

Toward Smart Polymeric Binders for Battery Electrodes

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18.1 INTRODUCTION

At the Paris Climate Summit in December 2015, 195 countries agreed to set out a global action plan to put the world on track to avoid dangerous climate change by limiting global warming to well below 2°C ([European Commission Climate Action, 2015](#)). To achieve this goal, the launch of research programs based on the development of innovative and more efficient carbon-free technologies for the electrification of the grid and the automotive transportation in cities will be needed. Energy storage in secondary or rechargeable batteries is a versatile and lower-emission option to achieve the goals mentioned previously ([Gholam-Abbas and Pistoia, 2003](#)). In the past several decades, the research of secondary Li-ion batteries has been driven by an increasing demand of portable electronic devices ([Tarascon and Armand, 2001](#); [Palacín, 2009](#)). However, some disadvantages, such as the loss of performance of the current battery electrode materials during use ([Palacín and de Guibert, 2016](#)) as well as the presence of scarce and expensive components in the electrodes, needs to be solved. Moreover, the necessary increase of the gravimetric and volumetric energy density of next-generation batteries will be facilitated by using the correct chemical strategies to raise both the operation cell voltage and capacity of the electrode materials ([Armand and Tarascon, 2008](#); [Goodenough and Kim, 2010](#)).

Problems associated with these high-capacity electrode materials, such as metal alloys, include the large volume expansion/contraction (~300% for Si) during discharge and charge. These volumetric changes

result in particle fracture (pulverization) causing continuous electrolyte decomposition (due to the exposure of fresh surfaces and destruction and subsequent reformation of the Solid Electrolyte Interphase [SEI] due to expansion-contraction); the formation of dead, nonelectrically connected particles; and delamination from the current collector. The net effect of these factors is poor long-term cyclability and large irreversible capacity loss during the first cycle. Structural and chemical investigations of this electrode material during electrochemical cycling seek a better understanding of those parameters limiting capacity as well as other failure mechanisms. With this knowledge, scientists have been designing new materials and electrode engineering strategies to improve the performance and also mitigate the degradation processes of these high-capacity anode materials. Among the main strategies to mitigate the weaknesses related to the use of high-capacity electrode materials are the implementation of alternative polymeric binders with new chemistries and electrode engineering routes. The use of earth-abundant precursors and the application of environmentally friendly synthetic routes during the preparation of the advanced polymeric binders have been also addressed. Success in these matters is surely based on first understanding the underlying chemistries of the currently used binders and electrode components by applying novel in situ testing and visualization techniques on functioning batteries. In addition, a combined application of experimental and theoretical techniques has shown high propensity to gain insights into many of the questions that arise from the “how do batteries work and why do they fail” challenge.

18.1.1 How Do Batteries Work?

A battery (Fig. 18.1A) fundamentally consists of an anode and cathode (mixed ionic/electronic conductors), electrolyte (ionic conductor), and external circuit (electronic conductor). As the battery is discharged, the anode (potential μ_a) is oxidized as electrons flow through the external circuit to reduce the cathode (potential μ_c). This redox reaction is enabled by the change of free energy ΔG expressed as the difference of the (electro)chemical potential of the two materials (redox pair); thus the energy from each electron is $\mu_a - \mu_c = V_0$ (Fig. 18.1B). To retain charge neutrality, the electron transfer is accompanied by a flow of cations from the anode to the cathode. In the absence of an applied voltage, the chemical potential (μ) and electrochemical potential ($\bar{\mu}$) are equivalent; however, to reverse the reaction, a potential is applied and the relevant thermodynamic quantity becomes $\bar{\mu} = \mu + zF\phi$, where z is the ionic charge, F is Faraday's constant, and ϕ is the applied potential.

The scientific community has exerted great effort to extend an enormous effort in the search for new electrode and electrolyte materials toward the

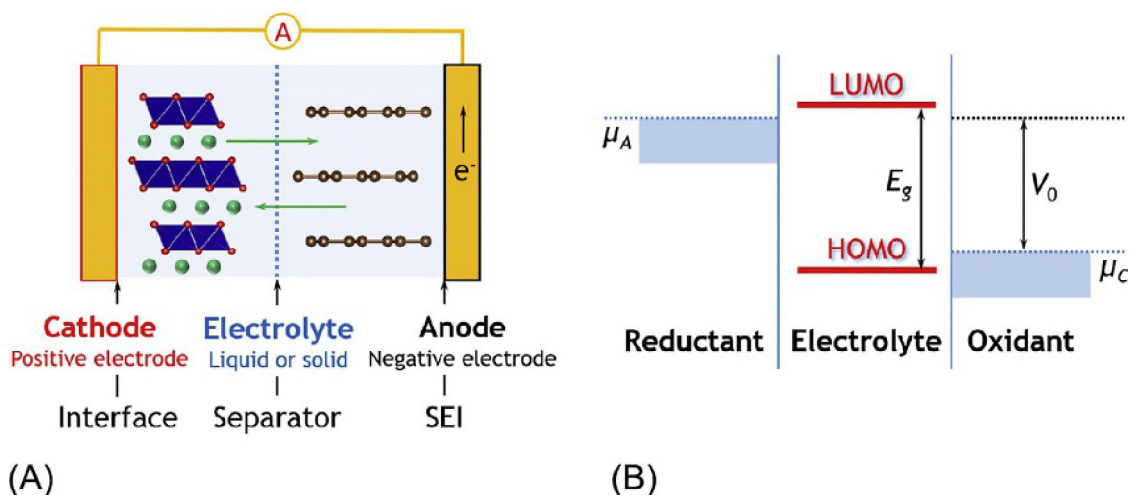


FIG. 18.1 Complex systems. (A) A battery generally comprises a cathode, an anode, electrolyte, and the respective interfaces between the components. (B) Relative energies of the electrolyte window E_g and the anode and cathode electrochemical potentials μ_A and μ_C , respectively.

goal of enhancing the amount of energy stored in the electrochemical cells. The energy density of a battery is determined by the product between the equilibrium voltage (V_0) of the electrochemical cell and the capacity (Q) of reversible charge transfer between the anode and the cathode per unit weight (Ah g^{-1} , gravimetric energy density) or unit volume (Ah cm^{-3} , volumetric energy density). Hence, maximization of Q and V_0 by choosing chemical redox couples of lightweight elements with dense particle morphologies and large electronegativity differences, respectively, is pursued. The resulting secondary batteries are complex systems with anodes, cathodes, and electrolytes that are constantly undergoing structural and chemical changes during operation. Finding the best-performing combination of these three components can only be achieved through the selective use of existing and new electrode materials, and of the right electrolyte combination so as to minimize detrimental reactions associated with the electrode-electrolyte interface—the critical component of any electrochemical system.

