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Advances in intrinsically self-healing solid polymer electrolytes for lithium-ion batteries. Review article.

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The demand for high safety and long cycle life of lithium-ion batteries has driven in-depth research on solid polymer electrolytes (SPEs), but the problem of mechanical damage has severely limited their practical applications. Intrinsic self-healing SPEs provide innovative solutions for healing micro cracks and inhibiting dendrite growth, enabling dynamic network reconfiguration capabilities. In this paper, we systematically review the design strategies and research progress of self-healing SPEs: SPEs based on supramolecular interactions (e.g., quadruple hydrogen bonds achieving >95% healing efficiency within 1–60 min at room temperature); SPEs based on dynamic covalent bonds (e.g., imine bonds enabling ionic conductivities up to 7.48×10^{-4} S cm^{-1}); and synergistic design strategies combining dynamic covalent bonds with supramolecular interactions. Critical limitations persist, including low intrinsic ionic conductivity (10^{-4} S cm^{-1} without plasticizers) impeding fast charging, unresolved trade-offs between mechanical strength (>10 MPa) and healing efficiency (>95%), along with unverified scalable manufacturing and long-term stability under extreme conditions such as high voltage or bending. Future research should prioritize cross-scale co-design of dynamic networks, develop intelligent sensing and adaptive healing systems, and advance engineering manufacturing processes. These developments will facilitate the transformation of self-healing SPEs from fundamental research to practical high-safety, long-lifespan energy storage devices.

Keywords: Self-healing, solid polymer electrolytes, lithium-ion batteries, supramolecular interactions, dynamic covalent bonds.

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INTRODUCTION

Lithium-ion batteries (LIBs) have become the mainstream electrochemical energy storage technology for portable electronic devices and electric vehicles due to their significant advantages, including high operating voltage, low self-discharge rates, long cycle life, and no memory effect[1, 2]. Furthermore, LIBs and other new energy sources play a crucial complementary role alongside traditional energy sources (e.g., fossil fuels, hydropower) within the evolving energy mix. This collaboration is essential for ensuring overall energy security by providing diversified, reliable, and increasingly sustainable power generation and storage solutions during the global energy transition[3, 4]. However, the liquid electrolyte system commonly used in current commercialized LIBs has significant safety hazards, which may lead to serious safety accidents such as short circuit, thermal runaway, and even fire and explosion[5–7]. In this context, solid polymer electrolytes (SPEs), which are lightweight, flexible, and have excellent film-forming and process ability properties, are regarded as the key materials to break through the safety bottleneck of liquid electrolytes and improve the energy density of batteries[8–11]. Notably, SPEs with thicknesses of tens to hundreds of micrometers face severe mechanical reliability challenges in practical applications. During battery assembly and cycling, external mechanical stresses (e.g., collision, extrusion) and stresses generated by internal electrode volume changes synergistically lead to structural damages and interface failures of SPEs, which in turn trigger the degradation of battery performance and the shortening of battery service life. In this regard, the study of smart polymer material systems with autonomous healing function provides innovative solutions for realizing highly reliable SPEs.

Self-healing polymers (SHPs) have become one of the most promising research directions in the field of smart materials since they were proposed in the 1980s[12]. Tracing back its development history, the self-healing phenomenon of poly(vinyl acetate) was first discovered by Kargin et al. in 1970, and this breakthrough discovery laid an important foundation for SHPs research[13]. The milestone work that really pushed the field into a rapid development stage was the first time that Viswanathan et al. realized the self-healing function of thermosetting polymers by embedding dicyclopentadiene microcapsules compounded with platinum catalysts into epoxy resin matrix in 2001[14]. The current SHPs are mainly used to endow materials with dynamic healing capabilities through physical or chemical methods. After research, two major healing mechanisms, extrinsic and intrinsic, have been developed. Extrinsic SHPs achieve immediate healing through a curing reaction by pre-embedding healing microcapsules or microvascular networks in the polymer matrix, and when the material is damaged, the encapsulated functional reagents are released into the damaged area[15]. However, this system has obvious limitations, not only the complexity of the microcapsule preparation process and the poor compatibility of the healing agent-substrate interface, but also the lack of dynamic interactions can lead to a significant decrease in the efficiency of multiple healings. In contrast, intrinsic SHPs provide materials with the ability to be reversibly reconfigured at the molecular level by designing dyna-

mic covalent bonds (e.g., imine bonds, disulfide bonds) or supramolecular interactions (e.g., hydrogen bonds, ionic interactions). These materials not only eliminate heterogeneous interfaces but also exhibit nearly infinite self-healing cycles, excellent healing efficiency (>95%), and long-term stability. Therefore, intrinsic SHPs show unique advantages in flexible electronics and energy devices[16].

The healing mechanism of intrinsic SHPs is mainly based on supramolecular interactions and dynamic covalent bonds[17]. Specifically, supramolecular interactions cover non-covalent modes of interaction such as hydrogen bonds, metal-ligand bonds, host-guest recognition (e.g., crown ether-ion pairs), π-π stacking effects, ion-dipole interactions, and hydrophobic associations. Dynamic covalent bonds, on the other hand, include reversible imine, acylhydrazone, disulfide/diselenide, and borate bonds, as well as reactions based on Diels--Alder cycloaddition, olefinic complex decomposition, ester exchange, and dynamic exchange of carbamates[18]. Recent studies have shown that supramolecular interactions and dynamic covalent bonds are complementary in material healing processes. Dynamic covalent bonds can effectively enhance the mechanical strength of materials by virtue of their high bonds energy, while supramolecular interaction can achieve >90% healing efficiency even at room temperature due to its low bonds energy, which confers a fast dynamic response to the system. By synergistic design on the molecular scale, combining the mechanical enhancement effect of dynamic covalent bonds with the highly efficient healing properties of supramolecular interaction, smart polymeric materials can be constructed with both high strength and high self-healing rate. In this paper, we systematically review the research progress of intrinsic self-healing polymer electrolytes (SHPEs) in LIBs based on the self-healing mechanism of supramolecular interactions, dynamic covalent bonds, and the combination of the two[19, 20]. The main focus is to elucidate the constitutive relationship between the dynamic bonds network design of SHPEs and the key battery performance indexes. In view of the key bottlenecks of SHPEs, we propose the direction of future research focus, which provides a theoretical framework and technical path for the development of a new generation of solid-state electrolytes with high safety and long cycle characteristics.

SHPES BASED ON SUPRAMOLECULAR INTERACTIONS

Hydrogen bonds

As the core driving force of supramolecular interactions, hydrogen bonds have become the most mature molecular design strategy for constructing self-healing materials due to their unique advantages of dynamic reversibility, orientation properties and environmental responsiveness[21]. Hydrogen bonds play a crucial role in conferring self-healing capabilities to SPEs[22]. The dynamic reversibility of hydrogen bonds, particularly the four hydrogen bonds in the uracil ketone unit, enables the interface that breaks upon damage to spontaneously reform. These hydrogen bonds not only provide the driving force for self-healing by allowing polymer chains to reconnect at damaged sites but also contribute to maintaining mechanical integrity and interface stability[23]. The reversibility of hydrogen bonds ensures that the electrolyte can repeatedly heal from mechanical damage (such as cracks or fractures caused by volume changes during lithium deposition/stripping cycles), thereby extending the lifespan of lithium metal batteries and enhancing their safety and reliability.

In 2018, Xue et al. reported poly(ethylene glycol)-based SHPEs (PEG-UPy)[24]. The material was prepared by free radical copolymerization reaction between ureido pyrimidinone (UPyMA) monomer containing quadruple hydrogen bonds and poly(ethylene glycol) methyl ether methacrylate (PEGMA) monomer (Fig. 1). The network of quadruple hydrogen bonds formed between UPy groups not only endowed the material with the ability of self-healing, but also significantly strengthened the adhesion strength of electrolyte/electrode interface through dynamic cross-linking effect. Mechanical tests showed that the PEG-UPy healed for 2 h at room temperature could withstand tensile deformation of more than 20 times of the original length without fracture. The ion-transport properties of the poly(ethylene glycol) side chains in the material resulted in an ionic conductivity of 2.1×10^{-5} S cm^{-1} at 30 °C, which was enhanced to 1.1×10^{-4} S cm^{-1}. The Li//Li symmetric cell assembled based on PEG-UPy maintained a stable lithium deposition/stripping behavior after 500 cycles at 60 °C, and the voltage polarization was always maintained within 50 mV. In the full-cell test, the $LiFePO_4$/PEG-UPy/Li cell exhibited an initial discharge capacity of 157 mAh g^{-1} and showed excellent capacity retention in long-term cycling.

In order to improve the mechanical strength and thermal stability of $SHPE_S$, Xue et al. developed dual-network SHPEs (DN-SHPE) based on the above mentioned research work (Fig. 2)[25]. DN-SHPE was prepared by employing a radical copolymerization reaction of polyethylene glycol-bis-carbamate dimethacrylate (PEGBCDMA) with PEGMA, UPyMA monomers in a ternary copolymerization to construct a physical-chemical double crosslinked network structure. The physical crosslinked network consists of quadruple hydrogen bonds of UPy groups, which gives DN-SHPE self-healing function, while the chemical crosslinked network is formed by the urethane fragments of PEGBCDMA, which significantly improves the mechanical strength and thermal stability of DN-SHPE. This synergistic network design effectively balances the hindering effect of the chemical cross-linking network on ion migration, and the poly(ethylene glycol) side chain of PEGMA and the ether-oxygen chain segments of PEGBCDMA work together to build a continuous ionic conduction channel, resulting in an ionic conductivity of DN-SHPE of 2.93×10^{-5} S cm^{-1}. Electrochemical tests showed that the Li/DN-SHPE/$LiFePO_4$ cell exhibited an initial discharge capacity of 137.9 mAh g^{-1} at 0.1C with a Coulombic efficiency of 99% in the first week. After 120 charge/discharge cycles, the discharge capacity remained at 128 mAh g^{-1} with a capacity retention rate of 92.8%, demonstrating excellent cycling stability.

On the basis of the previous research work (Figures 1 and 2), in 2019, Xue et al. reported a self-healing

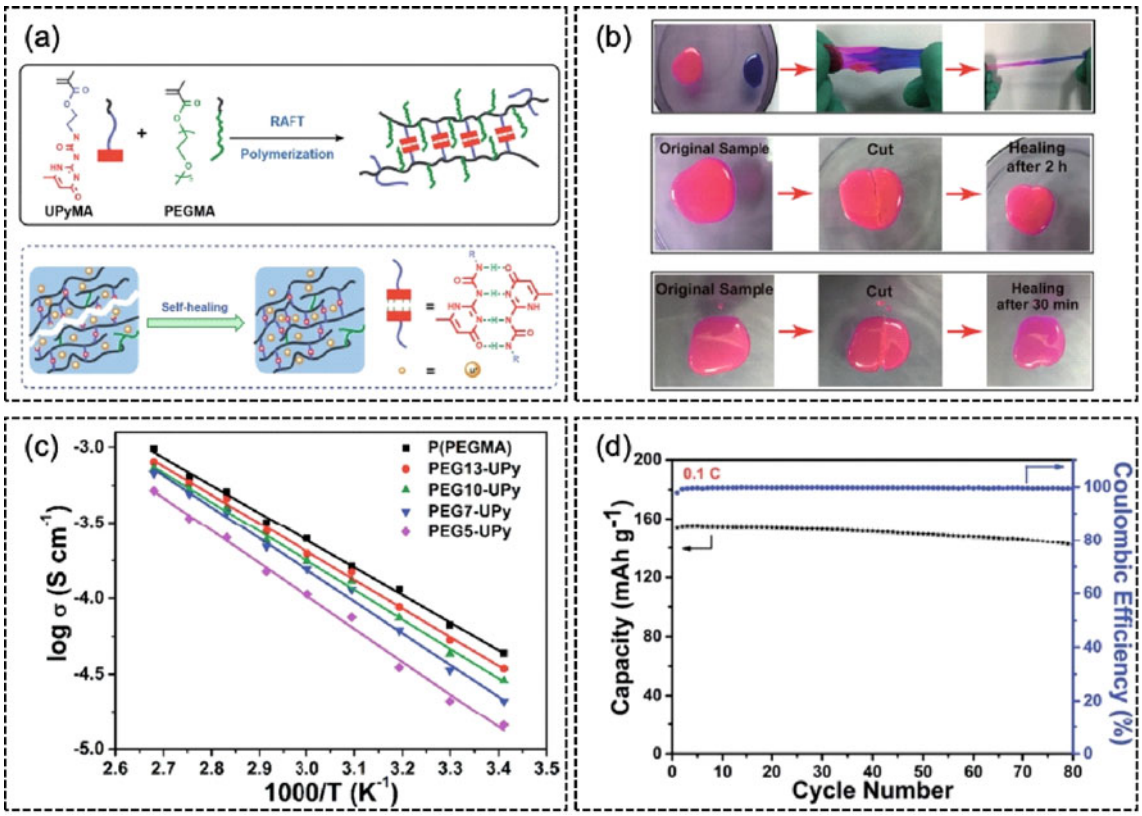

Figure 1. (a) Schematic illustration of the synthesis of the brush-like copolymer and the self-healing mechanism. (b) Optical images showing the self-healing process of PEG-UPy. (c)The ionic conductivities of PEG-UPy and P(PEGMA). (d) Cycling performance of the $LiFePO_4$ battery with healed PEG-UPy at 0.1C. Adapted from Ref.[24]

