Self-healable gels in electrochemical energy storage devices

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ABSTRACT

In the green energy and carbon-neutral technology, electrochemical energy storage devices have received continuously increasing attention recently. However, due to the unavoidable volume expansion/shrinkage of key materials or irreversible mechanical damages during application, the stability of energy storage and delivery as well as the lifetime of these devices are severely shortened, leading to serious performance degradation or even safety issues. Therefore, the utilization of self-healable gels into electrochemical energy storage devices, such as electrodes, binders, and electrolytes, is proven as an effective method to realize long-term stable operation of these devices via the self-repairing of mechanical and electrochemical characteristics. Herein, this review first summarizes the feature and fabrication of different gels, paying special attention to hydrogels, organohydrogels, and ionogels. Then, basic concepts and figure of merit of self-healable gels are analyzed with a detailed discussion at the healing mechanisms, from reversible dynamic bonds to physical molecular diffusion, and to external healing trigger. Then we introduce all the important parts of electrochemical energy storage devices, which could be replaced by healable gels to enhance the durability, including electrodes, binders, and electrolytes. Finally, the critical challenges and future perspectives regarding the future development of healable gels based high-performance electrochemical energy storage devices or electronics are provided.

1 Introduction

In recent years, the global scale energy crisis and the accompanying increasingly severe ecological issues urgently call for the development of clean energy system [1–3]. Electrochemical energy storage devices (EESDs), represented by secondary batteries and supercapacitors, can store electricity in the form of chemical energy and unleash them within electrochemical processes. Due to the high energy storage capacity, high power efficiency, and less pollution, these EESDs have been widely used in mobile electronic devices, new energy vehicles, and large-scale energy storage devices for national defense [4–6]. However, EESDs face with problems of stability and safety during operation due to the unavoidable volume expansion/shrinkage of key active materials, which causes the local cracks and rupture of electrodes, especially the high specific energy electrodes [7–9]. In addition, EESDs for powering the wearable electronics or under the extreme conditions (low temperature, high temperature, and high humidity) need to endure multiple bending or deformation processes, which probably leads to internal mechanical damages [10–12]. These irreversible physical or mechanical damages seriously reduce the capacity and cycle stability, shorten the lifetime, and even cause thermal runaway of EESDs [13]. In order to solve these problems, there is absolutely an urgency to develop EESDs with self-healing functionality, effectively decreasing the performance loss after the damages and reactivating their original properties, thus realizing the high security, high reliability, and ultra-long lifetime of EESDs fundamentally [14, 15].

Gels, including hydrogels, organohydrogels, and ionogels, are physically or chemically crosslinked polymer networks containing mobile liquids [16]. Owing to facile functionalization of polymer networks, the mechanical properties, conductivity, adhesion, or even self-healing ability of gels can be tuned towards different applications [17–19]. Thus, gels, especially the self-healable gels, are attracting the attention of researchers to improve the electrochemical performance as well as the durability of EESDs,

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due to their excellent flexibility and stretchability, easy workability, high theoretical capacity, and functional recovery ability after damage [20–22].

When utilized in EESDs, after facing internal or external mechanical damages, these gels can initiate the healing process, restoring the mechanical property and functionality with or without triggers, such as light, heat, or chemical reagents (Fig. 1). For instance, self-healable gel electrodes, which generally are fabricated via the incorporation of conductive agents inside healable gel matrix, can achieve multiple bending/stretching cycles and maintain good performance under mechanical damage, enabling the stable power supply for wearable electronic devices [23, 24]. When used as binder for electrodes, self-healable gels can also inhibit the volume expansion of the electrode and the shedding of active substances in the electrochemical processes, thus EESDs can sustain a good cycling stability [25]. Concerning electrolytes, gels with internal salts or ionic liquid (ILs) are ionically conductive and receiving great attention as polymer electrolyte in solid EESDs to overcome the problems of leakage and electrolyte flammability issues [26–28]. Healable gel electrolytes can prevent the growth of lithium dendrites as well as restore the device and functionalities after breakage or rupture due to the mechanical deformations in electrochemical cycling processes or under extreme conditions [29, 30]. Based on the good application prospects in these fields, the development of self-healable gels to fundamentally achieve energy storage with high safety, high reliability, and long life, has become a worldwide research hotspot.

Since the first discovery of healable gels in 1928, hydrogels, organohydrogels, and ionogels have been widely utilized as electrodes, binders, and electrolytes to advance the performance and durability of EESDs. From 1970 to 2022, the reports of self-healing devices for energy storage gradually increased (Fig. 2). Despite the many reports of self-healing gels, nevertheless, a detailed review of self-healable gels used in energy storage devices is lacked. This review prospectively summarizes the research progress of self-healing gels in various applications of electrochemical energy storage, introduces the classification and assembly of different gels, expounds the self-healing mechanism of gels, and discusses the research status of self-healing gels as electrodes, binders, and electrolytes in the field of energy storage.

The future development direction of the self-healing EESDs is prospected and predicted, which provides guidance for the research and application of self-healing EESDs.

2 Classification and fabrication of different gels

Gels can be categorized based on their composition and properties. Hydrogels are three-dimensional (3D) networks of hydrophilic polymers capable of absorbing and retaining large amounts of water or biological fluids. Based on the structure of hydrogels, organohydrogels formed from organic solvents and organic gelators, and ionogels formed by incorporating ILs into a polymer matrix or self-assembled structures, are fabricated to improve the stability and overall performance. The choice of preparation method depends on factors such as the desired gel properties, intended application, and the types of polymers and crosslinking agents used, whereas most common preparation methods of gels include chemical crosslinking (polymerization), physical crosslinking, enzymatic crosslinking, radiation crosslinking, and template assisted method [31–33]. This section will provide a brief overview of the properties and typical fabrication techniques for various types of gels.

2.1 Hydrogels

Hydrogels are polymers formed by chemical or physical crosslinking and swelled in a large amount of water due to the three-dimensional polymer network structure [34–36]. Based on their chemical composition, hydrogels can be divided into two categories: (i) natural polymers and (ii) synthetic polymers [37]. Hydrogels of natural polymers, such as agarose, alginate, and chitosan, are biocompatible and biodegradable, whereas they lack in the mechanical strength. Hydrogels made of synthetic polymers, including polyvinyl alcohol (PVA), polyacrylic acid (PAA), polyacrylamide (PAM), polyethylene oxide (PEO), or polyethylene glycol (PEG), possess desired mechanical properties and tunable physicochemical properties, and are used widely in the bioelectronics and energy storage devices [38].

Among all commonly used gel polymers, PVA is a biocompatible and water-soluble polymer with large amount of hydroxyl functional groups, which can be crosslinked to form hydrogels [39, 40]. Borax can easily crosslink with didiol groups of
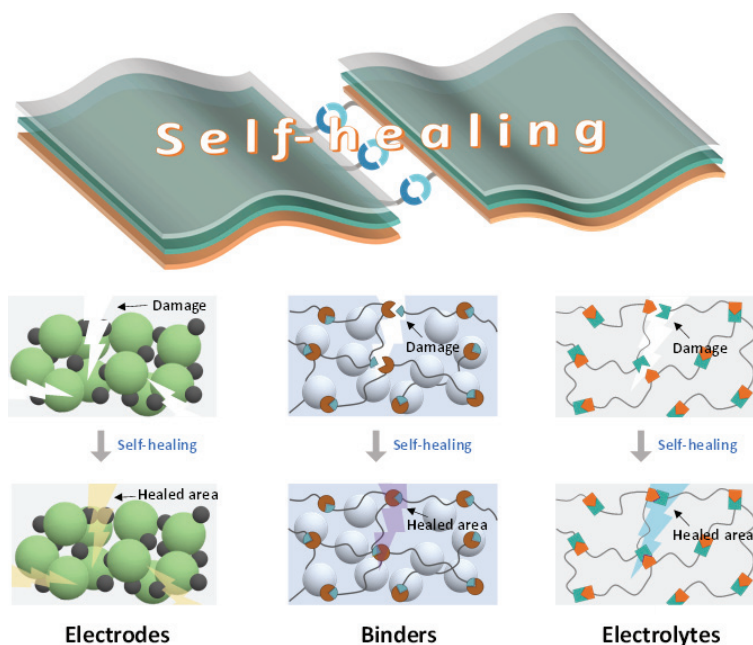

Figure 1 The scheme of working mechanisms of self-healable gels in EESDs. The gels can be used as electrodes, binders, or electrolytes to realize the self-healing functionality and improve the durability of EESDs.
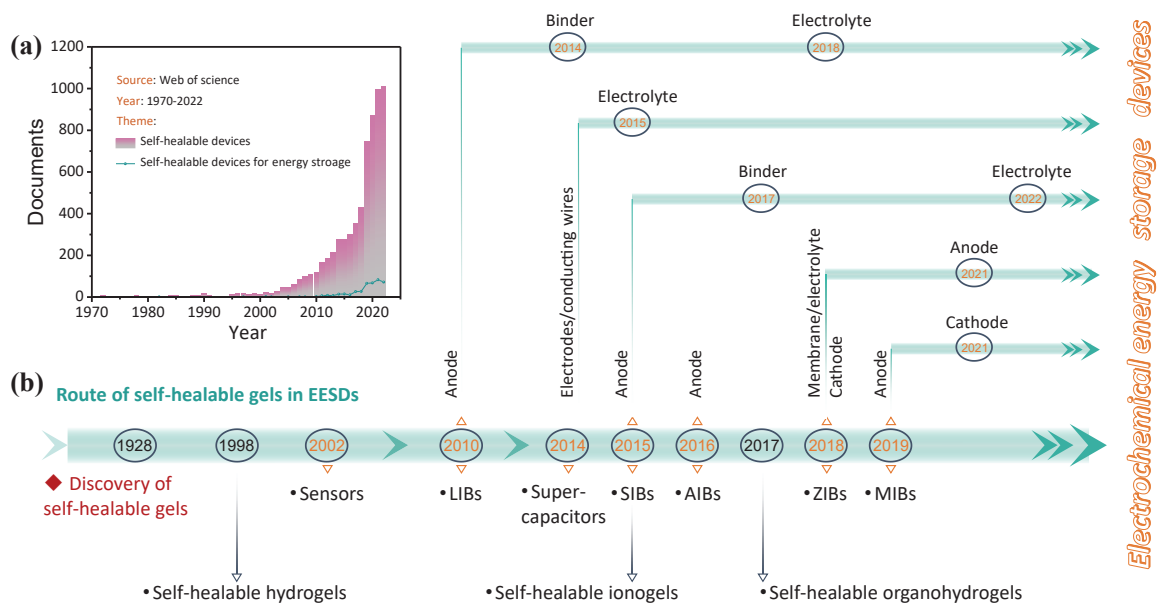
Figure 2 (a) Number of scientific documents per year from 1970 to 2022 (source: web of science. Search term: self-healable devices and self-healable devices for energy storage. Query date: March 18, 2023). (b) Research route of the self-healable gels, and their functionalities in diverse EESDs, including LIBs, supercapacitors, sodium ion batteries (SIBs), aluminum ion batteries, ZIBs, and magnesium ion batteries (MIBs).

PVA to generate reversible borax-ester interactions to form healable hydrogels, and additives such as microfibrillated cellulose (MFC) can further improve the mechanical stiffness and self-healing behavior (Fig. 3(a)) [41]. PAA is also a biocompatible, soft, adhesive, and charged polymer network, and it is often used to fabricate hydrogels with copolymers or interpenetrating networks to improve the mechanical properties [42, 43]. Sui et al. prepared a tough copolymer hydrogel based on sulfobetaine methacrylate (SBMA) and acrylic acid monomers, and the addition of LiCl further improves the ionic conductivity and freezing tolerance (Fig. 3(b)) [44]. PAM gels based on free radical polymerization of acrylamide and crosslinker N,N′-methylene-bis-acrylamide are inert and strong hydrogels with tunable mechanical properties (Fig. 3(c)) [45]. The PEG and PEO possess the same structure of repeated units of ethylene oxide, while the polymer whose molecular weight is above 20,000 g·mol^{-1} is referred as PEO [46]. PEO gels have high ionic conductivity, reasonable mechanical properties, better flexibility, wide electrochemical window, and excellent compatibility with electrodes, and are widely investigated as the gel electrolytes in the EESDs, which will be discussed in the following section [47].

The preparation methods depend on the properties required for the hydrogels and the intended application. The chemical crosslinking, which involves the polymerization of monomers with the trigger of free radicals or ionic crosslinking agents to form a covalent crosslinking based hydrogel network, provides excellent control over the mechanical properties and stability by manipulating the choice of monomers, crosslinking agents and initiators, degree of crosslinking, and post-modifications [48]. In contrast, physical crosslinking preparation methods (i.e., thermal gelation, pH-induced gelation, and salt-induced gelation) are able to create a three-dimensional work based on physical interactions between polymer chains (i.e., hydrogen bonding, hydrophobic interactions, and supramolecular interactions) [49]. Physical crosslinking of hydrogels often offers advantages such as simplicity, reversibility, and biocompatibility, however, disadvantages including lower mechanical strength and stability compared to chemically crosslinked hydrogels might be brought out [50].

2.2 Organohydrogels

Though various intriguing advantages of hydrogel are discussed in the last section, hydrogels still face the limitation of the poor stability as they tend to dehydrate in dry conditions or freeze at low temperatures. To address these problems, the organohydrogels are obtained via partial or fully substitution of water in hydrogels with high boiling temperature organic solvents (e.g., glycerol, ethylene glycol (EG), and dimethyl sulfoxide (DMSO)) [51, 52]. Generally, due to the non-volatile property of organic solvents, organohydrogels acquire the improved anti-drying and anti-freezing properties, even improved mechanical properties for the possible interactions between organic solvents and gel matrix as well as additives.

