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REVIEW

Self-healing polymer binders for the Si and Si/carbon anodes of lithium-ion batteries

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Abstract: A silicon anode with a high specific capacity is one of the most promising candidates for developing advanced rechargeable lithium-ion batteries (LIBs). However, the problems of low electrical conductivity, severe volume changes during use and an unstable solid electrolyte interface seriously hinder their use in LIBs. Although using the carbon materials used to construct Si/C composite anodes have demonstrated their advantages in improving the performance of Si-based anodes, the binder, another key component of the electrode, also has a significant effect on the electrochemical performance of a battery. A self-healing binder uses non-covalent and reversible covalent bonds to effectively improve the cycling stability of LIBs by repairing the internal/external damage caused by the huge volume change of a Si-based anode. As for the solid-state polymer electrolytes (SPEs) of flexible lithium batteries, the use of self-healing polymers can also quickly repair the damages or cracks in the SPEs, and have a promising prospect in the development of flexible and wearable electronics. The paper gives an overview of the synthesis, characterization and self-healing mechanisms of the self-healing polymer binders for use in Si and Si/C anodes and their recent application in flexible lithium batteries is briefly summarized. The related technical challenges and design requirements for self-healing polymer binders used in the Si and Si/C anodes of LIBs are discussed.

Key Words: Silicon; Carbon; Lithium-ion batteries; Self-healing polymer; Covalent bonds

1 Introduction

Lithium-ion batteries (LIBs) have been extensively used in mobile electronics, electric vehicles and energy storage systems due to their high energy density, good stability and technology population. Nevertheless, the innovations of LIBs are high expected from the electrode materials, electrolytes, separators and cell structures. A lot of studies have been reported to enhance the energy density of LIBs by developing the high capacity cathode and anode materials[1]. According to the different mechanisms, the anode materials used in LIBs include the intercalation/deintercalation type such as soft carbons[2], hard carbons[3], graphite[4,5] and lithium titanate[6], the alloying/dealloying type such as Tin-based materials[7] and Si-based materials[8], and the conversion type such as CoO, LiO_2[9] and Fe_3O_4[10]. Among them, the alloy type materials have the highest theoretical capacities and are attracting more attentions for next generation LIBs. As one of the most promising alloy type materials, Si has a theoretical capacity of 4 200 mA h g^{-1} and a low operating potential (~0.4 V vs. Li/Li$^+$) that is favorable to avoid the formation of lithium dendrites[11-13]. In addition, Si is the second abundant element in the earth crust and environmentally friendly, so it has the advantage for the LIBs with low cost.

However, developing Si-based anodes of LIBs for the practical applications still faces the challenges. Firstly, Si is a semiconductor material and its electronic conductivity is not enough for the LIBs with high power density. Secondly, the huge volume change more than 300% during the lithiation and delithiation of Si leads to a series of problems as shown in Fig. 1[14,15]. The large stress resulted from the volume effect causes cracking and pulverization of Si particles. An unstable solid electrolyte interface (SEI) is continuously formed around the Si surface, which consumes the electrolyte and leads to a low initial Coulomb efficiency (ICE). The volume expansion and contraction during the continuous lithiation/delithiation cause the lost of the electrical contact between the active materials and the current collectors and thus the rapid performance degradation of cells[16]. Therefore, the low Coulombic efficiency and the poor cycle life caused by the low electronic conductivity and the volume effect of Si seriously limit the commercialization of Si-based anodes of LIBs.

In recent years, some advanced strategies have been reported to solve the problems of Si-based anodes from the aspects of nano-sizing particles, surface coating, alloying, forming a cavity structure, compositing with carbon, adding

DOI: 10.1016/S1872-5805(22)60638-3

electrolyte additives, pre-lithiation and using functional binders (Fig. 2). In terms of material design, nano-sizing the active particles can relieve stress and improve the conductivity of electrons and ions in the electrode[17,18]. Surface coating with carbon materials can improve the conductivity and promote the formation of stable SEI by providing a stable interface layer[19-21]. The application of Si alloy materials can not only enhance the dispersion of nano-Si particles but also improve the electronic conductivity of electrodes[22]. The void space between the inner particles and the outer shell provides a buffer space for the volume expansion of the Si particles to hold the electrode structure and stabilize the SEI layer[23-25]. Si/C composite structure can bring the synergistic effect to improve the conductivity and to maintain the electrode structure by utilizing the mechanical and electronic properties of carbon materials[26,27]. From the view of using the unactive materials to improve the Si-based anode performance, the electrolyte additives can passivate the interphase between Si particles and electrolyte during the initial lithiation process to form a stable SEI film for improving the cycle life of Si electrodes[28-30]. Pre-lithiation can prevent the lithium from being consumed by the side reaction to produce SEI to increase the ICE of the Si electrodes[31-33]. Especially, the functional binders are requsted for most electrodes to integrate the active materials, the additives and the current collectors, which become a key factor affecting the performance of a battery. For Si-based anodes, the functional binders are also expected to alleviate the volume effect during the lithiation and delithiation[34-38].

Although the binders represent only a small fraction of materials used in the electrode (usually less than 10% of the total electrode mass), it has a significant impact on the electrochemical properties of the electrodes[39]. Commercial polyvinylidene fluoride (PVDF) is a commonly used binder for LIBs due to the good chemical, electrochemical and mechanical stabilities. The binding mechanism of PVDF is based on the van der Waals forces and thus it is very difficult to solve the problem of the stress resulted from the volume changes of Si[40]. However, the rational design of functional binders is an effective method to resolve the poor conductivity and buffer the volume expansion of Si anodes. As a functional binder of Si anodes, it must meet several basic requirements as below. The binder serves as both a dispersant and a thickener to allow a homogeneous dispersion of the active materials and the conductive additives. It can make the active particles firmly bound to the current collectors through mechanical interlocking or intermolecular forces/chemical forces. The binder has a wide electrochemical window and is chemically/electrochemically stable. Moreover, the binder with good wettability can facilitate the mass transport of lithium ion between the interface of the active particles and the electrolyte[41].

The rational design and use of binders including the natural biomass-based binders and the synthetic binders can significantly improve the cycling performance and ICE of Si anodes. Among the binders, self-healing polymer (SHP) binders have the reversible bonds with a sensitive dynamic at the molecular scale, and can quickly repair the microcracks in electrodes during long term cycling, which has exhibited the good potential on improving the electrochemical performance of the Si anodes in LIBs[42].

2 Intrinsic binding mechanisms of SHP

As the binder of Si or Si/C anodes of LIBs, SHPs can dissipate the mechanical stress caused by the volume change of Si particles during delithiation and lithiation to rapidly repair the microcracks inside the electrode or the mechanical damage outside[43,44]. SHP binders applied in electrode systems
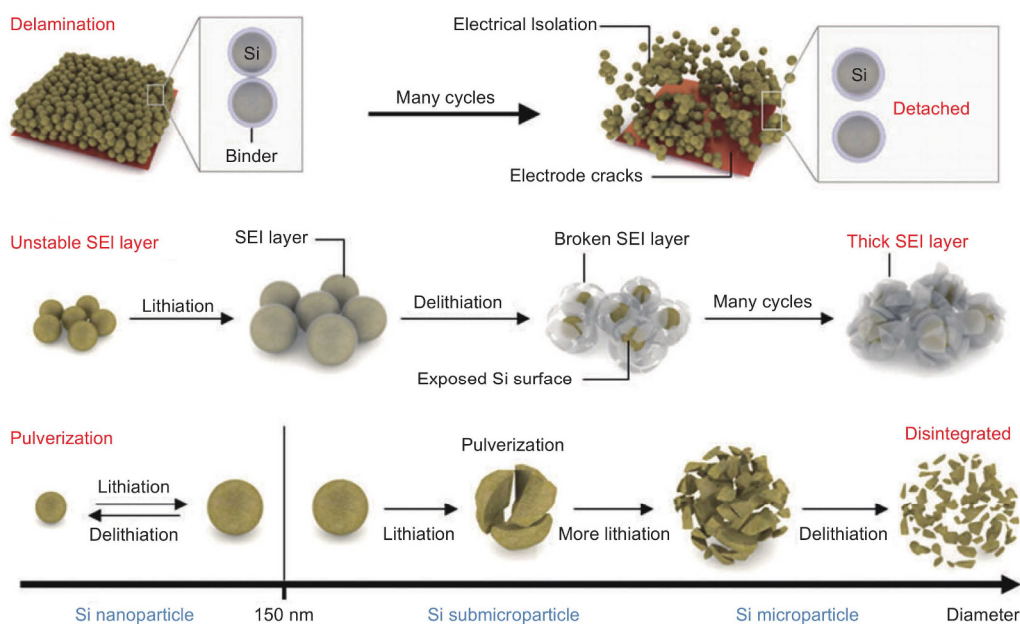

Fig. 1　Three representative failure mechanisms of Si-based anodes: delamination, unstable SEI layer formation and pulverization[15]. Reprinted with permission by Royal Society of Chemistry.

usually achieve the self-healing process by exploiting dynamic bond interactions at the molecular level[45]. A variety of reversible interactions at the molecular level include reversible covalent-bonds and non-covalent bonds. The covalent-bonds such as disulfide bonds[46], imine bonds[47], borate ester bonds[48,49] and acylhydrazone bonds[50] have been successfully formed in the SHP binders. Novel SHP binders with dynamic crosslinking properties can also be developed by Diels-Alder reaction[51], transesterification and disulfide exchange reaction[52]. SHP based on the reversible covalent bonds is generally considered to be a process of moving from a high energy state toward an equilibrium state. This equilibrium state shift can be controlled and changed by external conditions such as the pH value, irradiation and temperature[53]. Most of the SHP binders based on the covalent-bonds exhibit the excellent mechanical properties and the stable self-healing ability due to the stronger bond energy than the noncovalent bonds. SHP binders based on the non-covalent bonds including hydrogen bonds[54,55], metal-ligand interactions[56], host-guest interactions[57], ion-dipole interactions[38,58], and π-π interactions[59] have the lower kinetic stability and the weaker dissociation, however, they are easier constructed than the dynamic covalent bonds. SHP binders relying on the reversible non-covalent bonds can achieve the self-healing properties with mobility and flexibility. When the supramolecular polymers are mechanically fractured, the abundant supramolecular radicals will be generated on the fracture surface, and some radicals will contact and spontaneously recombine with the polymer chain, thereby to self-heal the fracture[60]. Multifunctional SHP binders with excellent self-healing properties can be synthesized by cross-linking the different kinds of polymers by the reversible covalent-bonds.

