

The Recent Advance in Fiber-Shaped Energy Storage Devices

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Wearable electronic devices that can be directly worn on the human body or combined with daily textiles have experienced a booming development with the rapid development of mobile electronics. These wearable electronic devices strongly demand indispensable, high performance power systems with small size, high flexibility, and adaptability to comfort frequent deformations during usage. Fabricating high-performance energy storage systems in a 1D shape like fiber is recognized as a promising strategy to address the above issues. These fiber-shaped power systems with diameters from tens to hundreds of micrometers can adapt to various deformations for stable operation in close contact with the human body. It is also possible to further weave such 1D energy storage devices into breathable textiles with matching electrochemical performances for the wearable electronics. Here, the key advancements related to fiber-shaped energy storage devices are reviewed, including the synthesis of materials, the design of structures, and the optimization of properties for the most explored energy storage devices, i.e., supercapacitors, aprotic lithium-based batteries, as well as novel aqueous battery systems. The remaining challenges are finally discussed to highlight the future direction of the development of fiber-shaped energy storage devices.

1. Introduction

Over the past decades, the rapid development of mobile electronics has brought enormous convenience to our daily life. With these miniature electronic devices, the communication and social networking become more prompt and frequent among people. In the course of its evolvement, wearable electronic devices that can be directly worn onto human body or combined with daily textiles, experience a booming development.^[1–3] These wearable electronic devices strongly demand indispensable, high performance power systems with small size, high flexibility and adaptability to comfort frequent deformations during usage.^[4,5] However, conventional energy storage systems such as supercapacitors and lithium batteries are typically rigid and limited by their lifespan, which cannot effectively satisfy the above requirements.

Fabricating high-performance energy storage systems in a 1D shape like fiber is recognized as a promising strategy to

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relieve the limitations of wearable electronics.^[6,7] On the one hand, these fibershaped power systems with diameters from tens to hundreds of micrometers can adapt to various deformations for stable operation in close contact with the human body. It is also possible to further weave such 1D energy storage devices into deformable textiles with breathability. On the other hand, the 1D energy storage devices exhibit matching electrochemical performances for the wearable electronics.

The recent advance in fiber-shaped energy storage devices is summarized with a brief chronology in evolution (**Figure 1**). Previously, two electrically conducting fibers were woven into a supercapacitor that may witness the most rapid development simply from the publication number possibly because it can be most easily fabricated and characterized among the fiber-shaped energy storage devices.^[8,9] Compared with the fiber-shaped supercapacitor, the fiber-shaped lithium-ion

battery appeared much later due to the difficulty in finding appropriate electrode materials and fabricating methods.^[10] Nevertheless, the invention of fiber-shaped lithium-ion battery boosted the interest at both academy and industry, and a lot of efforts are then made to develop more energy storage systems and expand their applications in wearable and biomedical electronics. The other kinds of batteries such as lithium-sulfur batteries, lithium-air batteries, sodium-ion batteries, zincion batteries, zinc-air batteries, aluminum-air batteries and integrated systems have been discovered in just a few years, and they are further widely explored for a variety of applications including wearable electronics, biomedical electronics, and artificial intelligence. Now the fiber-shaped energy storage devices are attracting more and more interests and become a mainstream direction in various fields such as energy, chemistry, physics, material science, biomedical science, and engineering.^[11] It is further evolved into a new discipline that we call fiber electronics.

In this review article, the key contents related to the fibershaped energy storage devices, including the synthesis of materials, the design of structures, and the optimization on properties are carefully discussed for the mostly explored energy storage devices, i.e., supercapacitors, aprotic lithiumbased batteries (such as lithium-ion batteries, lithium–sulfur batteries, and lithium–air batteries), and aqueous battery systems (such as aqueous lithium/sodium-ion batteries, zincion batteries, and aluminum–air batteries). The integration of energy storage with the function of energy

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harvesting in the 1D format is then highlighted. The remaining challenges in fiber-shaped energy storage devices are finally discussed to provide insights for the future development.

2. Fiber Electrode

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As the key component to construct fiber-shaped energy storage systems, fiber electrodes are required to accommodate various deformations such as bending, stretching, and twisting under the premise of relatively high electrical conductivity and mechanical properties. Two main issues to address for choosing the fiber electrodes are the high conductivity and flexibility. Generally, metal wires with excellent conductivity are rigid and heavy while lightweight polymer fibers with flexibility are less conductive. By contrast, carbonaceous fibers are usually adopted for their relatively low mass density, high tensile strength, and surface area for enhanced capacitance and electrical conductivity.^[12] At the early stage, as widely developed candidates, two aligned carbon nanotube (CNT) fibers coated with gel electrolyte were twisted to form a supercapacitor fiber.^[13] The resulting devices could work under bending deformations with stable specific capacity. Graphene fibers had also been proved to be proper fiber electrodes for energy storage in both coaxial and paralleled configurations.^[14,15] To further combine the high conductivity of CNT fibers and the high electrocatalytic activity of graphene fibers, CNT/graphene composite fibers were synthesized (Figure 2a,b).^[16] The interconnected microstructure comprising of graphene sheets and CNT bundles enhanced mechanical strength and charge transport due to the strong π - π stacking interactions. This effect enacted as an improved tensile strength of ≈630 MPa, an electrical conductivity of (450 \pm 20) S cm⁻¹ and an improved specific capacitance of ≈ 31.5 F g⁻¹ (Figure 2c). Similar tactic is applied for enhancing the incorporation of active MoS₂ into graphene fiber skeletons through a one-step hydrothermal process.^[17] Apart from the chemical incorporation inside fiber electrodes and active materials, the interfacial area is also a significant parameter to the electrochemical performance.^[18] In particular, higher interfacial area determines an improved capacitance for electric double layer capacitors (EDLCs), which store charges through a surface double layer capacitance mechanism and







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separate the charges at the electrode/electrolyte interface. To this end, hollow reduced graphene oxide (RGO)/conducting polymer composite fibers with high interfacial areas were synthesized (Figure 2d,e).^[19] The hollow structures were produced by the released gases during the GO reduction reaction, contributing to an excellent charge storage capacity of 27.1 μ Wh cm⁻² for the resulting supercapacitors.

