Stretchable Energy Storage Devices: From Materials and Structural Design to Device Assembly

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1. Introduction

In the past several years, wearable electronic devices have attracted tremendous interest because they have shown extensive potential applications ranging from artificial organs, electronic skin, healthcare monitoring to soft robotics with arbitrarily potential applications. Stretchability is one essential prerequisite of wearable electronic devices to achieve stretchability and material synthesis for stretchable electronics and separators as building blocks in the fabrication of SESDs are briefly introduced in this review. Representative SESDs including stretchable supercapacitors and stretchable Li-based and Zn-based batteries are also summarized from the perspective of design strategy and performance optimization in terms of voltage output, energy density and capacity retention under mechanical strain. Finally, challenges and future development directions in this promising field are presented.

Stretchable energy storage devices (SESDs) are indispensable as power supply for next-generation independent wearable systems owing to their conformity when applied on complex surfaces and functionality under mechanical deformation. Structural strategies with underlying fundamental mechanics to achieve stretchability and material synthesis for stretchable electrodes and separators as building blocks in the fabrication of SESDs are first assembled in 2010.[21] The battery could be stretched up to 100% without failure. Later, a stretchable Zn-MnO₂ battery on conductive fabric was reported with stretchability of 150%.[22] These assembled batteries could power electronic devices under mechanical deformation. However, these primary batteries were not rechargeable. Various stretchable rechargeable batteries were subsequently proposed and fabricated. A stretchable primary Zn-MnO₂ battery with coplanar structure was first assembled in 2010.[21] The battery could be stretched up to 100% without failure. Later, a stretchable Zn-MnO₂ battery on conductive fabric was reported with stretchability of 150%.[22] These assembled batteries could power electronic devices under mechanical deformation. However, these primary batteries were not rechargeable. Various stretchable rechargeable batteries were then introduced.[23,24] Furthermore, considering safety issues from organic electrolytes, aqueous electrolyte-based stretchable rechargeable batteries were also reported.[12]

In this review, the recent developments of SESDs are mainly covered. First, structural strategies (such as wavy structure, island-bridge configuration, origami/kirigami structure, helically coiled design and 3D porous structure) toward stretchability are briefly introduced, followed by the summary of advanced stretchable electrodes (such as CNT film, graphene fiber, and metal spring) and stretchable membrane/separators for SESDs. This is followed by a discussion of the recent state-of-the-art stretchable supercapacitors (including fiber-shaped, 2D planar, 3D structured stretchable supercapacitors, self-healable, and transparent stretchable supercapacitors) and batteries (such as stretchable Li-based and Zn-based aqueous and non-aqueous batteries). Additionally, the all-in-one self-driven integrated systems are emphasized. Finally, future perspectives of SESDs toward practical wearable applications are delineated.

2. Strategies for Stretchability

The electrodes in conventional ESDs are generally rigid and stiff, which cannot yield large strain values (>100%)[25,26] and thus fail to satisfy the requirements of deformation and stretchability in SESDs for wearable applications. Therefore, various
strategies have been proposed and demonstrated with significant improvements of stretchability in SESDs.

2.1. Wavy Structure Design

Pioneered by Bowden and Whitesides,[27] wavy structures, also known as buckled structures or pre-strained structures, have been developed into one of the advanced approaches to attaining stretchability of electronic devices. Through bonding materials onto a pre-strained elastomeric substrate followed by releasing the applied strain, periodic wavy structures can be generated.[28] The wavy structure design has been widely utilized in stretchable electrodes for SESDs.[18] It was first exploited in stretchable supercapacitor based on CNT macrofilms as electrodes with a stretchability of 30% (Figure 1a).[17] Biaxial pre-strain strategy was subsequently developed to generate biaxial wavy geometry with stretchability along in-plane directions (Figure 1c,d).[29,30] Hierarchically buckled sheath-core conducting fibers were also reported.[31] It was fabricated by wrapping CNT sheets along the fiber direction on stretched elastomeric fiber cores (Figure 1e). The conductivity change was less than 5% after a strain of 1000%, thus enabling their promising applications as superelastic electrodes for stretchable supercapacitors. Other morphology, such as wrinkled wavy geometry, was also obtained with a stretchability of 600% (Figure 1h,i).[19] The good mechanical and electrical conductivity properties contributed to their utilization in stretchable supercapacitors and batteries.

The wavy structures are able to withstand large tensile strains as well as compressions without destruction of the materials by tailoring the wavelengths and wave amplitudes.[18] Wavelengths are defined as the distance between two consecutive peaks/troughs and amplitude is referring to the change between peak and trough in a periodic wave. Based on the energy method, these parameters, including the degree of pre-strain onto the elastomeric substrate, the thickness and elastic modulus of active materials/film and the substrate,[12–15] can have effects on wavelengths (λ) and wave amplitudes (A) and further influence the stretchability and stability of the wavy structures.[16–18] In the range of small strains (5%), wavelengths (λ₀) and wave amplitudes (A₀) are determined through the following Equations:[19]

\[
\lambda_0 = 2\pi h\left(\frac{E_s}{3E_f}\right)^{\frac{1}{3}}
\]

(1)

\[
A_0 = h_1 \sqrt{\frac{\varepsilon_{pre}}{\varepsilon_c} - 1}
\]

(2)

\[
\varepsilon_c = 0.25 \left(\frac{3E_s}{E_f}\right)^{\frac{2}{3}}
\]

(3)

where \(\varepsilon_{pre}\) and \(\varepsilon_c\) is the pre-strain and critical strain of the buckling, respectively. \(h_1\) is the film thickness. \(E_s\) and \(E_f\) is the plane-strain moduli of substrate and film, respectively.

Figure 1. a) Fabrication process and b) scanning electron microscopy (SEM) image of a buckled CNT macrofilm on an elastomeric PDMS substrate. Reproduced with permission.[17] Copyright 2009, Wiley-VCH. c) Schematic illustration of biaxially stretchable supercapacitors. d) SEM image of a biaxially stretchable electrode. (c) and (d) reproduced with permission.[18] Copyright 2018, American Chemical Society. e) Fabrication process of buckled nanotube sheets on an elastomeric fiber. The circular arrow indicates the belt direction. f) Schematic illustration of the structure of a longitudinal section in the nanotube sheath, showing 2D hierarchical buckling. g) SEM image of the long- and short-period buckles in the buckled nanotube sheet. (e–g) reproduced with permission.[31] Copyright 2015, American Association for the Advancement of Science. h) Schematic illustration of a superstretchable supercapacitor. i) SEM image of the released paper electrode after pre-stretching. Scale bar, 50 mm. (h) and (i) reproduced under the terms and conditions of the Creative Commons Attribution License 4.0.[19] Copyright 2015, the Authors, published by Springer Nature.
According to Equation (1), wavelength ($\lambda_0$) is independent on pre-strain when pre-strain is smaller than 5%. By contrast, when the pre-strain is large, wavelengths ($\lambda$) and wave amplitudes ($A$) are dependent on the pre-strain, which are described as follows:

$$\lambda = \frac{\lambda_0}{(1 + \varepsilon_{\text{pre}})(1 + \xi)^{1/3}}$$  \hspace{1cm} (4)

$$A = \frac{A_0}{(1 + \varepsilon_{\text{pre}})(1 + \xi)^{1/3}}$$  \hspace{1cm} (5)

$$\xi = \frac{5}{32} \varepsilon_{\text{pre}} (1 + \varepsilon_{\text{pre}})$$  \hspace{1cm} (6)

As the active materials/film are bonded onto the pre-strained elastomeric substrate to generate the wavy structures, the adhesion and interfacial mechanical strength between active materials/film and the elastomeric substrate needs to be enhanced. However, it is not reflected in the above equations. It should also be noted that the above equations apply for uniaxial stretching modes and need to be modified for biaxial and omnidirectional stretching wavy geometries.

2.2. Island-Bridge Configuration

Island-bridge configuration, in which rigid island materials are interconnected by the bridges of stretchable metal traces onto an elastomeric substrate, is another efficient strategy to realizing stretch capability. The configuration is sketched in Figure 2a.[41] During stretching of the whole structure, rigid island materials will go through negligible strain while the junctures of rigid islands and stretching substrate will experience huge localization strain, thus resulting in cracking and failure of the metal traces.[42] The maximum bridge strain ($\varepsilon_{\text{bridge}}^\text{max}$), maximum island strain ($\varepsilon_{\text{island}}^\text{max}$), and device stretchability ($\varepsilon_{\text{stre}}$) can be given by the following Equations:

$$\varepsilon_{\text{bridge}}^\text{max} = 2\pi \frac{h_{\text{bridge}}}{L_{\text{bridge}}} \sqrt{\frac{\varepsilon_{\text{pre}}}{1 + \varepsilon_{\text{pre}}}}$$  \hspace{1cm} (7)

$$\varepsilon_{\text{island}}^\text{max} = \frac{\varepsilon_{\text{bridge}}^\text{max}}{E_{\text{bridge}} L_{\text{bridge}}^2} E_{\text{island}} h_{\text{island}}$$  \hspace{1cm} (8)

$$\varepsilon_{\text{stre}} = \frac{\varepsilon_{\text{pre}}}{1 + (1 + \varepsilon_{\text{pre}}) \frac{L_{\text{island}}}{L_{\text{bridge}}}}$$  \hspace{1cm} (9)

where $L_{\text{bridge}}$ is the distance between islands before releasing, $h_{\text{bridge}}$ is the thickness of interconnects, $h_{\text{island}}$ is the thickness of islands, $\varepsilon_{\text{pre}}$ is the pre-strain, $E_{\text{bridge}}$ is the Young’s modulus of the bridge, $E_{\text{island}}$ is the Young’s modulus of interconnects and $L_{\text{island}}$ is the length of islands.

It is advisable to employ thin and low modulus elastomers as substrates, reduce the size of islands, and increase the length of bridges to alleviate the localization strain and avoid metal interconnect failure for a high level of stretchability.[43,44] However, it

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Figure 2. a) Experimental and computational studies of the self-similar serpentine layouts. The scale bar is 2 mm. b) Schematic illustration of a device in the state of stretching and bending. c) Exploded view layout of the various layers in the battery structure. d) Illustration of “self-similar” serpentine geometries. (black: first level serpentine; yellow: second level serpentine). e) Optical images of the Al electrode pads and self-similar interconnects on a Si wafer (left panel), after transfer printing on a sheet of silicone (middle panel), and with slurries of LiCoO$_2$ (right panel). f) Optical images of the Cu electrode pads and self-similar interconnects on a Si wafer (left panel), after transfer printing on a sheet of silicone (middle panel), and with slurries of Li$_4$Ti$_5$O$_12$ (right panel). Scale bars in (e) and (f) are 2 mm. (a–f) were reproduced under the terms and conditions of the Creative Commons Attribution License 4.0.[41] Copyright 2013, the Authors, published by Springer Nature.
should be noted that the small size of islands and long bridges lead to low areal coverage of active materials, low utilization of surface area, and thus compromise areal capacity/capacitance of ESDs. Thus, there is always a tradeoff between larger stretchability and higher areal capacities. Self-similar serpentine interconnects with two level serpentines were designed to make use of the limited space of bridging Li-ion batteries,

2.3. Origami/Kirigami Structure Design

The inspirations from origami (paper-folding) and kirigami (paper-folding and cutting) with high linear and areal deformability\cite{45-49} have sparked another strategy to achieve stretchability in SESDs.\cite{50-52} The origami/kirigami-based ESDs are based on conventional sandwiched-type planar ESDs, in which the slurries of cathode and anode materials are coated on current collectors, separators, and electrolytes are sandwiched between cathode and anode, followed by encapsulation, while the thickness of origami/kirigami-based planar ESDs should be thin (hundreds of micrometers) to facilitate folding/unfolding/cutting processes for stretchability.\cite{50-53} Stretchable origami/kirigami-based Li-ion batteries have been assembled and demonstrated.\cite{50-53} Figure 3a displays an origami-based Li-ion battery with a thickness of 380 \(\mu\text{m}\) in its fold and unfold state.\cite{52} Parallelograms were formed on the thin planar battery when it was folded along predefined creases. Subsequently, pulling two parallel sides could unfold the battery along the creases, thus realizing stretch capability. An areal deformability of 1600\% could be obtained. During expanding and folding, strain takes place at the creases and vertices while the parallelograms experience body motion but strain-free. An areal capacity could be as high as 2 mAh cm\(^{-2}\) when the origami Li-ion battery was compressed. Additionally, output voltage consistency was observed in the folding and unfolding state. An auxetic-cut pattern was developed for stretchable kirigami-based batteries, as shown in Figure 3b.\cite{53} The auxetic-cut battery could accommodate extreme mechanical deformations through the hinge joints as the external force was highly localized in the hinges while the segmented motifs experienced no deformations. The hierarchy and number of segmentations are two important factors affecting stretchability in the auxetic-cut

Figure 3. a) Examples of origami Li-ion batteries using Miura folding. Reproduced under the terms and conditions of the Creative Commons Attribution License 4.0.\cite{52} Copyright 2014, the Authors, published by Springer Nature. b) Design concept of an auxetic-cut battery system. Reproduced with permission.\cite{53} Copyright 2019, Wiley-VCH. Illustrations of kirigami patterns for stretchable batteries: c) zigzag-cut, d) cut-N-twist and e) cut-N-shear pattern. (c–e) reproduced under the terms and conditions of the Creative Commons Attribution License 4.0.\cite{54} Copyright 2015, the Authors, published by Springer Nature.
battery systems. Other patterns, such as zigzag-cut pattern (Figure 3c), cut-N-twist pattern (Figure 3d) and cut-N-shear pattern (Figure 3e) were also introduced into kirigami-based batteries to enhance stretchability.\[54\]

As creases and hinge joints experience concentrated stress during cyclic and repetitive folding/unfolding, it is crucial to employ robust battery material/current collector/encapsulation layer with mechanical endurance to withstand stress/fatigue and guarantee device functionality/reliability. It is still challenging to achieve both high deformability and satisfactory cyclic stability under repetitive folding/unfolding modes via the origami/kirigami strategy for stretchable energy storage devices.

