Science for Energy and Environment

Review

A Review of Self-Healing Polymers for Lithium Batteries: From Mechanistic Insight to Application

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Abstract: Lithium batteries are crucial for powering portable electronic devices and electric vehicles, profoundly impacting our global society. However, their repeated charge and discharge cycles cause structural changes that lead to mechanical fractures in the internal components, significantly reducing cycling lifetimes of lithium batteries. Utilizing intrinsic self-healing polymers is a promising strategy to address these issues, as these materials can spontaneously repair mechanical cracks or damages, resulting in greatly enhanced electrochemical performance. In this review, we present and highlight how self-healing polymers contribute to improved electrochemical performance in lithium batteries. We first introduce the self-healing mechanisms identified in current self-healing functions, including external and intrinsic self-healing. Then, we discuss their effects on different electrolyte and binder materials. Key examples illustrating the efficacy of self-healing polymers in extending cycle life and improving battery stability are discussed. Finally, we propose some challenges and future opportunities in this evolving field to stimulate the rational design of advanced self-healing polymers for stable lithium batteries.

Keywords: lithium batteries; self-healing polymers; mechanisms; electrolyte; binder

1. Introduction

Lithium batteries are the preferred source of energy to power portable electronic devices and electric vehicles [1], due to their high operating voltage, low self-discharge, long lifespan, no memory effect and efficiency [2] as electrochemical energy storage systems. However, during charge and discharge cycles, the internal components of lithium batteries are prone to deformation [3,4]. The accumulation of these deformations can cause physical fractures [5], compromised safety, and reduced lifespan. This issue is particularly pronounced in high-capacity electrode materials [6] such as silicon and sulfur [7,8]. These volume changes [9,10] can induce substantial internal strain energy in active particles [11,12], leading to fragmentation and the formation of significant cracks on the material surface, which diminishes operational efficiency and reduces battery lifespan. Consequently, it is imperative to enhance the stability of lithium batteries to promote their application [13].

To address these challenges of lithium batteries [14], scientists have drawn inspiration from natural biological systems [15–18]. For instance, human skin heals automatically following an injury through platelet aggregation in the blood, which stops bleeding [19] and facilitates wound healing. Inspired by such biological processes [20–25], researchers have developed various biomimetic materials that mimic the dynamic mechanisms of human wound healing. By leveraging the regenerative properties of self-healing materials [26–29], it is possible to enhance their resistance to fatigue, thereby significantly prolonging the lifespan, stability, and dependability of lithium batteries.

Significant research has focused on integrating self-healing polymers into lithium batteries to improve lithium-ion storage performance [30,31]. Recent literature highlights significant progress in this field [32–36], demonstrating that self-healing polymers can efficiently extend cycle life and enhance the stability and reliability of lithium batteries [37]. Given the critical role of self-healing technologies in advancing lithium batteries [38], it is imperative to summarize the progress of self-healing mechanisms and approaches toward high-performance lithium batteries over the past decades [39–41].

This review aims to present and highlight how self-healing polymers contribute to improved electrochemical performance in lithium batteries. We begin with a comprehensive overview of various self-healing mechanisms identified in current self-healing functions, including external and intrinsic self-healing. We then detail the effects of self-healing polymers on the electrochemical performance of different electrolyte and binder materials used in lithium batteries (Figure 1). Key examples demonstrating how self-healing polymers enhance electrochemical performance are parsed and discussed. Finally, we outline the challenges and future opportunities in this burgeoning research field. This review is anticipated to stimulate the rational design of advanced self-healing polymers for stable lithium batteries, appealing to researchers in electrochemical energy science, materials science, physical chemistry, and nanotechnology.

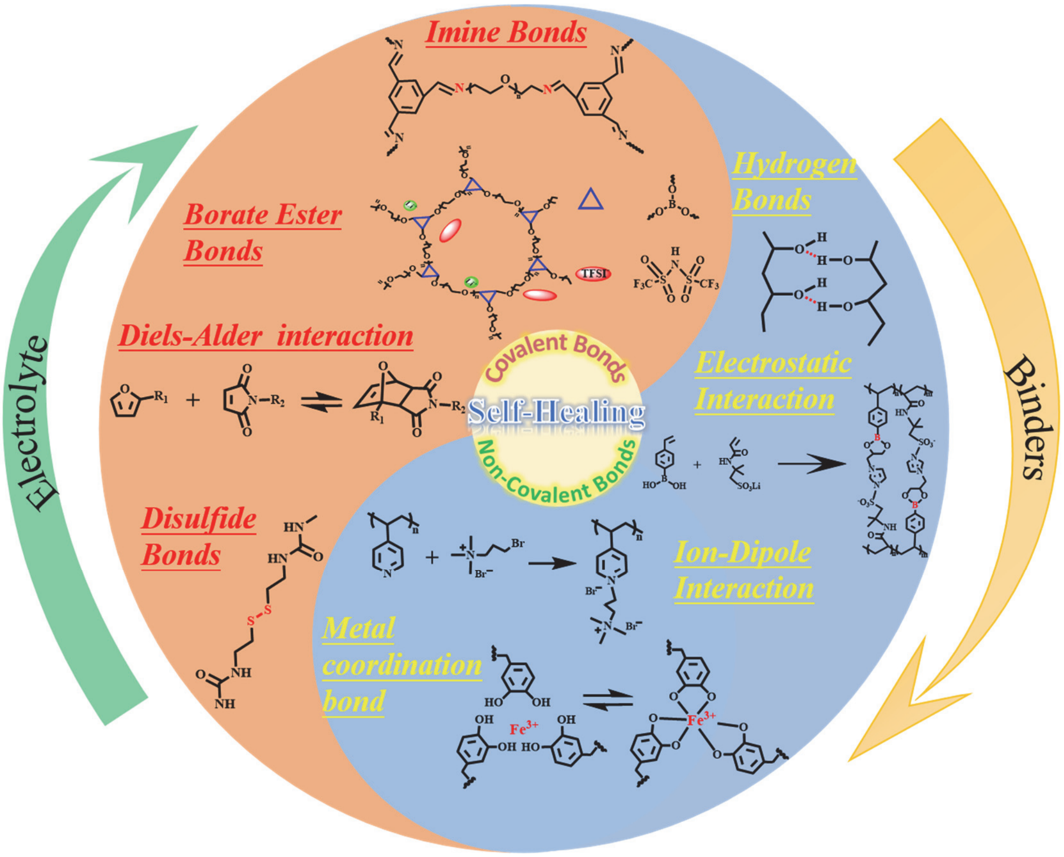


Figure 1. Chemical structures of the various reversible dynamic covalent bonds and non-covalent bonds used for self-healing polymers.

2. Self-Healing Mechanism of a Polymer

Self-healing is defined as utilization of existing resources to heal and restore functionality in the body following a rupture or damage. Self-healing strategies generally entail molecular-level physical or chemical reactions. Self-healing mechanisms are categorized into external and internal types based on the triggering factors initiating the healing process. External self-healing is primarily accomplished by incorporating healing agents [42], including pre-embedded microcapsules [43,44], which become active upon the release of the agent. They can autonomously detect and mend cracks, eliminating the need for external intervention. In contrast, internal self-healing [45], harnesses dynamic chemical processes [46] predicated upon reversible polymer bonds or supramolecular interactions [47] necessitating external triggers such as thermal or photonic stimuli to initiate repair. This process achieves re-healing and usually requires external stimuli, including heating or exposure to light. These methodologies rely on innate, dynamic chemical bonds sans the reliance on exogenous healing agents [48]. Leveraging distinct healing mechanisms, self-healing mechanisms offer two primary advantages for lithium batteries: theoretically infinite healing cycles due to reversible bonding, and optimized initial energy density by eliminating unnecessary electrochemically inactive components. Nevertheless, the naturally sluggish nature of dynamic chemical reactions in self-healing materials implies that the healing process may necessitate a longer duration. Subsequently, a comprehensive analysis of each category is provided. A meticulous dissection of each classification ensues to elucidate their respective merits and limitations.

2.1. External Self-Healing

Self-healing mechanisms are predominantly classified into two main types [49], i.e., capsule-based and microvascular systems [50–52]. Central to both modalities is the encapsulation of liquid healing agents within microcapsules or pre-embedded within a polymer matrix. Once electrolyte damage and rupture occur, the encapsulated agents are discharged, interfacing with the damaged region to instigate polymerization reactions to achieve healing.

Zhang et al. [49]. have classified capsule systems into five distinct types (Figure 2), i.e., single-capsule encapsulation [53–55], capsule dispersion [56–59], phase separation/droplet dispersion [60], dual-capsule [61–69], and integrated systems. In capsule-based systems, a single type of healing agent is encapsulated. This agent may consist of a reactive chemical, a suspension, a solvent, or a metal with a low melting point. The healing process is initiated when the agent is released and interacts with functional groups in the matrix triggers polymerization. Subsequently, environmental humidity or light exposure. As a result, the chains on the fractured surface become entangled or form conductive bridges. Capsule-dispersion catalyst systems consist of capsules containing monomers, within which catalysts are dispersed or dissolved in a matrix [70,71]. Microcapsule rupture induced by crack propagation prompts polymerization of liberated monomers catalyzed by adjacent catalysts. Systems characterized by phase-separated droplets or capsules entail phase separation of at least one healing component, with the other enclosed within capsules. Upon capsule rupture and subsequent liquid release, inter-component reaction ensues. Self-healing materials often require stringent processing conditions, such as heating and shear mixing, to encapsulate healing agents, including monomers and initiators, within a self-contained microcapsule system. These components are either contained within the core and shell of the same capsule, arranged in layers to form multilayered microcapsules [72], or encapsulated in smaller spheres stored within larger spheres to form capsules within capsules. Capsule rupture liberates healing agents, initiating polymerization upon catalyst contact sans additional chemicals. The commercialization of the self-healing technology based on microencapsulated [73] healing agents is significantly higher when compared to other methods. This is due to three reasons: firstly, there is no requirement to alter the molecular structure to incorporate polymers with self-healing properties; secondly, microencapsulation technology has advanced significantly since the 1950s; and thirdly, the process of integrating microcapsules containing healing agents into the polymer matrix can be easily achieved using existing mixing techniques. Widespread adoption of self-healing materials is essential. However, external healing systems face limitations in healing agent diversity and compatibility with polymer matrices. Constrained healing cycles, laborious pre-embedding processes, and challenges in managing compatibility and achieving controlled agent release impede widespread adoption. Consequently, internal self-healing materials have emerged as a focal area of investigation.

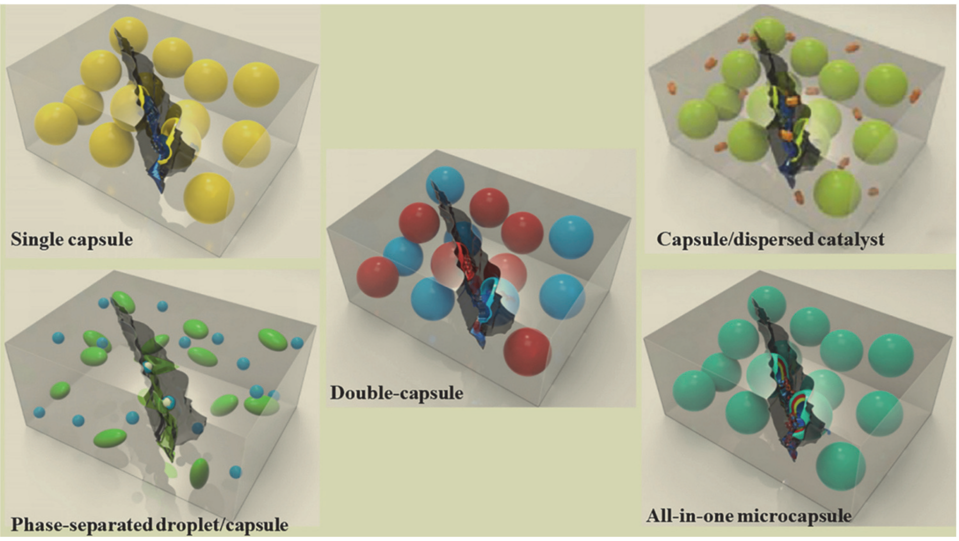


Figure 2. Various types of self-healing systems that rely on capsules. Reproduced with permission [49]. Copyright 2021, Nano Energy.

2.2. Intrinsic Self-Healing

Once the healing agent is depleted, the previously mentioned external self-healing methods no longer possess the ability to self-heal [74]. In addition, the presence of voids resulting from microcapsules or liquid-core fibers can potentially give rise to fresh flaws in the material. Consequently, researchers have developed internal self-healing [75] materials to tackle this issue [76]. When a material sustains damage, its internal self-healing electrolyte [77] utilizes its inherent self-healing capability to activate intermolecular forces [78,79], which then proceed to reassemble and heal the fractured chemical bonds. This approach enables simultaneous execution of multiple healing processes within a specific location without additional consumption of healing agents or catalysts. The reversible process can be classified into two primary categories determined by supramolecular interactions: reversible dynamic covalent bonds (Table 1) and reversible dynamic noncovalent bonds (Table 2) [80]. Reversible dynamic covalent bonds encompass a variety of chemical reactions, including Diels-Alder [81–84], imine [85–87], acylhydrazone, disulfide [88], diselenide, boronic ester [89–91], olefin metathesis [92], ester exchange, and polyurethane/urea transamination reactions. The reversible dynamic non-covalent bonds that are formed through supramolecular interactions encompass hydrogen bonds [93–95], metal coordination bonds [96], key interactions in these processes include electrostatic [97], host-guest [98], π-π stacking, ion-dipole, and hydrophobic interactions.

2.2.1. Reversible Dynamic Dovalent Bonds

Imine Bonds

Imine bonds, also called Schiff bases, possess a C=N bond length ranging from approximately 0.124 to 0.128 nm and a dipole moment of around 0.90D. Comprising two complementary elements, typically nitrogen and carbon, this chemical bond [99] displays stability and chemical properties akin to conventional covalent bonds. However, dynamic imine bonds possess distinct attributes, notably their propensity to form and break under mild conditions, facilitating swift, reversible reactions devoid of accompanying side reactions. Therefore, incorporating imine bonds into polymers may facilitate production of self-healing materials. The formation and cleavage of dynamic imine bonds occur under mild environmental conditions, obviating the necessity for high temperatures, high pressures, or strong acids. Xu et al. [100] proposed a novel design for a self-healing solid-state polymer electrolyte predicated on imine bonds. The electrolyte was synthesized by combining different proportions of polyethylene oxide and paraformaldehyde using a straightforward Schiff-base reaction. The crosslinking reactions of the self-healing network are illustrated in Figure 3a. The amine groups on the linear NH_2-PEG-NH_2 segments react with the aldehyde groups of terephthalaldehyde when heated, yielding a polymer structure containing imine bonds. The reversibility of imine bonds confers upon the polymer structure the ability to self-heal. When subjected to internal or external forces, the polymer promptly self-heals via reversible dynamic covalent bonds, reinstating its initial form and functionality. The reaction mechanism is depicted in Figure 3b. A notable reaction involves the condensation of amine groups on NH_2-PEG-NH_2 with the aldehyde groups of terephthalaldehyde. The presence of dynamic reversible imine bonds is responsible for the occurrence of dissociation reactions (imine hydrolysis and recombination) and coupling reactions (imine-amine exchange and imine condensation) between the primary amine groups of NH_2-PEG-NH_2 and the aldehyde groups of terephthalaldehyde, or the imine-containing polymer network. Notably, fully healed samples demonstrated excellent tensile properties, with no visible damage, indicating complete restoration of the supramolecular polymer elastomer's original integrity. This phenomenon is attributed to reversible imine bonds in the polymer network, which imparts high thermal stability and exceptional self-healing properties.

