Molecular design principles for polymeric binders in silicon anodes

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Polymer binders influence a wide range of physical and chemical properties of silicon electrodes, including mechanical durability, adhesion, electronic and ionic conductivity, morphology, and self-healing behavior. The design of polymer binders involves trade-offs between these various properties. For example, electrolyte uptake can enhance ion diffusion, but can also result in poor mechanical properties and reduced adhesion. Nonpolar polymers can be highly elastic, but typically exhibit poor adhesion to the silicon surface. Highly crosslinked polymers exhibit excellent mechanical strength, but poor elasticity and reversibility to mechanical deformation.

Our review of polymer binders for silicon anodes is organized in terms of specific molecular design principles that have been implemented in the design of polymeric binders: elasticity, adhesion, mechanical strength and crosslinking, multi-functionality, electronic and ionic conductivity, electrolyte uptake, and electrochemical stability. We critically review and evaluate studies aimed at implementing these design principles to achieve improved performance and stability in silicon anodes and we discuss trade-offs among different target properties. We comment on both successes in applying these design principles and areas where further work is needed. This review can provide both new and experienced researchers with a useful summary of the development of polymeric binders for silicon anodes.

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Molecular design principles for polymeric binders in silicon anodes

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Silicon anodes potentially offer a volumetric energy storage capacity significantly greater than that of commercial graphitic carbon anodes, but silicon electrodes exhibit poor stability under reversible charging and discharging. This has been attributed to several factors including large volume changes of Si during battery operation, the non-passivating nature of the Si surface which can result in uncontrolled growth of solid-electrolyte interface layers, and reactivity between the binder and lithiated silicon. To address these challenges, researchers have developed innovative compositons and architectures of polymer binders aimed at increasing storage capacities and improving stability. Polymer binders serve multiple functions in battery electrodes including maintaining adhesion between the electrode and current collector and cohesion of the electrode as a whole, ensuring the stability of the solid electrolyte layer that forms on the surface of silicon, and in some cases providing electronic and ionic conductivity. The goal of this review is to identify and critically evaluate underlying molecular design principles applied to the development of polymeric binders for silicon anodes. Molecular design principles include molecular functionalities, architectures, or compositions that can produce a desired physical or chemical property. The review specifically focuses on the molecular features of binders that facilitate self-healing, electronic conductivity, mechanical performance, and electrochemical performance.

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1. Introduction

Lithium-ion batteries are an integral part of our day-to-day lives and provide portable, rechargeable, and reliable sources of energy for commercial electronic devices. These batteries dominate the market for use in portable electronic devices because their energy densities and reliability exceed that of other commercial energy storage systems. However, there is a need for higher energy densities to power electric vehicles, homes and buildings, and provide grid-scale energy storage.[1,2]

Silicon is an abundant, stable, and non-toxic material with a high specific capacity for lithium storage, and it is therefore an attractive target for use as an anode active material in lithium ion batteries. However, developing silicon anodes that outperform commercial graphite anodes is a significant challenge. The challenge can be understood by comparing the volumetric capacities of full cell batteries with different anode materials.[3] Volumetric capacities are more relevant to applications than specific capacities, and the maximum volume of the anodes – at the state of full lithiation – should be used for comparisons. While silicon has a specific capacity more than 10 times that of graphite, the volumetric capacity is roughly 4 times that of graphite. When incorporated in a full cell and taking into consideration the average cell voltages, silicon anodes offer potentially a 30 % increase in volumetric capacity over graphite.[3] While still a significant improvement, this is much lower than might be expected based on the relative specific capacities. Also, this analysis does not account for irreversible capacity losses observed or the higher polymer binder contents used in silicon anodes. Binder contents of 3 – 5 wt % are used in commercial graphite electrodes, while silicon and alloy anode materials are typically fabricated with 10 wt % binder or more.[4] Therefore, in order to develop a superior silicon anode, irreversible capacity losses have to be reduced while also decreasing the content of polymer binders used.

The polymeric binder maintains the structure of the electrode, serving as a glue to hold the various components of the electrode together and maintain contact with the current collector. Effective polymeric binders for silicon and other alloy anodes perform multiple functions. This includes maintaining strong adhesion to silicon, conductive additives, and the charge collector, facilitating repeated and large volume changes of the silicon particles, and enhancing the transport of charges or ions through the electrode. The polymer binder also influences the electrode processing process through the choice of compatible solvents and the slurry viscosity[5] and can have a direct impact on electrochemical stability through potential side-reactions with the active material or electrolyte. The binder generally does not contribute to storage capacity or conductivity, and therefore the amount of binder used should be minimized. The need for a polymeric binder system designed specifically for silicon and other lithium alloy materials was recognized as early as 2003.[6–10] A series of studies demonstrated that poly(vinylidene fluoride) (PVDF) was inadequate as a binder and suggested an extensible composite matrix as a potential alternative. For example, a copolymer of vinylidene fluoride, tetrafluoroethylene, and propylene, poly(vinylidene fluoride-tetrafluoroethylene-propylene) (PVDF-TFE-P), was capable of accommodating much larger strains than PVDF and produced nanocomposite electrodes with better capacity retention under cycling when compared against PVDF.[6,9]

Table 1. List of target polymer binder properties, molecular design principles implemented to achieve these properties, and examples of polymer chemistries that meet these criteria. PVDF-TFE-P = poly(vinylidene fluoride-tetrafluoroethylene-propylene). PAA = poly(acrylic acid). CMC = carboxymethyl cellulose. PVA = poly(vinyl alcohol). HPAM = hydrolyzed polyacrylamide. PDA = polydopamine. PEO = polyethylene oxide. PANi = polyaniline. PPYE = poly(1-pyrenemethylmethacrylate-co-triethylene oxide methyl ether methacrylate. PEDOT:PSS = poly(3,4-ethylenedioxythiophene):poly(styrene-4-sulfonate). PVDF = poly(vinylidene fluoride). PTFE = polytetrafluoroethylene. PAN = polyacrylonitrile.

Target property	Molecular Design Principle	Polymer Binder Chemistries
Elastic polymer binders	Low T_g polymers, low crosslink density, mobile crosslinking functionalities	PVDF-TFE-P, polyrotoxane-modified PAA
Strong adhesion to silicon	Polar polymers, covalent binding to silicon	CMC, PVA, HPAM
Self-healing of cracks and fractures	Supramolecular polymers and reversible crosslinking	CMC, PAA
High-strength and modulus binders	Rigid and highly crosslinked polymeric binders, binders with little or no electrolyte uptake	crosslinked CMC-PAA, ionically-crosslinked alginate
Multi-functional binders	Polymer blends and copolymers	PDA-PAA-PEO block polymers
Electronically conductive binders	π-conjugated polymers, polymers with pendant organic semiconductors	Polyfluorenes, PANi, PPYE, PEDOT:PSS
Ionically-conductive binders	Polymeric binders that swell in liquid electrolyte, polymers that can store Li^+ ions	PVA, PVDF, crosslinked chitosan and natural rubber
Electrochemically stable binders	Wide bandgap polymers, broad thermodynamic stability window	PEO, PTFE, PAN

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Subsequent to these early studies, reports have followed with an impressive variety of polymer compositions, architectures, and design principles implemented towards the goal of producing stable, high-capacity silicon anodes. In addition to highly elastic polymeric binders, other design strategies include high modulus binders, polar polymers, supramolecular polymers that can reversibly associate and dissociate, branched polymers, block copolymers, charged and/or ion conductive polymers, conjugated polymers, and small molecular binders. Altogether, these studies have provided a variety of examples of polymer binder materials that can improve performance and stability while providing insight into the design of polymeric binder materials.