Following the fabrication of flexible fiber electrodes, realizing stretchability becomes the next focus to achieve since being stretched is a more frequent occurrence in most wearable



Figure 1. A brief chronology of the development of fiber-shaped energy storage devices. Reproduced with permission.^[46,78,85,87] Copyright 2014, Wiley-VCH; 2017, Elsevier; 2018, American Chemical Society; 2015, Wiley-VCH.

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Figure 2. a) Schematic illustration to the structure of the graphene/CNT composite fiber for high performance fiber electrodes. b) Cross section of a graphene/CNT composite fiber. The arrow shows a graphene/CNT composite sheet. c) Comparison of stress–strain curves of fiber electrodes. Reproduced with permission.^[16] Copyright 2014, Wiley-VCH. d) Schematic illustration to the charge distribution on the hollow structure. e) Cross-sectional SEM images of the hollow fiber electrode at low and high magnifications. Reproduced with permission.^[19] Copyright 2016, Wiley-VCH. f) The interaction among PANI, PA, and rGO in a gel electrode fiber. g) SEM images of the gel electrode fiber. h) Strain–stress curves of rGO, PANI/rGO, and PANI fiber electrodes. Reproduced with permission.^[22] Copyright 2018, Wiley-VCH.

electronics.^[20] Directly fabricating components of energy storage systems on the stretchable fibrous substrate has been developed as a typical strategy. For instance, the stretchable supercapacitor is first prepared by winding aligned CNT sheet incorporated with polyaniline (PANI) onto a prestretched polydimethylsiloxane (PDMS) wire as inner electrode, then coated with a thin layer of gel electrolyte, and enwrapped by another PANI/CNT composite sheet to form outer electrode.^[21] The electrochemical performances of the stretchable fiber remained almost unchanged at a strain of up to 300%. Another method for stretchable fiber electronics has recently been upgraded by designing intrinsically stretchable fiber electrodes and electrolyte. In a representative work, intrinsically stretchable fiber electrodes comprising of interconnected, self-standing 3D nanostructured conductive PANI/RGO (reduced graphene oxide) hydrogels are prepared by the self-assembly synthesis and then molded into fiber electrodes (Figure 2f-h).^[22] Two hydrogel fibers coated with gel electrolyte were assembled into a stretchable all-gel-state supercapacitor fiber, which can bear the strain up to 40%. In this kind of paradigms, the stretchability and the capacity are mainly limited by the conductivity as well as the active material content of the gel fiber electrodes.

3. Supercapacitor

Supercapacitors are of intensive interests among energy storage devices for powering a variety of electronic devices due to the advantages of high power density, short charging time and long cycling life.^[23,24] A supercapacitor is generally constructed by sandwiching gel electrolyte with two thin-film electrodes. Mimicking the sandwiched structure of the traditional planar supercapacitor, we may easily fabricate the fiber-shaped supercapacitor on an electrically conducting fiber as the inner electrode by sequentially coating gel electrolyte layer and winding the outside electrode.^[25] The above coaxial structure was further evolved into a twisting structure where two fiber electrodes with each coated with a layer of gel electrolyte were wound together to form the fiber-shaped supercapacitor later on. To date, carbon based materials and transition metal oxides were usually adopted as active materials incorporated on fiber substrates for supercapacitor fiber construction.^[26-28]

Compared with the other types of energy storage systems such as batteries, supercapacitors often reveal in a less complicated construction and require a less strict fabrication process. These advantages featured supercapacitor fibers with promising SCIENCE NEWS _____ www.advancedsciencenews.com





Figure 3. a) Schematic of the preparation procedures of the fluorescent fiber electrode. b) Photograph of 20 fluorescent supercapacitor fibers woven into a black textile under ultraviolet. c) 16 fluorescent supercapacitor fibers divided into 4 groups and woven into a glove to power 4 red LEDs. Reproduced with permission.^[30] Copyright 2017, Wiley-VCH. d) Schematic of the shape-memory supercapacitor fiber (SFSC). e) SFSC under flexural deformation and shape recovery. Reproduced with permission.^[31] Copyright 2015, Wiley-VCH. f) Schematic of the fabrication for an in-series fiber-shaped electrochemical capacitor. g) Dependence of the voltage on charging time for electrochemical capacitor fiber containing 100–1000 units connected in series. Reproduced with permission.^[35] Copyright 2015, Wiley-VCH.

potential as an intriguing platform for designs toward functional or smart energy storage devices in fiber format for more desirable environmental adaptability during usage. Typically, functional materials/components can be directly introduced into fiber electrodes to form functional supercapacitor fibers.^[29] As depicted in Figure 3a, functional component of fluorescence was incorporated into aligned CNT sheets through a co-spinning method.^[30] Under the premise of a stable electrochemical performance, the fluorescent component introduced fluorescent indication capability to the fiber, which was particularly promising for flexible and wearable devices applied in dark environment (Figure 3b,c).^[30] Modifying common elastic fiber substrate with functional layer was also effective to construct functional fiber-shaped supercapacitors with responsive behavior^[31,32] (i.e., shape-memory and self-healing) and stable electrochemical performance (Figure 3d,e). Interestingly, since pseudocapacitors with Faradic reactions at fiber electrodes are interlinked with some electrochromic processes,^[33] it is possible for integrating electrochromic function into supercapacitor fibers. Electrochromic polymer PANI that displayed different colors under charging/discharging were electrodeposited into aligned CNT fiber electrodes for supercapacitor construction. The resulted color-changing function could indicate the working state of supercapacitor in real-time.^[34]

In real-world applications, the output voltage and current provided by wearable supercapacitor fibers are of vital significance, which are generally adjusted by arranging supercapacitors in series and parallel connection, respectively. However, traditional circuit with external conducting wires suffer from many disadvantages in fabricating convenience, preparation cost and integrated stability. Efforts with an emphasis on novel structure designs have been made to address these practical issues. With tunable output voltage in a wireless manner, supercapacitors in series were constructed on a single elastic fiber based on aligned CNT (Figure 3f).^[35] As electrodes, aligned CNT sheets along the axial direction were separated with equal interval and share the same elastic fiber substrate. Gel electrolyte were then coated to connect each separated electrode, forming an integrated in-series connected supercapacitor fiber with tunable working voltage up to 1000 V (Figure 3g). In addition, this design was also leveraged in a continuous wet-spinning method to assemble poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) polymer into supercapacitor wires, achieving high energy density of 41.1 μ Wh cm⁻².^[36] The resulting fibers were further woven into a watchband and successfully powered an Apple Watch, demonstrating promise for practical applications in wearable electronics.

