

# Electrode Binder Design on Silicon-Based Anode for Next-Generation Lithium-Ion Batteries

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As an important part of the electrode material of lithium-ion batteries, the binder significantly affects the forming strength of the solid electrolyte interface (SEI), and also determines the mechanical properties and cycling stability. In the silicon anode, binder have greater effect in the chemical and electrochemical stability because of the volume of the silicon anode changes by more than 300%. Thus, the development of functional new binders with enhanced properties is one of the keys to

mitigating the instability of silicon anodes. This concept first briefly introduces the advantages and disadvantages of conventional electrode binders, then the current research progress of silicon anode binders is briefly summarized based on the different types of interaction forces of binders. Finally, we conclude the properties indicators of silicon anode binders with superior performance in batteries, and comment our previous work in detail.

Silicon has become the most promising anode material for next-generation lithium-ion batteries (LIBs) due to its high theoretical specific capacity and large natural reserves. The problem that restricts the large-scale commercial application of silicon anodes is the large volume expansion (>300%) in the continuous delithiation/lithiation process.<sup>[1]</sup> The large volume expansion could break the stability of formed SEI layer, the active silicon is frequently exposed to the electrolyte environment and continuously reacts with the electrolyte and SEI layer are being formed all the time.<sup>[2]</sup> This consumes a large amount of electrolyte and active silicon, which further reduces the cycling life of the battery.<sup>[3]</sup> The large volume expansion also breaks the structure of the material compositions and the whole electrode, resulting in the failure of the electrical contact between the silicon particles and between the silicon with the Cu substrate.<sup>[4]</sup> The binders play an irreplaceable role in the electrode, connecting the individual active particles and connecting them into a single unit, guaranteeing electrical contact between the particles.<sup>[5]</sup> The functional groups of silicon anode binders can be broadly divided into the following two categories: polar functional groups that act as adhesion and conjugated functional groups that act as electrical conductors (such as alkyl functional groups). The binder forms a covalent connection or strong intermolecular force with silicon particles and current collectors through polar functional groups such as –OH, –COOH, –F, –NH<sub>2</sub> and –CONH– to achieve a stable

connection, and the long chain structure of the binder can connect individual silicon active particles to ensure electrical contact between the particles<sup>[6]</sup>. The conjugated functional groups on the molecular chain can also improve ion transport and electron conductivity throughout the electrode.<sup>[6a, 7]</sup>

The main electrode binders used on a large scale are PVDF, CMC, SBR, and PAA. As shown in Figure 1, there is a schematic diagram of the structure of the four commonly used electrode binders and a summary of their respective advantages and disadvantages. PVDF is commonly used as an electrode binder due to its strong adhesion and stable electrochemical properties. However, PVDF mainly relies on the formation of hydrogen bonds between the F in the molecule and the particles. When the volume of the electrode material changes greatly, it will cause cracking and powder loss of the electrode sheet. PVDF has been reported to have greater swelling in carbonate electrolytes, which will lead to a decrease in its hardness and make it more difficult to stabilize silicon particles with large volume changes during cycling. In addition, PVDF requires NMP as a solvent, which is expensive and harmful, so PVDF is not considered as a binder for silicon anodes. CMC can form a strong interaction force, but CMC has high stiffness and low elongation at break, which cannot well adapt to the large-volume expansion of silicon. And in order to achieve the high load of the anode, the industry generally rolls the electrode piece to improve the compacting density of the electrode piece, and the pole piece that only uses CMC binder is very prone to powder loss and structural collapse when rolling. On the other hand, the dispersion performance of SBR is very poor, but its adhesive performance is delightful. In actual production, the application of CMC is always combined with flexible SBR, and the addition of SBR can improve the loss of electrode piece powder. The surface of silicon particles is generally covered with silicon oxide, and some silicon oxide will react with water in the environment to form silicic acid, while PAA with a large number of carboxylic acid groups can combine with silicic acid on the silicon surface to form strong hydrogen bonds and