The goal of this review is to identify and critically evaluate underlying molecular design principles applied to the development of polymeric binders for silicon anodes. Molecular design principles include molecular functionalities, architectures, or compositions that can produce a desired physical or chemical property. As examples, reversible bond formation enables healing of cracks that form in the electrode during operation, and polar polymers provide stronger adhesion to silicon compared with nonpolar polymers. By describing molecular design principles that have been proposed and critically evaluating the results detailed in literature reports, we aim to aid the development of rationally-designed polymeric binder materials for silicon and other alloy anodes.

We will not provide a comprehensive review of polymer binder chemistries, and instead direct the reader to several recent and excellent reviews[4,5,11–19]. We also will not detail capacities of different electrodes and formulations reported, as these can vary widely in terms of silicon loading, charge and discharge rates, thicknesses, and other testing conditions. Instead, we will take advantage of reported comparative studies to understand the success and drawbacks of different polymer binder chemistries. When reporting capacities, we include details on the silicon content in the electrode, porosity, thickness, and charge-discharge rate to place the results in proper context. This review also primarily focuses on polymer binders used in silicon nanoparticle electrodes, although some examples of polymer binders for silicon micro-particle electrodes are also discussed since similar design concepts have been applied to both. Finally, this review focuses on the polymeric binders and will not discuss strategies to engineer the nanostructure of silicon materials through, for example, etching[20] or encapsulation[21]. These approaches are covered in significant detail in other review articles[11].

2. Mechanical Properties and Performance

Lithiation of silicon is associated with large volume changes, and this volume expansion causes mechanical stresses that can fracture silicon nanoparticles, produce cracks in the electrode, cause delamination from the charge collector, and ultimately lead to irreversible capacity loss[3,22–27]. Polymer binders can potentially address this capacity loss by suppressing cracking, maintaining cohesion between the various materials in the anode, ensuring strong adhesion to the current collector, and sustaining large changes in volume during lithiation and de-lithiation without rupture. In this section, we describe different molecular design approaches that have been applied and tested to address the mechanical instabilities that arise in silicon anodes.

2.1 Elastic Polymer Binders

The earliest attempts at addressing the poor mechanical stability and irreversible capacity loss in silicon anodes focused on improving the elasticity of the polymer binder. This is an intuitively attractive idea as the binder will undergo large strains to accommodate volume changes in silicon particles. In a series of studies, poly(vinylidene fluoride–tetrafluoroethylene–propylene) (PVDF–TFE–P) binder was compared to poly(vinylidene fluoride) (PVDF).[6,7,9,10,28] The authors conducted stress-strain measurements on carbon composites of each polymer and found that PVDF composites could only sustain 10 % elongation before breaking, while PVDF-TFE-P composites could sustain up to 100 % elongation, both in air and swollen with electrolyte.[6] When implemented in anodes with amorphous $Si_{0.64}Sn_{0.36}$ as the active material with a 1:1 mass ratio of active material to polymer binder, the PVDF-TFE-P outperformed PVDF in terms of stability and reversible capacity under identical electrochemical testing conditions.[6,28] These studies were important in demonstrating the importance of polymer binder composition on alloy anode performance. However, this work was limited to comparisons with PVDF and focused exclusively on electrodes with very high polymer binder contents (approximately 50 wt %). Other examples of elastic polymeric binders include styrene-butadiene rubber (SBR),[29,30] polyacrylamide,[31,32] and supramolecular polymer binders.[33,34] A number of subsequent studies on non-elastic, polar polymeric binders concluded that binder elasticity may not be the most important factor determining electrochemical performance. Carboxymethylcellulose (CMC) is a brittle, non-elastic polymer, yet a series of studies on CMC[26,29,35–38] demonstrated it was a more effective binder than elastic polymers like SBR or PVDF-TFE-P. For example, a study comparing CMC and SBR rubber with matched binder content, thicknesses, silicon loading, and

electrochemical testing characteristics showed that CMC anodes produced more stable and higher capacity anodes.[36] These observations led to the hypothesis that elasticity may not be an important factor for polymer binders, or may be less important than other properties such as adhesion to the silicon surface.[37] Studies that show comparable performances using stiff polymers (e.g., pyrolyzed polyacrylonitrile (PAN)[39] or polyamide imide (PAI)[40]), highly crosslinked materials[41], and other non-elastic binders (Nafion[42–45]) are consistent with this hypothesis. At the same time, it is not possible to attribute the differences in performance to elasticity alone, since the polymer also differ in terms of polarity, adhesion, and electrolyte uptake.

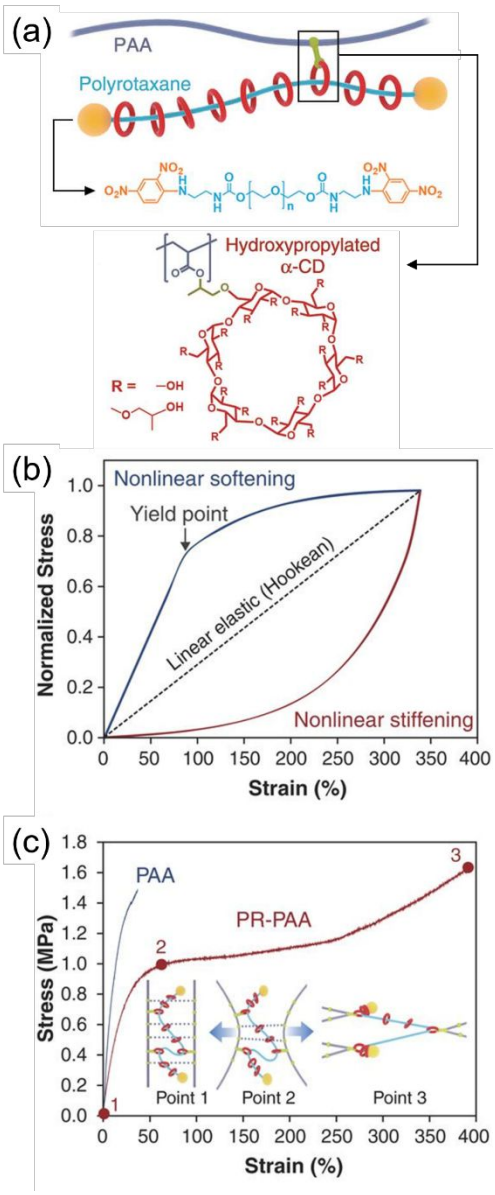

Figure 1. (Reproduced with permission from ref. 32): (a) Molecular structure and schematic for polyrotoxane-modified PAA ((PR-PAA) binder. (b) Representative curves for nonlinear softening, nonlinear stiffening, and a linear mechanical response to deformation and (c) stress-strain data for PAA and PR-PAA binder. The PR-PAA binder shows non-linear strain stiffening at strains in excess of 250 %.

In a recent study demonstrating that elasticity may still be a useful design concept for polar polymer binders, polyacrylic acid (PAA) was functionalized and crosslinked with polyrotoxanes.[32] Polyrotoxanes are molecular rings mechanically interlocked with a linear polymer that threads through rings. The novel crosslinking mechanism enables the rings to slide along the linear chain, resulting in a highly elastic material. The authors showed that the binders could sustain large strains (in excess of 200 %) and exhibited nonlinear strain-stiffening behavior (see Figure 1). This is in contrast to linear, non-modified PAA binders that exhibited non-linear strain-softening. The resulting electrodes fabricated using the polyrotoxane-PAA binder exhibited excellent reversible storage capacities in electrodes with only 10 wt % binder contents. This study is notable because it demonstrated that elasticity may indeed be an important molecular design property, in combination with other favorable polymer binder properties. The study also identified nonlinear strain-stiffening at large strains as a potentially general-applicable design concept. The significance of nonlinear strain-stiffening has not been tested in other polymer binder materials. Recently, the group implemented polyrotoxanes in SiO batteries through the development of a pyrene–poly(acrylic acid) (PAA)–polyrotaxane (PR) supramolecular network as a binder. The pyrene was included to associate with the carbon surface of the SiO particles, and the resulting electrodes achieved areal capacities up to 3 mAh/cm^2 with just 10 wt % polymer binder[46].