18.1.2 Properties of an Ideal Polymer Binder

Developing high-capacity battery systems to store a large amount of energy without sacrificing the safety, cost, power, and stability standards remains a formidable challenge and requires optimized performance of every battery component (Armand and Tarascon, 2008; Kang and Ceder, 2009). Polymer-binding agents are critical for the good performance of the electrodes of batteries during cycling as they hold the electroactive material together forming a cohesive assembly by means of mechanical and chemical stability as well as adhesion to the current collector. This function

is crucial when developing high-capacity electrode materials that usually evidence large dimensional changes. For example, the theoretical capacity of silicon anode materials is 4200 mAh g^{-1} to the $\text{Li}_{22}\text{Si}_5$ phase, more than 10 times higher than that of the current graphite anode electrode found in lithium ion batteries of commercial portable electronic devices; about 3500 mAh g^{-1} is accessible during electrochemical lithiation to the $\text{Li}_{15}\text{Si}_4$ stage (Bruce et al., 2008). However, around 300% of volume expansion was observed when Si is fully electrochemically lithiated. The binder of a battery should provide extraordinary tolerance of the large volume change of high-capacity materials during battery operation. For instance, traditional binder systems involving nonconductive polymers, and conductive additives face technical challenges when applied in high-capacity electrodes. In a conventional binder system, this large volume change disrupts the electrode integrity during electrochemical cycling.

An ideal binder system should present the following properties to the high capacity electrode material (Fig. 18.2): (1) Electronic conductivity under cycling conditions; (2) good mechanical adhesion to the metallic current collector and flexibility with inexhaustible tolerance for large volume change; (3) electrolyte uptake to ensure high ionic conductivity; and (4) electrochemical stability. In addition, from the theoretical and practical point of view, polymeric binders behave similarly than polymer adhesives: (a) The polymer must wet the surfaces by chemical and/or physical interactions; (b) after wetting, the polymer must provide adhesion and be cohesively strong.

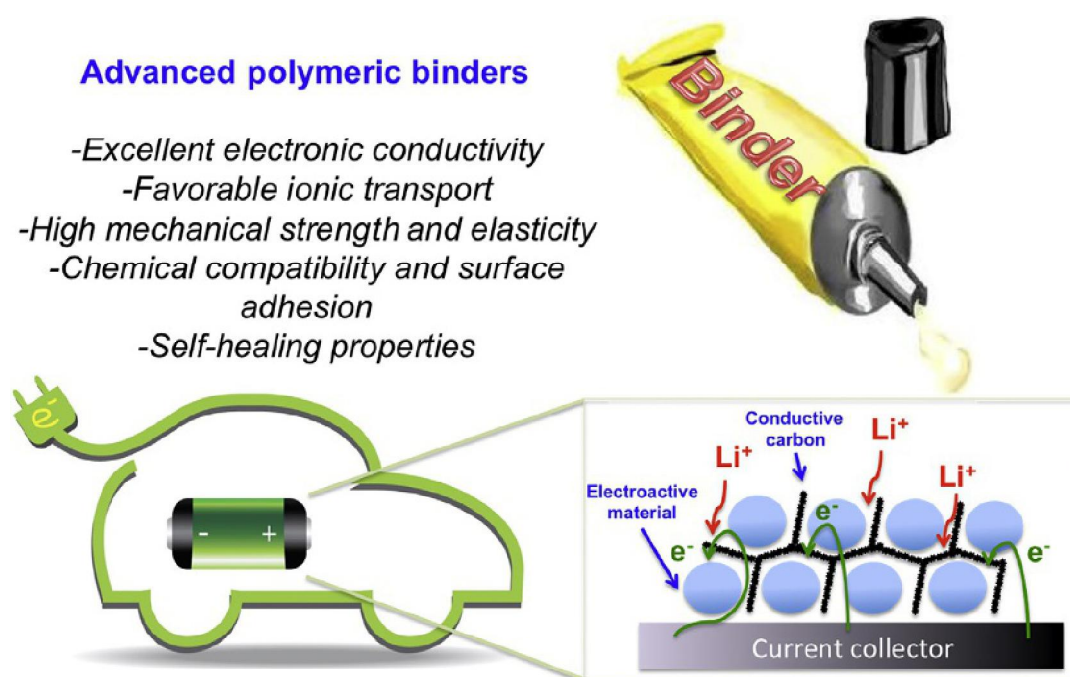


FIG. 18.2 Main properties of the polymeric binders. Electrode's battery components.

The preparation of active material and polymer binder suspensions should fulfill the first requisite, and a loss of solvent, chemical reaction, or cooling of the hot melt adhesives could cause this process. However, as shown in this chapter, these two requirements do not necessarily need to be satisfied to achieve the optimum performance of the binder system. The dimensional changes produced in the electrode during the electrochemical cycling would also need the application of novel and innovative strategies to be buffered such as the presence of self-healing properties on the polymer binder as well as advanced macromolecular chemistry and nanoengineering tactics to design multifunctional electrode materials.

18.1.3 Traditional Polymer Binders for Battery Electrodes

Among the polymeric binder systems used in the battery field, polyvinylidene fluoride (PVDF) has been one of the most extensively used (Fig. 18.3). The presence of fluorine atoms ensures low water content, and

