

The Review on of Novel Binders for Silicon Anode Based Lithium-Ion Batteries

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Abstract

Silicon is considered as a promising anode material for next-generation lithium-ion batteries due to its high theoretical capacity, natural abundance, and environmental benignity. However, the low conductivity and the drastic volume change of silicon (300%) during cycling cause the battery capacity degradation. Proper selection and application strategy of binders is of importance to accommodate volume changes of Si, maintain mechanical and electronic connections with Si anode during cycling. In this review, the bonding mechanism and structural design principles of binders are introduced. Recent advances in binders with various functional groups and different features (e.g., conductive binder, self-healing binder) are overviewed, perspectives of novel binders are mentioned. Finally, comparison of the properties different binders in electrode fabrication are proposed.

Keywords

Lithium-ion battery; Silicon anode; Binders

Introduction

Environmental problems (e.g., global warming, deforestation) and oil shortage increase severely, the overexploitation of resources by people leads to the depletion of the planet's energy and natural disasters. Researchers are developing a cleaner energy to reduce the effects on the environment. To date, the development of devices suitable for efficient conversion and stable storage of clean energy has become a research hotspot in the energy field. Among them, lithium-ion batteries (LIBs) are widely used in portable electronic devices and electric vehicles due to their high energy density, light weight, long cycle life, and environmental friendliness. The demand for higher energy density of LIBs in various fields has increased rapidly in recent years, necessitating the development of LIBs with higher energy density.

In an effort to further increase the energy density of LIBs, various anode materials have been developed. Graphite anodes are commonly used in commercial LIBs due to their low

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operation voltage and low price. However, graphite anodes with a low theoretical capacity of $372 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ fail to meet market expectations nowadays. Among promising anode materials of LIBs, silicon (Si) has the advantage of high theoretical capacity ($4200 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$). Si is recognized as the most promising anode material to replace or complement graphite in LIBs.

Silicon-based anodes are on the verge of large-scale commercial application, which can achieve higher energy density batteries than the state-of-the-art conventional batteries. For example, Tesla Inc. used Si/graphite anodes for the power batteries in their product Model 3 and revealed at 2020 Battery Day that it will explore low-cost, metallurgical-grade Si coated by a polymer; Xiaomi applied the batteries containing silicon oxide anodes in their smartphone product Xiaomi 11 Ultra. In addition, there are a great number of companies developing Si-based anodes. However, the huge massive change of Si (300%~400%) (Jin et al., 2017) and continuous side reaction caused low Coulombic efficiency.

Previous studies have shown that binder plays a vital role in the electrochemical performance of silicon anode. Although binders are very small and cost about only 1%-3% of the total battery fees (Li, Xia, & Zhang, 2019), they could play significant roles in silicon anode based batteries. In state-of-the-art LIBs, conventional polyvinylidene fluoride (PVDF) is the dominant binder due to its mechanical, chemical, and electrochemical stability benefits. Currently, the existing PVDF-based binding system has failed to meet the requirements of silicon based high-capacity active materials.

This review will introduce the binding mechanism between binders and silicon and

provide insights on the design principles of novel binders for silicon-based anodes. Following the introductory and literature review sections, the focus will be on binder property of electrochemical performance for silicon-based anode. Finally, perspectives for further development of novel binders are proposed.

Binding Mechanism

The binding mechanism is critical to the design of binders. Describing the mechanism of binding is a multi-disciplinary topic which includes surface chemistry, physics, polymer chemistry, rheology, stress analysis and fracture analysis. An effective binding process can be separated into two steps: the desolution/diffusion/penetration step and the hardening step. In the first step, the binder (either dissolved nonreactive binder or reactive binder precursors) wets the substrate surface and penetrates the pores of electrode material particles. In the second step, the binders are hardened via different reaction mechanisms (e.g., drying for nonreactive binders or polymerization for reactive binders) which leads to the mechanical interlocking effect. To produce significant mechanical interlocking, we need to increase the surface roughness and porosity of the electrode material, select a suitable adhesive system, and formulate a binder solution of the appropriate viscosity to ensure that the adhesive can effectively mix, disperse and penetrate the material within the electrode (Nunes et al., 1982). The strength of the force at the interface increases relative to the surface roughness and porosity, as more adhesive sites for the presence of these interactions.

So far, seven binding theories have been proposed (Nunes et al., 1982), including wetting theory, mechanical interlocking theory, adsorption theory, diffusion theory, electrostatic

theory, acid-base theory, and theory of weak boundary layers. Bonding is an interfacial phenomenon involving three processes: the binder wets the surface of the substrate, penetrates the pores of active material particles, and then creates a bonding force through different reaction mechanisms. Wetting theory, mechanical interlocking theory and adsorption theory are commonly used generally.

Binders in Silicon-Based Anode

Binders rich in polar functional groups (e.g., carboxyl, hydroxyl, amine, imine, nitrile groups) that can form strong interactions with the hydroxyl groups of the silicon surface have been widely investigated. Various functional groups facilitate chemical binding with active electrode materials, while innovative features including enhancing chemical/thermal stability, promoting electronic/ionic conductivity, creating self-healing property, are also designed for binders to improve electrochemical performance in LIBs. In this section, polymer binders with various polar groups, conductive binders and self-healing binders suitable for silicon-based anodes will be introduced.

Carboxyl-Rich Polymer Binders

1) Sodium carboxymethyl cellulose (CMC) based binders

CMC is a carboxymethylated derivative of cellulose, formed by etherification of the hydroxyl group on the β -linked glucopyranose residues by carboxymethyl (-OCH₂COONa) (Figure 1a). The existence of carboxymethyl groups is responsible for the aqueous solubility of CMC (Yang et al., 2018). CMC is rich in hydroxyl and carboxylate groups that form hydrogen bonds and ionic dipoles with the hydroxyl groups on the Si surface.