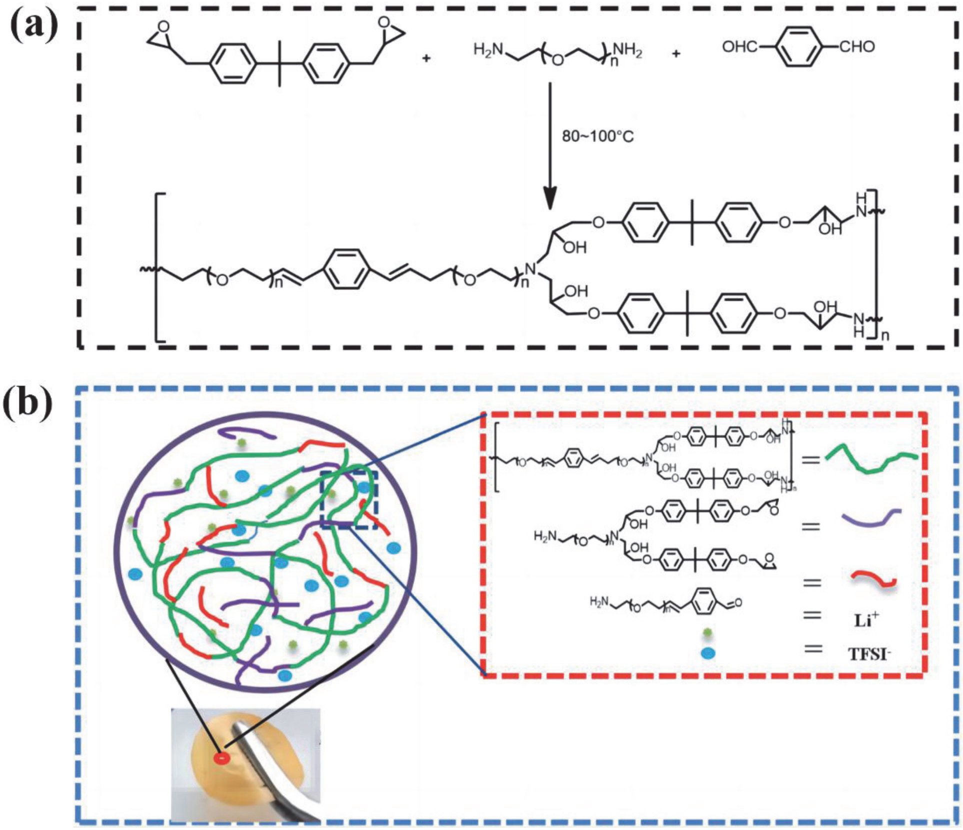


Figure 3. (**a**) A schematic illustration of the self-healing supramolecular polymer elastomer network, while (**b**) shows a mechanism diagram of the same network. Reproduced with permission [100]. Copyright 2021, RSC Advances.

Disulfide Bonds

Disulfide bonds exhibit lower bond energy than C-C bonds, rendering them susceptible to breakage and recombination. The conditions for the dynamic exchange of disulfide bonds [101–103] are gentle, allowing them to react to different stimuli. Materials derived from the reversible disulfide bond [104] exchange reactions showcase noteworthy properties such as self-healing, reshaping, and reconfiguration at low temperatures, sparking considerable interest with greater energy than non-covalent bonds, disulfide bonds enhance the mechanical properties [105] of materials. Solid-state polymer electrolytes are regarded as the most suitable for meeting the safety standards of advanced electrochemical devices, offering superior thermal and mechanical stability compared to liquid electrolytes. Nevertheless, certain fragile solid polymer electrolytes may lead to catastrophic battery malfunctions caused by short circuits. Xue et al. [106] outlined a new category within solid-phase extraction, characterized by disulfide bonds and urea groups (Figure 4). Incorporating self-healing materials [26–29] can enhance the fatigue resistance of lithium batteries, thereby extending their lifespan, stability, and reliability. Remarkably, the self-healing of this polymer is accelerated at higher temperatures. Fully rejuvenated solid polymer electrolytes retain their self-healing capabilities. Furthermore, ensuring the preservation of ionic conductivity and cycling performance in solid lithium metal/$LiFePO_4$ batteries, even after significant damage.

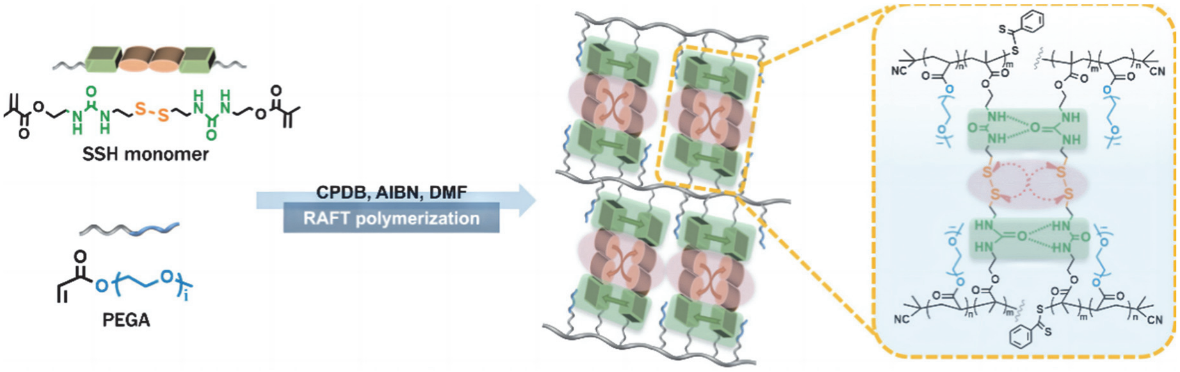


Figure 4. A schematic representation of the process by which self-healing polymer is formeddriven by the formation of disulfide bonds. Reproduced with permission. [106] Copyright 2020, American Chemical Society.

Borate Ester Bonds

Renowned for their remarkable thermodynamic stability and adaptable dynamics, borate ester bonds engage in dynamic reactions through multiple pathways [107], including hydrolysis/dehydration, uncatalyzed ester exchange with diols, and direct rearrangement between different borate compounds. Consequently, borate ester bonds emerge as a viable avenue for crafting self-healing polymers. Xue et al. [90] successfully developed a new SHPE (self-healing polymer electrolyte), employing a ring-opening reaction initiated by thermal stimulation involving thiols and epoxy groups. The resultant SHPE exhibited exceptional mechanical characteristics and interface durability. The schematic diagram of SHPE is depicted in Figure 5a,b. The integration of a cross-linked network substantially bolstered the mechanical integrity of the polymer electrolyte. The capacity of SHPE for self-healing stems from the cross-linked network's ability to undergo topological transformations via borate ester exchange reactions. Furthermore, the presence of numerous borate ester bonds within the interconnected structure, featuring vacant p orbitals, served as Lewis acid functional sites. Based on Lewis acid-base dynamics, the interaction between boron atoms and anions in the lithium salt ensures uniform the distribution of lithium ions on the lithium metal, augmenting stability at the interface between SHPE and lithium metal. In addition, diverse ester exchange reactions facilitate the formation of borate ester bonds, endowing SHPE with remarkable self-healing and recyclability properties. A Li/Li symmetric cell incorporating SHPE exhibited a consistent voltage plateau exceeding 1200 h. Additionally, the LFP/SHPE/Li cell, enriched with boron and featuring a cross-linked structure, demonstrated outstanding stability at the interface between SHPE and lithium metal.

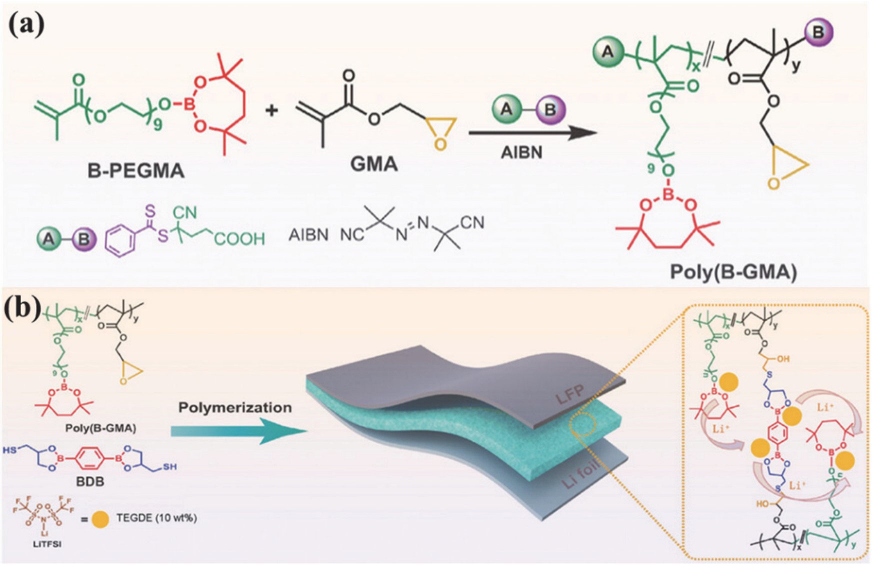


Figure 5. (**a**) Diagram illustrating the synthesis of poly (B-GMA) via RAFT polymerization. (**b**) Diagram illustrating the manufacturing process of the versatile SHPE. Reproduced with permission [90]. Copyright 2023, Wiley.

Diels-Alder Interaction

The Diels-Alder interaction, sometimes referred to as Diels-Alder cycloaddition or cycloaddition, is a chemical process in which a conjugated diene reacts with a substituted alkene to produce a substituted cyclohexene. This reaction can occur even though certain atoms in the resulting ring are not carbon atoms. Certain Diels-Alder reactions remain reversible, with ring cleavage reactions termed retro-Diels-Alder reactions [108–110]. Chen et al. [111] unveiled an innovative approach for fabricating polymer electrolyte membranes characterized by enhanced ionic conductivity, superior mechanical robustness, and intrinsic self-repair capabilities. These new polymer electrolyte membranes with self-healing properties leverage the superior conductivity of ions of polymethylmethacrylate and the inherent adaptability of polybutylacrylate, and its self-repairing capacity offered by Diels-Alder reactive groups.

The monomeric structures and synthesis methodologies of such SHP composite have been depicted in Figure 6a. Through the modification of methylmethacrylate with furfuryl alcohol, the creation of the monomer furfuryl methacrylate is achieved, serving not only as a cross-linking agent enhancing the self-healing polymer's structural integrity but also facilitating self-repair via activation of the Diels-Alder interaction. Displayed in Figure 6b is the self-repair mechanism inherent to the self-healing polymer composites. Through harnessing the thermally reversible Diels-Alder cycloaddition incorporating multifuran and maleimide functionalities, the self-healing polymer composite is synthesized. This process establishes a densely cross-linked matrix via the interaction between furan and maleimide molecules, enabling thermal reversibility owing to the reversible nature of the Diels-Alder reaction. The resulting intricately cross-linked matrix is similarly formed through the furan-maleimide Diels-Alder reaction, leveraging the reaction's reversible nature to achieve thermal reversibility. Damage to membranes resulting in a short-circuit rapidly elevates battery temperature due to significant current flow. Consequently, the ensuing heat facilitates repair of the fractures, thereby restoring the functionality of the self-healing polymer composite This inherent repair mechanism obviates the need for external substances, including catalysts, additional monomers, or targeted repair strategies at the compromised interface, enabling multiple restorations of the fractured segments of the polymer electrolyte. Thus, once assembled, the lithium-ion battery serves as an exemplary self-healing apparatus.

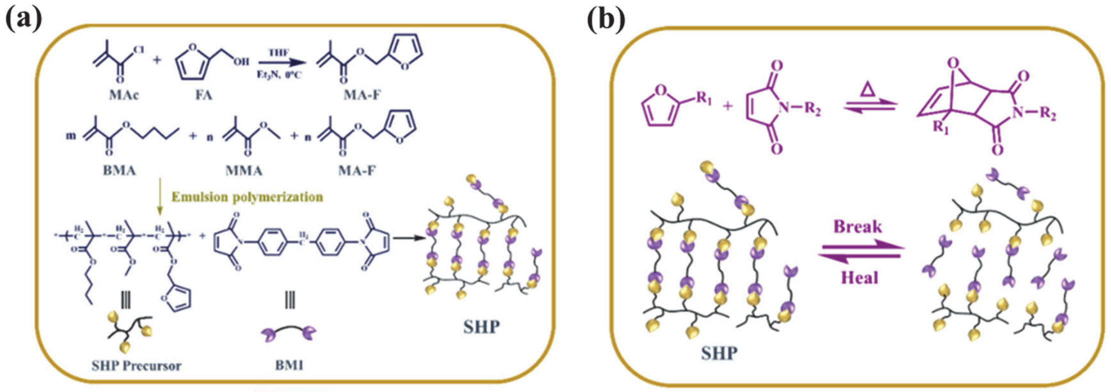


Figure 6. (**a**) Creation and chemical engineering of molecular architectures for MMA-F, precursors to self-healing polymers, and the resultant SHP composite. (**b**) Processes fundamental to the SHP composite, utilizing the thermally reversible Diels-Alder reaction. Reproduced with permission [111]. Copyright 2021, Polymers.

Olefin Metathesis Reaction

Olefin metathesis, also known as alkene metathesis, is the process in which two carbon-carbon double bonds are severed and recombined under the action of a metal catalyst. According to the change of molecular skeleton during the reaction, it can be classified into five cases: ring-opening metathesis, ring-closing metathesis, ring-opening metathesis polymerization, acyclic dienophthalic metathesis polymerization, and cross-metathesis reaction. The entire reaction process is reversible and can be used for polymer self-healing material applications.

In this context, Lu et al. [112] have introduced the inaugural instance of a self-healing polymer mediated by olefin metathesis, characterized by the reversible interchange of durable covalent carbon-carbon double bonds Figure 7. The olefin metathesis reaction stands out for its potential in this area due to its efficacy in rearranging strong C=C double bonds at room temperature. The polymer demonstrates efficient healing capabilities under gentle conditions. With moderate pressure, it can undergo effective self-repair in atmospheric conditions, at room or even below-room temperatures. This approach is streamlined, effective, and holds potential for widespread application across a spectrum of olefin-based polymers, including polyisoprene, butyl rubber, and polynorbornene, all of which feature double bonds amenable to metathesis reactions. The resilience of carbon-carbon double bonds augments the prospect of crafting resilient self-healing polymers.

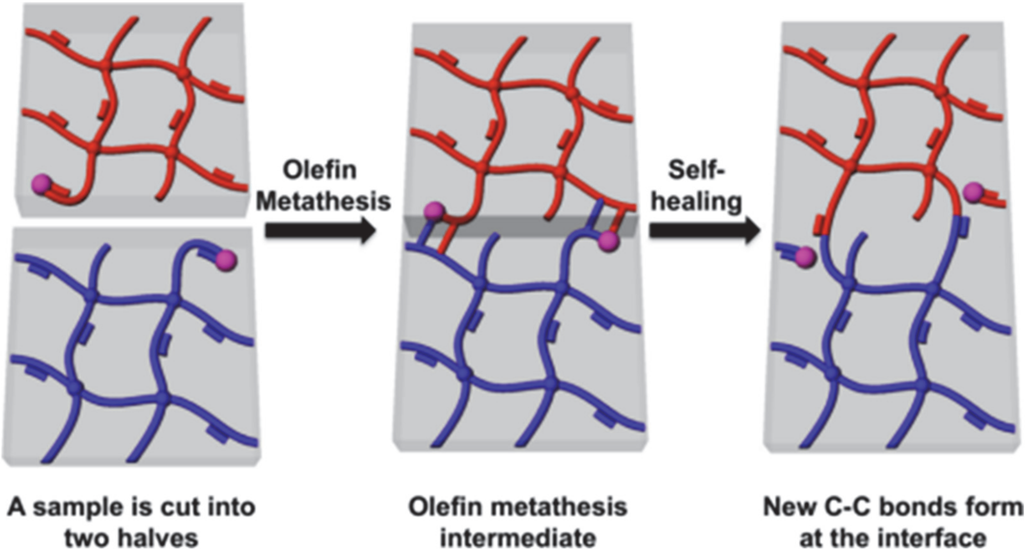


Figure 7. Implementing olefin metathesis for efficient polymer restoration through the reversible modification of strong carbon-carbon double bonds. Reproduced with permission [112]. Copyright 2012, J. Am. Chem. Soc.

2.2.2. Reversible Dynamic Non-Covalent Bonds

Hydrogen Bonds

Hydrogen bonds, renowned for their reversibility, directionality, and sensitivity, are extensively studied supramolecular interactions, frequently employed in developing self-healing systems [113,114]. This approach facilitates the spontaneous migration of polymer chains in the affected region, restoring the hydrogen-bond network to its pre-damaged state. Xue et al. [115] proposed a conceptual framework to tackle these concerns. The polymer electrolyte comprises a physically cross-linked network featuring brush-shaped polyethylene glycol chains embedded in urea-pyrimidinone. The synthesis and mechanism of the self-healing copolymer are elucidated in Figure 8a,b. The monomer employed for high-performance lithium-ion batteries is (2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)methyl acrylate), in conjunction with poly(ethylene glycol) methyl ether methacrylate. This innovative polymer electrolyte exhibits flexibility, enabling rapid intrinsic self-healing and high extensibility. Under ambient conditions, it autonomously repairs cuts within two hours and stretches over 20 times its original length without fracturing. Moreover, this novel polymer electrolyte showcases exceptional stability at the electrode interface, yielding a high-performance battery characterized by consistent reversible electrochemical reactions and cycling.

