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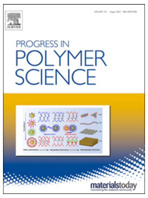

Polymers for flexible energy storage devices

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ABSTRACT

Flexible energy storage devices have received much attention owing to their promising applications in rising wearable electronics. By virtue of their high designability, light weight, low cost, high stability, and mechanical flexibility, polymer materials have been widely used for realizing high electrochemical performance and excellent flexibility of energy storage devices. In this review, flexible energy storage devices including supercapacitors and batteries are firstly introduced briefly. Then the design requirements and specific applications of polymer materials as electrodes, electrolytes, separators, and packaging layers of flexible energy storage devices are systematically discussed with an emphasis on the material design and device performance. The remaining challenges and future directions are finally summarized to guide future studies on the development of polymer materials for flexible energy storage devices.

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1. Introduction

Modern electronics has witnessed the rapid advancement of flexible devices, such as roll-up displays, wearable sensors, miniature robots, and implantable medical devices [1–9]. This has also accelerated the innovation of energy storage devices with flexibility and even wearable compatibility besides high energy density and safety [10,11]. A lot of flexible energy storage devices have been thus designed with different configurations and working mechanisms [12–14]. For instance, flexible fiber/fabric supercapacitors [15–23], lithium-ion batteries (LIBs) [13,24-26], sodium-ion batteries [27], lithium-sulfur batteries [28], lithium-air batteries [29–31], zinc-air batteries [20], and aluminum-air batteries [32,33] have been designed. Meantime, some interesting additional functionalities have been introduced to extend their application scopes of novel electronic devices including shape memory [34], self-healability [35], stretchability [24,36,37], biodegradability [38] and chromatic capability [39].

Material design is of fundamental relevance to the realization of high electrochemical performance and flexibility of energy storage devices. Metallic, nonmetallic, and organic materials have been extensively investigated as electrodes, electrolytes, or separators of energy storage devices. Materials are generally combined to synergistically enhance the electrochemical properties of energy storage devices. For example, highly conductive metals are commonly used as current collectors of flexible electrodes to load active electrode materials. Carbon and metal compounds are usually adopted in flexible electrodes to transmit electrons and store energy, while small-molecule organic solvents and metal-organic salts are vital in electrolytes. As a matter of fact, polymers are also indispensable and irreplaceable for flexible energy storage devices, which typically act as separators to guarantee ionic transport and electronic blocking, as binders to provide mechanical adhesion, or as packaging layers to ensure structural support and stable encapsulation for energy storage devices. For example, separators with pore sizes of approximately 30–100 nm are commonly made of uniaxially stretchinged polyethylene (PE) or polypropylene (PP), serv-

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Abbreviations: ANF, aramid nanofiber; BC, bacterial cellulose; Ca, calcium; CNT, carbon nanotube; COF, covalent organic framework; C-pHEMA, crosslinked poly(2-hydroxyethyl methacrylate); GO, graphene oxide; Li, lithium; LIBs, lithium-ion batteries; LLTZO, $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$; LGPS, $Li_{10}GeP_2S_{12}$; Mg, magnesium; M-PEF, modified polyester fibers; Na, sodium; PAA, poly(acrylic acid); PAM, polyacrylamide; PAN, polyacrylonitrile; PANI, polyaniline; PDB, poly(2,3-dithiino-1,4-benzoquinone); PDMC, poly(methacrylatoethyl trimethyl ammonium hydroxide; PDMS, polydimethylsiloxane; PE, polyethylene; PEDOT, poly(3,4-ethylenedioxythiophene); PEG, poly(ethylene glycol); PEGDA, poly(ethylene glycol) diacrylate; PEGDE, poly(ethylene glycol diglycidyl ether); PEI, polyetherimide; PEO, poly(ethylene oxide); PET, polyethyleneterephthalate; PI, polyimides; PP, polypropylene; PPy, polypyrrole; PS, polystyrene; PSS, polystyrenesulfonate; PTAM, poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl acrylamide); PVA, poly(vinyl alcohol); PVDF, poly(vinylidene difluoride); PVDF-HFP, poly(vinylidene fluoride)-*co*-hexafluoropropylene; SBS, poly(styrene-*b*-butadiene-*b*-styrene); SIBS, poly(styrene-isobutylene-styrene); SSLB, solid-state lithium battery; TMAC, *N*,*N*,*N*-trimethyl-1-(oxiran-2-yl)methanaminium chloride; VSNP, vinyl hybrid silica nanoparticles; Zn, zinc; ZSC, zwitterionic sulfobetaine/cellulose; α-CD, α-cyclodextrin.

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ing as electrical insulation layers but ionic conduction pathways through the liquid electrolyte filling the pores between the two electrodes [40–43]. Besides, polymers such as poly(vinylidene difluoride) (PVDF) are also used as binders to provide strong cohesion between active materials and conductive additives in the electrodes, to increase their adhesion to metal current collectors [44], and to ensure high-quality (uniform and smooth) coatings onto the current collectors. Meanwhile, polymer-based tubes, such as polyolefin-based heat-shrinkable tubes, are regularly exploited to encapsulate flexible fiber batteries [28].

Compared with metallic and inorganic nonmetallic materials, polymers possess several inherent advantages, such as flexibility, toughness, easy processability, and high designability. Additionally, polymers are composed of abundant elements (*e.g.*, C, H, O, N and S), thereby making them ideal for achieving high deformability, high energy density, good safety, or special functions of flexible energy storage devices. In essence, these advantageous properties make polymers an optimal choice for flexible energy storage devices. For instance, it is promising to use lightweight and flexible polymers with redox groups (*e.g.*, polyphenols [45–48], polyimides (PI) [49,50], radical polymers [51]) or oxygen reduction/evolution activity [52–54] to replace brittle inorganic metal compounds as active electrode materials, aiming to realize both high flexibility and energy density while also alleviating the problems of resource shortage and high costs associated with metal compounds. Polymers have also been used in current collectors to improve energy density, mechanical flexibility, or even stretchability of the entire device [55–57]. Besides, introducing polymers to electrolytes can alleviate electrolyte leakage and device combustion or even bring some unique functions (*e.g.*, stretchability [58–61], self-healability [59,62-64], freezing resistance [65–69], biocompatibility and biodegradation [64,70-73]). Notably, some all-polymer energy storage devices achieve extreme flexibility [74].

Despite previous great progress, the large-scale applications of flexible power systems are still largely limited by their low energy/power densities, short lifespans, low mechanical properties, and poor safety [75–77]. Developing novel polymer-based electrodes, electrolytes, and separators for flexible power systems has become more necessary than ever before. Some certain requirements should be followed in the design of polymers for flexible energy storage devices. Polymer electrode materials, which store energy by reversible redox conversion [78,79], hold great promise for flexible energy storage devices due to their high theoretical capacities, remarkable rate properties, intrinsic structural tunability, facile processability, good mechanical flexibility, and the possibility of low-cost green synthesis from renewable sources. Reversible redox activity and non-solubility in the electrolyte should be guaranteed in designing polymer electrode materials. To ensure high electrochemical properties and safety, gel polymer electrolytes, solid polymer electrolytes, and composite polymer electrolytes have been employed to replace conventional liquid electrolytes [80–82]. Favorable film-formability and processability, high mechanical strength, (electro)chemical robustness, and high ionic conductivity are vital for the design of polymer-based solid electrolytes [83,84]. Polymer separators, which are placed between two electrodes to prevent internal short-circuiting while storing electrolytes within pores to ensure efficient ionic conduction, should be electrical insulators. They should also feature high porosity and wettability for electrolyte and possess outstanding mechanical and (electro)chemical stability [41,85].

Due to the great development of polymers-based flexible energy storage devices, it is imperative to comprehensively review the applications of polymers in such devices to push forward future research on next-generation power systems. Simultaneously, understanding and clarifying the roles played by novel polymers in flexible energy storage devices contribute to establishing and completing the theoretical aspects of polymer-based flexible power devices. This includes exploring the use of redox-active polymers to enhance the flexibility of the devices, employing polymer-based binders to improve the mechanical properties and electrochemical performances of the flexible electrodes, utilizing ion-conductive polymers to increasie ionic conductivity and mechanical strength of the electrolytes while improving safety, and optimizing the interfaces between electrodes and electrolytes. Additionally, the design and use of polymer-based separators are crucial for maintaining the structural integrity, enhancing charge/discharge characteristics and improving cycling stability under repeatedly deformed states.

Some reviews related to polymer materials or flexible energy storage devices are available [86–92]. However, these reviews have certain limitations. In the first case, polymer energy materials were carefully discussed with an emphasis on the design, synthesis, and electrochemical properties, but without a specific focus on their use in flexible energy storage devices [78,79,93-99]. In the second case, a variety of energy storage devices were highlighted as the main development achievements, covering all types of materials but without a specific focus on polymers [100–110]. In the third case, polymers were primarily discussed in relation to their use as gel electrolytes [89,111] or electrodes (*e.g.*, conducting polymers) [112] for flexible energy storage devices, mostly limited to thin films. To summarize, there is currently no comprehensive review available that fully covers polymer materials in terms of synthesis, structure control, and property enhancement specifically for their applications in all formats of flexible energy storage devices, including both thin film and fiber shapes. Herein, such a comprehensive and deep review article is carefully presented, particularly on the basis of related studies in recent years. We will first systematically summarize the different types of flexible energy storage devices, including supercapacitors and different types of batteries, then highlight the design requirements and representative applications of polymer materials in electrodes, electrolytes, separators, and packaging layers, and finally figure out key challenges to guide future studies.

2. Flexible energy storage devices

Among the various energy-storage technologies, supercapacitors and batteries are the two main types of energy storage devices (Fig. 1) [113–116]. Supercapacitors can be adapted to specific applications which require high power density, while batteries have been in the spotlight in academia and industry due to their high energy densities. Currently, the rapid advancement of wearable electronics promotes the mechanism understanding and technological development of flexible supercapacitors and batteries [117]. This section briefly describes different types of supercapacitors and batteries to provide context for the construction of flexible energy storage devices.

2.1. Supercapacitors

Compared with batteries, supercapacitors can complete the discharge and charge processes within seconds or minutes, primarily based on fast electrostatic or non-Faradaic electrochemical processes. Supercapacitors generally exhibit a linear voltage change upon constant current during discharging/charging. Thus, the cyclic voltammetry curves of supercapacitors typically present a rectangular shape without characteristic redox peaks. The capacitance (C) is defined to evaluate the capability to store charge using Eq (1), where ΔQ means the stored charge and ΔU is the applied voltage

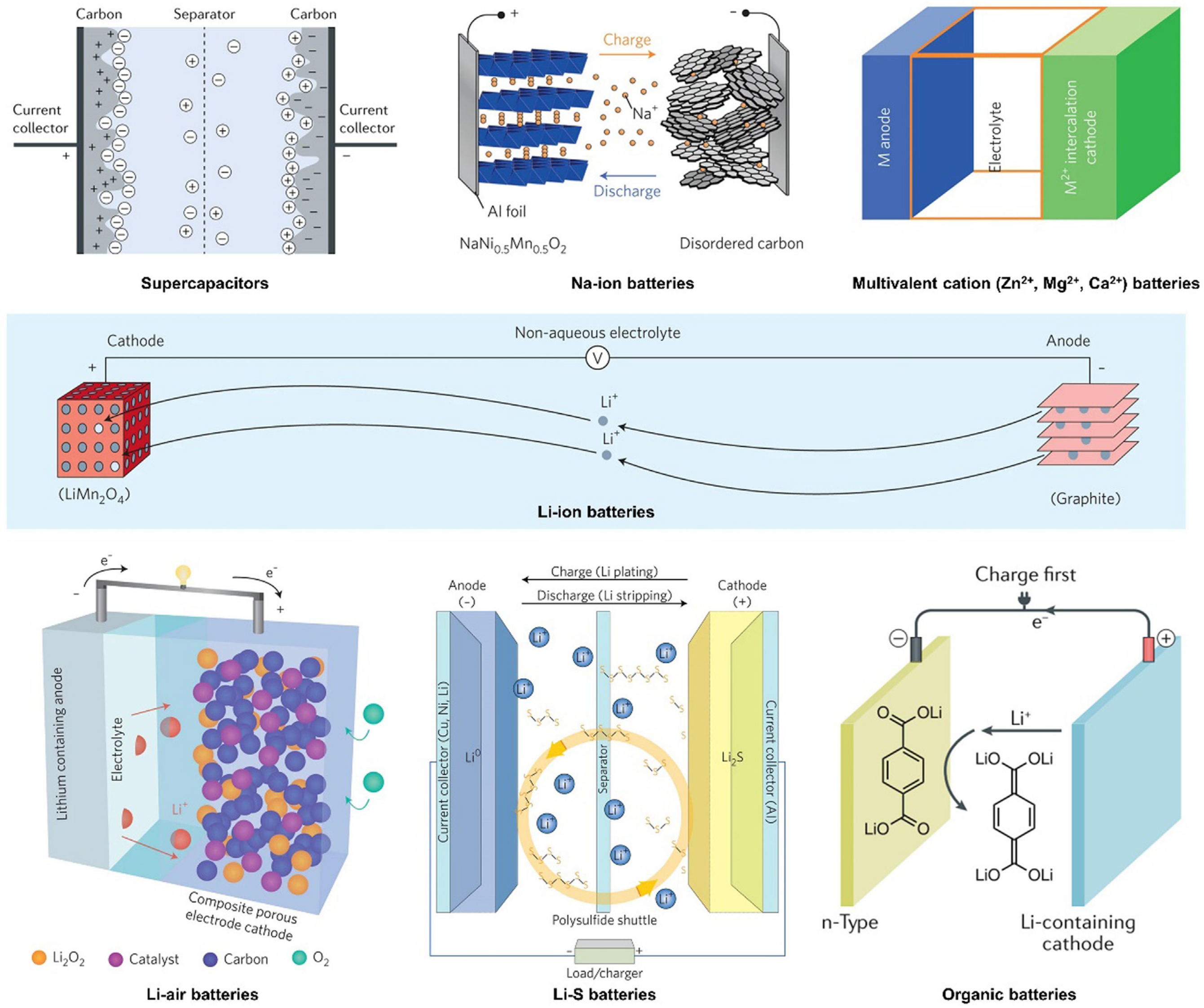

Fig. 1. Schematic of supercapacitors and different rechargeable battery systems. [115,116,173], Copyright 2016, 2019 and 2020. Adapted with permission from Springer Nature.

on the electrode.

$$C = \frac{\Delta Q}{\Delta U} \tag{1}$$

In general, electrode materials used for supercapacitors can be categorized into electric double-layer capacitors and pseudocapacitive capacitors based on the charge storage mechanism [114,118,119]. Electric double-layer capacitors store charges *via* physical electrostatic charge adsorption at the interfaces between the electrode and electrolyte [120–122], without involving redox reactions during discharging/charging, enabling a rapid charge storage process. Carbon materials are widely utilized in supercapacitors based on the electric double-layer capacitor mechanism, including activated carbons [123–125], templated carbons [126], carbon nanotubes (CNTs) [127–130], and graphene [131–133]. Efforts have been devoted to increasing specific surface areas for charge adsorption in recent years [134]. On the other hand, pseudocapacitive capacitors store energy through reversible surface redox reactions, providing higher energy densities compared to electric double-layer capacitors. Conductive polymers [135] and transition metal oxides [136,137] are typical pseudocapacitive materials [138]. It is worth noting that the intrinsic flexibility of conductive polymers is advantageous for achieving the deformability and wearability of supercapacitors.

2.2. Batteries

Battery technologies have made significant progress since the lead-acid battery. Nowadays, the development of portable and wearable electronics has presented higher demands for the advancements of battery technologies. Flexible batteries are expected to provide stably power to wearable electronics, even under various deformations. These flexible batteries operate on the same working mechanisms as conventional batteries. The following section will introduce the operating mechanism and material design of conventional batteries to guide the construction of flexible batteries.

2.2.1. Intercalation-based batteries

Lithium-ion batteries. Since being commercialized by SONY Corporation in 1990, LIBs based on $LiCoO_2$/graphite electrode materials have achieved a broad range of applications [139,140]. The working mechanism of LIBs is supported by a rocking-chair process. During charging, lithium (Li) ions are extracted from the Li-containing compounds of the cathode and intercalated into the anode materials, while discharging is a reversible process. Currently, the widely applied cathode materials mainly include metal layered oxides ($LiMO_2$, M=Co, Ni) [141,142], spinel-type compounds ($LiMn_2O_4$) [143], and olivine-type compounds ($LiMPO_4$, M=Fe, Co, Mn) [144]. Graphite is predominantly used as the anode materials. To achieve higher energy densities for electric vehicles, ternary cathode materials ($LiNi_xCo_yMn_zO_2$) are considered as one of the most promising alternatives in the future due to their high energy density, long cycling life, and low cost [145]. However, LIBs have almost reached the limits with the growing control and optimization of material and device engineering [146]. Therefore, it is urgent but challenging to develop advanced LIBs and explore battery technologies beyond them [147].

Sodium-ion batteries. The increasing necessity for more sustainable and low-cost battery technology has accelerated research into sodium-ion batteries. The significant progress in new materials and approaches has provided a leap forward for the advanced sodium-ion batteries [148,149]. Sodium-ion batteries operate on the same intercalation mechanism as LIBs, but with the advantage of abundant sodium (Na) resources and a suitable redox potential ($E_{(Na+/Na)} = -2.71$ V *vs.* standard hydrogen electrode) enable a promising energy storage technology [150]. Na ions cannot be inserted into the graphite due to their larger ionic radius. Instead, the hard carbon is applied as an anode material, while layered Na transition-metal oxides, Prussian blue compounds, and polyanionic compounds are widely used as cathode materials. One benefit of the larger ionic radius is the weak solvation energy in polar solvents, accelerating the intercalation kinetics at the interface between the electrode and electrolyte. Therefore, sodium-ion batteries can achieve high-rate performance and even maintain high-capacity retention at low temperatures.

Multivalent cation batteries. In addition, the safety of batteries during operation has been a major concern in recent years. In this regard, rechargeable multivalent cation (*e.g.*, Zn^{2+}, magnesium ions (Mg^{2+}), and calcium ions (Ca^{2+})) batteries have received significant attention due to their abundant metal reserves, low costs, and operational safety advantages. During the discharging and charging processes, multivalent metal ions are inserted and extracted from the cathode materials, enabling greater charge storage capacity compared to Li^+ and Na^+ ions.

Rechargeable aqueous zinc-ion batteries are a promising alternative for large-scale grid energy storage applications [151–153]. Zinc (Zn) metal is used as the anode due to its high stability in water and facile processability. Correspondingly, materials with a tunnel structure and large layer spacing, including manganese-based compounds, vanadium-based compounds, and Prussian blue compounds, are the most extensively studied materials for aqueous zinc-ion batteries [154]. However, issues such as dendrite growth on zinc metal and a narrow aqueous electrolyte window need to be addressed [155,156]. In addition, while Mg and Ca metals offer desirable gravimetric and volumetric capacities for energy storage, constructing batteries based on these elements is still far from practical applications due to poor plating/stripping efficiency [157–159].

2.2.2. Conversion-based batteries

To exceed the capacity limits of conventional intercalation-type electrodes, the novel battery systems based on conversion reactions have attracted much attention in recent years. Two representatives of these systems are lithium-air and lithium-sulfur batteries. Meanwhile, organic batteries, typically based on the valence change of carbonyl carbon, also provide the possibility of constructing high-capacity batteries.

Metal-air batteries. Metal-air batteries, comprising a metal anode (*e.g.*, Li, Na, Zn, Mg, Ca) and O_2/CO_2 as cathode active materials with catalyst layers for the reduction/evolution of gas, have the highest energy densities among all energy storage technologies [160–162]. However, sluggish reduction and evolution kinetics at the cathodes largely hinder the practical applications of metal-air batteries. This is mainly due to the complex and sluggish electrode reactions occurring at the solid (catalyst layer)-liquid (electrolyte)-air (O_2/CO_2) three-phase interfaces. In recent years, researchers have designed and prepared various porous catalytic cathode materials, such as carbonaceous materials, noble metal nanomaterials, transition metal oxides, and single-atom catalysis [163–165]. For example, wrinkled MoS_2/N-doped carbon core/shell nanospheres interfaced with single Fe atoms were designed as superior oxygen reduction reaction and oxygen evolution reaction bifunctional electrocatalysts for robust wearable zinc-air batteries with both high capacity and cycling stability [165]. However, these batteries still exhibit severe charging/discharging overpotentials and poor round-trip efficiency due to the limited driving force and structural instability of the catalyst layer. Developing high-performance and low-cost novel catalysts is still vital for advanced metal-air batteries, while the introduction of external field driving forces has been explored to tackle the aforementioned problems [100,166-169].

Metal-sulfur batteries. Metal-sulfur electrochemistry (*e.g.*, lithium-sulfur, sodium-sulfur, potassium-sulfur, magnesium-sulfur) has been regarded as a promising strategy to realize high energy densities due to the high theoretical capacity of 1672 mAh g^{-1} from sulfur cathode materials, low cost, and abundant reserves of sulfur [99,170,171]. Unlike the intercalation chemistry of conventional metal-ion batteries, metal-sulfur electrochemistry involves a complex phase transition process in which the solid sulfur is reduced to soluble polysulfides and then to solid sulfides during discharge. Charging is a reversible process accompanied by the conversion from solid sulfides back to sulfur. Up to now, metal-sulfur batteries are not yet available in the market. The challenges related to cathodes include the serious shuttle effect of intermediate polysulfides and the sluggish reaction kinetics of sulfur, while the dendrite formation and surface corrosion are also the main problems for the metal anodes [172]. Polymers have been widely used in metal-sulfur batteries because of their rich abundance, light weight, diverse molecular structures, and well-defined functional groups. Polymers can not only serve as elemental sulfur carriers, but also directly act as active cathode materials, such as organosulfur polymers. Furthermore, polymers also play vital roles as binders, separators, and electrolytes due to their excellent chemical stability, film-forming ability, and processability [99].

Metal-organic batteries. To alleviate the cost and performance pressure on inorganic materials, organic electrode materials are considered an alternative strategy [173,174]. Organic electrode materials can be synthesized and composed from a wide range of sources, and their performances can be further optimized by chemical modifications. Generally, organic electrode materials can be classified as conductive polymers and redox group-bearing structures [175], which store charges mainly based on the valence change of carbon, oxygen, and nitrogen in these redox groups [176]. The pursuit of sustainable energy storage technology has accelerated the development of organic electrode materials in recent years. To achieve practical applications, improving the electrical conductivity of organic electrode materials and measurements at the industrial standard (with high mass loadings and lean electrolytes) should be highlighted.

Benefiting from the improvement of device configuration and fabrication technology, an increasing number of energy storage devices (including but not limited to the devices mentioned above) have been endowed with flexibility and used to power wearable electronics. The typical strategy for achieving device flexibility is to construct intrinsically flexible electrodes or deposit active materials onto flexible substrates combined with quasi-solid or solid electrolytes. The mechanical stability of flexible electrodes and the full contact between electrodes and electrolyte enable the stable operation of devices during various deformations. Furthermore, polymers, with controllable physicochemical properties and facile synthetic methods, play a vital role in the construction of flexible energy devices. Polymers are promising to implement important effects in various parts of flexible energy devices, including active materials, binders, supporting scaffolds, electrolytes, and separators. The following chapters will systematically introduce the development and applications of polymers in flexible energy devices.