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covalent bonds. In addition, PAA is soluble in water, and the use of water as a solvent can reduce the cost of slurry mixing and improve safety. In the electrolyte environment, the PAA binders replaced with lithium exhibited superior electrochemical performance over PAA<sup>[15]</sup>. This may be due to the fact that the PAALi binder can facilitate the transport of Li at the electrode interface through the H<sup>+</sup>/Li<sup>+</sup> reversible exchange reaction between –COOH and –COOLi, and the high co-transport of electrons and Li in the battery enhances the kinetic performance of the electrode and provides a fast capacitive redox process, thereby improving the performance of the electrode.<sup>[16]</sup> In addition, there is an emerging strategy for solvent-free preparation of electrodes, in which solvent-free binders represented by polytetrafluoroethylene (PTFE) use the huge shear force brought about by high-speed rotation to achieve the fibrosis of PTFE, so as to achieve uniform dispersion and good adhesion of electrode powder slurry. However, there are still many problems that need to be solved urgently in the solvent-free strategy. How to achieve stable contact between the material and the current collector, how to achieve uniform dispersion of powder, and how to extrude a uniform thin electrode film. Wei *et al.*<sup>[17]</sup> showed that PTFE undergoes irreversible electrochemical reactions around 0.5 V and 1.2 V (vs. Li/Li<sup>+</sup>). This leads to irreversible degradation of PTFE, which leads to rapid battery failure. However, these conventional

binders do not provide a stable mechanical environment and conductive network, and often need to be used with silicon-active particles which have been synthesized in a complex process. As shown in Figure 2, we divide the silicon anode binders into three main types according to the different forces of the binders to maintain the integrity of the silicon anode structure: 1) the electrode structure is maintained by dissipating stress through a large number of hydrogen bonds; 2) the silicon particles are stabilized by strong covalent bonding; 3) the electrode structure is maintained by improving the self-repair of the electrode through healable ionic bonds.

When there are a large number of polar functional groups in the binder molecule, such as –OH, –COOH, –F the binder is easily bonded with the silicon surface. Although the strength of hydrogen bonds is not as strong as that of covalent bonds, hydrogen bonds can still be formed when the intermolecular distance is close again. The highly cross-linked hydrogen-bonded polymer binder is able to form more hydrogen bonds with the silicon particles, which can disperse more stress, making the structure of the silicon anode more stable in cycling.<sup>[18]</sup> Bao *et al.*<sup>[19]</sup> reported a self-healing polymeric binder (SHP) in which highly branched molecular chains are linked by hydrogen bonds, which greatly increases the binder's ability to accommodate large-volume expansion. Figure 3a is a schematic diagram of the structure of SHP and a schematic diagram of the