2.2 Polar and Adhesive Polymer Binders

Strong adhesion between the polymeric binder and silicon along with the other components of the electrode can help limit sintering and isolation of silicon fragments, loss of conductive pathways, and delamination from the charge collector. Strong adhesion to the silicon surface has been achieved using highly polar, water soluble polymers that contain carboxylic acid, hydroxyl, acetate, or amino functionalities that can associate or bind directly to the silicon surface. CMC is a non-elastic polymer that was found to be superior as a binder when compared with nonpolar elastic polymers or blends of polar and nonpolar polymeric binders[36]. A number of studies attributed the success of CMC as a binder to strong adhesive interactions between CMC and the silicon surface[35,37,38,47,48] and provided direct evidence for strong interactions between the binder and the silicon surface. For example, in one study IR measurements indicated the formation of ester linkages between CMC polymer binder and the silicon surface. The authors concluded that the binder formed a covalent bond with silicon nanoparticles after hydrolysis of acetate groups on CMC polymer followed by condensation with silicic acid functionalities on the surface (see Figure 2).[38] In another study, battery cycling and X-ray photoelectron spectroscopy (XPS) measurements were used to understand the impact of processing conditions on performance. The authors used XPS to quantify the content of ester linkages relative to unreacted acid groups, and found a larger number of ester bonds and improved stability for electrodes processed at low pH.[47] Recent ^{13}C solid state NMR

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studies indicated that the associations between CMC and the silicon surface were hydrogen bonding interactions rather than ester linkages. This study also systematically demonstrated the importance of polymer-silicon interaction through modification of the silicon surface to block hydrogen bonding and comparisons with polymer binders that did not form hydrogen bonding associations with silicon. The authors concluded that non-covalent interactions between the binder and silicon were important for maintaining cycling performance and stability.[37]

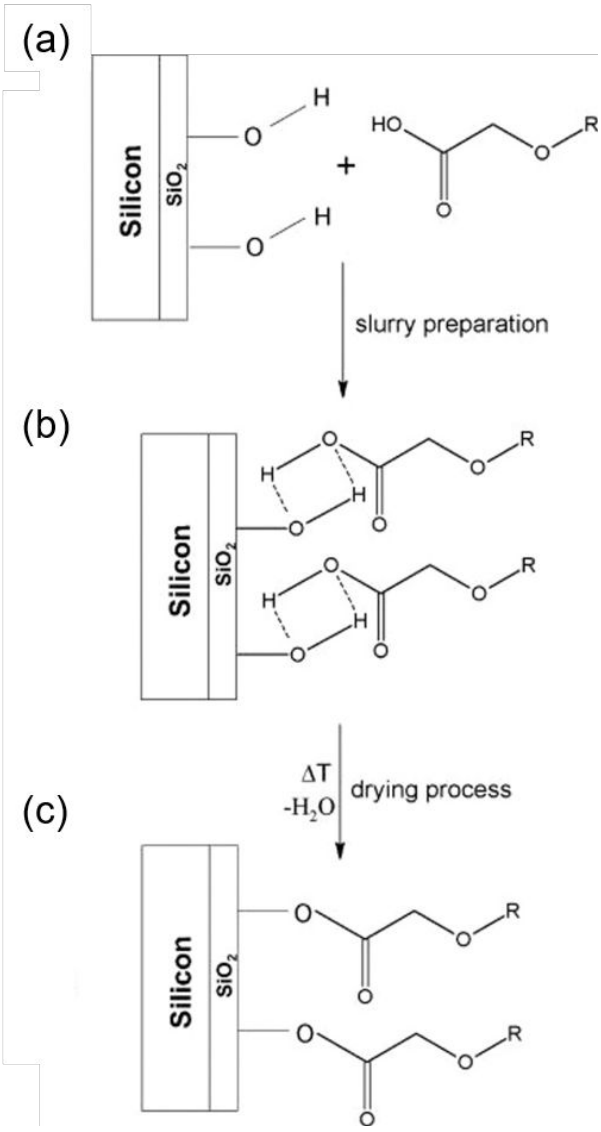

Figure 2. (Reproduced with permission from ref. 38): Schematic for binding between a polymer binder and hydroxyl groups on a silicon surface.

Poly(acrylic acid) (PAA) and sodium polyacrylate (PAANa) are additional examples of strongly adhesive polymeric binder materials.[49–53] Similar to the studies on CMC, XPS and FTIR measurements were used to study the interaction between the binder and silicon surface, indicating the formation of ester linkages. One study also produced evidence for anhydride linkages between PAA chains, which can serve to effectively crosslink and further strengthen the binder.[54] A comparative study analyzed PAANa and PVDF in silicon-carbon electrodes, and found greater adhesion strengths, higher capacities, and more stable batteries in electrodes with PAANa.[49]

Other examples of water-soluble polymers with strong adhesion to silicon include poly(vinyl alcohol) (PVA),[55] alginate,[56] catechol-functionalized polymers,[57] carboxymethyl chitosan,[58] Nafion,[42–45] and polyacrylamide.[31,59] A comparative study of many polar polymers along with other electrode characteristics (e.g. electrolyte used, silicon nanoparticle size and surface chemistry) identified high molecular weight PAA as the best-performing binder studied. This study also concluded that a thin surface oxide layer on the surface of silicon nanoparticles was important for adhesive forces.[18]

Some notable examples of water insoluble polymers have also been reported to be highly adhesive. These polymers are still more polar than PVDF, but less polar than PAA, CMC, and alginate. For example, polyacrylonitrile (PAN)[60] (processed in N-methyl pyrrolidone) was compared against PVDF and CMC binders in graphite and silicon/graphite anodes and found to have higher adhesion strength in both graphite and silicon/graphite anodes and outperform PVDF and CMC in long-term cycling tests. The improved stability was attributed to the polarity of the nitrile side-groups in the binder and binding to the silicon surface[5]. In another example, a polyimide copolymer termed P84 was studied in silicon anodes. The copolymer did not contain any pendant polar groups, but did have a variety of unique and potentially beneficial properties including redox activity with Li^+ and a high modulus.[61] The authors conducted a detailed analysis of adhesion forces using peel tests and the Surface and Interfacial Cutting Analysis System (SAICAS) technique, and they showed that P84 had strong adhesion and favorable long-term cycling. A mechanism for binding or adhesion to the silicon surface was not provided.

Altogether, these studies demonstrate that strong adhesion between the binder and silicon surface is an important design parameter for producing stable, high capacity silicon electrodes. The adhesive forces were generally attributed to the polarity and reactivity of the polymer functional groups.