2.4. Helically Coiled Spring Configuration/Textile Design

Helically coiled spring is another structure to achieve stretchability. As shown in Figure 4a, the stretchability can be obtained from Hooke’s law: \( F = k \times \Delta l \), where \( F \) is the applied force onto the fiber along coiled spring axis, \( k \) is a constant determined by geometric parameters and materials of the fiber and \( \Delta l \) is length change of the fiber.\[55,56\] Meanwhile, the fiber length can be described as: \( L = 2\pi r n \tan \theta \), where \( L \) is fiber length, \( r \) is radius, \( n \) is number of coils and \( \theta \) is pitch angle. Thus, the maximum strain stretch ratio (\( \nu_{\text{strain}} \)) is given by:\[55,56\]

\[
\nu_{\text{strain}}^{\text{max}} = \frac{2\pi r n}{L} = \frac{1}{\sin \theta}
\]

The smaller pitch angle, the larger strain stretch ratio. It should be noted that the calculated stretchability from the above equation is for fibers. If one fabric/textile is knitted with such helically coiled spring fibers, their stretchability can be further improved by pre-strain strategy\[57\] or twisting fibers onto elastomeric substrates.\[58\] Other factors, including fiber materials and spinning/knitting method, would also affect the stretchability of textile/fabric.\[59–61\]

2.5. 3D Porous Structure Design

3D porous structure design is another viable strategy for SESDs. As shown in Figure 5a, the prepared porous elastomer-based electrodes can accommodate strain while conventional electrodes would suffer from cracks under mechanical deformations.\[62–64\] With sugar cubes (Figure 5b) as the pore-creating agent,
stretchable 3D porous sponge-like polydimethylsiloxane (PDMS) scaffolds (Figure 5c) were prepared. Stretchable electrodes were then obtained by filling electrode materials in the sponges (Figure 5d). Figure 5e displays the stretching and releasing process of carbon/silicon/polymer composite electrode, which was realized with the help of foam structure and elastomeric polymer coating. Figure 5f illustrates the preparation process of such stretchable composite electrode. Graphitic carbon layer was first grown on nickel foam. After removal of nickel, silicon layer, and polymer layer were then subsequently and uniformly grown on carbon foam owing to the porous 3D structure.

2.6. Composite Design

One straightforward method for stretchability is to directly deposit active materials on the surface of stretchable polymeric substrates as films/coatings or disperse active materials into substrates as fillers, thus obtaining stretchable composites. Generally, 1D nanomaterials, such as nanowires and nanofibers, are promising candidates for such stretchable composites due to their large aspect ratio, which can to some extent alleviate decreased contact area resulting from active material sliding and maintain electrical connectivity during stretching/releasing process. A delicate balance should be pursued between stretchability and electrochemical performance as high loading mass of rigid active materials would increase energy storage property while impair stretch capability. The uniformity and distribution of coatings/fillers play a vital role in the stretchability of prepared composites, which is affected by coating/displacement processing methods, such as sonication, hot pressing, and ink casting. Furthermore, it is suggested to incorporate elastic binders into coatings/fillers to suppress their sliding/cracking and chemically

Figure 5. a) Schematic illustration of the stretchability comparison between the conventional electrode using metal foil and the electrode based on PDMS sponge. Illustration of synthesis process of the stretchable electrode and their optical images: b) sugar cubes, c) PDMS sponge, and d) stretchable electrode. (b–d) reproduced with permission. Copyright 2016, Wiley-VCH. e) Schematic illustration of the stretching and releasing process of the prepared carbon/silicon/polymer foam electrode. f) Preparation process and SEM images of the prepared carbon/silicon/polymer foam electrode. (e) and (f) reproduced with permission. Copyright 2016, Wiley-VCH.
modify coatings/fillers to enhance their interfacial adhesion with polymeric substrates to alleviate delamination during mechanical stretching/releasing process.

In summary, the above proposed strategies for stretchability in energy storage devices have their own advantages as well as drawbacks. These factors, such as loading mass of active materials, fabrication complexity, stretchability, and specific applications, need to be taken into account when choosing these strategies for stretchability. For example, pre-strain wavy structure design is a simple method to obtain stretchability. However, the loading mass of active materials on these pre-strain elastomer substrates should be limited to avoid delamination issue during cyclic stretching/releasing, which inevitably compromise areal/volumetric capacitances/capacities of assembled SESDs. Additionally, the stretchability is constrained by the interfacial mechanical strength between active materials and elastomer substrates. It is also challenging to integrate these pre-strain SESDs with other stretchable electronics. By contrast, helically coiled spring configuration/textile design for stretchability can be easily integrated into fabrics for wearable applications. However, the fabrication process of the spring/textile electrodes/devices is relatively complicated. The available choices for spring/textile electrodes are also limited, which are normally graphene- and carbon nanotube-based electrodes with enhanced mechanical strength but low energy storage capacity. As for origami/kirigami structures, they can be easily patterned/programmed to deliver large areal deformability/stretchability for SESDs. The main drawback is their complicated fabrication process. The island-bridge configurations suffer from a trade-off between stretchability and areal capacitance/capacities of SESDs. The complexity and the high cost in fabrication process are also the main disadvantages. While 3D porous structures can be designed for stretchability, they encounter delamination issue during mechanical deformation and complicated fabrication process. Composite design is simple but the stretchability is compromised.

3. Stretchable Electrodes for SESDs

As one core component, the electrode plays a significant role in the electrochemical performances of SESDs. Typically, the electrodes are prepared by coating electrode slurries (mixture of active materials, conductive additive, and polymeric binders) onto the surface of metal current collectors. As mentioned, electrode materials are typically rigid and stiff, which can lead to their delamination from the current collector during deformation/stretching and the consequent degradation of electrochemical performance in SESDs. Additionally, metal current collectors usually withstand low strain values (<2%), which may result in unstable electrical conduction or even disconnection with external wires during large strain.[31] Thus, it is of significance to explore and design stretchable electrodes for SESDs. In this section, three types of materials toward stretchable electrodes for SESDs are discussed, including carbon-based materials, metal-based materials and conducting polymer-based materials. There are reviews on stretchable electrodes for other applications such as bioelectric interface or human–machine interface.[65,66]

3.1. Carbon-Based Materials

Carbon-based materials, including CNTs and graphene, are widely employed as electrode materials in ESDs because of their high electrical conductivity, large surface area, and excellent chemical and thermal stability.[67,68] Incorporation of their outstanding mechanical robustness and structural integrity under deformation,[67,68] carbon-based materials can be prospective constructions in building SESDs.

In addition to the above-mentioned merits, 1D CNTs display a large aspect ratio,[69] thus enabling construction of electrically networks and maintaining electrical conduction under large strain. There are generally two ways to utilize CNTs in SESDs. One is fabricating CNT/polymer composites as stretchable current collectors/electrodes through various methods, such as spray-coating, spin-coating, dipping-coating, transfer, printing, and vacuum filtration.[70,71] For example, 3D porous CNT/PDMS composite was prepared as stretchable anode for Li-ion batteries.[72] The porous structures were obtained by mixing poly(methylmethacrylate) (PMMA) and PDMS and then removing PMMA, as displayed in Figure 4a. The other commonly utilized method is twisting aligned CNTs to form spring-like fibers as stretchable current collectors/electrodes. Figure 4h–m shows the stretchable single CNT fibers developed by Peng’s group.[61,73] The single CNT fibers could deliver an impressive stretch capability of 300% uniaxial strain along the fiber axis and a high electrical conductivity of 10^5–10^6 S cm^{-1}.[65] SEM images revealed that the initial structures could be preserved without damage during stretching/releasing. Additionally, electrical resistance did not change substantially after stretching/releasing to 100% strain. Subsequently, stretchable Li-ion batteries were assembled by incorporating active materials (Li_{4}Ti_{5}O_{12} (LTO) and LiMn_{2}O_{4} (LMO)) into CNT fibers to prepare stretchable electrodes and separating cathode and anode with gel electrolytes. Stretchable Zn-air batteries were also demonstrated with such spring-like CNT fibers as current collector and cathode.[74] The prepared CNT fibers would facilitate air diffusion from ambient atmosphere to the active sites of cathode.

Graphene is also attractive in SESDs owing to their high mobility and elasticity. For example, a stretchable current collector rGO/PDMS was prepared by immersing 3D porous PDMS sponge into graphene oxide (GO) solution, followed by reducing GO into rGO with enhanced electrical conductivity, as illustrated in Figure 6b.[63] The fabricated rGO/PDMS sponge with high stretchability could serve as current collector for a stretchable Na-ion battery. Graphene fibers were also prepared as stretchable electrodes for SESDs. An all-graphene core–sheath fiber was designed, in which the core graphene fiber was decorated with 3D porous graphene framework.[75] Spring-like supercapacitor with helical loops was then developed with highly stretchable properties.

3.2. Metal-Based Materials

Compared to carbon-based materials, metal-based materials deliver higher electrical conductivity and capacities, which are beneficial to facilitating electron transport and improving rate capability and energy density in ESDs. Various metals, such as
lithium, silver, copper, and gold, have been utilized as current collectors/electrodes. However, their intrinsically low elasticity prevents them from being directly utilized in SESDs. Thus, structural engineering introduced in Section 2 is adopted to realize stretch capability in rigid metal-based materials. Incorporating metal into stretchable current collector is one feasible strategy. For example, directly depositing Au onto pre-strained elastomer poly (styrene-block-isobutylene-block-styrene) was achieved as stretchable current collector.\(^{[76]}\) Cui’s group developed a stretchable Li metal anode by electrodeposition of Li onto Cu coil embedded in the poly(styrene-ethylene-butylene-styrene) (SEBS) rubber.\(^{[77]}\) The fabrication process is illustrated in Figure 6c. 1D Cu wire was first wrapped into 1D Cu coil and then self-wrapped into 2D Cu coil in an Archimedeian spiral pattern. Highly elastic rubber SEBS was then casted on the 2D Cu coil. After SEBS rubber was dried, one side of SEBS rubber was partly polished away to expose part of 2D Cu coil with small 3D microdomains. These 3D microdomains were then electrodeposited with Li metal. A stretchable Li metal anode was finally fabricated. Upon stretching, mechanical energy would be absorbed by elastic rubber while the 3D microdomains of Li metal on Cu coil would be unaffected, thus guaranteeing structural integrity of Li metal and its stable electrochemical performance. The hierarchical spiral structures of 2D Cu coil as well as highly elastic rubber SEBS endow the as-prepared Li metal anode with high stretchability. Additionally, the pattern of 3D microdomains was beneficial to reduce localized current density and homogenize Li-ion flux with improved cycling stability. With this design, the as-prepared Li metal anode could exhibit good mechanical and electrochemical stability under deformation (0.1% capacity loss per stretching/releasing cycle with a large strain of 60%). However, the full cell of Li battery was not assembled and demonstrated in this work due to the complicated manufacture process. Another drawback is the limited stretchability, which is dependent on 2D Cu coil. Metal spring, such as Li spring, Al spring and Zn spring, were prepared as stretchable electrodes for SESDs. A flexible and stretchable fiber-shaped Li-air,\(^{[78]}\) Zn-air,\(^{[74]}\) and Al-air\(^{[79]}\) battery was reported with Li, Zn, and Al spring as anode, respectively.

3.3. Conducting Polymer-Based Materials

With intrinsic stretchability, environmental compatibility, high capacities, and high electrical conductivity, conducting polymer-based materials are extensively explored in SESDs. For example, buckled polypyrrole (PPy) with wave structures were prepared as stretchable electrodes for Mg batteries, which could maintain good electrical conductivity and stable electrochemical performance when the prepared electrode was stretched/released 2000 cycles under 30% strain.\(^{[76]}\) Additionally, the proposed PPy/Mg battery system can be a promising power source for implantable devices as the biocompatibility of PPy and Mg metal. With textile structural configuration, nylon lycra fabrics coated with PPy were synthesized as electrodes for stretchable supercapacitors.\(^{[80]}\) The conductive textile-based supercapacitor could sustain 1000 stretching/releasing cycles with a strain of 100% and maintain stable electrochemical properties.

From the above discussion, it can be summarized that carbon-based stretchable electrodes exhibit high surface area and 3D percolation networks, thus beneficial to increase contact area and enhanced adhesion with substrates while maintaining structure integrity with desirable stretchability under mechanical deformation. Furthermore, the porous networks of carbon-based stretchable electrodes can buffer volume expansion of ion intercalation/de-intercalation during charge/discharge process, thus minimizing electrode stress and alleviating delamination issue, which is also one merit of polymer-based stretchable electrodes. By contrast, metal-based stretchable electrodes suffer from volume changes and possible delamination from substrates and even dendrite formation during stripping/deposition process due to their limited porosity. One challenge of carbon-based stretchable electrodes is their solid-electrolyte interface formation.
due to large surface area, resulting into low coulombic efficiency and capacity decay in stretchable batteries. The complex fabrication process of these stretchable electrodes is also one concern to assemble SESDs with reduced manufacture costs while enhanced gravimetric/volumetric power/energy densities.