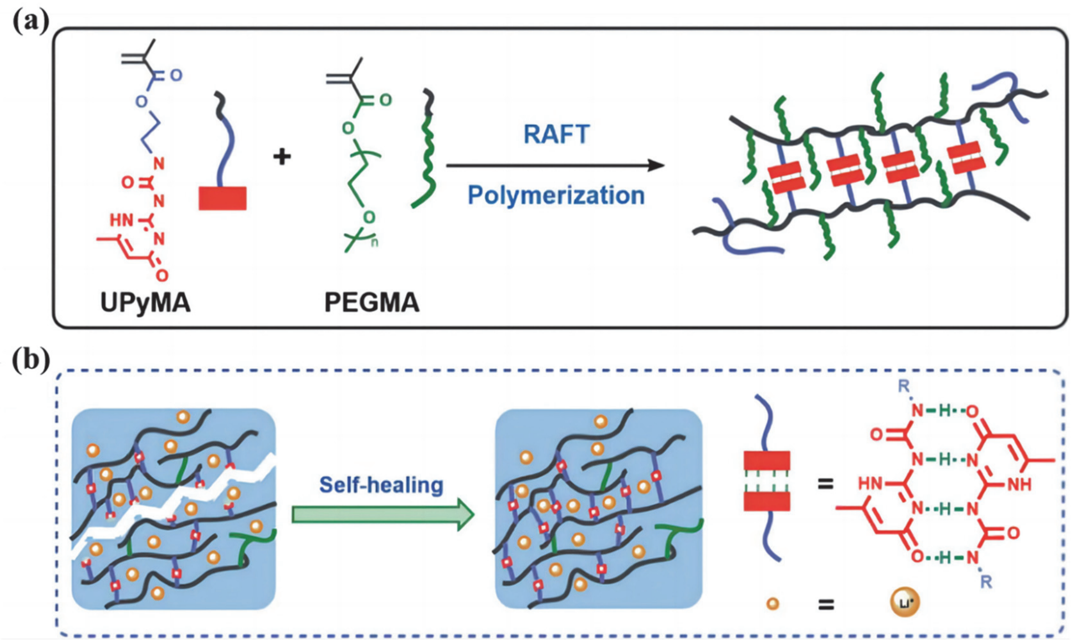


Figure 8. (**a**) Synthesis of copolymers (**b**) illustrates the formation and self-healing mechanism of self-healing polymer electrolyte. Reprinted with the authorization [115]. Copyright 2018, Royal Society of Chemistry.

Ion–Dipole Interaction

The term "ion-dipole interaction" was introduced in 2016 to describe the attractive interaction between ions and a polar substance, where the ions carry a positive or negative charge. Investigations have illuminated that stretchable solid polymer electrolytes, which are created using ion-dipole interactions, manifest remarkable Young's modulus, mechanical strength, and ultimate tensile strain energy under ambient conditions. Furthermore, these materials exhibit complete recuperation within a 24-h timeframe subsequent to mechanical deformation.

Solid-state polymer electrolytes have gained attention for their use in dependable and portable electronic gadgets due to their exceptional flexibility and self-healing properties. In 2022, Yang et al. engineered flexible, fire-resistant, and damage-resistant self-healing solid polymer electrolytes through the integration of hexa-armed poly(N,N,N-trimethyl-((2-(dimethylamino)ethyl)methacrylate)-7-propyl)-tris(trifluoromethanesulfonyl)imide), imidazolium-based ionic liquid, as well as Lithium bis(trifluoromethanesulphonyl)imide [116]. A biphasic polymerized ionic liquid was synthesized by infusing an ionic liquid along with lithium salt into the interstices of polymer chains (Figure 9). A self-healing polymerized ionic liquid was formulated by amalgamating an imidazole-based ionic liquid and ethyl acrylate via co-polymerization, succeeded by substitution of the Br^{-} counter-anions with volumetrically larger anions (Tf^{-}, FSI^{-}, as well as $TFSI^{-}$). Such combination of polymerized ionic liquid-solid state polymer electrolytes and $TFSI^{-}$ exhibited full recovery of damage following exposure to a temperature of 55 °C for a duration of 7.5 h. The hexa-armed cationic polymer ionic liquids feature a distinctive architecture comprising multiple arms and charged nuclei, augmenting ion attraction and van der Waals forces within the polymer domain. Consequently, DPIL-6-derived solid polymer electrolytes exhibit exceptional self-healing properties.

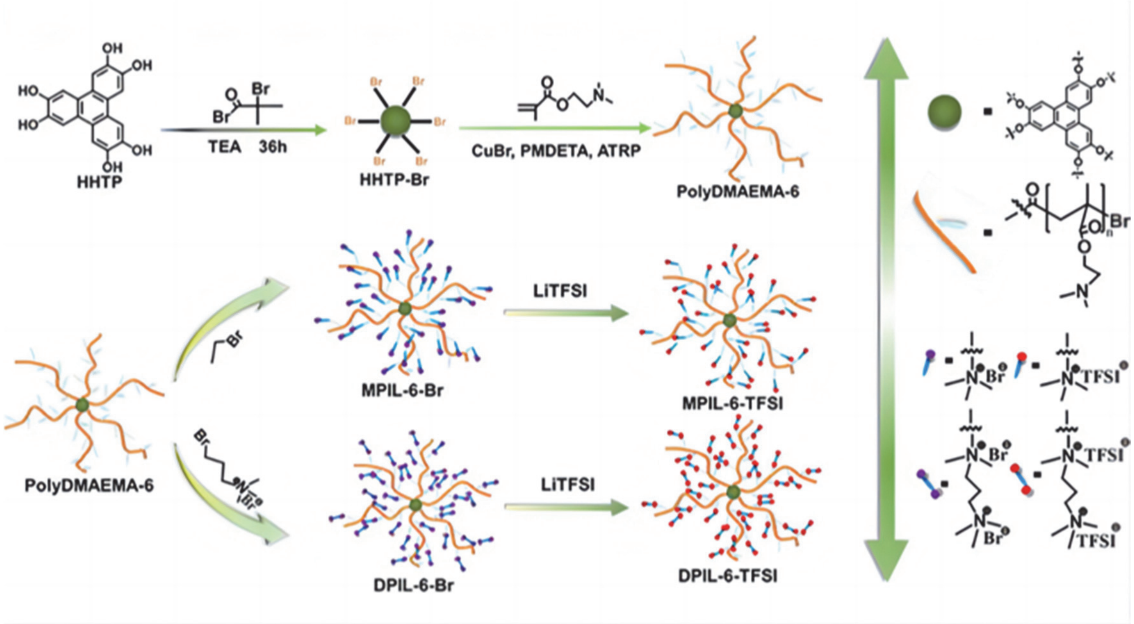


Figure 9. Synthetic approach for the six-arm MPIL-6 and DPIL-6. Reproduced with permission [116]. Copyright 2022, Chemical Engineering Journal.

Metal Coordination Bonds

Coordination compounds, also known as complexes, are formed when metal ions or atoms (referred to as central ions or atoms) combine with specific molecules or ions (referred to as ligands or coordinating entities) through coordination bonds [117]. Coordination complexes can be formed by metal ions and suitable ligands, including terminal or pendant groups, which connect polymer chains. Incorporating diverse metal ions and ligands allows for the ability to reverse and adjust the strength of metal-ligand coordination, resulting in dynamic mechanical properties that can be modified. The greater the electron-donating capacity of ligands, the higher the strength of the coordination bonds in the complex, resulting in increased stability of the complex. The metal-ligand coordination breaks apart when subjected to mechanical force, and its subsequent reorganization following the removal of the force results in self-healing. Temperature fluctuations or exposure to electromagnetic radiation can induce the rearrangement of metal-ligand coordination.

Despite significant strides in self-healing material advancement leveraging metal-ligand coordination, its application in self-repairing electronics remains relatively unexplored. In 2016, Bao et al. [118] achieved a breakthrough in self-healing dielectric elastomers by embedding metal-ligand coordination as cross-linking motifs within a nonpolar polydimethylsiloxane polymer. Employing metal-ligand interactions involving Fe^{2+} and Zn^{2+} ions coordinated with pyridine, the researchers (Figure 10) introduced dynamic metal-ligand coordination bonds possessing dual strength into the backbone of soft polydimethylsiloxane polymers. This strategic integration facilitated both exceptional stretchability and inherent self-healing capacity. The resultant materials showcased outstanding electrochemical resilience.

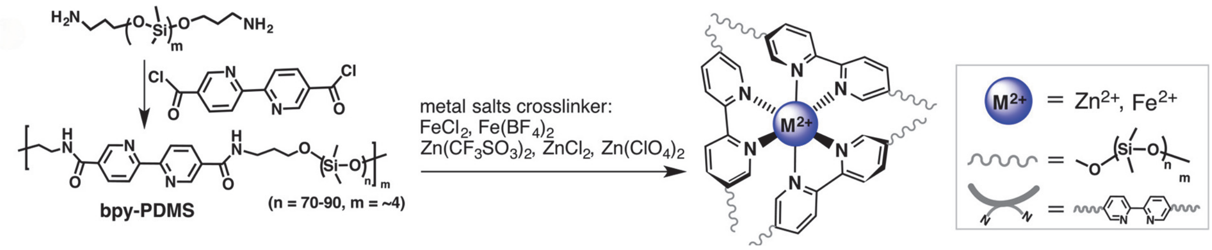


Figure 10. Process of creating self-healing polymers through the cross-linking of metal salts. Reproduced with permission [118]. Copyright 2016, Journal of the American Chemical Society.

Electrostatic Interaction

Electrostatic interaction is the force of attraction or repulsion involving ions formed when atoms or groups gain or lose electrons. The electrostatic interactions between ions can result in either repulsion or attraction, which allows materials to possess self-healing properties based on these interactions.

In September 2019, Feng et al. [119] devised a versatile gel polymer consisting of an ionic liquid and dynamic covalent bonds via a one-pot polymerization method, as illustrated in Figure 11. This gel polymer exhibits inherent self-healing capabilities. The prepared gel polymer showcased exceptional stretchability and high ion conductivity owing to reversible electrostatic interactions involving imidazole cations and boron esters. Electrostatic interactions between imidazolium cations and sulfonate anions, coupled with reversible dynamic covalent bonding, enhance polymer chain flexibility, thereby enabling remarkable self-healing properties. The presence of sulfonate anions in the gel polymer specifically curtailed the movement of negatively charged polysulfides, thereby facilitating the migration of positively charged lithium ions within lithium-sulfur battery systems. Consequently, this investigation introduces novel avenues to advance current progress.

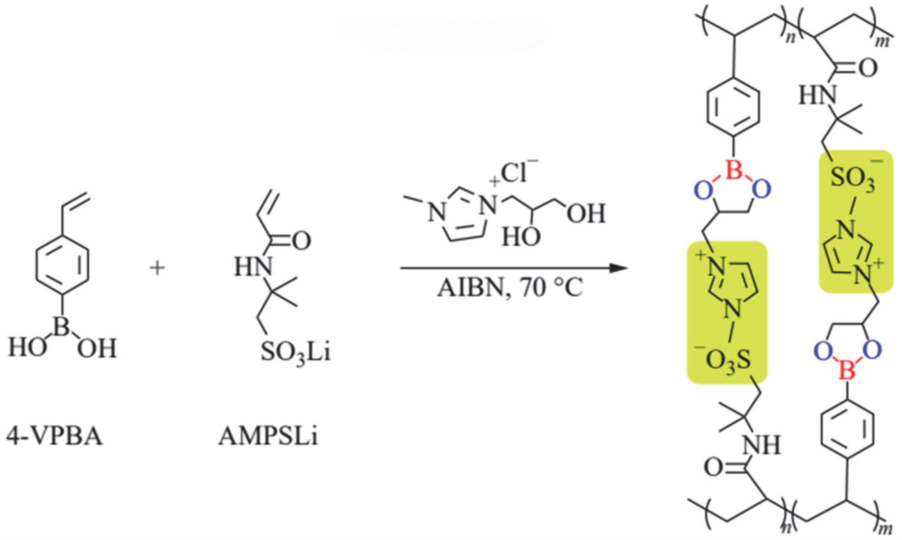


Figure 11. Synthetic approach for the gel polymer. Reproduced with permission [119]. Copyright 2019, Chinese Journal of Polymer Science.

Supramolecular host polymers comprise organized assemblies linked by non-covalent bonds, encompassing multiple hydrogen bonds, metal coordination, electrostatic interactions, and π-π stacking interactions. These non-covalent interactions confer upon self-healing polymers the capability to undergo self-healing owing to their dynamic and reversible nature. As depicted in Figure 12, the initial one is restored by rearranging the inner framework via the reversible linkage, which constitutes the primary self-healing approach deliberated within this manuscript; the latter is primarily fixed through the introduction of remedial substances, such as pre-inserted miniature containers, which primarily activate following the penetration of the additives [120–122]. Nevertheless, self-healing polymers reliant on supramolecular interactions encounter several challenges: the inclusion of weak and reversible non-covalent bonds often resulting in significant reduction in self-healing polymers rigidity; the integration of supramolecular interactions, particularly hierarchical ones involving multi-component systems, frequently necessitates intricate synthesis methodologies, thereby escalating self-healing polymers production costs; numerous self-healing polymers require the involvement or incorporation of external solvents to facilitate the recognition process of supramolecular interactions. Therefore, further advancements are necessary to optimize self-healing capabilities in lithium batteries.

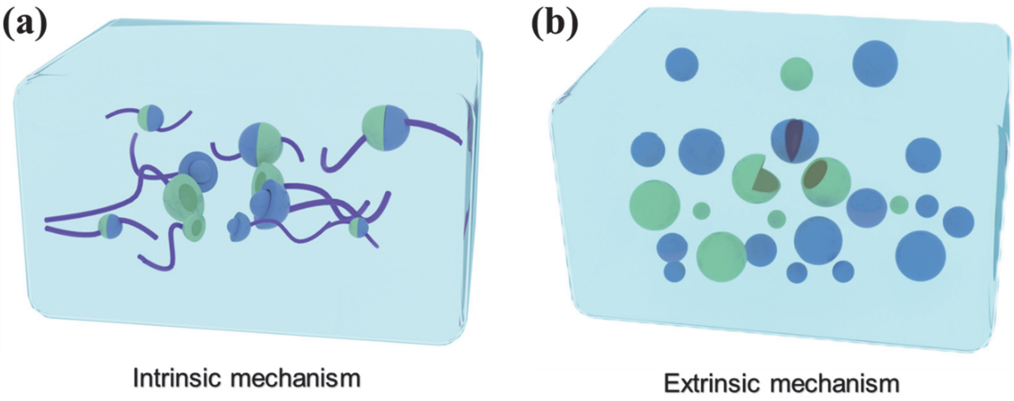


Figure 12. Schematic diagram of two types of self-healing mechanisms.

Table 1. Reversible Dynamic Covalent Bonds.

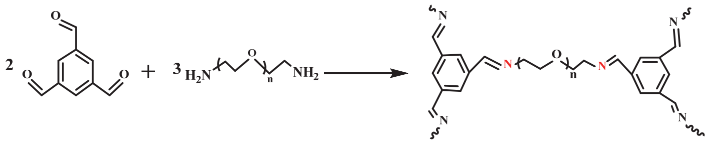
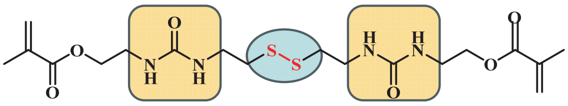
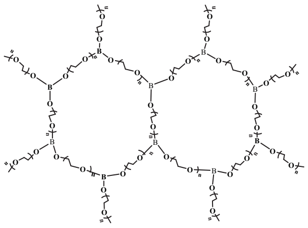
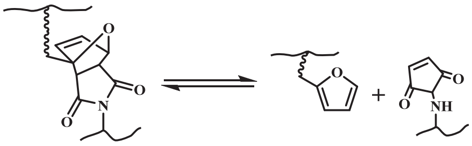
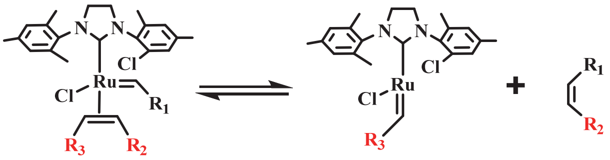
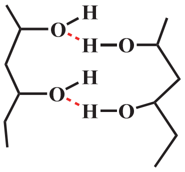
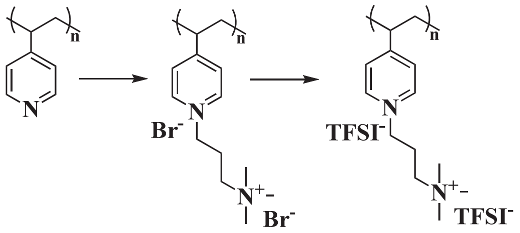
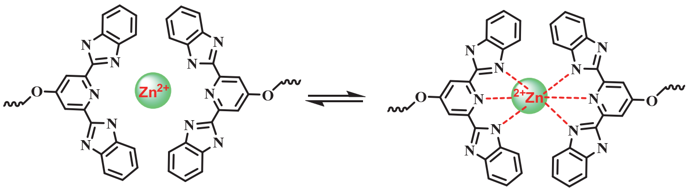
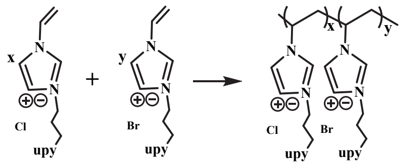
Entry	Healing Mechanism	Self-Healing Component	Healing Condition	Ref.
1	Imine bond		RT, 10 min 50 °C, 5 min	[123]
2	Di-sulfide bond		RT, 30 min	[106]
3	Boronic Ester bond		60 °C, 34 h	[124]
4	Diels-Alder reaction		110 °C, 20 min	[112]
5	Olefin Metathesis reaction		RT, 6 h	[92]

Table 2. Reversible Dynamic Non-covalent bonds.