2.3 Self-Healing, Reversible, and Supramolecular Polymer Binders

A number of studies have implemented supramolecular, reversible, or self-healing bonds and polymers in binders, with the hypothesis that a reversible bond is able to accommodate the large volume changes in silicon without permanent fracture. This reversible nature also allows for reorganization of the polymer chains bound to the silicon surface, and some examples are shown in **Figure 3**. One example focused on CMC binders in low-Si content electrodes (1:1:1 mass ratio of binder, Si, and carbon black). The authors proposed that reversible hydrogen bonds were important to the electrode stability and systematically explored the nature of associations between CMC and Si by comparisons with other polymer binders and modifications of the Si surface. Polymer binders which formed covalent bonds or did not interact with Si performed poorly in comparison with CMC binders that could hydrogen bond with the surface, which enabled the binder to reversibly associate with the surface and accommodate large volume changes.[37]

In an elegant study involving a multi-functional copolymer, the authors prepared copolymers containing different combinations of functional monomeric repeat units.[62] One repeat unit was designed to form crosslinks and bind to the silicon surface while another would associate through reversible supramolecular interactions. These two functionalities were created using Meldrum's acid (5-methyl-5-(4-vinylbenzyl)), which can covalently bind to the silicon surface when thermally annealed or, after hydrolysis, form self-healing supramolecular interactions. The authors systematically varied the composition of the polymer binder and the content of covalent crosslinking and self-healing functional groups in the binder. They found the highest initial coulombic efficiency and best stability in electrodes with the highest content of self-healing functional groups. The electrodes contained 60 wt % silicon nanoparticles and 0.2 mg cm^{-2} silicon loading. They also produced direct evidence for self-healing by analyzing the same spot on a nanocomposite electrode after the 1st and 2nd charge-discharge cycle using SEM.[62]

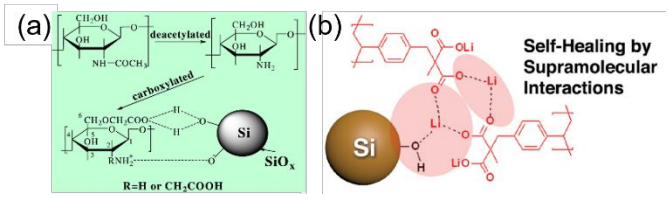

Figure 3. (a) (Reproduced with permission from ref. 58) Molecular structure and schematic for carboxymethyl chitosan forming hydrogen bonds with the surface of silicon nanoparticles. (b) (Reproduced with permission from ref. 62) Schematic for supramolecular interactions between lithium dicarboxylate functionalities and the silicon nanoparticle surface.

A series of studies designed and implemented supramolecular binders in electrodes with silicon microparticles[33,63,64]. In one formulation, a highly elastic and conductive network was formed using dynamic hydrogen bonding and carbon black nanoparticles. Electrodes with a 1:1 ratio of binder to Si microparticles produced an initial capacity of 3200 mAh/g and an areal capacity of approximately 2 mAh cm^{-2}.[63] The performance of this system was further optimized in a follow-up study to achieve areal capacities up to 4 mAh cm^{-2}.[64] In a more recent study, a second example of a supramolecular polymeric binder was reported using fatty acid polymers and urea functional groups[65]. By varying the composition of the supramolecular binder, the authors explored the role of modulus, rheological properties, adhesion, crosslink density, and ion mobility on performance. They identified an optimal network relaxation time and crosslink density that produced electrodes that could achieve stable cycling[65].

These studies clearly point to self-healing and reversible binding as an effective and important design strategy or polymeric binders. These materials in general combine some degree in elasticity with an ability for the binder to re-organize and self-heal. Recent reviews detail additional work towards the development of supramolecular polymeric binders.[12,66,67]

2.4 Crosslinked and High Strength Polymer Binders

One potential source of irreversible capacity loss in silicon composite electrodes is through pulverization and isolation of fragments of the silicon particles during cycling. Pulverization can be reduced by using silicon nanoparticles as the active material, but movement of the nanoparticles during cycling can still result in isolation of particles and loss of capacity. These problems can be potentially addressed through the use of a high-strength binder that prevents pulverization and maintains connectivity between the electrode components. For example, alginate was used effectively as a polymeric binder in a silicon nanocomposite electrodes, and its performance was attributed, in part, to its high strength that was maintained in the presence of electrolyte due to its limited electrolyte uptake.[56]

A general approach to directly tailor the mechanical properties of polymer binders is through reactive crosslinking. For example, PAA and CMC undergo interchain crosslinking when blended and annealed through esterification.[41] The resulting crosslinked networks have a higher modulus than both PAA and CMC separately and a higher modulus compared with alginate as measured by nanoindentation studies. In electrochemical cycling studies, the specific capacity and stability of electrodes with crosslinked PAA-CMC binders outperformed PAA and CMC separately. A similar approach was reported through the crosslinking of multi-functional copolymers containing a distribution of carboxylic acid, carboxylate, and hydroxyl functional groups that could be crosslinked by thermally annealing at elevated temperatures.[68]

Polymeric binders with pendant carboxylic acid or carboxylate groups may be ionically crosslinked using divalent cations. For example, Ca^{2+} can form physical crosslinks when added to sodium alginate, resulting in an increased strength, toughness, and strain resistance.[69,70] The improved strain resistance was attributed to the ability to break and reform ionic bonds.[70] Crosslinking with Ca^{2+} also improved the stability of electrodes relative to pure sodium alginate.[69,70]

Other examples of crosslinking in polymeric binders include polyborosiloxanes[71] and dual-crosslinked binders,[72] the latter containing both ionic crosslinks of a bio-derived alginate and covalent crosslinking between the alginate and polyacrylamide. The study of dual-crosslinked polymers provides an innovative way to independently tune the modulus and content of reversible crosslinks in the binder materials[72].

These studies demonstrate that crosslinking can enhance electrochemical performance and stability, and they attribute improvements to increased modulus of the binder and reduced electrolyte uptake. However, while crosslinking increases the network modulus, it also generally reduces network elasticity, and the optimal balance between elasticity and network modulus has not been studied.

2.5 Multi-functional Polymer Binders

The various design strategies described above include polymer polarity and adhesive properties, network reversibility, crosslinking and the nature of forming crosslinks or binding to the silicon surface, modulus, and elasticity. Studying each of these characteristics is difficult in even a single binder material,

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and identifying optimal characteristics across a broad library of material choices may be impossible. A potential approach to achieve a binder with many or all of these characteristics is through the blending or combination of different polymer binder materials. One strategy, for example, is through the synthesis of a copolymer containing a variety of different functional groups that perform various functions. This has been implemented in the design of conductive polymer binders[73] and adhesive and self-healing binders[62,68] and is an effective strategy to systematically screen libraries of copolymers and identify trade-offs in the design of polymeric binders. A related, and simpler, approach is to blend different polymeric binders in order to try to combine the favorable characteristics of different material in a single binder.[30,34,41,74]

A more demanding but potentially more effective approach is to utilize block copolymer materials as binders. While the synthesis of block copolymers is significantly more challenging than random copolymers, the use of multi-block copolymers can more effectively combine the properties of distinct polymer binders in a single macromolecule. For example, the synthesis of a triblock copolymer containing polydopamine (PDA), polyacrylic acid (PAA), and polyoxyethylene (PEO) required the preparation of a chain-transfer agent-functionalized PEO polymer followed by a sequential polymerization reaction, a polymer deprotection, and final modification step to produce from conversion of some acrylic acid groups. The resulting triblock copolymer binder exhibited favorable properties that combined many of the desirable characteristics of the separate polymeric binders.[75] Although not specifically discussed in the study, this is a potential way to design a binder with significant electrolyte uptake that can also maintain excellent mechanical properties since the swelling and adhesion would be mediated by micro-phase segregated polymer blocks.