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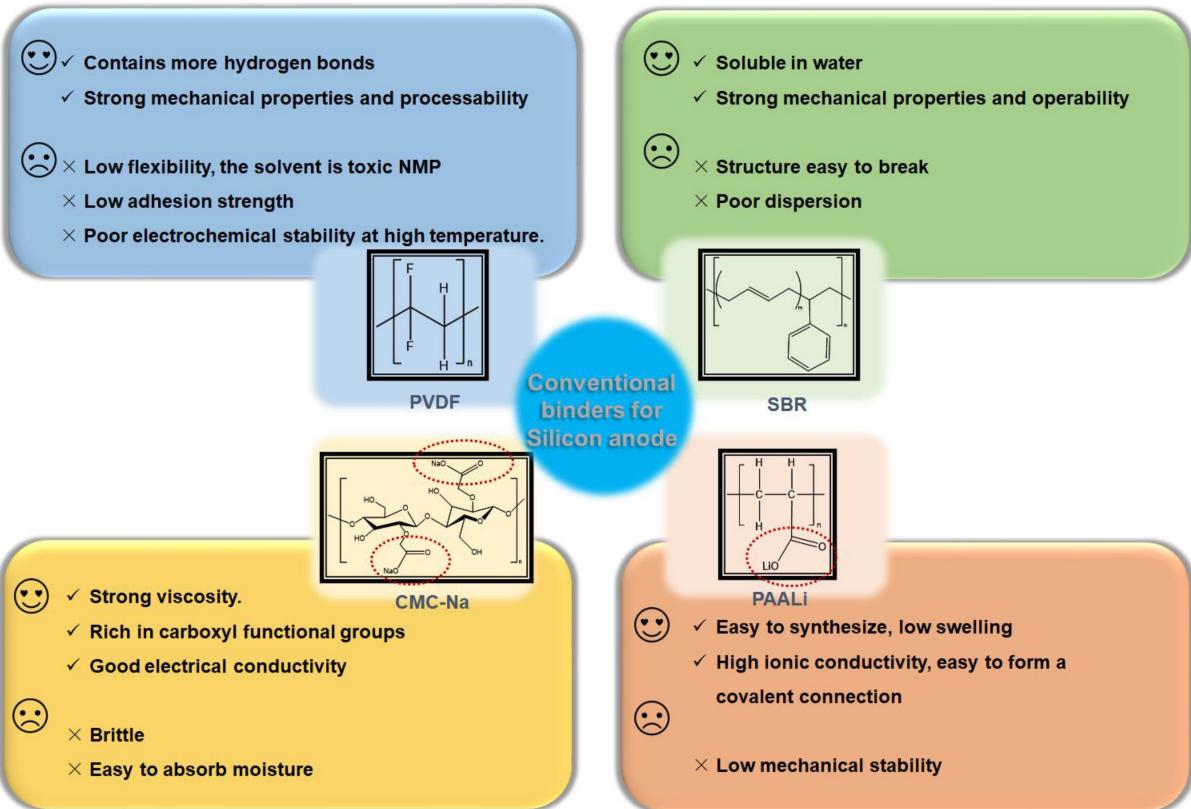
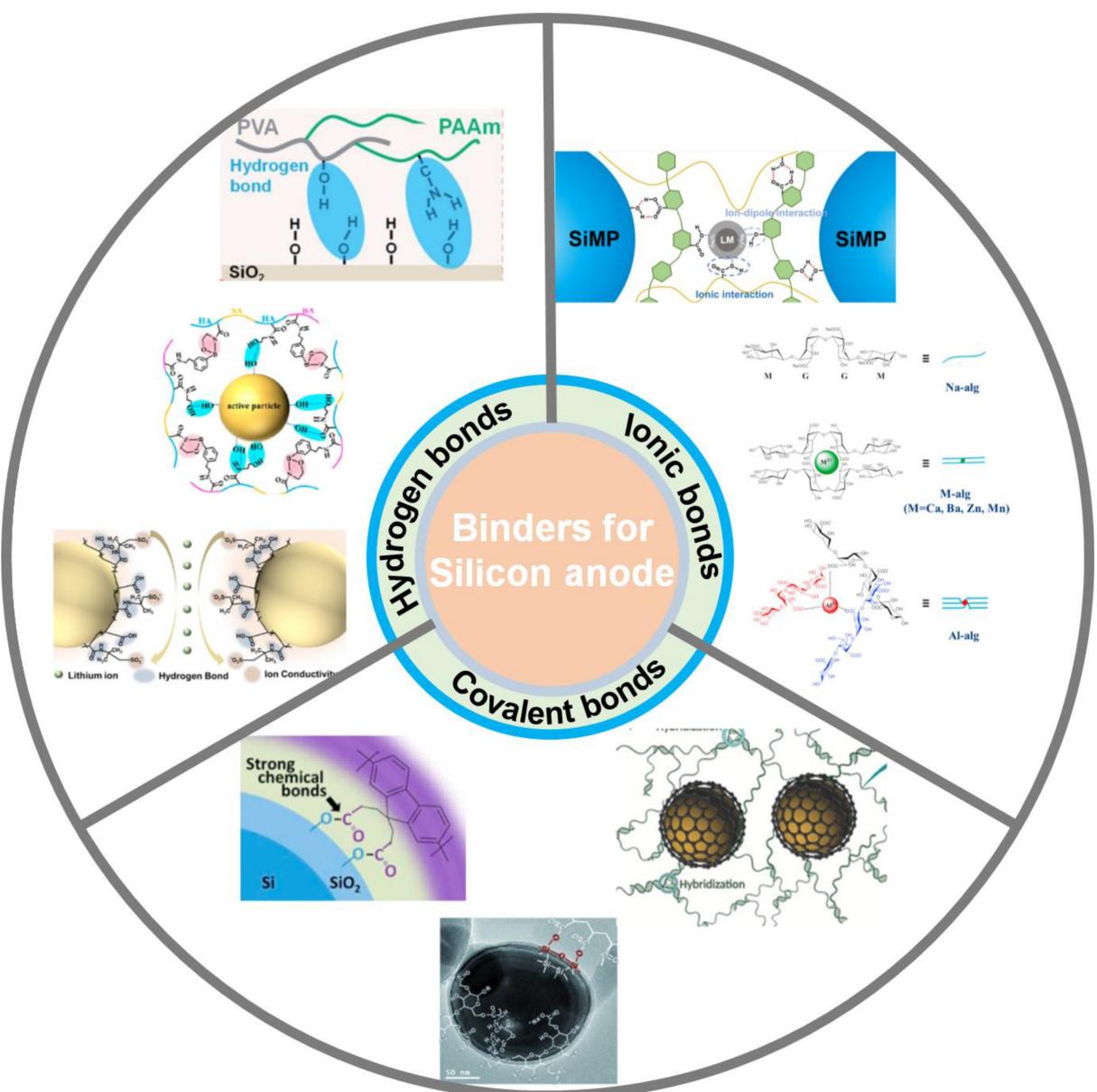


Figure 1. The structure of conventional binders is simple and its advantages and disadvantages.