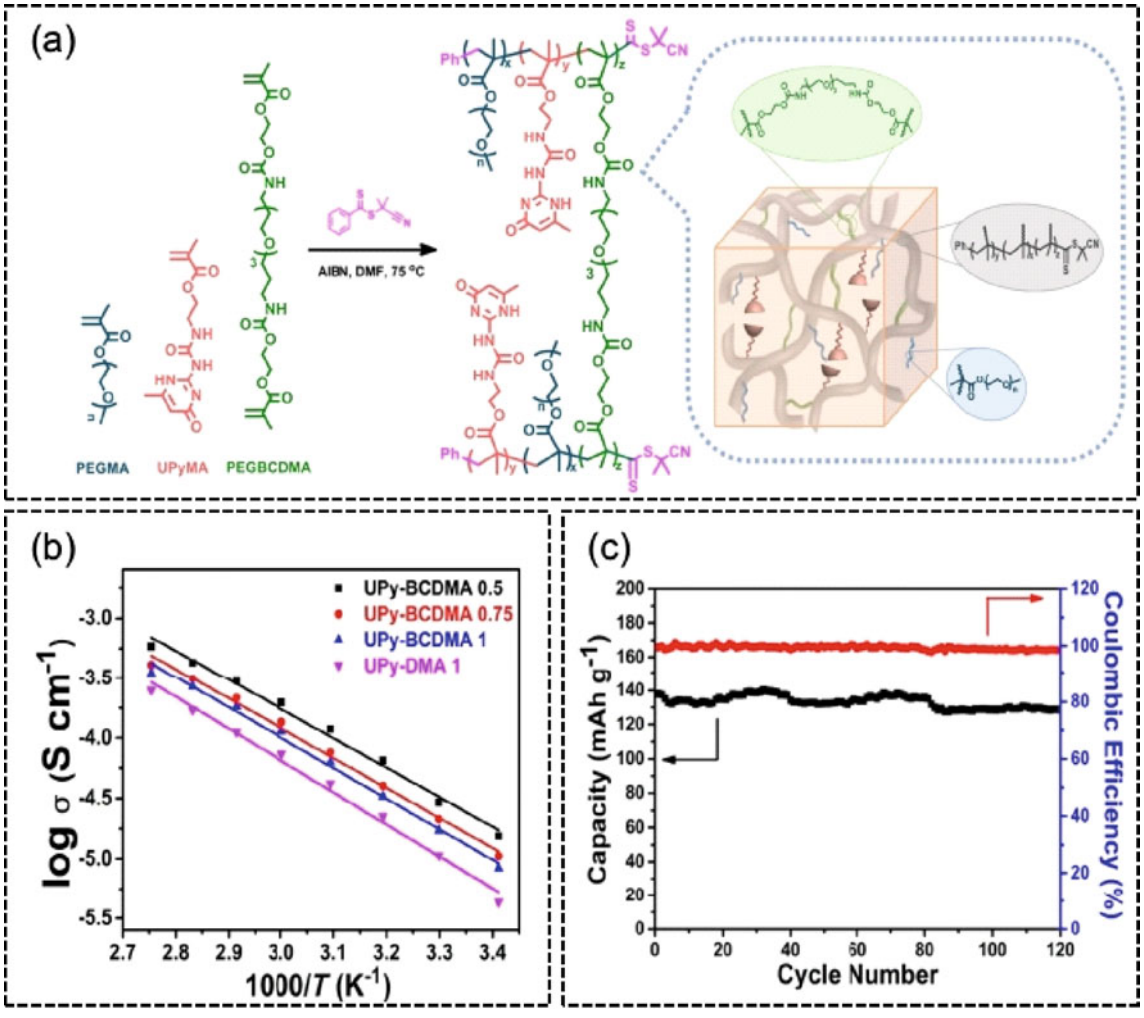

Figure 2. (a) Schematic illustration on the dual-network of DN-SHPE. (b) The temperature dependence of ionic conductivities of DN-SHPE. (d) Cycling performance of the DN-SHPE-based battery evaluated with a current density of 0.1C at 60 °C. Adapted from Ref.[25]

composite polymer electrolyte (SHCPE) with enhanced mechanical properties and higher ionic conductivity (Fig. 3)[26]. UPy-functionalized silica nanoparticles (SiO_2--UPy) homogeneously dispersed in a PEG-UPy matrix to construct three-dimensional lithium-ion transport channels through interfacial. The modified UPy groups on the surface of SiO_2-UPy formed dynamic cross-links with the quadruple hydrogen bonds network in the matrix, which not only significantly improved the dispersion of the nanofillers, but also enhanced the overall performance of the material by strengthening the polymer/filler interfacial interactions. The experimental results showed that the ionic conductivity of SHCPE reached 8.01×10^{-5} S cm^{-1} at 30 °C, which was nearly four times higher than that of the pure PEG-UPy system. The dynamic hydrogen bonds network endowed SHCPE with excellent self-healing properties, and its surface scratches were fully healed within 60 min. The $LiFePO_4$ full battery assembled based on SHCPE exhibited an initial discharge capacity of 139 mAh g^{-1}, and the capacity retention rate reaches 97.9% after 60 cycles, which verifies the significant advantage of this composite system in maintaining long cycle stability.

From the above reports, it can be seen that UPy is an efficient self-healing functional group with reversibility and strong quadruple hydrogen bonds, and a small amount of UPy in the polymer can confer excellent self-healing performance, while the good electrochemical stability of UPy will not affect the electrochemical performance of the battery. However, the room-temperature ionic conductivity of the above reported UPy functional group-based SHPEs only reach the order of 10^{-5} S cm^{-1}, which does not meet the requirements of practical applications. In 2019, Guo et al. constructed a flexible supramolecular skeleton through the polycondensation reaction of amino-capped poly(ethylene glycol) (PEG) and introduced a thermoplastic polyurethane (TPU) as a dynamic cross-linking agent (Fig. 4)[27]. The urethane--ester hydrogen bonds in the molecular chain of TPU formed a multistage hydrogen-bonds network with the PEG backbone, which enabled rapid self-healing (complete healing of the incision in 1 min) while breaking through the room-temperature ionic conductivity to 1.9×10^{-4} S cm^{-1}. Electrochemical performance tests show that the $LiFePO_4$ full cell maintains 90% of its initial capacity of discharge after 100 cycles at 0.2 C magnification.

To address the technical bottleneck that the ionic conductivity (10^{-7}~10^{-5} S cm^{-1}) of solid-state electrolytes is difficult to meet the practical application requirements (>10^{-3} S cm^{-1}), the gel polymer electrolytes (GPEs) have been developed by introducing plasticizers to construct a "solid-liquid synergistic" conduction mechanism[28]. At the same time, the efficient dissociation and migration of lithium salts is achieved by using the plasticizer microregion, which combines the safety of SPEs with the conduction advantages of liquid electrolytes, and is regarded as the electrolyte solution with the most commercialization potential. In this context, Liu et al. developed self-healing composite gel electrolytes (SHGPE) in 2019 (Fig. 5)[29]. SHGPE was developed by combining SHPs containing multiple hydrogen bonds, lithium-lanthanum zirconium-oxo-garnet (LLZGO) ceramic powder with electrolyte (1 M $LiPF_6$). The dynamic hydrogen bonds network in SHGPE could instantly healing microcracks when lithium dendrites punctured the electrolyte membrane, while the LLZGO filler achieved a room-temperature ionic conductivity of 1.2×10^{-3} S cm^{-1}. In addition, the viscoelastic property of SHGPE induced the formation of adaptive contact at the electrolyte/electrode interface, which effectively regulated the lithium ion deposition behavior and inhibited the growth of dendrites. Electrochemical tests showed that the Li/SHGPE/$Li_4Ti_5O_{12}$ battery maintained a discharge

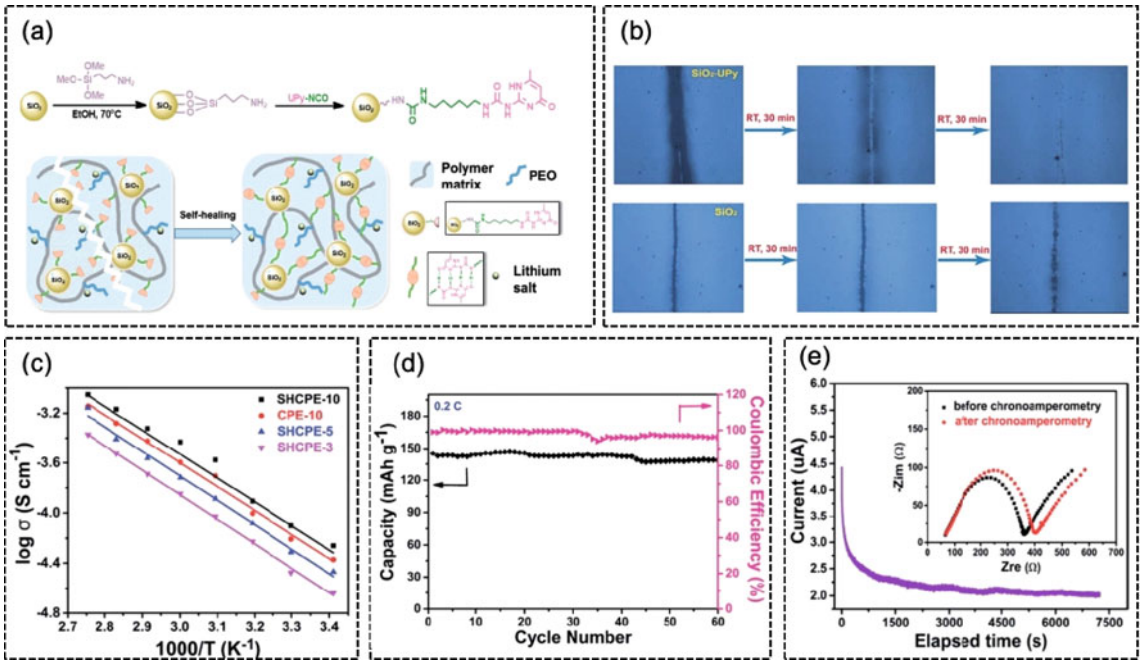

Figure 3. (a) Preparation procedure of SiO_2–UPy, and schematic illustration of the structure of the SHCPE with the supramolecular networks. (b) Optical microscope images of the self-healing process. (c) Temperature dependence of ionic conductivities of SHCPE/CPE. (d) The cycling performance of the Li/SHCPE-10/$LiFePO_4$ cell. (e) Chronoamperometry profile of the Li/SHCPE-10/Li cell at 60 °C. The inset displays the impedance spectra before and after chronoamperometry. Adapted from Ref.[26].