2.6 The Role of Processing on Performance

In addition to the various relevant polymer binder properties discussed, the role of processing cannot be neglected. Silicon electrodes are typically fabricated by deposition of a slurry, and the final characteristics of the electrode structure, including polymer conformation, distribution of silicon and conductive additives, and uniformity will depend on the casting conditions. As an example of how processing conditions can be leveraged to produce more uniform electrodes, polymer binders can be synthesized *in situ* during casting in order to produce a more uniform slurry and stronger interactions between the binder and silicon particles.[76,77] When comparing the performances of different polymeric binders, the slurry viscosity can have a significant impact on final performance.[35,50,59,78,79] Differences in viscosity can arise due to differences in processing conditions. For example, dissolving a high molecular weight hydrolyzed polyacrylamide in a planetary mixer decreased the viscosity compared to dissolving with a stir bar, possibly due to polymer shearing.[59] Addition of other more viscous agents or cross-linking may also have an impact on the viscosity. For example, addition of sodium alginate to an *in situ* polymerized binder increased the viscosity and also prevented over polymerization of the binder.[77] Changes in the solution pH can improve binder interactions with other slurry components as well as the degree of binder coiling or extension. In one example, neutralizing the acidic protons of PAA was shown to be a significant processing step.[53] In another example, changing the pH improved the solubility of CMC, resulting in a more extended polymer conformation in the final electrode with a greater number of contacts with the silicon surface[35,80]. Additional examples of slurry preparation affecting electrochemical testing can be found in a review by Mazouzi et al.[81]

The slurry casting and drying process afterward can also play an important role. Outgassing of slurries may be a necessary step to prevent bubbles of gas from creating nonuniformities in the cast film.[31,59] Gas can arise in the slurry from polymerization reactions, crosslinking reactions or binder interactions with the Si surface. Also, some reports specify the drying conditions of casted films, such as in the case of a Si electrode using a polyacrylamide hydrogel binder with good cycling performance. The electrode was specified to sit in a humid box after casting until *in situ* cross-linking was completed.[31,51] In general, processing conditions have a significant impact on the morphology and performance of a composite electrode.

3. Electrochemical Properties and Performance

To maximize electrode volumetric capacities, composite electrodes must be good conductors of both electrons and ions,[82,83] as shown schematically in **Figures 4** and **Figure 5**. Polymeric binders influence both electronic and ionic conduction through interactions with the electrolyte, their impact on the composite electrode morphology, and, in some cases, intrinsic electronic or ionic conduction of the polymeric binder. The polymeric binder furthermore can play a role in the electrochemical stability of the composite electrode through electrochemical degradation of the binder or impact on the formation of the solid-electrolyte interphase. In this section, we review polymer binder design principles related to electrochemical properties and stability of the nanocomposite electrode.

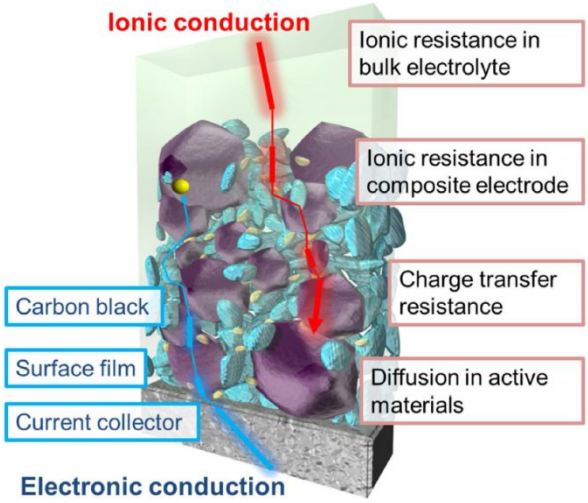

Figure 4. (Reproduced with permission from ref 83): Schematic for ionic and electronic conduction in nanocomposite electrodes.

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3.1 Electronically Conductive Polymer Binders

Silicon nanoparticles (SiNPs) are non-conductive and they typically require a conductive additive, such as carbon black, along with the polymer binder. Polymers that are electronically conductive can be used simultaneously as a polymeric binder and conductive additive and reduce the overall content of additives, leading to an increase in the content of active materials. In this section, we review only work on the design of electronically conductive polymeric binders, which usually consist of conjugated backbones or conductive side groups. These conducting polymeric binders can facilitate charge transport to and from silicon particles, as shown schematically in **Figure 5.**

A 2011 study demonstrated the potential utility of conductive polymer binders[84]. The study reported a series of polyfluorene polymers and copolymers containing functional groups for reaction with lithium and binding to the silicon surface. The polymers studied contained a π-conjugated backbone, and the functional groups included a carbonyl functionality that could react with lithium and a methylbenzoic ester functional group to improve adhesion to silicon (see **Figure 6**). The reactive carbonyl groups were necessary because the polymer is non-conductive in its native state, but is doped electrochemically during electrochemical cycling. The authors used a variety of methods including X-ray absorption spectroscopy, impedance measurements, and density functional theory calculations to understand the electrochemical doping of the polymer and design a binder that would remain doped in the working potential range of the anode, 1 to 0.01 V (vs. Li/Li^+). It was demonstrated that this polymer could be used as a binder without an additional conductive additive, despite a much lower electronic conductivity compared with acetylene black (4.9×10^{-6} S/cm for the binder after the first lithiation cycle compared with 0.1 to 100 S/cm for acetylene black)[73]. The use of the conductive polymer binder resulted in an impressive performance of the composite electrode, using silicon nanoparticles and 33 wt % polymer binder[84].

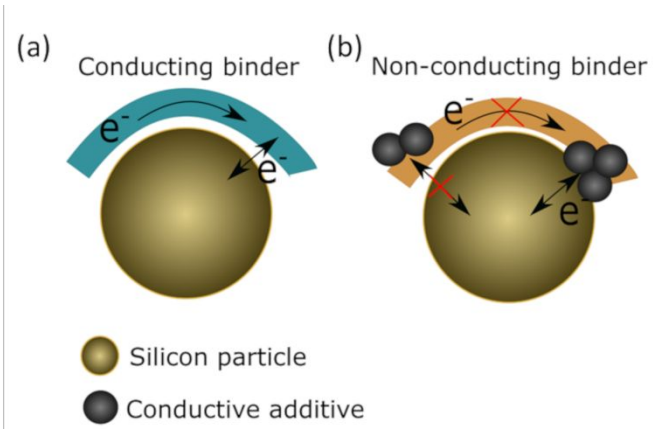

Figure 5. Schematic depicting charge transport and charge transfer between a silicon particle and (a) conductive binder and (b) non-conductive binder with carbon additive. The conducting binder transports electrons through the binder itself and transfers electrons between the binder and the silicon particle. The non-conducting (traditional) binder is insulating; conductive additives such as carbon facilitate electron transport and transfer.