The first way to prepare organohydrogels is to perform the gelation in the binary solvent (Fig. 3(d)) [53]. Cheng et al. fabricated cellulose nanofibrils/PAM organohydrogels via the radical polymerization in a DMSO/water solution and subsequent soaking in a CaCl$_2$ solution [54]. Due to the synergistic effect between ions and binary solvent, the organohydrogels demonstrated a high tensile strength, transparency, and ability to maintain flexibility as well as conductivity at −20 °C [55]. A silk fibroin organohydrogel was also reported via a convenient on-step regulation of a precursor mixture of silk fibroin, tannic acid, and EG under the ultraviolet light radiation [56]. Nevertheless, the solvent condition probably affects the gelation properties (e.g., solubility of monomers and polymerization time), and thus the second method concerning *in-situ* polymerization of organohydrogels on dehydrated hydrogel is proposed (Fig. 3(d)). Gao et al. obtained a heteronetwork organohydrogels via *in-situ* polymerization of oleophilic polymer within a crosslinked hydrophilic matrix swollen with amphiphilic solvents and resultant organohydrogel exhibited stable elasticity from −80 to 80 °C [57]. However, this method is generally complicated and non-universal for all organohydrogels, as the *in-situ* polymerization may affect the internal gel matrix.

The third strategy based on solvent displacement/soaking has become the most universal and facile way to transform hydrogels into organohydrogels (Fig. 3(d)). The "free water" molecules in the hydrogel are believed to be exchanged rapidly and freely with the organic solvents as they are not restricted by the polymer chains [58]. Liang et al. turned PAM-chitosan (CS) hydrogel into an organohydrogel by soaking the hydrogel in 1,2-propanediol for 12 h, and obtained organohydrogel displayed significantly
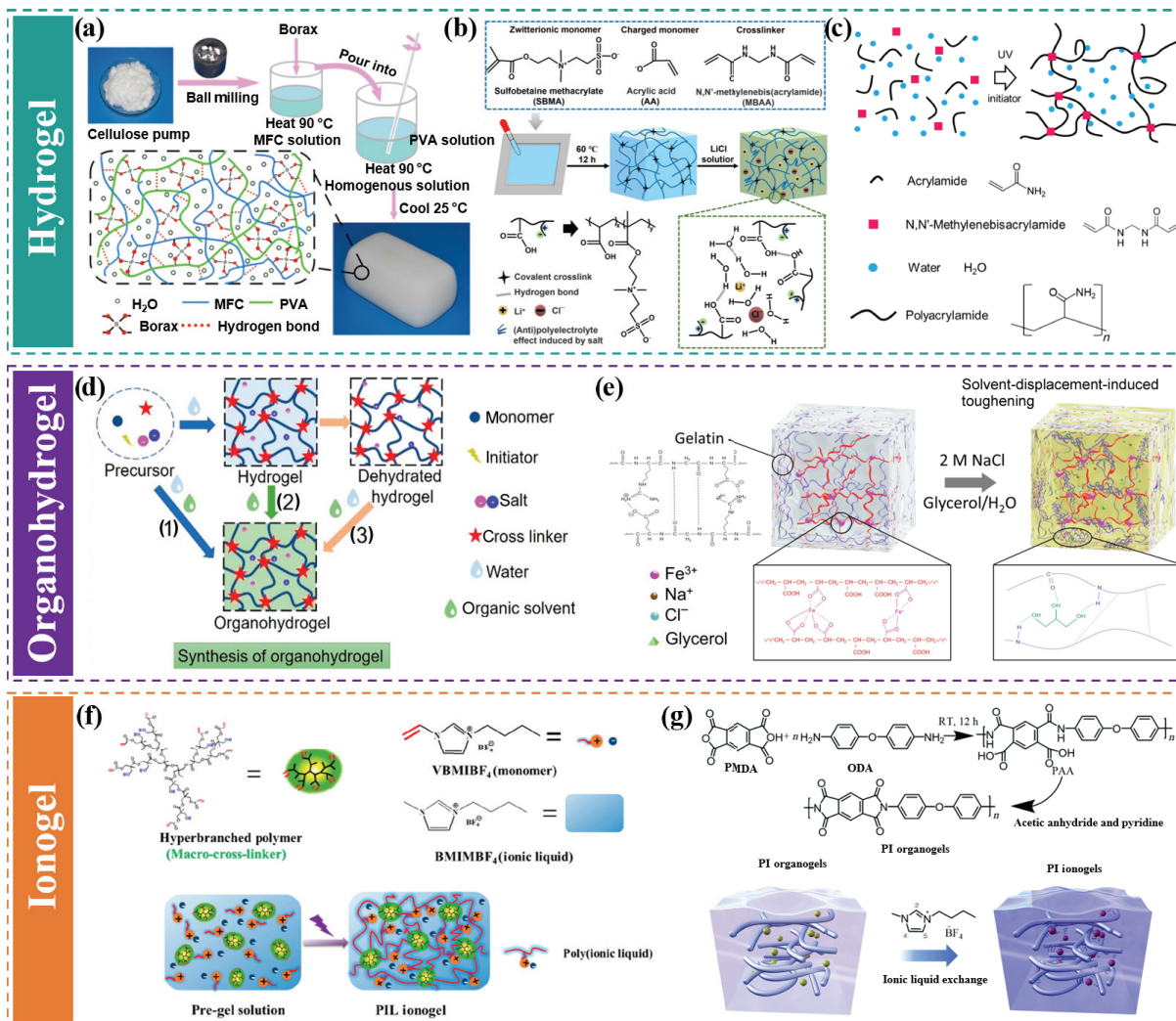
Figure 3 Summarization of different type of gels. (a) Schematic illustration of the preparation and synthesis process of the MFC-PVA-borax hydrogels via one-pot tandem reactions. Reproduced with permission from Ref. [41], © American Chemical Society 2016. (b) Preparation of ionic conductive poly(SBMA-co-AA) hydrogels. Reproduced with permission from Ref. [44], © Elsevier B.V. 2021 (c) Synthesis of a polyacrylamide hydrogel. The precursor is a mixture of the monomer (acrylamide), the crosslinker (N,N'-methylenebisacrylamide), the initiator, and water. A ultraviolet light triggers free radical polymerization, leading to a hydrogel. Covalent bonds link the monomer units into polymer chains and crosslink the polymer chains into a polymer network. Water molecules are mobile in the polymer network. Reproduced with permission from Ref. [45], © Elsevier Ltd. 2019. (d) Three approaches for the synthesis of organohydrogel: (1) gelation in binary solvent, (2) organic solvent displacement, and (3) *in-situ* polymerization of organohydrogel on dehydrated hydrogel. Reproduced with permission from Ref. [79], © American Chemical Society 2021. (e) Schematic illustration of the soaking-toughened gelatin/polyacrylic acid-glycerol organohydrogel electrolytes in which dual dynamic supramolecular networks were formed by Fe^{3+} coordination with carboxylic groups and physical crosslinking of gelatin in glycerol/H_2O solution containing 2 M NaCl. Reproduced with permission from Ref. [60], © American Chemical Society 2020. (f) Schematic illustration for synthesis of ionogel with hyperbranched polymer as macro-cross-linkers by photopolymerization. Reproduced with permission from Ref. [67], © American Chemical Society 2021. (g) Scheme of preparation of polyimide ionogels. Reproduced with permission from Ref. [69], © The Royal Society of Chemistry 2019.

improved mechanical strength, freezing resistance, and moisture retention [59]. A gelatin/ferric-ion-crosslinked PAA hydrogel was fabricated by soaking the dual dynamic supramolecular network into a NaCl glycerol/water solution to perform the solvent displacement, improving the toughness (~ 1.3 MJ·cm⁻³) and ionic conductivity (> 7 mS·cm⁻¹) (Fig. 3(e)) [60]. Although soaking method is facile and effective, the organohydrogels fabricated by soaking treatment can only maintain their mechanical performance in the as-prepared states, as their mechanical properties may face the weakening in aqueous environment, which needs to be improved for further utilization.

2.3 Ionogels

Different from hydrogels and organohydrogels, ionogels are polymer networks swollen with ILs which are constituted by ions with a melting point below 100 °C [61]. Different from another term "ionic hydrogel" that contains aqueous salt solution for conductivity, ionogels possess high ionic conductivity, significant

anti-dehydration, and anti-freezing properties due to the nonvolatility, high temperature, and chemical stability of ILs [62, 63]. The synthesis methods of ionogel are varied according to their potential applications, as ionogel electrolytes used in batteries and supercapacitors are mostly made by sol-gel, impregnation, and covalent grafting to obtain high porosity and specific surface area, while ionogels used in sensors prefer polymer matrix out of condition for molding devices [64].

Photopolymerization is a most popular way to synthesize ionogels owing to its simplicity, cheapness and ease of controllability [65, 66]. Wang et al. prepared a single network ionogel via by *in-situ* photopolymerization of 1-vinyl-3-butylimidazolium tetrafluoroborate (VBIMBF₄) as conductive elements and acrylate-terminated hyperbranched polymer as macro-crosslinker in 1-butyl-3-methylimidazolium tetrafluoro-borate (BMIMBF₄) (Fig. 3(f)) [67]. The ionogel was highly stretchable (> 1000%), conductive at room temperature (~ 6 mS·cm⁻¹) and stable in terms of thermochemical properties

from −60 to 250 °C. Similarly, an ultra-strong adhesive, self-healable, and 3D printable photoluminescent ionogel was developed via one-step photopolymerization of ascorbic acid (AA) and zwitterionic IL [68].

Besides photopolymerization, there are other ways to produce ionogels. Xiang immersed the polyimide organohydrogel prepared by chemical imidization of poly(amic acid) in BMIMBF$_4$ for the solvent displacement due to the formation of hydrogen bonds (Fig. 3(g)) [69]. The obtained ionogel exhibited excellent performance, including excellent mechanical properties (tensile strength ~ 7.1 MPa and elongation at break ~ 320%), high ionic conductivity (> 2 mS·cm^{-1}), and high thermostability. By a one-pot reaction scheme through simply mixing two solutions to obtain covalent crosslinking and ionic bonds crosslinking, a double network click ionogel was also reported [70]. The click-ionogels exhibited excellent toughness and resilience even after 10,000 fatigue cycles as well as high ionic conductivity, and maintained excellent performance from −75 to 340 °C. Although the incorporation of ILs in ionogels offers significant advantages, it often leads to a trade-off between improved ionic conductivity as well as stability, and compromised mechanical properties, as well as an increased risk of leakage.

3 Self-healing mechanisms of gels

Among all polymer materials, the self-healing behavior of gels is studied most, and plenty of designs are proposed to enhance the self-healing property via modification or functionalization of gel systems [71–73]. For self-healing gel systems, two parameters are generally denoted to evaluate the healing performance. The most important parameter, "healing efficiency η" is defined as the ratio of property change before and after healing: $\eta = (P_{\text{healed}} - P_{\text{damaged}})/(P_{\text{pristine}} - P_{\text{damaged}})$, where P is material property of interest [74]. Electronic properties, including conductivity or current and mechanical properties such as tensile stress or elongation at the break, are often involved in the calculation of healing efficiency. The second parameter is known as healing response time, which describes the recovery time of healing process. Due to the different polymer chain mobility and healing mechanisms, healing response time can be varied from less than one second to a few hours, or even several days. The reversibility R is related to the ability of the system to repeat the self-healing process every time when a stimulus (internal or external) has been applied and can be defined as a dimensionless parameter varying from 0 to 1 [75]. R is equal to 0 when the self-healing behavior can only happen once, while some healing behaviors are indefinitely repeatable at least theoretically, providing a value of 1 for R.

Depending on if an external trigger is needed for the healing process, self-healing materials are classified into "autonomic" and "non-autonomic" healing materials, and healing process initiates spontaneously when damage is performed on autonomic healing materials [76]. Self-healing materials can also be sorted into "intrinsic" or "non-intrinsic" healing materials, relying on if healing agents encapsulated in capsules or vascular network are needed to achieve healing of bulk material [77]. In this section, the different healing mechanisms of gels will be reviewed (Fig. 4).

3.1 Reversible dynamic bonds

The healing behavior of most reported self-healing gels is based on the existence of dynamic bonds distributed in the bulk material [78]. These bonds can be easily broken and restored, imparting the intrinsic healing ability to gels. As been reported so far, non-covalent bonds (e.g., hydrogen bonding, π–π interaction, metal–ligand interaction, and host–guest interaction) and several covalent bonds (e.g., Schiff base reaction) are adopted or potential in the design of healable gel systems (Figs. 4(a)–4(d)).