Novel fabrication methods toward scale-up production, fabricating convenience, and lower cost of fiber-shaped supercapacitors, have been developed during recent several years.^[37] Commonly, the fabrication process of supercapacitor fibers consists of several steps including preparing the fiber substrate, incorporating active materials, coating the electrolyte, and assembling as-prepared fiber electrodes into a device.^[38] As a simplification of above preparation process, the synchronous deposition strategy to continuously fabricate supercapacitor fibers was designed and achieved.^[39] The production line integrated the procedures of depositing active materials (including



manganese dioxide, polyaniline, and polypyrrole, etc.), polymerization, and device assembly together. The above integral fabrication could be accomplished within 5 min. The scale up production may bring the technology from the lab to commercialization for weaving supercapacitor fibers into power textiles in a continuous manner. In a more miniature paradigm, laser reduction was adopted to construct supercapacitor on single GO fiber, representing a typical method for microfabrication.^[40] Although the specific capacity was relatively low, the abovementioned intriguing paradigms combining novel fabrication and material design demonstrate a clear opportunity for practical applications of supercapacitor fibers.

4. Aprotic Lithium-Based Battery

In order to obtain high energy-density 1D energy storage devices, the development of fiber-shaped battery systems is highly desired. Limited to the electrochemical window of aqueous electrolyte, aqueous battery systems typically have an operating voltage less than 1.5 V, restricting their output energy. Aprotic battery systems are intriguing, because aprotic electrolyte enables the design of batteries with much higher voltages. Due to the light weight and high voltage, lithium-based batteries, known as the most successful aprotic system, have attracted enormous research interests. Initiated with fiber-shaped lithium-ion battery for its high maturity, fiber-shaped lithium-sulfur, and lithium-air systems were successively constructed in acquiring of a much higher specific energy.

4.1. Lithium-Ion Battery

Being one of the most common commercial power supplies, lithium-ion batteries (LIBs) are used in various mobile electronic products because of their high energy density, long cycle life, and high working voltage.^[41-43] It is more technically challenging to construct LIBs in a flexible or fibrous configuration compared with supercapacitors, since LIBs usually consist of more complicated components including cathode materials, anode materials, conductive additives, binders, separators, electrolytes as well as packaging materials. As a result, conventional LIBs are generally fabricated in a rigid and bulk structure, leading to space occupation as well as incapability for deformation and thus hindering their practical applications toward wearable electronics. With conventional components, once LIBs are constructed into flexible 1D configuration, the occurrence of deformation during usage may result in the detachment due to the poor interaction between different component layers, thus leading to the fail to work.[44]

The realization and development of fiber-shaped LIBs have been driven by the synthesis and fabrication of novel electrode materials, accompanied by optimized design of device structures. Sharing a similar development track with supercapacitor fibers, current 1D LIBs typically consist of two twisted fiber electrodes or occur in a coaxial cable configuration. Using a spring-liked Cu wire deposited with Ni–Sn active materials and an aluminum wire coated with LiCoO₂ slurry as anode and cathode, respectively, a cable LIB has been



fabricated (Figure 4a,b).^[45] The resulted device delivered a specific capacity of 1 mAh cm⁻¹ and flexibility to fit deformation (Figure 4c). However, its dimension, taking the diameter as example, was comparable to that of a commercial AAA battery, which unfortunately, limited the further application. Herein, efforts have been devoted for fabricating fiber-shaped LIBs in a more compact manner. Successfully, fiber-shaped LIBs with diameter within several micrometers were produced from a CNT/LiMn₂O₄ hybrid fiber cathode and a CNT/Li₄Ti₅O₁₂ (CNT/ LTO) hybrid fiber anode in a parallel structure (Figure 4d,e).^[46] The CNT fiber in this case simultaneously served as current collector and the host for active materials, thus reducing the weight and volume of the LIB. A relatively high lithiation potential of ≈1.5 V (vs Li/Li⁺) was provided by the introduction of Li4Ti5O12, which was beneficial for a dendritic-free anode surface for long-span work.^[47,48] A flexible poly(vinylidene fluoride) (PVDF) membrane was set between two fiber electrodes as separator and the integral fibrous device was inserted into a heat-shrinkable tuber. The resulting fiber-shaped LIB delivered a discharge plateau voltage of 2.5 V at 0.1 mA, and the specific capacity reached 138 mAh g⁻¹. Moreover, this fiber-shaped LIB was highly flexible with a stable electrochemical performance (i.e., the specific capacity could be retained at ≈85% after 100 bending cycles) and could be bent into various formats (Figure 4f).^[46]