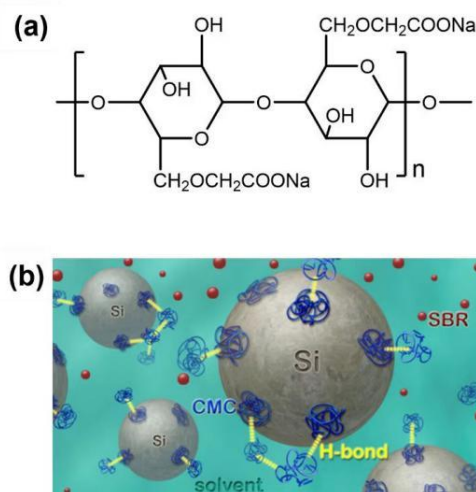


Figure 1. a) Structural formulae of CMC. b) Schematic showing the different migrations of SBR and CMC during drying of electrode slurry (Hebeish, Hashem, Elhady, & Sharaf 2013). Copyright 2020, American Chemical Society

CMC was found to promote the homogeneous dispersion of graphite in aqueous solution acting like a surfactant. It was also found that the mixture of styrene-butadiene rubber (SBR) and CMC in certain proportions further improved dispersion of graphite due to the existence of anionically charged surfactant on SBR, resulting in a more uniform and less porous microstructure (Lim, Kim, Ahn, & Lee 2015). With the rise of silicon-based anodes, Chen et al. early proposed the idea of using elastomeric binders to accommodate huge volume changes (Chen, Christensen, & Dahn, 2003). And the CMC/SBR binder for Si/graphite was further studied. Compared with PVDF, CMC/SBR exhibited high elasticity, strong adhesion and low electrolyte absorption. Such excellent properties optimized the cycling performance of Si/C anodes.

2) Poly acrylic acid (PAA) based binders

PAA is a water-soluble chain polymer with many carboxyl groups in its molecular chain, which can form a variety of interactions with silicon-based active materials and endow a strong binding force between the active

particles and the current collector (figure 2a). The degree of neutralization of -COOH in PAA largely affects its performance as a binder, and PAA dissolved in water is prone to intermolecular agglomeration due to the strong intermolecular hydrogen bonding forces. The PAH-M salt is prepared by neutralizing PAA with alkali. The electrostatic repulsion between the carboxylate groups improves the stretching of the molecular chains and helps to reduce the intermolecular agglomeration effect. Komaba et al. indicated that PAA as a binder significantly improved the electrochemical performance of SiO anode compared to PVDF, PVA, and CMC (Komaba et al., 2011). On the one hand, the strength, ductility and toughness of polymer were determined by the crystalline and amorphous regions. Crystalline polymers exhibited higher strength and lower ductility under dry condition compared to amorphous polymers. The amorphous property of PAA polymers improved the homogeneity of PAA film covered with SiO particles. On the other hand, the interactions between the carboxyl groups of PAA and the hydroxyls group on the SiO surface enabled PAA polymer to cover the SiO surface uniformly. And partial carboxyl groups of PAA were converted into carboxylic anhydride groups after drying, forming a chemically crosslinked network structure. In addition, PAA probably possessed a physical cross-linked structure, such as entanglement of the main chain. As a result, the SiO-PAA anode reached $826 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ at a rate of $100 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ and exhibited a reversible capacity of $700 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ after 50 cycles.

PAA can form polyacrylates with various metal ions (PAAX, X including Li, Na, and K...), and polyacrylates are also effective binders for anodes of LIBs (figure 2b). Among the PAAX series binders, PAALi and PAANa exhibit better cell performance because of a favorable polymer conformation in composites. In Dang

et al.' study, utilized Li-substituted PAA as binder for Si microparticle (SiMP) anodes and conducted a comparative study of Li-substituted PAA (PAA-xLi) (Dang et al., 2020). They proposed that the viscosity and hardness of PAA-xLi increased with increasing Li substitution owing to the electrostatic repulsion of the -COOLi groups. Low viscosity solution was unfavorable for the stability of slurry because of the rapid sedimentation of SiMPs during preparation. Appropriate high-viscosity solution, such as PAA-0.75Li solution, helped to slow down the sedimentation of SiMPs in slurry and make them uniformly dispersed. Due to high flexibility of the PAA-0.75Li binder and strong adhesion with SiMPs, the SiMP/PAA-0.75Li anode exhibited improved cycling stability with a reversible capacity of $2125 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ after 100 cycles in the current density of $1200 \text{ mA}\cdot\text{g}^{-1}$.

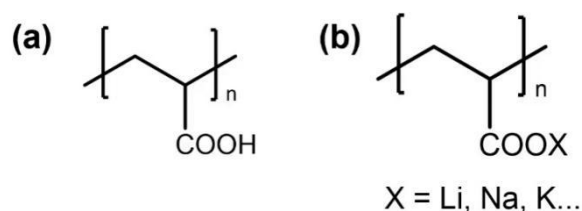


Figure 2. a) structural formula of PAA. b) structural formula of PAAX

At present, there are many studies on PAA binders, and PAA is regarded as a promising binder. Other than mentioned above, researches on PAA binder with other various compositions have been extensively reported, such as PAA-Rosin (Choi et al., 2016), PAA- poly(acrylic acid)-co-poly(maleic acid) (PAA-PAA/PMA) (Yim et al., 2015), Fe^{3+} -PDA-160/PAA (Guan et al., 2020), PAA- poly(ethylene-co-vinyl acetate) (PAA-EVA) (Guo et al., 2019), all of which have been demonstrated to be promising candidates for PAA based binders, while providing multiple design principles for novel PAA based binders.

3) Alginate (Alg) based binders

Alg is a polysaccharide extracted from brown algae which is very similar to CMC structure with a large number of carboxyl and hydroxyl functional groups in its molecular structure. A larger number of binder-Si bonds are mainly attributed to increased content of carboxyl groups in the alginate, which resulted in better Si electrode stability. In 2011, Kovalenko et al. introduced sodium alginate (SA) as binder for silicon anodes (Kovalenko et al., 2011). Compared to PVDF, SA showed minimal swelling in the electrolyte, and carboxylate groups in the molecular structure provided substantial transport channels for lithium ions. Because it has a large number of neatly arranged carboxyl groups, it can form a strong hydrogen bonding force with the silicon surface groups. The prepared silicon negative electrode is charged and discharged at a current density of 4.2A/g, and the specific capacity is 1700mA·h/g after 100 cycles.

