water   | Nanostructured Si powder | 20%         | 0.2–0.3                       | 88.3%     | 2222 mA h g\(^{-1}\) after 100 cycles | 3600/1C                       | 2015 | 69  |
| Konjac glucomannan | Water | Si@sio\(_2\) (40–100 nm) | 25%         | 0.2–0.3                       | 78.1%     | 1278 mA h g\(^{-1}\) after 100 cycles | 2000                          | 2018 | 72  |
| Carboxymethylated gellan gum | Water | SiNPs | 20%         | 1.31                          | 82.5%     | 900 mA h g\(^{-1}\) after 100 cycles | 1000                          | 2019 | 73  |
| PAA | NMP     | SiNPs (50 nm)  | 20%         | 0.7–1.2                       | 82.1%     | 1500 mA h g\(^{-1}\) after 500 cycles | 1000                          | 2017 | 77  |
| PDA-PAA-PEDO | Water   | SiNPs (50 nm)  | 20%         | 0.7                           | 74%       | 1597 mA h g\(^{-1}\) after 200 cycles | 0.5C                          | 2018 | 66  |
| Pectin/PAA | Water   | SiNPs          | 20%         | 0.5–0.7                       | 84.7      | 2386 mA h g\(^{-1}\) after 100 cycles | 2100                          | 2020 | 81  |
| Partially lithiated PAA and Nafion | Water | SiNPs (100 nm) | 10%         | 0.7–1.0                       | 90.76%    | 2143 mA h g\(^{-1}\) after 100 cycles | 0.2C                          | 2020 | 86  |
| Sequence-defined peptoids | Water | SiNPs (50 nm) | 20%         | 0.7                           | 72.8%     | ~3110 mA h g\(^{-1}\) after 500 cycles | 1000                          | 2020 | 96  |
| PMDOPA | DMF     | SiNPs          | 20%         | 0.7–0.8                       | 89.6%     | ~1300 mA h g\(^{-1}\) after 550 cycles | 840/0.2 C                      | 2020 | 111 |
| Branched PAA | Water   | Si/graphite (3/5) | 10%         | 0.6–1.0                       | ~77%      | >1000 mA h g\(^{-1}\) after 50 cycles | 100                           | 2015 | 75  |
| NaPAA-g-CMC | Water   | SiNPs (50–100 nm) | 20%         | 0.45                          | ~85%      | 1816 mA h g\(^{-1}\) after 100 cycles | 840/0.2C                       | 2016 | 86  |
| CS-g-PAANa | Water   | SiNPs (30–100 nm) | 30%         | ~0.22                         | 85.96%    | 1608 mA h g\(^{-1}\) after 100 cycles | 420                           | 2019 | 118 |
| PVA-g-PAA | Water   | SiNPs (30–80 nm) | 10%         | 0.5–0.6                       | 82.4%     | 1315.8 mA h g\(^{-1}\) after 1000 cycles | 400                           | 2018 | 85  |
| GC-g-LIPAA | Water   | Si/graphite (15/73) | 10%         | >2.5                          | 90.3%     | 495 mA h g\(^{-1}\) after 100th cycle | 0.1C                          | 2018 | 119 |
| PVDF-g-PAA | NMP     | 3D porous Si particles | 20%         | ~2.0                          | ~78%      | 1711 mA h g\(^{-1}\) after 50 cycles | 0.2C                          | 2016 | 120 |
| Branched PAA-PEG | Water | Si/graphite (15/73) | 10%         | 2.4                           | 97.1%     | 76% capacity retention after 100 cycles | C/3                           | 2020 | 88  |
| CS-g-PANI | Acid solution | SiNPs (50 nm) | 20%         | 0.8–0.9                       | 72.4%     | 1087 mA h g\(^{-1}\) after 200 cycles | 1C                            | 2020 | 121 |
| Hyperbranched β-cyclodextrin | Water | SiNPs | 40%         | 0.3                           | 85.9%     | 1471 mA h g\(^{-1}\) after 200 cycle | 4200/1C                       | 2014 | 125 |
| Double-helical native xanthan gum | Water | SiNPs (60 nm) | 20%         | 0.3                           | —         | 2150 mA h g\(^{-1}\) after 200 cycles | 3500/1C                       | 2015 | 126 |
| Li–Nafion | Water   | SiNPs (30–50 nm) | 25%         | 0.4                           | 76%       | 1200 mA h g\(^{-1}\) for more than 100 cycles | 0.1C                          | 2017 | 129 |
| PAA/CMC | Water   | SiNPs (<100 nm) | 20%         | 0.4                           | 88.2%     | over 2000 mA h g\(^{-1}\) after 100 cycles | 300                           | 2012 | 89  |
| Crosslinked PAA/PVA | Water | SiNPs (<100 nm) | 20%         | <1.0                          | 83.9%     | 1830 mA h g\(^{-1}\) after 300 cycles | 4000/1C                       | 2014 | 93  |
| Glycerol-crosslinked PEDOT:PSS | Water | SiNPs | 27%         | <0.7                          | 85.6%     | 1951.5 mA h g\(^{-1}\) after 200 cycles | 500                           | 2020 | 138 |
| MAH crosslinked corn starch | Water | SiNPs (<50 nm) | 20%         | —                             | —         | ~2106 mA h g\(^{-1}\) after 200 cycles | 0.5C                          | 2018 | 139 |
| MAH crosslinked CMC | Water | SiNPs | 20%         | 1-1                           | 87.6%     | 996 mA h g\(^{-1}\) after 120 cycles | 1000                          | 2019 | 140 |
| Crosslinked natural GG polymer | Water | SiNPs (50 nm) | 10%         | 0.7                           | 82.7%     | 87.3% capacity retention after 100 cycles | 0.2C                          | 2019 | 142 |
| Crosslinked chitosan | Acid solution | SiNPs (100 nm) | 20%         | —                             | 89.6%     | 1969 mA h g\(^{-1}\) after 100 cycles | 500                           | 2016 | 144 |
| Type of binder | Solvent | Si-based anodes | Binder ratio | Areal loading (mg cm$^{-2}$) | Initial CE | Cycling performance | Current density (mA g$^{-1}$) | Year | Ref. |
|----------------|---------|-----------------|--------------|-----------------------------|-----------|--------------------|-------------------------------|------|------|
| CS-GG + GA     | Water   | SiNPs (<100 nm) | 20%          | 0.40                        | —         | ~2144 mA h g$^{-1}$ after 100 cycles | —                            | 2019 | 145  |
| Crosslinked dextrin | Water | SiNPs (~100 nm) | 20%          | −0.9                        | 88.79%    | ~1100 mA h g$^{-1}$ after 150 cycles | 0.5C                          | 2020 | 146  |
| Crosslinked CMC-PEG | Water | SiNPs (≤50 nm) | 10%          | 0.4                         | 81%       | ~2000 mA h g$^{-1}$ after 350 cycles | 0.5 C                         | 2019 | 147  |
| Crosslinked hyperbranched PEI | Water | SiNPs (~160 nm) | 20%          | 0.5                         | 91.6%     | 2180 mA h g$^{-1}$ after 100 cycles | 500                           | 2019 | 148  |
| Crosslinked PAM hydrogel | Water | SiNPs          | 10%          | 1.0-1.1                      | 86.9%     | 2843 mA h g$^{-1}$ after 100 cycles | 0.1C                          | 2018 | 150  |
| Crosslinked PEI | THF     | SiNPs (≤50 nm) | 20%          | 0.55                        | —         | 2414 mA h g$^{-1}$ after 100 cycles | 0.2 C                         | 2019 | 153  |
| Crosslinked PVA–PEI | Water | SiNPs (≤50 nm) | 20%          | 1.8-2.7                      | 83.8%     | 1063.1 mA h g$^{-1}$ after 300 cycles | 200                           | 2016 | 103  |
| TMM functionalized PVA network | Water | SiNPs (~120 nm) | 20%          | —                           | 90.81%    | >95% capacity retention over 350 cycles | 0.2C                          | 2019 | 104  |
| Self-healing polymers | Chloroform | SiMPS (3–8 μm) | 50%          | 0.5–0.7                      | >80%      | 80% capacity retention after 90 cycles | 0.1C                          | 2013 | 41   |
| PAA-Upy supramolecular | Water | SiNPs (~70 nm) | 20%          | 0.4–0.6                      | 86.4%     | 2638 mA h g$^{-1}$ after 110 cycles | 2100/0.5 C                    | 2018 | 160  |
| Self-healing PAU-g-PEDOT | Water | SiNPs (~50 nm) | 20%          | 0.5-0.6                      | 70.4%     | 1450.2 mA h g$^{-1}$ after 350 cycles | 0.5 C                         | 2020 | 161  |
| Ca$^{2+}$ crosslinked SA hydrogel | Water | SiNPs | 29% | — | −77% | 1822 mA h g$^{-1}$ after 120 cycles | 420                           | 2014 | 162  |
| Ca$^{2+}$ crosslinked SA hydrogel | Water | SiNPs (200 nm) | 15%          | 1.0-1.1                      | 80.2%     | 2837.5 mA h g$^{-1}$ after 200 cycles | 420                           | 2014 | 163  |
| (Fe$^{3+}$) crosslinked (PAN$_{3x}$Fe$_y$) | Water | SiMPS (1–5 μm) | 20%          | 0.8                         | 92.3%     | −1400 mA h g$^{-1}$ after 400 cycles | 1790                          | 2020 | 166  |
| Sn$^{4+}$ crosslinked PEDOT: PSS | Water | SiNPs (~100 nm) | 20% | — | — | 1876.4 mA h g$^{-1}$ after 100 cycles | 1000                          | 2020 | 167  |
| PAA-PEG-PBI | NMP     | SiNPs | 10% | 0.7–0.91 | — | 1221 mA h g$^{-1}$ after 50 cycles | 1000/0.5 C | 2017 | 169  |
| Crosslinked CMC-CPAM | Water | SiNPs | 20% | −0.5 | 92% | 1906.4 mA h g$^{-1}$ after 100 cycles | 300                           | 2020 | 171  |
| Metallopolymers | NMP | SiNPs (~50 nm) | 15%          | 0.7                         | —         | 81.9% capacity retention after 3 50 cycles | 1500/1C                      | 2019 | 110  |
| Si@Fe$^{3+}$-FDA-PAA | Water | SiMPS | 20% | 3.0 | — | 2000 mA h g$^{-1}$ after 200 cycles | 0.5 C                         | 2020 | 176  |
| β-CDp/6 AD | DMSO | SiNPs (~50 nm) | 10%          | −0.8                        | 84%       | 1542.6 mA h g$^{-1}$ after 100 cycles | 1500/0.5C                    | 2015 | 177  |
| Slide-ring PR-PAA | DMSO | SiMPS (~2.1 μm) | 10%          | 1.07                        | 91.22%    | 91% capacity retention after 150 cycles | (0.64 mA cm$^{-2}$) | 2017 | 44   |
| Conductive PFFOMB | Chlorobenzene | SiNPs | ~33.3% | — | ~58% | 2100 mA h g$^{-1}$ after 650 cycles | 0.1 C                         | 2011 | 181  |
| PEG-coated PFPF | NMP | SiNPs | 10% | 0.6 | 72% | 605 mA h g$^{-1}$ after 1000 cycles | C/3                           | 2018 | 187  |
| PF–COONa | Water | SiNPs (~50 nm) | 33.3% | 0.19 | 68.4% | 2806 mA h g$^{-1}$ after 100 cycles | 420                           | 2017 | 188  |
| PFPPQ–COONa | Water | SiNPs | ~33.3% | 1.2 | ~71% | 901 mA h g$^{-1}$ after 400 cycles | 0.5C                          | 2018 | 189  |
| Pyrene-based (PPyE) | NMP | SiNPs | ~33.3% | 0.15 | 70.7% | 2300 mA h g$^{-1}$ after 180 cycles | 0.1C                         | 2015 | 190  |
| Pyrene-based (PPyMAA) | NMP | SiNPs (50–70 nm) | 10% | — | 82.08% | 2200 mA h g$^{-1}$ after 180 cycles | 420/0.1C                    | 2015 | 192  |
| Pyrene-based (PpyMADMA) | NMP | Si-alloy particles (1 μm) | 10% | ~0.5 | 64.64% | ~800 mA h g$^{-1}$ after 100 cycles | 0.1C                         | 2018 | 129  |
| PANI | In situ | SiNPs | 25% | 0.2–0.3 | ~70% | ~1420 mA h g$^{-1}$ after 1000 cycles | 1000                         | 2013 | 193  |
| FA doped PEDOT: PSS | Water | SiNPs (~60 nm) | 20% | 1.0 | ~79% | 1950 mA h g$^{-1}$ after 100 cycles | 1000                         | 2016 | 199  |
| Stretchable conductive glue | Water | SiNPs | 10% | 1.0 | ~80% | 1500 mA h g$^{-1}$ after 700 cycles | 840/0.2 C                    | 2017 | 200  |
| Poly(phenanthrenequinone) | NMP | SiNPs (<50 nm) | 30% | 0.46 | 81% | 2823 after 50 cycle | 0.1C                         | 2015 | 205  |
| Cyclized-PAN | DMF | SiNPs (~50 nm) | 30% | 0.5–0.6 | — | 1500 mA h g$^{-1}$ after 150 cycles | 0.1C                         | 2013 | 210  |
| PAA-PHEA-co-DMA) | Water | SiMPS (3–6 μm) | 10% | ~1.0 | ~89.3% | 2394 mA h g$^{-1}$ after 220 cycles | 1000                         | 2016 | 45   |
| PEDOT: PSS/PEO/PEI | Water | SiNPs (180 nm) | 10% | 1.0 | 82.0% | 2000 mA h g$^{-1}$ after 500 cycles | 1000                         | 2018 | 202  |
| PAA/PVA + Elastic gel polymer electrolyte | Water/DMAc | Micro-sized SiO | >10% | 3.7 | — | 1068 mA h g$^{-1}$ after 250 cycles | (0.3 mA cm$^{-2}$) | 2019 | 214  |
| PAA + BFPU | Water/DMF | SiNPs (100 nm) | 15% | 0.95 | 89.75% | 88% capacity retention after 200 cycles | 2000                         | 2020 | 215  |
PVA, and so forth, are the typical linear polymer binders for Si-based anodes.