Entry	Healing Mechanism	Self-Healing Component	Healing Condition	Ref.
1	H-bonds		RT, 5 min	[34]
2	Ionic interaction		RT, 10 min	[125]
3	Metal coordination bonds		Light, 30 s	[118]
4	Electrostatic interaction		55 °C, 1 h	[97]

3. Applications of Self-Healing Polymers

3.1. Self-Healing Electrolyte

3.1.1. Polyethylene Glycol-Based Self-Healing Polymer Electrolyte

Polyethylene glycol-based solid polymer electrolytes are among the earliest and extensively studied systems among various polymer electrolytes. They offer several advantages, including low density, excellent viscoelasticity, and facile film formation. Polyethylene glycol is a polyether characterized by the chemical structure $H\text{-}(O\text{-}CH_2\text{-}CH_2)_n\text{-}OH$. Polyethylene glycol can undergo polymerization via cationic or anionic ring-opening of ethylene oxide which is driven by a catalyst. Polyethylene glycol-based solid polymer electrolytes were among the pioneering subjects of inquiry in the field. In 1973, Wright et al. discovered that doping polyethylene glycol with alkali metal salts could serve as an ion conductor. Polyethylene glycol's exceptional compatibility with lithium salts has spurred extensive research and application in lithium-ion batteries. Lithium ions' continual coordination and decoordination with the ether oxygen atoms along the PEO chain facilitate ion movement as the chain segments reorient.

In 2023, Xie et al. [126] introduced a novel cross-linked network SHPE, synthesized via thiol-ene click polymerization. This process entailed the amalgamation of poly (ethylene glycol) diacrylate, ((((Disulfanediylbis(4,1-Phenylene))Bis(Azanediyl))Bis(Carbonyl))Bis(Azanediyl))Bis(Ethane-2,1-Diyl)Bis(2-Methylacrylate), 3,6-dioxa-1,8-octanedithiol, and pen-taerythritoltetra to form a crosslinked polymer matrix, as depicted in Figure 13a. The infrared spectrum of the raw materials (Figure 13b), displays the 1650 cm^{-2} absorption bands in the poly (ethylene glycol) diacrylate, signifying C=C bond stretching vibrations. Likewise, the 2553 cm^{-2} absorption peaks in the pen-taerythritoltetra and 3,6-dioxa-1,8-octanedithiol spectra represent S-H bond stretching vibrations. The absence of these bands in the SHPE spectrum confirms the completion of thiol ene click polymerization and the successful formation of a cross-linked network polymer. The assembled Li/SHPE/$LiFePO_4$ battery exhibits consistent cycling performance and remarkable tolerance to high charging and discharging rates. In addition, the Li/LFP battery, equipped with SHPE, demonstrates nearly identical ion conductivity and cycling performance restoration, as evidenced in Figure 13c.The researchers assessed the self-healing capability of the electrolyte via splitting a 900 µm thick electrolyte membrane into two (as depicted in Figure 13d) and conducting healing tests by rejoining the severed surfaces. Within 3 s, the two components could autonomously re-establish connection without external stimuli. After 24 h, the interface of the healed electrolyte remained visibly intact and could support a weight of 100 g without detaching, as depicted in Figure 13e. Incorporating the ionic liquid resulted in a simultaneous enhancement in ion conductivity and flame retardancy. SHPE melted within 3 s of exposure to a flame but did not combust. These findings suggest that SHPE can potentially reduce the risk of fires stemming from battery short circuits, thereby enhancing the safety of lithium-ion batteries (Figure 13f). The remarkable self-healing capacity of SHPE arises from the synergistic interplay involving dynamic disulfide bonds and hydrogen bonds in the poly(ethylene glycol) diacrylate backbone.

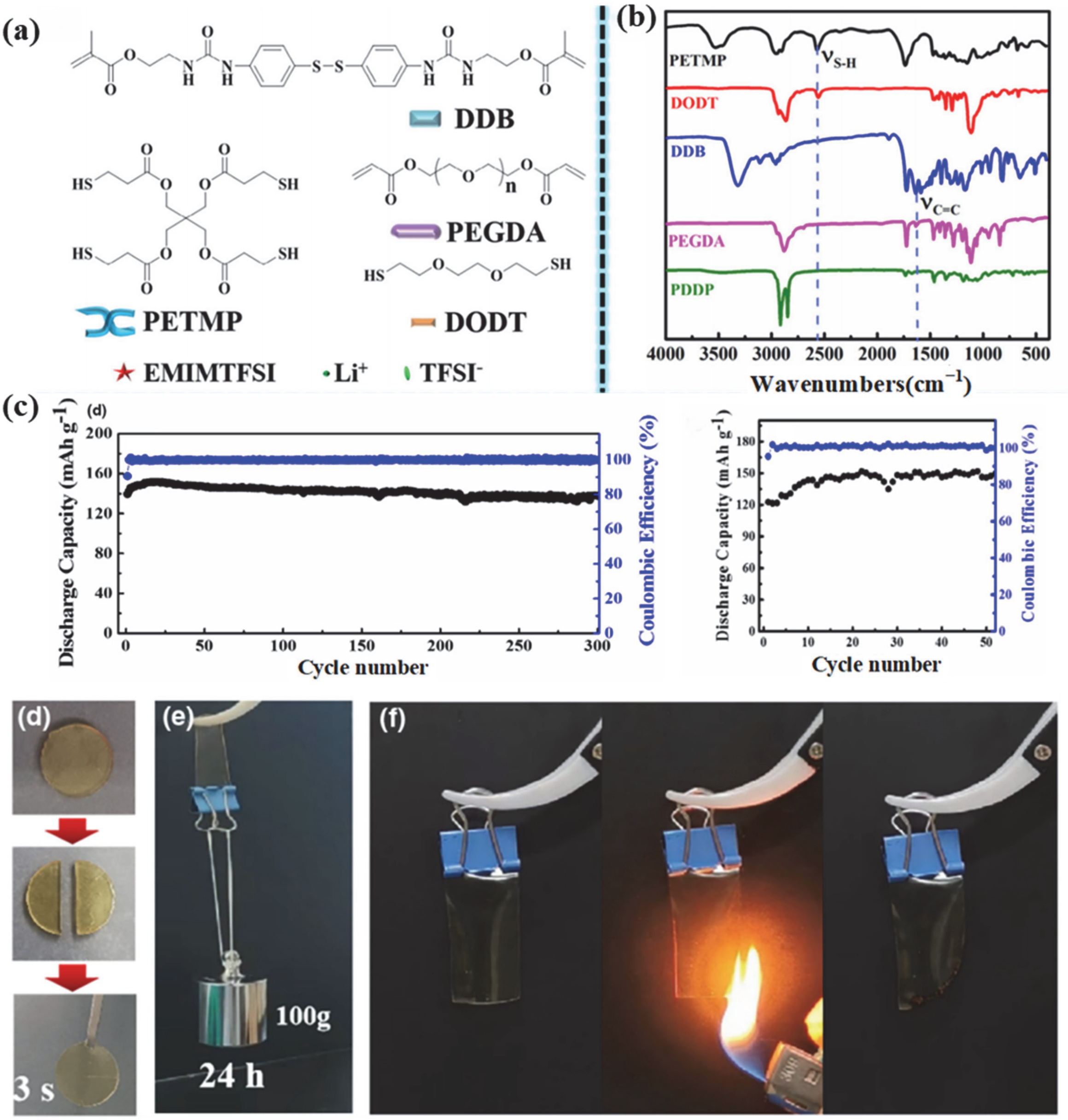


Figure 13. (**a**) Chemical structures of polyethylene Glycol Diacrylate, Pentaerythritol Tetraacrylate,1,2-Dithiolane-3-Pentanediol, and Dibenzoyl Peroxide. (**b**) Far-infrared spectra of different raw materials in self-healing electrolytes. (**c**) Long-term performance of Li/SHPE/LFP cells was evaluated at discharge rates of 0.2C and 0.1C (**d**) Photographs depicting the progression of the healing process of SHPE-5 at a temperature of 28 °C. (**e**) Regenerative capabilities of SHPE-5 are evident in its ability to support a weight of 100 g during the healing process. (**f**) Procedure for making the SHPE-5 membrane flame-retardant. Reproduced with permission [126], Copyright 2023, John Wiley & Sons.

3.1.2. Polyurethane-Based Self-Healing Polymer Electrolytes

Since the discovery of the first polymer, these versatile compounds have pervaded every facet of human life. Polyurethane has garnered considerable attention owing to its outstanding performance. Polyurethane is a broad term used to describe a group of polymers with urethane bonds in their main structure. These polymers are composed of flexible segments, also known as soft segments, which have a glass transition temperature below room temperature. They also contain rigid or hard segments, which have a glass transition temperature above room temperature. The flexible and rigid segments are linked by urethane bonds, exhibiting thermodynamic incompatibility. In the condensed state, the hard segments naturally aggregate and embed within the soft segment phase, resulting in microphase separation. The lower glass transition temperature of the soft phase enables polyurethane to undergo reversible deformation. while the hard phase, rich in hydrogen bonds, ensures robust binding, maintaining polyurethane's shape. Polyurethane's unique composition endows it with exceptional durability and tear resistance compared to other materials. Its distinct chemical makeup imparts exceptional water and degradation resistance and compatibility with living organisms, rendering it highly promising for a myriad of applications including packaging, coatings, biomedical engineering, flexible sensors, and beyond. Nevertheless, even minor damage to polyurethane can significantly diminish its lifespan, despite its extensive utility. In response, self-healing polyurethanes have emerged as a solution, garnering significant interest for their ability to extend material lifespan and minimize resource consumption. Self-healing polyurethane, akin to human skin, autonomously repairs itself without external triggers. However, in various applications, multifunctional self-healing polyurethane is essential to provide flexibility to flexible sensors and enable adaptation to complex surfaces and deformable environments, meeting specific usage requirements in diverse scenarios.

Guo et al. [127] devised a solid polymer electrolyte boasting swift self-healing capabilities, stable equilibrium between rigidity and flexibility, and high ionic conductivity. This electrolyte aims to regulate the electrochemical behavior of lithium metal, ensuring the safety and flexibility of solid lithium metal batteries. Elastic thermoplastic polyurethane was employed as a physical cross-linker to enhance the mechanical strength of solid-state hybrid polymer electrolyte. Molecular intra-hydrogen bonding between urea and ester groups, cross-linked with a supramolecular scaffold of polyethylene glycol groups, is depicted in Figure 14a. Amino-terminated polyethylene glycol was chosen for its dynamic hydrogen bonds, facilitating rapid self-healing and contributing to a highly polar structure. Amino-terminated polyethylene glycol was chosen for its dynamic hydrogen bonds, facilitating rapid self-healing and contributing to a highly polar structure. Incorporating lithium-ion salts significantly improved ionic conductivity. The regulation of this solid-state hybrid polymer electrolyte enhanced stability and efficacy of the lithium metal anode's coating and stripping behavior. Consequently, employing the distinctive supramolecular solid-state hybrid polymer electrolyte in full-solid lithium metal batteries resulted in enhanced cycle stability and flexibility under free bending. Swift self-healing of polymer chains primarily arises from dynamic and reversible intermolecular or intramolecular hydrogen bonds among numerous urea and ester groups. Electrostatic attraction between ions in the lithium salt also contributes to rapid self-healing, as depicted in Figure 14b. The exceptional attributes of the designed supramolecular solid polymer electrolyte render it an optimal choice for enhancing electrochemical efficiency for lithium metal batteries, particularly in Li/LFP and Li/NCM full cells. Adjustable self-healing solid polymer electrolytes in solid lithium metal battery fabrication yields exceptional flexibility and consistent cycling performance.

Presently, a substantial body of research exists on polymer electrolytes facilitating single-ion conduction. These electrolytes incorporate anions such as phosphate, carboxylate acid, and sulfate, chemically bonded to the polymer backbone comprising polyether, silanes, acrylic, methacrylic, and polyethylene oxide. The sole mobile species in these electrolytes are the Li^+ ions. However, despite exhibiting an almost perfect Li^+ transference number, the majority of these solid ionic-conducting polymer electrolytes demonstrate low electrical conductivity ranging from below 10^{-8} to 10^{-7} S cm^{-1} at ambient temperature. This limitation can be mitigated by incorporating weakly coordinating anionic species such as bis(trifluoromethanesulfonyl)imide and bis-(fluorosulfonyl)imide within the polymer backbone or as pendant groups. This enhancement is ascribed to the inadequate coordination between Li^+ and the counter-anions. Modifying the structure of solid ionic-conducting polymer electrolytes through random, cross-linking, and block co-polymerization techniques with various neutral polymers offers an alternative avenue for enhancing the conductivity value of solid ionic-conducting polymer electrolytes.

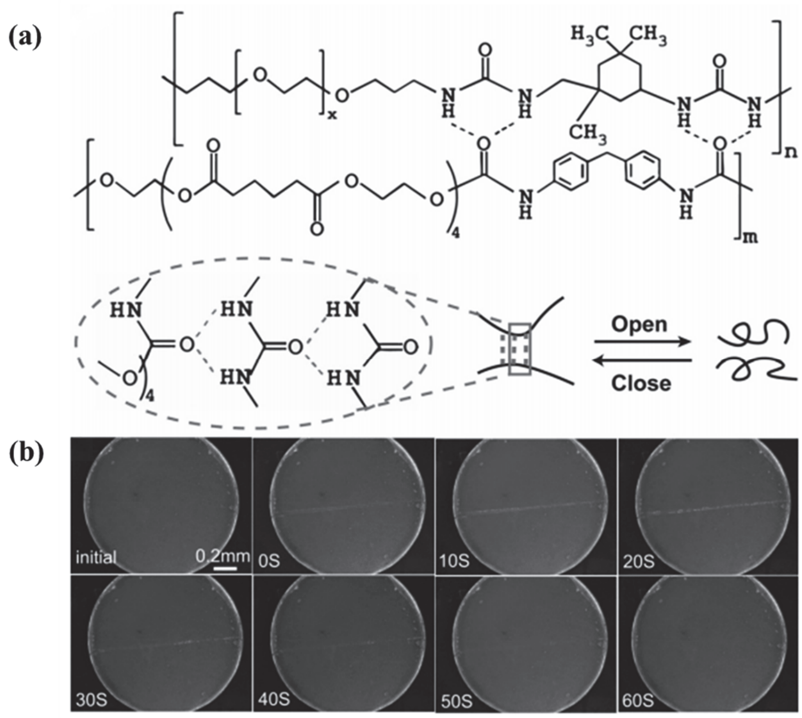


Figure 14. (**a**) Molecular arrangement and fluid hydrogen bonding of self-healing polymers. (**b**) Regenerative process of self-healing polyethylene following a cut. Self-healing polymer elastomer demonstrated the ability to heal the cut in under 60 s. Reproduced with permission [127], Copyright 2023, John Wiley & Sons.

In efforts to enhance the conductivity of polymer electrolytes, Kim et al. [128] introduced a novel random copolymer termed polyethylene-co-propylene lithium (fluorosulfonyl) imide, incorporating the acrylate (fluorosulfonyl) imide anion. This solvent-free and plasticizer-free solid ionic-conducting polymer electrolytes, based on PEALiFSI and, demonstrates remarkably high electrical conductivity coupled with self-healing capability. PEALiFSI exhibits exceptional characteristics, including high lithium-ion transport, thermal stability, fire resistance, and electrochemical cycle durability. Characterization plots depict the performance of self-healed electrolyte-based $LiFePO_4$/PEALiFSI/Li in half-cell and full cell configurations at various C rates, as illustrated in Figure 15a,c. Figure 15b illustrates changes in discharge specific capacity and coulombic effectiveness with increasing cycles at 0.1C. The discharge-specific capacity ratios of the self-healed PEALiFSI electrolyte-based half-cell were 159, 132, and 85 milliampere-hours per gram, respectively, at 0.1, 0.5, and 1C, respectively. The cyclic voltammetry plots exhibited minimal overpotential across all current rates, suggesting excellent electrolyte reversibility. Figure 15d demonstrates the changes in discharge specific capacity and coulombic effectiveness with increasing cycles up to 500 cycles. Additionally, it offers remarkable energy storage capacity and excellent capacity retention in an all-solid-state lithium-ion battery. Figure 15e depicts the reaction scheme for the synthesis of PEASF. These findings underscore PEALiFSI as a promising solid ionic-conducting polymer electrolyte capable of fostering practical lithium-ion batteries with enhanced security and stability.