In addition to SA, alginate could be coordinated with various cations, such as Ca^{2+} , Mg^{2+} , and Cu^{2+} . Wu et al. synthesized a series of alginate (Alg) hydrogel binders for SiNP anodes in lithium-ion batteries (Wu et al., 2017). As shown in Figure 3a, the Na-Alg molecule shows a linear structure, while M-Alg (Figure 3b) and Al-Alg (Figure 3c) show different cross-linked structures due to the coordination of multivalent cations to the alginate. More alginate chains are expected to be cross-linked by the higher valent cations. The cross-linked structures exhibit stronger coordination than the hydrogen bonding between the linear alginate chains and therefore M-Alg and Al-Alg show stronger binding strength than Na-Alg.

Many studies have shown that the cross-linking of alginate with specific cations improves the electrochemical properties of Alg (Liu 2014; Zhang 2014). On the one hand, the cations link

the Alg chains by strong coordination, and on the other hand, the free carboxyl groups of Alg form strong hydrogen bonds with the hydroxyl groups on the Si surface. The cross-linked network can withstand sharp volume changes in silicon and maintain the integrity of the electrode. More importantly, it is important to choose the right cation to cross-link with the alginate. Firstly, the cation should be able to form strong coordination interactions with the alginate. The Alg molecule contains both mannate (M) residues and gulonate (G) residues. It is more preferable to choose a cation that can coordinate with both G and M residues. Secondly, the radius of the cation should be appropriate. Cations with a larger radius can generate more negative charges on the aggregates and facilitate the adsorption of cations to COOH and OH groups.

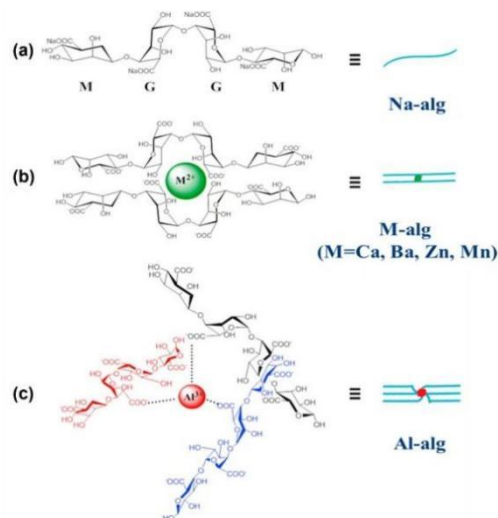


Figure 3. Schematic of a) Na-Alg, b) M-Alg and c) Al-Alg molecular structures. Copyright 2017, Elsevier

Hydroxyl-Rich Polymer Binders

1) Polyvinyl alcohol (PVA) based binders

PVA is a water-soluble polymer with high resistance to acid, alkali and heat. Extensive hydroxyl groups in PVA form strong hydrogen bonds with the active materials and the current collector (Figure 4a). These strong hydrogen bonds redouble the adhesion strength of the

electrodes. However, in comparison with CMC, PAA and Alg, PVA as a binder led to rapid capacity loss during cycling (Feng et al., 2013). In addition, but the current use of polymerization degree of 1700 PVA is too high in the actual use of the process which is easy to pulp skin. PVA's alcohol resolution affects the molecular content of hydrophobic groups and intermolecular hydrogen bonding, so the reduction in the degree of alcoholysis will also decrease the membrane mechanical properties. However, the change in hydrophobic group content, according to the "similarity compatibility" principle, has a significant impact on the mechanical properties. In contrast, amorphous CMC, PAA and Alg could be uniformly distributed in the electrode, which highly improved the stability. Secondly, CMC, PAA and Alg containing numerous carboxyl groups which could easily form hydrogen bonding or ester-like bonds with hydroxyl groups of active materials and thus exhibited excellent cycling performance.

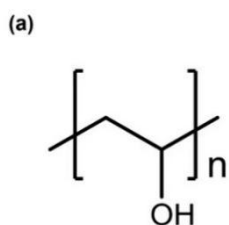


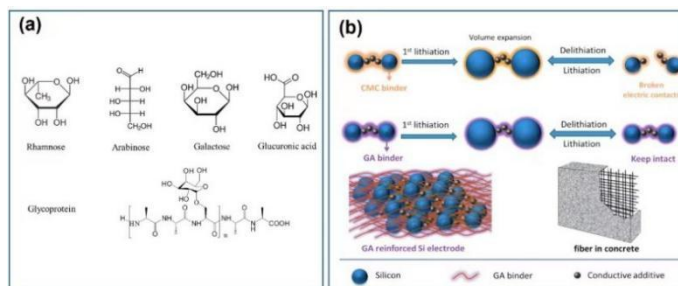
Figure 4. a) Structural formulae of PVA

2) Gum Arabic (GA) based binders

GA is composed of glycoproteins and polysaccharides (Figure 5a). Glycoproteins are proteins containing oligosaccharide chains, which are covalently bonded to each other. Polysaccharides are carbohydrates in which multiple monosaccharides are linked together by glycosidic bonds. Polysaccharides contain a large number of hydroxyl groups and glycoproteins are rich in polypeptide side chains. The silicon anode with GA as a binder prepared

by Ling et al. exhibited a reversible capacity of 1419 mA·h g⁻¹ after 500 cycles when measured at 1 C (Ling et al., 2015). Ling et al. attributed the excellent performance of the anodes to the concrete stretching structure formed by the polysaccharide and glycoprotein chains (Figure 5b). The hydroxyl groups in the polysaccharide enhanced the bonding force of the polysaccharide and the glycoprotein improved the mechanical properties, so that the synthesized anode had good adhesion to both the SiNPs and the current collector.

This low cost, naturally abundant, and environmentally benign polymer is a promising binder for future LIBs. Further, Ling et al. designed a GA-PAA flexible binder by in situ esterification reaction of GA and PAA, as shown in Figure 5c (Ling et al., 2015). The researchers found that the water vapor generated by the esterification reaction created micron-sized pores, which alleviated the stress and hindered the formation and propagation of cracks. The higher electrolyte uptake of the binder had been evidenced to benefit Li-ion transport. To improve ion transport capability in GA, PAA was cross-linked, resulting in improved Li-ion conductivity, reinforced mechanical strength, and enhanced coherent strength. The improved Li-ion coefficient was mainly ascribed to enhanced polarity and generated micron-sized pores, which improve electrolyte uptake.