3.1.1 Non-covalent bonds

Hydrogen bonding is generally weak and quite abundant in gel materials due to the presence of multiple functional groups (hydroxyl, amine, sulfonate, and carboxyl) [74]. The reversible nature and fast dissociation/association behavior of hydrogen bonding make it most popular in the design of healable materials (Fig. 4(a)) [75, 76]. π–π interaction is prominent in conjugated polymeric systems, with tunable bonding strength based on aromatic group size, insertion of heteroaromatics, and different substitutions, enabling that it could be used to restore the molecular structure in healable systems (Fig. 4(b)) [77, 78]. Metal–ligand interaction happens in coordination complexes and is considered as a σ-donor interaction with an additional π-interaction [79]. A stretchable and healable PVA hybrid hydrogels was simply by introducing Cu^{2+} and fibrous sepiolite (Sep) into PVA solution due to the construction of the hydrogen bonds between the silanol groups (Si–OH) on the Sep surface and the hydroxyls of PVA as well as the metal–ligand coordination between the hydroxyls of PVA and Cu^{2+} (Fig. 4(c)) [80]. Host–guest interaction is another non-covalent interaction and it often exists in supramolecular complexes, where two kinds of molecules or groups are contained; one is called the host and the other is the guest [81]. Xu et al. reported that the β-cyclo-dextrin-adamantane host–guest interaction can restore the polysaccharide based conductive hydrogel system after being damaged (Fig. 4(d)) [82]. Besides, though not widely investigated, hydrophobic interaction, which refers to the non-covalent interactions between hydrophobic (water-repelling) regions of polymer chains in an aqueous environment, is also presented in the design of self-healable polymer systems [83]. After being damaged, the dissociation and reassociation of hydrophobic regions in the damaged area facilitate the spontaneous repair of gels. In addition, ionic bonds also play a crucial role in the self-healing of gels. When a gel with ionic crosslinks gets damaged, the ionic bonds can dissociate, allowing the polymer chains to move and rearrange, and the ionic bonds reform, leading to the reconnection of the broken gel regions [84]. This rapid healing response, along with the ability to undergo multiple healing cycles, enhances the gel's resilience and mechanical properties [85].

3.1.2 Covalent bonds

Several covalent bonds can also be reversibly broken and reconstructed without external stimulus, such as Schiff base reaction and Diels–Alder (DA) reaction. The formation of a dynamic chemical bond between amine and aldehyde is called Schiff's base reaction, while DA reaction is referred as a chemical reaction to form a substituted cyclohexene derivative between a substituted alkene and a conjugated diene. Like the non-covalent bonds mentioned above, these covalent bonds are also easy to be broken and recovered. Xu et al. fabricated a self-healable electroconductive hydrogel based on reversible crosslinking Schiff base bonds, formed between aldehyde-modified hyaluronic acid (HA-ALD) and glycol chitosan (GC) (Fig. 4(b)) [86]. In addition, other reversible covalent bonds, including acylhydrazone bonds (between an aldehyde or ketone group and a hydrazide functional group), disulfide bonds (between two sulfur atoms present in cysteine residues within a polymer chain), and diol-boronic acid links (between diols and boronic acid groups), are receiving more attention in the design of tough healable gels [87]. These covalent bonds are advantageous for creating self-healing gels as they offer strong and stable crosslinks within the gel network while still being responsive to specific environmental cues [88].

3.2 Physical molecular diffusion

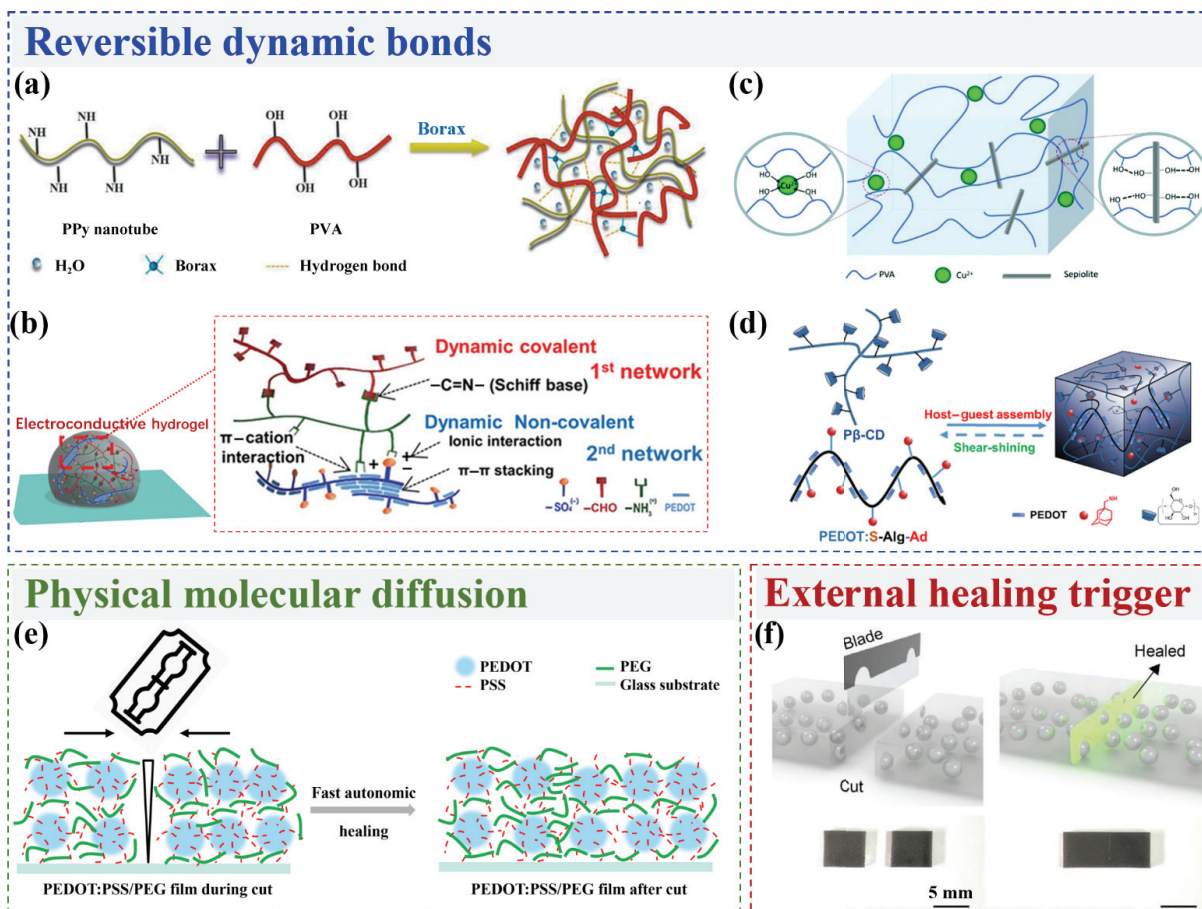For a self-healing gel system, the physical molecular diffusion

Figure 4 Examples of self-healing gel polymers based on (a)–(d) reversible dynamic bonds, (e) physical molecular diffusion, and (f) external healing trigger. (a) Schematic illustration of preparation and synthesis process of self-healable polypyrrole hydrogel and the multiple hydrogen bonds inside the gel. Reproduced with permission from Ref. [94], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2020. (b) Scheme of the interactions involved in the formation of the conductive and healable double network, including dynamic covalent bonds (Schiff based reaction) and π–π interaction. Reproduced with permission from Ref. [86], © Xu, Y. et al. 2019. (c) Schematic illustration showing the self-healing of the PVA-Cu-Sep hydrogels due to the metal-ligand coordination and hydrogen bonding. Reproduced with permission from Ref. [80], © The Royal Society of Chemistry 2016. (d) Schematic of dynamic cross-link formation utilizing guest–host complexation inside a self-healable conductive gel. Reproduced with permission from Ref. [82], © American Chemical Society 2019. (e) Schematic healing mechanism of an autonomic healable conducting polymer film via physical molecule diffusion. Reproduced with permission from Ref. [92], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2020. (f) Schematic illustrations and photographs of the LM-gelatin hybrid gel films before and after self-healing. Reproduced with permission from Ref. [93], © Wiley-VCH GmbH 2021.

mechanism, including the chain segment motion and material flow ability due to the increased softness or viscoelasticity, is often adopted [89]. The fundamental healing process in this case is the molecular interdiffusion and entanglement of polymer chains at the damaged interface [90]. One common approach to achieve molecular diffusion is to lower the glass transition temperature (T_g) below room temperature. Then at room temperature, the mobility of material segments or polymer chains are enough for healing [91]. After bringing the two pieces of the damaged gel materials connected, arising from the fast-molecular diffusion at room temperature, the polymer/polymer interface vanishes gradually, and the mechanical and conductive property are restored. As healing rate is determined by mobility of polymer chains to damaged area, the chemical nature of the polymer and length or molecular weight of polymer chains affects diffusion speed and then healing behaviour (Fig. 4(e)) [92].

3.3 External healing trigger

For these gel materials which do not possess healing ability intrinsically, healing agents, in the form of fibers, capsules, or vascular network, are embedded in the matrix to provide instant healing. When damage or crack is made on the material, the healing agents will be released into damaged areas and heal the crack as well as conductive network. Park et al. reported a self-

healable gel using capsulation of liquid metals (LMs) and their uniform embedding inside a gelation gel [93]. After the LM-gelatin gel film was cut into two parts and being reattached, the LM capsules located near the edges coalesced to counterpart capsules spontaneously, and the gelatin hydrogels were also re-bonded at the sliced surfaces, recovering the electrical and mechanical functionality (Fig. 4(f)). The disadvantage of this method is the difficulty of patterning of embedding conductive healing agents and the healing process can only happen one-time.

4   Self-healable gel electrodes in EESDs

The energy storage density of EESDs is strongly limited by the current-existed choices of electrode materials, thus, the advancing of the high specific energy electrodes remains a hot topic in the field of electrochemical energy storage systems. Nevertheless, most high specific energy electrodes suffer the problems of volume expansion during electrochemical processes and poor stability. Meanwhile, to match the requirement of wearable electronic devices, the electrodes need to maintain excellent mechanical and electrical properties even under multiple bending and stretching cycles or even mechanical damages [95]. Self-healable gels possess excellent flexibility and stretchability, ease of processability, high theoretical capacitance, and the ability to restore functionalities after damage, enabling its potential for electrodes in EESDs [96].

Depending on the electroactive materials inside the gel matrix, the self-healable conductive gel electrodes can be divided into three categories: (i) conducting polymers based gels; (ii) carbon-based materials based gels; and (iii) metal oxide composite materials based gels. In this section, electrodes in EESDs based on various self-healable gels will be introduced briefly.

4.1 Conducting polymer based healable gel electrodes

Conducting polymers, such as polyaniline (PANI), poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), and polypyrrole (PPy), are polymers based on intrinsic conductive conjugated systems, whose conductivity can be further tuned via doping [97, 98]. Conducting polymer gels are receiving gradual attention in electrodes for next-generation EESDs as they combine features of high electrical conductivity, outstanding electrochemical characteristics, ideal interaction with electrolyte, cost-effectivity, and unique three-dimensional porous morphology with swellable characteristics, robustness, environmentally compatibility, and mechanical flexibility [99]. While endowing the electrode with healing ability, conducting polymer gels are promising for advanced long-lasting EESDs [100].

PANI is an ideal electroactive material for electrodes in EESDs due to its easy preparation, good conductivity, and high theoretical capacitance [101]. For PANI hydrogel-based energy storage applications, all-hydrogel supercapacitors are more suitable as wearable electronic appliances owing to their high flexibility, fast ion transfer kinetics and good self-healing ability [102]. Zou et al. prepared a PANI/PVA hydrogel electrode by *in-situ* copolymerization of electroactive aniline and 3-aminobenzoic acid (MABA) to ensure the effective ionic interactions between MABA and calcium ions as well as PANI and PVA [103]. Due to this special assembly, the PANI/PVA hydrogel electrode exhibited excellent robustness, a high conductivity of ~ 140 S·m^{-1}, and a large specific capacitance of ~ 350 F·g^{-1}. In addition, this hydrogel electrode could successfully heal itself within 4 h after being cut off by reconstructing the ionic bonds and borate ester bonds (Figs. 5(a) and 5(b)). The integrated all-hydrogel supercapacitors possessed a capacitance of ~ 80 F·g^{-1}, an energy density of ~ 8 Wh·kg^{-1}, the ability to keep stable energy output even after being subjected to various deformations (e.g., stretching, compressing, bending, and even pinning), as well as to restore electrochemical properties with a healing efficiency of ~ 50% (Fig. 5(c)). In order to improve the self-healing performance, Lin et al. introduced the metal coordination and hydrogen bonds into PANI/PVA hydrogels via adding phytic acid (PA) and Fe^{3+} [104]. The as-fabricated gels possessed a self-healing efficiency of ~ 70% in tensile strain. Using the hydrogel as active electrodes, the all-slid-state capacitor displayed a high energy density of ~ 0.2 mWh·cm^{-2} with a power density of 0.25 mW·cm^{-2} and maintained ~ 0.08 mWh·cm^{-2} at 5 mW·cm^{-2}. Moreover, during the charging/discharging multi-cycling test, the self-healing ability enabled the hydrogel-based supercapacitors to keep a Coulombic efficiency of 99% and a capacitance retention of 92% even after 10,000 cycles.

PEDOT is an already commercialized conducting polymer in the form of PEDOT:PSS suspension and it has been widely researched in bioelectronics, energy storage, and harvesting devices due to its mixed electronic/ionic conductivity, stability, processability, and biocompatibility [105–107]. Among all PEDOT based composites, PEDOT:PSS hydrogels have been brought into focus of electronic and energy devices as them combine the high conductivity with other attracting properties, such as softness or healing ability [108]. A PEDOT:PSS hydrogel was prepared by dual treatment of commercial PEDOT:PSS suspension with diluted sulfuric acid and concentrated acid [109].