### 2.1.1 CMC binders

CMC is a derivative from cellulose, consisting of large amount of hydroxyl (−OH) and carboxymethyl groups (−OCH₂COONa) (Figure 2A). The combined CMC/SBR binder is the most widely applied aqueous binder for the conventional graphite anode. CMC is extremely stiff and brittle (Figure 2B), however, the earlier studies found that it is potentially a good binder for Si-based anodes. For example, Dahn et al. found that CMC binder showed much better cycling performances than the less brittle CMC/SBR binder and PVDF binder. Later, Hochgatterer et al. demonstrated that the carboxylic acid groups in CMC could react with the surface −OH groups on Si particles by a condensation mechanism to form chemical bonds (Figure 2C). This strong chemical interaction between CMC and Si particles played a key role in maintaining the long-lasting cycling stability of Si-based anodes. Besides, the binding ability of CMC is related to its molecular weight and degree of substitution (DS) by carboxymethyl groups (Figure 2D). At a constant DS (0.9), Si anode with higher $M_w$ (700 000 g mol$^{-1}$) CMC exerted higher capacity than Si anode with a lower $M_w$ (250 000 g mol$^{-1}$) CMC binder. For a given $M_w$ (250 000 g mol$^{-1}$) CMC binder, an optimum DS value (1.4) was observed. The existing of
optimum DS value for CMC binder has also been confirmed by Liu et al.\textsuperscript{59} Lestriez et al. found that a lower pH level (pH = 3) is more favorable for the condensation reaction between −COOH groups in CMC and the Si −OH groups on Si surface, thus leading to stronger chemical interaction between binder and active materials, and the significantly improved cycling performance of Si-based anodes.\textsuperscript{60} The excellent adhesive, together with its environmentally friendly and inexpensive features make CMC an important binder or binder additives for Si-based anodes. Xie et al. reported that the CMC binder is helpful to improve the binding ability of acrylic adhesive (the weight ratio between acrylic adhesive and CMC is 2:1) by increasing its adhesive strength and electrode activation.\textsuperscript{27} Zhang et al. developed a novel water-soluble conductive composite binder for Si anode by dispersing the conductive polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) in the CMC solution.\textsuperscript{61} In this design, CMC played a crucial role in homogenously dispersing the conductive PEDOT: PSS component and maintaining the integrity of Si anodes due to its strong adhesive strength. Si anode with the optimized composite binder (CMC/PEDOT: PSS = 1/1 by weight) showed better cycling and rate performances than using only CMC binder.

### 2.1.2 Alg binders

Except for CMC, other natural derived polymers, like Alg, CS, Guar gum (GG), and so forth, have also been studied for Si-based anodes. Alg is a natural derived linear copolymer of (1 → 4) β-D-mannuronic acid (M) and α-L-guluronic acid (G) (Figure 3A). In each of the M or G monomeric units, there are two hydroxyl groups and one carboxylic group, which makes Alg contains higher concentration and much more uniformly distributed carboxylic groups than CMC binder. At the same concentration, Alg solution exhibits extraordinarily higher viscosity than CMC solution.\textsuperscript{62} Yushin et al. firstly employed Alg...
polymer as a promising binder for SiNP anodes, showing greatly improved cycling performances (1700 mA h g\(^{-1}\) capacity retention after 100 cycles at a current density of 4200 mA g\(^{-1}\)) than that of CMC or PVDF binder (Figure 3A).\(^{62}\) The excellent cycling performances of Si anodes with Alg binder can be ascribed to its highly concentrated and more uniformly distributed carboxylic groups, leading to stronger interactions with Si particles, better transport of Li ions and more efficient formation of stable SEI layer. Recently, Choi et al. designed a mucin-inspired renatured DNA/Alg (reDNA/Alg) amphiphilic binder for Si and Si/graphite (Si/Gr) composite anodes by mixing reDNA and Alg (Figure 3B).\(^{63}\) The reDNA/Alg binder showed higher adhesion forces than the solely reDNA or Alg, and thus the best cycling performance (80.1\% capacity retention \ [-2000 mA h g\(^{-1}\)]\) after 160 cycles at a current density of 1750 mA g\(^{-1}\)) of SiNP anodes. Especially, the hydrophobic reDNA is favorable to bind with hydrophobic carbon conductive agent and graphite in blended electrodes, while Alg preferentially binds with hydrophilic Si particles. The combined effects by reDNA and Alg provide the Si/Gr anodes with greatly improved cycling stability (Figure 3B). Besides, modification of Alg with adhesive catechol functional groups could improve its adhesion strength and the cycling performance of SiNP anodes, as shown in Figure 3C.\(^{64}\)

### 2.1.3 | CS binders

CS is a linear polysaccharide derived from chitin (the second most abundant polysaccharide in the world after cellulose) and it is composed of randomly distributed β-linked D-glucosamine and N-acetyl-D-glucosamine.\(^{65}\) CS is insoluble in water, but it can become soluble after carboxymethylation. Zhang et al. employed the carboxymethyl CS (c-CS) as a water-soluble binder for Si anodes (Figure 4A).\(^{66}\) Due to the stronger interactions

![Figure 4](image-url)

**Figure 4** (A) Synthesis of carboxymethyl chitosan (c-CS) and the proposed bonding mechanism between c-CS and SiNP surface; The first galvanostatic charge and discharge curves of SiNP anodes with C-chitosan (c-CS), Alg, CMC, and PVDF binders.\(^{66}\) Copyright 2013, Elsevier. (B) Chemical structures of guar gum (GG) and the schematic illustration of Li-ion transfer in the GG binder; Cycling performances of SiNP anodes with GG, SA, and PVDF binders; The initial CE of SiNP anodes with GG, SA, and PVDF binders.\(^{67}\) Copyright 2015, WILEY-VCH.
between the hydroxylated Si surface and the polar groups (−OH, −COOH, and −NH₂) on c-CS, SiNP anodes with c-CS binder exhibited a super high first discharge capacity of 4270 mA h g⁻¹ and an initial CE of 89%. At the same cycling condition, SiNP anodes with c-CS binder showed better cycling stability and rate performance than that of Alg, CMC and PVDF binders. GG is a natural derived nonionic polysaccharide and consists of linear chains of (1 → 4)-β-D-mannopyranosyl units with α-D-galactopyranosyl units attached through (1 → 6) linkages (Figure 4B). Due to the large number of polar hydroxyl groups and the similar transport of Li ions to polyethylene oxide (PEO), GG has been studied as an effective binder for Si-based anodes. 36,67-70 Sun et al. found that GG can be a robust ion-conductive binder for SiNP anodes, showing greatly improved cycling performance (2222 mA h g⁻¹ capacity retention after 100 cycles) and rate performance in an electrolyte without fluoroethylene carbonate (FEC) additive. 69 Other natural derived linear biopolymers, like agarose, 71 konjac glucomannan, 72 and carboxymethylated gellan gum, 73 have also been studied as binders to alleviate the volume expansion and promote an improved cycling performance of Si-based anodes.