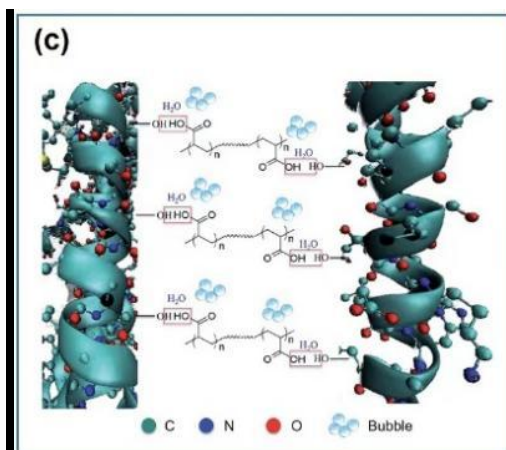


Figure 5. a) Chemical structure of GA which composed of polysaccharides and glycoproteins; b) Schematics of the concept to address volume change issue in battery materials. Copyright 2015, Elsevier. c) Schematic diagram of the polymeric reaction: the generation of water and formation of the crack-blocking GA–PAA composite binder. Copyright 2012, Royal Society of Chemistry

Nitrogenous Groups-Rich Polymer Binders

1) Polyimide (PI) based binders

PI refers to a type of polymer containing an imide ring (-CO-N-CO-) on the main chain (Figure 6a). The imide groups in PI molecules show superior tensile and elastic recovery ability, which effectively adjust the volume expansion of Si and ensure the integrity and stability of the whole electrode. In addition, charge transfer and π - π bonding interactions in the PI molecule can improve thermal stability and mechanical strength, thus improving electrochemical performance (Li et al., 2021). PI with high mechanical properties and processability can be used as silicon anode binder (Oh et al., 2017). Kim et al. prepared composite electrodes using SiMPs prepared by Ag-assisted chemical etching as the active materials and PI and PVDF as polymer binders, respectively (Kim et al., 2013). After 20 cycles, the capacity retention of PI-based electrodes and PVDF-based electrodes were 75.9% and 20.1%, respectively.

Polyetherimide (PEI) is a polymer with a heterogeneous structure, which is composed of repeating arrangements of ether and imide rings (Figure 6b). PEI was used for silicon-graphite electrodes by Yim et al (Yim, Courtel, Abu-Lebdeh, & Mater, 2013). The researchers found that Si-graphite electrode containing PEI binder exhibited the highest specific capacity, excellent cycling and rate performance compared to electrodes containing PVDF, NaCMC, and NaPAA binders. The PEI-based electrode had the highest first irreversible capacity of $733 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$. The high reversible specific capacity and the first irreversible specific capacity may be caused by the electrochemical reaction of carbonyl groups on the imide ring with Li^+ and e^- .

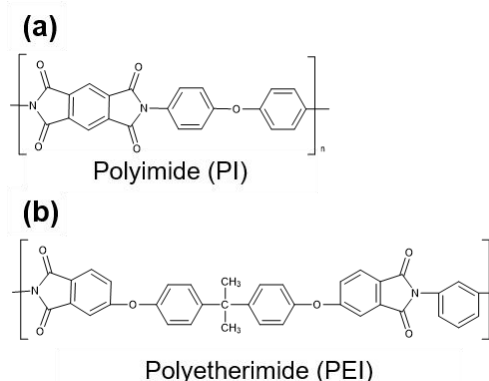


Figure 6. Chemical structure of a) polyimide and b) polyetherimide.

Polyamide imide (PAI) was applied in SiMP electrode fabrication by Choi et al. Although PAI binder reacted with Li^+ and electrons at the first cycle, cycling performance is remarkably improved due to strong binding force that tolerates volume expansion. Further, thermally treated PAI was used for the Si-alloy anode (Park et al., 2019). Yang et al. prepared Si-alloy anodes by embedding silicon nanoparticles in Cu - Al - Fe matrix phase with thermally treated PAI as a binder. The spatial restriction on PAI polymer chains by silica alloy particles and conductive carbon was overcome by thermally

treating the PAI polymer above its glass transition temperature. This increased the mobility of the polymer chains, allowing enhancement of secondary interactions intra- or inter-chain by polymer chain rearrangement. The shear stress cutting through the electrode layer increased as the thermal treatment temperature increased. Similar to the shear force behavior, the adhesion strength of the Si-alloy electrode increased with increasing heat treatment temperature.

Binder Properties on Electrode Fabrication

Binders make up only a small part of the electrode composition (2-5% of mass in commercial electrodes), but they play an important role in the electrochemical performance of the cell. This section will focus on the physical and chemical properties of binders.

The physical properties include thermal, mechanical, electrical conductivity and dispersion properties. Excellent physical properties are still required to improve electrochemical performance (Fan et al., 2015). Chemical properties include chemical and electrochemical stability, with an emphasis on the stability of the adhesive in harsh environments and wide voltage windows. These properties are highly correlated with molecular weight, molar volume, density, degree of polymerization and functional groups.

Thermal Properties

Thermal properties relate to the changes in the physical and chemical properties of a polymer as heat is added or removed. In the practical application of binders, thermal stability, diffusivity and expansion rate are key considerations as they can significantly affect the electrochemical properties and electrode stability when energy storage devices are operated at different temperatures. The strength

of binding forces between binders, the containing composites, functional groups and molecular mass are the factors influencing thermal properties.