3. Polymers for electrodes

3.1. Design requirements of polymers for electrodes

Polymers are indispensable components in electrodes. Firstly, polymers with redox activity have been regarded as promising cathode and anode materials by their intrinsic merits of low cost, low solubility, high rate performance, good electrochemical reversibility, accurately tunable chemical potential, high energy density, flexibility, processability, and recyclability. Polymer active materials can be categorized according to their electrochemically active groups, including conductive polymers, oxygen-containing polymers (carbonyl and ether), nitrogen-containing polymers (imine, nitrile, and azo), sulfur-containing polymers (thioether and disulfide), and radical polymers. Depending on their intrinsic structure and redox potentials, polymer active materials with low redox potentials can replace traditional carbon materials (*e.g.*, graphite and hard carbon) as anode materials [177–180], while other typical polymers undergoing oxidation first can serve as cathodes [181–183]. Further, several other requirements, such as stretchability [163,184-187], self-healability [188–190], and electrochromic ability [39,179,191-194] can meet the unique demands of flexible applications with novel multiple functions. Besides, polymers are extensively used as binders to enable firm cohesion between active materials and conductive additives as well as their adhesion to current collectors. Some functional polymer binders can enhance the electrochemical and mechanical performances of emerging flexible energy storage devices, such as flexible lithium-sulfur batteries, by inhibiting the shuttle effect of polysulfides [195,196]. Polymer binders should possess high electrochemical stability towards active electrode materials and decent chemical stability to withstand the corrosion of acidic or alkaline electrolytes and avoid the structural collapse of electrodes. In addition, binders are required to provide ionic transporting ways in the electrodes. Further, polymers are also being explored as flexible and stretchable current collectors, exhibiting ultra-low weight, low cost, and enhanced mechanical properties [197–199]. They are expected to have excellent film-forming properties and robust mechanical properties to withstand the tension of handing and winding operations during electrode fabrication and device assembly.

3.1.1. Stretchability

To match the mechanical properties of advanced flexible/stretchable electronic devices (*e.g.*, soft tactile sensors, motion sensors, and nervous sensors), novel energy storage devices are expected to be able to be stretched, bent, twisted, and even deformed into arbitrary shapes [200–202]. The key to fabricating stretchable supercapacitors/batteries lies in designing stretchable electrodes. The common strategy for fabricating stretchable electrodes is to load conductive material onto stretchable polymer substrates, such as poly(styrene-*b*-ethylene-butylene-*b*-styrene)/Ag membrane [203], SBS/Ag film [204], PDMS/CNTs film [198], SIBS/carbon black/CNTs film [199], graphene-modified PDMS sponge [55], elastic fibers [16,205] and fabrics [206,207]. Another strategy to fabricate stretchable electrodes is to design polymeric gel electrodes with cross-linking polymer chains and tunable amounts of solvents, which can tolerate large strains and reversible deformations [208]. Recently, polymeric gel electrodes with intrinsically stretchable properties have been widely explored, such as α-cyclodextrin/polyacrylamide/polyaniline (α-CD/PAM/PANI) hybrid hydrogel [184], poly(vinyl alcohol)/polyaniline (PVA/PANI) hydrogel [163,185], polyacrylamide/polyaniline (PAM/PANI) organohydrogel [186], polyaniline/graphene oxide (PANI/GO) [187] and poly(3,4-ethylenedioxythiophene): polystyrenesulfonate/polyacrylamide/polypyrrole (PEDOT:PSS/PAM/PPy) [209] for advanced supercapacitors. However, most current flexible and stretchable polymer-based electrodes often lack adequate softness and toughness to supply a stable energy output under severe and repeated deformations, especially severe mechanical stresses at the device level.

3.1.2. Self-healability

Self-healability, widely existing in living organisms, is an essential property to heal internal or external wounds spontaneously and restore their structure and function, which has greatly inspired researchers to develop artificial materials and devices with a long lifetime, good sustainability, and high safety [188,189,210]. With the emergence of wearable electronics, smart energy supply devices with self-healability have inspired great research optimism as they can recover their electrochemical and mechanical performances in the case of mechanical and structural damages under bending, twisting, stretching or other deformations. Most reported healable energy storage devices are fabricated by either employing extra self-healing polymer substrates to wrap/support the electrodes [211–213] or using patching electrodes with self-healable polymer-based electrolytes [59]. Unfortunately, these non-intrinsically self-healing electrodes give rise to low energy density and limited healing efficiency. Facing these challenges, the design and construction of an electrode with intrinsic self-healability is highly desirable and significant. Until now, self-healable polymer materials with various healing chemistries, including incorporation/release of curing agents [188] or dynamic/reversible covalent or noncovalent interactions as the mobile phases [189,190], have been studied to fabricate electrodes with intrinsic seal-healability [56,167,214].

3.1.3. Electrochromism

With the development of flexible energy storage devices and artificial intelligence, flexible energy devices are expected to have some extra smart functions beyond energy storage and conversion [14,215]. For example, it is greatly promising to design flexible devices that can perceive and exhibit voltage changes or charged/discharged states in a visual way [216,217]. Introducing electrochromic materials as redox-active electrodes enables the devices to show different applied voltages *via* displaying reversible and visible color changes [218,219]. In addition, when used in flexible electrochromic displays, the new electrochromic devices can significantly decrease energy consumption for coloration as they can recycle the consumed energy for bleaching, making them an optimum energy-efficient technology. However, it is still a great challenge to incorporate electrochromic ability into flexible devices, which imposes high demands for flexible electrochromic electrodes. Compared to inorganic and organic materials, conducting polymers like PANI and PPy are considered to be the most promising electrochromic electrode materials owing to their excellent physicochemical properties (color variation, charge storage ability, etc.) that can be accurately tuned by the applied voltage [39,192-194,220,221].

3.2. Redox-active polymers

The basic requirement for active materials utilized in batteries and pseudo-supercapacitors is a reversible electrochemical redox reaction. Organic polymer active materials can fulfill energy storage based on simple redox conversion reactions rather than the complex intercalation mechanisms of inorganic materials. This means that the same polymer active materials can be used in different metal-ion batteries, such as LIBs, sodium-ion batteries, and multivalent-ion devices [175]. In addition, the organic polymer active materials can also act as a catalyst layer to accelerate gas reduction and evolution reactions in metal-air batteries [222,223]. The structural designability and synthetic tunability of polymer materials enable them to function as redox conversion materials or catalyst layers in different systems.

The electrode of an electrochemical cell can be categorized into cathode and anode according to reduction and oxidation processes that occur during discharge, respectively. In general, polymer materials can be used as the cathode or anode, depending on the practical redox potentials of polymer active materials and counter electrodes. A significant potential difference between polymer active materials and counter electrodes is desirable to achieve a high output voltage, thus leading to increasing energy density. As a result, it is essential yet challenging to develop and modify polymer active materials with proper redox groups.

3.2.1. Conductive polymers

Since their discovery in the 1970s, conductive polymers and their composites have been extensively studied in a wide variety of applications [224]. Numerous reviews have been published on their synthetic strategies and diverse applications in fields such as biomedicine [225], waste water treatment [226], and photocatalysts [227]. The latest developments on the construction of conductive polymers with various functions are also discussed [228]. However, a comprehensive review on conductive polymer composites utilized as electrodes in flexible batteries and supercapacitors—encompassing all formats, including thin-film and fiber shapes—is currently lacking. Here, we aim to fill this gap by focusing on conductive polymers as promising electrode materials for batteries and supercapacitors.

The electrochemical activity of conductive polymers originates from the overlap of adjacent π-orbitals, leading to good electrical conductivity. Conductive polymers undergo redox reactions through doping and de-doping processes, where the polymer chain undergoes reduction or oxidation and incorporates cations or anions, respectively. In particular, PANI, PPy, polythiophene (PT) and PEDOT: PSS are well-known redox-active conductive polymers (Fig. 2) [14,229]. Despite their high electrical conductivities, the doping degrees of conductive polymers are below 50%, suggesting that less than half of redox-active centers undergo charge and discharge reactions and thus cause decreased capacities (~150 mAh g^{-1}) [229]. The redox potentials of conductive polymers depend on the doping level, and the degrees of doping gradually vary during charge and discharge, resulting in a sloping practical voltage.

For example, commercialized coin-type Li secondary batteries with PANI cathodes were developed in the 1980s [230]. However, the decreased capacities and sloping voltage limited the range of applications, and the production of batteries was soon taken off the market [173]. Although conductive polymers still suffer from these drawbacks, their improved electrical conductivity and reaction rate make them favorable for applications in high-power devices such as supercapacitors [228]. When utilized in supercapacitors, the conductive polymers possess the following advantages: (1) high specific capacitances, *e.g.*, pseudocapacitive-type conductive polymers achieve much higher specific capacitance than carbon-based materials based on an electric double-layer capacitor mechanism; (2) high energy and power densities, *i.e.*, the improved electrical conductivities of conductive polymers can reduce the use of conductive additives and binders, which decreases the overall weight of devices and improve energy and power density; (3) high flexibility, *e.g.*, the soft chains of conductive polymers make it possible to develop flexible and wearable supercapacitors. Therefore, the recent conductive polymer-based flexible supercapacitors will be highlighted in the following.

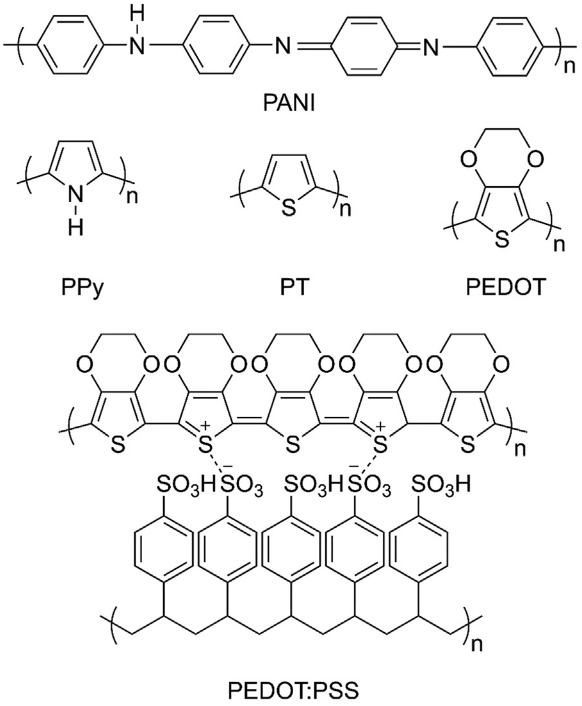

Fig. 2. Molecular structures of representative conductive polymers.

PANI. PANI demonstrates great application potential in energy storage due to its facile synthesis, environmental stability, and good electrochemical performance. PANI can be synthesized through electrochemical or chemical oxidation. The several redox states, which include fully reduced leucoemeraldine, intermediate emeraldine salt, and fully oxidized pernigraniline salt controlled by the doping of protons, enable enhanced electrochemical activity [231]. It is important to note that the fully oxidized state is not chemically stable due to its high electrophilicity and acidity. As a result, the theoretical specific capacity of PANI is determined into a limited value between fully reduced and half-oxidized states. Nowadays, many efforts have been devoted to improving the electrochemical performance of PANI by optimizing the polymer structure and fabricating novel composite electrode materials. It is particularly necessary to discuss the composite materials combined with carbon-based additives, metals, or other polymers [118].

Fabricating composites with other polymer materials is proposed to improve cycling stability. The single PANI-based electrode generally faces the problems of volumetric change during doping/de-doping processes and mechanical brittleness under deformations. The novel PANI-polymer composite features high structural porosity and intrinsic superelasticity, enhancing mechanical and electrochemical stability [163,185,232]. An intrinsically stretchable and bendable anisotropic PVA/PANI hydrogel was prepared through the cryopolymerization strategy, which can maintain stability under complex deformations for stretchable supercapacitors [163]. The crosslinking density of the composite with a unique double network can be enhanced by the dynamic hydrogen bonds

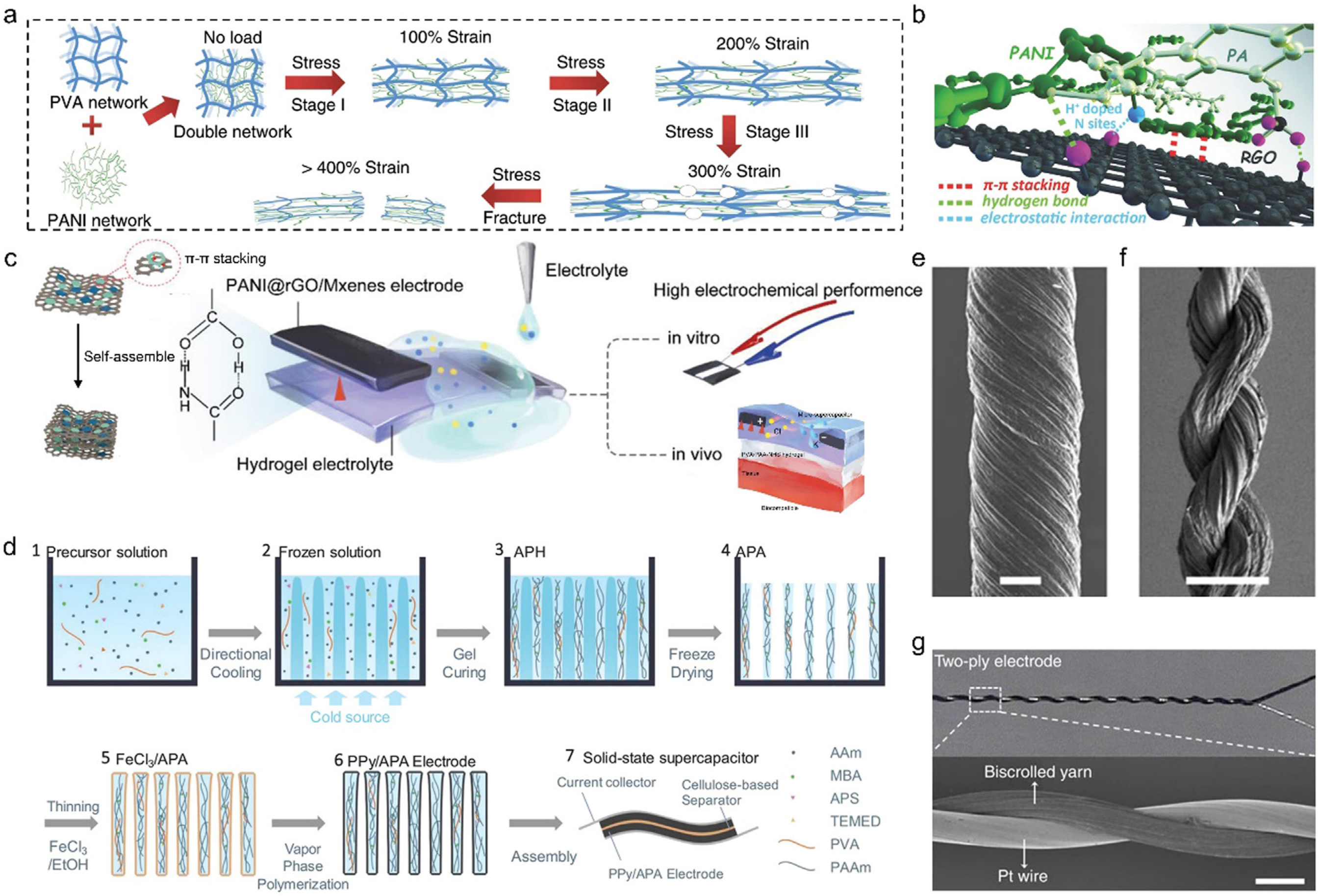

Fig. 3. (a) Schematic stretching illustration of PANI and PVA double networks. [163], Copyright 2020. Adapted with permission from Springer Nature. (b) Schematic intermolecular interaction among PANI, phytic acid, and rGO. [187], Copyright 2018. Adapted with permission from John Wiley & Sons Inc. (c) Fabrication process and application of all-hydrogel micro-supercapacitor based on PANI@rGO/Mxene gel electrodes. [238], Copyright 2021. Adapted with permission from John Wiley & Sons Inc. (d) Fabrication process of all-solid-state hydrogel supercapacitors based on aligned polyacrylamide aerogel matrix loaded with PPy. [243], Copyright 2020. Adapted with permission from John Wiley & Sons Inc. SEM images of (e) a biscrolled PEDOT/carbon multiwalled nanotube yarn with ~37° bias angle and (f) two PEDOT/carbon multiwalled nanotube yarns plied together. Scale bar, 10 and 50 μm, respectively. (g) Two SEM images of a PEDOT/carbon multiwalled nanotube biscrolled yarn plied with a 25 μm Pt wire. Scale bar, 40 μm. [247], Copyright 2013. Adapted with permission from Springer Nature.

between the PANI network and the PVA network (Fig. 3**a**). Benefiting from the improved mechanical properties, the obtained stretchable supercapacitors exhibited a high specific capacitance of 260 F g^{-1} and remarkable energy density of 27.5 Wh kg^{-1} and remained stable under severe deformations. Also benefiting from the electrical and mechanical support from carbon-based materials, fabricating composites with carbon-based materials such as GO [187,233,234] and CNTs [216,221,235] can improve the power density of supercapacitors. In this regard, the macromolecularly interconnected 3D graphene/PANI hydrogel as a free-standing electrode was synthesized through the self-assembly of two macromolecular structures [187]. The strong intermolecular interaction between PANI and graphene enabled enhanced mechanical properties and processibility in the fiber-shaping process (Fig. 3**b**). Moreover, the all-gel-state fibrous supercapacitor based on composite hydrogel electrode achieved a strain up to ~40% to overcome large structure deformation, and delivered a remarkable volumetric energy density of 8.80 mWh cm^{-3}. In addition, an electrochromic fiber-shaped supercapacitor based on aligned CNT/PANI composite sheet as the electrode was constructed [221]. The resulting intelligent fiber-shaped supercapacitor could be woven into fabrics and display reversible chromatic transitions under different working states. Even under different deformation conditions, 93.8% of the specific capacitance was maintained after bending for 1000 cycles and 97.9% after being fully stretched for 100 cycles.

By many unique properties of metal oxides (*i.e.*, MnO_2, RuO_2, TiO_2, WO_3, and Fe_3O_4), such as high energy storage capability and cycling stability, the PANI/metal oxide composite has received significant attention. A ternary reduced GO/Fe_3O_4/PANI nanostructure was synthesized through the scalable soft-template technique as the electrode for a semiflexible and all-solid-state supercapacitor [236]. The synergistic effects of double-layer capacitance from reduced graphene oxide (rGO) and pseudocapacitance from Fe_3O_4 nanoparticles and PANI nanorods enabled improved electrochemical properties. The resulting supercapacitor achieved a high energy density of 47.7 Wh kg^{-1} at 550 W kg^{-1} and remained at 78% of initial capacitance after 5000 cycles.

In addition, two-dimensional transition metal carbides and nitrides, also known as MXene, have been intensively investigated for energy storage and catalytic applications due to their layered nanostructure and superior electrical properties. For example, rational heterojunction engineering through intercalating PANI nanoparticles into an MXene interlayer demonstrated a high capacitance of 1167 F cm^{-3} [237]. The PANI nanoparticles enabled sufficient contact with the MXene substrate and favorable electron transport. The resulting asymmetric supercapacitor delivered a high energy density of 65.6 Wh L^{-1} at 1687.3 W L^{-1} and remained stable at different bending angles of 45°, 90°, and 180° Furthermore, a thin and stretchable micro-supercapacitor composed of PANI@rGO/MXene gel electrode and hydrogel electrolyte was presented (Fig. 3**c**), which could be implanted onto the heart of living mice and stably operate *in vivo* for 14 days [238]. The crosslinked interface between the gel electrode and hydrogel electrolyte ensured desired and stable electrochemical performances, even under various deformations.

PPy. PPy is another conductive polymer that has been extensively studied due to its environmental stability, high conductivity, and easy processing capability for various applications. Its better flexibility and greater mass density compared to other conductive polymers make it a promising candidate for constructing flexible and portable supercapacitors [74]. Similar to the optimization of PANI-based electrodes, efforts have been made to design novel nanostructures and composites with other materials (*i.e.*, polymers [239,240], carbon-based materials [54,202,241,242], and metal oxides [136,214]) to improve PPy-based electrodes. The process of fabricating composites generally involves optimizing the electrode structure; thus, the following part will focus on the former.

A wood-inspired flexible all-solid-state hydrogel supercapacitor was constructed by morphologically tuning the aligned PAM aerogel matrix loaded with PPy (Fig. 3**d**) [243]. The aligned structure was achieved through an ice-templating method, and the intrinsic pore size was reduced from 47 to 12 μm by adding PVA, which benefited ion transport and increased mass loading. Therefore, the resulting supercapacitor exhibited a high energy density of 73.8 μWh cm^{-2} and remained at 86.5% of its initial capacitance after 1000 cycles at 6.2 mA cm^{-2}.

Hybridizing with highly conductive carbon-based materials increases the pathways for electrons and accommodates an abundance of electrolytes for redox reactions. Meanwhile, carbon-based materials feature high porosity, flexibility, and robustness to maintain normal functions under deformations. For example, a core-sheath helical-structured fiber-shaped supercapacitor was constructed based on MnO_2 nanoflower decorated CNT fiber and CNT/PPy composite film [241]. The synergistic enhancement of MnO_2 and PPy improved the overall capacitance, while replacing traditional elastomer with a CNT substrate increased the resulting device's gravimetric and volumetric energy densities. In addition, incorporating the self-healing capability can restore electrochemical performance and mechanical integrity when the damage occurrs during various deformations [202]. A highly stretchable and real-time healable supercapacitor was constructed based on PPy-incorporated gold nanoparticle/CNT/PAM hydrogel electrodes and the gold nanoparticle/PAM hydrogel electrolyte. The hydrogel electrode possessed a hierarchical honeycombed network structure, which exhibited large stretchability with an elongation of 2380%. Benefiting from the stretchability and healability of the dynamic gold nanoparticle-thiolate interaction, the assembled device maintained 89.5% of its initial capacitance upon doubling the tensile strain to 800% and restored 80% of the initial specific capacitance over ten healing processes.

To widen the operating voltage range and remain stable during stretching, a coaxial stretchable asymmetric fiber-shaped supercapacitor was fabricated with MnO_2 nanoflower decorated CNT fiber and CNT/PPy composite film as positive and negative electrodes, respectively [241]. The operating voltage window was enlarged from 0.8 to 1.5 V with the decoration of MnO_2 and PPy, and the stretchability of the overall device was achieved by overtwisting the fiber to realize a helical structure. The helical supercapacitor exhibited a high gravimetric energy density of 2.41 mWh g^{-1} and maintained around 80% of its initial capacitance at 0% and 20% strains after 5000 cycles.

PT and its derivatives. PT and its derivatives have received wide attention in electrochemistry due to their broad potential windows, low bandgaps, high electrochemical stability, and fast electrochemical kinetics [118,244]. Typically, PTs are synthesized by chemical or electrochemical polymerization of thiophene and substituted thiophenes [229]. PT can accept *p*- and *n*-doping and is used for both positive and negative electrodes. In 1983, PT films (with a dopant concentration of 24 mol%) were used as cathode and anode active materials in batteries, delivering a voltage of 3.1 V and an energy density of 93 Wh kg^{-1} [245].

The practical capacitances of PT-based materials are lower than those of PANI and PPy because their high molecular weight, but the minimal side reactions and broad potential windows make them show unique advantages in asymmetric supercapacitors with high energy density and good cycling stability. PT and its derivatives, such as poly(3-methythiophene) and poly(3-(4-fluorophenyl)thiophene), have been extensively studied as electrode materials of supercapacitors. For instance, poly(3-methythiophene) was conformally coated on densified and horizontally aligned carbon nanotube arrays *via* modified oxidative chemical vapor deposition, and the combination of electronically conducting carbon nanotubes and pseudocapacitive polymers enabled a high areal capacitance of 3.1 F cm^{-2} at 5.0 mA cm^{-2} and high electrochemical stability even at high strains [246].

Benefitting from the dioxy bridge to stabilize the aromatic thiophene ring, PEDOT possesses favorable features for bioelectronic sensors and electrochemical supercapacitors, including high conductivity, electrochemical stability, and fast electrochemical kinetics [247–250]. In addition, the various functional groups can be introduced into monomers to enable more functionalities. The biscrolled yarns were prepared by twisting insertion in 100 nm thick PEDOT-infiltrated carbon multiwalled nanotube sheets (Figs. 3**e-f**) [247]. The biscrolled yarns plied with a metal wire current collector could construct supercapacitor yarns with enhanced structural stability and outstanding power performance.