A number of other studies on polyfluorene-based binders have focused on further improving performance and demonstrated the versatility of this class of materials. For example, polar side-chains can be incorporated to increase electrolyte uptake and improve capacity.[73] Polyfluorene binders can be utilized in SiO anodes, and calendaring reduces porosity and increases volumetric capacity.[85] By incorporating ionic side-chains, the polyfluorene copolymer can be made water soluble and used in aqueous-processed nanocomposite electrodes.[86] Finally, the kinetics of electrochemical doping of the binder can be tuned through incorporation of organic functional groups with fast reaction kinetics ((poly(phenanthraquinone), PPQ), resulting in a nanocomposite electrode with improved rate performance.[87]

Polyaniline (PANi) has also been studied as a conductive matrix for Si anodes. In one example, a conductive PANi hydrogel was produced in the presence of silicon nanoparticles by polymerizing and electrochemically doping polyaniline. The resulting conductive composite was cast immediately after the reaction to produce a nanocomposite electrode.[76] In other studies, PANi was used as a conductive additive rather than a binder.[88–91] For example, in one study the authors used PANi to first coat silicon nanoparticles and then fabricated a nanocomposite electrode using PAA as the binder.[91]

Poly(3,4-ethylenedioxythiophene):poly(styrene-4-sulfonate) (PEDOT:PSS) is a commercially produced conductive polymer mixture studied for use in a wide variety of electronic device applications, but only recently explored in silicon anodes (see **Figure 7)**.[92] In a systematic study using PEDOT:PSS as the binder for silicon anodes without any additional conductive additives, the authors detailed how the processing conditions, polymer loading, composite electrical conductivity, and electrochemical composition were optimized to produce a nanocomposite electrode. This included quantifying the electrical conductivity of the nanocomposite electrodes as a function of binder content, dopant concentration, and porosity, and the optimized electrodes produced an areal capacity of approximately 3 mAh cm^{-2}. In another study, PEDOT:PSS was used as a conductive additive along with CMC as the binder.[93]

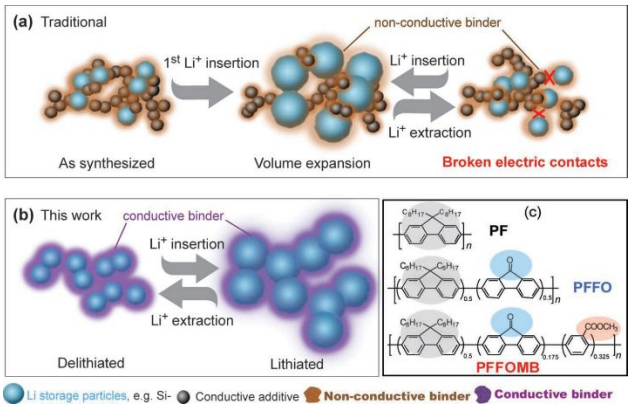

Figure 6. (Reproduced with permission from ref. 84): Schematic illustration of Si electrode (a) with and (b) without conductive binder during lithiation and delithiation. (c) Chemical structures of conductive polymeric binders polyfluorene

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(PF), poly(9,9-dioctylfluorene-co-fluorenone) (PFFO), and poly(9,9-dioctylfluorene-co-fluorenone-co-methylbenzoic ester) (PFFOMB).

Conductive polymer binders can also be fabricated using polymers with a flexible backbone and semiconductive or conductive side-chains. For example, poly(1-pyrenemethylmethacrylate-co-triethylene oxide methyl ether methacrylate) (PPYE) with pyrene and ethylene glycol side-chains was implemented in silicon nanocomposite electrodes without additional conductive additives at a 2:1 ratio of silicon to polymer and demonstrated excellent performance.[94,95] However, a follow up study found poor stability of these materials in silicon anodes due to preferential uptake of one electrolyte component, resulting in unstable growth of the solid-electrolyte interface (SEI) layer.[96]

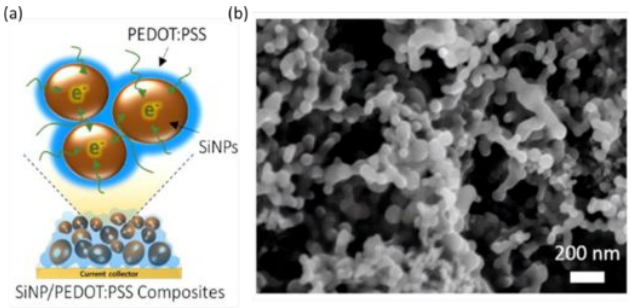

Figure 7. (Reproduced with permission from Ref. 92): (a) Schematic illustration of interaction of the conductive binder (poly(3,4-ethylenedioxythiophene):poly(styrene-4-sulfonate) (PEDOT:PSS)) with silicon nanoparticles. (b) Scanning electron microscopy (SEM) image of the as synthesized electrode (Si/binder=2/1 by mass) with 10 wt% (wrt to PEDOT:PSS) formic acid (FA).

A number of studies have reported the use of non-conductive polymers which can be subsequently pyrolyzed to produce a conductive or partially conductive material. For example, polyacrylonitrile (PAN) is non-conductive and can be thermally treated to produce conductive carbon fibers[97], and pyrolized PAN has been used as a conductive binder for microporous silicon anodes[20,98]. In these studies, porous silicon particles were produced from electrochemically etched silicon wafers. The pores in the microparticles were designed to enable reversible silicon expansion/contraction during charge and discharge cycles, resulting in electrodes with excellent cycling stability. The optimal polymer content for the system was found to be 30 wt % pyrolized PAN.[20] Pyrolyzed lignin can similarly be used as a conductive polymeric binder for silicon nanocomposite electrodes.[99] Electrodes with approximately 55 wt % silicon and pyrolyzed lignin along with poly(ethylene oxide) (PEO) as binder materials produced electrodes with excellent stability.

These studies on conductive polymer binders illustrate the potential and versatility of these materials for use in silicon anodes but also point to a number of questions related to their use in anodes. First, many of the materials reported are only conductive after electrochemical doping. As demonstrated by the development of polyfluorene binders, achieving electronic conductivities over the working potential of the silicon anode is not trivial and may require a combination of computational design and experimental verification to develop polymers that remain conductive over the operating window.[84] For example, PANi is known to be in the insulating leucoemeraldine form over silicon's potential window.[100,101] Follow up studies have not studied the electrochemical doping of the binder in nanocomposite electrodes, and it is therefore unclear what role doping/de-doping may have on the performance during electrochemical cycling. The conductive polymers studied also vary widely in terms of the intrinsic electronic conductivity of the binder, and the conductivities of are generally much lower than other, more commonly studied conductive additives such as carbon black. It is unclear what the optimal or minimum electronic conductivity needed for the anodes. In addition to these issues, the physical properties of conductive polymer binders such as modulus, elasticity, adhesion, electrolyte uptake are in general poorly understood.

3.2 Polymer Binder Interaction with the Electrolyte

Polymer binders can swell in electrolyte, and the amount of electrolyte swelling or uptake has an impact on morphology, ionic and electronic conductivities, mechanical properties, and the formation of the solid electrolyte interphase (SEI) layer. Electrolyte uptake by the polymer binder is often quantified by measuring the swelling ratio, defined as the weight ratio of the amount of electrolyte uptake to the binder film before swelling.

Polymeric binders can vary widely in terms of electrolyte uptake. For example, PVDF was shown to swell significantly in propylene carbonate, up to 25 wt % at room temperature and 60 wt % at 80 ^{o}C. By comparison, a 1:1 blend of SBR and CMC swelled by less than 1%.[30] Various polar binders with favorable adhesive properties take up little or no electrolyte. This includes PAM,[59] CMC,[29] CMC blended with SBR,[30] PAA,[49] and alginate.[56] The thickness of PAA and Na-CMC binder films increased by less than 2 % in the presence of diethylcarbonate vapor compared with 20 % for PVDF.[49] Similarly, ellipsometry studies showed no detectable uptake of solvent vapor and only a small reduction of Young's modulus in the presence of electrolyte for alginate binders.[56] Crosslinking also reduces electrolyte uptake, as reported PVDF-TFE-P compared with PVdF.[6]

A number of studies have demonstrated that electrolyte uptake is detrimental to the modulus and adhesive strength of the polymer binder.[49,54,56,102–104] For example, in a comparison of PVDF, alginate, and Na-CMC, atomic force microscopy was used to compare the Young's modulus of each polymer binder in the dry state and in the presence of electrolyte. Due to electrolyte uptake, the PVDF modulus decreased by an order of magnitude, while the modulus of alginate and Na-CMC, which did not significantly swell in electrolyte, did not change.[56] In another study, both PAA and CMC retained a high modulus even in the presence of electrolyte, due to little or no electrolyte uptake by the binder.[49] Studies based on XPS measurements have concluded that electrolyte uptake can also be detrimental to adhesion between the polymeric binder and the silicon surface.[54,56]