Additionally, more attention needs to be paid at the delamination issue, which usually occurs at the interface between active materials and stretchable polymeric substrates, and crack problem, that happens at active materials during repeated stretching/releasing process. Thus, it would be desirable to modify active materials or substrates to strengthen their interfacial adhesion and maintain active material integrity under mechanical deformations. Normally, elastic binders, containing a large number of hydrogen bonding sites or even covalent crosslinks, are introduced into active materials to alleviate crack issue and reinforce structural durability. Additionally, the hydrogen bonding/covalent crosslinks are beneficial to the enhanced adhesion of active materials to the stretchable polymeric substrates. The amount of elastic binders should be optimized as a large amount of binders would affect ionic conductivity and retard charge transfer kinetics, and thus degrade electrochemical performance. Nanostructure engineering of active materials is also one way to suppress material cracks during stretching/releasing process, such as replacing nanoparticles to nanowires/nanofibers, which can minimize resistance change from release status to stretch status as well. The stretchable polymeric substrates can also be modified to generate interfacial hydrogen bonding rather than weak van der Waals forces between active materials and substrates to alleviate delamination issue. Other surface treatments, such as oxygen plasma and ultraviolet light, are also employed to modify stretchable polymeric substrates with hydrophilic functionalities to enhance the interfacial adhesion.

4. Stretchable Separators

Compared with traditional rigid separator, stretchable separator is proposed to possess the dual merits of stretchability and ionic conductivity to ensure the normal operation or functionality of SESDs during the mechanical deformations. Hydrogel electrolyte that consists of organic polymer framework and liquid electrolyte has been proved to be a promising candidate for stretchable separator. Its abundant intermolecular and intramolecular chemistries, that is, covalent bond, ionic bond, hydrogen bond, etc., endow the separator network with a superior stretchability. A series of stretchable separators have been successively developed to realize and optimize the stretchability while incorporating smart functions as well. Despite these inspiring advances, there still are several challenges triggered by the repeated stretching deformation such as interface contact failure, electrolyte leakage, and stripping of electrode active materials. All these contents will be summarized and discussed in this section to provide a possible guidance for the future development.

4.1. Stretchable Separators and Their Smart Functions

Poly(dimethylsiloxane) (PDMS) with excellent chemical stability has been employed as stretchable substrate and encapsulation layer for a long time. With engineering pre-stain by stretching PDMS separator before assembly with electrodes, the as-fabricated SESDs can deliver stretchability to some extent. Suffering from the relatively rigid network constructed by curing the silicone-elastomer base, the PDMS separator only exhibits a low strain value of 30%. Polyvinyl alcohol (PVA) prepared by the sol–gel process in the liquid electrolyte was also used as stretchable separator with good stretchability (>100% strain). Similar preparation was achieved in poly(ethylene oxide) (PEO) separator with a limited stretchability of 21% (Figure 7b,c). Despite demonstrating simple preparation process, these separators still cannot meet the stretchability requirement of stretchable devices due to their linear polymer chains without intermolecular crosslinking. This structure-dependent stretchability was apparently enhanced on polyacrylamide (PAM) separator. The covalent bonds formed by the vinyl addition reaction of the acrylamide monomer and the hydrogen bonds based on the amino group enable PAM separator to be stretched with a super-large strain of 3000% (Figure 7d,e). In addition, polyacrylic acid (PAA) was also developed into a highly stretchable separator (600% strain for whole device) through constructing dual-crosslinked network with the help of vinyl hybrid silica nanoparticles and hydrogen bond (Figure 7f,g). All these attempts contribute to the gradual enhancement of separator stretchability.

Other than exploring new hydrogel species for stretchable applications, introducing functional components into the existed stretchable separator was proved to be effective for improving stretchability while bringing extra smart functions as well. For example, agar and hydrophobic micelles were introduced into the PAM network and thus achieved an excellent strain recovery capability of restoring near 100% original length after 500%-strain stretching for 30 times. This good removal of residual deformation after large-scale stretching is attributed to the as-introduced agar and hydrophobic interaction that substantially dissipate energy and restore the network after stretching. Besides, the PAM hydrogel was also modified with alginate to deliver the ultra-tough function that enable the SESDs to survive 20 times of random run-over by cars on road, which benefits much from the energy dissipation enabled by Zn2+-crosslinked alginate network. Furthermore, anti-freezing function of PAM stretchable separator was also achieved through adding low-freezing-point species of ethylene glycol-derived waterborne anionic polyurethane acrylates, which enables SESDs to deliver >80% of the room-temperature capacity at −20 °C.

4.2. Stretching Induced Interface Contact Issues

The repeated stretching deformation poses threat of contact degradation or even failure at the separator-electrode interface. One of the interface contact issues is the longitudinal detachment, which may directly increase the interface resistance and deteriorate the rate capability once it occurs. Moreover, the interface detachment may also lead to the failure of separator’s mediation toward ionic flow and thus results in the notorious dendrite problem in metal batteries. The other interface issue caused by stretching deformation refers to the
lateral displacement which is also known as dislocation.\cite{103,104} It will decrease the electrochemically effective contact area between separator and electrodes, resulting in the reduction of energy density of SESDs. Meanwhile, the electrode active materials may also delaminate from the current collector due to the stronger adhesion interaction by the separator.\cite{105} These two interface challenges impede the ideal incorporation of both mechanical properties and electrochemical performances into SESDs. Hence, we propose in this review work to develop structure and material strategies, such as the all-in-one construction strategy, to strengthen the interface contact between separator and electrode.

4.3. Liquid Electrolytes in Stretchable Separators

Stretchable separator networks should uptake liquid electrolytes to simultaneously achieve stretchability and ionic conductivity.\cite{106} However, under the condition of repeated stretching, the as-filled liquid electrolytes may leak or evaporate away, bringing about the corrosion of human skin in wearable applications and degrading the ionic conductivity as well.\cite{107} This was addressed by the construction of sodium polycrylate (PANa) hydrogel, which can remarkably uptake water (>200 times of its weight) and avoid the water evaporation (maintaining 97.3% of the weight after 200 h).\cite{108} This
good water-retention capability was attributed to the large solvent-accessible surface area favored by the high dispersion and the interaction energy between PANa and water molecules. Another long-standing concern about the liquid electrolyte is the electrochemically stable voltage window, especially for the aqueous energy storage systems. Toward this end, highly concentrated electrolyte was introduced into the separator network to widen the voltage window to >2.3 V and thus ensure a ultra-stable ion storage at ≈1.7 V. Besides, linear polymer of polyethylene glycol (PEG) was also reported to chemically passivate water molecule through extremely decreasing the amount of free water. Design of thermally stable and stretchable polymer gel with long shelf life and high ionic conductivity will be desirable for stretchable battery applications.

Therefore, it is desirable and challenging to prepare stretchable separators with high ionic conductivity and maintain strong adhesion between separators and electrodes during repeated mechanical deformation. It is essential and attractive to explore novel materials and structural designs for superior stretchable separators.

5. Stretchable Energy Storage Devices

5.1. Stretchable Supercapacitors

Because of high power density, superior cycle life and safe operation, stretchable supercapacitors are promising in wearable applications. Based on energy storage mechanism, there are two types of electrode materials in supercapacitors: electrochemical double layer capacitive (EDLC) and pseudocapacitive materials. EDLC materials, such as carbon materials, store energy through electrostatic accumulation of charges at the interface between electrodes and electrolytes, while pseudocapacitive materials, including conducting polymer and transition metal oxides, store energy through reversible redox reactions, thus pseudocapacitive materials deliver higher specific capacities than EDLC materials. Table 1 summarizes recently reported stretchable supercapacitors through structural and material engineering.

<table>
<thead>
<tr>
<th>Electrode materials</th>
<th>Stretchable strategy</th>
<th>Stretchability [%]</th>
<th>Voltage window</th>
<th>capacitance</th>
<th>Energy density</th>
<th>Capacitance retention</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO2/CNT//CNT</td>
<td>Coiled spring</td>
<td>100</td>
<td>0–1.5 V</td>
<td>35 F cm−1</td>
<td>1.6 mWh cm−3</td>
<td>&gt;99% after 10 000 cycles at 100% strain</td>
<td>[122]</td>
</tr>
<tr>
<td>MnO2/CNT//Fe2O3/CNT</td>
<td>Pre-strain</td>
<td>100</td>
<td>0–2 V</td>
<td>110 F g−1</td>
<td>46 Wh kg−1</td>
<td>&gt;95% after 6000 cycles at 100% strain</td>
<td>[125]</td>
</tr>
<tr>
<td>NiCo2O4/CNT//Fe2O3/CNT</td>
<td>Pre-strain</td>
<td>50</td>
<td>0–1.6 V</td>
<td>212 F g−1</td>
<td>75 Wh kg−1 (25 mWh cm−2)</td>
<td>90% after 10 000 cycles at 50% strain</td>
<td>[126]</td>
</tr>
<tr>
<td>MnO2/CNT (symmetric)</td>
<td>Kirigami</td>
<td>500</td>
<td>0–0.8 V</td>
<td>16 F cm−1 (227 mF cm−2)</td>
<td>21 µWh cm−2</td>
<td>98% after 10 000 cycles at 400% strain</td>
<td>[127]</td>
</tr>
<tr>
<td>PANI/rGO (symmetric)</td>
<td>—</td>
<td>80</td>
<td>0–0.8 V</td>
<td>4 mF cm−2</td>
<td>1.88 mWh cm−3</td>
<td>85% at 60% strain</td>
<td>[128]</td>
</tr>
<tr>
<td>Mxene//activated carbon</td>
<td>Pre-strain</td>
<td>100</td>
<td>0–1.0 V</td>
<td>95 F cm−1</td>
<td>5.5 Wh kg−1</td>
<td>93% after 3000 cycles at 100% strain</td>
<td>[129]</td>
</tr>
<tr>
<td>PANI/CNT (symmetric)</td>
<td>Pre-strain</td>
<td>200</td>
<td>0–0.8 V</td>
<td>1200 mF cm−2</td>
<td>51 µWh cm−2</td>
<td>97% after 20 cycles at 200% strain</td>
<td>[132]</td>
</tr>
</tbody>
</table>

5.1.1. Stretchable Fiber-Shaped Supercapacitors

Owing to their small size, light weight, high flexibility, and easy weavability with smart clothes, stretchable fiber-shaped supercapacitors have been developed significantly and integrated with various wearable electronics.

Stretchable fiber-shaped supercapacitors can be divided into two categories: co-axial configuration and non-coaxial configuration. The first stretchable fiber-shaped supercapacitor was reported with coaxial configuration by Peng’s group in 2013. It was fabricated by sequentially and coaxially wrapping gel electrolyte (PVA/H3PO4) and aligned CNT sheets onto an elastic fiber, as shown in Figure 8a. Aligned CNT sheets served as stretchable electrodes because of their remarkable electrical conductivity, high tensile strength, and good mechanical stability. The coaxial design could favor increased contact areas and decreased contact resistance between electrodes and electrolytes. Thus, the assembled fiber-shaped supercapacitor endured 1000 stretching/releasing cycles at a strain of 75% with capacity retention of 90% (corresponding to a specific capacitance of 17 F g−1 and a voltage window of 0.8 V). The capacitance could be enhanced to 41.4 F g−1 after incorporating ordered mesoporous carbon into aligned CNT sheets. However, the low stretchability and low capacities prevented the fiber-shaped supercapacitor from further developments. To further enhance specific capacities, pseudocapacitive materials polyaniline (PANI) were introduced into the CNT sheets. The elastic fiber was pre-stretched to 50% for the following process of wrapping electrodes (PANI/CNT composite) and electrolytes (PVA/H3PO4). As a result, a high stretchability of 400% could be achieved with a large specific capacitance of 111.6 F g−1 and an operating voltage window of 1.0 V. More importantly, 79.4 F g−1 could be retained after 5000 stretching/releasing cycles at a strain of 300%, indicating the excellent mechanical durability.

In addition to the employment of pseudocapacitive materials, asymmetric design by coupling positive and negative electrodes with separated potential windows was adopted to widen voltage window and enhance energy density of devices. A stretchable asymmetric fiber-shaped supercapacitor with coaxial design was prepared by employing MnO2 decorated CNT fiber as...
cathode, PPy and CNT composite film as anode and PVA/KOH as gel electrolytes. The operating voltage window could be widened to 1.6 V and the energy density could be reached to 2.41 mWh g$^{-1}$. Stretchability of 20% was achieved by twisting the coaxial fiber-shaped supercapacitor into helical loops. Electrochemical performance remained stable under applied strain, demonstrating structural deformability.