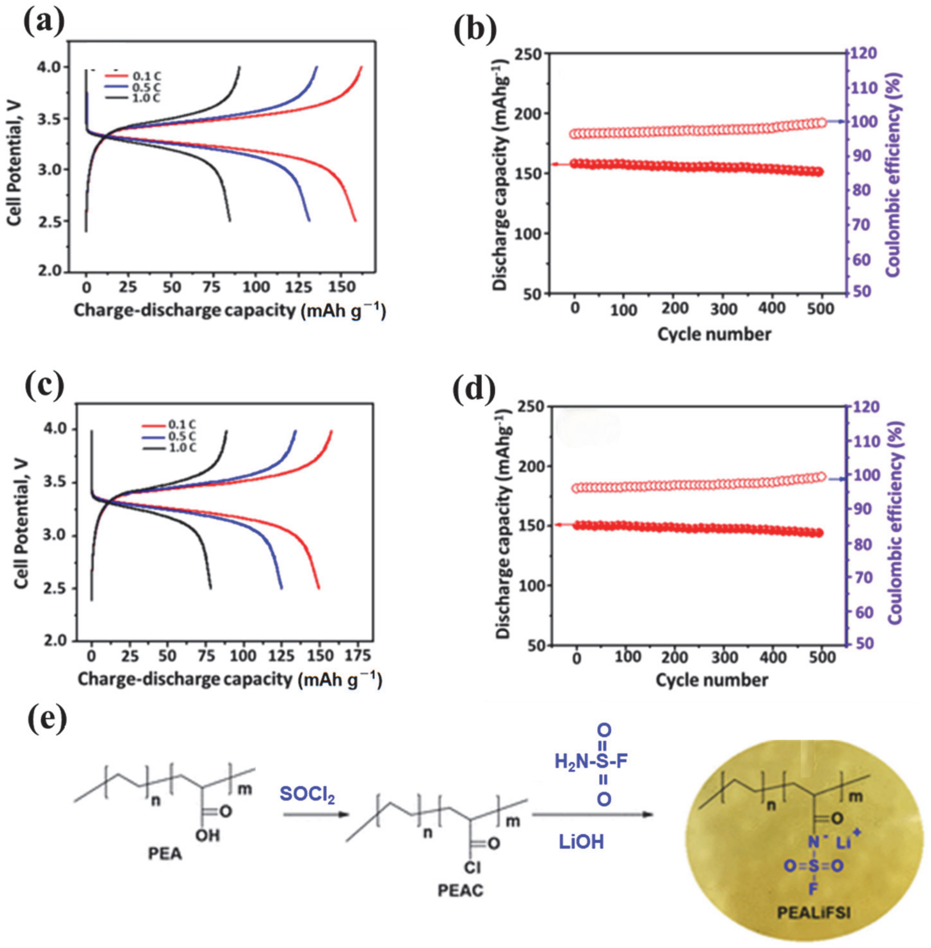


Figure 15. (**a**) CD plots depicting the performance of the half-cell at various C rates: 0.1, 0.5, and 1C. (**b**) Graphs depicting the trends of discharge specific capacity and coulombic efficiency of the half-cell over several charge-discharge cycles at a rate of 0.1C. (**c**) CD plots were generated for a complete cell with a self-healing electrolyte comprising LiFePO4, PEALiFSI, and graphite. The cell was analyzed at various C rates. (**d**) The charts display the discharge specific capacity and coulombic efficiency metrics of the full cell during CD cycles at a rate of 0.1C. (**e**) Schematic representation of the synthesis process for PEASF. Reproduction is authorized [128], Copyright 2019, Applied Materials.

3.1.3. Poly(Vinylidene Fluoride)-Based Self-Healing Polymer Electrolytes

Research on poly(vinylidene fluoride)-based electrolytes within lithium-ion batteries has been extensive, owing to poly(vinylidene fluoride)'s exceptional formability, high dielectric constant, elevated glass transition temperature, and presence of electron-withdrawing solid groups. Wang et al. [129] recommend embedding polyethylene glycol chains with urea-pyrimidinone into a matrix reinforced with PVDF-HFP (as depicted in Figure 16a) and polyethylene oxide to establish an inorganic cross-linked network. Urea-pyrimidinone groups are appended to the copolymer chains as terminal groups. The material's inherent hydrogen bonding facilitates its return to its original state post-damage under appropriate thermal or temporal conditions, preserving its mechanical and thermal characteristics. To assess the self-healing efficiency of this thin film, researchers simulated operational damage by incising the surface of the cross-linked network sample with a blade. Subsequently, they monitored the self-repair process under a 100x magnification optical microscope, with outcomes presented in Figure 16b. This innovative gel polymer electrolyte demonstrates significant flexibility, enhanced mechanical strength, high ion conductivity, and the ability for autonomous repair without external intervention.

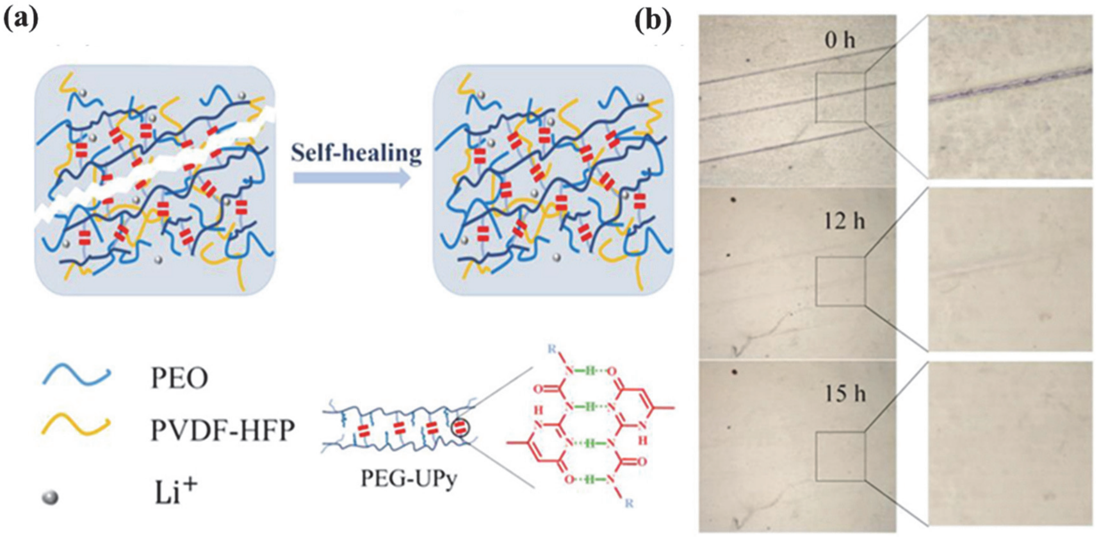


Figure 16. (**a**) Diagram depicting the formation of the PP-PU network and its self-healing mechanism across the cut interface. (**b**) Optical imagery capturing the self-healing process of cross-linked network under ambient conditions. Reproduction authorized [129], Copyright 2019, ACS Applied Energy Materials.

3.1.4. Siloxane Based Self-Healing Electrolyte

Siloxane materials are polymers that have a main chain structure consisting of Si-O-Si, with silicon atoms bonded to organic groups including methyl, phenyl, thiol, amine, or epoxy groups. Due to their distinctive organic-inorganic hybrid structure, siloxane materials possess exceptional properties, including resistance to aging, high and low temperatures, low surface energy, hydrophobicity, electrical insulation, and physiological inertness. They are extensively utilized in sectors such as construction materials, electronic packaging, aerospace, and transportation. However, polymer materials, particularly those with limited mechanical resilience like siloxane, are susceptible to irreversible micro-damage caused by external stresses during the manufacturing and utilization processes. This scenario significantly affects the material's durability and safety, leading to considerable resource waste and environmental pollution. Integration of sacrificial bonds through successive polymerizations within a trifurcated molecular network has yielded exceptionally robust elastomers with increased stretchability. However, initial stretching causes "irreversible" damage due to the rupture of these sacrificial networks. Introducing a reversible mechanism for energy dissipation is critical for restoring mechanical properties.

The development of rigid materials capable of rapid self-healing remains challenging, mainly due to the sluggish movement of molecular chains hindering rapid healing processes. In addressing this challenge, Bao et al. [130] investigated self-healing siloxane materials relying on metal-ligand interactions. To create materials that possess characteristics resembling those of biological muscles, including durability, flexibility, and the ability to self-heal, the researchers combined polydimethylsiloxane with a structure consisting of 2,6-pyridinedicarboxamide and $FeCl_3$. By exploiting varying bond strengths in the interactions between ligands and Fe^{3+}, ions, the researchers developed a remarkably flexible and self-healing organic silicon elastomer material dubbed FeHpdca-polydimethylsiloxane (depicted in Figure 17a). Consequently, the elastomer demonstrates exceptional stretchability, stretching up to about 45 times its initial length and then returning to its original shape when the strain is released. The material's exceptional self-healing performance, even at −20 °C, is attributed to the dynamic nature of the metal-ligand interactions, which do not require an external energy supply. In addition, the elastomer film boasts a high dielectric constant and rapid recovery at low tensile strains while minimizing hysteresis. When subjected to high pressure, the elastomer undergoes localized expansion without electrical breakdown, enabling self-healing as depicted in Figure 17b, rendering it suitable for artificial muscles. The urgent and challenging task is to devise a rational design that effectively imparts autonomous, rapid, and efficient self-healing properties to a microphase separation structure, enabling its effective operation in harsh environments.

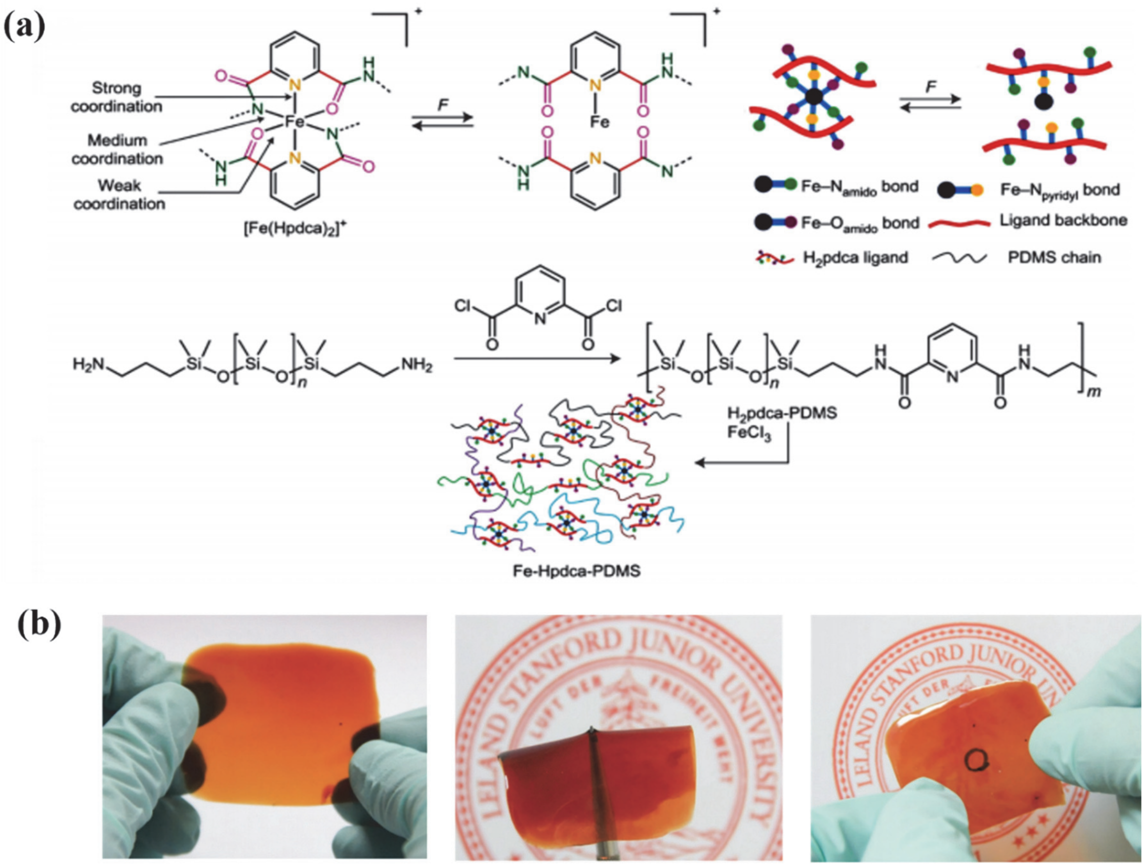


Figure 17. (**a**) Schematic illustration of stress fracture mechanism of Fe(III)-amide coordination interaction and synthesis of the Fe-Hpdca-polydimethylsiloxane; (**b**) Self-healing artificial muscle fabricated from a Fe-Hpdca-polydimethylsiloxane film. Reproduced with permission [130], Copyright 2016, Springer Nature.

To address the aforementioned challenge, Bao et al. [131] introduced various hydrogen donors and acceptors to establish both strong and weak hydrogen bonds, thereby enhancing control over the system. They reported the development of a self-healing electronic skin composed of a resilient self-healing polydimethylsiloxane elastomer and liquid metal EGaIn. The polydimethylsiloxane oligomer (polydimethylsiloxane-MPUx-IU$_{1-x}$) undergoes copolymerization with HN$_2$-PDMS-NH$_2$, 4,4’-methylenediphenyl diisocyanate (MP unit), and isophorone diisocyanate unit (IU unit) to yield a cross-linked elastomer that exhibits both strong and weak hydrogen bonding. The chemical structure of polydimethylsiloxane–MPUx–IU$_{1-}$x is depicted in Figure 18a. The relatively weak hydrogen bonds in the IU unit tend to selectively break and reform during elastomer deformation, dissipating energy and imparting a high level of toughness to the elastomer. This enhancement specifically targets fatigue issues commonly associated with conventional self-healing electronic skin under significant strains. Consequently, a stretchable self-healing electrode was devised, utilizing polydimethylsiloxane-MPU0.4-IU0.6 as the substrate and liquid metal EGaIn as the conductive layer (depicted in Figure 18b). This electrode exhibits remarkable stretchability (500%), the stability over 100 cycles, and maintain reversible low resistance (depicted in Figure 18c). Following a 12-h self-healing period in artificial sweat, the electrode regained its original electrical and mechanical properties. Notably, after immersion in water and artificial sweat for 24 h, the elastomer retained its mechanical characteristics and successfully self-heal in damaged areas (depicted in Figure 18d), indicating its ability to self-heal even in water. Moreover, the elastomer and EGaIn-based stretchable self-healing electrode demonstrated the capacity to restore its initial electrical and mechanical attributes following a 12-h healing period in artificial sweat (Figure 18e), positioning it as a highly promising material for advancing self-healing electronic skin.

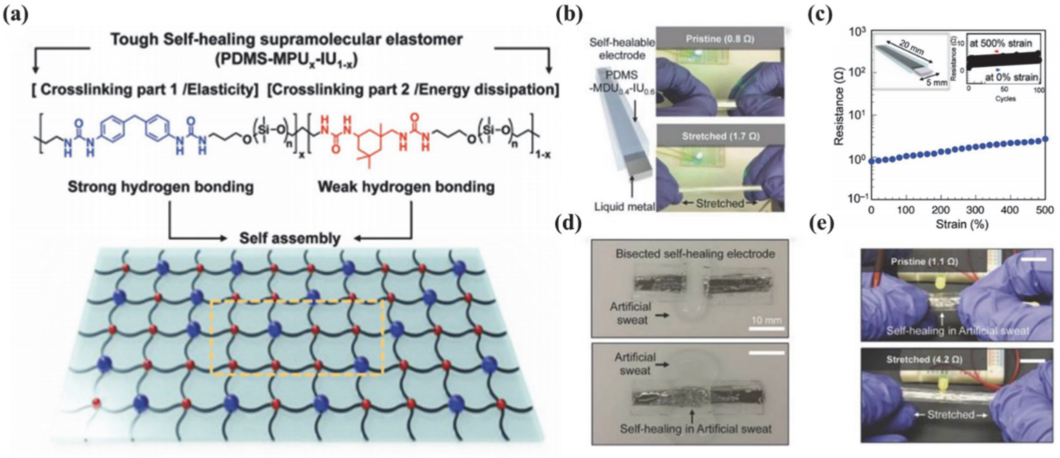


Figure 18. (**a**) Polydimethylsiloxane–MPU$_x$–IU$_{1-x}$ molecular structure. (**b**) Optical images displaying the self-healing electrode fitted with an LED lamp pre-stretching (middle) and post-stretching (right). (**c**) Graph depicting electrical resistance as a function of strain for the self-healing electrode, including cyclic stretching resistance (inset). (**d**) Self-healing electrode with severed conductive lines before (top) and after (bottom) realignment in artificial sweat. (**e**) After a 9-h self-healing interval in artificial sweat, the stretched electrode illuminated an LED lamp. Reproduced with permission [131], Copyright 2018, Advanced Materials.