Various negatively charged agents, especially the intensively explored PSS, can be incorporated with positively charged PEDOT to optimize electrical and mechanical properties [251–254]. In this regard, a flexible fiber-based supercapacitor was reported with high tensile strength and modulus, and desirable electrochemical performance. Ultrahigh molecular weight PE fibers were used as a substrate and modified continuously modified by polydopamine, Ag nanoparticles, and PEDOT:PSS [251]. The resulting composite fiber achieved a superhigh strength of up to 3.72 GPa, which made it possible to fabricate ultra-strong fabrics. The resulting supercapacitor exhibited a high specific capacitance of 563 mF cm^{-2} at 0.17 mA cm^{-2} and remained at 92% of the initial capacitance after bending for 1000 cycles. In addition, a sweat-based flexible supercapacitor with PEDOT:PSS as the active component was presented to power cloth-based electronics [254]. The mixed ionic and electronic conductivity, hydrogen bonding interactions with the cellulose substrate, and environmental friendliness from active electrodes enabled a high specific capacitance of 8.94 F g^{-1} in a sweat equivalent electrolyte and structure flexibility of the developed supercapacitor.

It is promising to improve the cycling stability and mechanical strength of individual conductive polymers by combining them with carbon materials, metals, or other polymers. However, critical issues related to conductive polymer composite materials need to be further understood and addressed. Directly physically mixing multiple materials result in poor interactions among different components, limiting the improvement of performances. Interfacial contacts among different components should be enhanced through feasible strategies such as chemical deposition or ball milling to enable capacity, rate, and long-term stability of flexible devices. In addition, the proportion and distribution of each component also need to be thoroughly considered, which leads to distinct electrochemical performances and mechanical properties of composite electrodes.

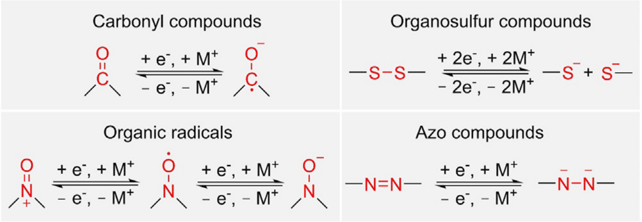

Fig. 4. Redox mechanisms and characteristics of different redox groups.

3.2.2. Redox group-bearing polymers

Since the conductive polymers suffer from limited capacity and sloping discharge voltage, many efforts have been made to explore redox group-bearing polymers [175], which consist of a non-conductive backbone bearing the electroactive groups. The redox group-bearing polymers have a distinct redox potential based on the specific redox active sites. As shown in Fig. 4, various redox groups, such as carbonyl compounds (*i.e.*, quinone, imide), organosulfur compounds, azo compounds, and radical compounds (*i.e.*, nitroxyl, phenoxyl), with stable operation voltage and high capacity, have been introduced into polymer backbones [244]. Redox group-bearing polymers permit access to various electrochemical performances and material properties through various polymerization methods, enabling a desirable alternative as active materials for batteries.

Carbonyl compounds. The carbonyl compounds are the most widely studied materials with fast reaction kinetics, high capacity, and structural tailorability [255–257]. The redox activity of carbonyl is based on the enolization process, in which the negatively charged oxygen can be attacked by positively charge carriers such as metal ions. The adjacent carbonyl groups or conjugated structures stabilize the negative charge over the delocalized system [176]. The first exploration of the tricarbonyl compound as a cathode for primary Li battery can be traced back to the 1960s [173,258]. However, the rapid decay in capacity due to their high solubility in aprotic electrolytes has limited the applications of carbonyl compounds. Since then, continuous research has been conducted to explore the reaction mechanism and broaden the application of carbonyl compounds.

As presented above, although the small carbonyl molecules exhibit high theoretical capacity (*i.e.*, 496 mAh g^{-1} for 1,4-benzoquinone), the severe dissolution in aprotic electrolyte leads to a rapid capacity decay [259–262]. Many strategies have been designed to improve cycling stability, including polymerization, optimization of electrolytes, and modification of separators [45–47]. Combining the carbonyl groups with insoluble polymer backbones effectively maintains structural stability during operation. Meanwhile, the distinct mechanical properties of polymer chains can enable the battery with flexibility and stretchability.

From the perspective of molecular design, the ladder-structured heterocyclic dithioether-containing poly(quinone), poly(2,3-dithiino-1,4-benzoquinone) (PDB) was designed as electrode active material for all-plastic battery [48]. The free-standing electrodes were prepared by mixing PDB and CNTs, which exhibited good flexibility and ultralong stability of 1000 cycles at high current density (Fig. 5**a-c**). Moreover, the all-plastic-electrode battery, with pristine PDB as a cathode and prelithiated PDB as an anode, maintained a capacity of 119 mAh g^{-1} after 250 cycles and reached a high energy density of 276 Wh kg^{-1} (Fig. 5**d-f**). The all-polymer-based battery offered guidance on rational design for more flexible and safe energy devices.

Imides are the other promising carbonyl electroactive materials [263–266]. Recently, a conjugated backbone with integrated redox sites was constructed for high-rate Li batteries [263]. The linear conjugated alternating naphthalene-bithiophene exhibited desired electronic conductivity, and a naphthalene dicarboximide realized the charge storage through a reversible two-electron pathway (Fig. 5**g, h**). Benefiting from the fast electrode kinetics provided by the desired electronic conductivity, the resulting battery could remain 96% retention of initial capacity and coulombic efficiency > 99.95% after 3000 cycles.

Radical compounds. The radicals are generally the intermediates during the reaction to initiate polymerization or react with other molecules. The unpaired electrons enable the radical compounds with fast electron transfer and favorable redox kinetics. Particularly, nitroxyl radical-bearing polymers such as 2,2,6,6-tetramethylpiperidinyl-*N*-oxyl are commonly used as electrode materials in batteries [267–270]. To achieve high loading areal capacity and operation at the high current density, poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl acrylamide) (PTAM) was introduced into a nanocarbon sponge of single-walled carbon nanotube to prepare electrodes [51]. The synergy of high electrochemical reactivity of PTAM and the current collection network by CNTs leads to a large current density of 1 A cm^{-2} and a high areal capacity of around 3 mAh cm^{-2}. Moreover, a thin and flexible polymer-based battery using NaCl electrolytes was fabricated to demonstrate the practicability.

3.2.3. Other redox-active polymers

Covalent organic frameworks (COFs), with highly ordered porous structures, have attracted widespread interests. The unique crystalline porous framework, large π-conjugated structure, and abundant transfer pathways enable COFs as a promising choice for energy storage devices [271–273]. For example, a fully conjugated COF (g-$C_{34}N_6$-COF) linked by C = C bonds was synthesized through a variant Knoevenagel condensation (Figs. 6**a-c**) [274]. This COF was assembled with singled-walled CNTs to prepare free-standing film electrodes, and the fabricated micro-supercapacitors achieved excellent areal capacitance of 15.2 mF cm^{-2} and a high energy density of 7.3 mWh cm^{-3} while remaining stable under bending (Fig. 6**d, e**). Moreover, COFs can composite with other conducting polymers to enhance charge transfer and structural stability. The hollow dioxin-based COF-316 microflowers were synthesized *via* a self-template strategy (Fig. 6**f-h**), enabling sufficient combination with PPy [275]. Benefiting from the hydrogen bond interaction, COF-316@PPy based supercapacitors reached an areal capacitance of 783 μF cm^{-2} and exhibited the same electrochemical capacitance and stability under various bending states (Figs. 6**i, j**).

In addition to linking with redox units, incorporating active units as the catalytic sites into COFs presents an effective strategy to accelerate oxygen reduction and evolution reactions of metal-air batteries. In this regard, covalently integrating cobalt coordinated porphyrin units with benzene linkages into two-dimensional layers was reported to design porphyrin covalent organic framework as a bifunctional cathode catalyst for Zn-air batteries [53]. Further compositing with CNT scaffolds enabled the device with mechanical robustness and improved flexibility. The assembled flexible Zn-air batteries delivered a small voltage gap and exhibited stable operation under bending.

3.3. Polymer binders

Binders are a key segment of electrode slurry, which provide strong adhesion between electrode components and current collector and maintain electrode robustness during operation [44,276,277]. Polymeric binders can be typically divided into natural binders (*e.g.*, guar gum, carboxyl methyl cellulose, gelatin, and chitosan) and synthetic binders (*e.g.*, PVDF, polytetrafluoroethylene, poly(acrylic acid) (PAA), PVA, and styrene butadiene rubber) [196,278-280]. Although the binder makes up only 2–10 wt% of a

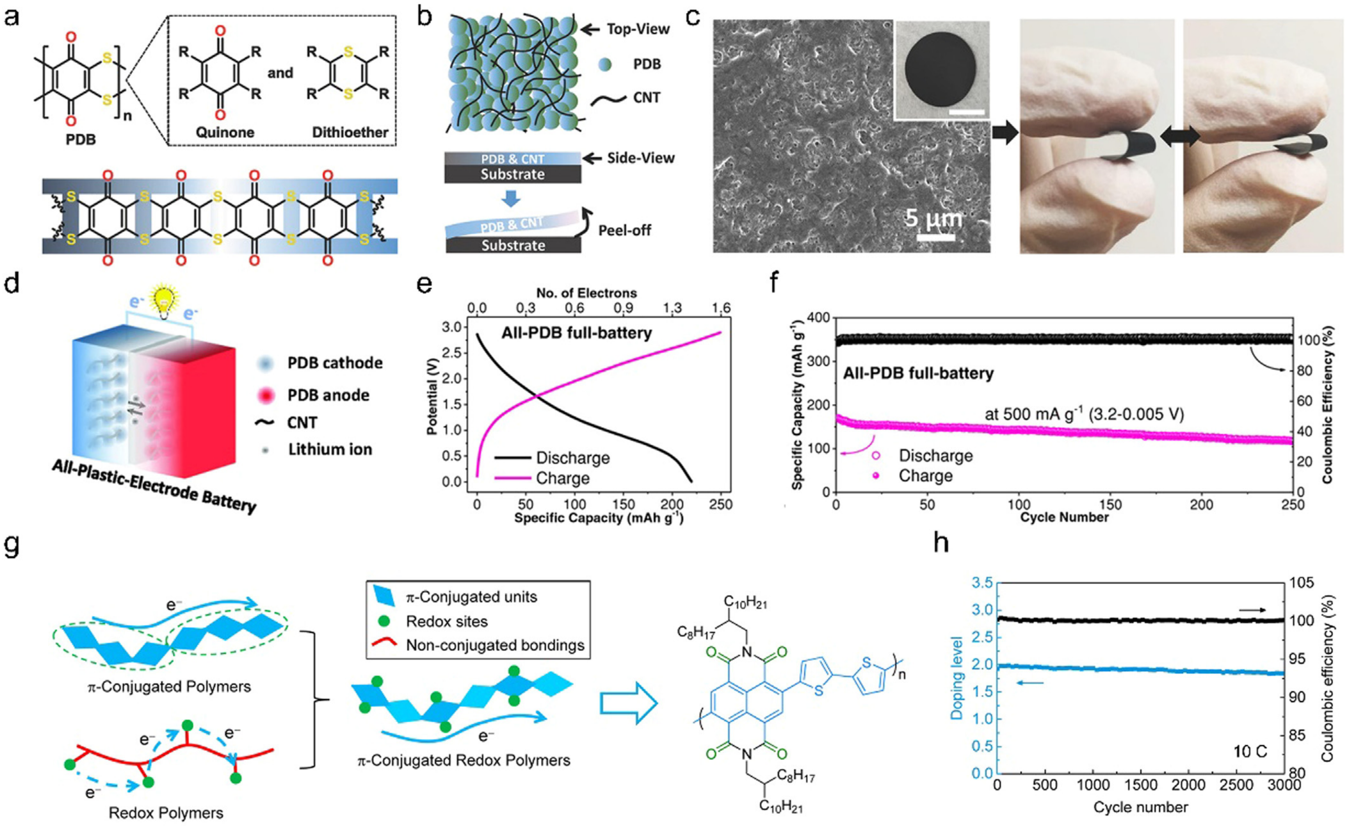

Fig. 5. (a) Chemical structure of PDB. (b) Schematic preparation of a free-standing PDB electrode film. (c) SEM image and photograph of a free-standing electrode film. (d) Schematic illustration of the all-PDB-electrode battery. (e) Charge and discharge profiles and (f) cycling performance of the all-PDB full battery. [48], Copyright 2020. Adapted with permission from John Wiley & Sons Inc. (g) Schematic structure of π-conjugated polymers, redox polymers, and π-conjugated redox polymers. (h) Reversibility of π-conjugated redox polymers during 3000 cycles at 10 C. [263], Copyright 2015. Adapted with permission from American Chemical Society.

composite electrode, it has a critical influence on the electrochemical performance of batteries [244]. Binders can provide the following functions during operation: (1) allow a homogeneous distribution of electrode slurry; (2) bridge electrode components with the current collector for mechanical stability; (3) provide pathways for the transfer of electrons and mass transport of ions. Several theory models are introduced to describe binding processes and mechanisms, including mechanical interlocking theory, chemical bonding theory, and thermodynamic mechanism. The adhesion strength between binders and electrode components is closely associated with interfacial bonding forces, including intermolecular forces and chemical bonds. The surface and porosity of electrode materials also affect the strength of the force.

PVDF is the most widely used binder in the Li-ion battery industry due to its good electrochemical stability and binding capability. However, a series of drawbacks, such as environmentally harmful fabrication process and limited electrical/ionic conductivity, need to be addressed for high-performance devices. Therefore, various novel polymeric binders have been designed to achieve strong binding capability [281–284], and high mechanical stability to preserve particle-particle cohesion under large volume changes of electrode materials, good chemical inertness to battery components, high electrochemical stability over a broad operation window (0–5 V), high wetting capability in electrolytes to enhance interactions with other electrode components, and minimal addition to ensuring high energy density. Particularly, providing strong adhesion to keep structural integrity is of great importance for flexible energy storage devices when faced with multiple deformations.

Recently, aramid nanofiber (ANF), a novel building block derived from Kevlar with exceptional mechanical properties, was used to reinforce the mechanical performance of electrodes [258]. The hybrid fiber electrode, with delaminated $Ti_3C_2T_x$ nanosheets as assembled units and 5% of ANF as a functional additive, exhibited a mechanical strength of 104 MPa. The assembled device maintained stable electrochemical performance under varying degrees of bending. In addition, ANF was used to tailor the microstructure of the bucky paper framework. strengthening CNT networks by π-π stackings and van der Waals forces. The resulting electrode achieved 6.5- and 24.4-times improvements in strength and toughness, without degradation in capacitance in supercapacitor [258].

Moreover, polymeric binders with dual or multiple functions (interconnection capability, conductivity, and self-healing ability) have attracted increasing attention. A unique alternate architecture of carbon nanocoil/PEDOT:PSS was constructed *via* a repeated drop-casting procedure [117]. The three-dimensional carbon nanocoils served as ion transfer channels, while the PEDOT:PSS ensured the stability of electrode structure and improved electron transfer kinetics. In addition, adopting the self-healing ability of polymers can accommodate large volume changes of electrode materials. To overcome the volume change of sulfur species and shuttle effect, a self-healing and polysulfide-trapping binder cross-linked by hydrogen bonds from polyvinylpyrrolidone and polyethyleneimine were designed [285]. The numerous carbonyl bonds (C = O) of polyvinylpyrrolidone and amino groups (-NH_2) of polyethyleneimine could regulate polysulfide redox kinetics, and the dynamic hydrogen-bonding networks enabled the self-healing ability to maintain stability during bending. The resulting flexible lithium-sulfur pouch battery remained over 95% of its initial capacity after 2800 bending cycles, contributing to the applications of high-performance flexible Li-S batteries.

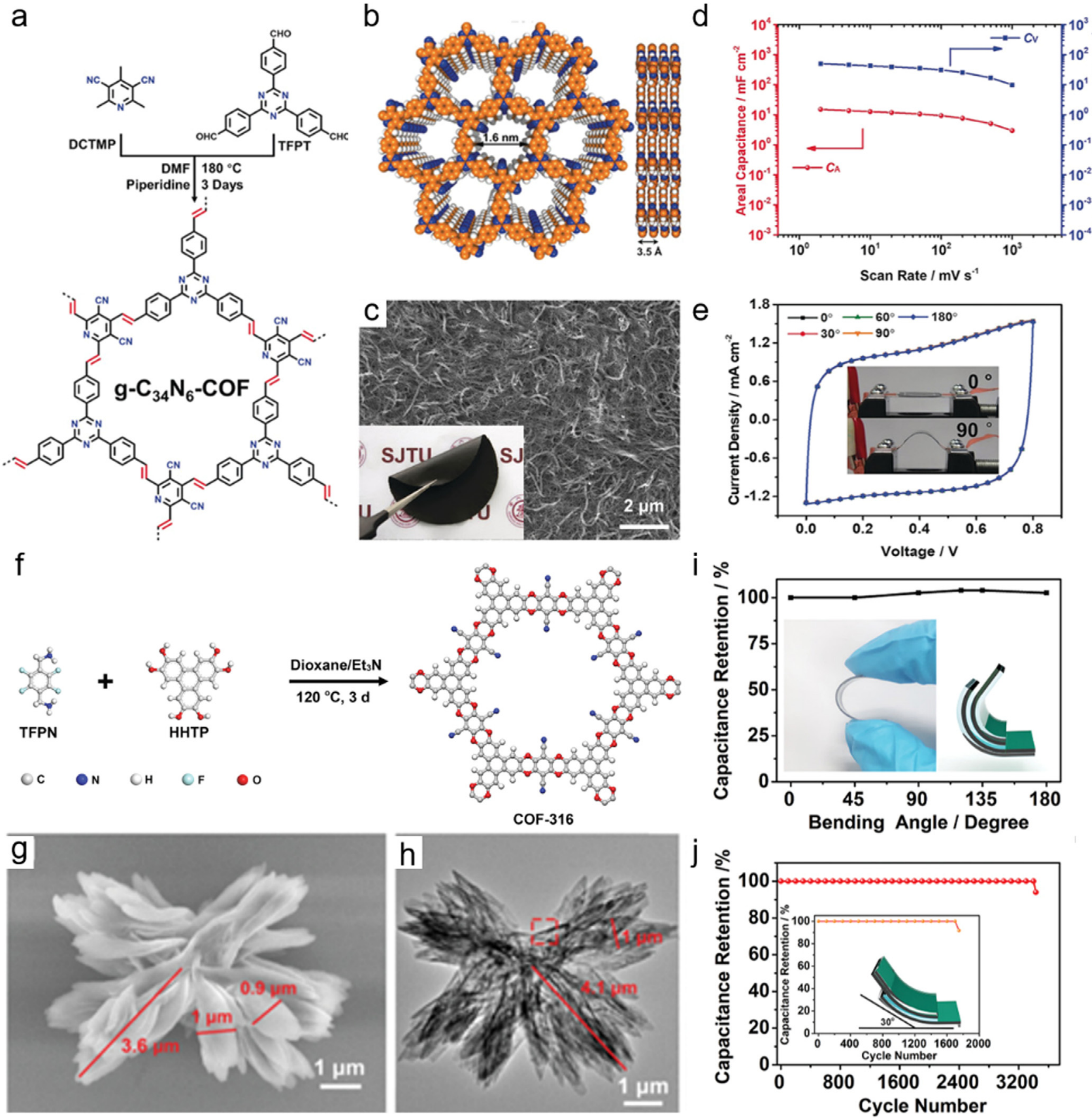

Fig. 6. (a) Synthesis and structure of g-$C_{34}N_6$-COF. (b) Eclipsed AA-stacking model of g-$C_{34}N_6$-COF. (c) SEM image of g-$C_{34}N_6$-COF/CNTs hybrid thin film (inset: optical photograph). (d) Specific areal and volumetric capacitances at different scan rates and (e) CV curves under different bending conditions at 50 mV s^{-1} of COF-based micro-supercapacitors. [274], Copyright 2021. Adapted with permission from John Wiley & Sons Inc. (f) Synthesis process of COF-316. (g) SEM and (h) TEM images of COF-316. (i) The capacitance retention curves under various bending angles at 50 mV s^{-1} and (j) the cycle stability of COF-316@PPy based supercapacitors. [275], Copyright 2019. Adapted with permission from John Wiley & Sons Inc.

3.4. Polymer-based supporting scaffolds

Traditionally, the electrode of a Li-ion battery is fabricated by coating the slurry on a metal-based current collector (*e.g.*, copper and aluminum foils) [286]. The planar metal-based current collector can ensure mechanical strength and charge transfer using a thin electrode with low mass loading. However, the development of commercial batteries with high-mass-loading electrodes and flexible configurations puts forward higher requirements for supporting scaffolds, which need not only ensure sufficient charge delivery through the bulk volume but also remain stable during deformations [115,197,287,288]. The unique mechanical flexibility and architectural designability of polymers offer the possibility of rational design for functional supporting scaffolds. The multiple-dimensional polymer-based supportive scaffolds can be used for energy devices with different configurations [289].

3.4.1. One-dimensional supporting scaffold

One-dimensional energy devices with high flexibility, multiple functions, and good tissue compatibility have received much attention for being weaved into textiles in recent years [117,251,290]. It can power a series of personalized electronics. One-dimensional

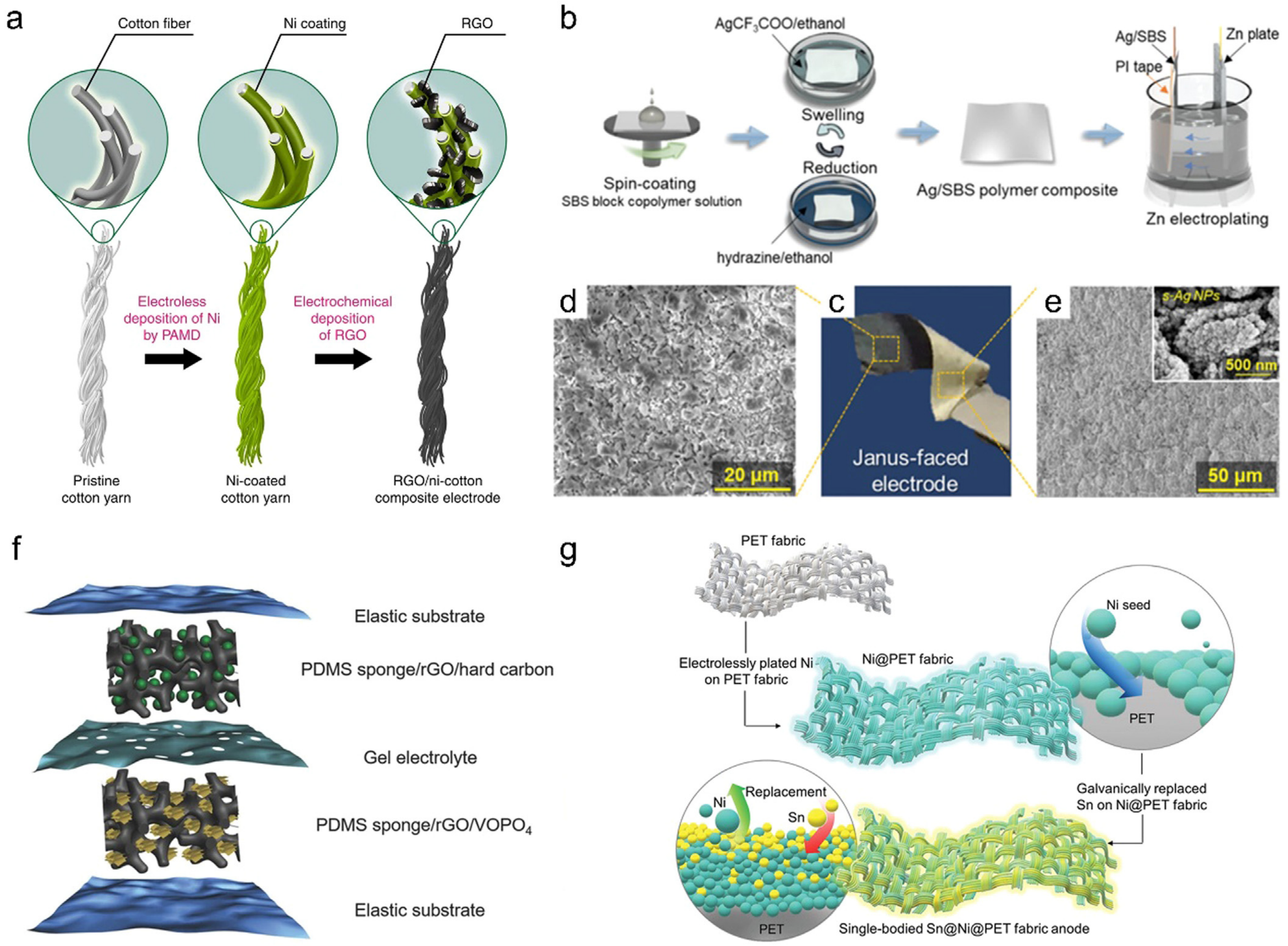

Fig. 7. (a) Schematic fabrication of rGO/Ni cotton yarn composite electrodes. [292], Copyright 2015. Adapted with permission from Springer Nature. (b) Schematic preparation of the Janus-faced electrode. (c) Optical image of the Janus-faced electrode. (d, e) SEM images of the Ag/SBS composite deposited with (d) zinc and (e) silver nanoparticles. [204], Copyright 2020. Adapted with permission from John Wiley & Sons Inc. (f) Schematic illustration of an all-stretchable-component Na-ion battery. [55], Copyright 2017. Adapted with permission from John Wiley & Sons Inc. (g) Schematic fabrication of the single-bodied Sn@Ni fabric electrode. [299], Copyright 2020. Adapted with permission from John Wiley & Sons Inc.

polymer substrates can be used as scaffolds to load electrode components. An efficient, scalable, and general strategy based on modified polyester fibers (M-PEF) was reported to construct high-performance textile and yarn electrodes [291]. The uniform rGO layer was anchored on the surface of M-PEF *via* a repeated dyeing and drying strategy to enable high conductivity for energy storage, and then PPy was electrodeposited as active materials. Benefiting from an efficient surface area and flexible substrate provided by the interconnected conductive fibers, the rGO/M-PEF-based supercapacitors achieved high electrochemical performance and remained stable when they suffered various deformations. In addition, a hierarchical graphene-metallic textile composite electrode was reported to achieve high-performance all-solid-state supercapacitor yarns (Fig. 7**a**) [292]. A thin layer of Ni was first deposited on the cotton yarns *via* the polymer-assisted metal deposition method to ensure flexibility, conductivity, and light weight, and then rGO nanosheets were coated on the inner and outer spaces of yarns by electrolyzing that provided enhanced double-layer capacitance.