Stretchable fiber-shaped supercapacitor with non-coaxial design is also prepared by intertwining two electrolyte-coated electrodes. For example, conductive polymer poly(3,4-ethylene-dioxythiophene)/poly(styrene sulfonate) was first incorporated into CNT film, followed by wrapping the composite film onto pre-stretched polymer wires (64% polyester and 36% polyurethane), coating gel electrolyte PVA/H$_3$PO$_4$ onto two such elastic wires and intertwining them together. The fabricated fiber-shaped supercapacitor exhibited a high stretchability of 350% with a corresponding capacitance of 30.7 F g$^{-1}$ (97% of its original value at 0% strain). Additionally, the fiber-shaped supercapacitor showed long-term stability to repeating stretching/releasing cycles at a high strain up to 200%. A fiber-shaped asymmetric supercapacitor with two separated intertwined electrodes was also fabricated for stretchable applications, which involved MnO$_2$/CNT hybrid fiber as positive electrode, CNT fiber as negative electrode and PVA/KOH as gel electrolyte. Owing to the widen potential window of 1.5 V and the enhanced volumetric capacitance of 21.21 F cm$^{-3}$, the obtained energy density and power density could reach 1.57 mWh cm$^{-3}$ and 2.08 W cm$^{-3}$, respectively. Mechanical stretchability was achieved by the simple pre-strain-then-releasing strategy. The fabricated fiber-shaped supercapacitor was first attached to a 100% pre-strained elastic fiber. Buckled fiber-shaped supercapacitor was then formed with a stretchability up to 100% after releasing the elastic fiber. The electrochemical performance was insensitive to the mechanical stretching/releasing cycles at the applied strain of 100%, implying mechanical robustness and durability of the prepared fiber-shaped supercapacitor.

Graphene fibers were also chosen as electrode materials for stretchable fiber-shaped supercapacitors. An all-graphene core-sheath fiber was designed, in which the core graphene fiber was decorated with 3D porous graphene framework. The core graphene fiber exhibited a low density of 0.23 g cm$^{-3}$ while maintaining good mechanical strength and high electrical conductivity. The sheath graphene framework provided high surface area for electrolyte penetration. The hybrid structure offered great advantages of such graphene core-sheath fibers as flexible electrodes for fiber-shaped supercapacitors. After pre-coating gel electrolyte PVA/H$_2$SO$_4$ onto two fiber-shaped electrodes and intertwining them together, the fiber-shaped supercapacitor was fabricated. Spring-like supercapacitor with helical loops was then developed with highly stretchable properties. The electrochemical performance was not affected by the applied strain of 200%.
5.1.2. Stretchable 2D Planar Supercapacitors

One direction to fabricating stretchable 2D planar supercapacitors is to prepare buckling carbon-based electrodes onto elastomeric substrates via pre-strain strategy. Wei’s group pioneered the preparation of buckled CNT microfilms as stretchable electrodes by releasing a 30% pre-strain PDMS substrate.[123] Electrospun elastic polyurethane was prepared as stretchable separator. The assembled stretchable supercapacitor displayed similar CV curves and unchanged specific capacitances under 0% and 30% applied strain, suggesting stable electrochemical stability under mechanical deformation. More importantly, electrochemical properties were also investigated under dynamic stretching/releasing modes at various strain rates to simulate the real situations in practical wearable applications. 98.5% capacity retention was achieved at a low strain rate of 1.11% strain s\(^{-1}\) and 94.6% capacity retention was obtained at a high strain rate of 4.46% strain s\(^{-1}\) after 1000 charge/discharge cycles. Such high capacity retention and slight variation on the long-term stability under various in situ dynamic stretching/releasing mode revealed the true performance of the prepared stretchable supercapacitor. However, the limited stretchability of 30% hindered their practical applications for powering wearable electronics. To achieve high stretchability, CNT films were directly grown on pre-strained PDMS substrate.[124] Upon releasing PDMS substrate, buckled CNT films were generated, which could be stretched up to 140% with slight resistance change. The better strain tolerance could be attributed to the unique continuous reticulate architecture of the prepared CNT film. Through employing the stretchable CNT electrode and gel electrolyte PVA/H\(_2\)SO\(_4\) stretchable 2D planar symmetric supercapacitor was integrated. The calculated specific capacitance was 48 and 53 F g\(^{-1}\) under the applied strain of 0% and 120%, respectively. The enhanced capacitance was ascribed to more exposure of active materials to electrolyte during stretching process. Asymmetric design and pseudocapacitive materials are also adopted in stretchable 2D planar supercapacitors to enhance capacitance and energy density. For example, a stretchable supercapacitor was prepared based on MnO\(_2\)/CNT film on PDMS as positive electrode, Fe\(_2\)O\(_3\)/CNT film on PDMS as negative electrode and PVA/Na\(_2\)SO\(_4\) as gel electrolyte.[125] The assembled supercapacitor could deliver a wide potential window of 2 V, a high energy density of 45.8 Wh kg\(^{-1}\) and a corresponding power density of 0.41 kW kg\(^{-1}\). The capacitance variation was less than 1% after the supercapacitor was subjected to dynamic 10 000 stretching/releasing cycles at a large strain of 100%. Another example was to employ NiCo\(_2\)O\(_4\)/CNT as positive electrode and Fe\(_2\)O\(_3\)/CNT as negative electrode for the stretchable asymmetric supercapacitor.[126] The voltage window could be as wide as 1.6 V and the energy density could be as high as 75 Wh kg\(^{-1}\) with a corresponding power density of 239 W kg\(^{-1}\) at a strain of 50%.

Textile/fabric structural engineering is another direction to fabricating stretchable 2D planar supercapacitors. By immersing fabric textiles into CNT inks, a stretchable CNT/fiber electrode with high conductivity was synthesized for stretchable supercapacitors.[160] After the assembled supercapacitor being stretched to 120% strain 100 times, negligible specific capacitance change was observed, revealing its impressive mechanical stability. Pseudocapacitive MnO\(_2\) was adopted to incorporate into CNT/cotton-based textile to increase capacitance and energy density.[157] Additionally, it is revealed that the pre-stRAINING process of the textile would be beneficial to the enhanced capacitance and energy density owing to the alignment between CNT and cotton fibers. Conductive polymer PPy was also introduced and coated onto nylon lycra fabric as electrodes with enhanced capacities for stretchable supercapacitors.[180] The PPy/fiber electrode could maintain its good electrical conductivity and electrochemical performance after being subjected to 1000 stretching/releasing cycles with 100% applied strain. However, the as-prepared stretchable supercapacitor suffered from inferior cycling stability, originated from the inherent structural destruction of polymer-based electrode materials during cycling.

Through the strategy of origami/kirigami, Chen’s group reported editable supercapacitors with customizable stretchability using MnO\(_2\)/CNT composite as electrodes (Figure 8c).[127] A supercapacitor edited with honeycomb structure delivered a high capacitance of 2272 mF cm\(^{-2}\) and a high stretchability of 500% with negligible capacitance degradation. Moreover, 98% capacitance retention could be achieved after 10 000 stretching/releasing cycles under a high strain of 400% (Figure 8e). The superior stretchability and mechanical deformability could be attributed to the interwoven ultralong MnO\(_2\) nanowires and CNTs composite as flexible electrodes and the deposition of mechanically strengthened porous cellulose film onto electrodes.

Graphene are widely utilized in stretchable supercapacitor with thin film configuration as well because of high mobility and good mechanical properties. Crumpled graphene film was prepared and employed as stretchable electrodes for supercapacitors.[29] Graphene film was first adhered to a biaxially pre-stretched elastomer substrate. After relaxing the substrate biaxially, crumpled graphene film with hierarchical structures was formed through harnessing mechanical instability. A high stretchability of 300% could be achieved with slight resistance change of the electrode based on the crumpled graphene film. The wavy strategy guarantees structural integration under stretching states. Our group also developed graphene-based electrodes for stretchable planar supercapacitors.[128] Vertical reduced graphene oxide (rGO) and gold (Au) bilayer heterostructures on PDMS substrate were prepared through a direct laser-patterning process and a transfer method. Planar microsupercapacitors with the rGO/Au/PDMS composite as electrodes were fabricated, exhibiting a stretchability up to 60%. After incorporation of pseudocapacitive PANI, the obtained energy density could be up to 1.88 mWh cm\(^{-2}\). Capacitance retention was 85% after 500 stretching/releasing cycles at a strain of 60%, indicating mechanical durability of the intrinsically stretchable microsupercapacitors.

MXenes, a new class of 2D materials, has also been considered as promising electrode materials for energy storage devices. Their high electrical conductivity and good mechanical properties make them promising candidates in SESDs. Chen’s group developed crumpled MXene nanocoatings on elastomeric substrate for stretchable supercapacitors (Figure 8f).[129] MXene nanosheets were first prepared and mixed with nonactive polymer binder sodium alginate (SA) to enhance mechanical
stability while maintaining good electrical conductivity. After drop-casting MXene/SA dispersions onto biaxially pre-stretched elastomer substrate and then releasing the substrate, the crumpled structure of MXene nanocoatings were thus achieved via localized mechanical instability during stretching/releasing. The as-prepared MXene electrode exhibited gravimetric capacitances of 118 and 108 F g\(^{-1}\) and volumetric capacitances of 395 and 362 F cm\(^{-3}\) at 0% and 80% strain, respectively. Additionally, it demonstrated mechanical durability, which could endure 1000 stretching/releasing cycles at a strain of 80% with capacity retention of 76%. The capacitance decrease was due to delamination and cracks of MXene nanocoatings under mechanical deformations, resulting in increased charge transfer resistance. A stretchable asymmetric supercapacitor was constructed based on the stretchable MXene electrode as positive electrode, stretchable activated carbon as negative electrode and gel electrolyte PVA/Li\(_2\)SO\(_4\). The volumetric capacitance was calculated to be 95 and 85 F cm\(^{-3}\) under 0% and 100% strain, respectively. The capacitance decrease under stretching states was also resulted from strain-induced cracks and delamination. The maximum energy density of 5.5 Wh kg\(^{-1}\) was achieved with a corresponding power density of 0.5 kW kg\(^{-1}\).

5.1.3. Stretchable 3D Supercapacitors

Sponge is an intrinsically stretchable and compressible porous structure for stretchable 3D supercapacitors. A highly compressible supercapacitor based on PANI/CNTs nanostructured sponge as electrodes and PVA/H\(_2\)SO\(_4\) as gel electrolyte was reported.\(^{[130]}\) The PANI/CNTs sponge electrode was prepared by coating a layer of CNTs on the skeleton of sponge by dipping and drying method and subsequent PANI growth on the CNT layer through chemical oxidation polymerization process. The as-prepared supercapacitor exhibited capacitance retention of 97% when compressed under a strain of 60%. Several supercapacitors were integrated in series or parallel to deliver improved potential/current output.

5.1.4. Biaxial/Omnidirectional Stretchability

In addition to uniaxial stretchability, biaxial/omnidirectional stretchability is also necessary in many applications, especially when the electronics are directly attached on human skin and required to adjust deformations as body moves. One strategy to achieve biaxial stretchability is to employ the island-bridge strategy, involving the integration of microsupercapacitors with serpentine interconnections.\(^{[131]}\) Elastomer Ecoflex was used as substrate and stiff polyethylene terephthalate (PET) film was locally implanted onto Ecoflex. Microsupercapacitors were subsequently placed onto PET film, where applied strain was mitigated. The fabricated microsupercapacitor array exhibited 100% uniaxial and 50% biaxial stretchability without electrochemical performance degradation. High energy density and power density of 25 mWh cm\(^{-3}\) and 32 W cm\(^{-3}\) could be obtained, respectively. Omnidirectionally stretchable supercapacitor was developed based on continuous and isotropic buckled CNT film, which was realized by transferring randomly oriented CNT film onto omnidirectionally pre-strained elastomer substrate and subsequently releasing it (Figure 9a).\(^{[132]}\) The obtained isotropic buckled CNT film displayed uniaxial, biaxial, and omnidirectional stretchability up to 200% with slight resistance increment of 3%, indicating superior mechanical deformability. Pseudocapacitive materials PANI was electrodeposited onto the isotropic buckled CNT film to enhance capacitance. Supercapacitor based on the hybrid PANI/CNT electrode and gel electrolyte PVA/H\(_2\)SO\(_4\) delivered a high capacitance of 1230.1 mF cm\(^{-2}\), a maximum energy density of 54.6 µWh cm\(^{-2}\) and a maximum power density of 30.0 mW cm\(^{-2}\). The electrochemical performance exhibited slight variation upon uniaxially, biaxially, or omnidirectionally stretching to 200%. Even after 20 omnidirectional stretching/releasing cycles, the capacitance loss was less than 4%, suggesting excellent mechanical stability.