This hydrogel exhibited extremely high conductivity of ~ 8.8 S·cm^{-1} and an excellent volumetric capacitance of ~ 200 F·cm^{-3} at 0.54 A·cm^{-3} as a supercapacitor electrode. Although the self-healing property of this hydrogel was not reported, the similar work about the self-healable PEDOT:PSS hydrogel prepared by blending of 4-dodecylbenzenesulfonic acid (DBSA) suggests its potential in healable electrode [110]. Due to the rigid conjugated backbones of PEDOT chains, the self-healing property of PEDOT is limited, thus various work was done to develop healable PEDOT based conductors via introducing reversible bonds inside the composites or tuning the mechanical properties [111, 112]. In order to improve the healing ability of PEDOT based hydrogel electrode, Zhu et al. fabricated a stretchable and healable PEDOT based hydrogels with excellent electrochemical properties via supramolecular assembly of PVA and thiophene-3-boronic acid (ThBA), as well as the activators regenerated by electron transfer (ARGET)-atom transfer radical polymerization (ATRP) grafting methodology (Fig. 5(d)) [113]. With a PVA hydrogel as electrolyte, the integrated hydrogel supercapacitor exhibited a specific capacitance of ~ 220 mF·cm^{-2}, with an energy density of ~ 20 μWh·cm^{-2}. The hydrogen bonds between PAA grafted thiophene and PVA offered the fast self-healing properties to the hydrogel electrode and integrated supercapacitor, thus the device could maintain ~ 96% of the initial capacitance after 1000 charging–discharging cycles and recover ~ 80% of the capacitance after the cutting–healing cycle (Fig. 5(e)).

PPy is another widely used conducting polymer due to its high conductivity and noncytotoxcity, and PPy based gels can be simply synthesized via the *in-situ* polymerization of pyrroles and gel matrix [114]. Self-healable PPy gels are widely used in the electrodes of batteries and supercapacitors due to their outstanding electrochemical properties and ability to improve the lifetime of device [115]. Liu et al. prepared a novel self-healing Li-S battery via embedding PPy gel-infilled microcapsules, which were fabricated by a microfluidic coaxial flow focusing technology, into the sulfur cathode (Fig. 5(f)) [116]. Once the cracks were formed on the cathode, the embedded gel microcapsules would break and release conductive gel core into the cracks, repairing the broken pathway for electron transportation. The incorporation of PPy gel microcapsules provided the self-healing battery with a stable capacity of ~ 800 mAh·g^{-1} after 200 cycles at a rate of 0.1 C, exhibiting a capacity decay rate of 0.23% per cycle (Fig. 5(g)). Besides, this battery could still maintain the behaviour of charging and discharging normally compared to the batteries without capsules even after being thrown at a 1 m height repeatably or being impacted before assembling. In addition to healing agents of electrodes, PPy gels could also function as electrodes in EESDs to improve the capacity and durability [117].

4.2 Carbon based materials based healable gel electrode

Carbon based inorganic materials are other important electroactive agents in hydrogels for their high conductivity, stability, and availability [118, 119]. A flexible and healable supercapacitor was fabricated via the *in-situ* polymerization and deposition of carbon nanotubes (CNTs) nanocomposites electrode materials onto the two-sided faces of healable PVA electrolyte separator [120]. At a current density 0.044 mA·cm^{-2}, the CNT nanocomposite-based supercapacitor exhibited an enhanced capacitive performance of ~ 16 mF·cm^{-2} compared to that for pure CNT at 0.16 mF·cm^{-2}. Good cycling stability and reliable self-healing capability with nearly 80% retention of the specific capacitance after the fifth self-healing cycle were also demonstrated. Xu et al. fabricated a graphene-based hydrogel fiber with continuous networks by combination of one-step confined hydrothermal synthesis, the introduction of PVA solution with
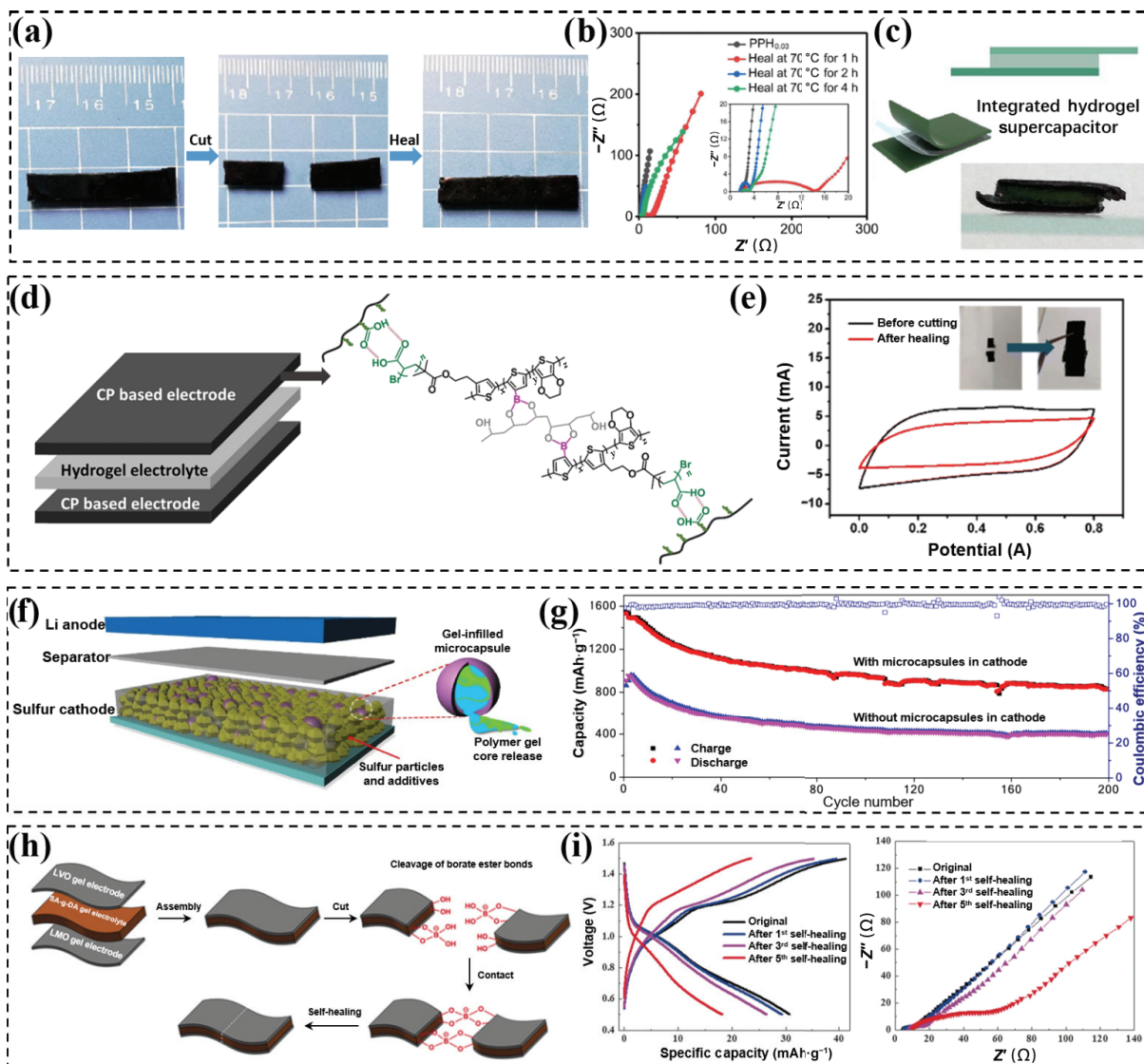
Figure 5 Self-healable gel electrodes in EESDs. (a) Optical graphs of the self-healing behavior of the PANI/PVA hydrogel electrode. (b) Nyquist plots of PANI/PVA hydrogel electrode (inset: enlarged high-frequency region) after different healing time. (c) Scheme and optical images of the integrated hydrogel supercapacitor based on PANI/PVA hydrogel electrode. Reproduced with permission from Ref. [103], © Elsevier B.V. 2021. (d) The "sandwich" structure of the supercapacitor and the chemical structure of the poly(EDOT-co-(Th-g-PAA)-co-ThBA)-PVA hydrogel. (e) Cyclic voltammetry measurements of the device before cutting and after self-healing, and where the inset photographs showing the device before cutting and after healing. Reproduced with permission from Ref. [113], © The Royal Society of Chemistry 2022. (f) Illustration of the self-healing Li-S battery constructed with PPy gel-infilled microcapsules in a cathode. (g) Cycling performances of the undamaged electrodes with and without using PPy gel-infilled microcapsules. Reproduced with permission from Ref. [116], © American Chemical Society 2021. (h) Schematic illustration of the assembly and self-healing of the LIB. (i) Electrochemical properties of the battery after different cut/healing cycles (left: galvanostatic charge–discharge profiles at 1.0 A·g⁻¹, and right: electrochemical impedance spectroscopy spectra). Reproduced with permission from Ref. [125], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2018.

cryoprotectants, and a following facile solvent replacement [121]. With a PVA gel electrolyte, the integrated supercapacitor based on the graphene-based hydrogel fiber electrode delivered a remarkable specific capacitance of ~ 280 F·g⁻¹ at 25 °C, showing an excellent cycling performance with a capacitance retention of ~ 90% after 5000 charge/discharge cycles.

Mxenes, whose general formula is $M_{n+1}X_nT_x$ (M, X, and T represent a transition metal, C and/or N, and a surface group (OH, O, or F), resectively), have recently emerged as promising electrode materials for energy storage devices due to their high capacitance and excellent electrochemical energy storage even at high charge/discharge rates [122]. Yu et al. designed a innovatory healable hydrogel electrode with high electrical conductivity by mixing conductive $Ti_3C_2T_x$ into PAA and chitosan hydrogels [123]. Due to the existence of hydrogen bonds and electrostatic attraction between –OH group of $Ti_3C_2T_x$ and the polymer chains, the gel could recover both electrical and mechanical properties.

The $Ti_3C_2T_x$ hydrogel electrode exhibited excellent maximum specific capacitance of ~ 290 mF·g⁻¹ at 0.5 mA·g⁻¹ and kept ~ 65% of initial capacitance after 2000 cycles.

4.3 Metal oxide composite based healable gel electrodes

Besides conducting polymers and carbon based inorganic conductive materials, other materials or composites have been tried to fabricate hydrogel electrodes for energy storage devices [124]. By integrating all the electroactive components into the PVA polymer network crosslinked by dynamic borate ester bonding, Hao et al. developed an omni-healable aqueous lithium ion battery (LIB) (Fig. 5(h)) [125]. The self-healable anodes and cathodes were fabricated by dispersing LiV_3O_8 (LVO) as well as $LiMn_2O_4$ (LMO) particles homogeneously into the PVA matrix, resulting in an electronic conductivity of ~ 0.7 mS·cm⁻¹ for the LVO anodes and ~ 1.1 mS·cm⁻¹ for the LMO cathodes at room temperature. The hydrogel electrolyte synthesized via a similar

process in the presence of dopamine grafted sodium alginate and Li₂SO₄ was then sandwiched between the LVO and LMO electrodes to assemble a LIB. The LIB showed a specific capacity of ~ 30 mAh·g⁻¹ and a Coulombic efficiency of ~ 83 % during the first lithiation/delithiation cycle at 1.0 A·g⁻¹. The battery possessed an excellent self-healing ability in recovering its tensile strength and specific capacity with a healing efficiency of ~ 99% and ~ 95%, respectively, after a self-healing process for only 20 min (Fig. 5(i)).

To summarize this section, self-healable gel electrodes, including conducting polymers based gels, carbon-based materials based gels, and metal oxide composite materials based gels, hold significant potential for advancing EESD technology by addressing mechanical degradation and enhancing the overall performance, durability, and flexibility. Ongoing research is needed to optimize their self-healing properties, mechanical strength, and electrochemical performance. Additionally, long-term durability and stability evaluations are essential to ensure that self-healable gel electrodes can withstand the rigorous demands of practical EESDs.

5　Self-healable gel binders in EESDs

With the rapid development of EESDs, many high specific energy electrode materials are emerging [126, 127]. Among all high-capacity electrodes, owing to the advantages of high theoretical specific capacity (4200 mAh·g⁻¹), safe lithium intercalation potential (< 0.5 V vs. Li/Li⁺), and environmental friendliness, Si is considered as a promising anode material for LIBs [128]. However, Si anode has serious volume expansion and contraction (volume change > 300%) in the lithiation/delithiation cycles, which will cause breakage and destruction of electrode structure, thus leading to a significant decline of cycle stability and limiting the practical application of Si anode materials [129]. In addition, Li-S batteries have also received increasing attention due to their ultra-high theoretical specific capacity (1675 mAh·g⁻¹) and energy density (2600 Wh·kg⁻¹) [130, 131]. Therefore, it can reduce the weight and size of the battery while ensuring adequate energy supply. S cathode will undergo serious volume changes during repeated cycling, leading to the crushing of the electrode and even battery failure [132]. In addition to the bonding properties of the general binder, LIB or Li-S electrode binder material also needs to be able to withstand the swelling and corrosion of the electrolyte, as well as withstand the electrochemical corrosion during the charge/discharge processes, and maintain stability within the operating voltage range of the electrode. Due to the lack of viscoelastic energy and structural strength, the traditional binders cannot adapt to the huge volume changes in the discharge/charge processes, which leads to the loss of connection between the active material and the conductive agent, the shedding of electrode and fluid collector, and the suppression of electrochemical activity [133, 134]. Based on the rich reversible bonds, self-healable gel binders can realize fracture-restructuring and appropriate stretchability and viscoelasticity, thus reducing the volume change of Si anode in the cycling process, maintaining the integrity as well as electric contact connectivity, achieving the long cycle stability ultimately [135]. In this section, multiple self-healable gel binders in EESDs will be discussed.

5.1　PAA-based gel binders

PAA is a commonly used binder of Si anode of LIBs due to its good mechanical strength and adhesion [136]. PAA gel binder contains many carboxyl groups, which can be bonded with functional groups on the surface of Si material, promoting the formation of solid electrolyte interface (SEI) film and improving the cycling performance of batteries [137]. However, the carboxyl

polymerization of PAA binder at high temperature may lead to the weakening of the force between PAA and Si material, and the capacity decreases greatly after several cycles. Therefore, many researchers focused on the PAA based composite binders, combining the advantages of different binders to cooperatively improve the electrochemical performance of Si anode [138–140].