3 SHP coating on the surface of Si and Si/C anodes

It has been well demonstrated that the surface coating strategy around the Si anodes can effectively block the direct contact between the electrolyte and the Si materials. The flexibility and stretchability of polymer can not only relieve the mechanical stress caused by the volume change of Si and improve the structure stability of an electrode, but also significantly inhibit the agglomeration of Si NPs caused by large surface energy[61]. In 2021, Xu and coworkers[62] summarized the different coating materials on the Si anodes of LIBs, such as the carbon materials, oxides, metals and conductive polymers. They also proposed a few feasible suggestions for designing the structure of the Si anode coating. This section mainly focuses on the roles of the composite coating of carbon and polymer and the SHP coating in the Si anodes of LIBs.
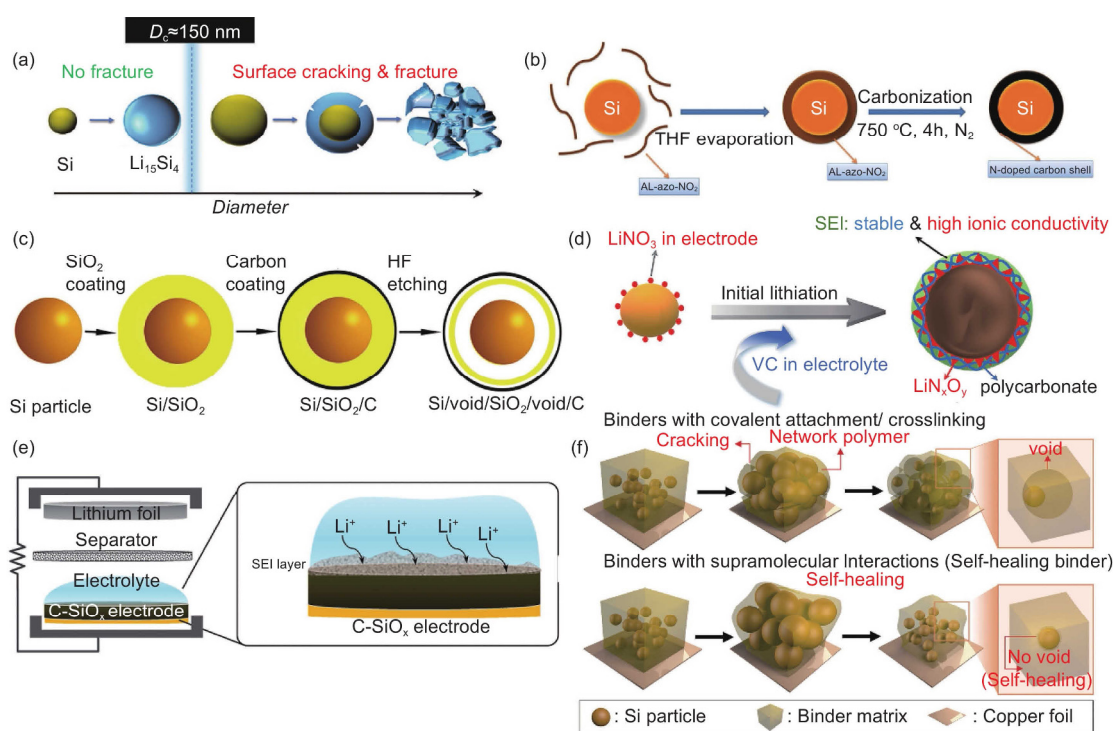

Fig. 2 (a) Size-dependent fracture of Si NPs by pulverization[18]. Reprinted with permission by American Chemical Society. (b) Schematic of preparation procedures of Si@C nanocomposites[20]. Reprinted with permission by Elsevier. (c) Schematic illustration of the fabrication process of the dual yolk-shell structure[25]. Reprinted with permission by Nature Research. (d) The surface modification mechanism of vinylene carbonate (VC) and lithium nitrate (LiNO₃) as effective electrolyte additives[29]. Reprinted with permission by Elsevier. (e) Graphical illustration of the pre-lithiation process of the carbon-coated SiOₓ (c-SiOₓ) electrode[33]. Reprinted with permission by American Chemical Society. (f) Graphical representation of the proposed mechanism for two types of binders for Si anodes[38]. Reprinted with permission by Wiley-VCH.

3.1 Composite coating of carbon and SHP

Carbon materials with structure variety, flexibility and good conductivity[62-68] have been well demonstrated the advantages in the electrochemical performance of Si anodes[69,70]. The carbon coating around the Si materials can not only alleviate the volume expansion and enhance the electrical conductivity, but also can improve the stability of SEI film by avoiding the direct contact between electrolyte and Si. Although carbon materials have many advantages, the polymers still play an important role in improving the performance of Si anodes. Carbon materials must be uniformly dispersed in a polymer to ensure electrical conductivity and maintain a dynamically stable interface between the materials during volume expansion and contraction of Si. Wu et al.[71] proposed a graphite oxide (GO) coating modified with polydopamine (PDA) on Si NPs. As the conductive support and buffer matter, the GO uniformly dispersed in polydopamine (PDA) provided the high electronic conductivity and maintained the integrity of the electrode structure (Fig. 3a). Compared with the pristine Si electrode, PDA with flexibility maintained the integrity of the electrode structure and inhibited the continuous reconstruction and destruction of SEI around Si NPs, and even showed a self-healing effect (Fig. 3b). The PDA/GO-Si electrode exhibited the improved capacity and cycling stability, achieving a first discharge capacity of 2903 mA h g^{-1} and maintaining a capacity of 1 300 mA h g^{-1} after 450 cycles.

Li et al.[72] polymerized LiOH with the acrylic acid (Li-AA) that was partially neutralized and then mixed with carbon nanotubes (CNTs) to get a flexible polymer/carbon coating on the surface of SiO$_x$ microparticles (Fig. 3c). The flexible lithium polyacrylate (LiPAA) provided a uniform interface for lithium ion conduction and exhibited excellent mechanical properties due to its high stretchability. The uniformly dispersed CNTs in the Li-PAA provided a rapid pathway for electronic conduction. As shown in Fig. 3d, the integral interface of C-SiO$_x$/C microparticles (MPs) was dynamically stable during the repeated volume expansion and
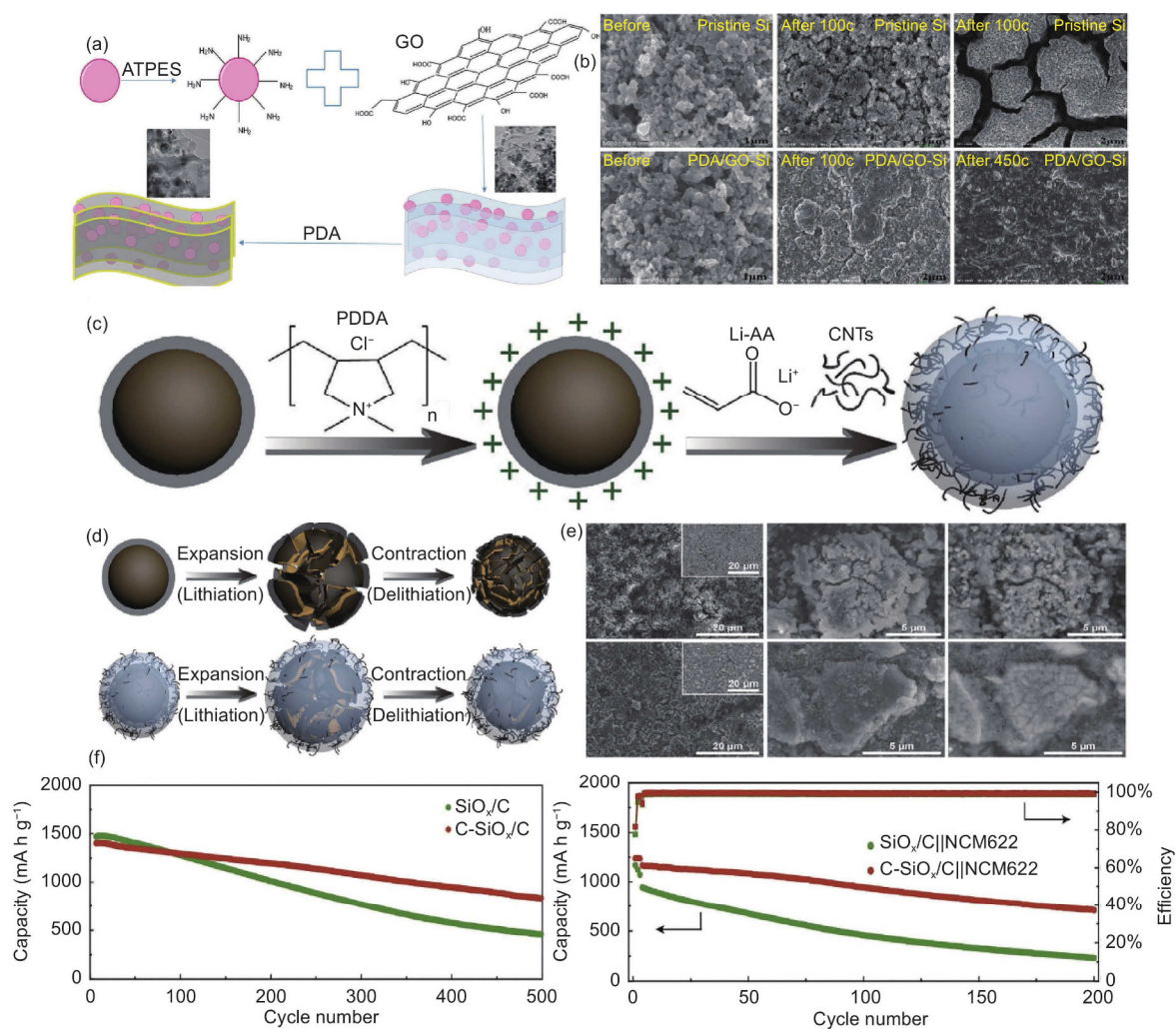

Fig. 3　(a) Schematic procedure for the fabrication of PDA/GO-Si. (b) SEM images of pristine Si electrode and PDA/GO-Si electrode before and after cycles[71]. Reprinted with permission by Elsevier. (c) Schematic illustration for the preparation of C-SiO$_x$/C. (d) Schematic illustration of lithiation and delithiation of SiO$_x$/C and C-SiO$_x$/C. (e) SEM images of SiO$_x$/C (top three) and C-SiO$_x$/C anodes (bottom three) after 200 cycles in full-cells. (f) Cycling performance of Li//SiO$_x$/C and Li//C-SiO$_x$/C at 0.2C. (g) Cycling performance and Coulombic efficiencies of SiO$_x$/C//NCM622 and C-SiO$_x$/C//NCM622 in full cells[72]. Reprinted with permission by Elsevier.

contraction, and no obvious crack generation was observed on the electrode surface after 200 cycles. Although the self-healing property of lithium polyacrylate (LiPAA) was not demonstrated, the excellent stretchability can suppress the pulverization of active particles and the continuous formation of SEI during lithiation and delithiation (Fig. 3e). The specific capacity of the C-SiO$_x$/C anode was 836 mA h g^{-1} (Li//C-SiO$_x$/C) after 500 cycles in a half cell, which was higher than the commercial graphite anode (372 mA h g^{-1}). When the current density was increased to 0.5 C, the capacity of the C-SiO$_x$/C//NCM622 decreased to 1 171 mA h g^{-1}, and the specific capacity was 709 mA h g^{-1} after 200 cycles (Fig. 3f and g).