action of self-healing hydrogen bonds in cycling. Charged polymer chains and oppositely charged polymer chains or metal ions produce Coulomb forces. The Coulomb force between chains favors the formation of three-dimensional cross-linked structures of polymers. And the ionic bond is similar to the hydrogen bond, the magnitude of the force is related to the distance, and the ionic bond is stronger when the oppositely charged species are approaching. This corresponds to the ability of particles to heal themselves like hydrogen bonds.<sup>[20]</sup> Zhao *et al.*<sup>[10]</sup> proposed a non-covalent assembly strategy to synthesize liquid metal-doped polymer binders by combining the softness of gallium-indium alloys (EGaIn) with the rigidity of PAA and cellulose nanofiber (CNF) matrices. Figure 3b shows a schematic diagram of the structure of EGaIn. The ingenious combination of liquid metal (LM) fluidity and polymer flexibility, liquid metal-doped polymer composites can not only eliminate the internal stress caused by the violent deformation of micron silicon particles, but also repair severe microcracks and rebuild the conductive connections between crushed Si fragments, thereby significantly improving electrochemical performance. In addition to ionic and hydrogen bonds, there is also a covalent connection between silicon and binder. The covalent bond has a strong anchoring effect and is able to firmly bond the silicon particles and the binder. However, once the covalent bond is broken, it is almost impossible to reconnect, so the researchers dispersed the stress changes caused by the expansion of the silicon by increasing

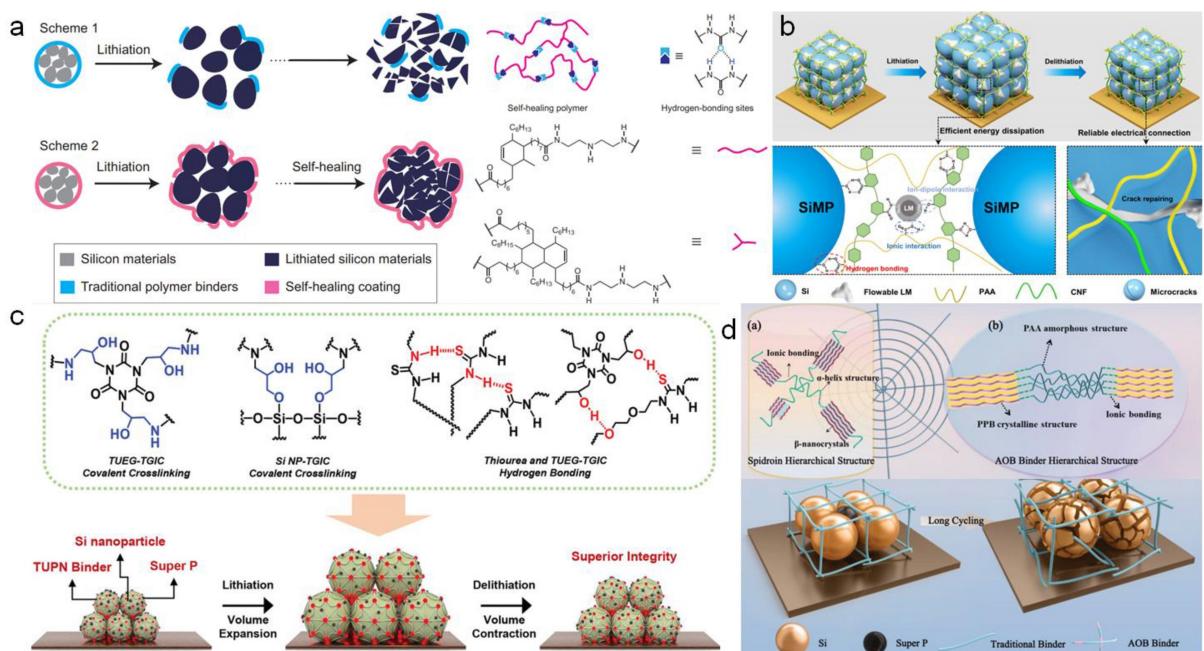
the degree of crosslinking of the binder, and by increasing the covalent junction site between the binder and the silicon particles<sup>[21]</sup>. As shown in Figure 3c, Hwang *et al.*<sup>[22]</sup> synthesized a thiourea polymer network (TUPN) binder by in-situ cross-linking between triethylene glycol (TUEG) amino groups and triglycidyl isocyanurate (TGIC) epoxy groups. The epoxy group of TGIC and the hydroxyl group of silicon form a covalent bond, forming a stable thin layer of SEI at the electrolyte-electrode interface. In addition, due to the presence of thiourea and isocyanurate molecules, a physical interaction is formed between the current collector and the TUPN10 binder, which improves the interfacial stability. In addition, many researchers have recently applied biomimicry to silicon anode binders. Inspired by the human tendon sheath, Jiang *et al.*<sup>[23]</sup> prepared a water-soluble double network binder (DNB), which had good adhesion properties, high mechanical properties and good self-healing ability thanks to its supramolecular hybrid network. As illustrated in Figure 3d, Mu *et al.*<sup>[24]</sup> developed a spider silk protein-inspired hierarchical structure binder. It is characterized by a spider-like hierarchical structure that withstands large volume changes in silicon-based electrodes. In an aqueous-oil binary solution-based blend (AOB) binders, polymers containing hydrophobic tetrazolium groups and water-soluble amorphous polyacrylic acid mimic the  $\beta$ -fold and  $\alpha$ -helix structures of spider silk proteins, respectively. Thanks to this biomimetic design, AOB binders combine high tensile strength and elasticity, strong electrode adhesion, significantly stabilize the silicon-based electrode structure, and