3.2. Self-Healing Binders

Binders are essential for maintaining the structural integrity of battery electrodes [132]. Recently, there's been an increased focus on the critical role of the minimal active materials in batteries, which typically comprise around 10% of the total electrode mass [133]. Binders enhance the electrical contact between the active materials and conductive carbon [134], improve the efficiency of lithium-ion transport, decrease the internal resistance of Lithium-ion batteries, and effectively prevent crack formation and phase separation. However, excessive binder incorporation [135,136], along with conductive additives, can increase the workload and inert substance proportions within the electrode [137]. Insufficient utilization of binders can result in problems, including the separation, flaking, and disintegration of active substances, resulting in diminished battery capacity and compromised cyclic performance [138]. Furthermore, excessive binder usage can elevate the chemical inertness of electrode materials, reducing conductivity and increasing internal resistance and polarization, thereby affecting battery electrochemical and safety characteristics. Conventional binders and conductive additives do not possess the capability to heal themselves [139], resulting in the mechanical breakage of the electrodes during repeated use. Therefore, implementing binders equipped with self-healing properties can effectively mitigate issues including the expansion of electrode volume during battery cycling.

Self-healing binders can be classified into three categories based on the source of the binder [140–142]: synthetic, natural [143], and conductive binders. Synthetic binders [144] are man-made, whereas natural binders are abundant in nature and usually found in deionized water in a dispersed form. Novel binders exhibit both conductive and adhesive properties, typically comprising active materials, conductive carbon, and binders within electrodes. Conductive carbon and active materials may naturally separate during battery cycling-induced volume expansion or contraction. Conductive polymer binders prevent losses resulting from this physical separation, ensuring robust electrical contact between active materials and conductive additives like carbon black and graphene. Therefore, electrode binders significantly influence lithium battery longevity and internal resistance [145–147], warranting a comprehensive understanding of their impact on lithium battery impedance. Conductive additives and chemical binders, such as carbon black and polyvinylidene fluoride, have been shown to enhance cycle longevity, albeit with increased weight and size. Researchers have explored cross-linked polymer binders to form three-dimensional networks around silicon particles, effectively withstanding mechanical stress and strain, preventing electrode separation, and preserving electrical contact. Consequently, these binders enhance electrochemical process performance.

3.2.1. Polyacrylic Acid Based Self-Healing Binders

In the field of self-healing binders, polyacrylic acid (PAA) stands out as a readily synthesized hydrophilic polymer. Its molecular structure features extended carbon chains and carboxyl functional groups, which are capable of forming robust hydrogen bonds, facilitating strong adhesion, and contributing to self-healing properties. Due to its abundant availability and high theoretical capacity, silicon is an excellent choice for the negative electrode material in lithium-ion batteries. Nevertheless, the swift growth experienced by the material during the cycling process leads to particle deterioration, detachment from the current collector, disruption of the electrical connection, and the creation of a substantial solid electrolyte interface. These issues lead to poor performance. To overcome these limitations, functional polymers have emerged as promising binder materials for silicon anodes.

In 2022, Matsumi et al. [148] published a study introducing a durable self-healing polymer composite, poly(bisaminonaphthoquinone)/poly (acrylic acid) (P-BIAN/PAA), notable for its strength and n-type characteristics. Figure 19a,b depict the structures of P-BIAN and PAA and the formation of electrostatic hydrogen bonds between the nitrogen atoms in P-BIAN's diimine main chain and the carboxyl groups in PAA. This allows for structural flexibility to accommodate the substantial volume fluctuations in silicon anodes. When applied in batteries, P-BIAN/PAA demonstrated remarkable stability across 600 charge-discharge cycles, achieving a reversible capacity of around 2100 mAh g^{-1}, 95% capacity retention (Figure 19c), and a Coulombic efficiency above 99%. Electrochemical impedance spectroscopy was utilized to evaluate the anode half-cell's internal resistance. Nyquist comparison curves, shown in Figure 19d,e, compare the Si/C/(P-BIAN/PAA)/AB anode half-cell and a control group post-cyclic voltammetry. The Si/C/(P-BIAN/PAA)/AB anode exhibited an internal resistance of 620 Ω, significantly lower than the control's 1100 Ω. This indicates the role of electrolyte decomposition in influencing the battery's internal impedance and long-term cycling performance. Therefore, the development and utilization of versatile binders that offer both conductivity and self-heal capabilities are crucia, enabling customization of a thin solid electrolyte interface layer, enhancing lithium-ion diffusion and potentially improving the stability of silicon anodes. Inspired by this research, a composite binder using P-BIAN as a conductive link for silicon anodes has been developed, combined with proton polymer to create a customized thin solid electrolyte interface and gain self-healing properties through hydrogen bond network formation.

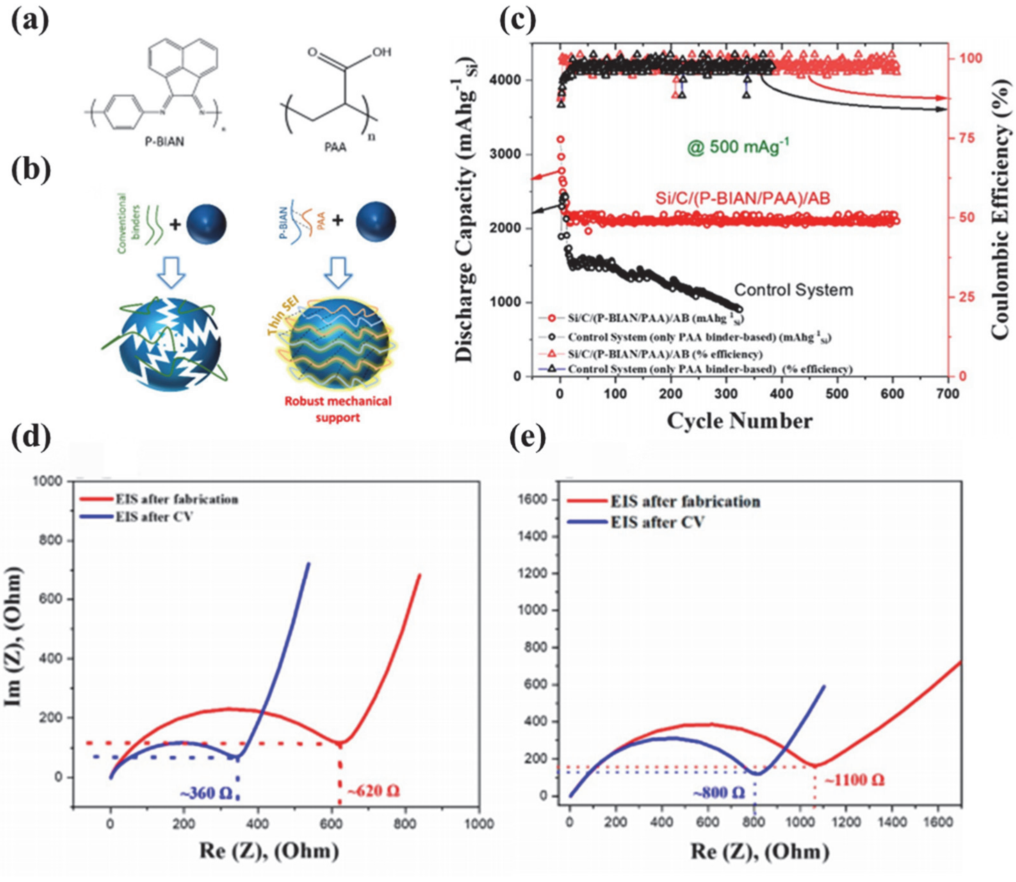


Figure 19. (**a**) Chemical structures of the polymers P-BIAN and PAA. (**b**) Conventional binders break too soon, whereas P-BIAN/PAA composite materials mend cracks by utilizing their self-healing properties. (**c**) A study comparing the extended cycling performance of conventional and self-healing binders in lithium-ion batteries.

Impedance profiles were acquired for the Si/C/(P-BIAN/PAA)/AB anodic half-cell (**d**) and the control system (**e**). Reproduced with authorization [148], Copyright 2022, ACS Applied Energy Materials.

In October 2020, Song et al. [8] developed a dual-layered binder that consists of a high Young's modulus polyacrylic acid internally and a low Young's modulus bi-functional polyurethane externally. This binder was designed to tackle the significant volume changes and internal stress that occur during the cycling of silicon-negative electrodes. Simultaneously, this binder also possesses a self-healing capability. Figure 20a depicts the configuration of a silicon electrode utilizing a binder based on polyacrylic acid. The Si/PAA electrode was prepared by dispersing Si nanoparticles, conductive additives, and PAA binder in a weight ratio of 70:15:5 and subsequently casting the mixture onto copper. Researchers utilized the PAA-Bi-functional polyurethane binder in commercially available silicon-based anodes to validate its practical implementation. Figure 20b illustrates that the Si/PAA-Bi-functional polyurethane electrode has an initial areal capacity of 2.7 mAh cm^{-2}, demonstrating excellent cycle stability. Following 200 cycles under a high current density of 2 A g^{-1}, the capacity retention surpasses 88%. Stress distribution within silicon anodes was evaluated under continuous lithiation using various polymer binders. Rigid binders, such as PAA, exhibited significantly higher stress compared to the more flexible bi-functional polyurethane binder (Figure 20c). The collapse of the electrode structure can be attributed to the mutual compression of Si particles. Remarkably, when the elastic binder is applied as a coating on the outside of the rigid binder, the stress distribution is significantly reduced compared to that of the rigid binder. Rigid binders can release internal stresses during the process of lithiation. On the other hand, elastic binders function as a protective layer, dispersing any remaining stresses and serving a self-healing function. Additionally, they help reduce the stress on silicon particles that are compressed together, thus restoring the structure of the silicon anode.

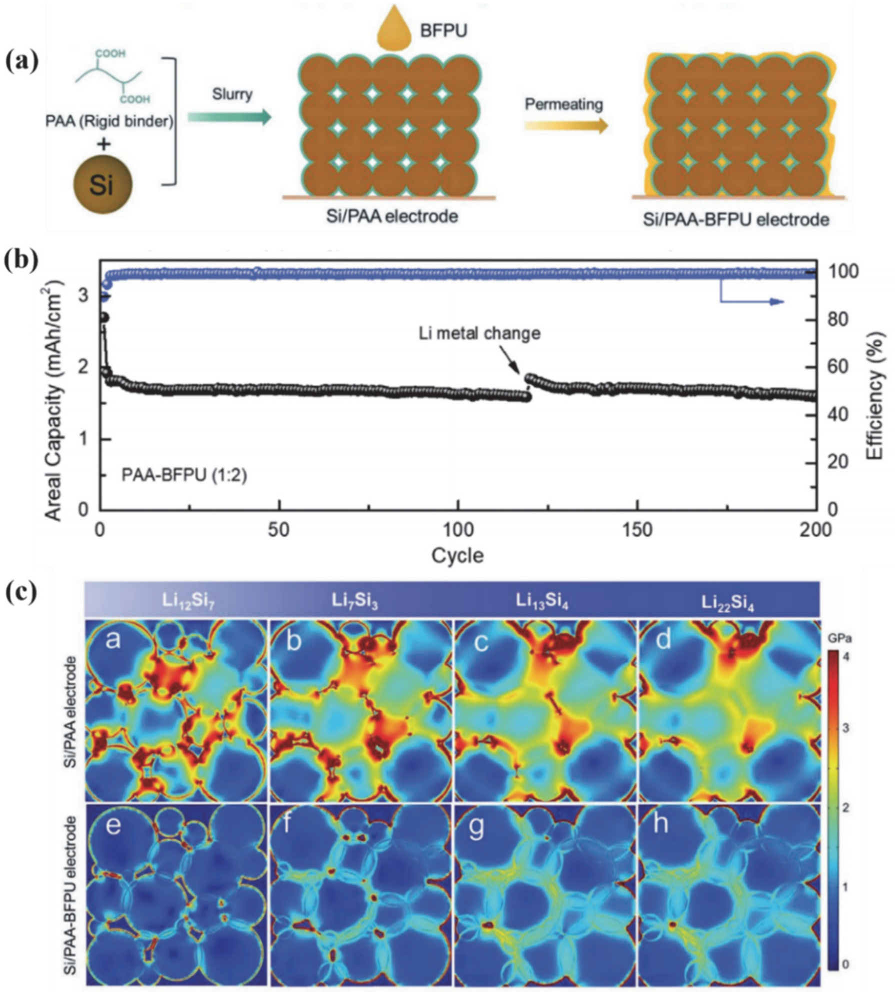


Figure 20. (**a**) Schematic diagram depicting the process of preparing a silicon anode using a PAA-bi-functional polyurethane binder. (**b**) Cycling efficiency of the Si/PAA-bi-functional polyurethane electrode was assessed at

a current density of 2 A g^{-1}. (**c**) Stress distribution of the PAA-based binder on the silicon negative electrode is analyzed at various lithiation states. Reproduced with permission [8], Copyright 2020, Wiley.

Furthermore, the newly introduced bi-functional polyurethane, endowed with rapid self-healing properties, effectively remedied micro-cracks induced by elevated stress levels, thus bolstering the resilience of the silicon anode. This versatile adhesive, employing an ingenious dual-layered packaging structure, offered valuable insights for prolonging the lifespan of high-energy-density lithium-ion batteries that undergo substantial volume fluctuations during cycling.

3.2.2. Polyvinyl Alcohol-Based Self-Healing Binders

Polyvinyl alcohol is a polymer with high affinity for water owing to its capacity to form hydrogen bonds with other molecules through its multiple hydroxyl groups. It exhibits favorable water solubility, film-forming capability, exceptional durability, and is non-toxic and non-irritating. Nevertheless, the thermal stability of polyvinyl alcohol is inadequate, as it undergoes decomposition at approximately 230 °C in the presence of air and experiences discoloration and brittleness when subjected to temperatures exceeding 100 °C. Although silicon has a high capacity, its decomposition is caused by significant volume changes during repeated charge-discharge cycles. Polymer binders are essential for preserving the structural integrity of electrodes and greatly enhancing their lifespan.

In 2020, Yu et al. [149] pioneered a novel binder termed ESVCA, a conductive self-healing hydrogel. Although there have been successful attempts to establish effective electrical connections between active materials using conductive binders and to enhance the structural stability of silicon anodes with self-healing binders, there are currently only a limited number of binders that possess both conductivity and self-healing properties. These binders can maintain the electrical contact and structural integrity of silicon electrodes over extended charge-discharge cycles. This study details developing and evaluating an innovative three-dimensional conductive self-healing hydrogel binder. The binder is notable for its excellent conductivity and rapid self-healing capabilities, making it ideal for use in high-performance silicon anodes. The self-healing conductive hydrogel binder is synthesized by merging poly (3,4-ethylene-dioxythiophene): poly (styrenesulfonate) with polyvinyl alcohol to create a 3D interpenetrating self-healing hydrogel network (Figure 21a). Compared to conventional conductive polymers, it demonstrates enhanced conductivity due to its distinctive 3D network structure, which enables more uninterrupted pathways for conduction, guaranteeing steady and swift electron transfer. Several tests were conducted to investigate the mechanical properties of the self-healing conductive hydrogel and the interactions among the polymer chains within the mixture. Figure 21b highlights the exceptional tensile strength of the self-healing binder, which remains intact even when stretched to approximately 300% of its original length. Furthermore, the hydrogel maintains exceptional mechanical performance even after undergoing self-healing. This strength is primarily attributed to the robust electrostatic interactions and dynamically reversible hydrogen bonds between the poly (3,4-ethylene-dioxythiophene): poly (styrenesulfonate) and polyvinyl alcohol chains. Figure 21c displays the long-term cycling performance of the silicon electrode at different current densities: 500 mA·g^{-1}, 1000 mA·g^{-1}, and 2000 mA·g^{-1}. At 500 mA·g^{-1}, the electrode exhibited a reversible capacity of 1786 mAh g^{-1}, maintaining 71.3% of this capacity after 200 cycles at room temperature. Impressively, it retained 74.1% capacity after 200 cycles at 2000 mA·g^{-1} and sustained a high reversible capacity of 1743 mAh g^{-1} even after 200 cycles at elevated temperatures. The binder was formulated by dissolving polyvinyl alcohol in deionized water heated to 90 °C. The resulting solution was then mixed with poly(3,4-ethylene-dioxythiophene), poly (styrenesulfonate) solution, and 5% 4-carbonxybenzaldehyde solution. After stirring for 30 min at room temperature, the binder displayed a stretchable, three-dimensional self-healing network structure when applied to silicon particle surfaces. The structure successfully reduced the volume fluctuations occuring following the addition and removal of lithium from silicon particles, thereby preserving the structural integrity of the silicon electrode.