5.1.5. Self-Healing and Stretchable Supercapacitors

Self-healability is one desirable feature in stretchable supercapacitors for wearable applications as supercapacitors are generally damaged and destroyed by external mechanical deformations. One simple way to achieve self-healability was to wrap self-healing polymer outside supercapacitors. Gao’s group coated stretchable and self-healing carboxylated polyurethane (CPU) on the spring-like fiber-shaped supercapacitor.\(^{[133]}\) Capacitance retention was 82.4% after the as-prepared supercapacitor was stretched to 100%. However, capacitance rapidly decreased to 54.2% after the third healing, resulting from misalignment of the broken electrodes. Zhi’s group developed a multifunctional electrolyte for stretchable supercapacitors.\(^{[134]}\) The electrolyte was comprised of polyacrylic acid dual crosslinked by hydrogen bonding and vinyl hybrid silica nanoparticles, thus contributing to the superior self-healability and stretchability. Without wrapping an extra layer of self-healing polymer into devices, volumetric/gravimetric capacitance based on the whole devices would not be compromised. Stretchable and self-healable supercapacitor was then assembled by pre-stretching the multifunctional electrolyte, paving flexible PPy coated CNT paper electrodes onto the electrolyte and incorporating small CNT patches on the cutting wounds. Enhanced capacitances were exhibited during stretching to 600% because of more active materials participating into electrochemical process. The healing efficiency was almost 100% after 20 breaking/healing cycles, which could be attributed to the high conductive CNT patches connecting broken parts. Our group prepared a stretchable and self-healing conductor for supercapacitors.\(^{[134]}\) The conductor was comprised of nickel flakes, CPU, and Ga-based liquid metal (Figure 9c). The conductor could be stretched to 700%. Additionally, a high healing efficiency of 97.5% could be achieved owing to electrical restoration by the flow of liquid metal and mechanical healing by the interfacial hydrogen bonding of CPU. A stretchable and self-healing supercapacitor was then constructed by sandwiching two such conductors around an ionic-liquid gel electrolyte. The CV and charge/discharge curves maintained the same under the applied strain of 200%. Upon restretching to 100% after healing from cutting, an increased electrochemical healability of 94% could be obtained, due to reversible faradaic reactions of Ga-based liquid metal in ionic liquid electrolyte.
5.1.6. Transparent and Stretchable Supercapacitors

In the rolled-up displays or wearable optoelectronics, both transparency and stretchability are required. As energy storage devices, transparent, and stretchable supercapacitors can be embedded into such systems as power sources for other transparent and stretchable electronics, like sensors and actuators, to facilitate human interactions and feedbacks. Additionally, it would be more desirable to incorporate and integrate transparent and stretchable energy storage devices and energy harvesters together in such systems to obtain self-powered capability. Thus, achieving optical transparency of stretchable supercapacitors is another step toward such power-integration with rolled-up display and wearable optoelectronic systems. One attempt was to prepare free-standing, flexible, and transparent graphene paper (Figure 9d) for transparent and stretchable supercapacitors. By employing prismlike graphene as building blocks, the graphene paper was prepared with outstanding electronic conductivity and mechanical properties and could be transferred to any substrates of interest. A transparent (transmittance of 59% at a wavelength of 800 nm) and stretchable (elongation of 38%) supercapacitor was assembled after transferring the prepared graphene paper onto transparent PDMS as electrodes and coating a thin layer of gel electrolyte PVA/H$_2$SO$_4$. It delivered stable electrochemical performance under alternating bending, stretching and releasing states during cycling. In addition to carbon-based transparent electrodes, Ag nanowire percolation network can also be a promising candidate for transparent and stretchable supercapacitors. To mitigate the oxidation issue of Ag nanowires, Au with a thickness of 5 nm was coated outside Ag nanowires as a transparent and stretchable electrode. The electrode could be stable at ambient atmosphere for 4 weeks while significant decrease of peak currents in CV curves were observed after
50 cycles, indicating electrochemical process resulted in 45% Ag loss and thus electrode degradation. To address the concern, our group prepared electrochemically stable Ni-Ag and Fe-Ag core–shell networks and transferred them to polyurethane acrylate matrix as stretchable (strain of 35%) and transparent (transmittance of 50%) electrodes for asymmetric supercapacitors, as shown in Figure 9c. The electrochemical stability was ascribed to the physical barrier and the electrochemical redox reactions of metal shell rather than the core Ag nanowires. Metal oxides/hydroxides were formed on the surface of metal shell, contributing to enhanced capacitance. Thus, the fabricated 1.6 V asymmetric supercapacitor delivered a high energy density of 0.68 mWh cm\(^{-3}\), a high power density of 313 mW cm\(^{-3}\), excellent cycling stability (92% capacity retention after 5000 cycles) and good stretchability (91% capacity retention under the strain of 35%). Typically, there is always a trade-off and balance between transmittance and electrochemical performance for transparent energy storage devices. Higher loading mass of active materials would enhance capacitance/capacities but inevitably compromise transmittance. The challenge would be to explore novel materials with optical transparency while providing electrochemical performance. Currently, the developments of transparent energy storage devices are lagging behind, not to mention transparent and stretchable energy storage devices. So far, the transmittances of assembled transparent and stretchable supercapacitors are reported to be at the range of 30–60%. It would be desirable to further enhance the transmittance and energy storage capacity simultaneously.

Owing to relatively simple configuration, stretchable supercapacitors are designed and introduced with additional functionalities, such as the above-mentioned optical transparency and self-healability, to meet their requirements in advanced wearable electronics. Other functionalities, such as biodegradability, temperature tolerance, and shape memory, would also be desirable to incorporate into stretchable supercapacitors. Biodegradability would be beneficial to reducing e-waste for environmental protection or contribute to the practicability of body implantable stretchable energy storage devices. Shape memory property would allow stretchable devices to resist external dynamic mechanical deformations and recover to their original shapes after stimuli. Temperature tolerance would prevent stretchable energy storage devices from power loss at extreme low temperatures or ignition at extreme high temperatures. However, these additional functionalities would inevitably complicate the synthesis/manufacture process and limit material selection of electrodes, current collector, gel/solid electrolyte and encapsulation layer in stretchable supercapacitors. Meanwhile, the low energy density would be further compromised by implementing multi-functionalities, which is another critical challenge for stretchable supercapacitors.

5.2. Stretchable Batteries

Stretchable batteries, which store energy through redox reactions, are widely considered as promising energy storage devices for wearable applications because of their high energy density, low discharge rate, good long-term stability, and lack of memory effect. In this section, recently reported stretchable Li-ion batteries are covered. Table 2 summarizes various stretchable batteries from the aspects of battery type, stretchability, average potential, energy density and capacity retention under mechanical deformations.

5.2.1. Stretchable Li-Based Batteries

Li-based batteries with Li\(^+\) as charge carriers, including Li-ion batteries and Li-air batteries, are of great interest because of low redox potential of Li/Li\(^+\) (~3.04 V versus SHE) and low weight and small radius of one-charge Li\(^+\), thus contributing to their wide working potential, enhanced energy density and improved kinetics of ion intercalation/de-intercalation. Recently, various stretchable Li-based batteries have been designed and reported with stable electrochemical performance under external mechanical influences.

**Stretchable Li-Ion Batteries:** As mentioned, wavy configuration is widely adopted in stretchable electrodes/batteries. A gum-like super stretchable Li-ion battery was assembled based on the wavy structures, consisting of highly stretchable and stable cathode and anode, gel electrolyte and elastic package. The battery was fabricated as illustrated in Figure 10a. Two aligned CNT sheets served as current collector and skeleton of electrodes. Random CNTs were blended with LMO and LTO nanoparticles, which were active materials of cathode and anode, respectively. The mixture of LMO-CNT and LMO-CNT were subsequently inserted into two aligned CNT sheets, forming a sandwich structure. Followed by introducing un-curing PDMS fluid into the mixture and placing the sandwich structure onto a pre-strained PDMS substrate, the electrodes were prepared. Owing to the novel wavy strategy and electrode material engineering, the as-prepared arched electrodes could maintain stable electrochemical performance after 500 stretching/releasing cycles with a high strain of 400%. Additionally, the assembled battery with the arched electrodes could deliver an areal capacity of 0.11 mAh cm\(^{-2}\), an average voltage of 2.4 V and an energy density of 1.6 mWh cm\(^{-2}\), which remained almost the same after the battery was stretched to a strain of 400% 200 times. Furthermore, dynamic electrochemical tests revealed less than 1% voltage fluctuation when the battery was subjected to repeated stretching/releasing cycles at a high speed of 3 cm s\(^{-1}\) (Figure 10b). These results verify the superior mechanical stretchability of the gum-like Li-ion battery.

A stretchable Li-ion battery via the wavy structures at battery level was reported by Cui’s group, in which all the components including electrodes, the separator and package materials could be stretched equally, as shown in Figure 10c. The prepared polyurethane/poly(vinylidene fluoride) membrane was considered as a promising separator in stretchable batteries because of its porous, sticky, and stretchable properties. These properties could avoid detachment between electrodes and separator and guarantee efficient ion transport especially under dynamic states. Owing to the unique separator, the wavy battery with commercial LiCoO\(_2\) as cathode and graphite as anode delivered constant areal capacity of 2.2 mAh cm\(^{-2}\) and energy density of 110 Wh L\(^{-1}\) at stretched and released states. The intensity of LED powered by the wavy battery remained steady even under the applied strain of 50%. Moreover, the wavy battery...
exhibited stable electrochemical performance at dynamic states of repeated stretching/releasing cycles (85% capacity retention at 0.5 C after 60 cycles under 50% strain). Enhanced areal capacity of 3.6 mAh cm$^{-2}$ and energy density of 172 Wh L$^{-1}$ were achieved by stacking double units in series.

Porous framework design is also employed in stretchable Li-ion batteries. 3D graphitic carbon/Si foam coated with elastomer (Figure 5e) was reported to be a high-capacity anode for stretchable Li-ion batteries.[64] The foam structure could be recovered after releasing the applied mechanical force. The highly elastic polymer coating could guarantee electrode integrity during stretching/releasing process. Thus, the as-synthesized electrode could display a high stretchability of 88% and sustain 1000 repeated stretching/releasing cycles at a strain of 25% with acceptable resistance change. As the foam was stretched, small cracks would be generated to dissipate stress and accommodate strain, thus resulting in resistance increase. Unfortunately, full cell of stretchable Li-ion batteries with the prepared carbon/Si foam anode were not assembled and demonstrated. Similarly, 3D porous sponge-like electrodes (Figure 5b–d) were prepared and could be stretched in all directions, superior to those stretchable electrodes which could only accommodate strain unidirectionally.[62] However, due to either electrode material aggregation or detachment during stretching and releasing, the sponge-like electrodes displayed reduced specific capacity and enlarged voltage hysteresis between charge and discharge profiles after 500 stretching/releasing cycles. Likewise, the electrochemical performance of the full cell under stretched states were also not evaluated.

Helically coiled spring configuration is also applied in the preparation of stretchable Li-ion batteries. Yarn cathode and anode was synthesized by coating LMO and LTO nanoparticles onto aligned CNT yarns, respectively.[73] Afterward, yarn electrodes were wound around an elastomeric substrate, followed by coating a thin layer of gel electrolyte. A stretchable fiber-shaped Li-ion battery was successfully fabricated through the spring structure and the elastic substrate. As shown in Figure 10d, the assembled fiber-shaped battery could be stretched to 100% with the elongation as high as 300%, as shown in Figure 4h–m. Subsequently, a highly stretchable battery was assembled with the elongation as high as 300%, as shown in Figure 4h–m. As the foam was stretched, small cracks would be generated to dissipate stress and accommodate strain, thus resulting in resistance increase. Unfortunately, full cell of stretchable Li-ion batteries with the prepared carbon/Si foam anode were not assembled and demonstrated. Similarly, 3D porous sponge-like electrodes (Figure 5b–d) were prepared and could be stretched in all directions, superior to those stretchable electrodes which could only accommodate strain unidirectionally.[62] However, due to either electrode material aggregation or detachment during stretching and releasing, the sponge-like electrodes displayed reduced specific capacity and enlarged voltage hysteresis between charge and discharge profiles after 500 stretching/releasing cycles. Likewise, the electrochemical performance of the full cell under stretched states were also not evaluated.

Table 2. Summary of the reported stretchable batteries.