Binders performance varies when they are exposed to heat over a range of temperatures. For example, GA starts to carbonize at 210 °C, while CMC remain stable until 235 °C when they are tested under the same conditions (Ling et al., 2015). Among PVDF, PAA, and CMC binders, PVDF has largest thermal expansion rate, while PAA has the largest thermal diffusivity between 20 and 80 °C (Zhang et al., 2014). Thermal property and stability of binders are crucial for electrode fabrication and operation of energy-storage devices, especially at elevated temperatures. In electrode fabrication, the electrode including the active materials and binders are subject to a high-temperature treatment for the sake of binder curing and solidifying, the removal of organic solvent, and sometimes the electrochemical cycling (e.g., 100 °C for solid-state batteries) at high temperatures, which requires appropriate thermal stability of the binder (Tan, 2015; Liu 2017). In practical application, the electrodes need to work in a wide temperature range (from -20 to 55 °C) (Lu et al., 2013). Most of the binders are stable at or above 150 °C. Hence, the thermal properties of binders are important for electrode fabrication and operation of energy-storage devices at elevated temperatures.

Mechanical Properties

The most important mechanical properties in electrodes fabrication are strength, elasticity, flexibility, hardness and adhesion of materials. The strength of a material refers to its strength under tension or compression with the same material able to display different tensile and compressive strengths. Compressive strength relates to intrinsic properties of a material.

The tensile strength of a material is quantified as tensile stress which can withstand before mechanical failure (Mark, 2007). Tensile strength is determined by a polymer's molar mass and functional groups (Nunes et al., 1982). In general, polymers such as polyethylene (Perkins et al., 1976) and CMC (Dadfar & Kavooosi, 2015) display a relatively high tensile strength. For polyethylene, higher molecular weight could give higher strength fibers while having no apparent effect on the Young's modulus (Perkins et al., 1976). CMC films showed good tensile strength, young's modulus, water solubility, water swelling, water uptake. Incorporation of multi-walled carbon nanotubes caused a significant increase in the tensile strength, increase in young's modulus, decrease in water solubility, decrease in water swelling, decrease in water uptake (Dadfar & Kavooosi, 2015). As a result, CMC binders show higher tensile strength than PVDF and they also can better withstand forces from repeated cycling.

Materials' elasticity and flexibility are as vital as tensile strength. Elasticity relates to a material's ability to recover to its original form after a stress is applied and removed. Flexibility refers to the ability of a material to handle bending without breaking (Mark, 2007). As with tensile strength, a polymer's molar mass and functional groups largely determine its elasticity and flexibility. Alg and CMC binders are more flexible than PVDF, and being more elastic, as shown by cyclic tensile testing (Tabor, 1970). The hardness of a material measures its resistance to indentation (Dadfar & Kavooosi, 2015). A harder material implies better binding capability and higher stability. Nanoindentation, used to evaluate hardness, can also be used to investigate the elasticity of materials, the benefits of which are mentioned above. For example, guar gum binder is more elastic and homogeneous than PVDF, resulting in a binder which was better able to withstand

large volume expansion in Li-S electrodes (Li et al., 2015).

Adhesive strength is a measure of the strength of bonding between an electrode film and the current collector (Mark, 2007). The molecular weight and functional groups of a polymer strongly influence adhesive strength (Lee & Oh, 2013). Various polymers have better adhesion than PVDF, including CMC, PAA, and Alg, which can provide strong hydrogen and chemical bonding. In battery applications, repeated volume expansion of active materials (silicon anodes) and bending (wearable energy devices) are the main source of loss of contact between electrode components. Binders with a high adhesive strength can withstand this volume expansion and are able to maintain contact between the active material, the conductive additive, and the current collector, which minimizes capacity fading and enhances cycle life.

Electrical and Ionic Conductivity

Both electrical and ionic conductivity are significant properties in any electrochemical batteries. Polymers were long known to be insulating materials until the first conductive polymers were produced in the 1970s (Shirakawa, 1977; Fenton, 1973). Binders can provide either electric or ionic conductivity, leading to new electrode systems which shift the status quo from conventional electrodes comprised of active material, polymer binder, and conductive additive. In other words, conductive binders can act as binders and conducting additives simultaneously. Therefore, the transition from conventional electron/ion-inert binders to ones with inherent conductive properties provides an alternative route to enhance the overall capacities of electrodes without relying on mechanical and chemical advances. The adoption of conductive polymers could eliminate the use of conductive additives

and therefore increase the specific capacity of batteries. Electrical conductivity of polymers depends on the presence of highly π -conjugated polymeric chains. The polymers, although brittle, interact well with the surface of Si and are therefore able to withstand volume changes during cycling; very high capacity and good rate capability were achieved with this type of polymeric binder compared to other binders using either high-capacity silicon. In the case of the silicon anode, initial capacities of $3000 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ (and reaching $1700 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ after 100 cycles) with a coulombic efficiency 98% were obtained, which highly increased electrical and ionic conductivity.

Many polymers, such as natural chitosan (Osman & Arof, 2003) starch (Liew & Ramesh, 2013) and Nafion (Schneider et al., 2012) have been explored and add them into binders could enhance the ionic conductivity (Ngai, Ramesh, Ramesh, & Juan, 2016). The ionic conductivity of polymers plays an important role in the electrochemical performance of batteries, especially power density.

Dispersion Properties

Dispersion properties of polymers refer to the ability to disperse the electrode materials into the binder solution and obtain a uniform composite. A polymer that helps this process and prevents aggregation is usually called a dispersant (Pirung, Quednau, & Auschra, 2002). The electrochemical performances of the cells depend dramatically on the cathode morphologies influenced by the dispersibility of the binders. In electrode fabrication processes, polymers can act as a binder as well as an effective dispersion agent, such as CMC, gelatin (Wang et al., 2011), PAA, (Lee, Paik, Hackley, & Choi, 2006) PVP (Seh et al., 2013). The dispersibility of these binders can be affected by the charge density, chain flexibility, and electrostatic repulsion and depletion.

Besides, higher chain flexibility is required for the binder to resist the depletion effect that break the adsorption. In spite of the similar chemical compositions of CMC and SA, the dispersability of CMC is much higher than SA, resulting from its higher chain flexibility stemming from the equatorial linkages with lower rotational barriers (Hong et al., 2016). The overall dispersion performance is also dependent on electrode materials. The uniform dispersion of particles, especially for silicon anodes, remains a big challenge (Su et al., 2017).