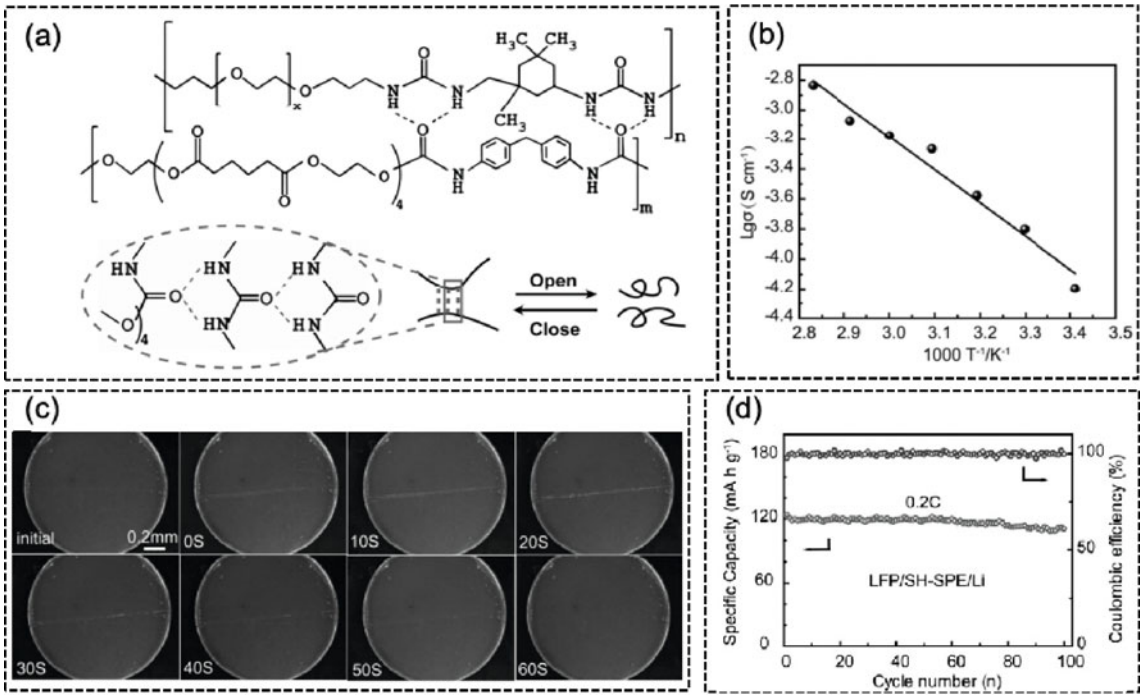

Figure 4. (a) Supramolecular structure and dynamic hydrogen bonds of SHSPE. (b) Log plot and linear fit of SHSPE σ vs. temperature ranging from 20 to 80 °C. (c) The self-healing process of SHPEs after being cut. (d) The cycling performances for a solid-state battery cycled at 0.2C and 60 °C. Adapted from Ref.[27]

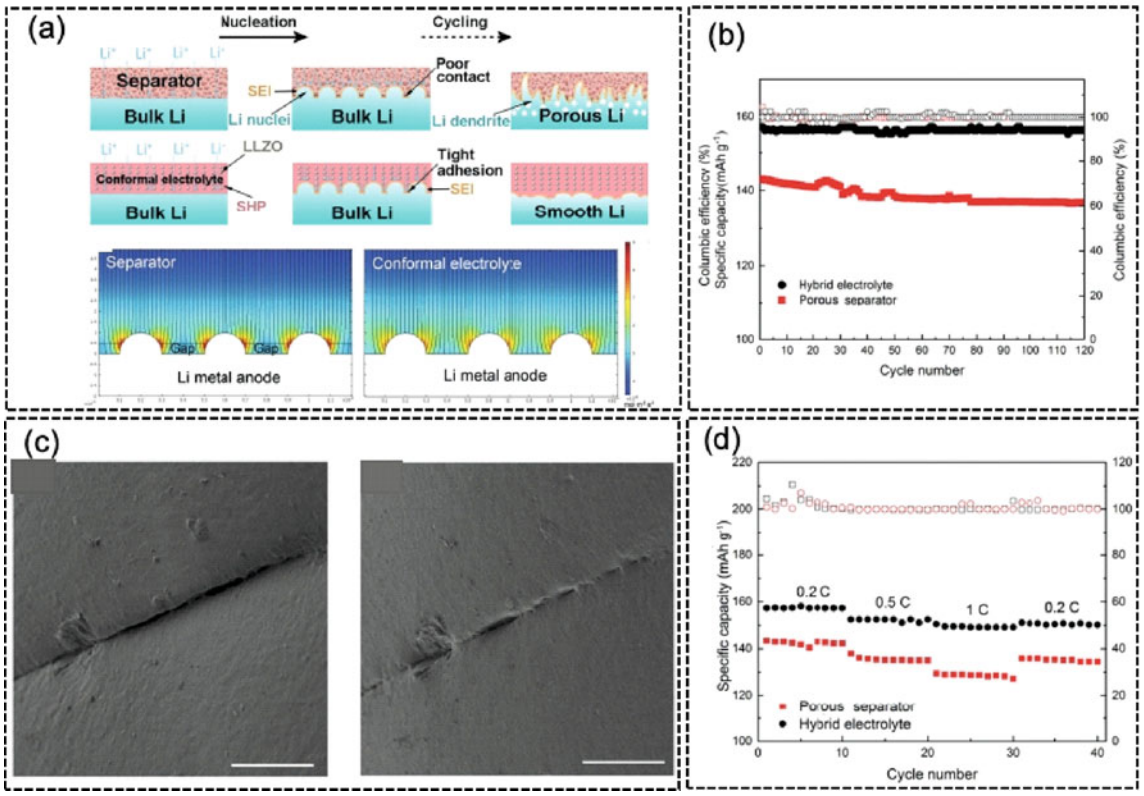

Figure 5. (a) Mechanism illustration of the solid–liquid hybrid electrolyte with volume conformable functionality and strong adhesion with Li metal anode. (b) Cycling performance and Coulombic efficiencie (CE) of the Li||LTO cells using porous separator and hybrid electrolyte/PVDF. (c) SEM images of the CPE surface showing the self-healing functionality after 1 h. Scale bar 100 μm. (d) Rate capability of the Li||LTO cells based on porous separator and hybrid electrolyte/PVDF. Adapted from Ref.[29]

capacity of 157 mAh g^{-1} after 120 cycles at 1C, with a capacity retention rate of 99.4%.

In 2020, Wang et al. proposed an innovative design strategy for low-eutectic solvent (DES)-based gel electrolytes (DSPs), which successfully integrated self-healing and flame-retardant functionalities in a single package (Fig. 6)[30]. The DSPs were constructed via in situ radical polymerization of UPyMA with pentaerythritol tetraacrylate (PETEA) monomers in a low-eutectic solvent of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)/N--methylacetamide (NMA)/ 4-fluoro-1,3-dioxolan-2-one (FEC), with a three-dimensional interpenetrating ne-

twork structure. The dynamic hydrogen bonds network imparted self-healing properties to DSPs, and its porous structure adapted to the change of electrode volume to maintain stable interfacial contacts. The FEC additive promoted the formation of dense SEI interfacial layer, which effectively inhibited the growth of lithium dendrites, and at the same time, imparted intrinsic flame retardant properties to DSPs[31, 32]. The DSP was shown to have an ionic conductivity of 1.79 × 10^{-3} S cm^{-1} at 25 °C, and the electrochemical stabilization window was extended to 4.5 V vs. Li/Li^+. The $LiMn_2O_4$ battery assembled based on the DSP exhibited excellent multiplicative response characteristics, with a capacity retention of 98.6% after a multiplicative cycling test of 0.1C→1C→0.1C.

Recently, the gel SHPEs developed by Guo et al. realized the synergistic design of dynamic hydrogen bonds network and porous structure through the copolymerization reaction of ethylene glycol methyl ether acrylate (EGMEA) and UPyMA (Fig. 7)[33]. The carbonyl (C=O) and amino (NH) groups of the UPy moiety in the SHPEs formed an intermolecular hydrogen bonds network, which endowed SHPEs with self-healing ability through the dynamic fracture-reorganization mechanism. The hierarchical porous structure immobilized the liquid electrolyte components through a physical domain-limiting effect, which promoted the formation of a stable SEI/CEI interfacial layer while maintaining a high ionic conductivity (2.2 mS cm^{-1} at 25 °C). Electrochemical performance tests showed that SHPEs possessed a lithium ion transference number of 0.75 and an oxidation stability of >5.9 V vs. Li/Li^+. The $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ full cell assembled based on this electrolyte exhibited an initial discharge capacity of 228.8 mAh g^{-1} at 0.1 C.

In 2021, Manthiram et al. proposed an interfacial grafting modification strategy to provide an innovative solution for interfacial engineering of organic-inorganic composite solid-state electrolytes (Fig. 8)[34]. In this study, a composite electrolyte (LSnS-UPy) with dynamic bonds properties was constructed by grafting UPyMA monomers containing quadruple hydrogen bonds onto the surface of a sulfide solid-state electrolyte ($Li_{3.85}Sn_{0.85}Sb_{0.15}S_4$). This design realized molecular-level interfacial coupling between the sulfide ionic conductor and the elastic polymer binder. the dynamic hydrogen bonds network of the UPy moiety endowed the electrolyte with self-healing capability, while the sulfide backbone guaranteed a lithium ion conductivity of up to 1.2 × 10^{-3} S cm^{-1} (25 °C). In practical application tests, the Li/LSnS-UPy/$LiNi_{0.9}Mn_{0.05}Co_{0.05}O_2$ cell has a capacity retention of 82% after 140 cycles at a high surface capacity of 2.0 mAh cm^{-2}, which maintained its surface area capacity higher than 1.65 mAh cm^{-2} at 0.3 C.

The reviewed studies demonstrate diverse strategies for constructing hydrogen bond driven SHSPEs, primarily

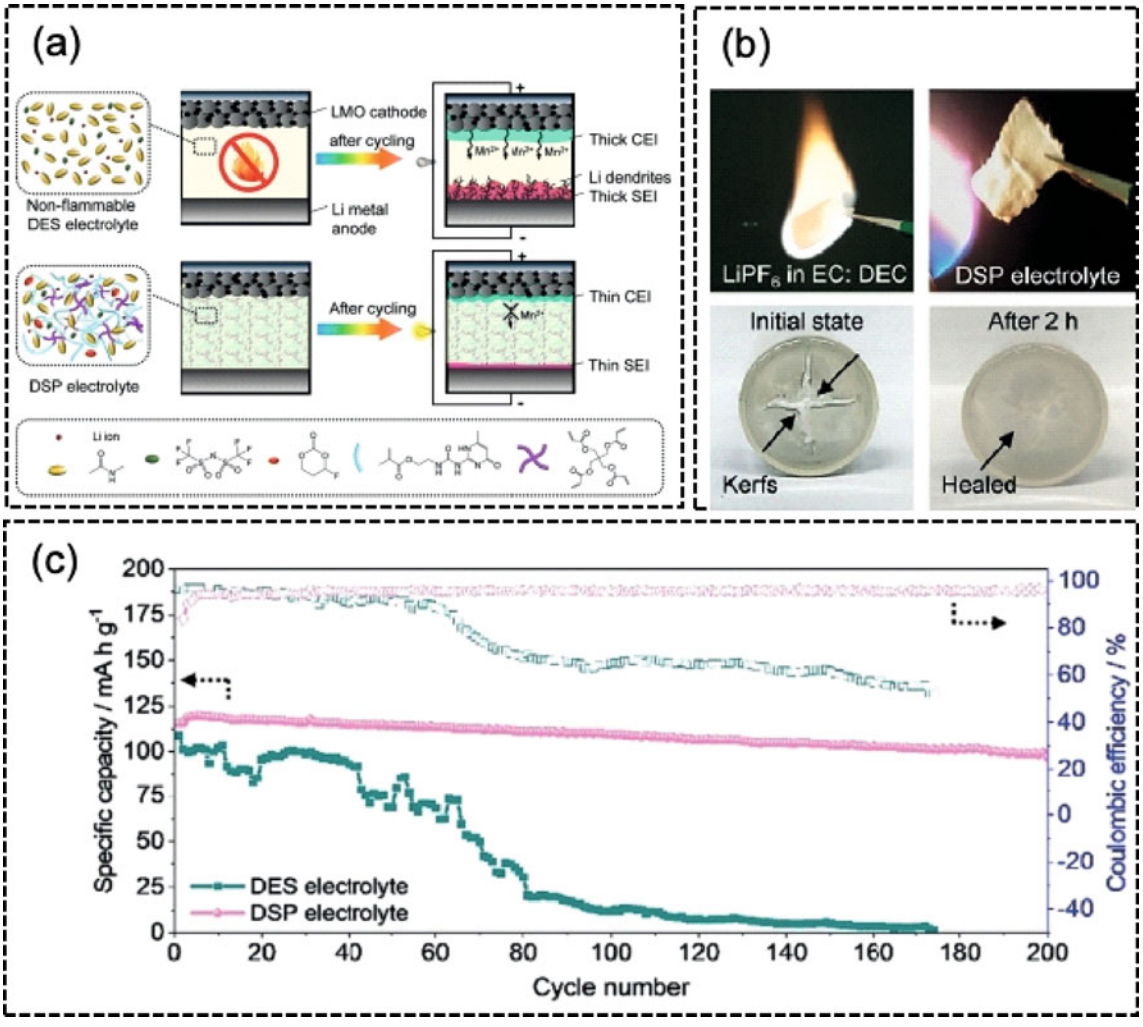

Figure 6. (a) DES and DSPs in Li||LMO cells. (b) Optical images of the 1 M $LiPF_6$ in EC/DEC electrolyte (top left) and DSP electrolyte (top right) under a combustion test, and the self-healing process of the DSP electrolyte after being cut (bottom). (c) Cycling performance at 0.1C of Li|DES|LMO and Li|DSP|LMO cells. Adapted from Ref.[30].