<table>
<thead>
<tr>
<th>Battery type</th>
<th>Stretchable strategy</th>
<th>Stretchability [%]</th>
<th>Average voltage [V]</th>
<th>Capacity</th>
<th>Energy density</th>
<th>Capacity retention</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-ion battery</td>
<td>Wavy</td>
<td>400</td>
<td>2.4</td>
<td>0.11 mAh cm$^{-2}$</td>
<td>1.6 mWh cm$^{-2}$</td>
<td>87% after 100 cycles at 0% strain</td>
<td>[140]</td>
</tr>
<tr>
<td>Li-ion battery</td>
<td>Wavy</td>
<td>50</td>
<td>3.7</td>
<td>2.2 mAh cm$^{-2}$</td>
<td>110 Wh L$^{-1}$</td>
<td>85% after 60 cycles at 50% strain</td>
<td>[141]</td>
</tr>
<tr>
<td>Li-ion battery</td>
<td>Coiled spring</td>
<td>100</td>
<td>2.2</td>
<td>138 mAh g$^{-1}$</td>
<td>27 Wh kg$^{-1}$</td>
<td>84% after 200 cycles at 100% strain</td>
<td>[73]</td>
</tr>
<tr>
<td>Li-ion battery</td>
<td>Coiled spring</td>
<td>100</td>
<td>2.5</td>
<td>2.2 mAh m$^{-3}$</td>
<td>–</td>
<td>85% at 100% strain</td>
<td>[61]</td>
</tr>
<tr>
<td>Li-ion battery –</td>
<td>100</td>
<td>1.2</td>
<td>90 mAh g$^{-1}$</td>
<td>30 Wh kg$^{-1}$</td>
<td>80% at 100% strain</td>
<td></td>
<td>[146]</td>
</tr>
<tr>
<td>Li-ion battery –</td>
<td>50</td>
<td>0.9</td>
<td>43 mAh g$^{-1}$</td>
<td>35 Wh kg$^{-1}$</td>
<td>65% after 50 cycles at 50% strain</td>
<td></td>
<td>[151]</td>
</tr>
<tr>
<td>Li metal battery</td>
<td>Coiled spring</td>
<td>100</td>
<td>1.5</td>
<td>1132 mAh g$^{-1}$</td>
<td>–</td>
<td>90% after 100 cycles at 100% strain</td>
<td>[157]</td>
</tr>
<tr>
<td>Li-air battery</td>
<td>Wavy</td>
<td>100</td>
<td>2.5</td>
<td>7111 mAh g$^{-3}$</td>
<td>2540 Wh kg$^{-1}$</td>
<td>–</td>
<td>[78]</td>
</tr>
<tr>
<td>Zn-MnO$_2$ battery –</td>
<td>100</td>
<td>1.4</td>
<td>3.5 mAh cm$^{-2}$</td>
<td>–</td>
<td>–</td>
<td></td>
<td>[21]</td>
</tr>
<tr>
<td>Zn-MnO$_2$ battery –</td>
<td>100</td>
<td>1.3</td>
<td>3.88 mAh cm$^{-2}$</td>
<td>–</td>
<td>–</td>
<td></td>
<td>[22]</td>
</tr>
<tr>
<td>Zn-MnO$_2$ battery –</td>
<td>Sponge</td>
<td>100</td>
<td>1.0</td>
<td>3.6 mAh cm$^{-2}$</td>
<td>–</td>
<td>89% at 100% strain</td>
<td>[171]</td>
</tr>
<tr>
<td>Zn-MnO$_2$ battery –</td>
<td>Coiled spring</td>
<td>300</td>
<td>1.25</td>
<td>302 mAh g$^{-1}$</td>
<td>53.8 mWh cm$^{-3}$</td>
<td>95% after 100 cycles at 300% strain</td>
<td>[95]</td>
</tr>
<tr>
<td>Zn-Ag battery –</td>
<td>100</td>
<td>1.5</td>
<td>0.11 mAh cm$^{-2}$</td>
<td>0.17 mWh cm$^{-2}$</td>
<td>81% at 80% strain</td>
<td></td>
<td>[176]</td>
</tr>
<tr>
<td>Zn-Ag battery –</td>
<td>100</td>
<td>1.1</td>
<td>2.5 mAh cm$^{-2}$</td>
<td>–</td>
<td>–</td>
<td></td>
<td>[178]</td>
</tr>
<tr>
<td>Zn-Ag battery –</td>
<td>Coiled spring</td>
<td>100</td>
<td>1.5</td>
<td>3.5 mAh cm$^{-2}$</td>
<td>–</td>
<td>103% at 100% strain</td>
<td>[179]</td>
</tr>
<tr>
<td>Zn-Ni/Co battery –</td>
<td>Wavy</td>
<td>400</td>
<td>1.6</td>
<td>73 mAh g$^{-1}$</td>
<td>–</td>
<td>87% after 500 cycles at 400% strain</td>
<td>[183]</td>
</tr>
<tr>
<td>Zn-air battery –</td>
<td>Wavy coiled spring</td>
<td>800</td>
<td>1.2</td>
<td>800 mAh g$^{-1}$</td>
<td>930 Wh kg$^{-1}$</td>
<td>–</td>
<td>[186]</td>
</tr>
<tr>
<td>Zn-air battery –</td>
<td>500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-ion battery –</td>
<td>Sponge</td>
<td>100</td>
<td>1.3</td>
<td>595 mAh g$^{-1}$</td>
<td>573 Wh kg$^{-1}$</td>
<td>–</td>
<td>[187]</td>
</tr>
<tr>
<td>Al-air battery –</td>
<td>Coiled spring</td>
<td>30</td>
<td>1.3</td>
<td>935 mAh g$^{-1}$</td>
<td>1168 Wh kg$^{-1}$</td>
<td>–</td>
<td>[79]</td>
</tr>
</tbody>
</table>
Stretchable Aqueous Li-Ion Batteries: Organic electrolytes are predominately employed in Li-ion batteries because of their wide potential window, which can contribute to improved energy density. However, their flammability, volatility, and toxicity can lead to potential safety risks, such as exploding and catching fire, under repeated mechanical deformations, which makes them undesirable to be utilized in stretchable Li-ion batteries. Additionally, organic electrolyte exhibits inherently low ion transport, resulting in low power density of Li-ion batteries. Furthermore, organic electrolyte is expensive. Thus, stretchable aqueous Li-ion battery based on safe, cheap, and high ionic conductivity aqueous electrolyte is proposed as alternative power supply for wearable electronics.

One example is developed by Park’s group. First, they prepared the hybrid carbon/polymer composite (HCP) as stretchable current collector, which could effectively maintain its good electrical conductivity (150 $\Omega$ $\square^{-1}$) even under a high strain of 200%. Afterward, active materials LMO@CNT and polyimide-coated activated carbon (PI@AC) were synthesized as cathode and anode material. Stretchable electrodes were fabricated by integrating the electrode materials onto the elastic current collector. A stretchable aqueous Li-ion battery was then assembled with 1 M Li$_2$SO$_4$ as electrolyte and packaged with stretchable polymer ecoflex. The battery could sustain a strain of 100% with capacity retention of 80%. When the strain was back to 0%, the capacity returned to its original value. However, it should be noted that, because of the utilization of aqueous electrolyte, the average potential was around 1.2 V and the maximum energy density obtained was 30 Wh kg$^{-1}$, less than the reported stretchable Li-ion batteries with organic electrolyte, even though the delivered maximum power density could be as high as 1260 W kg$^{-1}$. Additionally, the liquid electrolyte in this stretchable battery could result in possible electrolyte leakage issue especially under mechanical deformations.

Recently, stretchable water in salt (WiS) aqueous gel electrolyte was then brought up and applied in stretchable aqueous Li-ion battery to widen electrochemical window. WiS aqueous electrolyte with extremely high concentration of lithium salt in water can deliver high ionic conductivity as well as wide electrochemical window because water decomposition is suppressed by solvation process of lithium salt. Through immersing a PAM hydrogel membrane into water and then the prepared WiS electrolyte (22 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)), PAM-WiS was prepared, as shown in Figure 11a. Water in the network of cross-linked PAM chain was replaced by WiS. The obtained PAM-WiS could simultaneous possess mechanical stretchability (300%) as well as electrochemical functionalities (high ionic conductivity ($10^{-3}$–$10^{-2}$ S cm$^{-1}$) and broaden electrochemical window (1.95–4.3 V versus Li/Li$^+$)), presenting promising in stretchable aqueous Li-ion battery. Another important component is stretchable current collector. The author designed
a composite layer (SEBS/CNT/CB) (SCC) with a uniform top layer of Ag microflakes as stretchable current collector (SCCA) (Figure 11b). Both the top Ag layer and the bottom percolating carbon network (CNT/CB) could provide fast electron transport path. Even if small cracks occurred on the top Ag layer upon stretching, the bottom percolating CNT/CB network could bridge the gap of cracks to guarantee fast electron transport. The sheet resistance of SCCA at 0% and 100% was 0.53 and 2.71 $\Omega \square^{-1}$, respectively. By contrast, without the top Ag layer, SCC exhibited sheet resistance increase from 115 to 200 $\Omega \square^{-1}$ when the strain was from 0% to 100%, underlying positive effects of Ag flakes toward the significant improvement of electrical conductivity. However, it could be noticed that the sheet resistance largely increased to 137 and 200 $\Omega \square^{-1}$ after SCCA was subjected to 100 stretching/releasing cycles at the strain of 0% and 100%, respectively. It could be attributed to oxidation and destruction of Ag microflakes during cyclic strains. LMO and prelithiated V$_2$O$_5$ was selected as cathode and anode active materials, respectively, as their redox peaks were located within the stable voltage window (1.95–4.93 V versus Li/Li$^+$). To ensure robust adherence and avoid delamination between active materials and current collector, a mask-assisted spray-coating method was adopted to deposit electrode slurries onto SCCA. The full battery was assembled with sandwiched...
structure: cathode, gel electrolyte, and anode, as shown in Figure 11c. As the PAM-WiS hydrogel was sticky, the interface between electrodes and gel electrolyte would maintain robust even under mechanical deformations. The assembled battery could be subjected to twisting, bending and stretching which could maintain structural integrity. However, it was observed that capacity loss was 35% and energy density decreased from 35 to 17 Wh kg$^{-1}$ when the thin film battery was stretched to 50%. It could be ascribed to large internal resistance and the following severe polarization under stretched states. The introduction of mechanical strain resulted in the compromised electrochemical performance. It could be due to the multilayers of the thin film battery with various interfaces, which could suffer from delamination and thus increased internal resistance under stretching states. Another possible reason was the designed current collector with Ag microflakes, which would significantly degrade upon exposure to air and moisture. Potential improvements might be achieved by protecting the conductive Ag flakes.

**Stretchable Li Metal Batteries**: Compared to traditional Li-ion batteries commonly using LTO or graphite as anode materials, Li batteries directly employing Li metal as anodes can deliver enhanced energy density because of low redox potential of Li/Li$^+$ (≈3.04 V versus SHE) and high theoretical specific capacity (3860 mAh g$^{-1}$) of Li$^{[147,152–154]}$. Li metal anodes cannot accommodate strain. Above 25% strain would lead to irreversible elongation and subsequent fracture. Additionally, dendrite growth of Li metal anode during charge/discharge lead to non-uniform Li-ion flux and poor cycling stability, thus further hindering their applications in stretchable energy storage devices.$^{[155,156]}

Inspired by spring structures to realize stretch capability, a fiber-shaped Li metal anode (Li-ZnO@CNT fiber) was fabricated, as illustrated in Figure 11d.$^{[157]}$ The introduction of ZnO arrays could overcome the issue of low Li affinity onto large surface-tense CNT fibers. The as-prepared Li metal anode on ZnO arrays with large surface area could effectively homogenize Li-ion flux and generate Li stripping/deposition with low overpotential. The fabrication process of a stretchable Li battery was displayed in Figure 11e. An elastic fiber was first pre-strained to 100%, followed by coating a thin layer of PEO-based gel electrolyte. The as-prepared fiber-shaped Li metal anode was then winded onto the pre-strained and coated elastic fiber, indicating that a stretchable Li metal anode was synthesized. Similarly, the prepared fiber-shaped cathode (MoS$_2$@CNT) was winded on the elastic fiber, followed by another thin layer of gel electrolyte was coated on the Li anode. Subsequently, the third layer of gel electrolyte was coated to encapsulate the battery and the elastic fiber was released to its original length. Hence, a stretchable fiber-shaped Li battery was assembled, which could be stretched to 100% with negligible capacity loss. Additionally, the Li battery could endure 100 stretching/releasing cycles at a strain of 100% with capacity loss of less than 10%. These results verified good stretchability of the assembled fiber-shaped Li battery.

Li-air batteries based on Li metal as anode and O$_2$ as cathode, are regarded as promising energy storage devices because of an ultrahigh theoretical energy density of 3500 Wh kg$^{-1}$, five to ten times higher of traditional Li-ion batteries.$^{[158–160]}$ The preparation of stretchable Li metal anode as well as stretchable carbon-based electrodes have been discussed earlier. Thus, stretchable Li-air batteries can be prepared as attractive power source for wearable electronics.

The first Li-air battery was fabricated by Peng’s group.$^{[78]}$ Stretchable air electrode was prepared by stacking aligned CNT sheet onto pre-strained elastic polymer substrate (Ecoflex) and then releasing the polymer substrate to its original state. Stretchable Li anodes were prepared by paving Li sheets on Cu sheets current collector, which were connected with Cu springs. After the prepared gel electrolyte was sandwiched between stretchable air electrode and stretchable Li anode, the stretchable Li-air battery was finally accomplished (Figure 11f). It is shown that the stretchable air electrode could endure 1000 stretching/releasing cycles at a strain of 100%, during which electrical resistance fluctuation was less than 4%. Owing to Cu springs, Li anode could also sustain 1000 repeated stretching/releasing cycles at a strain of 100% while maintaining structural integrity. Stretchability of the Li-air battery was then investigated. We can see that discharge voltage plateau (≈2.5 V), internal resistance and charge transfer resistance could be well maintained after the Li-air battery was stretched to 100%. Even at high stretching speed and after 1000 stretching cycles, the electrochemical performance remained stable. It should be noted that the energy density obtained in the Li-air battery could be as high as 2540 Wh kg$^{-1}$, much higher compared to previous reported stretchable Li-ion batteries (<150 Wh kg$^{-1}$). However, the electrochemical performance of the prepared Li-air battery would suffer from remarkable degradation at high humidity of 20%. The reason for that was the reaction of permeated H$_2$O with discharge product Li$_2$O$_2$, thus leading to byproduct (LiOH and Li$_2$CO$_3$) accumulation at the air electrode. Therefore, further modifications are needed for practical applications, such as introducing a hydrophobic diffusion layer.

In addition to the above mentioned issues in stretchable Li-ion/Li-metal batteries, another critical challenge is the high interfacial impedances between electrodes and gel/solid electrolytes, leading to sluggish charge transfer kinetics and undesirable electrochemical performance including cycling stability, rate capability, and power density for practical applications. Unlike liquid electrolyte, gel/solid electrolytes exhibit poor wetability/contact with electrodes. More loss of effective contact area takes place when electrodes/Li metal anode experience large volume change during ion intercalation/de-intercalation/ Li stripping/deposition or devices are being stretched/released, inducing ion insulating. It is challenging to construct stretchable batteries with conformal and continuous ionic contact at the interface of electrodes and electrolytes during operation at dynamic stretching/releasing states. Besides, stretchable Li-based batteries with high energy density and satisfactory cycling performance have not been demonstrated. Other high-capacity cathodes, such as S, can also be explored and assembled into stretchable Li-S batteries to achieve high energy density.