2.1.4 | PAA binders

PAA contains much higher concentration of carboxylic groups than CMC or Alg polymers, and is the most important and widely explored synthetic polymer binder for Si-based anodes. In 2010, Yushin et al. first reported the using of PAA as binder for SiNP anodes. 40 The results showed that PAA film exhibited a similar swellability and mechanical properties with the CMC binder, but obviously improved cycling stability of SiNP anodes. 40 They ascribed the superior performance of SiNP anodes to the higher concentration of carboxylic groups in PAA binder, which is favorable for the stronger interaction with SiNP, transport of Li ions and formation of stable SEI layer at the
surface of SiNPs. Later, Komaba et al. demonstrated that SiO anode with PAA binder showed the best performances compared to that of PVDF, PVA or CMC binders (Figure 5B). Many studies have demonstrated that PAA could react with the surface hydroxyl group on Si to form covalent bonds (Figure 5C) and PAA is helpful to form a concomitant SEI layer on the surface of Si particles. In addition, the binding ability of PAA can also be regulated or optimized though neutralization by NaOH or LiOH, and controlling its $M_w$ (Figure 5C).

Besides, a series of PAA-based polymer binders have been developed for Si-based anodes through polymerization, blending and post-modification methods. Deng et al. designed a water-soluble triblock copolymer polydopamine-polyacrylic-polyethylene oxide (PDA-PAA-PEO) binder for Si anodes via reversible addition fragmentation chain transfer (RAFT) polymerization and a coupling reaction (Figure 6A). The coexisting of carboxyl, catechol and ethylene oxide moieties provides the PDA-PAA-PEO binder with strong adhesion and high ionic conductivity, thus improved cycling performance of SiNP anodes (1597 mA h g$^{-1}$ reversible capacity after 200 cycles at a current density of 0.5C) (Figure 6A). Blending PAA with other polymers, such as CMC, pullulan, pectin, polyvinyl butyral, PVA, polyaniline, Nafion, and so forth, can obtain composite binders with better performance than the individual polymers. For example, SiNP anode with mixed pectin/PAA (1/9 by weight) binder exhibited a higher capacity retention (2386 mA h g$^{-1}$ after 100 cycles) than the pure PAA binder (1508 mA h g$^{-1}$ after 100 cycles) (Figure 6B). It is believed that the pectin/PAA composite binder could exert strong adhesive forces to various interfaces, including binder/SiNPs, binder/carbon black and binder/copper foil, so that to stabilize the SiNP anodes. Lin et al. developed a hard/soft modulated trifunctional network binder (N-P-LiPN) for SiNP anodes by complexing the partially lithiated PAA (P-LiPAA, 90 wt%) and Nafion (P-LiNF, 10 wt%) via the hydrogen bonding effect.

**Figure 6** (A) Chemical structure of triblock copolymer polydopamine-polyacrylic-polyethylene oxide (PDA-PAA-PEO) and the cycling performances of SiNP anodes with PDA-PAA-PEO, PAA-PEO, and PVDF binders at a current density of 0.5C. Copyright 2018, The Royal Society of Chemistry. (B) Cycling performances of SiNP anodes with mixed pectin/PAA (1/9 by weight) binder and PAA binder (0.05 C for the first three cycles, 0.1 C for the 4th to the 6th cycles and 0.2 C for the 7th to the 100th cycles). Copyright 2020, WILEY-VCH. (C) Schematic of the preparation of the N-P-LiPN binder. Copyright 2020, WILEY-VCH. (D) Chemical structure of catechol, glycinamide, and rosin modified PAA binder for Si-based anodes.
Due to the strong adhesion, good mechanical properties and facilitated Li ion transport, SiNP anodes with the N-P-LiPN binder showed the highest initial CE (93.18%) and significantly enhanced cycling performances, compared with other individual (P-LiPAA, PAA, P-LiNF, and NF) or the non-lithiated composite (N-PN) binders. Meanwhile, ultrahigh Si mass loading of 28.88 mg cm$^{-2}$ and ultrahigh-areal-capacity of 49.59 mA h cm$^{-2}$ can be achieved by using this N-P-LiPN binder. Finally, modifying PAA with other functional groups, such as catechol, glycinamide or rosin (abietic acid), can also improve its binding ability for Si-based anodes (Figure 6D). Especially, due to the reactivity of carboxyl groups in PAA, it is widely employed to construct the in situ crosslinked networking polymer binders for Si-based anodes.

### 2.1.5 Other synthetic linear polymer binders

Except for PAA, other synthetic linear polymers have been studied as binders for Si-based anodes. PVA contains large amount of hydroxyl groups on the polymer chain (Figure 7A), which is benefit to form strong hydrogen bonding with Si particles or other electrode components. Oh et al. first studied the high $M_w$ PVA as a potential binder for Si/Gr anodes. In fact, the employing of PVA as binder for Si-based anodes often involves a branching, crosslinking and modification designing, which will be discussed in the following sections. The –COOH and –OH groups are the most important functional groups in many polymer binders for Si-based anodes. To make better use of the
advantages of −COOH and −OH, Zhang et al. fabricated a sequence-defined peptoids (P1) with programmed −COOH and −OH groups on the chain as a crosslinkable binder for SiNP anodes (Figure 7B).\textsuperscript{106} The results showed that SiNP anodes with P1 binder showed excellent cycling performance (−3110 mA h g\textsuperscript{−1} after 500 cycles at 1.0 A g\textsuperscript{−1}) and good rate capability (1328.2 mA h g\textsuperscript{−1} even at 7 C), compared with CMC or P2 (substituting the −OH groups in P1 by −OCH\textsubscript{3} groups) binders (Figure 7C). Mussel-inspired polymer binders have attracted a lot of research interests due to the excellent adhesion by the catechol groups.\textsuperscript{107-110} Wang et al. synthesized a series of PEG and carboxyl groups containing PI binders for Si anodes, showing stable cycling of SiNP anode introduced a copolyimide (P84) binder for the SiNP binders (Figure 7C). Mussel-inspired polymer binders have attracted a lot of research interests due to the excellent adhesion by the catechol groups.\textsuperscript{107-110} Wang et al. synthesized a series of poly(N-methacryloyl-3,4-dihydroxy-L-phenylalanine) (PMDOPA) polymers containing ultrahigh content of catechol groups via radical polymerization of MDOPA monomer (Figure 7D).\textsuperscript{111} As the increase of \(M_w\) (PMDOPA-9 < PMDOPA-14 < PMDOPA-20), both flexibility and adhesive strength of PMDOPA binders increased. Especially, the highest \(M_w\) PMDOPA-20 showed the best flexibility, adhesive strength and cycling stability of Si anodes, compared to that of the PMDOPA-9, PMDOPA-14 and PAA binders. Finally, polyimide (PI) can be an effective binder for Si-based anodes, despite that an organic solvent (e.g., N-methyl-2-pyrrolidone, NMP) usually needs to be applied (Figure 7E).\textsuperscript{112-116} Abu-Lebdeh et al. reported that Si/Gr (1/15 by weight) composite anodes using a polyetherimide (PEI) binder showed the highest capacity retention (500 mA h g\textsuperscript{−1} at C/12 after 350 cycles) and best rate performance (200 mA h g\textsuperscript{−1} at 5 C) compared with NaCMC, NaPAA and PVDF binders.\textsuperscript{112} Lee et al. introduced a copolyimide (P84) binder for the SiNP anodes, showing stable cycling of SiNP anode (1313 mA h g\textsuperscript{−1} after 300 cycles at 1.2 A g\textsuperscript{−1}).\textsuperscript{113} Particularly, Wang et al. synthesized a series of PEG and carboxyl groups containing PI binders for Si anodes, allowing for the aqueous processing of Si electrode (Figure 7E).\textsuperscript{117} Si anode fabricated by the PI-200 (copolymerized with PEG-200) binder exhibited the best cycling stability (2235.5 mA h g\textsuperscript{−1} after 200 cycles at 0.1 C), compared to CMC, PI, PI-400 (copolymerized with PEG-400) and PI-800 (copolymerized with PEG-800) binders.

2.2 Branched polymer binders for Si-based anodes

Due to the high concentration of carboxylic groups and strong interactions with Si particles, PAA is widely employed to construct the branched polymer binders for Si-based anodes. For example, copolymerization of acrylic acid (AA) monomer with a certain amount of diallyl ether crosslinker could obtain a branched PAA binder (Figure 8A).\textsuperscript{75} The degree of branching could be regulated by controlling of usage of crosslinker to achieve the best cycling performance of Si-based anodes. Wei et al. developed a NaPAA grafted CMC (NaPAA-g-CMC) binder for SiNP anodes through free radical graft polymerization of AA monomer onto the linear CMC backbone (Figure 8B).\textsuperscript{51} The branched NaPAA-g-CMC binder tends to form multipoint interactions with Si surface, leading to stronger binding ability and much improved cycling performances of SiNP anodes than the corresponding linear CMC, NaPAA or mixed NaPAA/CMC binders. The same polymerization method has been employed to fabricate the PAA grafted chitosan (CS-g-PAA)\textsuperscript{118} and PAA grafted PVA (PVA-g-PAA)\textsuperscript{85,100} binders for the Si-based anodes (Figure 8C,D).