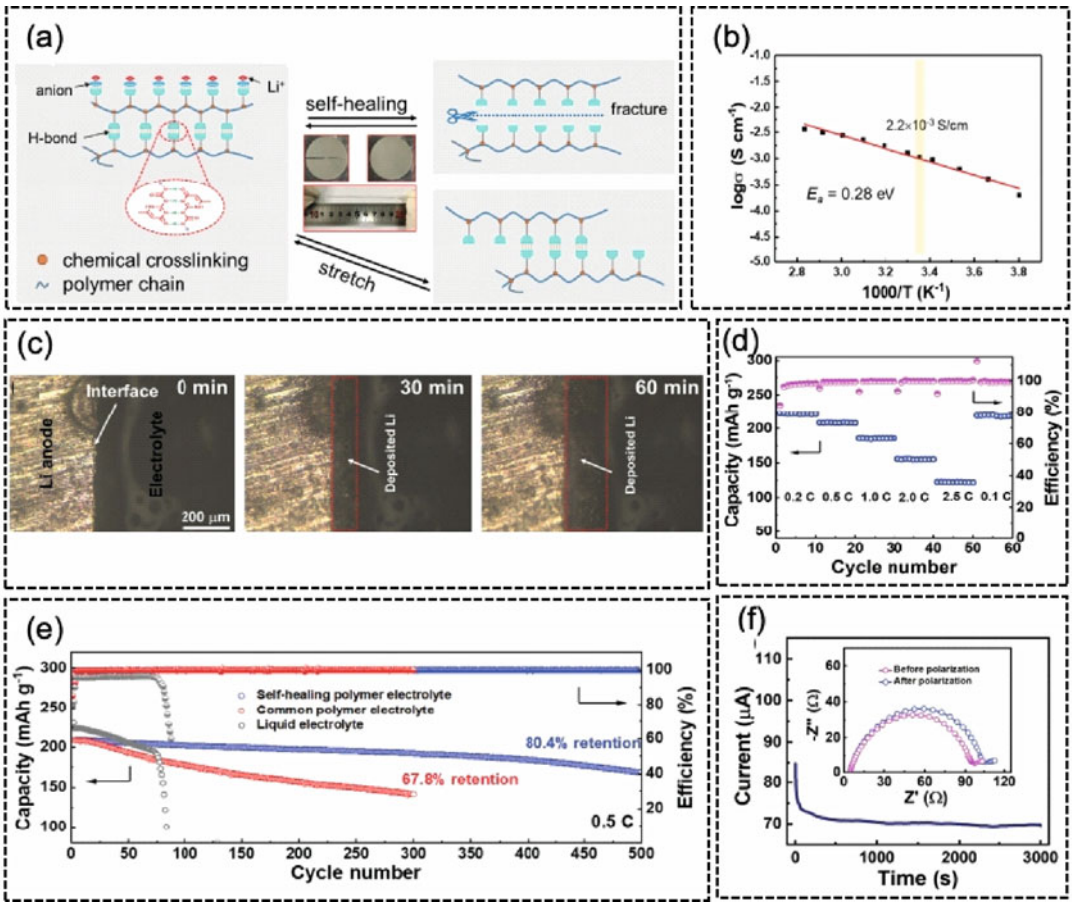

Figure 7. (a) Schematic diagram of the self-healing mechanism. (b) Ionic conductivities as a function of temperature. (c) In situ optical microscopy images showing the Li deposition behaviors with the SHPEs. (d) Rate performance. (e) Cycling performance with CE. (f) Chronoamperometry profile. Adapted from Ref.[33]

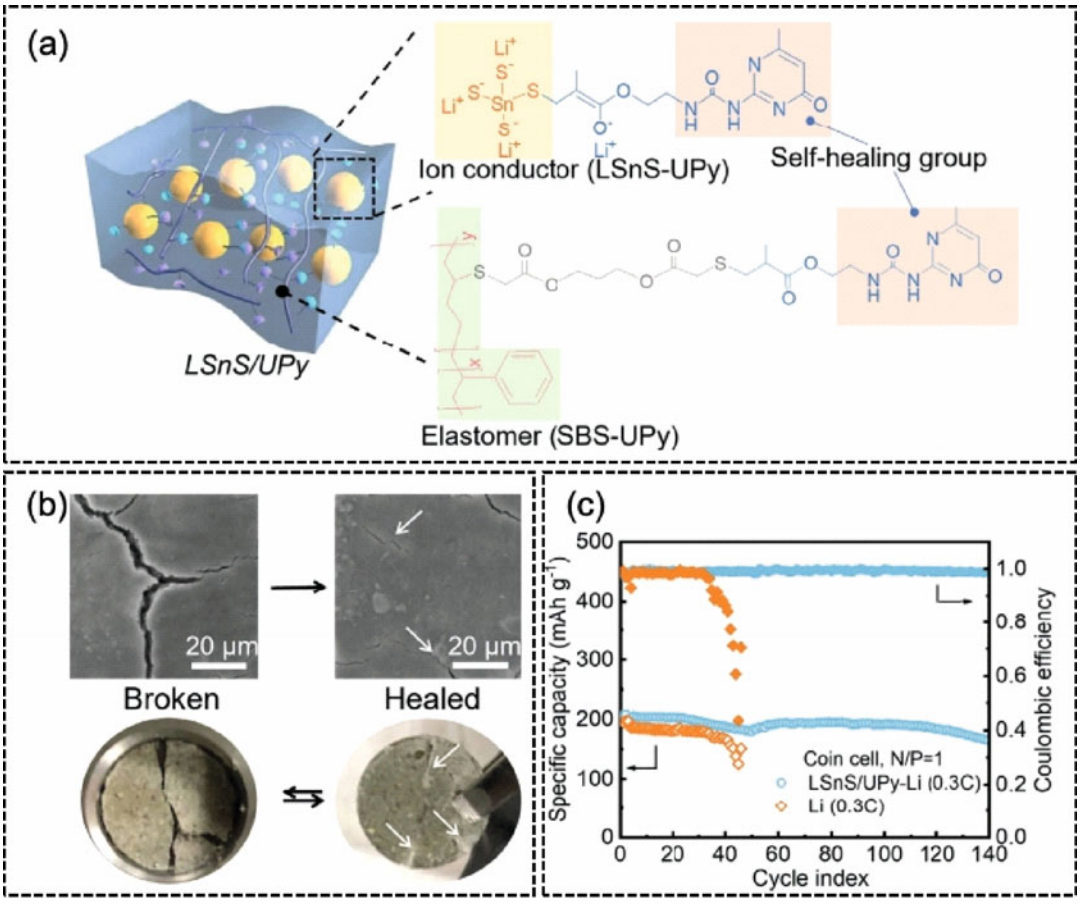

Figure 8. (a) Schematic of the composition of the self-healable composite electrolyte (LSnS/UPy). (b) Self-healing of the composite electrolyte after cycling (upper column) and after mechanical breakdown (lower column). The arrows indicate the remaining signs of cracks. (c) Cyclability. Adapted from Ref.[34]

leveraging UPy units, TPU, or hybrid networks. Key findings reveal that UPy-based systems exhibit tunable ionic conductivities (2.1×10^{-5} to 8.01×10^{-5} S cm^{-1} at 30 °C) by integrating quadruple hydrogen bonds with PEG backbones, enabling self-healing within 0.5–2 h at room temperature or 60 °C. The introduction of dual networks enhances mechanical strength while maintaining high healing efficiency. Hybrid systems combining hydrogen bonds networks with inorganic fillers further boost conductivity by creating continuous ion transport channels. Gel electrolytes integrate hydrogen bonds with liquid electrolyte components, achieving higher conductivities and rapid healing by balancing network dynamics and ion mobility. However, a trade-off persists between ionic conductivity and mechanical strength[35], with pure hydrogen bonds systems typically exhibiting lower conductivities compared to gel-based counterparts. Future research should prioritize integrating dynamic hydrogen bonds networks with high-conductivity pathways to bridge this gap.

Ion-dipole interaction

As an important molecular interaction mode, ion-dipole interaction has shown unique application value in the field of flexible electronic devices in recent years[36]. Ion-dipole interaction achieves energy dissipation and structural reorganization through the electrostatic attraction between charged ions and dipole moments of polar molecules, which provides a new idea for the construction of high-performance self-healing materials[37]. Ion-dipole interactions play a key role in conferring self-healing capabilities to SPEs[38]. These interactions form between ionic species (such as imidazolium cations) and polar groups (such as -CF_3 in PVDF-HFP) and exhibit high reversibility, enabling bonds at damaged interfaces to dynamically reform[39]. This reversible interaction not only promotes the migration and rearrangement of polymer segments to bridge damaged regions but also ensures the structural integrity and ionic conductivity of the repaired electrolyte, making it highly suitable for use in SHSPEs.

In 2018, Zhong et al. reported ionic liquid composite gel electrolytes (SHGPE), revealing the key role of ion-dipole interaction in the design of multifunctional electrolytes[40]. SHGPE was developed by subjecting 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonimide) (EMI-TFSI) and poly(vinylidene fluoride)-hexafluoropropylene copolymer (PVDF-HFP) to a solution blend modification, a dynamic ion transport self-healing bifunctional network was constructed by utilizing the directional dipolar interaction between the strongly polar -CF_3 group in the polymer chain segments and the ionic liquid cations. This interaction mechanism endowed the material with room-temperature self-healing capability (surface scratches were completely eliminated in 12 h), while the system obtained an ionic conductivity of 1.4×10^{-3} S cm^{-1} through the high lithium dissociation capability of the ionic liquid. Characterization of the material properties showed that the dynamic ion-dipole network gave SHGPE excellent thermal stability and flame retardancy. The $LiFePO_4$ full cell assembled based on this electrolyte maintained 96.5% capacity retention and 99.8% average CE after 200 cycles at 1 C.

In 2021, Fu et al. developed an amphiphilic ionic SHPE, which achieved a synergistic optimization of ion transport and interfacial stability[41]. SHPE was prepared by an amphiphilic monomer copolymerization strategy, in which sulfobetaine methacrylate (SBMA) was copolymerized with hexafluorobutyl methacrylate (HFBM) to construct a polymer skeleton that combines both amphiphilic ions (N^+/SO^{3-}) and fluorinated groups to construct a functionalized polymer backbone (Fig. 9). On this basis, EMI-TFSI ionic liquid and LiTFSI lithium salt were introduced to form a dynamic physical crosslinked network by utilizing the strong ion-dipole interactions between the -CF_3 groups in the chain segments of HFBM and the imidazole cations. This design provides the material with rapid self-healing capability

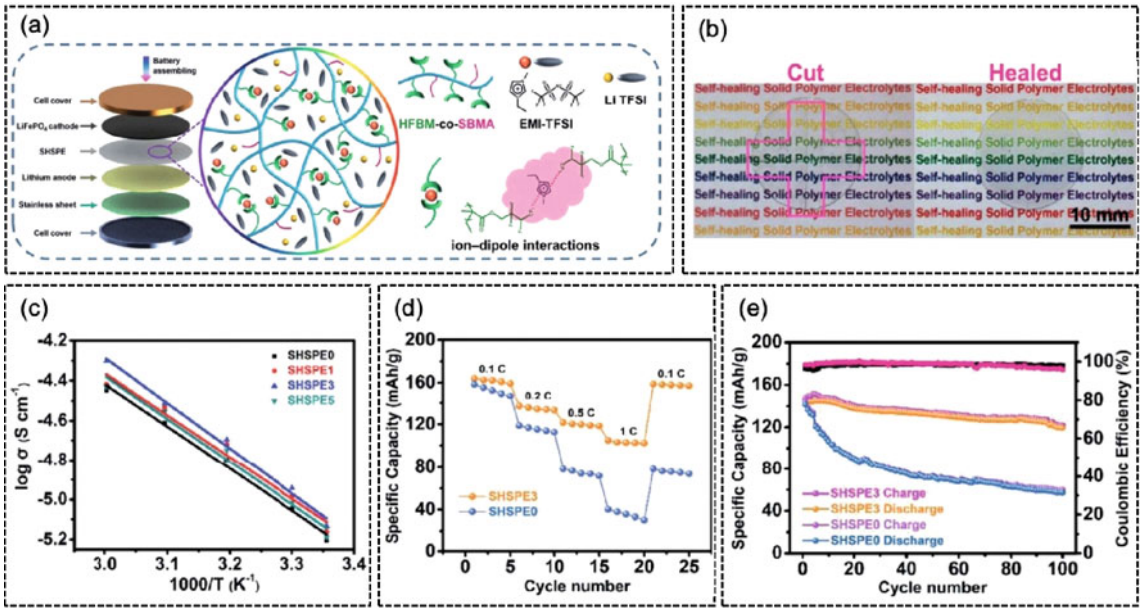

Figure 9. (a) Schematic illustration of the configuration of the Li/SHSPE/$LiFePO_4$ cell and macromolecular structure of SHSPE. (b) Self-healing of SHSPE3. (c) Temperature dependence of the ionic conductivity of SHSPE. (d) Reversible capacity of Li/SHSPEs/$LiFePO_4$ at 60 °C and various current rates (0.1C to 1C). (e) Long-term cycling performances of Li/SHSPE0/$LiFePO_4$ and Li/SHSPE3/$LiFePO_4$ at 0.2C and 60 °C. Adapted from Ref.[41]

at room temperature (3 h to restore the intact structure by cutting off the specimen). Electrochemical tests show that the Li/SHPE/Li symmetric cell maintained a stable polarization voltage of 0.22 mV for 100 h of cycling at a current density of 0.1 mA cm^{-2}, verifying the effective inhibition of lithium dendrite growth by the electrolyte. The assembled Li/SHSPE3/$LiFePO_4$ cell has a high discharge capacity of 144.8 mAh g^{-1} at 0.2C, a capacity retention of 82% after 100 cycles, and a CE of 97%.