3.4.2. Two-dimensional supporting scaffold

Compared with the rigid metal-based current collector, the two-dimensional polymer-based supporting scaffolds show the advantages of constructing intrinsically stretchable energy devices [198,203]. The SIBS was explored to construct an inherently stretchable zinc-manganese dioxide battery [199]. The SIBS could act as a membrane separator to transfer Zn ions, an adhesion agent to combine electrode components, and even an encapsulation layer to inhibit the permeation of gas and moisture. For example, an intrinsically stretchable supporting scaffold was obtained by mixing SIBS and highly conductive carbon black/carbon nanofibers. The resulting polymer-based battery could keep operation after 150 cycles at 100% strain. In addition, a novel Janus-faced electrode was reported with good mechanical robustness (200 cycles at 200% strain) and high electric conductivity (2.1 Ω at 100% strain) [204]. The SBS block-copolymer film was fabricated as a supporting scaffold by spin coating, and Ag nanoparticles and metallic zinc were deposited on the front and back sides of the polymer film, respectively (Fig. 7**b-e**). The resulting zinc-silver battery, based on the unique design, exhibited enhanced cycling stability and fixed discharge-charge platforms even under 200% strain.

3.4.3. Three-dimensional supporting scaffold

The conventional two-dimensional current collectors are hindered by the limited transport depth for a thick electrode with highly loaded active materials. By contrast, the three-dimensional supporting scaffold can offer efficient charge delivery and ion transport even for a practical electrode with high loadings. In general, a variety of elastic polymers with high mechanical flexibility and surface area, including PET, PDMS, PVDF, PEDOT, and PP have acted as the supporting scaffolds to load active materials [167]. Three-dimensional porous PDMS is the most widely used polymer-based supporting scaffold due to its high mechanical strength and flexibility [55,57,293]. In this regard, highly porous, stretchable, and conductive PDMS nanocomposites embedded with CNTs were synthesized for flexible LIBs [293]. The porous morphology was optimized by the controllable phase separation of poly(methyl methacrylate) (PMMA) in PDMS and the removal of polymethylmethacrylate. 670% higher storage capacity than a nonporous sample was achieved by optimizing the scale and distribution of pores. In addition, an all-stretchable-component Na-ion battery was constructed by graphene-modified PDMS sponge electrodes (Fig. 7**f**) [55]. The battery maintained high electrochemical performance under different stretched states and even after hundreds of etching-release cycles, providing a novel strategy for the applications of wearable energy devices.

In addition to the three-dimensional porous structure, the three-dimensional interwoven supporting scaffold can also provide efficient pathways for electrons and ions [237,294-297]. Meanwhile, softness is also a key parameter to evaluate the flexibility of wearable electronics. A universal electroless plating strategy was reported for decorating various metals (Ni, Co, Cu, and Ag) on different substrates including cotton cloth, paper, and sponge. High loading of active materials and high conductivity (4–200 kS/m) were achieved without sacrificing the softness. These decorated soft clothes could be directly used for Zn batteries which demonstrated high flexibility over 2000 cycles of folding [298]. Moreover, a hierarchical structure of a textile network fabricated by cotton fibers with a conductive layer of CNTs was developed as an air cathode for Li-O_2 battery [295]. The woven textile-based air cathode provided noncompetitive transport for O_2 and electrolyte, while O_2 flowed through the woven holes, and the electrolyte diffused along the fibers. Meanwhile, the textile-based air cathode could recover to its original shape after bending and twisting. Due to the decoupled pathways, the resulting Li-O_2 battery exhibited a low overpotential of 1.15 V and a high discharge capacity of 8.6 mAh cm^{-2}. To enhance the electrical conductivity of three-dimensional structures, there have been attempts to anchor metal nanostructures on the interwoven supporting scaffold. Apart from cotton cloth as a supporting scaffold, the thin metallic nickel layers were deposited on PET fabrics *via* electroless plating to produce a flexible current collector (Fig. 7**g**) [299]. And then, the metallic tin as active material was galvanically embedded in a nickel layer due to the difference in electrochemical potential. The tin@nickel fabric electrodes could maintain their dimensional integrity after 2000 bending cycles and multi-folded deformations. Benefiting from the well-interconnected ion transport channels and charge-conductive network, the fabric electrode provided enhanced electrochemical performance.

3.5. Summary and discussion

Developing flexible electrodes is crucial for flexible energy storage devices. By their intrinsic flexibility and high designability, polymers have been widely used as active materials, binders, and supporting scaffolds to achieve energy storage, structural stability, and provide mechanical support in flexible electrodes [244,300-302].

As active materials, conductive polymers, and redox group-bearing polymers show remarkable electrochemical properties in supercapacitors or batteries. Especially, redox-active polymers not only function as redox centers but also act as bridges to interact with other components and enhance device resistance to deformations. For example, the intramolecular valence bonding (grafting to/from substrates) or intermolecular interaction (π-π interaction/stacking) between organic polymers and conductive additives provide multiple pathways for electron transfer and enhanced stability at discharged/charged states. Meanwhile, by their good affinity to organic solvents, fast penetration of electrolytes accelerates mass transport to redox-active polymers. The strong adhesion between polymers and current collectors and the high mechanical properties of polymer backbones can avoid detachment and delamination under various deformations of electrodes. Therefore, many efforts have been devoted to enhancing these interactions. In addition to improving the electrochemical performance of redox-active polymers, further research should also focus on understanding the mechanism of polymer chains under deformations and achieving a trade-off between the electrochemical performance and flexibility of devices.

Binders are mainly divided into natural and synthetic polymer materials. PVDF is a classical and common synthetic binder in cathodes, while styrene-butadiene rubber and polytetrafluoroethylene are typical anode binders. To keep the structural integrity of electrodes under deformations, polymeric binders with higher mechanical strength and additional functionalities have been developed for flexible devices. ANF, as a building block with superior mechanical performance, has been introduced to preserve cohesion among electrode components, ensuring stable electrochemical performance even under extreme deformations. Meanwhile, developing polymeric binders with dual or multiple functions (*e.g.*, ion transport, electron conduction, and self-healing) can improve the mechanical and electrochemical performances of flexible energy storage devices. These multiple roles could be achieved through compositing or bonding with functional additives. For example, covalent linking traditional binders with single-ion conducting polymers can facilitate ion transport in the electrodes. Besides, further research should consider the crosslinking efficiency to ensure stable operations with minimal additions.

Polymers used as supporting scaffolds should be mechanically robust and flexible to maintain the structural integrity of electrodes under repeated deformations. To this end, supporting scaffolds are commonly made by high-strength (*e.g.*, aramid [290], PE [251], polyester [291], and polyethyleneterephthalate (PET) [299,303]) or high-elasticity resins (*e.g.*, poly(styrene)-*b*-poly(ethyleneran-butylene)-*b*-poly(styrene) [203], polydimethylsiloxane (PDMS) [55,57,198,293], poly(styrene-isobutylene-styrene) [199], and poly(styrene-*b*-butadiene-*b*-styrene) (SBS) [204]). In addition, the supporting scaffolds are expected to have high electrical conductivities. Thus, polymers are generally composited with highly conductive materials such as metal and carbon. And the engineering and structural design of flexible polymer-based supporting scaffolds are required to enhance the compatibility of interfaces between the supporting scaffolds and active materials. A good interfacial contact can strengthen the adhesion of active materials on the supporting scaffolds, avoid detachment of active materials from supporting scaffolds after repeated deformations, and increase the loading contents of active materials for higher energy densities.

Currently, the low-efficiency preparation techniques of flexible electrodes are hindering the large-scale production of flexible energy devices. However, the design of an ideal current collector has the potential to significantly accelerate the continuous fabrication of flexible electrodes. There are facile and scalable strategies, such as mix-weaving polymer fibers with metal wires or plating metal layers on polymer substrates, to produce polymer/metal composite current collectors which are expected to meet the demand for scalable production of flexible electrodes. These composites not only provide high conductivity equivalent to that of a metal current collector, but they also inherit outstanding mechanical properties, such as tensile strength and fatigue resistance, from the polymer substrate.

4. Polymers for electrolytes

The electrolyte is a vital component of energy storage devices as it provides ion-transfer pathways through the electrodes and maintains the required electrochemically stable potential windows for the charging/discharging process. it is an indispensable component and largely impacts performance of energy storage device. Electrolytes used in flexible devices share the same basic property requirements as traditional devices, such as high ionic conductivity, superior electrochemical stability, and extraordinary safety. Nevertheless, conventional liquid electrolytes, despite their inherent high ionic conductivities, face practical limitations due to persistent side reactions, leakage issues, and safety concerns, hindering their practical applications.

In recent years, there has been a growing interest in solid-state electrolytes as potential solutions to the challenges associated with conventional liquid electrolytes. These solid-state electrolytes, both inorganic and polymer-based, offer enhanced electrochemical and thermal stability. They are highly appealing for flexible energy storage devices due to their non-toxic, non-flammable, and leak-free nature. The inorganic solid-state electrolytes without any rubber-like additives cannot be deformed due to their brittle and rigid nature, thus inapplicable to deformable cells. In comparison, polymer-based solid-state electrolytes exhibit excellent mechanical stability and flexibility, enabling successful assembly of bendable devices due to their favoring interfacial compatibility with electrodes. Polymer-based solid-state electrolytes can be further classified into solid-state, gel, and composite polymer electrolytes. In this section, the design requirements of polymer electrolytes with the specific applications are introduced.

4.1. Design requirements of polymers for electrolytes

As one of the major components of an electrochemical power device, electrolyte plays an important role in the electrochemical process. For example, the electrochemical stable potential window of the electrolytes determines the operating voltage and thus the capacitance of supercapacitors. Widening the electrochemical stable potential window of electrolytes will improve energy density effectively [76]. For the batteries, many redox chemistries only exhibit their energy storage capability at high potentials. The electrochemical process between $LiCoO_2$ and graphite (the typical redox reactions of commercial batteries), for instance, only delivers its high energy-density and reversibility in the electrolyte with a stable potential window of $>$ 4.5 V.

However, the traditional electrolytes with high electrochemically stable potential windows are commonly composed of volatile and combustible organic solvents, which brings serious safety hazards. This is a fatal defect, especially for flexible and wearable power sources. To this end, non-flammable aqueous and ionic liquid electrolytes are employed to enhance the safety of flexible power devices [304]. However, these safe electrolytes suffer from either relatively low electrochemically stable potential windows or high economic costs, which limits their applications in flexible electrochemical power devices.

In this context, solid-state electrolytes inspired great research interests owing to its higher safety and thermal/(electro)chemical stability compared with liquid electrolytes [305]. The inorganic solid electrolyte is known for its high ionic conductivity of up to 10 mS cm^{-1} and high mechanical strength [306]. However, the poor interfacial contacts with electrodes, hazardous parasitic reactions with high-active anodes like Li metal, [307,308] and the brittle nature and bare flexibility pose challenges in device assembly and practical applications, especially for flexible devices requiring high deformability. On the contrary, polymer-based solid electrolytes present higher flexibility, stable interfacial property and good adhesion to electrodes, low cost, light weight, and manufacturing scalability, making them promising for use in practical flexible batteries and supercapacitors [309,310]. In recent years, the rise of solid-state flexible and wearable energy storage devices also boosts the development of polymers as electrolytes.

In consideration of the promising advantages of polymer-based solid-state electrolytes, a large number of research efforts have been devoted to designing new polymer electrolytes to enable flexible power sources with high safety and energy densities and novel properties like stretchability and self-healability. To meet the demands of fast ionic transport kinetics and reversible redox chemistry for energy storage, the polymer-based electrolytes are expected to satisfy the following several key parameters: (1) have a wide electrochemically stable potential window; (2) have electrical insulation and ionic conduction to deliver charge carriers upon redox reactions; (3) well dissociate the ion pairs of the electrolyte salts; (4) match with the electrode materials to maximize the electrochemical activities of electrode materials; (5) have good thermal stability at the wide range of temperatures for the safe operation of devices; (6) exhibit good interfacial contact with electrodes to endow efficient mass transport at the interfaces; and (7) have moderate mechanical robustness to avoid direct contact of two electrodes and the short circuit of cells [84,311-313]. The difficulties in designing ideal polymer electrolytes not only lie in the rareness of integrating all these requirements in a single polymer material but also stem from maintaining all these features for thousands of charge-discharge cycles. Currently, a variety of electrolyte materials have been designed for electrochemical power devices according to the aforementioned requirements [59,61,309,314,315].

In addition to the universal requirements introduced above, polymer-based electrolytes for flexible energy storage are supposed to deliver some other unique characteristics, such as stretchability [61,74,186,202,316], self-healability [61-63,317], adhesiveness [238,285,318], freezing resistance [186,318-321], biocompatibility [238], and biodegradability [64] to expand the applications and enhance the adaptation of the flexible devices in a complicated and volatile environment.

4.1.1. Stretchability

The emerging stretchable electronics have recently aroused wide attention owing to their excellent flexible, smart, and anti-deformation properties [117]. This also comes with the urgent need for designing matchable stretchable energy storage devices. Generally, the stretchability of energy storage devices is supported by elastic electrolytes [317]. In this consideration, polymer-based materials with intrinsic elasticity can easily provide superior stretchable properties, thus representing promising candidates as electrolytes for stretchable energy storage devices. In particular, polymeric hydrogels with intrinsic stretchability have been extensively studied as electrolytes, such as anionic polyurethane acrylates/PAM hydrogel [58], vinyl hybrid silica nanoparticles/PAA hydrogel [59], Al^{3+} ionically crosslinked alginate [60] and poly(2-acrylamido-2-methylpropane sulfonic acid-*co-N, N*-dimethylacrylamide) hydrogel [61], for stretchable supercapacitors.

4.1.2. Self-healability

Self-healing refers to the capacity to recover from mechanical failure spontaneously, which is a critical survival property in nature [59,188]. Inspired by this unique feature, a variety of self-healing polymers are developed to get over the mechanic damage of materials *via* restoring the broken interfaces by hydrogen bonding, host-guest interaction, thermoplastic elastomers, reversible chemical bonds, and coordination [188,190,210]. It is almost inevitable for flexible devices to suffer from damage after thousands of deformations. To improve the dependability of flexible/stretchable energy storage devices, various self-healable polymer materials, such as PVA [62], ferric-ion-crosslinking sodium polyacrylate [63], flour [64], and PAA [59], are employed into their systems to serve as electrolytes. With these self-healable electrolytes, flexible and wearable power devices, coupled with self-healability, have particularly become mainstream in portable electronics.

4.1.3. Adhesiveness

In practical applications, flexible devices tend to fail from mechanical deformation, especially after numerous cycles, resulting generally from the interface detachment between electrolyte and electrode. Hence, in addition to the fundamental demand like high ionic conductivity, electrolytes used in the deformable devices should possess good adhesiveness to electrodes to avoid the separation between electrolyte and electrode and construct stable electrolyte-electrode interfaces [285]. Benefiting from their abundant functional groups, polymer electrolytes commonly possess intrinsic adhesiveness to electrodes allowing for the formation of strong and continuous electrode-electrolyte interfaces, favoring lowering interfacial resistance and enhancing deforming robustness of flexible energy storage devices.

4.1.4. Freezing resistance

Low temperatures will lead to significant performance degradation of power devices resulting from the considerably reduced ionic conductivity of electrolytes. This problem worsens for flexible devices due to the serious mechanical deformation at low temperatures. In general, polymer-based electrolytes with poor temperature tolerance will lose their conductivity and flexibility at freezing temperatures, and the devices can only operate a few cycles with limited deformability [322–324]. The poor low-temperature resistance of electrolytes significantly limits their applications in cold environments, and thus remarkable freezing resistance is constantly pursued for the polymer-based electrolytes. Currently, temperature-tolerance of polymer-based electrolytes has been enhanced by compositing deicing agents, such as inorganic salts (*e.g.*, NaCl, LiCl, and $CaCl_2$) or organic solvents (*e.g.*, ethylene glycol and glycerol), into the polymer matrices [65–69].

4.1.5. Biocompatibility and biodegradation

Implantable energy-supply devices are the key components of emerging implantable medical devices for disease diagnosis and treatment. For a power device implanted inside the human body, it should be flexible enough to match the modulus of biological tissue and biocompatible and biodegradable to avoid potential safety hazards or toxicity and surgical removal after completing their missions, aiming to decrease the patients' pain, the risk of wound infection, and various chronic inflammations resulted from secondary trauma to patients [325,326]. As an important part of implantable power device, the electrolyte is also expected to be biocompatible and biodegradable. The key to fabricating biocompatible and biodegradable electrolytes lies in using biocompatible polymers and natural biodegradable materials, such as cellulose [70], agarose [71,72], flour [64], and sodium alginate [73], instead of toxic or non-degradable materials.

4.2. Solid polymer electrolytes

Solid polymer electrolytes are fabricated by solvating metal salts, especially alkali metal salts, in polymer matrices. Driven by electric fields, metal ions move from the electron-donor groups along polymer long chains to the adjacent electron-donor sites by a hopping process. Due to high metal-ion mobility, polymers with high metal-ion dissociation ability, such as poly(ethylene oxide) (PEO) [327–329], poly(vinylidene fluoride)-*co*-hexafluoropropylene (PVDF-HFP) [330–334] and PMMA [335], are commonly used.

4.2.1. Polyether-based solid polymer electrolytes

Polyethers consist of a sequential chemical structure of ether bonds, which can dissociate and complex metal salts by the coordination effect between metal ions and oxygen atoms, as well as ensure superior flexibility of macromolecular backbone and sufficient ionic dynamics within the polymer matrices. Therefore, PEO and its derivatives, the typical polyethers, are the most widely used polymer matrices of solid polymer electrolytes. However, high crystallinity of PEO leads to low ion conductivity (10^{-8}–10^{-6} S cm^{-1}) and inferior metal-ion transference number (0.2–0.3) at room temperature, which seriously deteriorates the capability of the energy storage devices. For this reason, various methods have been designed to synthesize PEO-based solid polymer electrolytes with good mechanical properties, superior electrochemical stability, and high ion conductivity.

Crosslinking is an effective method to decrease crystallinity while substantially improving the mechanical strength and thermal stability of solid polymer electrolytes. Hence, a polyether-based self-healing solid-state electrolyte was prepared by the polycondensation of amino-terminated poly(ethylene glycol) (PEG) and thermoplastic polyurethane (Fig. 8**a**) [336]. The electrolyte with a cross-linked network with dynamic intermolecular/intramolecular hydrogen bonds showed rapid self-healing and rigid-soft coexisting stability. The electrolyte could regulate the electrochemical behavior of metallic Li to prepare solid Li metal batteries with excellent cycling stability and free bending flexibility. Another cross-linked PEG-based resin was also constructed by a ring-opening reaction of poly(ethylene glycol diglycidyl ether) (PEGDE) with epoxy groups and poly(ether amine) with amino groups [337]. By confining the hydroxyl groups with inferior oxidative stability to the PEG backbone, the oxidation potential of the PEG-based polymer material with reduced reactivity was boosted to 4.36 V, providing new insights for high-voltage flexible LIBs.

Blending with other polymers has also been widely used to increase the ionic conductivity of solid polymer electrolytes by suppressing crystallization and improving T_g of PEO. In this consideration, a polyether-based solid polymer electrolyte with a double network was developed by reasonably controlling the chain length of the constitutional unit (Fig. 8**b**) [338]. With the self-plasticization of its double network, the bendable double-network electrolyte exhibited increased ionic conductivity (from 10^{-5} to $10^{-4.5}$ S cm^{-1} at room temperature), high thermal stability (up to 200 °C) and good capacity to suppress the growth of Li dendrite. The pouch cells maintained their electrochemical functions under bending and truncated conditions.

4.2.2. Poly(vinyl fluoride)-based solid polymer electrolytes

PVDF-based polymers with a semi-crystalline structure and strong electron-withdrawing functional groups (-CF) have a high dielectric constant ($\varepsilon = 8.4$) and great solubility of metal salts, thus delivering higher electrochemical stability and increased ionic conductivity. For instance, PVDF-HFP, a typical type of poly(vinyl fluoride)-based polymers, was introduced to design the polymer-in-salt solid electrolyte with high ionic conductivity of 1.24×10^{-4} S cm^{-1} at room temperature (Fig. 8**c**) [334]. The as-fabricated pouch cells exhibited robust flexibility and excellent electrochemical performance even under bending. In addition, the flexible cells also exhibited high safety after abuse tests without internal short circuits or burns, showing great potential in practical applications.