Along with the innovations of flexible LIB fibers, a series of superstretchable LIB fibers was developed to further enhance the device adaptability toward various deformations. Noting here that compared with stretchable supercapacitor fibers, fabricating stretchable LIB fibers is challenging since it involves much more components and packaging technology. First, depositing active materials onto a stretchable substrate, such as wounding aligned CNT/LiMn₂O₄ (cathode) and CNT/ Li₄Ti₅O₁₂ (anode) composite onto a PDMS fiber,^[49] is a universal strategy because it simultaneously enables the close contact and stable incorporation, benefiting a compact construction. A layer of gel electrolyte was infiltrated onto the resulting fiber, followed by wrapping a PDMS membrane as the packaging layer. The as-fabricated LIB fiber could endure a large tensile strain up to 600%, which was sufficient for normal movements of human body. The electrochemical performances of the battery were comparable with their planar counterparts, and could be stably retained upon stretched to 200%. This strategy for stretchable LIB fibers was efficient, but at the cost of a decreased energy density since the introduction of the stretchable substrate increases the additional weight of fiber-shaped LIBs.^[50,51] Synthesizing an intrinsic stretchable fiber electrode may introduce the stretchability and in the meanwhile retain the battery performance. Using a stretchable, spring-liked CNT fiber electrode prepared by over-twisting several CNT fibers together,^[52] intrinsically stretchable LIBs were developed and delivered a reversible capacity of 92.4 mAh g⁻¹, which could be well retained at 85% at a 100% strain without the introduction of an additional elastic substrate. The stretchable deformation achieved according to this strategy may be limited by the low dimensional material in LIB components and can hardly surpass 100%.

To scale up the preparation of the flexible all-fiber LIB, many advanced manufacturing technologies have been applied to ADVANCED SCIENCE NEWS _____ ADVANCED ELECTRONIC MATERIALS www.advelectronicmat.de



Figure 4. a,b) Schematic illustration and photograph of the cable LIB with hollow-helix anode, respectively. c) First charge/discharge profiles of cable batteries. Reproduced with permission.^[45] Copyright 2012, Wiley-VCH. d,e) Schematic illustration and photograph of the flexible fiber-shaped LIB, respectively. f) Galvanostatic charge and discharge curves before and after bending for 500 and 1000 cycles. Reproduced with permission.^[46] Copyright 2014, Wiley-VCH. g) Schematic of the design concept and fabrication process of 3D printed 1D LIB. h) Photographs of the fiber electrode during the printing process. i) Life-span of the as-printed LIB fibers. Reproduced with permission.^[54] Copyright 2017, Wiley-VCH.

continuously fabricate the hybrid fiber electrodes with high efficiency.^[53] As a creative attempt, by means of 3D printing, the cathode and anode fibers could be directly prepared from electrode inks prepared by incorporating lithium iron phosphate (LFP) and $LiMn_2O_4$ (LMO) into the PVDF solution with CNT conductive additives, respectively (Figure 4g,h).^[54] PVDFco-HFP was coated onto the electrode fibers, and two electrode fibers were then twisted and assembled in a heat shrinkable tube. The state-of-art fabrication method yielded fiber-shaped LIB with a discharge specific capacity of ≈ 110 mAh g⁻¹ at 50 mA g⁻¹ and good flexibility for wearable applications (Figure 4i). To date, there was one pitying point for this kind of research because the continuously fabricated electrode fibers should still be assembled in argon-filled glove boxes, which accurately prevented the scale-up LIB fibers from moving forward. Therefore, significant effort should be further devoted for designing and transplanting advanced technologies into continuous LIB fiber fabrications.

4.2. Lithium-Sulfur Battery

With conventional intercalation transition metal oxide and phosphate cathode materials approaching their theoretical capacity, LIBs have been limited from further improvement to meet the growing requirements. In the case of wearable electronics, traditional battery and supercapacitor systems may be unable to provide a desirable longevity. As successors of LIBs, post-lithium batteries, mainly referred to lithium–sulfur (Li–S) batteries, and lithium–air (Li–air) batteries, have aroused wide attentions in recent years due to their much higher theoretical specific energy.^[55]

The lithium-sulfur batteries outperform with a high theoretical energy density of 2600 Wh kg⁻¹ and become a promising replacement of LIBs to be applied in electronic devices. Generally, in Li-S battery system, the sulfur-based cathode can effectively lower the cost of devices, while its lithiated intermediate, soluble polysulfides are prone to make capacity degradation and decreased lifespan. This obstacle has been initially overcome by developing stable sulfur host for flexible cathodes. Flexible, highly conducting and self-standing sulfur cathode were successfully prepared with activated carbon fiber cloth and template-synthesized CNT membranes,[56,57] blazing the direction for the realization of fiber-shaped Li-S battery. Evolved from those flexible sulfur hosts, fibrous cathode that stably embraces the sulfur-encapsulated particles was synthesized for fibershaped Li-S batteries.^[58] Using MC-CMK-3 as host to reserve sulfur, the CMK-3/S composite particles were synthesized







Figure 5. a) Schematic of the fabrication of the fiber-shaped Li–air battery. b) Charge and discharge curves at current density of 1400 mA g^{-1} . Reproduced with permission.^[63] Copyright 2016, Wiley-VCH. c) Schematic of the working mechanism of the redox mediator with LDPE film in 1D Li–air battery in ambient air. d) Cycling performance of the Li–air battery under different conditions in ambient air. Reproduced with permission.^[65] Copyright 2017, Wiley-VCH.

and then incorporated into a CNT porous fiber as the cathode. Assembled with a lithium wire anode and electrolyte, the flexible fiber-shaped Li–S battery exhibited improved longevity, i.e., over 83% of capacity retained after running for 100 cycles at 0.1 C, and could light a LED up for 30 min with a 10 cm length. The fiber-shaped Li–S battery is now at its early stage although its gravimetric energy density has already surpassed lots of LIB fibers and supercapacitor fibers. Several safety issues should be considered and addressed including the direct use of metallic Li wire and the hazardous electrolyte for further translation toward commercial applications.

4.3. Lithium-Air Battery

Along with the development of Li-S batteries, rechargeable lithium-air batteries, with a high theoretical energy density (3600 Wh kg⁻¹), have emerged as another competitive candidate for potential applications in a "fiber electronics" society.[59,60] Despite the demonstrated potential, several challenges have to be accomplished for its realization in wearable electronics including: i) the absence of effective structural design for flexible 1D configuration; ii) poor cyclability; iii) insoluble reaction product Li2O2 blocking air passage; iv) severe side reactions with water and carbon dioxide in air. Many efforts have been firstly made to fabricate flexible lithium-air batteries and successfully achieved flexibility in planar electrodes (e.g., a flexible film).^[61,62] However, the widely adopted cell configurations of them are still the coin cell and Swagelok cell, which were exclusively packaged with relatively rigid and bulky device dimensions.