3.2 Coating of SHP

Compared with the composite coating of carbon material and polymer, a flexible SHP coating can response and repair the microcrack caused by the volume change during lithiation/delithiation to maintain the electrode dynamic stability. The conductive polymers and conductive additives in anodes can form a fast electronic transfer channel. It has been reported that intrinsic SHP coating can improve the electrochemical performance of the Si and Si/C anodes, significantly[73]. The flexible SHP coating can dissipate the inner stress caused by the volume change, prevent the disintegration of the pulverized active particles and avoid the contact of the new interface between the pulverized particle and the electrolyte to generate new SEI. For the application, the SHP coating can also maintain the integrity of the Si and Si/C anodes by restoring the electrode microcracks during cycles.

Although nanosized Si particles could provide more free space alleviating the volume effect to improve the cycle performance of the battery, Si microparticles (MPs) have the lower costs and the higher volumetric energy density. But the extremely poor cycle stability restricts the development of Si MPs. SHPs have exhibited huge potential to improve the stability of Si MP anodes. Wang et al.[74] reported the coating of SHP on Si MPs (Fig. 4a). The amorphous SHP with the randomly branched hydrogen-bond allows the polymer chains at the fracture interface to rearrange and recombine. Therefore, the self-healing process is driven by the hydrogen bonds at room temperature to spontaneously repair the mechanical damages and cracks within electrodes caused by the huge volume change of Si MPs during lithiation/delithiation (Fig. 4b). Meanwhile, the good stretchability of SHP ensures the stable electrical contact between the active particles (Fig. 4c). Kim et al.[75] dispersed the Si MPs and the multi-walled CNTs (MWCNTs) in a SHP matrix and prepared a freestanding electrode. The stretchable and self-healing ability of the SHP enhanced the mechanical stability through the reversible hydrogen bonds, which can spontaneously repair any fractures inside the electrode materials caused by the repeated volume expansion at room temperature (Fig. 4d). The design of freestanding electrode without a current collector greatly avoided the stress caused by the volume change and

maintained the integrity of the electrode structure and electrical conductivity (Fig. 4e). The freestanding Si and Si/C anodes with the SHP has an improved capacity retention of 91.8% after 100 cycles at 0.1C (Fig. 4f).

It has been demonstrated that the coating thickness of SHP has a great influence on the specific capacity and cycle stability of Si and Si/C anodes. The thicker coating will increase the diffusion paths of lithium ions and the series resistance of electrode, resulting in a relatively lower capacity. In contrast, the suitable coating thickness can greatly improve the cycling stability of anodes. Sun et al.[76] designed a graphitic carbon/Si foam electrode coated by an elastic SHP with hydrogen bonds and covalent crosslinking. The supramolecular polymer coating containing a mass of hydrogen bonding sites can be mechanically healed at room temperature (Fig. 5a). The stretchable SHP can build a robust interface and maintain the electrode integrity during the volume change of the carbon/Si materials to improve the stability of LIBs. As shown in Fig. 5b, the electrodes coated with different amounts of SHP exhibited the different electrochemical performances. The optimized amount of the polymer made the carbon/Si foam electrode exhibited a specific capacity of 722 mA h g^{-1} after 100 charge/discharge cycles at 0.1 A g^{-1}, and the corresponding capacity retention was up to 83% after 100 cycles.

In the practical applications of Si and Si/C anodes, the rate performance is as important as the cycling life. It has been confirmed that increasing the electron and lithium transport rates of materials is an effective method to improve the kinetics and the rate performance of the LIBs[77]. Jiao et al.[78] implanted the polyethylene glycol (PEG) into a new tape of SHP binder since PEG can tune Young's modulus and provide ionic conductivity, simultaneously (Fig. 5c). PEG and polyethylene oxide (PEO) are common materials in polymer electrolytes because the lone pair electrons from the ether-oxygen bond can facilitate the transfer of lithium ions through coordination interaction, effectively. The self-healing property of polymer coatings is conferred by the dynamic disulfide bonds. The synthesized double-wrapped binder used in Si anodes can utilize the rigid polyacrylic acid (PAA) to dissipate the internal stress during the lithiation, while the elastic SHP coating can minimize the residual stress as a buffer layer and to maintain the integrity of the electrode during delithiation. As shown in Fig. 5d, the double-wrapped SHP binder with the rigidity and flexibility for Si anodes showed a high areal capacity of 3.5 mA h cm^{-2} and an excellent cycling stability with a capacity retention of over 88% after 200 cycles.

The structural design of SHP coating on Si and Si/C anodes can be summarized as follows. The polymer chain designs must have sufficient dynamics, and the molecular structure must contain multiple dynamic interactions[42]. The introduction of multiple covalent/non-covalent interactions with multiple bonds can enhance the mechanical property and the self-healing efficiency of polymers[79]. SHPs containing

abundant reactive functional moieties such as hydroxyl, carboxylate, carbonyl, nitrogenous groups, methyl benzoic ester groups, catechol groups, and sulfonic acid groups can interact with Si—OH and Si—O bonds on the surface of Si particles to form electrostatic bonds, hydrogen bonds and covalent bonds, which can effectively mitigate the stress and strains caused by the volume change of Si and Si/C anodes[80].

SHP coatings with the excellent ionic/electronic conductivity are beneficial to increase the specific capacity and the rate capability of batteries. Therefore, the rational design of SHP molecular structures as coatings of electrode materials becomes an effective strategy to address the main challenges of Si and Si/C anodes.
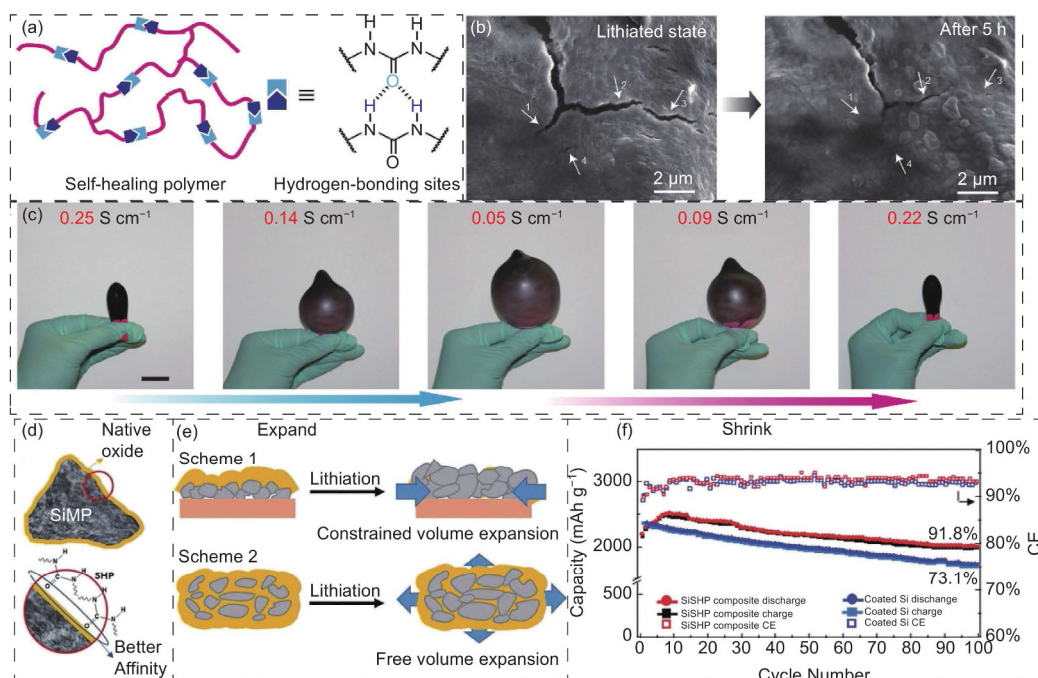

Fig. 4   (a) Chemical structure of the SHP. Polymer backbones (magenta lines), hydrogen-bonding sites (light-blue and dark-blue boxes).
(b) Structure of the self-healing Si MP electrode during electrochemical cycling. (c) The SHP/CB composite was coated on an inflatable balloon to mimic the volume and electrical conductivity changes of Si particles during cycles[74]. Reprinted with permission by Nature Research.
(d) Schematic illustration of the affinity between the SHP and Si MPs due to the presence of the native oxide layer. (e) Schematic illustration comparing the freestanding design and a conventional electrode. (f) Capacity retention and Coulombic efficiencies of the freestanding Si SHP composite anode (red) and the coated Si SHP electrode (blue) over 100 cycles at C/10[75].
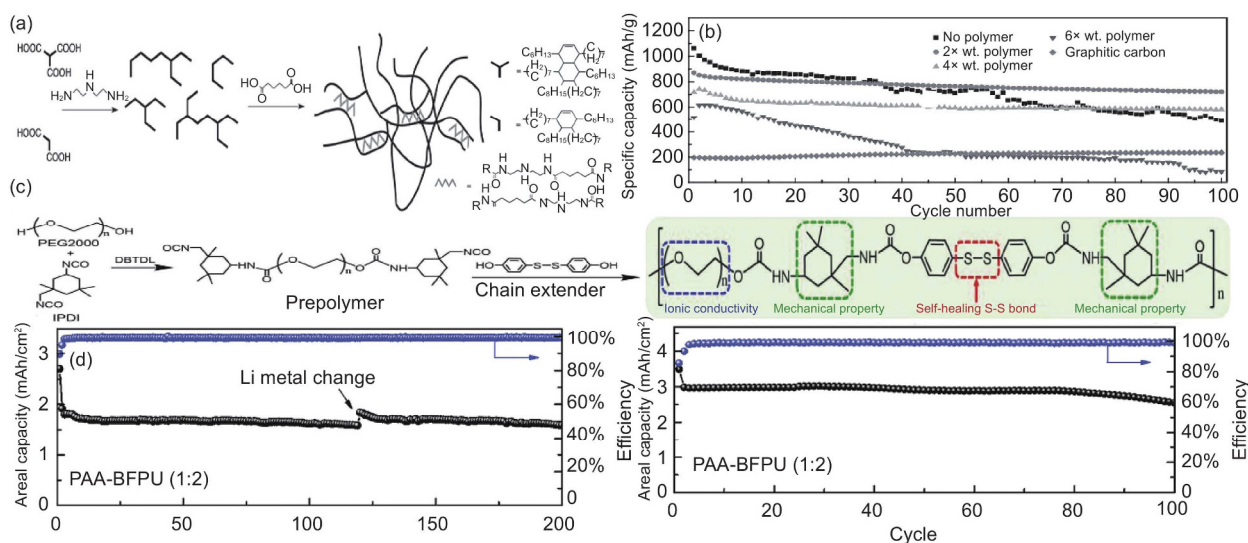Reprinted with permission by Royal Society of Chemistry.