In response to the bottleneck of high cost of traditional ionic liquids that restricts their scale-up application, Panzer et al. developed an economical self-healing gel electrolyte (SHGPE) based on solvated ionic liquids (SILs) in 2019[42]. SHGPE complexed a fully ampholytic polymer network with SIL ([Li(G4)]-[TFSI]) by in situ photopolymerisation, where the polymer backbone was built by co-polymerising methacryloyloxyethylphosphorylcholine (MPC) and sulphobetaine vinyl imidazole (SBVI) (Fig. 10). The ampholytic groups of MPC and the cations of SIL formed a dynamic crosslinked network by ionic-dipolar interactions, giving the material self-healing properties and excellent ductility. At the same time, the dipole-dipole self-association between SBVI molecules formed dense physical cross-linking points, which enhanced the elastic modulus of the material. Electrochemical performance tests showed that SHGPE exhibited high ionic conductivity, and the assembled lithium-ion battery stably cycled for 100 cycles at 0.5 C.

In 2024, our group developed self-healing poly(ionic liquid) block copolymer electrolytes (PIBCPEs), which realized the fusion of high ionic conductivity and room-temperature self-healing performance through the dual ion-dipole synergistic interactions of imidazole cations with the oxygen atoms of the PEO chain segments and the -CF_3 group in PVDF-HFP[43]. The preparation was carried out by atom transfer radical polymerization (ATRP) technique, in which 1-(4-vinylbenzyl)-3-methylimidazolium bis(trifluoromethanesulfonyl) imide salt ([VBMIm][NTf_2]) was copolymerized with PEO macromolecular initiator to form a block structure, and doped with PVDF-HFP to enhance the mechanical properties. Among them, the ion-dipole interaction of imidazole cations with PEO oxygen atoms (binding energy –53.09 kJ mol^{-1}) reduced the crystallinity of PEO, while the interaction of imidazole cations with -CF_3 in PVDF-HFP (binding energy –44.64 kJ · mol^{-1}) endowed the material with self-healing ability (scratches completely healed within 1 h). Molecular dynamics simulations showed that the rapid migration of lithium ions (diffusion coefficient 0.13 × 10^{-7} cm^2 s^{-1}) in the continuous phase of PEO formed by the microphase separation resulted in an ionic conductivity of PIBCPE_27 of 3.7 × 10^{-4} S cm^{-1} at 25 °C, and the lithium ion transference number was enhanced to 0.57. Electrochemical tests showed that the Li/PIBCPE_27/Li symmetric cell was stably cycled for 3,700 h at 0.1 mA cm^{-2} with a polarization voltage of only 0.15 V; the capacity retention of the assembled Li/PIBCPE_27/$LiFePO_4$ battery reached 97.1% after 250 cycles at 0.5 C (discharge capacity 144.0 mAh g^{-1}), and the self-healing electrolyte almost completely restored the electrochemical performance (capacity retention 98.2% at 0.1 C). In addition, the electrolyte exhibited an oxidative stability window of 5.0 V and a discharge capacity of 107.7 mAh g^{-1} when matched with the NCM622 cathode.

Current self-healing SPEs based on ion-dipole interactions are mainly achieved by integrating imidazolium-based ionic liquids with fluorinated polymers (e.g., PVDF-HFP, HFBM) or zwitterionic copolymers (e.g., MPC-SBVI). These systems form dynamic networks where reversible interactions between ionic species and polar functional groups (e.g., -CF_3, ether oxygens) enable self-healing while maintaining ionic transport. Ionic conductivities span from 3.7 × 10^{-3} to 1.79 × 10^{-3} S cm^{-1} at room temperature, with self-healing times ranging from 1 to 12 h depending on temperature and network crosslink density. Mechanical properties vary from elastic moduli

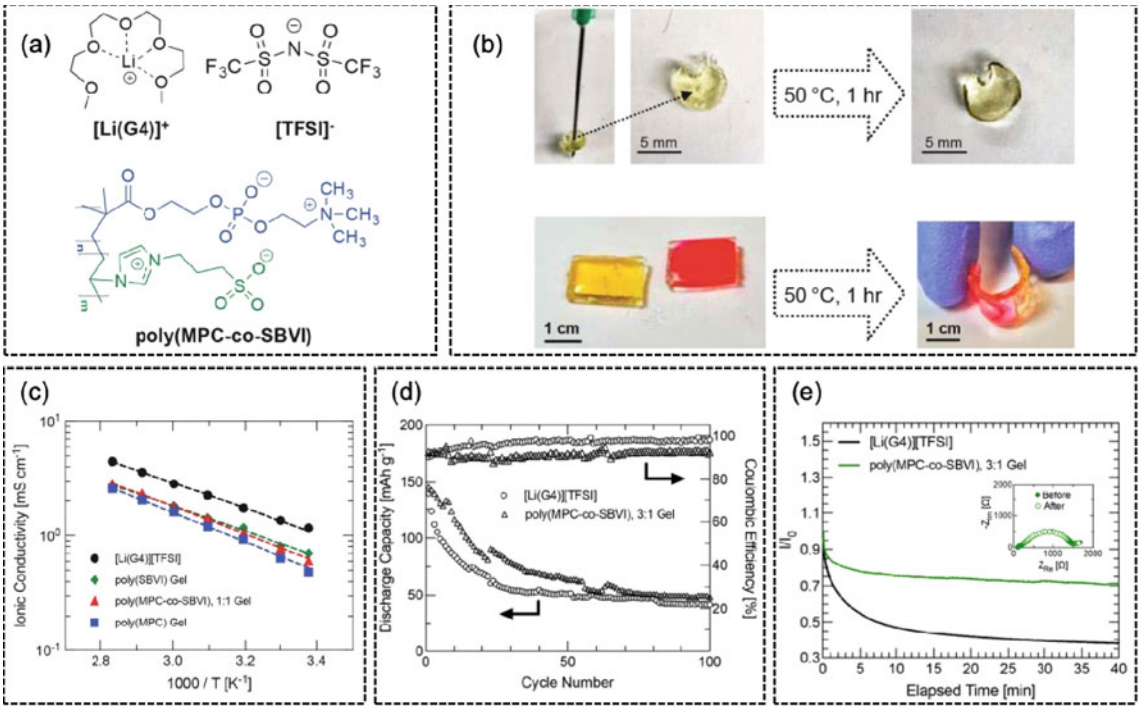

Figure 10. (a) Molecular structures. (b) Photographs showing a puncture test. (c) Temperature dependence of ionic conductivity. (d) Discharge capacity and CE profiles over 100 cycles. (e) Chronoamperometry responses to dc polarization at 80 mV. Adapted from Ref.[42]

of 23 kPa to 7.3 MPa and tensile strengths up to 5.39 MPa, reflecting a trade-off between conductivity and mechanical resilience—higher ionic liquid content enhances conductivity but reduces stiffness, while zwitterionic or chemical crosslinking improves mechanical strength at the cost of conductivity[44]. Future research should prioritize multi-scale dynamic network design, integrating ion-dipole interactions with dynamic covalent bonds (e.g., disulfide or borate esters) to achieve simultaneous enhancement of conductivity and mechanical toughness.

Electrostatic interaction

Electrostatic interaction, as an important driving force in the design of self-healing materials, originates from the Coulombic interaction between charged groups[45]. Electrostatic interactions play a key role in conferring self-healing capabilities to SPEs[46]. The interactions arise from the attractive forces between charged particles (such as imidazolium cations) and anions (such as $TFSI^-$) as well as other polar groups, exhibiting high reversibility, thereby enabling bonds at damaged interfaces to dynamically reform. Electrostatic interactions not only promote the re-bonding of polymer segments at damaged sites but also help maintain the structural integrity of the electrolyte, ensuring that ionic conductivity and interface compatibility remain largely unchanged after repair[47]. The dynamic nature of these interactions enables the electrolyte to repeatedly repair mechanical damage, such as cuts or fractures, thereby enhancing the durability and safety of LIBs, particularly in flexible and wearable electronic devices.

In 2019, Sun et al. reported the poly(ionic liquid)-based self-healing gel electrolyte (SHGPE) (Fig. 11)[48]. In this study, a dynamic dual network structure was constructed by compositing a polyionic liquid containing UPy groups (PIL-UPy), a bifunctional ionic liquid (DE-IM/TFSI) and a lithium salt (LiTFSI). Among them, the quadruple hydrogen bonds of the UPy group and the electrostatic cross-linking of the poly(ionic liquid) formed a dual network structure, which realized the damage healing through the reorganization of hydrogen bonds and the dynamic balance of ion pair. The electrolyte showed spontaneous healing capability at 55 °C, and moreover breakthrough the in-situ healing function inside the encapsulated battery, and the charge/discharge capacity of the damaged battery can be restored and maintained after heat treatment. Characterization of the material properties showed that the ionic conductivity of SHGPE reached 1.41×10^{-3} S cm^{-1}. The $LiFePO_4$ full battery assembled based on SHGPE maintained a discharge capacity of 147.5 mAh g^{-1} after 120 cycles at 0.2 C, with a capacity retention rate of 98.6% and a stable CE of 99.7%.

In 2021, Fu et al. developed a star-shaped topologically structured bicationic poly(ionic liquid) electrolyte (DPIL-6-SPE), which achieved a breakthrough enhancement of ion transport kinetics through molecular architecture innovation[49]. DPIL-6-SPE was a solid-state polymer electrolyte system constructed via a six-armed star-shaped bis-cationic quaternary ammonium polyionic liquid (DPIL-6). The synergistic effect of its multi-arm topology and multiple charge centres significantly enhanced the ionic gravity and van der Waals interactions between the polymer chain segments, and the resulting three-dimensional network structure confered excellent dynamic reversible properties. Experiments showed that the system could achieve rapid self-healing (recovery time <2 h) at 25 °C, which was attributed to the dynamic equilibrium of intermolecular forces and the topological entanglement effect of the polymer backbone. In addition, DPIL-6-SPE exhibited excellent adhesion strength to lithium metal electrode (load weight ~200 g) and good interfacial compatibility. The multiple cationic centers of DPIL-6-SPE facilitated the dissociation of lithium salts, releasing more Li^+ trapped by $TFSI^-$, resulting in higher ionic conductivities (more than 10^{-5} S cm^{-1}) and lithium ion transference number (0.46). The assembled $LiFePO_4$/DPIL-6-SPE/Li cells were able to discharge up to 152.6 mAh g^{-1} at 0.1C, with 94% capacity retention and 96% CE after 50 cycles. In particular, the mechanical proper-

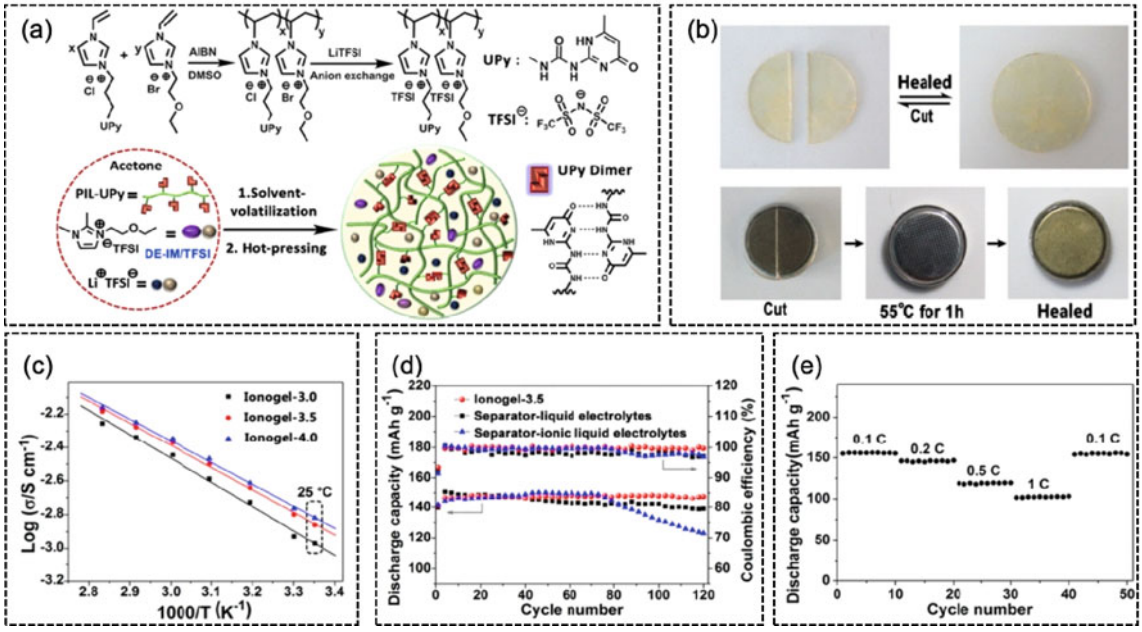

Figure 11. (a) Schematic illustration of the synthesis of the PIL-UPy copolymers and the preparative process of the ionogel membranes. (b) Photos of the membranes healed. (c) Ionic conductivities. (d) Cycling performances. (e) Rate performance. Adapted from Ref.[48]

ties and electrical conductivity of DPIL-6-SPE could be fully recovered after multiple damages, which enabled the derived soft-packed batteries to have stable power supply capability when bent and folded at multiple angles.