Electrolyte uptake influences both electronic and ionic conduction in nanocomposite electrodes. This was demonstrated, for example, in a comparative study of different

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polymeric binders in SiO nanocomposite electrodes.[54] The authors showed that both PVDF and PAA swelled to some degree electrolyte, with a 43 and 8 % swelling ratio, respectively. The corresponding nanocomposite electrodes exhibited only electronic conduction in the dry state and mixed electronic and ionic conductors when swollen with electrolyte, reflecting enhanced ionic conduction due to electrolyte uptake (see **Figure 8**). On the other hand, the electronic resistance increased for both nanocomposite electrodes due to swelling, and the increase was more significant for PVDF, which swelled more significantly in electrolyte (see inset in **Figure 8**). The authors found that the PAA nanocomposite electrodes were more stable, and the authors attributed this to the relatively poor mechanical properties of electrolyte-swollen PVDF polymer as compared to PAA.[54] This study demonstrates the complexity in tailoring the properties of polymer binders for optimal performance due to the impact on various electrode characteristics relevant for performance.

Despite the negative impact of electrolyte uptake on mechanical properties and adhesion, some studies have tried to leverage electrolyte uptake for increasing ionic conductivity.[60,73,105–109] For example, one study focused on a crosslinked mixture of chitosan and natural rubber.[106] Pure chitosan swelled significantly more in the electrolyte compared with natural rubber, and the degree of electrolyte uptake decreased with increasing rubber content. The authors also demonstrated an increasing ionic resistance with increasing rubber content and poorer rate performance with increasing rubber content. At the same time, electrodes with pure chitosan binders exhibited poor stability, due in part to excessive electrolyte uptake. The optimal chitosan content of the binder was determined to be in the range of 50 – 70 %.[106] In another study focused on semiconductive, multifunctional binders, the authors purposefully engineered copolymers to include polar side-chains that increased electrolyte uptake.[73] The resulting copolymer took up more than 25 wt % electrolyte, compared with a similar copolymer that did not contain polar side-chains and did not swell appreciably in electrolyte. The authors also measured a lower modulus in the (dry) polymer that contained the polar side-chains. Using 33 wt % polymer binder, the authors demonstrated higher capacity and stability in the binders with significant electrolyte uptake. Finally, a study of a molecular weight series of PVA in comparison with PVDF and PAA found that PVA outperformed PAA. PVA showed significant electrolyte uptake (30 – 40 wt % swelling) while PAA did not swell in the electrolyte. The authors also reported a higher adhesion strength for the PVA binders.[55]

A recent study conducted a detailed analysis of electrolyte uptake and transport of a silicon nanocomposite electrode.[96] The study focused specifically on poly(1-pyrenemethyl methacrylate) (PPy) conductive polymer binder, but the methods applied are relevant to all energy storage systems. Through analysis of electrolyte uptake and swelling of polymeric thin films, the authors demonstrated that the polymer binder preferentially swelled in diethyl carbonate (DEC), resulting in an increased concentration of DEC over ethylene carbonate (EC) at the silicon/PPy interface. Despite the favorable adhesive, mechanical, and electronic properties of PPy, this selective electrolyte uptake resulted in continuous degradation and electrolyte decomposition.[96] Very few studies have looked at selective uptake of one electrolyte component, and this selective uptake has not been reported for other binder materials.

Altogether, a large number of studies have demonstrated effective polymer binders using polar binders which do not appreciably swell in electrolyte. While the general consensus is that swelling can be detrimental to mechanical properties, a number of studies have shown that swelling can be beneficial by enhancing ionic conductivity. There is no consensus on the optimal degree of swelling, and this is likely dependent on the particular system and characteristics including binder content, mechanical properties, morphology, and adhesive strength.

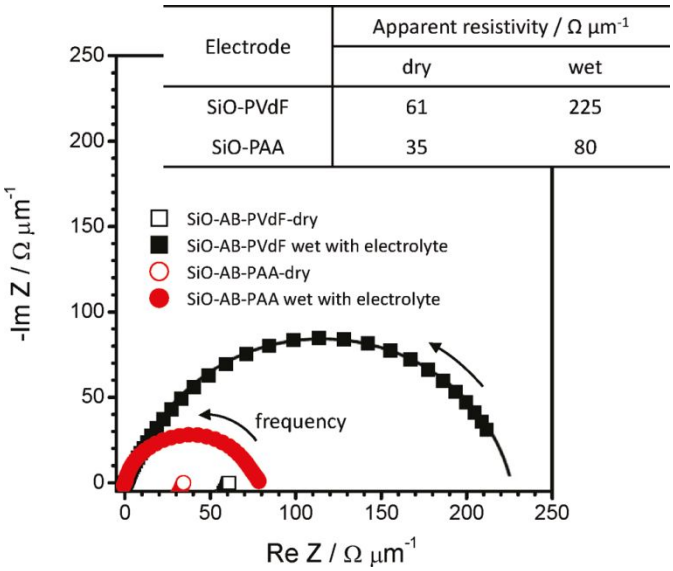

Figure 8 (Reproduced with permission from ref. 54): Nyquist plots of wet and dry SiO electrodes containing either PVdF or PAA binder. Wet electrodes exhibit higher electronic resistance but lower ionic resistance compared with dry electrodes.

3.3 Electrochemical Stability

Polymer binders can degrade during battery operation due to exposure to the electrolyte, mechanical stresses, or electrochemical reactions. Here, we review general considerations and studies focused on understanding the stability of polymer binders in silicon-based anodes.

As a first condition for binder stability, the binder should not dissolve in the electrolyte, which is typically a blend of carbonate solvents. The solubility of 98 different polymers in cyclic carbonates, EC and propylene carbonate (PC) have been compiled in a report that is useful as a starting point for selecting a polymer binder.[110] Solubilities were determined by adding 0.3 g of polymer to 5.7 g of carbonate solvent. As examples, Na-alginate, methyl cellulose, polyacrylamide, PI, PAA, and styrene/butadiene (SB) copolymer are not soluble in pure and binary carbonate solvents at neither 25 °C nor 60 °C. PVdF, PVP, PMMA, and styrene/acrylonitrile (SA) copolymers are soluble at 25 °C.

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The polymer binder (and electrolyte) can degrade due to reduction or oxidation reactions at the electrodes. Polymer HOMO and LUMO levels provide a rough estimate of stability windows and can be estimated from calculations.[109,111] In general, lower HOMO levels correspond to improved stability in an oxidative environment (cathode) and higher LUMO to improved stability in reductive (anode) environments. As examples, PVDF and PTFE, and PAN have sufficiently low HOMO levels for use in the cathode, while SBR, PEO, and PPO have sufficiently high HOMO and LUMO levels, corresponding to good electrochemical stability in the anode and cathode.

A recent study on electrolyte stabilities showed that using HOMO and LUMO levels can lead to significant discrepancies with the experimental electrochemical stability window.[112] The electrolyte stability window is determined by the reductive and oxidative potential of the binder in the electrode environment, and for good stability the potential window of the binder should be larger than the working potential of the battery. This also applies to the liquid electrolyte, and is demonstrated for liquid electrolytes with an energy level diagram in **Figure 9.**[112] The diagram shows that the liquid electrolyte is unstable when its thermodynamic potential window is narrower than the cell voltage, which is the difference in the electrochemical potentials of both electrodes. Similarly, the polymer binder should have lower reduction potential than the electrochemical potential of the anode and a have higher oxidation potential than the electrochemical potential of the cathode.