Fig. 5   (a) Synthesis of the elastic SHP. (b) Cycling performance of the bare carbon electrode and the carbon/Si electrodes with different amounts of the SHP at a current density of 100 mA g^{-1}[76]. Reprinted with permission by Wiley-VCH. (c) Synthesis of the bifunctional polyurethane (BFPU) polymer. Fabrication of the Si anodes with double-wrapped polyacrylic acid (PAA)–BFPU binder. (d) Cycling performance of the Si/PAA–BFPU (1:2) electrode at a current density of 2 and 0.8 A g^{-1}[78]. Reprinted with permission by Wiley-VCH.

4 Construction of SHP binder networks around Si and Si/C materials

The SHP might only play the role around the surface of Si materials. However, the coating thickness and uniformity are hard to control when SHP is used as the surface coating of Si and Si/C anodes. In contrast, direct mixing the SHP with Si and Si/C materials is able to construct the SHP binder networks and the preparation process is controllable[42].

The SHP is bonded with Si and Si/C anodes by the physical type of non-covalent bonds and the reversible covalent bonds according to the self-healing mechanisms. SHP based on the covalent bonds consists of polymer chains to form polymer networks through the reversible bonds. When the polymer chains are broken, these reversible chemical bonds reconstruct at the damaged interface[53]. The chemical nature of the polymer determines its adhesion strength as a binder. SHP binders based on the non-covalent bonds and the reversible covalent bonds can be classified into three categories according to their reversibility and strength as the weak supramolecular interactions, the strong supramolecular interactions and the covalent bonds crosslinking (Fig. 6)[15]. In this section, the SHP performance is mainly discussed from the bonding properties and their effects.

4.1 SHP binders based on non-covalent bonds

Non-covalent bonds are dynamically reversible that are represented by hydrogen bonds, metal-ligand coordination, π-π interactions, ionic bonds, guest-host interactions and van der Waals forces[81]. Although the interactions of these bonds are relatively weak compared to the covalent bonds, they still can be used to construct the dynamic self-healing systems around the electrode materials[60].

SHP binders of non-covalent bonds can repair the damaged sites/microcracks through the formation of transient bonds and the non-covalent networks, taking into account the reversibility and the interactions between the bonds and the polymer chains[82]. When the polymer network is damaged,

the divorced interfaces could be produced. Around the interfaces, the multiple supramolecular bonds can move to recover and recombine the polymer chains and thereby to close and heal the cracks. The gluiness of non-covalent bonds determines the strength of the self-healing network[83]. In this part, the applications of dynamic non-covalent bond based self-healing binders for Si and Si/C anodes of LIBs are shortly summarized and commented.

4.1.1 SHP design based on hydrogen bond

Hydrogen bonding can be defined as the directional dipole-dipole attraction between a hydrogen atom and an electronegative atom (such as oxygen, nitrogen, or fluorine), which is bonded to another negatively charged atom by a pair of electrons[84]. Hydrogen bonding is one of the strongest non-covalent interactions, since its high per-volume concentration and relatively large strength. The dynamic properties of the SHP binder based on hydrogen bonds are critical for the process of repairing electrode microcracks, and thus improving the cycling stability of Si and Si/C anodes[53].

Recently, Su and coworkers[85] synthesized a multifunctional polymeric binder (1-phenyl-3-(2-pyridyl)-2-thiourea, PPTU) by hydrogen bond cross-linking of a conducting polymer, poly (3,4-ethylenedioxythiophene): poly (styrenesulfonic acid) (PEDOT:PSS) with a stretchable polymer, poly(ether-thiourea) (PETU). The PPTU can be curved on the surfaces of Si NPs to form an interwoven continuous 3D network, which is beneficial to the mechanical stability and the electron transfer. In addition, the excellent self-healing ability of PPTU binder can accommodate the huge volume change of Si to maintain the integrity of the electrode. Xu et al.[86] designed a water-soluble SHP binder of poly(acrylic acid)-poly(2-hydroxyethyl acrylate-co-dopamine methacrylate) (P(HEA-co-DMA)) by a free radical co-poly-merization reaction. As shown in Fig. 7a, the self-healing network composed of the soft/rigid chains and the hydrogen bonds not only provide the sufficient mechanical support, but also buffer the mechanical stress during lithiation/delithiation
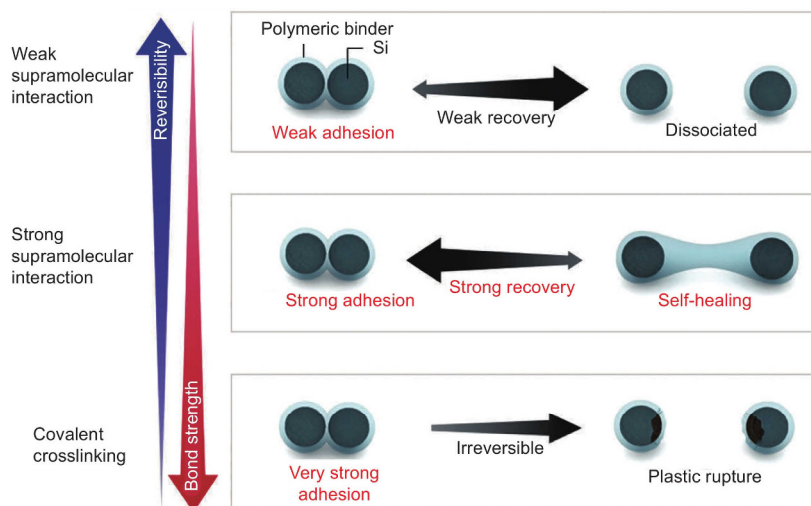

Fig. 6 Classification of chemical bonds, supramolecular interactions and their adhesion behaviors in Si anodes[15]. Reprinted with permission by Royal Society of Chemistry.

of Si. The catechol groups and the high content of hydrogen bonding sites endowed the flexible polymer with the self-healing capability to enhance the microscopic stability of the network structure[87]. Therefore, the capacity of P(HEA-co-DMA) was 2 394 mA h g^{-1} after 220 cycles with a capacity retention of 93.8% at 1.0 A g^{-1} (Fig. 7b). Li et al.[88] synthesized a glycinamide (GA) -modified PAA binder by the simple coupling method. The double amide groups of PAA-GA can bring the reversible double hydrogen bonds by the interchain condensation (Fig. 7c). Compared with PAA containing a single hydrogen bond, PAA-GA alleviated the mechanical stress resulted from the volume change of Si particles and maintained the structural integrity of the electrode (Fig. 7d). Si and Si/C anodes using PAA-GA as a binder exhibited a high ICE (86.5%), a satisfactory initial capacity (3 739 mA h g^{-1}) and an excellent cycling stability (81% retention after 285 cycles).

It is generally believed that quadruple-hydrogen-bonds have the higher self-healing efficiency than single or double hydrogen bonds due to the formation of more stable hydrogen

bonded dimers[89]. Zhang et al.[90] prepared the polyacrylic acid-2-ureido-4-pyrimidinone (PAA-UPy) with the reversible-quadruple hydrogen bonding through covalently integrating the UPy with the linear polymer PAA. The fractures of PAA-UPy as the binder can be reversibly recovered during cycles of battery (Fig. 8a). As shown in Fig. 8b, the electrodes with PAA-UPy clearly showed the less and smaller cracks than the other 2 linear binders. The damage caused by the Si volume change can be repaired immediately and the electrical connection of materials can be also kept during the repeated lithiation/delithiation. Therefore, the Si anode with a discharge capacity of 4 194 mA h g^{-1} and cycling stability with a capacity of 2 638 mA h g^{-1} after 110 cycles can be obtained. Yang et al.[91] investigated a self-healing binder (UPy-PEG-UPy) by introducing UPy with the quadruple hydrogen-bond ureido-pyrimidinone moiety to the PEG oligomers. Similar to the previous work, the strong self-healing ability of the UPy dimer can drive the rees-tablishment of quadruple hydrogen bonds (Fig. 8c) to prevent
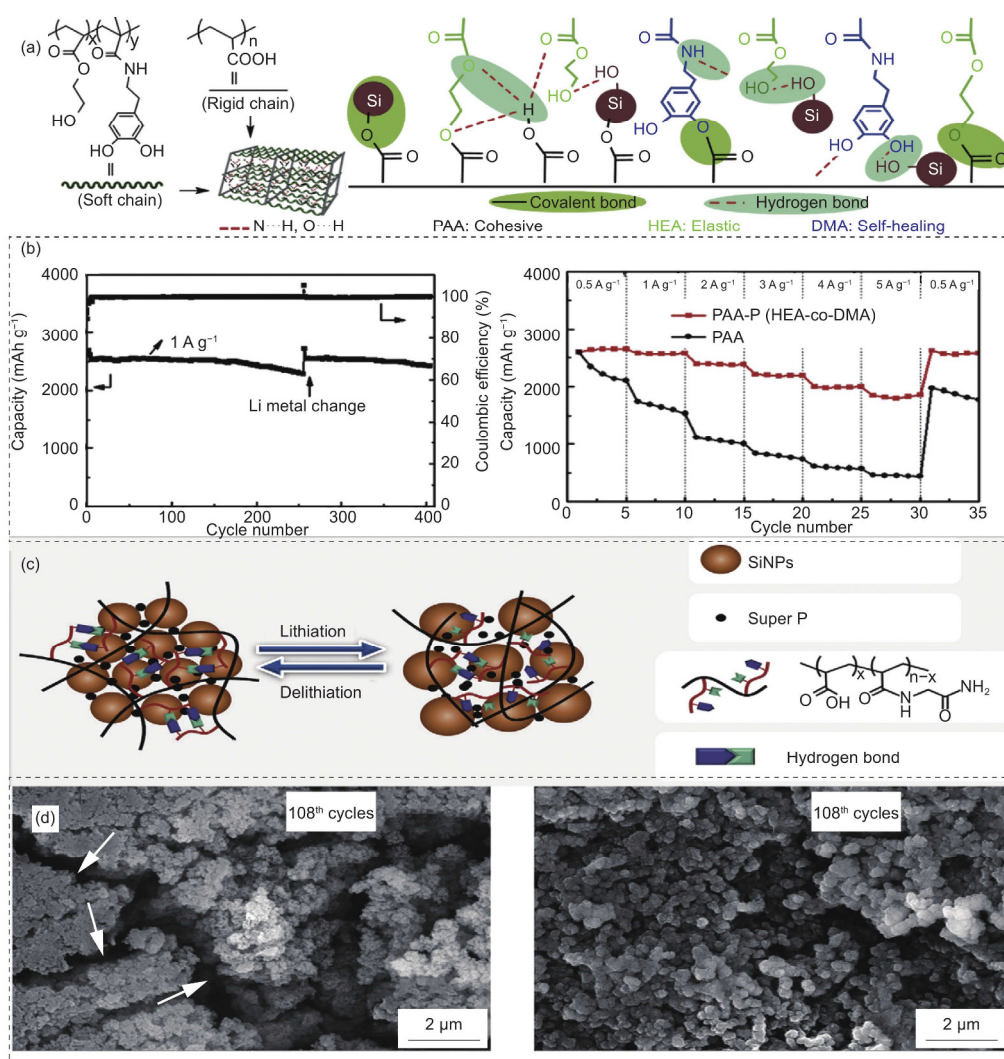

Fig. 7　(a) Chemical structures of P(HEA-co-DMA) and their interaction with Si. (b) Cycling and rate performance of P(HEA-co-DMA)[86]. Reprinted with permission by Elsevier. (c) Schematic illustration of the lithiation/delithiation process of Si electrodes using PAA-GA polymer with reversible double hydrogen bonds as a binder. (d) SEM images of Si/PAA and Si/PAA-GA electrodes after 108 cycles at 0.2 C[88]. Reprinted with permission by Elsevier.