The path toward above target was first realized by constructing a coaxial structure for 1D Li–air batteries.^[63] Interestingly, the 1D battery configuration allows air to diffuse in all directions around compared with the planar counterpart of which air only diffuse in one direction. As a presentative fabrication, the gel electrolyte was first coated on a lithium wire and then a layer of aligned CNT sheet was wrapped around as the air electrode, finally a heat shrinkage tube was introduced as the protect layer (Figure 5a).^[63] In this coaxial structural design, the gel electrolyte also serves as a protect layer to prevent oxygen diffusing to the lithium anode, restraining parasitic reaction between the lithium anode and oxygen to some extent. As a result, the fiber-shaped lithium-air battery exhibited a cyclability of 100 cycles at 500 mAh g^{-1} (Figure 5b). The limited cyclability was mainly attributed to the side reactions of the Li₂O₂ with water and carbon dioxide in air to produce lithium carbonate and blocking the air electrode.^[64] To achieve a more stable cyclability in fiber-shaped Li-air batteries, efforts have been devoted to developing novel electrolyte and packaging technologies.^[61] A waterproof polyethylene (PE) film was introduced to the battery system as well as a redox mediator LiI through the combination of the PE film and LiI,^[65] the parasitic conversion of reaction product Li₂O₂ to electrochemically inert Li₂CO₃ was retarded dramatically. The resulting battery fiber realized an ultrastable Li-air battery with a superior cyclability of 610 cycles in ambient air (Figure 5c,d), which may further meet the practical requirements.

Besides the problematic air cathode, the employment of lithium anode poses severe safety hazardous especially for applications of portable and wearable electronic devices. The dendrite growth nature of the lithium also leads to a low coulomb efficiency of Li–air batteries. Replacing metallic lithium wire with composite fiber electrodes represents a promising strategy. For instance, lithiated Si/CNT hybrid fibers are synthesized as a substitute for the pure Li metal as anode fiber.^[66] The Si nanoparticles were introduced for Li accommodation and the high specific capacity of silicon has endowed the lithiated silicon/CNT hybrid electrode sufficient lithium ion for the battery reaction with a resulting energy density of 512 Wh kg⁻¹ in a miniature device diameter of \approx 500 µm, suggesting its promising potential for the fabrication of high

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performance power textile. Other composite lithium anodes have also been successfully explored. For instance, using 3D microarchitectures of highly elastic polymer rubbers to accommodate the metallic lithium, a stretchable lithium composite anode has been realized,^[67] revealing the potential applications in wearable electronics.

5. Aqueous Battery Systems

Toward applications in wearable electronics that work in close contact to human body, safety is essential for fiber-shaped batteries. However, aprotic batteries are increasingly scrutinized for the safety issues since fire/explosion accidents cloud their extensive use in mobile electronic devices.^[68,69] The main cause of those safety hazards can be attributed to the aprotic electrolyte based on organic solvents, which could induce inflammability if the battery collapsed or produced leakage. Replacing the non-aqueous electrolyte with the aqueous one represents an important step for developing LIB fiber with higher safety.^[70,71] Moreover, an aprotic battery relies on a highly reliable packaging that features an ultralow water vapor permeability. This calls for the development of flexible packaging technique with ultrahigh barrier performance, which may disturb the practical application of these batteries. And it would be difficult to reconcile this requirement with water washing needs of some wearable devices. Accordingly, aqueous fiber-shaped battery systems were developed. Apart from aqueous lithium-ion (and its analogue sodium-ion) battery, high performance aqueous Zinc and Aluminum based systems of fiber-shaped batteries have been demonstrated, which can adopt their metallic form as high capacity anode because of their stability to water.

5.1. Aqueous Lithium/Sodium-Ion Battery

Attempts have been made through introducing aqueous Li₂SO₄ solution-based electrolyte into LIB fiber systems with polyimide/CNT and LMO/CNT hybrid fibers serving as anode and cathode, respectively.^[72] The resulting LIB fiber indeed became safer while delivered a limited specific capacity of 86 mAh g⁻¹. The performance gap was resulted from a rather narrow electrochemical stability window provided by water, which is \approx 1.23 V under thermodynamic equilibria.^[73] Fortunately, the above stability window of water has recently been expanded to \approx 4.0 V,^[74] which may be transplanted into aqueous LIB fibers to combine high-energy density and safe electrolyte for wearable electronics.

Sharing the similar mechanism of Li-ion batteries including intercalation or deintercalation, sodium-ion batteries (SIBs) can be fabricated within similar strategies and technologies of LIBs. The availability and low cost of sodium make SIBs as a promising candidate to replace LIBs in portable and wearable electronics. In recent several years, efforts have been made to develop flexible electrodes for SIBs, i.e., carbon coated FeS on carbon cloth,^[75] free-standing flexible nitrogen-doped carbon nanofiber film,^[76] and electrodes based on urchin-like Na₂Ti₃O₇ and peanut shell derived carbon^[77] are successfully fabricated.



Benefiting from the above intriguing evolutions, a family of flexible fiber-shaped aqueous SIBs was achieved with electrodes comprising of Na_{0.44}MnO₂ (NMO) and nanosized carbon-coated NaTi₂(PO₄)₃ (NTPO/C) as cathode and anode, respectively.^[78] In this system, the NMO and NTPO/C were introduced and incorporated into aligned CNT fibers via a wet-spinning process. No extra conductive agents or additional current collectors were needed for the 1D SIB, which could be directly integrated into daily necessities. Interestingly, this kind of fiber-shaped SIBs could work in various Na⁺-containing aqueous solutions including normal saline and cell-culture medium, which boosted the safety and confirms its potential for wearable and even implantable electronics.