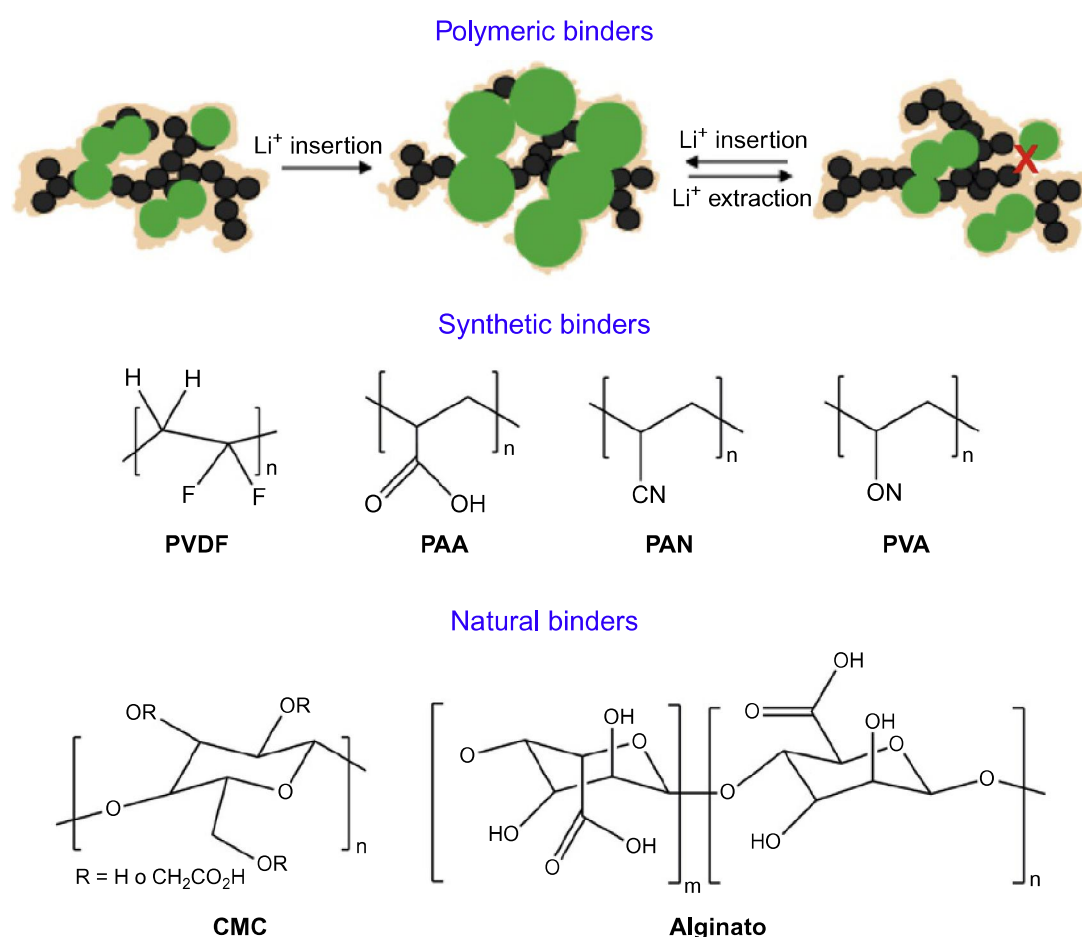


FIG. 18.3 Schematic representation of the electrode's structure in lithium ion batteries: active material (*green circles*), conducting additive (*black circles*), and polymeric binder (*peach-color circles*). The molecular structure of traditional natural and synthetic polymeric binders is also indicated.

then low hydrophilicity (water reacts violently with alkali metal such as lithium and sodium), high dielectric constant, lithium ion conductivity, and also electrochemical stability will ensure stability and also exhibit high mechanical properties (Tsuchida et al., 1983; Kurihara and Nagai, 1998). Different block copolymers derived from PVDF have been used, to also increase the plasticizer effect and allow the increase of ionic conductivity (Chen et al., 2003a,b). The PVDF copolymer binder has also been combined with nanosized conductive carbon additive to sustain the electronic conductivity. Elongation up to 100% strain have been evidenced whereas pristine PVDF binder films could not tolerate more than 10% of elongation. The improvement of the mechanical properties has also resulted in an enhancement of the cycling performance of the battery.

Nafion (sulfonated polymer) has also been studied as a binder in Silicon anodes (Garsuch et al., 2008), showing capacity retention up to 74% after 100 cycles when a current of 150 mA g^{-1} was applied. Poly-acrylic acid (PAA) (Magasinski et al., 2010; Erk et al., 2013), polyvinyl alcohol (PVA) (Masiak et al., 2007), and blends of both polymers have also been used with silicon particles. Particularly successful was the case when the PAA and PVA was cobindered with a 9:1 ratio and then heated at 150°C for 1 h inducing an esterification reaction to form a cross-linked gel polymer network (Song et al., 2014). The area capacity achieved by using these binders was 4.3 mAh cm^{-2} , and the volume variation after being cycled went up to 4.5%, much lower than for PVDF (19.7%) due to the 3D interpenetrated polymeric gel network.

18.2 BIO-BASED POLYMER BINDERS

Biopolymers from nature such as cellulose, alginate, and chitosan have evidenced binder properties for high-capacity alloy-anodes in lithium-ion batteries (Fig. 18.3). In general, the binder properties rely in the functional groups, such as carboxylic acids and hydroxyl groups for adhesion. Bio-based or natural polymer binders are abundant and inexpensive, and the preparation of the electrode and binder suspensions or slurries can be prepared in water making these systems extraordinary promising for the development of a sustainable battery technology. However, the use of natural polymers also exhibits drawbacks: the uncontrollability of certain polymer properties such as the molecular weight, presence of different types of functional groups that could be electrochemically instable and then will provoke side reactions that produce large and irreversible capacities during cell cycling, and also poor mechanical and binding properties due to the presence of oligomer fractions.

Different polysaccharides (amylose, amylopectin, glycogen, agarose) were studied as polymer binders for silicon/graphite composite

electrodes (Murase et al., 2012). Among the main advantages observed by using these bio-based binders in comparison to PVDF are the following: an improved first cycle coulombic efficiency (CE), suppressed electrolyte decomposition, and better cycling performance and capacity retention. Among all of them, amylopectin exhibited the best electrochemical performance. Naturally abundant gum arabic (GA), composed of polysaccharides and glycoproteins, was applied as a dual-functional binder (Ling et al., 2015a): hydroxyl groups of the polysaccharide in GA ensure the strong bonding to Si, whereas the long chain glycoproteins provides further mechanical tolerance to the large volume expansion by Si nanoparticles. Specific capacitances up to 2000 mAhg^{-1} at 1 C rate and 1000 mAhg^{-1} at 2 C rate were achieved after 500 cycles. GA was also combined with PAA to induce esterification reaction and establish a flexible network, which provides reinforced mechanical and enhanced coherent strengths. The porosity developed during the network formation relieves the stress and block the formation and propagation of cracks, leading to high areal capacity Si anode (Ling et al., 2015b).