Chemical Stability

Binders must have a certain chemical stability to resist corrosion from electrolyte and electrochemical reactions. The chemical stability of binders depends on their chemical composition and structure as well as chemical environment. For example, PVDF, one of the most chemically stable binders in LIBs, reacts with lithiated graphite and metal lithium at elevated temperatures (Du, 1998; Maleki, 1999) and swells in organic solvents. The reactions of PVDF with lithiated carbon (Li_xC₆) attribute to the exothermic heat generation of lithiated carbon materials and also form LiF and hydrogen on the surface of electrodes (Du et al., 1998). The instability of binders may cause the collapse of electrodes and trigger safety issues. Therefore, the chemical stability of binders in a specific battery system (including types of electrode materials, electrolyte, and cycling potential range) is an essential condition of electrode design to ensure electrochemical performance and longevity of batteries (Baryskov & Khomenko, 2010). The instability of binders may cause the collapse of electrodes and trigger safety issues. Therefore, the chemical stability of binders in a specific battery system (including types of electrode materials, electrolyte, and cycling potential

range) is an essential condition of electrode design to ensure electrochemical performance and longevity of batteries (Barsykov & Khomenko, 2010).

Electrochemical Stability

The most fundamental requirement of binders is that they cannot be reduced under a low negative potential and not oxidized under a high positive potential. Activation energy is one of the determining factors for electrochemical stability of binders. Existing binders, such as PVDF, CMC, PAA, PVA, show quite high electrochemical stability (Nguyen et al., 2013). However, the increase of operating voltage for high-voltage materials bring in bigger challenges for the electrochemical stability of binders.

Strategies in Developing Binders and Binding Process

To address these drawbacks of the traditional PVDF binder, we need to design or choose binders with enhanced relevant properties as mentioned previously. The specific goals can be summarized as follows: (i) introduce stronger interfacial forces by grafting reactive functional groups to form polar inter-molecular forces and chemical bonds, (ii) reduce the cost of the binder and binding process, (iii) consider eco-friendliness in binder design and binding processes, (iv) accelerate excellent electron and ion transport, (v) improve mechanical flexibility and ductility, (vi) boost electrolyte uptake of binder and dispersion ability of electrode materials and conductive additive, and (vii) adopt emerging technology, such as self-healing ability of polymers to accommodate large volume changes (Huang, 2018; Kwon, 2018).

Conclusion

Binder is one of critical parts in the electrode configuration, which generally serves to hold

active material and conductive additive together in contact with the current collector to maintain electrode integrity during cycling. Due to the continuous volume expansion and contraction of Si-based materials during lithiation/delithiation process, higher demands are placed on binder in the electrode. In this review, we first introduce the bonding mechanism between binders and active materials. The binder wets the surface of the substrate, penetrates into the pores of the active material particles, and then produces adhesion mainly through mechanical interlocking mechanism and adsorption mechanism. Then, we review the recent progresses of binders with various functional groups (e.g., carboxyl, hydroxyl, amine, imide, nitrile groups) and different features (e.g., conductive binders and self-healing binders). Binders should have polar groups that form strong interactions with active materials and current collector to effectively buffer drastic volume change of Si. Additionally, strong interactions should be formed between polymer chains of the binder, which can construct a crosslinked 3D network structure, thus effectively preventing irreversible slipping of Si particles, buffering the volume change and maintaining the electrical connection and integrity of the electrode. Furthermore, conductive binder combining conductivity and adhesion can be used in electrodes to reduce the proportion of inactive materials and thus increase the electrode energy density. And the conductive network of conductive binder can effectively maintain the electrical contact of the electrodes. Self-healing polymer materials are the key to solve the existing issues of silicon anodes. Self-healing binder is able to self-repair the mechanical damage generated by the electrode during cycling.