5.2. Zinc-Ion Battery

Over decades, alkaline Zn-MnO2 battery is one of the most popular primary cells for their low costs, desirable specific capacity, convenient fabricating process and high safety.^[79,80] Above attractive features make zinc ion battery systems promising to be applied in flexible and wearable electronics. Flexible alkaline batteries based on polymer gel electrolytes for Zn-MnO₂ systems have been proposed by Gaikwad et al.^[81,82] The resulted zinc-ion batteries exhibited high discharge performance and good flexibility. Then the carbon fibers were introduced as current collectors for the fabrication of a primary Zn-MnO₂ battery in fiber format with flexibility.^[83] However, these primary Zn batteries were not rechargeable and suffered from sharp capacity attenuation. Recently, aqueous rechargeable Zn-ion batteries of high capacity (819 mAh g^{-1}) have been studied based on a Zn metal anode and an α -MnO₂ nanofibers based cathode.^[84] The highly reversible conversion in aqueous Zn/MnO₂ system makes it possible to achieve flexible zinc-ion battery (ZIB) fibers with rechargeable, high electrochemical performances.

With similar fabricating strategies of fiber-shaped supercapacitors and LIBs, a typical paradigm of a quasi-solid-state elastic Zn-ion battery has been very recently reported by Zhi et al.^[85] As shown in **Figure 6**a, two double-helix CNT yarns modified with α -MnO₂ and Zn were prepared as cathode and anode, respectively (Figure 6b). A polyacrylamide (PAM) based polymer electrolyte was optimized as a flexible host immersed with neutral solution of ZnSO4 and MnSO4. The resulted yarn Zn-ion battery delivered desirable specific capacity of 302.1 mAh g⁻¹, and 98.5% capacity retained after 500 cycles (Figure 6c). The stretchability up to 300% strain was further achieved by winding two fiber electrode yarns to an elastic substrate fiber. Unlike active alkali metals like Li and Na, Zn can work in open air, leading to numerous advantages for the battery fabrication, as well as providing opportunities for novel design with additional environmental responsibility during use to satisfy various requirements. As an attempt, the shapememory function was introduced by using Zn electrodeposited Nitinol wire as flexible anode fiber.^[86] A stainless steel yarn electrodeposited with MnO2 and polypyrrole was synthesized as the fiber cathode. The resulting ZIB fiber achieved a discharge capacity of 174.2 mAh g⁻¹ with shape-memory function for the resulted Zn-ion battery fiber.







Figure 6. a) Schematic diagram of fabrication of the yarn ZIB. b) TEM image of the MnO_2 nanorods in the cathode fiber. c) Initial two discharge/ charge curves of the yarn ZIB. Reproduced with permission.^[85] Copyright 2018, American Chemical Society. d) Schematic of the construction of the fiber-shaped Zn-air battery. e) SEM image of a cross-stacking CNT based air cathode. f) Galvanostatic discharge curves of the fiber-shaped Zn-air batteries. Reproduced with permission.^[87] Copyright 2016, Wiley-VCH.

5.3. Zinc-Air Battery

Compared with rechargeable Zn-ion batteries, the zinc-air battery has been developed as a relatively mature technology. The zinc-air battery delivers a higher theoretical energy density of 1086 Wh kg⁻¹ (\approx 5 times higher than that of LIBs). The main challenge of fabricating fiber-shaped zinc-air battery lies in the preparation of the air electrode, which requires high catalytic activity, good air permeability, and structural stability under various deformations. The CNT sheet with porous nanoalignment has been developed as an ideal candidate for rational design to serve as the air electrode due to its minor thickness, light weight, and favorable electrical and mechanical properties. Using a high performance air electrode of aligned CNTs, fibershaped Zn-air batteries have been successfully fabricated.^[87] The air electrode comprising of cross-stacked CNT network provided both mechanical stability and enhanced electrical conductivity along the axial direction of the integral battery fiber (Figure 6d,e). The zinc spring anode was prepared with hydrogel polymer electrolyte for the oxygen-reduction reaction (ORR) as well as a RuO₂-based catalyst for the oxygen-evolution reaction (OER). Endowed with high flexibility and stability, the zinc-air battery fiber can be discharged/charged at 1 V at a high current density of 1 A g^{-1} (Figure 6f). In this case, the porous architecture of the air cathode not only serves as a gas diffusion layer, but also a current collector for electron transport, enabling lightweight, high compact assembly of the integral device.

5.4. Aluminum-Air Battery

During the evolvement of metal anode for batteries, aluminum shows a leading position due to low mass density and ability to exchange three electrons in the electrochemical process $(Al^{3+} + 3e^- \rightarrow Al)$.^[88] From the environmental point of view, it

is the most abundant metal element in the earth, and thus fabricating batteries with Al is promising for sustainable development. Moreover, aluminum possesses the highest volumetric capacity of 8040 mAh cm⁻³. When it comes to aluminum-air batteries, the theoretical energy density is 2796 Wh kg⁻¹, which far exceeds that of LIBs. While in practical fabrications, similar to the Li-air and Zn-air battery systems, the electrochemical performance of flexible Al-air batteries highly depended on the air cathode. In a representative work, using porous CNT layer coated with Ag nanoparticles, flexible air cathode for Al-air battery fibers have been successfully explored. The air-cathode layer was coated with a gel electrolyte and then wrapped onto a spring-liked Al wire.^[89] The resulting Al-air battery fiber exhibited desirable flexibility, stretchability, and an energy density of 1168 Wh kg⁻¹. The Al-air batteries are not rechargeable because thermodynamically aluminum cannot be electrodeposited in aqueous solutions, which may hinder their practical application toward wearable electronics. Developing room temperature aluminum-ion batteries with nonaqueous electrolyte (e.g., room temperature ionic liquids) may also be a promising successor for powering wearable electronics.^[90]