The application of carboxymethyl cellulose (CMC) as binder material has evidenced excellent electrochemical performance for Silicon powders when used as anode material in lithium-ion batteries. Exhibiting specific capacities up to 1100 mAhg^{-1} for 70 cycles was a huge improvement in comparison to PVDF-based Si laminate (Li et al., 2007). These preliminary studies have shown that CMC has been an excellent binder option for alloy anode materials because of their water solubility, low cost, and higher electrochemical performance. In addition to these works, other advantages of using CMC binders have been published by other researchers such as: (a) suppression of the increase of the open circuit potential after full discharge of lithium-silicon electrode (Key et al., 2009); (b) possibility of preparation of CMC porous scaffolds of CMC containing Si as an anode electrode due to the stiff nature of the polymer (Guo and Wang, 2010); and (c) increase of cycle life by neutralizing the charge of the CMC by controlling the pH of the slurry during the lamination process (Lestriez et al., 2007).

Another excellent natural polysaccharide used as binder is alginate. It is a copolymer of 1–4 linked β -D-mannuronic acid (M) and α -L-guluronic acid (G) residues extracted from brown algae. The application of alginate in Si anodes had shown high SEI stability during 200 cycles as a consequence of the optimum interaction between the electrolyte and the functional groups on alginate (Kovalenko et al., 2011).

Carboxymethyl chitosan was also explored as a water-soluble binder for a silicon/graphite composite electrode (Yue et al., 2014). This polymeric binder exhibited optimum bonding properties to the silicon nanoparticle surface, enabling better cycling performance of Si/graphite electrodes than CMC or alginate.

Natural polymers showing excellent adhesion properties due to the presence in the macromolecular chain of catechol units have also inspired novel polymeric binders (Lee et al., 2006, 2007). These catechol units have been incorporated into different synthetic polymer matrices such as PAA improving binding properties and cycling performance compared to the pristine polymer (Ryou et al., 2013). A β -cyclodextrine with epichlorohydrin polymer (Jeong et al., 2014) exhibiting multidimensional hydrogen network has also offered a strong interaction with the silicon anode particles. The origin of the excellent binding properties observed in this material might be due to the self-healing properties of the polymer that favors the recovery of the polymer chain network even if the silicon nanoparticles lose their contact with it during the electrochemical cycling.

18.3 MULTIFUNCTIONAL POLYMER BINDERS

As shown in the previous section, conventional polyvinylidene fluoride (PVDF) binders are not appropriate for high-energy anodes such as Si because of their weak Van der Waals interactions with Si, and the copper current collector (Ling et al., 2015b) cannot avoid the severe structural deformation during charge and discharge. Moreover, although PVDF has been the preferred binder for lithium ion batteries currently in the market (Oltean et al., 2016), it is known to decompose at voltages close to Li^+/Li (Julien et al., 2016) as well as Na^+/Na . In spite of the strategies that have been applied to minimize the failure of the electrode such as creation of novel metal alloys, Si/C composite electrode materials (Sheehan, 1976; Wang et al., 2015), Si wires (Shen et al., 2014; Zhou et al., 2013) and nanotubes (Zhu et al., 2013), and especially nanoengineering of the electrodes (Choi et al., 2014), an efficient battery binder system for assembling high-capacity electrodes still has not been developed yet.

A practical polymer binder must be multifunctional, because it is not feasible to use a blend of binders to satisfy each requirement at once yet. Therefore multifunctional polymers are the most suitable matrix for integrating the properties required in a single framework because they can incorporate many types of surface functionalities to achieve the target function. In addition to the binding properties among the more significant functionalities required by the polymeric binder are the following: electronic and ionic conductivity, processability, electroactivity, reversible elasticity, and self-healing properties.

To achieve some of these properties, researchers have adopted the following strategies: (i) implementation of covalent (Koo et al., 2012) and noncovalent (Kwon et al., 2014) interactions between the polymeric binder and the electroactive material to enhance binding affinity; (ii) preparation of three-dimensional polymer networks with well-defined interchain

interactions to endure the structural instability of the Si electrode during cycling (Ling et al., 2015b); (iii) conducting components, highly elastic components (elasticity property), and self-healing ability within the chemical glues have been recently introduced (Zhao et al., 2015a).

One of the simplest initial strategies adopted by researchers to increase the electrical conductivity of the binder was the use of these classical binders together with conductive carbons. However, a large porosity pushed the electrolyte inside and then its weight had to be also included in the mass balance that penalizes the gravimetric capacity of the electrode. Thus many authors have cleverly designed intrinsic electronically (Han et al., 2012) and ionically (Cui et al., 2013) conducting binders for large volume-change silicon anodes. These materials, exhibiting binding force along with conductivity, enable the reduction of the amount of binder and also suppress the use of conducting additives. A profoundly different approach to combine a conducting and binding additive is the use of self-standing electrodes made with carbon nanotubes (Tran et al., 2012; Park et al., 2015) or graphene (Zhu et al., 2016; Lima et al., 2011). Although they have the added advantage of not needing current collector and are important for wearable electronics, which require flexible and lightweight components, they cannot be processed with the standard electrode fabrication techniques. The requirements of special equipment, as well as energy and time-consuming preparation, prevent their use with industrial purposes.

One of the pioneering works that include a conjugated conductive block in the polymer binder chain was done by Prof. Gao Liu's group (Fig. 18.4) (Liu et al., 2011). In this work, researchers used poly(9,9-dioctylfluorene-*co*-fluorenone-*co*-methylbenzoic ester) (PFM), which has a polyfluorene-based structure. This polymer is doped during the electrochemical reduction process, and lithium ions are inserted into the silicon structure. The presence of polyfluorene blocks with additional functionalities such as carbonyl and aliphatic chains contribute to the optimization of the conduction band. The benzoic functionalities improve the adhesion properties of the binder. These electrodes evidenced capacities up to 2500 mAh g⁻¹ in silicon particles with only 20% of capacity fade after 650 cycles. The same group has also performed the most recent advances in the area of conductive polymer binders in the last few years by designing single-component battery binders that improve only one of the functions of the binder without being unfavorable to the others. For instance, they were able to incorporate triethylenoxide monoethylether chains into the fluorene units to improve the polarity and electrolyte uptake capability of the polymer. XAS and DFT calculations show that the incorporation of the ionic conductive block has no effect on the electronic properties.