Si NPs from the agglomeration and to maintain the integrity of the Si and Si/C electrode. As shown in Fig. 8d, the application of UPy-PEG-UPy SHP binder results a high performance of the Si anode that exhibits an ICE of 81% and a reversible capacity of 1 454 mA h g^{-1} after 400 cycles.

In 2021, Liu et al.[92] synthesized a polymer binder with highly stretchable and elastic property for Si and Si/C anodes by an in-situ cross-linking PAA with isocyanate-terminated polyurethane oligomers (CPAU) that consisted of UPy moieties and PEG chains during the electrode preparation. In CPAU, the UPy moieties supplied the reversible and strong quadruple-hydrogen bond cross-linkers, and the soft PEG chains can dissipate the stress caused by the volume expansion of Si particles (Fig. 8e). As a result (Fig. 8f), although the cross-sections of both the Si@CPAU and the Si@PAA electrode had the same thicknesses of 16.3 μm before cycling, the Si@CPAU electrode can well maintain the integrity of electrode and there were only a few cracks after 10 cycles. However, the severe cracks were observed in the Si@PAA electrode. The binder of CPAU resulted in the formation of the elastic three-dimensional network around Si and Si/C particles (Fig. 8g), which can provide high resistance to immobilize the structure of the Si anodes and improve the cycling performance of the battery[86,93].

4.1.2 SHP design based on metal-ligand non-covalent bond

Among the non-covalent interactions, metal-ligand interactions are more favorable due to their unique properties. At the end of the polymer chain or as a side group, the metal ions and the appropriate ligands will spontaneously combine to form a coordination complex, linking the polymer chains together[60]. The strength of the coordination bond is between van der Waals interactions and covalent bond, which can be tuned over a fairly wide range (approximately between 25% and 95% of covalent bonds)[94,95]. The dissociation and recombination of metal ions ligands can promote the recovery of mechanical damage. The bond strength can be adjusted by carefully selecting the combination of metal ions with ligands, which can improve the self-healing efficiency of polymer materials[95].

In 2019, Jeong and Choi[96] firstly presented the SHP binder based on the coordination bonds. They synthesized a metallopolymer network built by Fe^{3+}-(tris)-catechol coordination crosslinking, poly (DMA_{33}-co-BA_{66}-co-$PEGdA_1$, PDBP) from dopamine methacrylamide (DMA), aliphatic butyl acrylate (BA) and polyethylene glycol diacrylate (PEGdA). The effective self-healing property of the binder played an important role in maintaining the integrity of the Si electrode during the continuously expand and contract of Si particles (Fig. 9a). It was found that pH value had a great influence on
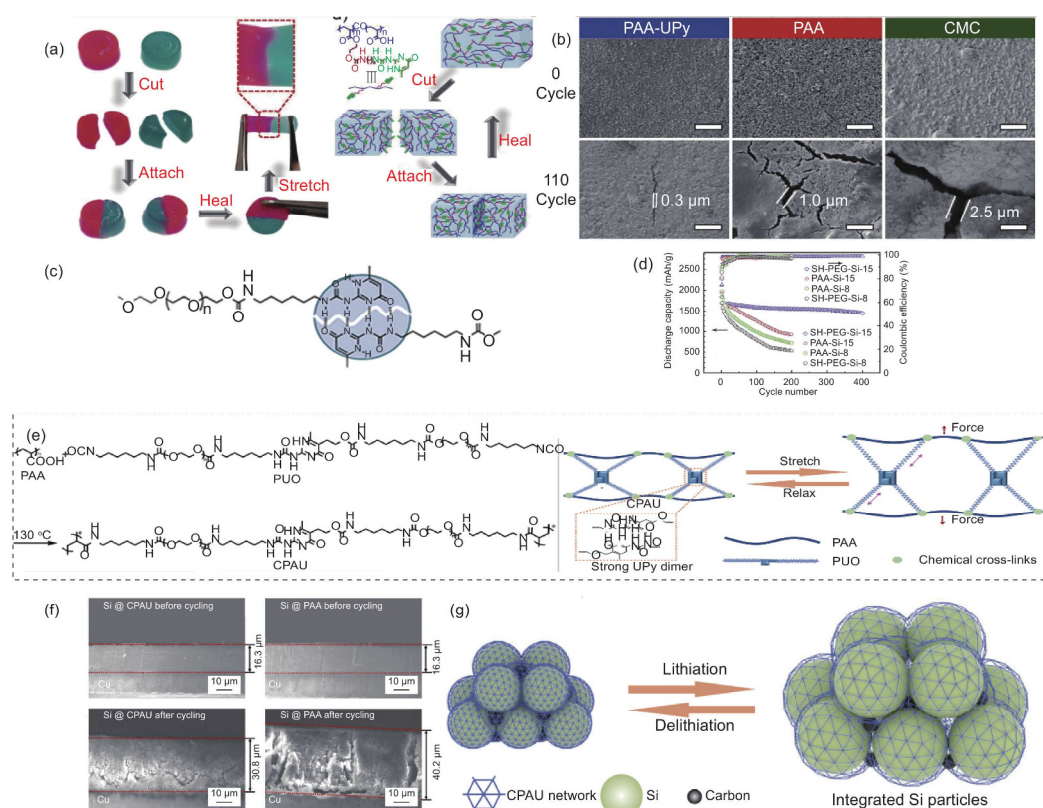

Fig. 8   (a) The schematic illustration of self-healing mechanism and self-healing test of PAA–UPy based hydrogel. (b) SEM images of Si electrodes with different binders before and after 110 cycles[90]. Reprinted with permission by Wiley-VHC. (c) Self-healing mechanism of UPy-PEG binder crosslinked via quadruple hydrogen bonds. (d) Cycling performance and Coulombic efficiency of UPy-PEG-Si-15[91]. Reprinted with permission by Elsevier Science INC. (e) Schematic illustration of the synthesis scheme and self-healing properties of CPAU. (f) Cross-sectional view of Si electrodes before and after cycling. (g) Schematic illustration of CPAU binder maintaining the integrity of the electrode materials[92]. Reprinted with permission by American Chemical Society.

the strength of Fe^{3+}-catechol coordination bond (Fig. 9b). When the pH value was increased from neutral to 10, a stable tridentate ligand structure was gradually formed between the Fe^{3+} and the catechol. As shown in Fig. 9c, the binders based on coordination bond had a high self-healing efficiency, the microcracks on the surface of Fe-PDBP@pH10 electrode almost disappeared after 50 cycles. The corresponding Si electrode exhibited a capacity retention of 81.9% after 350 cycles and an excellent rate performance, which was superior to the Si anode using the linear polymer of PAA or PVDF as the binders (Fig. 9d).

Recently, Kim and coworkers[56] successfully synthesized the CMC-PEG-Im-Zn^{2+} binder by in-situ cross-linking of carboxymethyl cellulose (CMC) with the Zn^{2+}-imidazole backbone during electrode fabrication (Fig. 10a). The flexibility of the PEG chains and the self-healing property of the Zn^{2+}-imidazole coordination bonds synergistically ensured the high elasticity of the binder network, enhanced the contact between the Si particles and sustained the integrity of the electrode structure. The 3D network structure can dissipate the stress generated by the volume expansion of active particles. As shown in Fig. 10b, the interparticles in Si/C composite electrodes using styrene-butadiene rubber (SBR)/CMC as the binder was filled by the SEI layer, which led to an unstable solid interfacial layer. In contrast, most spaces between the interparticles in the electrode using SBR/CMC-PEG-Im-Zn^{2+} as binder were still empty after cycles, proving that the Zn^{2+}-imidazole coordination bond can significantly inhibit the continuous formation of SEI. Therefore, the Si/C anode and the full cell paired with $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode exhibited an excellent performance (Fig. 10c).

4.1.3 SHP design based on ionic interaction

Polymers based on the ionic interactions are generally composed of ions or ionizable groups with the opposite charges[45]. Ionic groups or clusters mainly include phosphate ($—PO_3^{2-}$), sulfonate ($—SO_3^{2-}$), and carboxylate ($—COO^-$) by the physical cross-linking, they can endow the polymers with flexibility[97]. The level and types of ionic groups have a great influence on the mechanical properties of the polymers. For example, the fracture resistance and the tensile strength of the polymers can be improved with the increase of the ionic content within a certain range[98]. Some ionic type polymers have the excellent self-healing functions due to the unique complex microstructures and dynamic reversible physical crosslinks[45].