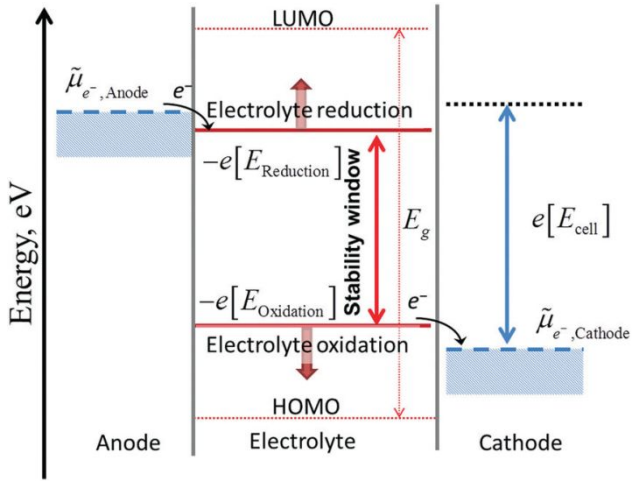

Figure 9. (Reproduced with permission from ref 112): Diagram showing the anode and cathode potential limits for the electrolyte stability and electrolyte HOMO and LUMO levels. The diagram shows that the electrolyte will react when its stability window is narrower than the cell potential, and HOMO and LUMO levels may be poor predictors of this stability window.

Polymer binders can also react with electrode active materials, and these reactions are in general undesirable. One recent study investigated the stability of polymer binders in the presence of lithium silicate (LC).[113] The reaction of PVDF or Li-PAA polymer binders with lithium silicate (LS) was studied by physically mixing Li_7Si_3 powders with each polymer binder (10 or 30 wt %) in an argon-filled glovebox. NMR and Raman spectral studies revealed the formation of new Li complexes from the reaction between PVdF and lithium ions produced by delithiation. The defluorination of PVDF by HF generation was also confirmed by GC mass spectrometry. Based on the characterization results, the authors of the study proposed a number of carbon-carbon and carbon-hydrogen bond-breaking reactions in PVDF consistent with the NMR and Raman spectral analysis. They concluded that reaction between the binder and LS reduces the amount of Li available for reaction and degrades the binder, resulting in poor electrochemical performance.[113] In contrast, unlike the LS/PVdF system, new Li species were not observed in mixtures of LS and Li-PAA, indicating that Li-PAA was chemically stable against LS. Consequently, the Si/Li-PAA anodes exhibited much better electrochemical performance[113].

3.4 Effect of Polymer Binder on Solid Electrolyte Interphase

Carbonate electrolytes decompose on the surface of active materials during the charge process and produce a passivation layer known as the solid electrolyte interphase, or SEI. This is an electronically insulating but ionically conductive layer, and in silicon anodes the SEI can grow uncontrollably during cycling because of the volumetric changes of silicon, resulting in loss of capacity and, eventually, failure.[50] Polymer binders are partially coated on the surface of active materials[55,78,114,115] and can influence the formation of SEI layer. Here we briefly review studies focused on understanding the impact of polymer binders on SEI growth.

In one study in silicon anodes and PAA binder, carboxylate groups in the PAA binder were shown to react with the electrolyte salt, producing a protective layer comprised of $Li_xPF_yO_z$ and LiF. This protective layer resulted in improved performance and stability when compared against other materials without the film[19,116,117]. The polymer coating layer acted as a stable SEI that enables surface passivation despite of large volumetric change during cycling[118,119].

The polymer binder can also influence the interaction between lithium ions and the active material surface. In studies of graphite anodes, polar binders such as PAA, PVA, and poly(methacrylic acid) (PMA) have been shown to suppress decomposition of the electrolyte by promoting de-solvation of lithium from the liquid electrolyte to the active particle surface[115,120]. The coated polymers behave like an artificial SEI layer on the surface of graphite active materials. Gelatin-modified graphite can serve as nucleation sites for the formation of passivation layers[121,122]. PAA binder can help form a stable SEI and suppress the generation of HF[123]. Certainly, the binder can play a large role in SEI layer formation or suppression whether it blocks access to the active material or becomes part of the SEI itself.

4. Conclusions and Outlook

A review of the history of the Li-ion battery shows many technological innovations and compromises were needed to produce commercial Li-ion batteries. The initial hopes of the technology were to produce capacities in excess of 3000 mAh/g, but the final commercialized devices reached about 10 % of this value[124]. Similar compromises will be necessary in the commercialization of silicon, most notably through making composites of silicon and carbon. By diluting the silicon content of the anode with carbon, batteries with stable performance can be produced, but at a cost of lower capacities[125]. However, efforts are underway to make higher-content silicon batteries, with 50 % or more silicon in the anodes, and the chemistry of the polymer binder will play an essential role in these efforts.

An impressive variety of polymeric binders have been developed towards the aim of producing stable, high-capacity silicon anodes. This variety reflects the wide range of molecular

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design principles and changes in emphasis and direction in developing new and better polymer binders. While early work focused on polymer binder elasticity, more recent work has emphasized adhesion and self-healing in polymer binders. Nevertheless, all of the design principles listed in Table 1 have proven to be useful, and the most successful polymer binders have considered the impact across a variety of electrode properties. This includes understanding and optimizing the level of electrolyte uptake by the binder, balancing elasticity and reversibility with mechanical strength, and characterizing electrochemical degradation mechanisms.

The study of novel polymer binders presents new challenges to understanding the enhancement of performance and optimizing the electrode composition. In the case of electronically conductive polymer binders, these materials typically exhibit electronic conductivities several orders of magnitude lower than conventional conductive additives such as carbon black, yet they are able to produce working electrodes. This leads to the question: what is the optimal electronic conductivity for these binders, and how and why is that different than for other conductive additives? In the case of polyrotoxane crosslinkers which have produced silicon anodes with impressive capacities, the underlying source of performance enhancement remains unclear. Can this be attributed to improved elasticity, or the combination of increased elasticity along with non-linear strain stiffening at large strains? Finally, self-healing and supramolecular systems raise a number of intriguing and still unanswered questions regarding the optimal balance of network reorganization, modulus, and reversibility required to produce optimal electrodes.

Further progress in the development of new and more effective polymer binder systems for silicon anodes will require a greater emphasis on model systems and computational studies. Model studies are important for isolating the impact of a specific chemical functionality or physical property. For example, model studies with random copolymer binders have enabled the systematic control over binder chemistry, and these studies can help isolate the effects that a particular monomeric repeat unit has on electrode characteristics [62,68,73]. Another example is the study of model, thin film electrodes, which can help in understanding both adhesive properties and the chemistry that occurs at the silicon-binder interface[59,96]. Computational studies of polymer binders in composite electrodes are in general limited, but can potentially be instrumental in advancing the development of binders and providing insight into molecular design principles. A challenge of these studies is appropriately capturing the multi-scale complexity of binders and the electrode environment. Recent work has implemented computational simulations to aid in understanding performance degradation due to stress generation and/or loss of conductivity[126–130] and to understand molecular-level phenomena that govern adhesion to the silicon surface[131]. Pairing computational and experimental studies can provide an effective, iterative approach to the design of next-generation polymeric binders for silicon anodes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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We review molecular design principles for polymer binders for silicon anodes. Their impact on performance is complex and includes mechanical properties, adhesion, electrolyte uptake, ionic and electronic conductivity, and electrochemical stability.