In addition, living radical polymerization methods, including atom transfer radical polymerization (ATRP) and RAFT, have been employed to construct the graft copolymer binders for Si-based anodes. By these means, branched polymers with uniformly distributed side chains and customized length can be easily prepared. Thus, the effects of grafting structure on the cycling performance of Si-based anodes could be well studied. For example, Cao et al. synthesized a series of well-defined LiPAA grafted glycol chitosan (GC-g-LiPAA) polymers via the RAFT polymerization method (Figure 9A).\textsuperscript{119} They found that the peeling force and cycling performance of Si/Gr anodes are greatly related to the grafting structure of GC-g-LiPAA binders. Among all grafted or linear binders, GC\textsubscript{22}%g-LiPAA\textsubscript{62} binder showed the highest peeling force and best cycling performance of Si/Gr anodes. Yang et al. prepared a poly(tert-butylacrylate) (PtBA) grafted PVDF (PVDF-g-PtBA) copolymer binder via the ATRP polymerization method (Figure 9B).\textsuperscript{120} Especially, it can be transformed into PVDF-g-PAA after an in situ pyrolysis process, leading to greatly enhanced mechanical properties and cycling stability of Si/Gr anodes. Zhang et al. developed a branched PAA-PEG binder for Si-based anodes by copolymerizing AA monomer and tetra (ethylene glycol) diacrylate (TEGDA) crosslinker via the RAFT polymerization (Figure 9C).\textsuperscript{88} Due to the improved both mechanical properties and ionic conductivity, greatly improved cycling performance can be achieved for the Si/Gr anodes.

Besides, grafting electrically conductive polymers onto chitosan can increase the electronic conductivity of the derived binders.\textsuperscript{121,122} For example, Kim et al. reported a chitosan-grafted-polyaniline (CS-g-PANI) polymer as new electrically conductive, mechanically robust, and water-soluble binder for SiNP anodes (Figure 10A).\textsuperscript{121} CS-g-PANI binder with 50% PANI and
50% CS exhibited the well-balanced electronic conductivity and adhesive strength, and the best cycling performance of SiNP anode. Other natural derived branched polymers, such as karaya gum\textsuperscript{123} and amylopectin,\textsuperscript{124} can also be used as effective binders for Si-based anodes. Choi et al. found that the hyperbranched β-cyclodextrin (β-CD) polymer can be an excellent binder for Si anode, showing much improved cycling performance of SiNP anodes (Figure 10B).\textsuperscript{125} Furthermore, they found that the double-helical native xanthan gum (XG) can be an promising binder for SiNP anodes, showing greatly improved cycling performances than that of CMC, Alg, or other polysaccharide binders.\textsuperscript{126} The double-helical native XG with a lot of highly adhesive trisaccharide side chains is similar to the millipedes, showing great ability to maintain the integrity of overall electrode and promote the stable cycling of SiNP anodes (Figure 10C). Nafion is a graft copolymer composed of polytetrafluoroethylene...
backbone and perfluoroalkyl vinyl ethers side chains terminated by sulfonic acid (−SO₃H) or sulfonate (−SO₃⁻Na⁺ or −SO₃⁻Li⁺) groups. Dahn et al. demonstrated that Nafion or the ion exchanged Nafion (Li-Nafion) can be effective binders for Si-based anodes.

Dahn et al. and Cheng et al. demonstrated that Nafion or the ion exchanged Nafion (Li-Nafion) can be effective binders for Si-based anodes.
Crosslinked polymer binders for Si-based anodes

Crosslinked structure will increase the mechanical strength and resistance to deformation of polymer binders, which is benefit for suppressing the huge volume change of Si-based anodes and maintaining the integrity of overall electrodes. According the crosslinking chemistry, polymer binders can be divided into the covalently crosslinked polymer binders and dynamically crosslinked polymer binders. For covalently crosslinked polymer binders, in order to match the slurry processing, many in situ chemical reactions have been utilized for fabricating the 3D interconnected polymer binders for Si-based anodes. For dynamically crosslinked polymer binders, dynamic interactions, including hydrogen bonding, electrostatic interaction, metal ion coordination, host–guest interaction, and so forth, have been employed to construct the restorable or self-healing polymer binders for Si-based anodes.

2.3.1 Covalently crosslinked polymer binders

Esterification reaction has been widely employed for constructing the covalently crosslinked polymer binders for Si-based anodes. Due to the high availability of –COOH and –OH groups in a lot of water-soluble polymers, thermally activated esterification reaction between these two groups has been widely used to fabricate the 3D crosslinked polymer binders for Si-based anodes. Cho et al. reported a 3D crosslinked PAA/CMC binder for SiNP anodes by thermally curing the electrodes at 150°C under vacuum (Figure 11A). The crosslinked binder exhibited high mechanical resistance to strain due to the covalently crosslinking of polymer chains. SiNP anodes with the crosslinked PAA/CMC (1/1) binder showed greatly improved reversible capacity (over 2000 mA h g⁻¹ after 100 cycles at 30°C) than the linear PAA, CMC or PVDF binders. Meanwhile, they pointed out that the
dimerization of –COOH groups on PAA to form anhydride and the condensation between PAA and the surface –OH groups on the Si surface can also contribute to the crosslinking. Wang et al. developed an interpenetrated gel polymer binder for SiNP anodes by in situ thermally crosslinking PAA and PVA (9/1 by weight) (Figure 11B).\(^{93}\) The crosslinked PAA/PVA binder could effectively accommodate the volume change of SiNP electrode, enabling the SiNP anodes with excellent cycling stability (e.g., 2283 mA h g\(^{-1}\) capacity retention after 10 cycles at a current density of 400 mA cm\(^{-2}\)), even at a high mass loading of 2.4 mg-Si cm\(^{-2}\). Ryu et al. employed the PAA-co-PVA (6/4) random copolymer to fabricate the 3D interconnected networks for SiNP anodes, showing improved cycling performances than that of PVA, PAA, and mixed PAA/PVA binders (Figure 11C).\(^{130}\) Except for the crosslinking reaction between macromolecules, small molecules containing two or more –COOH or –OH groups can be applied as crosslinkers to fabricate the interconnected networks for Si-based anodes (Figure 11D). For example, D-sorbitol crosslinked PAA,\(^{136}\) fumaric acid crosslinked PVA\(^{102}\) and citric acid crosslinked CMC\(^{137}\) have been reported to show enhanced mechanical strength and greatly improved cycling performances of Si-based anodes, compared to that of linear PAA, PVA or CMC binders.

Other esterification reaction between –OH and sulfonic acid,\(^{138}\) anhydride,\(^{139,140}\) or boronic acid\(^{141,142}\) groups can also be employed to fabricate the covalently crosslinked polymer binders for Si-based anodes. Qian et al. reported an crosslinked conductive binder for SiNP anodes by thermally crosslinking PEDOT: PSS and glycerol at 180°C (Figure 12A).\(^{138}\) The glycerol crosslinked PEDOT: PSS (GP) binder showed greatly enhanced peeling force and superior conductivity, leading to improved cycling and rate performances (1951.5 mA h g\(^{-1}\) and 804 mA h g\(^{-1}\) at a high current of 8.0 A g\(^{-1}\)) of SiNP anodes containing no conductive additive. Maleic anhydride crosslinked corn starch\(^{139}\) or CMC\(^{140}\) binders have been demonstrated to be promising binders for the Si-based anodes (Figure 12B). Besides, Song et al. employed the inorganic sodium borate to crosslink CMC, making the obtained binder with strong ability to buffer the volume change of Si particles and maintain the integrity of overall electrode (Figure 12C).\(^{141}\) SiNP anodes with the crosslinked binder showed greatly improved cycling stability (1211.5 mA h g\(^{-1}\) capacity retention after 600 cycles at 0.33C rate) than that of the non-crosslinked CMC binder. Recently, Park et al. developed a room-temperature crosslinked multifunctional polymer binder for SiNP anodes via the spontaneous crosslinking reaction between a boronic acid containing polymeric crosslinker and natural GG polymer at room temperature (Figure 12D).\(^{142}\) The boronic acid containing polymeric crosslinker was prepared by radical polymerization of vinyl phenylboronic acid and a vinyl functionalized PEO monomer. The systematic design imparted the binder with strong adhesive strength, networking structure and high ionic conductivity, enabling the SiNP anodes with excellent cycling and rate performances.

Schiff base reaction between amine (–NH\(_2\)) and aldehyde (–CHO) groups has been employed to fabricate the crosslinked polymer binders for Si-based anodes. Chitosan is a linear derivative from chitin and it is soluble in the dilute acetic acid solution. The massive amine groups on chitosan make it readily react with aldehyde compounds.\(^{143}\) Lee et al. developed a glutaraldehyde (GA) crosslinked chitosan binder for SiNP anodes, showing high initial CE of 89% and capacity retention (1969 mA h g\(^{-1}\) at the current density of 500 mA g\(^{-1}\) after 100 cycles).\(^{144}\) Saito et al. reported a catechol functionalized and GA crosslinked chitosan (CS-CG + GA) binder for SiNP anodes (Figure 13A).\(^{145}\) The optimized networking CS-CG10% + 6%GA binder showed the most improved peeling force and the best cycling performance of SiNP anodes. In addition, Yan et al. reported a crosslinked dextrin binder for Si-based anodes, employing the aldolization reaction between hydroxyl groups in dextrin and aldehyde groups in GA (Figure 13B).\(^{146}\) The GA crosslinked dextrin binder showed enhanced mechanical property, enabling the SiNP anodes with much improved electrochemical performances, compared to that of PVDF, CMC or pristine dextrin binders.

Epoxy group could readily react with –NH\(_2\) or –OH groups through addition reaction. The di- or multifunctional epoxy compounds can be used to crosslink the –NH\(_2\) or –OH rich polymers. Paik et al. reported an in situ crosslinked CMC-PEG (6.4/1.6) binder for SiNP anodes via the crosslinking reaction between polyethylene glycol diglycidyl ether (PEGDE) and CMC (Figure 14A).\(^{147}\) SiNP electrodes with the crosslinked CMC-PEG binder exhibited greatly enhanced peeling strength and cycling performance (~2000 mA h g\(^{-1}\) up to 350 cycles at 0.5 C) than that of the pure CMC binder. Besides, Chen et al. developed a crosslinked hyperbranched polyethyleneimine (PEI) binder for Si anodes by using 1,4-butandiol diglycidyl ether (BDE) as crosslinker (Figure 14B).\(^{148}\) Both high density of amino groups in PEI and the interconnected 3D network contributed to enhance the electrochemical performance of SiNP anodes (2180 mA h g\(^{-1}\) capacity retention after 100 cycles at a current density of 500 mA g\(^{-1}\)).