**Figure 2.** Schematic diagram of different silicon anode binders. The left is some of new anode binders that are mainly connected with silicon particles through hydrogen bonds. From top to bottom: a schematic diagram of the action between a multifunctional silicon anode binder and silicon surface force.<sup>[8]</sup> Copyright 2021, The Royal Society of Chemistry. A schematic diagram of the interaction of a covalently bonded cross-linked network adhesive with silicon for Si/C<sub>450</sub> and Si/C<sub>600</sub> electrodes was developed by reversible addition-fragmentation chain transfer (RAFT) polymerization.<sup>[6b]</sup> Copyright 2024, American Chemical Society. Schematic diagram of the molecular structure of a sulfonic group modified binder.<sup>[9]</sup> Copyright 2024, Wiley-VCH GmbH. On the right, some novel binders that maintain the electrode structure by improving the electrode's self-healing with healable ionic bonds. From top to bottom: Schematic diagram of the action of a non-covalently cross-linked liquid metal-doped polymer binder based on multiple dynamic bonds.<sup>[10]</sup> Copyright 2021, Elsevier. Schematic diagram of the structure of various alginic acid hydrogel binders for silicon anodes.<sup>[11]</sup> Copyright 2017, Elsevier. At the bottom are some of the new binders that interact with the surface of silicon particles primarily through covalent bonds. From left to right: Schematic diagram of the action of a conductive polymer binder covalently bonded to a silicon surface.<sup>[12]</sup> Copyright 2017, Elsevier. Mechanism diagram of a polymer binder with a 3D interconnected network with silicon.<sup>[13]</sup> Copyright 2012, Wiley-VCH GmbH. Diagram of the mechanism of action of a novel DNA binder and graphene oxide with silicon particles.<sup>[14]</sup> Copyright 2024, Wiley-VCH GmbH.

extend the cycle life of the electrode. Han *et al.*<sup>[25]</sup> designed a layered conductive polymer binder that can efficiently integrate high-capacity anodes using strong and reversible Coulombic interactions and abundant hydrogen bonding. Zhang *et al.*<sup>[26]</sup> constructed a three-dimensional network adhesive in which a long chain of polyacrylic acid (PAA) was crosslinked with an amino acid lysine (Lys). The abundance of polar groups in PAA/

Lys allows it to adhere tightly to Si particles by hydrogen bonding. PAA/Lys binders have high elasticity and strong adhesion, which can effectively maintain the structural integrity of Si electrodes and improve their electrochemical performance. The construction of the conductive network of the binder is mainly realized by the long chain structure of the binder, which can connect a single silicon active particle, so that the single



**Figure 3.** (a) Schematic illustration of the design and behavior of the stretchable self-healing electrode and the chemical structure of the SHP.<sup>[19]</sup> Copyright 2013, Springer Nature Limited. (b) Mechanism diagram of a novel liquid metal-doped polymer composite binder.<sup>[10]</sup> Copyright 2023, Elsevier. (c) Schematic diagram and mechanism of multifunctional interlocking binders with in-situ covalent and hydrogen bonds.<sup>[22]</sup> Copyright 2023, The Authors. (d) Schematic diagram of the structure of a multi-level structural binder inspired by spirochals and its role in silicon anode.<sup>[24]</sup> Copyright 2023, Wiley-VCH GmbH.

silicon active particle is connected by the polymer chain to form a conductive network across the electrode. How to achieve the stable contact between the long chain of binder and the silicon active material is the core problem that silicon anode binder needs to solve. At present, the main way is to design a variety of polymer chain structures to achieve or introduce special functional groups that interact more strongly with silicon, or to improve the cross-linking degree of polymers, so that the binder and silicon have more contact sites, so as to dissipate the stress changes caused by the volume expansion of silicon, so as to achieve more stable contact between the binder and silicon particles.