When cycling commercial silicon electrode composites, a drop in lithium diffusion was observed as a consequence of the migration of the

Multifunctional binders

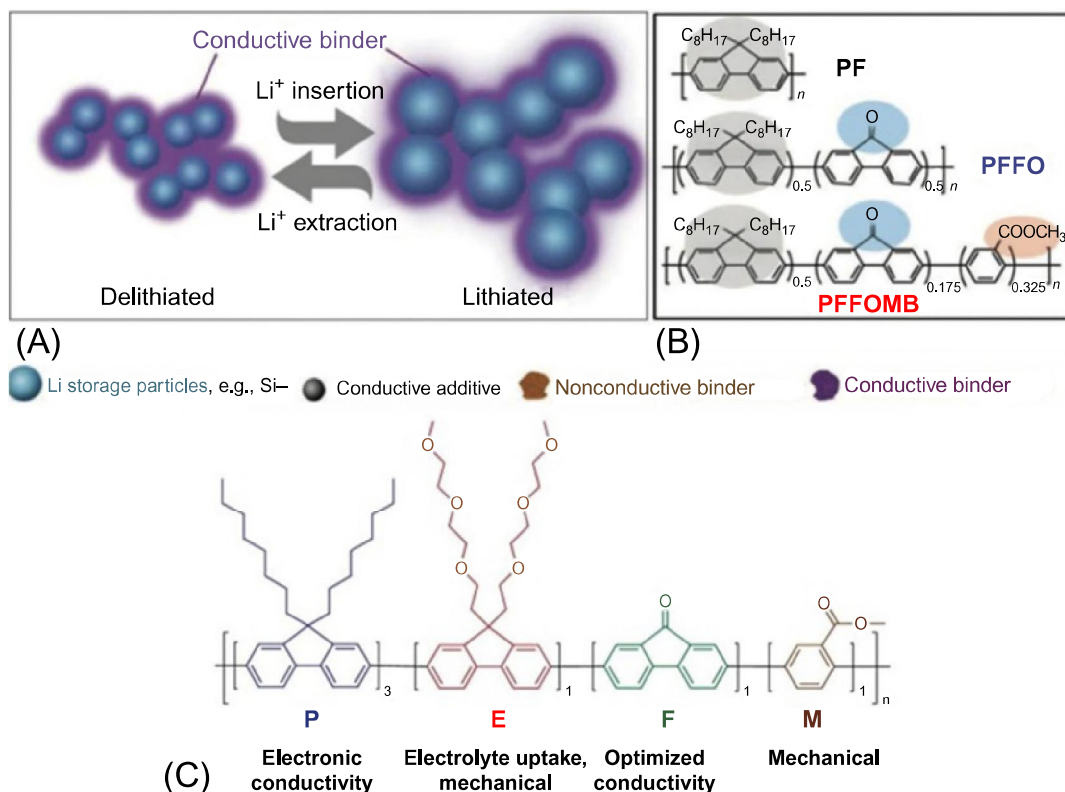


FIG. 18.4 Multifunctional binders. (A) Conductive polymer binder is able to hold the volumetric changes after lithium ion insertion. (B) Polyfluorene block is the conjugated unit providing electron conductivity to the binder. (C) Copolymer binder showing different block functionality.

conductive carbon additive and the polymer binder to the surface of the electrode materials. To improve lithium diffusion and try to avoid these types of problems, researchers have designed innovative nanostructures such as the preparation of Si-PFM particles with an average diameter of $10\ \mu\text{m}$ by spray/precipitation method (Fig. 18.5) (Xun et al., 2013). This new hierarchical design electrode incorporating the secondary $10\text{-}\mu\text{m}$ -sized particles of Si-PFM exhibited current densities up to $4\ \text{mAh cm}^{-2}$ with an improved capacity retention and rate performance compared to thin film Si-PFM electrodes of $10\ \mu\text{m}$ thickness.

Silicon nanoparticles (n-Si) have been combined with micron-sized Si particles (m-Si) and PFM conducting polymer binder as conductive and structural additive instead of using conventional m-Si and PVDF binders. Among the main advantages of these types of composite electrodes are the following: (a) the presence of the high surface area n-Si alleviated mechanical stress due to the dimensional changes occurring during the lithiation and de-lithiation processes; (b) because of the unique polymer structure, this binder operates like a cross-linked polymeric network confining the

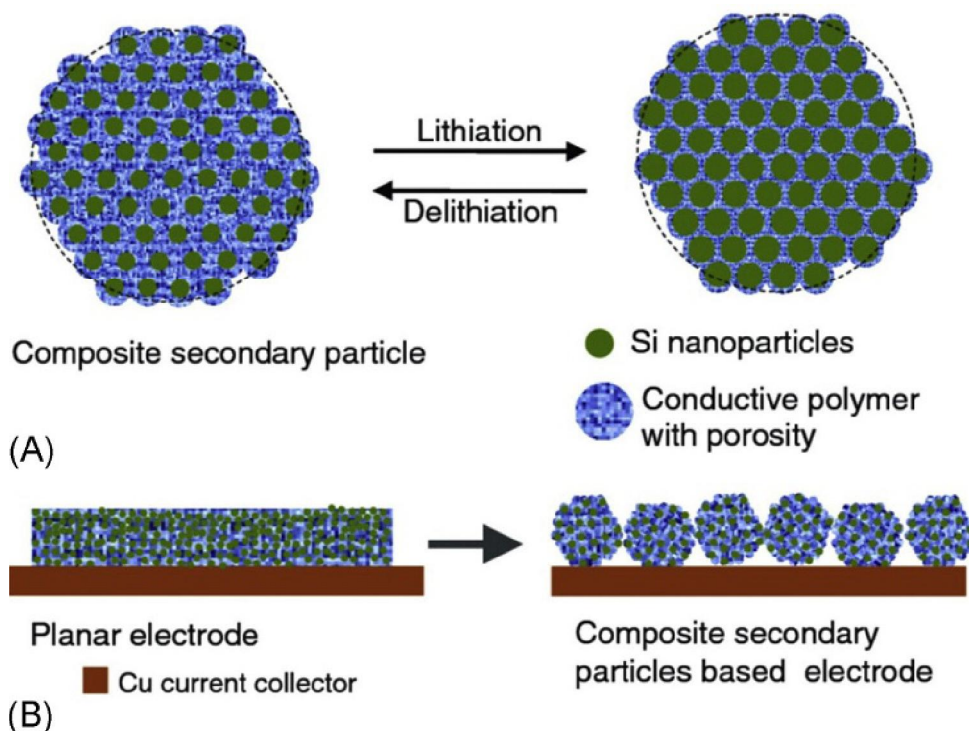


FIG. 18.5 Schematic representation of Si/conductive polymer composite secondary particles. (A) Composite secondary particles during lithiation and delithiation. (B) A planar electrode made with a conductive polymer binder and Si nanoparticles vs. an electrode made with composite secondary particles. There are larger pores between the composite secondary particles.