In situ polymerization of crosslinkable monomers can be an effective method to fabricate the crosslinked...
FIGURE 12  (A) The glycerol crosslinked PEDOT: PSS (GP) binder and the cycling performances of SiNP anodes with different binders.\textsuperscript{138} Copyright 2020, Elsevier. (B) Fabrication SiNP anode with maleic anhydride crosslinked corn starch binder.\textsuperscript{139} Copyright 2018, Elsevier. (C) Graphical interaction between the sodium borate crosslinked CMC binder and the SiNPs, and the corresponding lithiation/delithiation process.\textsuperscript{141} Copyright 2018, Elsevier. (D) Schematic of boronic acid crosslinked guar gum (BC-g) binder in Si electrode; The spontaneous crosslinking reaction between boronic acid and vicinal alcohol at room temperature; Peeling tests of Si electrodes with CMC, guar gum, and BC-g binders; Ionic conductivity of guar gum and BC-g binder films.\textsuperscript{142} Copyright 2019, WILEY-VCH

FIGURE 13  (A) Illustration of the glutaraldehyde (GA) crosslinked and catechol functionalized chitosan (CS-CG + GA) binder.\textsuperscript{145} Copyright 2019, American Chemical Society. (B) Schematic illustration of the crosslinking and the interaction between the crosslinked dextrin and SiNPs.\textsuperscript{146} Copyright 2019, Elsevier
polymer binders for Si-based anodes. Liu et al. introduced a highly stretchable crosslinked polyacrylamide (PAM) hydrogel binder for Si anodes by in situ free radical polymerization of acrylamide monomer and bifunctional N,N-methylenebisacrylamide (MBAA) monomer (Figure 15A). The degree of crosslinking of PAM can be regulated by varying the usage of MBAA. The crosslinked PAM binder showed much better stretchability and adhesion strength than linear PAM binder, and thus much improved cycling performance of SiNP anodes. SiNP anode with 1% crosslinked PAM (Si-c-PAM-0.001) binder showed the highest reversible capacity of 2843 mA h g\(^{-1}\) after 100 cycles, corresponding to a capacity retention of 90.1% (Figure 15A). Park et al. further dementated that the MBAA crosslinked PAM can be a promising binder for Si based anodes. Poly(ether urethane) (PEU) is usually prepared by the polyaddition reaction of diisocyanates and diols. In order to obtain a crosslinked PEU, Lee et al. introduced a trifunctional gallic acid (GA) crosslinker in the polyaddition reaction of methylene di-p-phenyl diisocyanate (MDI) and poly(ethylene glycol) (PEG) (Figure 15B). The crosslinked PEU showed good resistance to electrolyte solvents, greatly improved adhesion strength and cycling stability (2414 mA h g\(^{-1}\) after 100 cycles at 0.2 C) of SiNP anodes, compared with linear PEU and PVDF binders. Other in situ crosslinked polymer binders based on PAA or PVA have been developed for Si-based anodes. Okada et al. reported an in situ crosslinked PVA-PEI (8/2 by weight) polymer binder for Si anodes by heat treatment of electrodes at 100 and 120°C (Figure 16A). The condensation reactions between hydroxyl groups in PVA, imido groups in PEI and hydroxyl groups on the surface SiO\(_2\) layer of SiNPs, lead to formation of an interconnected network and strong covalent bonding with SiNPs. Thus, SiNP anodes with this crosslinked PVA-PEI binder showed excellent cycling (1063.1 mA h g\(^{-1}\) capacity retention after 300 cycles) and rate (1590 mA h g\(^{-1}\) capacity even at a current density of 10 A g\(^{-1}\)) performances, compared to that of CMC and PVDF binders (Figure 16A). Zheng et al. employed the trimethylol melamine (TMM) to functionalize and crosslink PVA polymer through the dehydration of \(-\text{OH}\) groups on TMM and PVA chains under heat treatment, and used as a binder for SiNP anodes (Figure 16B). The network structure and existing of triazine structure are benefit for improving both mechanical properties and ionic conductivity of TMM-PVA binder. Especially, the optimized TMM-PVA binder, with 0.08 molar fraction of TMM and reacted under 50°C for 4 days, showed very impressive cycling (> 95% capacity retention over 350 cycles) and rate (~2300 mA h g\(^{-1}\)) capacity at a current density of 84 A g\(^{-1}\)) performances of SiNP anodes (Figure 16B).
Besides, chemical reaction between carbodiimide (–N=C=N–) and –COOH groups has been used to fabricate a polycarbodiimide (PCD) crosslinked PAA binder for Si/Gr composite anodes, showing improved cycling performance than that of the linear PAA or PVDF binders (Figure 17A). Ryu et al. synthesized a novel copolymer poly(tert-butyl acrylate-co-triethoxyvinylsilane) (TBA-TEVS) as efficient binder for SiNP anodes (Figure 17B). In this design, the tert-butyl groups can be in situ deprotected upon thermal treatment and transformed to –COOH groups, and then crosslinked to form an interconnected structure via dimerization of –COOH groups. Meanwhile, the siloxane groups are helpful to form a stable SEI layer for SiNPs. SiNP anodes with the optimized TBA-TEVS-21 binder (containing 21% of TEVS) showed the best cycling performance, compared to that of Alg, CMC, PAA/CMC and PVDF binders. Wrapping Si particles with polydopamine (PD) or polyphenol (e.g., tannic acid, TA) can make Si particles to covalently bond with carboxyl containing polymer binders, so that to form an interconnected structure and enhance the cycling stability of Si anodes (Figure 17C).

Wei et al. prepared a vinyltriethoxysilane (VTES) crosslinked NaPAA polymer binder (PVTES-NaPAA) for SiNP anodes by hydrolyzing the VTES component in the copolymer precursor (Figure 17D). The crosslinked structure and large amount carboxyl groups made the PVTES-NaPAA polymer a promising binder for SiNP anodes.

2.3.2 | Dynamically crosslinked polymer binders

Dynamically crosslinked polymer binders with self-healing property are potentially more benefit for accommodating the repeated huge volume change of Si-based anodes. The reversible dynamic bonds enable the networking structure of polymer binder can be repaired at the fracture points and maintain the integrity of Si particles or electrodes at any time. Rationally designed dynamically crosslinked polymer binders are highly desirable for alleviating the volume expansion of Si-based anodes and promoting their long-term stable cycling.
Hydrogen bond

Hydrogen bond is a type of dipole–dipole attraction between a hydrogen atom covalently bonded to an electronegative atom (such as nitrogen, oxygen, or fluorine) and another electronegative atom bearing a lone pair of electrons. Single hydrogen bond is usually too weak to fabricate the supramolecular polymers. While multiple hydrogen bonds with increased strength and directionality can be used for fabricating the supramolecular polymers.157 Bao et al. first employed the hydrogen bond based supramolecular self-healing polymers (SHP) as effective binder for SiMP anodes (Figure 18A).43 The crosslinked SHP binder with good mechanical stretchability could accommodate the huge expansion of SiMPs and spontaneously repair the mechanical damages in the electrode. SiMPs anode with the SHP binder showed greatly improved cycling performances (2617 mA h g$^{-1}$ discharge capacity at the first cycle and 80% capacity retention after 90 cycles) than the conventional PVDF, CMC or Alg binders. Based on above results, they further improved and optimized the SHP binders for Si-based anodes, including 3D spatial distribution of SHP binder into Si electrodes with controlled particle sizes,158 controlling the crosslinking density of SHP to understand how viscoelastic properties affect cycling stability,46 and incorporating PEG segments into SHP to facilitate Li ionic conduction and improve high rate performance of Si anodes (Figure 18B).45 Besides, Bao et al. developed a stretchable graphitic carbon/Si anode by conformal coating of a self-healing elastic polymer on the 3D foam structured carbon/Si (Figure 18C).159 Due to a combination covalent crosslinking and the sacrificial hydrogen bonding, the new polymer was much tougher and more elastic than the abovementioned SHPs. The stretchable carbon/Si foam anode presented a high specific capacity of 719 mA h g$^{-1}$ and maintained 81% of its original capacity after 100 cycles.

Deng et al. developed a water-based quadruple-hydrogen-bonded supramolecular binder for SiNP anodes by copolymerization of tert-butyl acrylate and an ureido-pyrimidinone (UPy) containing acrylate monomer followed by hydrolysis (Figure 19A).160 The obtained PAA-UPy binder showed improved adhesive strength and excellent self-healing ability due to its quadruple-hydrogen bonding dynamic interactions. Si anode with the self-healing PAA-UPy binder exhibited a super high
initial discharge capacity of 4194 mA h g$^{-1}$ and CE of 86.4%, and superior cycling stability (2638 mA h g$^{-1}$ after 110 cycles), compared with that of the linear PAA, CMC or PVDF binders. Furthermore, Kim et al. designed a UPy functionalized PAA grafted with PEG (PAU-g-PEG) binder for SiNP anodes by free radical copolymerization of tert-butyl acrylate monomer, Upy-containing monomer and poly(ethylene glycol) methyl ether methacrylate monomer followed by hydrolysis (Figure 19B). The coexistence of UPy and PEG units imparted the PAU-g-PEG binder with excellent self-healing property, improved adhesive strength and high ionic conductivity, rendering the Si anodes with excellent cycling (capacity retention of 1450.2 mA h g$^{-1}$ and CE of 99.4% after 350 cycles under a C-rate of 0.5 C) and rate (capacity of 2500 mA h g$^{-1}$ under a C-rate of 3 C) performances.