Although there are various methods for synthesizing silicon anode binder, and the structure of the synthesized binder has its own characteristics. However, the purpose is to maintain the stability of the electrode structure and the connectivity of the conductive network of the silicon negative electrode in the process of continuous delithiation/lithiation. In order to realize this purpose, as shown in Figure 4, the new binder design takes into account the following properties: 1) strong adhesion properties and mechanical properties; 2) high ion transport capacity; 3) simple preparation method and use condition, 4) feasible, low-cost and ecofriendly.

However, the silicon anode binder currently prepared is either too expensive to prepare or is toxic and harmful to the environment. All these factors hinder its mass production. As shown in Figure 5, Wang *et al.*<sup>[27]</sup> proposed a carbonization process for electrode sheets, which differs from other approaches used by other researchers, who typically synthesize the target polymer first, and then mix the synthesized polymer binder with the silicon active material to obtain the final

electrode sheet. In contrast, the polymer binder used by Wang *et al.* is a low-cost starch without any treatment, which is then physically mixed with micron-sized silicon particles, and finally heat treated at 500 °C to obtain a silicon anode with excellent performance. Impressively, the solvent used in the electrode slurry is water, which is non-toxic and harmless, and the cost is desirable. The electrodes are dried at room temperature without any instrumental assistance. Soluble starch, a polymer with a lower branching density, was used in this experiment. Starch itself is not a binder with conductive properties, but carbonized starch is a conductive binder that plays a role in the binding and conductivity of the entire electrode. The starch raw material is simply mixed with micron-sized silicon, and then the slurry-poured electrode is carbonized to obtain an in-situ carbon-coated micron silicon anode. In-situ carbon-coated silicon particles allow for lower swelling and a more stable interface. The raw materials used for the whole electrode are only starch and  $\mu$ -Si, and no conductive agent is added, which greatly increases the content of active silicon. Studies have shown that polymers treated at different temperatures can selectively remove certain functional groups. By heat treating the polymer over a range of temperatures, the increase in the conductivity of the polymer is achieved by enhancing the electron cloud conjugation between the polymer chains. Therefore, starch will also lose part of its branched chain structure during the carbonization process and transform into a long-chain structure that retains the carbon backbone. Not only can the carbon skeleton connect individual silicon particles, but the long-chain carbon skeleton is more likely to form  $\pi$ - $\pi$  electron conjugation between the chains, resulting in high ionic conductivity.<sup>[2]</sup> At the same time, the authors proved through scanning electron