6. Integration System

Although numerous efforts have been made to realize and maximize the electrochemical performance of fiber-shaped energy storage systems like batteries and supercapacitors, these flexible energy storage devices still cannot avoid frequent charging process, which lead to inconvenience for usage. Toward their real applications of wearable electronics, the integration of energyharvesting technologies from ambient environment delivers a promise to address such issues, which may pave the way for further construction of multifunctional (e.g., photodetecting and sensing) microintegration systems.^[91,92] Currently, the





explored fiber-shaped integrated energy devices mainly focused on combining energy harvesting and storage devices (mainly including supercapacitors) to realize self-powering function in a compact and effective 1D architecture.^[93]

Harvesting power from solar energy is environment friend and renewable. To efficiently utilize solar energy and store it in wearable electronic devices, solar cells and energy storage devices are integrated together in a highly compact 1D configuration. An effective strategy to realize above integration is designing fiber electrodes that can simultaneously serve for solar energy harvesting and energy storage.^[94,95] In 2014, a wire-shaped device serving as both dye-sensitized solar cell and electrochemical capacitor has been developed by assembling two twisted fiber electrodes,^[96] with one comprising of a TiO₂ nanotubes modified Ti wire and the other of an aligned CNT fiber, followed by incorporation of an I_3^-/I^- redox ion couple containing electrolyte. Under illumination, the fiber device functioned as a dye-sensitized solar cell with a high energy conversion efficiency of 6.58%. The two fiber electrodes also serve as an electric double-layer capacitor to store the energy immersed with proper electrolyte and delivered a specific capacitance of 85.03 µF cm⁻¹. Compared with switching function on an integrated device between energy harvesting and energy storage, simultaneously realizing the bifunction requires a more compact energy fiber with the high flexibility and integration. Toward this end, a flexible fiber with both photoelectric conversion and lithium ion storage was proposed in a coaxial configuration.^[97] Using LMO/CNT and LTO/CNT fibers, the energy storage unit was fabricated in the inner space. A spring-liked photoanode and additional CNT layer were then fabricated to form the outer energy harvesting part. This fiber-shaped integrated fiber delivered both high photovoltage up to 5.12 V and high output voltages up to 2.6 V.

The integration of liquid-based fiber-shaped dye-sensitized solar cells with LIBs or supercapacitors generally required necessary sealing process for stable operation, which is complex and may increase the burden for integral weight and flexibility of the resulting energy devices. In this regard, the allsolid-state solar cells such as polymer solar cell (PSC) that can directly work in air may be a promising selection. A design of a coaxial structure was adopted to integrate PSC and supercapacitor by sharing a fiber electrode.^[98] For the PSC part, a layer of TiO₂ was fabricated on the left region of a Ti wire, followed by coating of poly(3-hexylthiophene):phenyl-C₆₁ butyric acid methyl ester (P3HT:PCBM) and PEDOT:PSS on the surface. Then a layer of aligned CNT sheet was fabricated on the outer layer, serving as another electrode for PSC part (Figure 7a). As for the supercapacitor part, the right region of Ti wire serves as the current collector, wrapped by two layers of aligned CNT layers for electrodes with electrolyte sandwiched between. Without sealing process, the integrated energy fiber could work for weeks with the entire efficiency maintained at \approx 75% (Figure 7b,c). Following that, perovskite solar cells that deliver high power conversion efficiencies have also been integrated



Figure 7. a) Schematic diagram showing the circuit connection in the fiber-shaped integrated energy system. b,c) Charging–discharging curve of the PSC-SC integrated system. Reproduced with permission.^[98] Copyright 2014, Wiley-VCH. d,e) Systematic configuration of the self-charging knitting power textile for wearable electronic device. f) Circuit diagram of the TENG-SC integrated system. g) Charging curves of SCs by manually tapping the TENG fabric. Reproduced with permission.^[106] Copyright 2017, American Chemical Society.



with lithium ion batteries or supercapacitors with desirable performances. $^{\left[99-101\right] }$

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Apart from harvesting energy from solar energy to power wearable electronics, triboelectric nanogenerator (TENG) is also effective to convert various forms of mechanical energy of daily activities from our bodies,[102-104] especially considering the usage scenario of wearable electronics. Since TENGs usually exhibited uncontrollable fluctuation/instability in their outputs, they cannot be directly used to drive most electronics that require a stable and continuous input power.^[105] Integrating the energy harvesting TENG with an energy storage unit can provide more clear opportunities for sustainable and maintenance-free applications. As an effective attempt, Wang et al. reported a facile and scalable all-yarn-based self-charging knitting power textile comprised of fiber-based TENGs and supercapacitors (Figure 7d-f).^[106] Serving as energy harvesting unit, highly stretchable and shape-adaptive TENG fabric was fabricated from groups of energy-harvesting yarns prepared by coating silicone rubber on the surface of three-ply twisted stainless steel/ polyester fiber blended yarn. When an active object (such as glove, fabric, hand, or foot) contacts with the silicone dielectric layer, electrification occurs at the interface and induce charge polarities for electrical generation. Regulated by a rectifier, the generated energy was stored in supercapacitor yarns. The integrated energy fabric can deliver the maximal peak power density of $\approx 85 \text{ mW} \text{ m}^{-2}$ with high elasticity, flexibility and stretchability (Figure 7g). The utilization of mechanical energy from daily motions offers promise to sustainable power system especially for the miniature wearable electronic devices.

7. Conclusions and Perspective

In conclusion, to meet the growing requirements of energy supplying units for wearable electronics that work in close contact to human body, efforts have been devoted to developing energy storage devices in flexible, fiber-shaped configurations to better adapt to various deformations. In this review, we discussed and highlighted the recent advances of wearable fiber-shaped energy storage devices with an emphasis on material synthesis, novel structural design as well as electrochemical properties, as summarized in **Table 1**. To date, numerous energy storage mechanisms have been successfully realized in flexible fibershaped configuration with acceptable performances. However, there still exists several important challenges that need further enhancement.