**Electrostatic interaction**

A charged polymer and oppositely charged metal ions or two oppositely charged polymers could form interconnected polymer networks through the electrostatic interaction or ionic bonds. The reversible electrostatic interaction makes the polymer networks with self-healing property, which is favorable for accommodating the continuous volume variation of Si particles. SA is a natural derived linear copolymer of ϕ-mannuronic acid (M) and α-L-guluronic acid (G) units. In aqueous solution, the G blocks in SA can be crosslinked by different metal cations (e.g., Ca$^{2+}$, Zn$^{2+}$, Al$^{3+}$, etc.) to form a self-healing SA hydrogel. Sun et al. firstly employed the Ca$^{2+}$ crosslinked SA hydrogel as an efficient binder for Si/C anode (Figure 20A). Due to the crosslinking by Ca$^{2+}$, SA hydrogel binder exhibited much enhanced mechanical properties and electrochemical performances (e.g., 1822 mA h g$^{-1}$ capacity retention after 120 cycles at a current density of 420 mA g$^{-1}$) of Si/C anodes, compared to the linear SA binder. In this work, only 1 wt% of CaCl$_2$ has been used to obtain the SA hydrogel with a low degree of crosslinking. Later, Zheng et al. increased the usage of CaCl$_2$, setting the molar fractions between Ca$^{2+}$ and alginate residues at 0.05, 0.1 and 0.15, to obtain a series of highly crosslinked SA network binders for SiNP anodes (Figure 20B). In this preparation, the SA containing Si anode slurry was immediately crosslinked to form a viscous gel upon adding the Ca$^{2+}$ ions. Then, the viscous gel was stirred at high shear rate and immersed in water to remove residual chloride ions. The filtered gel was casted onto copper foil to prepare the electrode. Due to the high degree of crosslinking by Ca$^{2+}$ and the strong interactions between the carboxylic groups in SA and the hydroxylated Si surface, the highly crosslinked SA binder showed greatly increased...
mechanical properties and ability to suppress the volume change of Si particles. Finally, the highly crosslinked SA binder with 0.15 molar ratio of CaCl₂ showed the best cycling performance (reversible capacity of 2837.5 mA h g⁻¹ after 200 cycles at a current of 0.42 A g⁻¹) of Si anodes. Hwang et al. further demonstrated that the Ca²⁺ mediated electrostatic crosslinking could improve the toughness, resilience, electrolyte desolvation of the SA binder, making the Ca²⁺ crosslinked SA a promising binder for SiNP anodes. Recently, Sun et al. further studied the different metal ions (Ca²⁺, Ba²⁺, Mn³⁺, Zn²⁺, Al³⁺) crosslinked SA as binders for SiNP anodes (Figure 20C). They found that Al³⁺ and Ba²⁺ crosslinked SA showed the most improved Vickers hardness, viscosity, peeling strength, as well as cycling performances of Si anodes than that of other metal ions, which can be ascribed to the higher valence of Al³⁺ that can crosslink with more alginate chains and the larger ion radius of Ba²⁺ that can interact more strongly with alginate chains. Except for the metal ions crosslinked SA binders, Park et al. developed a ferric ion (Fe³⁺) crosslinked polyacrylate (PANa₀.₈Fe₀.₀₁) binder for SiMP anodes via the ionic coordination between Fe³⁺ and carboxylate groups in PANa₀.₈ (Figure 20D). Si-MP anode with the optimized PANa₀.₈Fe₀.₀₁ binder showed a greatly improved cycling performance (a capacity retention of ~1400 mA h g⁻¹ after 400 cycles at a current density of 1790 mA g⁻¹) compared with the linear PAA or PVDF binder. Qian et al. studied the crosslinking of electrically conductive PEDOT: PSS polymer by multivalent cations in the 5th period and Group 2, including Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, In³⁺, Sn⁴⁺ (Figure 20E). They found that the variation trend of viscosity and conductivity of crosslinked PEDOT: PSS was consistent with that of ionic potential and softness parameters. Especially, the Sn⁴⁺ crosslinked PEDOT: PSS binder displayed more increased viscosity, electrical conductivity, and mechanical properties due to the higher ionic potential and positive softness parameter of Sn⁴⁺. Si anode with the Sn⁴⁺ crosslinked PEDOT: PSS binder showed most improved cycling
stability (1876.4 mA h g\(^{-1}\)) capacity retention after 100 cycles at a current density of 1.0 A g\(^{-1}\)) compared to other cations crosslinked PEDOT: PSS binders.

Two oppositely charged polymers are able to form a reversibly interconnected network through the electrostatic interaction of charged groups. Kim et al. reported an electrostatically crosslinked PAA-PBI binder for Si/Gr composite anode via electrostatic interaction between the acidic PAA and the basic poly(benzimidazole) (PBI) polymer (Figure 21A). The strong electrostatic interaction between PAA and PBI made the PAA-PBI-2 (containing 2 wt% of PBI) binder with obviously improved binding property and cell cycling performance compared to that of pure PAA binder. However, the rigid structure makes PBI with poor solubility in solvent, which is not benefit for fabricating high loading Si anodes from the PAA-PBI binder. Therefore, Kim et al. incorporated a PEG component into PBI to obtain a PEGPBI binder with improved flexibility, solubility, and ionic conductivity (Figure 21B). SiNP anodes with the physically crosslinked PAA-PEGPBI-2 (containing 2 wt% of PBI) binder exhibited improved cycling and rate performances compared with pure PAA binder. Recently, Yang et al. introduced a self-healing alginate and carboxymethyl chitosan (Alg-C-chitosan) composite binder for SiNP anodes through the electrostatic interaction between –COO\(^-\) groups in Alg and the protonated amines (–NH\(_3^+\)) groups in C-chitosan (Figure 21C). The electrostatic interaction and self-healing properties made the Alg-C-chitosan composite binder be able to tolerate the tremendous volume change of Si particles and maintain the stable cycling of Si-based anodes. Besides, they employed the CMC and cationic polyacrylamides (CPAM) to fabricate a self-healing network binder for Si-based anodes (Figure 21D). The electrostatically crosslinked self-healing CMC-CPAM binder exhibited excellent mechanical and adhesive strength, and greatly improved cycling performances (e.g., 1906.4 mA h g\(^{-1}\)) capacity retention after 100 cycles at a current density of 300 mA g\(^{-1}\)) of SiNP anodes.

**Metal ion coordination bond**

The extraordinary adhesion of mussel byssus is originated from the substantial strong and reversible Fe\(^{3+}\)- (tris)catechol coordination complex, which has been widely employed for designing of robust self-healing polymer network materials. Inspired by the mussel byssus, Choi et al. developed a Fe\(^{3+}\)-(tris)-catechol coordination crosslinked metallopolymer binder for SiNP anodes (Figure 22A). Firstly, they synthesized a branched catechol containing poly(DMA\(_{33}\)-co-BA\(_{66}\)-co-PEGdA\(_3\)) (PDBP) copolymer by free radical copolymerization of dopamine methacrylamide (DMA) monomer, butyl acrylate (BA) monomer and a difunctional...
polyethylene glycol diacrylate (PEGdA) monomer. After adding FeCl₃ (in a molar ratio of catechol/Fe³⁺ = 3:1) into PDBP solution and increasing the pH value to 10, Fe³⁺-(tris) catechol coordinated self-healing metallopolymers could be obtained, which is denoted as Fe-PDBP@pH 10. The strong Fe³⁺-(tris) catechol coordination and self-healing property of Fe-PDBP@pH 10 lead to superior stable cycling of SiNP anodes (e.g., 81.9% of the initial capacity after 350 cycles at 1C rate) (Figure 22B).

Figure 20  (A) Schematic illustration of mechanical integrity of the Si/C electrodes with pure SA binder and Ca²⁺ crosslinked SA hydrogel binder, and the cycling performances of Si/C anodes with pure SA binder and Ca²⁺ crosslinked SA hydrogel binder at 420 mA g⁻¹. Copyright 2014, The Royal Society of Chemistry. (B) Schematic illustration of the robust Ca²⁺ crosslinked SA binders for SiNP anodes; Force-displacement curves and cycling performances of the Si-PVDF, Si-Alg, Si-Alg-Ca-0.05, Si-Alg-Ca-0.1, and Si-Alg-Ca-0.15 electrodes. Copyright 2014, The Royal Society of Chemistry. (C) Schematic structures of multiple divalent metal ions crosslinked Alg and Al³⁺ crosslinked Alg. Copyright 2017, Elsevier. (D) Schematic illustration of the Fe³⁺ crosslinked polyacrylate (PANa₀.₈Feᵧ) binder. Copyright 2020, WILEY-VCH. (E) Schematic illustration of the metal ions crosslinked PEDOT: PSS binders and Sn⁴⁺ was chosen as an example. Copyright 2020, American Chemical Society

Host–guest interaction

Choi et al. reported a dynamically crosslinked polymer binder for SiNP anodes based on the host–guest interactions between hyperbranched β-cyclodextrin polymer (β-CDp) and a supramolecular crosslinker with six adamantane units (6 AD) (Figure 23A). The host–guest interaction between β-CD and AD rendered the β-CDp/6 AD binder with self-healing property that can
FIGURE 21  (A) Physically crosslinked PAA-PBI binder through electrostatic interactions between the acidic PAA and the basic poly(benzimidazole) (PBI) polymer. Copyright 2015, American Chemical Society. (B) Physically crosslinked PAA-PEGPBI binder based on the electrostatic interactions between PAA and ion-conducting poly(ethylene glycol-co-benzimidazole) PEGPBI. Copyright 2017, Elsevier. (C) Schematic illustration of the electrostatically crosslinking between Alg and C-chitosan. Copyright 2016, Springer Nature. (D) Schematic illustration of the electrostatically crosslinking between CMC and CPAM. Copyright 2020, Elsevier.

FIGURE 22  (A) Schematic illustration of the cycling of SiNP anode with Fe$^{3+}$-(tris)catechol coordinated self-healing metallopolypolymer PDBP binder. Copyright 2019, American Chemical Society. (B) Cycling performances of SiNP anodes (Si mass loading = 0.7 mg cm$^{-2}$) with Fe-PDBP@pH 10, PAA, and PVDF binders at 1C rate (1500 mA g$^{-1}$). Copyright 2019, American Chemical Society.
recover the broken linkages between polymer chains during continuous cycling, enabling the intimate Si-binder interaction, structural stability of electrode film, and controlled SEI formation. SiNP anodes with the optimized β-CDp/6 AD (β-CD/AD = 1/0.5) binder showed the best cycling performance compared to other host or guest alone and other linear (including PAA, CMC and Alg) binders. Furthermore, they developed a highly elastic slide-ring polyrotaxane (PR) crosslinked PAA binder for SiMP anodes (Figure 23B). In this design, the α-cyclodextrins (α-CDs) molecules were firstly threaded on a PEG chain through host–guest interaction, and then trapped by capping the PEG chain with bulky 1-fluoro-2,4-dinitrobenzene end groups. Crosslinked PR-PAA binder was obtained by crosslinking some of the α-CDs on PR with PAA through the esterification reaction. Due to the ring sliding motion of α-CDs along the PEG chains, the PR-PAA binder containing 5 wt% of PR exhibited extraordinary elasticity of 390% strain before rupture, keeping even the pulverized Si particles coalesced without disintegration. SiMP anode with the PR-PAA binder showed greatly improved CE (91.22% at the first cycle and 99.10% at the fourth cycle) and excellent cycling stability (91% capacity retention after 150 cycles at a current density of 0.64 mA cm⁻²) at commercial-level areal capacity (2.67 mA h cm⁻²).

2.4 | Conjugated conductive polymer binders for Si-based anodes

Due to the inherently low conductivity of Si, well-designed Si/C composites and conductive additives usually need to be used to improve the electrical conductivity.