Inspired by the organic solvents commonly used in experiments, self-healable water-soluble glycinamide modified PAA (PAA-GA) binder was synthesized via a low-cost coupling method for assembling Si anode [141]. The hydrogen bonds formed by the reaction between the carboxyl and diamide groups of PAA-GA with the hydrated silica layer are strong reversible supramolecular interactions and allow more efficient recovery with the removal of mechanical stress to alleviate massive volume change. The Si/PAA-GA electrode displayed the good cycling stability of ~ 81% retention after 285 cycles and high rate performance of ~1000 mAh·g⁻¹ capacity at 5 C. Wang et al. also designed an elastic self-healing PAA composite binder to achieve long-term stable cycling of Si anode [142]. Multiple hydrogen bonds formed by *in-situ* crosslinking of water-soluble citric acid (CA) and PAA could establish reversible networks for Si particles. CA molecules served as a protective buffer layer to release internal stress and stabilize SEI, but also connected with PAA to form a specific structure of soft inside and rigid outside (Fig. 6(a)). When two different color binders were connected, the volume deformation could reach 280% due to the self-healing effect (Fig. 6(b)). Therefore, the Si/CA-PAA electrode exhibited good cycle performance with a ~ 90% capacity retention after 300 cycles at 0.1 C (Fig. 6(c)).

The strong quadruple hydrogen bonding in the ureido-pyrimidone (UPy) group is mostly used to achieve self-healing because it is easy to implement and possesses good reversibility due to the relative instability of the bonds [143, 144]. Deng et al. prepared a new polymer by copolymerizing a small amount of UPy monomer with linear PAA polymer [145]. This supramolecular polymer realized self-repairing ability through the dynamic action of quadruple hydrogen bonds, facilitating the usage as a self-healing binder for nano-silicon anode. The first discharge capacity of the Si/PAA-Upy anode was ~ 4200 mAh·g⁻¹ with a Coulombic efficiency of ~ 86% and the battery showed an excellent electrochemical performance even after 110 cycles, with a capacity remaining at ~ 2600 mAh·g⁻¹. Similarly, a new composite Si anode binder combining a rigid PAA as a protective layer and an elastic bifunctional polyurethane (BFPU) as a buffer layer was designed [146]. By introducing BFPU with rapid self-healing ability, the microcracks caused by large stress could be dynamically recovered, further ensuring the integrity of Si anode. During the lithium insertion process, the stress distribution in the Si/PAA electrode was extremely high, demonstrating the severe damage of Si particles at edge, which eventually leaded to the collapse of the electrode structure (Fig. 6(d)). However, the stress distribution in Si/PAA-BFPU electrode was much lower when BFPU was coated on PAA surface. By adjusting the ratio of PAA to BFPU, the Si/PAA-BFPU (1:2) electrode showed good cycling performance at 1.2 A·g⁻¹, with a capacity retention of 97.0% after 100 cycles (Fig. 6(e)).

Besides, PAA chains can also be crosslinked or grafted to other polymer network to achieve healable copolymer gel binders [147]. Xu et al. prepared a viscoelastic and healable copolymer via crosslinking PAA chain segments with poly(2-hydroxyethyl acrylate-co-dopamine methacrylate) (P(HEA-co-DMA)) and obtained a gel binder with three-dimensional network structure [148]. The tensile and shrinkage of PAA-P(HEA-co-DMA) binder could adapt to the volume change of Si particles during the insertion/desertion of Li⁺, which significantly improved the cycling
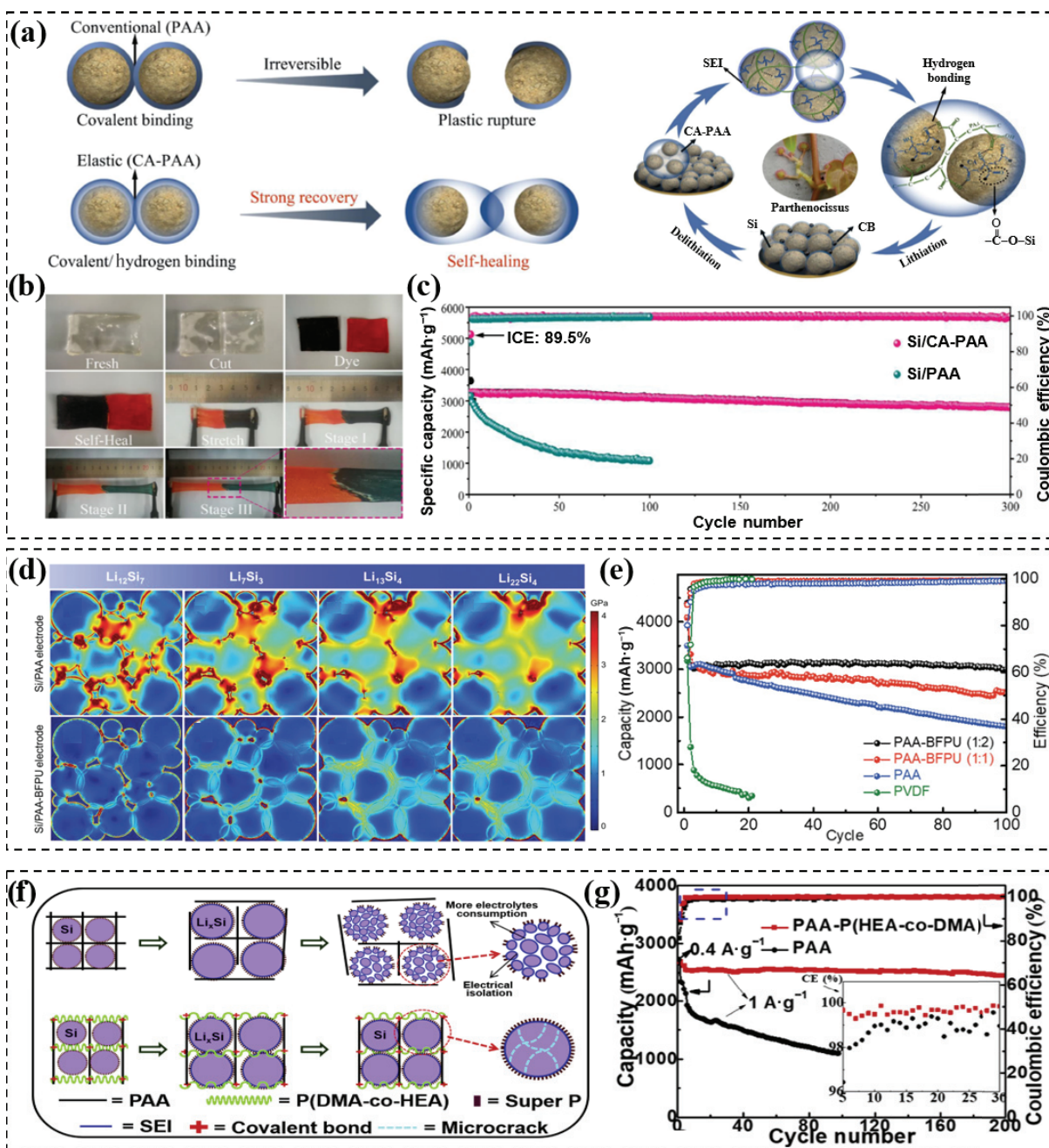
Figure 6 Self-healable PAA gel-based binders in EESDs. (a) Schematic diagram of chemical interaction type between binders and Si particles, schematic design of CA-PAA binder, and the chemical bonding between CA-PAA binder and Si particles, (b) digital photos of self-healing test of CA-PAA polymer membranes, and (c) cycling performance of Si electrode with self-healing CA-PAA and pure PAA binder after 300 cycles at 0.1 C (the mass loading of Si is 0.6 mg·cm⁻²). Reproduced with permission from Ref. [142], © Elsevier B.V. 2021. (d) Stress distribution on Si anode with PAA and PAA-BFPU binders at different lithiation states and (e) the cycling performance and Coulombic efficiencies of Si electrodes with PAA-BFPU (1:1 and 1:2, weight ratio), PAA, and PVDF binders at a current density of 1.2 A·g⁻¹. Reproduced with permission from Ref. [146], © Wiley-VCH GmbH 2020. (f) The proposed schematic of Si electrode using different binders during cycling and (g) cycle performances of the Si electrodes with different binders. Reproduced with permission from Ref. [148], © Elsevier Inc. 2018.

stability and rate performance of the electrode (Fig. 6(f)). The Si anode using PAA-P(HEA-co-DMA) binder showed the good cycle performance compared with PAA binder, with almost no capacity fading up to 200 cycles (Fig. 6(g)). In addition, the PAA-P(HEA-co-DMA) binder was also suitable for micron silicon oxide anode materials to improve the cycling stability as well as surface density, which could be beneficial for the design and preparation of EESDs with large volume effect.

5.2 PVA/PEO/PAM-based gel binders

PVA, an industrialized and mass-produced polymer, has been widely used in wearable bioelectronics and EESDs due to its excellent mechanical properties and low toxicity [149]. Since a

large number of hydroxyl groups in the PVA chains can form strong hydrogen bonds with functional groups on the surface of Si or Si/C particles, PVA gel is also used as binders for Si-based anodes [150]. However, with the continuous charging/discharging process of the active material, the polymer chain of the binder changes irreversibly, leading to the loss of reversible capacity [151]. Crosslinking is a feasible strategy to enhance the structure stability and mechanical adhesion of PVA binder, and conducting polymer PEDOT:PSS is considered as a functional adhesive owing to its tunable high conductivity and good water solubility [152]. Hu et al. designed a novel three-dimensional network conductive self-healing hydrogel binder for Si anode in LIBs based PEDOT:PSS/PVA gel [153]. Compared with the traditional

conductive polymer, the special 3D network structure of this gel binder promoted more continuous conduction paths, enabling faster electron transport and more prominent conductivity. The Si-PEDOT:PSS/PVA electrode possessed a high reversible capacity of ~ 1200 mAh·g⁻¹ at a current density of 2000 mA·g⁻¹ over 200 cycles, implying that the self-healing conductive hydrogel with 3D conductive network structure could maintain the integrity of the electronic pathway and repair fragments instantaneously due to the good self-healing ability.

PEO is a common binder material as it promotes the ionic transport, thus high-performance durable batteries can be realized via incorporating healing ability with PEO based binders [154, 155]. Ryu et al. prepared boronic crosslinker-guar (BC-g) binders via spontaneous formation of covalent bonds between guar gum and boronic acid groups conjugated to polystyrene skeleton (Fig. 7(a)) [156]. The hydroxy-rich guar gum was highly adhesive to the surface of the collector fluid and Si particles, increasing the stability of the electrode. Interestingly, as a part of BC, PEO dissolved the crosslinker in aqueous solvent and enhanced the Li⁺ transport efficiency of Si electrode due to the existence of coordination bonds in PEO (Fig. 7(b)) [157]. The addition of BC not only improved the transport of Li⁺, but also exhibited higher capacity retention of ~ 87% at 0.2 C after 100 cycles, while guar binders only retained ~ 54% of initial capacities, due to the

formation of stable electrode network structure, which effectively prevented the comminution of Si particles (Fig. 7(c)). Based on the recovery capability of metal-ligand coordination between Fe³⁺ and catechol moieties, a self-healing metal polymer (Fe-PDBP@pH10) binder for maintaining the integrity of Si anode during the cycling process was fabricated [158]. During the lithiation/delithiation stage, even if the volume expansion of Si particles can break the original Fe³⁺-catechol coordination bonds, the internal bonding of catechol moieties was easy to recover, thus greatly improving the cycle stability, as the self-healing phenomenon was sustainable throughout the cycles (Fig. 7(d)). Compared with polyvinylidene fluoride (PVDF) or PAA-based binder electrodes, the Fe-PDBP@pH10-based Si electrode showed much better and more stable cycling performance (Fig. 7(e)).