Fiber-shaped energy storage devices generally deliver at best a comparable or relatively poor performance compared with their planar counterparts. This can be attributed to the unique 1D configuration with high curvature interface, which demonstrates good flexibility but in the meanwhile deactivates the efficiency of conventional electrodes and active materials to some extent. More systematic research should focus on synthesizing novel electrode fibers and active materials, aiming at improved enhanced performance on curved interfaces. For instance, combined with high flexibility and conductivity, aligned CNTs with microstructured open architecture are promising materials to serve as the air cathode in metal–air battery fibers including Li–air, Zn–air, and Al–air systems. Besides, planar energy storage devices typically adopt a structure where the anode and

Table 1. R	epresentative	fiber-shaped	energy	storage	devices	discussed	in this	review.
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Fiber device	Fiber electrode	Assembly	Capacity	Flexibility	
Supercapacitor	rGO/CNT fibers ^[16]	Twisted	31.5 F g ⁻¹ at 0.04 A g ⁻¹	Can be bended	
	rGO/MoS_2 fibers ^[17]	In parallel	368 F cm ⁻³ at 0.1 A cm ⁻³	No significant capacitance decay after 1000 bending cycles	
	Hollow rGO/PEDOT:PSS fiber ^[19]	In parallel	304.5 mF cm $^{-2}$ at 0.08 mA cm $^{-2}$	Can be tied into a knot	
	PDMS fiber wounded with CNT/PANI sheets $\ensuremath{^{[21]}}$	Coaxial	100.8 F g^{-1} at 1 A g^{-1}	Well maintained after stretching at a strain of 300% for 5000 cycles	
	3D PANI/rGO hybrid hydrogel ^[22]	In parallel	112 F g ⁻¹ at 0.08 A g ⁻¹	Maintained after 1000 stretching cycles	
Lithium-ion battery	Cu wire coated with Ni–Sn; Al wire coated with ${\rm LiCoO_2^{[45]}}$	Cable type	1 mAh cm ⁻¹ at 0.1 A cm ⁻¹	Can be bended	
	$\rm Li_4Ti_5O_{12}/CNT$ and $\rm LiMn_2O_4/CNT$ composite yarns $^{[46]}$	In parallel	138 mAh g ⁻¹ at 0.01 mA	High stretchability	
	Polyimide/CNT hybrid fiber; LiMn ₂ O ₄ /CNT hybrid fiber ^[49]	In parallel	86 mAh g ⁻¹ at 600 C	Can be woven into flexible battery textile	
	$\rm Li_4Ti_5O_{12}/CNT/PVDF$ and $\rm LiFP_6/CNT/PVDF$ inks $^{[54]}$	Twisted	110 mAh g ⁻¹ at 50 mA g ⁻¹	Can be woven into fabric	
Lithium-sulfur battery	CNT fiber incorporated with CMK-3/S; lithium wire ^[58]	Cable type	First discharge capacity of 1051 mAh g ⁻¹ at 0.1 C	Little influence at varying bending states	
Lithium-air battery	Lithium wire coated with gel electrolyte and CNT sheet ^[63]	Coaxial	12 470 mAh g ⁻¹ at 1400 mA g ⁻¹	No capacity decay after 100 bending cycles	
Sodium-ion battery	Na _{0.44} MnO ₂ /CNT and NaTi ₂ (PO ₄) ₃ /CNT fibers ^[78]	In parallel	46 mAh g ⁻¹ at 0.1 A g ⁻¹	Flexible	
Zinc-ion battery	lpha-MnO ₂ /CNT and Zn/CNT yarns ^[85]	Twisted	Initial discharge capacity of 302.1 mAh g ⁻¹ at 60 mA g ⁻¹	Good knittability and stretchability	
Zinc-air battery	Zn spring and cross-stacked CNT layer coated with RuO ₂ -based catalyst ^[87]	Coaxial	6 Ah L ⁻¹ at 1 A g ⁻¹	Bendable and stretchable	
Aluminum-air battery	Al wire and CNT sheet incorporated with Ag nanoparticles ^[89]	Coaxial	935 mAh g ⁻¹ at 0.5 mA cm ⁻²	Little influence at varying bending states	





cathode plates closely face each other, which facilitates a fast working ion migration. Due to the curvature of the fiber electrodes, fiber-shaped devices usually exhibit a longer working ion migration length between the two electrodes, deteriorating mass transportation. Future research efforts should be made to design a more desirable architecture for fiber-shaped devices. Moreover, the electrical conductivity of fiber electrodes needs to be further improved. Although endowed with higher flexibility compared with metal wires, fiber electrodes of carbon nanomaterials adopted in most research exhibit undesirable, high electrical resistances. This feature results in the fact that fibershaped devices can effectively work at centimeter scale while fail to retain the efficiency as length of meters.

In order to fully realize real-world applications of fibershaped energy storage devices in commercial wearable electronics, the safety, packaging and continuous production are essential. In respect of safety, all components in the flexible fiber-shaped devices including electrode, electrolyte, separator, and encapsulation should demonstrate stability under various deformation. As a potential mainstream, aqueous electrolyte, gel electrolyte, and ionic liquids that exhibit higher safety level in the case of leakage or short circuit are promising candidates to replace conventional flammable liquid electrolyte. In regard to fiber-shaped device packaging, aprotic systems rely on a highly reliable packaging with an ultralow water vapor permeability. Though conventional aluminum-plastic film can easily meet this requirement, their flexibility is far from satisfactory. The development of flexible packaging technique with high barrier performance is highly desired, which would be a problem disturbing the practical application of this kind devices. However, this would not be an issue for aqueous systems. As for the scaled-up, continuous production, machinebased fabricating procedure should be developed to further fabricate fiber-shaped energy storage devices into breathable power textiles with flexibility. To date, only a few related studies are available and most current fiber-shaped devices are fabricated and woven into textiles by hand. In addition, the integration for multifunctional fiber-shaped devices, e.g., integrated with sensors for health caring, is of great significance for higher application value since the wearable electronic is of the interdisciplinary research area.

The fiber-shaped energy storage devices with high flexibility are moving towards a higher level of efficiencies and stability. It can be expected that these energy devices with unique 1D configuration will open up a revolutionary direction of fabricating power textiles for wearable electronics.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

batteries, energy storage, fibers, flexible, supercapacitors

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