5.2.2. Stretchable Aqueous Zn-Based Batteries

Even though stretchable Li-based batteries are attractive in wearable applications, they present potential safety issues related with flammable and toxic organic electrolyte and high-cost problems...
associated with limited resources of Li.[161,162] Thus, researchers have been exploring alternatives with material abundance, high safety, environmental friendliness, and high energy density. One of the substitutes is stretchable aqueous Zn-based battery with Zn metal as anode. Zn metal exhibits rich abundance, eco-friendliness, and high theoretical capacity (819 mAh g\(^{-1}\), 5851 mAh cm\(^{-3}\)).[163–165] More impressively, Zn is inert at ambient atmosphere and can be safely handled in air, thus simplifying battery assembly process.[166] Moreover, high redox potential of Zn/Zn\(^{2+}\) (−0.76 V versus SHE) allows Zn metal to be applied in aqueous electrolyte without electrolyte decomposition.[167] Various stretchable aqueous Zn-based batteries, including Zn-MnO\(_2\), Zn-Ag, Zn-Co/ Ni, and Zn-air batteries, have been reported through structural and material engineering.

**Stretchable Aqueous Zn-MnO\(_2\) Batteries:** Aqueous Zn-MnO\(_2\) battery system has been widely reported with advantageous electrochemical performance and merits of low costs, environmental friendliness and simple fabrication.[168–170] In 2010, the stretchable aqueous Zn-MnO\(_2\) battery was first fabricated and demonstrated (Figure 12a).[21] An elastic substrate was coated with a layer of carbon black and silicon oil paste as elastic current collector. Afterward, Zn anode paste and MnO\(_2\) cathode paste were laterally applied to the elastic current collector, followed by aqueous gel electrolyte coating. The prepared aqueous Zn-MnO\(_2\) battery exhibited open-circuit potential of 1.5 V, areal capacity of 3.5 mAh cm\(^{-2}\) and a lifetime of 1000 h. Moreover, the battery could be stretched to 100%. However, the high-level strain of 100% would cause irreversible depercolation effects in

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**Figure 12.** a) Schematic illustration of a stretchable aqueous Zn-MnO\(_2\) battery. Reproduced with permission.[21] Copyright 2010, Wiley-VCH. b) Scheme of a stretchable Zn-MnO\(_2\) battery in top configuration. Reproduced under the terms and conditions of the Creative Commons Attribution NonCommercial License 4.0.[171] Copyright 2017, the Authors, published by American Association for the Advancement of Science. c) Schematic diagram of fabrication and encapsulation of the stretchable and fiber-shaped Zn-MnO\(_2\) battery. Reproduced with permission.[172] Copyright 2018, American Chemical Society. d) Cross-sectional schemes of the stretchable Zn-Ag battery. e) Charge/discharge curves of the stretchable Zn-Ag battery at 0% and 80% strain. (d) and (e) reproduced with permission.[173] Copyright 2013, Wiley-VCH. f) Screen-printing steps of the stretchable Zn-Ag\(_2\)O battery. (Inset: Redox reactions at cathode and anode side.) g) The first charge/discharge cycle of the stretchable battery at 0% and 100% strain. (f–h) reproduced with permission.[174] Copyright 2016, Wiley-VCH. i) The assembly flow diagram of the flexible and stretchable fiber-shaped Zn-Ag battery. j) Areal capacity and coulombic efficiency of the assembled battery under alternating relaxed and stretching states during cycling. Reproduced under the terms and conditions of the Creative Commons Attribution NonCommercial License 4.0.[175] Copyright 2017, the Authors, published by American Association for the Advancement of Science.
the electrodes and decreased short-circuit current of the device. Further optimization and developments toward more reliable stretchable aqueous Zn-MnO$_2$ batteries are desirable. Subsequently, a stretchable wavy silver fabric, made from weaving silver-coated nylon threads into rubber matrix, was introduced into stretchable aqueous Zn-MnO$_2$ system (Figure 4d–g). The fabric could act as robust current collector to support cathode (MnO$_2$) and anode (Zn) active materials and withstand mechanical deformation. The assembled battery delivered a capacity as high as 3.88 mAh cm$^{-2}$ at initial states, which maintained the same under a strain of 100%. Sponge-based electrodes were also prepared for stretchable aqueous Zn-MnO$_2$ batteries. A stretchable current collector was fabricated by coating silver nanowires onto polyurethane (PU) sponge via a facile dipping coating process. The porous networks of current collector enabled high mass loadings of active materials (MnO$_2$ and Zn particles). An areal capacity of 3.6 mAh cm$^{-2}$ was obtained in the fabricated Zn-MnO$_2$ battery. Capacity retention of 89% was achieved when the battery was stretched to 100%. However, in the above reported stretchable Zn-MnO$_2$ batteries, the cathode and anode were laterally separated by a certain distance. It was found that such lateral configuration would increase internal resistance because of large distance between cathode and anode. By contrast, a top configuration, in which cathode, separator, and anode are sandwich-like placed, would be beneficial to reducing internal resistance and increasing specific capacity. Moreover, the sandwich-structured Zn-MnO$_2$ battery exhibited better electrochemical performance under stretched states because of thinner gel electrolyte with lower electrolyte resistance (Figure 12b).

A stretchable aqueous spring-structured Zn-MnO$_2$ battery was fabricated, which was composed of MnO$_2$ coated CNT yarn as cathode, Zn coated CNT yarn as anode and highly stretchable and high ionic-conductivity electrolyte based on PAM hydrogel (Figure 12c). The assembled battery delivered good electrochemical performance (a high specific capacity of 302.1 mAh g$^{-1}$), a discharge plateau of 1.25 V, a volumetric energy density of 53.8 mAh cm$^{-3}$, capacity retention of 98.5% after 500 cycles at a current density of 2 A g$^{-1}$). Additionally, the battery could endure 100 stretching cycles at a strain of 300% with capacity retention of 95%. Thus, with good electrochemical performance as well as mechanical robustness, the battery presents promising in integration with other electronics for wearable applications.

**Stretchable Aqueous Zn-Ag Batteries**: As one of the most mature battery systems, aqueous Zn-Ag batteries with Ag as cathode and Zn as anode can deliver high power density and comparable energy density to Li-ion batteries. In addition, these virtues, including their environmental benignity, low toxicity, air stability, enhanced safety, and simple manufacture process, enable them to be applied in both large and small scales and make them attractive in wearable electronics. Our group developed a stretchable Zn-Ag battery based on embedded Ag nanowires (AgNW) into elastic substrate PDMS. The stretchable cathode AgNW/PDMS was prepared through a lithographic filtration method. It could deliver an areal capacity of 0.27 mAh cm$^{-2}$ and maintain stable after 1000 charge/discharge cycles at a strain of 80%. The stretchable anode was fabricated by electroplating Zn onto AgNW/PDMS. The stretchable Zn-Ag battery could be assembled with lateral layout of cathode and anode in 10 m NaOH electrolyte (Figure 12d). The full cell delivered an areal capacity of 0.11 and 0.09 mAh cm$^{-2}$ at relaxed (0%) and stretched (80%) states, respectively (Figure 12e). However, the full cell experienced poor cycling stability, originated from reactive Zn anode in alkaline electrolyte. Zn anode would be consumed after tens of cycles. Wang’s group fabricated an epidermal tattoo-based Zn-Ag battery with lateral arrangement of cathode and anode as power supply for wearable electronics. The inexpensive, facile, and mass-production screen printing technology was employed to the fabrication process. However, the battery could only endure a small strain of 11.1%. Additionally, the prepared Zn-Ag battery suffered from inferior cycling stability. The capacity significantly dropped from 1.48 to 0.5 mAh cm$^{-2}$ after 13 cycles. It was also resulted from the loss of Zn anode during charge/discharge process. Another reason for capacity decay would be hydrogen evolution at anode side. Later, Wang’s group developed highly elastic and conductive inks for the screen-printed stretchable Zn-Ag batteries (Figure 12f). Hyperelastic polystyrene-block-polysoprene-blockpolystyrene was introduced into the electrode ink preparation as elastic binder with high mass loading, which would enhance mechanical properties of electrodes/battery while maintain their electrochemical performance. As a result, an areal capacity as high as 2.5 mAh cm$^{-2}$ and a corresponding discharge plateau of 1.1 V at a current density of 3 mAh cm$^{-2}$ was obtained when the prepared battery was stretched to 100% (Figure 12g). However, the all-printed Zn-Ag battery also encounter the issue of limited charge/discharge cycles (up to 30 cycles) (Figure 12h), due to the reaction of Zn anode with alkaline electrolyte and hydrogen evolution at Zn anode.

As shown in Figure 12i, a novel serpentine-shaped Zn-Ag battery with high stretchability was fabricated based on helical band spring as current collector. Zn anode was electroplated at high current densities on current collector to generate hyperdendrite morphology, which could effectively accommodate strain because of void spaces among dendrites. PVA-based gel electrolyte was dip-coated on Zn anode, followed by wrapping a layer of cellophane. The cellophane layer could protect Zn anode and gel electrolyte and mitigate Ag cathode migration. The fabrication of Zn-Ag battery was accomplished after Ag cathode was wrapped onto the cellophane. Owing to the unique design, the prepared Zn-Ag battery could endure 500 stretch cycles at a strain of 100% while maintain stable capacity as high as 3.5 mAh cm$^{-2}$ (Figure 12i). The internal resistance changed little between relaxed and stretched states, indicating structural robustness under mechanical deformations.

**Stretchable Aqueous Zn-Ni/Co Battery**: Aqueous Zn-Ni batteries are attracting increasing attentions because of high output voltage (~1.8 V). Bimetallic (Co, Ni) hydrides exhibit higher capacity and energy density than individual metal counterparts owing to synergistic effects. Thus, a highly stretchable Zn-Ni/Co battery was fabricated based on pre-strain strategy and elastic hydrogel separator. Nickel cobalt hydrides and Zn nanosheets were electrodeposited on flexible current collector (Au coated on CNT paper) as cathode and anode, respectively. The PANi polyelectrolyte was prepared as stretchable separator. Afterward, it was pre-stretched to 400%. Each side of the stretched hydrogel was paved with...
cathode and anode, followed by releasing it to relaxed state. Hence, wavy structures were formed in the sandwiched battery. When the battery was subjected to 400% strain, capacity enhancement (from 53.7 to 72.9 mAh g$^{-1}$) was observed, which could be attributed to decreased thickness of hydrogel electrolyte, increased contact area between active materials and electrolyte and thus better utilization of active materials. Owing to the wavy structures and highly stretchable hydrogel electrolyte, the prepared Zn-Ni/Co battery could maintain 87% of its initial capacity after 500 stretching cycles at 400% strain.

**Stretchable Aqueous Zn-Air Batteries:** Zn-air batteries are attractive as power supplies for wearable electronics because of their high theoretical energy density up to 1086 Wh kg$^{-1}$, much higher than the current dominant commercial Li-ion batteries, and simple assembly process favorable to scale up at low prices.[184,185] A flexible and stretchable fiber-shaped Zn-air battery was reported with Zn spring as anode, a hydrogel electrolyte PEO/PVA/KOH as separator and electrolyte, and aligned and porous CNT sheets as O$_2$ diffusion layer and current collector of air cathode.[44] The power and energy densities were calculated to be 6 Ah L$^{-1}$ and 5.7 Wh L$^{-1}$, respectively. The discharge plateau was ~1.0 V. Owing to the spring structure, the prepared Zn-air battery exhibited stretchable properties. However, the elongation was limited to 10%, hindering their applications in wearable electronics. The limited elongation of the assembled Zn-air battery could be ascribed to the poor stretchability of PVA-based gel electrolyte with high concentration of alkaline solution. To achieve better output power density, the electrolyte commonly used in Zn-air batteries is 6 M KOH. However, most hydrogels would lose their stretchability and display poor ionic conductivity under such strong alkaline environment. Thus, Zhi's group prepared alkaline-tolerant hydrogel electrolyte with high stretchability and ionic conductivity for stretchable Zn-air battery.[186] The hydrogel was developed based on PANa, N,N-methylene-bis-acrylamide and cellulose. The cross-linking among them contributed to enhanced mechanical robustness and stretchability of the prepared hydrogel in strong alkaline solution. After infiltrated by 6 M KOH, the obtained hydrogel electrolyte displayed a high stretchability of 100% with a good ionic conductivity of 0.28 S cm$^{-1}$. CNT paper-based was employed as air diffusion layer and current collector of air cathode owing to its high porosity and good electrical conductivity. Zn was deposited on CNT paper as anode. The hydrogel electrolyte membrane was pre-stretched to 800%, followed by attaching air cathode and Zn anode on each side of the electrolyte membrane. The 800% stretchable flat-type Zn-air battery with wavy structures was subsequently constructed (Figure 13a) after releasing the electrolyte membrane to its relaxed state. The Zn-air battery delivered a high specific capacity of 800 mAh g$^{-1}$, a discharge voltage of 1.2 V and a corresponding energy density as high as 930 Wh kg$^{-1}$. The electrochemical performance remained stable after repeated stretching/releasing cycles. A stretchable fiber-shaped Zn-air battery (Figure 13b) was also fabricated to realize weavability within textiles. Zn spring was coated with 500% pre-stretched hydrogel electrolyte. CNT paper was then attached to the pre-stretched hydrogel electrolyte. After releasing the electrolyte to its relaxed state, a stretchable fiber-shaped Zn-air battery was accomplished. It could be stretched to 500% with enhanced capacity of 800 mAh g$^{-1}$ and discharge voltage of 1.2 V. The electrochemical performance could be maintained after 100 stretching/releasing cycles at 500% strain, suggesting mechanical reliability of the prepared Zn-air battery. The weavability was demonstrated by integrating four stretchable fiber-shaped Zn-air batteries into wristband to power up an electronic watch.