Both systems by Li et al. and Guo et al. rely on electrostatic interaction and ionic liquids to balance mechanical flexibility and ionic transport. However, self-healing efficiency remains temperature-dependent, and interfacial instability during cycling leads to capacity fade in full cells. Synthetic complexity of multi-armed polymers and reliance on fluoroinated ionic liquids also hinder scalability. Future efforts should focus on integrating multi--scale dynamic networks, developing stimuli-responsive healing systems, and optimizing interface stability for high-voltage applications.

Although the supramolecular interaction-driven intrinsic SHPs exhibit unique healing properties by virtue of dynamic non-covalent bonds, its practical application still faces three key challenges: (1) the low bonds energy of reversible non-covalent bonds (5–50 kJ mol^{-1}) leads to the elasticity modulus of the material being generally confined to the order of 0.1–10 MPa; (2) the construction of multicomponent hierarchical supramolecular systems requires precise control of intermolecular forces, which significantly increases the synthesis cost; (3) the need to rely on the solvation medium to maintain the dynamic network reconfiguration capability, leading to performance degradation under extreme operating conditions such as high temperature/vacuum. These bottlenecks constrain the engineering application of supramolecular interaction-driven intrinsic SHPEs in solid-state batteries.

SHPES BASED ON DYNAMIC COVALENT BONDS

Imine bonds

Imine bonds, a chemical bond that combines covalent bond strength with dynamic reversibility, shows unique advantages in the field of self-healing materials. The high bond energy of 615 kJ mol^{-1} ensures the basic mechanical properties of the material, while the water molecule-mediated hydrolysis-condensation reversible mechanism (pH-responsiveness) confers the system with dynamic reconfiguration capability. This "strong and reversible" property breaks through the contradiction between mechanical strength and self-healing efficiency in traditional dynamic bonds systems, which has led to a wide range of applications in precision engineering fields, such as flexible electronic device packaging and smart coatings[50]. At present, dynamic covalent network design based on imine bonds has become one of the mainstream strategies for constructing high-strength self-healing materials.

In 2021, Pu et al. developed dynamic imine-bonded crosslinked SHPE to achieve synergistic optimization of mechanical strength and self-healing properties (Fig. 12)[51]. The material was prepared by the conden-

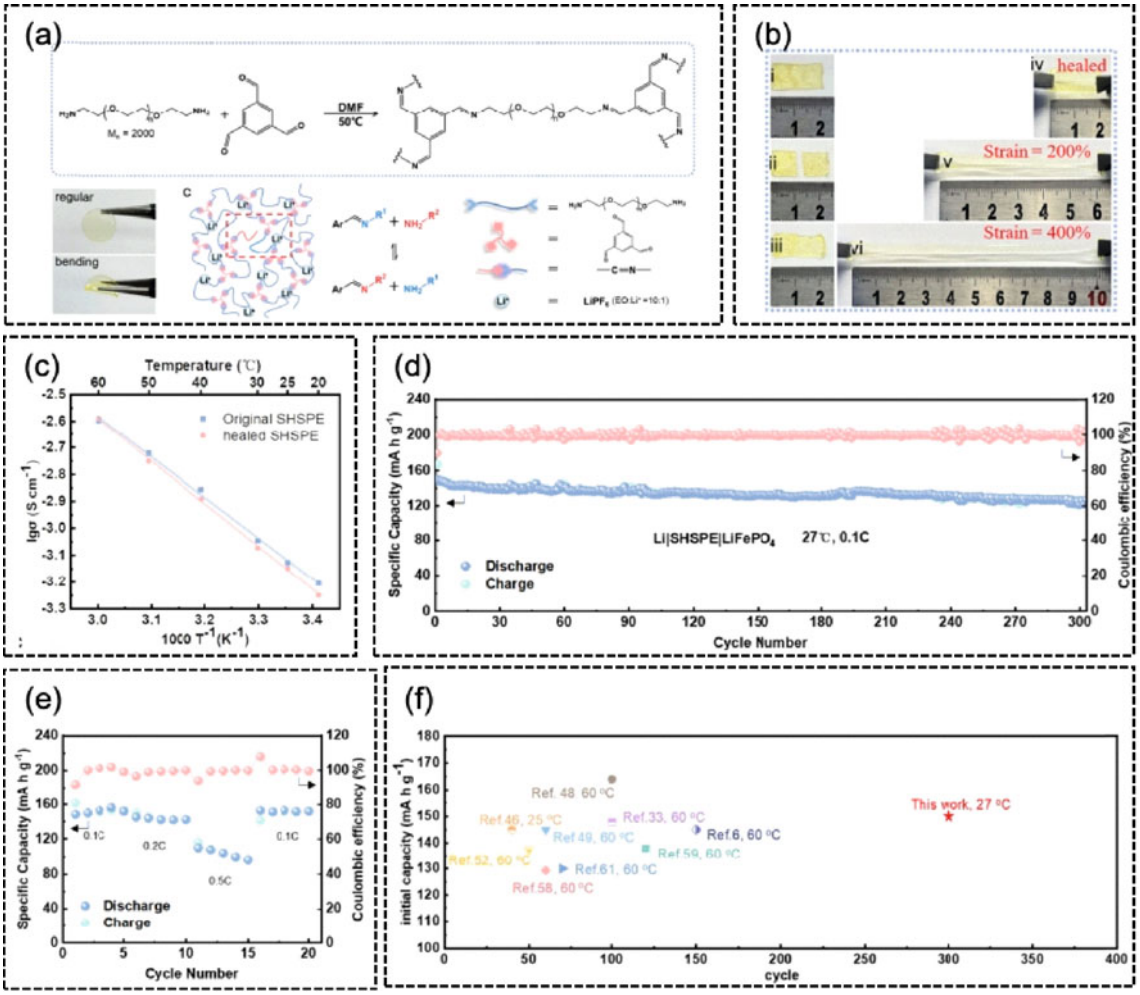

Figure 12. (a) Chemical precursors and synthesis scheme for the SHSPE. (b) Optical images of the SHSPE being healed. (c) The temperature-dependent ionic conductivity. (d) The long-term cycling performance. (e) Rate capability. (f) Comparison of the SHSPE to other LMBs with self-healing SPEs reported in the literature. Adapted from Ref.[51]

sation reaction of PEG diamine and homotriphenylaldehyde to construct a dynamic covalent network, in which the pH-responsive reversible property of imine bonds endowed SHPE with a dual advantage: (1) fractured specimens could be restored up to 500% of the tensile deformation capacity after 24 h of healing at room temperature; and (2) the dynamic network maintained a high elastic modulus, which was significantly higher than that of the conventional hydrogen-bonded network. Electrochemical characterization showed that SHPE achieved ionic conductivity of $6.23 \times 10^{-4} \sim 7.48 \times 10^{-4}$ S cm^{-1} in the temperature region of 20–25 °C, and electrochemical stabilization window (5.0 V vs. Li/Li$^+$) could compatible with high-voltage cathode materials. The assembled Li/SHPE/Li symmetric cell was operated continuously at 0.1 mA cm^{-2} for 1200 h with only 12% growth in interfacial impedance, verifying the sustained inhibition effect of the dynamic network on lithium dendrite growth.

In 2022, Deng et al. developed a novel SHPE, PBPE[52]. PBPE constructed a dynamic covalent network through the Schiff base condensation reaction of PEG diamine with homotriphenylaldehyde. Reversible bond exchange of imine bonds enabled PBPE to achieve rapid self-healing for 1 h at room temperature. After damage healing, the ionic conductivity and elastic modulus of PBPE could be almost completely restored. Electrochemical performance tests showed that the healed Li/PBPE/$LiFePO_4$ cell exhibited an initial capacity of 142.2 mAh g^{-1} comparable to that of the pristine battery at 0.5 C, with a capacity retention rate of 97.7% after 80 cycles (139.0 mAh g^{-1}). Mechanistic studies confirmed that the dynamic reconfiguration of the Imine bonds not only healed the electrolyte body damage, but also restored the lithium ion transport channel between the electrode/electrolyte through the regeneration of interfacial bonds.

In 2022, Li et al. reported bio-based smart electrolytes (Fig. 13)[53]. In this study, a dynamic imide crosslinked network was constructed through a multicopolymerization strategy of soybean isolate protein (SPI) with hyperbranched polyamide (HBPA), p-phenylene terephthalaldehyde (PA), and 1,4-butylene glycol diglycidyl ether (BDE). The abundant amino acid residues in the SPI anchored the TFSI$^-$ by electrostatic interaction, forming a selective lithium ion transport channel, enabling the system to obtain a room-temperature ionic conductivity of 3.3×10^{-4} S cm^{-1}. The dynamic imine bonds network endowed the material with self-healing properties, and the hyperbranched structure of HBPA enhanced the mechanical constraints of the polymer matrix on lithium deposition and inhibited the growth of lithium dendrites. Electrochemical tests showed that the Li/SHPE/$LiFePO_4$ cell exhibited a stable discharge capacity of 32.6 mAh g^{-1} at 0.5 C, with a CE close to 100%.

The SHSPEs based on dynamic imine bonds all utilized the reversible dissociation-recombination of imine bonds to balance mechanical resilience and ionic transport, with polymer backbones modulating segmental mobility[54]. In the three examples, SHSPEs are prone to structural instability in humid environments due to Imine bonds hydrolysis. Furthermore, the dynamic network lacks long-term compatibility with the lithium metal interface, and increased interface impedance during cycling may affect battery performance. In addition, although networks constructed from certain bio-based materials are recyclable[55], the synergistic optimization of ionic conductivity and mechanical strength still needs to be improved. Future directions include improving Imine bonds hydrolytic stability, integrating dual dynamic bonds for enhanced durability, and developing bio-based composites for sustainable scalability, alongside engineering smart interfaces with LiF-rich SEI layers to boost battery reliability.

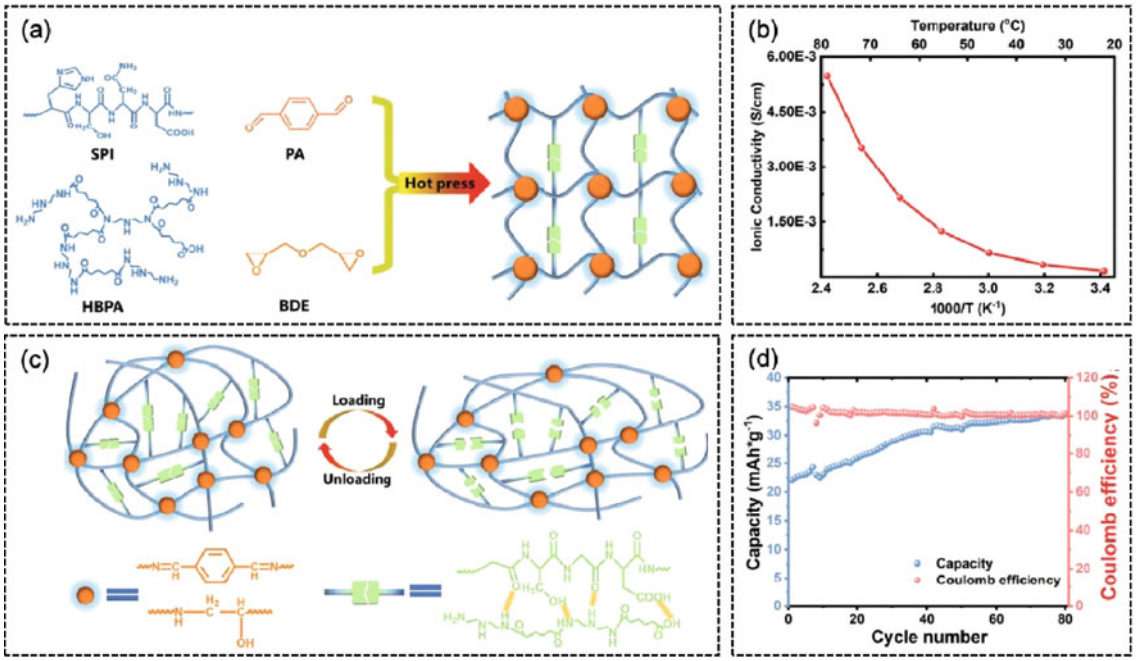

Figure 13. (a) Preparation of the dynamic covalent networks of SPI-based vitrimer. (b) The ionic conductivity of the SPI-3Li under different temperature. (c) Schematic illustration of the energy dissipation mechanism through reversible breaking and reformation of hydrogen bonds under deformation. (d) Galvanostatic cycling performances of Li|SPI-3Li|$LiFePO_4$ cells at 0.2C (60 °C). Adapted from Ref.[53]

Disulfide bonds

Disulfide bonds (-S-S-) play a crucial role in the effective self-healing process of SPEs due to their unique dynamic exchange characteristics and significantly lower bond energy compared to C-C bonds. This is attributed to their highly reversible nature and the ability to undergo dynamic exchange reactions under mild conditions[56]. Through the breaking and reformation of disulfide bonds via exchange reactions, polymer chains reconnect at damaged interfaces, thereby restoring structural integrity and functionality. Additionally, disulfide bonds enhance interface stability with lithium metal anodes by enabling the electrolyte to accommodate volume changes during cycling, thereby inhibiting dendrite growth and extending battery life[57]. Beyond their immediate self-healing capability, the dynamic nature of disulfide bonds supports recyclability, as the polymer network can be decomposed by reducing agents and reprocessed, further promoting the sustainability of battery technology. The combination of reversibility, mechanical robustness, and electrochemical compatibility makes disulfide bonds an ideal tool for developing durable and long-lasting SHSPEs.