Developing rigid-flexible coupling composite electrolytes to combine the merits of two kinds of electrolytes can be a

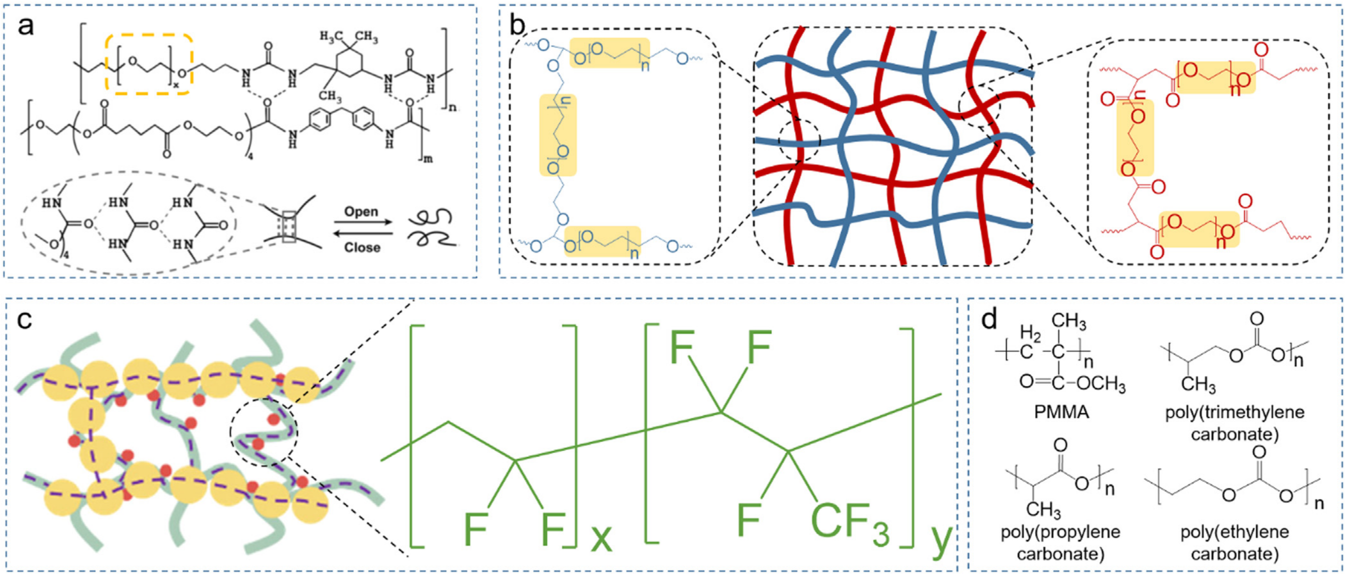

Fig. 8. (a) Molecular structure and dynamic hydrogen bonding for polyether-based self-healing solid-state electrolyte. [336], Copyright 2019. Adapted with permission from John Wiley & Sons Inc. (b) In situ formed polyether-based electrolyte with double network. (c) Schematic diagram of poly(vinyl fluoride)-based polymer-in-salt solid. [334], Copyright 2021. Adapted with permission from John Wiley & Sons Inc. (d) Molecular structures of PMMA, poly(propylene carbonate), poly(trimethylene carbonate), and poly(ethylene carbonate).

feasible strategy to achieve excellent comprehensive properties. A poly(vinylidene fluoride)-polyetherimide@poly(ethylene glycol) (PVDF-PEI@PEG) solid polymer electrolyte was developed by an *in situ* thermal curing approach [332]. The homogeneous PVDF-PEI composite porous membrane with an optimized PVDF and PEI weight ratio increased the amorphous phase, while the fast Li-ion transport channels were formed through the filled poly(ethylene glycol) electrolytes. The as-fabricated flexible $LiFePO_4$//Li battery delivered high specific capacities of 132.4 and 111.5 mAh g^{-1} with retention of 86.6% and 85.9% after 200 cycles at 2 C and 100 cycles at 3 C rate under 60 °C, respectively, demonstrating the feasibility as an energy storage device with high-rate capability.

4.2.3. Polyester-based solid polymer electrolytes

Polyesters containing the ester functional group in each repeat unit, such as PMMA, poly(ethylene carbonate), poly(trimethylene carbonate), and poly(propylene carbonate), have also been investigated as polymer host in solid polymer electrolytes due to their high ionic conductivity, wide electrochemical stability window, and good compatibility with electrode materials (Fig. 8**d**). For example, an ultrathin and high-strength solid polymer electrolyte with excellent interface compatibility was reported for flexible all-solid-state lithium-metal batteries [335]. The electrolyte was prepared by modifying PE separators with porous interfacial layers poly(methyl methacrylate)-polystyrene (PMMA-PS) and filling the separator with poly(ethylene glycol methyl ether acrylate)/LiTFSI electrolyte. PMMA improved the electrode compatibility while PS enhanced the mechanical strength of solid polymer electrolytes. The resulting 10 μm-thick electrolytes exhibited a room-temperature ionic conductivity of 34.84 mS cm^{-1} and mechanical properties of 103.0 MPa with elongation up to 142.3%. The $LiFePO_4$//Li pouch cells could work stably after various deformations, demonstrating their excellent flexibility and safety.

4.3. Gel polymer electrolytes

Despite of the above advantages, solid polymer electrolytes with low ionic conductivity cannot meet the requirements of many practical applications due to the extremely dense packing of polymer chains and limited chain segments. Typically, gel polymer electrolytes consist of a polymer matrix, a solvent, and an electrolyte salt. PEO, polyacrylonitrile (PAN), PVDF, PVDF-HFP, and PMMA have been commonly employed as polymer matrices. Plasticizers preferentially include water, carbonates, ethers, and ionic liquids. The transport of metal ions mainly occurs in the liquid plasticizers, while the polymer matrices provide the electrolytes with mechanical strength and keep them in a quasi-solid state, thus minimizing safety risks caused by the leakage of liquid components. The applications of gel polymer electrolytes have stimulated the development of flexible and wearable energy storage devices due to their high flexibility, sufficient ionic conductivity, and enhanced safety. In the following section, recent progress related to the gel polymer electrolytes used in flexible energy storage devices will be reviewed and discussed.

4.3.1. Poly(vinyl alcohol)-based gel polymer electrolytes

Among various polymer-based hydrogels reported, PVA-based hydrogels have been widely used due to their low cost and facile fabrication [62,163,185,282,317,319,339-344]. More importantly, PVA with abundant hydrophilic hydroxyl functional groups has a good affinity for the aqueous solution and good tolerance to strong acidic (*e.g.*, H_2SO_4 and H_3PO_4) [345] and alkaline (*e.g.*, KOH) environments [204,346].

Wearable electronics require the energy-storage systems to possess outstanding reliability in case of mechanical damage. PVA-based hydrogel prepared under appropriate conditions can self-heal once damaged owing to a large amount of hydroxy side groups in PVA chain segments and the O–H···O hydrogen bonds. A self-healing gel polymer electrolyte with a dynamic PVA grafted with *N,N,N*-trimethyl-1-(oxiran-2-yl)methanaminium chloride (TMAC) network cross-linked *via* diol-borate ester bonding was designed recently (Fig. 9**a**) [317]. The grafting of quaternary ammonium groups could reduce the coagulation of PVA chains and improve the malleability and salt-tolerance of the resulting copolymers, while the introduction of dynamic diol-borate bonding endowed PVA-*g*-TMAC network self-healing capability (Fig. 9**b**).

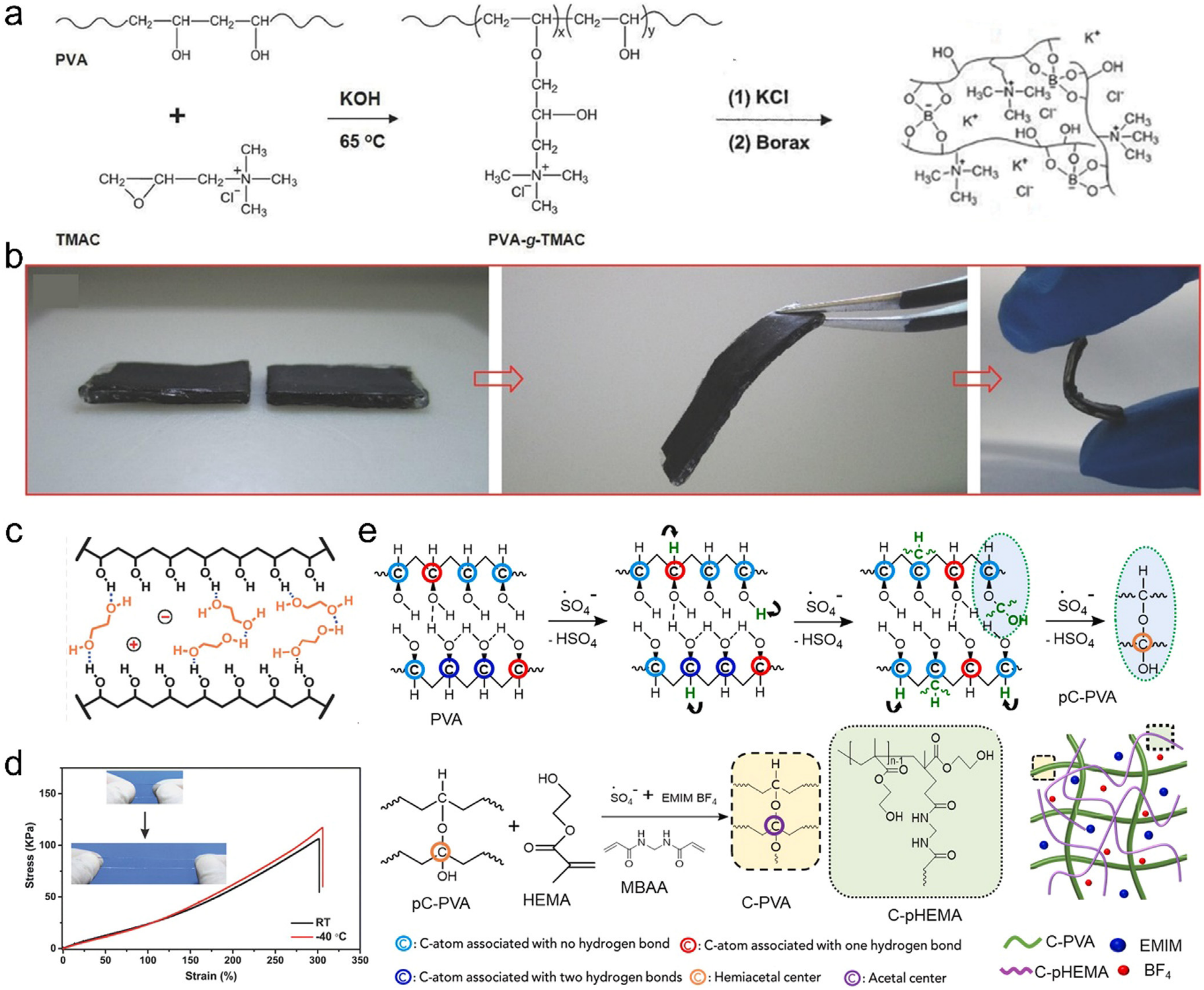

Fig. 9. (a) Illustration of the PVA-based anti-freezing organohydrogel. (b) Cut and self-healing of the capacitor of the PVA-based anti-freezing organohydrogel. [317], Copyright 2017. Adapted with permission from John Wiley & Sons Inc. (c) Schematic of the ethylene glycol/PVA anti-freezing gel electrolyte. (d) Tensile stress–strain curves of the organohydrogel electrolyte at room temperature and −40 °C. Inset: photographs of the organohydrogel electrolyte at a released state and 300% strain. [319], Copyright 2018. Adapted with permission from John Wiley & Sons Inc. (e) Synthetic chemical reaction of the PVA/C-pHEMA double network ionogel. [349], Copyright 2019. Adapted with permission from Elsevier Science Ltd.

The as-fabricated capacitor recovered its configuration, mechanical properties, and ion migration paths after self-healing. Other self-healing PVA/Zn(CF_3SO_3)$_2$ hydrogel was also applied in Zn-ion batteries [62].

A wide temperature window is also important for battery application. A new anti-freezing organohydrogel was constructed by incorporating H_2O/ethylene glycol solvent into PVA networks by hydrogen bonds and PVA crystallization (Fig. 9**c**) [319]. The H_2O/ethylene glycol binary solvent could lower the freezing point of water and dissolved ions, making PVA gels good ionic conductors at low temperatures even at −40 °C. Besides, the solvent molecules could form hydrogen bonds with PVA chains, which greatly improved the mechanical strength of the organohydrogels that could be stretched up to 300% (Fig. 9**d**). The as-fabricated supercapacitors based on this organohydrogel electrolyte exhibited good flexibility and electrochemical performance at low temperatures, paving the way for future flexible energy devices used in subzero temperatures. Montmorillonite materials are reported to be excellent dopants with the capability of enhancing the thermal properties of polymers [159,347,348]. Montmorillonite flake/PVA organic hydrogel electrolytes were reported for full-temperature flexible fiber supercapacitors operated at a wide temperature range of −40 to 80 °C [282].

Ionic liquid-based gel electrolytes with non-volatility, non-flammability and wide potential window (up to 3.5 V) could widen the operating temperature window. Hence, a double network ionogel film consisting of densely crosslinked PVA and sparely crosslinked poly(2-hydroxyethyl methacrylate) (C-pHEMA) was synthesized *via* a two-step thermally-initiated free-radical polymerization for high-temperature flexible supercapacitors (Fig. 9**e**) [349]. The double network of hard and soft components could effectively dissipate mechanical stress and maintain flexibility, demonstrating the tensile strength of 1.4 MPa, stretchability of 500%, and dissipation energy of 216 kJ m^{-3}. Besides, high amounts of ionic liquids (> 60 wt%) confined within the double network provided a high ionic conductivity of 36.8 mS cm^{-1}. In addition, ionogels exhibited good thermal stability to 100 °C. The fabricated supercapacitor achieved an energy density of

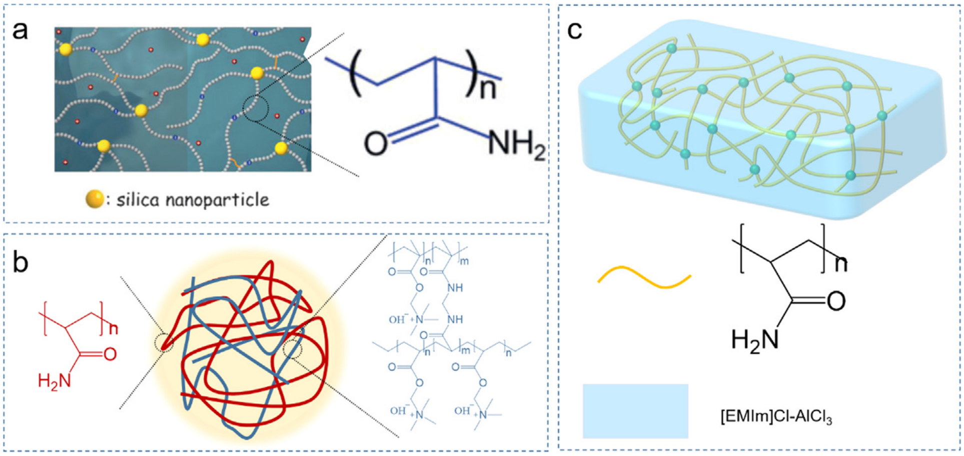

Fig. 10. (a) Illustration of vinyl hybrid silica nanoparticles cross-linking PAM-based gel electrolyte. [350], Copyright 2017. Adapted with permission from John Wiley & Sons Inc. (b) Schematic diagram of PAM/PDMC bioinspired polymer gel electrolyte. (c) Schemes of the PAM-based ionogel electrolytes.

51.0 Wh kg^{-1} at 180 °C and a durability of 91% over 100,000 cycles.

4.3.2. Polyacrylamide-based gel polymer electrolytes

PAM-based hydrogels with numerous hydrophilic amide groups (-CONH$_2$) and network structures have attracted much attention because they can accommodate water molecules and facilitate ion mobility [74,203,238,253,319,320,350-355]. However, pure PAM exhibits poor mechanical properties. Therefore, chemically crosslinked network was introduced in PAM-based gel polymer electrolytes [186,202,356]. For example, a hydrogel polyelectrolyte was developed by comprising PAM cross-linked by vinyl hybrid silica nanoparticles (Fig. 10**a**) [350]. The PAM as a hydrogel matrix provided good toughness, while the vinyl hybrid silica nanoparticles as stress buffers dissipated energy when a large strain was applied. The polyelectrolyte could be stretched to 1500% strain. The supercapacitors could be stretched to 1000% strain and compressed to 50% strain with good capacity retention. This work paved the way for the development of modern electronics, such as flexible energy devices and soft robot.

Besides, combining different kinds of polymer networks can also improve the mechanical properties of gel polymer electrolytes [351,353,357,358]. A bioinspired gel polymer electrolyte with a dynamic dual-penetrating network structure was developed by *in situ* formation of OH$^-$ conductive ionomer network (poly(methacrylatoethyl trimethyl ammonium hydroxide), PDMC) within a hydrophilic PAM hydrogel polymer (Fig. 10**b**) [351]. The OH$^-$ conductor could improve the water-retention capacity and ion conductivity of PAM electrolytes. The gel polymer electrolytes exhibited good water uptake of 107 g^{-1} and water retention and high ion conductivity of 215 mS cm^{-1}. The fabricated solid-state Zn–air batteries exhibited outstanding flexibility and electrochemical performance with cycling stability of 320 h.

PAM-based ionogels were also employed to construct robust electrode-electrolyte interfaces. A PAM-based [EMIm]Cl-AlCl$_3$ gel polymer electrolyte was prepared for flexible solid-state Al-ion batteries, which could accommodate the strain upon mechanical bending and suppress the production of gasses (Fig. 10**c**) [352]. Such gel polymer electrolytes enabled the Al-ion battery to present an ultra-fast charge capability within 10 s at 600 mA g^{-1} and an impressive specific capacity ~120 mAh g^{-1} at 60 mA g^{-1}, highlighting a novel approach for achieving high-performance flexible energy storage systems with enhanced stability and safety.

4.3.3. Poly(acrylic acid)-based gel polymer electrolytes

In addition to PAM-based hydrogels, PAA with carboxyl groups has excellent water retention capability, interesting mechanical and electrochemical functions after swelling in aqueous electrolyte, which has also been applied as hydrogel electrolyte for flexible energy storage devices [59,63,69,238,318,359-362]. For example, the sodium polyacrylate-based hydrogel demonstrated a good ionic conductivity of 11.5 mS cm^{-1} after soaking in KOH and Zn(CH$_3$COO)$_2$ mixture electrolyte. A flexible solid-state Zn battery was constructed by combining the sodium polyacrylate-based hydrogel electrolyte and carbon cloth-based electrodes, displaying a high capacity retention of 84.7% after 1500 cycles at 5 A g^{-1} [362]. However, the fabrication of hydrogels with adhesiveness and high robustness in harsh-temperature conditions and long-term use remains a challenge. The glutinous-rice-inspired adhesive organohydrogels were reported by introducing amylopectin into a PAA-based copolymer network through a “one-pot” crosslinking procedure in a glycerol-water mixed solvent containing potassium chloride as the conductive ingredient (Fig. 11**a**) [318]. The PAA-based organohydrogels exhibited excellent transparency ($>$ 90%), conductivity, stretchability, tensile strength, adhesiveness, anti-freezing properties, and moisture retention ability. Detachable and durable batteries and all-in-one supercapacitors were also fabricated utilizing the organohydrogels as electrolytes.

Besides, PAA will lose its mechanical robustness when incorporated with a strong alkaline electrolyte. To solve this problem, an alkaline gel electrolyte was developed through multiple crosslinking reactions among PVA, PAA, and GO, followed by infiltration of KOH and KI solution for flexible Zn-air batteries (Fig. 11**b**) [360]. The highly hydrophilic PAA-based network hydrogel exhibited improved water retention capability and ion conductivity of 155 mS cm^{-1}, and I^- anions as reactive modifier additive reduced the charging potential. The fabricated flexible Zn-air batteries delivered low charging potential of 1.69 V, long working life of 200 h, and high reliability under extreme deformations. In addition, another kind of dual-network hydrogel electrolyte was also developed by physically and chemically cross-linking sodium polyacrylate and cellulose, which enable a super-stretchable, flat-(800% stretchable) and fiber-shaped (500% stretchable) zinc–air batteries (Fig. 11**c**) [361]. This as-fabricated super-stretchable fiber-shaped battery demonstrated high power density of 108.6 mW·cm^{-2}, even increasing to 210.5 mW·cm^{-2} upon stretched by 800%.

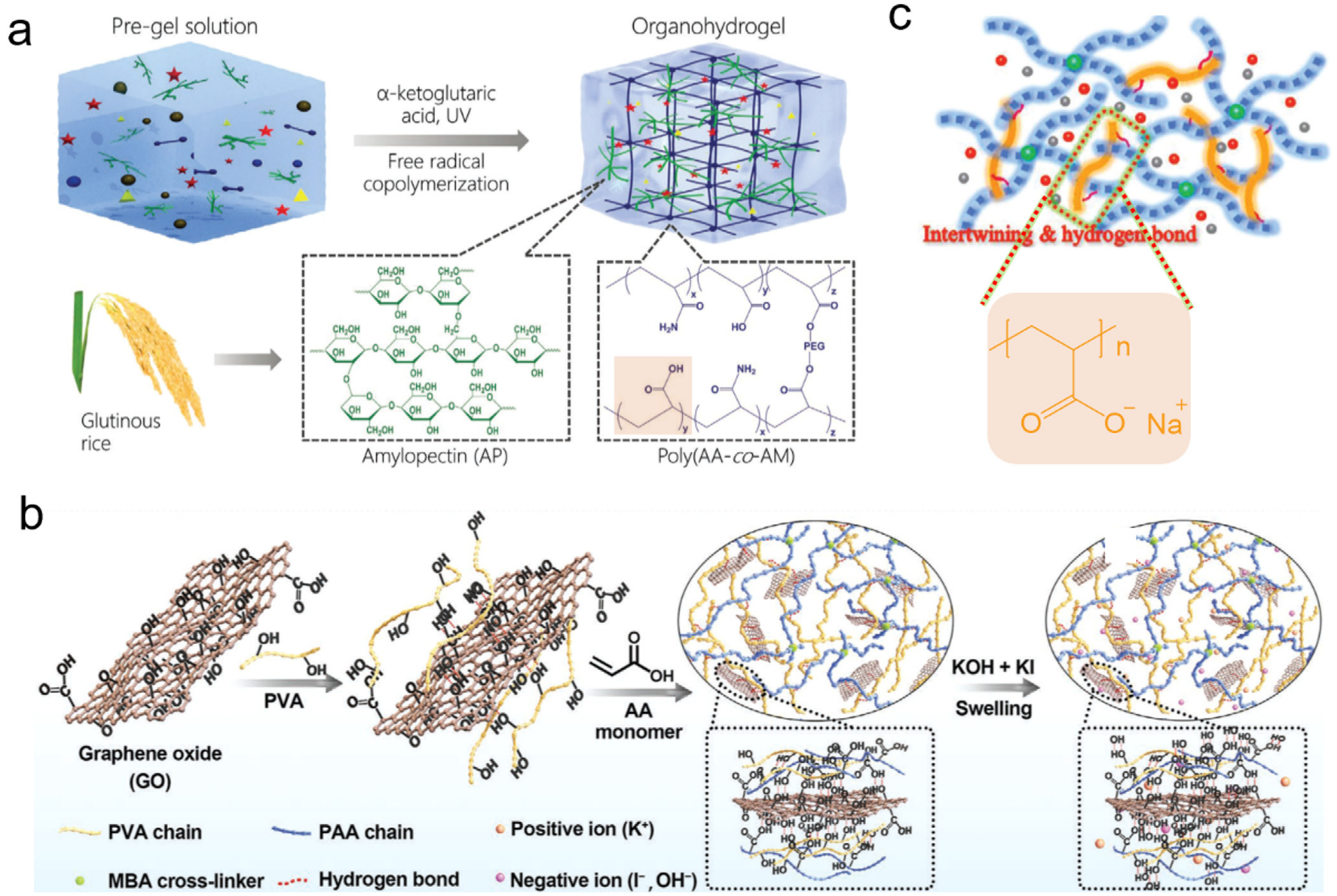

Fig. 11. (a) Illustration of the "one-pot" gelation procedure and the network structure of the glutinous-rice-inspired adhesive organohydrogels. [318], Copyright 2022. Adapted with permission from John Wiley & Sons Inc. (b) Schematic of the fabrication process for PAA-GO gel electrolyte. [360], Copyright 2020. Adapted with permission from John Wiley & Sons Inc. (c) Schematic of sodium polyacrylate/cellulose dual-network hydrogel electrolyte. [361], Copyright 2019. Adapted with permission from John Wiley & Sons Inc.

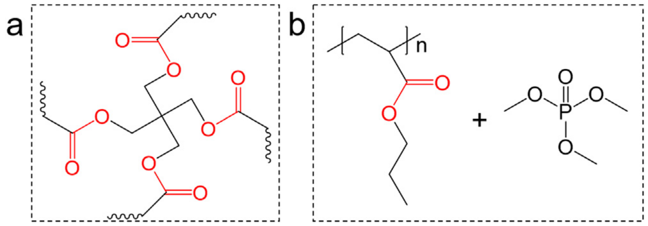

Fig. 12. (a) Structures of pentaerythritol tetraacrylate-based gel polymer electrolytes. (b) Structures of poly(butyl acrylate) and trimethyl phosphate employed in non-flammable elastic polymer gel electrolyte based on *in situ* polymerization.