Kang et al.[99] utilized the carboxylic acid-deprotonated PAA and the amine-functionalized Si particles (denoted as Si-NH_2) to produce ionic ammonium carboxylate salts at the interface during electrode preparation (Fig. 11a). Compared with the hydrogen-bonded binder (Si-CH_3/PAA), the Si-NH_2/PAA composite anode with ionic interactions exhibited a capacity retention of 80% after 400 cycles at 2.1A g^{-1} and a good rate capability (Fig. 11b). Recently, Jin et al.[100] reported a self-healing polyelectrolyte binder for Si and Si/C anodes. A self-healing binder was prepared by crosslinking phytic acid, polydopamine and poly (acrylamide-co-2-(dimethylamino)ethyl acrylate) (poly(AM-co-DMAEA)) in-situ through the reconfigurable hydrogen bonds and the ionic bonds. On this basis, a trace amount of dopamine was
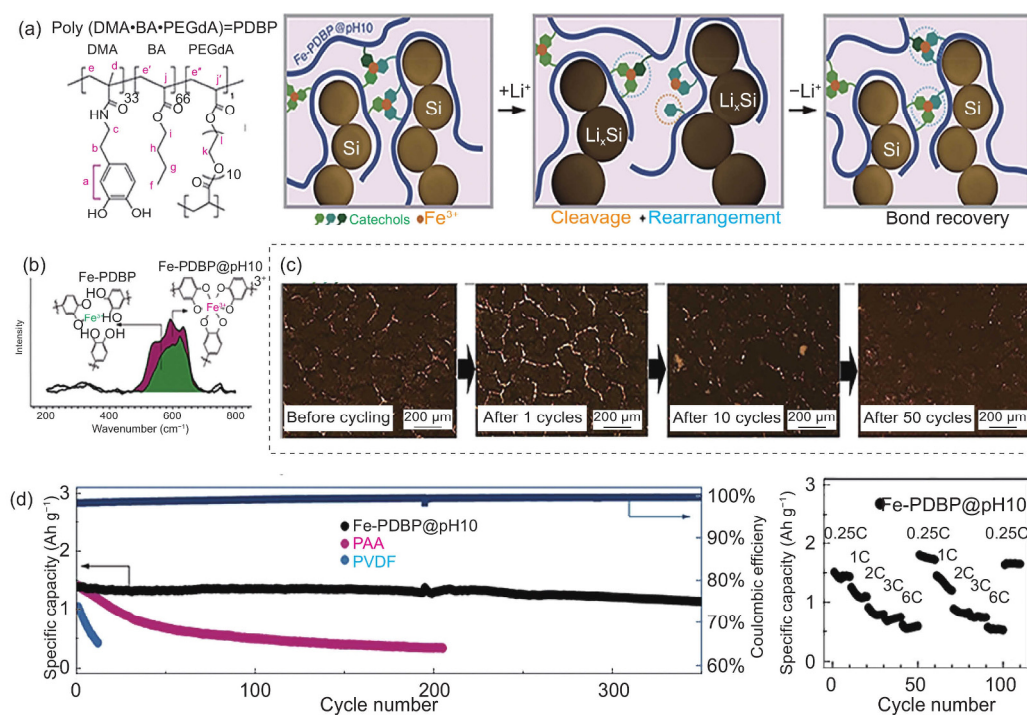

Fig. 9   (a) Molecular structure of PDBP polymer as a binder for Si anodes (left) and schematic illustration of Si-binder network configuration during cycling (right). (b) Raman spectra and mapping of Fe-PDBP prepared at pH 10 (magenta) and pH 5 (green). (c) Optical microscopy images of Fe-PDBP@pH10 based Si electrodes before and after self-healing process. (d) Cycling and rate performance of Si electrodes based on Fe-PDBP@pH10[96]. Reprinted with permission by American Chemical Society.

first added to auto-polymerize the alkaline poly(AM-co-DMAEA) in aqueous environment, while the reversible hydrogen bonds could be formed. Subsequently, the phytic acid ionizing H$^+$ can initiate the protonation of tertiary amine groups in polyDMAEA chains to form the dynamic ionic bonds (Fig. 11c). During the volume shrinkage, the self-healing binder can quickly glue and heal a majority of cracks emerged on electrodes due to volume expansion of Si particles. This excellent self-healing performance was due to the hydrogen bonds formation, π-π stacking and ionic interactions to tightly bind the fractured samples together (Fig. 11d, e). From Fig. 11f, the change of electrode thickness before and after cycles can confirm that the self-healing binder had the ability to repress the volume expansion of Si and Si/C electrodes compared to the linear binder PAA. The high loading amount of SiO-graphite and Si electrodes with self-healing binder exhibited high areal capacity and satisfactory cycling stability, which retained a reversible capacity of 1 000 mA h g^{-1} after 200 cycles at 0.3 A g^{-1} and a retention of 77% after 500 cycles (Fig. 11g).

4.2 SHP binders based on reversible covalent-bonds

As the self-healing binders based on the non-covalent bonds are generally weak and labile, the polymers have the reversible covalent bonds with high bonding strength are attracting more attentions. The mechanical strength of self-healing binders can be enhanced by the covalent cross-linking to optimize the electrochemical performance of Si and Si/C electrodes[101-103]. The reversibility of covalent bonds is generally evaluated by the bonding and debonding of chemical bonds between the different molecules or functional groups of the polymer[104]. Self-healing binders based on the reversible covalent bonds such as imine bonds[105], boronate ester bonds[106], disulfide bonds[78], and Diels-Alder reactions[107] have been demonstrated to improve the electrochemical performance of Si and Si/C electrodes.

It is generally considered that the reversible imine bonds involve Schiff base chemistry, which can be reversibly produced by the reaction of the carbonyl compounds and the primary amines[108,109]. Nam et al.[105] prepared a crosslinking polymer network with the reversible imine linkages via the dialdehyde-terminated PEG with glycol chitosan (GCS) (Fig. 12a). The conduction of lithium ions between the Si particles and the electrolyte around the binder layer was improved by introducing PEG with the capability of coordinating with lithium ions. As shown in Fig. 12b, the crosslinking polymer network formed by the imine bonds provided a rapid self-healing ability, which can alleviate the physical stress caused by Si volume change to ensure the structural stability of the electrode. By observing the electrode before and after cycles, it was found that the cycled self-healing electrode showed a very similar morphology with the pristine electrode
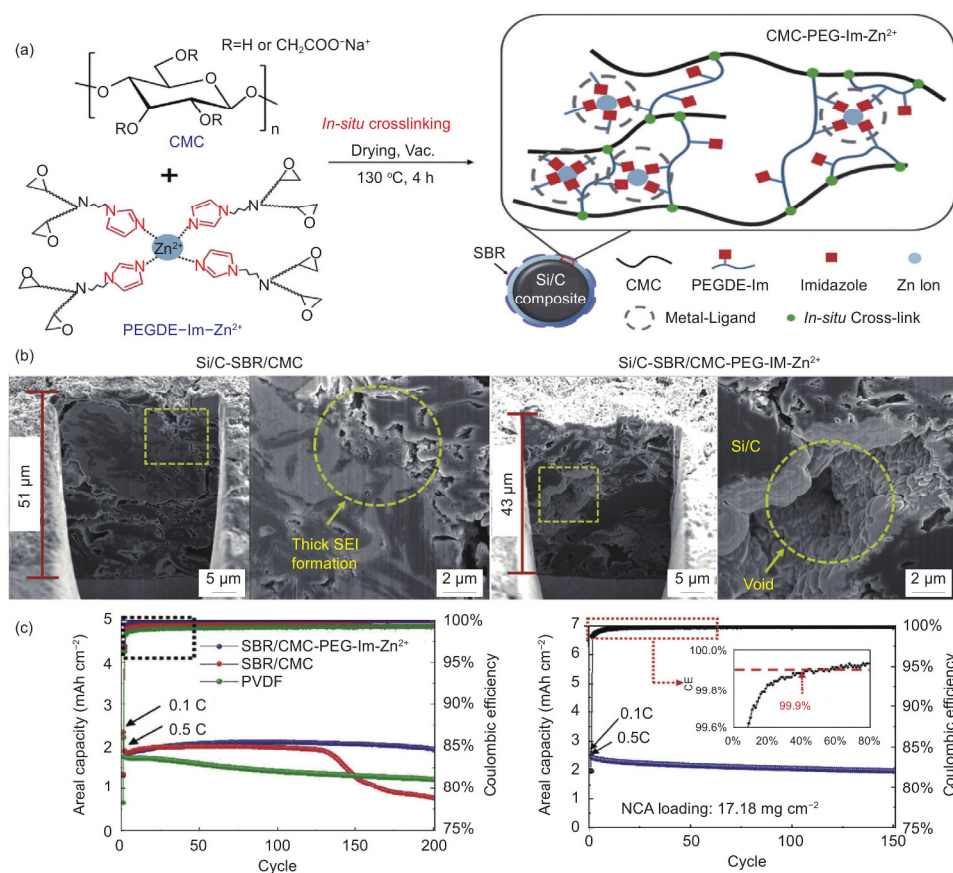

Fig. 10　(a) Schematic illustration of the supramolecular network formed by crosslinking between CMC and PEGDE-Im-Zn^{2+} in situ on the Si/C composite. (b) Cross-sectional SEM images of Si/C electrodes. (c) Cycling performance of Si/C electrodes and the full-cells using SBR/CMC-PEG-Im-Zn^{2+} measured at 0.5 C along with their Coulombic efficiencies[56]. Reprinted with permission by Wiley.

before cycle, besides some fine cracks. Furthermore, the SEI layers appeared to be uniform and stable (Fig. 12c). As shown in Fig. 12d, the Si electrode using the xPEG-GCS-0.5 polymer

binder exhibited an excellent cycling stability and a rate capability (a reversible capacity of 2 716 mA h g^{-1} at 3 C was maintained).
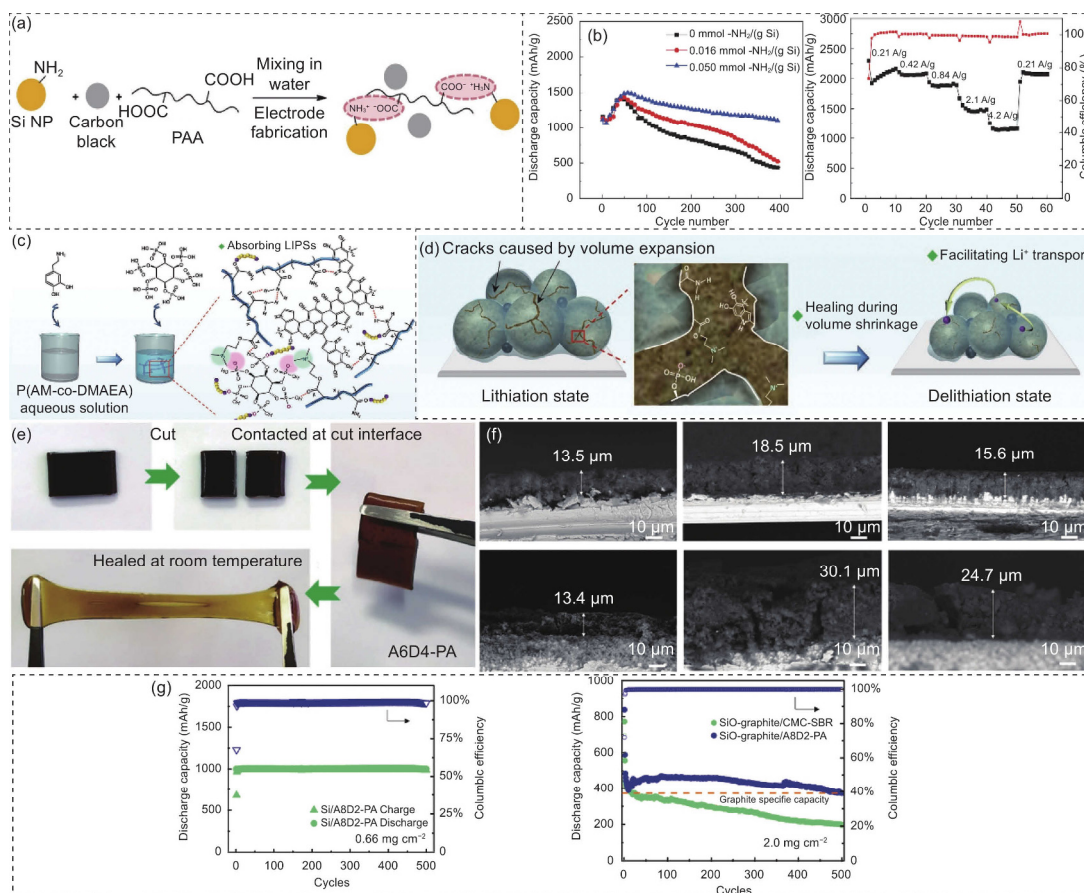