A highly stretchable Zn-air battery array was developed by integrating individual Zn-air battery with serpentine electrical connections. The individual Zn-air battery was prepared with Co$_3$O$_4$ grown on carbon cloth as air diffusion and catalyst layer and current collector of air cathode, Zn foil as anode and PVA/KOH as gel electrolyte.[187] Owing to the island-bridge configuration, the fabricated 2 × 2 Zn-air battery array displayed stable electrochemical performance under repeated and dynamic stretching/releasing cycles with a strain of 100%. The energy density could be achieved as high as 573 Wh kg$^{-1}$. Additionally, the Zn-air battery array could be designed through circuit connection to enhance voltage or current output for practical applications.

From the above discussions of the stretchable aqueous Zn-based batteries, we can see that in spite of various merits including low costs, high safety, simplified manufacture process, acceptable areal/gravimetric capacity, and satisfactory stretchability via materials, structure and device engineering, there are still some drawbacks/challenges needing to be addressed inheriting from aqueous Zn-based batteries. One issue is the inferior cycling stability, especially in the stretchable alkaline Zn-air and Zn-Ag batteries (less than 500 cycles). It is resulted from the utilization of alkaline electrolytes (KOH/NaOH) and subsequent dendrite growth on Zn anode and formation of irreversible and insulating by-products, leading to poor coulombic efficiency and fast capacity decay. It is advisable to modify alkaline electrolytes to neutral/mildly acidic electrolytes with better stability and compatibility with Zn anode. In the stretchable Zn-MnO$_2$ battery with Zn$^{2+}$ insertion/extraction mechanism, the strong electrostatic interaction between bivalent Zn$^{2+}$ and MnO$_2$ would result in sluggish kinetics of Zn$^{2+}$ insertion/extraction and structure transformation/dissolution of MnO$_2$, which are also responsible for the undesirable cycling stability. Some strategies including introducing vacancies into MnO$_2$ cathode materials and incorporating monovalent Li$^+$ into electrolytes would be effective to enhance cycling performance. Loss of effective contact resulting from volume change during Zn stripping/plating and the consequent large interfacial resistance between Zn metal anode and gel/solid electrolytes is another reason for the capacity degradation in the stretchable batteries. Further improvements of the cycling stability in the stretchable aqueous Zn-based batteries are still needed for practical applications.

Another issue is the moderate operating voltage output (<2 V) leading to insufficient energy density, which is commonly encountered in aqueous batteries. The voltage output in a battery cell is generally dependent on electrochemical window of electrolytes and the redox potentials between cathode and anode. Increasing concentration of the stretchable hydrogel electrolytes would be beneficial to suppression of electrolyte decomposition and water splitting and widening of electrochemical window. However, it is at the expenses of high electrolyte viscosity, low ionic conductivity, retarded reaction kinetics
Figure 13. a) Schematic illustration of a stretchable sandwich-structured zinc-air battery. (a) and (b) reproduced with permission.[186] Copyright 2019, Wiley-VCH. c) Schematic illustration of the integrated fiber-shaped device for photoelectric conversion and energy storage. Reproduced with permission.[199] Copyright 2012, Wiley-VCH. d) Working mechanism of the self-charging package for wearable electronics. e) Systematic configuration of the self-charging power clothes to harvest the mechanical energy from the body and then to directly power wearable electronics. f) Photographs of the power package under various mechanical deformations (scale bar: 5 cm). g) V–t curve of the self-charging power package under various operating modes. (Inset: circuit diagram of the power package). h) V–t curve of the self-charging power package charging by mechanical motions. (Inset: photograph of charging the package by hand flapping). i) Enlarged V–t curve of the power package connected to an electric watch under various operating modes, including discharging, sustainable, and charging mode. (d–i) reproduced with permission.[207] Copyright 2016, American Chemical Society.
and thus inferior rate capacity. Thus, further optimizations of electrolyte electrochemical window, rate capacity as well as stretchability are required in the stretchable aqueous Zn-based batteries. Exploring cathode electrode with high redox potential is more promising to deliver higher voltage output. Unfortunately, so far, limited cathode materials are capable of exhibiting electrochemical performance in the aqueous Zn-based batteries. It is even more challenging to achieve high voltage output, satisfactory electrochemical performance and favorable stretchability in the stretchable aqueous Zn-based batteries.

5.2.3. Other Stretchable Batteries

In addition to the widely investigated Li-based and Zn-based batteries, other batteries, like Na\[^{+}\][188,189] and Al-based\[^{190}\] batteries, are also attracting considerable attentions in stretchable energy storage devices for wearable technologies. As both Na\[^{+}\] and Li\[^{+}\] are monovalent cations, Na-ion batteries exhibit similar electrochemical performance to Li-ion batteries while Na is lower costs compared to Li. Thus, Yu’s group developed an all-stretchable-component Na-ion battery.\[^{63}\] Electrically conductive and elastic graphene-modified PDMS sponge was prepared as stretchable current collector. VOPO\(_4\) and hard carbon was casted onto the current collector as stretchable cathode and anode, respectively. With sodium-ion-conducting gel polymer as stretchable separator, the all-stretchable-component Na-ion battery was assembled, which could be stretched to 50% with capacity retention of 89%. No delamination was observed in the battery after 100 stretching/releasing cycles, indicating its mechanical robustness. Compared to monovalent-based batteries, multivalent-based batteries theoretically store more energies due to multiple electron transfers.\[^{162,191}\] Al-air battery is one example to deliver high theoretical energy densities.\[^{192}\] Peng’s group developed an all-solid-state fiber-shaped Al-air battery with a high specific capacity of 935 mAh g\(^{-1}\) and a corresponding energy density of 1168 Wh kg\(^{-1}\).[79] With Al spring as anode, followed by coating hydrogel electrolyte and wrapping Ag-coated CNT sheets as air cathode, stretchable Al-air battery was fabricated. It could endure an elongation of 30% with stable output voltage. Two series-connected Al-air batteries could be woven into textiles to power up LED watch. However, cycling performance was not demonstrated in this stretchable Al-air battery. It should be noted that, similar to Zn-based batteries, Al-based batteries suffer from side reactions and formation of irreversible by-products at Al metal anode side. Additionally, owing to strong electrostatic interactions between trivalent Al\(^{3+}\) and the framework of electrode materials, sluggish reaction kinetics take place in Al-based batteries, thus leading to the inferior cycling stability. Lower voltage output and few cathode materials available are also the practical challenges needing to overcome in Al-based batteries.

Regarding to multi-functional properties, such as self-healability, biodegradability, shape memory, and temperature tolerance, it is still challenging to accomplish in stretchable batteries for advanced wearable electronics. It can be attributed to the complicated manufacture process and limited material selection of all the components in stretchable batteries. Numerous efforts are needed to put into the realization of multi-functional stretchable batteries.

Therefore, these key parameters, including operational voltage, energy density, long-term cycling stability, stretchability, safety, and fabrication process, are evaluated in SESDs for wearable applications. Generally, compared to stretchable supercapacitors, stretchable batteries display higher energy density and larger operational voltages, thus enable them to be applied in wearable gadgets for long-term operations, such as human-health monitoring. Stretchable Zn-based batteries with improved safety and acceptable energy density can be one promising option for such applications. By contrast, owing to fast charge/discharge process, excellent cycling stability, and desirably safe, stretchable supercapacitors can be ideally integrated with energy harvesters for wearable self-driven systems. Especially for fiber-shaped stretchable supercapacitors, their superior flexibility and stretchability enable them to be potentially adopted into modern textile (weaving/knitting) technology to realize true wearable energy storage fabrics and allow air/moisture to pass through. Thus, various SESDs have their own advantages and corresponding applications.

So far, the main challenges of SESDs are the delamination issues and complex fabrication process. Under repeated mechanical deformations, delamination would possibly occur at these interfaces, including separator/electrodes, active materials/substrate as well as package layer/device, thus resulting into short life span of SESDs. The complex fabrication process of each component in SESDs, including stretchable electrodes, stretchable separators, and stretchable package layer, make it challenging for low manufacture costs of SESDs and their practical applications. Thus, it remains essential to explore novel materials and structure designs for SESDs with desirable durability and simple manufacture process.

6. Integrated Systems Powered by SESDs

Integrated systems with SESDs as power sources to drive various electronic devices are urgently desired to realize multifunctional features.\[^{16,193}\] In 2016, Peng’s group integrated the prepared stretchable Li-air battery with a sensor suite for physiological monitoring.\[^{78}\] Owing to its superior elastic deformation, the stretchable battery could be adapted to be worn on the head to collect physiologic signals or woven into textiles to power LED. The body-attachable stretchable integrated system demonstrated promising prospects in monitoring health signals without external power source.

Even though the merits of the above-mentioned integrated systems, it would be much better to generate self-driven integrated systems by incorporating energy harvester units.\[^{194-196}\] As solar power is regenerative and clean, one kind of such self-driven integrated systems is based on solar cell as energy harvester and supercapacitor as energy storage unit, which was proposed by several groups.\[^{197,198}\] Peng’s group reported an integrated energy wire to simultaneously realize photoelectric conversion and energy storage in one device, as shown in Figure 13c.\[^{199}\] The overall efficiency could reach up to 1.5%. Later, Li’s group fabricated an integrated photo-supercapacitor device with TiO\(_2\) arrays as electrode materials for both solar cell and supercapacitor, thus the overall efficiency increased to 1.64%.\[^{200}\]
In addition to solar energy, mechanical energy from human motions, such as walking and running, can be harvested as well through nanogenerators. Wang’s group developed various self-powered systems based on nanogenerators, energy storage devices, and electronics.[201–206] Due to complex mechanical deformations (twisting, stretching, and bending) from harvesting body motion energy, they designed all-in-one shape-adaptive self-powered package unit for wearable applications (Figure 13d).[207] By combining a kirigami-structured supercapacitor with stretchability up to 215%, a silicon rubber triboelectric nanogenerator with stretchability of 100% and a full-wave rectifier, a stretchable, bendable, and twistable self-charging power package was achieved to sustainably power wearable electronics. The $V-t$ curve of the self-powered system in Figure 13g–i demonstrated that the electronic watch was continuously powered up by nanogenerator under various operating modes, including discharging, sustainable and charging mode. This work initiated prospective developments in self-powered wearable electronics and flexible display

Even though such sustainable self-powered systems are promising for wearable applications, it is necessary and challenging to reduce their size and thickness to improve volumetric/gravimetric energy/power density at the device level. Furthermore, the overall energy conversion efficiency needs to be improved. It would be desirable to match voltage and current between energy harvesters and energy storage devices without incorporation of transformer and rectifier, which would inevitably compromise energy conversion efficiency.

7. Conclusions and Perspectives

In summary, stretchability is one critical and indispensable feature of energy storage devices for wearable applications. Strategic design for stretchability, fabrication of highly stretchable electrodes and separators for SESDs and various assembled SESDs (such as stretchable supercapacitors, stretchable Li-ion batteries and stretchable Zn batteries) are introduced. Additionally, the applications of SESDs in integrated systems are discussed. Despite the inspiring achievements in the past years, considerable challenges still remain to achieve reliable SESDs for practical applications.

First, it is desirable to increase energy density of SESDs. So far, the achieved energy density in the prepared SESDs are moderate, which cannot reach the practical electrochemical performance level of the conventional ESDs. One reason for that is the utilization of low ionic-conductivity gel/solid electrolyte in SESDs to avoid electrolyte leakage and enhance safety. Moreover, only a handful of electrode materials have been investigated in SESDs, like carbon-based materials, LMO, and ITO. Thus, developing high-capacity electrode materials and novel durable and biocompatible gel/solid electrolytes with high ionic conductivity are effective approaches to enhancing energy density of SESDs.

Second, delamination under repeated mechanical deformation is another issue needing to be urgently solved for SESDs. In stretchable electrodes, electrode materials tend to be delaminated from current collectors under applied strain, especially when the mass loading of electrode materials in current collectors are high, resulting in rapid capacity degradation. One reason for the delamination is resulted from the incompatible interfacial adhesion between electrode materials and the underlying current collectors, which can have significant effects on the size of localized cracks and continuous networks at elevated strains. However, it receives less attention and is often ignored. Introduction of elastic binders into electrode materials can be one option to accommodate mechanical deformation to mitigate delamination. Another direction to mitigate the delamination problem is to directly grow electrode materials on current collectors. Currently, most of the stretchable electrodes are prepared by slurry or deposition methods. Thus, the delamination issue undoubtedly needs further investigations.

Third, encapsulation of SESDs has not yet received much attention. Ideally, SESDs can maintain functional and stable electrochemical performance under harsh environmental conditions and extreme mechanical deformations. Waterproof is one requirement to guarantee reliable operation of SESDs. More importantly, a wearable SESD should be thin and elastic enough to be compliant to our curved and soft biological surfaces. However, most of current SESDs are still too bulky and large-sized. Thus, more efforts should be devoted to developing thin, stretchable, durable, and biocompatible packaging materials for SESDs to realize practical wearable applications.

Additionally, the seamless integration between SESDs and other components to realize complete and independent wearable systems still need to be addressed. The all-in-one self-driven integrated system will be the main trend. Currently, the low power density of energy harvester would lead to unstable output voltage of energy storage units. Thus, multidisciplinary collaboration among materials science, electronics and biology is crucial.

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Conflict of Interest

The authors declare no conflict of interest.

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