Si particles and offering high resistance to deformation; (c) the addition of carbon additives is not needed because of the presence of the electron-conducting units in the polymer backbone. However, there are some disadvantages with using silicon nanoparticles as it is the presence of a high irreversible capacity (50%–70%) in the first cycle due to the formation of a large amount of SEI as a consequence of the higher reactivity of the nanoparticles in comparison with micron-sized particles. In any case, the use of this polymeric binder has resulted in high specific capacities of 2500 mAh g^{-1} after 30 cycles and good rate performance during the electrochemical insertion and deinsertion of lithium ions. PFM binder has also enabled the reversible electrochemical cycling of SiO above 100 mAh g^{-1} during more than 400 cycles by using a high loaded SiO amount of 98 wt% (Zhao et al., 2015b).

In-situ polymerization methods have also been applied for the development of novel multifunctional hierarchical electrodes containing electron-conducting binders. Particularly interesting is the case of the development of hierarchical conductive hydrogel framework with carbon nanotubes, which offered a continuous electron transport network and high porosity to accommodate the volume expansion of Si particles.

By 3D wrapping of silicon nanoparticles/single-wall carbon nanotubes with conducting polymer nanostructures, a greatly improved cycling performance is achieved with reversible discharge capacity over 1600 mAh g^{-1} and 86% capacity retention over 1000 cycles at the current rate of 3.3 A g^{-1} (Liu et al., 2013).

18.4 SMART POLYMER BINDERS

One of the main goals of creating a smart polymeric binder is reducing the weight of the inactive components while keeping conventional lamination techniques by combining the redox activity and adhesion properties within the same processable polymer. Therefore an ideal design of polymer binders should be able to improve elasticity of the polymeric binder and electrodes, which help inhibit current collector delamination, particle isolation, and crack generation during lithiation and delithiation of the active particles. In addition, the state-of-the-art roll-to-roll lamination process in the industry also specifically requires a flexible and ductile nature of the polymer binders and electrode, which will also help to prevent crack generation and delamination during processing. Polymers extracted from natural sources such as alginate, dextrin, agarose, and carboxymethyl cellulose contain surface-functional groups that can be used to improve the adhesive properties of the binder (Oltean et al., 2016). However, these biopolymers usually form a rigid network that does not accommodate the dimensional changes experienced by the electroactive materials as they undergo changes in shape during the lithiation-delithiation.

Prof. Gao Liu's group carried out the first studies related to the effect of the mechanical properties of the binder-electrode system on the electrochemical properties. To unveil the role of the polymer binders in the inhibition of failure of electrode interfaces, the researchers chose PMAA as rigid polymer binder. Then the PMAA was chemically modified with different contents (0, 5, and 10 wt%) of triethylene glycol methacrylate (TEGMA) to bring the ethylene glycol moiety into the polymer binder. The methacrylate structure in this monomer allows the radical copolymerization chemistry with MAA, and a uniform distribution of TEGMA in the final polymer binder is achieved. Incorporation of TEGMA structure into the polymer allows systematic investigating of the influence of the mechanical properties of the binder when it is used in lithium ion batteries. Mechanical tests were conducted at the surface of the electrodes to reveal the different mechanical responses from the electrode made with the rigid binder and with and without containing the flexible unit. Graphite electrodes assembled using the modified flexible binder can inhibit the generation of cracks, leading to improved cell cycling performance. Moreover, by adding a 10 wt% TEGMA, the cell cycling electrochemical performance

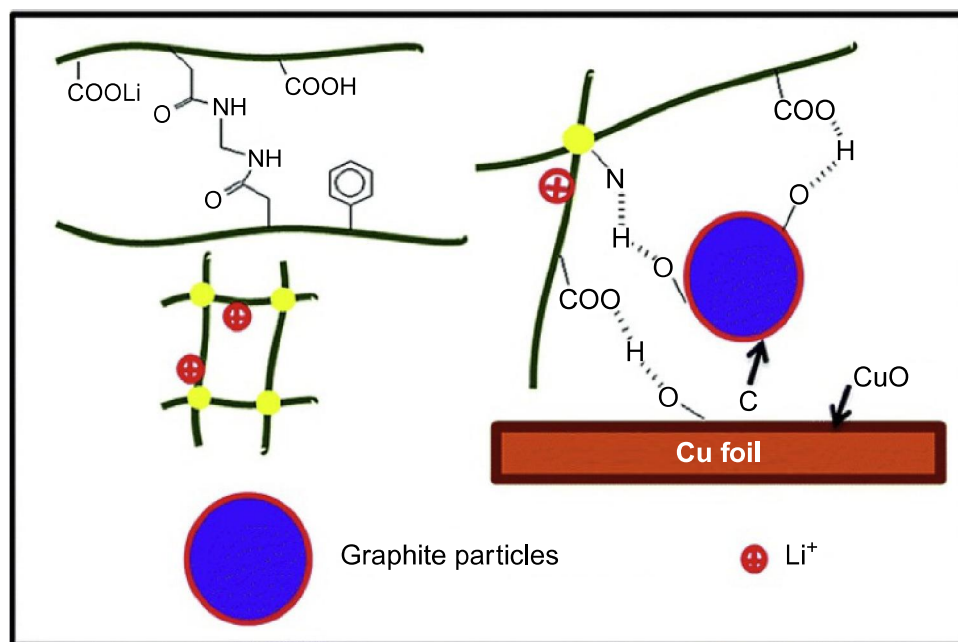


FIG. 18.6 Chemical structure of the c-Li-PSBM binder and the interaction between the c-Li-PSBM binder and graphite particles.

achieved a reversible capacity of $\sim 270 \text{ mAh g}^{-1}$ at 1C in comparison to 190 mAh g^{-1} for the unmodified PMAA polymer binder.