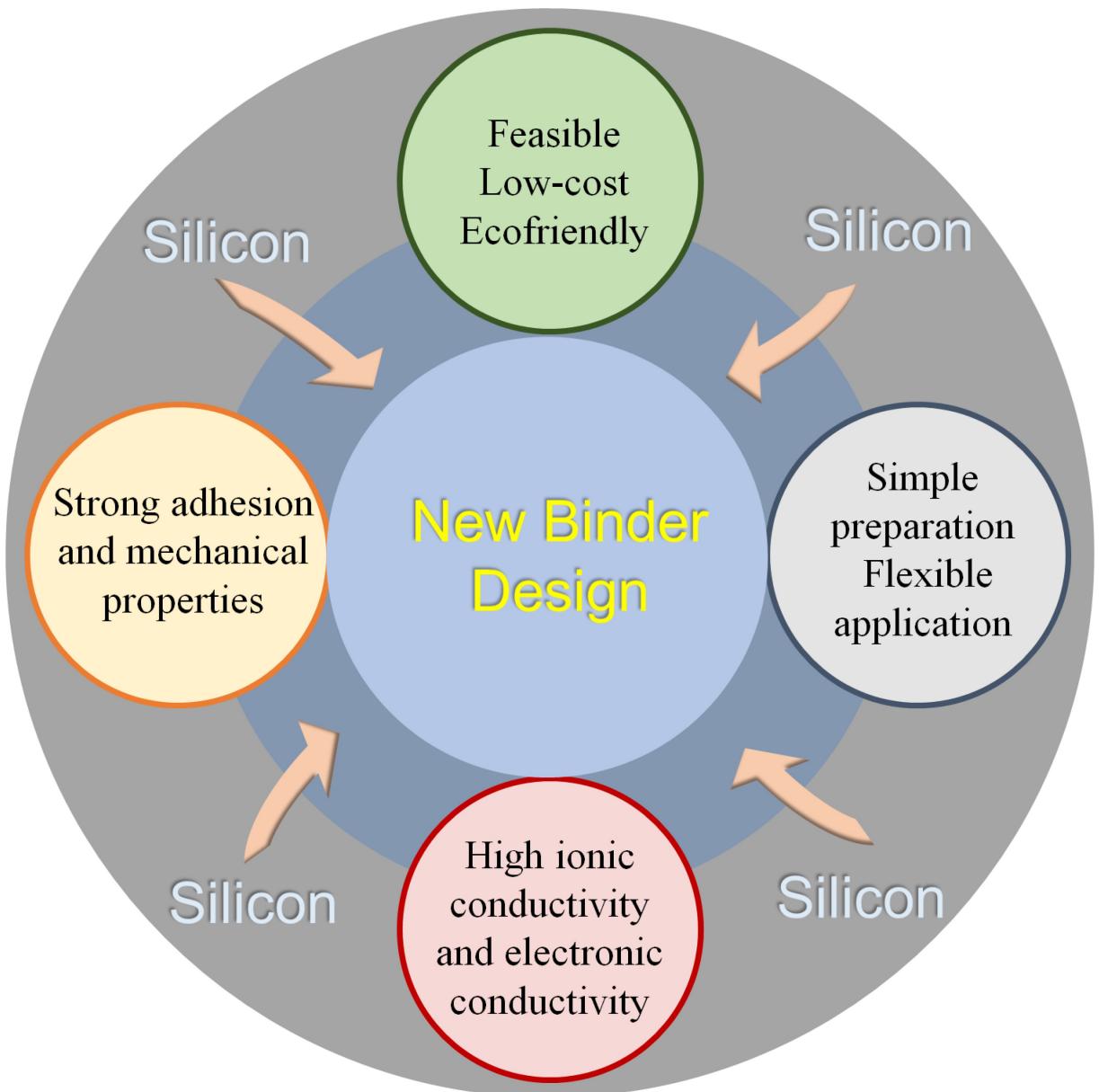
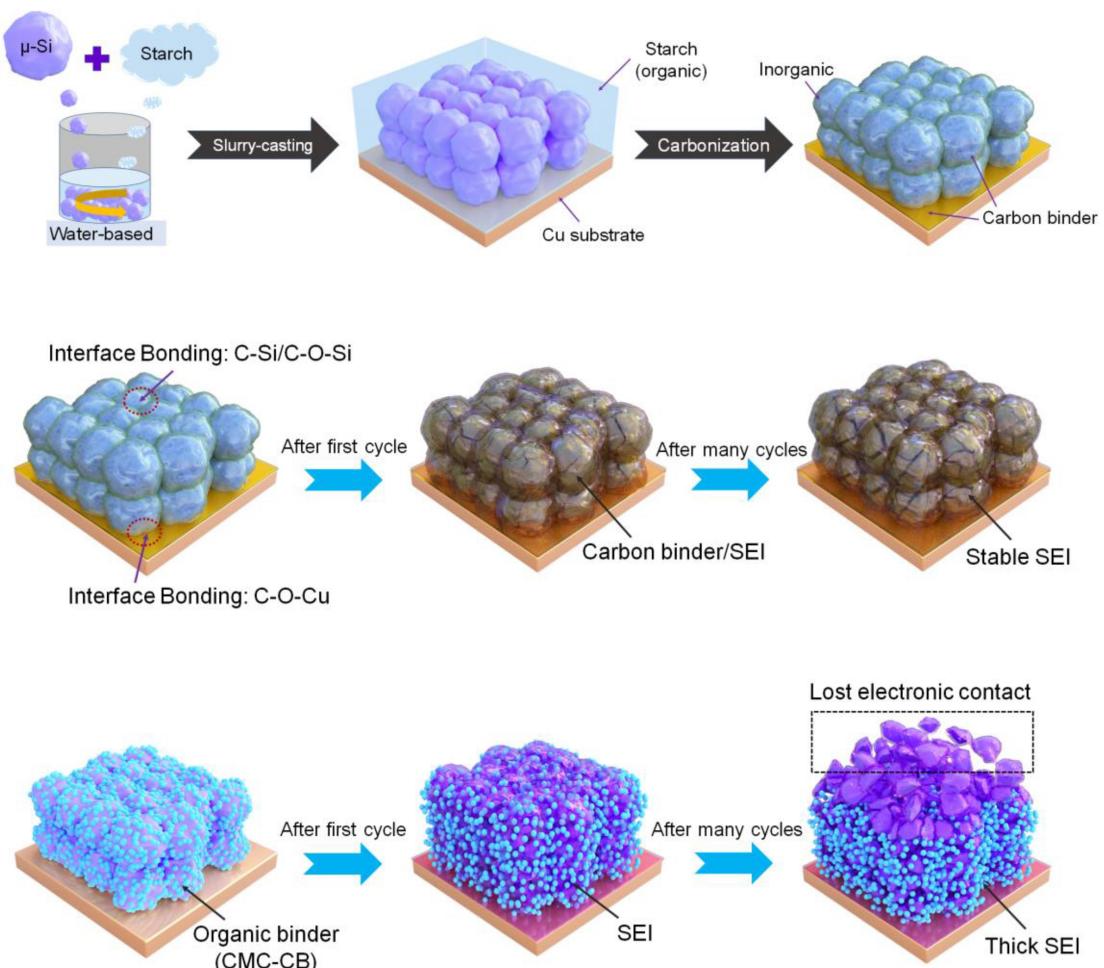