![Figure 23](image-url)
of overall electrode. The commonly used carbon-based conductive agents are nonadhesive and prone to disconnect with Si particles during the continuous volume change. Besides, both conventional binders and conductive additives are electrochemically inactive and contribute no capacity to the cell. Using conductive polymer binders as both binder and conductive agent are expected to maintain the overall electrode conductivity, and meanwhile boost the energy density of cell by increasing the proportion of active material in the electrode. Many reports have demonstrated that the conductive polymer binders with high electrical conductivity and strong binding ability can promote improved cycling performances of Si-based anodes at high areal capacities.179-180

2.4.1 PF-based conductive binders

In 2011, Liu et al. studied the polyfluorene (PF) based conductive polymers as binders for SiNP anodes (Figure 24A).181 The introduction of carbonyl (C=O) groups into PF could lower its lowest unoccupied molecular orbital (LUMO) energy level, making PFFO can be cathodically doped with high electronic conductivity under the reducing environment for anodes. Further introduction of methylbenzoic ester (−PhCOOCH₃) (MB) units into PFFO could provide PFFOMB with improved chain flexibility and mechanical binding force without compromising the electronic conductivity. SiNP anodes prepared by the PFFOMB binder, without
addition of any conductive additive, were demonstrated to show high specific capacity and excellent cycling stability (2100 mA h g\(^{-1}\) capacity retention after 650 cycles at 0.1 C). In addition, Liu et al. optimized the PFFOMB binder by introducing a triethylenoxide monomethylether on the polymer chain to increase its electrolyte uptake capability, enabling the conductive additive free SiNP anodes with a high initial capacity of 3750 mA h g\(^{-1}\) and stable cycling over 3000 mA h g\(^{-1}\) capacity after 50 cycles (Figure 24B).\(^{182}\) The versatility of PF based conductive binders for different Si-based anodes and toward practical application have been demonstrated by the same group.\(^{183-186}\) Recently, Taskin et al. developed a PEG (\(M_n = 2000\)) grafted poly(fluorene phenylene) (PFP) conductive copolymer as binder for SiNP anodes.\(^{187}\) The grafted PEG chains could increase the polarity, electrolyte uptake capability and mechanical properties of the PFP-g-PEG binder, enabling the stable cycling of SiNP anodes (2625 mA h g\(^{-1}\) at the first cycle and 605 mA h g\(^{-1}\) after 1000th cycles at C/3 rate). The above introduced PF based conductive binders need to be dissolved in organic solvent (e.g., NMP) for the slurry process. Pan et al. developed a water-soluble PF based conductive binder (PF-COONa) for SiNP anodes by introducing large amount of carboxyl groups on the polymer chain (Figure 24C).\(^{188}\) The carboxyl groups could react with the polar groups on the surface of Si particles to form strong chemical bonds, rendering the PF-COONa binder with strong adhesive strength. SiNP anodes prepared by the PF-COONa binder, without any conductive additive, exhibited a high reversible capacity (2806 mA h g\(^{-1}\) at a current density of 420 mA g\(^{-1}\)) and good cycling stability (85.2% capacity retention after 100 cycles). Later, they introduced 10% of phenanthraquinone (PQ) into PF-COONa to obtain a novel PFPQ-COONa conductive copolymer binder with enhanced electronic conductivity (Figure 24D).\(^{189}\) SiNP anodes with the PFPQ-COONa binder showed greatly improved cycling stability and rate performances, compared with PF-COONa binder.

2.4.2 | Pyrene-based side chain conductive binders

Electronically conductive polymers that conduct electrons via the side chain π–π stacking have been developed as binders for Si-based anodes. Liu et al. reported a pyrene-based side-chain conductive polymer binder (PPy) for Si-based anodes via free radical polymerization of the pyrene containing methacrylate monomer (Figure 25A).\(^{190,191}\) PPy polymer exhibited good electronic conductivity with an electron mobility of 1.9 × 10\(^{-4}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\). Due to the low binding ability, Si anodes with the PPy binder showed a fair cycling performance. By copolymerizing with other functional monomers, such as triethylene oxide methyl ether methacrylate (Figure 25B)\(^{192}\) and dopamine methacrylate (Figure 25C),\(^{109}\) enhanced electronic conductivity, adhesive strength and mechanical integrity can be achieved for the PPy based binders, so that to improve the cycling performance of Si-based anodes.

2.4.3 | PANI-based conductive binders

Polyaniline (PANI) can be applied as an effective binder for Si-based anodes due to its facile aqueous-phase synthesis, high electronic conductivity, and environmental stability. Cui et al. demonstrated an in situ polymerization technique to fabricate a 3D interconnected
conducting hydrogel embedded with SiNPs conformally coated by the PANI conducting polymer (Figure 26A). The continuous electrically conductive PANI network and the strong binding between Si particles and PANI network by the phytic acid crosslinker enabled the superior stable cycling of SiNP anodes (90% capacity retention after 5000 cycles at a current density of 6.0 A g\(^{-1}\), as shown in Figure 26B). Besides, the PAA crosslinked PANI, carboxyl group functionalized PANI and polyvinyl pyrrolidone (PVP) functionalized PANI were reported to show improved electrolyte uptake, mechanical properties and adhesive strength, and capability to maintain the integrity of electrode, enabling the Si anodes with greatly enhanced cycling performance and stability. Liu et al. found that the star-structured PANI binder is more benefit for improving cycling performance of Si anodes compared to the crosslinked and linear PANI binder.

2.4.4 PEDOT: PSS-based conductive binders

PEDOT: PSS is one kind of low-cost, water-soluble, and commercially available polythiophenes based conductive polymer with tunable conductivity, electrochemical stability, mechanical robust and good processibility. Coleman et al. reported an in situ secondary dopped PEDOT: PSS as both binder and conductive additive for the SiNP anodes (Figure 27A). SiNP electrodes with 20 wt% of the formic acid (FA) dopped PEDOT: PSS showed a high conductivity of 4.2 S cm\(^{-1}\), which is over 100 times that of SiNP electrodes with the FA free PEDOT: PSS (36 mS cm\(^{-1}\)) and over 3800 times of SiNP electrodes with 10 wt% of LiPAA binder and 10 wt% of carbon black (CB) (mS cm\(^{-1}\)). The usage of FA, proportion of PEDOT: PSS in electrodes, and areal loading of SiNP on the electrochemical performances of SiNP anodes have been systematically studied. Super high first cycle capacity (3685 mA h g\(^{-1}\)) and excellent cycling stability (1950 mA h g\(^{-1}\) capacity retention after 100 cycles at a current density of 1 A g\(^{-1}\)) have been demonstrated for SiNP anodes with the FA secondarily dopped PEDOT: PSS binder. Besides, Huo et al. developed a novel stretchable conductive glue (CG) polymer binder for SiNP anodes by crosslinking D-sorbitol and vinyl acetate-acrylic (VAA) onto electrically conducting polymer PEDOT: PSS chains (Figure 27B). The CG binder can be stretched up to 400% in volume without losing conductivity and mechanical fracture. Due to the inherent high conductivity, excellent stretchability, and ductility, CG binder could accommodate the large volume change.

FIGURE 26 (A) Schematic illustration of 3D porous SiNP/conductive polymer hydrogel composite electrodes. Copyright 2013, Springer Nature. (B) Cycling performance of SiNP-PANI electrode at a current density of 6.0 A g\(^{-1}\) for 5000 cycles. Copyright 2013, Springer Nature
of SiNPs, and maintain the mechanical integrity and high electrical conductivity of overall electrode, so that enable the stable cycling of SiNP anodes with high Si mass loading. Finally, due to the water-solubility and conductive property, PEDOT: PSS has also been widely employed to construct 3D interconnected composite binders for Si-based anodes combined with other water-soluble polymer binders or functional materials.61,138,201–204

2.4.5 Other conductive binders

Other conductive polymers, including poly(phenanthrenequinone),205 carboxylate functionalized poly(thiophene),206,207 polyisoindigo derivative,208 and in situ polymerization derived polyimine209 have been demonstrated to show improved electrical conductivity and cycling stability for Si-based anodes. In addition, partially
carbonizing the nonconductive polymer binders by in situ thermal treatment have been demonstrated to be an effective method to improve both adhesion and electrical conductivity of overall electrodes. For example, in situ heat treatment of Si anodes with PAN\textsuperscript{210,211} or CMC-g-PAA\textsuperscript{212} binder at high temperature led to partially carbonization of polymer chains, and thus greatly enhanced electrical conductivity and mechanical property of electrodes, enabling the stable cycling of Si-based anodes.

2.5 Multifunctional designing of polymer binders for Si-based anodes

Multifunctional polymers with various architectures and properties can be realized by a combination of (co)polymerization, branching, crosslinking, post-modification, blending, and so forth. In the same way, polymer binders with desired multiple functionalities, including water solubility, flexibility, strong adhesive, chemical and electrochemical stability, low swelling by electrolyte, ionic and electronic conductivity, strong interaction with the Si surface, and so forth, could be tailored to accommodate the huge volume change of Si particles and stabilize the long-term cycling of Si-based anodes. Designing of multifunctional polymer binders for Si-based anodes has been widely employed in many reports, showing great promise for the practical application of Si-based anodes in high energy density LIBs.