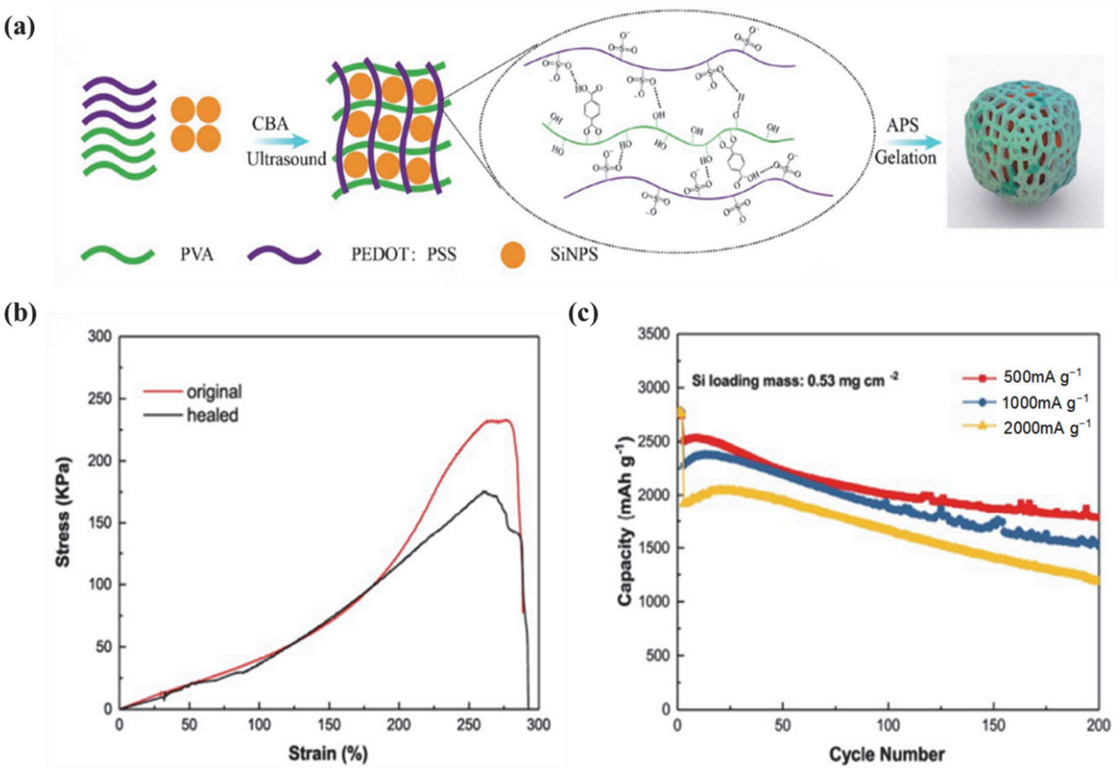


Figure 21. (**a**) Schematic diagram of the self-healing conductive hydrogel binder preparation process. (**b**) Stress-strain relationship of the conductive hydrogel that can heal itself. (**c**) Ability of the silicon electrode to perform consistently during repeated cycles at various levels of electric current. Reproduced with permission [149], Copyright 2019, Elsevier.

3.2.3. Carboxymethyl Cellulose-Based Self-Healing Binders

As a linear derivative of cellulose, carboxymethyl cellulose (CMC) exhibits diverse properties depending on the degree of substitution, showing increased solubility with higher degrees of substitution. It is soluble in water and can absorb water thus, functioning as a water-soluble binder.

In October 2020, Yang et al. [150] introduced a composite material named carboxymethyl cellulose-cationic polyacrylamide as a network binder to enhance the electrochemical performance of silicon-based negative electrodes in lithium-ion batteries. This material effectively enhanced battery performance. Carboxymethyl cellulose and polyacrylamide solutions demonstrate excellent viscosity at ambient temperatures. However, upon their combination, they undergo a spontaneous reaction to create a three-dimensional interconnected polymer structure, resulting in a distinct transition from a sol state to a gel state. The findings indicate that the carboxyl groups of carboxymethyl cellulose and the cationic groups of binder are predominantly linked together through reversible electrostatic interactions (Figure 22a). The network structure of the material, which was formed naturally at room temperature, exhibited self-healing properties that were distinct from traditional covalent cross-linking binders. Furthermore, the utilization of a high-molecular-weight binder resulted in the carboxymethyl cellulose-cationic polyacrylamide network binder exhibiting exceptional mechanical and adhesive potency, effectively enduring the alterations in silicon volume. As a result, silicon electrodes incorporating self-healing carboxymethyl cellulose-cationic polyacrylamide composite binders exhibited exceptional cycling stability, maintaining a capacity of 1906.4 mAh·g^{-1} after 100 cycles (Figure 22b). This attribute is most likely ascribed to the self-healing qualities of carboxymethyl cellulose-cationic polyacrylamide, which can efficiently mend structural damage to the electrode caused by the fluctuating size of silicon particles during repeated cycles of charging and discharging.

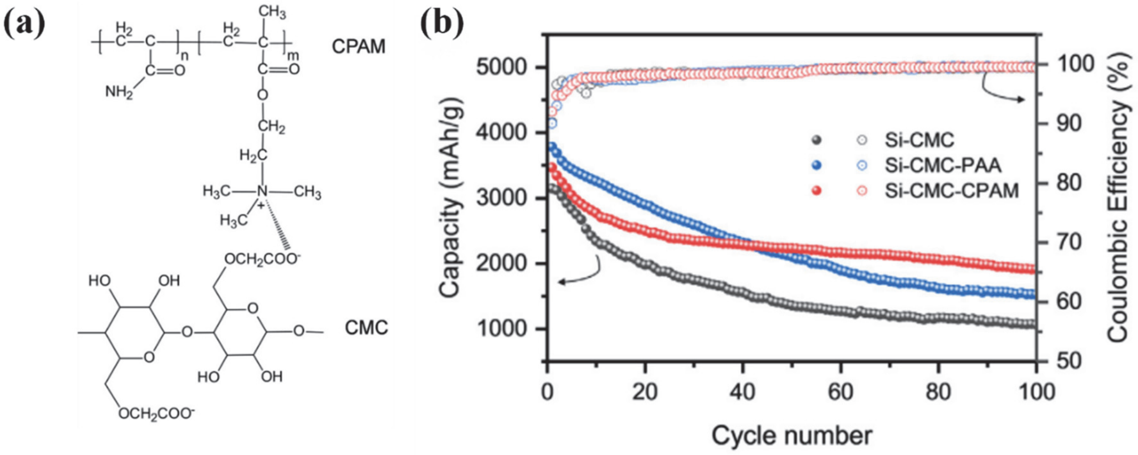


Figure 22. (**a**) Self-healing cross-linking process, which is initiated by electrostatic interactions between carboxymethyl cellulose and cationic polyacrylamide. (**b**) Evaluation of the electrochemical characteristics of silicon-based electrodes using various binders. Reproduced with permission [150], Copyright 2020, Elsevier.

3.2.4. Alginates Based Self-Healing Binders

Alginates, also referred to as alginic acid gels, brown algae salts, or alginate salts, are compounds that consist of salts derived from alginic acid. Their composition consists of long-chain polymers of (1→4)-β-linked D-mannuronic acid and (1→4)-α-linked L-guluronic acid. These polymers have a molecular weight of around 106. They are predominantly located in the cell walls and intercellular mucilage of brown algae. They can also be found in specific bacteria, such as pseudomonads and nitrogen-fixing bacteria, which generate capsules made of mucilage. Alginates form robust solid electrolyte interphase films by hydrogen bonding with hydroxyl groups on the surface of silicon particles. These films have high polarity and strong adhesion, effectively preventing the clumping and separation of silicon particles.

In 2021, Tae-Hyun et al. [151] explored the use of cross-linked polyethylene glycol chitosan as a sustainable, economical, and water-soluble polymer binder for silicon anodes within lithium-ion batteries. A self-healing, three-dimensional network was created by utilizing Schiff base reactions to connect the amino groups of polyethylene glycol chitosan with the dialdehyde groups of oxidized alginate salts. The oxidized alginate salt cross-linking agent underwent a spontaneous reaction with natural polymers, forming imine bonds and establishing a supramolecular network (Figure 23a). This approach facilitated the creation of strong and dynamic covalent bonds within the polymer binder, which effectively accommodated the significant volume changes of silicon during lithiation and de-lithiation processes. Figure 23b shows the comparative cycling performance of silicon electrodes. When combined with polyvinylidene fluoride binder, the silicon electrode exhibited inferior cycling performance compared to other binders, possibly due to inadequate strength of van der Waals forces to compensate for the discontinuities in the conductive network caused by substantial volume expansion during repeated cycling. Figure 23c illustrates the potential profiles of the silicon electrode during the charge and discharge processes, as measured using galvanostatic methods. The profiles are shown for both the 1st and 100th cycles. The self-healing imide-crosslinked glycol chitosan and oxidized alginate network effectively controlled the significant displacement of silicon nanoparticles and reduced the deformation of the composite electrode during changes in volume. The glycol chitosan and oxidized alginate glycol chitosan and oxidized alginate binder demonstrated the greatest reversible specific capacity compared to the glycol chitosan and polyvinylidene fluoride binders. This is due to its capacity to rapidly restore damage resulting from fluctuations in volume during the repeated processes of lithiation and de-lithiation of the silicon anode. This research holds significant promise for practical application in lithium-ion batteries.

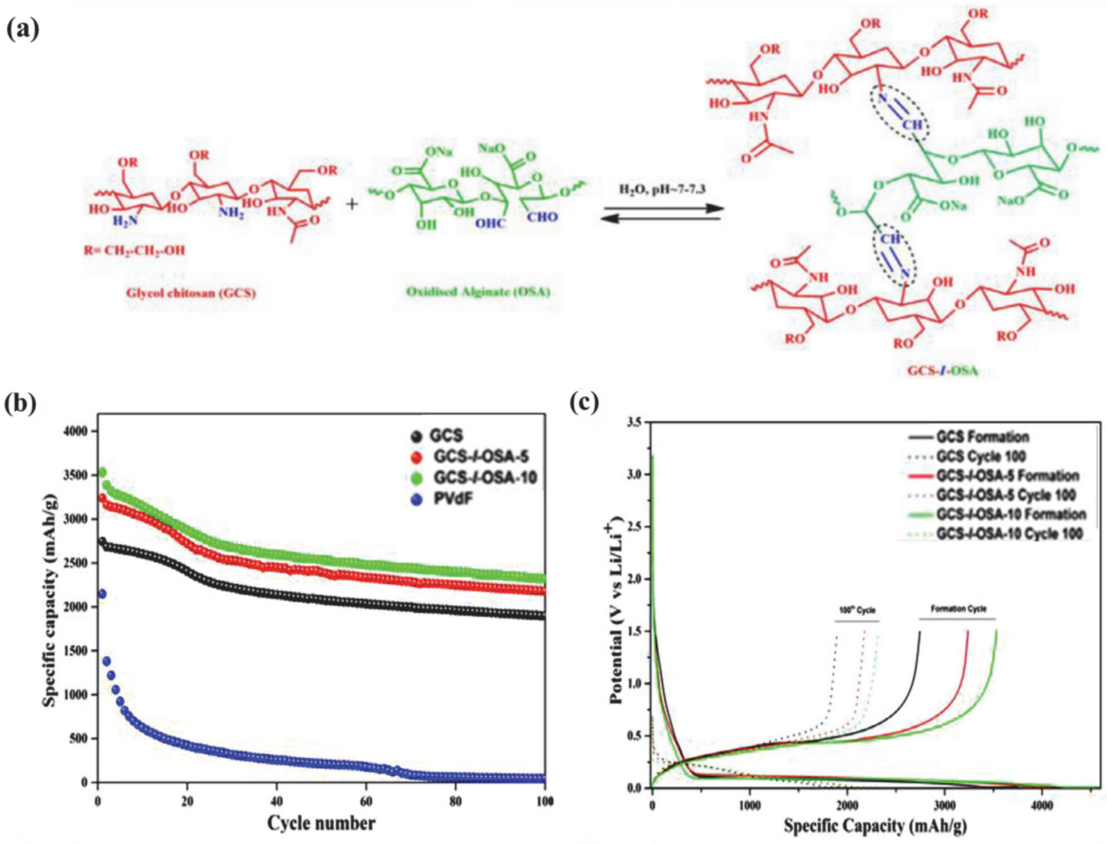


Figure 23. (**a**) A three-dimensional crosslinked network that is created by a dynamic Schiff base reaction. (**b**) Assessment of silicon electrode cycling performance using various polymer binders through 100 cycles. (**c**) Galvanostatic charging/discharging profiles of the electrodes with various binders. Reproduced with permission [151], Copyright 2021, Elsevier.

3.2.5. Cyclodextrins-Based Self-Healing Binders

Cyclodextrins refer to a group of cyclic oligosaccharides that are derived from linear starch through the action of the cyclodextrin glucosyltransferase enzyme produced by Bacillus. Usually, they consist of 6–12 D-pyran glucose units. Alpha-, beta-, and gamma-cyclodextrins, which are molecules composed of 6, 7, and 8 glucose units, respectively, have been thoroughly researched and are highly valuable in practical applications. Results of X-ray crystallography, infrared spectra, and nuclear magnetic resonance spectroscopy analyses have shown that each D (+)-pyran glucose molecule within a cyclodextrin adopts a chair conformation. The glucose units are linked through 1,4-glycosidic bonds to create the ring structure. Cyclodextrins possess a slightly conical ring shape due to the limited rotation of glycosidic bonds that connect glucose units.

An area of active research focuses on enhancing the energy density of lithium-ion battery units by increasing silicon content in silicon-graphite (Si-Gr) composite negative electrodes. In February 2022, Jang et al. [152] published a study introducing a composite binder for silicon electrodes. This binder comprises two components: pyrene-conjugated polyacrylic acid and hyperbranched γ-cyclodextrin polymer. The binder is designed to interlock and exhibit both hydrophilic and hydrophobic properties tightly, resulting in improved performance of the silicon electrodes. Figure 24a,b depicts a schematic diagram showcasing the creation of two affinity binders. The pyrene units in pyrene-conjugated polyacrylic acid increased the attraction to the Gr surface and intertwined with γ-cyclodextrin polymer hosts as guest molecules. This resulted in the formation of a self-healing crosslinked network consisting of both polymers. Nevertheless, the contrasting surface characteristics of silicon and graphene pose difficulties in achieving a consistent dispersion of electrode components and ensuring their adherence during cycling processes, which involve substantial changes in the volume of silicon. The effective interaction between the host and guest components preserved the electrode's integrity, leading to outstanding cycling performance (Figure 24c) for silicon-graphene electrodes with commercially significant areal capacities. The study demonstrated that biphilic, multifunctional supramolecular binders can improve the battery performance of new high-capacity electrodes, consisting of components with distinct surface characteristics, compared to conventional binders of a single type.

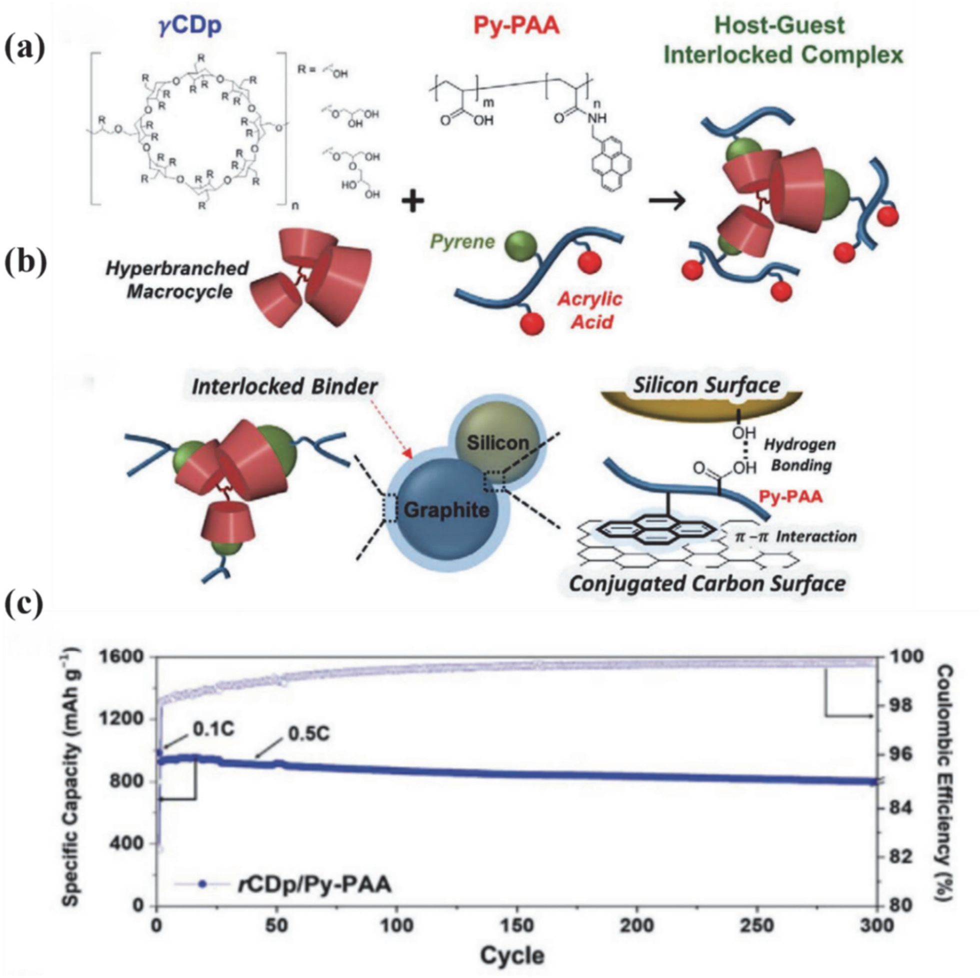


Figure 24. (**a**) Structural formula and synthesis process of the composite binder. (**b**) Interplay between the composite binder and the silicon electrode. (**c**) Battery's endurance in terms of cycling performance with the silicon electrode. Reproduced with permission [152], Copyright 2022, Wiley.