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References

- Jin Y, Li S, Kushima A, Zheng XJ, Sun YM, Xie J, Sun J, Xue W, Zhou G, Wu J, Shi F, Zhang R, Zhu Z, So K, Cui Y, Li J (2017) Self-healing SEI enables full-cell cycling of a silicon-majority anode with a coulombic efficiency exceeding 99.9%. *Energy Environ Sci* 10(2):580–592. <https://doi.org/10.1039/C6EE02685K>
- LI Y L, XIA Q H, ZHANG J. Application of water-soluble binder in Si-based anodes[J]. *Guangdong Chemical Industry*, 2019, 46:106-107(in Chinese).
- N. Liu, Z.D. Lu, J. Zhao, M.T. McDowell, H.W. Lee, W.T. Zhao, Y. Cui, A pomegranate-inspired nanoscale design for large-volume-change lithium battery anodes, *Nat. Nanotechnol.* 9 (2014) 187–192.
- Nunes, R. W.; Martin, J. R.; Johnson, J. F. Influence of Molecular Weight and Molecular Weight Distribution on Mechanical Properties of Polymers. *Polym. Eng. Sci.* 1982, 22, 205–228.
- H. Chen, M. Ling, L. Hencz, H.Y. Ling, G.R. Li, Z. Lin, G. Liu, S.Q. Zhang, Exploring chemical, mechanical, and electrical functionalities of binders for advanced energy-storage devices, *Chem. Rev.* 118 (2018) 8936–8982.
- H.Y. Yang, D.W. Wang, J. Deng, J. Yang, C. Shi, F.L. Zhou, Z.J. Shi, Activity and structural characteristics of peach gum exudates, *Int. J. Polym. Sci.* 2018 (2018), 4593735.
- A. Hebeish, M. Hashem, M.M. Abd El-Hady, S. Sharaf, Development of CMC hydrogels loaded with silver nano-particles for medical applications, *Carbohydr. Polym.* 92 (2013) 407–413.
- a) S. Lim, S. Kim, K. H. Ahn, S. J. Lee, *J. Power Sources* 2015, 299, 221-230; b) J. H. Lee, S. Lee, U. Paik, Y. M. Choi, *J. Power Sources* 2005, 147, 249-255.
- Z. H. Chen, L. Christensen, J. R. Dahn, *Electrochem. Commun.* 2003, 5, 919-923.
- S. Komaba, K. Shimomura, N. Yabuuchi, T. Ozeki, H. Yui, K. Konno, *J. Phys. Chem. C* 2011, 115, 13487-13495.
- D. Y. Dang, Y. K. Wang, M. Wang, J. Z. Hu, C. M. Ban, Y. T. Cheng, *ACS Appl. Energy Mater.* 2020, 3, 10940-10949.
- S. J. Choi, T. Yim, W. Cho, J. Mun, Y. N. Jo, K. J. Kim, G. Jeong, T. H. Kim, Y. J. Kim, *ACS Sustainable Chem. Eng.* 2016, 4, 6362-6370.
- T. Yim, S. J. Choi, J. H. Park, W. Cho, Y. N. Jo, T. H. Kim, Y. J. Kim, *Phys. Chem. Chem. Phys.* 2015, 17, 2388-93.
- X. Guan, Y. X. Yong, Q. P. Wu, X. W. Zhang, X. H. Guo, C. L. Li, J. Xu, *Energy Technology* 2020, 8.
- R. Guo, S. Zhang, H. Ying, W. Yang, J. Wang, W. Q. Han, *ACS Appl. Mater. Interfaces* 2019, 11, 14051-14058.
- I. Kovalenko, B. Zdyrko, A. Magasinski, B. Hertzberg, Z. Milicev, R. Burtovyy, I. Luzinov, G. Yushin, *Science* 2011, 334, 75-9.
- Z. Y. Wu, L. Deng, J. T. Li, Q. S. Huang, Y. Q. Lu, J. Liu, T. Zhang, L. Huang, S. G. Sun, *Electrochim. Acta* 2017, 245, 363-370.
- J. Liu, Q. Zhang, Z.-Y. Wu, J.-H. Wu, J.-T. Li, L. Huang, S.-G. Sun, *Chem. Commun.* 2014, 50, 6386-6389.
- L. Zhang, L. Y. Zhang, L. L. Chai, P. Xue, W. W. Hao, H. H. Zheng, *J. Mater. Chem. A* 2014, 2, 19036-19045
- X. J. Feng, J. Yang, X. L. Yu, J. L. Wang, Y. N. Nuli, *J. Solid State Electrochem.* 2013, 17, 2461-2469.
- M. Ling, Y. N. Xu, H. Zhao, X. X. Gu, J. X. Qiu, S. Li, M. Y. Wu, X. Y. Song, C. Yan, G. Liu, S. Q. Zhang, *Nano Energy* 2015, 12, 178-185.
- M. Ling, H. Zhao, X. C. Xiao, F. F. Shi, M. Y. Wu, J. X. Qiu, S. Li, X. Y. Song, G. Liu, S. Q. Zhang, *J. Mater. Chem. A* 2015, 3, 2036-2042.
- S. Li, Y. M. Liu, Y. C. Zhang, Y. Song, G. K.

- Wang, Y. X. Liu, Z. G. Wu, B. H. Zhong, Y. J. Zhong, X. D. Guo, *J. Power Sources* 2021, 485, 229331.
23. a) J. Oh, D. Jin, K. Kim, D. Song, Y. M. Lee, M. H. Ryou, *ACS Omega* 2017, 2, 8438-8444; b) Q. F. Yuan, F. G. Zhao, Y. M. Zhao, Z. Y. Liang, D. L. Yan, *J. Solid State Electrochem.* 2014, 18, 2167-2174; c) L. Zhu, H. Q. Hou, D. Zhao, S. W. Liu, W. Ye, S. L. Chen, M. Hanif, *Int. J. Electrochem. Sci.* 2015, 10, 9547-9555.
24. J. S. Kim, W. Choi, K. Y. Cho, D. Byun, J. Lim, J. K. Lee, *J. Power Sources* 2013, 244, 521-526.
25. C.-H. Yim, F. M. Courtel, Y. Abu-Lebdeh, *J. Mater. Chem. A* 2013, 1, 8234-8243.
26. H. I. Park, D. G. Lee, D. J. Chung, M. Sohn, C. Park, H. Kim, *Bull. Korean Chem. Soc.* 2019, 40, 248-253.
27. Fan, Q.; Zhang, W.; Duan, J.; Hong, K.; Xue, L.; Huang, Y. Effects of Binders on Electrochemical Performance of Nitrogen-Doped Carbon Nanotube Anode in Sodium-ion Battery. *Electrochim. Acta* 2015, 174, 970–977.
28. Ling, M.; Xu, Y.; Zhao, H.; Gu, X.; Qiu, J.; Li, S.; Wu, M.; Song, X.; Yan, C.; Liu, G. Dual-Functional Gum Arabic Binder for Silicon Anodes in Lithium Ion Batteries. *Nano Energy* 2015, 12, 178– 185.
29. Zhang, Z.; Zeng, T.; Lai, Y.; Jia, M.; Li, J. A Comparative Study of Different Binders and Their Effects on Electrochemical Properties of LiMn₂O₄ Cathode in Lithium Ion Batteries. *J. Power Sources* 2014, 247, 1–8.
30. Liu, B.; Fu, K.; Gong, Y.; Yang, C.; Yao, Y.; Wang, Y.; Wang, C.; Kuang, Y.; Pastel, G.; Xie, H. Rapid Thermal Annealing of Cathode-Garnet Interface toward High-Temperature Solid State Batteries. *Nano Lett.* 2017, 17, 4917–4923.
31. Tan, R.; Yang, J.; Zheng, J.; Wang, K.; Lin, L.; Ji, S.; Liu, J.; Pan, F. Fast Rechargeable All-Solid-State Lithium Ion Batteries with High Capacity Based on Nano-Sized Li₂FeSiO₄ Cathode by Tuning Temperature. *Nano Energy* 2015, 16, 112–121.
32. Lu, L.; Han, X.; Li, J.; Hua, J.; Ouyang, M. A Review on the Key Issues for Lithium-ion Battery Management in Electric Vehicles. *J. Power Sources* 2013, 226, 272–288.
33. Mark, J. E. *Physical Properties of Polymers Handbook*; Springer: Berlin, 2007.
34. Nunes, R. W.; Martin, J. R.; Johnson, J. F. Influence of Molecular Weight and Molecular Weight Distribution on Mechanical Properties of Polymers. *Polym. Eng. Sci.* 1982, 22, 205–228.
35. Perkins, W. G.; Capiati, N. J.; Porter, R. S. The Effect of Molecular Weight on the Physical and Mechanical Properties of Ultra- Drawn High Density Polyethylene. *Polym. Eng. Sci.* 1976, 16, 200– 203.
36. Dadfar, S. M. M.; Kavooosi, G. Mechanical and Water Binding Properties of Carboxymethyl Cellulose/Multiwalled Carbon Nanotube Nanocomposites. *Polym. Compos.* 2015, 36, 145– 152.
37. Tabor, D. The Hardness of Solids. *Rev. Phys. Technol.* 1970, 1, 145–179.
38. Li, G.; Ling, M.; Ye, Y.; Li, Z.; Guo, J.; Yao, Y.; Zhu, J.; Lin, Z.; Zhang, S. Acacia Senegal-Inspired Bifunctional Binder for Longevity of Lithium–Sulfur Batteries. *Adv. Energy Mater.* 2015, 5, 1500878.
39. Mark, J. E. *Physical Properties of Polymers Handbook*; Springer: Berlin, 2007.
40. Lee, B.-R.; Oh, E.-S. Effect of Molecular Weight and Degree of Substitution of a Sodium-Carboxymethyl Cellulose Binder on Li₄Ti₅O₁₂ Anodic Performance. *J. Phys. Chem. C* 2013, 117, 4404– 4409.
41. Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. Synthesis of Electrically Conducting Organic Polymers: Halogen Derivatives of Polyacetylene,(Ch)_x. *J. Chem. Soc., Chem. Commun.* 1977, 578–580.
42. Fenton, D.; Parker, J.; Wright, P. Complexes of Alkali Metal Ions with Poly (Ethylene Oxide). *Polymer* 1973, 14, 589.