In 2022, Yang et al. developed a SHPEs (RFSPE-3) based on rigid-flexible epoxy resin and dynamic cross-linking of disulfide bonds to achieve efficient synergistic optimization of mechanical strength and self-healing properties[58]. The electrolyte was prepared using a co-polymerization strategy of rigid DGEBA and flexible PEGDGE chain segments, and a functionalized polymer backbone with both rigid-flexible coupling network and reversible disulfide bonds was constructed by introducing 2-aminophenyl disulfide (2-AFD) as a cross-linker. The exchange reaction of dynamic disulfide bonds endowed the material with rapid self-healing ability at room temperature (complete structure recovery within 2 h of cutting off the specimen, tensile strength retention >95%), while the rigid epoxy backbone provided excellent mechanical properties up to 20 MPa. Electrochemical tests showed that the room-temperature ionic conductivity of RFSPE-3 reached 1.5×10^{-3} S cm^{-1} and remained stable after multiple self-healing cycles, and the Li/RFSPE-3/Li symmetric cell maintained a stable polarization voltage of 16 mV even after 1800 h of cycling at a current density of 1 mA cm^{-2}, which significantly inhibited the growth of lithium dendrites. The capacity retention of the assembled Li/RFSPE-3/$LiFePO_4$ cell reached 92.1% after 100 cycles at 0.2 C, and the CE was close to 100%. In addition, the electrolyte can be efficiently recycled and reprocessed through the reversible fracture and reorganization of disulfide bonds, which provides a new idea for the development of green lithium metal batteries.

Borate bonds

Borate bonds play a crucial role in the self-healing process of SPEs, thanks to their dynamic covalent nature. Under mild conditions, these bonds can undergo reversible formation and cleavage through multiple pathways, including hydrolysis/dehydration equilibrium, diol ligand exchange reactions, and complex decomposition reactions between borate ester groups. This facilitates the reconnection of polymer chains at damaged interfaces, thereby restoring structural and functional integrity[59]. Additionally, borate bonds enhance the recyclability of electrolytes, as the network can be decomposed in water to recover the original monomers, which can then be reprocessed into new electrolytes. The combination of reversible bonding, tunable dynamics, and recyclability makes borate bonds a versatile tool for developing durable and sustainable SHSPEs, thereby enhancing the lifespan and safety of LIBs.

In 2019, Evans et al. developed dynamic borate ester electrolyte by constructing a dynamic covalent network through the esterification reaction of triethylene glycol monomethyl ether with boric acid (Fig. 14)[60]. When the electrolyte was damaged, the reversible dissociation of the borate ester bond caused the network to temporarily depolymerize into monomers, followed by network reconfiguration via a dynamic bond exchange reaction, a process that fully restored the ionic conductivity of the healed electrolyte to its original value (3.5×10^{-4} S cm^{-1}). The research team innovatively adopted an electrochemical real-time monitoring method to verify the self-healing efficiency. When the electrolyte membrane was cut off, the system current dropped from the initial ±12 μA to ±3 μA, and then spontaneously recovered to the initial current level after 34 h without external

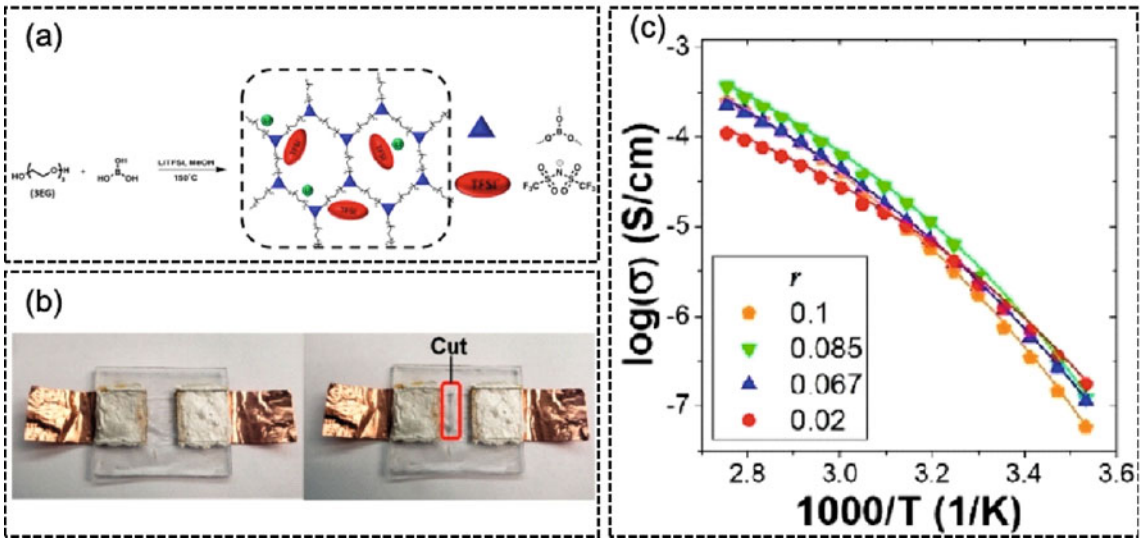

Figure 14. (a) Synthesis of dynamic network electrolytes from 3EG and boric acid. (b) Application of a force accelerates healing. (c) Conductivity as a function of temperature. Adapted from Ref.[60]

intervention. The healing time could be reduced to 10 min if mechanical pressure was applied to assist the bond exchange process.

SHSPEs designed based on dynamic covalent networks formed by borate bonds not only endow the electrolyte with unique self-healing capabilities but also enable the boron atoms in the boron ester bonds to form Lewis acid-base interactions with lithium salt anions, promoting lithium salt dissociation and constructing continuous ion transport channels. Some boron ester-containing electrolytes exhibit room-temperature ionic conductivity as high as 10^{-4} S cm^{-1}, and their electrochemical stability window is compatible with high-voltage cathode materials[61]. However, at low temperatures, the kinetics of the ester exchange reaction in borate bonds slow down, potentially reducing self-healing efficiency and ionic conductivity. This can be addressed by introducing other dynamic bonds to enhance low-temperature responsiveness.

Dynamic covalent bonds strategies provide innovative solutions for the design of SHPEs by precisely modulating the fracture-reorganization equilibrium mechanism of chemical bonds. Such bonds systems can be dynamically reconfigured at room temperature to achieve dynamic network reorganization at the molecular level, and their reversible properties stem from the synergistic effect of moderate thermodynamic stability and fast kinetic response[62].

SHPES BASED ON THE COMBINATION OF SUPRAMOLECULAR INTERACTION AND DYNAMIC COVALENT BOND

Supramolecular interactions have low bond energies and can be rapidly fractured and reorganized under ambient or mild conditions for instant self-healing. However, the strength of materials with supramolecular interactions alone is low. Dynamic covalent bonds have high bond energies that confer a rigid framework to the material, and although external stimuli (e.g., heat, light) are required to trigger healing, dynamic bond breaking and reorganization can healing a larger range of damage. The combination of supramolecular interactions and dynamic covalent bonds in SHSPEs produces a synergistic effect, significantly enhancing self-healing capabilities and overcoming the limitations of systems that rely solely on a single type of dynamic bond[63]. Supramolecular interactions (such as hydrogen bonds) enable polymer chains to spontaneously reconnect through reversible non-covalent bonds, achieving rapid initial healing at damaged interfaces and closing cracks swiftly without external stimulation. Meanwhile, dynamic covalent bonds (such as disulfide bonds and imine bonds) form a more robust covalent bond network and can undergo bond exchange reactions, enabling stable and durable repair[64]. This mechanism ensures that the repaired electrolyte exhibits significant recovery in both mechanical and electrochemical properties. This dual mechanism enables the electrolyte to not only rapidly repair surface damage through supramolecular interactions but also achieve deep, effective repair through the rearrangement of covalent bonds, maintaining high repair efficiency even after multiple damages. Additionally, the synergistic effects of these interactions help balance the flexibility and mechanical strength of the electrolyte, maintaining structural stability during cycling while allowing sufficient chain mobility for repair, thereby enhancing the durability and reliability of LIBs in practical applications.

In 2020, Xue et al. copolymerized poly(ethylene glycol) methyl ether acrylate (PEGMEA) with a bifunctional cross-linker containing disulfide bonds/urea groups using reversible addition-fracture chain transfer (RAFT) polymerization to construct a hydrogen bonds dynamic covalent bonds synergistic network (PEG-SSH) (Fig. 15)[65]. The urea-based quadruple hydrogen bonds were autonomously healed by dynamic reorganization at room temperature. And the disulfide bond recombination reaction activated the ultrafast healing mechanism. The dynamic network reconfiguration process did not destroy ion transport channels, and the ionic conductivity

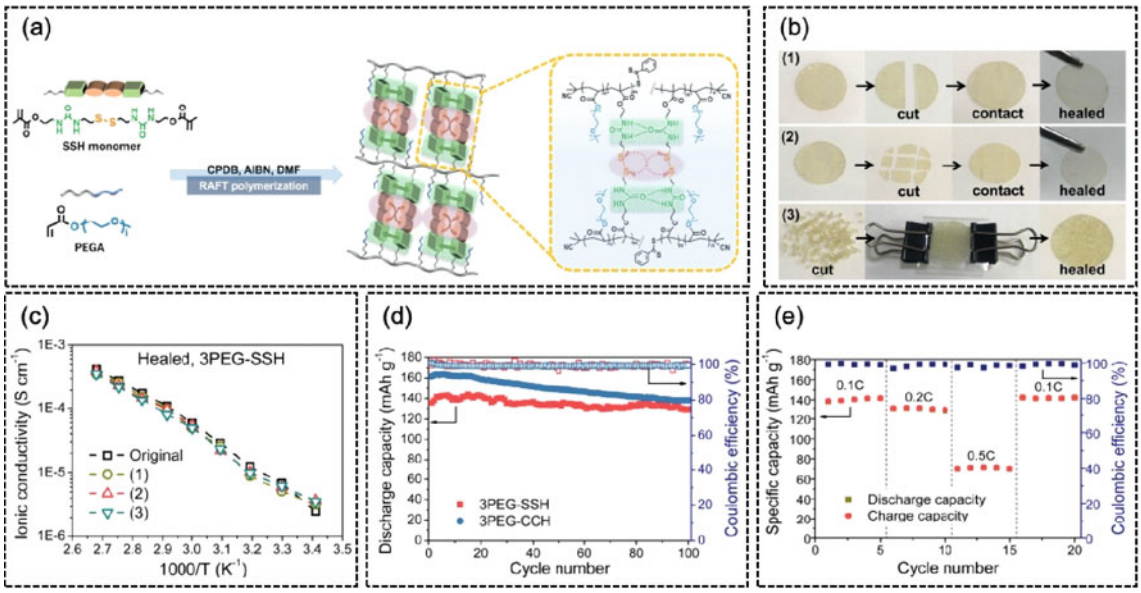

Figure 15. (a) Schematic illustration of the formation of PEG-SSH containing disulfide bonds and hydrogen bonds. (b) Photographs of disk-shaped 3PEG-SSH cut into different forms. (c) Temperature dependence of ionic conductivity of healed 3PEG-SSH. (d) Cycling performances of Li/3PEG-SSH/$LiFePO_4$ and Li/3PEG-CCH/$LiFePO_4$ cells at a specific current of 0.1C. (e) Cycling of Li/3PEG-SSH/$LiFePO_4$ cell at 0.1, 0.2, and 0.5C. Adapted from Ref.[65]

remained unchanged after healing. Electrochemical tests showed that the $LiFePO_4$ full battery assembled based on this electrolyte exhibited an initial discharge capacity of 135 mAh g^{-1} at 0.2C, a capacity retention rate of 97.5% after 100 cycles, and a stable CE of 99.8%.