3.2.6. Chitosan-Based Self-Healing Binders

Chitosan is a compound that is derived from chitin by a process called N-deacetylation [153]. It has chemical structures that are similar to both chitin and cellulose. Cellulose possesses a hydroxyl group at the C2 position, whereas chitin and chitosan feature an acetyl amino and amino group at the C2 position. Chitin and chitosan exhibit several distinctive characteristics, including biodegradability, cell affinity, and biological effects. Chitosan, which contains unbound amino groups, is the sole alkaline polysaccharide within the category of natural polysaccharides. Pastes containing chitosan, which can dissolve in water, have a favorable thickness and are regarded as efficient agents for binding electrodes.

Due to their abundant availability and high theoretical capacity, silicon electrodes have attracted considerable interest as potential materials for the next generation of lithium-ion batteries. Before the commercialization of silicon electrodes, several obstacles must be addressed, particularly the degradation of battery performance caused by significant fluctuations in the volume of the active material. In 2021, Tae-Hyun et al. [154] created a self-healing polymer binder with ion-conductive properties specifically designed for high-performance silicon electrodes. Ethylene glycol chitosan, acting as a substantial cross-linking agent with dialdehyde terminals, created a polymer network through imine double bonds with oxidized alginate salts using a straightforward technique (Figure 25a), thereby improving ion conductivity. The presence of robust and reversible imine double bonds enabled the self-healing capability of the cross-linked polymer. During the preparation of the polyethylene glycol-crosslinked-glycol chitosan-0.5 hydrogel, two chemical indicators, methyl orange and bromothymol blue, were included to observe the self-healing properties of the hydrogel electrolyte. Subsequently, the obtained hydrogel underwent self-healing tests by inflicting physical damage using the previously mentioned method at room temperature (Figure 25b). Remarkably, the polyethylene glycol-crosslinked-glycol chitosan-0.5 hydrogel demonstrated the ability to self-heal to the same degree at room temperature as at elevated temperatures. This validates the exceptional ability of the polymer network, which relies on reversible imine bonds, to heal itself even when exposed to room temperature. Subsequently, battery performance tests were conducted utilizing the polyethylene glycol-crosslinked-glycol chitosan-0.5 adhesive-based electrode, while a pure glycol chitosan adhesive-based electrode was employed as a control for comparative purposes (Figure 25c). The utilization of the polymer network in the silicon electrode yielded an initial Coulombic efficiency of 82.2%, a discharge capacity of 2141 mAh g^{-1} after 150 cycles, and a reversible capacity of 2700 mAh g^{-1} at a current density of 3C. The remarkable electrochemical performances demonstrate substantial enhancements in the functioning of silicon electrodes as a result of the self-healing network and ion-conductive properties of the polymer binder that was created.

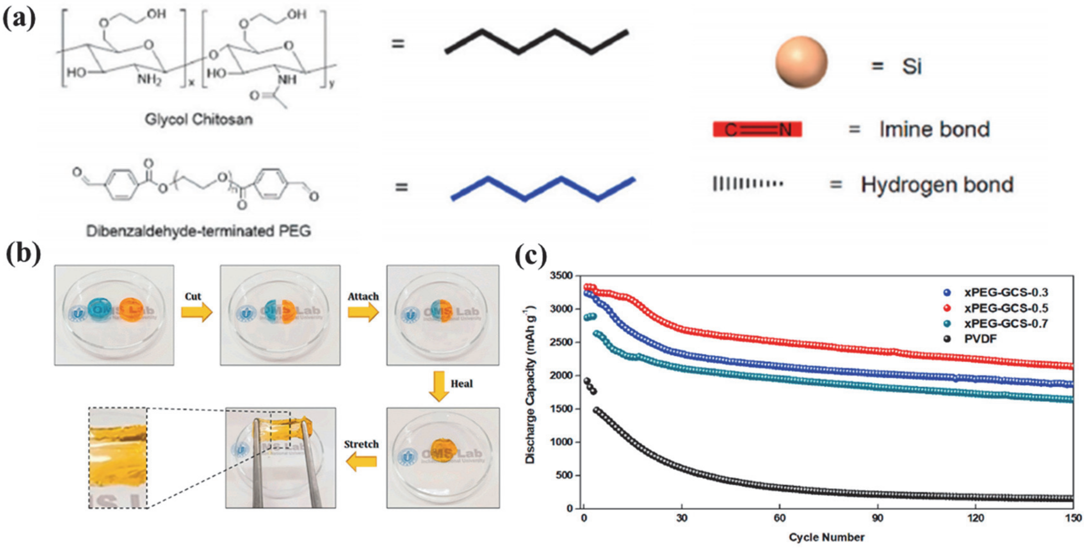


Figure 25. (**a**) Synthesis process of xPolyethylene glycol -glycol chitosan adhesive in a silicon electrode through a schematic diagram. (**b**) Evaluation of the self-healing capability of xPolyethylene glycol-glycol chitosan hydrogel following physical damage at ambient temperature. (**c**) Electrochemical performance of the polymer adhesive in the silicon nanoparticle (SiNP) electrode. Reproduced with permission [154], Copyright 2021, Elsevier.

3.2.7. Polypyrene Monomer Based Self-Healing Binders

In its pure form, the pyrrole monomer is a colorless, odorless liquid with an oily consistency, maintaining its liquid state at standard room temperature. This is a pentagonal heterocyclic molecule that can undergo electrochemical oxidation polymerization to produce a film when exposed to acidic water solutions and different organic electrolytes. The characteristics of the resulting polymer, including its electrical conductivity and mechanical strength, are intricately linked to the conditions under which polymerization occurs. These conditions include the type of electrolyte anions used, the choice of solvents, the pH level, and the temperature. The oxidation potential of poly(pyrole) (PPy) is approximately 1 volt less than that of its monomer. Chemical doping methods can be used to dope poly(pyrole), resulting in the introduction of counterions and the subsequent development of ion-conducting capabilities. Poly(pyrole) is utilized not only as a conductive material, particularly in specialized electrodes, but also finds application in electrochromic materials. poly(pyrole) is a linear conjugated polymer with specific optoelectronic characteristics.

Gallium, a liquid metal, has gained significant attention as a self-healing substance, particularly in energy storage systems. Nevertheless, the lack of regulation over electrode failure resulting from the volume expansion during the "liquid-solid-liquid" transformation remains a significant obstacle to achieving the self-healing properties of liquid metals when used as anodes in lithium-ion batteries. In September 2022, Ting et al. [155] presented a method for using conductive and adhesive poly(pyrole) to fix liquid metal nanoparticles (EGaSn-gallium-tin alloy) within integrated electrodes. These electrodes were used as anodes in lithium-ion batteries.

The in-situ polymerization resulted in the formation of tightly encapsulated structures of EGaSn nanoparticles, effectively preventing the separation of solid alloy by-products. By utilizing the properties of poly(pyrole), the inclusion of polyacrylic acid improved the strength of the electrode by forming hydrogen bonds. The current collector is coated with the poly(pyrole) slurry adhesive, as depicted in Figure 26a. The Nyquist plots of EGaSn and EGaSn@Poly(pyrole) are displayed in Figure 26b,c, illustrating the initial state as well as the fully charged state following the 50th and 100th cycles. The EGaSn@Poly(pyrole) anode exhibits excellent discharge capacities of 773, 675, 607, 462, and 350 mAh g^{-1} under the regularly changing current densities of 0.1, 0.2, 0.5, 1.0, and 2.0 A g^{-1}, respectively (Figure 26d). Incorporation of a “double insurance” design in EGaSn resulted in outstanding electrochemical kinetics and notable self-healing effects. As a result, the modified anode demonstrated exceptional durability during repeated cycles (499.8 mAh g^{-1} after 500 cycles at 1.0 A g^{-1}) and excellent ability to charge and discharge quickly (350 mAh g^{-1} at 2.0 A g^{-1}). This study enhances the methods used to engineer electrodes for liquid metal nanoparticles and opens possibilities for creating personalized, self-healing anodes in lithium-ion batteries.

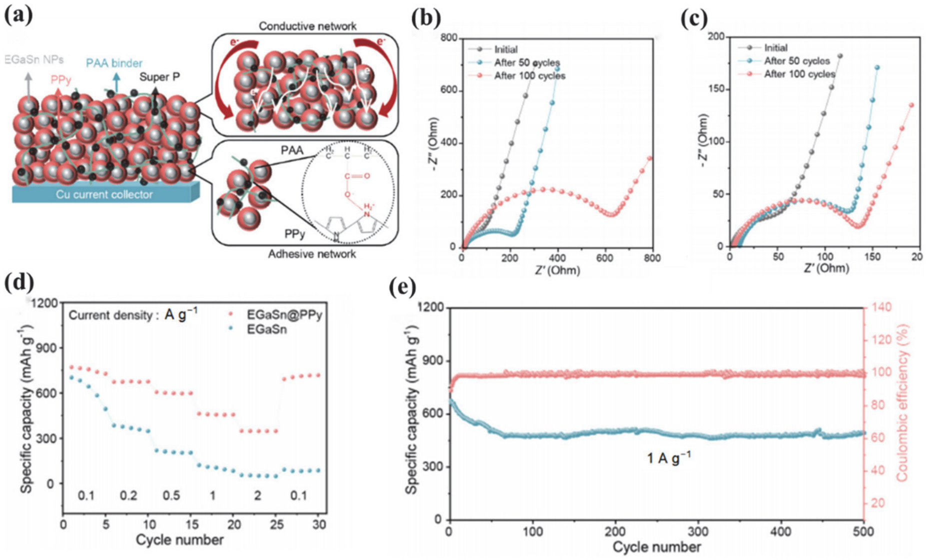


Figure 26. (**a**) Schematic diagram of the electrode structure. EIS curves of EGaSn (**b**) and EGaSn@Poly(pyrole) anodes (**c**) At initial and different charged states. (**d**) The rate performance of EGaSn@Poly(pyrole) and EGaSn anodes is being evaluated. (**e**) Durability of the EGaSn@Poly(pyrole) anode over an extended period of time. Reproduced with permission [155], Copyright 2022, Elsevier.

4. Conclusion and Outlook

In recent years, the rise of mobile intelligent electronics and the Internet of Things has driven significant progress in lithium batteries [156]. However, the diverse application scenarios and inevitable folding and breakage during use have imposed new demands on batteries' cycling life and endurance. Introducing self-healing polymers can endow lithium batteries with intelligent self-healing capabilities, effectively improving mechanical durability and extending life cycles. When damaged by external mechanical impacts and internal stresses [157,158], microcracks in the internal components of lithium batteries can be repaired on time, enhancing battery durability, reducing capacity degradation, and increasing safety [159,160].

The investigation and application of self-healing polymers in lithium batteries are still at an early stage [161], with most documented polymers confined to laboratory settings and far from real-world applications. Therefore, additional functional self-healing polymers must be further examined and developed to enhance device performance and address existing limitations [162,163]. Enhancing self-repair strategies and investigating self-healing polymers face numerous obstacles, particularly the need for a novel generation of wearable, flexible, and high-safety batteries. Moreover, internal self-healing processes should harmonize the compatibility among the electrode [164–168], electrolyte, and interface layers. Based on the breakthrough progress achieved, future research directions on self-healing polymers for advancing batteries are suggested herein (Figure 27).

1. Simplifying process. While various self-healing substances show remarkable restoration efficiency, some require specific external conditions, such as oxygen, elevated temperatures, and light, to trigger or hasten the process. This contradicts the design of enclosed batteries meant to be kept away from air. Investigating high-efficiency self-repairing polymers that do not require external activation can significantly lower the barriers to commercial use in the battery industry.
2. Balancing properties. Achieving a balance among electrochemical characteristics, self-repair capabilities, and mechanical properties is essential for improved electrical output performance and cycle longevity of lithium batteries. For instance, many self-healing polymers with numerous self-healing functional units exhibit diminished ionic conductivity, constraining battery energy density. Researchers must understand the molecular mechanisms to balance self-healing functional groups and dissociated ions within the materials. Given that mechanical harm often accompanies bending, stretching, and shock, ensuring batteries retain their electrochemical performance and recovery capability poses a significant challenge. At the same time, there is often a conflict between self-healing efficiency and tensile robustness. For instance, polymer gel electrolytes [169–171] can quickly regain their physical and chemical characteristics but often lack sufficient post-healing mechanical resilience. Considering both self-repairing functional bonds and rigid covalent bonds (or stiff polymer backbones) is essential to avoid this issue.
3. Expanding application fields. Building on the success of self-healing lithium batteries, researchers are now exploring similar strategies for zinc and sodium-based energy storage systems. Adapting these strategies to specific conditions is essential to improve the performance and address the existing challenges. For instance, hydrogels possess excellent self-repair capabilities, however, they are not ideal for lithium-based and sodium-based batteries. Nevertheless, they hold significant potential in self-healing zinc-based batteries [172–174].
4. Strengthening source control. Choosing self-healing polymers necessitates considering important social aspects, such as using non-toxic, harmless, and eco-friendly materials during the manufacturing process and the necessity for energy efficiency and waste minimization [175–178].

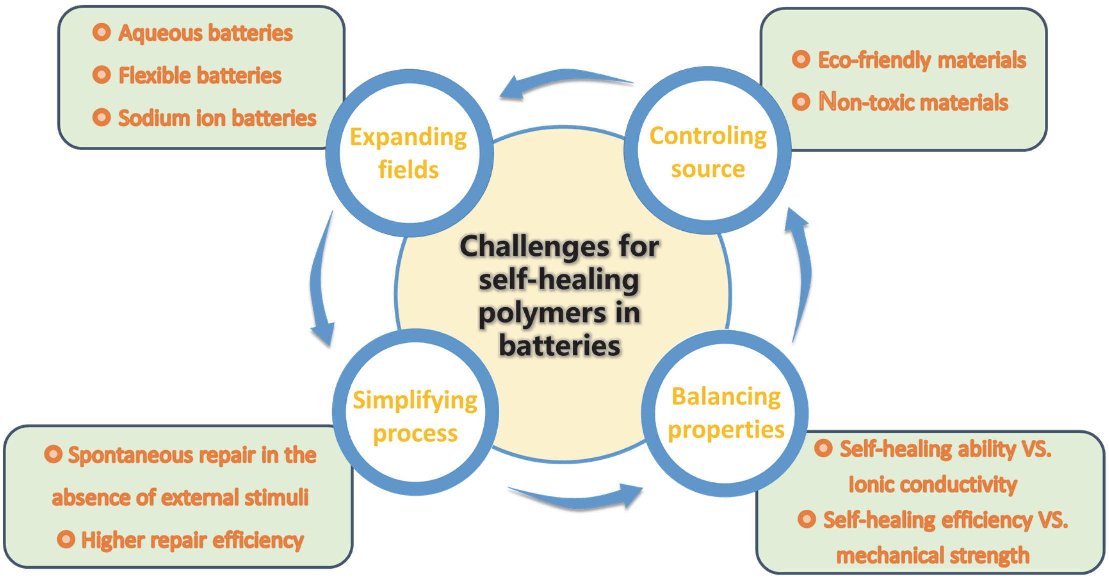


Figure 27. The challenges for self-healing polymers in batteries.

Self-healing polymers have diverse applications due to their advantages. These polymers exhibit diverse self-healing mechanisms. With advancements in engineering technology and a deeper understanding of self-healing functionalities, we are confident that self-healing flexible and stretchable lithium batteries will become vital in wearable and implantable functional devices.

Author Contributions: Q.S.: writing—original draft preparation; Y.W.: writing—review and editing; Q.C.: visualization; H.H.: supervision; M.Z.: project administration; Y.X.: funding acquisition; Y.L. (Yingliang Liu): Conceptualization.; Y.L. (Yeru Liang) Literature investigation, visualization. All authors have read and agreed to the published version of the manuscript.

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