Due to the abundant side chains and polar functional groups, PAM binder can form strong multidimensional interaction sites with hydroxyl groups on the silicon surface, resulting in strong interfacial adhesion, which generally greatly improves the strain resistance of the working electrode [159, 160]. Via compounding PAM onto an ionic conductive guar gum (GG) skeleton, a GG-g-PAM binder with high-ionic conductivity was constructed [161]. Through the self-healing effect of PAM, the mechanical stress distribution on the surface of GG-g-PAM binder and Si particles could be adjusted, thus the stable electrode-electrolyte interface
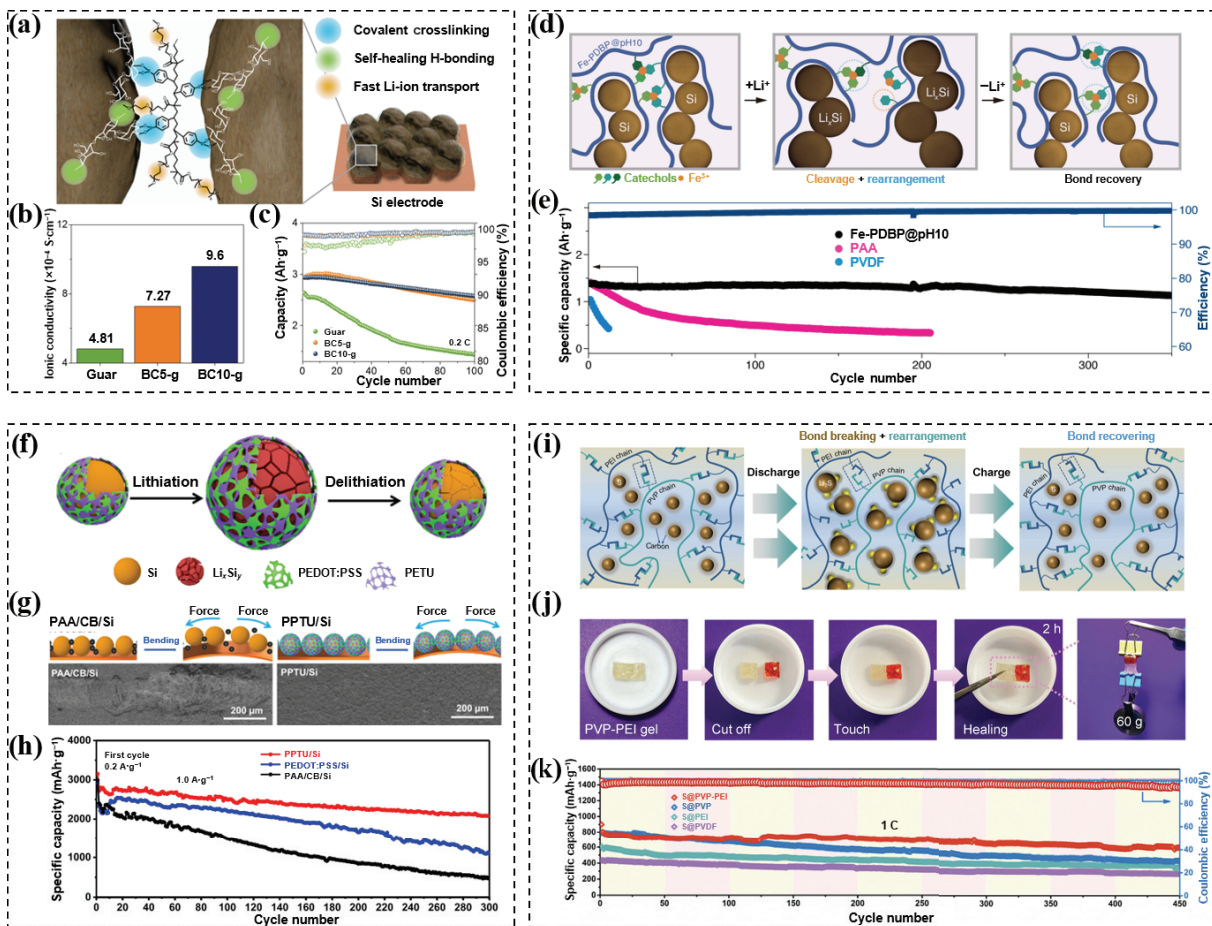

Figure 7 Self-healable gel binders based on other gel systems (a) Schematic of BC-g binder in Si electrode, (b) ionic conductivity results of guar and BC-g binder films, and (c) cycling performance of guar, BC5-g, and BC10-g at 0.2 C with the corresponding Coulombic efficiencies. Reproduced with permission from Ref. [156], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2019. (d) Schematic illustration of Si-binder network configuration during cycling, (e) cycle lives of Si electrodes based on Fe-PDBP@pH10, PAA, and PVDF and the Coulombic efficiencies of Si electrode based on Fe-PDBP@pH10 (right axis). Si mass loading = 0.7 mg·cm⁻². C-rate = 1 C (1500 mA·g⁻¹). Reproduced with permission from Ref. [158]. © American Chemical Society 2019. (f) Schematic illustration of the reaction mechanism for Si-based anodes using multifunctional polymeric binder during the lithiation/delithiation procedure, (g) schemes and scanning electron microscopy (SEM) images of the PAA/CB/Si and PPTU/Si anodes after bending tests, and (h) cycling performance of PPTU/Si, PEDOT:PSS/Si, and PAA/CB/Si anodes at 1.0 A·g⁻¹. Reproduced with permission from Ref. [165]. © American Chemical Society 2021. (i) Schematic of the self-healing process of S@PVP-PEI during one cycle, (j) optical photographs of the self-healing effect for PVP-PEI gel, and (k) long-term cycling performance of different binder-based cathodes at 1 C. Reproduced with permission from Ref. [167]. © Wiley-VCH GmbH 2021.

was maintained during the cycling. Wang et al. prepared a double crosslinking separated soybean protein (SPI-PAM) binder with self-healing ability for sulfur cathode [162]. Through hydrogen bonding and double crosslinking, this binder held the particles firmly to the fluid collector. Meanwhile, the self-healable SPI-PAM binder could also maintain a certain strength to resist external stretching and the self-healing interface has good fusion, as the sulfur cathode with self-healable SPI-PAM binder showed an initial specific capacity of ~ 850 mAh·g^{-1} at the current density of 1 C. Even after 350 cycles, the capacity retention was kept around 80% and the Coulomb efficiency remained at ~ 99%.

5.3 Other gel binders

At the beginning of the development of binders for secondary batteries, a variety of binders are reported. The preparation method of PAA based gel binders is relatively complex while PAM-based gel binders generally have a low electrical conductivity, so it is necessary to develop new healable gel binders to meet the requirements of improving the comprehensive performance of secondary batteries [163]. Dufficy et al. prepared a composite hydrogel binder consisted of carbon black (CB) and guar gum crosslinked by glutaraldehyde [164]. This chemical crosslinking method could enhance the stability of electrode microstructure, increasing the transport path of Li$^+$ and electrons, thus further improving the cycling performance of electrode materials. The Si electrode still presented a discharge capacity of ~ 1200 mAh·g^{-1} and Coulombic efficiency of ~ 100% even after 300 cycles at current density of 1 C. Moreover, a multifunctional polymer binder (PPTU) by crosslinked conducting polymer of PEDOT:PSS and stretchable polymer of polyether thiourea was used as a conducting spring between Si particles to obtain self-healing ability, superior elasticity, and enhanced conductivity (Fig. 7(f)) [165]. After continuous 1000 bending experiments, partial active particles of PAA/CB/Si anode exhibited the state of separation, while the PPTU/Si anode remained intact feature (Fig. 7(g)). The PPTU/Si anode showed excellent long-term cyclic stability, with a reversible capacity of ~ 2100 mAh·g^{-1} at a current density of 1.0 A·g^{-1} with the capacity retention of ~ 77% after 300 cycles (Fig. 7(h)).

The development of healable gel binders is not only limited to Si anodes, while the research on binders on other anodes are also in progress [166]. A self-healable binder composed of polyvinylchloride pyrrolidone (PVP) and polyethyleneimine (PEI) was studied to regulate redox kinetics of polysulfide in Li-S battery [167]. Upon discharging, Li$_2$S occurred because the conversion reaction of S and the volume expansion induced the fracture of partial hydrogen bonds of the binder, resulting in tiny cracks on the electrode surface. On charging, Li$_2$S returned to the state of S and the volume contraction brought the repair of crack on the electrode surface, attributed to the hydrogen bonds of the binder (Fig. 7(i)). To observe the self-healing effect of binder, a whole PVP-PEI gel is being cut into two pieces and reassembled for 2 h, and the fracture interface of PVP-PEI gel was healed, keeping the initial mechanical strength (Fig. 7(j)). Due to the healing property and strong 3D crosslinked hydrogen bond network of PVP-PEI binder, the integrity of S@PVP-PEI electrode after repeated cycles was ensured, with a reversible capacity of ~ 600 mAh·g^{-1} at 1 C maintained after 450 cycles, which was much higher than the capacity of S@PVDF, S@PEI, and S@PVP electrodes at the same condition (Fig. 7(k)).

To sum up, the current research on self-healing gel binders, including PAA-based gel binders, PVA/PEO/PAM-based gel binders, and other gel binders, is mainly focused on Si anode for LIBs and S cathode for Li-S batteries. The self-healing gel binders maintain the structural integrity of the electrodes under external mechanical stress and internal electrode volume changes. In subsequent studies, it is necessary to optimize their conductivity, adhesion, and stability. In addition, the search for composite gel materials with excellent comprehensive properties is still an important direction.

6 Self-healable gel electrolytes in EESDs

Gel electrolytes are gels with mobile ions inside and can be classified into hydrogel electrolyte, ionogel electrolyte, and organohydrogel electrolyte, depending on its composition discussed in Section 2. Due to the adequate ionic conductivity, excellent flexibility, favorable interfacial compatibility, and low cost, gel electrolytes are receiving significant attention for flexible/stretchable EESDs [168–170]. To ensure that EESDs can withstand repetitive deformation to extend their life, it is essential to functionalize the gel electrolyte with the self-healing property. The progress of gel electrolytes in supercapacitors was frequently discussed in recent literatures [171–174]. Therefore, as the prerequisites for gel electrolytes in mostly studied LIBs and zinc-ion batteries (ZIBs), including reasonable healing ability and excellent electrochemical and mechanical property, generally suit all EESDs, we will briefly introduce the progress of healable gel electrolytes in LIBs and ZIBs in this section [175].

6.1 Self-healable gel electrolytes in LIBs

For safer operation of LIBs, the replacement of organic liquid electrolytes by solid-state electrolytes is essential because the solid-state electrolyte plays a fundamental role as an ionic conductor and separator, hindering or even stopping the propagation of dendrites [176, 177]. In general, soft polymer solid-state electrolytes exhibit much lower interfacial resistance disadvantages, including the low ionic conductivity, narrow electrochemical stability window, and disappointing cracks or breakage after cycling, hindering the development of high-performance LIBs [178]. Fortunately, healable gel electrolytes with high ionic conductivity, high flexibility, good heat resistance, and the ability to recover from structural damages, are invented and many works have been extensively investigated towards high-performance durable LIBs [179, 180]. Compared with hydrogel electrolyte, ionogel electrolytes and organohydrogel electrolytes are receiving more attention due to their better stability and operability. They are mostly composed of healable host matrix, lithium salts, and ILs/liquid organic solvent plasticizers. The self-healing functionalities are provided by the polymer host matrix, which can prevent leakage of liquid components and thus ensure the safe operation, while the Li$^+$ mainly transports in the plasticizers with the ability to dissolve lithium salts.

6.1.1 Ionogel-based self-healable electrolytes

In the study of ionogels, the choice of the plasticizer is crucial for ion transport and safety concerns. ILs have been studied as a suitable plasticizer due to the intrinsic high ionic conductivity, electrochemical stability, thermal stability, and flame retardancy. Recent studies have shown that the ILs can also be incorporated into covalently self-healing crosslinked polymer networks to obtain ionogel-based self-healing electrolytes, which provide good electrochemical performance and received the most attention among the gel electrolytes in LIBs. Chen et al. developed an ionic liquid-immobilized poly(vinylidene fluoride-co-hexafluoropropylene) (IL-P(VDF-HFP)) based gel electrolyte, which provided both high ionic conductivity and excellent intrinsic self-healing properties due to the strong ion-dipole interactions between the polar –CF groups of P(VDF-HFP) and imidazolium cations inside the polymer network (Fig. 8(a)) [181].
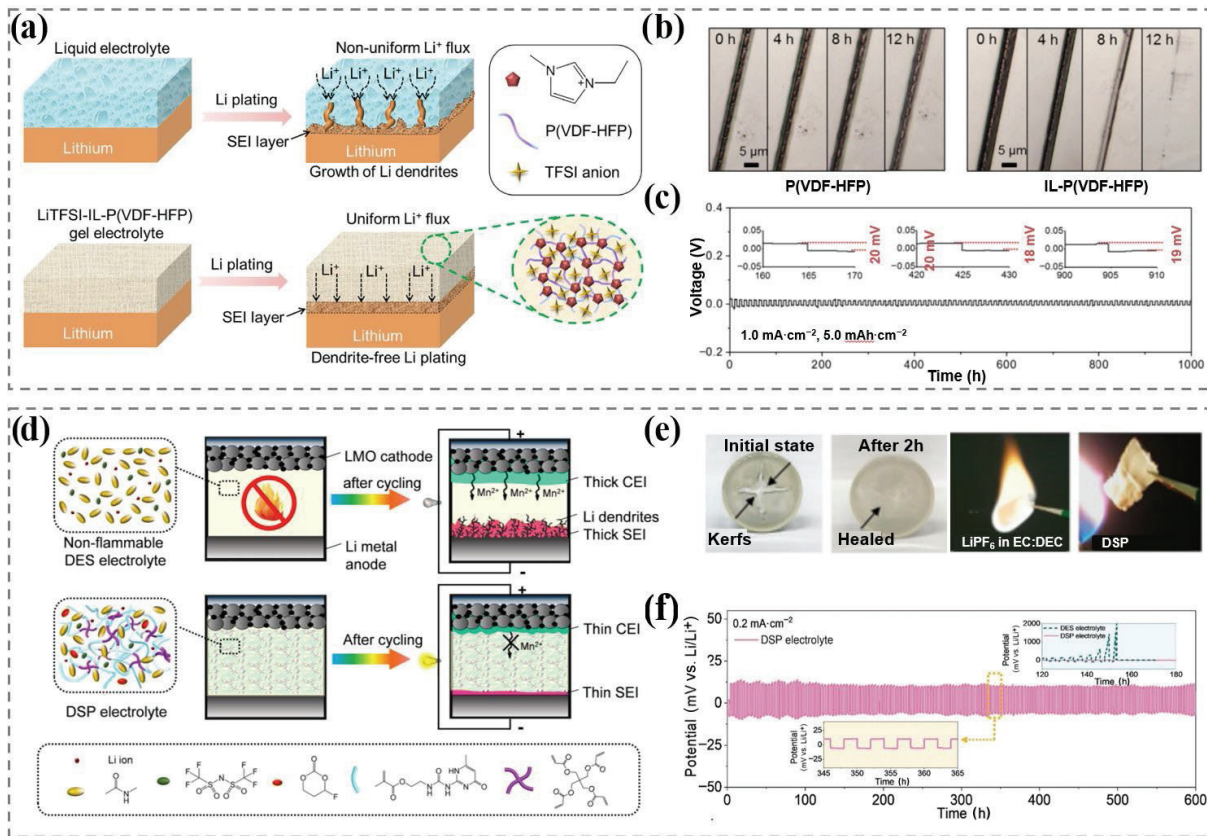
Figure 8 Self-healable gel electrolytes in LIBs. (a) Schematic illustration of the electrochemical deposition behavior of lithium metal anodes with liquid organic solution electrolyte and IL-P (VDF-HFP) gel electrolyte, (b) optical microscopic observations of the self-healing capability of scratched pristine P(VDF-HFP) and IL-P(VDF-HFP) after immersing in a mixed dimethoxyethane/dioxolane (1:1 in volume) solution of 1.0 M LiTFSI at room temperature for 0, 4, 8, and 12 h, respectively, and (c) cycling stability of LiTFSI-IL-P(VDF-HFP) gel electrolyte at 1.0 mA·cm⁻² for 5.0 mAh·cm⁻² per plating/stripping. The insets show magnified voltage profiles between the time intervals of 160–170, 420–430, and 900–910 h, respectively (right down). Reproduced with permission from Ref. [181], © Elsevier Ltd. 2018. (d) Schematic illustration of the DES and DSP electrolytes in LIB, (e) the self-healing process of DSP after being cut; and the optical images of the 1 M LiPF₆ in EC:DES electrolyte and DSP under combustion test, and (f) voltage profiles of Li‖Li symmetric batteries using DES (cyan line in the upper inset) and DSP (pink lines) electrolytes at 0.2 mA·cm⁻² with a cut-off capacity of 0.4 mAh·cm⁻². Reproduced with permission from Ref. [191], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2020.