Coskun et al. performed a systematic investigation of structure–property relationship of Si binder with varied ratio of functional monomers, namely 5-methyl-5-(4-vinylbenzyl) Meldrum’s acid (K) for dimerization/crosslinking and covalent attachment to Si, styrene (S) for stiffness, methyl methacrylate (M) for flexibility, and lithium 2-methyl-2-(4-vinylbenzyl)malonate (C) for self-healing effect via ion-dipole interactions between polymers and also with the Si surface (Figure 28A).\textsuperscript{213} They found that

**Figure 28** (A) Chemical structures of polymers and copolymers incorporating various monomeric units with distinct functionalities, and their interactions with Si.\textsuperscript{213} Copyright 2014, WILEY-VCH. (B) Chemical structures of PAA-P(HEA-co-DMA) and the illustrative interactions between binder and Si, and the spring expanders model of their complex.\textsuperscript{47} Copyright 2018, Elsevier. (C) Chemical structure of PEDOT: PSS, PEO, and PEI; Schematic diagram of improving Li ion transport by PEI and PEO; Schematic diagram of the interactions inside the binders with high ionic and electronic conductivities.\textsuperscript{202} Copyright 2018, WILEY-VCH
the higher ratio of K is more effective to improve the cycling performance of Si anodes than binder with higher ratio of S and M, which means that crosslinking/covalent attachment is more critical than the stiffness or flexibility of polymer binder in improving the cycling performance of Si anodes. Besides, the self-healing effect by C is more critical for high capacity, good cycling performance, and high initial CE of Si anodes, than the crosslinking/covalent attachment by K. Wang et al. designed a water-soluble poly(acrylic acid)-poly(2-hydroxyethyl acrylate-co-dopamine methacrylate) (PAA-P(HEA-co-DMA)) copolymer binder for SiMP anodes (Figure 28B). The abundant carboxyl and catechol groups made the PAA-P(HEA-co-DMA) binder with strong interactions with SiMPs and enhanced wet/dry adhesion force. And the multiple networks including covalent and non-covalent crosslinking, and a combination of rigid-soft chains, made the binder with strong ability to maintain the integrity of electrodes and buffer the huge volume change of SiMP anodes. Finally, SiMP anodes with the PAA-P(HEA-co-DMA) binder exhibited excellent cycling performances under even a high electrode loading (1.74 mg cm$^{-1}$). Besides, the combination of self-healing and ionic conductivity will render binder with both self-healing property and high ionic conductivity, enabling the greatly improved cycling and rate performances of Si-based anodes. Zhou et al. developed a composite polymer binder with both high ionic and electronic conductivities by assembling ionic conductive polymers (PEO and PEI) onto the electronically conductive polymer chains (PEDOT: PSS), to promote the superior cycling performances of SiNP anodes (Figure 28C).

**FIGURE 29**  (A) Chemical structure of the highly elastic copolymer 1; Stress–strain curves of the copolymer 1 before and after swelling by electrolyte; Schematic illustration of the cycling process of SiO electrode with the supremely elastic GPE intra-electrode cushion. Copyright 2019, Springer Nature. (B) Chemical structure of the highly elastic and self-healing bifunctional polyurethane (BFPU) polymer; The charging and discharging voltage profiles of SiNP electrodes with PAA-BFPU (1:2), PAA-BFPU (1:1), PAA, and PVDF binders at a current density of 0.2 A g$^{-1}$; Cycling performances of SiNP electrodes with PAA-BFPU (1:2), PAA-BFPU (1:1), PAA, and PVDF binders at a current density of 1.2 A g$^{-1}$. Copyright 2020, Wiley-VCH
Recently, Wang et al. proposed a new strategy that employing the supremely elastic gel polymer electrolyte (GPE) as an intra-electrode cushion to buffer the volume expansion of SiO particles and reduce the damage by electrode cracking, so that to maintain the integrity of electrode during cycling and enable the super stable cycling of micro-sized SiO anodes at high areal loadings (Figure 29A).\(^{214}\) GPE contains an ether-based soft domain and a 4,4’-methylene diphenyl diisocyanate (MDI) based hard domain, showing extreme elasticity with an elongation more than 2300% and good mechanical strength. When GPE was uniformly filled in the SiO electrode and served as an intra-electrode cushion, the thickness change of SiO electrode after cycling was greatly reduced, due to the efficient buffering effect by GPE. Finally, SiO anode with the GPE cushion showed greatly enhanced adhesion strength and significantly improved cycling stability (a reversible specific capacity of 1068 mA h g\(^{-1}\) over 250 cycles at a loading of 3.7 mg cm\(^{-2}\)). SiO|NCM523 full cell with the GPE-incorporated SiO anode (4.7 mg cm\(^{-2}\)) at a commercial-level capacity (3.0 mA h cm\(^{-2}\)) exhibited 70.0% capacity retention after 350 cycles and an average CE of 99.9%. Using the same strategy, Song et al. further developed a highly elastic and self-healing bifunctional polyurethane (BFPU) buffer layer to dissipate the deformation stress by Si particles and maintain the integrity of Si-based anodes (Figure 29B).\(^{215}\) SiNP anodes with this BFPU buffer layer displayed a higher initial CE of 89.06% and much improved cycling stability (97.0% capacity retention after 100 cycles) than SiNP anodes without BFPU.

3 | SUMMARY AND OUTLOOK

Despite the small usage, polymer binder plays a key role in keeping the integrity and stability of electrodes in LIBs. Especially, due to the intrinsic huge volume expansion of Si-based materials during lithiation and the resulting severe capacity degradation, polymer binder plays an even more critical role in alleviating the volume expansion, and maintaining the mechanical and electrochemical integrity of Si-based anodes. Over the past decade, numerous polymer binders with different structures, properties, functionalities, conductivities, flexibility, or derived from different chemical reactions and sources (natural or synthetic polymers), have been developed, aiming to promote the stable cycling and practical application of Si-based anodes in high energy density LIBs. In this review, to simplify the problem, we divided the polymer binders into four categories according to their structures, namely the linear, branched, crosslinked, and conjugated conducting polymer binders. In each of the categories, we summarized the corresponding polymer binders based on the type of polymers and fabrication methods or chemistries. For example, the natural derived CMC, Alg, and CS, and the synthetic PAA and PVA, are the most widely explored linear binders for Si-based anodes, showing great potential to alleviate the volume expansion of Si particles and improve the cycling stability of Si-based anodes. Based on CMC, Alg, CS, PAA and PVA, a series of branched polymer binders with increased binding strength and capability to alleviate the volume expansion of Si-based anodes have been developed. To further increase the binding strength and efficiency in buffering the volume expansion of Si-based anodes, 3D interconnected polymer binders have been proposed, which can be divided into the covalently and dynamically crosslinked polymer binders based on the reversibility of the crosslinking bonds. In situ chemical reactions, like the esterification reaction, Schiff base reaction, addition reaction of epoxy group, in situ crosslinking polymerization, and so forth, have been extensively adopted to construct the covalently crosslinked polymer binders for Si-based anodes. Dynamic interactions, like hydrogen bond, electrostatic attraction, metal ion coordination, host–guest interaction, and so forth, have been widely employed to fabricate the dynamically crosslinked polymer binders for Si-based anodes. Besides, as a special kind of polymer, the conjugated polymers with electronic conductivity have been studied to serve as both binders and conductive additives in the Si-based electrodes, with potential to maintain the electrical contact of overall electrode and increase the proportion of active materials in electrodes. The PF-based, PANi-based, PEDOT: PSS-based, side-chain conductive pyrene-based, and so forth, are some of the most widely explored conductive polymer binders for Si-based anodes. Finally, the comprehensive designing of multifunctional polymer binders for Si-based anodes, such as a combination of different structures, interactions, crosslinking chemistries, ionic or electronic conductivities, soft and hard segments, and so forth, is emphasized, which would be promising to promote the high performance of Si-based anodes.

Replacing the conventional graphite anode with the high-capacity Si-based anodes is one of the most promising strategies to remarkably boost the energy density of LIBs. Currently, only a small amount of Si or SiO\(_x\) can be introduced into the conventional graphite anode to achieve a balanced energy density and minimized capacity fading. Despite numerous polymer binders have been developed in the lab-scales, the widely employed polymer binder for Si/Gr composites is still the CMC/SBR binder. Aiming to develop a practical polymer binder that can
effectively alleviate the volume expansion of Si-based anodes and promote the large-scale application of high-capacity Si-based anodes in high energy density LIBs, the following aspects need to be considered in the future design of polymer binders for Si-based anodes. First, the designed polymer binders should be easily synthesized at low cost. In this respect, the water-soluble polymer binder is preferred due to avoiding usage of volatile, flammable, and toxic organic solvents and the expensive solvent recycling systems. After reviewing the progress of polymer binder for Si-based anodes, the -COOH and -OH groups containing polymers are undoubtedly the most important water-soluble binders. Other hydrophilic polarized groups, like catechol, ethylene oxide units, amine, sulfonic acid, and so forth, have been widely employed to functionalize the water-soluble binders. PANi and PEDOT: PSS, which are compatible with the aqueous process, can be employed to increase the electronic conductivity of water-soluble binders. Well-designed low cost and water-soluble polymer binders with highly integrated functionalities and structures are highly desirable in the near future. Second, most of the reported electrochemical evaluation of polymer binders for Si-based anodes are conducted in half coin cells, which usually contain enormously excess Li and electrolyte, so it is difficult to reflect the actual effectiveness of polymer binders in the Si-based anodes. Therefore, it is important to evaluate the polymer binders in full cells, preferably the punch-typed full cells, under extreme conditions, such as low binder usage, commercial level areal loading and electrolyte addition. Except for that, the physical and chemical characterizations, including the mechanical properties, adhesive strength, slurry stability, electrochemical stability, swelling property in liquid electrolyte, ionic and electronic conductivity, contribution of binder to SEI formation, the distribution of binder in the electrode, the interactions between binders and active materials, and so forth, are necessary to be conducted to screen or optimize the binders and guide the future binder designing for Si-based anodes. Third, the high initial CE of Si-based anodes, which reduces the irreversible capacity loss or cathode consumption during the first charge/discharge cycle, is significantly important to realize the high energy density of full cells. So it is crucial that the designed polymer binders should not consume active Li during the formation process, thus leading to a lower initial CE of Si-based anodes. Fourth, the designed polymer binder should be also compatible with the conventional graphite anode, since the Si/Gr composites is currently the best choice for the large-scale commercialization of Si-based anodes. Finally, extra efforts need to be made on understanding the working and failure mechanism of polymer binder in the Si-based anodes or Si/Gr composite anodes via some advanced in situ characterization techniques and modeling studies, so as to guide the future advanced design of polymer binders for Si-based anodes.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

ORCID

Yu-Guo Guo https://orcid.org/0000-0003-0322-8476

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AUTHOR BIOGRAPHIES

Yu-Ming Zhao is currently a postdoctoral researcher in Prof. Yu-Guo Guo’s group at ICCAS. He received his PhD degree in Polymer Chemistry and Physics from ICCAS in 2016. He worked as a postdoctoral fellow at The Pennsylvania State University from 2017 to 2019. His research focuses on synthesis of functional polymeric materials and developing materials for energy storage and conversion application.

Yu-Guo Guo received his PhD in physical chemistry from ICCAS in 2004. He worked at the Max Planck Institute for Solid State Research at Stuttgart (Germany) first as a guest scientist and then as a staff scientist from 2004 to 2007. He joined ICCAS as a full professor in 2007. His research focuses on nanostructured energy materials and electrochemical energy storage devices, such as Li-ion, Li-S, Li-metal, solid-state batteries, and Na-ion batteries.

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