Fig. 11   (a) Formation of ionic bonds between the interface of PAA binder and Si NPs in Si composite anodes. (b) Cycling performance and Coulombic efficiency of Si-NH$_2$/PAA composite anode at various current densities[99]. Reprinted with permission by Wiley-VHC. (c) The synthesis process of the self-healable polyelectrolyte binder. (d) Self-healing process of self-healable polyelectrolyte binder in lithiation and delithiation. (e) Self-healing process of A6D4-PA. (f) Cross-section view of Si/PAA and Si/A8D2-PA. (g) Cycling performance of the Si/A8D2-PA and SiO-graphite/A8D2-PA[100]. Reprinted with permission by Wiley-VHC.
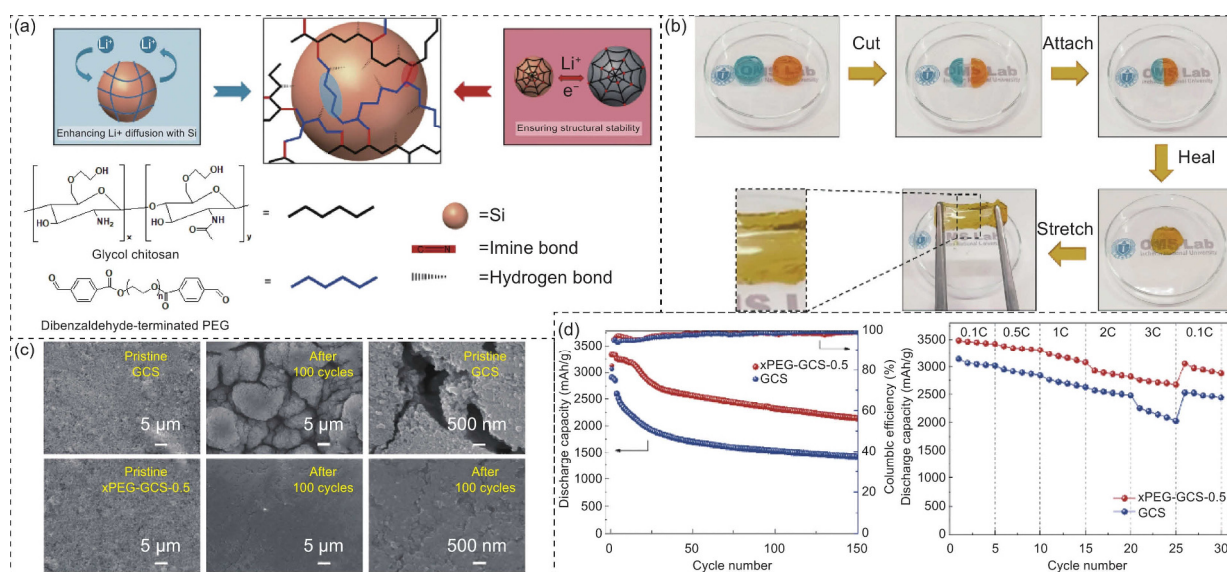

Fig. 12   (a) Schematic illustration of the adhesion mechanism of the xPEG-GCS binder in the Si electrode. (b) Self-healing tests of the xPEG-GCS-0.5 hydrogel after physical damage at room temperature. (c) Top-view images of the GCS and xPEG-GCS-0.5 based Si NP electrodes before and after 100 cycles. (d) Long-term cycling performance and rate performance[105]. Reprinted with permission by Elsevier.

Borate ester bonds are very important components in the intrinsic SHP[110]. Because of electron deficiency, the boronic acid prefers to form the dynamic borate ester bonds with electron-rich diols via the favorable tetrahedral geometry. Meanwhile, the pH value has a great influence on the stability of the borate ester bonds[111]. Ryu et al.[106] designed a SHP binder based on the vicinal alcohols of commercial polysaccharide polymer and the reversible borate ester bonds between the boronic acid group of the rigid polystyrene backbone. The PEO groups as another branch to impart high ionic conductivity of the polymer (Fig. 13a). As shown in Fig. 13b, the 180° peel testing confirmed that the introduction of reversible covalent bonds into the hydroxyl-enrich polysaccharides can delocalize the stress to the multiple side chains (i.e., borate ester groups). Hence, the total strength of electrodes can be enhanced. With the combination of hydrogen bonds and covalent bonds, the boronic crosslinker (BC) incorporated guar gum binder possessed the highly mechanical strength to make the polymer network to exhibit an excellent self-healing performance and a fast rate of lithium ions diffusion, which improved the cycling stability and rate performance of the Si and Si/C electrode of LIBs (Fig. 13c).

The most widely studied exchange reaction in the field of SHPs is the Diels-Alder (DA) reaction that is controllably reversible cycloaddition reaction of dienes with dienophiles[112]. By utilizing the DA reaction, Rajeev et al.[107] prepared a 3D crosslinking polymer network (Fig. 13d). It was the first report on the synthesis of polymer binder for Si anodes by DA reaction. Because of the reversible nature of DA chemistry reaction, the 3D crosslinking network binder exhibited a good self-healing property. As shown in Fig. 13e,

after 100 cycles, the Si@DA-PAA self-healing electrode still maintained a smooth surface. However, a series of linear structural binders such as furfurylamine-functionalized polyacrylic acid (FPAA), PAA, cold-mix asphalt (CMA), sodium alginate (SA) and PVDF had produced numerous cracks on the surface of the electrode. It indicated that the DA crosslinking binder had the excellent adhesive strength and self-healing property, which can prevent the Si particles from pulverization during charge-discharge.

5 SHP for solid-state polymer electrolyte in the flexible lithium batteries

Flexible lithium batteries (FLBs) can enable the power supply to the flexible and wearable electronic devices and thus have attracted much attention[113]. Lithium batteries with flowable liquid electrolyte are not suitable for use in flexible and wearable electronics due to its possible leakage, combustion and explosion when the battery suffers a large stress and strain[114]. Solid-state polymer electrolytes (SPEs) have lightweight, good flexibility, well film-forming property and high mechanical strength. Applying SPEs in FLBs can resolve the problems caused by liquid electrolyte and restrict the growth of lithium dendrite, improving the long-term cycling stability of LIBs, and thus presenting a promising prospect for the development of flexible and wearable electronics. However, SPEs are easily damaged or cracked under external force during assembly and application, resulting in battery failure. SHPs have ability to spontaneously repair the damaged parts of materials and thus have been proposed as ideal candidates for high performance SPEs[115].
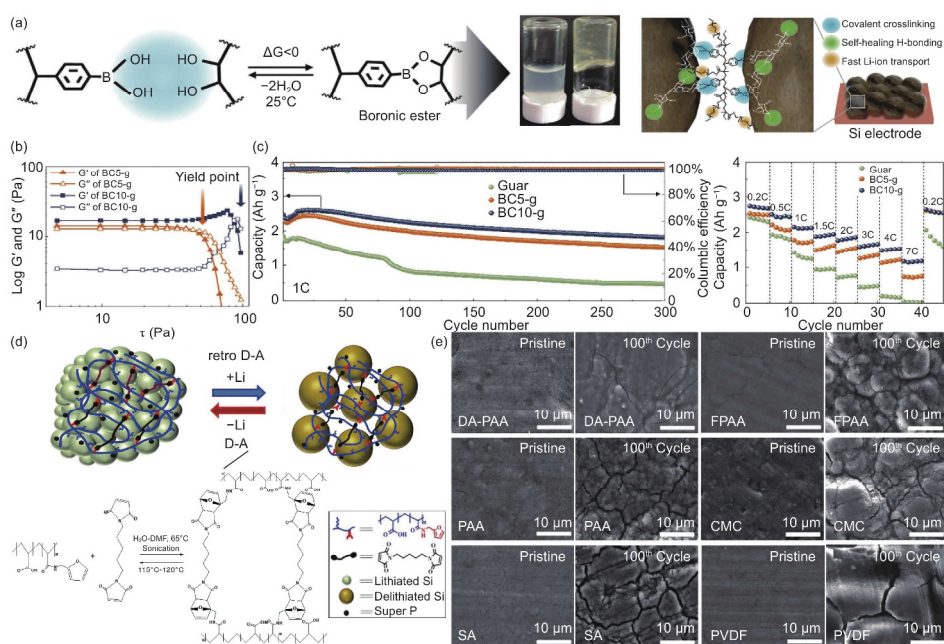

Fig. 13   (a) Schematic illustration of synthesis of the borate ester bond-based BC-g binder and its mechanism of action on Si electrodes. (b) Mechanical characterization of the nonlinear rheological response of BC-g hydrogel. (c) Long-term cycling performance of BC-g and guar electrodes at 1 C for 300 cycles and rate performance at various C-rates[106]. Reprinted with permission by Wiley-VCH. (d) Schematic representation of the SHP binder based on DA reaction. (e) Surface SEM images of Si electrodes with DA-PAA and conventional binders before and after 100 cycles[107]. Reprinted with permission by Pergamon-Elsevier Science Ltd.

Li et al.[114] based on the six-arm architecture and the dicationic charge scaffold, a self-healing SPE that can be applied in FLBs was developed through the combination of the six-arm dicationic polymeric ionic liquid (DPIL-6), imidazole-based ionic liquid (EMIM-TFSI) and LiTFSI (Fig. 14a). The combination of the multi-arm structure with the multi-charge centers strengthened the ionic attractions and van der Waals forces between the polymer segments, thus conferred DPIL-6-SPE with excellent self-healing ability (recovery time < 2 h at 25 °C). As shown in Fig. 14b, the repairing process after polymer disconnection showed good self-healing properties of DPIL-6-SPE. The mechanical properties (Fig. 14c) and the conductivity (Fig. 14d) of DPIL-6-SPE can be fully recovered after repeated damage. The cell of LiFePO₄/DPIL-6-SPE/Li maintained a discharge capacity of 152.6 mA h g⁻¹ and good cycling stability at 0.1 C with a Coulombic efficiency of 96% (Fig. 14e). The DPIL-6-SPE derived soft-pack battery had the stable powering capability during multi-angle folding and bending. Recently, Zhu et al.[116] prepared a self-healing SPE (PEO@BPIL). PEO@BPIL was combined with an imidazolium-based polymerized ionic liquid (poly(ethylene glycol) monomethacrylate (PEGMA)) block polymer. A large number of imidazole groups conferred PEO@BPIL with abundant ionic interactions and non-covalent bonds, thereby the PEO@BPIL exhibited an excellent self-healing performance (recovery time < 30 min, 60 °C) (Fig. 14f). After the SPE repeatedly broken and healed 1-5 times on the same location, its electrochemical impedance spectra (EIS) almost

overlapped, the impedance was closed, and the electrochemical performance was restored to the same as before (Fig. 14g). The PEO@BPIL-3-SPE used in a soft-pack battery can maintain a stable output in both multiangle folding and bending at room temperature, and showed an excellent application potential in wearable electronics (Fig. 14h).