Figure 4. Four characteristics that new electrode binder needs to have.

microscopy analysis of the cross-section of the electrode piece that the starch was carbon-coated with the silicon particles after the electrode piece was carbonized. In the process of carbonization of the electrode piece, the carbon converted from starch forms a C–O–Cu bond with the copper current collector, which shows the strong bonding between the electrode material and the current collector, and the Si 2p analysis shows that the Si–O–C bond and Si–C bond are formed between the carbon converted by starch and the micron silicon during the carbonization process of the electrode piece, which proves that the carbon binder forms a carbon coating with strong covalent bonding to the silicon particles.<sup>[28]</sup> Subsequently, through the scanning analysis of the electrode electrode pieces before and after cycling, it can be seen that the carbide electrode can still maintain the integrity of the electrode structure after cycling,

while the negative electrode prepared by CMC, conductive carbon black and micron silicon direct slurry mixing is cracked after cycling. Based on XPS depth analysis and SEM data, it can only be determined that the SEI formed after cycling of carbide electrodes is stronger and thinner. Because the preparation process of the carbide electrode is very simple, the raw materials used are micron silicon and starch, the manufacturing cost of the entire electrode is delightful, and the final silicon anode has an area specific capacity of more than 2 mAh cm<sup>-2</sup> and an ICE of more than 90%.<sup>[28,29]</sup> Besides, we considered the possibility of commercialization. The only difficulty in the whole electrode preparation process is how to solve the carbonization process problem of the large electrode piece. Industrial production is continuous large-scale automated production, how to achieve the continuous carbonization of electrode



**Figure 5.** Flow diagram of the preparation of an integrated electrode containing a carbon binder and a schematic diagram of the electrode structure before and after different electrode cycles.<sup>[27]</sup> Copyright 2023, Wiley-VCH GmbH.

pieces is an urgent problem to be solved. This requires a customized heating equipment, but I firmly believe that it is possible to work with equipment manufacturers and other research institutes to develop heating equipment suitable for large-scale carbonization of pole pieces such as ours. As for the electrochemical properties, our experiments have verified that the anode prepared by starch and silicon has good electrochemical properties. In addition, our subsequent experiments have also proved that the simple combination of silicon and starch with commercial graphite can significantly improve the electrochemical performance of carbide electrode sheets.

There are many other innovative ways to synthesize new adhesives. For example, studies have shown that the branching density of binders affects the conductive and mechanical properties of binders, and more functional groups are introduced, heteroatom doping is introduced, or biologically inspired to synthesize more characteristic silicon anode binders. These methods can all obtain excellent silicon anode binders. However, most of the synthetic silicon anode binders in academia are not suitable for large-scale industrial production due to their high production cost and environmental friendliness, and most of the work will use nano-silicon in order to

get a better performance, which further increases the production cost of the entire silicon anode. The preparation and production of silicon anode binder should consider the following factors: preparation cost, safety factor, mechanical properties, low swelling, high ionic conductivity and high electronic conductivity. Our work fulfills these requirements by using inexpensive micron silicon and starch as raw materials, which can be combined into silicon anodes with potential for commercial applications through simple heat treatment. The final electrode had excellent electrochemical properties. This one-step synthesis method provides a new idea for the research of silicon anode and further promotes the commercialization of silicon anode with high silicon content.

### Conflict of Interests

The authors declare no conflict of interest.

**Keywords:** lithium-ion batteries • silicon anode •  $\pi$ - $\pi$  conjugation • carbon binder • side chain density

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