Therefore, the surface scratches on this electrolyte completely vanished after being immersed in a 1.0 M lithium bis(trifluoromethanesulphonyl) imide (LiTFSI) solution for 12 h, while the pristine P(VDF-HFP) exhibited almost no self-healing performance (Fig. 8(b)). After coupling with this ionogel electrolyte, Li//Li symmetrical battery showed a consistent low voltage polarization and a flat voltage plateau for 1000 h without any short-circuiting, indicating that this ionogel electrolyte could effectively stabilize the Li stripping/plating processes and suppress the growth of Li dendrites (Fig. 8(c)). To further enhance the ionic conductivity, a healable ionogel electrolyte was prepared by immobilizing the ILs and Li salts within a hydrogen-bonded supramolecular polyionic liquid copolymer network bearing UPy pendant groups [182]. This ionogel electrolyte demonstrated a comparable high ionic conductivity of 10⁻³ S·cm⁻¹ to the conventional liquid electrolytes. The electrostatic interactions between ILs and copolymer network as well as the quadruple hydrogen bonds of UPy moieties provided the ionogel electrolytes with the capability to autonomously heal damages outside or inside the battery and to restore the battery performance even after the electrolyte breakage. Consequently, this ionogel based LIBs showed excellent cycling performance and notable resistance to Li dendritic growth, delivering a steady high discharge capacity of ~ 150 mAh·g⁻¹ and a Coulombic efficiency close to 100% after 120 cycles at the current rate of 0.2 C. Very recently, Chen et al. designed a novel copolymer via ultraviolet irradiation of monomers in the presence of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulphonyl)imide (EMIMTFSI) [183]. The

introduction of EMIMTFSI not only further enhanced the ionic conductivity of ionogel electrolyte up to 0.19 mS·cm⁻¹, but also endowed with the ability of repairing physical breakage as the EMIMTFSI can partially dissolve the copolymer chain segments and form reversible ionic bonds.

Traditional ionogel electrolytes of LIBs are generally prepared by dissolving lithium salts into ILs, and the ion conductivity can reach a high level of ~ 10⁻³ S·cm⁻¹ due to the nature of ternary ionic species systems [184, 185]. However, the most ILs have a complex synthesis routine, therefore only slight ILs are accessible on the market with extremely high price [186]. Recently, D'Angelo et al. explored a novel class of solvate ILs via an equimolar combination of LiTFSI with the organic ligand tetra(ethylene glycol) dimethyl ether, and fabricated an ionogel electrolyte after pairing the as-synthesized IL with zwitterionic polymer matrix obtained by copolymerization of 2-methacryloyloxyethyl phosphorylcholine (MPC) and sulfobetaine vinyl imidazole (SBVI) [187]. This optimized ionogel electrolyte showed an amorphous crystalline structure, a high ionic conductivity of 0.7 mS·cm⁻¹, high Li⁺ transference number of 0.60, and a favorable mechanical strength of 7.3 MPa. Besides, the cationic species of the IL could interact strongly with phosphorylcholine functional groups in the polymer network, thereby enhancing the ductility and self-healing performance of LIBs, with a safe operation of galvanostatic cycling for 100 cycles at a rate of C/2.

6.1.2 Organohydrogel based healable electrolytes

In addition to self-healable ionogel electrolytes, organic solvents

plasticized organohydrogel were also reported as healable electrolytes in LIBs [188]. Self-healable organohydrogel electrolytes, on the one hand, have the advantages of traditional organic solvent-based electrolytes, which can provide fast ion transport and wide electrochemical window. On the other hand, their polymer host matrix can limit the volatility of solvent molecules and eliminate leakage due to the interaction between the solvent molecules and polymer host matrix, thus ensuring the safety. Besides, the decrease in mechanical properties caused by the introduction of solvents could be avoided due to the incorporation of organic solvents. Chen et al. reported a healable organohydrogel electrolyte prepared by incorporating supra-molecular copolymer polyethylene glycol chains containing urea-pyrimidinone (PEG-UPy) into the crosslinked host of P(VDF-HFP) and PEO, and followed by the absorption in organic liquid electrolyte [189]. The introduced UPy units provided the quadruple hydrogen bonding network in the matrix, enabling considerable self-healing capacity of this electrolyte. The crosslinked P(VDF-HFP) with PEO segment guaranteed enhanced mechanical properties and good ionic conductivity (up to 7.5×10^{-4} S·cm^{-1}). Although the above electrolytes have excellent properties, the description of liquid electrolyte dosage is still ignored in this study, while the use of organic solvent raises the risk of safety accidents of the devices.

To obtain a safer self-healing organohydrogel electrolytes, Deng et al. used modified LiPF$_6$-based liquid electrolyte instead of base carbonate solvent to prepare self-healing organohydrogel electrolytes via Schiff-base reaction of amino-terminated polyethylene glycol with benzene-1,3,5-tricarbaldehyde (BTA) [190]. Due to the highly reversible and stable imine bonds from BTA, the organohydrogel electrolytes exhibited excellent self-healing capability and could quickly repair the cut damage within 1 h at room temperature, contributing to the excellent cycling performance of the as-assembled LiFePO$_4$/Li battery. Jaumaux et al. developed a novel deep eutectic solvent (DES)-based electrolyte to prepare a healable organohydrogel electrolyte to enhance the safety and cyclability of LIBs [191]. This DES-based self-healing polymer (DSP) electrolyte was synthesized via *in-situ* copolymerization of 2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)ethyl methacrylate (UPyMA) and monomer pentaerythritol tetraacrylate (PETEA) in a DES electrolyte, and fluoroethylene carbonate (FEC) as an additive (Fig. 8(d)). The DES obtained by eutectic ratio of LiTFSI and N-methylacetamide (NMA) exhibits highly flame-retardant, while the quadruple hydrogen bonding between the ester groups and urea groups in the UPyMA units ensures that the electrolytes could completely self-heal within 2 h at 25 °C after a through cut (Fig. 8(e)). Furthermore, with the SEI film on the anode surface provided by FEC, the uniform Li plating/stripping could even be obtained at high current over 600 h, which is much longer than that of in symmetric batteries (Fig. 8(f)).

6.2 Self-healable gel electrolytes in ZIBs

Hydrogel electrolytes, which can be expanded sufficiently and display outstanding rubber-like high elasticity due to the strong solubilization effect of water, are widely used in supercapacitors and aqueous metal-ion batteries [192]. With the existence of abundant non-covalent interactions (hydrogen bonding, etc.) formed in the water, hydrogel is the easiest type in gel systems to realize self-healing ability [85]. Thus, in the field of EESDs, extensive research based on healable hydrogels are widely used as electrolytes in ZIBs [193]. In 2018, Huang et al. firstly adopted a healable crosslinked hydrogel electrolyte via copolymerization of sodium polyacrylate (PANa) together with ferric chloride (FeCl$_3$)

for ZIBs [194]. Owing to the highly ferric ion-mediated ionic interactions, this hydrogel exhibited excellent mechanical performance and the ability to reconnect damaged surfaces after being cut off, thus ZIBs using this hydrogel electrolyte can be autonomically healed with over ~ 87 % of capacity retained after 4 cycles of breaking/healing. Via a facile freezing/thawing method, Huang et al. developed a PVA/zinc trifluoromethanesulfonate (PVA/Zn(CF$_3$SO$_3$)$_2$SO$_3$)$_2$) hydrogel electrolyte, which delivered high ionic conductivity of ~ 13 S·cm^{-1}, as well as excellent autonomous self-healing behaviour due to the hydrogen bonds between PVA chains (Fig. 9(a)) [195]. After multiple cut/healing cycles, the compact all-in-one aqueous ZIB assembled with PVA/Zn(CF$_3$SO$_3$)$_2$SO$_3$)$_2$ electrolyte displayed a high Coulombic efficiency of about 100% and a specific capacity of ~ 78 mAh·g^{-1} which is ~ 97% of the initial capacity (Fig. 9(b)). Recently, Huang's group continued to develop healable hydrogel electrolytes with triple network structures by crosslinking polymerization of agarose and PAM, followed by the introduction of the carboxymethyl cellulose (CMC) to strengthen the mechanical property [196]. The hydrogel electrolyte, with a porous crosslinking network and more hydrophilic groups, offered a high ionic conductivity (~ 23 mS·cm^{-1} at 25 °C) and excellent mechanical strength, as well as good interfacial compatibility between electrode and electrolyte, prompting much more disciplined Zn metal plating/stripping. Moreover, the dense dynamic network formed by high concentrations of hydrogen bonds provided highly stretchable (> 1300%) and self-healing (> 1000%) property of gel electrolytes (Fig. 9(c)). Thus, the flexible ZIBs with assembling this self-healing electrolyte could recover electrochemical performance with over 95% healing efficiency after 5 cycles of complete breaking/healing and endure numerous hammering strikes during the discharging process without substantial capacity loss (~ 89% of initial capacity retained) (Figs. 9(d) and 9(e)).

Akin to the liquid electrolyte-based LIBs, the additives in healable gel electrolyte can form a protective electrolyte interface film on the surface of Zn electrode, effectively reducing the interface reaction between electrolyte and anode in ZIBs [197–199]. For instance, amphiphilic macromolecule was used to manipulate he electrode/electrolyte interphases in ZIBs and enhance the stability during repeated Zn stripping/plating in cycles [200]. As amphiphilic macromolecules could not enter the inside of the formed defects, zinc was only deposited in the defects during cycling, thus healing the corroded electrode surface. In addition, the "electrostatic shield" effect formed by the basic groups of the amphiphilic molecules suppressed the two-dimensional (2D) diffusion and accumulation of Zn^{2+}, further guiding the repair of the damaged electrode surface (Fig. 9(f)). A small amount of gelatin was reported to enhance the storage and cycling stability of Zn electrode, as ZIBs using the base electrolyte with 0.5 and 1.0 g·L^{-1} gelatin could stably operate for 3000 cycles, while 0 and 0.1 g·L^{-1} gelatin added ZIBs appeared an initial capacity increase but a rapid capacity drop after only 1200 cycles (Fig. 9(g)). Despite the considerable success of healable gel electrolyte-based ZIBs, their operational regime is typically around room temperature, since the transportation ions in hydrogel electrolytes depends on the solubilization effect of water. Operation at low temperatures (< 0 °C) generally deteriorates the performance and leads to safety risks, rendering batteries with a wide working temperature range quite urgent for applications under extreme climate conditions, such as electric vehicles, advanced electronic devices, and grid-scale energy storage [201]. However, presumably due to the absence of suitable gel electrolytes, healable aqueous ZIBs with wide-working temperature are rarely reported. Jin et al. prepared an anti-freezing
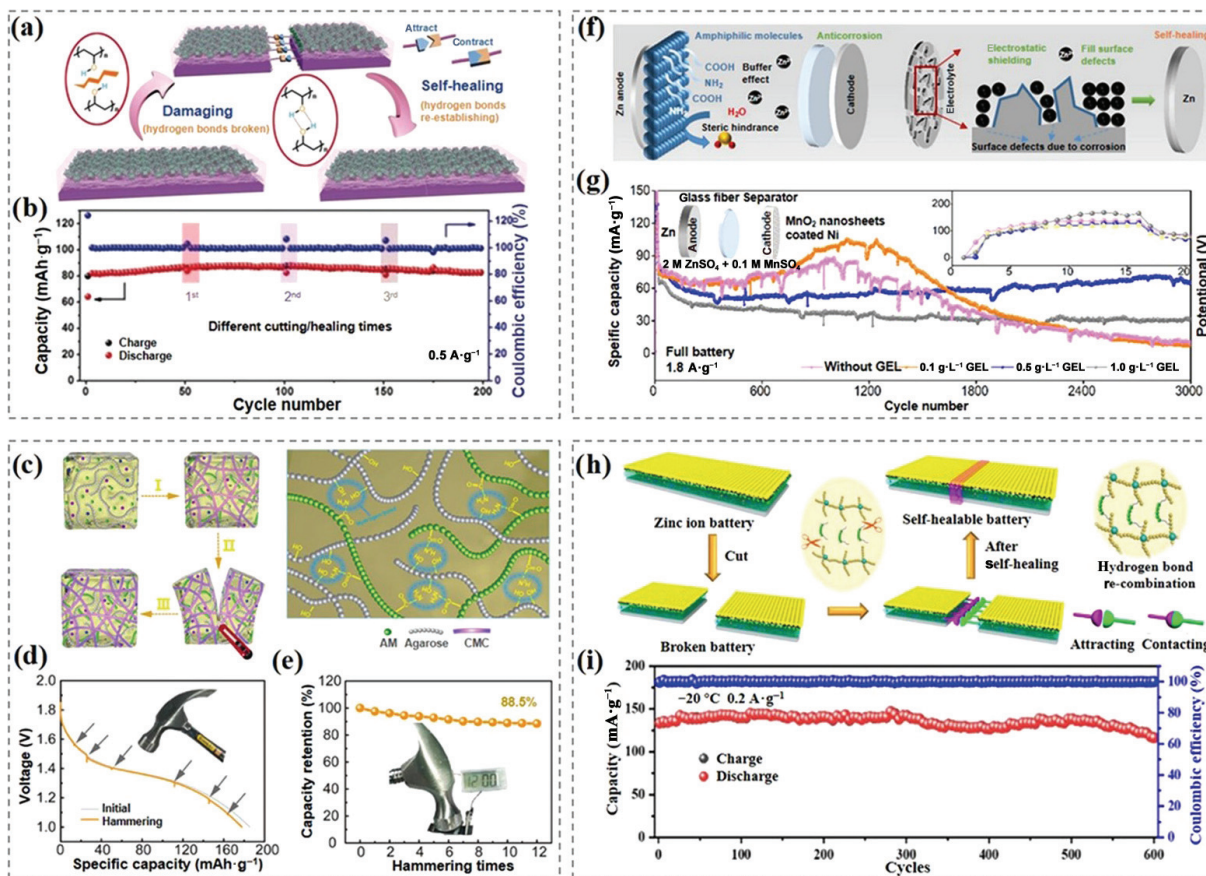
Figure 9 (a) Illustration of the structure of self-healing integrated all-in one ZIBs and (b) cycle performance of the self-healing ZIBs at original state and after multiple cutting/self-healing times. Reproduced with permission from Ref. [195], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2019. (c) Composition of self-healable hydrogel electrolyte and ((d) and (e)) its self-healing illustration and impact resistance, and capacity retention of flexible Zn‖MnO2 batteries after different hammering tests at 3.0 A·g⁻¹. Reproduced with permission from Ref. [196], © Elsevier Ltd. 2021 (f) Schematic illustration of the role of amphiphilic macromolecules as dielectric additives during placement and (g) cycling, the digital photos of the dissembling process for the symmetrical battery using the base electrolyte, and the cyclability profiles at 1.8 A·g⁻¹ of the full batteries using the base electrolyte (2 M ZnSO₄ + 0.1 M MnSO₄) with 0, 0.1, 0.5, and 1.0 g·L⁻¹ gelatin. Reproduced with permission from Ref. [200], © Elsevier Inc. 2022 (h) Schematic diagram of self-healing process and (i) the cycle performance of AF-SH-ZIB under −20 °C. Reproduced with permission from Ref. [202], © Elsevier B.V. 2021.