Wang and coworkers[115] developed a unique self-healing SPE through the combination of poly (2,2,3,4,4,4-hexafluorobutyl methacrylate-co-sulfobetaine methacrylate) (poly(HFBM-co-SBMA)), imidazole-based ionic liquid (EMI-TFSI) and LiTFSI. The prominent self-healing ability of self-healing SPE (recovery time < 60 min, 25 °C) was attributed to the supramolecular bonds (ion-dipole interactions) formed by a fluorine atom and imidazole cation inside the electrolyte framework (Fig. 15a). As shown in Fig. 15b, the self-healing SPE film recovered from the two parts being cut can be stretched up to more than 6 times as its original length after self-healing for 2 h at room temperature. The functional recovery of the materials is vitally important to its practical application. The ionic conductivity of self-healing SPE was tested after repeated breaking/healing at the same location. The healed sample showed a negligible change in the Nyquist plot compared with the original state (Fig. 15c). The self-healing SPE derived soft-pack battery can power five LEDs and maintain its function during multi-angle folding and bending (Fig. 15d). The self-healing SPE showed fully recoverable conductivity and mechanical properties after the repeated damages, and presented a great promise for use in safe and reliable flexible electronics.
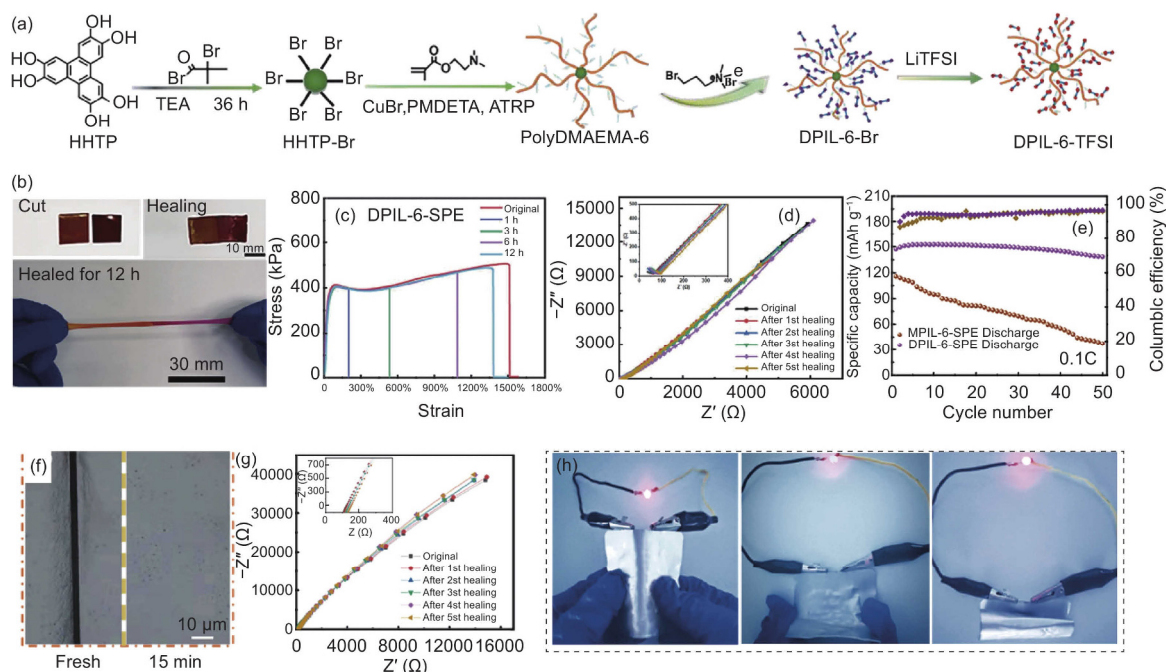

Fig. 14　(a) Synthetic approach for the six-arm DPIL-6. (b) Images of DPIL-6-SPE stretched after self-healing for 12 h. (c) Stress strain curves of DPIL-6-SPE at different repairing times. (d) Nyquist plots of DPIL-6-SPE after five breaking and self-healing cycles. (e) Cycling performance of LiFePO₄ /DPIL-6-SPE/Li batteries at 0.1C at 60 °C[114]. Reprinted with permission by Elsevier Science SA. (f) The damage and self-healing photos of PEO@BPIL SPE at 60 °C. (g) Nyquist plots of PEO@BPIL SPE after five breaking and self-healing cycles. (h) The powering of LEDs with a PEO@BPIL SPE soft-packed lithium metal battery under different bending conditions[116]. Reprinted with permission by American Chemical Society.
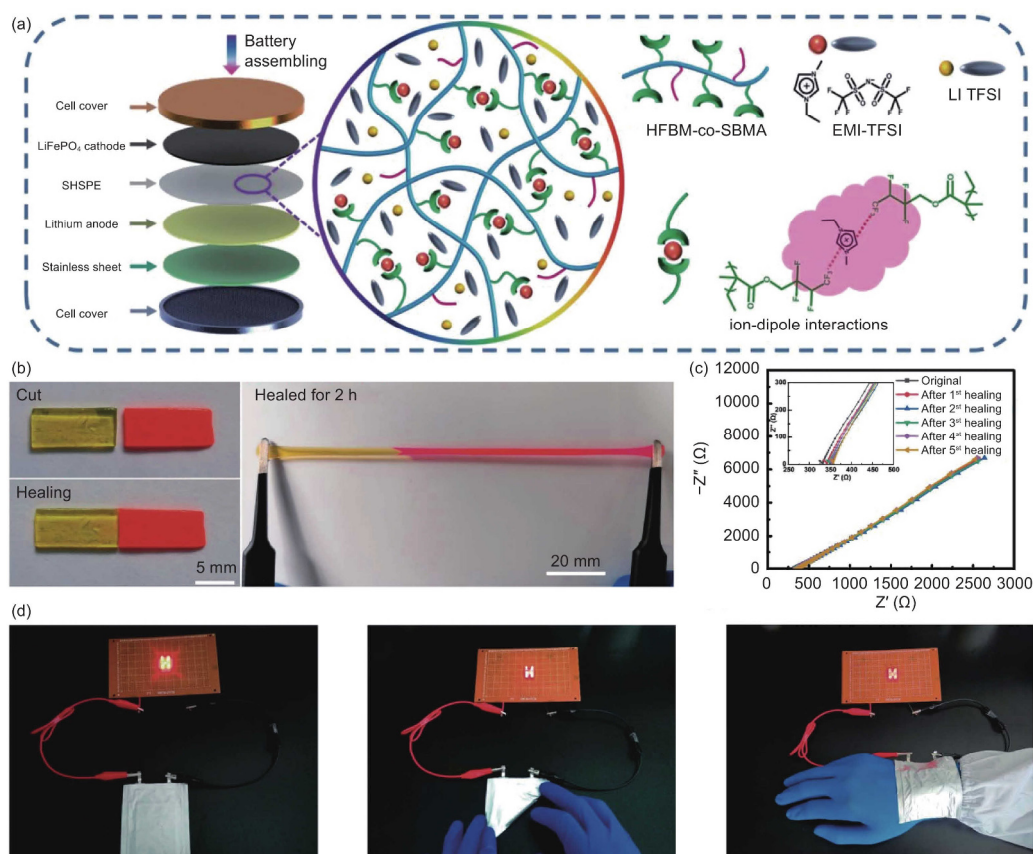
Fig. 15   (a) Schematic illustration of the configuration of the Li/Self-healing SPE/LiFePO₄ cell and macromolecular structure of self-healing SPE.
(b) Photos of self-healing SPE tretched after self-healing for 2 h. (c) Nyquist plots of self-healing SPE after five breaking/healing cycles.
(d) Photos showing the soft-packed battery under bending and unbending[115]. Reprinted with permission by Royal Society of Chemistry.

6 Summary and perspective

Self-healing polymer (SHP) binders have demonstrated the great potential in improving the performance of electrode materials of LIBs. The recent progress of SHPs on addressing the challenges of Si and Si/C anodes of LIBs have been summarized and commented from the aspects of SHP coatings, SHP/carbon coatings, SHP binders. The design and applications of SHP binders on Si and Si/C anodes by utilizing the interactions of non-covalent bonds and covalent bonds are critically reviewed.

The huge volume expansion of Si and Si/C anodes inevitably causes the destruction of the electrode. The flexibility and self-healing properties of the coatings containing SHPs can relieve the mechanical stress caused by the volume expansion of Si and maintain the structure stability of electrode in some degree. However, the coating thickness and uniformity are hard to control during electrode preparation, and the SHPs might play a role only around the surface of the Si and Si/C particles. In contrast, SHP binders based on the non-covalent bonds or the reversible covalent bonds can be directly mixed with Si and Si/C materials, which has more potential for the practical applications and commercialization. SHP binders of non-covalent bonds can rapidly repair the damaged sites/microcracks through forming the transient bonds and non-covalent networks. SHP binders

having the reversible covalent bonds with higher bonding strength and mechanical strength are attracting more attentions in recent years. The SHPs can effectively maintain the integrity of Si and Si/C anodes and enhance the cycle stability of LIBs. The applications of SHPs have become an ingenious strategy to address the most important challenges of Si and Si/C anodes of LIBs. SHPs can rapidly restore the mechanical properties and ionic conductivity of electrolytes of SPEs after multiangle folding and bending, which provides a great promise for the development of the reliable and safe flexible lithium metal batteries.

Although the developments of SHPs have a significant progress in recent years, the applications of SHPs as binders and SPEs for battery systems are still in the infancy stage. In near future, the critical aspects on exploring SHPs with good performance should be paid more attentions. (1) The introduction of self-healing components into the electrode system could affect the electrochemical window. It is necessary to design SHP binders with wide electrochemical windows and high voltage stability. (2) Most of SHPs are ionically and electrically insulated. The polymers only having the self-healing ability are not suitable as high-performance binders and SPEs in battery systems. Cross-grafting side chains or groups with lithium transport functions or electronic conductivity is an effective approach to achieve SHP binders and SPEs with an excellent electrochemical performance. (3)

The SHP binders are required to have good chemical stability and thermal stability. The designed SHP binders are insoluble, non-decomposable in the electrolyte system, and have a good absorption capacity for the electrolyte. (4) The self-healing mechanisms of SHP binders and self-healing SPEs need further investigation by the experiments and the theoretical simulation.

Acknowledgements

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