4.3.4. Polyacrylate-based gel polymer electrolytes

Polyacrylate with carbonyl groups exhibits strong affinity and high uptake for carbonate electrolyte [290,363-365]. Therefore, polyacrylate-based gel polymer electrolytes exhibit high ionic conductivity, excellent electrochemical stability, and low interface impedance, which is a common host material for organogel electrolytes [366,367].

In general, the enhanced ionic conductivity of gel polymer electrolytes with PMMA sacrifices its mechanical properties. Blending, copolymerization and introduction of nanofillers have been attempted to improve the mechanical stability of gel polymer electrolytes based on PMMA [364,366,368]. For instance, a pentaerythritol tetraacrylate-based gel polymer electrolytes with a network structure was prepared via a facile *in situ* synthesis strategy (Fig. 12**a**) [368]. Due to the immobilization of soluble polysulfides imparted by gel polymer electrolyte and the tight adhesion between the electrode and electrodes, a high-performance flexible polymer lithium-sulfur batteries battery was successfully achieved.

To further improve the safety of organic Li metal batteries, a non-flammable elastic gel polymer electrolyte based on poly(butyl acrylate) was prepared *in situ* (Fig. 12**b**) [369]. The large butyl side groups of poly(butyl acrylate) provided more free volume for polymer chains to move and endowed the electrolyte with better flexibility and elasticity. The incorporation of trimethyl phosphate rendered the electrolyte non-flammable. The gel electrolyte-based battery was stably operated for 500 cycles at 0.5 C with a 94% capacity retention, showing potential for next-generation wearable devices.

4.3.5. Poly(vinylidene difluoride)-based gel polymer electrolytes

In normal, PVDF with strong electron-withdrawing groups -CF_2 exhibits a high relative permittivity of 8.3, which can weaken the interaction between ion pairs and contribute to the dissociation of Li. Besides, PVDF material has good mechanical toughness, thermal stability, and electrochemical stability, which endows PVDF-based gel polymer electrolytes with excellent performances.

To improve the ionic conductivity of PVDF-based electrolytes, a PVDF-HFP gel polymer electrolyte co-doped with PEO and GO was fabricated *via* weak bond interactions for dual-ion batteries (Fig. 13**a**) [370]. PVDF-HFP as the polymer matrix exhibited lower crystallinity, higher conductivity, and better mechanical stability. PEO could improve the pore configuration. GO could effectively enhance the mechanical property and thermal stability of polymer.

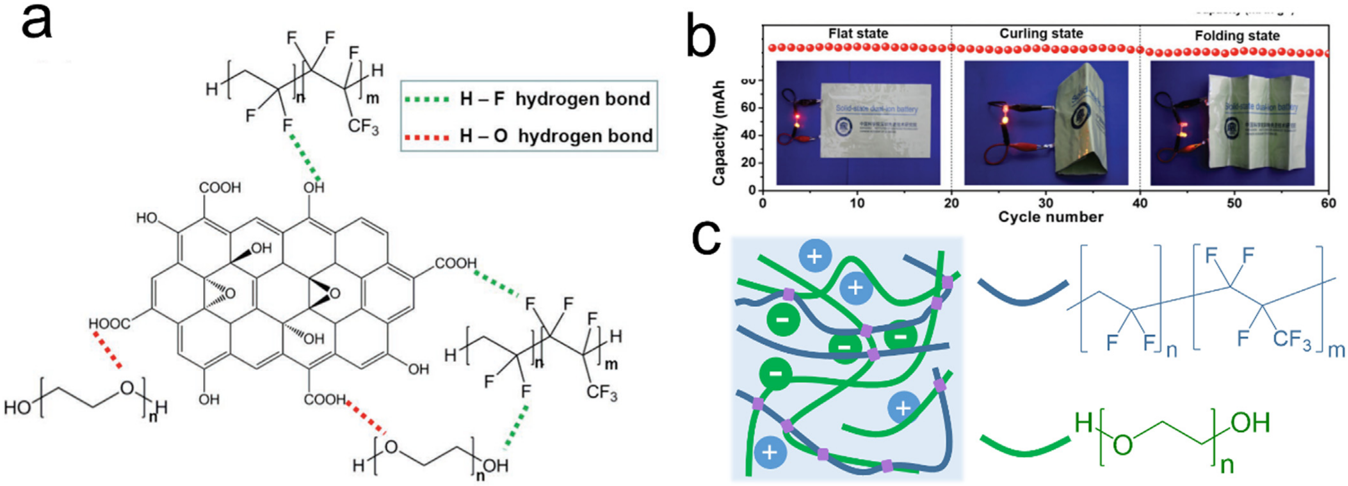

Fig. 13. (a) Schematic of the intermolecular hydrogen binding effect between PVDF-HFP, PEO, and GO in the porous copolymer network. (b) Cycling performance of the flexible dual-ion battery under flat, curling, and folding states at 2 C. Insets, LED powered by the flexible dual-ion battery with a porous copolymer network gel electrolyte at different states. [370], Copyright 2018. Adapted with permission from John Wiley & Sons Inc. (c) Schematic of PVDF-HFP-based ionogel electrolyte.

Moreover, PVDF-HFP could form H···F hydrogen bonds with GO and PEO, and GO could form H···O hydrogen bonds with PEO, leading to the formation of a highly porous copolymer network. The gel polymer electrolyte showed an improved ionic conductivity up to 2.1×10^{-3} S cm^{-1}. Therefore, the dual-ion batteries exhibited good cycling stability with a capacity retention of 92% after 2000 cycles at 5 C, good flexibility, and thermal stability (up to 90 °C, Fig. 13**b**).

PVDF-HFP-based ionogel with good mechanical properties also plays an important role in suppressing dendrite growth and side reactions. A PVDF-HFP gel polymer electrolyte film filled with PEO/ionic-liquid-based Zn salt was developed for an all-solid-state Zn-ion battery (Fig. 13**c**) [371]. The electrolyte could effectively suppress side reactions of hydrogen evolution reaction and Zn-dendrite growth. The all-solid-state Zn-ion batteries show excellent cycling performance of 30,000 cycles at 2 A g^{-1} at room temperature and withstand high temperatures up to 70 °C, low temperature to –20 °C, and bending deformation up to 150° for 100 cycles and eight times of cutting.

4.3.6. *Polyzwitterions-based gel polymer electrolytes*

Polyzwitterion is a charged polymer with repeating units of zwitterionic groups that have strong water retention ability [50,314,372-375]. A zwitterionic poly(propylsulfonate dimethylammonium propylmethacrylamide)-based gel polymer electrolyte was fabricated for supercapacitors (Fig. 14**a**) [314]. The polyzwitterions was composed of repeating units with a positively charged quaternary ammonium group and a negatively charged sulfonate group. The strong electrostatic interaction between charged groups and water molecules endowed poly(propylsulfonate dimethylammonium propylmethacrylamide) with high water retention. Meanwhile, the ion migration channel was formed in the hydration layer along the polyzwitterion chains when an external electric field was applied, which greatly enhanced ion transport in the gel electrolytes. The resulting flexible solid-state supercapacitor exhibited a high volume capacitance of 300.8 F cm^{-3} at 0.8 A cm^{-3}, and a rate performance of only 14.9% capacitance loss as current density increased from 0.8 to 20 A cm^{-3}.

However, the "salt-like structures" of the polyzwitterions usually lead to brittle polymerized hydrogels. A reliable approach is desired to enhance the mechanical properties. Cellulose nanofibrils, composed of nanofiber assemblies with diameters of 2 to 20 nm, exhibit unique structural hierarchies and have been widely used as reinforcing agents. Poly[2-(*methacryloyloxy*)*ethyl*]diethy-(3-sulopropyl), a zwitterionic sulfobetaine/cellulose hydrogel electrolyte was fabricated by using raw materials from natural plants, which exhibited good biocompatibility with mammalian cells [50]. The intrinsic zwitterionic groups on sulfobetaine chains can provide separated ion migration channels for positive and negative ions, which could facilitate electrolyte ion transport (Fig. 14**b**). A solid-state Zn-MnO_2 fiber battery with a fabricated zwitterionic gel electrolyte exhibited good electrochemical performance and flexibility (Fig. 14**c, d**).

4.3.7. *Other polymer-based gel polymer electrolytes*

Numerous gel polymer electrolytes based on renewable biopolymers (*e.g.*, chitosan [26,376], cellulose [70,237,285,321,377], and sodium alginate [60,73,378]) have been investigated recently. Biopolymers contain many hydrophilic functional groups such as $-NH_2$, -OH, -CONH-, $-CONH_2-$, and $-SO_3H$, which have high absorption affinity for polar solvent molecules and high salt solubility. Besides, biopolymers are nontoxic, renewable, and low-cost, exhibiting great potentials in wearable energy storage devices.

Cellulose, the most abundant natural polymer, is a macromolecular polysaccharide composed of glucose with intrinsic mechanical strength and flexibility. A high-performance bacterial cellulose (BC) nanofiber reinforced hydrogel electrolyte was designed for high-performance flexible supercapacitor (Fig. 15**a**) [237]. The hydrophilic BC could improve the mechanical properties and water retention of the hydrogel. The BC-based gel polymer electrolyte exhibited a high ionic conductivity of 125 mS cm^{-1} at room temperature and elasticity to ~1300% of its original length. The as-fabricated flexible supercapacitor with the BC-based gel polymer electrolyte exhibited stable electrochemical performance under deformation.

Chitosan is a biopolymer named poly[(1,4)-*N-acetyl-glucose-*2-*amine*)]. It is a linear polysaccharide composed of repeating units of β-(1,4)-linked 2-amino-2-deoxy-D-glucopyranose. The amine group ($-NH_2$) in the structure acts as an electron donor to interact with inorganic salts. The nitrogen atom serves as a complexation site for the cation coordination. An anti-freezing chitosan-biocellulosics super-ionic conductor electrolyte was synthesized *via* crosslinking between partially oxidized 2,2,6,6-tetramethylpiperidine-1-oxyl chitosan-biocellulosics and 1,4-diazabicyclo[2.2.2]octane quaternized chitosan-biocellulosics for deformable Zn-air pouch cells (Fig. 15**b**) [321]. The crosslinking structure reduced the crystalline domains and enhanced the

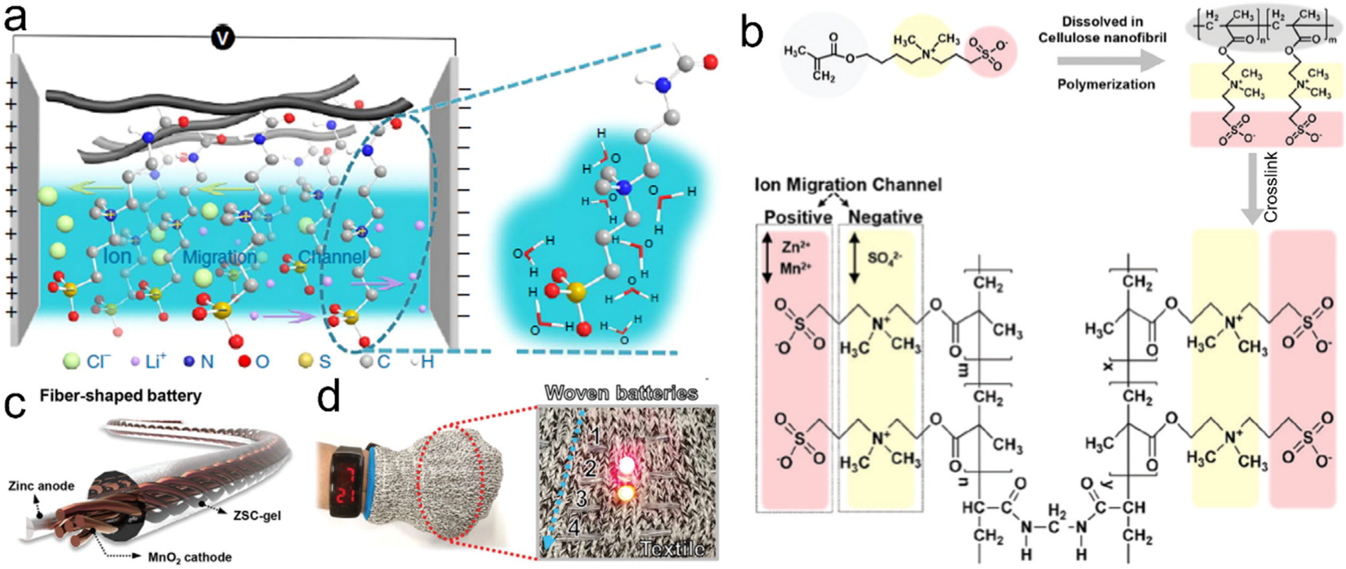

Fig. 14. (a) Schematic of the zwitterionic poly(propylsulfonate dimethylammonium propylmethacrylamide) gel electrolyte applied on electrodes. [314], Copyright 2016. Adapted with permission from Springer Nature. (b) Synthesis of the zwitterionic sulfobetaine/cellulose-gel. (c) Schematic of the fiber-shaped polyzwitterion-battery. (d) Fabric integrated with four fiber-shaped batteries in series. [50], Copyright 2020. Adapted with permission from John Wiley & Sons Inc.

local hydrophilic domains, resulting in good ionic conductivity. Besides, a dynamically strengthened network was formed due to inter/intramolecular hydrogen bonding, and thermodynamically stable antiparallel packing of chitosan-biocellulosics chains with covalent interactions of oxidized 2,2,6,6-tetramethylpiperidine-1-oxyl chitosan-biocellulosics and 1,4-diazabicyclo[2.2.2]octane quaternized chitosan-biocellulosics, which could effectively dissipate stress energy. The gel electrolyte exhibited a high conductivity of 86.7 mS cm^{-1} and dynamic mechanical behaviors with 119% strain and 195 MPa stress under 40% relative humidity at room temperature. The resulting flexible Zn-air batteries showed remarkable cycling performances for 6000 cycles without significant decays in discharge capacity (~95%) even under 180° bending (*i.e.*, folding) at 25 mA cm^{-2} and retained ~94% of its initial capacity after 1500 cycles at –20 and 80 °C. Besides, a new general solution-extrusion method was discovered to produce continuous fiber batteries in a single step at industrial scale [26]. The gel electrolyte inks for fiber LIBs were made by chitosan in acetic acid.

4.4. Composite polymer electrolytes

Despite of the great advantages of polymer-based solid electrolytes over liquid electrolytes, low ionic conductivity and poor mechanical properties remain challenges for commercial development. To address these issues and improve overall performance, various composites have been incorporated into polymers, mainly including fast-ion conductive ceramics (active) fillers and inert ceramic (passive) fillers. The room temperature conductivity and mechanical strength of composite polymer electrolytes, and the interfacial stability with the electrode, can be greatly improved through the synergistic effect of polymer and inorganic filler.

4.4.1. Active ceramics-based composite polymer electrolytes

Fast ion conductor ceramics, also known as active inorganic electrolytes, exhibit a high ionic conductivity as high as 10^{-2} S cm^{-1} at 25 °C. However, poor interfacial contacts limit their direct use as solid electrolytes. Therefore, the composite of fast ion conductor ceramics and polymer can make full use of these two parts. Fast ion conductors generally include garnet-type (*e.g.*, $Li_7La_3Zr_2O_{12}$, NASICON-type (*e.g.*, $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$), and LISICON-type (*e.g.*, $Li_{10}GeP_2S_{12}$) ceramics. Among them, $Li_7La_3Zr_2O_{12}$ shows an ionic conductivity of 10^{-4} S cm^{-1} at room temperature with superior stability toward Li metal. A flexible PVDF/$Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ (LLZTO) composite electrolyte membrane was designed using the traditional solution-casting method [379]. La atoms of LLZTO could complex with N atoms and $C = O$ groups of solvent molecules (such as *N,N*-dimethylformamide), and electrons were enriched on N atoms, which behaved like Lewis bases and induced PVDF chemical dehydrofluorination (Fig. 16**a**). The partially modified PVDF chains activated the interactions between the PVDF matrix, Li salts, and LLZTO filler, which significantly enhanced performance of flexible electrolyte membranes (*e.g.*, high ionic conductivity of about 5 × 10^{-4} S cm^{-1} at 25 °C, high mechanical strength, and good thermal stability).

However, the composite polymer electrolyte suffers from poor electrode wettability and high interface resistance. To enhance the electrode/electrolyte interfacial compatibility, a flexible $Li_{10}GeP_2S_{12}$ (LGPS) and polymers were tightly bonded by strong chemical bonds, which solved the interface compatibility problem, and the ions could transport rapidly through an expressway (Fig. 16**b**) [380]. The as-prepared membrane exhibited an ionic conductivity of 9.83 × 10^{-4} S cm^{-1} at room temperature and a high Li-ion transference number of 0.68. The *in situ* coupling reaction method provides an effective way to solve the interface compatibility problem.

4.4.2. Inert ceramics-based composite polymer electrolytes

In recent years, many studies have been made to incorporate inert oxide ceramic particles into polymer electrolytes to improve the mechanical properties, reduce polymer crystallinity, and thus solve the problem of low ionic conductivity of solid polymer electrolytes. Different types of inert ceramics have been incorporated into the polymer such as SiO_2, Al_2O_3, TiO_2, and zeolite [381–383]. A stable hydrophobic composite polymer electrolyte film composed of thermoplastic polyurethane and hydrophobic SiO_2 nanoparticles was designed to protect Li anodes from corrosion for flexible Li-air batteries (Fig. 16**c**) [383]. The film demonstrated good thermostability and mechanical properties. After adopting the protected Li anode, the prepared pouch-type flexible Li-air battery exhibited high flexibility, stable performance, water/heat resistance,

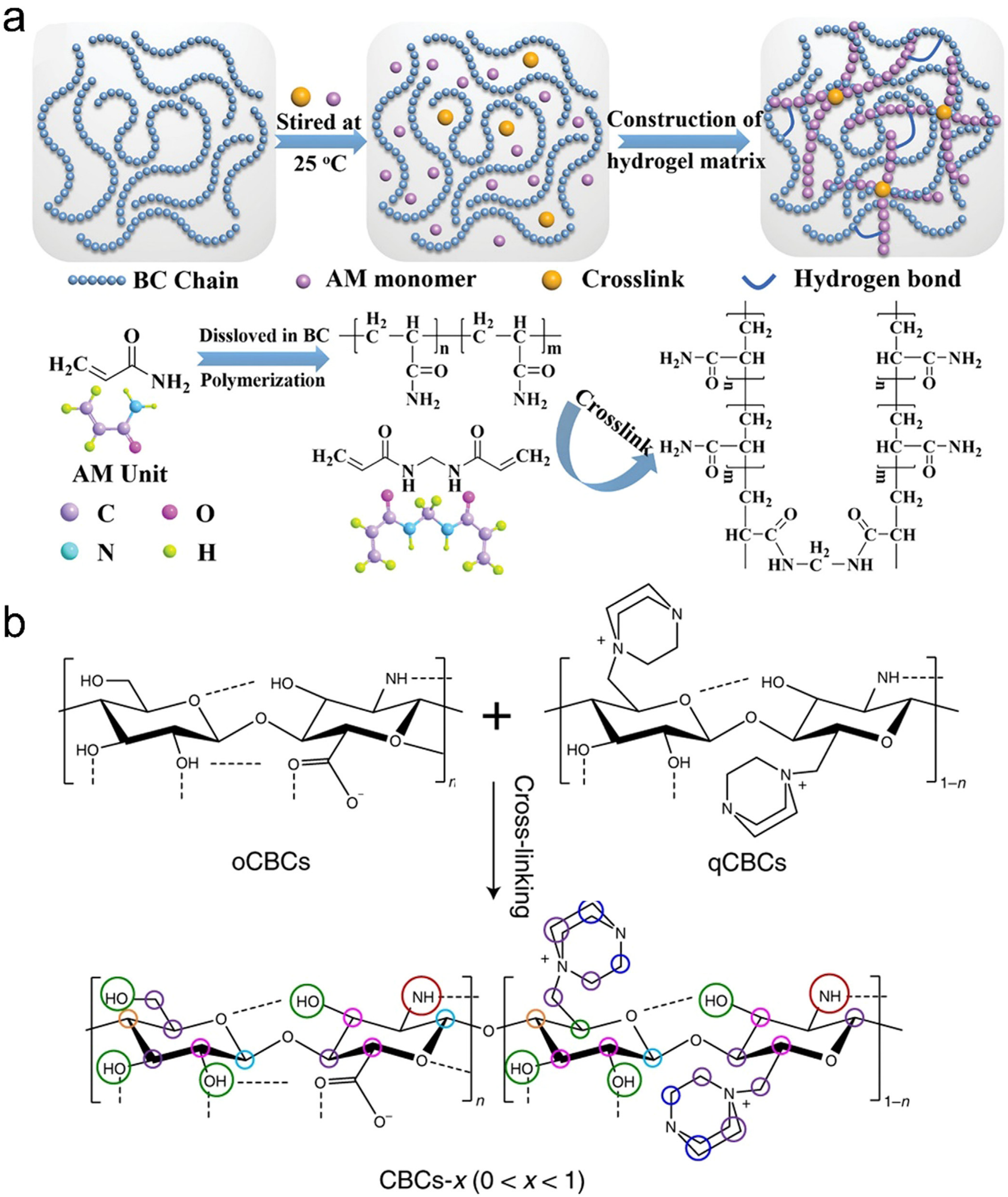

Fig. 15. (a) Synthesis process for the BC-based hydrogel *via* a simple polymerization approach. [237], Copyright 2021. Adapted with permission from John Wiley & Sons Inc. (b) Overall reaction illustrating the fabrication of anti-freezing chitosan-biocellulosics electrolytes. [321], Copyright 2021. Adapted with permission from Springer Nature.