Recently, Shu Huang and collaborators ([Huang et al., 2017](#)) developed a waterborne cross-linked ionomer binder with a cross-linking structure for graphite anode for Li-ion batteries ([Fig. 18.6](#)).

They used a low binder content of 1.5% without conductive additive. The binder is a polymer containing three monomers: styrene, butyl acrylate, and methacrylic acid (PSBM), and formed a strong interaction with graphite particles and facilitated the release of more free Li^+ upon lithiation/delithiation leading to enhanced electrochemical properties, including cycling, electrochemical impedance spectroscopy, and rate performances, compared to SBR based binders: retention of 85.2% after 300 cycles at a rate of 1C. The rate capacity retention of soft-package batteries with the PSBM binder was higher than that with SBR, especially at high rates of 2C and 3C.

Sunghun Choi and collaborators developed a novel binder that imparts extraordinary elasticity to the polymer network originating from the ring-sliding motion of polyrotaxane through a polyacrylic chain. The polymeric binder involves a linear polymeric frame [polyacrylic acid (PAA)] covalently bonded to a cyclic polysaccharide [α -cyclodextrin (α -CD)] threaded by polyethylene glycol "axle" (PEG) chains.

This cross-linked supramolecule, also known as polyrotaxane (PR), has unusual mechanical properties that arise from the sliding movement of the ring. The sliding of the ring lowers the Young's modulus of entire

electrode's material, which is a measure of its stiffness. The ring moves freely along the thread and acts like a moving pulley. This binder kept even pulverized silicon microparticles coalesced without fragmentation, enabling stable cycle life for silicon microparticle anodes at commercial-level areal capacities. The impact of the polyrotaxane cross-linking was revealed by examining the mechanical properties of a PR-PAA film binder. In addition, the PR-PAA-SiMP electrode exhibited far better cycling performance as compared with that of the PAA-SiMP electrode. When measured at 0.2 C (0.64 mA cm^{-2}), the PR-PAA-SiMP with an initial areal capacity of 2.67 mAh cm^{-2} preserved 2.43 mAh cm^{-2} after 150 cycles, corresponding to 91% capacity retention. By contrast, when measured under the same condition, the PAA-SiMP electrode began to lose its capacity from the outset and retained only 48% of the initial capacity after 50 cycles. The Coulombic efficiency of the PR-PAA-SiMP increased to 97.37% at the first cycle upon C-rate change (0.033–0.2 C) and then rose to 99.10% and 99.82% at the 4th and 22nd cycle, respectively. The average Coulombic efficiency in cycles 23–150 was 99.64%.

Yu Wang and collaborators have developed a gum-like nanocomposite as a conformable, conductive, and adhesive electrode matrix for energy storage applications (Fig. 18.7) (Wang et al., 2017). The new material used as a polymer matrix was based on ultrahigh molecular weight poly(ethylene oxide) and lithium salt, UHMWPEO-Li⁺ complex. The strong adhesion property is mainly contributed by a combination of Van Der Waals forces, hydrogen bonding, and electrostatic (ion-ion) interactions generated at the interface. The new electrode matrix was proposed based on a gum-like nanocomposite, a dual-conductive polymer adhesive. As an electrode matrix, the gum-like nanocomposite integrates the functions of binder, electrolyte, and conductive fillers. In particular, it shows strong adhesion, high electrical/ionic conductivities, and appropriate mechanical and self-healing properties. It is demonstrated that, with the electrode matrix, battery electrodes can be fabricated into nonporous composites showing not only excellent mechanical flexibility and stability but also improved electrochemical performance when working with a gum-like electrolyte.

The O-Li⁺ ratio is critical as it dramatically affects not only the morphology as described previously but also the properties, such as adhesion and ionic conductivity. Conformable integrated electrodes have been fabricated by using the UHMWPEO-Li⁺ as an electrode matrix. With appropriate loading of UHMWPEO-Li⁺ ($\approx 30 \text{ wt}\%$), the final composites showed integrated structures and excellent mechanical flexibility and conformability.

The ability to repair damage spontaneously, which is termed self-healing, is an important survival feature in nature because it increases the lifetime of most living creatures. This feature is highly desirable for rechargeable batteries because the lifetime of high-capacity electrodes, such as silicon anodes, is shortened by mechanical fractures generated during