Our group applied the strategy of combining dynamic disulfide bonds and hydrogen bonds to the preparation of self-healing gels and composite solid-state polymer electrolytes. In 2022, we developed a crosslinked network SHPEs (PDDP-5), which achieved room-temperature self-healing performance combined with flame-retardant properties through the synergistic effect of hydrogen bonds and dynamic disulfide bonds (Fig. 16)[66]. The electrolyte was constructed using a thiol-alkene click reaction to build a crosslinked network, with poly(ethylene glycol) diacrylate (PEGDA) as the flexible backbone, 4-aminobenzene disulfide derivative (DDB) as the source of dynamic disulfide bonds, and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide salt (EMIMTFSI) ionic liquid introduced. Hydrogen bonds endowed PDDP-5 with rapid self-healing ability (fragment splicing for weight bearing in 3 s and 100 g of weight after 24 h), while dynamic disulfide bonds enhanced mechanical strength (tensile strength of 0.105 MPa). The incorporation of EMIMTFSI enhanced the ionic conductivity of PDDP-5 to 1.13×10^{-4} S cm^{-1} (28 °C), widened the electrochemical window to 4.8 V, and exhibited excellent flame retardancy. Electrochemical tests showed that the polarization voltage of the Li/PDDP-5/Li symmetric cell was stabilized at 0.22 V after 300 h of cycling at 0.05 mA cm^{-2}, and the capacity of the assembled Li/PDDP-5/$LiFePO_4$ cell was maintained at 137.6 mAh g^{-1} after 300 cycles at 0.2 C, with a CE of 99.9%, and the electrolyte conductivity and cycling performance were almost completely restored after self-healing.

In 2024, we also reported three-dimensional crosslinked network deep eutectic gel polymer electrolytes (CNGPE), which achieved a combination of high ionic conductivity and room-temperature self-healing ability through the synergistic action of hydrogen bonds and dynamic disulfide bonds[67]. CNGPE was prepared using a thiol-alkene clicking reaction by copolymerization of Jeffamine dimethacrylate (JDMA), poly(dimethylsiloxane) dimethacrylate (PDMS-DMA) copolymerized with monomers containing dynamic disulfide bonds to construct a three-dimensional crosslinked network structure. A deep eutectic solvent (DES) consisting of LiTFSI and N-methylacetamide (NMA) as well as a LiDFOB/$LiNO_3$ composite lithium salt were introduced to endow the CNGPE with room-temperature self-healing capability (scratches were completely healed within 2 h) by utilizing the dynamic reversibility of hydrogen bonds and disulfide bonds. Electrochemical tests showed that the ionic conductivity of CNGPE reached 7.71×10^{-4} S cm^{-1} (30 °C), and the Li/CNGPE/Li symmetric cell was stably cycled for 800 h at 0.1 mA cm^{-2}, with a polarization voltage of only 0.07 V. The assembled Li/CNGPE/$LiFePO_4$ cell maintained a discharge capacity of 126 mAh g^{-1} after 960 cycles at 0.5 C, with a capacity retention rate of 99.9%. In addition, the electrolyte also exhibited a discharge capacity of 154.9 mAh g^{-1} when matched with a high-voltage ternary ortho-material (NCM811), demonstrating its potential for application in high-voltage lithium metal batteries.

In 2025, we prepared a self-healing composite solid electrolyte (PBHL@LLZTO@DDB) with a dynamic 3D inorganic/organic hybridization network, which effectively solved the problems of poor compatibility of inorganic/organic interfaces, growth of lithium dendrimers, and susceptibility of electrolyte membranes[68]. The electrolyte was based on polyurethane (PBHL) as a polymer matrix, modified by silane coupling agent (DDB) with $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO@DDB) as an inorganic filler. The disulfide bonds in the DDB molecule under-

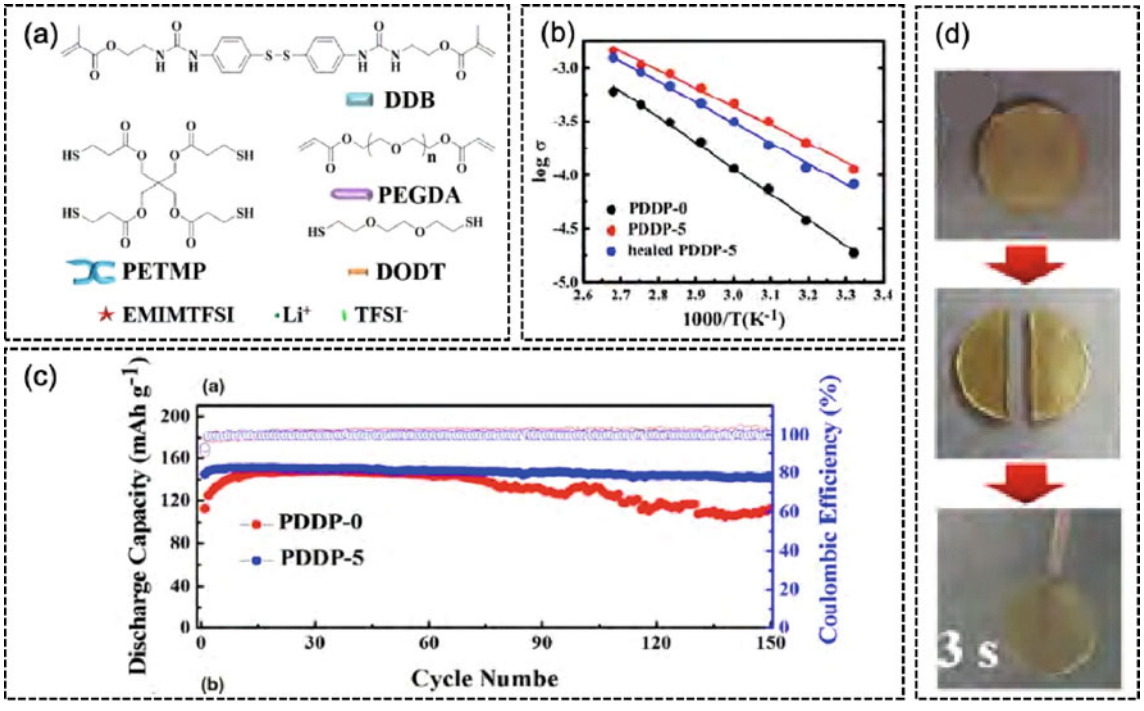

Figure 16. (a) The chemical structures of PEGDA, PETMP, DODT, and DDB. (b) Temperature dependence of ionic conductivity of PDDP-0, PDDP-5 and the healed PDDP-5. (c) Long-circulating performance of Li/PDDP-0/ $LiFePO_4$ and Li/PDDP-5/ $LiFePO_4$ cells at 0.1 C. (d) Photographs of healing process of PDDP-5 at 28 °C. Adapted from Ref.[66]

went an exchange reaction with the disulfide bonds in the PBHL to form a dynamic three-dimensional hybridization network, which promoted the homogeneous dispersion of LLZTO in the PBHL. Meanwhile, the combination of dynamic disulfide and hydrogen bonds endowed the electrolyte with excellent self-healing performance, which could autonomously healing the damaged area without additional stimulation, and the mechanical properties of the healed electrolyte were almost completely restored. Electrochemical tests showed that PBHL@LLZTO@DDB had a lithium ion conductivity of $1.24 \pm 0.08 \times 10^{-4}$ S cm^{-1} at 30 °C and a wide electrochemical stabilization window of 5.16 V (vs. Li^+/Li). The assembled Li/PBHL@LLZTO@DDB/Li symmetric cell can be stably cycled for more than 3200 h at a current density of 0.05 mA cm^{-2}, demonstrating excellent lithium metal compatibility. In the Li/PBHL@LLZTO@DDB/$LiFePO_4$ full cell with an initial discharge capacity of 140 mAh g^{-1} at 0.2 C, the capacity retention rate is 95% after 700 cycles, the CE is close to 100%, and the healed PBHL@LLZTO@DDB could almost fully recover the original electrochemical performance.

The studies collectively demonstrate SHSPEs that integrate dynamic covalent bonds (disulfide/imine) and supramolecular interactions (hydrogen bonds) to balance mechanical resilience and ionic transport. A common design principle involves dynamic bond reorganization: disulfide/imine bonds provide mechanical strength, and hydrogen bonds facilitate rapid healing, addressing interfacial instability and dendrite growth. However, current designs face trade-offs. Imine bonds suffer from hydrolytic degradation, disulfide systems show limited conductivity ($\leq 1.24 \times 10^{-4}$ S/cm), and bio-based matrices lack optimized ion transport pathways. Future research should prioritize hydrolytically stable hybrid networks, stimuli-responsive healing motifs (such as pH/thermal sensitivity), and sustainable feedstocks to enable scalable.

SUMMARY AND OUTLOOK

During assembly and cycling of LIBs, SPEs are susceptible to structural damage caused by mechanical stresses, leading to interfacial failure, dendrite penetration, and other coupled mechanical-electrochemical failure modes. In this context, SHPEs provide an innovative solution to solve the above problems through the dynamic bonds network reconfiguration capability. In this paper, we systematically review the research progress of SHPEs in the field of LIBs, analyze its design strategy from the dimensions of supramolecular interactions (hydrogen bonds, ion-dipole, etc.) and dynamic covalent bonds (Imine bonds, disulfide bond, etc.), and establish a constitutive relationship between the self-healing mechanism and the performance of the batteries. A comparison of various dynamic interactions is shown in Table 1. Supramolecular interactions, with their relatively low bond energies, can rapidly break and reform at room temperature or under mild conditions, enabling instant self-healing of materials. However, when acting alone, these interactions result in materials with low mechanical strength, making it difficult to meet high mechanical performance requirements. Dynamic covalent bonds possess higher bond energies, providing materials with a rigid framework. They enable damage repair through reversible bond exchange reactions. Although external stimuli may be required to trigger the process, the repair effects are more stable and long-lasting, and they confer higher mechanical strength to materials. However, their healing speed is relatively slow, making rapid repair difficult when used alone. The strategy of combining supramolecular interactions with dynamic covalent bonds demonstrates significant synergistic effects. Supramolecular interactions leverage their rapid response characteristics to achieve preliminary rapid healing of damaged areas, while dynamic covalent bonds ensure the material's mechanical strength and the durability of the repair by constructing a robust network structure. The combination of supramolecular interactions and dynamic covalent bonds addresses the challenge of balancing healing efficiency and mechanical performance under a single mechanism, offering an optimal solution for the design of high-performance self-healing polymer electrolytes.

Despite the significant progress, SHPEs still face four core challenges: (1) the balance between ionic conduction and self-healing. The conductivity of intrinsic SHPEs without plasticizers is mostly lower than 10^{-4} S cm^{-1}, making it difficult to meet the demand for fast charging; (2) Mechanical-functional balance dilemma. There is an intrinsic contradiction between high modulus (>10 MPa) and high healing efficiency (>95%); (3) Missing synergistic mechanism. Dynamic covalent bonds (bonds energy >150 kJ mol^{-1}) and supramolecular interactions (bonds energy <50 kJ mol^{-1}) cross-scale synergistic network design research is insufficient; (4) Engineering

Table 1. Comparison of Dynamic Interactions in SHSPEs

Types	Bond energy (kJ mol^{-1})	Self-healing time	Ionic Conductivity (S cm^{-1}, RT)	Mechanical Strength (MPa)
Hydrogen bonds	5–50	RT, 1–60 min	10^{-5}–10^{-4}	0.1–10
Ion-dipole interaction	10–60	RT, 1–12 h	10^{-4}–10^{-3}	0.1–7.3
Electrostatic interaction	20–100	55 °C or RT (thermal activation)	10^{-5}–10^{-3}	Topology dependent
Imine bonds	~615	RT, 1–24 h	10^{-4}–10^{-3}	>10
Disulfide bonds	~240	RT, 2–24 h	$\leq 1.24 \times 10^{-4}$	20
Borate bonds	150–200	RT, 10 min–34 h	$\sim 3.5 \times 10^{-4}$	Crosslinking dependent

bottleneck. The existing research is mostly limited to the laboratory scale, and lack of continuous preparation process and lifetime evaluation standards. Future research should focus on three breakthrough directions: (1) molecular scale, the development of dynamic covalent/supramolecular synergistic network, through the design of bond energy gradient to achieve a wide temperature range (-40 ~ 120 °C) adaptive healing; (2) device level, the construction of the "damage sensing-in situ healing-performance recovery" intelligent system, breakthrough in the failure of traditional batteries irreversible limits; (3) Engineering level, the development of roll-to-roll coating, 3D printing and other large-scale preparation technology, the establishment of a new battery based on ASTM/ISO standards. Only by realizing the multi-level innovation of materials-devices-processes can SHPEs be promoted from laboratory to industrialization and provide technical support for the next-generation high-security energy storage system.

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