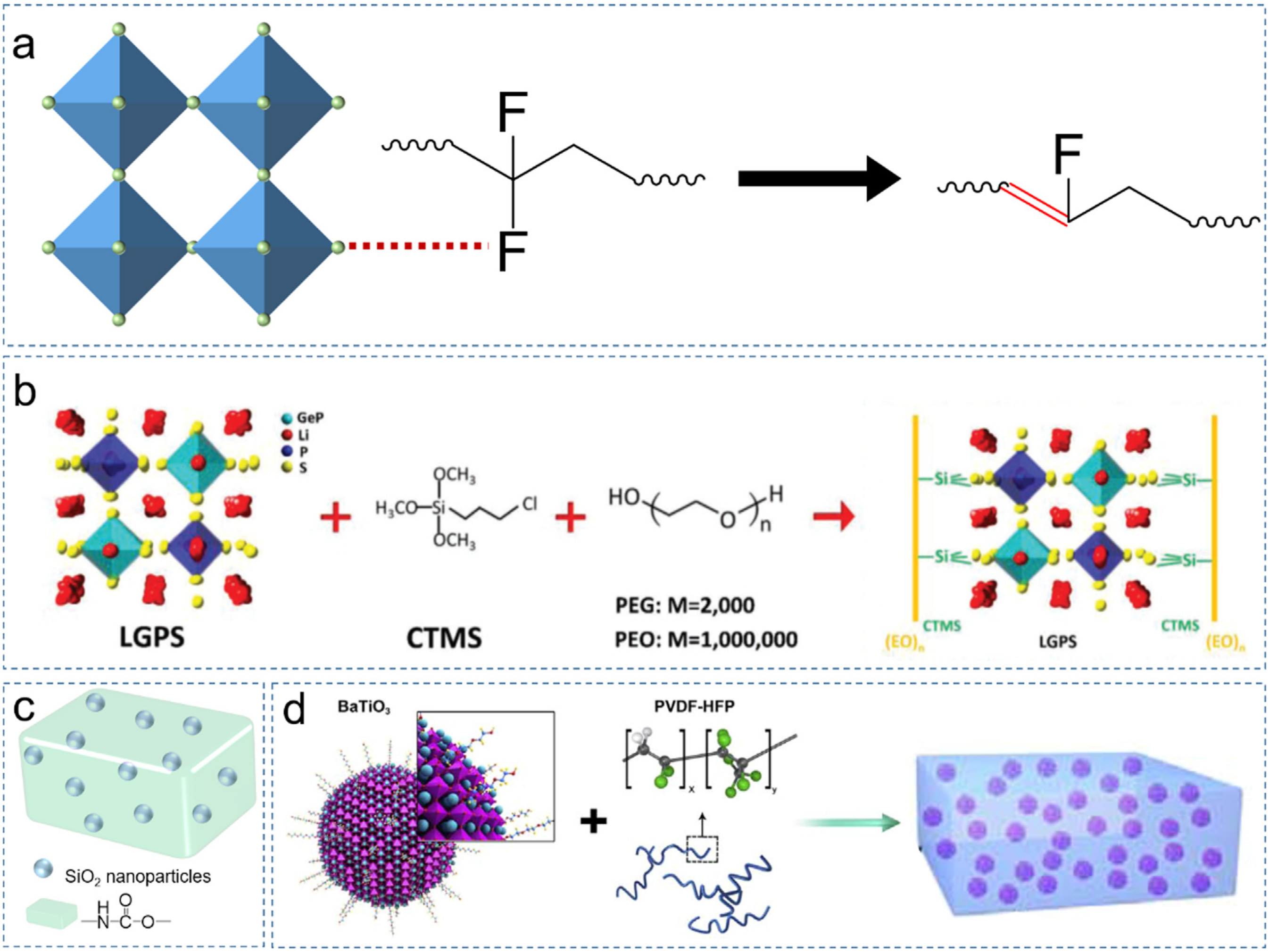

Fig. 16. (a) Possible complex structures in the PVDF/LLZTO-composite polymer electrolytes. (b) Schematic of the LGPS/polymer composite electrolyte. [380], Copyright 2020. Adapted with permission from John Wiley & Sons Inc. (c) Schematic of polyurethane/SiO_2 composite electrolyte. (d) Schematic of the formation of $BaTiO_3$/PVDF-HFP nanocomposite film. [384], Copyright 2017. Adapted with permission from Elsevier Science Ltd.

and even nail penetration endurance. Additionally, ferroelectric ceramic fillers of $BaTiO_3$ have also been incorporated into composite polymer electrolytes [384]. The interaction between the spontaneous polarization of the ferroelectric fillers and polymer backbone could increase the dipole moment of the polymer chain, which enhanced conductivity at the interfacial region (Fig. 16**d**). The surface charge of ferroelectric particles can also produce a high volume of the amorphous phase because of high nucleation rate during the solidification by acting as facile nucleation centers.

The difficulty in polymer/inert ceramic solid electrolytes is how to construct a good dispersion and strengthen the interaction between the filler and the polymer, which restricts the further improvement of ionic conductivity. In comparison, polymer/fast ion conductor composite electrolytes have both high ionic conductivity at room temperature and good mechanical properties. The future development direction of solid polymer electrolyte is likely to be the combination of fast ion conductors and polymers, which can combine the advantages of high ion conductivity of fast ion conductors and solve the problem of poor interface contact.

4.5. Summary and discussion

In this section, the recent advances and future development of polymer electrolytes for high-performance flexible energy storage devices have been presented (Fig. 17). The solid, gel and composite polymer electrolytes are further introduced in terms of their compositions, properties, and applications. Meanwhile, novel design strategies to improve the electrochemical and mechanical performance of polymer electrolytes are discussed. Despite these great progresses, many challenges still remain towards the practical applications of polymer electrolytes.

Improving performances of polymer electrolytes. To replace flammable liquid electrolytes, polymer electrolytes are supposed to achieve high ionic conductivity, good interfacial contact with electrodes, good mechanical properties to accommodate various deformations, and high thermal stability. Remarkably, the dynamics of polymer chains can be adjusted by their topology structure. For instance, branched polymers such as star-like, comb-like, bottlebrush-like, and hyperbranched polymers, which have shorter chains compared to their linear counterparts, are more difficult to arrange into an ordered structure, resulting in complete hindrance of crystallization and eventually a high ionic conductivity. In addition, some unique topologies imbue branched polymers with distinct properties such as high solubility in common solvents, controllable self-assembly structures, and adjustable thermal characteristics. Thus, creating branched polymers with carefully designed topologies is an effective approach to enhancing chain mobility and fabricating high-performance polymer electrolytes [315]. Meanwhile, the ion transport mechanism in polymer electrolytes is still unclear, which cannot provide effective rules for their syn-

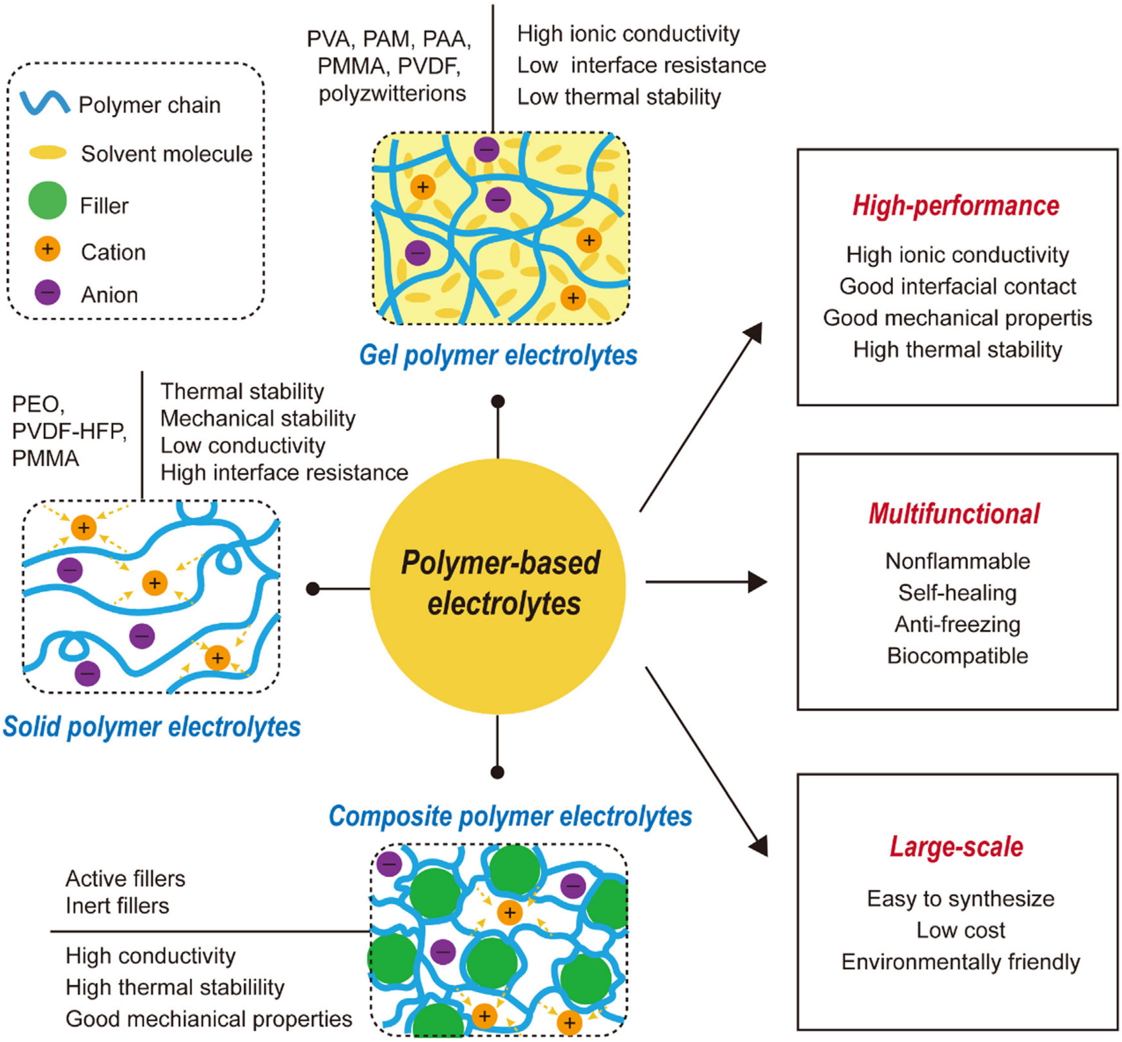

Fig. 17. Summary and perspective of polymer-based electrolytes.

thesis and applications. Therefore, more efforts are expected to optimize the compositions and investigate the ion transport mechanism of polymer electrolytes.

Designing multifunctional polymer electrolytes. To meet different application requirements, multifunctional polymer electrolytes needed to be designed and synthesized. Nonflammable polymer electrolytes are prepared with flame-retardant solvents and ionic liquids for safe, wearable Li-ion batteries. Self-healing polymer electrolytes *via* supramolecular interactions are synthesized to accommodate severe deformations. Anti-freezing polymer electrolytes can be prepared by introducing low freezing-point solvents to achieve Zn-ion batteries effectively working at low temperatures. Besides, bio-based polymer electrolytes can be used to prepare biocompatible, biodegradable, and implantable energy storage devices.

Producing polymer electrolytes at a large scale. Currently, most polymer electrolytes are prepared before assembling devices, which consumes large amounts of organic solvents and increases costs. To accommodate industrial productions of energy storage devices, it should be easy to synthesize polymer electrolytes at low cost under environmentally friendly conditions. Recently emerging *in situ* synthesis of polymer electrolytes can directly adapt to industrial production and form intimate electrolyte/electrode interfaces to enable high performances. It is necessary to pay more attention to the *in situ* synthesis of polymer electrolytes for the continuous production of flexible energy storage devices in the future.

Owing to their relatively low shape adaptability, polymer-based electrolytes are difficult to be used in the flexible energy storage devices, particularly in the fiber devices. However, *in situ* polymerization can take advantage of the beneficial properties of liquids, including low viscosity and easy handling, and the ability to wet the surface of flexible and even high-curvature electrodes and adapt the deformable shapes, ultimately creating good interfacial contacts between electrodes and electrolytes at essentially all length scales and establishing well-connected pathways for ionic transport between the electrodes. Subsequent *in situ* polymerization of the liquid electrolyte in the fully assembled cells transforms liquid electrolyte to a solid one with well-maintained interfacial contact. Therefore, *in situ* polymerization is a powerful strategy to achieve (quasi) solid-state flexible energy storage devices.

5. Polymers for separators

A conventional definition of the separator is an electronically insulating and porous membrane sandwiched between electrodes [40–42]. The porous separator influences the internal resistance, operating temperature, charge and discharge characteristics, durability, and cycling stability of the devices [85,385-387]. Herein, a separator is expected to possess good mechanical, thermal, and (electro)chemical properties, remarkable wettability of the electrolyte, uniform dimension, and cost-effectiveness [40-42,85,385-387]. A successful separator should play several specific roles. First, it should be electrically insulative to prevent the direct contact of the electrodes; second, it must process remarkable wettability toward electrolytes and be permeable to ionic fluxes; third, it ought to be (electro)chemically inert to electrolytes and electrodes; fourth, high thermal stability is required to avoid shrinkage at elevated operating temperatures; fifth, sufficient physical strength is needed to resist the tension and deformation during the fabricating and applying of the flexible devices [40-42,85,385-387]. Moreover, appropriate thickness and porosity are required to balance the mechanical strength and the internal resistance [41,388].

Due to their intrinsic capacities to meet and sometimes exceed the aforementioned requirements, polymers emerged quickly as promising materials to manufacture separators, which resulted in their large-scale applications in a wide range of energy storage devices such as supercapacitors, commercial lead-acid batteries, alkaline batteries, and LIBs [43]. Although a variety of microporous polymer membranes and nonwoven fibers were explored to serve as the separators, main attention focused quickly on polyolefin-based materials, mostly PP and PE, giving rise to their ability to achieve property, performance, manufacturability, and cost requirements simultaneously.

However, PE (T_m = 135 °C) and PP (T_m = 165 °C) deliver relatively low melting points, which limited the high-temperature operating of the devices since they are easy to shrink or even melt at high temperatures to induce dangerous short circuit. This can lead to a potential hazard, especially thermal runaway situations [389–391]. Besides, the porous polyolefin separators with low surface energy exhibit limited wettability of liquid electrolytes, leading to finite electrolyte uptake and restricted Li-ion transport and inhomogeneous Li-ion flux between the electrodes, which results in the increase of internal resistance and even accelerates the formation of Li dendrites in Li-metal batteries [392–394]. Generally, it has been difficult to extend the successes of commercial polyolefin separators to meet more complex challenges associated with flexible supercapacitors and batteries with deformability, high energy density, long lifetimes, and other unique functions like self-healability, heat resistance, and flame-retardance. This has opened opportunities for novel separators with various characteristics designed explicitly to achieve specific functions, including regulating the migration of conversion products (*e.g.*, polysulfides), suppressing detrimental dendritic growth at metal electrodes, and improving the voltage stability window of electrolyte, adhering to the electrodes to achieve elasticity of the whole device, and accommodating random shape changes of the deformable cell.

To meet the demand for flexible devices, various novel polymer materials have been used to prepare separators. Modifying commercial polyolefin separators or fabricating novel separators with functional polymer materials can drastically enhance the performance and safety of flexible devices. Grafting or coating polymer (*e.g.*, polydopamine [389], PPy [395,396], poly(ionic liquid)s [397], Nafion [398], polysulfone [366], chitosan [399] and GO-*g*-PAM molecular brushes [400]) on the surface of commercial polyolefin separator can improve mechanical strength, thermal stability, and electrolyte wettability [388,401]. On the other hand, porous polymeric membranes fabricated by functional polymers like PI [402], PVDF-HFP [403], PVA-PAA copolymer [404], PAN [405,406], and cellulose [407] have been investigated as promising separators due to their excellent chemical stability, good wettability to liquid electrolytes, high polarity, high thermal stability and adaptability toward deformable devices.

5.1. Design requirements of polymers for separators

Although separators are not directly involved in any electrochemical process of energy storage devices, their structure and properties determine the performances of the devices, including lifespan, safety, energy density, and rate capability by influencing mass transport and reaction kinetics [400,408]. Over the decades, various separators have been explored in power supply devices. Starting with cedar shingles and sausage casing, separators have been manufactured from cellulosic papers and cellophanes to nonwoven fabrics, foams, ion exchange membranes, and microporous flat sheet membranes made from polymeric materials [43]. They should be extremely electronic insulative by the intrinsic insulativity of the polymers while considerably ionic conducted with the electrolyte adsorbed in the pores of the polymer membranes. In addition, they should minimize the processes that adversely impact the electrochemical energy storage of the devices. With the emergence and development of deformable and wearable energy storage devices, the design of polymer-based separator becomes more demanding and complex [409].

The flexible devices are designed in many different shapes and configurations, such as planer and fibrous structures. The separators, which are either stacked between the electrodes or wound together with electrodes, should be built to accommodate these particular shapes and deformations of the devices. Stacked/wound separators and electrodes should be bonded/laminated as tightly as possible to ensure good interfacial contact and minimize the internal resistance between the separators and electrodes. The structures and characteristics of the separators should keep stable without significant change under the deformed state of the devices. Following the winding process, the electrolyte is filled; hence, the separators must possess good wettability to absorb the filled electrolyte quickly and completely.

To design the separator for a particular power device, many factors should be considered. The properties of separator must be traded off the application requirements. The design requirements mainly include the following: (1) moderate porosity, pore size, and tortuosity; (2) high ionic conductivity; (3) good electrical insulative; (4) favorable mechanical and dimensional stability; (5) thermal stability; (6) chemical resistance to degradation by electrolyte and electrode; (7) remarkable wettability toward electrolyte; (8) uniform and moderate thickness.

The importance of the aforementioned criteria varies, depending on the specific device and application. In many cases, a compromise in the separator property will be made to optimize the electrochemical performance and safety of the devices with the economic effectiveness of the manufacture. For instance, supercapacitors or batteries with minimal internal resistance require the separators to be as porous and thin as possible, while these properties tend to sacrifice the physical strength of separators and the safety of the devices.

In addition to the general design requirements listed above, some properties, particularly mechanical properties, are also required for separators in flexible or wearable energy storage devices to maintain their original functions under deformations (*e.g.*, bending, twisting, and stretching). While, compared with deformable electrodes (*e.g.*, embedding conductive materials in soft or elastic substrates) [19,216,235,410], electrolyte membranes [342,355,375,411], or structural layouts [199,412], a deformable separator membrane for flexible energy storage devices attracts little attention, which dramatically inhibits the development of the flexible devices. The requirements that influence the selection of the separators used in the flexible cells are discussed as follows.

5.1.1. Stretchability

With the emergence of stretchable electronics, the need for energy storage devices that can maintain electrochemical performance and safety under stretching has become urgent. Many efforts have been devoted in recent years to the design and fabrication of stretchable configurations and internal stretchable components including electrodes and electrolytes. As an important component of the device, the separator membrane with intrinsic stretchability has been developed to ensure its integrity and avoid failure when used in the deformable energy storage devices, which will guarantee good electrochemical performances and long-term stability at repeatable releasing-stretching cycles. Herein, polymer materials with intrinsic elasticity, such as SIBS [199] and polyurethane [413], are adopted to fabricate stretchable porous separator membranes, which endow the deformable devices with stable charge/discharge performances during dynamic stretching/releasing processes.

5.1.2. *Stickiness*

When the device is deformed, severe detachment between separators and electrodes will occur easily, leading to a dramatic increase in internal resistance and even failure of the devices. Therefore, a separator with strong stickiness or adhesion toward the electrode can maintain tight and firm contact between the electrode and separator to ensure a connected ion pathway and thus excellent cycling stability under a dynamic state [414].

5.1.3. *Polarity*

To facilitate the practical applications of high-energy-density flexible energy storage devices, such as lithium-sulfur batteries, the separators are expected to be polar to interact with soluble polysulfides to inhibit the detrimental shuttle effect. Additionally, the polar separator with abundant functional groups can regulate the depositing behavior of alkali metal ions to achieve dendrite-free and stable alkali metal anodes. Accordingly, a variety of functional polymers with an abundance of polar groups or heteroatoms like nitrogen, oxygen, and sulfur are employed to modify commercial polyolefin separators or fabricate novel separators *via* various strategies [366,396,399]. With these functionalized or novel separators, the remarkable cycling performance and mechanical flexibility of high-energy-density batteries can be simultaneously achieved.

5.2. *Functionalized commercial separators*

For commercial polyolefin, separators are unable to completely meet the demands for deformability, stretchability, and even self-healability of the flexible power systems and/or the requirements of deformable devices assembled by the high-energy-density electrodes like sulfur, oxygen, carbon dioxide, and metal anodes. Modifying porous polyolefin separators with functional materials is a natural strategy to enable the separator with the desired properties to fulfill these requirements. Owing to their intrinsic adhesivity and processability, polymer materials are frequently used as functionalized coating layers. For example, in the polyolefin separators functionalized by inorganic ceramics, the polymer binders such as PVDF, gelatin, and PI are often mixed with the ceramic particles to achieve firm adhesion between the ceramic layer and the polyolefin separator substrates [415–418].

In addition to binders in the modified layers, polymer materials can also serve as the coating layers of functionalized separators for flexible and high-energy devices (Fig. 18). For example, PPy was coated on a commercial separator to design a functional separator for flexible Li-S battery [396]. Due to its unique chain structure and the lone pair electrons of the nitrogen atoms on the polymer chains [419], the PPy layer demonstrates strong polarity to capture dissolved polysulfides and mitigates the shuttle effect, which eventually gives rise to enhanced cycling stability of the flexible Li-S battery. After repeated bending, the flexible Li-S battery can still achieve stable cycling capacity and power a device containing 24 white light-emitting diode, indicating the excellent mechanical flexibility of the designed Li-S battery. Additionally, polysulfone, composed of benzene rings and sulfone groups and thus possessing high thermal stability, mechanical strength, and oxidation resistance, was also employed to modify the commercial separators *via* a phase inversion strategy [366]. With the polysulfone-functionalized separator, the flexible Li-S battery exhibited prominently mitigated capacity degradation caused by the shuttle effect of the polysulfides in the battery. Thus, this modified separator, assembled with an ultrastable Li cloth anode and a boron nitride nanosheets/graphene interlayer-protected free-standing graphene/sulfur cathode, enabled the flexible Li-S battery with a superlong lifetime of 800 cycles in the folded state and high volumetric density of 468 Wh L^{-1} owing to the effective inhibition of the shuttle effect and dendrite formation. Furthermore, the as-designed flexible Li-S pouch cell can power light-emitting diode lights or an electronic watch, and even a light-emitting diode screen with a single chip was lit when three of the flexible cells were connected regardless of whether under either flat or bent states.

Chitosan displays a strong chemical affinity toward polysulfide in Li-S battery, given by its abundant hydroxyl and amino functional groups. Accordingly, chitosan, blended with activated expanded graphite, is employed by coating at top of the separator to mitigate polysulfide shuttling due to dual physical/chemical interaction toward polysulfides, which results in high performances of the flexible batteries incorporating this functional separator under various stress conditions [399].

5.3. *Novel separators based on functional polymers*

Other than serving as the modified layer of the traditional separators, various polymer materials (*e.g.*, cellulose nanofiber, nanofibrillated cellulose, PAN, PVDF-HFP, PI, SBS, polyurethane, SIBS, and PVA-PAA copolymer) with intrinsic processability and film-formability are also engaged to fabricate the novel separators *via* a variety of strategies like freeze-casting, paper-making sequential filtration, electrospinning, tape casting, and nonsolvent-induced phase separation to achieve the high-performance flexible devices (Fig. 19) [199,404,407,420].

A Neosepta® CMS ion exchange membrane was used to assemble a novel flexible hybrid battery-supercapacitor configuration, demonstrating excellent integrity and superior performance under mechanical stress [421]. Furthermore, a commercial copy paper fabricated by cellulose was utilized as a separator laminated with the electrodes to construct a flexible Li-ion film battery [422]. This paper functioned as not only a separator membrane with lower impedance than commercial separators but a mechanical substrate for the battery. Herein, the film battery with ultrathin thickness of only about 300 μm displayed robust mechanical flexibility (capable of bending down to $<$ 6 mm) and a high energy density (108 Wh kg^{-1}). A flexible all-in-one zinc-ion battery was further constructed, where the cellulose nanofiber separator and the rGO/PANI cathode and exfoliated graphene/Zn anode were integrated using an all-freeze-casting strategy [407]. Overall, with such an all-in-one configuration, the battery showed high flexibility and superior electrochemical stability under different bending states. Additionally, such a flexible all-in-one configuration was fabricated by a paper-making process using nano-fibrillated cellulose membrane as a battery separator [420]. In this cell, the nanofibrillated cellulose separator and electrodes were integrated into a single flexible but still mechanically strong, multi-layered structure *via* vacuum filtration. Furthermore, PVA-PAA copolymer had been also used to design an alkali-resistant separator for a flexible alkali battery [404].

In addition, electrospun nanofiber membranes delivering high porosity and electrolyte uptake can also be promising and attractive candidates for separators. Here, the amphiphilic separators were fabricated by chemical cross-linking of the PAN and

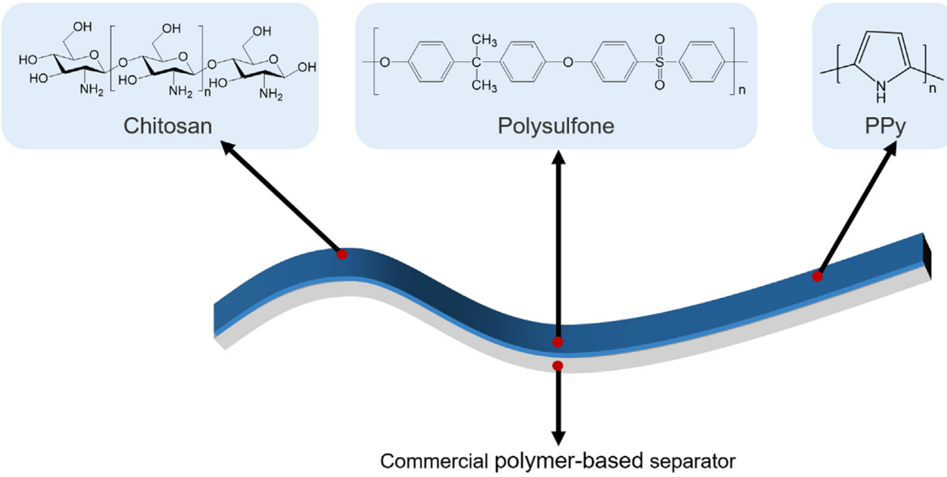

Fig. 18. Schematic illustration of commercial separator functionalized by various polymers, including chitosan, polysulfone, and PPy.