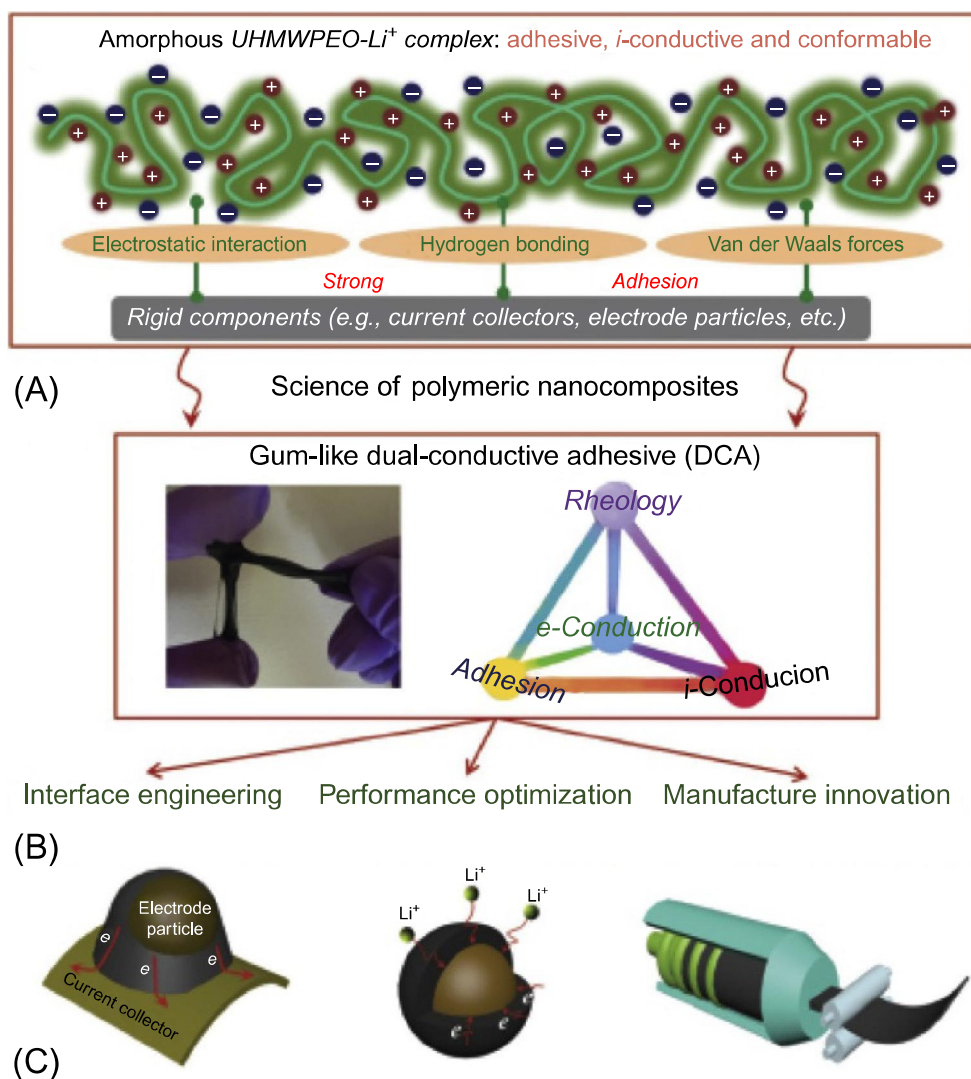


FIG. 18.7 Design of gum-like dual-conductive adhesive (DCA) as electrode matrix for nonporous electrodes. (A) Schematic of the amorphous complex formed by ultrahigh molecular weight poly(ethylene oxide) (UHMWPEO) and lithium salt. (B) Strategy for achieving high-performance DCA by compositing the UHMWPEO- Li^+ complex with electronically conductive nanomaterials and plasticizer. (C) Schematic of the primary benefits from DCA to battery technology.

the cycling process. To date, artificial self-healing materials developed for energy applications are all polymer-based. Further, conducting components and self-healing ability within the polymeric binder materials have been recently introduced.

Yi Cui and Zenan Bao groups apply self-healing chemistry to silicon microparticle anodes to overcome their short cycle-life (Wang et al., 2013) (Fig. 18.8). They showed that anodes made from low-cost SiMPs ($\sim 3\text{--}8\ \mu\text{m}$), for which stable deep galvanostatic cycling was previously impossible, now has excellent cycle lives when coated with a self-healing polymer (SHP).



FIG. 18.8 Self-healing binders.

The authors also evidenced a cycle life 10 times longer than state-of-art anodes made from SiMPs and still retain a high capacity (up to $\sim 3000 \text{ mA h g}^{-1}$). The randomly branched hydrogen-bonding polymer used can heal cracks and damage in the coating during cycling spontaneously. The SHP is made conductive (0.25 S cm^{-1}) by uniformly dispersing carbon black (CB) into the polymer. The composite undergoes simultaneous mechanical and electrical self-healing at room temperature. The self-healing capability shows that, after an electrical circuit is broken, when the two pieces of SHP acting as the conductors are brought together, the circuit is completed in about 1 min, and a light-emitting diode illuminates again. At the same time, the composite can withstand mechanical bending at the healed location, which indicates the quick electrical and mechanical healing at room temperature.

On the basis of this pioneering work, it can be concluded that the cycling performance of Si electrodes mainly depends on the healing ability of the polymer binder. Accordingly, the good adhesion at the interface between the silicon materials and the self-healing polymer is essential to maintain electrode integrity. However, because the self-healing polymer was only coated on top of the silicon particle electrodes, it showed poor adhesion between a majority of silicon materials and self-healing materials, making it difficult to achieve long-term cycling stability and high silicon mass loading. To overcome this shortcoming, the same groups presented a new electrode design with 3D spatial distributed self-healing

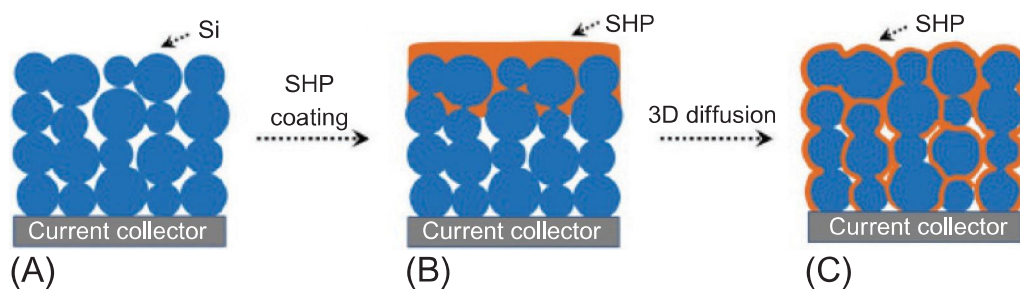


FIG. 18.9 Schematic design of self-healing Si electrodes with 3D spatial distribution of self-healing polymer into silicon electrodes. Reproduced with permission from Chen, Z., Wang, C., Lopez, J., Lu, Z., Cui, Y., Bao, Z., 2015. *Adv. Energy Mater.* 5, 1401826.

polymer into the Si electrodes (Chen et al., 2015). The new strategy allows the self-healing polymer to diffuse into the entire thickness of the Si layer to form robust interfaces between Si particles and the self-healing polymer (Fig. 18.9). The as-prepared self-healing electrodes with high mass loading of Si particles ($1\text{--}1.6\text{ mg cm}^{-2}$) demonstrated more stability at 140 cycles at high areal capacity ($3\text{--}4\text{ mAh cm}^{-2}$).

18.5 CONCLUSIONS AND OUTLOOK

The polymeric binder is a crucial component in the preparation of negative electrodes with a high capacity such as silicon and tin for lithium ion batteries. The main goal in the application of polymeric binders has been to achieve high and stable capacity values as a sign of an optimum performance of the battery. Traditional polymer binders such as PVDF has shown good properties for electrode materials such as graphite but not for high capacity anodes. New strategies for the development of advanced polymeric materials have been implemented to improve the cohesion between the active particles and also exhibiting the property of buffering the dimensional changes occurring during the insertion-deinsertion of lithium ions. New and advanced polymeric binders with hierarchical structures, high elasticity, and self-healing properties has allowed the mitigation of the failure mechanisms in the batteries.

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