and self-healable crosslinked polyacrylamide polyelectrolyte (AF-SH-CPAM) via *in-situ* polymerization of acrylamide monomer in a water/ethylene glycol solution [202]. Ethylene glycol not only improved the anti-freezing performance of the gel electrolyte by inhibiting the freezing of water molecules, but also endowed the gel with self-healing property by the dynamic adjustment of enhanced hydrogen bonding interactions between polymer chains, ethylene glycol and water (Fig. 9(h)). As a result, even under −20 °C, this healable ZIB could still achieve the high specific capacity of ~ 160 mAh·g⁻¹, with a high capacity retention of ~ 87% and a Coulombic efficiency of ~ 100% after 600 cycles, and recovered ~ 90% of initial capacity after three cutting/self-healing cycles at −20 °C (Fig. 9(i)).

In brief, different intrinsic interactions, such as hydrogen bonding, ion-dipole interaction, and electrostatic interaction, are introduced into the polymer host to manufacture gel polymer electrolyte mainly for LIBs and ZIBs. These electrolytes can autonomously repair cracks and fractures with or without external stimuli, leading to a long-term lifespan. In addition to the self-healable capacity, ionic conductivity, Li⁺ transport number, and interfacial resistance also have an important influence on the performance of electrolytes. Besides, the polymer networks loaded with high bulk solvents ultimately lead to insatiable mechanical properties that cannot withstand severe mutual stresses. Therefore, how to reinforce the mechanical properties of electrolytes without sacrificing electrochemistry performances is another current research hotspot.

7 Conclusions and perspective

In this review, we have conducted an in-depth analysis of the emerging field of self-healable gels and summarized their application in EESDs (Table 1). The healable gels, utilized as electrodes, binders, or electrolytes, offer a solution to some critical challenges that conventional energy storage devices face, such as mechanical degradation, volume changes, and reduced lifetime. The versatility of using different gel types, including hydrogels, organohydrogels, and ionogels, allows for the optimization of gels for specific applications, tailoring their properties to meet the needs of various EESD designs. However, there are still some problems to be dealt with in future work to realize the further advancement or even commercialization.

The first challenge is to improve the overall healing performance and stability of gels. The efficiency of self-healing mechanisms in gels is crucial for maintaining device performance. Achieving rapid and effective healing of mechanical and electrochemical damage is essential to ensure that the energy storage devices can continuously function optimally over their operational lifespan. Since the healing property is mainly endowed by the reversible interactions inside the gel matrix, the optimization of chemical bonds and components is worthwhile studying here. The long-term reliability of healable gels is relatively low, due to unavoidable evaporation at ambient conditions. Via using encapsulation or more volatile additives, it is expected that, under normal working conditions, the healable gels can provide

Table 1 Summary of the key self-healable gels in EESDs

Application	Gel	Healing response time	Healing efficiency	Self-healing mechanism	Cycling ability	References
Electrode	PANI/PVA hydrogel	2–4 h	~ 50% in capacitance	Dynamic borate ester bonds and ionic bonds	~ 87% capacitance retention after 3000 cycles in supercapacitors	[103]
	PANI/PA/Fe³⁺/PVA hydrogels	36 h	~ 70% in tensile strain	Coordination bonds between Fe^{3+} and PA, hydrogen bonds between PVA	~ 92% capacitance retention after 10,000 cycles in supercapacitors	[104]
	poly(EDOT-co-(Th-g-PAA)-co-ThBA)–PVA hydrogel	—	~ 80% in capacitance	Hydrogen bonds between PAA grafted thiophene and PVA	~ 96% capacitance retention after 1000 cycles in supercapacitors	[113]
	PPy/PA gel-infilled microcapsules	—	—	Release of gel capsules upon the break of S electrode	A capacity decay rate of 0.23% per cycle in Li-S battery	[116]
	CNT/PANI/PVA hydrogel	—	~ 80% in capacitance	Dynamic hydrogen bonding between PVA	~ 80% capacitance retention after 2400 cycles in supercapacitors	[120]
	$Ti_3C_2T_x$/PAA/chitosan hydrogels	—	~ 50% in tensile strain	Hydrogen bonds and electrostatic attraction between $Ti_3C_2T_x$, chitosan, and PAA	~ 65% capacitance retention after 2400 cycles in supercapacitors	[123]
Binder	LVO/PVA gel and LMO/PVA gel	20 min	~ 99% in tensile strain and ~ 95% in specific capacity	Dynamic borate ester bonds	~ 88% capacitance retention after 50 cycles in LIBs	[125]
	PAA/CA gel	—	—	Reversible hydrogen bonds	~ 90% capacity retention after 300 cycles in LIBs	[142]
	PAA/BFPU gel	1 h	~ 93% in tensile strength	Reversible aromatic disulfide metathesis and hydrogen bonds	~ 97% capacitance retention after 100 cycles in LIBs	[146]
	PAA-P(HEA-co-DMA) gel	10 min	—	Reversible hydrogen bonds and abundant catechol groups	~ 94% capacity retention after 220 cycles in LIBs	[148]
	PEDOT:PSS/PVA gel	2 min	~ 75% in tensile strength	Dynamic hydrogen bonds and electrostatic interactions	~ 74% capacity retention after 200 cycles in LIBs	[153]
	Fe-PDBP@pH10	24 h	—	Reversible Fe^{3+}–(tris)catechol coordination bonds	~ 82% capacity retention after 350 cycles in LIBs	[158]
	SPI-PAM polymer	—	—	Dynamic hydrogen bonds between the amide groups in PAM and SPI	~ 80% capacity retention after 350 cycles in Li-S battery	[162]
	CB/guar composite gel	—	—	Reversible hydrogen bonds	~ 75% capacity retention after 300 cycles in LIBs	[164]
Electrolyte	LiTFSI-IL-P (VDF-HFP)	12 h	—	Reversible ion-dipole interactions	~ 97% capacity retention after 200 cycles in LIBs	[181]
	PEG-UPy/PVDF-HFP/PEO	15 h	—	Dynamic quadruple hydrogen bonds	~ 97% capacity retention after 200 cycles in LIBs	[189]
	NH_2-PEG-NH_2/BTA	1 h	~ 88% in tensile strength	Reversible imine bonds	~ 98% capacity retention after 125 cycles in LIBs	[190]
	UPyMA–PETEA/LiTFSI/NMA/FEC	2 h	—	Reversible hydrogen bonds	~ 86% capacity retention after 200 cycles in LIBs	[191]
	PANa-Fe³⁺	—	—	Reversible ferric ion-facilitated ionic bonds	~ 87% capacity retention after 4 cycles of breaking/healing in ZIBs	[194]
	(PVA/Zn(CF₃SO₃)₂)	30 min	—	Reversible hydrogen bonds	~ 97 % capacity retention after 1000 cycles in ZIBs	[195]
	AF-SH-CPAM	—	—	Reversible hydrogen bonding between carbonyl groups of PAM chains and hydroxyl groups of EG	~ 87 % capacity retention after 600 cycles in ZIBs	[202]

stable healing performance upon multiple external damages, improving the durability of devices, especially the EESDs.

In the case of gel-based electrodes, the trade-off between conductivity, mechanical property, and healing ability needs further investigation. Therefore, research needs to pay attention on building gel network with adequate conductive percolation paths for high conductivity and plenty dynamic reversible interactions for healing while enough strong interactions needed for robustness. In addition, while self-healing gels can repair mechanical damage, their mechanical strength should not be compromised. The gel electrodes must exhibit sufficient mechanical properties to withstand mechanical stresses and maintain structural integrity during cycling and operational conditions. As the introduction of self-healable gel electrode may impact the electrochemical performance of the EESDs, maintaining high electrical conductivity, ion diffusion rates, and specific capacitance or capacity is vital to ensure that the devices retain their energy storage capabilities. Therefore, the optimization of the conductive fillers or the surface functionalization of gels could be adopted to improve the overall energy storage performance.

Current research on self-healing gels as binders mainly focuses on the silicon anode of LIBs. With the deepening of research, a small number of reports have appeared in Li-S battery system. The research focus is gradually shifting from single self-healing gel to other conductive polymer/gel composites. Nevertheless, self-

healable gels may affect the electrochemical performance of the electrodes. The presence of the gel matrix and self-healing functionalities can influence ion diffusion, charge transfer kinetics, and specific capacitance or capacity, potentially impacting the overall energy storage performance. In addition, the gel binder should provide sufficient mechanical strength to maintain the structural integrity of the electrode during mechanical stress and electrode volume changes. Ensuring good adhesion between the active materials and the current collector is critical for long-term device stability. Therefore, finding self-healing gel binders with high conductivity and adhesion, low cost, and easy preparation is still the goal of efforts.

With respect to the self-healable gel electrolytes, most research mainly focusses on lithium/zinc-ion batteries system, in which the healing ability endows the batteries with favorable safety performance and stability. However, the intrinsic properties of electrolytes, including room temperature ionic conductivity, self-healable capability, rebound resilience after deformation, and mechanical strength, still need to be further optimized to meet the practical application. When designing self-healable electrolytes, it is necessary to consider the reasonable match between the selection of self-healable functional monomers, the rate of ion transfer, and the strength of repaired network, to obtain the electrolytes with a combination of efficient healing capability, fast ion transport, and robust mechanical properties. In addition, the interface contacts between electrolytes and electrodes, which is crucial for the assembling and operation of EESDs, needs to be specially deciphered, as compatibility issues between the electrolyte and active materials should be carefully addressed to prevent hindered ion transport. In addition, current synthesis processes of self-healable gel electrolytes are not easily scalable for commercial production, and developing scalable cost-effective methods for synthesizing self-healable gel electrolytes is essential for practical applications.

Developing scalable and cost-effective methods for synthesizing self-healable gel electrolytes is essential for practical applications. Incorporating self-healable gels in EESDs also raises safety considerations. The chemical and physical properties of the gels should be thoroughly assessed to ensure that they do not introduce additional safety risks during device operation. By using self-healable gels, EESDs can be designed to be more flexible and stretchable, thus more studies are needed for the integration into wearable electronics, conformable devices, and bendable energy storage solutions. Additionally, scaling up the fabrication of self-healable gel-based EESDs for commercial applications will require further investigation.

In summary, self-healable gels in EESDs is highly promising and holds the potential to revolutionize the field. The integration of self-healable gels in electrochemical energy storage devices offers an exciting prospect for achieving long-term stable operation, improved performance, and enhanced safety. With ongoing research and development, self-healable gel-based energy storage devices could pave the way for more sustainable and efficient energy storage technologies in the future.

Acknowledgements

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