43. Osman, Z.; Arof, A. Ftir Studies of Chitosan Acetate Based Polymer Electrolytes. *Electrochim. Acta* 2003, 48, 993–999.
44. Liew, C.-W.; Ramesh, S. Studies on Ionic Liquid-Based Corn Starch Biopolymer Electrolytes Coupling with High Ionic Transport Number. *Cellulose* 2013, 20, 3227–3237.
45. Schneider, H.; Garsuch, A.; Panchenko, A.; Gronwald, O.; Janssen, N.; Novák, P. Influence of Different Electrode Compositions and Binder Materials on the Performance of Lithium–Sulfur Batteries. *J. Power Sources* 2012, 205, 420–425.
46. Ngai, K. S.; Ramesh, S.; Ramesh, K.; Juan, J. C. A Review of Polymer Electrolytes: Fundamental, Approaches and Applications. *Ionics* 2016, 22, 1259–1279.
47. Pirrung, F. O.; Quednau, P. H.; Auschra, C. Wetting and Dispersing Agents. *Chimia* 2002, 56, 170–176.
48. Wang, Q.; Wang, W.; Huang, Y.; Wang, F.; Zhang, H.; Yu, Z.; Wang, A.; Yuan, K. Improve Rate Capability of the Sulfur Cathode Using a Gelatin Binder. *J. Electrochem. Soc.* 2011, 158, A775–A779.
49. Lee, J.-H.; Paik, U.; Hackley, V. A.; Choi, Y.-M. Effect of Poly (Acrylic Acid) on Adhesion Strength and Electrochemical Performance of Natural Graphite Negative Electrode for Lithium-Ion Batteries. *J. Power Sources* 2006, 161, 612–616.
50. Seh, Z. W.; Zhang, Q.; Li, W.; Zheng, G.; Yao, H.; Cui, Y. Stable Cycling of Lithium Sulfide Cathodes through Strong Affinity with a Bifunctional Binder. *Chem. Sci.* 2013, 4, 3673–3677.
51. Hong, X.; Jin, J.; Wen, Z.; Zhang, S.; Wang, Q.; Shen, C.; Rui, K. On the Dispersion of Lithium-Sulfur Battery Cathode Materials Effected by Electrostatic and Stereo-Chemical Factors of Binders. *J. Power Sources* 2016, 324, 455–461.
52. Su, H.; Barragan, A. A.; Geng, L.; Long, D.; Ling, L.; Bozhilov, K. N.; Mangolini, L.; Guo, J. Colloidal Synthesis of Silicon@ Carbon Composite Materials for Lithium-ion Batteries. *Angew. Chem.* 2017, 129, 10920–10925.
53. Du Pasquier, A.; Disma, F.; Bowmer, T.; Gozdz, A.; Amatucci, G.; Tarascon, J. M. Differential Scanning Calorimetry Study of the Reactivity of Carbon Anodes in Plastic Li-ion Batteries. *J. Electrochem. Soc.* 1998, 145, 472–477.
54. Maleki, H.; Deng, G.; Anani, A.; Howard, J. Thermal Stability Studies of Li-ion Cells and Components. *J. Electrochem. Soc.* 1999, 146, 3224–3229.
55. Barsykov, V.; Khomenko, V. The Influence of Polymer Binders on the Performance of Cathodes for Lithium-Ion Batteries. *Sci. Proc. Riga Technol. Univ. Ser. 1* 2010, 21, 67–71.
56. Nguyen, V. H.; Wang, W. L.; Jin, E. M.; Gu, H.-B. Impacts of Different Polymer Binders on Electrochemical Properties of LiFePO₄ Cathode. *Appl. Surf. Sci.* 2013, 282, 444–449.
57. Huang, S.; Ren, J.; Liu, R.; Yue, M.; Huang, Y.; Yuan, G. The Progress of Novel Binder as a Non-Ignorable Part to Improve the Performance of Si-Based Anodes for Li-ion Batteries. *Int. J. Energy Res.* 2018, 42, 919–935.
58. Kwon, T.-w.; Choi, J. W.; Coskun, A. The Emerging Era of Supramolecular Polymeric Binders in Silicon Anodes. *Chem. Soc. Rev.* 2018, 47, 2145–2164.