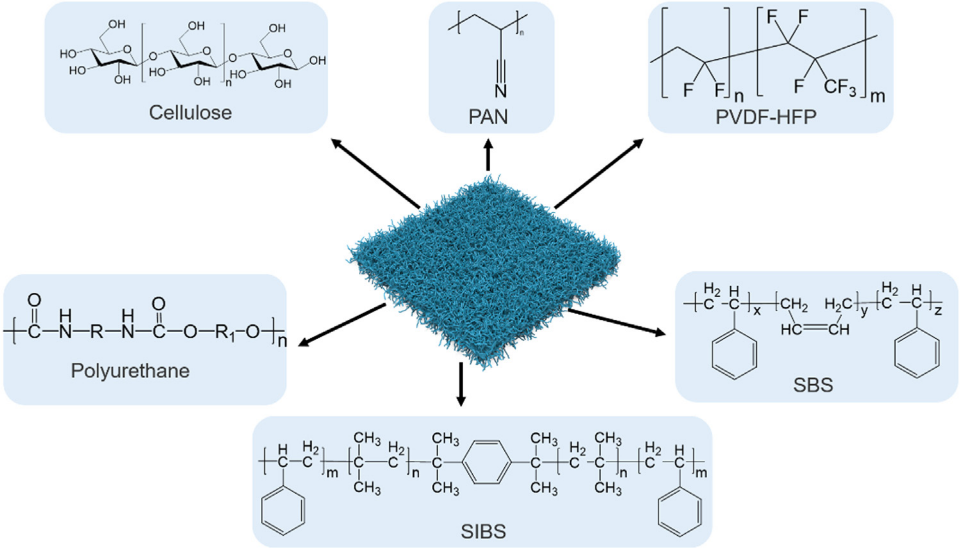

Fig. 19. Schematic illustration of novel separators prepared from different polymers, including cellulose, PAN, PVDF-HFP, SIBS, SBS and polyurethane.

the poly(ethylene glycol)diacrylate-grafted siloxane hybrid electrospun nanofiber. The membrane presented good mechanical properties, high chemical/thermal stability, and superior electrolyte-wettability which enabled the remarkable and steady electrochemical performance of flexible aqueous LIBs [405].

In comparison to the flexible separators mentioned above, elastic separators used in stretchable devices are less studied and discussed due to the more serious mechanical properties required. High-quality stretchable separators represent a crucial component of soft devices and dramatically impact electrochemical, thermal, and mechanical performances and safety independent of the devices. To meet the demands for intrinsically deformable energy storage devices, the porous and elastomeric polyurethane membrane was prepared by electrospinning as a separator of stretchable supercapacitors, which exhibited steady electrochemical properties under dynamic stretching/releasing and bending states with various strain rates applied [413]. Identically, polyurethane elastomer, composited with PDVF, was also introduced to fabricate an electrospun porous membrane with good stretchability and stickiness [414]. This resultant porous polyurethane/PVDF membrane was implemented as a separator for stretchable LIBs, which could preserve firm contact with electrodes to keep consecutive and unimpeded ion pathways under extreme physical deformations. This polyurethane/PVDF separator exhibited a high Li-ion transport and good stretchability (up to 100% strain) in the wavy battery during repeated stretching/releasing cycles. Additionally, a stretchable separator with considerably high porosity was constructed with 2-ethylhexylacrylate and urethane diacrylate as monomers *via* polymerization of high internal phase emulsions [423]. Utilization of this separator with high stretchability, porosity, and fast ion transport endowed stretchable batteries with an internal resistance of less than 3 Ω and a capacity of 16.8 mAh cm^{-2}, which was sufficient to power on-skin processing and communication electronics. Subsequently, SBS-based stretchable separator membrane was used for deformable power sources *via* facile nonsolvent-induced phase separation [304]. By precisely tuning several critical parameters for the phase separation process, the as-prepared porous stretchable separator membrane with a porosity of 61% exhibited high stretchability (270% to the uniaxial direction, and 60% to the biaxial direction). More importantly, this separator membrane was proved to be compatible with both organic and aqueous electrolytes to enable stretchable energy storage devices with stable electrochemical performances without internal short-circuit or mechanical failure even under 100% strain. Similarly, another elastic and thermoplastic copolymer, SIBS, was also involved in preparing the stretchable separator with a significantly high ionic conductivity of 0.5

mS cm^{-1} by solvent evaporation-induced phase separation [199]. Such extensible separators, together with other SIBS-based components like electrodes and package, were encapsulated by SIBS membranes into a full cell with a thin-film configuration, creating a single, polymer-based intrinsically stretchable battery, which was able to be fully functional after 150 cycles of 100% strain and withstand 39 washing cycles.

5.4. Summary and discussion

Currently, commercial separators (*e.g.*, porous PP and PE separators) are directly used in most cases, with little attention to designing specific separators for flexible energy storage devices. Obviously, in addition to the basic requirements (*e.g.*, insulativity, porosity, and wettability), separators for flexible devices should also possess some unique properties, such as stickiness, stretchability, and self-healing capability. In this section, the design requirements of separators used in flexible devices are first introduced. Then the specific designs of separators are presented based on the source and functionality with an emphasis on the emerging stretchable separators. The available stretchable separators, mostly made by elastomers via various pore-making strategies, delivered high adaptability toward stretching deformations of the devices. Noticeably, current separators are generally prepared by polymers derived from fossil feedstocks, while natural polymers with naturally abundant resources and great potential for biodegradation are more sustainable with low costs and recycling capabilities.

In planar flexible energy storage devices, electrodes and separator tend to detach from each other when the devices are deformed, thus leading to a dramatic increase in internal resistance and may even result in failures of the cells. Therefore, there is a pressing need to develop a scalable strategy to produce polymer-based separator with good stickiness. This stick separator would maintain tight contact between electrode and separator, resulting in a strong and connected ion pathway and thus excellent cycling stability under deformed states. In fiber-shaped cells, GPEs are typically used as the separators. However, the mechanical strength of polymer-based electrolytes is still insufficient for realistic requirements, especially when large deformations are imposed to the devices, which can pose a risk of short circuits of the cells. Considering the long-slender and high-curvature structure of fiber-shaped devices, developing effective separators to ensure the long-term stability of the cells and optimizing the adaptability of the separators to the vimineous electrodes to adapt complex deformations is still quite challenging.

6. Polymers for packaging layers

Packaging layers are vital in keeping reactive species, such as oxygen and water, away from sensitive materials like electrodes and electrolytes, thereby ensuring the long-term stability of the energy storage devices. Therefore, as the outer protecting layers, the packaging layers are required to possess low gas permeability and high solvent resistance and abrasion resistance; thus, the packaging layers generally comprise a moisture barrier layer, an electrolyte barrier layer, and a sealant layer. Currently, commercialized packaging layers are usually aluminum-plastic films. In flexible energy storage devices, the packaging layers can also provide mechanical supports, which are widely used to encapsulate LIBs. Yet, when applied in flexible energy storage devices, these metal-based packaging layers easily fatigue and damage under repeated deformation. In order to meet the application requirements of flexible batteries, packaging layers should have similar mechanical properties as electrodes and polymer-based electrolytes.

With good processability, film-formability, flexibility, wearability, and corrosion resistance, polymers are more promising packaging layers for flexible devices. Elastomers, such as PDMS, poly(styrene-isobutylene-styrene), and poly(styrene-b-ethylene-butylene-b-styrene) have been widely investigated as packaging layers for constructing intrinsically stretchable energy storage devices, of which elastic modulus can be flexibly regulated [199,203]. However, the high permeability of oxygen and water of the elastomers resulting from the large free volume and high chain mobility leads to poor cycling stability of the devices. Therefore, there is an ongoing need to explore packaging layers combining strong blocking properties with desired flexibility. Inorganic materials generally share a dense atomic packing structure and thus extremely low gas permeability, but the dense packing structure also lead to their limited deformability. To this end, compositing polymers with inorganic materials is a promising way to achieve highly flexible and lowly permeable packaging layers. For example, plating dense yet thin metal films on surfaces of polymer layers is a promising strategy for preparing desiring packaging layers. Furthermore, integrating ductile inorganic materials with low gas permeability and low melting points, such as liquid metals, into elastic polymer layers with low Young's modulus can develop stretchable and hermetic seals. These inorganic materials should have comparable hermetic sealing performance to metals, while at the same time possessing lower Young's modulus than the common elastic polymer layers that have limited hermetic performances. Such configuration may lead to ideal stretchable and hermetic seals for stretchable devices.

7. Conclusion and perspective

A variety of flexible energy storage devices have been reported based on different energy storage mechanisms. Flexible supercapacitors with high power density and simple configuration are first designed but they suffer from low energy densities. Therefore, more attention is drawn to LIBs with high nominal operating voltage, high energy, and power densities, and long cycle life. The high costs and limited resources of lithium have also promoted the development of sodium-ion and potassium-ion batteries, while their relatively low energy densities still could not meet growing energy demands. This promotes the development of high-energy flexible lithium-metal batteries, lithium-sulfur batteries, and metal-air batteries in recent years. Flexible energy storage devices should be both electrochemically and mechanically outstanding. Compared with metallic and inorganic nonmetallic materials, polymers have intrinsic flexibility and toughness, superior processibility, flexible designability, and are composed of abundant elements, thus endowing devices with high deformability, high energy density, high safety, and multiple functionalities.

Polymer materials play important roles in electrodes, (quasi)solid-state electrolytes, separators, and packaging layers. In terms of the applications in the electrodes, polymers have been recognized as promising active materials for flexible electrodes to replace carbon materials, transition metal compounds, and metal-ion compounds. Besides, polymers are also extensively used as binders to ensure good adhesion within active materials for ion conduction along with robust mechanical and chemical stability; some functional binders are used to endow flexible electrodes with unique functions like self-healability and super-elasticity. Further, polymers are employed as flexible and stretchable current collectors or supporting scaffolds, enabling flexible electrodes with ultra-low weights, low cost, and high mechanical properties.

In addition to electrodes, polymers are also widely used to make electrolytes. PEO is the most widely used polymer matrix of solid polymer electrolytes. Many strategies have been proposed to overcome its low ionic conductivity and inferior stability at high potentials, such as crosslinking or compositing with materials. PVDF-based polymers with a semi-crystalline structure and strong electron-withdrawing functional groups (-CF) exhibit high dielectric constant ($\varepsilon = 8.4$) and great solubility of metal salts, thus delivering higher electrochemical stability and increased ionic conductivity. Polyesters have also been investigated as polymer hosts in solid polymer electrolytes due to their superior ionic conductivity, electrochemical stability window, and compatibility with electrode materials compared to PEO-based polymer electrolytes. To further improve ionic conductivities of polymer-based electrolytes, solvents such as water, ethers, carbonates, and ionic liquids are employed in polymer matrices (*e.g.*, PVA, PAM, PAA, polyacrylate, PVDF, polyzwitterions, cellulose, and chitosan) to form polymer gel electrolytes. Compositing polymer matrices with inorganic fillers can also improve mechanical strength and provide pathways for the rapid transport of ions.

Currently, separators are almost prepared by polymers like PP and PE due to their good mechanical, thermal, and (electro)chemical properties and high insulativity. When used in flexible devices, separators are required to possess some special properties, such as stickiness, stretchability, and self-healing ability. To this end, functional polymers like chitosan, polysulfone, PPy, cellulose, PVDF-HFP, PAN, and polyurethane have been introduced to functionalize commercial separators or design novel separators.

The packaging layers are important in maintaining the long-term electrochemical and mechanical stability of flexible energy storage devices. Polymers with good processability, film-formability, flexibility, wearability, and corrosion resistance can meet the requirements of packaging layers for flexible devices. Further, compositing polymers with inorganic materials is highly desired to realize high flexibility and low gas permeability

Although flexible energy storage devices have achieved great advancements, they are still rarely used in current wearable electronics due to far more satisfactory performances. The following aspects are highlighted to convert existing academic achievements into future practical applications (Fig. 20).

7.1. High energy density

Wearable devices require deformable, thin, lightweight, and flexible power supply devices, which inevitably reduces the energy density to a certain extent. Although Li-ion fiber batteries with a high energy density of 80 Wh kg^{-1} had been achieved [75], the energy density of flexible energy storage devices lags far behind conventional LIBs (~250 Wh kg^{-1}), which is the stumbling block on the path of their practical applications. Fabricating high-energy-density devices while maintaining mechanical flexibility and deformability remains unmet but urgent. In the pursuit of high energy densities, adopting new energy-conversion chemistries (*e.g.*, Li metal, Li-S, and metal-air batteries) beyond commercial energy storage systems (*e.g.*, LIBs) presents an effective route, which require lightweight and high-conductivity current collectors. For example, CNTs and rGO have been widely introduced as current collectors to produce flexible LIBs or supercapacitors [37,424-427], but the efficiency of electron transmission from active materials to these current collectors is relatively low.

Additionally, adopting polymer-based active materials with higher specific capacities and increasing the mass loadings of redox-active polymer materials can largely improve the energy densities of cells. However, thick and dense electrodes may suffer from poor electrolyte wettability, inner cracks, and material delamination, thus leading to increased resistance and lowered flexibility of devices and even performance degradation or death of the cells. Using a thinner and lighter substrate, such as a polymer substrate coated by high conductive metal layers, can also enhance energy density with the lower mass portion of inactive materials in the device. As an indispensable part of energy devices, polymer-based electrolytes have light weight and wide electrochemical stable window, which can undoubtedly improve the energy density of flexible cells and keep them in a good operating condition, especially for flexible supercapacitors. Furthermore, designing novel configurations for flexible devices can also facilitate the energy density of the cells. For example, compared with the parallel and twisted types, the coaxial or rolled configurations can enhance the energy density of fiber batteries owing to larger, closer, and more efficient interfacial contact between electrodes, which prefer higher mass loadings of active materials, as well as a more stable and unitary structure to withstand repeatable deformations.

7.2. High safety

Wearable devices with close contact with the human body should be absolutely safe. However, current energy storage devices often face many safety hazards owing to the intrinsic toxicity of battery materials or the combustion/explosion of the whole device resulted from the thermal runaway of the cells. For example, corrosive and toxic electrolytes can leak out of the devices and do harm to the human body. Developing gel or solid polymer electrolytes to replace conventional liquid electrolytes is promising to solve the issue. Some heavy-metal-containing materials, such as cobalt-based electrodes or catalysts, are also toxic, and this raises the need to develop nontoxic electrode materials, such as redox-active polymers. Notably, it is worth noting that the polymer-based encapsulated materials also need to be explored to simultaneously achieve antileakage and retain high device flexibility. On the other hand, thermal runaway has been a notorious issue for energy devices, especially under repeated deformation or hazardous conditions such as ultrafast charging/discharging, overcharging, and short-circuiting. Therefore, efficient thermal management systems, such as polymer-based thermo-responsive current collectors [428,429] and electrolytes [430–434], and fire-resistant polymer separators [435,436] are necessary to develop and apply flexible energy storage devices to avoid overheating.

7.3. High flexibility and stretchability

Wearable energy storage devices should have high flexibility to keep stable in various applications by the design of materials (*e.g.*, soft electrodes, electrolytes, separators, and packaging layer) and configurations (*e.g.*, fiber and fabric). Unfortunately, Young's moduli of most existing energy storage devices are much higher to match that of soft human skin (~0.1–1.0 MPa), leading to inferior wearing comfort. This is mainly caused by the low flexibility of electrodes and packaging based on metallic compounds. Replacing electrodes and packaging with polymers with inherent flexibility and malleability is a promising way to match Young's modulus of the human body. Further, the all-polymer configurations can realize high mechanical flexibility comparable to the strength of native human tissues, making it possible for high-safety and minimally invasive implantation of the devices. In fact, human skin is soft and malleable. To achieve conformal wearable power supply devices, polymer materials are also expected to have intrinsic stretchability for achieving malleable and comfortable usage.

7.4. Intellectualization

Intellectualized design plays a significant role in expanding the application of flexible energy storage devices. For example, many deformable devices have achieved self-healing by facilely employing a self-healable polymer as an inner supporting substrate or an external protective layer. However, an additional component would inevitably increase the volume and mass of the entire device, leading to decreased mechanical flexibility and energy density.

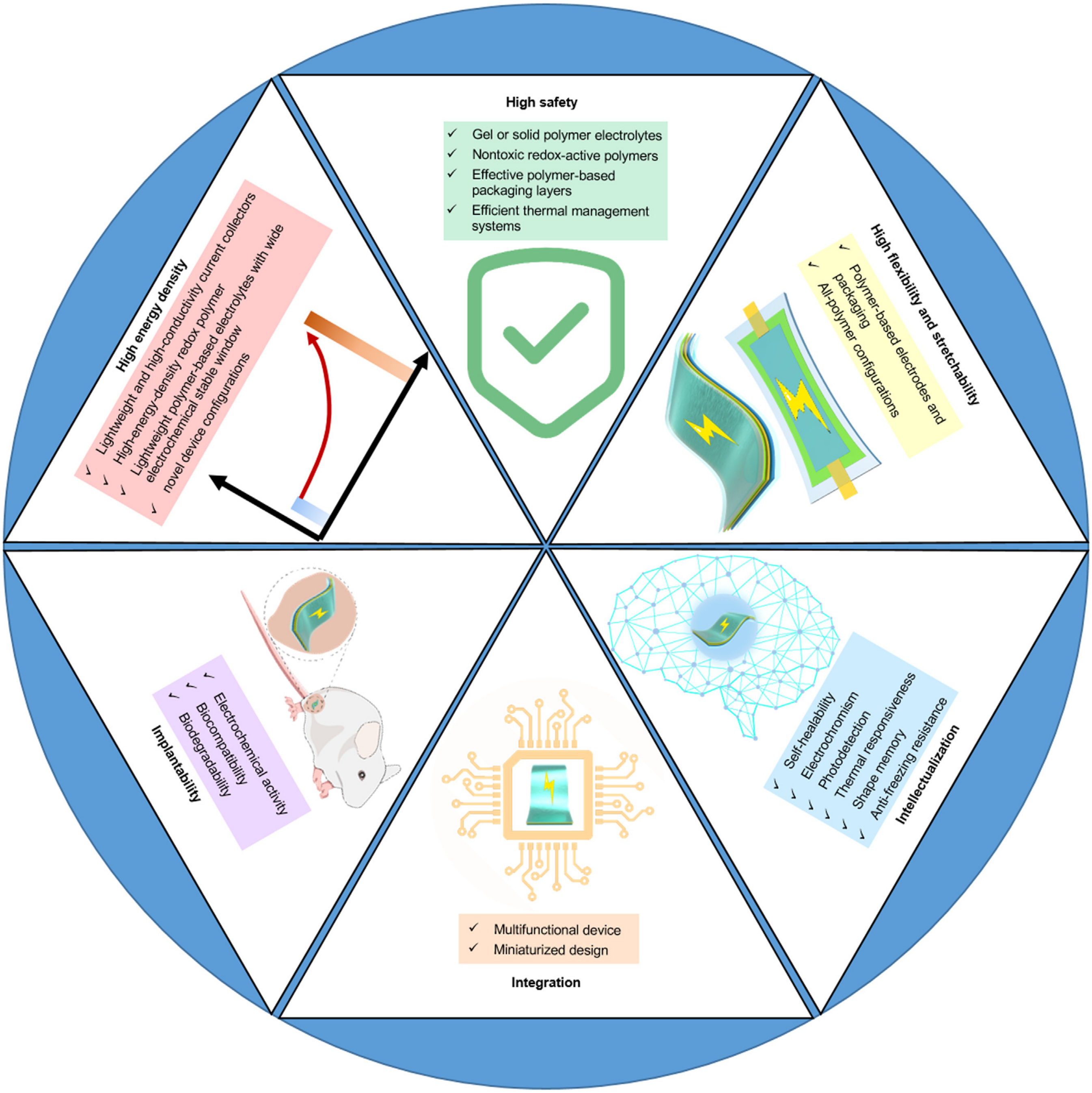

Fig. 20. Future perspectives of flexible energy storage devices.

Here, it is necessary to design electrolytes, electrodes, or separators with intrinsic self-healing capabilities by using intrinsically self-healable polymer materials. Meanwhile, the peculiar characteristics related to stimulus-response, such as electrochromism, photodetection, thermal responsiveness, shape memory, and anti-freezing resistance, are also attractive to flexible devices, but they are challenging because flexible devices require the materials selected to be more electrically conductive, optically transparent, mechanically strong, etc., for fabricating deformable devices than rigid ones because of the harsh operating environments and complex mechanical deformation. On that account, polymer materials, due to their inherent flexibility, easy processibility, and various stimuli-responsiveness, are potential candidates for the production of these smart and deformable devices. In the future research, numerous efforts should be made to design and fabricate deformable energy storage cells aiming to intellectualized flexible devices.

7.5. Integration

A large-scale production process from flexible energy storage devices to their integrated systems with high throughput and wearing comfort is of great significance for wearable applications. The integration of flexible energy storage devices with other systems, such as power generators [437–439], displayers [75,342] and sensors [75,440], is also a very promising direction for the future research. However, with most of the reported integrated systems being proposed by directly connecting the flexible energy storage modules with generators, solar cells, biosensors, and displayers, it would ineluctably lead to a large volume, lowered flexibility, and inferior portability. Compared with the simple connection technology, integrating flexible energy units and other electronic modules into one device can simultaneously realize multifunctionality and miniaturization with superior portability. However, fabricating such a highly integrated device is considerably complicated, relating to the intersection of various disciplines from scientific to technical fields. The easy processing of polymers may offer promises in developing new integration methods and enhancing the integration property, and this direction deserve more efforts aiming to solve the above problem.

7.6. Implantability

The last decades have witnessed the rapid development of implantable electronics for physiological monitoring and modulation [441], disease treatment, and artificial enhancement [442–444]. In the future, electronic devices are expected to be implanted into the human body for health monitoring and management as well as disease treatment. Designing the matching power supply for them should be prioritized. Unfortunately, so far, the power systems used for the operation of implanted electronic devices are usually primary and non-biodegradable, with additional surgical operations being required to replace batteries when it runs out, which will aggravate the pain and risks for patients. Besides, the existing implanted batteries usually possess limited softness or deliver even bulky and rigid configurations, demonstrating high Young's moduli and being quite unmatched with mechanically soft and dynamic biological tissues [445]. This mechanical mismatch may result in irritations and foreign body immune responses. It is challenging but significant to design implantable energy storage devices with superior safety, flexibility, biocompatibility, biodegradability, and electrochemical cyclability to resolve the energy supply issues in the human body for *in vivo* diagnosis and therapy. With the rapid development of polymer subjects, a variety of polymers with biocompatibility, biodegradability, and electrochemical activity as well as intrinsic flexibility, have been designed and synthesized. The as-synthesized polymers can fully meet the demands for mechanical properties, biocompatibility, and energy-storage capacity on implantable energy-storage devices. In addition, being critical for broadening the application range of these flexible devices, intellectualization and implantability can be achieved by designing new biocompatible, biodegradable, and smart functional polymers as well as their ingenious synergy with the basic deformable structure. In some cases, it is difficult to take into account of specific functions and electrochemical performances; hence, a balance must be reached. To summarize, rare studies are available for implantable batteries based on polymers, although they are highly desired.

Considering the increasing applications of polymers in flexible energy storage devices recently, this review first discusses design requirements of polymers in different parts of flexible energy storage devices. Then some representative polymers and their specific applications as key electrodes, electrolytes, and separators in energy storage systems are specially introduced. Finally, the key challenges and future perspectives of polymer-based flexible power supply systems are analyzed for practical commercial applications. The above challenges involve multiple fields, including materials, chemistry, electrochemistry, flexible electronics, and engineering. Therefore, it is necessary to involve researchers with different backgrounds to work together to tackle these issues. We believe that polymer-based flexible energy storage devices will gradually approach our daily life and even transform our work and life style in the future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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